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UNIVERSITY OF CINCINNATI

June 22 - 1951

I hereby recommend that the thesis prepared under my supervision by Martin K. Barnett

entitled A Critical History of the Concepts and Laws of Classical Thermodynamics.

be accepted as fulfilling this part of the requirements for the degree of Doctor of Philoosphy

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A CRITICAL HISTORY
OF THE CONCEPTS AND LAWS
OF CLASSICAL THERMODYNAMICS

A dissertation submitted to the
Graduate School of Arts and Sciences
of the University of Cincinnati
in partial fulfillment of the
requirements for the degree of
DOCTOR OF PHILOSOPHY
1951
by

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CONTENTS

	Page
I. The Development of Thermometry and the Temperature Concept	1
II. The Development of the Concept of Heat from the Fire Principle of Heraclitus through the Caloric Theory of Joseph Black.	98
III. The Development of the Energy Concept and First Law of Thermodynamics.	138
IV. The Development of the Entropy Concept and the Second Law of Thermodynamics.	225
Appendix--The Temperature Concept.	1A

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I. The Development of Thermometry and the Temperature Concept.

		Page
1.	Ancient and Medieval Period: Hot and Cold as Qualities.	1
2.	The Invention of the Air Thermometer: The Objectification of Sensation.	5
3.	Early Liquid Thermometers: The Residual Nature of Temperature.	11
4.	Alternative Scales and Thermometric Substances: The Principle of Indifference.	23
5.	The Revival of Gas Thermometry: The Quest for the Most Rational Scale.	38
	References and Figures.	87

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DEVELOPMENT OF THERMOMETRY AND THE TEMPERATURE CONCEPT.

1. Ancient and Medieval Period: Hot and Cold as Qualities.

Although observations of various thermal phenomena led the ancients to speculations which may be regarded as forerunners of our modern conceptions of the nature of heat, there is no record of their ever having made any systematic use of an instrument for detecting the degree of hotness of a body. Quantitative experiments or observations of thermal phenomena which would have entailed the introduction of the temperature concept and the use of a thermometer are therefore lacking.

The essential basis for the formulation of the temperature concept is the realization that a quantitatively observable property of a test-body needs to be substituted for our unreliable sense of hot and cold. Although the groundwork for this realization was provided by the theoretical materialism of Democritus, the fact that little headway was made can be largely attributed to the influence of Aristotle. To be sure, in the latter's system, the concepts of hot and cold along with moist and dry, were given the status of fundamental qualities, the essence of an individual body being determined by the extent to which each of the four qualities was present. However, Aristotle opposed on principle the notion that these qualities, which we would consider secondary or derived, might be reduced to more fundamental primary ones, i.e. to properties denotable by quantitative symbols. Thus the replacement of the sense of hot and cold by the concept of temperature was, with Aristotle and the multitude of medieval thinkers who followed him, out of the question from the beginning.

Nevertheless, phenomena which might have been made the basis for a systematic science of thermometry were well-known to the Ancients.

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Thus Philo of Byzantium, writing about 200 B.C., described a thermal device closely resembling the air thermometer introduced by Galileo eighteen hundred years later. One end of an inverted U-tube was sealed into a hollow lead sphere, and the other end was dipped into an open vessel of water (cf. Fig. 1). When the air in the sphere was cooled, said Philo, water rose from the vessel up into the tube; when it was heated, the water was driven down into the vessel and bubbles of air emerged from the end of the tube. The reference to bubbles of air emerging from the tube precludes the possibility that Philo might have used this device as a thermometer, since the latter application would require a constant quantity of air in the apparatus. Indeed, Philo stated that his experiment merely proved that "fire is closely connected with air and for that reason is drawn along with it."[1]

This reference to the close connection between fire and air was undoubtedly based on an acceptance of the Aristotelian "four-element" theory, according to which the four fundamental forms of matter were fire, air, water, and earth. Fire was associated with the properties, hot and dry; air with the properties, hot and wet; water, with the properties, wet and cold; and earth, with the properties, cold and dry. Thus air had the property hot in common with fire and could be converted into fire by substitution of the property dry for the property wet.

Somewhat later, near the beginning of the Christian era, we find a "thermoscope" described in the works of Hero of Alexandria.[2] A closed hollow sphere was filled with water except for an air space at the top (cf. Fig. 2). An inverted U-tube was sealed into the sphere, one end reaching to the bottom of the sphere, the other extending over a funnel.

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The stem of the funnel protruded into a hollow base, which also contained water. A straight tube extended from the water in the base to the air space in the sphere. Hero described how placing the sphere in the sun caused the air to be heated, thus forcing liquid out of the sphere, through the U-tube and into the base. When the sphere was placed in the shade, water was sucked up from the base through the vertical tube and thus returned to the sphere.

In one respect, Hero's thermoscope was more suggestive of the air thermometer than Philo's: the quantity of air in it remained constant during its operation. Actually, however, Hero himself did not consider this to be the case. He assumed the decrease in volume of the air on cooling to indicate a decrease in its amount and so supposed that the air must have escaped through the pores of the material composing the sphere.

Although Hero's reference to the effect of sun and shade on the behavior of the air of his thermoscope reveals an interest in what we would call variations in atmospheric temperature, there is no evidence that either he or his followers used any sort of device to indicate those temperatures. The Greek work for "climate" comes from a work meaning latitude, and, in fact, the only climatic measurements known to have been made by them were of the sun's altitude as it varied according to season and latitude.[3]

Aristotle's influence in physical science was promulgated largely through the writings of the physician, Claudius Galen of Pergamum, who died in 200 A. D. In the medical practice of the time, attention was directed to the therapeutic value of drugs supposedly associated with their ability to produce heat or cold. Following Aristotle, "heat" and "cold" were not regarded as relative terms, but as qualities, opposite in nature, and

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capable of separate identification. In this connection, Galen introduced the conception of "degrees" of hot and cold to indicate the extent to which these qualities were present in a body. Cold bodies, in which the quality hot predominated over the quality cold, were assigned to the 1st, 2nd, 3rd, or 4th degrees of cold. Similarly, hot bodies were relegated to four classes, according as they were hot in the 1st, 2nd, 3rd, or 4th degree. These degrees of hot and cold were strictly qualitative categories associated with the physician's perception. Only in connection with the conception of normal body temperature do we find a suggestion of the modern treatment of thermal phenomena. For, evidently recognizing the variability of sense perception, Galen suggested that the normal or "equal" temperature of the body be identified with that of a mixture of equal quantities of cold and boiling water.

Galen's rendition of Aristotle exercised wide influence through an Arabic translation about 850 A.D. and a Latin one three hundred years later. In the century following 1150, the works on physical science of Aristotle himself passed from the east into Europe, and these served to reenforce the traditional doctrine of the qualities, "hot" and "cold."

The very slow process of physical science in the medieval period is exemplified by the close similarity of the views of the fifteenth century Italian theorist, Giovanni Marliani,[4] and Galen, For, although these men are separated in time by some twelve hundred years, we find in their writings the same qualitative scale of hot and cold, comprising four degrees of "calidity" and four of "frigidity." Following Aristotle, Marliani supposed that everybody generally contained both hot and cold in varying proportions; he also assumed that the degree of frigidity and the degree of calidity would always total eight. In spite of the assumed additive property of these

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degrees, the latter were actually still the qualitative categories of Aristotle. No attempt to make them correspond with the quantitative properties of a test-body had yet been made.

Up to this point, the views of Marliani followed closely those of Galen. However, in proposing the concept of the "power" of heat (or cold) as distinct from its degree, he was breaking new ground. The ability of a body, e.g. a drug, to give up heat, reasoned Marliani, depends not only on the body's location in the scale of hot and cold but also on how much of it is used, i.e. on its extent. He thought that the actual power of heat (P) of a body might be expressed as the product of its degree of heat (T), its volume (V), and its density (D). Then P = DVT. The remarkable formal similarity of Marliani's "power" of heat to Joseph Black's "quantity of heat", developed about three hundred years later, is evident.

2. The Invention of the Air Thermometer: The Objectification of Sensation.

The initial stage in the development of modern thermometry and the temperature concept, which occurred in the early part of the seventeenth century, resulted from the fusion of two complimentary tendencies. The first of these was the tendency toward abstraction whereby all qualitative aspects of phenomena were deleted, leaving mathematically determined entities. For just as Galileo's conception of "pure motion," stripped of all the complicating phenomena imposed by friction, hailed the birth of modern mechanics, so the conception of temperature, devoid of all the complex sensations of hot and cold, marked the beginnings of modern thermometry. The second tendency, the trend toward instrumentation, was essential to implement the process of abstraction; that is, an instrument or test-body had to be devised whose quantitative readings could determine the degree of

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hot or cold without reference to sensation.

If the first tendency may be related to the revival of the pre-Aristotelian views of Democritus and Plato, according to which the essence of reality is that portion capable of quantitative or numerical expression--so the second tendency may be traced in part to familiarity with the thermoscopes of Philo of Byzantium and Hero of Alexandria. Hero's Pneumatica was known in Sicily as early as 1156 and was probably translated into Latin at that time.[5] It was published at Urbino in 1575 and at Amsterdam in 1680, and Italian versions appeared in 1542 and 1589. Although Philo's work remained relatively unknown until the twentieth century, his treatise, in manuscript form exerted determinative influence on at least one of the early workers in thermometry.

The circumstance that Hero's thermoscope had utilized the thermal expansion of air to force a liquid through a tube no doubt provided at least a partial explanation for the fact that the earliest thermometers were air thermometers. This would no doubt have been the case even without Hero's influence since the volume of air, the commonest gas, is far more sensitive to temperature changes than is that of liquids or solids. Furthermore, in the still prevalent four-element theory of the ancients, "fire" was more closely associated with "air" than with "water" or "earth."

If we characterize thermodynamics as an attempt to formulate a set of principles for thermal phenomena analogous to those provided by theoretical mechanics for non-thermal phenomena, it will not seem surprising that historians have usually attributed to Galileo Galilei, one of the founders of modern mechanics, the invention of the first air thermometer about the year 1592. The air thermometer attributed to Galileo is shown in Figure 3.

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The bulb B, containing the air, was brought into contact with the body whose hotness or coldness was being investigated. The resultant contraction or expansion of the air governed the height of the liquid column, the latter being regarded as an indication of the hotness or coldness in question. The stem was graduated but it is not known in what fashion. As enclosing liquid, Galileo probably used both water and wine.

Our knowledge of Galileo's thermometer, along with our basis for his priority as inventor, rests chiefly on the correspondence of colleagues and friends, since in his extant writings there is but one reference to his thermometer. In this fragment, he invoked the Aristotelian dictum, "Nature abhors a vacuum" to account for the rise of the liquid in the tube which accompanied the contraction of the air. On the other hand, he also expressed the view that "cold is nothing but the absence of heat,"[6] thus rejecting the Aristotelian view that hot and cold were two distinct properties capable of separate identification. The latter had dominated the thinking of Marliani and other medieval writers and had been one of the chief obstacles to the development of the modern concept of temperature.

One of the fundamental requirements of thermometers is posed by the necessity that different instruments shall give identical readings. The most obvious solution of this problem of comparibility might seem to lie in the production of identical thermometers; however, this solution presents great difficulties in manipulation. A far more feasible method consists in rendering un-identical instruments comparable by a process of calibration employing the concept of a "fixed point" or "reference state."

The concept of a "fixed point" and the validity of its use in connection with the calibration of a thermometer rest upon a simple application of the

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principle of causality that like effects always have like causes. Thus one begins with the observation that a particular thermometer always assumes the same reading whenever it is conjoined with e.g. any one of various samples of melting ice. From the constancy of the effect (the invariability of the reading) one infers the constancy of the cause and is thus led to conclude that, in the various instances of melting ice, we have encountered one and the same phenomenon characterized by a constant temperature. It now follows that if another thermometer be conjoined with melting ice, it must be made to give the same temperature reading as was recorded on the first thermometer when it was so conjoined, since one and the same cause must always have one and the same effect.

Because of the simplicity of this concept of the fixed point, it is not surprising that it was developed quite early in the history of thermometry. In fact, it was evidently already employed by Galileo's friend, Francesco Sagredo, who built a number of air thermometers modeled after the former's instrument. These were rather coarse devices by modern standards, for the capacity of the bulb was "three or four drinking glasses" and the tube was a "finger wide."[7] Nevertheless, Sagredo spoke of his thermometers agreeing well with one another, the liquid in instruments of different size rising and falling "in the same ratio." Since he also mentioned that his thermometer read 360 degrees in the greatest summer heat, 100 degrees in snow, and zero degrees in a mixture of snow and salt, it seems likely that comparability was attained by regarding the temperatures of snow, and snow and salt, respectively, as fixed points. As early as 1615, Sagredo referred to having made regular meteorological observations with his thermometer over a period of several years. He was thus able to compare the extremely cold weather of one winter with that of another.

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Credit for the first use of the thermometer in medicine must go to another associate of Galileo, Sanctorius Justipolitamus, who taught theory of medicine from 1611 to 1624 at Galileo's own University of Padua. Indeed, the evidence is strong that Sanctorius invented the air thermometer independently of, though somewhat later than Galileo; at any rate, his description of the thermometer in his "Commentary on the Medical Art of Galen," which appeared in 1612, was the first published account of the instrument.[8] Sanctorius modified the air thermometer to make it suitable for use in recording body temperatures; and, in a work published in 1626, several modifications, illustrated with drawings were described. In one form, the air bulb was inserted into the patient's mouth, and the position of the liquid in a long S-tube attached to the bulb was noticed. Sanctorius was the first physician to observe variations in the temperature of the human body and to interpret these as indicative of ill health. Of greater significance for the history of thermometry and the temperature concept was Sanctorius' employment of two reference points in graduating the tube. These were taken as the temperatures of snow and the flame of a candle.

An essential feature of the modern concept of temperature is the faith in the validity of the instrument even though it contradict the sense of hot and cold. That this aspect of the new science of thermometry was attaining recognition in the minds of the early workers in the field is evidenced by certain passages in their writings. Thus Sagredo spoke of the water of springs being colder in winter than in summer "although our feelings seem to indicate the contrary." Sanctorius stated that because of its moisture some air feels colder than it really is, i.e. than the thermometer indicates. Again, writing of the air thermometer in 1620, Francis Bacon stated that "the sensibility of the air with regard to heat and cold is so delicate and exquisite, that it far exceeds the human touch."[9]

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Whereas Galileo was undoubtedly familiar with Hero's thermoscope and Sanctorius openly acknowledged his debt to him, the work of the Englishman, Robert Fludd, in this field was most probably instigated by a familiarity with the writings of Philo of Bysantium. In 1617, Fludd published a drawing of a thermoscope exactly similar to Philo's although no reference to Philo was made; however, the similarity of his language to that originally employed by Philo leaves little doubt that he had access to a manuscript of Philo's treatise.[10] Later, in 1626, he described, along with Philo's thermoscope, an air thermometer of the Galilean type, claiming to have invented it some years before.

In 1644 the French theologian, Father Marin Mersenne, described a modification of Galileo's air thermometer, designed to improve its delicacy.[11] Instead of inverting the bulb and tube permanently in a vessel of water, the bulb was warmed and the end of the tube then plunged under water only long enough to permit entry by suction of a short column of the liquid. The thermometer was then ready to use, the position of the column of liquid on the scale indicating the temperature of the air in the bulb.

All of the early thermometers thus far described conformed to the same pattern; the inverted bulb and tube called, after its earliest inventor, the "Galilean tube." Another early type was illustrated in 1624 by Jean Leurechon in his "La recreation mathematique."[12] In this "two-bulbed" or "J" type (cf. Fig. 4), a bulb was blown on either end of a J-tube. The apparatus was partially filled with water through a hole in the bulb. The body whose degree of heat was to be determined was applied to bulb B, and the resulting motion of the liquid column in the longer leg noted.[13] A thermometer described by van Helmont in 1648 differed from Leurechon's

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illustration only in that it operated with a short column of liquid in the tube. This J-type design has an obscure origin but was probably invented by the Dutchman, Cornelius Drebbel, sometime between 1598 and 1622. The latter did not employ it as a thermometer, however, but as a "perpetu al motion tube," i.e. he thought the motion of the liquid back and forth in the tube, resulting from thermal fluctuations, demonstrated perpetual motion.[14]

One of the chief difficulties in the early practice of thermometry was associated with the lack of any generally accepted scale of degrees. The importance of reliable and reproducible reference points had not been fully established. Leurechon spoke of the "philosopher's scale" and the "physician's scale." According to the former, the length of the tube of the air thermometer was divided into eight degrees, whereas, according to the latter, it was divided into four degrees. The influence of Galen's doctrine of hot and cold is seen in the scale recommended by Robert Fludd in which, beginning at the mid-point or zero of the scale, the tube divisions were numbered from one to seven in either direction. A scale employed by the Roman engineer Telieux in 1611 purported to measure temperature in degrees and minutes. Again, none of these alternatives could correspond to the scale of Sagredo which indicated 360 degrees in summer heat, 100 degrees in ice and snow. The situation was described with considerable candor by Francis Bacon in his "Novum Organon," published in 1620, where he spoke of the scale of the inverted "Heat-glass" being "divided into as many degrees as you please."[15]

3. Early Liquid Thermometers: The Residual Nature of Temperature.

A well-known characteristic of the modern concept of temperature is its residual nature, in accordance with which the interaction between the

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thermometer and a given body, by means of which the position of the latter in the temperature series is determined, is a residue to be observed only under conditions which eliminate all "extra-thermal" effects. This residual character first received emphasis when it was realized that temperature readings recorded on the scale of the open air thermometer were vitiated by fluctuations in the external air pressure. This serious shortcoming of the conventional air thermometer was partly responsible for the early development of liquid thermometers.

However, the earliest liquid thermometers, as we shall see, pre-dated the classical experiments on air-pressure, performed by Torricelli and Pascal, which resulted in an understanding of the influence of the barometric pressure on the readings of the Galilean air-thermometer. Therefore, the reduction in popularity of the latter in favor of liquid thermometers must have been partly the result of other reasons; and these are not difficult to find.

Thus, the marked sensitivity of air thermometers to the presence of small amounts of moisture in the bulb and air sample must have presented a formidable obstacle to the construction of comparable instruments. Also, the awkward two-piece construction was unsatisfactory where portability was required. Again, it was difficult to establish thermal contact between the rather large bulb of air and the body being tested, particularly so if the latter was a liquid. On the contrary, if the bulb were made smaller, the stem error would have been increased, since a greater fraction of the air would have been at the temperature of the tube. Finally, the circumstance that the vessel of enclosing liquid was uncovered introduced errors resulting from evaporation of the liquid, in addition to those attributable to a variable barometer.

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In 1643 the Jesuit, Athanasias Kircher, published a description of a thermometer which was really a hybrid water-air type (cf. Figure 5).[16] The tube of the original Galilean tube was extended to the bottom of the bulb and the latter partially filled with water. Besides being a simpler one-piece instrument, Kircher's thermometer, having the bulb at the bottom, facilitated determination of liquid temperatures by immersion. Since the bulb contained both air and water, two thermometric substances were involved. The fact that the stem was unsealed incurred two kinds of accidental variation: that associated with the effect of variable atmospheric pressure on the volume of the air, and that associated with the effect of evaporation on the volume of the liquid.

Still another hybrid, liquid-air type was in use as early as 1656. This type, evidently generically related to the Dutch J-type of air thermometer, had one arm of a U-tube sealed to the bottom of the bulb. Vinegar was introduced into the apparatus until the bulb was about half full.[17]

A full-fledged liquid thermometer had already been designed and used as early as 1632 by the French physician, Jean Rey.[18] In this instrument a Galilean tube was placed bulb downward and the latter completely filled with water. As in Kircher's instrument, the tube was left unsealed so that readings were still affected by evaporation.

The first closed liquid thermometer of which we have any record is the one invented sometime before 1644 by the Grand Duke Ferdinand II of Tuscany, a former pupil of Galileo. The bulb of this instrument was about the size of a gun-ball and was filled with alcohol, colored or uncolored. The tube was hermetically sealed, thus eliminating evaporation.

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It cannot be stated with certainty that the realization of the influence of variable barometric pressure on open air thermometers is what prompted Ferdinand to invent the alcohol thermometer, since he may have invented the latter as early as 1641, two years before Evangelista Torricelli, mathematician to the Duke of Florence and another student of Galileo, demonstrated the Torricellian vacuum and correctly attributed day-to-day variations in the height of the mercury column to variations in the weight or pressure of the air. Knowledge of Torricelli's experiments was communicated to the French physicist, Blaise Pascal, through Father Mersenne, who first heard of them in 1644. Beginning in 1646, Pascal repeated and extended Torricelli's experiments. Particularly famous are the experiments, carried out under Pascal's direction by his brother-in-law, F. Perier, on the variation of air pressure with altitude.

Pascal was fully aware of the significance of his work for thermometry. In his "Treatise on the Weight of the Mass of the Air," published in 1663, one year after his death, he stated that his experiments on variable barometric pressure show "that degrees of heat are not correctly marked even in the best thermometers since in them all the different heights at which the column of water stands are ascribed to the rarefaction or condensation of the air inside the tube, whereas from our experiments we learn that the changes that take place in the outer air, that is, in the mass of the air, contribute markedly to those changes."[19] Again, in the "Story of the Great Experiment on the Equilibrium of Fluids," published at the same time, we read that a consequence of variable barometric pressure is the "unreliability of the thermometer in marking degrees of heat (which is not commonly recognized), as is shown by the fact that its liquid sometimes rises when the heat

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increases and sometimes, on the contrary, falls when the heat decreases, even though the thermometer be kept always at the same location."[20]

While the invention of the closed alcohol thermometer is generally attributed to Ferdinand II, considerable credit for its improvement and the extension of its use must likewise be assigned to Italian efforts and influence, in particular, to the work of the famous Accademia del Cimento (Academy of Experiments), which flourished in Florence from 1657 to 1667. The Academy was founded by Ferdinand II and his brother Leopold and was constituted largely of disciples and former students of Galileo. A record of their experimental work, in which no credit to individual members was given, was published in Italian in 1667. This book, entitled "Saggi di naturali experienza (Records of Natural Experiments),"[21] was destined to exert wide influence on the development of European science.

The members of the Academy evidently used closed alcohol thermometers almost exclusively in their experimental work, and the residual character of temperature provided them with at least one basis for this preference. They were quite familiar with Torricelli's experiments and probably with Pascal's as well. Not only did they repeat a number of these experiments but they also performed many new ones relating to the Torricellian vacuum and variations in air pressure. Thus, in one experiment, they employed an instrument identical to Kircher's air thermometer (cf. Figure 5) except that mercury was used in place of water. The level of the mercury in the tube was observed to rise when the instrument was taken to the top of a tower, and this, following Pascal, was correctly explained as due to the decrease in external air pressure. In a second instrument, consisting of a bulb of air sealed at the bottom to an open U-tube containing mercury

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and essentially identical to the Drebbel-type of air thermometer, similar phenomena were observed. We find it clearly stated that the level of the mercury in these instruments depends both on the temperature of the confined air and the barometric pressure.

On the other hand, attempts to demonstrate the compressibility of liquids were unsuccessful. They subjected a quantity of water to the pressure of a long column of mercury but were unable to observe any decrease in its volume, although a similar column had decreased the same volume of air to one-thirtieth of its original volume. From this, we may assume that they regarded the prevention of evaporation as the chief reason for sealing liquid thermometers.

Three closed alcohol thermometers were described in the opening pages of the Sagi. They were filled, first by warming the bulb and immersing the end of the stem in the liquid, and then, by pouring liquid through a small-stemmed funnel. The practice of coloring the alcohol was abandoned because the coloring agent deposited a sediment in the stem.

The Academicians undoubtedly recognized the importance of providing thermometers with comparable scales. During the years in which the Academy flourished, their thermometers were dispatched to cities and monastaries all over Europe for the purpose of making meteorlogical observations. These records were subsequently returned to Florence for comparison, a comparison which would have been meaningless had the thermometers themselves not been at least approximately comparable.

To attain this comparability, they probably relied mainly upon the skill of the glass blower in maintaining a constant relation between the volume of the bulb and the diameter of the stem. Thus, the stem of the first thermometer was divided into one hundred equal degrees or divisions,

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the glass blower being required to "make the Ball of this Instrument of such a Capacity, and joyn thereto a Cane of such a bore, that by filling it to a certain mark in the Neck with Spirit of Wine, the simple cold of Snow or Ice Externally Applied, may not be able to condense it below the 20 deg. of the Cane; nor... the greatest vigour of the Sun's Rays at Midsummer, to Rarifie it above 80 deg."[22]

Their second thermometer was divided into fifty degrees, the greatest heat of the midday sun giving a temperature of 40 degrees, the "greatest cold of our Winter" giving a reading of 12 or 11 degrees compared with a reading of 17 or 16 degrees on the first thermometer. The maintenance of such correspondence between scales was only attained "by Practice, teaching how to proportionate the Ball to the Cane, and so to adjust the Quantity of Liquor, as they shall not vary in their motions."[23] The stem of their third thermometer was longer and narrower than those of the other two and divided into 300 degrees. The fourth thermometer had a large bulb sealed to a very long stem consisting of a coil of glass tubing. Since, in coiling the stem, the uniformity of its bore was destroyed, this instrument was regarded as little more than a laboratory curiosity.

The exact manner in which the Florentines employed the ice-point in sealing their thermometers was not described in the Sagi. In their description of the 100-degree thermometer, they stated that, by means of the capillary funnel, "you may fill the Instrument up to what mark in the Neck you please." Later, they spoke of the "proportion of the spirit of wine found with the proof of Sun and Ice." These passages suggest that they might have introduced alcohol, with the bulb in an ice bath, until the level in the stem came to the 20-degree mark.

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The following circumstances, however, cast doubt on this conclusion. In the first place, their mention of the ice-point in the same phrase with the heat of the midday sun is scarcely consistent with the assumption that they employed these as fixed points in thermometry. For the variability of the sun's heat must have been a matter of every-day experience. However, if we take the other horn of the dilemma and assume that they did use both sun and ice as fixed points, we are left with no explanation for their concern about the ratio between bore and bulb. For with two fixed points, this ratio need not be constant. Again, in their description of the scale of the 50-degree thermometer, there is no mention of the use of ice or snow. However, in one experiment in which they had occasion to immerse a 50-degree thermometer in an ice bath, they stated that the instrument registered 13 1/2 degrees, and this was the reading at the ice point for a number of such thermometers discovered by Antinori in 1829. If the members of the Academy had employed the ice-point as a fixed point, it seems unlikely that they would have denoted it by such an odd number of degrees.

Thus the most likely conclusion is that these pioneers of thermometry, in seeking comparable thermometers, depended primarily on the glassblower's skill in attaining the correct relation between the dimensions of the bulb and that of the stem. Thus, for thermometers employing the same liquid, one inch of stem length would always correspond to the same number of degrees provided the ratio of volume of bulb to the square of the stem radius was constant. Although they were undoubtedly familiar with this simple geometric relationship, there is no evidence that they actually used it in making thermometers. Rather, they relied on trial and error, though probably guided by knowledge of the geometrical requirements. <u>After</u> the

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thermometer was completed, they probably immersed it in melting ice to determine whether or not, in the case of the 100 degree thermometer, they had succeeded in making the ice point come at 20 degrees. The advantage of reversing this procedure and allowing the ice bath to determine the location of the 20-degree mark on the stem evidently escaped them, although Sanctorious had employed this method over half a century earlier in calibrating the air thermometer. Thus, in referring to the 300-degree thermometer, they stated that they "can lay down no certain Rule to make it Practice, and often Trials being the only way to effect it, by increasing, and diminishing the size of the Ball, or the bore of the Cane, or the quality of the Liquor, till at length it hits right."[24]

Since such awkward methods were used to attain reproductibility, one naturally wonders how comparable the Florentine thermometers actually were. On this question, we read in the Sagi that a famous glass blower "could make Two or Three, or as many as you desired, of 50 deg. which being encompassed with the same Ambient, should all agree: but that the case was otherwise in those of 100 deg. especially of 300 deg. the smallest Inequality and Error committed, in making one with a large Ball, and small Neck, being very easie to be discovered: so that they will show great Disagreement and inequality when compared together." The claims made in this passage for the 50-degree thermometers agree with the performance of those found in Florence in 1829 by Antinori: these agreed excellently with one another not only at the ice point but at other points on the scale.[25]

Perhaps because they were familiar with Rey's thermometer, the members of the Academy considered "simple spring water" as a possible substitute for alcohol, in the closed liquid thermometer. They rejected the water for three reasons: first, the alcohol responded more quickly to temperature

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changes (we would say it had a lower heat capacity); second, they thought the lower density of alcohol enabled it to rise and fall more easily in the tube; and thirdly, unlike the spring water, the alcohol left no sediment in the tube. In this third objection they revealed that they were unaware of the importance of using distilled water.

To the above objections, they might have added their observations that the usefulness of water as a thermometric substance ceases at its freezing point where it begins to expand instead of contract with extraction of heat, and that, even while still completely liquid, in the neighborhood of the freezing point, it actually undergoes expansion instead of contraction on cooling. These observations were made in their work on artificial freezing which might be described as the first time-temperature experiments, or, equally well, as the first dilatometric observations. A Galilean tube was filled with water to a convenient point in the stem which was graduated. The bulb was immersed in a freezing mixture of snow and salt, and the level of the water in the stem recorded at regular time intervals. Temperature readings were also made at these time intervals but were recognized as being erratic because the thermometer was immersed in the freezing mixture instead of in the water. Incidentally, a slight rise of the liquid in the tube immediately upon immersion in the cooling mixture was correctly interpreted as resulting from the initial thermal contraction of the glass.

Similar studies were made of the thermal contraction of mercury, oil, and many other liquids. Also the relative effectiveness of different freezing mixtures, e.g. salt and ice, sugar and ice, saltpeter and ice, and sal ammoniac and ice, was determined, using comparable thermometers.

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In all of these experiments, the importance of the temperature concept was becoming increasingly evident; so that the thermometer, instead of being regarded as an interesting toy or, at most, a device of interest only to the practicing meteorologist or physician, came to be recognized as an instrument of strategic significance for general scientific investigation.

In the year 1668, a copy of the Sagi was dispatched to the Royal Society in England. However, the closed alcohol thermometer had already been introduced into that country some years before by the Englishman, Robert Boyle, and we find it described, along with many other findings of significance for thermometry, in his famous "New Experiments and Observations touching Cold, or a new Experimental history of Cold begun," first published in 1662.[26]

Boyle spoke of having been shown a closed alcohol thermometer by a traveler from Florence but did not give the date of this meeting. It is uncertain whether he first constructed such thermometers after seeing the Italian thermometer or before. However, regardless of the answer to this question, Boyle's position as a great pioneer in the development of thermometry will remain secure, since this rests primarily on his discussion and appreciation of the general principles of thermometry, supplemented, to be sure, by crucial experiments. Such generalizations were largely lacking in the writings of the Florentine Academy, which confined itself, for the most part, to a report of the experimental results.

In Boyle's time, the open air thermometer was still in common use in England. Indeed, Boyle mentioned at one point that his friends, never having been a closed liquid thermometer, did not believe that such an instrument was possible. Assuming the validity of the doctrine that nature abhors a vacuum and being unaware of the presence of the vapor of the liquid,

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they did not think it possible that the liquid could contract unless the air could enter to fill the vacuum. Boyle, however, was not one to worry about the impossibility of the actual. In constructing closed liquid thermometers, he not only demonstrated their possibility, but also pointed out the following advantages enjoyed by them but not shared by the open air type: independence of barometric pressure, impossibility of spilling the liquid, elimination of evaporation, and ease of immersion in liquids.

Boyle was very cogent in his demonstration of the residual character of temperature; he clearly emphasized the necessity of isolating the air thermometer from the influence of the pressure of the atmosphere. He was familiar with Torricelli's experiment and its correct explanation. Employing the air-pump which had been invented by Otto von Guericke sometime before 1655, he substantiated and extended Torricelli's findings. This was done by introducing a barometer into a bell jar, gradually evacuating the latter, and noting the progressive fall of the mercury. This experiment was reported by Boyle in 1660 in his "New Experiments Physico-Mechanicall touching the Spring of the Air,"[27] and its significance for thermometry was clearly pointed out in the "Experiments touching Cold:" the reading of the open thermometer depends, in part, upon "the height or weight of the atmospherical pillar." This conclusion was substantiated by a series of readings made on a pair of thermometers, identical except that one had a closed stem, the other an open one. The thermometers chosen for the experiment were of the hybrid liquid-air type described by Kircher (cf. Figure 5), alcohol being employed instead of water as the enclosing liquid. Boyle noted the external air temperatures indicated by the two instruments over a period of time and successfully correlated the discrepancies between

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their readings with variable atmospheric pressures observed on the barometer. Indeed, in his discovery in 1662 of his famous law governing the relation between the volume of a mass of air and its pressure or "spring," Boyle made it possible, for the first time, to correct readings of the open air thermometer for variations in the barometer.

4. Alternative Scales and Thermometric Substances: The Principle of Indifference.

The arbitrariness inherent in an elementary temperature scale is well recognized today. This characteristic flows from what may be called the Principle of Indifference. According to this principle, a body's position in the temperature series (scale of hot and cold) is independent of or indifferent to the particular choice of thermometric substance, thermometric property, and functional relation defining temperature in terms of the property.[28]

This arbitrary nature of temperature, particularly with respect to the choice of thermometric substance and manner of graduating the scale, began to make itself evident quite early in the history of thermometry. Thus, we have seen air, water and alcohol alternatively employed as thermometric substance. We have also referred to the wide variety of procedures used to graduate the scale.

However, it is in Boyle's writings that we find for the first time a clear realization of the arbitrariness of temperature scales, both in respect to the choice of thermometric substance and the method of graduating the scale. The operation of the Principle of Indifference was thus appreciated. We have just described experiments in which he used thermometers of the hybrid water-air type. In other experiments, he employed straight air thermometers because of their greater sensitivity. Although he preferred

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alcohol to any other thermometric liquid, he considered water as a possible substitute. The latter was rejected because it froze too easily and because it responded less readily than alcohol to changes of temperature (higher heat capacity). Turpentine was also mentioned as a possible thermometric liquid. Boyle was evidently aware that each of these liquids would expand in its own peculiar way upon application of heat and that each would therefore give a different temperature scale if employed in a thermometer. This was based not on conjecture but on actual measurement of the thermal coefficients of expansion of the liquids. Thus he filled a Galilean tube with turpentine up to a convenient point on the neck, and, noting the extent of fall of the meniscus when the bulb was immersed in ice water, was able to calculate from this and the dimensions of stem and bulb that turpentine contracts by 1/94 of its original volume when it is cooled from room temperature to the freezing point of water. He referred to similar experiments with water but gave no data. He also reported that the mean coefficient of expansion of water was determined by the method based on Archimedes' Principle, i.e. by weighing a glass object first in air and then in water at each of the two temperatures.

Even after choice of thermometric substance had been made, the method of graduating the stem had still to be determined. It was with respect to this feature, the method of graduation, that Boyle's thermometers definitely excelled those of the Florentine Academy. For Boyle clearly advocated the use of a fixed point for this purpose, allowing it to determine the starting point on the scale. As such a fixed point, Boyle considered both the freezing point of water and that of oil of aniseed, thus implying that the choice was largely arbitrary. He actually adopted aniseed oil because it froze at a more convenient temperature than water, and also because he

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entertained some doubt about the constancy of the latter. He suggested that each degree of temperature then be made to correspond to a constant fractional increase in volume of the thermometric substance above its volume at the reference point. The functional relation between temperature t and volume V, advocated by Boyle, may therefore be represented by

$$t = t_R + \frac{V - V_R}{\frac{V_R}{h}}$$

where t_R is the temperature number assigned to the reference point, V_R is the volume at the reference point, and 1/n is the fraction of V_R which is set equal to one degree. Boyle recognized that this procedure, if applied to different sized thermometers containing the same thermometric substance, would make the degree correspond to one and the same length on the stems of the different thermometers only if a constant relation were maintained between the volume of the bulb and the diameter of the stem.

Still another contribution of Boyle to thermometry stemmed from quite a different source, namely, from his promulgation of the modern concept of chemical element and particularly the concept of a chemical compound as contrasted with a physical mixture. For the concept of a pure substance, having a fixed composition and a correspondingly fixed set of properties, was essential for the complete description and determination of both the thermometric substance and those substances whose freezing and boiling points determined the scale. Without such a concept, together with its experimental realization, the various arbitrary choices of thermometric and reference substances would have tended toward anarchy, and the attainment of comparibility in thermometry would have presented an impossible goal.

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In Boyle's time, the four-element theory of Aristotle, together with the so-called three-element theory of Paracelsus, were still widely accepted in scientific circles. According to the first, the four fundamental forms of matter were earth, water, air and fire; these latter, however, were by no means analogous to our modern elements. Thus they were regarded as transmutable, one into the other, by alteration of their properties. Also, since Aristotle believed matter to be perfectly continuous, there was no theoretical basis for de-limiting the number of possible combinations of the four elements which might produce materials encountered in nature or in the laboratory. Indeed, quantitative aspects of these elements, such as their mass, were not emphasized, so that they were often regarded as qualities rather than elements in the modern sense. Similar considerations applied to the three elements, salt, sulfur, and mercury, of Paracelsus, although these gradually came to acquire a substantial character. However, there was no limit to the manner in which the elements might combine to form a compound, so that the idea of a compound having a discrete set of properties and composition was missing.

Boyle's thinking on these subjects, as recorded in his "Skeptical Chymist" (1661),[29] was dominated by his adoption of the atomic theory of Democritus, which had already been revived by Pierre Gassendi. According to Boyle, matter is composed of discrete atoms, there being as many kinds of atoms as there are kinds of elementary substances. Elements are, by definition, incapable of resolution into anything simpler, and this property arises from the fact that their atoms are indestructible. Compounds form by combination of the atoms of different elements to form larger particles. In this connection, he clearly distinguished between a compound of several elements and a physical mixture in which the original elementary properties

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were still to be found. Since the atoms were definitely substantial in character, the Law of Constant or Definite Composition was implied. Boyle emphasized strongly that the number of elementary substances into which all materials could be resolved far exceeded four.

Boyle's ideas on the nature of matter and chemical combination were not fully appreciated for over a hundred years. This was partly a result of authority and prejudice, partly a result of the scarcity of evidence supporting his views. Accumulation of the latter had to await the very slow development of analytical chemistry. In the meantime, the four-element theory continued to be accepted by many as the best working hypothesis, and the concept of the pure substance with fixed composition and properties was slow to take hold.

Particularly important for thermometry is the distinction between a chemical compound and a solution-- a distinction not made by Boyle since he referred to compounds as "perfectly mixed bodies", a term equally applicable to solutions, which are also homogeneous but, unlike compounds, of variable composition. Indeed, the confusion between these two concepts was not entirely cleared away until the first decade of the nineteenth century when, as a result of the famous controversy between Claude Berthollet and Joseph Proust, the universal validity of the Law of Constant Composition was finally established.

Since pure substances did not occur in nature and since the concept of the pure substance, as the goal of a series of purifying operations, was not clearly formulated, most of the materials employed in the early thermometers as well as those used for reference points were either solutions or mixtures subject to accidental variations in composition. A

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solution, of course, would have constituted an acceptable thermometric substance, provided identical samples of it could have been reproduced. Such reproduction, however, would have been generally possible only by means of a description of its composition in terms of pure substances. Thus alcohol was not prepared in the pure, water-free condition until the end of the eighteenth century,[30] so that variations in its composition undoubtedly imposed serious limitations on the attainment of comparable alcohol scales. Mysterious references in the Sagi to variations in the "quality of the liquor" must have referred to this situation. Also, we have seen that the members of the Florentine Academy did not appreciate the importance of using pure water when they considered it for possible use in thermometers. This same oversight probably caused Boyle to doubt the constancy of the freezing point of water and to prefer that of oil of aniseed in its stead. He was evidently unaware that the latter was not a pure substance but a solution and exhibited therefore a composition and freezing point which varied with its source and mode of preparation.

The importance of distilled water for thermometry was recognized by Boyle's colleague and former assistant, Robert Hooke. Adopting Boyle's practice of graduating a thermometer by employment of a single fixed point and equating the degree to a constant fractional increase or decrease in the volume at the fixed point, he recommended that the temperature on the alcohol thermometer be reckoned by assigning zero degrees to the volume at the freezing point of distilled water and by making each degree correspond to a volume change equal to one one-thousandth of the volume at zero. In the same year, 1665, the Dutch scientist, Christian Huyghens, first proposed the boiling point of water as a fixed point, only, however, as an alternative to the freezing point, and not to be used along with the latter.

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Since pure substances with invariable freezing and boiling points were generally unavailable and since, further, it was not always certain that such substances even existed, other, generally unsatisfactory environments were often employed to provide reference points in graduating the scales of the early thermometers. As examples, we may cite the candle flame of Sanctorious, the heat of the summer noon-day sun of the Florentine Academy, and the temperature of the "first night frost" of von Guericke. To this category of "fixed points" may be added the temperatures of deep cellars and mines. Both Galileo and Boyle expressed the belief that the temperature of such places remained quite constant. In a paper presented to the Royal Society in 1693,[31] entitled "On the Expansion and Contraction of Fluids by Heat and Cold, in order to Ascertain the Divisions of the Thermometer, and to make that instrument in all places, without adjusting by a standard," Edmund Halley definitely recommended the temperatures of such places "deep underground" as providing more reliable fixed points than the freezing points of water or oil of aniseed which he considered of doubtful constancy. He also suggested an alternative, the boiling point of pure alcohol. In the same paper, the thermal expansion of several fluids was studied with a view to their possible adoption as thermometric substances. He reported that water expanded 1/26th of its volume in going from room temperature to its boiling point, whereas mercury exhibited a fractional increase of only 1/74th over the same temperature interval. He found the volume of alcohol much more sensitive to temperature since it expanded about 1/12th of the original volume on being heated from room temperature to its boiling point. In spite of this, however, he preferred air to alcohol as thermometric substance, because he though alcohol varied in quality and lost some of its expansive power after continued use.

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The use of two reference points, in place of one, in graduating a thermometer, results in a great practical advantage: it then becomes possible to make different sized thermometers, employing the same thermometric substance, give identical readings without the necessity of determining either the volume of the bulb or the volume or diameter of the stem. For, regardless of the total volume of thermometric substance, the increase in volume in going from the lower fixed point to the higher one will always be the same fraction of the volume at the lower point and therefore will always correspond to the same number of degrees. The functional relation implied between temperature t and volume V in this method of graduating the scale is clearly the following:

$$t = t_{R1} + \frac{V - V_{R1}}{(V_{R2} - V_{R1})/k}$$

where t_{R1} is the temperature number assigned to the lower reference point, V_{R1} the volume at the lower reference point, V_{R2} the volume at the upper reference point, and 1/k the fraction of the difference between these two volumes which is to be set equal to one degree. Also, assuming the stem to be uniform, its volume will be proportional to its length, so that a constant fraction of the total distance travelled by the meniscus in going from one fixed point to the other in the various thermometers will always correspond to the same number of degrees. Thus, if V_o is the volume of the bulb, and l is the length of stem filled by the liquid, we will have $V = sl + V_o$, where s is the constant cross-sectional area of the stem. Substitution of this relation into the equation given above, we have

$$t = t_{R1} + \frac{l - l_{R1}}{(l_{R2} - l_{R1})/k}$$

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Sanctorious, or possibly Sagredo, was evidently the first individual to use this method of graduating the termometer, but this aspect of his work was, as we have seen, either unknown or, at least, unappreciated by both Boyle and the members of the Florentine Academy. The method, however, was revived in 1669 by Honoré Fabri, a French Jesuit, who had been a corresponding member of the Accademia del Cimento. He graduated a Florentine thermometer by marking the position of the meniscus, first when the bulb was surrounded by snow, and again when it was exposed to the "highest summer heat." He divided the intervening distance into eight equal parts. Nineteen years later we find Dalence[32] again employing the two-point method of graduation. He graduated a colored alcohol thermometer, whose bulb had been flattened for better heat conduction, by taking as fixed points the freezing point of water and the melting point of butter, dividing the intervening distance into twenty equal degrees, and logically extrapolating this scale four degrees in either direction. As an alternative method, he recommended the temperature of a mixture of ice and salt and the temperature of a very deep cave as fixed points, the distance between them to be divided into 15 equal degrees with the scale extrapolated another fifteen degrees above the cave temperature.

To Carlo Renaldini, another former member of the Florentine Academy, goes the credit for first using the two-point method of graduation in connection with points which were actually satisfactory. His choice, made in 1694, of the freezing and boiling points of water as the fixed points was a truly epoch-making one. He divided the intervening distance into twelve equal parts.

Sanctorious, early in the seventeenth century, had recognized the

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constancy of normal body temperature, and Borelli is said to have employed blood temperature as a reference point in thermometry in 1685. Isaac Newton[33] also employed body temperature along with the ice point in graduating his linseed oil thermometer. He assigned 0 degrees to the latter and 12 degrees to the former and found that, assuming the degree of heat to be proportional to the expansion of the oil, the boiling point of water came at 34 degrees, the melting point of an alloy containing equal parts of tin and bismuth came at 48 degrees, while lead melted at 96 degrees.

The temperature of the human body was also employed as a fixed point by Daniel Gabriel Fahrenheit, a Dutch instrument maker of German lineage, whose temperature scale in a modified form was destined for wide adoption. This scale, as described in a paper submitted to the Royal Society in 1724,[34] was really over-determined since it was based, according to his description, not on two but three reference points: body temperature, assigned the number 96; the ice point, assigned the number 32; and the temperature of a mixture of ice, water, and sal ammoniac, or alternatively, ice, water, and common salt, to which was assigned the number zero. If we ask ourselves how these three numbers were arrived at, we must conclude that only two of them were arbitrary and the third must have been determined from the other two, although Fahrenheit did not state this to be the case. It is possible that he specified three points so that, if conditions made the use of one infeasible, there would still remain two others to determine the scale. Thus, in referring to the determination of the zero point, he stated that "this experiment succeeds better in winter than in summer."

Fahrenheit used both alcohol and mercury as thermometric substance; and, in this connection, his method of calibration led to an interesting

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discrepancy. For he tacitly supposed that the application of the same two reference points to two thermometers, one employing mercury and the other alcohol, would lead to identical scales. Thus, when confronted with a discrepancy between an alcohol and a mercury thermometer, he attributed this entirely to a difference in the quality of glass used in the two instruments.[35] This supposition rested on the unwarranted assumption that the expansion of mercury was proportional to the expansion of alcohol. In Fahrenheit's day only a few mean coefficients of thermal expansion had been investigated, and his view that the two scales were identical probably went unquestioned.

In advocating the use of mercury as a thermometric substance, Fahrenheit performed a real service to the advance of thermometry. This liquid had been in common use in barometers where, because of its high density, no other liquid could seriously compete with it. It had also been used in small clinical thermometers in England as early as 1684.[36] However, its low thermal expansion had prevented its general adoption in thermometers. Fahrenheit showed that, in spite of this property, very precise and comparable mercury thermometers could be manufactured with sufficient care. An important point in favor of mercury at this time was the circumstance that it, unlike alcohol, was available in a high state of purity.[37] Additional points in its favor arose from its high conductivity, its low vapor pressure, its chemical stability, and its high boiling point.

The high boiling point of mercury was put to good use by Fahrenheit in his determination of the boiling points of high-boiling liquids.[38] Thus, using a mercury thermometer whose scale was extrapolated to 600 degrees, he found that water boiled at 212 degrees, nitric acid at 242 degrees, oil of vitriol at 546 degrees, and fixed oils at temperatures above the

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boiling point of mercury. Particularly significant for the concept of a pure substance was his observation that volatile oils boiled with increasing temperature.

Although Fahrenheit did not employ the boiling point of water as a fixed or reference point, he paved the way for its consistent use by others. We refer to his observation that the boiling point of water increases with increasing barometric pressure. Boyle had already noted that, under the partial vacuum of his air pump, water boiled at a relatively low temperature, but Fahrenheit made the first systematic investigation of this phenomenon. In his hypsobarometer, described in a paper submitted to the Royal Society in 1724,[39] he made use of this property of water to measure barometric pressures. This instrument was an open mercury thermometer, the upper portion of whose stem was quite small in cross-section (cf. Figure 6). At ordinary temperatures, encountered in weather fluctuations, the meniscus came on the lower scale which was graduated in the ordinary manner in degrees. To determine the barometric pressure, the same instrument was immersed in boiling water whereupon the meniscus rose to the constricted region of the stem which was graduated directly in inches of mercury.

Mention should also be made of Fahrenheit's work on the ice point.[34] Boyle and Halley had doubted the constancy of this point. Fahrenheit demonstrated that, in the absence of air, water could indeed be cooled to 15 degrees on his scale. Agitation, however, caused it to freeze at the customary temperature. It is possible, also, that he realized that ordinary, i.e. impure water freezes over a temperature range, since he referred to the ice point as the "commencement of freezing."

Fahrenheit's thermometers were dispatched from Amsterdam, the home of their maker, to cities all over Europe. Because they were very carefully

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constructed and hence exhibited excellent comparability, they attained wide usage, particularly in England. The latter country honored Fahrenheit in 1724 by electing him to the Royal Society.

Boyle's method of employing a single fixed point to determine the scale was reverted to by the aristocratic French scientist, Rene Antoine Ferchault de Reaumur, whose papers on the "Rules for Construction of Thermometers with comparable Scales" appeared in 1730 and 1731.[40] Assigning zero to the ice-point, he defined an increase of one degree as that rise in temperature which would increase the volume of his thermometric substance by one one-thousandth of its volume at the ice point. Reaumur designated as thermometric substance a solution of alcohol and water. He recognized that the exact composition had to be specified, since the thermal expansion of such a liquid would increase with its alcohol content. Finding that the solution, which he employed and which contained about one-fifth water by volume, expanded 80/1000 of its volume at the ice point when heated from the latter to a temperature just below its boiling point, he adopted this observation as a standard of composition, stating that the thermometric liquid should be an aqueous alcohol solution exhibiting just this amount of thermal expansion. Although a much simpler property such as specific gravity might have been employed to designate composition, we must nevertheless admit that Reaumur's specification of composition by means of a physical property was an important contribution to alcohol thermometry. For water-free alcohol was not yet available, and chemical analysis was still in a very rudimentary stage. Although Reaumur went to great pains to determine accurately the volumes of bulb and stem, he completely ignored Fahrenheit's observations of the effect of barometric pressure on boiling point and made no correction for this variable when specifying the thermal expansion of the

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thermometric substance.

In a paper published in 1742 entitled "Observations of Two Fixed Degrees on a Thermometer,"[41] the Swedish astronomer, Andreas Celsius, clearly contrasted the two fundamentsl methods of scaling a thermometer; the single fixed-point method of Boyle, and the two-point method first used by Sanctorious. He recommended the latter method, recognizing that it eliminated the necessity of measuring the volumes of bulb and stem. Celsius' paper is chiefly famous for his adoption as two fixed points, the freezing and boiling points of water, a choice which was destined to receive universal confirmation in later scientific work. The small dependence of the freezing point of water had yet to await another hundred years for its discovery, on barometric pressure so that we find Celsius asserting that this point is entirely independent of weather conditions. On the contrary, he fully recognized the importance of Fahrenheit's discovery of the dependence of the boiling point on the barometer. For purposes of thermometer graduation, he defined the boiling point as the temperature at which water vigorously boiled under mean barometric pressure, which he took as twenty-five and three-hundredths inches of mercury. For pressures deviating from this, he recommended a linear correction, a change of one inch of mercury in the pressure corresponding to a change of one degree in the boiling point. This was a novel and important application of the principle of Residues: elimination of the influence of an extra-temperature factor by calculation rather than by laboratory manipulation. He likewise recommended corrections for the expansion of the glass.

Apparently wishing to avoid the use of negative numbers for commonly encountered meteorological temperatures, Celsius assigned the number 100 to the freezing point of water and zero to the boiling point, dividing the intervening distance into one hundred equal degrees. This method was

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evidently applied mainly to mercury thermometers, although alcohol was also mentioned as a thermometric liquid. In the following year, 1743, Celsius' choice of temperature numbers for the ice point and boiling point was inverted, thus giving a scale which was, except for minor refinements, identical to the modern Centigrade scale.

The prestige of Reaumur evidently accounts for the delay, especially in France, in recognizing the superiority of mercury as a thermometric fluid. In 1772 Andre Deluc successfully advocated the adoption of mercury for this purpose.[41a] Like Celsius, he graduated his scale, using the ice point and the boiling point of water. The influence of Reaumur prevailed, however, in his decision to assign the numbers, zero and 80, respectively, to these two points. Thus was born the modern Reaumur scale, which achieved wide adoption on the Continent.

To Deluc also evidently goes credit for firmly establishing the fact that the thermal expansion of one liquid is not, in general, proportional to that of another. The difference in mean coefficients of expansion of different liquids was recognized quite early in the history of thermometry; and, after Boyle, it became obvious that, if one used the single point method of graduating the scale and identified the degree with a fixed fraction (the same for all liquids) of the volume at the fixed point, then each liquid would give a different scale. There still remained the possibility that the expansion of one liquid was proportional to the other in which case identical scales would be obtained by merely making thermometers, employing the two liquids, coincide at two fixed points. We have noted that Fahrenheit tacitly assumed that this would be the case for thermometers employing alcohol and mercury. Deluc, however, after constructing thermometers of various liquids, including mercury and alcohol, and noting their behavior,

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found that each liquid not only has a mean expansion coefficient but also a law of thermal expansion which is peculiar to itself, so that no simple procedure will suffice to bring the scales of different thermometric liquids into general correspondence. In this connection, Deluc showed that the peculiar behavior of water a few degrees above the freezing point resulted from the existence of an actual maximum in its density.

Many thermometer scales, in addition to those already described, were proposed and used in the eighteenth century.[42] In this respect, the period might be described as a veritable heyday for the Principle of Indifference. Unfortunately, however, the requirements of comparability and reproducibility were frequently not satisfied. Thus the biologist, Stephen Hales, in greenhouse experiments reported in 1727, used a thermometer, one of whose fixed points was described as the temperature of the hottest water which could be endured by the hand.[43] This ambiguous temperature was assigned the number 90. Again, in 1741, Jacques Micheli du Crest, defining a scale widely used in Switzerland, chose as fixed points for his "universal" alcohol thermometer the temperatures of boiling water and that of the cellar of the Paris observatory. He pretentiously referred to the latter as the "temperature of the terrestrial globe." Celsius, in the paper referred to, complained that the Florentine thermometers still in common use were unsatisfactory because of their poor comparability. Such thermometers, having their zero at the middle of the tube to indicate "temperate" air, were still employed as late as 1741 in Danzig for meteorological observations.

5. The Revival of Gas Thermometry: The Quest for the Most Rational Scale.

The Principle of Indifference, according to which the position of a body in the temperature series is independent of the particular thermometric substance employed in the thermometer used to determine that position, is

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today properly recognized as arising from the inherent nature of temperature. Indeed, it is this principle which provides the temperature concept with its universality.[44] However, this point of view was by no means prevalent among the early workers in thermometry nor was it generally accepted by the scientific world before the establishment of the First Law of Thermodynamics in the middle of the nineteenth century.

As already pointed out, the fact that different thermometric substances gave different scales, any one of which sufficed for practical thermometry, was commonly recognized after the time of Boyle. This situation, however, in which no particular scale seemed to have logical preference over any other, was often viewed with misgiving. The basis for this feeling was the theoretical conviction that heat was substantial in character and therefore capable of quantitative formulation in terms either of the amount of heat fluid in a body (theory of fire matter or caloric) or in the magnitude of the motion of its particles (kinetic theory of heat). For, this being the case, it was thought there ought to exist a single, "true" temperature scale whose readings would either directly represent or be simply related to the amount of heat in a body.

Thus, until the fall of the caloric theory in the nineteenth century, the Principle of Indifference was regarded as an empirical law of practical thermometry rather than as a first principle, and the arbitrariness of temperature scales as a feature to be eliminated by the march of science rather than as an essential characteristic of the temperature concept. There was thus posed the problem of the establishment of the most rational scale--a problem which engaged many of the best minds of the period. It was in connection with the culmination of the search for the true scale that the gas thermometer, after a century of unpopularity, returned to the scene to provide a temperature scale which, if not the most rational, at least

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seemed to have better claim to that title than any other.

Regret about the arbitrariness of temperature scales and the implied hope that time would remedy this situation were already expressed in the writings of Boyle. For there we read: "I consider that we are very much to seek for a standard, or certain measure of cold, as we have settled standards for weight and magnitude and time; so that when a man mentions an acre, or an ounce, or an hour, they that hear him know what he means and can easily exhibit the same measure: but as for the degrees of cold... we have as yet no certain and practicable way of determining them."[45] This passage clearly reveals that Boyle did not consider any arbitrary scale as constituting a satisfactory standard scale. To command universal adoption, a standard scale, he thought, should provide a "certain measure" of heat. That this was indeed his view is corroborated in another passage where he complained that the "best" proportion between the diameter of the tube and that of the bulb was unknown, also that the question as to the "best" thermometric liquid was <u>as yet</u> unanswered.

Thinking along the same line in 1693, Halley observed that any thermometer would suffice to determine whether or not two bodies were equally hot and, if they were not, which was the hotter; but that no thermometer readings permitted us to say that one body was e.g. twice as hot as another.[46] In other words, the temperature of a body, as recorded on an arbitrary temperature scale, is not a quantity but merely an order number referring to the position of the body in the temperature series.[47] According to Halley, however, this state of affairs is not a result of the nature of temperature but is incurred by the fact that we are ignorant of the "cause of expansion of fluids by heat."

In the writings of Newton, 1701, we find regret about the unavailability

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of a true temperature scale replaced by the claim that such an ideal scale was already provided by his own linseed oil thermometer. This claim was put forward in connection with the discovery of his famous law of cooling, according to which the rate of cooling of a hot body, when placed in a uniform draft of air, was proportional to the excess of its temperature over that of the air. He reasoned that since, in equal times, equal quantities of air particles came in contact with the body, equally many air particles were heated by the body by an amount proportional to the "heat" of the body. Hence the "heat loss" of the body must have been proportional to the "heat" of the body. But this loss was actually proportional to the readings of the linseed oil thermometer. Hence, said Newton, the "heat" of the body must be proportional to the readings of this thermometer.[48]

We note from this argument that the concepts of temperature and heat were by no means clearly differentiated as yet, also that the essential arbitrariness of temperature scales was not appreciated. Thus, in stating that the "heat loss" of the body was proportional to the "heat" (temperature) of the iron, Newton had already naively defined a thermometer scale. Whether or not this scale agreed with some other scale, e.g., that of the linseed oil thermometer, could only have been determined by experiments unknown to Newton.

The confusion between temperature and heat, present in the thought of Newton, was also shared by Boyle, as is evident from the quoted passage in which he assumed temperature to be a quantity analogous to weight, length, or time. Indeed, the failure to distinguish between these two concepts was frequently encountered until the latter part of the eighteenth century when Joseph Black finally distinguished between quantity of heat and intensity of heat or temperature.

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In the logical system known today as "classical thermodynamics," quantity of heat is defined in terms of an arbitrary temperature scale. The reverse procedure, that of determining the temperature scale by arbitrary units of heat, was implied by a practice first adopted by Renaldini in 1694--the graduation of the thermometer by mixture experiments. We have already referred to his graduation of the Florentine thermometer by division of the distance between the ice point and the boiling point of water into twelve equal parts. And an alternative method, he used mixture experiments, the first degree above the ice point corresponding to the temperature resulting from mixing eleven parts of cold (probably freezing) water with one part of boiling water, the second degree corresponding to the temperature of a mixture of ten parts of cold water and two of boiling water, and so on.[49]

The same method was applied by Brook Taylor[50] in 1723 to Newton's linseed oil thermometer. Finding that the readings of this thermometer were proportional to the quantity of boiling water in the mixtures, he concluded that Newton's scale did indeed have a just claim to rationality.

In 1760 the same procedure was applied to mercury thermometers by Joseph Black[51] and a dozen years later by Andre Deluc[52] in France. Their conclusion, in Deluc's words, was that "mercury is of all liquids hitherto employed in the thermometer, the one which most exactly measures differences of heat by differences in its volume."

The arbitrariness inherent in this method of graduating a thermometer was evidently not yet appreciated, though it would have revealed itself had these mixture experiments been repeated with liquids other than water. Only after the researches of Dulong and Petit established the general variability of heat capacity with temperature, in the second decade of the

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nineteenth century, did this arbitrariness attain full realization.

In fact, as we shall see, it was the gas thermometer scale which Dulong and Petit, as a result of their classical researches, put forward as the most likely candidate for the rational scale. Their point of view, however, had to await the identification of different gases and the subsequent discovery of the marked similarity in their thermal behavior--a process which did not complete itself until the appearance of the work of John Dalton and Gay-Lussac about 1800.

We have cited the close association of air with "fire" in the Greek four-element theory as one of the probable reasons for the early development of the air thermometer. This same association may partly explain the fact, that, even after the practical superiority of liquid instruments had been demonstrated by Boyle and the Florentine Academicians and long before the similarity in thermal behavior of different gases had been established, the air thermometer continued to be advocated from time to time.

The fundamental theoretical objection to the air thermometer, as emphasized by Boyle, had been the susceptibility of the instrument to variations in barometric pressure. This, however, was readily taken care of by closing that part of the apparatus containing the enclosing liquid. Thus Joh. Christoph Sturm described in 1676 a two-bulbed or J-type thermometer identical to that shown by Leurechon (cf. Fig. 4) except that both bulbs were sealed.[53] This would best be called a differential thermometer, since the position of the liquid in the J-tube depended on the difference in the temperatures of the air in the two bulbs.

The closed air thermometer advocated by Dalence in 1688 was also of the J-type and similar in design to that of Kircher (cf. Fig. 5).[54] However, mercury was used instead of water as enclosing liquid, the side tube was

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sealed, and the space above the mercury evacuated. In the same year, Guillaume Ammontons also described an air thermometer in which the expansion of the heated air pushed mercury into an evacuated space.[55] This thermometer is represented in Figure 7. A Torricelian vacuum existed in the bulb A below which mercury extended through the J-tube and into the bulb C. Above the mercury and extending up into a portion of the narrow tube D, was a layer of colored potash solution. Above the latter an oil layer extended to the bottom of bulb B which contained the air. The temperature of the air was identified with the location of the oil-potash boundry in the narrow tube. Air thermometers of this design were strongly recommended at this time by the French instrument maker, Hubin, who emphasized their great sensitivity compared to the new Florentine thermometers employing alcohol.[56]

Elimination of the influence of a variable barometric pressure on the readings of the open air thermometer was accomplished by von Guericke in 1672, not by closing the instrument, but by varying the amount of air in the bulb by means of a valve attached to the latter. Alcohol was the enclosing liquid, and the quantity of air in the bulb was frequently adjusted so that, regardless of the barometric pressure, the level of the alcohol in the side tube always came to the same position on the scale when the bulb was exposed to the "first night frost."[57]

Up until the end of the seventeenth century, the volume of the enclosed air was always regarded as the thermometric property in the air thermometer. Actually, the design of these instruments was such that even though external air pressure was eliminated, the pressure of the air was not held constant, but varied with the difference in the level of the enclosing liquid. Thus the position of the liquid in the tube might equally well have referred to the pressure of the confined air since this increased with the volume when the air was heated.

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However, the concept of the pressure or "spring" of air was not formulated until the time of Boyle. Even after this formulation, volume rather than pressure continued throughout the seventeenth century to be regarded as the sole thermometric property for air thermometers. This was doubtless because volume seemed to be a simpler property than pressure, and also because it appeared to be more intimately associated with the supposed substantial nature of heat.

This being the case, it seems paradoxical that the first air thermometer employing a "pure" thermometric property --one unaffected by the simultaneous variation in another property --was not a constant pressure but a constant volume instrument. For it was such an air thermometer that Guillaume Amontons proposed in his epoch-making paper of 1702.[58] Indeed, Amontons' Amontonser instrument, already described, was very nearly a constant-volume one because of the use of mercury in the side tube. Nevertheless, the volume change, small as it was, had been regarded as indicative of temperature. In the new J-type instrument (cf. Fig. 8) mercury was again employed as enclosing fluid. Because the diameter of the bulb containing the air was about three and a quarter inches or fifty-eight times the diameter of the side tube, the volume of the air on heating remained essentially constant, and its pressure was taken as representing its temperature. Since the side tube was open, the pressure was correctly computed as the sum of the barometric height and the difference of mercury levels in the bulb and side tube.

In Amontons' earlier instrument equal temperature increments were identified with equal volume increments (though not at constant pressure) which, in turn, were assumed to correspond to equal increments in length of the narrow tube through which the air expanded. Amontons recognized the difficulty of making a long narrow tube of uniform diameter, and, for this

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reason, claimed superiority for his new thermometer since, in the latter, small variations in the diameter of the side tube had very little effect on the pressure reading.

Amontons had begun his experiments on the effect of heating on air pressure with the tacit assumption that the increase in pressure experienced by "cold" air when exposed to boiling water would be independent of the initial pressure and mass of the air. He soon found this not to be the case, but that, instead, it was the ratio of the final pressure to the initial pressure which was always the same. He reported for the value of this ratio the fraction 4/3. Thus he concluded that, in passing at constant volume from a certain lower temperature to a certain higher temperature the pressure of any quantity of air always increased by a constant fraction of its intial pressure.

This discovery made it possible for Amontons to completely determine the scale of his air pressure thermometer by merely specifying the pressure at a single fixed point. He chose for this fixed point the boiling point of water and required that at this temperature the air in the bulb should be under a pressure of 73 inches of mercury. The figure 73 was evidently no more than an accidental result of the circumstances that 28 inches of mercury was adopted as the standard barometric pressure and that a difference of 45 inches in mercury levels corresponded to the capacity of the side tube. On this temperature scale according to which temperature was identified with the pressure of the enclosed air in inches of mercury, the ice point, according to Amontons, came at 51-1/2. Of course, areading on this instrument had to be accompanied by a simultaneous reading of the barometer and a correction made for any departure of the latter from 28 inches.

The proportionality of air pressure, measured at constant volume to

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temperature originally came to Amontons as an experimental law, but he soon realized that it was a necessary consequence of Boyle's Law. Thus, at the lower reference point, Boyle's Law gives $p_0V_0 = k_0m$ where m is the mass of the air, and at the upper reference point, assuming Boyle's Law to still hold, we have, $p_1V_1 = k_1m$. In the approximately constant pressure air thermometer, division of one equation by the other gives k_1/k_2 for the value of the volume ratio. However, if the volume be held constant division will also give k_1/k_2 as the value of the pressure ratio so that it is independent of p_1 and V_1. Thus Amontons evidently arrived at the important realization that constant-volume and constant-pressure air thermometers should give the same scale provided the same method of graduation be applied to each of them.

A logical implication of the idea of a true temperature scale is the concept of the "absolute zero" of temperature where a body is completely devoid of heat. Thus the quest for the most rational temperature scale was frequently associated with the identification of the true zero of temperature. Amontons was one of the first to concern himself with this question. In a later paper[59] he subscribed to the kinetic view that heat was associated with the motion of the "fire particles" of a body. The lowest attainable temperature he thought should correspond to a state where this motion had ceased and where the body could no longer exert a pressure against its surroundings. He thus arrived at the theoretical point where his own air pressure thermometer provided the true temperature scale.

Because of its large size, Amontons' thermometer was rather unsuitable for practical use. The inventor himself intended it to be employed primarily as a standard to calibrate alcohol thermometers. However, such an instrument was used by the Marquis of Poleni in meteorological observations extending from 1725 to 1736. In the meantime, Jacob Hermann had, in 1716, suggested

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that the need for the barometer correction might be eliminated by sealing the side tube. This improvement was adopted three years later in the thermometer used by Balthaser for weather temperatures.

In spite of the important theoretical advance in air thermometry made by Amontons, air thermometers continued to give way to liquid thermometers throughout the eighteenth century. In Herman Boerhaave's popular textbook published in 1732 we still find the air thermometer described along with Fahrenheit's mercury thermometer together with the claim that the former, because of its sensitivity, is particularly fit for discovering "the quantity of fire."[60] On the contrary, Joseph Black, one of the leading workers in the field of thermal phenomena in the latter part of the century, wrote an extended discussion of thermometry in which the air thermometer was not even mentioned.[61]

Ample evidence for the poor performance of air thermometers in the eighteenth century, in spite of their theoretical superiority, is found in the wide variation among the values reported by different investigators for the fractional increase in volume of air between the ice point and the boiling point of water. After Amontons work, it was obvious that, so long as Boyle's law held, this quantity might be measured either directly by noting the increase in volume at constant pressure or indirectly by observing the increase in pressure at constant volume. Amontons himself found a value of 0.380 for the fractional increase. The measurement was repeated many times in the following century with results varying from 0.333 to 0.500 and even higher.[62] This variation meant that the air thermometers in use during this period gave scales which were far from identical;

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such thermometers were therefore quite inadequate for serious scientific work and particularly for the precise thermal measurements of Lavoisier, Laplace, Black, and others in the latter part of the century.

Only after the more careful researches of John Dalton and, particularly, Gay-Lussac, performed a full one hundred years after that of Amontons, did the most likely cause of variation among air thermometer scales establish itself. These workers found that different samples of air would indeed exhibit identical thermal expansions provided sufficient care were taken to remove moisture from both air and bulb, a precaution of far greater significance than in the case of liquid thermometers. By this time, however, the fact that the air thermometer could be made to perform consistently was beginning to be overshadowed by a discovery of much greater import for the quest for the most rational scale--namely, that air was only one of a great class of gaseous bodies, all of which, though differing markedly in chemical composition, conformed, at least very approximately, to one and the same law of thermal expansion.

It is important to realize that this law, known in English-speaking countries as "Charles Law," according to which the volume of each gas at constant pressure is one and the same linear function of the temperature, could have only the status of a definition so long as air was the sole known gas and temperatures were reckoned from the air thermometer. For there could be no question of different gases conforming to the same law when only one gas was available for testing: nor could the law governing

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the thermal expansion of air be a conceivable object of investigation if its increase in volume was already not merely proportional but, by definition, identical to its temperature. To be sure, there existed the discrepancy, already pointed out, that, in the early air thermometers, purporting to identify temperature with air volume, the pressure was not held constant. However, in the open type instruments, the fractional change in the pressure was small, so that in these, at least, the definition of temperature was approximately tantamount to Charles Law.

Once liquid thermometers came into general use, the question of the law of the thermal expansion of air relative to the temperature readings of such an instrument became a possible subject of investigation. However, not until near the end of the eighteenth century does this problem appear to have attracted attention. Instead, studies on the thermal expansion of air were largely limited to measurements of the net or mean expansion between the ice point and the boiling point of water, with the widely varying results already mentioned.

On the other hand, the other aspect of Charles Law, relating to the identical thermal behavior of <u>different</u> gases, had to await the discovery and identification of these gases as well as the mastery of the techniques of their manipulation. Here, once again, we see the progress of thermometry dependent upon and limited by the progress of chemistry.

The earliest workers in chemistry tended to concentrate their attention on liquids and solids and to ignore the various gases resulting from different chemical reactions. This was undoubtedly because

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gases seemed intangible, compared with liquids and solids and, in any case, were more difficult to isolate and study. The observation that such gases often exhibited marked differences in properties, such as color and odor, was readily explained by the supposition that they were different forms of air or, perhaps mixtures of air with various solid or liquid impurities.

In fact, the generic term "gas" did not exist until its introduction in the first half of the seventeenth century by J. B. van Helmont whose works were first published in 1644. Although this chemist appears to have followed his predecessors in regarding these gases as varieties of air, nevertheless, by preparing them in various ways, by noting qualitatively their chemical and physical properties, and by assigning them different names, he initiated that process of classification and identification which culminated, toward the end of the following century, in their recognition as chemical individuals. Thus he showed that carbon dioxide is a common product of the burning of charcoal and various organic substances, the fermentation of wine and beer, and the action of acids on crab shells, containing carbonates. He named it "gas silvestre" ("wild" gas), referring to his belief that it could not be condensed or contained. However, he also applied this same name to oxides of nitrogen, prepared by heating potassium nitrate or by the action of silver on nitric acid, and to sulfur dioxide, the product of the burning of sulfur. Van Helmont knew that carbon dioxide would not support combustion and contrasted it with the gas resulting from the action of metals on acids which we now call hydrogen and which he called "inflam-

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mable gas", a term he also applied to other combustible gases.

Van Helmont did not suceed in isolating the gases which he prepared or confining them in containers, so that all of them, as obtained by him, were contaminated with air. In fact, he was of the opinion that such gases were by nature incapable of confinement by virtue of their "wild" character. The first step in the solution of this problem of the collection of gases was made by Boyle who in 1661 first described the collection of pure hydrogen by inverting a bottle of dilute sulfuric acid containing several iron nails in a vessel filled with acid. Eight years later John Mayow showed how a gas could be transferred from one bottle to another by opening the mouth of the bottle containing the gas under the mouth of the other bottle which had been filled with and inverted in water. Mayow emphasized the importance of pressure in measuring gas volumes and recommended that volumes be brought to atmospheric pressure by equalizing the water levels inside and outside the bottle. In this connection, he found that Boyle's law, which had been applied only to air, also held for hydrogen and nitric oxide. Boerhaave made use of this discovery, sometime before 1732, when he conducted gas-producing reactions <u>in vacuuo</u>, noted the increase in pressure, and then employed Boyle's law to reduce all volumes to the same pressure.

It was only a short step from Boyle's gas-collecting apparatus to the pneumatic trough, described by Stephen Hales in 1727, in which gases from an exterior generator were led by means of a tube into the mouth of a bottle, which was filled with water and inverted in the

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trough. Using this collection technique, Hales heated definite weights of a wide variety of solids and measured the volume of gas evolved in each case. He also noted the diminution in volume accompanying the solution of certain gases as they stood over water. In this way, Hales produced and collected many of the common gases, except those which were extremely soluble in water.

These improvements in the technique of manipulating gases greatly facilitated the task of observing their physical and chemical properties. Nevertheless most chemists continued to regard them as different varieties of air. Their recognition as chemical individuals, toward the end of the eighteenth century, came only as the culmination of a long and painful evolution, involving such complex historical processes as the rise and fall of the phlogiston theory, the elucidation of the function of air in respiration and combustion, the increased emphasis on weight relationships in chemical reactions, and the development of the distinction between elements, compounds, and mixtures.

By 1774, when the English chemist, Joseph Priestley, published the first volume of his Experiments and Observations on Different Kinds of Air, the different gases were beginning to be recognized as distinct substances, although they were still referred to as "airs", Van Helmont's generic term "gas" not yet having been adopted. Priestley, whose name is closely associated with the discovery of oxygen, introduced an important innovation in gas manipulation technique when he substituted mercury for water in the pneumatic trough. With this procedure he was able to generate and preserve such water-soluble gases

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as sulfur dioxide, hydrogen chloride, and ammonia, which had escaped his predecessors.

However, Priestley's significance for thermometry lies primarily in his pioneer work on the thermal expansion of different gases.[62a] The apparatus for these measurements consisted of an inverted bottle equipped with a stopper through which a side tube, bent to an unspecified angle with the horizontal, just protruded. The gas to be tested was confined in the inverted bottle over mercury. The thermal expansion of the gas caused the mercury to flow to a higher level in the tube. He reported the thermal expansions in terms of the inches of tube length traversed by the mercury when a certain volume of the gas was heated through four degrees Reaumur. These were obviously not constant-pressure experiments, and as Gay-Lussac noted later, Priestley's data could not be compared with that of others since he failed to give the angle of inclination of the tube and its capacity relative to that of the bottle. Nevertheless his measurements were presumably comparable with each other and hence should have revealed similar thermal behavior for different gases. Actually, he reported widely different expansions for the ten gases which he investigated. He obtained the following values, listed in the order of increasing expansions: air, 1.32: hydrogen chloride, 1.33: nitrogen, 1.65: nitric oxide, 2.02: hydrogen, 2.05: carbon dioxide, 2.20: oxygen, 2.21, sulfur dioxide, 2.37: hydrogen fluoride, 2.83: and ammonia, 4.75. The presence in his gas samples of varying quantities of moisture, which vaporized on heating, is suspected as a likely explanation of these differences in thermal expansion reported by Priestley. This suspicion is strengthened by the very high value, 0.9375, for the fractional increase in volume of

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air between the ice point and the boiling point of water, which he obtained from another experiment.[63]

Unsatisfactory as Priestley's measurements were, they served to draw attention to the problem. Monge, Berthollet, and Van der Monde, in 1786, investigated the thermal expansion of air and hydrogen and found nearly the same behavior for both gases. This agreement must have been largely accidental, however, as their values were quite high, again suggesting wet gases. Their results gave, for the fractional increase in volume in going from the ice point to the boiling point, 0.433 for air and 0.442 for hydrogen.[64] G. G. Schmidt obtained 0.357 for air and 0.321 for oxygen but much higher values for hydrogen, carbon dioxide, and nitrogen, namely, 0.440, 0.435, 0.478, respectively.[65]

The experiments of Guyton de Morveau and Duvernois, reported in 1790, constituted an attempt to determine, not merely the net expansion of each gas between two fixed points, but also the law of expansion relative to the Reaumur scale, obeyed by the gas within this temperature interval. Each gas, initially confined in a flask in an ice bath, was heated at approximately constant pressure through successive intervals of twenty degrees Reaumur up to the boiling point of water. The gas expelled during each heating stage was collected over mercury, cooled to the ice point, and its volume measured. However, not only did they report, for different gases, widely different values of the net fractional increase in volume between the ice point and the boiling point, but they also found, for each gas, a marked increase in

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the rate of thermal expansion with increasing temperature, a result probably caused by the progressive vaporization of moisture at higher temperatures.

Credit for first establishing the essential identity of the mean coefficients of expansion of a number of the common gases evidently should go to the French physicist, J. A. C. Charles, inventor of the hydrogen balloon. Unfortunately, his experiments, carried out around 1787, were not published and evidently remained little known until briefly described by Gay-Lussac in the historical introduction to his famous paper of 1802 on the same subject. In Charles' experiments, the gas to be investigated was confined in a flask over mercury. Sealed into this flask with its open end extending down into the mercury was a barometer tube having a long evacuated space above the mercury. The increase in the mercurial height in the barometer, incurred by heating the gas from the ice point to the boiling point of water, was, following Amontons, taken as a measure of the dilatation of gas. In this way Charles found the same net dilatation for oxygen, nitrogen, hydrogen, carbon dioxide, and air but varying values for certain of the water-soluble gases. According to Gay Lussac, the diameter of Charles' barometer tube was too large for the capacity of his flask, so that the increase in pressure fell short of what would have been observed had the volume been kept constant.

The paper by Charles' countryman, Gay-Lussac, which was published in 1802 under the title, "Investigations of the Dilatations of Gases and Vapors," [67] constituted a definite climax in the study of the thermal expansion of gases. It was characterized bybreadth of historical perspective, by ingenuity of experimental methods, and, above all,

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by the conclusion that all gases do exhibit, at least very approximately the same mean coefficient of expansion between the ice point and the steam point.

By this time, the hypothesis that heat is an imponderable fluid, under the name of the "caloric theory," had, as a result of its success in quantitatively correlating many types of thermal phenomena, attained wide acceptance and great prestige. As a result, the quest for the most rational temperature scale, since it constituted a search for a true measure of caloric, received still greater emphasis. Referring to this quest in the opening lines of his paper, Gay-Lussac admitted that "the thermometer, as used today, does not give exact indications of heat because one does not yet know what relation exists between the degrees of the thermometer and the quantities of heat which they may indicate." Again, he remarked that there was no proof for the claim that equal numbers of degrees on a thermometer correspond to equal increases in the pressure of caloric.

Gay-Lussac did not declare himself as to the bearing which the thermal expansion of gases might have on these theoretical questions. He did, however, point out the significance of such studies in practical problems dealing with the dependence of humidity on temperature, the thermal relations in heat engines, and the effect of temperature on the relation between barometric pressure and altitude.

Several methods for measuring the thermal expansion of gases were described by Gay-Lussac. In the first of these, a bulb equipped with a stopcock was filled with the gas at atmospheric pressure in a bath of melting ice. The bulb was then heated at constant pressure to the

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boiling point of water, a portion of the gas being expelled through the open stopcock. The stopcock was then closed, the flask and contents re-cooled to the ice point, and the stopcock opened under water. The volume of the water which entered was equal to the increase in volume which the gas remaining in the flask would have experienced as a result of heating. Gay-Lussac claimed special accuracy for this method because all volumes were obtained from weighing operations. Thus the volume which the gas remaining in the flask occupied at the ice point was calculated as the excess of the weight of the flask completely filled with water over its weight when containing the water which entered after cooling, and the increase in volume which this quantity of gas would have experienced on heating to the steam point as the excess of the latter weight over the weight of the empty flask.

In a modified procedure Gay-Lussac used the apparatus shown in Figure 9 in which no stopcock was required. Upon heating from the ice point to the boiling point, while maintaining the same mercury level inside and outside the flask, a portion of the gas was expelled through the delivery tube. The delivery tube was then withdrawn and the flask returned to the ice point. After adjusting to atmospheric pressure, the decrease in volume was read directly on the graduated neck of the flask.

In the historical survey that preceded the account of his own work, Gay-Lussac concluded that the presence of moisture had been an important cause of discrepancies in the work of his predecessors. Accordingly, he himself took great pains to remove moisture from both apparatus and

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gas. All gases were collected by displacement of mercury in the pneumatic trough.

After repeated trials with these methods, Gay-Lussac reported the following average values for the fractional increase in volume between the two fixed points: air, 0.3750; hydrogen, 0.3752; oxygen, 0.3748; and nitrogen, 0.3749. He thought that the differences among these values were sufficiently small to be attributed to experimental error.

The expansion coefficients for nitric oxide and the water-soluble gases, carbon dioxide, hydrogen chloride, sulfur dioxide, and ammonia, were not determined directly but by comparison with air. Equal quantities of air and the gas to be tested were introduced into a pair of identical graduated tubes inverted in mercury. The tubes were heated simultaneously and the thermal expansions of the two gases compared. From such experiments, Gay-Lussac concluded that nitric oxide and the water soluble gases exhibited the same expansion coefficients as air and the other gases.

In experiments with moist air and ether, he attempted to extend these conclusions to vapors. He verified a previous observation of deSaussure that moist air, so long as it contained no liquid water, exhibited the same thermal expansion as dry air. He also found that ether vapor expanded at the same rate as air between 60° and 100° Reaumur, although a discrepancy was observed at lower temperatures in the neighborhood of the boiling point of ether.

Generalizing, Gay-Lussac concluded that all gases and vapors expanded by the same fraction of their initial volume on being heated

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through equal numbers of degrees from a common temperature. As the most probable value of the mean coefficient of expansion between the ice point and the boiling point of water, he gave 0.00375 per degree Centigrade.

In the meantime, in England, John Dalton, working simultaneously with, but independently of Gay-Lussac, arrived at similar conclusions.[68] His procedure consisted in confining the gas sample over mercury in a barometer tube where it was heated from room temperature to the boiling point of water. Although he gave no data except for air, he reported that all gases investigated expanded in the same way with increasing temperature. Presumably using Boyle's law to reduce all volumes to the same pressure, he found that 1000 volumes of atmospheric air on heating from 55° F. to 212° F., expanded to 1321 volumes. Allowing 4 parts for the expansion of the glass, this gave a dilatation of 325 parts per 1000 for an increase of 157 degrees on the Fahrenheit scale of the mercury thermometer. To compare this with Gay-Lussac's results, let x equal the mean coefficient of expansion per degree Centigrade between the ice point and the boiling point. Since 55° F. equals 12.78° C., we have $(1 + 12.78\ x) / (1 + 100\ x) = 1000/1325$. This yields $x = 0.00392$ or a fractional increase of volume of 0.3912 compared with Gay-Lussac's value of 0.375. Although Dalton was aware of the importance of eliminating moisture, his higher value showed that he was less successful in accomplishing this than was Gay-Lussac.

Dalton associated the identical thermal expansions of gases with

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his belief that, in them, the expansion depended only on heat, whereas, in solids and liquids, this was determined by both heat and chemical affinity. Consequently, he thought that general laws, concerning the amount and nature of heat, would follow more readily from observations on gases than from observations on liquids and solids. Thus, Dalton arrived at the logical position from which gas thermometers were viewed as providing the most rational temperature scale.

This being the case, the question of whether or not the thermal expansion of air was proportional to the readings of the mercury thermometer was of considerable interest. Dalton himself thought there existed a slight departure from proportionality: he reported that, for the first 77 1/2 degrees above 55° F., 1000 parts of air expanded 167 parts but, for the next 77 1/2 degrees, it expanded only 158 parts. Although this result was far closer to the truth than that previously reported by deMorveau and Duvernois, it was not as correct as that established by Gay-Lussac sometime before 1815.[69] The latter placed a mercury thermometer and an air thermometer together in a heating bath and made simultaneous readings on the two instruments while elevating the temperature from the ice point to the boiling point of water. The air thermometer was an open Galilean tube in which the air was confined by a short column of mercury which also served as index. The air thermometer readings were corrected for any variation in barometric pressure during the experiment. To minimize temperature differences between the two thermometers, both were mounted horizontally at the same level in the bath. After repeated trials and

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after correcting all observations for the expansion of glass, Gay-Lussac concluded that, in this temperature range, the thermal expansion of air was exactly proportional to that of mercury. This meant that, if the two thermometers were made to correspond at two fixed points, they would then furnish identical scales. Or, regarding temperature as defined by the expansion of mercury, it meant that Charles Law, at least for air, was finally established.

For those who, like Amontons, associated the "absolute zero" of temperature with that point on the scale at which gas pressure, measured at constant volume, became zero, Gay-Lussac's work now provided a more sound basis for calculation. For assuming Boyle's Law, the pressure and volume coefficients were equal, so that for each degree Centigrade fall below the ice point, the gas would decrease in pressure by the fraction, 0.00375, of its pressure at the ice point. The absolute zero, or temperature of vanishing pressure, would thus come at (1/0.00375 = 267 Centigrade degrees below the ice point.

Dalton, on the other hand, thought he could deduce an entirely different value of the absolute zero from his data on the thermal expansion of gases. By a hazy reasoning process, he concluded that the absolute temperature, since it measured the "repulsive force" of the particles had to be proportional to the cube root of the total volume occupied by the gas. Thus, from his data, the absolute temperature of the gas at 212° F. stood to its value at 55° F. as the cube root of 1325 stood to the cube root of 1000. This gave the result that the absolute zero was 1727 Fahrenheit degrees below the boiling point of water.

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These were by no means the only values of the absolute zero proposed at this time. An entirely different calculation, often employed, was based on the view that the latent heat of fusion of a substance represented the excess of heat present in the liquid over that in the solid at the same temperature and that the heat capacities of solid and liquid were invariable with respect to temperature measured on the mercury thermometer. Thus if c' and c denoted the heat capacities of liquid and solid at the absolute temperature (reckoned from the absolute zero) t of the freezing point, then the heat of fusion q would be given by $q = c't - ct$. Substitution of measured values of q, c', and c into this relation permitted the calculation of t. Applying this method in 1788 to the heat of fusion of ice, Irvine and Crawford located the temperature, where water and ice contained no caloric, at -160° C. Gadolin in 1792 found that a similar calculation applied to wax yielded -480° C. for the lowest attainable temperature; and Dalton himself applied it to mercury to get -2021 C. for this very elusive quantity. Still other "absolute zeros" were calculated from the heat developed in mixture experiments and from the heat of chemical reactions.

Permeating this confused picture, the famous paper of Dulong and Petit, "On the Measure of Temperatures and on the Laws of the Communication of Heat," [70] published in 1817, came as a great clarifying influence. In their work, we see the problem of the most rational temperature scale viewed with the greatest generality consistent with the progress of science at this time. Also, on the purely experimental

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side, the paper was a true milestone in the history of thermometry, introducing, as it did, new and effective methods for the measurement of thermal expansion, particularly of liquids and solids.

The early portion of their paper was concerned with refining and extending to wider temperature limits the work of Gay-Lussac on the comparison of the air and mercury thermometers. They applied Gay-Lussac's first method [71] for the thermal expansion of gases (cf. p. 57) to temperatures ranging from the freezing point of mercury to its normal boiling point, subjecting the mercury to pressure to prevent the actual occurrence of boiling. In this way, they substantiated Gay-Lussac's law of proportionality between the expansion of air and the expansion of mercury for temperatures up to the boiling point of water. However they found an increasing departure from this law at higher temperatures as the following table shows:

Centigrade Temperature from Mercury Thermometer	Volume of Air Relative to Volume at Ice Point	Centigrade Temperature from Air Thermometer
-36	0.8650	-36
0	1	0
100	1.3750	100
150	1.5576	148.70
200	1.7389	197.05
250	1.9189	245.05
300	2.0976	292.70
360	2.3125	350.00

Air thermometer temperatures, recorded in the last column, excepting the values at the fixed points, were calculated on the assumption that temperature, by definition, was proportional to the increase in volume measured from the ice point. Thus, to find the air thermometer temperature corresponding to the mercury temperature of 360, they needed

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only to solve the proportion, $t/100 = 1.3125/0.375$. Dulong and Petit also found that hydrogen behaved in the same way as air over this extended temperature range, and, no doubt influenced by the work of Gay-Lussac, concluded that all other gases would do the same.

These results must have constituted a true revelation to those who had supposed that no real conflict was presented by the rival claims of the mercury and air thermometers for the honor of providing the true temperature scale. Dulong and Petit, however, were not satisfied with their work because they realized that it was affected in an undetermined way by the thermal expansion of the glass of which the thermometers were made. In this connection, their paper was distinguished by its phenomenal success in dealing with the problem of measuring the absolute thermal expansion of a fluid as contrasted with its apparent expansion.

The fact that the thermal expansion of the glass bulb may influence the readings of liquid-in-glass thermometers had been common knowledge since the Florentine Academy first recorded and explained the initial rise of the liquid in the stem when such a thermometer was plunged into a colder medium. Early in the eighteenth century, Fahrenheit had recommended that, in order to attain the best comparability, different thermometers should be made of the same kind of glass, and Celsius, in keeping with the residual character of temperature, had recommended that stem readings be corrected for any alteration in the volume of the bulb. However, because of the presence at this time of more serious uncertainties, such as the lack of precision in defining fixed points, such corrections, except at very high tem-

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peratures, must have seemed largely academic.

Later in the century, thermometry began to attain the stature of an exact science, and the question of the expansion of the container assumed a more real significance. This question was of particular importance for the commonest thermometric liquid, mercury, for two reasons: first, because of the small thermal expansion of mercury, thermometers filled with this fluid were unusually sensitive to the thermal behavior of the glass; and, second, because of attempts to identify the mercury scale with the most rational scale, the true or absolute expansion of mercury attracted special attention. Thus, when Dulong and Petit attacked this problem, a large number of values for the absolute fractional increase in volume of mercury in going from the ice point to the boiling point of water had already been reported. These values, obtained by adding the cubical expansion of glass to the apparent expansion of mercury, ranged from 1/67, obtained by Casbois, to 1/50, reported by Dalton. Their variability reflected the inherent difficulty of measuring the small thermal expansion of solids with exactitude, the differences in thermal behavior of different kinds of glass, and the dependence of the thermal behavior of a single glass on its own history. Also, as Dulong and Petit pointed out, those values of the thermal expansion of mercury, which depended, as did the value of Lavoisier and Laplace, upon the calculation of the cubical expansion of glass by multiplying by three the measured linear expansion, were necessarily triply sensitive to experimental error.

In the wake of this uncertainty, it was only by a stroke of sheer

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genius that Dulong and Petit came to measure the absolute thermal expansion of mercury by a method which was entirely independent of the behavior of the glass containers. This method of "equilibrating columns", which these illustrious French scientists graciously ascribed to Boyle, employed the apparatus diagrammatically illustrated in Figure 10. Two vertical tubes, A and A', were connected by a narrow, horizontal cross tube BB'. Mercury having been placed in the apparatus, tube A was surrounded by a constant-temperature ice bath, while tube A' was surrounded by an oil bath which was heated to various temperatures. At each temperature, the vertical heights of the mercury levels in the tubes, measured from the horizontal tube, were recorded. Since the two mercury columns balanced each other, the simplest principle of hydrostatics required that $h'd = hd$, where h and d denoted the height and density of the mercury in tube A held at the ice point and h' and d' their values in tube A' heated to temperature t'. If v and v' were the corresponding values of specific volume, Dulong and Petit could write $v'/v = d/d' = h'/h$, so that the fractional increase in volume between the ice point and temperature t' was $(v' - v)/v = (h' - h)/h$. To determine the temperature t' of the mercury in the heated tube, an approximately constant-volume air thermometer with a very long bulb and very narrow side tube was used (cf. Fig. 11). The volume which the air would have occupied at constant pressure was readily reckoned from the barometric pressure, the manometer reading, and the small tube volume through which it had expanded. This volume was also corrected for the expansion of the bulb, the cubical coefficient of expansion of glass having been determined by

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a method which will presently be described.

In the following table, the results obtained by this new method are summarized.

Centigrade Temperature Calculated from Absolute Expansion of Air	Mean Coefficient of Absolute Expansion of Mercury per Degree Centigrade between Ice Point and Temperature Indicated	Centigrade Temperature Calculated from Absolute Expansion of Mercury
0	0	0
100	1/5550	100
200	1/5435	204.61
300	1/5300	314.15

Comparison of this table with the earlier one reveals that the glass correction brought into still greater prominence the difference between the two thermometer scales at high temperatures.

Having measured the absolute thermal expansion of mercury, Dulong and Petit were able to determine the absolute expansion of glass by merely noting the apparent thermal expansion of mercury. To determine the latter quantity, they wisely employed the mercury "weight thermometer" illustrated in Figure 12. This consisted of a glass bulb equipped with a capillary side tube through which mercury was expelled upon heating. If when completely filled with mercury at the ice point, the bulb and tube contained W_o grams of mercury and if w grams were expelled by heating to temperature t, the weight $(W_o - w)$ remained. At the ice point, where its density was d_o, this weight occupied a volume $(W_o - w)/d_o$. Hence the mean coefficient of apparent expansion could be calculated as $w/(W_o - w)\,t)$. The practical advantages of the weight thermometer over the conventional type for this work were two-fold: first, the weights could be measured more accurately than volumes; and second,

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the necessity for a stem correction, which would have been large at high temperatures, was eliminated.

Using this method, Dulong and Petit obtained the following results which they found to hold equally well for several varieties of glass.

Centigrade Temperature from Air Thermometer	Mean Coefficient of Apparent Expansion of Mercury in Glass Between Ice Point and Indicated Temperature	Mean Coefficient of Absolute Expansion of Glass Between Ice Point and Indicated Temperature	Centigrade Temperature Calculated from Absolute Expansion of Glass
100	1/6480	1/38700	100
200	1/6378	1/36300	213.2
300	1/6318	1/32900	352.9

The overflow or apparent expansion of the mercury had of necessity to equal the amount by which the thermal expansion of the mercury exceeded that of the glass. Thus Dulong and Petit could calculate the coefficient of absolute expansion of the glass, given in the third column of this table, as the excess of that for the mercury, tabulated in the earlier table, over the coefficient of apparent expansion of the mercury. Characteristic of their general point of view was Dulong and Petit's consideration of an imaginary "glass thermometer" calibrated with the usual fixed points and having scale readings proportional to the cubic expansion of glass. The marked departure of such a glass scale from that of the air thermometer is revealed in the last column of the table.

Dulong and Petit completed their survey of thermal expansion with

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an account of their work with several solid metals. A portion of the Sagi of the Florentine Academy had been devoted to experiments on the thermal expansion of metal rings and wires, and throughout the eighteenth century numerous attempts had been made to measure the linear thermal expansion of metals and other solids. In the simplest method, the increase in length of a heated bar of the solid was observed against a scale held at a fixed temperature. Once having determined the thermal expansion of a standard bar, the expansion of other solids could be ascertained by the differential method. In this latter procedure, the standard bar and the bar to be investigated were placed side by side, fastened together at one end, and the difference in their expansions noted on a scale at the opposite end. The difficulty in obtaining accurate results in such experiments arose from the smallness of the quantity being measured and the necessity for uniformly heating a long bar to a high temperature without at the same time affecting the temperature of either the scale or any auxiliary apparatus used to magnify and measure the expansion. The first really accurate measurements of the linear thermal expansion of solids have been attributed to Laplace and Lavoisier.[72] In their work, prosecuted shortly before the French revolution, but little known until publicized by Biot,[73] one end of the heated bar was fixed while the other end operated a lever on which was mounted a telescope focused on a distant scale. They investigated the linear expansion of a large number of metals and glasses between the ice point and the boiling point of water. Although these different materials exhibited widely different total expansions,

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Lavoisier and Laplace reported that, in this temperature range, the expansion of each was linearly related to the temperature recorded on the mercury thermometer.

The work of Dulong and Petit in this field was distinguised by its extension of measurements to higher temperatures and by its introduction of a new procedure for direct determination of the cubical expansion of metals. They first sought to measure this cubic expansion by the same procedure they had employed for glass; i.e. by observing the apparent expansion of mercury when heated in a container made of the metal. They soon abandoned this, however, in favor of a much more convenient method depending on the overflow incurred by heating a mercury weight thermometer into which a sample of the metal had been introduced. If W_o' denoted the weight of the metal sample and d_o' its density at the ice point, then its initial volume was W_o'/d_o' and its volume at temperature t was $(W_o/d_o')\ (1 + x\ t)$ where x was the mean coefficient of absolute expansion of the solid. At the ice point, the remainder of the bulb and side tube was filled with W_o grams of mercury, but on heating to t, w grams were expelled, so that $W_o - w$ grams remained. If d_o was the density of the mercury at the ice point, the weight of mercury remaining initially occupied a volume of $(W_o - w)/d_o$ but at temperature t had a volume of $(W_o - w)/ d_o)\ (1 + mt)$ where m denoted the mean coefficient of absolute expansion of the mercury. Finally, since the initial volume of the glass bulb and tube was $(W_o/d_o + W_o'/d_o')$, its volume at t was $(W_o/d_o + W_o'/d_o')\ (1 + gt)$ g denoting the mean coefficient of absolute expansion of the glass. Since, at temperature t, the expanded bulb

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was completely filled by the expanded solid and the expanded mercury which remained, there resulted the fundamental relation

$$(W_o/d_o + W_o'/d_o')\ (1 + gt) = (W_o'/d_o')\ (1 + xt) + (W_o - w)/d_o)(1 + mt).$$

Having previously determined the coefficients g for glass and m for the mercury, Dulong and Petit solved this equation for x, the coefficient for the metal.

Taking care to protect the metal against amalgamation, Dulong and Petit used this method to determine the absolute expansion coefficients of iron and copper. In the case of platinum, the cubic coefficient was computed from the linear coefficient, the latter having been determined by the differential method of using a bar of copper as standard. Their values, for the three metals, of the mean coefficients of absolute expansion between the ice point and the indicated temperature, together with the Centigrade temperature readings which would result from the employment of their cubical expansion as thermometric property, are summarized in the following table:

Air Thermometer Temperature in Degrees Centigrade	Mean Expansion Coefficient for Iron	Centigrade Temperature on the Iron Scale	Mean Expansion Coefficient for Copper	Centigrade Temperature on the Copper Scale	Mean Expansion Coefficient for Platinum	Centigrade Temperature on the Platinum Scale
100	1/28200	100	1/19400	100	1/37700	100
300	1/22700	372.6	1/17700	328.8	1/36300	311.6

As early as 1731, Musschenbroek had employed a metal bar as thermometric substance and its length as thermometric property, and, later in the century, various workers had recommended such "pyrometers" for the determination of high temperatures. If the conclusion of Laplace and

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Lavoisier, that the linear expansions of two different metals were proportional to one another, had been generally true, all such pyrometers should have yielded the same temperature scale provided agreement was established at two fixed points. Also, assuming the cubical expansion coefficient to be three times the linear coefficient, a similar conclusion should have held for pyrometers which reckoned temperatures from the cubical expansion. Dulong and Petit, however, assuming their findings in the above table to be typical of all metals, concluded that the different metals, like different liquids, exhibited their own peculiar laws of thermal expansion, so that, when employed as a thermometric substance, each metal would furnish a temperature scale whose agreement with that of another could not be attained by any simple device.

In spite of these complexities, Dulong and Petit, being firm adherents of the still prevalent caloric theory, did not recommend that the quest for the most rational temperature scale be banished from physical science; indeed, in the opening lines of their paper they had expressed the opinion that the simplest laws of heat could never be discovered while employing a purely arbitrary temperature scale. However, as a result of their researches, they concluded that only gases conformed to one and the same law of thermal expansion; this conclusion, no doubt supported by metaphysical convictions about the nature of caloric, led them to the belief, previously advocated by Dalton, that the thermal expansion of gases was more immediately related to the "force of heat", than was that of liquids and solids. Consequently, they considered it probable that the laws of heat would assume a

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simpler form if referred to the scale of the air thermometer than if referred to one depending on the expansion of a liquid or solid. However, Dulong and Petit were by no means dogmatic on this point: they also hazarded the guess that the laws governing the thermal behavior of a particular liquid might be most simply expressed with reference to a thermometer employing that liquid as thermometric substance.[74]

As a matter of fact, the situation with respect to arbitrary scales was even more complex than Dulong and Petit believed it to be: not even the gases conformed to the same law of thermal expansion. For nearly thirty years after its publication, Gay-Lussac's data on the thermal expansion of gases continued to be accepted. Then, in the year 1835, the Swedish physicist, F. Rudberg, published the results of experiments which, though very carefully performed, indicated that the mean coefficient of expansion of dry air between 0° and 100° Centigrade was appreciably lower than Gay-Lussac and Dulong and Petit had supposed.[75] His procedure was the modified Gay-Lussac method adopted by Dulong and Petit involving simultaneous variation of pressure and volume. (cf. p. 57). After taking the utmost precautions to remove all moisture, the Swedish scientist concluded that the true value of the fractional increase in volume lay between 0.364 and 0.365 as compared with Gay-Lussac's value of 0.375. In the following year Rudberg refined the constant volume method of Amontons to measure the same quantity and again ob tained the same result.[76]

Unfortunately, Rudberg's death in 1839 prevented the extension of his excellent technique to the study of other gases. In the next year, Gustav

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Magnus took up the subject.[77] Evidently unaware that Dulong and Petit used Rudberg's first method, and thinking it unlikely that both Dulong and Petit, and Gay-Lussac would have obtained an identical, incorrect value for the expansion coefficient of air, Magnus entertained the possibility that the discrepancy between their value and that of Rudberg arose from the circumstance that the Swede, but not the Frenchman, had used Boyle's Law in the calculation.[78] Boyle's Law, he thought, might not be rigorously obeyed at temperatures as high as 100° Centigrade. Therefore, he undertook to repeat the experiments of Gay-Lussac in which the increase in volume, at constant pressure, of the air was observed directly as it pushed a confining index of mercury through a horizontal tube. Many trials, however, yielded only erratic results which he attributed to the failure of the mercury droplet to completely seal the tube. Magnus then turned to Rudberg's second, constant-volume method; and, after repeating the Swede's experiments on air, extended the method to hydrogen, carbon dioxide, and sulfur dioxide. His result for air agreed well with Rudberg's, and he also observed nearly the same value for hydrogen. On the other hand, carbon dioxide, and particularly sulfur dioxide, exhibited consistently greater expansions. The average fractional increases in volume between the ice point and the steam point which he obtained were as follows: air, 0.3665; hydrogen, 0.3657; carbon dioxide, 0.3691; and sulfur dioxide, 0.3856.

At this time, the illustrious French scientist, Henri Victor Regnault, directed his penetrating attention to an exhaustive study of the entire field of the thermal expansion of gases. The skill displayed

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by his experimental work, which was described in three papers appearing in 1842,[79] was matched only by the wisdom which characterized its interpretation. Although the immediate outcome of his investigations was the refutation of the claim that gas thermometric scales were peculiarly rational, its final result was the establishment of the whole subject of gas thermometry on a more secure basis.

Regnault first resolved to eliminate, once for all, all doubt as to the correct value for the fractional increase in volume of air between the ice point and steam point. He determined this quantity, first by Dulong and Petit's method, involving simultaneous variation of pressure and volume, then by a modification of this procedure in which, because the flask was equipped with a longer tube, the volume was nearly constant, and, finally, by Rudberg's constant volume method. Repeated trials with these methods gave results differing only in the fourth decimal place, differences which Regnault thought could reasonably be attributed to experimental error. Since one method involved a substantial Boyle's Law correction while the other two did not, Regnault rejected the possibility that previous discrepancies in the values reported for the coefficient for air had been caused by departures from Boyle's Law and gave, as the best value for the fractional volume increase, the mean of the values obtained by the different methods, 0.3665.

Turning now to the other gases and employing principally the modification of the method of Dulong and Petit, he obtained the following values for the fractional increase in volume between the two fixed points: nitrogen, 0.3668; carbon monoxide, 0.3667; hydrogen, 0.3668; nitrous oxide, 0.3676; hydrogen chloride, 0.3681; carbon dioxide, 0.3686;

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cyahogen, 0.3829; and sulfur dioxide, 0.3845. Regnault thus showed what had already been indicated by the experiments of Magnus, that not all gases conformed to the same law of expansion as was required by Charles' Law. Nitrogen, carbon monoxide, and hydrogen appeared to conform to essentially the same law as air, but the remaining gases investigated, exhibited progressively greater expansions.[80]

In all of Regnault's experiments, undertaken up to this time, the pressures of the gases at 100° C. had differed little from atmospheric pressure. According to the classical experiments of Amontons, the pressure coefficient for air was independent of the initial pressure, and, for over a century, the correctness of this conclusion appears to have been assumed with little additional proof. Davy, in 1823, had sought to show that the coefficient for air had the same value for pressures extending from one-sixth of an atmosphere to two atmospheres, but, according to Regnault, the experiments had not been performed with sufficient care to give accurate results. Therefore, Regnault, devoting his second paper to this matter, and, using Rudberg's constant volume method, measured the pressure coefficient for air over a range of pressures, beginning at about one-seventh of an atmosphere and ending at nearly five atmospheres. As shown in the last column of the accompanying table, he obtained a small but consistent increase in the pressure coefficient with increasing pressure, the total increase over the entire pressure range amounting to several per cent. Similar results, also recorded in the table, were obtained for carbon dioxide, except that the coefficient for the latter was about four times as sensitive to pressure changes as that for air. Thus Regnault demonstrated that the scale of

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the constant volume air thermometer, and still more that of one employing carbon dioxide, varied with the pressure at which the bulb was filled.

If Boyle's Law could have been assumed to hold over this pressure range, the equality of pressure and volume coefficients would have followed immediately, so that the same conclusions would have applied to the scales of constant pressure thermometers employing these gases. Already, Dulong and Arago, in a study of the compressibility of air published in 1830, had found only very small and uncertain departures from Boyle's Law over a pressure range up to twenty-seven atmospheres. Regnault, however, wishing to take nothing for granted, decided to measure the volume coefficients directly while heating the gases at constant pressure. After finding, as did Magnus, that Gay-Lussac's horizontal tube, enclosed by a short column of mercury, gave unsatisfactory results, he designed his own constant-pressure apparatus, In this new procedure, the gas was allowed to expand at constant pressure into an auxiliary tube which was kept at a constant, known temperature and where its volume was noted.

The volume coefficients which Regnault obtained in this way are entered in the second column of the table. Like the pressure coefficients, the volume coefficients for air and carbon dioxide also increased with pressure. Hydrogen, on the contrary, showed no pressure effect, while the volume coefficient for sulfur dioxide was even more sensitive to pressure change than that for carbon dioxide. It was thus established that, in general, the scales of constant pressure gas thermometers, like those for constant volume instruments, would not be strictly comparable unless the bulbs were filled at the same pressure.

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Effect of Pressure on Volume and Pressure Coefficients (Regnault).

Pressure at 100°C. (mm)	Volume Coefficient X 10^2	Pressure Coefficient X 10^2
	Air	
109.7		0.3648
266.1		0.3654
375.2		.3657
Atmospheric	0.3671	.3665
1678.4		.3676
2306.2		.3680
2526.4	.3694	
2621.5	.3696	
2924.0		.3689
3655.6		.3709
	Carbon Dioxide	
Atmospheric	0.3710	0.3686
901.1		.3694
1742.7		.3752
2523.0	.3846	
3598.1		.3860
	Hydrogen	
Atmospheric	0.3661	0.3668*
2543.7	.3662	
	Nitrous Oxide	
Atmospheric	0.3720	9.3676*
	Carbon Monoxide	
Atmospheric	0.3669	0.3667*
	Sulfur Dioxide	
Atmospheric	0.3903	0.3845*
982.0	.3980	
	Cyanogen	
Atmospheric	0.3877	0.3829*

*Obtained by the modification of Dulong and Petit's method in which only a small volume change occurred.

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To determine whether or not the gases departed from Boyle's Law, Regnault had only to compare the values of volume and pressure coefficients at corresponding pressures. For air at atmospheric pressure, the data revealed only a small and uncertain difference. At higher pressures, however, the volume coefficient appeared to be definitely larger. A similar behavior was observed for carbon dioxide, except that, in this case, the departure from Boyle's Law already made itself evident at atmospheric pressure. For the remaining gases studied, the data permitted a comparison of the two coefficients at atmospheric pressure only. The permanent gases, carbon monoxide and hydrogen, presumably conformed to Boyle's Law at this pressure. However, nitrous oxide, sulfur dioxide, and cyanogen, behaving like carbon dioxide, gave pressure and volume coefficients which were markedly different. The fact that, in all cases where a difference occurred, the pressure coefficients were smaller than the volume coefficients, indicated to Regnault that the pressure required to keep the volume constant on heating was smaller than it should have been according to Boyle's Law; in other words, the gases were too compressible to follow this simple generalization.

When Regnault did this work, all of the gases studied, except the permanent ones, had been liquefied so that their boiling points were known, at least approximately. The fact that these boiling points were intimately related to the extent to which the gases departed from the laws of Charles and Boyle did not escape the keen perception of this great Frenchman. To facilitate the comprehension of his conclusions on this point, the volume and pressure coefficients at atmospheric pressure,

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together with their differences, have been assembled in the following table in the order of increasing boiling point of the gas. As the boiling points of the gases decreased, their coefficients decreased and approached the values obtained for the permanent gases. A slight discrepancy appeared with carbon dioxide, but that this might have been attributed to the fact that the gas solidified on cooling at atmospheric pressure instead of forming liquid. Equally marked was the decrease in the difference between the two coefficients with decreasing boiling point, indicating progressively smaller departures from Boyle's Law.

Relation of Volume Coefficient, Pressure Coefficient, and Their Difference to Boiling Point. (Atmospheric Pressure.

Gas	Boiling Point	Volume Coefficient X 10^2 (a)	Pressure Coefficient X 10^2 (b)	a - b
Hydrogen	very low	0.3662	0.3668	negligible
Air	very low	.3671	.3665	negligible
Carbon monoxide	very low	.3669	.3667	negligible
Nitrous oxide	-90	.3720	.3676	.0044
Carbon dioxide	-78.5*	.3710	.3686	0.0024
Cyanogen	-21	.3877	.3829	.0048
Sulfur dioxide	-10	.3903	.3845	.0058

Regnault was thus able to formulate the hypothesis, abundantly confirmed by later work, that the deviations of gases from Charles and Boyle's Laws were associated with the extent to which their states were

*Sublimation Point.

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removed from their points of condensation;[81] and that, although each gas, when examined under ordinary conditions, might exhibit its own peculiar pressure and volume coefficients, nevertheless, with diminishing pressures, all such coefficients would approach one and the same value. With respect to Boyle's Law, Regnault directly confirmed this hypothesis five years later by an exhaustive study of the compressibility of gases.[82] From this work it appeared that not even the permanent gases conformed strictly to Boyle's Law, but that, in all cases, the extent of the departure decreased with decreasing pressure, and that, for all gases studied except hydrogen, this departure was in the direction of excessive compressibility.

Thus, although, by revealing that real gases under ordinary conditions did not conform to the same law of thermal expansion, Regnault destroyed the foundation on which previous claims for the rationality of the gas thermometer scale had been based, nevertheless he simultaneously provided such claims with a new type of support. For since, with decreasing pressure, the thermal behavior of such gases approached identity, one might have argued that a thermometric scale, based on this limiting law of thermal expansion, had prior claim to rationality since it was the same for all gases.

Although the concept of the "perfect" or ideal gas, as the arch-type approached by all real gases when rarefied and for which the simple laws of Boyle and Charles were exact, was clearly formulated by Regnault at the close of his second paper, still the thought that such a concept might serve, through extrapolation of data to zero pressure, to define the most rational temperature scale did not occur, or at least did not appeal, to

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him at this time. Thus he concluded his third 1842 paper with this statement: "The simple laws which were previously assumed to govern the expansion of gases, led physicists to regard the air thermometer as a normal thermometer whose readings were actually proportional to the increase in quantity of heat. Now that these laws are known to be incorrect, one sees that the air thermometer belongs in the same class as all other thermometers whose temperature readings are related in a more or less complicated way to the heat added. Thus one sees how far we still are from possessing any means for the absolute measurement of quantities of heat, and how feeble is the hope, in the present state of knowledge, of finding through experiment simple laws among the phenomena dependent upon these quantities."

Even though, in these words, Regnault disavowed any theoretical preference for the air thermometer, he nevertheless came to recommend it as an arbitrary standard for practical reasons. This recommendation came as a result of an attempt, described in his third paper, to check the work of Dulong and Petit on the comparison of the scales of the mercury and air thermometers. For this purpose, he used a constant volume air thermometer and a mercury weight thermometer. Between the ice point and the steam point, Regnault found, as did his predecessors, that the two scales were practically identical, although he observed that the mercury thermometer read about two-tenths of a degree higher midway between the two fixed points. Above the steam point, substantial agreement was noted until 250°C. where the mercury thermometer again read higher by about three-tenths of a degree. With increasing temperature, this difference increased, becoming about three degrees at 350°C. However, because of

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uncertainties about the thermal behavior of the glass Regnault did not lay great weight on these measurements. Dulong and Petit had reported that all of the several varieties of glass studied by them exhibited the same thermal expansion, and, as a result, it had been commonly assumed, since that time, that any two mercury thermometers would furnish identical scales provided they were made to agree at the ice and steam points. Regnault showed that this was by no means true, but that, because of differences in the glass, two mercury thermometers calibrated in the customary way, generally exhibited marked discrepancies at higher temperatures, the difference becoming as great as five degrees at 300°C. Furthermore, because of inconsistent behavior of the same glass, a single mercury thermometer did not always give the same readings after heating to an elevated temperature as before. For these reasons, Regnault strongly recommended the constant pressure air thermometer, particularly for accurate work at elevated temperatures, because of its larger expansion or pressure coefficient and its consequent relative independence of the behavior of the glass.

Thus the great quest for the most rational temperature scale deteriorated, with Regnault, into a practical preference for the air thermometer based only on the most mundane considerations. Furthermore, this was only a forerunner of that complete banishment of the problem, in its original form, from physical science--a banishment which, indeed, was almost at hand. The half-century preceding the publication of Regnault's papers had witnessed a steady accumulation of experimental facts with which the caloric hypothesis could not cope. In the very year, 1842, in which Regnault released his researches on the thermal expansion

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of gases to the scientific world, Robert Mayer published his classical paper on the Energy Principle, embodying a system of thought in which the caloric theory had no place; and, even while the Frenchman struggled with pressure and volume coefficients, James Prescott Joule was performing equally careful experiments in England on the conversion of work into heat — experiments which, beginning in 1843, found expression in a series of open and successful attacks on the hypothesis that heat was an indestructible fluid.

As a result of these factors and others, the caloric theory had become a historical oddity by the middle of the eighteenth century. Since, deprived of the assumption that the heat of a body was a definite measurable entity, the question of how much heat the body contained became meaningless, the problem of the true temperature scale, as formulated by the caloricists, was likewise relegated to the archives. Yet, so unpredictable is the progress of scientific discovery that the gas thermometer returned to the scene almost immediately to establish its claim to rationality, in an entirely new guise. Extending the earlier speculations of Sadi Carnot on the efficiency of an ideal heat engine, Sir William Thompson showed that the ratio of the heat absorbed to the heat expelled during the cyclic operation of such an engine might be employed to define a temperature scale, which would be absolute or rational in the sense of being definable without reference to the properties of any particular thermometric substance, and that such a scale was, in fact, very nearly proportional to that of the air thermometer. However, the complex historical process which culminated in this result, because it was only indirectly related to that history of temperature which has now been traced

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from Philo through Regnault, is more appropriately assigned to the history of the Second Law of Thermodynamics.

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Footnotes for Chapter I (Development of Thermometry and the Temperature Concept).

[1]Morris Cohen, Sourcebook of Greek Science, New York, 1948, pp. 255,256.

[2]Herons von Alexandria, Volume 1: Druckwerke und Automatentheater. herausgegeben von Wilhelm Schmidt, Leipzig, 1899, p. 255.

[3]Lancelot Hogben, Science for the Citizen, London, 1938, p. 560.

[4]Marshall Clagett, Giovanni Marliani and Late Medieval Physics, New York, 1941, Chapter II.

[5]Charles H. Haskins, Studies in the History of Medieval Science, Harvard University Press, 1927, pp. 181, 182.

[6]Fritz Burckhardt, Die Erfindung des Thermometers and Seine Gestaltung im XVII Jahrhundert, Basel, 1867, p. 19.

[7]Henry C. Bolton, Evolution of the Thermometer, 1592-1743, Easton, Pa., 1900, p. 17.

[8]F. Sherwood Taylor, "The Origin of the Thermometer", Ann. Sci., 5, pp. 129-156, 1942.

[9]Francis Bacon, Advancement of Learning and Novum Organum, Colonial Press, London, 1900, p. 387.

[10]F. Sherwood Taylor, op. cit.

[11]Burckhardt, op. cit., p. 27.

[12]From the fact that Leurechon's book went through seventeen editions, one may conclude that the J-type thermometer was widely known. cf. Martha Ornstein, The Role of Scientific Societies in the Seventeenth Century, Chicago, 1928, p. 65.

[13]Bolton, op. cit., pp. 11-14.

[14]F. Sherwood Taylor, op. cit.

[15]Francis Bacon, op. cit., p. 387.

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[16]Burckhardt, op. cit., p. 27.

[17]Burckhardt, op. cit., p. 25.

[18]Bolton, op. cit., pp. 31, 32.

[19]The Physical Treatises of Pascal: The Equilibrium of Liquids and The Weight of the Mass of the Air, translated by I.H.B. Spiers, New York, Columbia University Press, 1937, pp. 61,62.

[20]Pascal, op. cit., p. 109

[21]Essays of Natural Experiments made in the Acadamie del Cimento, English by Richard Waller, London, 1684. A Latin translation appeared in 1731, a French one in 1755. The work was widely used as a laboratory manual until the end of the eighteenth century.

[22]Cimento, pp. 2, 3.

[23]Cimento, pp. 4, 5.

[24]Cimento, p. 5.

[25]Antineri, Ann. Chim., 45, 354, 1829.

[26]Life and Works of Hon. Robert Boyle, London, 1772, v. II, p. 494

[27]Boyle, op. cit., vol. I, p. 33.

[28]However, the test body, its thermometric property, and the temperature function must meet certain elementary requirements. For a complete discussion of M. K. Barnett, "The Temperature Concept," Journal of Physical Chemistry, 46, pp. 715-723, 1942.

[29]John M. Stillman, The Story of Early Chemistry, New York, 1924, pp. 393-397

[30]Carl Craebe, "Geschichte der Organische Chemie, Berlin, 1920, p. 15.

[31]Edmund Halley, Philosophical Transactions of the Royal Society of London, Abridged, London, 1809, volume 3, 1683-94, p. 505.

[32]Burckhardt, op. cit., pp. 44, 45.

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[33]Isaac Newton, "A Scale of the Degrees of Heat," Philosophical Transactions Abridged, volume 3, pp. 572-575.

[34]Daniel Gabriel Fahrenheit, "Experiments and Observations on the Freezing of Water in Vacuue," Philosophical Transactions Abridged, vol. 33, p. 22. Later, when the ice point and steam point came into general usage as fixed points, the "Fahrenheit Scale" was defined by assigning 32 to the former and 212 to the latter.

[35]Bolton, op. cit., p. 23.

[36]R. T. Gunther, Early Science at Oxford, Oxford, 1921, III, p. 69.

[37]Purification of mercury by distillation was employed as early as 1655 by Dobczensky. Removal of foreign particles by filtration has been accredited to Fahrenheit who may also have removed air and moisture by the method described by von Bergen in 1745, namely, heating the mercury under a receptacle attached to an air pump and allowing it to cool in a vacuum. c.f. E. Gerland and F. Traumiller, Geschichte der Physikalischen Experimentierkunst, Leipzig, 1899, pp. 249, 320.

[38]Fahrenheit, "Experiments concerning the degrees of heat of boiling liquors," 1724, Philosophical Transactions Abridged, vol. 33, p. 1

[39]Fahrenheit, "Description of a New Barometer (Hypsobarometer)," Philosophical Transactions Abridged, vol. 33, p. 54.

[40]Rene Antoine Ferchault de Reaumur, "Ru les for Construction of Thermometers with comparable Scales (which give an idea of the heat and cold which are associated with known masses)," Hist. et Mem. de L'Acad. de Paris, annee 1730-31, Reprinted in Ostwald's Klassiker der exacton Wissenschafton, nr. 57 Abhandlungen u ber Thermometric von Fahrenheit, Reaumur, Colsius, Leipzig, 1894.

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[41] Andreas Celsius, "Observations of two fixed Degrees of a Thermometer," Reprinted in Ostwald's Klassiker, no. 57.

[41a] A. Wolf, A History of Science, Technology, and Philosophy in the Eighteenth Century, New York, 1939, pp. 293-297.

[42] Thirty-five different thermometer scales, in use at various times during the eighteenth and latter part of the seventeenth centuries, are listed by Bolton, op. cit., pp. 88, 89.

[43] Bolton, op. cit., p. 80.

[44] M. K. Barnett, op. cit.

[45] Boyle, op. cit., p. 489.

[46] Halley, op. cit.

[47] Barnett, op. cit.

[48] Ernst Mach, Die Principien der Warmelehre, Leipzig, 1923, pp. 58-61.

[49] J. C. Peggendorff, Geschichte der Physik, Leipzig, 1879, pp. 385, 386.

[50] Brook Taylor, "An Account of an Experiment, made to Ascertain the Proportion of the Expansion of the Liquor in the Termometer, with regard to the Degrees of Heat," Philosophical Transactions Abridged, vol. 6, p. 641, 1723.

[51] Joseph Black, Lectures on the Elements of Chemistry, Edinburgh, 1803, vol. 1, pp. 52-68.

[52] Wolf, op. cit., p. 294

[53] Burckhardt, op. cit., p. 30.

[54] Burckhardt, op. cit. p. 32.

[55] A. Wolf, A History of Science, Technology, and Philosophy in the 16th and 17th Centuries, New York, 1935, pp. 85, 86.

[56] Burckhardt, op. cit., p. 31

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[57]Ferd. Rosenberger, Die Geschichte der Physik, Braunschweig, 1882-1890, zweiter teil, p. 150.

[58]Guillaume Amontons, "Discourse on some properties of air and the means of determining temperature in all climates of the world," Memoirs de l'Academie Royale des Sciences, 1702, Reproduced in part by W. P. Magie, A Source Book in Physics, New York, 1935, pp. 128-131.

[59]Mach, op. cit., pp. 8, 9.

[60]Herman Boerhaave, A New Method of Chemistry, English by Peter Shaw, 1753, Part II, pp. 224-236.

[61]Black, op. cit., pp. 52-68.

[62]Rosenberger, op. cit., dritter teil, p. 100.

[62a]This work was described in Gay-Lussac's paper in Annales de Chimie et de physique, 1^se^, t. 43, pp. 137-156, An X, 1802. Gay-Lussac's paper was republished in Ostwald's Klassiker der Exacton Wissenschaften Nr. 44, Das Ausdehnungsgesetz der Gase, Leipzig, 1894.

[63]Rosenberger, op. cit., dritter teil, p. 100.

[64]Rosenberger, op. cit., dritter teil, p. 100.

[65]Rosenberger, op. cit., dritter teil, p. 100.

[66]Guyton de Morveau, "On the Expansion of Air and of Gases by heat and the necessity of determining this with exactitude in order to perfect the method of reducing volumes of these fluids to the volumes they would have at a given temperature." Annales de Chimie, vol. 1, p. 256, 1790.

[67]Gay-Lussac, op. cit.

[68]John Dalton, "On the Expansion of Elastic Fluids by Heat," Memoirs of the Literary and Philosophical Society of Manchester, v. 5, pp. 595-602, 1802, Republished in Ostwald's Klassiker Nr. 44.

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[69]J. B. Biot, Precis Elementaire de Physique Experimentale, Paris, 1821, t.1, pp. 246, 253. Gay-Lussac's experiments had already been described in the 1816 edition of Biot's book.

[70]Dulong and Petit, Annales de Chimie et de physique, t. VII, p. 8, 1817, Republished in Ostwald's Klassiker Nr. 44.

[71]The procedure used by Dulong and Petit had been described in their earlier paper, "Experiments on the laws of expansion of solids, liquids, and elastic fluids and on the exact measure of temperature," Annales de Chimie et de physique, vol. 2, p. 240, 1815. The bulb used by Dulong and Petit was equipped with a narrow tube instead of a stopcock. After entry of mercury at the ice point, the bulb was sealed off at the reduced pressure indicated by the difference in mercury levels inside and outside the tube. Thus a Boyle's Law correction was required to convert the volume of the cold air to atmospheric pressure.

[72]Rosenberger, op. cit., dritter teil, p. 110.

[73]Biot, op. cit., vol. 1, pp. 236-239.

[74]In this same paper Dulong and Petit considered the possibility of defining a true scale by means of heat capacity measurements. This work will be described in a later section. Because they found that the heat capacity of each substance varied with temperature in a manner peculiar to that substance, they concluded that it was impossible to define a temperature scale whose readings would be generally proportional to the amount of heat absorbed by a body.

[75]F. Rudberg, "On the Expansion of Dry Air Between 0 and 100 Degrees Centigrade." Republished in Ostwald's Klassiker Nr. 44

[76]F. Rudberg, "Second Series of Experiments on Expansion of Dry Air Between 0 and 100 Degrees Centigrade," Republished in Ostwald's Klassiker Nr.44.

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[77]Gustav Magnus, "On the Expansion of Cases by Heat," Republished in Ostwald's Klassiker Nr. 44.

[78]The only Boyle's Law correction involved in Gay-Lussac's methods was the small one entailed by any variation in barometric pressure during the experiment.

[79]V. Regnault, "Investigations of the Expansion of Gases" and "Investigations of the Expansion of Gases, Part 2," Annales de Chimie et de physique, series 3, vol. 4, pp. 5-67, 1842. The third paper was "On the Comparison of the Air Thermometer with the Mercury Thermometer," Annales de Chimie et de physique, series 3, vol. 5, p. 83, 1842. All three papers will be found in Ostwald's Klassiker Nr. 44.

[80]Regnault obtained erratic results with oxygen and ammonia, reporting that they reacted with mercury at elevated temperatures. Later, however, oxygen was found to have essentially the same coefficient as air while ammonia gave a much higher value, 0.3860.

[81]This generalization was foreshadowed by Gay-Lussac's observation that ether vapor exhibited an abnormally high thermal expansion in the neighborhood of its boiling point. (cf. page 54)

[82]Thomas Preston, The Theory of Heat, London, 1919, p. 464. Boyle himself thought air became too compressible at pressures above four atmospheres to conform to his law. However, in 1853, Sulzer and Robison concluded that the deviations from the law were in the opposite direction. In 1826, Oersted and Swendsen could find no deviations from the law. On the other hand, Despretz's experiments, performed the next year, showed that gases like ammonia and carbon dioxide were definitely more compressible than

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air and hydrogen, and similar conclusions were indicated by the work of Pouillet, Dulong and Arago, in 1830, tested the conformity of air to Boyle's law for pressures up to 27 atmospheres but were unable to establish any certain departures from the law.

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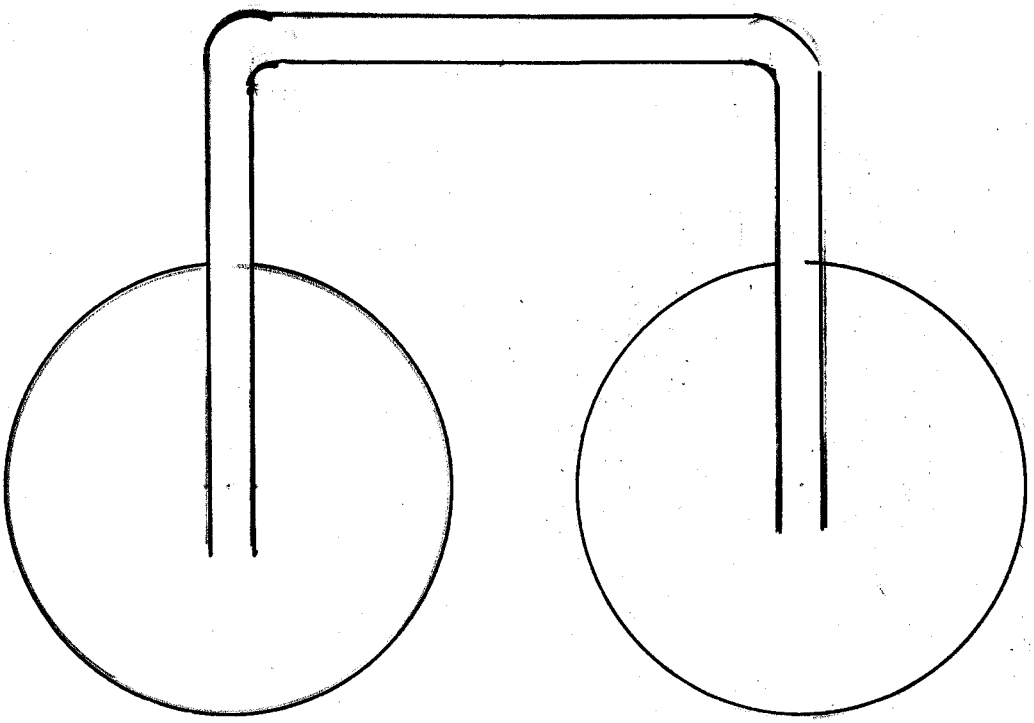

Figure 1. Philo's Thermoscope.

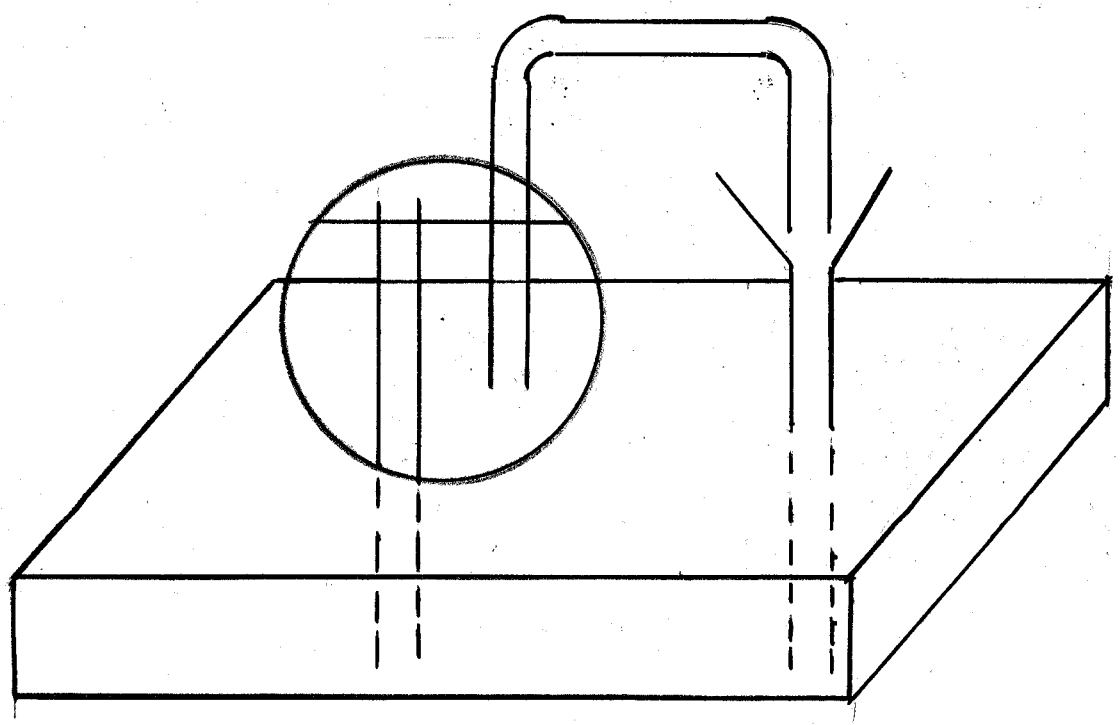

Figure 2. Hero's Thermoscope.

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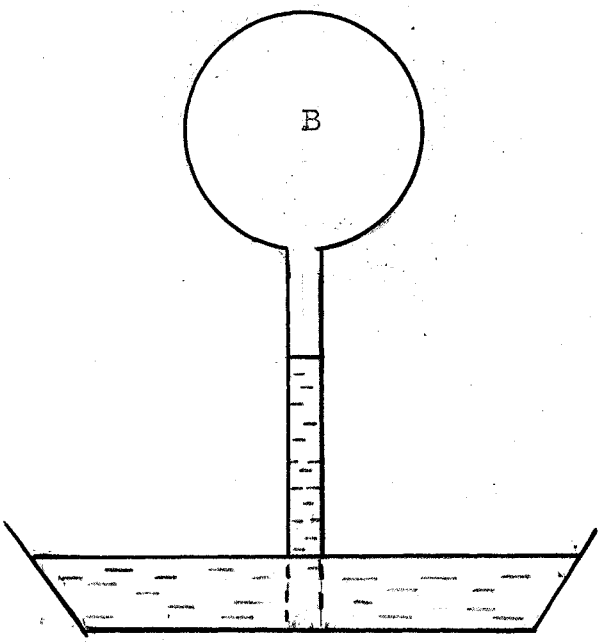

Figure 3. Galileo's Air Thermometer.

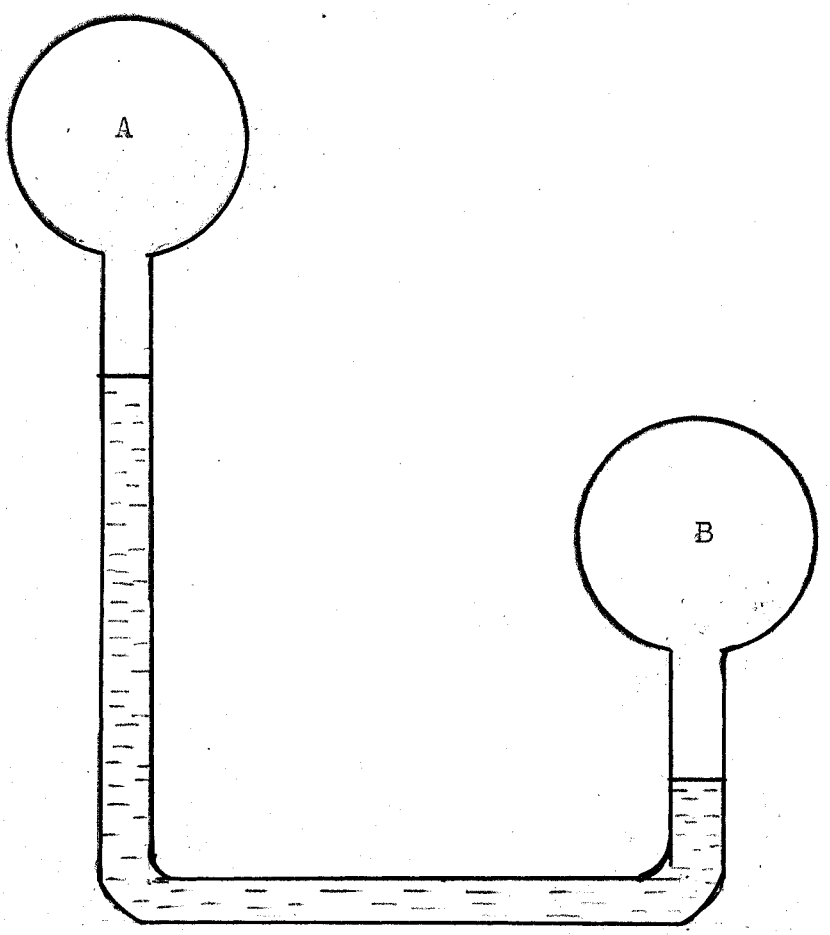

Figure 4. Early Two-Bulbed Thermometer.

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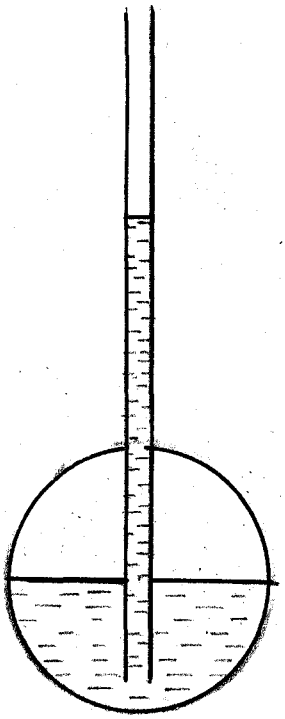

Figure 5. Kircher's Hybrid Thermometer.

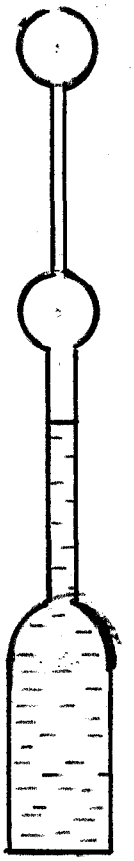

Figure 6. Fahrenheit's Hypsobarometer.

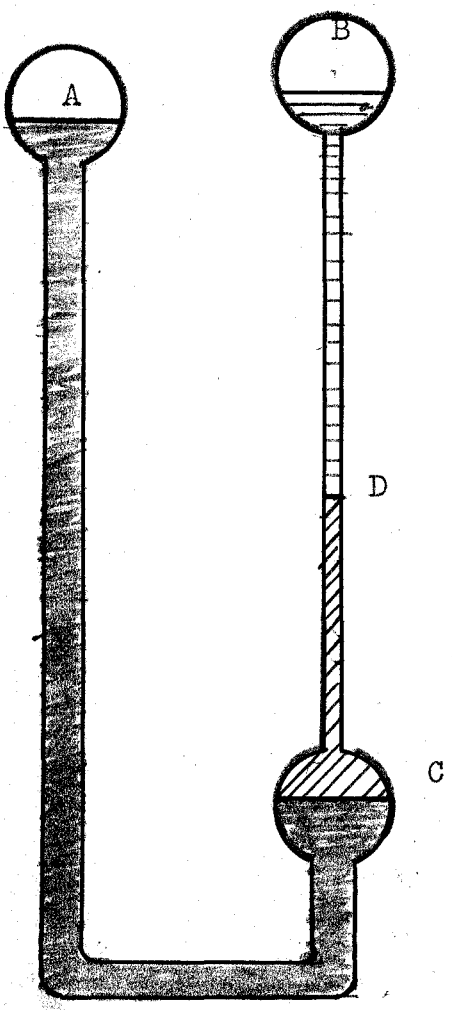

Figure 7. Amontons' Closed Air Thermometer.

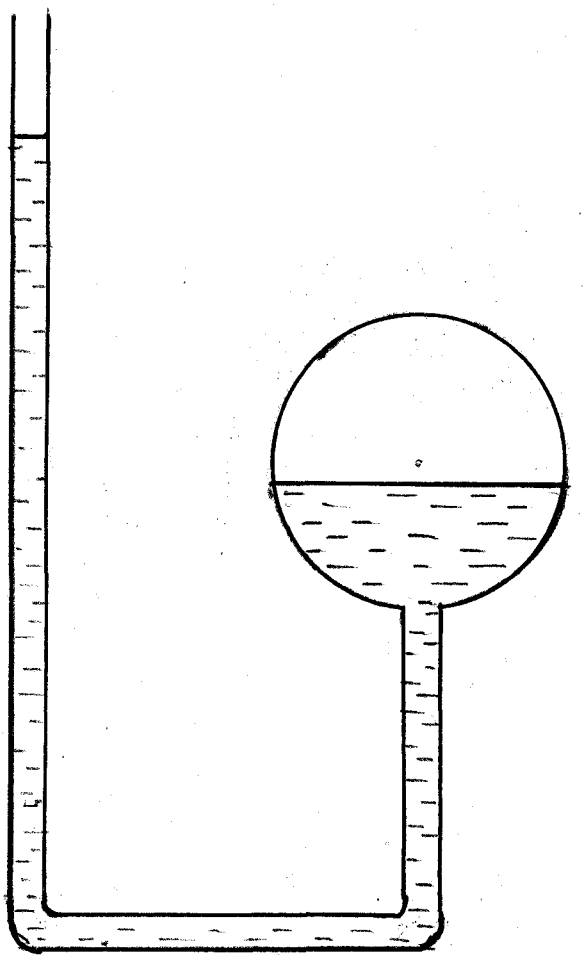

Figure 8. Amontons' Air Pressure Thermometer.

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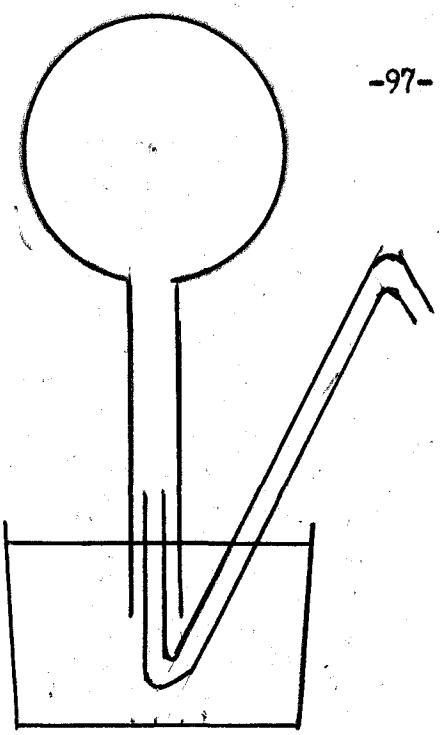

Figure 9. Gay-Lussac's Apparatus for Thermal Expansion of Gases.

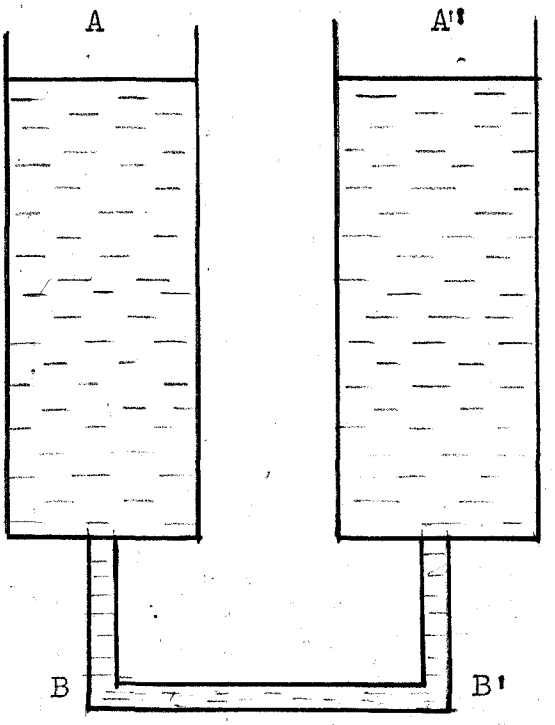

Figure 10. The Equilibrating Columns of Dulong and Petit.

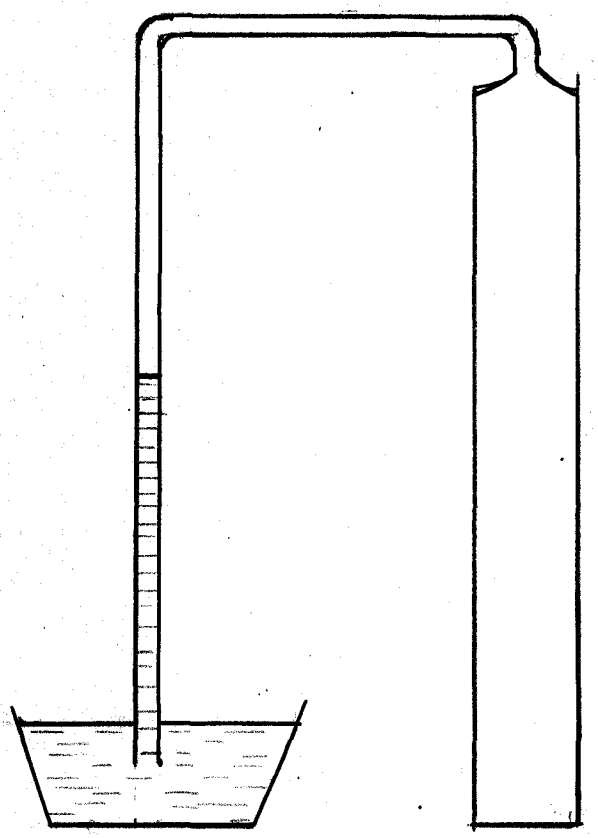

Figure 11. Air Thermometer of Dulong and Petit.

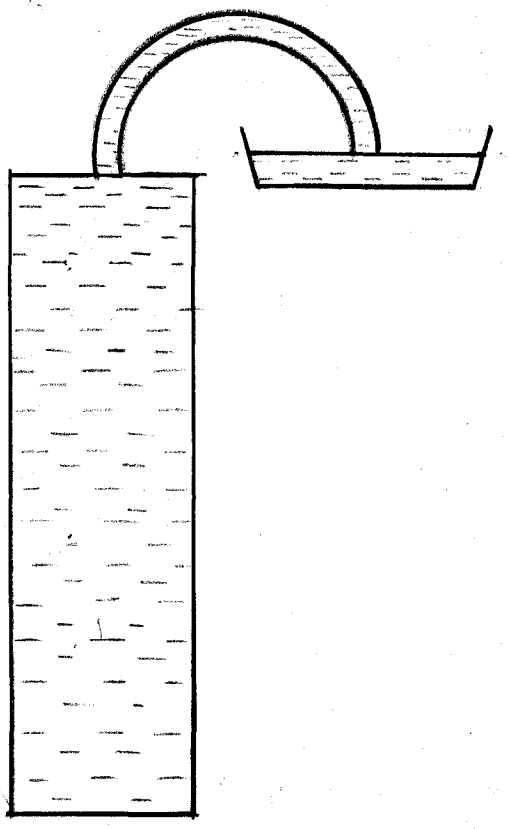

Figure 12. Mercury Weight Thermometer of Dulong and Petit.

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II. The Development of the Concept of Heat from the Fire Principle of Heraclitus through the Caloric Theory of Joseph Black.

		Page
1.	Greek Theories of Heat: Fire Matter and Fire Atoms	99
2.	The Alchemical Principles and Phlogiston	103
3.	Rise of the Kinetic Theory of Heat	108
4.	Development of the Caloric Hypothesis	114
	References and Footnotes	134

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II. The Development of the Concept of Heat From the Fire Principle of Heraclitus Through the Caloric Theory of Joseph Black.

1. Greek Theories of Fire: Fire Matter and Fire Atoms.

The development of modern investigations on the phenomena of heat is connected with two distinct notions as to the nature of heat, the one asserting the substantial ("fluid") nature of heat, the other maintaining that what we perceive as heat is essentially a rapid vibration of the particles of the body which feels hot. It will be of interest to trace the history of these ideas, the roots of which are to be found in antiquity.

The Greek Notion of Fire. The phenomena of combustion must have early excited wonder and speculation, but the first European to give the concept of "fire" a prominent position in a system of natural philosophy was the Greek philosopher Heraclitus (cir. 500 B.C.). However, as Windelband (1, p. 36) notes, when Heraclitus declared fire "to be the essence of all things, he understood by this not a material or substance which survived all its transformations, but just the transforming process itself in its ever-darting, vibrating activity, the soaring up and vanishing which corresponds to the becoming and passing away." Hence, it would be a superficial view, indeed, which regarded the Fire Theory of Heraclitus as the root of the phlogiston theory or the caloric hypothesis which flourished over a thousand years later. Rather, in his conviction that all things are in a continual flux, that permanence is illusion due to the strife of opposites, he is closer to the kinetic view of heat.

A much closer approach to the substantial view of heat is found in Empedocles' (450 B.C.) four-element theory. He postulated as elements

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earth, water, air, and fire and thought that all change must consist in the dividing, intermingling, and separation of these fundamental constituents, regarded as imperishable, homogeneous, and unchangeable. The four-element theory gained great influence through its adoption by Plato (427-347 B.C.) and Aristotle (384-322 B.C.), the latter, however, introducing an important modification, namely, the postulate that the elements may be transmuted into one another by modification of their properties.[1]

Ellis (2, p. 76) thinks that earth, water, air, and fire of the Greek four-element theory correspond to the modern terms, solid, liquid, gas, and energy. With respect to the first three of these, we may agree with Ellis: all solids, all liquids, all gases were no doubt referred to as earth, water, and air, respectively, the generic terms not yet having been formulated. The identification of the Greek fire-element with energy is, however, objectionable. In the burning process, a bright fluid appears to emerge and it was no doubt this which Empedocles, and Aristotle after him, called "fire." On the other hand, the recognition of the peculiar nature of this "element" is already evidenced by the fact that Heraclitus chose fire as symbolic of the principle of change and restless activity, Aristotle (1, p. 147) regarded fire as endowed with a peculiar centrifugal force, and Democritus (460-360 B.C.) considered the "fire atoms" to be the cause of life processes.

Thus we see that in the Greek notion of "fire," three ideas representing different aspects of the combustion process are confused and they remained confused until modern times, when they finally received clear formulation in the distinct concepts of "quantity of matter," "quantity

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of heat" (or, more generally, "quantity of energy"), and "available energy" or "motive power."[2]

Greek Atomism. In the meantime, there had developed another view of the world which was destined to become, many centuries later, the foundation of the kinetic theory of heat. That view was Greek atomism. We have already noted how Heraclitus, captivated by the manifold change and variety in nature, had asserted that the essence of reality was simply flux or continual change, symbolized by "fire." On the other hand, Parmenides (470 B.C.), founder of the Eleatic School, adopting as his definition of Being, that which fills space (corporeality), reasoned that, since non-Being can neither be conceived of nor exist, therefore, there exists only one Being which fills all space. Further, Being, if it were to change, could only pass into non-Being; because this is inadmissible, since non-Being does not exist, it follows that Being is eternal and unchangeable, and that all change as well as qualitative distinctions, must be illusory.

Democritus, the great systematizer of the Atomistic School, confronted with the opposition between the doctrines of Heraclitus and Parmenides, attempted to effect a compromise. He adopted Parmenides' notion of Being, as a stuff whose sole properties are eternality and corporeality (space-filling). But to explain the world of changing phenomena so insistently emphasized by Heraclitus, he supposed this Eleatic Being divided into small bits, scattered throughout empty space, and endowed with random motion. The continual flux of natural process, observed by Heraclitus, is nothing more, according to atomism, than the unceasing coming together and disintegration of the atoms, which, to be

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sure, are assumed to differ in size and shape. "All becoming, or change, is in its essence motion of atoms in space" (1, p. 43).

However, it is only insofar as the kinetic theory of heat may be regarded as derived from the general notions of atomism that Democritus and his followers may be regarded as the true fathers of the modern kinetic notions regarding the nature of heat. For when we inquire how the Greek atomists regarded the phenomena of fire and heat, we find that these were attributed not to any particular state of motion or configuration of the atoms of a body but to the presence in it of a particular species of atoms, namely, the "fire atoms." The "fire atoms," says Democritus, constitute a particular kind of atoms, namely, "the finest, smoothest, and most mobile." This phrase "most mobile" may be interpreted to mean that the "fire atoms" were characterized by a greater velocity than the other atoms. But the modern notion that an ordinary atom, by acquiring through impacts a greater velocity, can become a "fire atom" is implicitly denied by Lucretius, the great popularizer of Greek atomism, when he states that atoms have always moved and always will move with the same velocity (3, p. 139).

The manner in which the Greek atomists regarded the phenomena of fire and heat is typical of the manner in which they explained many of the properties of matter: these properties were regarded as due to intrinsic, unchangeable properties of the atoms in question rather than to the momentary condition of these atoms. Thus the peculiar fluid nature of liquids was attributed to the smoothness and roundness of their atoms. Things which were painful and harsh to the senses were supposed to consist of hooked, rough atoms.

Thus, with respect to the nature of heat, Greek atomism is seen to

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occupy an intermediate position, which, indeed, was revived in modern times, especially by continental Europeans (4, p. 31). Insofar as all things were regarded as constituted of atoms moving in space, Greek atomism foreshadowed the kinetic theory of heat. But in postulating that fire and hot bodies contain particular kinds of atoms (although, to be sure, they were not considered to be atoms of an imponderable fluid), it tended to agree with the Aristotelian postulate of a fire-matter, which was the forerunner, not only of phlogiston, but also of a much more fertile conception, namely, Black's caloric.[3]

2. The Alchemical Principles and Phlogiston

The Hellenistic-Roman and Medieval Periods contributed relatively little to the heat concept. The best European minds of these centuries were occupied with questions of logic, ethics, or theological metaphysics. The only advances in the knowledge of heat were those gleaned by the alchemists of Egypt and Arabia and later of Europe, in their practical, partly magical, attempts to prepare gold from the baser elements and to discover the elixir of life.

Throughout this period, the teachings of Aristotle functioned as the guiding light, especially among the Arabians, who introduced them into Europe through the invasion of Spain in the eighth century and also through contacts made during the Crusades.[4] Like Aristotle they regarded the one fundamental matter as capable of appearing in four different elementary forms (fire, earth, air, and water) which could be changed one into another by a proper variation of properties. However, in their practical work with the metals, they came to regard Aristotle's particular choice of properties as inadequate. Thus we find Geber, an Arabian alchemist of the ninth century, introducing the properties ("principles"),

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"mercury" and "sulfur," the first to account for the luster, volatility, fusibility, and malleability of metals, the second to account for their color, combustibility, affinity, and hardness. To these Valentine added the principle "salt" which was supposed to remain intact on chemical treatment and was regarded as serving as a sort of base for the union of the principles, mercury and sulfur. By variation of these three properties, the metals were thought to be capable of transmutation into one another.

It is not difficult to understand how the alchemists came to associate sulfur with combustibility. A mixture of sulfur and nitre was used as a fusion mixture for the metals, so that sulfur was thought to have the property (intense heat) of fire in this respect. Further, its yellow color suggested the bright color of "fire-matter," which appears to emerge from a substance, leaving an uncombustible residue.

We must realize that the terms "sulfur," "mercury," and "salt" were used, at least in the earlier centuries of the period, in a manner which, from our point of view, was metaphorical.[5] They denoted properties rather than substances, although this distinction seems gradually to have been obliterated.

System of Paracelsus. Thus we find Paracelsus (1493-1541) attemping to reconcile the Aristotelian four-element theory with the three principles of the alchemists by assuming that sulfur is the product of the action of fire on air; mercury, that of the action of air on sulfur; and salt, that of the action of water on mercury. Paracelsus was a man of great influence, and his system, however imaginative, reveals an important fact, namely, that the three principles had come, in the minds of the

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alchemists, to acquire a substantial character so that they were placed in the same category as Aristotle's four elements.[6]

What had happened was, no doubt, that the three-element theory, because of its value in explaining the behavior of the metals, had come more and more into the foreground with the consequent neglect of the Aristotelian doctrine, and that, as a result, the former finally usurped the province of the latter, at least in the field of metallurgy, so that the three principles came to be regarded, not only as properties, but as substances as well. Then the system of Paracelsus may be regarded simply as an attempt to justify current alchemical ideas by referring them back to Aristotelian doctrine, regarded as fundamental.

That by the latter part of the seventeenth century, the sulfur principle, in particular, had come to acquire a definitely substantial character and, indeed, to be more or less identified with the substance which we now denote by that name, is evident from Becher's (1635-82) criticism of the alchemical combustion theory. Sulfur, he says, itself burns and therefore cannot be the principle of combustibility but must, like the metals, contain it. Becher definitely postulates that combustion is a process of decomposition, a view which seems to have been held by all of Aristotle's followers, and states that in the burning of a substance the combustible principle, which he calls terra pinguis (fatty earth), is evolved.

Advent of Phlogiston. Stahl (1630-1734) substituted the term "phlogiston" for Becher's terra pinguis and skillfully employed the hypothesis, under the name of the "phlogiston theory," to correlate the phenomena of calcination, combustion, reduction, and metallic displace-

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ment of hydrogen from acids.

Although the phlogiston theory came to exert a commanding influence on most of the chemists of the eighteenth century, it nevertheless shared the fundamental weakness of the sulfur theory which had preceded it, namely, the confusion between property and substance. Nor was this alleviated by Stahl's statement that phlogiston is "the material and principle of fire, not fire itself" (5).

The increase in weight of a substance, on burning, and the essential part played by the surrounding air were the main facts which finally overthrew the phlogiston theory of combustion. The advocates of the theory met the first objection in two ways. Some of them regarded phlogiston, not merely as an imponderable, but as actually endowed with negative gravity; they regarded its presence as functioning to decrease the effective weight of a body. This idea was advocated by numerous alchemists before Becher's time and indeed was shared by Aristotle who, as we have noted, endowed his fire-matter with a peculiar centrifugal force. Others maintained that the increase of weight was due to the addition of ponderable fire-matter during the combustion process: the fire in the flame was thought to penetrate the container to which it was applied and combine with the burning substance. The second objection, that the presence of air was necessary for combustion, was met by the assumption that it (the air) functioned as an absorbing agent for the phlogiston liberated.

By the latter part of the eighteenth century, the phlogiston theory had become extremely unwieldy; in fact, phlogiston had been variously identified as light, electricity, soot, and hydrogen, and indeed, in

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France, was still associated with sulfur (5). Hence the penetrating researches of Lavoisier (1775) on the weight relations involved in combustion were quite sufficient to cast out from the minds of most chemists the 2,000-year old notion that burning is a process of decomposition and to establish in its place the postulate that combustion consists in the union of the burning substance with the oxygen of the atmosphere.

However, as Merz (6, Chap. VIII) has noted, the phlogiston theory, insofar as it asserted that something was liberated in combustion, contained an element of truth which was destined to bear fruit. Lavoisier's great service showed that the mysterious phlogiston had no place in a description of the weight changes incurred by burning. But a more careful investigation of the changes occurring in the surroundings was to lead to a sort of reincarnation of the phlogiston theory. Our modern phraseology still bears witnes to that reincarnation, for we say that heat is liberated in burning.

Nor had the concept of an imponderable fluid, exemplified by phlogiston, reached the end of its scientific usefulness. Rather, this end had come only in the case of chemistry proper, which, following the example of Lavoisier, proceeded to concentrate on the study of the weight relationships in chemical change. In those branches of physics concerned with changes of state or condition, the concept of an imponderable fluid continued to be of service. We shall see that, as caloric, it rendered invaluable service in comprehending and classifying the phenomena of change of state, expansion, compression, and reciprocal changes of temperature. In the eighteenth century Watson (1746) and Franklin

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(1706-90) independently proposed fluid theories of electricity. Later, Coulomb (1785-1789) advocated the two-fluid theory to correspond to positive and negative electricity. He also proposed two magnetic fluids. These fluid theories of electricity and magnetism served as the basis for the mathematical formulation of the laws in these branches of physics.

3. Rise of the Kinetic Theory of Heat.

In the meantime, epoch-making advances in astronomy and mechanics had brought the motion concept into great scientific prominence, and this fact, together with the revival of Greek atomism, led more imaginative minds to the formulation of the modern kinetic theory of heat.

It is of interest to note that in the cases of Bacon (1620) and Descartes (1640), motion theories of heat are advanced independently of atomism. This was done, in the crudest form, by Francis Bacon (7, Chap. VIII) who, impressed by the motion of boiling liquids and fire, asserted heat to be the outward, upward, expansive motion of the small parts of a body. His doctrine is not a revival of atomism, for he states, specifically, that the motion is "not in the very minutest particles but in those of some tolerable dimensions," nor does he postulate a void. He does not explain how a liquid can be in violent motion without being hot or how, on the other hand, a red-hot iron may be in a state of rest. Descartes, though denying the existence of a void and postulating the infinite divisibility of matter, nevertheless states motion to be the cause of all change. In particular, he regards the sensation of heat as due to motion communicated to the nerves, an old idea of Democritus (1, p. 114).

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Greek atomism was revived and popularized through the efforts of Magnenus (1646) and especially Gassendi (1647). The union of the motion and atomic concepts to account for thermal phenomena had not long to wait, for we find Boyle (1629-91) asserting, in quite the modern fashion, that heat is a molecular motion and Locke (1690) describing it as "a very brisk agitation of the insensible parts" of an object (8, p. 24). Hooke (1665) adopted a similar view toward the property of fluidity, attributing this, not to the shape of the atoms of the fluid, as the Epicureans had done, but to "a certain pulse or shake of heat."[7]

Newton, too, who as Merz (6, Chap. VI) notes, first made the kinetic view of nature scientifically possible through the publication of his Principia (1687), states that "heat consists in a minute vibratory motion of the particles of bodies," (9, p. 84). These views were strengthened when Bernoulli (1738) laid the foundation of the kinetic theory of gases.

Relation of Light and Heat. The tendency to associate heat with motion received a fresh impulse from the establishment, by experiment, of the close relationship existing between light and radiant heat. For whether light be viewed according to the corpuscular emission theory favored by Newton or the undulatory theory of Huygens (1690), it is, in either case, a motion (in the first case, a streaming motion of particles; in the second, a vibratory motion in the ether), so that radiant heat, so closely related to it, must also be of the nature of motion. We have just noted Newton's kinetic view of heat. Huygens also held such a view, for he not only states that light is a motion, but also that the solvent properties of heat and flame, the causes of

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light, indicate that they too are of the nature of motion (10,p. 211).

The close connection between light and heat had already been vividly exhibited by the properties of the burning-glass of Archimedes (287-212 B.C.), and in the thought of the medieval alchemists the two were pretty thoroughly confused. In modern times we find a renewed interest in these phenomena. Tschirnhausen (1699), concentrating the rays of the sun with two large lenses, succeeded in burning wood, boiling water, and melting lead and iron. By coating the metals with charcoal, he was able to volatize them, from which he deduced the salient conclusion that black bodies absorb the most heat. At the same time he cast doubt on the legitimacy of generally identifying light and heat when he observed that the rays of moonlight could not be made to produce any noticeable heating effect.

Boyle, by noting that the burning-glass remains operative in a vacuum, had already demonstrated that the propagation of heat and light is independent of the material medium, and Scheele (1777) verified this with the observation that heat felt ten feet from an oven is unaffected by an intervening stream of air. Scheele also made the important distinction between this sort of heat which he called "radiant heat" (strahlende Warme), and the heat passing out through the chimney with the smoke (convected heat).

Lambert (1779), no doubt influenced by the emission theory of light, assumed that radiant heat consists of streams of "fire-particles," reminiscent of Democritus. He was also convinced that these "fire rays" obeyed the same laws as light, and proceeded to deduce the laws of the burning lens from the principles of optics. At the same time, he was

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aware that the rays of "dark heat" (infrared rays) were reflected in the same manner as light.

The close similarity of light and radiant heat was further demonstrated by Pictet (1790), who noted that a thermometer placed at the focus, or "burning point," of a concave mirror immediately registered a rise in temperature when a hot body was placed at the focus of a second mirror, coaxial with the first but at a long distance from it. From this he concluded that radiant heat must be propagated in straight lines at a very great velocity, perhaps at the velocity of light itself. He contrasted this with conducted heat which, unlike radiant heat, must proceed from particle to particle of the medium and consequently travels much more slowly. However, a complete distinction between radiant and conducted heat is not attained by Pictet, for, on failing to concentrate the heat from boiling water by means of a glass mirror, he thinks this might be done with a mirror which is a better conductor of heat, e.g., a metal mirror.

Hutton (1794) identifies light with radiant heat and postulates that dark bodies also emit radiation, even though undetectable by the eye. A hot body, he says, converts heat to light which, on absorption, becomes heat again. A step backwards appears to have been made by Herschel (1800) when he stated that every ray consists of a light ray and a heat ray.

Rumford (1805), famous for his experiments on frictional heat, regarded a body which radiates heat as analogous to a bell sending out vibrations (heat waves). The temperature of the hot body, he says, is determined by its period of vibration. A series of experiments led

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Rumford to further important conclusions: (1) all bodies radiate at every temperature; (2) the intensity of radiation is different at the same temperature for different bodies (substances); (3) bodies at the same temperature do not influence each other through radiation.

To Leslie (1804) is due the important observation that strongly reflecting surfaces are also poor emitters of radiation and that heat absorption and heat emission increase and decrease together. He also discovered that the intensity of radiation (from a unit area of surface) at a point outside of the radiating body decreases with the angle made by the surface of the body with the line of propagation of radiation to the point. Leslie's speculations on the nature of heat are less fortunate. For, ignoring Boyle's discovery that radiant heat is propagated in a vacuum, he attributed radiant heat to air pulsations set up by the radiating (vibrating) body, thus confusing radiation with convection.

Prevost (1809), who clearly distinguished between the radiation and conduction of heat, adopted the emission theory of radiant heat (calorique rayonnant) and developed it along lines suggested by Bernoulli's kinetic theory of gases. He notes that glass retains "dark heat" but allows radiant heat to pass through and thinks this may be due to the fact that there are several kinds of heat particles. Rumford had already postulated that all bodies radiate at every temperature,[8] and Prevost brought this principle into great prominence in his celebrated "Theory of Exchanges." A hot body is simply one which emits heat particles at a greater rate than colder bodies. The apparent state of rest characterized by equality of temperatures is really, says Prevost, a state of dynamic equilibrium in which the bodies emit the particles of "radiant caloric" at the same rate.

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It will be unnecessary to describe here Fourier's (1817) mathematical systematization of the facts of radiation, nor shall we relate the long series of investigations, extending through the nineteenth century, which served to establish the agreement of radiant heat and light in all their properties, with the resultant triumph of the undulatory theory of Huyghens, the latter having been revived and developed by Young (1801) and Fresnel (1819). Rather, it will suffice, for our purposes, to point out just what significance is to be attached to that period of the history of the subject, ending in the early years of the nineteenth century.

In the first place, we cannot ignore the heuristic significance which these investigations had for the establishment of the First Law of Thermodynamics. For, entirely independent of the question of the precise nature of light and heat, the facts of their close association, conformity to the same laws, and their convertibility constituted undeniable evidence in support of that comprehensive, though vague, view that all of the "forces" of nature are "correlated." The precise manner in which this notion of "correlation of forces" contributed to the founding of the Energy Principle naturally belongs to a history of that principle.

Of more immediate concern is the effect of these radiation studies on current ideas concerning the nature of heat. We have already remarked that, insofar as radiant heat, like light, is regarded as a motion of something, the study of it tended to bolster up the kinetic theory of heat. If, nevertheless, the caloric or fluid theory continued to maintain its supremacy throughout the eighteenth century, this may be

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attributed, to a large extent, to the circumstance that Newton's emission theory, not Huyghens' wave theory, of light (hence of radiant heat) prevailed among most of the physicists of that period.[9] For if light is to be regarded as a rectilinear motion of very fine particles, radiant heat must also be so regarded. And, since the radiating body exhibits no loss in weight, the particles must be those of an imponderable fluid, naturally identified as heat fluid, or caloric, since the radiating body suffered a fall in temperature.[10]

4. Development of the Caloric Hypothesis.

As a matter of fact, the caloric theory was scarcely in need of the support coming to it by virtue of the popularity of Newton's emission theory of radiation, for the hypothesis of an imponderable heat fluid was already proving most fruitful in explaining "mixture experiments", as well as the phenomena of liquefaction and vaporization. And if these investigations appear as over-whelmingly important not only for the heat concept but for thermodynamics generally it is precisely because, in them, attention is concentrated on that particular aspect of changes which we now characterize as "their initial and final states," an attempt being made to define the imponderable heat fluid in such a manner that it will appear as quantitatively conserved in the processes in question.

"Mixture experiments" were not new to the eighteenth century; indeed, Renaldini (1694) had already employed mixtures of boiling and freezing water in varying proportions for the purpose of thermometer graduation. However, the mixture experiments of Fahrenheit, carried out at the request of Boerhaave (1732) were viewed from an entirely

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new standpoint: the thermometer scale was regarded as already given, the final reading of the thermometer being interpreted as indicative of the amounts of heat contributed to the mixture by the constituents. Fahrenheit found that two equal volumes of water at different temperatures attain, on rapid mixing, a temperature which is the arithmetical mean of the two initial temperatures,[11] but that when equal volumes of water and mercury at different temperatures are mixed, the temperature of the mixture is higher or lower than the arithmetical mean, depending on whether water is the warmer or colder constituent. Only when two volumes of water were mixed with three of mercury was the final temperature found to be the arithmetical mean of the initial temperatures.

The standpoint which Boerhaave assumes in attempting to explain Fahrenheit's experiments is typical of the fluid theory adherents. He regards, as a fundamental axiom, the proposition that there exists an imponderable, indestructible fluid which, in the mixture experiments, merely suffers redistribution. The fundamental question then becomes: How was this fluid distributed between the different bodies before mixing? From the viewpoint of historical criticism, Boerhaave's fundamental question is seen to amount to just this: How may the imponderable fluid be defined so as to satisfy the axiomatic requirement of conservation?

Fahrenheit's experiments revealed one weight of water to have the same heating effect, per degree change of temperature, as twenty weights of mercury. Although his experiments had, at the same time, revealed that two volumes of water are equivalent to three volumes of mercury, Boerhaave, no doubt preferring to attribute to experimental error the deviation of three-halves from unity rather than that of twenty, sees fit to state

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that heat is probably distributed between bodies at the same temperature in accordance with their volumes. Thus we see that Boerhaave's heat fluid was endowed with precisely those properties which, more than two thousand years earlier, were attributed to the Eleatic Being, namely, corporeality (space-filling), homogeneity (uniform distribution), and indestructibility.[12]

Confusion of Temperature and Heat. In the thought of Boerhaave we can detect a confusion of the intensity and capacity factors of heat which was quite prevalent in his day. This had already been evident in the case of Newton (1701), who thought that the "heat" of a hot body must be proportional to its "heat loss" and, at the same time, considered the readings of his actually arbitrary thermometric scale to be a measure of the latter and therefore, he thought, of the former as well. When Boerhaave decides, as a result of the mixture experiments, that heat is probably distributed according to volume, he thinks this view substantiated by the fact that bodies in contact come to a common temperature, thus revealing his confusion between uniform temperature and uniform distribution of heat.

The same confusion in terminology exists in the writings of Richmann (1750), who attempted to give mathematical formulation to the results of mixture experiments employing different quantities of the same substance.[13] He does not distinguish between temperature and quantity of heat but refers to both as "heat" (calor). On the basis of experiment and theoretical considerations, he stated that the "heat" u of a mass m on being distributed between the masses m and m' yields the "heat" $mu/(m+m')$, so that if two masses m and m' with "heats" u and u', respective, are

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mixed, the resulting "heat" is $(m\,u + m'u')/(m + m')$. In general, when masses m, m′, m″,. . . of "heats" u, u′, u″, . . . are mixed, the final "heat" will be

$$U = \frac{m\,u + m'u' + m''u'' + \ldots}{m + m' + m'' + \ldots}$$

The close relation of Richmann's "m u" product to our "quantity of heat" is obvious. We must also accredit him with a certain insight into the relative nature of his measurements, for he states that is is not the "absolute heats" but only the excesses over the zero point of his thermometer that come into consideration.

From the appearance of masses in his formula, we might suppose that Richmann leaned to the opinion that heat is distributed according to mass. This does not seem to have been the case, although he disproved Boerhaave's assertion that the rate of cooling of a body is inversely proportional to its density by observing that a body of mercury cooled more rapidly, also was heated more rapidly, than lighter bodies of the same size, shape, and initial temperature. However, in his mixture experiments with water, he considered the experimental error due to the heating of flask and thermometer to be eliminated by regarding these as replaced by the same volumes of water.

Classic Work of Black. By definitely distinguishing between "heat" and "temperature" and by the introduction of the "heat capacity" and "latent heat" concepts, Joseph Black (1760)[14] probably did more than any other man to convert confusion into order in this most important domain of physical science. He begins, in a thoroughly empirical, yet critical, vein by pointing out that the well-known truth that "all bodies

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communicating freely with each other, and exposed to no inequality of external action, acquire the same temperature as indicated by a thermometer," is really a remarkable experimental fact which could not have been predicted from any known relation of each of the bodies, separately to heat. This fact, which had previously been referred to as the "equality of heat," Black wisely prefers to call the "equilibrium of heat," since it is not heat equality but temperature equality which is involved. Boerhaave's view, also adopted by Muschenbroek, that two bodies of equal volume and at the same temperature contain the same heats, he recognizes as an instance of confusion between the quantity and intensity factors of heat. Nor is the heat required to raise different bodies through the same number of degrees proportional to their density. Fahrenheit's experiments clearly show that "the same quantity of the matter of heat has more effect in heating quicksilver than in heating an equal measure (volume) of water.... Quicksilver, therefore, has less capacity for the matter of heat than water...has"; in fact, mercury has only two-thirds the capacity for heat that water has.[15] Heat, then, is distributed in a body, neither according to the body's mass nor its volume but "according to its (the body's) particular capacity, or its particular force of attraction for this matter."

Several investigators on the Continent were led to ideas similar to Black's. With Wilke (1781), the heat capacity notion finds expression in the statement that every body is equivalent to some quantity of water at the same temperature, i.e., the given body will have the same effect as its equivalent quantity of water in raising the temperature of a definite quantity of water through a definite temperature interval.[16]

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Lambert (1775), like Black, distinguishes between quantity of heat (Menge der Warme) and its intensity (Kraft or Starke der Warme). For bodies of the same substance at the same temperature, the first, he says, is proportional to the volume of the body, but the same quantity of heat has in bodies of different substances of the same volume a different force. Lambert regarded heat as consisting of "fire-particles" (Feuerteilchen) and described the Boerhaave-Fahrenheit experiment by stating that three "fire-particles" in water had the same "force of heat" as two "fire-particles" in an equal volume of mercury. From his own observations of the temperature equalization between a liquid contained in a thermometer and a second liquid into which the thermometer was introduced, he concludes that four "fire-particles" have the same heating effect in mercury that six in the same volume of alcohol, and seven in the same volume of water, have.

Concept of Latent Heat. Quite as epoch-making as his ideas concerning heat capacity, was Black's extension of the heat concept to changes of state (liquefaction and vaporization) by means of the notion of "latent heat." When Black first took up the study of these phenomena (around 1760), only one kind of heat was recognized, namely, "sensible heat"; in other words, it was assumed that the addition or subtraction of heat to or from a body must, in every case, make itself evident by a change in the reading of a thermometer in contact with the body. Black demonstrated, with considerable finality, that this view, in the light of observed facts, was quite unscientific and untenable. Thus, he notes that in the case of fusion, if the accepted view be correct, a body of ice at the freezing temperature would be converted, wholly and

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instantaneously, into liquid by the smallest addition of heat. But the well-known slowness of the melting process shows us that this never happens. To confirm his opinion, Black suspended a body of ice and a body of cold water in a warm room and noted the changes in temperature of each. The temperature of the water rose continuously, but that of the ice rose to the freezing point, remained there until fusion was complete, then again rose continuously. The experiment, says Black, reveals clearly that during fusion heat is absorbed without change of temperature, since the body of ice and the body of water were both receiving heat under exactly the same exterior conditions. This was substantiated when he detected a stream of cold air descending from the ice during fusion, this being correctly described as air which had given up its heat to the ice. On solidification of the melted ice, Black reasoned that the same heat must be liberated which had been absorbed on fusion (Principle of Conservation of Heat). The liberation of heat on freezing was ably proven by reference to the supercooling and subsequent solidification of water accompanied by the rise in temperature of the mixture to the freezing point, a phenomenon known to Fahrenheit. The sudden rise of temperature shows, says Black, that it is not the loss of "sensible," but that of "latent," heat which is the condition of freezing.

From these experiments Black feels himself forced to conclude that the addition of "latent heat" at constant temperature is the "principal and most immediate cause of fluidity," whereas the subtraction of the same is the cause of solidity.[17]

Black gives added weight to his views by determining the heat of

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fusion of ice by two different methods. The first was based on the observation already referred to: a body of ice and a body of water, each at the freezing temperature and of known weight, were placed in a warm room, and from the rise in temperature of the water, the amount of heat absorbed by the ice during fusion was readily calculated. The second method was modeled after the mixture experiments of Boerhaave and Fahrenheit; a small piece of ice at the freezing point was introduced into a large body of warm water and the fall in temperature of the water during fusion noted. This with the weight of the water gave the heat absorbed by the ice which, divided by the initial weight of the ice gave the heat of fusion per unit weight. When we consider that this determination was being made for the first time in the history of physics, Black's value of 77 calories per gram for the latent heat of fusion of ice appears remarkably close to the modern value.

Black advanced exactly similar views to account for the facts of vaporization and liquefaction. Entirely unacquainted with any notion of "latent," as opposed to "sensible," heat many of Black's predecessors had held that the bubbles of gas which are generated in, and subsequently expelled from, a boiling liquid are bubbles of heat itself, and that the temperature of the liquid does not rise simply because this heat passes through the liquid instead of being absorbed. At the same time, others maintained that the bubbles were those of air. Black's careful reasoning, coupled with shrewd observation and cleverly designed experiments brought order into this wilderness of confused ideas. Having identified the bubbles as those of the vapor of the liquid, he shows that the constant temperature during vaporization is consistent with

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only one assumption, namely, that the absorption of "latent heat" is the cause of the formation of vapor, just as it had been the cause of fusion or liquidity. Indeed, says Black, if this were not the case, the liquid on reaching the boiling point, would, on the addition of the smallest quantity of heat, explode into vapor. Black's analysis of vaporization also explained why hot water, on being brought to boiling by subjecting it to reduced pressure, experienced a sudden and decided cooling, a phenomenon first noted by Boyle.

Black determined the heat of vaporization of water and then checked this against a determination of the heat of liquefaction, which, he correctly reasoned, should be equal to the former. The first was determined by steadily heating an initially cold body of water until vaporization was complete. By assuming that the rate of heat absorption during boiling was the same as that before the boiling point was attained, he was able to calculate, from the time elapsing during boiling, the latent heat of vaporization. The heat of liquefaction was measured by distilling a definite quantity of water into a known quantity of cooling water whose rise in temperature was noted. In another experiment the water was distilled into an ice calorimeter and the weight of melted ice noted. Black's first values for the heat of vaporization of water were too low (445, 456 calories per gram). James Watt, his famous student and assistant, introducing several refinements, concluded that the correct value lay between 495 and 525 calories per gram, values which compare favorably with the accurate value, 536, obtained over half a century later by Regnault.

Speculations on the Absolute Zero. Black insisted that hot and cold

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were purely relative terms and stated that there was no evidence for any lower limit of the temperature scale. Irvine and Crawford (1778), on the other hand, regarded the fusion experiments as supplying data for the determination of the absolute zero, i.e., the temperature corresponding to the state of zero heat content. Instead of regarding the latent heat of fusion as simply the direct cause of fluidity, as Black had done, they reasoned that, since the heat capacity of water is greater than that of ice, the latent heat must represent the net excess of total heat of the water at the freezing temperature over that contained in the ice at the same temperature. This assumption, coupled with the supposed invariability of heat capacity with temperature, provided all that was necessary for the calculation of the absolute zero of temperature. Thus if c and c' be the heat capacities (specific) of water and ice, respectively, and the absolute zero be t degrees below the freezing point, the view of Irvine and Crawford requires that Q, the heat of fusion, be given by

$$Q = tc - tc'$$

Substituting $Q = 80$, $2c' = c$, we obtain $t = 160$, i.e., the absolute zero is at - 160° C. Further, this view requires that the heat of fusion decreases with decreasing temperature. Thus, for ice, if T be the Centigrade temperature, we have $Q = \frac{1}{2}ct = \frac{1}{2}(160 + T)$.

Dalton, who also adopted this view, showed that the same reasoning, applied to the heat of fusion of mercury, gave the absolute zero as - 2021° C. Gadolin, adopting similar assumptions to account for the heat developed on mixing two liquids at the same temperature, found that the heat of solution of sulfuric acid in water indicated the absolute zero to be between - 830° C. and - 1720° C. Still other "absolute

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zeros" were calculated from other mixture experiments and from the heat of chemical reactions.[18]

Specific Heat Determinations. Through introduction of the concepts heat capacity and latent heat, Black provided a secure theoretical basis for the measurement of quantities of heat, and hence specific heats, by two distinct methods, the method of mixtures and the method of melting ice. Black himself determined a number of specific heats, but most of the determinations date from those of Irvine (1763), Black's student, who measured the specific heats of mercury, glass, iron filings, and numerous other substances by the method of mixtures.[19]

Wilke (1772) employed the ice calorimeter for the measurement of specific heats as also did Laplace and Lavoisier (1780). To the latter is due the recognition of the general variation of specific heat with temperature and the realization that the specific heat can be precisely defined only by means of the calculus. They thus wrote: $s=dQ/dt$. They are with Black in refusing to assume any absolute zero of temperature, nor do they accept the view that the heat of a chemical reaction is to be attributed generally to the difference in heat capacities of reactants and products.

The first accurate measurements of specific heats were those of Dulong and Petit (1813), who employed the water calorimeter. They confirmed the variability of specific heat with temperature, already observed by Laplace and Lavoisier. They also discovered (1819) the law, for which they are best known, that the atomic heat capacities of most solid elements have approximately the same value, namely, about six calories. A similar generalization for the molecular heats of certain classes of solid compounds was later discovered by Newmann (1831).

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The determination of the specific heats of gases have a special significance for the history of thermodynamics because it was to bodies in the gaseous state that the first and second laws were first developed analytically. The first attempts in this direction were those of Crawford (1778) who introduced heated metal cylinders, containing weighed quantities of the gases, directly into a calorimeter. The results were unsatisfactory because of the relatively small weights of gas employed and the consequently small heating effect of the gas.[20] Laplace and Lavoisier (1784) remedied this by sweeping a large quantity m of gas through the coiled tube of an ice calorimeter, noting the fall of the temperature of the gas θ and the weight μ of ice melted. Then $ms\theta = 80\mu$, where s is the specific heat of the gas.

Clement and Desormes (1819) filled the same flasks with different gases, in turn, at the same temperature and pressure, and introduced it into the water calorimeter, whereupon the heat capacities of these gases were placed proportional to the times required to warm the gases through the same temperature interval.

The first accurate measurement of specific heats of gases were those of Delaroche and Berard (1813). The gas at temperature u_1 and constant pressure was led at the rate of m grams per minute through the coiled tube of a water calorimeter where it was cooled to u_2. If a steady state has been reached, indicated by a constant temperature of the calorimeter, the latter must be losing heat to the surroundings at the same rate at which it is absorbing heat from the gas. Hence, if the water value of the calorimeter (at the constant final temperature) be w and if the calorimeter is known to cool at the rate of v°C. per minute, when no gas is supplied, then

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$$ms(u_1 - u_2) = wv,$$

where s is the specific heat of the gas.

Delaroche and Berard's experiments indicated that different gases have different heat capacities, but Haycraft (1824), refining their methods, thought he could conclude that equal volumes of different gases at the same pressure have equal heat capacities, a view supported later by Delarive and Marcet (1827). However, the most careful investigations of Regnault (1837), by the method of Delaroche and Berard, showed this to be true only for oxygen, hydrogen, and nitrogen, whose specific heats he also found to be independent of temperature. He was not able to detect any variation in the specific heats (unit weight) of gases with variation in pressure.

We must note that some of the above methods yield the specific heat at constant volume, others the specific heat at constant pressure. The early workers in this field did not clearly appreciate the significance of this distinction, and the confusion arising from attempts to explain the discrepancy involved, along with that of the cooling of a gas incurred on expansion as well as its heating on compression, constituted a principal factor in the fall of the caloric theory and the enunciation of the First Law of Thermodynamics.

Heat of Chemical Reaction. However, in the meantime, the caloric hypothesis was also demonstrating its great service in other branches of the phenomena of heat. Lavoisier, in researches carried out with Laplace on specific heats and latent heats, had further demonstrated the great scientific value of these concepts, and he attempted to extend the idea of latent heat to account for the heat of chemical reactions. In this line of thought, caloric (calorique), though admittedly imponderable,

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nevertheless plays somewhat the role of a chemical element.[21] Since to convert solids to liquids, and the latter to gases, a great amount of caloric must be supplied, Lavoisier supposed that gases, air in particular, contain the greatest amount of caloric. Accordingly, when a solid burns in air to form a solid oxide, Lavoisier supposes the caloric liberated to be that which was latent in the air, and states that the heat of combustion must be greatest when two gases combine to form a solid. He thus associates the liberation of caloric in a chemical reaction with the change of state of aggregation occurring (12, p. 27). However, in the case where both reactants and products are gaseous, he is forced to explain the heat effect as due to the difference in specific heats of reactants and products.

The conviction that caloric is a conservative quantity led Laplace and Lavoisier to assert that the heat liberated when a system changes its state is equal to that consumed when the system goes through the reverse change, a generalization of the principle employed by Black in dealing with fusion and vaporization. This generalization, which Laplace and Lavoisier were able to verify experimentally to a certain extent, later attained great significance in the work of Hess (1840) where it assumed the form that the heat liberated in a chemical change is independent of the path of the change.[22]

The caloric theory also served to clarify the phenomenon of cooling. As early as 1740, Martine had discovered deviations from Newton's Law of Cooling and these were verified by Kraft, Richmann, Leslie, and Dalton; in fact, the latter had proposed a new temperature scale for which Newton's law would be exact. The exact investigation of the rate of cooling of a body was first carried out by Dulong and Petit (1817).

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Whereas Newton's treatment had been obscured by the confusion of temperature and heat, Dulong and Petit, profiting by the advances instituted by Black, clearly distinguish between these two concepts. Adopting the fundamental notion of heat as a conservative quantity, they regard the net heat lost per unit time by a cooling body as equal to the excess of the heat radiated over that absorbed per unit time. The rate of heat radiation and absorption was, in turn, recognized as being dependent on the temperatures of body and surroundings, on the form and extent of surface of the cooling body, on the total mass of the body, on the peculiar nature of the surface of the body (coefficient of emissivity) and on the nature of the surrounding medium (4, p. 504).

Caloric and Heat Conduction. Another great support of the fluid theory was found in the firm foundation it provided for the theory of heat conduction which attained its highest stage of development in the hands of Fourier (1822). The earliest problems in heat conductivity seem to have been associated with the variation in temperature at the different points of an iron bar subjected to a constant source of heat at one end. The first attempt at a quantitative treatment was that of Amontons (1703), who thought that the temperature increased linearly with the distance from the cold end. To Lambert (1778) is due the realization that the "steady state" attained by such a bar is really a dynamic one in which the heat gained by any element from the hot end equals the sum of the heat given up by the element to the surrounding air and that passed on to the colder part of the bar.

The confusion of radiated heat and conducted heat was naturally associated with the confusion of emissivity and conductivity (often referred to as "outer," or "surface conductivity," and "inner conducti-

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vity," respectively). Thus Franklin supposed that, if bars of different metals, but having the same dimensions, be coated with wax and all exposed, at one end, to the same source of heat, then the distances over which the wax was melted, in the steady state, would be proportional to their conductivities for heat. Ingenhouss (1785) adopted this point of view and carried out the experiments. But J. T. Mayer (1791), reasoning that the best conductors of heat should be those which lose their heat to the air most rapidly, concluded that Ingenhouss' best conductors were actually the worst.

The first sound theoretical treatment of the stationary state of a unilaterally heated bar is due to Biot (1804). He reasoned that, at any point, the heat gained from the hot end equals that lost to the air throughout the remainder of the bar, which, in turn, may be computed from Newton's law of cooling. In this way, he deduced the law that, for distances from the cold end which form an arithmetical progression, the corresponding temperature excesses over the surroundings form a geometric progression, also verifying it experimentally over a considerable temperature range.

All of the laws of heat conduction were developed in a marvellously systematic and comprehensive way by Fourier, working from 1807 to 1822, when his great Theorie analytique de la Chaleur was published. He distinguished clearly between heat capacity, emissivity, and conductivity, and formulated the first precise analytical definition of the latter concept. His whole theory of conduction followed rigorously from a simple fact, taken as first principle: the quantities of heat exchanged between two parts of a conducting body, lying very close together, are proportional to their temperature difference. The solution of the problem of the dis-

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tribution of heat in a long bar in the steady state appeared as a mere detail in Fourier's comprehensive elaboration: he showed that, assuming invariability of conductivity with temperature, the distances over which the wax was melted in Ingenhouss' experiment were proportional not to the conductivities themselves but to their squares.

Although Fourier does not commit himself on the nature of heat, the latter concept appears in his equations precisely as if it were an imponderable fluid which suffers change of distribution but never gain or loss in total quantity, and which strives to attain a uniform "temperature level" just as a ponderable fluid seeks a condition of uniform height above sea level. The fluid theory of electricity had already been advanced in the eighteenth century by Franklin, Aepinus, Coulomb, and others; and Ohm (1826), impressed by Fourier's work, conceived of the analogy between flow of electricity and flow of heat. He argued that an analogue of the temperature difference of Fourier's theory should exist for electric currents and was thus led to formulate that most useful concept, electromotive force ("electroscopic force").

Caloric as Substance. With so many victories to its credit, it is not surprising that the caloric theory came to occupy a position of commanding influence and relative security, a position which it did not completely relinquish until the middle of the nineteenth century. In particular, the growing number of facts consistent with the caloric hypotheses had the effect of bringing increasingly into prominence the conviction that caloric was an actual substance.

This is already evident in the terminology of Boerhaave who, by referring to heat by the latin term ignis, reveals the close relationship between the eighteenth century heat fluid and the Greek "fire-matter."

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It is significant that Black, who carefully warned scientists against attempts at ultimate explanations in terms of hypothetical abstractions (15, pp. 282-285), nevertheless revealed, in his terminology, a firm belief in the substantial nature of caloric. For he refers to heat as "matter of heat" and characterizes the "equilibrium of heat" by the very materialistic phrase "equality of saturation." Moreover, adopting Cleghorn's assumption that caloric exhibits an attractive force for different substances, he identifies the heat capacity of a body as "its particular force of attraction for this matter."

Berthollet, to whom Ellis (2, p. 186) attributes the introduction of the term caloric, cautiously defined it simply as the "cause of heat." Lavoisier was, at times, equally careful, for he says (2, p. 186), "rigorously speaking, we are not even obliged to suppose that caloric is a real substance; it suffices that it may be any cause whatever which separates the molecules of matter, and we can thus consider its effects in an abstract and mathematical way." Yet the phraseology of this very excerpt ("we are not even obliged" to consider it a substance) indicates that Lavoisier considered it both natural and legitimate, even though unnecessary, to regard caloric as a "real substance." That this was indeed his view is corroborated by his explanation of the explosive force of gunpowder: this, he said, is due to the sudden liberation of caloric, "that highly elastic fluid," also by his reference to fusion as a process of "solution in caloric." But the most convincing evidence of his belief in the substantial nature of heat is found in the circumstance that even after he had, by his investigation of combustion, banished phlogiston from science, he nevertheless continued to retain "caloric" in his table of chemical elements.

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Cleghorn and Black had endowed caloric with the fundamental Newtonian property of matter, that of attraction (for other kinds of matter), and Lavoisier had even placed caloric in his table of elements. From these circumstances, it is not surprising that some eighteenth century calorists thought that caloric possessed at least some mass (4, p. 32). Otherwise Rumford, a great opponent of the caloric theory, would hardly have considered it worth-while to carry out his investigation, An Inquiry Concerning the Weight of Heat (1799). He was able to show conclusively that caloric, if it exists at all, does not possess mass.

After Rumford's investigations, all calorists recognized that caloric, like electricity and magnetism, must be an imponderable. However, the property of weight had never been regarded as fundamental, except insofar as it was implied by the postulated attraction of caloric for matter. A more fundamental property, which had been assumed from the beginning, was that of the elasticity and self-repellent nature ascribed to the heat fluid.[23] Thus Dalton (16, ii, p. 393) says that besides the force of attraction between particles, "we find another force that is likewise universal, ... a force of repulsion. This is now generally, and I think properly, ascribed to the agency of heat. An atmosphere of this subtle fluid constantly surrounds the atoms of all bodies and prevents them from being drawn into actual contact." Also Fourier speaks of "the equilibrium which exists, in the interior of a solid mass, between the repulsive force of heat and molecular attraction." He also says that "heat is the origin of all elasticity."

This self-repellent property of caloric explained why the volumes of bodies quite generally increased on heating (at constant pressure).

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The anomalous cases of the fusion of ice and the contraction of water between the freezing point and 4°C. were "explained" by reference to analogous cases in mixtures of ordinary matter; e.g., the solution of water and alcohol, also that of copper in tin, and numerous chemical reactions are accompanied by a decrease in volume.

Indeed, the magnificent edifice comprising both theory and experiment, erected on the basis of the caloric hypothesis, must cause us to place it among the most fruitful hypotheses in the history of science. However, in the meantime, the facts of frictional and electrical generation of heat and the heating and cooling of gases on compression and expansion, respectively, were coming into increased prominence and were destined, after a battle of half a century, to bring about the fall of the fluid theory. This fall was coincident with the establishment of the First Law of Thermodynamics and, in many cases, with the revival of the kinetic theory of heat.

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Footnotes:

[1]Aristotle's properties were hot, cold, dry, and wet. Of these, hot and dry, especially hot, were supposed to belong to fire; hot and wet, especially wet, to air; cold and wet, especially cold, to water; and cold and dry, especially dry, to earth. By alteration of properties the one basic kind of matter could assume the form of fire, air, earth, or water.

[2]As an element in the same category as earth, water, and air, "fire" is "matter"; as identified with perpetual process (Heraclitus), it is "quantity of energy"; and as endowed with a peculiar force (Aristotle), as the "principle of disturbance" (Empedocles), as endowed with unusual mobility (Democritus), or as the principle of restless activity (Heraclitus), it corresponds roughly to "available energy," or "motive power."

[3]This statement is not intended to divert attention from the fundamental opposition between Greek atomism and Aristotelianism. For Democritus the only primary, i.e., real, properties of matter are extension in space and motion. Aristotle, on the other hand, was quite opposed to any attempt to reduce phenomena to mechanical causes, e.g., "hotness" itself was, for him, a primary quality.

[4]Of Aristotle's works, only a portion of his logic was transmitted directly to European posterity by means of the Christian theology. The remainder arrived much later via Arabia (1, p. 268).

[5]Wisely avoiding confusion, Brown (5) calls the alchemical principles "philosophical sulfur," "philosophical mercury," etc.

[6]This is particularly evident from Paracelsus' description of the burning process: "That which smokes and evaporates over the fire is mercury, that which flames and is burnt is sulfur, and all else is salt" (2, p. 161).

[7]For heat being nothing else but a very brisk and vehement agitation of the parts of a body," these "are thereby made so loose from one another, that they easily move any way and become fluid" (2, p. 96).

[8]Hutton first noted the contradiction involved in assuming that only the hot body radiates: the same body, at the same temperature and in exactly the same state, is assumed to radiate, or not radiate, depending on whether it is the hotter or the colder of the two bodies.

[9]This we may attribute to the failure of Huyghens' theory to account for the nature of shadows and for rectilinear propagation, together with the fact that Newton's great authority opposed it. Young (1800) revived and expanded the wave theory in England, but his work was hardly noticed. It was Fresnel (1817), working in France, who finally convinced scientific authority of the superiority of the undulatory theory, but only after overcoming vigorous opposition. Thus his most important memoir on the subject, though submitted to the French Academyin 1821, was not published until 1827 (11, ii, p. 115).

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[10]A curious dilemma must have presented itself to those scientists who opposed, on general principles, the assumption of an imponderable fluid. For if the existence of an imponderable heat fluid be denied, that of another, namely, Huyghens' ether, must be admitted to account for the propagation of radiation through a vacuum.

[11]Strictly speaking, if the final temperature is the arithmetical mean of the initial temperatures when one thermometer is employed, it will not be so when another thermometer, employing a different thermometric substance, is used instead, unless the expansion of the first thermometric substance is proportional to that of the second. The appreciation of this fact had to await the exhaustive investigation of thermometric scales by Dulong and Petit (1817).

[12]To be sure, the analogy is not perfect, for Boerhaave did not deny the existence of a vacuum nor that of matter or fluids, other than caloric.

[13]Kraft (1746) had already made an attempt in this direction when he advanced for U, the final temperature of a water mixture, the empirical formula

$$U = \frac{11\,m\,u + 8\,m'u'}{11\,m + 8\,m'}$$

where u and u′ denote the initial temperatures of the bodies of water of masses m and m′, respectively. The asymmetry of Kraft's formula must have been due to experimental error.

[14]Black's pothumous Lectures on the Elements of Chemistry, which contained his ideas on heat, was not published till 1803. However, a surreptitious publication, containing an account of his views, appeared in London in 1770. Moreover, after 1760, he disseminated his views among his students orally by means of his lectures (11, ii, p. 161). In this way, many of Black's ideas became dissociated from the name of their originator. (4, p. 180).

[15]Black observes that this fact also explains why, if equal volumes of water and mercury are placed at the same distance before a fire, the mercury warms faster, and when the fire is removed, cools more rapidly than the water.

[16]To Wilke is due the introduction of the term "specific heat," which was suggested by the analogy with specific gravity (11, ii, p. 159).

[17]Some investigators of this time, e.g., Muschenbroek, adopting an ancient view of Democritus, held that water was a fluid not by virtue of heat imparted to it but because of an "essential quality," depending upon the supposed spherical shape of its particles. Freezing, they supposed due to the addition of "frigorific particles," a view supported, in the case of water, by the increase in volume on freezing (4, p. 33).

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[18] As Mach (10, p. 168) notes, even though the assumption that the heat of fusion represents the net excess of the heat of the liquid over that of the solid at the freezing temperature, along with that of the invariability of heat capacity with temperature, be accepted, still the data need not necessarily be regarded as indicative of an absolute zero: if the temperature calculated be assumed to be that at which the heat of fusion in question assumes a zero value, then one may assume, equally well, that below this temperature the heat of fusion acquires negative values. Indeed, such a point of view would have eradicated the apparent discrepancies between the different "absolute zeros," since there would be no reason for supposing that all substances exhibited a zero heat of fusion at one and the same temperature.

[19] Let m and m' be, respectively, the mass of the body introduced and the water value of the calorimeter in grams of water. Then if the initial temperatures of body and water calorimeter are t and t', respectively, whereas the final common temperature is t'', we have

$$m(t - t'')s = m'(t'' - t')$$

from which s, the specific heat of the substance composing the body in question, is determined.

Again, if a body of mass m, specific heat s, and temperature t causes by its introduction into the ice calorimeter the melting of μ grams of ice, we have

$$mst = 80\mu$$

from which s may be calculated.

[20] Thus Crawford found, for the specific heat of air, 2 calories per gram (1). Lavoisier and Laplace, with their much improved method, got 0.33, the correct value being 0.2374.

[21] Light (lumiere) and caloric (calorique) appeared at the very top of Lavoisier's table of elements (tableu des substances simples), followed by the chemical elements known in his day. As older terms for caloric, he lists heat, principle of heat, igneous fluid, fire, matter of fire, matter of heat, but not phlogiston. Yet, in expounding his theory of combustion (1777), he states that caloric, as well as light, are evolved in every combustion, quite in the manner of the phlogistinians (17, p. 55). The essential point here is, of course, that Lavoisier recognizes that the liberation of the imponderable caloric is only one aspect of combustion and is accompanied by combinations with the ponderable oxygen of the air.

[22] The influence of Lavoisier's relegation of caloric to the same class as the chemical elements is seen in Hess's attempt to extend the law of multiple proportions to caloric, i.e., he tried to show that "when two substances combine in several proportions, the quantities of heat which are produced in the formation of the different compounds stand to one another in multiple proportions" (13, p. 504).

[23] As early as 1733, the same property had been attributed to each of the two electric fluids by Dufay (11, ii, p. 201).

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III. THE DEVELOPMENT OF THE ENERGY CONCEPT AND THE FIRST LAW OF THERMODYNAMICS.

page

1. The Greek Being as Precursor of Energy. 139

2. The Modern Revival of the Substance Hypothesis: Kinetic Theory versus Caloric.

A. The Cartesian Substance in Specialized Science. 143

B. The Existence of Frictional Heat. 147

C. Thermal Phenomena Accompanying Expansion and Compression of Gases. 150

D. Thermal Effects Related to Electricity, Magnetism, Light and Chemical Action. 160

E. The Explanation of Animal Heat. 163

F. The Precursors of the First Law: Mohr, Seguin, Liebig, and Grove. 168

3. The Development of the Concept of Mechanical Work.

A. Excluded Perpetual Motion. 172

B. Momentum versus Vis Viva. 176

C. The Work Concept in French Technical Mechanics. 182

4. The Formulation of the First Law of Thermodynamics.

A. Mayer and the Principle of Equivalence. 185

B. Joule and the Mechanical Equivalent of Heat. 193

C. Helmholtz and the Mechanistic Hypothesis. 199

Footnotes 214

References 399

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III. THE DEVELOPMENT OF THE ENERGY CONCEPT AND THE FIRST LAW OF THERMODYNAMICS.

1. THE GREEK BEING AS PRECURSOR OF ENERGY.

If we characterize the history of the heat concept as a long and laborious search for a quantity which is conserved in thermal phenomena, we may similarly describe the evolution of the energy concept as a search for a quantity which is conserved in all physical phenomena, of which thermal changes constitute only a special class; and, if, to bring to light the beginnings of the notion of heat, we must delve into Greek philosophy, this is all the more necessary in the case of the energy concept.

For Greek philosophy, at its very start, concerned itself with the question, How can identity be consistent with change, reality with process, Being with Becoming? It is most significant that, in framing solutions of this problem, the early Greeks were everywhere guided by the naive conviction of the unity of the world, i.e. by the assumption that the question did, indeed, possess an answer.

Among the Ionian natural philosophers (Thales, Anaximander, Anaximenes (640-500 B.C.)) the question of how identity may persist through change, which we may refer to as the philosophical problem of substance, took the rudimentary form, What is the nature of the cosmic matter or "world-stuff" which constitutes "the abiding ground of all these changes,..., which experiences all these transformations, from which all individual things arise, and into which they become again transformed." (15,p.32) Thales, no doubt influenced by the phenomena of solidification and vaporization, also probably aware of the essential part played by moisture in organic processes, declared the "world-stuff" to be water.

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Just as in the Greek "fire-matter" we saw intermingled concepts which many centuries later were destined to separate out as "matter," motive power" or "available energy," and "heat," so in the Ionian "world stuff," we see "matter," "available energy," "energy," and "path of change" likewise confused. As endowed with materiality or corporeality, the "world-stuff" is matter. Also, because of their naive hylozoistic viewpoint, the Ionian philosophers supposed that things which change must be alive, and hence capacity for change (animation) was regarded as a fundamental property of the cosmic matter. Further, in its passive aspect, as the fact of completed process, the "world-stuff" corresponded to quantity of change (our energy).[1] Finally, as actual process, it calls to mind the modern notion of path of change of state.

These considerations render intelligible Anaximenes' preference for air as cosmic matter, on the ground that it possessed an essential characteristic which water, in his opinion, lacked, viz. that of infinity. For, since the changes of nature appeared to be unceasing, the "world-stuff," in so far as it was identified with capacity for change and Becoming, had to be infinite: for "a finite cosmic matter would exhaust itself in the ceaseless succession of productions"(15, p.33). Anaximander, however, thought that this essential characteristic of infinity was possessed no more by air than by water or any other substance which we may perceive. No object of experience, he said, corresponds directly to the "world-stuff;" yet, to explain experience, we must assume such a conception as real and conditioning all phenomena. Hence, he simply called the cosmic matter "the Infinite" and attributed to it the qualities which Thales and Anaximenes had attributed to water and air, respectively, viz. "it has never begun to be, it is imperishable, inexhaustible, and indestructible." However, Anaximander's vague terminology should not

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lead us to suppose that, in his system, the concept of matter was no longer a constituent element in the notion of "world-stuff." Rather, it is probable that his substance was "an infinite Corporeal mass, in which the various empirical substances were so mixed that no definite quality could be ascribed to it as a whole." (15,p.34)

It is in the system of Heraclitus that we find the concept of matter ejected from the notion of the "world-stuff;" for the latter was for him just the fact of change itself, which he symbolized by declaring "fire" to be the essence of all things. At the same time, he introduced the most important principle that allchange takes place in conformity to a definite law. "All flows, and nothing abides... The rhythm of events is therefore the only permanent... In this ceaseless transformation of all things nothing individual persists, but only the order, in which the exchange of contrary movements is effected--the law of change, which constitutes the meaning and worth of the whole.[2]

In tracing the history of the heat concept, we saw how, in opposition to Heraclitus, there was set up the purely logical system of Parmenides, who declared all change and qualitative differences to be illusory and answered the problem of substance by postulating one timeless, changeless, indestructible, homogeneous Being, filling all space. It was also observed how, as an attempt at compromise between the views of Heraclitus and the Eleatics, there arose the Atomistic School, which explained phenomena on the hypothesis of an Eleatic Being split up into extremely small bits (atoms) of various shapes which were supposed to be in rapid, random, ceaseless motion.

For our purposes, it will be sufficient to point out how the notion of conservation, so important for the First Law, played with Parmenides and the Atomists a dominant role as it had already done with the Ionian

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philosophers of nature. With Parmenides, the conservation postulate caused the doctrine of substance to take the extreme form where it necessitated the denial of the reality of process. With the atomists, it played a double role: on the one hand, the atoms themselves were supposed to be indestructible and to have ahd no beginning, and, on the other hand, their motion, too, was assumed never to increase or decrease.

Indeed, this idea of conservation was employed in one form or another by all of the Greek philosophers. Empedocles supposed it applicable to each of his four elements; Anaxagoras attributed it to each of his elements, supposed infinite in number, and especially to his "force-element" (15,p.41), regarded as the cause of all motion. With Plato and Aristotle, Empedocles' four elements were supposed to be different inter-convertible formsof a single fundamental matter, the conservation attribute being ascribed to the latter only.

In the case of Plato and Aristotle, however, this notion of matter was thoroughly overshadowed by the new content which the concept of substance had, in the meantime, acquired. Following on the speculations of the earlier Greeks, which were confined almost wholly to the philosophy of nature, there had arisen an awareness of, and interest in anthropomorphic problems, with the result that the task of formulating the concept of an all-embracing substance was seen to involve new and more complex aspects. Thus, with Aristotle, whose system constituted the union and culmination of the various trends in Greek thought, the concept of substance possessed a double meaning. On the one hand, the individual thing was the truly real, i.e. it was the essence or substance. On the other hand, since the individual thing existed only if the species manifested itself in it, the species also were called substances.

Both of these meanings of the substance concept are opposed to the one

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which lies at the basis of the modern theory of energy. For if the individual things are real, as such, they are not identical. Thus, according to this notion of substance, the task of knowledge is not to reduce the individual things to instances of one and the same substance(as the early Greek natural philosophers, also the atomists, had supposed), but rather to predicate of the individual thing the qualities which belong to it.. Thus the individual thing, according to this view, is never predicate but always subject of a proposition (15, p. 141). Nor was Aristotle's second meaning of substance much nearer to that advocated by modern physical realism. Thus when plants were said to be instances of the same species (substance), this was not meant to imply that they were identical; rather they were thought of as exemplifying, in different degrees, the plant species regarded as archtype or Platonic idea.

The reception of Aristotle's works by the Christian church began about 1150 and continued until the middle of the thirteenth century. Thereafter, his ideas, through their incorporation into church doctrine, came to exercise a commanding influence, which, indeed, played no small part in delaying the development of physical science. A revolt, however, was gradually gathering weight and culminated in the seventeenth century in the philosophical system of Descartes.

2.THE MODERN REVIVAL OF THE SUBSTANCE HYPOTHESIS: KINETIC THEORY VERSUS CALORIC.

A. The Cartesian Substance in Specialized Science.

In the Cartesian philosophy, the notion that "beneath the various qualities, which are the appearances of the phenomenal world, there is a single Substance which is only capable of quantitative distinctions" found clear expression. At the same time, the process of abstraction, whereby different

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individual things could come to be regarded in their "real" light as instances of one and the same substance, involved the mechanistic despiritualization of nature.

In the development of modern physical science, it is precisely the belief in a Cartesian substance which is conserved, which functions as the guiding idea through which order is won out of the manifold variety of nature. However, in accordance with the restriction of scientific study and investigation to special fields of phenomena, regarded as mutually distinct, the Substance motion assumed, among the scientists of the eighteenth century, the form in which a peculiar substance was allotted to each special domain of phenomena. In mechanics, the substance idea appeared as the "force" of a moving body, a quantity which the Cartesians regarded as synonymous with Newton's "quantity of motion" (momentum), but which Leibnitz and his followers thought should involve the square of the velocity. Lavoisier's great researches served to show that the substance, which remains conserved in chemical processes is "quantity of matter" as defined by the process of weighing. In establishing a definite substance concept in chemistry, Lavoisier simultaneously performed the great service of separating out from the vague "world-stuff" the element of corporeality, although the significance of his achievement was slow to be appreciated. Thus the substances alloted to the phenomena of heat, electricity, magnetism, and light, though generally referred to, after Lavoisier, as imponderables, were still endowed with the property of filling space as is evident from the fact that they were referred to as "fluids."

Until the dawn of the First Law of Thermodynamics, each of the above-mentioned substances was supposed to function as exclusive lord in its own domain: it was more or less generally assumed that each possessed

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the traditional attributes of "Being without Becoming, imperishability, and indestructibility.[3] However, with the advent of the nineteenth century, the border-line phenomena, i.e. those involving relations between fields of physical experience previously regarded mutually distinct, pressed forward with increasing demands for recognition, with the result that physical science became conscious once again of the age-old problem of how to attain unity from variety, constancy from change. Thus it is as the progressive attempt to solve the philosophical problem of substance, in its general, physical aspect, that the history of the development of the energy concept is best understood.

The universality and inevitability of the problem is evidenced by the wide variety of fronts on which the new conceptions were being advanced, conceptions which were destined to find unity, toward the middle of the century, in the First Law of Thermodynamics.[4] On the one hand, the frictional generation of heat and the heating and cooling of gases on compression and expansion were raising insurmountable objections to the old caloric theory, with the result that, in some quarters, the kinetic theory of heat was being revived, and, in still others, there developed a tendency to assume a purely positivistic attitude toward the fact of interdependence of the phenomena of heat and mechanics. Further, newly discovered facts in the domains of electro-chemistry, electro-magnetism, electro-kinetics, thermo-electricity, radiant heat, physiological chemistry, bio-physics, and others, pointed unflinchingly to manifold connections between the older divisions of science, heretofore supposed distinct. Finally, the whole movement was given a vital impetus by the clear formulation, during the first quarter of the century, of the concept of "work" in mechanics.

To be sure, the kinetic theory of heat had never completely died out,

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and its ascension to a position of prominence was already foreshadowed by the peculiar form taken by the caloric theory among numerous continental scientists in the eighteenth century: caloric was supposed to be corpuscular in nature, and its particles, assumed to be in rapid motion, were thought, by some, to impart their motion to the particles of the heated body through successive impacts (32,p.7). Corpuscular caloric probably got its start through the spread of the fire-particle concept of Greek Atomism, previously revived by Gassendi[8/]. Early in the eighteenth century, the idea was promulgated by Herman Boerhaave. Later, we find that certain passages of Baron de Holbach's pseudo-scientific, but highly influential work, Systeme de la Nature, published in 1770, are very reminiscent of Lucretius. Thus, after attributing all modifications of matter to the motions of elementary particles, he said that "fiery particles are in play in all the events of life, and,now visible, now concealed beneath the rest of matter, produce numerous phenomena" (27, ii,p.101). This corpuscular theory of caloric, which was no doubt given added impetus by the popularity of Newton's emission theory of light, was adopted by Lambert, and the progressive change exhibited in his views may perhaps be taken as indicative of a trend in the direction of the motion theory of heat even in the very years when the caloric theory was exhibiting its greatest strength. For, in a work written around the middle of the eighteenth century, Lambert merely spoke of the mutually repelling forces of his fire-particles, but, twenty-four years later, he ascribed velocities to them (4, p.160). Prevost, as we have already noted, explained the phenomena of radiant heat by the assumption of heat particles moving in straight lines. Even Fourier exhibited a leaning toward the motion theory of heat. For, he said (25,p.39): "The effects of heat can by no means be compared with those of an elastic fluid whose molecules are at rest...

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The free state of heat is the same as that of light; the active state of this element is then entirely different from that of gaseous substances."

B. The Existence of Frictional Heat.

In the meantime, the fact of frictional heat was causing the caloricists increased embarrassment. That the evolution of heat appears to result from friction and percussion was, of course, well-known to the adherents of the caloric theory. However, in those instances where the friction or percussion incurred changes of state, they were able to account for the heat evolved in the same way in which they explained the heat of solidification or the heat of chemical reaction; that is to say, they could regard the heat as the direct result of the change of state, or they could make the more specific assumption that the heat evolved corresponded to the difference in the heat capacity of the body in the two states. Thus, the rise in temperature of a nail when hammered, they could attribute to the circumstance that the particles of the iron are pressed closer together and that, as a result, heat, previously latent, becomes sensible, just as occurs when a gas is liquefied; or adopting a line of reasoning employed by Irwin and Crawford, they could suppose the heat evolved indicative of the difference in the total heats of the iron in the two states and, assuming a definite absolute zero, attributable to a change in heat capacity. To be sure, these sorts of explanation taxed the imagination less in cases where a change of state was clearly evident, e.g. when the evolution of frictional heat incurred a pulverization of a solid.

On the other hand, the adherents of the kinetic theory of heat, taking special note of the sensible motion consumed in friction and

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percussion, had early recognized, in these processes, strong evidence for the view that sensible heat is a motion of the insensible parts of a body. Thus, Boyle stated that a nail on hammering becomes hot because of "the forcible motion of the hammer, which impresses a vehement and variously determined agitation of the small parts of the iron." He supported this view with the observation that, when a nail is being driven into a board, the same blow of the hammer will cause a greater heating effect, once the motion of the nail stops.

However, such explanations as these must have seemed far more speculative to the calorists than any they themselves were called on to make. It was not until the quantitative investigations of Count Rumford, in 1798, that the generation of frictional heat began to give serious trouble to the caloric theory. Noticing the production of large amounts of frictional heat in the boring of cannon, Rumford's attention was drawn to the question of the nature of heat,[5] and he decided to attempt to illuminate this problem by quantitative experiments. He prepared a hollow gun-metal cylinder, mounted it on a horizontal axis so that it could be driven by horse-power, while the blunt end of the borer pressed against its bottom. Through a radial hole, he immersed the bulb of a thermometer in the cavity of the cylinder; and, to diminish heat loss to the outside, he surrounded the cylinder with flannel. He found that in the course of one-half hour, 960 revolutions of the cylinder produced 837 grams of metallic dust and raised the temperature of 113 pounds of gun metal through 70 degrees Fahrenheit. To overthrow the common caloric theory explanation, that the heat produced was due to the change in heat capacity, he determined the specific heats of solid metal and that of the small metallic chips and discovered no appreciable difference.

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In another experiment, he placed the cylinder and boring apparatus in a box of water and calculated that the heat liberated in two and one-half hours was enough to raise 26.58 pounds of ice-cold water to the boiling point.

Rumford emphasized that heat may be produced in unlimited amount by this process, and this, together with the agreement of the heat capacities of solid metal and powder, caused him to attack the caloric hypothesis and to advocate the acceptance of the kinetic theory of heat.[6]

A very significant experiment was the one first performed in 1799 by Sir Humphrey Davy: he melted ice by rubbing two blocks of it together. The process was accomplished by clock-work, under the exhausted receiver of an air-pump surrounded by ice, so that very little heat was exchanged with the surroundings. Davy saw, immediately, the peculiar significance of his experiment, namely, that, in it, the production of frictional heat was accompanied by a change of the substance into a state characterized by a greater heat capacity than that of the original state.[7] He did not proceed to make his observations the basis for advocation of the motion theory until several years later when he said that "heat...or that power which prevents the actual contact of the corpuscles of bodies, and which is the cause of our own sensations of heat and cold, may be defined as a peculiar motion, probably a vibration of the corpuscles of bodies tending to separate them. It may with propriety be called the repulsive motion. Bodies exist in different states, and these states depend upon the action of attraction and of the repulsive power of their corpuscles..."(35,p.46).

The experiments of Rumford and Davy attracted very little attention before they were revived about forty years later by Joule. In the case of Rumford, this may be attributed, in the first place, to the fact that his work did not provide conclusive evidence against the caloric theory. For

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even though it be assumed that the heat capacities of solid metal and powder remain equal at lower temperatures, still the heat generated could be regarded as a direct result of the change of condition of the metal.[8] With Davy, however, this was not the case. For not only was water known to have a greater heat capacity than ice, but, further, heat had been recognized, since Black's experiments, to be the cause, not the result, of liquefaction.

If Davy's, along with Rumford's work, remained, nevertheless, quite uninfluential, this may be attributed, aside from the circumstance that it was probably not very well-known, to the fact that the motion theory was still a very vague hypothesis, as compared with the caloric theory. The latter defined heat as a definite, measurable quantity, and we have already described the great advances that were made, with this definition regarded as the premise. Rumford and Davy, on the other hand, called heat a motion, but they gave no indication of how much a motion was to be measured. Many of the phenomena of heat, readily explained with the caloric hypothesis, must have seemed to present difficulties to the kinetic theory. Thus, the calorists might very well have queried, What is meant by saying that the conduction of heat consists of a flow of motion?

C. Thermal Phenomena Accompanying the Expansion and Compression of Gases.[9]

That the nemesis of the caloric theory, at least in its traditional form, was nevertheless not far distant, was further evidenced in the confused attempts of the calorists to account for the temperature changes incurred in gases on compression and expansion, together with the lack of temperature change on free expansion. E. Darwin in 1788 and M. A. Pictet, eleven years later, had noted the temperature changes incurred on expansion, but the first systematic experiments were those of John Dalton

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in 1800. The latter placed a thermometer in a container of air and noted the fall in temperature on evacuating with the air pump and the rise resulting when the air was allowed to stream in again. From the circumstance that the change in the thermometric readings, though small, occurred very rapidly, he concluded that the actual change in temperature of the gas was much greater than that recorded by the thermometer, and this conclusion was substantiated when thermometers with smaller bulbs exhibited greater temperature changes. To determine the actual temperature of the gas, Dalton observed the initial rate at which the thermometer reading changed when the air pump was applied to the flask. Then, in a separate cooling experiment, he determined the temperature difference corresponding to this rate of cooling. Thus, in one experiment, he found that, on applying the air pump, the thermometer reading fell at the rate of 1°F. in $3\frac{1}{2}$ seconds from which he was able to deduce that the fall in temperature of the gas amounted to 50 Fahrenheit degrees.

To account for these phenomena, Dalton resorted to the hypothesis, then popular among many of the adherents of the caloric theory, that the appearance or disappearance of sensible heat must be due to a change in heat capacity incurred by the change of state. Thus, he supposed that the diluted air had a greater heat capacity than the denser air, so that, on expansion, a fall in temperature resulted. More specifically, it was assumed that, on expansion, sensible calorique became latent by associating itself with the increased space at its disposal.[10] A substantial nature was thus attributed to the empty space; in fact, Dalton thought that, through such experiments, the specific heat of a "vacuum" could be determined.

It was with Dalton's point of view in mind that Gay-Lussac, in company with Laplace and Berthollet, first performed the famous

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"free expansion" experiments in 1806 (6,p.170). Supposing that the cooling effect on expansion was due to the greater specific heat of the diluted gas, he hoped, by expanding different gases under exactly the same conditions, to arrive at their (relative) specific heats. For this purpose, he placed the gas to be investigated in the Flask A (Fig.1) and connected the latter by means of a tube equipped with a stop-cock,

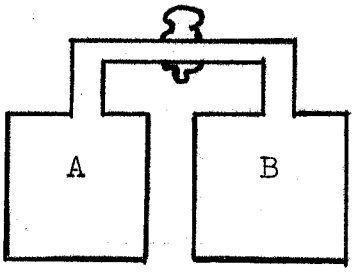

Figure 1

to the evacuated flask B. The cock was then opened, thus allowing the gas to stream into B, whereupon the temperature changes in A and B were noted. To the observers' great surprise, the small temperature changes in A and B were approximately equal and opposite, as exemplified by the results obtained with air for various pressures:

Initial Pressure in A	Temperature Decrease in A	Temperature Increase in B
0.79 meters	0.61 degrees	0.58 degrees
0.38 "	0.34 "	0.34 "
0.19 "	0.20 "	0.20 "

If the heat capacity of air increased as its density decreased, the greatest heat capacity being assigned to a vacuum, then the temperature rise in B might have been attributed to the "decrease of the vacuum" there. Gay-Lussac rejected this explanation because no temperature change was incurred by volume changes of Torricelli's vacuum (i.e. the vacuum over the mercury of a barometer tube). Leslie had suggested that the temperature rise was the result of the imperfect vacuum in B. That is, the large decrease in volume of the air left in B, incurred by the entrance of air from A. After finding that the same heating effect was produced in B no matter how great the care taken to evacuate it, Gay-Lussac also discarded Leslie's explanation.

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From the circumstance that the temperature rise in B was exactly compensated by its fall in A, Gay-Lussac was forced to reject Dalton's assumption that the specific heat of air increased on dilution. He said: "If, actually, in our experiment, the expanded air which remains in the flask has absorbed caloric, that which has gone out of it has carried some away, and it has not been demonstrated that the quantity of that which is absorbed is greater than that carried away, i.e. the temperature fall in A is no greater than the temperature rise in B. Consequently, the opinion of those who believe that an empty space dontains more caloric than a space filled with air, and which is grounded only on these considerations, is absolutely without foundation." (4, p.465)

Gay-Lussac himself did not propose any explanation of the unexpected heating effect in B. but cautiously contented himself with the remark that "it seems to me that for the theory of heat, it is of the greatest importance to know the source of it."

The discrepancies between Gay-Lussac's experiment and the current views on the specific heats of gases appear to have been little recognized. Thus in 1812 Clement and Desormes attempted to determine , by ingenious expansion experiments, the specific heat of a vacuum at two different temperatures from which they proceeded to calculate the temperature at which the vacuum contained no caloric, i.e. the absolute zero of temperature. More specifically, they supposed that the rise in temperature of air, on rushing into a vacuum, was caused by the absorption of all of the vacuum's heat by the air and the simultaneous vanishing of the vacuum. Knowing the heat capacity of the gas employed, they were able to calculate from the observed temperature rise the amount of heat absorbed by the gas from the vacuum. In this way, they determined the total caloric contained in a vacuum at 0° C. (and 100°C.) The difference between

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these two values gave the caloric required to raise the vacuum (of a given volume) through one hundred degrees. This, divided into the vacuum's "heat content" at 0°C. gave, for the state of zero heat content (absolute zero of temperature), -267°C.

The apparatus employed by Clement and Desormes is shown in Figure 2. The air in flask K was diluted by attaching an air pump at L, thus causing the mercury to rise to the height h in the manometer. Connection with the air pump was then cut off by closing the cock M. When the large cock H was opened, air rushed in causing the height of the mercury to fall to zero. However, on closing H, the mercury rose gradually to the height h'. This was because the air, on rushing into the vacuum, was heated so that it was this warmer air which came to the outside barometric pressure b, indicated by zero height of the mercury column. However, after closing H, the air gradually cooled to the temperature of the surroundings, with consequent fall of pressure indicated by the rise of the mercury to the height h'. These data sufficed for the calculation of the temperature rise experienced by the measured quantity of air, a rise which Clement and Desormes attributed to the absorption, by the air, of the vacuum's heat. For if t was the temperature centigrade of the gas in K, when the mercury was at level h' and hence, the gas at pressure b - h', and, if t + ϑ was the temperature immediately after H was closed, i.e. when the gas was at atmospheric pressure b, we would have by a combination of Boyle's and Gay-Lussac's Laws,

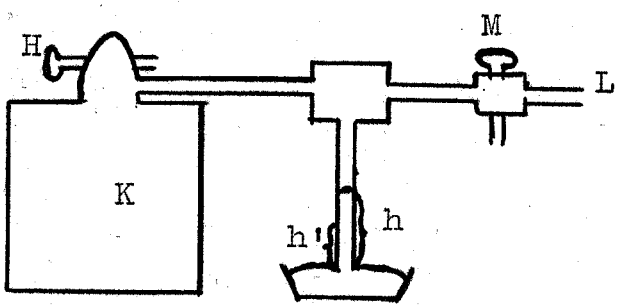

Figure 2

$$\frac{1 + \alpha (t + \vartheta)}{1 + \alpha t} = \frac{b}{b - h'}$$

whence,

$$\vartheta = \frac{h' (1 + \alpha t)}{\alpha (b - h')}$$

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where α is Gay-Lussac's thermal coefficient of expansion.

By determining the value of ϑ at 0° and again at 100°, using known quantities of air, Clement and Desormes were led to their calculation of the absolute zero, as already described.

Instead of interpreting Gay-Lussac's experiment as throwing doubt on the validity of the caloric theory, they regarded it as showing that caloric, like ordinary gases, was distributed according to volume, i.e. there was no net temperature change in Gay-Lussac's experiment because the total volume remained the same. They defined temperature as the "pressure of caloric" and, assuming it to behave like a perfect gas, they stated that its pressure, hence temperature, must be proportional to its density. Hence the absolute zero of temperature had to correspond to absolute absence of caloric. This supposition that caloric was of the nature of a perfect gas was strengthened by the approximate agreement of the absolute zero, calculated as above from the temperature changes on compression, with the absolute zero calculated from Gay-Lussac's Law of thermal expansion of gases, i.e. the temperature at which the volume of a given quantity of gas would be reduced to nothing.[11]

The first clear distinction between the heat capacity of a gas at constant pressure and that at constant volume was made by P.S. Laplace in 1816. He was led to make this distinction partly by the facts of thermal behavior of gases on expanding and compressing, but especially as an attempt to account for the discrepancy between Newton's calculated value of the velocity of sound in air and the observed value.

Newton found, by calculation from first principles, that the velocity of sound, c, should be given by

$$c = \sqrt{\frac{E}{\rho}}$$

where E is the coefficient of elasticity of the medium, ρ, its density.

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If we assume, as Newton did, that the successive condensations and rarefactions of the medium, which constitute the propagation of sound, take place in accordance with Boyle's Law, we have pv = constant. Whence, $\frac{dp}{p} + \frac{dv}{v} = 0$, and $E = -dp\ \frac{v}{dv} = p$, so that $c = \sqrt{\frac{p}{e}}$.

Newton himself knew that the observed velocity of sound was considerable greater than the value calculated from his formula, and he supposed this due to the neglect, in his calculation, of the volume occupied by the molecules of air. Lagrange later suggested that the discrepancy was caused by the increase in the coefficient of elasticity with density. Laplace (1816), confronted with the discrepancy between the observed value of 337.2 meters per second (at 7.5°C.) and the value of 283.4 meters per second, calculated from Newton's formula, concluded that such a difference could not be ascribed to the volume of the air molecules. Instead, he proceeded somewhat along the lines suggested by Lagrange; that is, he assumed that in the rapid condensation of air which occurs in sound propagation, the increase in pressure is greater than that corresponding to Boyle's law because the latent caloric rendered sensible by the compression does not have time to be conducted away and hence goes to raise the temperature of the air. In this way, Laplace was led to his famous formula for the velocity of sound: $c = \sqrt{\gamma \frac{p}{\rho}}$ where $\gamma = c_p/c_v$, c_p and c_v denoting the specific heats of air at constant pressure and constant volume, respectively.[12]

Laplace saw that the data from the above described experiment of Clement and Desormes were sufficient for the Calculation of γ, the ratio of specific heats. Imagine a unit weight of gas at temperature t°C., pressure p, and volume v. Its volume when heated at constant pressure to any temperature

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$t_i^{\circ}C.$ is given by $v_{t_i} = v_o (1+\alpha t_i)$. Hence when heated from t° to $(t+1)^{\circ}$, at constant pressure (I), the volume increase is $v(\frac{\alpha}{1+\alpha t})$, and the heat absorbed is C, the specific heat at constant pressure.

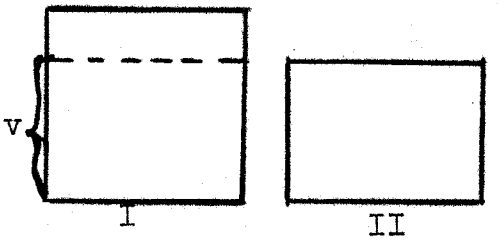

Figure 3

If, instead, the gas be heated from t° to $(t+1)^{\circ}$ at constant volume (II), the heat absorbed is c, the specific heat at constant volume. Hence if after heating to $(t+1)^{\circ}$ at constant pressure, the gas be suddenly compressed to its original volume, the heat C-c will be liberated raising the temperature through the interval τ to $(t+1+\tau)^{\circ}$. Hence, $C - c = \tau c$, $\frac{C}{c} = 1+\tau = \gamma$. If we assume that, for small decreases in volume, the rise in temperature ϑ is generally proportional to the fractional volume decrease β, we shall have, very approximately, $\beta : \frac{\alpha}{1+\alpha t} :: \vartheta : \tau$, or $\tau = \frac{\vartheta \frac{\alpha}{1+\alpha t}}{\beta}$.

Now in Clement and Desormes' experiment (cf. figure 2), suppose the original volume of diluted air in K was v. On opening the cock H, air rushed in, causing a sudden compression of the air already in K with a consequent liberation of heat and rise in temperature through ϑ°. Let v' be the volume of the air, originally in K, after the air in K cooled to the original temperature and the pressure fell to b - h'. Then, since the temperature was the same as at the start, Boyle's Law gave $(v'/v) = (b-h)/(b-h')$. The fractional decrease in volume suffered by the air initially in K was

$$\beta = \frac{v - v'}{v} = \frac{h - h'}{b - h'} .$$

We have already shown that Gay - Lussac's Law gives for the temperature elevation, on compression, $\vartheta = \frac{h'(1+\alpha t)}{\alpha (b - h')}$.

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Hence, $\gamma = 1 + \tau = 1 + \left(\vartheta \frac{\alpha}{1+\alpha t} \Big/ \beta\right) = 1 + \frac{h'}{h - h'}$.

In this way, Laplace obtained from the data of Clements and Desormes the value, $\gamma = 1.357$, for air. Employing this value in his formula for the velocity of sound, he obtained, for the latter, 345 meters per second, a value much closer to the observed value (337.2) than Newton's calculated value (283.4) had been.

Laplace had noted that his formula for the velocity of sound might equally well be used for determining γ from sound velocity. Dulong (1829) carried out a systematic investigation along this line. He measured the velocity of sound in air, oxygen, hydrogen, carbon dioxide, carbon monoxide, nitric oxide, and ethylene and, from his results, deduced the value of γ for each gas.

The general mathematical treatment of the behavoir of a gas subject to the conditions of Clement and Desormes' experiment was given by Poisson in 1823. Proceeding in full conformity with the caloric hypothesis, he supposed the quantity of heat q contained in a unit weight of gas to be a definite function of its pressure p and density ρ, i.e.

$$q = f(p, \rho). \qquad (1)$$

From the general gas law, $p = k\rho(1 + \alpha t)$, there resulted $\left(\frac{\partial \rho}{\partial t}\right)_p = -\frac{\alpha\rho}{1+\alpha t}$ and $\left(\frac{\partial p}{\partial t}\right)_\rho = k\alpha\rho = \frac{\alpha p}{1+\alpha t}$. For the specific heat at constant pressure, the theory gave $c_p = \left(\frac{\partial q}{\partial t}\right)_p = \left(\frac{\partial q}{\partial \rho}\right)_p \left(\frac{\partial \rho}{\partial t}\right)_p = -\left(\frac{\partial q}{\partial \rho}\right)_p \frac{\alpha\rho}{1+\alpha t}$

and $c_v = \left(\frac{\partial q}{\partial t}\right)_\rho = \left(\frac{\partial q}{\partial p}\right)_\rho \left(\frac{\partial p}{\partial t}\right)_\rho = \left(\frac{\partial q}{\partial p}\right)_\rho \frac{\alpha p}{1+\alpha t}$.

Supposing the ratio of specific heats to be a constant γ, Poisson found

$$\gamma = \frac{c_p}{c_v} = -\left[\left(\frac{\partial q}{\partial \rho}\right)_p \Big/ \left(\frac{\partial q}{\partial p}\right)_\rho\right] \frac{\rho}{p}$$

and $$\gamma p \left(\frac{\partial q}{\partial p}\right)_\rho + \rho \left(\frac{\partial q}{\partial \rho}\right)_p = 0$$

whose integral was $$q = \phi\left(\frac{p^{\frac{1}{\gamma}}}{\rho}\right)$$

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where ϕ was an undetermined function. If ψ denoted the inverse function of ϕ, then, finally $\frac{p^{\frac{1}{\gamma}}}{\rho} = \psi(q)$

If the gas was thermally insulated (q = constant), this equation of state reduced to $\frac{p^{\frac{1}{\gamma}}}{\rho}$ = constant

Thus Poisson obtained a correct result by a method which we must now certainly consider incorrect. Indeed, the same must be said about Laplace's distinction between the specific heat at constant volume and that at constant pressure. For the fact that the latter was noticeably greater than the former never suggested to him that caloric could be destroyed and converted into mechanical work. Instead, the extra heat which was added on increase of volume, and which we now regard as converted into external work, he simply classified as "latent." Indeed, far from relinquishing the caloric hypothesis, the latter became in his hands one of the most pretentious of scientific theories. He supposed that each of the molecules of a gas attracted to itself molecules of caloric and that the mutual repulsions of the latter caused the fluid to expand. The pressure in the interior of a gas he thought proportional to the product of the square of the number of molecules of gas per unit volume and the square of the caloric contained in unit volume. To account for the tendency of a body to come to a uniform temperature, he assumed mutual radiation between all the particles of caloric and defined temperature as the density of this internal radiation. We have already noted that he attempted to deduce from the caloric postulates the laws of Boyle and Gay-Lussac. Also, for the total heat (latent heat and sensible heat) V of a fluid he deduced (36, p.142) the interesting formula: $V = F + H \frac{p^{\gamma}}{\rho}$, where F and H were constants.

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In all of this theory, however, Gay-Lussac's free expansion experiment remained unexplained. Why did not a gas cool in free expansion as it did when pushing back a piston? There was no satisfactory answer forthcoming on the basis of the caloric hypothesis. That this state of affairs did not cause more unrest among the calorists, Mach (4, p.200) thinks due to the fact that Gay-Lussac's experiment was little known.

At any rate, like Davy's melting of ice by friction, it was ignored by the calorists, and its significance was not appreciated until 1842 when Robert Mayer relied on it to justify his famous calculation of the mechanical equivalent of heat from the difference between the specific heat of air at constant pressure and that at constant volume. In the meantime, the cooling of a gas in expanding against an external force, along with the converse phenomenon, continued to be attributed to Dalton's hypothesis of change of heat capacity with density or pressure.[13] This old assumption was not invalidated until 1837 when Regnault's very careful investigations revealed no change in the heat capacity (per unit weight) of gases with change in pressure or density.

The tenacity of the caloric theory thus prevented, for the time being, the facts of frictional heat and temperature changes of gases on expansion and compression from causing any general recognition of a mutual relation between the phenomena of mechanics and those of heat. In the meantime, however, new discoveries in the "border-line" divisions of physical science were pointing, with increased vigor, not only to the recognition of mutual relationships between heat and other phenomena but to the general correlation of all physical phenomena.

D. Thermal Effects Related to Electricity, Magnetism, Light, and Chemical Action.

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We have already observed how investigations into the phenomena of radiant heat served to revive the old belief in the close association of heat and light. Thus Hutton stated in 1794 that heat and light are the same thing, that, in a hot body, heat is converted into light, which, on absorption, becomes heat again. Young, who advocated the wave theory of light and the kinetic theory of heat, held that in these exchanges between heat and light, the total amount of both remained constant.

The relationship between electricity and chemical (action) provided still another front for the advancing concept of correlation. The history of this relationship begins with the discovery of "galvanic" electricity by Galvani in 1786. He found accidentally that the limb of a frog could be made to contract convulsively by placing it in contact with a piece of copper and a piece of iron, which are also in contact with each other. Since he had, six years earlier, observed that similar convulsions were produced by the application of frictional electricity, he supposed the convulsions, in this case also, to be associated with electricity. However, he supposed the electricity to be already present in the muscle and attributed the convulsion to its discharge through the metals.

Volta, in 1792, discarded Galvani's explanation of the phenomenon; instead he supposed the flow of electricity to arise from the tensions set up at the surface of contact between the different metals. However, in the same year, Fabroni suggested that chemical action might be the cause of galvanism. Nine years later, Wollaston substantiated this view and, having demonstrated the identity of galvanic with frictional electricity, even went so far as to attribute the latter, also, to chemical action.

The electrolytic action of the galvanic current on a variety of chemical substances was studied in the first decade of the nineteenth century by Davy, Nicholson, Carlisle, Berzelius and Hissinger, and others.

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The quantitative study of the relation between the amount of chemical action and the electricity conveyed through the solution culminated in the formulation of Faraday's Law of Electrolysis in 1831.

In the meantime, the relations observed between electricity and chemical action led, in chemistry, to the rise of Jons Jacob Berzelius' very influential theory of electrochemical dualism. According to this theory, every chemical reaction consists in a partial neutralization of opposite electric charges, supposed residing on the reactants. The facts of electrolysis indicated that the compounds decomposed must have consisted of two parts, one negative and the other positive. Berzelius supposed this true of all compounds, with the stipulation that the negative charge is not, in general, equal in magnitude to the positive. Hence, the compound has a net charge and will consequently exhibit a tendency to react with another compound so as to effect a new distribution of charge corresponding more closely to complete electrical neutralization. This Dualistic System, in which chemical affinity and electrical attraction were regarded as identical, held its ground until the facts of organic chemistry, especially Dumas' Law of Substitution, which was advanced in 1834, showed it to be of very restricted applicability.

However, Berzelius' theory may have retarded the growth of organic chemistry, it performed a permanent service for thermodynamics in so far as it fostered the correlation of electrical and chemical phenomena. In the meantime, relations between electricity and other of the so-called "forces" of nature were being established. The evolution of heat and light on the discharge of frictional electricity had long been known, and Davy, by means of the voltaic arc which he discovered in 1810, revealed that the same phenomena were incurred by the discharge of galvanic electricity.[14] The relation of heat to electricity was brought into further

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prominence in 1821 when Johann Seebeck discovered the difference in electrical potential between the junctions of two different metals, when the junctions were maintained at different temperatures. The converse phenomenon was observed by Pierre Pelletier in 1834. In the year prior to Seebeck's discovery, Oersted broke down the old barrier between electricity and magnetism when he discovered the magnetic field which surrounds a conductor carrying a current. Eleven years later, the converse phenomenon, magneto-electricity, was demonstrated by Faraday who observed the current incurred in a conductor on its motion through a magnetic field.

In 1801, Cruickshank observed that the presence of light increases the velocity at which hydrogen and chlorine combine to form hydrogen chloride, and Dalton checked this observation in 1811. In 1843, Dupin showed that the acceleration of chemical action in such cases was proportional to the intensity of the incident radiation.

E. The Explanation of Animal Heat.

The relationships, which we have just outlined, helped pave the way for the adoption of that universal principle of correlation which we now know as the First Law of Thermodynamics. Of greater immediate significance for that law, however, were the investigations on the relation of heat to chemical action. We have already described the researches of Laplace and Lavoisier on this subject, and how they came to formulate the principle that the heat liberated in the forward reaction equaled that absorbed in the reverse reaction. In 1840, G.H. Hess greatly extended their researches and placed the principle in the form that the heat liberated in a chemical process (at constant volume) is independent of the path of the change.

However, the greatest stimulus, in this connection, to the founders of the energy principle, especially Robert Mayer and Herman Von Helmholtz, came as a result of the investigations of the phenomenon of animal heat.

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Of great historical significance was Albert Haller's theory that animal heat arises as a result of the friction associated with the movement of the blood in the lungs. This theory was promulgated in Haller's "Outline of Physiology," a standard text of that time first published in 1747. The theory was probably widely accepted by physicians of the period (cf. 62, pp.27-34). Even after the chemical theory of animal heat had been given strong experimental support, Haller's mechanical explanation continued to be employed to account for a residual heat effect which Lavoisier's experiments could not attribute to chemical action. Not until 1843, which year marked the publication of Dulong's new and accurate determination of the heat of combustion of hydrogen, was it finally shown that Haller's theory could account for no more than a negligible fraction of animal heat.

Haller's theory of animal heat, though almost entirely erroneous, nevertheless served to propagate and keep alive a most important scientific concept: the inter-convertibility of heat and motion. The popularity of this theory among physicians in its original or modified form must account in part for the otherwise paradoxical fact that two of the three founders of the First Law (Mayer and Helmholtz) were not scientists but physicians.

Foundations for the modern chemical theory of animal heat were laid by the investigations of Irvine Crawford, published in 1777. He measured the heat given off to a water calorimeter, by burning wax, together with the oxygen consumed. He then placed a pig in his calorimeter, determining the heat developed by the pig on inhaling a definite quantity of oxygen. He found that, for every one hundred ounces of oxygen consumed, the calorimeter was elevated 2.1° F. by the burning wax, and 1.73°F.

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by the breathing pig. The agreement was for him close enough to warrant the statement that the heat of the animal resulted from the transformation of "pure air" (oxygen) to "fixed air" (carbon dioxide) and water.

Lavoisier, as early as 1777, also attributed animal heat to the oxidation of carbon to carbon dioxide. Three years later, he carried out systematic experiments, in company with Laplace. The heat given off by a guinea pig was compared with the quantity of heat corresponding to the carbon dioxide exhaled, assuming the reaction in the animal to be simply the oxidation of free carbon. In one experiment, the total heat developed by the pig, when placed in the calorimeter for ten hours, was 31.82 calories; whereas, the theoretical heat corresponding to the carbon dioxide evolved was only 25.408 calories. However, Lavoisier also found that the oxygen consumed was somewhat in excess of that equivalent to the carbon dioxide evolved and, noting the water vapor in the breath, was logically led to attribute the excess oxygen, together with some of the excess heat, to the oxidation of hydrogen to water.

Of especial significance is Lavoisier's enumeration of the factors which control the rate of oxidation consumption (and carbon dioxide evolution). He found that this rate increases as the temperature of the surroundings decreases, as the rate of muscularity activity increases, and as the rate of digestion increases. Of particular significance for the later-developed idea of "correlation of forces," is Lavoisier's discovery that the more work a man does, the more oxygen he consumes and the more nitrogenous matter he excretes.

Stimulated by Lavoisier's work, similar investigations were performed in the domain of plant respiration. In researches carried out in the late years of the eighteenth century, it was found that growing plants take in carbon dioxide and give off oxygen, simultaneously increasing the carbon

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content of their tissues.

All of these studies provided a great stimulus to the growth of organic chemistry. The analysis and identification of a great variety of compounds occurring in plant and animal life was undertaken. At first, these compounds were supposed in their behavoir to conform to laws different from those prevalent in the inorganic domain. With Wohler's systhesis of urea from ammonium cyanate in 1828 and the subsequent extension of the weight relationship laws to organic compounds, this view was more or less abandoned.

As a result of the great interest in organic chemistry, the notion of "Stoffwechsel," or exchange of matter, assumed a dominant influence in the description of physiological processes. In the meantime, other aspects of these processes, in addition to the thermal, were coming into prominence.

This development was perhaps foreshadowed by Lavoisier's observation that the rate of oxygen intake increases with muscular activity. In 1823, repeating Lavoisier's experiments on animal heat, Despretz found that the heat of combustion, corresponding to the water and carbon dioxide exhaled, amounted to only 74-90% of the actual animal heat. Although most of this discrepancy was the result of the circumstance that he employed in his calculation a low value for the heat of combustion of hydrogen, we must nevertheless ascribe considerable significance to his explanation of the difference. For he ascribed the extra heat to food, the motion of the blood, and friction. (37,Chapt. 1).

While the study of the purely chemical aspect of physiological processes was probably due to Liebig, more than to any other man, the study of the physical and mechanical aspects of these processes may be ascribed mainly to the influence of Weber and Muller. The definite conception of the exchange of "energy," as well as matter, in life processes

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probably dates from Schwann's (1839) microscopical work on the changes occurring in cell growth. He regarded the cell as a definite physical mechanism whose changes of state are quite as significant as the chemical reactions occurring in the organism. This meant that biochemistry needed to be supplemented by biophysics. With this in mind, Schwann introduced, in place of the term "Stoffwechsel" (chemical process), the broader Greek term, "metabole." (18, p. 421)

Of far-reaching import for physical science was the influence which this trend of thought exerted on Robert Mayer and Hermann von Helmholtz, two of the greatest founders of the First Law of Thermodynamics. Mayer's interest in the problem of the correlation and transformation of the "forces" of nature was first aroused while employed as ship's physician on a cruise in the East Indies in the year 1840. In the course of his duties he was obliged to bleed natives of the tropics, whereupon he was struck with the fact that the venous blood of these people was of a much brighter red than that of his patients in Germany. This brighter color he correctly attributed to the smaller amount of carbon dioxide in the venous blood of the tropical natives. Then he recalled Lavoisier's theory of animal heat and realized that the smaller carbon dioxide content, hence brighter color, of the venous blood was in conformity with the fact that less heat, hence less oxidation, should be required to maintain body temperature in the tropics than in a colder climate. At this point, there occurred to him the fact that the animal body, by means of muscular activities, can produce frictional heat. Unschooled in the subtle explanations offered by the calorists for the generation of frictional heat, Mayer thought that this frictional heat, like that directly produced in the animal body, must have as its ultimate cause, the food and oxygen consumed. But here it occurred to him that the amount of heat which can

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be obtained from a given quantity of food should be the same regardless of whether all of it is given off by the bodydirectly, or a part of it is developed through the expenditure of muscular work in frictional processes. In this way, Mayer was led to postulate a definite, invariable mechanical equivalent of heat.

Helmholtz, likewise a physician, was also led to physical studies through the study of physiology. In 1845, in a paper on "Metabolism During Muscular Activity," he described experimental studies proving that the activity of a frog's muscle incurs definite chemical changes in the components of the muscle. The following year, he published his "Report on the Theory of Animal Heat for 1845." In this, he noted that, in accordance with the still prevalent caloric theory, animal heat must be already present as latent heat in oxygen and food. He then described an experiment by Brodlie in which a beheaded or poisoned animal, in which respiration was continued by artificial means, was found nevertheless to develop considerably less heat than a normal animal, respiring at the same rate. From this experiment, Brodlie supposed that at least some of the animal heat must come, not from respiration, but from the activity of the nervous system. Liebig, evidently interpreting "nervous activity" as an hypothetical spontaneous phenomenon, rejected Brodlie's view and re-asserted the chemical view. Helmholtz himself then advocated the motion theory of heat and stated the conviction that mechanical, electrical, and chemical forces can generate only a definite quantity of such motion(heat).

F. The Precursors of the First Law: Mohr, Seguin, Liebig, and Grove.

The full account of the views of Mayer and Helmholtz we shall postpone till later. We may note here, however, that even before the appearance of their famous papers and those of Joule on the First Law, the above

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described discoveries in physics, chemistry, and physiology had led to general, though rather vague statements that all of the "forces"[15] of nature are correlated as well as conserved in their total amount.

Probably the earliest enunciation of this kind appeared in 1837 in a paper, "On the Nature of Heat," by K. F. Mohr. In this short, quite remarkable paper the author came very close to the notion of "equivalence" so ably expounded by Mayer five years later. Thus Mohr said: "If heat force has been used to destroy another force (cohesion), it must apparently cease to exist as force; accordingly, every latent production of heat is associated with a change of state of aggregation; that is, with the destruction of material forces." In other words, the creation of latent heat (regarded as a form of "force") is, as we should say, compensated by the destruction of material forces, i.e. by the overcoming of the cohesive forces between the material particles whose change of mutual position characterizes the change of state. The old Greek notion of a substance whose identity persists throughout the manifold changes of nature appeared in Mohr's statement that force (Kraft) behaves like ponderable matter, since, in all the processes where it suffers division and redistribution, it remains constant in quantity. The following statement of Mohr has been regarded, in some quarters (18, p. 108), as the earliest enunciation of the Principle of Conservation of Energy: "Besides the known fifty-four chemical elements there exists in nature only one agent more, and this is called "Kraft;" it can under suitable conditions appear as motion, cohesion, electricity, light, heat and magnetism."[16]

In Mohr's association of the production of latent heat with a change of state, the circumstance that external work is simultaneously done was apparently neglected. The importance of this circumstance was recognized

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in 1839 by the Frenchman, M. Seguin, in a work, "On the Influence of Railroads." He knew that the immediate condensation of steam yields more heat than if the steam is first expanded to yield work and then condensed. He supposed the cooling of a gas on expansion to be the cause of the work done and postulated, "an identity of nature between caloric and motion, such that these two phenomena are only the manifestation, under different forms, of one and the same cause."(4, p. 238) Seguin made unsuccessful attempts to show that the heat absorbed from the boiler of a steam engine is greater than that given up to the condenser, and he did not calculate the mechanical equivalent of heat from the cooling of a gas until 1847.

Liebig, whose interests were mainly chemical, was nevertheless thinking along lines similar to those of Mohr, as is revealed in portions of his "Chemical Letters" for 1841. Thus he wrote: "Heat, electricity, and magnetism are related to each other as are the chemical equivalents of carbon, zinc, and oxygen. By a given quantity of electricity we bring forth a corresponding quantity of heat or magnetic force, which are mutually equivalent. With electricity I buy chemical affinity which, used in one form, produces heat, in another, electricity and magnetism. Out of nothing no force can arise... If the carbon needed for obtaining zinc from its ore were burned under a vapor machine instead, it is most probable that we would obtain far more force, than we could obtain from the zinc (pure), if it were used (as fuel) in this apparatus (vapor machine)." These views in which the concept of equivalence of forces, regarded as the analogue of the principle of chemical equivalents, occupied a prominent position, resemble those of Mayer on whom they probably exerted considerable influence (32, p. 10).

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General ideas, quite similar to those of Mohr, were promulgated in England in 1842 by W. R. Grove in his very popular Lectures on the Correlation of Physical Forces. "Light, heat, electricity, magnetism, motion, and chemical affinity," he said, "are all convertible material affections; assuming either as the cause, one of the others will be the effect..." He then proceeded to describe , qualitatively, a great many experimental facts, known at this time, which, he thought, clearly indicated that these "affections" or "forces" were indeed mutually convertible. He took note of the tendency, then growing in England, to regard these affections as different modes of motion, but, perhaps due to Faraday's influence, preferred to adopt a positivistic viewpoint. Thus he said, "Cause and effect, therefore, in their abstract relation to these forces, are words solely of convenience; we are totally unacquainted with the ultimate generating power of each and all of them, and probably shall ever remain so... We must humbly refer their causation to one omnipresent influence, and content ourselves with studying their effects and developing by experiment their mutual relations." (38, p.5)

These citations from the writings of some of the precursors of the Energy Principle show how the rapidly widening domain of experimental knowledge resulted in simultaneous and, for the most part, independent enunciations of the principle of correlation of natural forces. In this great movement, which is grounded, not only in experimental fact, but also in the inner demand for a unified world of phenomena, the inadequacy of the old caloric theory of heat appears only as a particular consequence. At the same time, it must be acknowledged that, of the precursors just discussed, only Mohr and Seguin are definitely dependent on the motion theory of heat: for Liebig the analogy with chemical equivalence is apparently sufficient, whereas Grove is contented to call the different "affections"

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of matter by the common term, "force." [17]

It is important to realize why the above-discussed writers (Mohr, Seguin, Liebig, and Grove) are denoted "precursors" rather than founders, proper, of the Principle of the Conservation of Energy. This is precisely because their generalizations were still vague, uncertain of terms and relations, and lacked quantitative interpretation and support. All of the writers appear to be obsessed with an inner conviction that the "forces" of nature, while changing their particular form, nevertheless remain constant in total amount. Yet there is lacking, for the most part, any suggestion as to just how "force" is to be measured in particular cases in such a way as to exhibit this conservative property. To be sure, this state of affairs was largely a result of the circumstance that the data necessary for such quantitative correlation were not yet available.

3. THE DEVELOPMENT OF THE CONCEPT OF MECHANICAL WORK.

A. Excluded Perpetual Motion.

A development of the greatest significance for this quantitative correlation of "forces" had, however, already taken place in the technical mechanics of France. We refer to the evolution of the concept, "mechanical work." The latter had been vaguely suggested by Newton's Principle of Action and Reaction, Huygens' Principle of Living Force, and the general conviction of the impossibility of perpetual motion, but it was not until the first few decades of the nineteenth century that it finally received clear formulation as a definite, quantitative, substantial concept, which was destined to function as the prototype and measure of all the various "forces" of physical science.

With respect to the principle that "it is impossible to create work out of nothing or to construct a perpetuum mobile," the so-called principle of the impossibility of perpetual motion, Mach's historical

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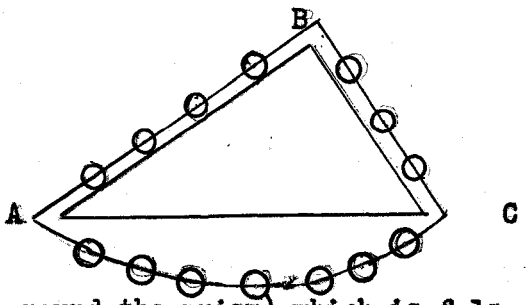
studies (40) have shown that, far from being a result of mechanics, the principle, in one form or another, has always been assumed as a starting point in the proof of mechanical theorems. Thus, Stevinus in 1605 argued that if an endless chain of fourteen balls of equal weight be hung over a prism in the manner shown in Figure 4, the lower symmetrical part of the chain may be imagined taken away, whence the four balls on AB must exactly balance the three balls on BC. For otherwise, he said, the smallest displacement would result in "a continuous and unending motion

Figure 4



(of the balls around the prism) which is false."

We so not find Stevinus' argument altogether acceptable now, since we, unlike him, prefer to think in terms of an abstract mechanism devoid of friction. Nevertheless, his principle that we cannot get something out of nothing immediately appears familiar and acceptable to us.[18]

The principle again appeared in Stevinus' demonstration that "A given mass of water preserves within water its given place (Figure 5). "For," he said, "assuming it to be impossible by natural means, let us suppose that A does not preserve the place assigned to it, but sinks down to D. This being posited, the water which succeeds A will, for the same reason, also flow down to D; A will be forced out of its place in D; and thus this body of water, for the conditions in it are everywhere the same, will set up a perpetual motion, which is absurd." From this Stevinus deduced the laws of

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hydrostatics.

Several decades later the principle of excluded perpetual motion took with Galileo the form of the postulate that the velocity acquired by a falling body is uniquely determined by the vertical height of descent. Galileo associated this with the conviction that a body on rolling down an inclined plane must acquire a velocity just sufficient to carry it up any other inclined plane of the same height. On the other hand, the principle requires that the body , having fallen down one plane, must continue to preserve the same velocity as long as it moves in a horizontal plane (law of inertia).

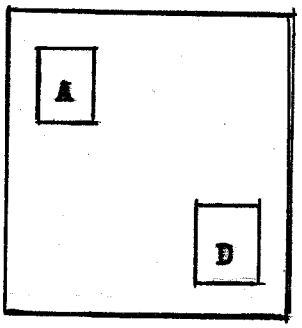

Figure 5

The a priori element in Galileo's principle thus makes itself evident. For bodies, in fact, do not continue their motion indefinitely on a horizontal plane, nor are the velocities acquired, on rolling down an inclined plane, actually sufficient to carry them to their original heights.

In 1673 Christian Huygens, following Galileo, gave a sharper form to the law of inertia. He stated that bodies would continue to move on a horizontal plane with the same velocity, if it were not for gravity and the presence of the atmosphere. He also generalized Galileo's principle respecting the heights of ascent. In the first place, he stated that the principle amounts to saying that heavy bodies do not of themselves move upwards; that is, if the principle were not true, a body, having rolled down one inclined plane, might attain a height, greater than its initial height, on rolling up another plane of different inclination. This suggested the following generalisation of the principle: "If any number of weights be set in motion by the force of gravity, the common center of gravity of the weights as a

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whole cannot possibly rise higher than the place which it occupied when the motion began." (Principle of the Conservation of the Center of Gravity)

The principle of excluded perpetual motion also found expression in Isaac Newton's famous laws of motion. The First Law postulated the law of inertia already enunciated by Galileo. The Second Law provided acting forces to account for changes of motion. The Third Law, the law of equality of action and reaction, was employed by Newton in two senses. In the first place, it was construed to mean the equality of force and counter-force, and it was this interpretation of the law which Newton emphasized. But it was also understood to apply when action and reaction were measured in terms of the products of the forces of the bodies and their respective velocities, the velocities being resolved along the directions of the fordes. Interpreted in this way, Newton's Third Law postulated the Conservation of Power, or what amounts to the same thing, since the times were equal, the Conservation of Work.[19]

The substantial element at the basis of the principle of excluded perpetual motion is quite evident in Newton's laws of motion. The First and Third Laws concern the cases where motion or work is conserved. In the Second Law, the fact of accelerated motion is brought into conformity with excluded perpetual motion by the postulation of forces which may act at a distance.

Regardless of which of the various possible principles we choose to regard as fundamental starting point for the systematic development of mechanics, the idea of the impossibility of perpetual motion continues to play the dominating role. We have shown this to be the case with Galileo's principle relating to velocities acquired by falling bodies, Huygens' Principle of the Conservation of the Center of Gravity, and Newton's laws of motion. It is likewise true of the Principle of Vis Viva, the Principle

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of Virtual Displacements, D'Alembert's Principle, the Principle of Least Action, and others.

B. Momentum versus Vis Viva.

In which of these various forms the fundamental principle of excluded perpetual motion is clothed is a question of relatively little import for pure mechanics. For each is found to implicate the others, so that regardless of which is adopted as the fundamental one, the final results are the same. However, so far as the relation of mechanics to the development of thermodynamics is concerned, it is a fact of great significance that, in the actual, historical choice of fundamental mechanical principles, the concepts of force and momentum appeared more primitive than the concepts of work and vis viva.

This point of view received its initial impetus from the historical accident that the law of falling bodies was formulated by Galileo as a relation between the time and velocity rather than as one between the distance and velocity. To be sure, the notion of vertical distance of descent occupied an important position in Galileo's thought, as we have already seen. Accordingly, we find Galileo advancing the tentative hypothesis that the velocity of a falling body is proportional to the distance through which it has fallen. However, because he thought this led to self-contradictory results, he discarded it in favor of the assumption that the velocity is proportional to the time, i.e.

$$v = g\,t. \qquad (1)$$

By means of the definitive relation between distance s and velocity v, namely, $v = s/t$, he converted his hypothesis to the form

$$s = \tfrac{1}{2} g t^2, \qquad (2)$$

a relation which he found to agree with experiment.

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Of course, elimination of t from (1) and (2) gives a relation between the velocity and the distance, namely,

$$gs = \tfrac{1}{2}v^2 \quad . \qquad (3)$$

However, this relation was not employed by Galileo. Instead, equations (1) and (2) were regarded as fundamental. In keeping with this point of view, he regarded the "force" of a moving body, which he variously designated as its "momentum," "impulse,"or "energy," to be measured by the product of its weight and the first power of its velocity.

Descartes adopted this view in 1644, maintaining that the total "quantity of motion" in the world, as measured by the product of weight and velocity, is constant.

Quantity of motion or momentum also occupied the dominant position in the thought of Newton, who, however, saw fit to substitute for weight the more refined concept of mass. He showed that in a free system unacted on by external forces the total momentum (Σmv) remains constant. And, in cases where such forces act, he was naturally led to define their magnitude in terms of the change which they effect in unit time in the momentum of the bodies upon which they act.

The square of the velocity first appeared of determinative significance in 1673 when Huygens enunciated the celebrated Principle of Vis Viva, which resulted from his application of the Principle of the Conservation of the Center of Gravity to the solution of the problem of the center of oscillation of the compound pendulum. By the center of oscillation of a compound pendulum is meant its center of gravity. Suppose that on a compound pendulum AO (Figure 6) the element at unit distance from the point of suspension O, in passing from the position of greatest exdursion to the equilibrium(vertical) position, descends through a height k. Then the elements of mass m,m',m'', ...

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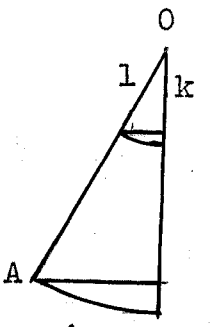

Figure 6

at distances r, r', r'', ... from 0 will simultaneously fall through the heights kr, kr', kr'', ..., so that the decent of the center of gravity is given by:

$$\frac{mrk+m'r'k'+m''r''k+\ldots}{m+m'+m'''+\ldots} = k\,\frac{\sum mr}{\sum m}. \qquad (4)$$

By a stroke of genius, Huygens now imagined that, when the compound pendulum reaches the vertical, equilibrium position, the connections between its mass points are destroyed so that each is allowed to rotate about 0 as a separate pendulum. If the velocity , at the equilibrium position, of the mass point which is at unit distance from 0 be v, then the corresponding velocities of the other mass points will be rv, r'v, r''v, ...; and, having been freed of their connections, their heights of ascent are, according to equation (3), (which Huygens obtained from Galileo's equations (1) and (2)), $(rv)^2/2g$, $(r'v)^2/2g$, $(r''v)^2/2g$,... Whence the height of ascent of the center of gravity of the liberated masses is

$$\frac{m(rv)^2/2g+m'(r'v)^2/2g+m''(r''v)^2/2g+\ldots}{m+m'+m''+\ldots} = \frac{v^2}{2g}\,\frac{\sum mr^2}{\sum m} \qquad (5)$$

But by Huygens' fundamental Principle of the Conservation of the Center of Gravity, the center of the gravity of the system of the liberated masses, when they each reach their extreme positions, must be at the same height as that of the compound pendulum in its extreme position. Hence the right-hand members of equations (4) and (5) are equal, or

$$k\,\frac{\sum mr}{\sum m} = \frac{v^2}{2g}\,\frac{\sum mr^2}{\sum m} \qquad (6)$$

Now, if y is the length of a simple pendulum having the same period of oscillation as the given pendulum, ky will be the distance of its descent and vy will be its velocity at the equilibrium position. Application of (3) gives:

$$\frac{(vv)^2}{2g} = ky$$

or

$$y\,\frac{v^2}{2g} = k \qquad (7)$$

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Elimination of k from (6) and (7) gives for y, the distance of the center of oscillation from O,

$$y = \frac{\Sigma mr^2}{\Sigma mr} \tag{8}$$

Huygens' result (8) is of little interest to us, but the relation (5) whereby he attained it is of the greatest significance. More generally expressed, equation (5) says that if any system of weights p, p', p'',... falls through the heights h, h', h'',..., thereby attaining velocities v, v', v'',... the Principle of the Conservation of the Center of Gravity requires that

$$\frac{ph + p'h' + p''h'' + \ldots}{p + p' + p'' + \ldots} = \frac{p(v^2/2g) + p'(v'^2/2g) + p''(v''^2/2g) + \ldots}{p + p' + p'' + \ldots}$$

or $$\Sigma ph = 1/g \, \Sigma(pv^2/2) \, . \tag{9}$$

If we introduce the mass m for the ratio p/g, a step which Huygens did not take, we have

$$\Sigma ph = \tfrac{1}{2}\Sigma mv^2 \tag{10}$$

which is the Principle of Vis Viva in its modern form.

The application of the Principle of Vis Viva to the impact of elastic bodies on a horizontal plane was made by Huygens in a posthumous work published in 1702. In this case, the principle takes the form

$$\tfrac{1}{2}MV^2 + \tfrac{1}{2}mv^2 = \tfrac{1}{2}MV_1^2 + \tfrac{1}{2}mv_1^2 \tag{11}$$

where V and v are the velocities before impact of the masses M and m, and V_1 and v_1, their velocities after impact.

Nowhere, however, did Huygens give to his Principle of Vis Viva the status of a first principle. Rather, it is regarded as a derived principle resulting from the Principle of the Conservation of the Center of Gravity. Nor did he introduce any new name for a term involving the square of the velocity.

The case is otherwise with Leibnitz who precipitated a long and famous

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controversy by his publication in 1686 of a treatise entitled, "A Short Demonstration of a Remarkable Error of Descartes and Others, Concerning the Natural Law by Which They Think That the Creator Always Preserves the Same Quantity of Motion; By Which, however, the Science of Mechanics is Totally Perverted." It is certainly logical to assume, he said, that the same "force" must be required to raise a body m a height 4h as to raise a body 4m to a height h. But we know (cf. equation (3)) that the velocity acquired in descent , in the first case, is not four times, but only twice that acquired in the second case. Hence, said Leibnitz, the true measure of force is given by the product of the "body" [20] and the square, not the first power of its velocity. In 1695 Leibnitz reverted to this subject, introducing the term vis viva for the product mv^2, regarded as the true measure of the "force" of a moving body. This he distinguished from the simple pressure exerted by a body at rest, which he called its vis mortua.

The dispute, thus precipitated with the followers of Descartes, lasted until 1743 when D'Alembert pointed out that the whole controversy really amounted only to a question of how force is to be defined. Indeed, Newton in 1687 had already defined force in still a third way as the time rate of change of the mv product, a definition which is still accepted. Nor can the dispute be settled by postulating that what we define as force must be conserved. For, although the investigations of Huygens showed that the sum $\sum mv^2$ remains constant for a system of bodies in the absence of the action of external forces, so did Newton show that the Cartesian sum $\sum mv$ also remains constant under these conditions.

Nevertheless, we must recognize the service which the Leibnitzians performed in emphasizing the significance of the product of the mass of a body and its increase in height and the product of its mass and the square of its velocity. For these simple

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of its velocity. For these products were destined to become of determinative significance for the development of thermodynamics.

As a matter of fact, however, the efforts of the Leibnitzians were not so fruitful as they might have been. Throughout the eighteenth century, the notions of work and vis viva continued to be regarded as artificial, so that the general practice was to replace them by the Newtonian concepts of force, mass, and momentum. It has already been observed that this is no more than an historical accident, since mechanics can be erected just as well on the basis of the concepts of work, mass, and vis viva, regarded as fundamental.

About the middle of the eighteenth century Huygens' Principle of Vis Viva was revived and extended by John and Daniel Bermoulli. They placed the principle in the form given by equation (10). Following Leibnitz, John Bernoulli evidently attributed a substantial nature to vis viva ($\sum mv^2$) for he stated that "where vis viva disappears, the power to do work is not lost, but is only changed into some other form."(18,p.99)

Galileo and Huygens knew that the velocity acquired by a falling body depends only on the vertical distance of descent, and Daniel Bernoulli, extending this, stated that the gain in vis viva of a body subject to forces of attraction from several fixed centers depends only on the initial and final distances of the body from these fixed centers. These ideas were given general, analytical form in 1788 by J.L. Lagrange. He showed that, if the three components of each of the forces acting may be expressed as the derivative of a function of the coordinates and, further, if the only restrictions imposed on the motion of the system are those expressible by equations between the coordinates, then

$$\sum \tfrac{1}{2} mv^2 + \sum mV = H \qquad (12)$$

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where V is a function of the coordinates and H a constant. Hence, he wrote for the vis viva of the system

$$\sum mv^2 = 2H - 2\sum mV \qquad (13)$$

C. The Work Concept in French Technical Mechanics.

For pure mechanics, equation (13) is of great importance. It reveals that, in the case of so-called conservative systems, the sum $\sum mv^2$ is uniquely determined by the configuration of the system. For the aims of technical mechanics, it is of little service, since the forces operative in machines are not conservative. Accordingly, in the French technical mechanics of the early nineteenth century, the Principle of Vis Viva was reformulated. The concepts of work and transformation also received sharper formulation and, in accordance with their value for practice, acquired a new significance.

Let us briefly trace this important development with which are associated the names of the Frenchmen, L. N. M. Carnot, M$_o$nge, Coulomb, Navier, Coriolis, and Poncelet. Suppose a point mass m has the coordinates x, y, z, and velocity components x', y', z' at the time t. If X, Y, Z are the net components of all forces acting, the dynamical differential equations (Newton's definition of force) give

$$m\frac{dx'}{dt} = X, \qquad m\frac{dy'}{dt} = Y, \qquad m\frac{dz'}{dt} = Z$$

Multiplying these equations into

$$x'dt = dx, \qquad y'dt = dy, \qquad z'dt = dz,$$

respectively, and adding, we obtain

$$m(x'dx' + y'dy' + z'dz') = Xdx + Ydy + Zdz.$$

If v is the velocity, Q the working force, dq the projection of the element of path on the direction of the force, the last equation may be written

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$$mvdv = Qdq$$

which, for a system of points, becomes,

$$\Sigma mvdv = \Sigma Qdq. \qquad (14)$$

Integration gives:

$$\tfrac{1}{2}\Sigma mv_2^2 - \tfrac{1}{2}\Sigma mv_1^2 = \Sigma \int_1^2 Qdq. \qquad (15)$$

The great significance of the development which we are tracing lies less in equation (15) itself than in the point of view from which its members were regarded. For the right-hand member was now recognized as being a measure of the changes which incur the production of a state of increased motion as represented by the left-hand member, or, conversely, as the measure of the effect resulting when the motion decreases. Thus, by virtue of their association with definite physical operations, encountered in practice, the members of (15) came to acquire a substantial, as distinct from formal, character. At the same time, there naturally arose the idea of transformation, whereby the cause, represented by the right-hand member, is conceived as being transformed into the effect represented by the left-hand member, or vice versa.

This novel trend of thought is exemplified by the new terminology which began to be adopted at this time. The motion of transformation is clearly evident in the term, latent vis viva (force vive latente), which was introduced by L. N. M. Carnot for twice the right-hand member of (15). Other terms advanced for $\Sigma \int_1^2 Qdq$, or its double, included "mechanical power" (puissance mecanique), "moment of activity" (moment d'activite), "dynamic effect" (effet dynamique), and "quantity of action" (quantite d'action). Finally, Poncelet (1824) introduced the term, "mechanical work" (travail mecanique), for $\Sigma \int_1^2 Qdq$, and established the kilogram-meter (work done in lifting a kilogram weight through a height of one meter) as its unit of measure.[21]

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Poncelet also referred to the left-hand members of (14) and (15) by the term "work." Thus he called $-m\frac{dv}{dt}$ and $-mvdv$, the force of resistance, and the work of resistance, respectively. Writing (14) in the form,

$$\sum Qdq + \sum -mvdv = 0,$$

he regarded it as expressing the following relation between the virtual moments: the sum of the elements of work developed, including both those produced by the forces changing the motion ($\sum Qdq$) and those developed by the forces of resistance brought into being by those changes ($\sum -mvdv$) is equal to zero. No doubt appreciating the novelty of this point of view, Poncelet referred to the old Principle of the Conservation of Vis Viva as the Principle of the Transformation of Work (principe de la transmission du travail).

To Coriolis (1829), who advocated views quite similar to those of Poncelet, is due the logical step of assigning the name vis viva to $\frac{1}{2}mv^2$ rather than to mv^2, a change of terminology which was, however, slow to be adopted.

Anticipating our subsequent exposition, we may point out the threefold significance of these developments for the First Law of Thermodynamics. In the first place, they provided mechanics itself, regarded as a branch of thermodynamics, with clear formulations of the all-important notions of conservation and transformation. Secondly, in doing this, a basis was simultaneously provided for the quantitative, substantial treatment of all changes which occur in connection with mechanical changes, either directly or indirectly. Finally, the new ideas of mechanics provided a more logical basis for the kinetic theory of heat.

However, the thermodynamical significance of these developments in French technical mechanics was slow to be appreciated. The writings of the precursors of the First Law (e.g. Mohr, Liebig, Grove) although

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although coming ten to fifteen years after Poncelet expounded his notion of mechanical work, were quite lacking in the quantitative formulations which a proper appreciation of his ideas might have provided. Although the concept of mechanical work played an important role in the experiments of Joule, the first decided influence on thermodynamics of the new developments in mechanics appeared in Helmholtz's (1847) attempt to develop systematically the mechanistic view of phenomena. The real significance of the work concept for thermodynamics, however, remained unappreciated until the classical developments of Sir William Thomson and Rudolph Clausius at the middle of the century.

4. THE FORMULATION OF THE FIRST LAW OF THERMODYNAMICS.

A. Mayer and the Principle of Equivalence.

We are now in a position to resume the main thread of our exposition of the history of the First Law of Thermodynamics. Before our digression into the history of mechanics, we had just completed a resumé of the views of the precursors of the Energy Principle. We may now describe the work of the founders proper of the First Law, the most important of whom were Mayer, Joule, and Helmholtz.

Robert Mayer is distinguished from the precursors of the First Law by the fact that, although he was guided by the same metaphysical belief in a Cartesian substance which dominated the speculations of the precursors, he, unlike them, succeeded in definitely showing how this substance could be interpreted in scientific practice. On the other hand, the great generality of his treatment sets him off from Joule, his English contemporary, while his complete independence of the kinetic theory of heat places him in a class by himself among the great founders of thermodynamics.[22]

In his first published paper entitled, "Remarks on the Forces of

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Inorganic Nature (1842)," (38; 43)[23], Mayer made no mention of the happy accident which brought his mind to bear on the subject (cf. p.67), but began with considerations of the most general nature. The influence of the substance hypothesis and, more specifically, of Lavoisier's Principle of the Conservation of Mass, is evidenced in Mayer's opening characterization of his paper as "an attempt to make the concept of force (Kraft) just as precise as that of matter."

Forces, he defined as "instructible, changeable, imponderable objects." Their instructibility and changeability is associated with the fact that they stand to each other in the relation of cause and effect and are hence governed by the principle: causa aequat effectum. Since forces, in exemplifying the relation of cause and effect, pass into one another, they must be regarded as different, changeable forms of the same object. Finally, the characteristization of the forces as "imponderables" differentiates them from bodies of matter which also exhibit the relation of cause and effect.

The notion of equivalence was clearly set forth. If a cause c has ann effect e, $c = e$. If e is again the cause of f, $e = f$, etc. So we may write $c = e = f = \ldots = c$. Just as the object of chemistry is to develop casual relations between the different forms of matter (chemical equations), so the object of physics should be to develop similar relations between the different forces.

Mayer now passed to several concrete illustrations of his ideas. In the combustion of hydrogen, water is formed, and the chemical formulation of the causal relation between the ponderables involved is represented by:

$$H_2 + \tfrac{1}{2}O_2 \longrightarrow H_2O.$$

But, said Mayer, heat is also produced which must have a cause x. So we

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may write:

$$x = \text{heat.}$$

He did not discuss the nature of the cause (force) x.

In the application of his ideas to mechanics, Mayer clearly formulated the ideas which are now embodied in the terms, "potential energy" and "kinetic energy."[24] Since the expenditure of force is the necessary cause of the lifting of a weight above the surface of the earth, space differences of ponderable objects must be considered forces. He called such forces, fall-forces (Fallkrafte), because they cause bodies to fall. Mechanics shows us that a fall-force can be the direct cause of a new species of force, motion, and provides us with a quantitative relation between the two. Thus, a weight m, on being lifted through a height d, acquires, on falling, a velocity c such that

$$md = mc^2 = v,$$

where v is the fall-force.[25] Mayer here observed that the Principle of the Conservation of Vis Viva is a particular instance of the general law of the indestructibility of causes.

However, motion often disappears without the appearance of other motion or the lifting of a weight. Our fundamental principle of the indestructibility of force clearly requires, said Mayer, that some new form of force appear; but only experience can reveal just what this new form will be in any particular case. Thus, when heat appears and motion disappears, the motion can be said to be the cause of the heat, only when the motion is the sole cause and heat the sole effect. Since this actually occurs, as when frictional heat is produced by the motion of metal parts which undergo no permanent change, we must assume that heat is a force, capable of arising out of motion.

Mayer rejected the supposition of the calorists that the production

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of frictional heat is caused by the decrease in volume. For water may be heated by shaking whereupon its volume increases. He likewise rejected the kinetic theory of heat, although he apparently adopted the undulatory hypothesis of light and radiant heat. We can no more say that the essence of heat is motion than we can say that the essence of fall-force is motion. Rather, said Mayer, motion (either simple or vibrating, as in light and radiant heat) must cease to be motion when it becomes heat.

The relation observed between the forces, heat and motion, and that between fall-force and motion provide us with a relation between fall-force and heat. At the same time, Mayer noted that heat need not always be the effect of motion. Thus a change of state of aggregation may also be the effect as in Davy's experiment on the melting of ice by friction. Also heat and volume increase may be produced simultaneously as the effects of motion. Finally, the vanishing of heat may result in motion, increase of volume, elevation of a weight, etc.

As further illustrations, Mayer cited the water works, the vapor machine, and the locomotive. In the first, the expenditure of fall-force (which Mayer said may also be regarded as a decrease in volume of the earth) produces motion which, in turn, is converted into heat. In the vapor machine, heat becomes motion, which, in turn, may be employed to raise a weight. In the locomotive, heat produces motion which is partially converted back into heat by the friction of the wheels on the rails.

Mayer concluded his remarkable paper with the result of his calculation of the mechanical equivalent of heat. It remains for future experiments, he said, to determine directly the height to which a weight must be raised in order that, on falling, a certain weight of water will be raised from 0° to 1° C. However, he stated that from the ratio $c_p/c_v = 1.421$ for gases he found that a unit weight must fall through a

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distance of 365 meters in order to raise a unit weight of water from 0° to 1°C. From this, he concluded that only a small part of the heat of combustion is converted into work in the steam engine and suggested that other means, e.g. electrical, be employed for attaining this motion.

In a paper privately published three years later and whose title, "Organic Motion in Connection with Nutrition," suggests the sphere of of phenomena in which the ideas contained in the first paper originated, Mayer extended his great generalization to the whole phenomenal world, including the organic. To the historian of thermodynamics, however, the paramount importance of this paper lies in the fact that it gives in detail the method whereby the mechanical equivalent of heat, cited in the first paper, was obtained and thereby establishes Mayer as the author of the first unambiguous calculation of the mechanical equivalent of heat.[26]

For, in the 1845 paper, we learn that the calculation from the ratio c_p/c_v was based on the long-forgotten free-expansion experiment of Gay-Lussac. The latter shows, said Mayer, that the mere increase in volume of air does not require any heat. Hence, the excess of the heat capacity at constant pressure over that at constant volume must be regarded as the cause, i.e. equivalent, of the fall-force generated (work done). Now Mayer imagined a cubic centimeter of air confined at 0°C. in a vertical tube of one square centimeter cross-section under a column of mercury 76 centimeters high. If the air be heated under these conditions to 1°C., its volume increases by (1/274)th of the original volume (Gay-Lussac's Law of Thermal Expansion), thereby raising the mercury column, whose weight is 1033 grams, through a height of 1/274 centimeters. Now the specific heat of air is 0.267 (Delaroche and Berard). Hence the total heat absorbed by the cubic centimeter of air, whose weight is (0.0013 grams, is) (0.0013)(0.267)= 0.000347 .

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since the ratio $c_p/c_v = 1.421$ for air (Dulong), the heat which would have been needed if the volume had been constant is 0.000347/1.421 = 0.000244. The difference, 0.000347 - 0.000244 = 0.000103, represents the heat used to lift a weight of 1033 grams through a height of 1/274 centimeters. By reduction, Mayer found that one unit of heat (calorie) is equivalent to the raising of a one-gram weight a height of 367 meters.[27]

In his 1845 paper Mayer also explained a phenomenon which had long bothered scientists, namely, the charging of the electrophorus. If a negatively charged wax disc be placed parallel to an uncharged metallic disc, the side of the metal nearest the wax will become positively charged, its reverse side negatively charged (Figure 7). The negative charge may be removed by grounding, whereupon the metal may be removed from the neighborhood of the wax disc and its positive charge imparted to the electrophorus by conduction. This process may be repeated as many times as we please, the wax and metal discs having resumed their initial states after each operation. The charging of the electrophorus thus appears to be an effect which has no cause; indeed, Volta, who first observed the phenomenon in 1775, thought it violated the principle of excluded perpetual motion.

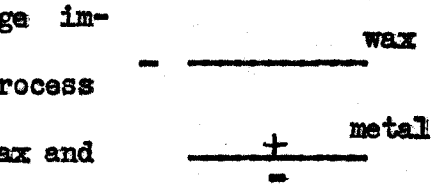

Figure 7

Mayer's explanation was simple and to the point. He observed that, because of the attraction of unlike electricities, more force (work) must be expended in removing the charged metal disc from the vicinity of the wax disc than would be required if the metal were uncharged. It is this additional force which is the cause of the charging of the electrophorus.

In the 1845 paper we find Mayer adopting Dalton's atomic hypothesis long enough to suggest that the heat of chemical reaction may be the result of collisions of the atoms of the reactants which rush together

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under the forces of chemical affinity.

However, with this exception, the positivistic view of the 1842 paper is maintained. The object of future investigation must be the study of the transformations of force, whose various species he listed in the following table:

Forms of Force

	I.	Fall-Force	(mechanical forces)
	II.	Motion	(mechanical effects)
Imponderables	III.	Heat (simple, vibrating)	(light, radiant heat)
	IV.	Magnetism, electricity, galvanic current	
	V.	Chemical Change (separation, combination)	chemical forces

The designation of vibratory motion, heat, magnetism, and electricity as "imponderables" is undoubtedly a concession to the popular terminology of the day. For Mayer had already stated in his 1842 paper that, actually, all forces are imponderable.

In his 1845 paper Mayer postulated that the heat of the sun is the ultimate source of all activity in the world. This heat is converted by growth processes into the woody fibers of plants where, either by direct burning or through the intermediary of the animal body, it is re-converted into heat. Several years later, in a paper, "Contributions to Celestial Dynamics", he devloped the hypothesis of colliding meteors to account for this enormous heat of the sun.

Mayer's last work, "Remarks on the Mechanical Equivalent of Heat", appearing in 1851, (38), was no more than a resumé of views that had been set forth in his previous papers. Its chief historical interest arises from its account of the observations made on the Java trip of 1841 which led finally to the great paper of 1842.

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Contemporaneous with, but independent of Mayer's work were the views of L.A. Colding of Copenhagen and James Prescott Joule of England. Colding, in a paper, "Thesis on Force" (35, p. 56; 32, p. 129), which was presented to the Royal Society of Copenhagen in the year 1843, proposed the Energy Principle in a form which was quite as general, though less definite than that of Mayer. All forces, he said, being of spiritual origin, cannot be destroyed but only changed in form. Further, he maintained that his principle that the total force of the world is conserved, is required by the principle of excluded perpetual motion.[28] Like Seguin, Colding assumed, without resort to Gay-Lussac's free-expansion experiment, that the cooling of a gas on expansion against a piston is equivalent to the mechanical force generated in pushing back the piston. Further, he even regarded the work of compression of solids and liquids as also equivalent to the heat generated. Fortunately, however, his calculation of the mechanical equivalent was based, not on these faulty considerations, but on his observations of the frictional heat generated by rubbing metals together. From such experiments he obtained the value 350 for the mechanical equivalent of heat.

Colding's work appeared to have been unknown outside the circle of his immediate associates until after the establishment of thermodynamics by Thomson and Clausius, when it was rediscovered. It hence exerted no influence on the development of thermodynamics. For many years Mayer's work was also unappreciated, even in Germany. Helmholtz made no reference to Mayer in his 1847 paper, and Clausius, in his great memoir of 1850, mentioned him only once and then in the most casual fashion. Not until the last quarter of the century was the true significance of Mayer's work appreciated whereupon he came to be hailed as the true father of energetics.

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B. Joule and the Mechanical Equivalent of Heat.

Fortunately, fate ruled otherwise in the case of Joule of England. Although his careful and pains-taking experiments received little notice up until 1847, in that year they attracted the attention of Thomson; and it was their influence which led to Thomson's abandonment of the caloric theory and subsequent modification of Carnot's theory to form the great system of classical thermodynamics. Since, as we shall note later, Helmholtz's paper of 1847, like those of Mayer and Colding, was quite uninfluential, we may say that, of the work of the great founders of the Energy Principle, Joule's played by far the greatest part in the historical development of classical thermodynamics.

It would be difficult to find two scientific men whose inclinations, as revealed in their work, differed more than those of Mayer and Joule. From the very beginning of his studies, Mayer appears to have been thoroughly convinced of the a priori validity and logical necessity of the Energy Principle in all its generality, although his actual knowledge of the detail of physical science was quite meager. Further, with the exception of an experiment in which he raised the temperature of a body of water from 12°C. to 13°C. by shaking, he is not known to have performed a single quantitative experiment.

The work of Joule, on the contrary, was almost exclusively experimental. He was most cautious about making generalizations; indeed, for the most part, he dispensed with them altogether, preferring to let the experiments speak for themselves.

However, it is scarcely conceivable that Joule's famous and remarkable experiments could "just happen." They were planned, of course, and, behind those plans, there must have been a motive and a conviction. In fact, Joule himself gave expression to this conviction on several occasions. As early as 1843, he spoke of the forces of nature being "by the

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Creator's fiat, indestructible." (32, p. 31) Again, at the conclusion of his 1845 paper, he wrote: "Since I am of the view that only the Maker possesses the power to destroy, I agree with Roget and Faraday that every theory which points in its consequences to the annihilation of force is necessarily false. The principles which I have developed are free of this difficulty." (32,p. 32) These quotations seem to justify the characterization of Joule's experimental work as an attempt to give definite, quantitative form to the vague notions of transformation and conservation of force, known to him through the writings of Faraday and Grove.[29]

It is impossible to say just how much Joule was influenced, in advance, by Rumford's kinetic theory of heat. We do know that he referred to it in 1843, definitely subscribed to it in 1845, and stated in 1847 that "we might reason a priori that such absolute destruction of vis viva cannot possible take place, because it is manifestly absurd to suppose that the powers with which God has endowed matter can be destroyed any more than they can be created by man's agency." (44, I, p. 265)

Joule's interest in the problem of the transformation of force grew out of his unsuccessful attempt, in 1837, to construct an electro-magnetic engine which could replace the steam power employed in his father's brewery. He found that the work obtained in this way from a pound of zinc was less than one-fifth of that obtained from one pound of coal in the best steam engines. This, together with the higher price of the zinc, caused him to conclude that the electro-magnetic machine was impractical as a source of power except for special purposes.

In the course of these investigations, Joule noted the heat developed in the conductors carrying the current and decided to determine the relation of this heat to the current strength. Profiting by Faraday's law, he measured the current by noting the weight of metal deposited per

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unit time in an electrolytic cell introduced into the circuit. By immersing the conductors in a calorimeter, he then discovered his famous law that the heat developed in a conductor (metallic or electrolytic) is proportional to the product of its resistance and the square of the current strength. He further showed that the net heat developed in such a circuit, when no other effects were produced, was equal to the heat effect characteristic of the chemical reaction occurring in the battery,[30] and that this net heat was proportional to the product of the electromotive force of the battery into the number of chemical equivalents transformed. Finally, he demonstrated that, by the insertion of a water coulometer into the circuit, the total heat of the circuit was diminished by an amount equal to the heat evolved when the liberated hydrogen and oxygen recombined to form water. All of these results appeared in Joule's 1840 paper entitled, "On the Production of Heat by Voltaic Electricity."

Joule evidently did not consider these experiments as evidence against the caloric postulate that heat is always conserved in total amount, for he spoke of the diminished heat effect, occasioned by the introduction of the coulometer, as compensated by the production of "latent heat" associated with the hydrogen and oxygen. Instead, his attack on the caloric theory was not publicly launched until three years later, in 1843, when his paper, "On the Calorific Effects of Magneto-Electricity and on the Mechanical Value of Heat," appeared.

If heat is not a substance but a state of vibration, said Joule in this 1843 paper, we might expect that it could be brought about through motion. He then proceeded to describe his discovery that, by means of Faraday's magneto-electricity, the heat effect corresponding to a given chemical action occurring in a voltaic battery may be decreased or

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increased depending on whether "mechanical power" is expended or developed. By rotating a spool of wire with an iron core between the poles of an electromagnet, measuring the induced current by means of a galvanometer, and noting the total heat developed, he first showed that the heat developed by the induced current, like that of the voltaic current already studied, is proportional to the product of the resistance of the circuit into the square of the current intensity. He then introduced a voltaic battery into the circuit containing the spool and the galvanometer and found, of course, that, by rotation of the spool, the battery current, hence the amount of chemical action occurring in the battery per unit time, may be diminished or increased, depending on the direction of rotation. After showing that the heating effect of this current, which may be regarded as a combination of the battery current and the induced current, is also proportional to the product of the resistance into the square of the current intensity, Joule realized that he had, in magneto-electricity, a means whereby the heat corresponding to a given cell reaction may, by mechanical means, be increased or decreased by an amount proportional to the intensity of the induced current. This follows from the fact that the effect, on the chemical action, of the induced current is proportional only to the first power of this current's intensity, whereas the increase or decrease in the heating effect is proportional to the square of the induced current. [31]

Thus suppose q is the heat developed per unit time per unit current in a voltaic circuit unaffected by induced currents. Let the resistance of the circuit and the current flowing be denoted by R and I, respectively. By choosing as the unit of electromotive force that electromotive force required to produce in unit resistance a current corresponding to the heat q, we may write for the total heat of the circuit, $qI \equiv RI^2$, where

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Ohm's Law requires that $IR = q$. If, now, there be introduced an induction current i, and if we denote by Q the heat now developed per unit time per unit current, we shall have

$$Q\ (\ I \pm i) = R(I \pm i)^2$$

or

$$Q = RI \pm Ri = q \pm Ri,$$

i.e. the increase or decrease in the heating effect, Q-q, is proportional to the intensity i of the induced current.

In the case where the induced current assists the voltaic current, Joule recognized that the increased heating effect, Q-q, which he carefully measured, must come from the "mechanical power" expended in turning the spool through the imposed magnetic field. To determine the magnitude of this work, he devised a mechanism whereby rotation of the spool was effected by means of a falling weight suspended over a pulley. With this modification, the experiment was repeated , care being taken that the magnitude of the weight W was such as to produce the same velocity of rotation of the spool as prevailed when the heating effect Q-q was determined. Disconnecting the battery operating the electromagnet, Joule next determined the weight w which will just overcome the frictional resistance opposing rotation of the spool. Then, if h is the height fallen through by the weight W in the time t, the mechanical power (W-w)h has evidently generated the heat (Q-q)tI. From a series of such experiments, Joule obtained, as the mean value for the mechanical equivalent of heat, 838 foot pounds per British Thermal Unit.

In a footnote to this same paper, Joule stated that, by measuring the temperature rise caused in water by forcing it through the small holes of a piston, he obtained the value 770 foot pounds per B.T.U. for the mechanical equivalent.

In the above-described investigations Joule supplied definite

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quantitative evidence for the principle of the correlation and conservation of "forces," so far as chemical action, heat, electricity, magnetism, and mechanical action were concerned. In the same year that saw the publication of his second paper (1843), he attempted to bring light into the same fold with the other "forces" by comparing the heat of a galvanic current which rendered the wire incandescent with the heat effect when the wire was kept cool by immersion in water. Finding the heat effect for a given current in the latter case slightly in excess of the heat effect in the former, he attributed the difference to the production of light in the first instance. (35, p. 65)

In a paper published in 1845, entitled "On the Changes of Temperature produced by the Rarefaction and Condensation of Air," Joule described new determinations of the mechanical equivalent. In one experiment, a given volume of air at a known pressure was sucked into a compression flask contained in a water calorimenter, whereupon it was compressed to a smaller volume and the rise in temperature of the water noted. By employing a large quantity of water, the temperature rise was sufficiently small so as to make the work of compression calculable from Boyle's Law. Joule found that, if the work of compression be assumed to be equivalent to the heat developed, this method gave the value 795 for the mechanical equivalent. The fair agreement of this value with the value obtained from the thermal effects of magneto-electricity (where there was no possibility of the heat having been latent) caused Joule to suspect that the volume changes of air likewise did not, in themselves, incur any heat to become free or latent, and he confirmed this suspicion by performing the free expansion experiment which, unknown to him, had been carried out by Gay-Lussac many years before.

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As a further check, he measured the heat absorbed by air when it expanded practically isothermally against atmospheric pressure, thereby obtaining the 820 for the mechanical equivalent. In conclusion, pointed out that his experimental results contradicted the assumptions (caloric hypothesis) which Carnot had made in developing his theory of the steam engine, whereas they confirmed the theory that heat is a state of motion of the smallest particles of a body.

The method for the determination of the mechanical equivalent which Joule finally found most reliable was the direct one in which frictional heat was generated by the arms of a paddle rotated in water by means of lead weights attached to the shaft of the paddle by cords drawn over pulleys (17, p. 289). Experiments of this type, employing mercury as well as water as frictional medium, were carried out by Joule from 1845 through 1849 and gave as the most probable value of the mechanical equivalent, 772 foot-pounds per B. T. U. (423.5 kilogram-meters per calorie), a value which stood for nearly thirty years.[32]

C. Helmholtz and the Mechanistic Hypothesis.

Mayer, as we have seen, vigorously opposed the kinetic theory of heat; and Joule, although he accepted it, appears to have been guided in his experimental researches far more by Grove's general notion of the correlation and conservation of forces than by any hypothesis as to the ultimate nature of thermal phenomena. On the contrary, the dominating stimulus in the case of Helmholtz's 1847 paper, "On the Conservation of Force" (45), was the conviction that not only heat but magnetism, electricity, light, and chemical "forces" as well were ultimately mechanical in nature and were hence subject to the laws of pure mechanics. However, if, in spite of the fact that Helmholtz fell far short of attaining this postulated goal of universal

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mechanical explanation, his paper nevertheless contains numerous results of lasting value, this is because these latter are in conformity with Mayer's principle of equivalence.

In the introduction to his paper, Helmholtz clearly revealed the fundamental opposition of his point of view with that of Mayer. The proper function of theoretical science, said Helmholtz, is, starting from the visible effects of phenomena, to seek out their common, hidden causes. The hypothesis that all phenomena are, in fact, reducible to the same fundamental causes is simply the scientifically necessary assumption that nature is comprehensible.

Science, said Helmholtz, regards phenomena from the standpoint of two abstractions: (1) matter in its purely existential aspect, i.e. matter constant in quantity and occupying space; (2) matter as acting and producing qualitative effects, i.e. matter endowed with "forces" (Krafte). He observed that these two aspects are actually inseparable since matter is observable only through its forces, and, conversely, the observation of forces implies the existence of matter.

Particles of matter endowed with unchangeable forces(indestructible qualities) are particles of the chemical elements. If we imagine the whole world analyzed into particles of the chemical elements, then the only changes possible are the motions of these particles relative to one another. Hence science's search for final causes must consist in reducing all phenomena to the motions of particles of matter endowed with unchangeable forces.[33]

Having adopted this mechanistic point of view, Helmholtz considered it immaterial whether he take as fundamental axiom, (1) the Principle of Excluded Perpetual Motion (impossibility of obtaining work from nothing), or (2) the hypothesis that all phenomena can be traced back to the action of

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attracting and repelling forces whose intensity depends only on the distance, since he regarded these two starting points as mutually equivalent.

Let us see how he came to regard these two axioms as identical. In the first place, the Principle of Excluded Perpetual Motion, when applied to an isolated system of mass particles moving under the influence of their mutual , conservative forces, requires that the change in total vis viva ($\sum \frac{1}{2}mv^2$) of the system when it goes from one configuration to another shall be independent of the path (that is, independent of the intermediate velocities and configurations) or, what is the same thing, that the total vis viva of the system shall be uniquely determined by the system's configuration. For suppose the total change in vis viva for a given change of configuration were greater by one path than by another. Then, by allowing the change of configuration to occur along one of these paths and then restoring the system to its initial configuration by reversing the other path, the excess vis viva, equivalent to a certain amount of work, would have been obtained from nothing. But this would violate the Principle of Excluded Perpetual Motion.

Further, it is equally evident that the assumption that the configuration of such a system uniquely determines its total vis viva, implies the Principle of Excluded Perpetual Motion, a truth which Helmholtz did not take the trouble to point out explicitly. Consequently, Helmholtz considered the form which the Principle of the Conservation of Vis Viva takes for such an isolated system of mass particles as tantamount to the Principle of Excluded Perpetual Motion. Lagrange had already shown that this form of the Principle of the Conservation of Vis Viva followed from the assumption that the acting forces could be expressed as derivatives of a function of the coordinates, i.e. that their intensities depended only on the distance between

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the centers of emanation. Hence Helmholtz's second axiom (hypothesis of central or conservative forces) was sufficient for the first (Principle of Excluded Perpetual Motion).

Helmholtz thought that the first axiom was likewise sufficient for the second. If the kinetic energy T of a particle be a function of the coordinates (x, y, z) alone, we have

$$dT = \frac{\partial T}{\partial x} dx + \frac{\partial T}{\partial y} dy + \frac{\partial T}{\partial z} dz.$$

Further $$dT = Xdx + Ydy + Zdz$$

where X,Y, and Z are the components of the force acting on the particle. Equating like coefficients of dx, dy, dz, Helmholtz deduced the conclusion that the force-components are uniquely determined by the coordinates (x,y,z), and hence that the action of forces in such a system depends only on the distance between the particles. Lipschitz, however, has shown that this conclusion does not rigorously follow. (32, p. 38)

Helmholtz derived the analytical formulation of the Principle of Conservation of Vis Viva in the following manner. Suppose a particle of mass m is subject to the conservative force ϕ whose components are X, Y, Z. At time t, the coordinates of the particle are x,y,z, its velocity is v, whose components are x', y', z', and its distance from the point of emanation of the conservative force is r. Now

$$v^2 = x'^2 + y'^2 + z'^2$$

whence $$d(v^2) = 2x'dx' + 2y'dy' + 2z'dz'. \qquad (16)$$

But the force components are given by the fundamental relations:

$$X = m\frac{dx'}{dt}, \quad Y = m\frac{dy'}{dt}, \quad Z = m\frac{dz'}{dt}$$

so that $dx' = Xdt/m$, etc. Substituting these values, also $x' = \frac{dx}{dt}$, etc., in (16), we obtain $$dv^2 = \frac{2X}{m} dx + \frac{2Y}{m} dy + \frac{2Z}{m} dz.$$

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Introducing ϕ by means of the relations $X = -\frac{x}{r}\phi$, $Z = -\frac{z}{r}\phi$, $Y = -\frac{y}{r}\phi$,

we find

$$mdv^2 = -2\frac{\phi}{r}(xdx + ydy + zdz),$$

or

$$\tfrac{1}{2}mdv^2 = -\phi\, dr.$$

Integration between the limits V and v, and R and r, gives

$$\tfrac{1}{2}mV^2 - \tfrac{1}{2}mv^2 = -\int_r^R \phi dr, \qquad (17)$$

where the Principle of Excluded Perpetual Motion requires that the integral on the right-hand side be independent of the path. Helmholtz next shows that, when applied to a system of any number of mass particles, equation (17) assumes the form:

$$-\sum\int_{r_i}^{R_i}\phi_i\, dr_i = \sum(\tfrac{1}{2}m_i V_i^2) - \sum(\tfrac{1}{2}m_i v_i^2). \qquad (18)$$

The Principle of Vis Viva expressed in the form (18) Helmholtz called the Principle of the Conservation of Force. The right-hand member of (18) was called the gain or loss of living force (vis viva), the left-hand member, the corresponding change in the system's "tension-force" (Spannkraft). The Principle of Conservation of Force was hence expressed in words, as follows: "In all cases of the motion of free material points under the influence of their attracting and repelling forces, whose intensities depend only on the distance, the loss in the quantity of tension-force always equals to the gain in living force, and the gain in the first equals to the loss in the second." Hence the sum of tension force and living force remains constant.[34]

As instances of the fruitful results obtained by the application of the Principle of Conservation of Force to mechanics, pure and applied, Helmholtz cited the laws of motion of the heavenly bodies, the laws of falling terrestrial bodies, the laws of collision of elastic bodies, the Principle of the Conservation of the Center of Gravity, the Principle of Virtual Velocities, the laws of statics, principle of conservation of elastic vibrations, and

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and

Fresnel's laws of the reflection, refraction, polarization of light.

Helmholtz's Principle of the Conservation of Force is, of course, nothing more than Poncelet's Principle of the Transformation of Work applied to conservative systems. However, by emphasizing the close relationship of his principle to the Principle of Excluded Perpetual Motion and by pointing out that it may be taken as the starting point in the systematic exposition of mechanics, Helmholtz rendered a real service to pure mechanics.

In so far as its relation to pure mechanics is concerned, Helmholtz's paper constituted an extension of the "energetic" view already advocated by Poncelet and Mayer. On the other hand, in postulating that all changes, including electrical, magnetic, chemical, optical, and acoustic processes, are really mechanical in nature and hence subject to his Principle of the Conservation of Force, Helmholtz placed himself in direct opposition to the "energetic" view, substituting in its place the ideal of molecular(or atomic)physics. According to the latter, every body is a Newtonian system of mass particles, too small to directly observe, and whose changes in vis viva and tension-forces are to be inferred from the macroscopic changes of the body.[35]

Turning to the consideration of thermal phenomena, Helmholtz showed that his mechanistic hypothesis was consistent with the known facts. The view that an absolute loss of vis viva occurs in frictional processes and in the collision of inelastic bodies neglects the increased tension-forces caused by compression, also the production of heat and electricity in such processes, which can, in turn, produce mechanical actions. The question, whose answer the mechanistic hypothesis requires to be affirmative, is, Does the sum of the forces produced always correspond to the mechanical force which has been lost?

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Does heat really have a force equivalent? In answering this question, Helmholtz was led to a criticism of the caloric theory, which was still widely accepted at this time, e.g. by William Thomson in England. According to the caloric hypothesis, the force-equivalent of heat can mean only the work obtained in the transfer of a certain quantity of heat ffom a higher to a lower temperature. To explain frictional heat, the calorists had assumed: (1) that the heat is conducted from the surroundings; or (2) that it arises from compression of the surface particles where it was previously latent. The first of these assumptions, said Helmholtz, is unsupported by experimental evidence. The second, besides ascribing a large and highly improbable thermal effect to a very small compression, completely fails to account for the frictional heat producible from soft bodies in which no large surface compressions could be maintained, e.g. as in Davy's melting of ice by friction and in the softening of iron by hammering.

As positive evidence against the caloric theory and in favor of the kinetic theory of heat, Helmholtz cited Joule's measurement of the work-equivalent of frictional heat, also the production of heat by mechanical means in the magneto-electric machine. He observed, as Mayer had done before him, that mechanical work must be expended to charge the electrophorus and that the heat generated on discharge must be equivalent to the work originally expended. He noted that similar considerations apply to the work expended in charging a battery.[36]

"From these facts," said Helmholtz, "it follows that the quantity of heat(of a body) can be absolutely increased by mechanical forces, that therefore calorific phenomena cannot be deduced from the hypothesis of a species of matter, the mere presence of which produces the phenomena, but that they are to be referred to changes, to motions, either of a peculiar species

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of matter, or of the ponderable or imponderable bodies already known, for example, of electricity or the luminiferous ether."[37] Thus Helmholtz refused to commit himself on the question of just what it is whose motion constitutes heat; likewise, he admitted that the precise nature of this motion is unknown. Indeed, he said, "Of what nature the motion is we have no means whatever of ascertaining; the possibility of conceiving the phenomena of heat as being due to motion is, however, sufficient for our present object. The conservation of force in case of these motions will hold good in all cases where hitherto the conservation of caloric has been assumed."

In this connection, Helmholtz stated that it is only free or sensible heat which is to be attributed to the vis viva of the calorific motion. Latent heat is an expression for the quantity of "tension-force" (potential energy of position) of the atoms of the body. Thus when latent heat becomes sensible, tension-force has been transformed into the vis viva of calorific motion.

Concerning the heat of chemical processes,[38] Helmholtz observed that Hess's Law of Constant Heat Summation becomes a special instance of the Principle of Conservation of Force, if, instead of supposing that every chemical compound possesses a characteristic quantity of latent caloric, we assume that the heat developed by chemical processes is a measure of the "vis viva produced by the chemical attractions."

If, in applying the Principle of the Conservation of Force to electrical phenomena, Helmholtz obtained more definite results, this is because his mechanistic viewpoint has, in this case, an unambiguous significance for <u>macroscopic</u> systems. Electricity, says Helmholtz, may generate force in either of two ways: (1) the electricity may move the body which bears it; (2) the electricity itself may move through the

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body generating heat. In particular, he showed that K. F. Gauss' potential theory, completed in 1839, is in complete conformity with the Principle of the Conservation of Force. Thus, if two bodies of charges e_2 and e_1 are located at a distance r from each other, the force of attraction is, according to Coulomb's Law, $\phi = -\frac{e_1 e_2}{r^2}$. When one of the bodies passes from the distance R to r, the gain in vis viva is $-\int_R^r \phi \, dr = \frac{e_1 e_2}{R} - \frac{e_1 e_2}{r}$. Because ϕ is a central force, this gain in vis viva (which may correspond to a visible motion of the bodies or to an increase in the invisible calorific motion, representing a development of heat) is independent of the path in going from the distance R to r.

As an application of the potential concept, Helmholtz obtained, for total "tension-force" expended in giving to a body of capacity c a charge e and potential V, the well-known expression

$$\tfrac{1}{2} e V = \tfrac{1}{2} \frac{e^2}{c} .$$

If, on discharge, all visible motion is avoided (also light and sound), this represents the mechanical equivalent of the total heat generated. As experimental confirmation of his law, Helmholtz cited the work of P. T. Riess which had revealed the heat of discharge to be proportional to the square of the charge.

Turning to galvanic electricity, Helmholtz began by distinguishing between metallic and electrolytic conductors. No combination of metallic conductors can result in the generation of an electric current except that occasioned by the process of establishment of electric equilibrium. In the conjointment of metallic conductors with electrolytic conductors, however, electric currents are generated even though the metallic conductors themselves are in electric equilibrium. The Principle of the Conservation of Force requires that this

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production of galvanic electricity be accompanied by chemical action as, indeed, Faraday's experiments have shown to be the case. For if it be caused by the mere contact of unlike metals (contact theory), an infinite amount of electricity, hence mechanical force, could be obtained without expenditure of any other kind of force.

Helmholtz then discussed Lenz's Law for the heat of the electric current ($Q = I^2Rt$) and cited Joule's experimental verifications of it. Like Joule, Helmholtz assumed the heat developed by the current to be equal to that of the cell reaction when it occurred alone outside of the battery. The total heat Q, developed in time t, by the galvanic current I of a battery of electromotive force E is by Lenz's Law,

$$Q = I^2 R t = EIt,$$

where R is the resistance of the circuit. Let q_a be the heat of solution of one equivalent of the anodic substance (e.g. zinc) and q_c that for one equivalent of the cathodic material (e.g. copper). Then, if I be measured as equivalents of e.g. water decomposed by the current per unit time, the heat which would have been developed by the chemical reaction if it had occurred outside the battery is

$$Q' = I t (q_a - q_c) .$$

But , if $Q = Q'$, this requires that the electromotive force be related to the heats of reaction as follows (cf. footnote 30):

$$E = q_a - q_c.$$

To be sure, the mechanistic hypothesis does not appear to play any determinative role in this treatment of galvanism. However, said Helmholtz, if we imagine charged atoms (ions) of the cell fluid attracted and repelled by the electrodes, the term $I (q_a - q_c)$ may be supposed to represent the amount of their tension-force which, per unit time, is transformed into the

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vis viva of the calorific motion given by I^2R.

After discussing the phenomenon of polarization, Helmholtz undertook to apply his principle to thermo-electric currents. A thermo-element (Fig. 8) absorbs, in a unit of time, the heat q_1 at the hot junction, develops heat q_2 at the cold junction, whereas the electrical current I, which is generated , develops the heat I^2R. If E is the total potential drop in the circuit, EI represents the heat, per unit time, developed by a chemical reaction which would have produced by galvanic means the same current I. Since the Principle of Conservation of Force requires that this hypothetical "chemical heat" be equal to the heat actually produced, we have

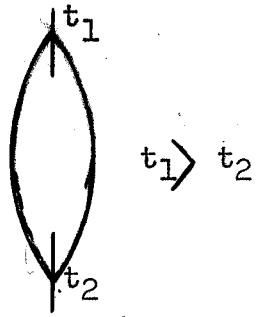

Figure 8

$$EI = I^2 R \quad q_1 - q_2. \tag{19}$$

Also, if B_1 and B_2 denote the e.m.f.'s developed at hot and cold junctions, respectively, Ohm's Law requires:

$$I = \frac{A - B_1 - B_2}{R} . \tag{20}$$

Comparing equations (19) and (20) we obtain

$$(B_1 - B_2)\, I = q_1 - q_2 .$$

i.e. "with the same intensity of current, both the force which generates heat and that which absorbs heat increase with temperature in the same proportion as the e.m.f."[39]

In the case of magnetic attractions and repulsions, the Principle of the Conservation of Force takes the same form as in the electrical case since the inverse square law of attraction still holds.

When we come to magnetic induction, the Principle of the Conservation of Force requires, according to Helmholtz, that, "if a magnet moves under the influence of a current, the vis viva which it thereby gains, must be

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obtained at the expense of the tension-forces, which are consumed in the current." Now suppose the drop in e. m. f. in the primary circuit is E and its current is I and its resistance R. Let V be the potential of the magnet toward the conductor. Now it is not clear why aEIdt, where a is the mechanical equivalent of heat, should represent the tension-force consumed in the current in time dt, nor why $I \frac{dV}{dt}$ dt should equal the corresponding gain in vis viva of the magnet. Yet by assuming this and that aI^2Rdt gives the vis viva generated in the path of the current, Helmholtz obtained the correct equation,

$$aEIdt = aI^2R\,dt + I\frac{dV}{dt}\,dt,$$

whence

$$I = \frac{E - \frac{1}{a}\frac{dV}{dt}}{R}.$$

In attempting to extend these results to the case where several conductors are set in motion by the mutual magnetic actions of their respective currents, Helmholtz obtained incorrect equations (cf. 32, p. 46).

Helmholtz concluded his essay with a few remarks relative to the extension of the Principle of Conservation of Force to organic processes. In the growth of plants, "chemical tensions" are stored up, accompanied by the absorption of solar rays. By burning, these chemical tensions are obtained as heat. Animals consume chemical tension, as plant food, and generate heat and mechanical force in their place. In this connection, the experiments of Dulong and Despretz on animal heat are cited as confirming the Principle of Conservation of Force.

Because he was far better trained in mathematical physics than Mayer, Helmholtz was able to definitely show how the equation provided by the First Law could yield many new and fruitful results. However, as a general statement of the Energy Principle, Helmholtz's exposition suffered from the vagueness occasioned by his adoption of the hypothesis that all phenomena are

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ultimately mechanical in nature. Even when regarded as an outline of the aims of molecular physics, his paper is still ambiguous because of his attempt to include imponderables in the Newtonian mechanistic scheme.[40]

A more precise, also bolder exposition of the mechanistic hypothesis, as applied to heat, was the celebrated theory of molecular vortices which was advanced in 1850 by W.J.M.Rankine with the publication of his paper on "The Mechanical Action of Heat" (47, p. 234). Joule's experiments, said Rankine, confirm conclusively Davy's contention that heat is a motion of some sort, and it only remains to develop this theory quantitatively by introduction of suitable assumptions. Rankine then supposed that each atom of matter consists of a nucleus imbedded in an elastic (ponderable) atmosphere. The expansive force characteristic of heat he attributed to the centrifugal forces set up by the vortex motions of the atomic atmospheres; in fact, quantity of heat in a body at a given temperature was regarded as numerically equal to the product of the weight of the body and the height through which a body of unit weight must fall in order to acquire the velocity of the molecular oscillations of the given body. In these considerations the term "mechanical power" was employed where Helmholtz had used "force."[41]

In opposition to Carnot's postulate of the conservation of caloric, Rankine, like Helmholtz, set up the Principle of Conservation of Vis Viva,which, for a cyclic process, yielded the result that "the algebraical sum of the vis viva expended and produced, whether in the shape of expansion and compression, or in that of heat, must be equal to zero." The manner in which Rankine applied this theorem to obtain a relation between the specific heat of a liquid, its latent heat of evaporation, the specific heat of the saturated vapor, and the pressure and volume changes occurring, as well as several other results, will be related in connection with the development of the

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Second Law of Thermodynamics.

Nor is this the place to enter into the details of Rankine's theory of vortices which now, even for molecular physics, possesses no more than purely historical significance. It will suffice to note that the vortex theory, after further elaboration by its author, was, beginning in 1867, adopted and expanded by Thomson until it acquired great scienfific prestige in England. Along with the revival and development of Bernoulli's kinetic theory of gases by Joule, Clausius, and Maxwell, it exerted a great influence in favor of the general, kinetic view of nature.

Although numerous results arrived at in Rankine's paper were actually independent of any mechanistic hypothesis, still they were, for the most part, at least colored (hence, from the energetic point of view, confused) by the assumption of molecular vortices. [42] The combination of a clear, unambiguous statement of the Energy Principle, formally free from mechanistic hypotheses, together with a systematic and detailed analytical elaboration of its consequences, was first attained at the middle of the nineteenth century through the efforts of Rudolph Clausius in Germany and William Thomson in England. Although both acclaimed the kinetic theory of heat, they did not allow this hypothesis to enter into the statement of the general principle nor to affect the form of the analytical results. Thus, while in full sympathy with the mechanistic view of Helmholtz and Rankine, their formal results appear rather as the fulfillment of the energetic ideal of Mayer.

However, the truly great service of Clausius and Thomson lay, not in their elaboration of the First Law proper but rather in their union of it with the older ideas of Carnot and Clapeyron on the motive power of heat to form the

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the Second Law of Thermodynamics. In fact, the whole thought of Clausius and Thomson, in spite of its significance for the First Law, is best understood as a correction and extension of the ideas of Sadi Carnot, so that we had better delay its consideration until we come, in the next section, to expose those ideas.

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FOOTNOTES

(The Development of the Energy Concept and The First Law of Thermodynamics)

1. This confusion in early Greek natural philosophy was finally cleared up only ninety-five years ago, when the fundamental distinction between energy and available energy was formulated. Indeed, the confusion still persists in most of the text-books of physics: there we commonly find energy defined as "work or Capacity for work!" Thus a vagueness continues to surround "energy" which surrounded the term "force" which preceded it.

2. The more consideration we give to these speculations of Heraclitus, the more we may appreciate their significance for modern thermodynamics, especially the First Law. Thus Poincaré (30,Chapt. VIII), after a careful analysis of the First Law, concludes that no general definition of energy is possible. We may only say, he holds, that, if the universe is governed by laws, there will be quantities which remain constant in it. Thus the important fact appears to be, as Heraclitus suspected, the fact of law itself. Again, Heraclitus' refusal to assume any permanent substance underlying phenomena may be instructively compared with Ostwald's (31,Lec. 12) statement that the assumption of matter, as a carrier of energy, is superfluous.

3. Of course, ever since the revival of Greek materialism by Gassendi and Descartes, there had existed proponents of the mechanistic view that all natural phenomena are the results of the actions of forces and motions, either sensible or hidden. However, definite scientific progress outside pure mechanics had been made only through the assumption of the various "fluids," supposed conservative.

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4 Merz (18, p. 96) has very appropriately described the development of the First Law in the following words: "The complex of ideas and the manifold courses of reasoning which are centered in this conception (of energy) form such an intricate net-work, the interests involved are so great, the suggestions which led up to it so numerous, the consequences which resulted for science and practice so far-reaching, that the historian has no little difficulty in laying bare the many lines of thought which apparently cross and re-cross each other."

5 "The more I meditated on these phenomena, the more they appeared to me to be curious and interesting. A thorough investigation of them seemed even to bid fair to give a further insight into the hidden nature of Heat; and to enable us to form some reasonable conjectures respecting the existence, or non-existence, of an igneous fluid: a subject on which the opinions of philosophers have, in all ages been much divided."(35,p.39)

6 "We have seen that a very considerable quantity of heat may be excited by the friction of two metallic surfaces, and given off in a constant stream or flux in all directions, without interruption or intermission, and without any sign of diminution or exhaustion...

"It is hardly necessary to add that anything which any insulated body or system of bodies can continue to furnish without limitation cannot possibly be a material substance; and it appears to me to be extremely difficult, if not quite impossible to form any distinct idea of anything capable of being excited and communicated in the manner the heat was excited and communicated in these experiments except it be Motion." (17,p.39)

7 "From this experiment it is evident that ice by friction is converted into water, and according to the supposition, its capacity is diminished; but it is a well-known fact that the capacity of water for

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heat is much greater than that of ice; and ice must have an absolute quantity of heat added to it before it can be converted into water. Friction, consequently, does not diminish the capacity of bodies for heat" (35, p.46)

8 In his text-book of 1829, Biot associated the heat liberated in Rumford's experiment with the separation of the surface particles of the metal from the particles underneath. This caloric, he said, must have been present between the particles of bronze which were separated in the boring process. (4, p. 200)

9 The author acknowledges his dependence, in this section, on the excellent discussion by Mach. (4, pp.195-210)

10 The caloric view of this phenomenon has been likened to the changes which occur on changing the volume of a moist sponge: on compressing a sponge (space filled with gas) water (caloric), previously unobservable (latent), appears as liquid (sensible heat).

11 The excellent standing of the caloric theory at this time was evidenced by the fact that Clement and Desormes were honored by the French Academy for their researches.

12 We shall not show in detail just how Laplace obtained his formula but shall content ourselves with revealing how it readily follows from Newton's general formula, $c = \sqrt{\frac{E}{\rho}}$, by employment of Poisson's formula for adiabatic expansion and compression, $pv^{\gamma} =$ constant. For then, $\log p + \gamma \log v = 0$, and $\frac{dp}{p} + \gamma \frac{dv}{v} = 0$. Whence, $E = -v\frac{dp}{dv} = \gamma p$ and $c = \sqrt{\frac{E}{\rho}} = \sqrt{\gamma \frac{p}{\rho}}$.

13 Biot, in a standard textbook (1829), ascribed the heating of a gas on its introduction into a flask, to, first, the cooling of the gas with simultaneous liberation of caloric (?), and, second, to the reduction in volume of the gas first entering by the gas which followed it.

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To arrive at the true laws of gases, he said that these two effects should be studied separately.

He also stated that the heat developed in Rumford's experiments must have been hidden between the surface particles of the iron before boring.

14 This did not imply for Davy, that a relation existed between light and heat on the one hand, and chemical action on the other, since he, like Volta, associated galvanic electricity not with chemical action but attributed it to the mere contact of the heterogeneous substances.

15 The term "force" was borrowed from mechanics where it already was used with a variety of meanings. Newton and his followers had used it in the modern sense as the product of a body's mass and its acceleration. The Cartesians had employed it for momentum; while, as "dead force" (vis mortua), the Leibnitzians used it to denote the product of mass and height of elevation, and, as "living force"(vis viva), for the product of mass and the square of the velocity. When Grove, Mohr, and Liebig, adopted the term in their rather vague speculations on the First Law, its meaning must have become still less definite. In the work of Mayer in 1842 however, "force" is definitely synonymous with our "energy," and this is also true, for the most part, with Helmholtz (1847).

In England, Watt introduced "horse power" to denote the capacity of an engine to do work, and Joule calls this by the name "mechanical power," which term was employed by Rankine (1850) in the extended sense in which Helmholtz used "Kraft." Carnot also refers to work as "motive power." About 1825, Poncelet introduced the term "mechanical work" for what we now would call mechanical energy. Clausius, in his first memoir, in 1850, adopted this term with the same meaning.

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In 1852, Thomson introduced the general term "energy" for that which Helmholtz and Mayer had called "Kraft." This term (energy) had already been used by Young (1802) in place of vis viva and, indeed, had been employed by Galileo, though not consistently. (41, p. 271) Finally, in 1853, Rankine divided energy into "potential" and "actual," and this terminology was soon adopted by Thomson and others.

16 Mohr's paper appeared in an obscure Vienna publication in the year 1837. It exerted practically no influence whatsoever on the development of thermodynamics; in fact, its publication was generally unknown, until the paper was unearthed some twenty years later by the historical researches of Akin. (18, p. 107)

17 The motion theory of heat thus constituted only one of the of the stimuli which let to the formulation of the First Law: firmer bases were to be found in the facts of correlation. However, we cannot attribute to mere accident the fact that Joule, Helmholtz, Rankine, Kelvin, Clausius, and even Carnot (before he died), were all adherents of the kinetic theory of heat. Among the great founders of thermodynamics, only Robert Mayer opposed it. However, we shall see that, of these founders, only Helmholtz and Rankine allowed the kinetic theory of heat to influence the actual form in which the principles of thermodynamics were developed: in the others, the motion theory served merely as a source of subjective stimulus.

18 From our modern, abstract point of view, the name, "Principle of Excluded Perpetual Motion," is incorrect. Indeed, Newton's First Law of Motion states that "a continuous and unending motion," far from being impossible, is the rule. Nevertheless this obsolete terminology has still been retained with the understanding that "Excluded Perpetual Motion" refers to the impossibility of creating motion without the expenditure of

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permanent changes in other bodies.

19 The passage of the Principia which expresses this interpretation of the Third Law reads as follows: "If the action of an agent be measured by the product of its force into its velocity, and if similarly the counter-action of the resistance be measured by the velocity of its several parts multiplied into their several forces, whether these arise from friction, cohesion, weight, or acceleration, action and counter-action in all combinations of machines will be equal and opposite."

Tait (35, p.34) and Thomson (48, p. 78) have claimed unjustly that this statement amounts to the general principle of the conservation of energy. As a matter of fact, except for the case of forces arising from acceleration, where the law amounts to the conservation of mechanical energy, Newton's statement is ambiguous, if not incorrect. For how may the resisting forces of friction, cohesion, and weight be measured in terms of velocities, e.g. if the resisting bodies remain at rest? Of course, we say today that the heat produced by overcoming frictional forces, the changes of state occasioned by overcoming cohesion, and the increased height acquired by a body in overcoming its weight are all forms of energy which are expressible as, i.e. equivalent to definite velocities of a body of given mass. But there is no reason to assume that Newton attached any such meaning to the statement quoted above.

20 Neither Galileo, Huygens, Descartes, or Leibnitz attained the clear notion of mass formulated by Newton.

21 "Working mechanically, "said Poncelet, "means to destroy, for the purposes of the arts, resistances such as cohesion, gravity, inertia of matter, etc. Mechanical work does not assume a resistance overcome once for all but a resistance continually destroyed throughout the path traversed, at the point where it is exerted, and in the direction of the path." (42)

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22 Carnot made his great contribution while under the influence of the caloric theory, but, before his death in 1832, abandoned caloric in favor of the kinetic theory of heat.

23 A similar paper, couched, however, in vaguer terminology and retaining the old Cartesian measure of motion, was submitted by Mayer to Poggendorff in 1841, but was not published till forty years later. Poggendorf, editor of the famous Annallen, also refused to publish Helmholtz's great paper of 1847, "Uber die Erhaltung der Kraft," also Mohr's paper of 1837.

24 It is not probable that Mayer was influenced by the similar views of Coriolis and Poncelet, since the work of the latter remained generally unknown in Germany until after 1845 when German editions of their lectures appeared. Besides, it is doubtful if Mayer's knowledge of classical mechanics and mathematics was sufficient to make such works intelligible to him.

25 Mayer's omission of the factor $\frac{1}{2}$ before mc^2, which was supplied in his later papers, may have been an oversight but, more likely, bears witness to his very sketchy knowledge of mechanics.

26 Rumford did not calculate the mechanical equivalent from his data; and, indeed, as we have already noted (cf.p. 12), his experiments were not altogether conclusive. In Sadi Carnot's notebook, first published in 1878, a value of the mechanical equivalent was given as 370 k.g.m. but the method of calculation was not stated. In 1839 Seguin calculated the mechanical equivalent on the assumption that the cooling of a gas, on expansion, is equivalent to the work of expansion, but he did not justify this procedure by reference to the free expansion experiment of Gay-Lussac. Joule's first calculations of the mechanical equivalent were not published until 1843.

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Mayer's failure to explain his method of calculation in the 1842 paper proved to be very unfortunate. The 1845 paper, like Gay-Lussac's free expansion experiment, was unknown abroad, so it was assumed in England that Mayer's calculation, like Seguin's, rested on unwarranted assumptions.

27 The deviation from the correct value (427) was due principally to the inaccurate value of Delaroche and Berard's c_p.

28 In a letter to Griesinger written in 1842, Mayer also advanced, as evidence for his theory, the fact that it may be regarded as logically dependent on the principle of the impossibility of perpetual motion which he regarded as subjectively certain. (32, p.26)

29 As Merz observes (18, p. 111), Joule could hardly have inferred the constancy of the mechanical equivalent of heat from his early determinations, which varied from 742 to 890 foot pounds per B.T.U., if he had not been possessed of an a priori conviction in this direction.

30 Joule tacitly assumed that no exchange of heat with surroundings, apart from the chemical heat, was occasioned by the working of the battery. Helmholtz also made the same assumption in 1847. This error later found expression in Berthelot's view that the heat of chemical action is a measure of chemical affinity and was not cleared up until the appearance of the work of Gibbs (1875).

31 "Now the increase or diminution of the chemical effects occurring in the battery during a given time is proportional to the magneto-electrical effect, and the heat evolved is always proportional to the square of the current; therefore the heat due to a given chemical action is subject to an increase or to a diminution directly proportional to the intensity of the magneto-electricity assisting or opposing the voltaic current.

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"We have therefore in magneto-electricity an agent capable by simple mechanical means of destroying or generating heat." (44, I, p. 146)

32 In 1858 Hirn obtained the value 425 k.g.m. from the heat of percussion of lead; and by an interesting method, depending on the comparison of oxygen intake and body heat of the human body when engaged in muscular activity with that obtaining when at rest, he deduced the value, 436.7 k.g.m., for the mechanical equivalent. From the heat developed in a copper disc when rotated in a magnetic field, Violle obtained, in 1870, the value 435 k.g.m. per. In 1878 Joule refined his paddle-wheel experiment, obtaining 772.55 foot pounds per B. T. U.

In all of Joule's work, the invariability of the specific heat of water had been assumed. Rowland (1879), repeating Joule's experiments on a larger scale so as to effect greater temperature differences in the calorimeter, and taking account of the slight variation in the specific heat of water, obtained, for the mechanical equivalent, the value 427.52 k.g.m. at 14.6°C. (latitude of Baltimore), while the value obtained by Joule in 1878, expressed in these units, was 426.75. (For a complete list of determinations made up until 1899 see 17, p. 319). Because the electrical calorimeter has now supplanted the water calorimeter in accurate work, the calory is logically defined in terms of the international volt and the international ohm, thus eliminating from the mechanical equivalent any vagueness associated with the thermal properties of water. See the review by Mueller and Rossini (63).

33 Helmholtz employed the term "force" (Kraft) in three different ways. In the passages just cited, "force" is snyonymous with "quality" or "physical property." Again, he also uses "force" for the Newtonian force of attraction. Finally, in the phrase, conservation of force, "force" is synonymous with "energy"," as it had already been with Mayer.

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34 Suppose a particle subject to an attractive, conservative("central") force ϕ whose distance from the point of emanation is r at time t. Then the tension force remaining is $\int_0^r \phi dr$ while that consumed is given $\int_\infty^r \phi dr$. The former can "immediately act" whereas the latter can only be "called into action by an equivalent loss of vis viva."

35 At the same time, the notion of equivalence as applied to macroscopic changes was necessarily involved by this mechanical hypothesis, since if all changes are really mechanical in nature, they are capable of quantitative representation in terms of the same (mechanical) unit and hence enter, of necessity, into the relations, "equal to," "greater than." and "less than."

36 Like Joule, Helmholtz did not consider the heat of voltaic electricity as conclusive evidence against the caloric hypothesis, since this heat might be supposed to have already been present as latent in the chemicals of the charged battery. He also suggested that the heat of frictional electricity might similarly be explained.

37 Helmholtz did not explain how an "imponderable," such as electricity, could possess vis viva. Clausius, commenting on this difficulty five years later (46), said "To give, however, the quantity $\frac{1}{2}\sum mv^2$... a meaning so general as to embrace the motion both of the material masses and of the electricity, we must...decide whether the electricity is subject to the laws of inertia, so as to permit of vis viva being ascribed to it." Clausius did not attempt to make any such decision.

38 An account of Helmholtz's views on the work of Carnot and Clapeyron will be found in the history of the Second Law (next section).

39 Thomson's correct treatment of thermo-electricity will be found in the history of the Second Law.

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40 As we have seen, caloric was the only imponderable which Helmholtz specifically rejected. Evidently out of respect for the important analytical results obtainable with the fluid concepts in electrical theory, Helmholtz retained the imponderable electrid fluid. The success of Fresnel's undulatory theory of light likewise must have caused his retention of the luminiferous ether.

41 "The quantity of heat in a given mass of matter, according to the hypothesis of molecular vortices, as well as every other hypothesis which ascribes the phenomena of heat to motion, is measured by the mechanical power to which the motion is equivalent, that being a quantity the total amount of which in a given system of bodies, cannot be altered by their mutual actions, although its distribution and form may be altered." (47, p. 244)

42 In the next section, we shall see that by 1855 Rankine's views had undergone a complete change so that he became the leading proponent in England of the "energetic" view of physical phenomena.

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IV. THE DEVELOPMENT OF THE ENTROPY CONCEPT AND THE SECOND LAW OF THERMODYNAMICS.

page

1. Introduction. 226

A. The Essence of the Second Law. 226

B. The Opposition of Greek Philosophy to the Second Law. 227

C. The Absence of Second-Law Ideas in Modern Physical Theory Prior to Carnot. 229

2. Carnot and the Motive Power of Heat.

A. The Problem of Improved Efficiency. 234

B. The Thermal Properties of Gases. 244

C. The Significance of Carnot's Work. 255

3. The Elucidation of Carnot's Ideas.

A. Clapeyron and the Pressure-Volume Diagram. 257

B. The Views of Holtzmann and Helmholtz. 268

C. Carnot's Theorem and the Absolute Temperature. 273

D. The Effect of Pressure on the Freezing Point of Water. 275

E. Thomson's Exposition of Carnot's Theory. 277

4. The Rejection of the Caloric Hypothesis.

A. The Efforts of Rankine: Molecular Vortices versus Energetics. 281

B. Clausius and the Directional Flow of Heat. 295

C. Thomson and the Postulate of Restricted Conversion. 312

5. The Entropy Concept and the Dissipation Law.

A. The Generalization of Carnot's Theorem. 340

B. The Dissipation of Mechanical Energy. 344

C. Equivalence Values and Entropy. 353

D. Objections to the Second Law. 362

E. Applications to Thermo-Electricity and Phase Equilibria. 365

Footnotes and References 372

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IV. THE DEVELOPMENT OF THE ENTROPY CONCEPT AND THE SECOND LAW OF THERMODYNAMICS

1. INTRODUCTION

A. The Essence of the Second Law

Under the heading, "Second Law of Thermodynamics," we find embraced a series of ideas which function to condition and, to a certain extent, contradict the substantial view of the world expressed by the First Law. As the term, "Second Law," is generally understood, these ideas, broadly stated are: first, among the various forms of energy (modes of substance) there may be distinguished two classes, a class of active, useful, or "available" forms arising by virtue of the external, spatial, and temporal relationships which the members of a macroscopic system of bodies bear to each other, and a class of inactive, "unavailable" forms associated with the internal conditions of temperature, density, pressure, and state of aggregation prevailing within each of the bodies supposed chemically homogeneous; second, whereas "available" forms of energy are capable of complete transformation into those of the "unavailable" type, the extent of transformation of the latter into the former can never, even under ideal (reversible) conditions, exceed a definite maximum which must always fall short of complete convertibility; and, third, because the necessary ideal conditions can never be altogether attained, every real transformation of energy incurs an irretrievable loss of "available" energy and a consequently ineradicable gain of the "unavailable" form, thus imparting a definite direction to cosmic processes taken as a whole.

The task of exposing the history of the Second Law of Thermodynamics is thus seen to involve the examination of those systems of thought, catering to the substantial view of physical realism, for the answers to two questions. First, Are the forms of the universal substance regarded

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as divisible into classes which bear any resemblance to the active or "available" and the inactive or "unavailable" forms of energy, respectively? Second, if such a division is made, what relationship is postulated between these two form of substance?

B. The Opposition of Greek Philosophy to the Second Law.

In the case of Greek natural philosophy, we may search in vain for any answers to these questions which would indicate even an approach to the Second Law of Thermodynamics. With the Ionians (Thales, Anaximander, Anaximenes) and Heraclitus, the standpoint of hylozoism prevented the adoption of even the elementary segregation of substance into the active and inactive forms. Instead, they naively supposed all nature to be "alive" and innately endowed with the capacity for ceaseless change, i.e. for them, all energy was "available."

Empedocles overstepped the bounds of hyozoism to postulate a separate cause of motion which was supposed to produce changes in matter, regarded as passive. But nowhere did Empedocles regard this active cause of motion, which he designated by the vague terms "love" and "hate," as capable of entering into a relationship of convertibility with passive matter. Rather, the active cause was not a form of substance at all, but a power acting on substance while remaining, at the same time, independent of it. With Anaxagoras, the active cause of natural change was itself considered a form of substance; at least this would seem to follow from the author's reference to it as the "force element." But, as with Empedocles, there was no possibility of its convertibility into other forms, since Anaxagoras specifically stated that the "force element" was imperishable and unchangeable.

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Like the hylozoists, Parmenides failed to differentiate Being into active and inactive forms, though for a different reason: with him, this failure was a consequence of the denial of the reality of all change and the resultant postulation of one timeless, changeless Being forever remaining identical to itself. Leucippus, in incorporating the notion of the Eleatic Being into the atomistic doctrine, likewise rendered foreign to the latter any differentiation of substance into "available" and "unavailable" types: all substance consists of atoms whose sole attributes are size and shape, and all change is simply the motion of these atoms. Democritus, as we have seen , departed far enough from this purely mechanistic scheme to postulate the existence of particular kinds of atoms, namely, "fire-atoms," which he supposed to be more mobile and active than the other atoms. But, as with the "force-element" of Anaxagoras, so with the "fire-atoms" of Democritus, there was no question of the transformation of this more active form of substance into inactive forms or vice versa: the "fire-atoms," like the other atoms, were eternal and unchangeable.

Thus, of these Greek philosopphers of nature, some (the hylozoists, Parmenides, and Leucippus) made no distinction between active and inactive forms of substance; and, of those who did (Empedocles, Anaxagoras, Democritus) , all supposed the active form to be conserved throughout the phenomenal changes. Hence, there could be no question here of any transformation of the active form of substance into an inactive form, let alone an irreversible transformation. The notion of the "dissipation" of substance, entailing a "running down" of the world, was therefore completely foreign to Greek philosophy. Thus the Milesians regarded the cosmic process as a ceaseless succession of productions, and attained, in Anaximenes, to the clear realization that this requires that the "World-Stuff" be possessed of an infinite capacity for change; Heraclitus and Empedocles spoke of the ceaseless strife of oppàsites resulting in a succession of periodic

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changes in nature; whereas, according to Leucippus, natural processes, though not necessarily periodic, must go on forever because the motion, with which atoms are endowed, is itself eternal. Still another type of contrast to the notion of irreversibility is encountered in the teleological view of Anaxagoras. For the latter, to explain the order of the world, supposed the elements endowed with a rational, purposive motion.[1]

C. The Absence of Second-Law Ideas in Modern Physical Theory Prior to Carnot.

It is not only among the Greeks that the ideas constituting the Second Law of Thermodynamics are found wanting: this shortcoming also characterized modern physical philosophy as it was developed in the seventeenth and eighteenth centuries. Indeed, we may say that the ideas forming the nucleus of the Second Law were as alien to that development as the notion of substance, lying at the basis of the First Law, was intimately akin to it.

This state of affairs may be largely attributed to the apparent opposition of the ideas embraced by the Second Law with the fundamental assumption behind the First Law. For the acceptance of the Cartesian doctrine that all qualitative changes are really manifestations of a single substance, capable only of quantitative distinctions, incurs the postulation of the homogeneity of all parts of the universe and is hence opposed to any fundamental differentiation of substance into active and inactive forms. At the same time, the notion of irreversibility, involving the transformation of one form of substance into another, is likewise excluded.

This opposition to the ideas embraced by the Second Law found its principal expression in the extension of the highly influential science of mechanics, whose foundations were laid in the latter part of the seventeenth century by Galileo, Huygens, and Newton, to form a materialistic philosophy of

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nature, closely resembling Greek Atomism. To be sure, Leibnitz's classification of forces as "dead" and "living" may be regarded as corresponding to a division of substance into inactive and active forms. However, aside from the fact that this energetic view of mechanics was not generally considered fundamental until long after the work of Pencelet, the notions of partial convertibility and irreversibility was quite as foreign to it as they were to the Greeks, since the two forms of force were regarded mutually and completely interconvertible.

The extension of mechanics to form a general "astronomical view of nature" (51, Chapt. IV) received its greatest stimulus from Newton's Principia, published in 1687. The conclusion that falling terrestrial bodies are governed by the same law of attraction as the heavenly bodies (Universal Law of Gravitation) provided a most powerful influence in favor of this astronomical view. Following Newton's cue, the view that all phenomena arise from the exertion of attractive and repelling conservation forces between the particles of bodies, gradually gained weight and culminated in the publication of Laplace's Exposition du Systems du Monde in 1796 and his Mecanique Celeste from 1799 to 1825.

Newton himself set the example for this sort of speculation when he explained the refraction of light by the hypothesis of corpuscles of light subject to attractive forces. In 1713 Hauksbee supposed capillary action to be the result of molecular attractions. By the extension of the notion of mass to include the imponderables, electricity and magnetism, electrical and magnetic actions were incorporated into the Newtonian scheme, a step receiving added support by the discovery of Cavendish and Coulomb, toward the end of the eighteenth century, that these electrical and magnetic actions conformed to an inverse square law of the same form as Newton's law of gravitation. About the same time, the inverse square

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law was also found to govern the variation of the intensity of radiation with distance.

The extension of the astronomical view to molecular forces was early recognized as necessitating the admission of repulsive as well as attractive forces, an hypothesis whose feasibility was no doubt favored by the existence of such forces in electrified and magnetic macroscopic bodies. Pursuing the Newtonian ideal, R.G. Boscovich, in 1758, sought to formulate a truly universal law of attraction and repulsion which would govern both the attractive, e.g. gravitational forces of macroscopic systems as well as the repulsive forces of molecular systems. Although the general law which he advanced was scientifically impractical, his point of view was essentially that adopted by Poisson, Navier, and Cauchy in explaining the elasticity of solid bodies as due to molecular forces.

In the works of Laplace, already referred to, the astronomical view of nature foreshadowed by Newton was systematically elaborated. Thus the solidity of bodies, the aberration of light, chemical affinities, and thermal phenomena were all explained on the basis of central forces between the minute particles of bodies. In the case of heat, the repellent forces were attributed to particles of imponderable molecules.

Again, we must call to mind the complete opposition of this view of nature to the Second Law of Thermodynamics. For, if in this mechanistic scheme, astronomy is regarded as the model science, this implies that all phenomena possess the eternality and periodicity which seem to be characteristic of the motions of the heavenly bodies. According to this view, there are no fundamental or lasting changes which are distinct from temporary or reversible ones. Instead, all changes are of precisely the same kind, i.e. motion and consequent change of configuration of

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particles of matter, ponderable and imponderable. And, just as, according to Newton, a body unacted on by an external force continues its rectilinear motion unchanged, so the whole cosmic process must continue on its cyclical path precisely because there is nothing to stop it.

The acquirement, in the later years of the eighteenth century and the first half of the nineteenth, of a new wealth of experimental knowledge, revealing a great variety of complex relationships between widely different phenomena, presented new difficulties to the mechanistic view of nature. At the same time, the fact that such relationships existed seemed to strengthen the mechanistic view that all phenomena possess the same ultimate character. Hence, the net result in numerous quarters was the alteration, rather than the abandonment of the mechanistic view. Thus the hypothesis of light corpuscles gave way to the vibratory theory, and caloric was gradually supplanted by the kinetic theory of heat.[2]

The existence of this mechanistic tradition explains, to a limited extent, the almost universal neglect of the Second Law of Thermodynamics by the precursors and founders of the Energy Principle. Thus Rumford, Mohr, Seguin, and, above all, Helmholtz, by their adoption of the kinetic theory of heat, became, in a way, theoretically opposed to the Second Law, i.e. if heat is already motion (of invisible particles), there appears to be no reason for supposing it cannt be completely changed into macroscopic motion or potential energy.[3] For example, Helmholtz in 1847 carelessly stated that Joule's experiments showed that "the heat which raises one kilogram of water through 1°C. raises 452 kilograms through a height of one meter." Again he said that, in cases where only mechanical and thermal changes are involved, the Principle of the Conservation of Force requires that the two following questions shall possess affirmative answers: (1) Does a definite loss of mechanical force always incur the production of a

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definite quantity of heat?; (2) Does a definite loss of heat correspond to the production of a definite quantity of mechanical force? The essential difference in these two questions completely escaped him (cf. 32, p. 44), in spite of the fact that he was familiar with Carnot's ideas.

If, however, the influence of the mechanical hypothesis cannot, by itself, suffice to account for the delayed formulation of the Second Law, this is precisely because the thought of numerous precursors and founders of the Energy Principle was, at least to a large extent, independent of the classical Newtonian tradition.

It was not the astronomical, or the atomic, or the kinetic view of nature that led men like Faraday, Grove, and Joule in England and Liebig and Mayer in Germany to postulate the Principle of the Conservation and Correlation of Forces. Rather, the stimulus for this came, in the first place, from the newly discovered facts of correlation and, secondly, from an inner, naive belief in the existence of a Cartesian substance underlying all change. Yet the Second Law was quite as foreign to these thinkers as it was to the proponents of the mechanistic hypothesis, for they all spoke unreservedly of the "equivalence of forces," i.e. each form of force was supposed completely convertible into every other form.[4]

From this it follows that a general explanation of the delayed establishment of the Second Law cannot be the mechanistic hypothesis itself but rather must embrace the latter as a special case. This general explanation can be none other than the existence of the wide-spread conviction that all phenomena are manifestations of a single substance whose identity is maintained throughout all change. For whether this substance be identified as matter subject to Newtonian forces (mechanical view of nature) or whether it simply be referred to by a common name such as "force," the

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hypothesis of the World-Stuff appears to be, in either case, intrinsically opposed to the ideas embodied in the Second Law of Thermodynamics. This would seem to result from the implication, by the substance hypothesis, of the notion of the mutual convertibility of its forms.

This is not the place to undertake an analysis of the substance concept with the object of determining to what extent it represents a generalization of sense-experience as distinct from an a priori construct imposed by the human mind on the external world. It must suffice here to point out that, as a consequence of the wide-spread acceptance of physical realism, the Second Law, unlike the First, appeared foreign and unnatural. In the words of Lewis and Randall (49, p. 110), the Second Law "seemed in no recognizable way to accord with existing thought and prejudice. The various laws of conservation had been foreshadowed long before their acceptance into the body of scientific thought. The Second Law came as a new thing, alien to traditional thought, with far-reaching implications in general cosmology."

2. CARNOT AND THE MOTIVE POWER OF HEAT.

A. The Problem of Improved Efficiency

Considering this alien nature of the Second Law, the fact that its foundations were laid by Sadi Carnot over fifteen years before Mayer's general enunciation of the Energy Principle, constitutes somewhat of a paradox. On the other hand, the narrow range of technical interests relative to the economy of heat engines, which constitutes the sole historical source of the Second Law, presents a sharp contrast to the wide variety of roots leading to the Energy Principle--a contrast in full conformity with the novel character of the ideas of restricted convertibility and irreversibility. At the same time, there follows, happily for the historian of thermodynamics, the result that, whereas, because of the great variety of interests involved, the chain of discoveries and enunciations

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constituting the history of the First Law was exceedingly difficult to expose, the development of the Second Law, on the contrary, takes a direct and relatively simple course, which begins definitely and undisputedly with Carnot and culminates, twenty-five years later, in the systematic treatments of Clausius and Thomson.

At the time of publication of Carnot's epoch-making paper, "On the Motive Power of Heat" in 1824, (50), no general theory of the action of heat engines existed. To be sure, the improvements introduced by the English engineer, James Watt in 1765,[5] had greatly increased the efficiency of the steam engine. However , Watt had approached the problem in a rather empirical fashion. His improvements aimed at correcting the specific deficiencies of the older Newcomen engine and were brought about by his study of the particular properties of steam rather than by any attempt to formulate universal principles governing the economy of the steam engine, let alone steam engines in general. On the other hand, "Watt's successors had strayed still farther from the goal of general theory, since they had concerned themselves less with Watt's problem of increasing the efficiency of the engine than with the mechanical one of increasing the capacity, i.e. the power obtainable for a given size of cylinder.

Carnot's paper represented a definite return to Watt's problem of improved efficiency. If, at the same time, the French engineer's contribution contained results of far-reaching significance for theoretical physical science, this arose from the circumstance that he insisted on establishing a general theory of the motive power[6] of heat, which would include the action of the steam engine as a special case. Thus, from the very start, he aimed at the establishment for heat engines of a set of general principles such as French technical mechanics was already providing for non-thermal machines.[7]

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Having adopted this broad point of view, Carnot found himself confronted with the question of whether or not there existed a definite theoretical limit to the extent which improvements of the heat engine may increase its economy, and whether or not this limit is the same for engines employing different substances as the working body. "The question has often been raised," he said, "whether the motive power of heat is limited or not; whether there is a limit to the possible improvements of the steam engine which, in the nature of the case, cannot be passed by any means; or if, on the other hand, these improvements are capable of indefinite extension. Inventors have tried for a long time, and are still trying, to find whether there is not a more efficient agent than water by which to develop the motive power of heat... We propose to submit these questions to a critical examination."

Before describing the remarkable process of abstraction whereby Carnot attained his desired general theory, we should note, at the outset, that his treatment of the subject was, from our point of view, confused and, to a certain extent, invalidated by his acceptance of the caloric hypothesis; that is, he supposed, along with Laplace, Poisson, and other eminent French scientists of his day, that heat is an imponderable, indestructible fluid whose amount in a given body is uniquely determined by the body's sensible state.

With the view of determining the essential features of the process whereby motive power is obtained from heat, Carnot turned his attention to the steam engine. In the operation of the latter, caloric developed by combustion in the fire box passes through the walls of the boiler where it produces steam. The steam, in some way incorporated with the caloric, then passes into the cylinder where, by its expansion and consequent cooling, motive power is developed. Finally, the steam is passed into the

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condenser where is it liquefied by means of the cooling water which receives its caloric. To the question, What is the essential feature of this process whereby motive power is obtained from heat, Carnot replied that is is the passage of a definite quantity of caloric from the heated air of the fire-box to the cooling water of the condenser. "The production of motive power in the steam engine is therefore not due to a real consumption of the caloric but to its transfer from a hotter to a colder body—that is to say, to the reestablishment of its equilibrium, which is assumed to have been destroyed by chemical action such as combustion, or by some other cause."

Hence, said Carnot, heat in itself is not sufficient for the production of motive power: a colder body is also necessary. It all bodies were at the temperature of the fire-box, the steam engine could not operate. For there would then exist no means of condensing the steam or removing it from the cylinder.

Carnot recognized that these considerations apply not only to the steam engine, but to any heat engine. For steam is only one particular agent by means of which motive power is obtained through the lowering of the temperature of the caloric. "All bodies can be applied to this purpose, for they are all susceptible to changes of volume, to successive contractions and dilatations effected by alterations of heat and cold; they are all capable, by this change of volume, of overcoming resistances and thus of developing motive power."

Just as "wherever there is a difference of temperature the production of motive power is possible," so "conversely, wherever this power can be employed, it is possible to produce a difference of temperature or to destroy the equilibrium of caloric." As common examples of this converse phenomenon, Carnot cited the elevation of temperature of bodies by friction and percussion and the heating of gases by compression.

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Carnot now turned to the fundamental question, "Is the maximum motive power obtainable by the fall of a definite quantity of caloric from one given temperature to a certain lower temperature dependent on the working body employed in the heat engine?" To answer this, Carnot imagined the operation of a steam engine to be carried out as follows: (1) the body A (fire-box), supposed maintained at the temperature of boiling water, was brought into contact with water, also at the boiling point, thereby causing the production of a definite quantity of steam and the incorporation into the latter of a definite quantity of caloric; (2) the steam was now introduced into the cylinder where it was expanded against a piston until its temperature fell to the temperature of the condenser B; (3) the steam was now condensed by placing it in contact with B, whose temperature was supposed invariable, and exerting on it a constant pressure until liquefaction was conplete.[8]

What meaning can be attached to the "maximum motive power" of such an engine? Carnot's answer to this question amounted to the formulation of the concept of reversibility. Since every transfer of caloric from a higher to a lower temperature may be made the means of production of motive power, it follows that whenever such production fails to accompany the transfer, the latter constitutes "a veritable loss." But this production of motive power can only take place when the transfer of caloric, which occasions a change of temperature, is accompanied by a change of volume. Hence the necessary and sufficient condition for maximum efficiency is "that in bodies used to obtain the motive power of heat, no change of temperature occurs which is not due to a change of volume." Carnot failed to state explicitly that the attainment of maximum efficiency must also require that the expansion be carried out infinitely slowly or that the pressure exerted by the piston must differ only infinitesimally from the internal pressure of the fluid.

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Yet his conditon for reversibility may be regarded as sufficiently general, since, if expansion (or compression) were carried out at a finite rate, temperature gradients would develop between the various elements of the working body and heat transfers would occur between these elements without any net volume change, i.e. a portion of the temperature change of any given element would not be due to its change but to the direct transfer of heat from contiguous elements.

It was quite clear to Carnot that the maximum efficiency is a limit which can never be attained but only approached. At the same time, the fact that it can conceivably be approached justifies its employment as a theoretical artifice. Thus, strictly speaking, said Carnot, the transfer of caloric between the fire-box A and the working body will not occur if these are at the same temperature. Yet the smallest imaginable difference suffices for the transfer of this finite quantity of caloric, and this is "sufficient to establish the propriety of our reasoning. In the same way, in the differential calculus, to obtain an exact result it is sufficient to be able to conceive of the quantities neglected as capable of being indefinitely diminished relative to the quantities retained in the equation."

For the purpose of his demonstration, Carnot needed to assume that the working body after its employment in the development of motive power was again in its initial state. In the ideal three-stage operation above described, this assumption might be realized if, after the condensation of the steam, the resultant water were raised from the temperature of the condenser to the temperature of the fire-box A by direct contact with A. But this would destroy the ideal character of the process by introduction of an irreversible heat transfer. To get around the difficulty, Carnot supposed the temperature difference between A and B infinitely small. For, if this was the case, restoral of the working body to its initial

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temperature and state by direct contact with A would entail only a negligible departure from ideality (maximum efficiency).

Supplemented by this fourth stage, the process becomes a cyclic one, i.e. the water vapor is returned to its initial liquid state. Hence, according to the caloric hypothesis, it must contain the same amount of caloric as it did at the beginning of the operation, so that all of the supposedly indestructible caloric given up by A must have been absorbed by B. Since each of the four stages was carried out without any appreciable waste, the whole operation may be described as one in which, by means of the transfer of a definite quantity of caloric from a given higher temperature to a given lower temperature, the maximum motive power obtainable with steam has been realized.

May we hope to obtain more motive power by simply substituting some other working body for steam in the operation? According to Carnot, the Principle of Excluded Perpetual Motion requires that the answer to this question be negative. In the first place, he noted that all of the stages of the above process may be carried out in the reverse order, in which case the same quantity of motive power is expended which was developed in the forward process and the same quantity of caloric which, in the forward process, passed from A to B, now passes from B to A. Suppose now, said Carnot, that there is some other agent which is capable of producing a greater maximum motive power, for the same amount of caloric and the same temperature fall, than is the steam. Then, after allowing this agent to develop its said maximum power, we could, by reversing the steam engine, employ only a portion of this power to restore that caloric to A which was transferred to B in the operation of the hypothetical engine. At the end of this series of operations, all bodies, including the caloric, are in their initial state, the only change being that represented by the excess

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motive power developed by the hypothetical engine. Further, the whole operation could be repeated as many times as we please. "There would thus result not only the perpetual motion, but an indefinite creation of motive power without consumption of caloric or of any other agant whatsoever. Such a creation is entirely contrary to the ideas now accepted, to the laws of mechanics and of sound physics; it is inadmissible. We may hence conclude that the maximum motive power resulting from the use of steam is also the maximum motive power which can be obtained by any other means." (Carnot's Theorem)

To the objection that the Principle of Excluded Perpetual Motion (impossibility of obtaining work from nothing) is a mechanical theorem which may not apply to the production of motive power by thermal means, Carnot replied in two ways: (1) heat, also electricity, is probably due to "some motion of bodies" and hence should be governed by the laws of mechanics (mechanistic hypothesis of Laplace and Helmholtz); (2) aside from this mechanistid hypothesis, experience teaches a posteriori that the production of perpetual motion is impossible by any means whatever, so that we are justified in giving to the Principle of Excluded Perpetual Motion this general interpretation (positivistic view of Mayer).[9]

Having established "Carnot's Theorem" for the case of an ideal engine whose fire-box and condenser are at temperatures only infinitesimally removedffrom each other, Carnot stated that it may be extended to the case of an engine whose fire-box A and condenser Z are at temperatures differing by a finite amount, by employment of the following artifice. Imagine an infinite series of bodies B, C, D, ... whose temperatures exhibit a gradual fall from the temperature which is just infinitesimally below that of A to the temper ature which is just infinitesimally above that of Z. Let us first carry out the ideal four-stage process, already described, using A and B as fire-box and

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condenser, whereby our given quantity of caloric is carried from A to B. Let this be followed by a similar ideal process employing B and C as fire-box and condenser, respectively, thereby carrying the given quantity of caloric to the temperature of C. Continuing this process, we finally transfer the caloric to Z. Since the maximum motive power is produced in each of the simple cycles, the same must be true of the compound cycle. Further, by reversing each of the simple cycles in turn, beginning with the last, the whole compound cycle may be reversed. Hence, said Carnot, the same considerations apply to the compound cycle as applied to the simple cycle, i.e. Carnot's Theorem also holds for the compound cycle.

This artifice employed by Carnot is by no means theoretically satisfactory; that is, a fall of caloric through a finite temperature interval does not become negligible by supposing it replaced by a series of successive infinitesimal falls whose sum equals to the finite fall. Carnot himself certainly did not regard his demonstration altogether satisfactory, for he stated that a cyclic process employing air instead of steam, which we will now describe, provides the basis for a more rigorous proof of Carnot's Theorem.

The process which Carnot next proceeded to describe, clearly in detail, was none other than the "Carnot Cycle" as it is still found in every text-book of thermodynamics. Suppose, he said, that we have at our disposal a body of air at the temperature t_1 enclosed in a cylinder under a movable piston, also two constant temperature reservoirs A and B at temperatures t_1 and t_2, respectively, where $t_1 > t_2$. Conduct the air through the following reversible process: (1) placing A in thermal communication with the air, expand the latter isothermally, its volume thereby increasing from v_1 to v_2; (2) thermally isolate the air, and continue the expansion until its temperature falls to t_2 and its volume

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acquires the value v_3; (3) establish thermal communication with B and compress the air isothermally until its volume is again v_1; (4) thermally isolate the air and continue compression until the original temperature t_1 is attained, the volume simultaneously decreasing to v_4; (5) again establish thermal communication with A and expand isothermally till the volume increases to v_2. For the sake of clarity, we represent the series of operations on the p—v diagram of Figure 1, although no such representation was employed by Carnot.

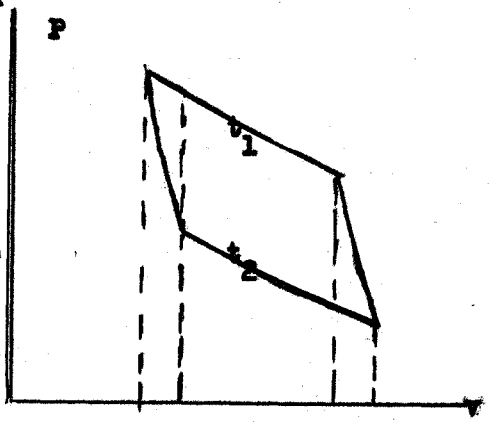

Figure 1

Regarding the state (t_1, v_4) as the initial state, the operations (5), (1), (2), (3), and (4), when carried out reversibly, successively, and in this order, constitute a cyclic process whereby the maximum motive power is obtained by the fall of a given quantity of caloric from t_1 to t_2. Carnot recognized that the production of motive power, rather than its consumption, is the result of the circumstance that the pressure of the gas at every point of the expansion is greater than its corresponding value during the compression. On the other hand, if the process be reversed, the same quantity of motive power will now be expended and the caloric which formerly was transferred from A to B will now be carried back to A.

Because adiabatic compression, rather than an infinite number of infinitesimal temperature falls of caloric, is employed to return the working body to its initial state, the cyclic process just described, said Carnot, is more vigorously reversible than the earlier described process with steam. By employing the former in a line of reasoning exactly similar to that already employed in connection with the latter, we

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hence obtain a more rigorous proof of the fundamental theorem, which Carnot now worded as follows: "The motive power of heat is independent of the agents employed to develop it; its quantity is determined solely by the temperatures of the bodies between which, in the final result, the transfer of the caloric occurs."

In Fourier's great work on heat conduction , heat appeared to behave precisely as a material fluid whose direction of flow was governed by a temperature gradient just as the direction of flow of water is determined by the difference of levels. Now Petit, in 1818, had already presented the energetic treatment of the hydraulic engine, and it seems most probable that the supposed analogy of the action of caloric in the heat engine to that of water in the hydraulic engine exerted a determinative influence on Carnot at the very start. At any rate, we find him referring, at this point in his exposition, to the analogy between the fall of water and the fall of caloric. "The motive power of falling water depends on the quantity of water and on the height of its fall; the motive power of heat depends also on the quantity of caloric employed and on... its descent. In the fall of water, the motive power is strictly proportional to the difference of level between the higher and lower reservoirs. In the fall of caloric, the motive power doubtless increases with the difference of temperature between the hotter and colder bodies, but we do not know whether it is proportional to this difference." We shall soon see how, in attempting to determine the precise form of dependence of the motive power on the temperature limits, Carnot obtained incorrect results.

B. The Thermal Properties of Gases.

By means of his fundamental theorem (Carnot's Theorem), Carnot derived several principles governing the thermal behavior of perfect gases. For this purpose he imagined the Carnot cycle to operate between

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temperatures which differed only infinitesimally. Now, he said, suppose such a cycle to be carried out with each of two different gases. That is, each of two gases, initially at the same temperature, pressure, and volume is expanded isothermally by the same amount, then expanded adiabatically by an infinitesimal amount until they both reach the lower temperature limit, then compressed isothermally to practically the original volumes, whereupon infinitesimal adiabatic compressions carry each of them into their initial states. Since the adiabatic portions of the cycle are infinitesimal in extent, their contributions to the motive power may be neglected. Hence, the motive power of the cycle equals to the excess of the motive power developed the isothermal expansion over that absorbed in the isothermal compression. But, by the laws of Charles and Boyle, the pressure and volume change occurring in the isothermal expansions must be the same in the two cycles, and this is also true for the isothermal compressions. Hence the motive powers of the two cycles are the same. Finally, this must mean , according to the fundamental theorem, that each of the two cycles has transferred the same quantity of caloric from the higher to the lower temperature, i. e. one and the same quantity of caloric has been absorbed, by each of the gases, in isothermal expansion and developed in the isother mal compression. This leads to the general theorem: "When a gas passes without change of temperature from one definite volume and pressure to another, the quantity of caloric absorbed or emitted is always the same, irrespective of the nature of the gas chosen as the subject of the experiment."

Carnot used the theorem just stated in his proof that the ratio of the specific heats, $\gamma = c_p/c_v$, is the same for all perfect gases. Poisson had already calculated β, the fractional decrease in volume resulting from the elevation of temperature of a body through $1^{\circ}C$. by sudden compression,

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from the velocity of sound.[10] Carnot now imagined unit volume of gas at 0°C. and volume V (Figure 2). Sudden compression to $V - \beta V$ raises its temperature to 1°C., whereas addition of its specific heat at constant pressure c_p raises its temperature to 1°C . and causes its volume to increase to $V+\alpha V$ (III). Hence isothermal expansion from state II to state III, whereby the volume increases by $\alpha+\beta$, must entail absorption of the heat c_p. Again, neglecting any possible effect of t the small volume change on the specific heat, we see that, in order to expand isothermally from $V - \beta V$ to V, the specific heat at constant volume, c_v, must be supplied. Placing the quantities of heat absorbed in small volume changes proportional to the latter we obtain $\gamma = \frac{c_p}{c_v} = \frac{\alpha+\beta}{\beta}$

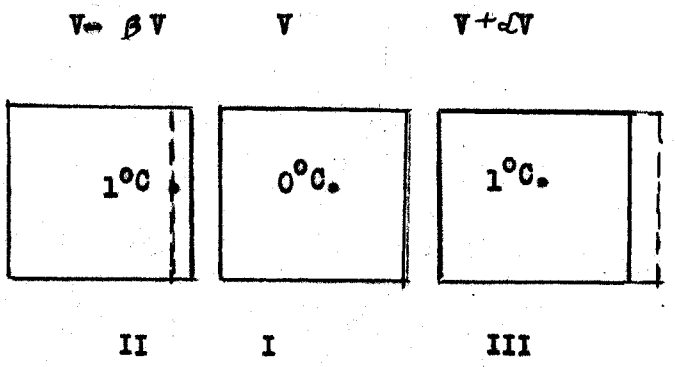

Figure 2

But, as already seen, the heat absorbed by a gas at a chosen constant temperature in passing from one volume to another (reversibly) is the same for all perfect gases. Hence, supposing α and β to be the same for all, γ must likewise have the same value for different gases.

Carnot next employed his fundamental theorem (Carnot's Theorem) to obtain a relation between the volume and the amount of caloric absorbed (developed) in the isothermal expansion (compression) of one and the same gas. Here again, the cycles employed are supposed to operate between two bodies A and B whose temperatures are infinitely close to each other. Let a body of gas at the temperature of the hot body A be confined under a piston in the cylinder (Figure3). Let the gas be carried through a Carnot cycle between the given temperature limits such that the distance through

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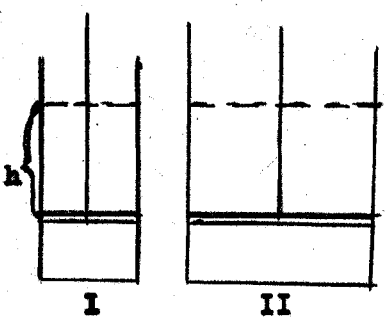

Figure 3

which the piston advances during isothermal expansion, which differs only infinitesimally from the distance through which it recedes in isothermal compression, is represented by h. Imagine, now, that the gaseous body is transferred to a similar cylinder (II) of greater cross-section and that the initial temperature of the gas as well as the height of the piston is the same as before. Let the gas be again carried through a Carnot cycle operating between the same temperature limits as before and such that the distance through which the piston advances during isothermal expansion, which differs only infinitesimally from that through which it recedes during isothermal compression, is again represented by h. This means that the ratio of the volume at the beginning of the isothermal expansion to its value at the end of this expansion has the same value in the two cases, and similarly for the initial and final volumes of the isothermal compression. Now the increase in volume of the gas, hence by Boyle's law, the decrease in its pressure, occasioned by its transfer from cylinder I to cylinder II, is, for the same temperature and height of the piston, proportional to the increase in the cross-sectional area of the piston. Consequently, the total force exerted on the two pistons at corresponding instants is the same, and, since the distances through which the pistons advance during isothermal expansion, like those through which they recede during isothermal compression, are also identical, it follows that the motive power of the two cycles is likewise the same. Finally, this entails, according to Carnot's Theorem, that one and the same quantity of caloric is absorbed in the isothermal expansions and developed in the

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isothermal compressions. This chain of reasoning thus leads to the following proposition: "When the volume of an elastic fluid changes, without change of temperature, from U to V, and the volume of a quantity of the same gas, equal in weight and at the same temperature, changes from U' to V', the quantities of heat absorbed or set free from each will be equal when the ratio of U' to V' is equal to that of U to V;" or, as otherwise expressed, "When a gas changes its volume without change of temperature, the quantities of heat which it absorbs or gives up are in arithmetical progression when the increments or reduction of volume are in geometrical progression."

Aside from the proof of his fundamental theorem, which was vitiated by the hypothesis of the conservation of caloric, we may say that all of Carnot's theorems and methods of proof, which have been so far discussed, are valid. In the case of the proofs of the two main theorems relating to the thermal properties of gases, this is due to his employment of cycles whose temperature limits differ only infinitesimally; in this case, Carnot's assumption that the heat absorbed from the hot body equals to that given up to the cold body, is practically correct.

In some of Carnot's deductions the postulates of the caloric theory led him astray. One of the most interesting of these cases is his proof that the difference between the specific heat (referred to unit volume) at constant pressure and that at constant volume is the same for all gases provided they conform to the laws of Charles and Boyle and are at the same pressure and temperature. Like the other calorists, Carnot thought this difference corresponded to the quantity of caloric required to effect the volume increase at constant temperature; that is, he imagined the specific heat at constant pressure to be composed of two factors,

one, [illegible]

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one representing the caloric required to raise the temperature of the gas by one degree (specific heat at constant volume), the other representing the caloric required to effect the volume increase at constant pressure. But this latter factor, the caloric absorbed by the gas in expanding isothermally from one definite pressure and volume to another definite pressure and volume, is, by a theorem already proved, the same for all gases at the same temperature. Hence the difference in the two specific heats must be the same for all gases at the same temperature and pressure.

Carnot thus obtained a correct result by an incorrect method. For Gay-Lussac's free expansion experiment, which Carnot never mentioned and which was perhaps unknown to him, had shown that no appreciable heat is required merely to increase the volume of a gas. Indeed, we now know that it is precisely those gases that do absorb (or develop) heat on a mere isothermal increase in volume, which do not conform to Carnot's law respecting the difference of specific heats, since, in these cases, the heat absorbed on isothermal, reversible expansion is not entirely equivalent to the work developed.

This same faulty line of reasoning led Carnot to two other conclusions respecting the heat capacities of gases, one of which was true, the other false. The true one was that the difference in heat capacities at constant pressure and constant volume of a given quantity of gas is independent of the pressure of the gas if the temperature is the same; the false one, that the specific heat of a gas (referred to unit weight) increases in arithmetical progression when its volume increases in geometrical progression.

The most remarkable instance in which Carnot obtained a formally correct result by a completely erroneous demonstration is found in his

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attempt to determine the nature of the dependence of the motive power of heat on the temperature as distinguished from the fall of temperature. Is the maximum motive power of a given quantity of caloric, like that of a mass of water, dependent only on the total fall of potential (temperature), or is it also dependent on the particular values of the heights (temperatures) between which the transfer occurs? Carnot attacked this problem by imagining the same body of air to be employed in two different Carnot cycles, the first working between the temperatures 100° and $(100-h)^{\circ}$, the second 1° and $(1-h)^{\circ}$, where h is an infinitely small quantity. Further, he supposed the initial volume of the gas to be the same in both cases and also that the changes of volume which it undergoes are precisely the same in both cycles. Hence, since the rate of change of pressure with respect to the temperature is independent of the temperature, the motive power of the two cycles will be the same, so that the question of the dependence of the motive power of a given quantity of caloric on the temperature limits resolves itself into the question of whether or not the isothermal expansion of the gas at 100° in the first cycle absorbed the same amount of caloric as did the isothermal expansion of the gas at 1° in the second cycle.

To answer this latter question, Carnot invented the device, so important for subsequent theory, of carrying out the same process along two different routes. Let the initial and final volumes of the gas in the isothermal expansions be V_1 and V_2. Then the gas may be carried from the state in which its volume is V_1 and temperature 1° to the state in which its volume is V_2 and its temperature 100°, by two different paths: (1) it may first be heated at constant volume to 100°, whereby it absorbs a units of caloric, and then expanded isothermally to V_2, while absorbing b units of caloric; or (2) it may first be expanded isothermally to V_2,

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while absorbing b' units of caloric, and then heated at constant volume to 100°, while absorbing a' units of caloric. To facilitate the exposition, we represent these two paths on the p—v diagram (Figure 4), which, however, was not employed by Carnot.

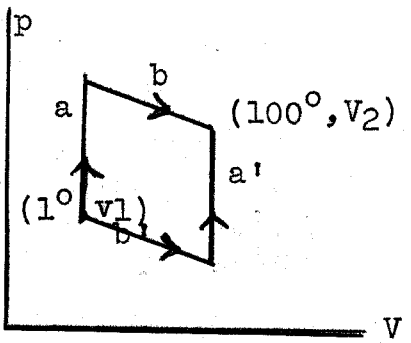

Figure 4

Since the initial and final states of the gas for the two paths are not the same, the caloric theory requires that $a+b \cong a'+b'$ or $a'-a \cong b-b'$. The experiments of Delaroche and Berard had indicated that the heat capacity of air increases slightly as the density decreases. Hence $a' > a$, whence $b > b'$. In other words, of the two cycles yielding the same maximum motive power and incurring the same net descent of caloric, the one operating at the higher temperatures consumes the more caloric. We have therefore the following theorem: "The descent of caloric produces more motive power at lower degrees of temperature than at higher."

This correct result Carnot obtained, as we have just seen, by introducing into his demonstration two errors which had the effect of cancelling each other. The first was the caloric assumption that the quantity of heat absorbed by a body depends only on the latter's initial and final states; the second was the assumption of the correctness of Delaroche and Berard's data which indicated an increase in the specific heat of gases with decreasing density. (Regnault's researches later showed the heat capacities of the ideal gases to be independent of density, as well as temperature.)

Indeed, the smallness of the variation in specific heat with density, revealed by Delaroche and Berard's experiments, indicated to Carnot that it might very well be due to experimental error.[11] Hence he considered it

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not improbable that the maximum power of caloric is independent of the particular limits and dependent solely on the total fall in temperature.

Carnot relegated to a footnote the analytical expression of some of his theorems. Pet p denote the pressure of a given body of air when its volume is v and temperatuse t, and p_1, its pressure when $v = 1$ and $t = t$. Boyle's Law then gives $p = p_1/v$. If p_0 is the pressure of the gas when $v = 1$ and $t = 0$, we have $p_1 = p_0 (1+\alpha t)$, whence $p = p_0 (1 + \alpha t)/v$. The work w, when the gas expands isothermally at t from $v = 1$ to $v = v$ is

$$w = \int_1^v pdv = p_0 (1+\alpha t) \log v. \qquad (1)$$

If the expansion took place at $t + dt$ instead of t, the work would be

$$w + \delta w = p_0 (1+\alpha t + \alpha dt) \log v. \qquad (2)$$

Subtracting (1) from (2),

$$\delta w = p_0 \alpha \log v \, dt \qquad (3)$$

where δw is the work developed by a cycle working between $t + dt$ and t in which isothermal expansion occurs between $v = 1$ and $v = v$. Such a cycle transfers a quantity of caloric, denoted by e, from $t+dt$ to t.

Let u denote the motive power developed by a cycle which transfers one unit of heat from t^0 to 0^0C. By the fundamental theorem (Carnot's theorem), $u = F(t)$, where F(t) is a function of t only. When t receives the increment dt, this work becomes $u + du = F(t + dt)$, so that $du = F(t + dt) - F(t) = F'(t)\, dt$ where $F'(t) = dF(t)/dt$. Here du is the motive power developed by a cycle absorbing unit heat at $t + dt$ and working between $t + dt$ and t. If, instead, e units of heat be absorbed, the work is

$$e\, du = e\, F'(t)\, dt. \qquad (4)$$

Finally, since $e\, du = \delta w$, (3) and (4) give $e\, F'(t)\, dt = p_0 \alpha \log v \, dt$, or

$$e = (p_0 \alpha / F'(t)) \log v = T \log v. \qquad (5)$$

Since the coefficient of log v is a function of t only, (5) is the analytical expression of the law relating the heat absorbed in isothermal

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expansion to the volume.

Up to this point, Carnot's analytical treatment was completely satisfactory, even from the standpoint of modern thermodynamics. However, the remainder of his deductions were completely invalidated by the introduction of an obviously incorrect expression for the specific heat at constant volume.[12]

Carnot now turned to the direct experimental verification of his fundamental theorem: by utilizing the available data on the specific properties of air, water, water vapor, and alcohol vapor, he attempted to show that the motive power of heat, for a given temperature fall, would be the same regardless of which of these substances be employed as working body.

Thus he imagined a reversible cyclic process employing one kilogram of air initially at atmospheric pressure and 0°C. and working between 0° and -0.001°C. If the air expands isothermally from 0.77 cubic meters, its initial volume, to $0.77\ (1+\alpha+\beta)$, where $\alpha = 1/274$, $\beta = 1/116$, the heat absorbed will be c_p, the specific heat at constant pressure. Regarding the volume changes and hence the work effects of the adiabatic portions of the cycle to be negligible, the volumes occupied by the air in the isothermal compression at $(0 - 0.001)^{\circ}$ will be the same as in the isothermal expansion at 0° except that they will be traversed in the reverse order. The difference in pressures at corresponding positions of the two isothermal portions of the cycle will be (1/267)(1/1000) atmospheres, i.e. the pressure of a water column whose height is (1/267000)(10.4) meters. Therefore the motive power developed by the cycle is $(1/116 + 1/267)\ (0.77)(10.4)(1/267000) = 0.000000372$ where the unit of work corresponds to 1000 kilogram meters. The caloric transferred is the specific heat of air at constant pressure or 0.267 kilogram calories. Therefore the work developed per 1000 kilogram calories is

$$\frac{(0.000000372)(1000)(1000)}{0.267} = 1.395 \text{ k.g.m. x } 10^3 \text{ per k.g.cal. x } 10^3 \text{ per } 1^{\circ} \text{ temperature fall.}$$

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Carnot made similar calculations, utilizing the isothermal vaporization and condensation, at a temperature one degree lower, of water and alcohol, respectively. In these cycles, unlike his previously described ideal cycle with steam, he regarded the net motive power developed to be equal to the excess of that developed in the isothermal expansion over that absorbed in isothermal compression. Also, the initial and final volumes for the expansion were supposed to be the same as to the final and initial ones, respectively, of the compression. Finally, the irreversible heat effects, occasioned by raising and lowering the working body isometrically through one degree by direct contact with the fire box and condenser, respectively, were assumed to be negligible. The results obtained in this way, together with the one for air, comprise the following table:

Working Body	Temperature Fall	Motive Power ($k.g.m. \times 10^3 / k.g.ca. \times 10^3$)
Air	0° to -1°	1.395
Water (liquid vapor)	100° to 99°	1.112
"	0° to -1°	1.290
"	[illegible] to 77°	1.212
Alcohol (liquid vapor)	78.7° to 77.7°	1.230

Carnot noted that, of these data, only those taken at the same temperature are strictly comparable. The discrepancies occurring in these cases he thought could very well be due to experimental error. However, he was by no means dogmatic about the correctness of his theory: indeed, as we shall see, he expressed serious doubts as to the validity of the caloric hypothesis upon which the truth of his fundamental theorem had been made to rest.

Carnot devoted the remainder of his paper to an enlightening discussion of practical heat engines and how their efficiencies might be improved.

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C. The Significance of Carnot's Work.

If, in spite of the fact that Carnot did not formally advance what we today refer to as the Second Law of Thermodynamics, he is nevertheless referred to as the founder of the Second Law, this is precisely because two of the three general ideas embraced by the Second Law (cf. p.226) are to be found in his 1824 paper. In the first place, his contrast of caloric at a definite temperature, with the motive power which it may yield by suffering a fall in temperature, corresponds to the fundamental differentiation of substance into inactive and active (useful) forms: the caloric at a certain number of degrees above a reference temperature ("potential energy of caloric") represents the inactive form of substance, whereas motive power (a raised weight or a ponderable body endowed with motion) is the active form. However, the notion that, even in the ideal limiting case, the inactive form of substance is only partially convertible into the active form, is not found in Carnot's papers: he supposes that the potential energy of caloric and the corresponding motive power would be completely and mutually convertible in the perfect engine. On the other hand, in the concept of "maximum motive power" as a limit which is never achieved, it is clearly implied that every actual transfer of caloric incurs an irretrievable loss of motive power. Hence the fundamental idea of "irreversibility" would seem to be present in Carnot's work.

However, as Helm notes (32, p. 54), the admission of the notion of irreversibility into Carnot's argument incurred a contradiction with the fundamental notion of substance. This contradiction arose out of Carnot's retention of the caloric hypothesis, i.e. of his assumption that the development of motive power incurred no diminution in the total quantity of caloric. Thus suppose that a quantity of heat Q falls directly

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from the temperature t_1 to t_2, without the production of motive power. According to Carnot, this quantity of heat may, in the limiting case, be completely restored to its initial condition by means of an ideal cycle absorbing a certain quantity of work. At the end of this series of changes, everything is the same as before except that a certain quantity of work has been completely annihilated, i.e. expended without producing any result whatsoever. Since the whole operation might be repeated an indefinite number of times, we see that Carnot's reasoning implies the possibility of an unlimited destruction of work without any compensating changes whatsoever. To be sure, this does not involve any contradiction with the Principle of Excluded Perpetual Motion as Carnot generalized it. But the substance hypothesis, on which the First Law is based, excludes the possibility, not only of perpetual motion, but also that of the absolute destruction of motion or work.[13]

Carnot thus occupies a somewhat peculiar position in the history of thermodynamics. On the one hand, his line of reasoning involves a flat contradiction of the Energy Principle; on the other, although Clausius' postulate of the impossibility of heat passing "of itself" from a lower to a higher temperature is tacitly acknowledged, it is never introduced as a fundamental principle.

If Carnot's paper is nevertheless of the greatest significance, this is because it not only advanced numerous concepts and principles which remain completely valid today, but also presented many of its erroneous conclusions and methods of proof in such a form that only a single step—the relinquishment of the caloric hypothesis in favor of the Energy Principle—was necessary to convert them into their modern form.[14]

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I. THE ELUCIDATION OF CARNOT'S IDEAS

A. Clapeyron and the Pressure-Volume Diagram

Carnot's paper was privately published in pamphlet form, and this fact, together with the circumstances that many of the ideas set forth in it were novel, hence difficult to grasp, probably accounts for the failure of his contemporaries to appreciate its significance. Not until ten years after its publication and two years after the author's DEATH did the seed which the great founder of the Second Law had sown begin to bear fruit. In that year, 1834, E. Clapeyron, also a French engineer, published his "Memoir on the Motive Power of Heat" (52).

The resemblance of the title of Clapeyron's paper to that of Carnot's is in keeping with the close similarity of the contents of the two papers. For Clapeyron's contribution was essentially no more than an elucidation and elaboration of Carnot's ideas. At the very start, he paid tribute to Carnot's general mode of reasoning and contrasted it with the questionable hypotheses introduced by Laplace and Poisson in their treatments of thermal phenomena.[15] While appreciating the virtues of Carnot's theory, Clapeyron also failed to discern its weakness. For he, like Carnot, accepted as a fundamental axiom, the principle of the conservation of caloric, and he reiterated the proof of Carnot's Theorem, respecting the independence of the motive power on the working body, in precisely the same form in which Carnot had given it. Indeed, the possibility of the re-formulation of the proof into its modern form appeared more remote than it had with Carnot, since the doubt in the validity of the caloric hypothesis, which Carnot explicitly expressed several times in the course of his paper, nowhere found expression in the memoir of Clapeyron.

Of the first importance is Clapeyron's graphical representation of Carnot cycles on the p-v diagram. Such diagrams had already acquired great practical significance in connection with Watt's indicator, but

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their introduction into theoretical reasoning dates from Clapeyron. The form taken by Clapeyron's diagram for a cycle employing a perfect gas as working body is well-known (cf. Figure 5).

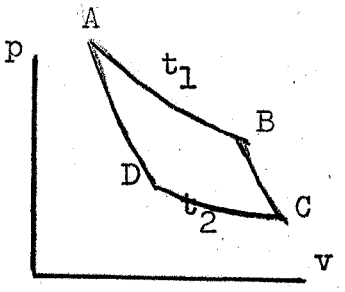

Figure 5

The gas, whose initial state corresponds to point A, is subjected, successively, to isothermal expansion (AB), adiabatic expansion (BC), isothermal compression (CD), and adiabatic compression (DA). Following Carnot, Clapeyron supposed that, in order for the adiabatic compression (DA) to return the gas to its initial state, the isothermal compression (CD) must be continued until the caloric, which is received from the hot reservoir during isothermal expansion (AB), has been imparted to the cold reservoir. If this be done, the gas will supposedly contain the same amount of caloric at the end of the isothermal compression as it did at the beginning of the isothermal expansion, so that when adiabatic compression restores it to its initial volume, both its volume and its total caloric will be the same as at the start of the cycle. Hence, its pressure and temperature, also its state, must be the same. This follows from Clapeyron's assumption that, of the variables Q (quantity of caloric), p, t, and v which characterize the state of a body, the values of any two determine the values of the remaining two.

Carnot's cycle with steam was unsatisfactory because the last stage, that of adiabatic compression, was lacking. This deficiency was supplied by Clapeyron whose diagrammatic representation on the p-v diagram is shown in Figure 6. A quantity of liquid at temperature t_1 and pressure and volume corresponding to C is supposed carried through the following reversible,

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cyclic process: (1) the liquid is subjected to isothermal evaporation at t_1, until a certain portion of it has been vaporized, the pressure and volume of the system during this process corresponding to the points of the horizontal segment CE; (2) thermal isolation of the system is established whereupon adiabatic expansion, represented by EG, results in further vaporization of the liquid at the expense of the sensible caloric of the system., the temperature consequently falling to t_2; (3) communication with the cold reservoir is extablished whereupon isothermal compression and condensation, represented by GK, is continued until the caloric which was received from the hot reservoir at t_1, is imparted to the cold reservoir at t_2; (4) adiabatic compression, hence liquefaction, restores the system to its initial volume and, since the total caloric is also the same as at the start, to its initial state.

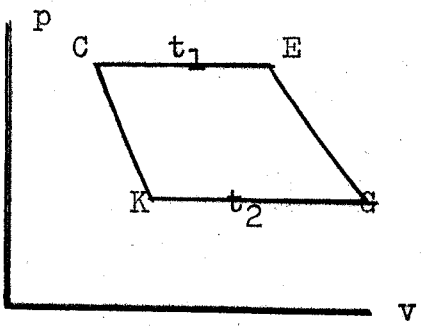

Figure 6

By application of simple geometrical principles to the p-v diagrams of Carnot cycles of infinitesimal dimensions, Clapeyron was able to clothe Carnot's Theory in a new analytical form. Thus suppose the p-v diagram of Figure 7 represents an infinitesimal Carnot cycle, employing a perfect gas as working body. Neglecting infinitesimals of higher order, this figure may be treated as a parallelogram.[16] The work developed will equal to the area of abcd which is given by the product, $eg \cdot bn$. But $eg = dv$, and $bn = dp_v$; hence, evaluating dp_v from the gas law, $pv = R(267 + t)$,

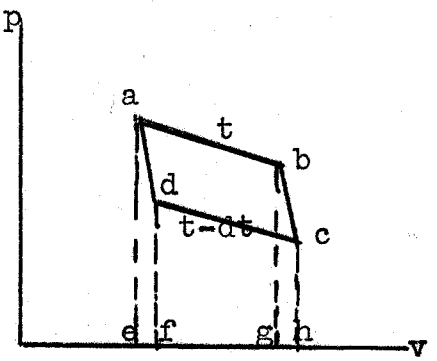

Figure 7

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we obtain:

$$\text{Work developed} = dv \cdot dp_v = R\,\frac{dt \cdot dv}{v}\,. \qquad (6)$$

Supposing Q to be a definite function of p and v, the element of heat absorbed by the gas in the isothermal expansion is, except for infinitesimals of higher order,

$$dQ = \left(\frac{\partial Q}{\partial v}\right)_p dv + \left(\frac{\partial Q}{\partial p}\right)_v dp. \qquad (7)$$

[17]

But, for isothermal expansion, the gas law gives $pdv + vdp = 0$, or $dp = -\frac{p}{v}\,dv$. Substitution of this in (7) gives, for the heat element,

$$dQ = \left(\frac{\partial Q}{\partial v}\right)_p dv - \left(\frac{\partial Q}{\partial p}\right)_v \frac{p}{v}\,dv = \left[\left(\frac{\partial Q}{\partial v}\right)_p - \frac{p}{v}\left(\frac{\partial Q}{\partial p}\right)_v\right]dv \qquad (8)$$

The maximum quantity of work obtainable by the transfer of unit quantity of caloric from t to t - dt is the ratio of (6) to (8), or

$$\frac{R\ dt}{v\left(\frac{\partial Q}{\partial v}\right)_p - p\left(\frac{\partial Q}{\partial p}\right)_v} = \frac{dt}{\theta}\,. \qquad (9)$$

which ratio, by Carnot's Theorem, is a function of t only, or of the product $p \cdot v$. But the numerator of (9) involves t only, so that this must also be true of the denominator. Whence

$$v\left(\frac{\partial Q}{\partial v}\right)_p - p\left(\frac{\partial Q}{\partial p}\right)_v = F(p \cdot v), \qquad (10)$$

an equation which, we now know, has no meaning other than for isothermal processes, whose integral is

$$Q = f(p \cdot v) - F(p \cdot v) \log ((\text{hyp})\ p).$$

Substituting for f (p•v) and F (p•v), the corresponding functions RB and RC, of t, we have

$$Q = R(B - C \log p), \qquad (10)$$

an equation which, we now know, has no meaning other than for isothermal processes.

Clapeyron regarded equation (10) and the gas law

$$pv = R\,(273 + t) \qquad (11)$$

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as two fundamental relations connecting the four variables p, v, t, and Q.

Since the denominator of (9) equals to F (p ,v) = RC (t) we may write

$$\frac{R\,dt}{v\left(\frac{\partial Q}{\partial v}\right)_p - p\left(\frac{\partial Q}{\partial p}\right)_v} = \frac{dt}{C}. \qquad (12)$$

The true nature of the function C(t) thus becomes evident: the product of its reciprocal into the differential of the temperature equals to the maximum work obtainable by the fall of a unit of heat from t^0 to $(t - dt)^0$. By Carnot's Theorem, C is a positive function of the temperature, the same for all bodies.[18]

For an isothermal expansion of a perfect gas from (p, v) to (p', v'), equation (10) gives for the heat absorbed

$$Q - Q' = RC \log (p'/p) = RC \log (v/v'), \qquad (13)$$

which is the analytical expression of Carnot's law that the heats absorbed by a gas in isothermal expansion are in arithmetic progression when the reductions of volume are in geometric progression. Substituting $R = \frac{pv}{267+t}$, Clapeyron obtained the law in the form

$$Q - Q' = \frac{pvC}{267 + t} \log (v/v'), \qquad (14)$$

which shows that "equal volumes of all the gases , taken at the same temperature, being compressed or expanded by the same fraction of their volume, disengage or absorb quantities of heat proportionate to the pressure," a result not stated by Carnot.

Clapeyron also observed that, according to (13), "equal volumes of all the elastic fluids, taken at the same temperature and under the same pressure, being compressed or expanded by the same fraction of their volume, disengage or absorb the same absolute quantity of heat." This result, already obtained by Carnot , had been experimentally verified by Dulong.[19]

Equation (10) led to correct results when applied to isothermal processes because, in these cases, the caloric supposition that Q was a definite function

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of the state variables was valid. However, according to the calorists, Q was a definite function of these variables under all circumstances. Hence, Clapeyron incorrectly supposed equation (14), obtained by the integration of (10), to apply also to non-isothermal processes in which the initial and final temperatures were the same. He thus fallaciously regarded equation (14) as a general law which embraced Carnot's law, relating to isothermal volume changes, as a special case.

The same false assumption of the general validity of equation (10) led Clapeyron to the law that the difference in the two specific heats is the same for all perfect gases at the same temperature. Thus, by differentiation of (10), he concluded that:

$$c_p - c_v = \left(\frac{\partial Q}{\partial t}\right)_v - \left(\frac{\partial Q}{\partial t}\right)_p = \frac{R}{267 + t} C$$

This calls to mind that Carnot also obtained this correct result by an incorrect method. (cf. p.251)

In these considerations involving perfect gases, Clapeyron obtained practically the same results already obtained by Carnot by non-graphical methods. However, the application of the same mode of reasoning to the thermal behavior of vapors yielded new results not obtained by Carnot.

The p-v diagram of Figure 8 represents a Carnot cycle employing the isothermal vaporization and condensation of a pure liquid for the transfer of caloric, and working between temperatures which differ only infinitesimally. For reasons similar to those advanced in the case of the cycle of Figure 7, the figure cdef may be

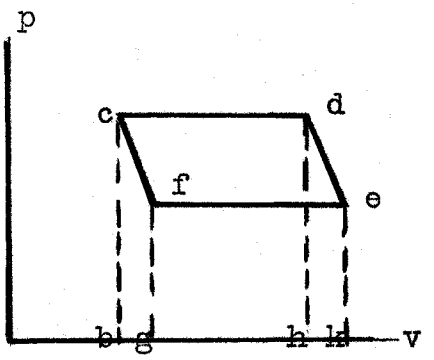

Figure 8

treated as a parallelogram, so that its area, hence the net work developed, is given by cd • (dh-ek). Suppose v is the volume of the saturated vapor

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resulting from the isothermal evaporation. Then, if ρ and δ denote the densities of liquid and saturated vapor, respectively, we have, for the volume of liquid evaporated, $v\ \delta\ /\ \rho$; whence the increase in volume of the system during isothermal evaporation is $cd = (1 - \delta/\rho)v$. Further, $(dh - ek) = \left(\frac{\partial p}{\partial t}\right)_v dt$. This gives:

$$\text{Work developed} = (1 - \delta/\rho)\, v \left(\frac{\partial p}{\partial t}\right)_v dt. \qquad (15)$$

Also, if k denote the latent heat of vaporization per unit volume of saturated vapor at p and t, we have

$$\text{Total heat absorbed} = kv. \qquad (16)$$

Division of (15) by (16) gives the maximum work developed by the fall of a unit of heat at t through the temperature interval dt. This being the same for all working bodies, it must by equation (12) equal to dt/C. Therefore

$$\frac{(1 - \delta/\rho)v \cdot \left(\frac{\partial p}{\partial t}\right)_v \cdot dt}{kv} = \frac{dt}{C} \qquad (17)$$

so that

$$k = (1 - \delta/\rho) \cdot \left(\frac{\partial p}{\partial t}\right)_v C \qquad (18)$$

which is none other than the famous Clausius-Clapeyron equation expressed in terms of the unknown function , C(t).

At ordinary temperatures, Clapeyron noted that ρ , the density of the liquid, greatly exceeds δ , the density of the vapor. Hence, under these conditions, we (have), very approximately:

$$k = C \left(\frac{\partial p}{\partial t}\right)_v , \qquad (19)$$

i.e. "the latent caloric contained in equal volumes of the vapor of different liquids at the same temperature, and under the corresponding pressure, is proportional to the coefficient $\frac{dp}{dt}$ of the pressure with regard to the temperature."[20]

Clapeyron incorrectly concluded from equation (19) that liquids of feeble vapor pressure,and consequently small $\left(\frac{\partial p}{\partial t}\right)_v$ coefficients, must have small latent heats: he failed to note the possibility that C(t) may be

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correspondingly larger for such liquids. From (18), however, he correctly deduced that the latent heat of vaporization must approach zero as the density of the vapor approaches that of the liquid, assuming C and $\left(\frac{\partial p}{\partial t}\right)_v$ to remain finite.

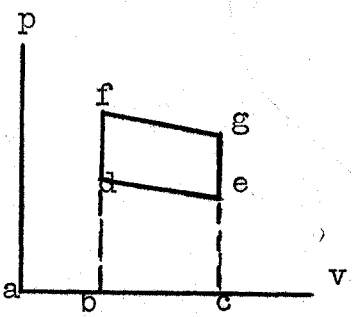

Figure 9

With the object of placing Carnot's theory in a more general analytical form, which shall apply to any body whatsoever, Clapeyron next employed still a third type of infinitesimal cycle. Starting with any body whatsoever at the temperature T and whose volume and pressure are represented by point d on the p-v diagram of Figure 9, imagine it carried through the following infinitesimal, reversible, cyclic process: (1) heat isometrically until the temperature $T + dT$ is attained, thereby entailing a pressure increase represented by the length of the segment df; (2) expand isothermally until the heat element dQ is absorbed, the volume and pressure assuming the values represented by point g; (3) cool isometrically to the temperature T, the pressure falling by an amount represented by the length of the segment ge; (4) compress isothermally in contact with the cold reservoir until the original volume, hence the original state, is attained.[21] Because all the operations are only infinitesimal in extent, the figure dfge may be regarded a parallelogram whose area, hence the work developed, is given by the product, bc · df. Hence

$$\text{Work developed} = bc \cdot df = dv \left(\frac{\partial p}{\partial T}\right)_v \cdot dT = \frac{dv\, dT}{\left(\frac{\partial T}{\partial p}\right)_v} . \quad (20)$$

Regarding the heat absorbed in the isometric heating exactly to cancel that developed in isometric heating cooling,[22] the work developed must have resulted from the transfer, from $T + dT$ to T, of the caloric absorbed in isothermal expansion. During this isothermal expansion,

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$$dT = \left(\frac{dT}{dp}\right)_v dp + \left(\frac{dT}{dv}\right)_p dv = 0, \quad \text{or} \quad dp = -\frac{\left(\frac{dT}{dv}\right)_p dv}{\left(\frac{dT}{dp}\right)_v} \quad . \quad (20')$$

Therefore the heat absorbed is given by:

$$dQ = \left(\frac{dQ}{dp}\right)_v dp + \left(\frac{dQ}{dv}\right)_p dv = dv\left[\left(\frac{dQ}{dv}\right)_p - \left(\frac{dQ}{dp}\right)_v \frac{\left(\frac{dT}{dv}\right)_p}{\left(\frac{dT}{dp}\right)_v}\right] \quad (21)$$

The ratio of (20) to (21) represents the maximum work developed by one unit of heat in falling from $T + dT$ to T and, as before, must equal to $\frac{dT}{C}$.

Therefore

$$\frac{dT}{\left(\frac{dQ}{dv}\right)_p \left(\frac{dT}{dp}\right)_v - \left(\frac{dQ}{dp}\right)_v \left(\frac{dT}{dv}\right)_p} = \frac{dT}{C}, \quad (22)$$

so that

$$\left(\frac{dQ}{dv}\right)_p \left(\frac{dT}{dp}\right)_v - \left(\frac{dQ}{dp}\right)_v \left(\frac{dT}{dv}\right)_p = C. \quad (23)$$

In the special case of perfect gases, Clapeyron observed that evaluation of the coefficients $(dT/dP)_v$ and $(dT/dv)_p$ converts the general equation (23) into equation (9'), already obtained by another method.

Supposing Q to be a definite function of p and v, Clapeyron integrated equation (23) as he had already done with equation (9'), thus obtaining

$$Q = F(T) - C \cdot \phi(p,v), \quad (24)$$

where F(T) is an arbitrary function and $\phi(p,v)$ satisfies an accessory equation. However, he made no attempt to apply this incorrect result to particular cases.

By substitution of the value of C, given by (23), into the expression (21) for the element of heat absorbed in isothermal expansion, Clapeyron obtained the new relation:

$$dQ = \frac{1}{\left(\frac{dT}{dp}\right)_v} C dv \quad (24')$$

which, by virtue of equation (20'), becomes

$$dQ = -\frac{C dp}{\left(\frac{dT}{dv}\right)_p} = C dp \left(\frac{dv}{dT}\right)_p, \quad (25)$$

i.e. "if the pressure supported by different bodies, taken at the same temperature, be augmented by a small quantity, quantities of heat will be

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disengaged from it, which will be proportional to their dilatibility by heat."[23]

Clapeyron devoted the remainder of his paper to the numerical calculation of 1/C and the coefficient dC/dt by several different methods. We have already observed that the product of 1/C and dt represents the maximum work obtainable by the fall, through the interval dt, of a unit of heat at the temperature t. Clapeyron assumed, as Carnot had already done, that the maximum work obtainable from a unit of heat is, for a small temperature fall, namely, one degree, is proportional to this fall. Hence he regarded the value of 1/C at a given temperature as numerically equal to the maximum motive power obtainable by the fall of a unit of heat from the given temperature to a temperature one degree lower. Therefore Clapeyron's values of 1/C are comparable with Carnot's calculations of the motive power of heat. (cf. table, p.254)

Clapeyron's first method of calculation of C was based on the equations $pv = R(267 + t)$ and $Q = R(B - C \log p)$ for perfect gases. Differentiatig the second, we obtain

$$dQ = R\left(\frac{dB}{dt} - \log p \ \frac{dC}{dt}\right)dt - RC\frac{dp}{p} = \left(\frac{dQ}{dt}\right)_p dt - RC\frac{dp}{p}. \quad [24]$$

But, by virtue of the first, $(R/p)dp = R(Rdt - pdv)/vp = (Rdt - pdv)/(267+t)$. Therefore the expression for dQ becomes

$$dQ = \left(\frac{dQ}{dt}\right)_p dt - C\frac{(Rdt - pdv)}{267 + t}$$

so that, for an adiabatic process ($dQ = 0$), we have

$$(1/C) = \frac{(Rdt - pdv)}{(267 + t)dt} \cdot \frac{1}{\left(\frac{dQ}{dt}\right)_p}$$

Dulong and had calculated that air, as well as the other gases, taken at 0°C. and one atmosphere pressure, when compressed suddenly (adiabatically) by 1/267 of its volume, develops a quantity of heat capable of raising the

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same volume of air (measured under the same conditions) through 0.421°. Suppose a kilogram of air, occupying a volume of 0.77 cubic meters at 0°C. and one atmosphere (10230 k.g. per square meter) pressure, be subjected to such an adiabatic compression. Substituting $v = 0.77$, $p = 10230$, $c_p = 0.267$, $dv = 0.77/267$, $dt = 0.421$, the above equation yields, for such a process, the result, $1/C = 1.41$, for $t = 0°C$.

Clapeyron next deduced values of 1/C by substitution of values of dp/dt and k, the latent heat of vaporization, in the equation $1/C = \frac{(dp/dt)}{k}$. His results by this method comprise the following table:

Liquid	dp/dt at B.P.	Density Vapor at B.P.($d_{air} = 1$)	k per k.g. of Vapor	B. P.	1/C
Sulfuric ehter	1/26.12	2.280	90.8	35.5	1.365
Alcohol	1/25.19	1.258	207.7	78.8	1.208
Water	1/29	0.451	543	100	1.115
Essence of turpentine	1/30	3.207	76.8	156.8	1.076

From the values, $1/C = 1.41$ for $t = 0$ and $1/C = 1.115$ for $t = 100$, Clapeyron deduced the mean value, $dC/dt = 0.00187$, i.e. the work value of a unit of heat per unit fall of temperature decreases slightly with increasing temperature, a result also obtained by Carnot but by incorrect reasoning (cf. p.375).

As a check of the above values of 1/C, Clapeyron next employed the same equation to calculate 1/C from values of dp/dt for water vapor at a series of temperatures. Assuming k to be independent of temperature, he obtained in this way:

t	1/C
0	1.586
35.5	1.292
78.8	1.142
100	1.102
156.8	1.072

These results compared favorably with the values already obtained for 1/C

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same
at the temperatures.

The concordance of these values of 1/C at corresponding temperatures, together with Dulong's verification of the law respecting the heat developed by compression of a perfect gas, greatly strengthened Clapeyron's confidence in Carnot's theory. As already noted, he nowhere expressed any doubt as to the validity of the caloric hypothesis.

We must not under-estimate the impottance of Clapeyron's paper. Although his fundamental ideas were all borrowed from Carnot, he nevertheless performed a gdnuine service by clothing them in precise analytical form. For, in this way, the merits, as well as the demerits, of Carnot's theory were brought clearly into prominence, and the way was paved for its modification into a form consistent with the Energy Principle.

This modification, however, was slow to arrive. We have already observed the general neglect of Carnot's and Clapeyron's work by the founders of the Energy Principle. Mayer did not mention it. Joule contented himself with simply observing that, according to the First Law, Carnot's assumption that, in the operation of the ideal engine, the heat absorbed in isothermal expansion equals that developed in isothermal compression, must be abandoned in favor of the supposition that the former exceeds the latter by the amount of heat equivalent to the work developed. Helmholtz, as we shall see, made several comments on the relative merits of Clapeyron's views and those of Holtzmann, about to be described, but made no attempt to develop Carnot's ideas in a manner consistent with the Energy Principle.

B. The Views of Holtzmann and Helmholtz.

The modification of Clapeyron's views so as to accord with the Energy Principle was approached, however not attained, by Holtzmann in his pamphlet, "On the Heat and Elasticity of Gases and Vapors", published in 1845 (55). His description of the effect of adding heat to a gas would

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seem to accord with the Energy Principle. For he said, "The effect of the heat added to the gas is either increase of temperature combined with increase of elasticity, or a mechanical action; and a mechanical action is the equivalent of the increase of temperature." That is to say, if a temperature rise has occurred, the gas may always be expanded until the initial temperature is reattained. Naively neglecting the change of state of the gas, Holtzmann, like Seguin, regarded the total mechanical action developed as the measure of the heat absorbed. Hence, he adopted, as his unit of heat, that "heat which on its addition to any gas is capable of producing the mechanical action $\underline{a}$, i.e. to use a definite measure, which can raise $\underline{a}$ kilograms one meter."

Thus, for an infinitesimal isothermal expansion of a perfect gas, the work is pdv and the heat absorbed, dQ. Hence Holtzmann wrote

$$\frac{pdv}{dQ} = \underline{a} \quad . \tag{26}$$

However, at this point, Holtzmann fell back on the caloric assumption that Q is a definite function of the state variables and wrote with Clapeyron:

$$dQ = \left(\frac{dQ}{dp}\right)_v dp + \left(\frac{dQ}{dv}\right)_p dv \quad .^{25} \tag{26'}$$

For isothermal expansion $dt(p,v) = 0$, so that

$$dp = - dv \frac{(dt/dv)_p}{(dt/dp)_v} = dv(p/v).$$

Substituting this in the expression for dQ and combining the result with the expression for $\underline{a}$, Holtzmann obtained

$$v(dQ/dv)_p - p(dQ/dp)_v = (pv)/a \tag{27}$$

whose integral is

$$Q = F(t) - \frac{R(272 + t)}{a} \log p. \tag{28}$$

Holtzmann's equations (27) and (28) closely resemble equations (9') and (10) obtained by Clapeyron. At first, this state of affairs startles the reader, since Holtzmann has apparently not employed Carnot's theorem to

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obtain his results. A closer examination of equation (26), however, explains the agreement with Carnot's theory. We should note, in the first place, that if equation (26) be regarded as expressing the equivalence of work and heat (and Holtzmann evidently intended that it should be so regarded), it cannot but contradict equation (26'). For the heat absorbed by a gas cannot be determined by the work done and, at the same time, by the initial and final states, since the work done is not determined by the initial and final states. On the other hand, if we regard equation (26) as expressing Carnot's theorem for an infinitesimal cycle employing a perfect gas, it is the analogue of Clapeyron's expression (12):

$$\frac{R(dt/v)\,dv}{dQ} = \frac{dt}{C}\ .$$

Comparison of the two yields the result $C = (1/a)t$. Thus Holtzmann's equation (26) amounts , formally, to Carnot's Theorem supplemented by the assumption of the linearity of C(t). This explains the forms taken by equations (27) and (28).

By differentiation of (28), Holtzmann obtained the results:

$$C_p = (dF/dt) - (R/a) \log p \qquad (29)$$

and

$$C_v = (dF/dt) - (R/a) \log p - R/a \qquad (30)$$

whence

$$C_p - C_v = R/a. \qquad (31)$$

Clapeyron had already obtained this difference in terms of his C function, but he did not employ the result to evaluate C. Holtzmann, however, employed equation (31) to calculate a. By virtue of the perfect gas law, equation (31) becomes

$$a(C_p - C_v)(273 + t) = pv.$$

The quantity $(C_p - C_v)$ for air was evaluated from Delaroche and Berard's value of C_p and the value of $\gamma = C_p/C_v$ calculated from the velocity of sound. Whence a = 374, i.e. "The heat which warms one kilogram of water

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1°C. is capable of raising 374 kilograms 1 meter." Holtzmann stated that this value of a may be in error by as much as forty units.

Holtzmann's method for the calculation of a was precisely the one already employed by Mayer three years earlier. In 1845 Mayer justified his calculation by reference to Gay-Lussac's free-expansion experiment, but Holtzmann made no attempt to justify his calculation in this manner.

Of the remainder of the results obtained by Holtzmann, the correct ones had already been formulated by Carnot and Clapeyron. Thus from equation (28) he obtained Carnot's law respecting the heat effect of the isothermal volume change of a perfect gas (cf. equation (13)). Like Clapeyron, however, he supposed this heat effect to be the same when the path was a non-isothermal one connecting the same initial and final states.

Supposing equation (28) to be generally valid, he obtained an incorrect relation for the variation of the temperature of a perfect gas with its pressure during adiabatic expansion. Similar assumptions, together with the supposed linearity of $F(t)$, led to the incorrect expression for the variation of the vapor pressure of a liquid with temperature, namely,

$$\log(p/p_0) = \frac{Bt}{(1/\alpha)+t}$$

where p_0, B, and α are constants. Because of faulty data for the specific heat of steam and its coefficient of expansion, the above formula appeared in Holtzmann's day to be approximately correct (53).

Holtzmann's description of the vaporization of a liquid would seem to accord with the modern view. For he stated that the latent heat w is used to overcome the forces of cohesion and to increase the volume of the system against the external pressure. Let the work of overcoming cohesion per cubic meter of liquid vaporized be C. Then, if p be the external pressure, ρ and Δ the densities of vapor and fluid, respectively, we have $w = a\left(\frac{1}{\rho} - \frac{1}{\Delta}\right) + C$.

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Neglecting $1/\Delta$ and supposing the vapor to obey the gas law, we get

$$\frac{C}{a} = w - \frac{R(1 + \alpha t)}{a} .$$

Assuming, with de Pambour, that w decreases linearly with t, i.e. $w = w_0 - ct$, where c is the specific heat of the liquid, we have,

$$\frac{C}{a} = w_0 - dt - \frac{k(1 + \alpha t)}{a} ,$$

i.e. the work of cohesion decreases as the temperature increases.

This mode of regarding the matter appeared to conform to Mayer's Energy Principle (which Holtzmann nowhere mentions). Confusion again appeared, however, in his statement that in the adiabatic expansion of steam, "the steam retains its quantity of heat, its temperature sinks, and the temperature passes over into its equivalent mechanical force." (!)

All in all, Holtzmann's presentation of his subject was far less clear than the treatments of Carnot and Clapeyron. Its importance for us is almost purely historical, i.e. it reveals how, as late as 1845, the caloric theory was still holding its own against the advances of the Energy Principle.

Helmholtz devoted several paragraphs of his famous paper of 1847 (45) to the comparison of Clapeyron's and Holtzmann's work. He did not reject Carnot's proof of Carnot's Theorem, although he pointed out its dependence on the principle of the conservation of caloric. He observed that, according to Clapeyron's equation (25), the compression of water between the temperature of maximum density and the freezing point should be accompanied by the absorption of heat, and this seemingly paradoxical, theoretical result caused him to doubt the validity of the formula. He noted that Holtzmann's equation (26) for the mechanical equivalent assumed that the energy (Kraft) of the gas is independent of its volume, and pointed out Joule's (but not Gay-Lussac's) experimental confirmation of this assumption but failed to point out Holtzmann's employment of the caloric hypothesis, along with the notion of the mechanical equivalence of heat. To compare Clapeyron's

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theory with Holtzmann's he observed that Clapeyron's expression for C,

$$C = \frac{1}{R}\left[v\left(\frac{dQ}{dv}\right)_p - p\left(\frac{dQ}{dp}\right)_v\right]$$

and Holtzmann's expression for a,

$$\frac{pv}{a} = v\left(\frac{dQ}{dv}\right)_p - p\left(\frac{dQ}{dp}\right)_v,$$

when taken together, require that $(1/C) = \frac{ak}{pv} = \frac{a}{1+\alpha t}$. Comparing the values of 1/C calculated from this last expression with Clapeyron's values, Helmholtz obtained good agreement and concluded that, for gases, Clapeyron's formula was equivalent to Holtzmann's.

C. Carnot's Theorem and the Absolute Temperature.

In the last years of the eighteen forties the work of Carnot and Clapeyron began to attract considerable attention in England mainly though the efforts of William Thomson. The latter's contributions began with his short, but epoch-making paper, "On the An Absolute Thermometric Scale Founded on Carnot's Theory of the Motive Power of Heat, and Calculated From Regnault's Observations"(56), published in 1848. Carnot and Clapeyron had both attacked the question of the dependence of mechanical effect of heat per unit fall of temperature on the Centigrade scale of temperature. However, the observation that Carnot's Theorem provided the basis for the definition of an absolute temperature scale independent of the particular properties of any substance, had escaped them. It was first pointed out by Thomson in the paper just cited.

Gauss and Weber had already introduced absolute mechanical units into electricity and magnetism, and it seems probable that their work may have stimulated Thomson to undertake the establishment of an absolute unit of temperature. After pointing out the complications arising from the varia-

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bility of the specific heats of substances with temperature, he correctly characterized the conventional Centigrade scale as no more than "an arbitrary series of numbered points of reference sufficiently close for the requirements of practical thermometry." He then proposed the question, "Is there any principle on which an absolute thermometric scale can be founded," and stated that Carnot's Theory provided an affirmative answer. For "the relation between motive power and heat as established by Carnot, is such that quantities of heat, and intervals of temperature, are involved as the sole elements in the expression for the amount of mechanical effect to be obtained through the agency of heat; and since we have, independently, a definite system for the measurement of quantities of heat, we are thus furnished with a measure of intervals according to which absolute differences of temperature may be estimated."

After a brief reference to Carnot's line of reasoning, Thomson proposed an absolute scale, clearly, in the following words: "The characteristic property of the scale which I now propose is, that all degrees have the same value; that is, that a unit of heat descending from a body A at the temperature T° of this scale, to a body B at the temperature $(T-1)^\circ$ would give out the same reversible mechanical effect, whatever be the number T. This may justly be termed an absolute scale, since its characteristic is quite independent of the physical properties of any specific substance."

Using Regnault's data for the latent heat of steam and its saturation pressure at a series of temperatures and estimating the corresponding densities of the vapor by means of the laws of Boyle and Gay-Lussac, Thomson calculated the mechanical effect of a unit of heat per unit Centigrade degree of temperature fall at a series of temperatures ranging from $230^\circ C$ to $0^\circ C$, by means of Clapeyron's equation (19). $k = \sigma \frac{dp}{dt}$.

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Like Clapeyron, Thomson found only a small variation in the mechanical effect $\frac{1}{C}$ with change of temperature, thus indicating (to him) that the centigrade scale is approximately an absolute scale.

D. The Effect of Pressure on the Freezing Point of Water.

Following a suggestion made by Thomson, his brother, James Thomson in 1849 deduced another remarkable consequence from Carnot's Theory, namely, that the freezing point of water should be lowered by an increase in pressure. (56, p. 156) Suppose we have a body of air A at $0^{\circ}C$ confined in a cylinder under a piston, a heat reservoir W maintained at $0^{\circ}C$, and a body of water W^{1}, initially at $0^{\circ}C$ and one atmosphere pressure, and confined under a piston. (cf. Fig. 10) James Thomson now conceived the following reversible process: (1) placing A and W in thermal contact, compress the air isothermally thus transfering a certain quantity of heat from A to W; (2) placing A and W^{1} in thermal contact, expand A to its original volume while simultaneously expanding W^{1} and freezing a certain quantity of water. The expansion of W^{1} is supposed retarded so that its variable pressure, during expansion, is greater than the original atmospheric pressure; this retardation, however, is supposed subject to the condition that when the initial volume of A is reattained its temperature, hence that of W^{1}, will again be $0^{\circ}C$. Hence W^{1}'s pressure will again be one atmosphere. (3) By thermal contact of W with W^{1}, remelt the ice, thus restoring W^{1} to its initial state. According to the caloric theory, since W^{1} and A contain their original quantities of heat, W must also. Hence W, A, and W^{1} are all

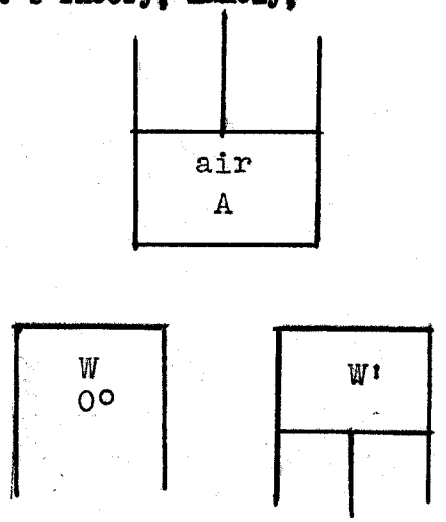

Figure 10

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restored to their initial states. A certain amount of work has been developed by the expansion of the solidifying ice in stage (2) of the process. This must have been compensated by a net absorption of work by A in the course of the whole process, which means that the average pressure, hence temperature of A, was less during its expansion than during its compression, which requires, in turn, that the temperature of W' was less than 0° when its pressure exceeded one atmosphere. In other words, the freezing temperature of water must have been lowered by the increased pressure.[26]

To obtain this result in analytical form James Thomson imagined a Carnot cycle, similar to that already used by Clapeyron in the deduction of the Clausius-Clapeyron equation, but employing the system, liquid water-icem as working body. Suppose the working body to be initially at 0°C and at a pressure and volume corresponding to point a on the p-v diagram of Figure 11, and let it be subjected to the following cyclic process: (1) isothermal compression along ab, with liquefaction of ice and absorption of heat from a reservoir at 0°C; (2) adiabatic compression along bc, lowering the temperature (freezing point) to $-t^{\circ}$C.; (3) isothermal expansion along cd, with solidification of the water and development of the heat which was absorbed during isothermal compression; (4) adiabatic compression along da, restoring the body to its initial state.

Neglecting the small volume changes occurring during the adiabatic portions of the cycle, the net work equals to the excess of the work developed during isothermal expansion over that absorbed during isothermal compression. If we suppose t to be such that

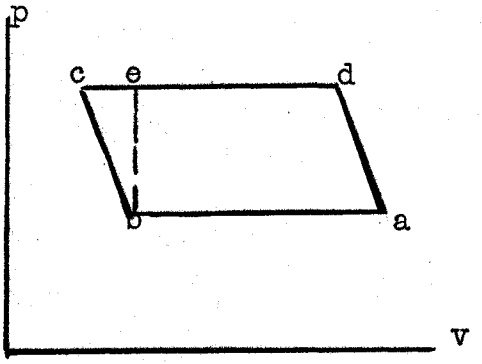

Figure 11

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the pressure difference bc equals to Δp and if we suppose the isothermal compression is accompanied by the melting of one cubic meter of ice (whose initial state corresponds to point a), then the work developed by the cycle amounts to $10333 \cdot 0.09$ k.g.m. The heat transferred from 0° to $-t^\circ$ is the latent heat of a cubic meter of ice, 80,000 calories. Then by Clapeyron's theory,

$$\frac{10333 \cdot 0.09 \cdot \Delta p}{80000} = \frac{1}{C} \tau = 1.553\tau$$

where the assumption of the linearity of the work-value of the heat with respect to the temperature difference is justified by the smallness of τ. This formula was experimentally verified by William Thomson in 1850, the following year.

E. Thomson's Exposition of Carnot's Theory.

The year 1849 which saw James Thomson's theo. prediction of the lowering of the freezing point of water by in d pressure, also saw the publication of William Thomson's paper, "A count of Carnot's Theory of the Motive Power of Heat; with Numerical sults Deduced from Regnault's Experiments on Steam." The paper was mainly a resumé of the work of Carnot and Clapeyron, although a few minor modifications were introduced. Thus, the analytical expression of Carnot's Theorem for an infinitesimal cycle with a perfect gas was developed without resort to Clapeyron's p-v diagram. Let the volume, temperature, and pressure of the body of gas, say air, at the beginning of each of the four stages of the infinitesimal Carnot cycle be given by the table:

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	Volume	Temperature	Pressure
Beginning of isothermal expansion	v	$t + \tau$	p
Beginning of adiabatic expansion	$v + dv$	$t + \tau$	$p(1-dv/v)$
Beginning of isothermal compression	$v + dv + \phi$	t	$p(1-dv/v) - \omega$
Beginning of adiabatic compression	$v + \phi$	t	$p - \omega$

Neglecting infinitesimals of the second order, the average pressures during isothermal expansion, adiabatic expansion, isothermal compression, and adiabatic compression will be $p(1-\frac{1}{2}dv/v)$, $p(1-dv/v) - \frac{1}{2}\omega$, $p(1-\frac{1}{2}dv/v) - \omega$, and $p - \frac{1}{2}\omega$, respectively. Multiplying these mean pressures into the corresponding volume changes, we find $p(1-\frac{1}{2}dv/v)dv$, $\left[p(1-dv/v) - \frac{1}{2}\omega\right]\phi$, $-\left[p(1-\frac{1}{2}dv/v) - \omega\right]dv$, and $-(p - \frac{1}{2}\omega)\phi$ for the amounts of work developed in the four operation, respectively. By addition, the net work is found to be $\omega\,dv - p\,\phi\,dv/v$, or $(v\omega - p\phi)dv/v$.

By the perfect gas law,

$$pv = p_0 v_0 \{1 + \alpha(t + \tau)\}$$

and

$$(p - \omega)(v + \phi) = p_0 v_0 (1 + \alpha t)$$

where p_0, v_0 denote the pressure and volume for ice and α is the thermal coefficient of expansion. By subtraction,

$$v\omega - p\phi + \omega\phi = p_0 v_0 \alpha\tau .$$

or neglecting $\omega\phi$,

$$v\omega - p\phi = p_0 v_0 \alpha\tau$$

Substituting this value in the expression for the net work, the latter becomes $p_0 v_0 \alpha\tau \frac{dv}{v}$ or $\frac{\alpha p_0 v_0}{v\frac{dq}{dv}}\,dq\,\tau$ where dq is the element of heat transferred from $\tau + t$ to t. Then the mechanical effect M of H units of heat, descending through the temperature interval τ, is

$$M = \frac{\alpha p_0 v_0}{v\left(\frac{\partial q}{\partial v}\right)_t} H\tau$$

The coefficient of $H\tau$ evidently represents the mechanical effect of

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a unit of heat falling through a unit interval of temperature, which, by Carnot's Theorem, is some function $\mu(t)$, the same for all bodies. Then

$$\mu(t) = \frac{\alpha p_0 V_0}{V \left(\frac{dq}{dV}\right)_t} \qquad (1)$$

is the expression for Carnot's Theorem for this case. This is seen to be a special form of Clapeyron's general equation (24').

Although Thomson adhered to the principle of the conservation of caloric throughout this 1849 paper, still, at several points, he expressed considerable doubt in its validity. Of the first importance, in this connection, was his recognition that Carnot's proof of Carnot's Theorem involved the assumption of the absolute destruction of work (cf. p.33') For he said, "When 'thermal agency' is spent in conducting heat through a solid, what becomes of the mechanical effect which it might produce? Nothing can be lost in the operations of nature—no energy can be destroyed. What effect then is produced in place of the mechanical effect which is lost? A perfect theory of heat imperatively demands an answer to this question; yet no answer can be given in the present state of science."

If, in spite of this contradiction and Joule's experiments, which Thomson had been acquainted with since 1847, the latter nevertheless continued, in 1849, to regard the caloric theory as "the most probable basis for an investigation of the motive power of heat," this must be largely due to the experimental verification of numerous consequences of Carnot's Theory. We have already observed, in connection with Carnot and Clapeyron, the general agreement of the values of "Carnot's function" C as calculated by a variety of different methods employing data from several branches of physics. Thomson now found that by the

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substitution, into Clapeyron's equation (18), of Regnault's recently determined data on the saturation pressure and latent heat of steam together with the values of the density of steam calculated from the perfect gas law, values of μ (or $1/C$) were obtained, which were in substantial agreement with the older values of μ obtained by Carnot and Clapeyron by applying the same method to data on air, sulfuric acid, alcohol, water, and turpentine. And, like the older values, Thomson's also revealed a gradual decrease of μ with increasing temperature. The agreement between the two sets of values of μ is shown in the following table, taken from Thomson's paper:

Substance	Temperature (°C)	Value of μ (ft.-lbs./C.U./°C.)		μ from Regnault's Data on Steam (ft.-lbs./C.U./°C.)
Air	0.5	(Carnot)	4.377	4.960
Sulfuric ether	35.5	(Clapeyron)	4.478	4.510
Alcohol	78.8	"	3.963	4.030
Water	100	"	3.658	3.837
Turpentine	156.8	"	3.530	3.449

Further, Thomson was able to show that the values of μ calculated from Regnault's observations in the manner just described were in approximate agreement with Joule's experimental results on the heat of compression of air. (cf. p. 198). Write (1) in the form

$$dq = \frac{\alpha p_0 v_0}{\mu} \frac{dv}{v} \qquad (2)$$

In an isothermal process $\frac{\alpha p_0 v_0}{\mu}$ is constant; hence integration of (2) gives, for the heat evolved by the isothermal compression of air from the volume V to V',

$$Q = (\alpha p_0 v_0/\mu) \log V/V'. \qquad (3)$$

The work done in this compression will be

$$W = \int_{V'}^{V} p\,dv = \int_{V'}^{V} p_0 v_0 (1 + \alpha t)\,dv/v = p_0 v_0 (1 + \alpha t) \log V/V'.$$

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Therefore the ratio of work done to the heat developed should be

$$W/Q = \mu (1 + \alpha t)/\alpha . \qquad (4)$$

Introducing his values of μ, calculated from Regnault's data, into this formula, Thomson obtained values of the ratio in fair agreement with Joule's experimental determination of the same quantity.[27]

In addition to the above verifications of Carnot's Theory, we should recall that Dulong had already verified Carnot's formula for the heat effect of the isothermal compression of a perfect gas, and that James Thomson's prediction of the depression of the freezing point of water by increase of pressure was soon to be verified. Finally, Thomson had shown how Carnot's theory provided the basis for that most important concept, the absolute temperature.[28]

In the face of these successes scored by Carnot's Theory, Thomson did not yet regard Joule's experiments as conclusive enough to justify the rejection of the caloric postulate. While admitting that Joule's experiments prove that heat can be generated at the expense of mechanical action, he pointed out that the converse phenomenon, which should be perfectly possible according to the Energy Principle as stated by Mayer, Joule, and Helmholtz, had never yet been observed: the development of heat by one body and the absorption of work by another appeared always to be accompanied by the change of state of an auxiliary body. Thus Mayer's Principle of Equivalence seemed to be beset with objections just as formidable as the Principle of the Conservation of Caloric.[29]

4. THE REJECTION OF THE CALORIC HYPOTHESIS.

A. The Efforts of Rankine: Molecular Vortices versus Energetics.

In his 1845 paper, Joule had urged the modification of Carnot's

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theory so as to make it accord with the Principle of Equivalence, but the first definite attempt to do this came in February, 1850, with the publication of Rankine's paper, "On the Mechanical Action of Heat, Expecially in Gases and Vapors" (47, p. 234). Although his point of view was dominated by the hypothesis of molecular vortices, still some of the results of Rankine's paper were formally independent of this hypothesis (cf. p. 212)

According to the caloric theory, the heat required to bring a body of liquid at a certain volume and temperature into the gaseous state at a certain volume and temperature must be independent of the path, e.g. of the temperature at which the liquid boils, but, according to the mechanical theory of heat, this so-called "total heat of evaporation" must depend on said path.[30] Rankine derived an analytical expression for this dependence in the following manner. Suppose that a unit weight of liquid has, at the temperature t_0, the volume v_0 and vapor pressure P_0, and latent heat of evaporation L_0. Suppose the volume of unit weight of the saturated vapor, at this temperaure, be V_0. At the temperature $t_1 > t_0$, let the values of these quantities be v_1, P_1, L_1, and V_1. Imagine a unit weight of the liquid , initially at t_0 and v_0, carried through the following reversible, cyclic process: (1) let the unit weight of liquid be brought into the state (t_1, v_1) in such a manner that its mean specific heat between t_0 and t_1 is represented by $c_1 L$.

$$\text{Heat absorbed} = c_L(t_1 - t_0)$$

$$\text{Work developed} = \int_{v_0}^{v_1} P\,dv.$$

(2) Evaporate the unit weight of liquid isothermally at t_1.

$$\text{Heat absorbed} = L_1$$

$$\text{Work developed} = P_1(V_1 - v_1).$$

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(3) Expand under saturation pressure until the temperature falls to t_0. If K_s is the specific heat of the saturated vapor,

Heat absorbed $= \int_{t_1}^{t_0} K_s dt$

Work Developed $= \int_{v_1}^{v_0} PdV$

(4) Liquefy the vapor isothermally at t_1.

Heat absorbed $= -L_0$

Work developed $= -P_0 (V_0 - v_0)$.

Since the body is restored to its initial state, the total heat absorbed equals to the total work developed, or

$$L_1 - L_0 + K_1 (t_1 - t_0) = \int_{t_0}^{t_1} K_s dt = P_1(V_1 - v_1) - P_0(V_0 - v_0) + \int_{v_0}^{v_1} Pdv + \int_{v_1}^{v_0} PdV.$$

The quantity K_s, the specific heat of the saturated vapor, Rankine clearly defined for the first time: it represents the "quantity of heat which unity of weight of vapor receives or gives out, while its temperature is increased by 1°, its volume being at the same time compressed so as to bring it to the maximum pressure corresponding to the increased temperature." By means of the molecular vortices hypothesis, Rankine predicted that K_s was negative for the vapors known in his day, i.e. "the heat generated by the compression is greater than that which is required to produce the elevation of temperature, and a surplus of heat is given out; and, on the other hand, if the vapor at saturation is allowed to expand, and at the same time maintained at the temperature of saturation, the heat which disappears in producing the expansion is greater than that set free by the fall of temperature: and the deficiency of heat must be supplied from without, otherwise a portion of vapor will be liquefied in order to supply the heat necessary for the expansion of the rest." (47) This prediction was confirmed by Clausius later in the same year by a method independent of any hypothesis as to the nature of heat.

In his 1850 paper, Rankine calculated the work done by a reversible

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steam engine absorbing a definite quantity of heat at one temperature and discharging a correspondingly smaller amount at a lower temperature and he refers to this as the "maximum mechanical effect." Without explicitly stating it, he seemed to imply the validity of Carnot's Theorem, respecting the independence of the maximum work on the working body, but he gave no proof for the existence of such a maximum. In the following year, 1851, in a paper "On the Economy of Heat in Expansive Machines" (47), we find him insisting that "Carnot's Law (Theorem) is not an independent principle in the theory of heat but is deducible, as a consequence, from the equations of mutual conversion of heat and expansive power." And he maintained this in the face of the classical treatments of Thomson and Clausius which had, in the meantime, appeared. From the hypothesis of molecular vortices, he thought he could deduce, for the efficiency of a heat engine working between the absolute temperatures T_1 and T_2, the value

$$\frac{T_1 - T_2}{\varkappa}$$

where $\varkappa$ is a constant, $\frac{\quad}{\varkappa}$ small compared to ordinary values of T_1, and which must be the same for all substances in order that molecular equilibrium be possible.[31]

Beginning in the year 1853, Rankine expounded the positivistic or "energetic" view of thermodynamics which he was careful to distinguish from the hypothetical, mechanistic standpoint of his previous papers. This new viewpoint found expression in three papers, whose contents considerably overlap: "On the Mechanical Action of Heat; Section VI. A Review of the Fundamental P rinciples of the Mechanical Theory of Heat" (1853); "On the General Law of the Transformation of Energy" (1853); and "Outlines

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of the Science of Energetics" (1855), all of which are included in his Miscellaneous Scientific Papers (47).

Unfortunately, however, Rankine's attempt to make his considerations extremely general caused much of his reasoning to be cloaked in obscurity. Thus his term "energy" is frequently surrounded by a vagueness reminiscent of that which had associated itself with the term "force" in the writings of the precursors of the First Law of Thermodynamics.

Rankine's vagueness is somewhat exemplified by the definitions of "actual" and "potential" energy with which he began his paper, "On the General Law of the Transformation of Energy." "Actual, or Sensible Energy," he says, "is a measurable, transmissible, and transformable condition, whose presence causes a substance (body) to change its state in one or more respects." By the occurrence of changes, actual energy is replaced by "potential, or Latent Energy, which is measured by the product of a change of state into the resistance against which that change is made." As examples of actual energy, he cited "the vis viva of matter in motion, thermometric heat, radiant heat, light, chemical action, and electric currents," and as instances of potential energy, he gave "the mechanical powers of gravitation, elasticity, chemical affinity, statical electricity, and magnetism."

Helm(32, p.112) has detected, in this segregation of energy into actual and potential, the influence of Rankine's earlier proposed mechanistic hypothesis of molecular vortices; that is, Rankine's supposition that this segregation, which, for mechanical energy, corresponds to the scientifically valid classification of energy as "kinetic" and "potential," also applies to every other species of energy, e.g. heat energy, may well have been suggested by the conviction that all energy is really mechanical.

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Whether this be true or not, Rankine's classification did not correspond to the fundamental division of substance into active and inactive forms, required by the Second Law (cf. p.220. Thus, the energy of sensible heat and the energy of motion of macroscopic bodies, which we now recognize as instances of inactive and active energy, respectively, Rankine regarded to be of the same general type, namely, "actual energy." Indeed, the failure to recognize the peculiar nature of heat energy was characteristic of Rankine's treatment.

The Law of the Conservation of Energy, Rankine formulated in the statement that the sum of all energies, actual and potential, of the universe is constant.

Now, said Rankine, let V denote the "magnitude of the measurable state of a substance," i.e. the value of some extensive property of the body in question; U, the species of potential energy developed when V. increases; and P , the common magnitude of the tendency of V to increase, and of the equal and opposite resistance against which it increases. Then

$$dU = PdV, \qquad p = \frac{dU}{dV}.$$

At this point, Rankine seriously obscured his whole treatment by choosing Q, the actual energy of the body, as an independent variable, a step reminiscent of the caloric theory. Suppose Q denotes the actual energy of a body which produces the tendency for V to increase, and imagine Q divided into infinitely small parts of magnitude dQ. Since these elements dQ are "altogether alike and similarly circumstanced, the effect of the total actual energy Q in causing V to increase, must be $\frac{Q}{dQ}$ times the effect of a single element dQ. But the effect of dQ in causing the development of potential energy of species U, during the increment dV, is

$$\frac{dP}{dQ} dQdV,$$

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so that the effect of the whole actual energy Q is

$$Q\frac{dP}{dQ}dV, \qquad (1)$$

ie. this represents the "amount of actual energy Q transfromed to potential energy of species U in the change dV."

The expression (1), Rankine refered to as the "General Law of the Transformation of Energy," which he stated as follows: "The effect of the whole actual energy present in a substance, in causing the transformation of energy, is the sum of the effects of all its parts." Although he later referred to this proposition as an "axiom" and as "The Second Law of Thermodynamics," he nevertheless did not regard it as an independent postulate, for he describes it, in his 1855 paper, as "a consequence of the definition of actual energy, as a capacity for performing work possessed by each part of a substance independently of its relation to other parts." Thus his previously expressed conviction that all of the principles of thermodynamics flow from the hypothesis of molecular vortices now has its analogue in the view that said principles are derivable from a single concept, that of "energy."[32]

The expression (1) represents the portion of potential energy due to the actual energy Q present in the body. Then the difference

$$(P-Q\frac{dP}{dQ})dV$$

Rankine regards as equal to that por tion of the potential energy developed which arises from causes other than the actual energy Q.

Rankine next undertook to derive an expression for the "quantity of actual energy of the form Q which must be transmitted to the substance from without, in order that its total actual energy may receive the increment dQ, and its state V (parameter) at the same time the increment dV." This actual energy added, denoted by d.Q, Rankine regarded as divisible into three parts: (1) the actual energy which preserves its form, dQ; (2) the

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the actual energy which transforms itself to some unknown form because of resistance offe red to the increase of total actual energy, LdQ; (3) the actual energy which transforms itself into potential energy of the form U, $Q\frac{dP}{dQ}dV$. Hence,

$$d.Q = (1 + L)dQ + Q\frac{dP}{dQ}dV \quad (2)$$

Subtracting the potential energy developed, P dV, from the expression for d.Q, Rankine obtained, for the net energy received during the change dV, the expression

$$d\psi = d.Q - dU = (1 + L)dQ + (Q\frac{dP}{dQ} - 1)PdV \quad (B)$$

which, by the principle of the conservation of energy, must be an exact differential. Hence,

$$\frac{dL}{dV} = \frac{d}{dQ}(Q\frac{dP}{dQ} - P) = Q\frac{d^2P}{dQ^2} + \frac{dP}{dQ} - \frac{dP}{dQ} = Q\frac{d^2P}{dQ^2}$$

and

$$L = f'(Q) + Q\frac{d^2}{dQ^2}\int PdV$$

where f' (Q) is a function of Q and " PdV denotes a partial integral taken in treating the particular value of Q, to which it corresponds, as a constant quantity." Substituting this value of L in (B), he obtained

$$d\psi = d.Q - dU = (1 + f'(Q) + Q\frac{d^2}{dQ^2}\int PdV)\,dQ + (Q\frac{dP}{dQ} - P)dV$$
$$= d\left\{Q + f(Q) + (Q\frac{d}{dQ} - 1)\int PdV\right\} \quad (3)$$

These general considerations parted with some of their vagueness when Rankine applied them to the relations between heat and work in his paper, "On the Mechanical Action of Heat, Section VI" in 1853. For this case, Q denotes the sensible or actual heat of a body, PdV the work done by its volume increase dV at the pressure P. Then the expression (1) supposedly represents the work developed during the expansion dV, which is due to the presence of the heat Q. Then the difference

$$(Q\frac{dP}{dQ} - P)\,dV \quad (4)$$

must represent the work consumed in overcoming molecular attraction (assuming no heat has been added from the outside). This internal work,

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Rankine supposed to be a definite function of Q and V, namely, S(Q,V). (dS would seem to correspond to the quantity L.dQ of equation (B).) By (4),

$$\frac{dS}{dV} = Q\frac{dP}{dQ} - P \qquad (5)$$

$$S = \int (Q\frac{dP}{dQ} - P)dV + \phi(Q). \qquad (6)$$

Rankine called S the "potential of molecular action."

The total heat absorbed when the actual heat of a body increases its volume by dV, Rankine placed equal to the sum of three quantities: the increase in sensible heat dQ; the work of molecular action (internal work), dS; and the external work, PdV. Hence,

$$\begin{aligned} \text{Total heat consumed} &= dQ + dS + PdV \\ &= (1 + \frac{dS}{dQ})dQ + (\frac{dS}{dV} + P)dV \\ &= (1 + Q\int \frac{d^2P}{dQ^2}dV + \phi'(Q))dQ + Q\frac{dP}{dQ}dV \end{aligned} \qquad (7)$$

where the last transformation results from the substitution of $\frac{dS}{dV}$ from (5) and that of $\frac{dS}{dQ}$ from (6). Equation (7) supposedly expresses the relation between heat, molecular work, and external work, during reversible expansion.

Rankine now defined a new function, "the heat potential" F, by means of the relation:

$$F = \int \frac{dP}{dQ}dV \quad (Q = \text{constant}). \qquad (8)$$

Since, according to Rankine, $\int Q\frac{dP}{dQ}dV$ represents the total work (molecular and external) developed due to the presence of the heat Q, in the volume change dV, we see that ΔF represents the ratio of this total work, done at constant heat Q, to the amount of heat present.

Now, from the definition of F,

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$$dF = \frac{dF}{dQ}\,dQ + \frac{dF}{dV}\,dV = \left(\int \frac{d^2P}{dQ^2}\,dV\right) dQ + \frac{dP}{dQ}\,dV,$$

so that the general equation (7) becomes, for an adiabatic change,

$$0 = \left[1 + \phi'(Q)\right] dQ + Q\,dF$$

or

$$-dF = \frac{1 + \phi'(Q)}{Q}\,dQ, \qquad (9)$$

i.e. "when the quantity of heat in a body is varied by variation of volume only, the variation of the heat potential depends on the heat only and is independent of the volume."

Rankine now attempted to derive Carnot's Theorem by applying these considerations to a Carnot cycle, and regarding F and Q as independent variables. The cycle is described as follows: (1) Maintaining the body at constant heat (hence, constant temperature) Q_1, expand till its heat potential passes from F_A to F_B. Since all heat absorbed is converted to work (internal and external), the heat absorbed is

$$H_1 = Q_1 (F_B - F_A);$$

(2) Expand adiabatically till the heat falls to Q_2 and the heat potential, varying according to (9), becomes F_C, THE HEAT $Q_1 - Q_2$ being converted into work (internal and external); (3) Compress at constant heat Q_2 till the heat potential becomes F_D, the heat absorbed being

$$H_2 = Q_2 (F_C - F_D);$$

(4) Compress adiabatically until the heat potential and the heat again have their original values, the heat converted into work (internal and external) being $Q_2 - Q_1$. Rankine evidently assumed that isothermal compression is continued just to the point where adiabatic compression will return the working body to its initial state, but he does not state what condition must hold in order that this be possible. The heat absorbed at the higher temperature is $H_1 = Q_1 (F_B - F_A)$, that developed at the lower temperature is $H_2 = Q_2 (F_C - F_D)$. Since the body is returned to

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its initial state, $H_1 - H_2$ represents the external work developed. Therefore, the efficiency of the cycle is

$$\frac{H_1 - H_2}{H_1} = \frac{Q_1 (T_B - T_A) - Q_2 (T_C - T_D)}{Q_1 (T_B - T_A)} = \frac{Q_1 - Q_2}{Q_1} \qquad (9')$$

since, by (9), $T_B - T_A = T_C - T_D$.[34]

Rankine's 1855 paper, "Outlines of the Science of Energetics", constitutes the author's final attempt to develop systematically the laws of energy in a manner independent of all hypotheses of occult forces and motions. Although this paper frequently partakes of the vagueness which characterized the 1853 papers, still it is noteworthy for certain valid results which it contained.

Among these, we may include the general definition of intensive and extensive properties which Rankine called "efforts (active accidents)" and "passive accidents," respectively. He began by defining an "accident" as "every variable state of substances, whether consisting in a condition of each part of a substance, how small soever, (which may be called an absolute accident), or in a physical relation between parts of substances, (which may be called a relative accident)." An "effort", he then defined as "every cause which varies, or tends to vary, an accident," whereas a "passive accident" is a condition which an effort tends to vary.

On the basis of these definitions, Rankine generalized the concept of work to mean any "variation of an accident (passive) by an effort." Quantity of work W is then measured by the line integral of the effort X with respect to the passive accident x. Thus

$$W = \int_{x_0}^{x_1} X dx. \qquad (10)$$

This generalized notion of work is made the basis for Rankine's definition of energy as that which "comprehends every state of a substance

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which constitutes a capacity for performing work." A quantity of energy is then measured by the quantity of "work" which it can perform.

We have already noted Rankine's failure to appreciate the peculiar nature of heat. This shortcoming again appeared in the form of his "First Axiom" that "any kind of energy may be made the means of performing any kind of work." As "Second Axiom" he stated the Law of Conservation of Energy in the form: "The total energy of substance cannot be altered by the mutual actions of its parts." As "Third Axiom" he advanced the "General Law of the Transformation of Energy," already cited (cf. p.237).

Proceeding in a manner similar to that of the 1853 paper (cf. p.286), Rankine now attempted "to determine the amount of effort X arising from the actual energy Q which tends to perform a particular kind of work W by the variation of a particular passive accident." The total effort to perform this kind of work is by (10), $X = \frac{dW}{dx}$. Dividing Q into small parts δQ, the portion of the effort X due to each of these parts is $\delta Q \frac{dX}{dQ}$, and the effort due to the whole actual energy Q (supposed of a single kind) is $Q \frac{dX}{dQ} = Q \frac{d^2 W}{dQ\, dx}$. If this effort caused by the actual energy is less or greater than the effective effort, the difference $(1 - Q \frac{d}{dQ})X$ or $(Q\frac{d}{dQ} - 1)X$ is due to other causes.

For a small increment of the passive accident, dx, the amount of actual energy which disappears is

$$dH = Q \frac{dX}{dQ} dx = Q \frac{d^2 W}{dQ dx} dx = Q\, d\frac{dW}{dQ} . \qquad (10')$$

"The function of actual energy, efforts, and passive accidents, denoted by

$$F = \int \frac{dW}{dQ} = \int \frac{dH}{dQ} \qquad (11)$$

whose variation multiplied by the actual energy gives the amount of actual energy transformed in performing wht work dW is called the Metamorphic Function of the kind of actual energy Q, relatively to the kind of work W."

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Thus the actual energy of kind Q which is reversibly transformed to W is given by

$$H = \int Q \, dF, \qquad (12)$$

Rankine next attempted to prove that when two bodies are in equilibrium, the ratio of their actual energies of a given kind is constant. Denoting the values of these actual energies by Q_A and Q_B, he thus wrote for an equilibrium condition: $(Q_B/Q_A) = (K_B/K_A)$ or $(Q_A/K_A) = (Q_B/K_B) = \Theta$.

Rankine called Θ "the metabatic function" for the kind of actual energy Q.

Because of the proportionality of Q and Θ, the operators $Q\frac{d}{dQ}$ $\frac{d}{d}$ are are equivalent so that (10') becomes $dH = \Theta \frac{dW}{d\Theta}$.

Defining ϕ ("a kind of metamorphic function") by the relation $d\phi = \frac{dW}{d\Theta}$, Rankine finally wrote

$$H = \int \Theta \, d\phi \qquad (13)$$

for "the quantity of actual energy of kind Q transformed to the kind of work W during any finite variation of accidents."

Considering the cloak of obscurity which surrounds the above considerations, the reader is considerably surprised to find that in the case of where Q denoted actual heat energy, they led Rankine to apparently correct results. For, in this case, Rankine stated that Θ is none other than the absolute temperature, i.e. the actual heat of a body is proportional to its absolute temperature, a proposition which Rankine assumed without proof. The constant of proportionality K is, for this case, the "real specific heat."

Equation (13) would then appear to be the expression for the heat absorbed and transformed into some sort of work W. Because of the vagueness which surrounds Rankine's term "work," we cannot say whether equation (13) represented a truly correct result or not. However, the formal analogy of the "metamorphic function" with the entropy function, introduced ten years

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later by Clausius, is evident. In fact, Rankine explicitly observed that for a reversible adiabatic process, the ϕ function corresponding to heat energy, remains constant.

The criticism which Helmholtz, in 1853, aimed at Rankine's paper, "On the General Law of the Transformation of Energy," might very well be extended to the latter's whole "Science of Energetics." "Mr. Rankine," said Helmholtz, "has arrived, in his own way, at many results which other investigators, starting out from entirely different premises, also found to be correct. However, it is quite impossible to follow him over the route through which he endeavors to derive his laws, so that one gets the impression that he gained his results rather by a kind of correct instinct than by rigorous mathematical analysis. Or, he has suppressed so many of the intermediate steps leading to his final conclusions that the reader is forced to rediscover the latter for himself." (32, p. 114)

However, we must admit that these attempts of Rankine--vague and pretentious as they are--to formulate a set of general physical principles devoid of "explanatory" hypothesis, constitute a continuation of the worthy ideal of Robert Mayer--an ideal which was not fully appreciated till later in the century, in the writings of such men as G. Kirchoff, George Helm, Ernst Mach, Wilhelm Ostwald, and Pierre Duhem (14). Apart from this, the numerous contributions of Rankine to technical thermodynamics, his extension of graphical methods, and the fact that he was the author of the first formal text-book of thermodynamics, must also insure for him a permanent place in the history of thermodynamics.[35]

At the same time, we must admit that one of the chief advantages, which ensues from the inclusion, in our history of thermodynamics, of an outline of Rankine's "Science of Energetics," is the contrasting

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background which it provides for the far more careful and precise treatments of Clausisus and Thomson. Rankine, following the ideal of Grove and Mayer, sought to lay down perfectly general principles which should govern every conceivable kind of energy; but, because he was unwilling to approach the general case through the rigorous and detailed consideration of particular cases, his treatment was vague and frequently meaningless. Clausius and Thomson, on the contrary, were content to follow along the lines laid down by Carnot and Clapeyron, their work consisting essentially of a modification of Carnot's Theory so as to bring it into conformity with the Energy Principle. However, in working out the solution of this seemingly special problem of the "motive power" of heat, they succeeded in attaining results which actually proved to be of greater significance for a general science of energetics than Rankine's pretentious attempts already described.

B. Clausius and the Directional Flow of Heat.

In the same month , February, 1850, that saw the publication of Rankine's first paper, "On the Mechanical Action of Heat, Especially in Gases and Vapors," there was submitted to the Berlin Academy the epoch-making paper by Clausius, "On the Moving Force of Heat and the Laws of Heat Which May be Deduced Therefrom" (57).

Like Rankine, Calusius began with a definite rejection of the fluid theory of heat, on the ground that the principle of the conservation of caloric contradicts Joule's experiments on the generation of heat by expenditure of mechanical work. In the place of the caloric theory, Clausius advocated the kinetic theory of heat, so that the principle of equivalence of heat and work followed as a result of the Principle of the Conservation of Vis Viva of pure mechanics.[36]

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Clausius took note of Holtzmann's modification of Carnot's theory (which was known to Holtzmann and Clausius only through the work of Clapeyron) and observed, as Helmholtz had failed to do, that Holtzmann, while professing to adopt Mayer's Energy Principle, really contradicted it by retention of the postulate of conservation of caloric. Clausius was also acquainted with Thomson's 1849 "Account of Carnot's Theory," and he cited, as a definite objection to Carnot's reasoning, Thomson's observation of the possibility, implied by it, of the absolute destruction of work. (cf. p. 279)

Nevertheless, said Clausius, the agreement with experience of numerous deductions from Carnot's Theory indicates that the essential part of the latter must not be abandoned. This essential part is retained and the Principle of Equivalence remains unviolated, if we assume that, in the working of a heat engine, the heat developed along the lower isotherm, instead of being equal to that absorbed along the higher, is less than the latter by an amount proportional to the net work developed, after the working body is returned to its initial state.

As the fundamental "Principle of the Equivalence of Heat and Work," Clausius laid down the following proposition; "In all cases where work is produced by heat, a quantity of heat proportional to the work done is consumed; and, inversely, by the expenditure of a like quantity of work, the same amount of heat may be produced." The form of this statement is significent in that it does not contradict the theoretical possibility that a given quantity of heat may not be completely transformable into work, i.e. without anything else happening. It merely requires that, <u>if</u> a conversion occurs, the work produced shall be proportional to the heat consumed. Allowance is thus made for Thomson's objection that heat has never been

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observed to be completely transformed into work without other changes simultaneously occurring.

As a consequence of the above principle, the "total heat" of a body in a given state, a phrase freely employed by the calorists, can have no definite meaning. For, said Clausius, the work developed by a body in passing from one state to another will depend on the path of the change of state; hence, the heat absorbed, being dependent on this work, must also vary with the path.

Clausius retained the distinction, made by the calorists, between "sensible" and "latent" heat. The sensible heat of a body is indicated by the body's temperature. The latent heat represents that portion of the absorbed heat which is converted into work, external and internal. Like Rankine, Clausius supposed that the change in a body's sensible heat (heat corresponding to the vis viva of the elementary particles of the body), also the heat expended as internal work (work done in changing the configuration of the system of particles which constitute the body) is independent of the path of the change.[37]

Following the graphical method introduced by Clapeyron, Clausius first developed the Principle of Equivalence for perfect gases, for which

$$pv = R(\alpha + t)$$

where $R = \frac{p_o v_o}{\alpha + t_o}$, the subscript "o" denoting the value of the corresponding variable in a state of reference. Let the figure abcd on the p--v diagram of Figure 12 represent a Carnot cycle of infinitesimal extent, employing a perfect gas as working body, and operating between the temperatures t and t-dt. Neglecting infinitesimals

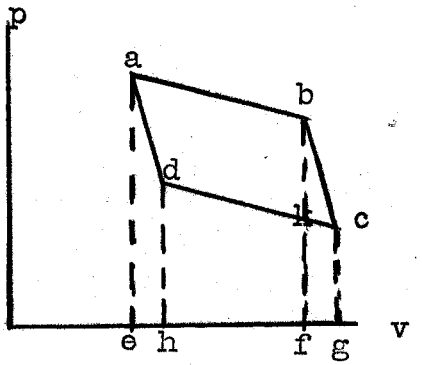

Figure 12

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of the third order (the area of abcd being itself an infinitesimal of the second order), abcd may be treated as a parallelogram. Hence, Clausius found, as Clapeyron had already done (cf. p.260), that the area of abcd, and hence the work, is given by

$$\text{work done} = \frac{Rdtdv}{v} \quad . \qquad (1)$$

According to the fundamental Principle of Equivalence, this work must correspond to a definite consumption of heat. Clausius obtained an analytical expression for this quantity of heat in terms of the independent variables, v and t, in the following way. Let $dv = ef$ denote the increase in volume along with isotherm ab at the temperature t; $dv = hg$, that along the isotherm dc at the temperature t-dt; $\delta v = eh$, that long the adiabatic path ad; and $\delta' v = fg$, that along the adiabatic path bc. The heat received along ab will be

$$\left(\frac{dQ}{dv}\right)dv;$$

and that received along the lower isotherm cd will be

$$-\left[\left(\frac{dQ}{dv}\right) + \frac{d}{dv}\left(\frac{dQ}{dv}\right)\delta v \frac{dv}{dt}\left(\frac{dQ}{dv}\right)dt\right] d'v.$$

The net quantity of heat consumed in the cycle will therefore be the difference of these two quantities, or

$$\left(\frac{dQ}{dv}\right)dv - \left[\left(\frac{dQ}{dv}\right) + \frac{d}{dv}\left(\frac{dQ}{dv}\right)\delta v - \frac{d}{dt}\left(\frac{dQ}{dv}\right)dt\right] d'v. \qquad (2)$$

Now, from the figure,

$$dv + \delta' v = \delta v + d'v.$$

Also, since the heat absorbed along the adiabatic path ad is zero, we have

$$\left(\frac{dQ}{dv}\right)\delta v - \left(\frac{dQ}{dt}\right) dt = 0.$$

Similarly, for the adiabatic bc,

$$\left[\left(\frac{dQ}{dv}\right) + \frac{d}{dv}\left(\frac{dQ}{dv}\right)dv\right] \delta' v - \left[\left(\frac{dQ}{dt}\right) \frac{d}{dv}\left(\frac{dQ}{dt}\right)dv\right] dt = 0 \quad .$$

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Eliminating d'v, δv, and $\delta' v$ from these three equations and equation (2), and discarding infinitesimals of higher order than the second, we obtain in place of equation (2), the relation

$$\text{Heat Expended} = \left[\frac{d}{dt}\left(\frac{dQ}{dv}\right) - \frac{d}{dv}\left(\frac{dQ}{dt}\right)\right] dv\, dt. \qquad (3)$$

By virtue of the Principle of Equivalence, we have

$$\frac{\text{Heat Expended}}{\text{Work Produced}} = A \qquad (4)$$

where A is the mechanical equivalent of heat. Substituting (1), and (3) in (4), Clausius obtained

$$\frac{d}{dt}\left(\frac{dQ}{dv}\right) - \frac{d}{dv}\left(\frac{dQ}{dt}\right) = \frac{AR}{v} \qquad (II)$$

as the analytical expression of the Principle of Heat and Work for the case of perfect gases. Clausius observed that the circumstance that the right-hand member of (II) is not equal to zero corresponds to the truth that the expression $\frac{dQ}{dv}dv + \frac{dQ}{dt}dt$ is inexact, i.e. Q is not expressible as a function of t and v.[38]

Clausius next stated that equation (II) may be transformed into a complete differential equation of the first order, namely,

$$dQ = dU + \left[(AR(\alpha + t)/v)\right]dv \qquad (IIa)$$

where U is an arbitrary function of v, t. He stated that the first term of the right-hand member of (IIa) represents that portion of the absorbed heat which corresponds to the increase in sensible heat of the gaseous body and expenditure of internal work, whereas the second term represents that portion converted into external work.[39]

In order to place equation (IIa) in a form capable of yielding specific results capable of experimental test, Clausius introduced the fundamental assumption that the heat absorbed by a perfect gas in isothermal expansion is equivalent to the external work developed.[40] This means that the internal

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work is to be neglected so that the term dU of (IIa) represents simply the increase of sensible heat. Therefore dU = c dt where c is a function of t only. Equation (IIa) then becomes

$$dQ = c\,dt + AR\frac{\alpha + t}{v}dv \quad . \qquad \text{(IIb)}$$

When the prescribed path is perpindicular to the v-axis, we have from (IIb)

$$\frac{dQ}{dt} = c, \qquad (5)$$

i.e. c is the specific heat at constant volume. For a path perpindicular to the p-axis, the perfect gas law gives for a unit weight of gas, $\frac{dv}{v} = \frac{dt}{\alpha + t}$, which substituted in (IIb) yields the result,

$$\frac{dQ}{dt} = c' = d + AR, \qquad (6)$$

where c' is the specific heat at constant pressure.[41]

From (6) and (5) we have

$$c' - c = AR = A\frac{p_o v_o}{t_o} \quad , \qquad (7)$$

i.e. the difference in the specific heats at a given temperature, referred to unit weight, has, for one and the same perfect gas, the same value under all conditions; and, for different perfect gases, the difference is proportional to the specific volume v_o of the gas in the standard state (p_o, t_o). Dividing equation (7) by v_o, we obtain for the difference of specific heats referred to unit volume,

$$\underline{c}' - \underline{c} = AR/v_o = Ap_o/t_o, \qquad (8)$$

i.e. this difference not only has the same value for a single gas under different conditions, but is is also the same for different gases.[42]

From either (7) or (8) we obtain the ratio of specific heats,

$$\gamma = \underline{c}'/\underline{c} = c'/c = Ap_o/\underline{c}\,t_o, \qquad (9)$$

i.e. this ratio is constant if $\underline{c}$ (or c) is.[43]

For an adiabatic expansion equation (IIb) takes the form

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$$cdt + AR(\alpha + t)\frac{dv}{v} = 0$$

or $v^{\left(\frac{AR}{c}\right)}(\alpha + t) = v^{(\gamma-1)}(\alpha + t) = K$;

since, by (6), $AR/c = \gamma - 1$. Here K is a constant. Applied to the reference state (p_o, v_o, t_o), the above equation is $v_o^{\gamma-1}(\alpha + t_o) = K$. Dividing the second equation by the first,

$$\left(\frac{v_o}{v}\right)^{\gamma-1} = \frac{\alpha + t}{\alpha + t_o} \qquad (10)$$

By the perfect gas law, $v_o/v = \frac{\alpha + t_o}{\alpha + t}\frac{p}{p_o}$, so that (10) may be written

$$\left(\frac{p}{p_o}\right)^{\gamma-1} = \left(\frac{\alpha + t}{\alpha + t_o}\right)^{\gamma}. \qquad (11)$$

Finally, since $\frac{\alpha + t}{\alpha + t_o} = \frac{pv}{p_o v_o}$, (10) becomes

$$\frac{p}{p_o} = \left(\frac{v_o}{v}\right)^{\gamma}. \qquad (12)$$

Equation (12) had already been obtained by Poisson (cf. p.159) from the caloric theory and the assumption of the constancy of γ. Clausius now showed that it was a necessary consequence of the Principle of Equivalence as applied to perfect gases regardless of whether γ be constant or not.

Clausius also showed that Clapeyron's equation for isothermal expansion (cf. p.261) followed from the Principle of Equivalence. For if T be constant, equation (IIb) may be integrated (because Q is a definite function of v when the temperature is fixed), the result being

$$Q = AR(\alpha + t)\log v + \text{const.} \qquad (13)$$

or

$$Q - Q_o = AR(\alpha + t_o)\log(v/v_o) \qquad (14)$$

where $Q-Q_o$ is the heat absorbed on expanding at t_o from v_o to v. Equation (14) Clausius also placed in the form:

$$Q - Q_o = Ap_o v_o \log(v/v_o), \qquad (15)$$

i.e. when equal volumes (v_o) of different gases at the same initial pressure (p_o) are compressed or expanded isothermally by the same fraction of the

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original volume, the same quantity of heat is developed or absorbed. Carnot (cf. p.248) and Clapeyron (cf. p.261) had derived this theorem for the case where the different gases are at the same temperature, and it was for this special case that Dulong had verified it experimentally.

By a method analogous to that by which he derived equation (II) for perfect gases, Clausius obtained an analytical expression of the Principle of Equivalence for a vapor, say steam, at its maximum density. On the p--v diagram of Figure 13, let abcd represent the variations of pressure and volume occurring in a Carnot cycle of infinitesimal extent, employing liquid water and steam at its maximum density as working body, and operating between the temperatures t and t-dt. Clausius treated abcd as a parallelogram, as Clapeyron had already done.(cf.p.) The work developed by the cycle is equal to the area of this parallelogram, so we have

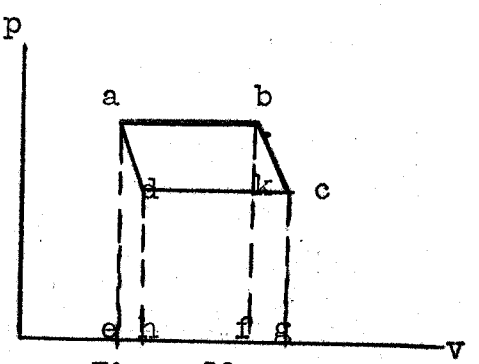

Figure 13

$$\text{Work Developed} = \overline{ef} \cdot \overline{bk} = (s-\sigma)dm \cdot \left(\frac{\partial p}{\partial t}\right)_v dt \qquad (16)$$

where s, σ, and dm denote, respectively, the specific volume of the saturated steam at the temperature t, the specific volume of the liquid at the same temperature, and the weight of liquid evaporated in the isothermal expansion $\overline{ab}$. This was Clapeyron's equation (15) (p.263) expressed in terms of specific volumes instead of densities and the mass of vapor evaporated instead of its volume.

If r denote the specific heat of vaporization of water at the temperature t while in equilibrium with the saturated vapor, and d'm denote the mass of liquid precipitated during the isothermal compression $\overline{cd}$, we shall have

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$$\text{Net Heat Expended} = r\,dm - \left(r - \frac{\partial r}{\partial t}\,dt\right)d'm \qquad (17)$$

Now let δm be the mass of liquid precipitated in the adiabatic compression $\overline{da}$: and $\delta' m$, the mass evaporated in adiabatic expansion $\overline{bc}$. Then $dm + \delta' m = d'm + \delta m$.

Let μ and m be the masses of liquid and vapor, respectively, which are originally present; c, the specific heat of the liquid at the temperature t; and hdt, the quantity of heat which must be communicated to unit weight of vapor to raise its temperature from t to $t + dt$., the vapor being preserved, by means of pressure control, at its maximum density. Then the condition that the expansion ad be adiabatic is

$$r\,\delta m - \mu\,c\,dt - m\,h\,dt = 0.$$

Similarly, for the adiabatic expansion, $\overline{bc}$.

$$r\,\delta' m - (\mu + dm)\,c\,dt - (m + dm)\,h\,dt = 0.$$

By eliminating d'm and $\delta' m$ from (17) and the last three equations and neglecting infinitesimals of higher order than the second, there results:

$$\text{Net Heat Expended} = (dr/dt + c - h)\,dm\,dt. \qquad (18)$$

Then, by combination of (17) and (18), we obtain finally, as the analytical expression of the Principle of Equivalence for this case, the relation

$$dr/dt + c - h = A(s - \sigma)\left(\frac{\partial p}{\partial t}\right)_v. \qquad \text{(III)}$$

If, in place of the Principle of Equivalence, we adhere to the Principle of the Conservation of Caloric, we have, instead of (II), the relation

$$dr/dt + c - h = 0 \qquad (19)$$

Now Watt had concluded from insufficient evidence that the heat required to convert unit weight of liquid water at the freezing point into saturated vapor is a constant quantity independent of the pressure (temperature) of the vapor. This opinion, which up to the time of

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Regnault's experiments was generally accepted, was called "Watt's Law" and received the analytical expression:

$$r + \int_0^t c\,dt = \text{constant}$$

or $$dr/dt + c = 0.$$

Combined with (19), this yielded

$$h = 0,$$

a result which was long believed to be true and found expression in the statement that, if a saturated vapor changes its volume in a vessel impermeable to heat, it always remains saturated.

However, Regnault had shown that "Watt's Law" should be replaced by

$$dr/dt + c = 0.305$$

which, according to (19), would mean that $h = 0.305$, i.e. in adiabatic expansion of water vapor, initially saturated, the maximum density is not preserved.

However, Clausius observed that if Regnault's result be combined with the relation (III), expressing the Principle of Equivalence, different results follow. Since the right-hand member of (III) is positive, we can conclude, and only conclude, that $h = 0.305$. We shall see that, by the introduction of Carnot's Theorem, Clausius was able to prove that, for water vapor, h is not zero, but negative, a result simultaneously obtained by Rankine from his hypothesis of molecular vortices. (cf.p.283)

In the case of the founders of the First Law and, to a large extent, Rankine, the great significance of the Energy Principle overshadowed the fact that, in the work of Carnot and Clapeyron, there lay the foundations of a new axiom, not deducible from the Principle of Equivalence. On the contrary, that which most characterizes the genius of Clausius is his recognition that the proof of Carnot's Theorem necessitates the

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introduction of a "Second Law of Thermodynamics."

For, says Clausius, even though the Principle of Equivalence be accepted, " it is still possible that the transfer (of heaat from a higher to a lower temperature) accompanies the consumption (of heat to form work) and also bears a definite relation to the work produced." Indeed, the agreement with experience of many of the results of Carnot's Theorem, respecting the independence, of the maximum work[44] value of heat, of the working body, indicates that such a definite relation does, in fact, exist.

However, with the abandonment of the Principle of the Conservation of Caloric, Carnot's Theorem, that the maximum work obtainable from a Carnot Cycle employing a given heat transfer and working between given temperature limits is independent of the working body--this theorem can obviously no longer be based on the Principle of Excluded Perpetual Motion. Neither does it follow from the Principle of Equivalence. However, said Clausius, it can be shown to follow from the cogent postulate that heat cannot pass from a colder to a warmer body without any other change. For suppose that, in violation of Carnot's Theorem, the maximum efficiency of a heat engine, for given temperature limits, is greater for a cycle employing the working body A than for one employing the working body B. Then if the cycle employing A absorbs heat Q_1 at t_1 operates between t_1 and t_2, develops the heat Q_2 at t_2, and develops the work W, one employing B, absorbing heat Q_1 and t_1, and working between t_1 and t_2, will develop the heat Q_2' at t_2 and will develop the work W', where $W = W' + h$ and $Q_2 = Q_2' - h$, h being a positive quantity. Imagine now that, after the completion of the cycle employing A as working body, we exactly destroy the work W by carrying out a reversed cycle with B which absorbs

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the work $W = W' + h$, which was developed in the cycle with A. For this purpose, the cycle employing B must evidently absorb the heat $Q_2' = Q_2 + h$ at t_2, so that, by the Principle of Equivalence, the heat developed at t_1 is $W + Q_2 + h = Q_1 + h$. At the end of this double process, a quantity of heat h has passed from t_2 to the higher temperature t_1 without any other change occurring, thus violating the postulate referred to.[45] Hence, by adhering to the latter, the proof of Carnot's Theorem is established.

Suppose a Carnot Cycle to operate between temperature limits t and t-dt, differing only infinitesimally from each other. By Carnot's Theorem, the ratio of the work developed to the heat transferred from t to t-dt is a function of the temperature only. Following Clapeyron, Clausius represented it by (1/C)dt, where C is a function of t only.

To obtain the analytical expression of Carnot's Theorem for perfect gases, Clausius again considered the infinitesimal cycle of Figure 12. The heat transferred is rigorously given by the excess of the heat absorbed, $\left(\frac{dQ}{dv}\right)dv$, over the heat expended, given by (3), and is therefore equal to

$$\frac{dQ}{dv}dv - \left[\frac{\partial}{\partial t}\frac{dQ}{dv} - \frac{\partial}{\partial v}\frac{dQ}{dt}\right] dvdt.$$

However, since the second term of this expression is an infinitesimal of the second order, it may be neglected, so the heat transferred becomes simply $\frac{dQ}{dv}\,dv$. Dividing this into the expression (1) for the work developed and placing the quotient equal to dt/C, we obtain

$$\left(\frac{dQ}{dv}\right) = RC/v. \qquad \text{(IV)}$$

The same line of reasoning when applied to an infinitesimal Carnot Cycle, employing saturated vapor as working body (cf. Figure 13), led to

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the famous Clausius-Clapeyron equation. As before, the heat transferred is rigorously equal to the excess of the heat absorbed, rdm, over that expended, given by (17), and is therefore equal to

$$rdm - (dr/dt + c - h)\, dmdt.$$

Neglecting infinitesimals of the second order, this becomes simply rdm. Dividing this into the work developed, given by (16), and again placing the quotient equal to (1/C)dt, we obtain

$$r = C(s - \sigma)\left(\frac{\partial p}{\partial t}\right)_v , \qquad (V)$$

the famous Clausius-Clapeyron equation,

The relation (IV) had already been obtained by Clapeyron in the more general form (cf. p.)

$$\frac{dQ}{dv} = C\left(\frac{\partial p}{\partial t}\right)_v , \qquad (IV')$$

and relation (V) is the same as Clapeyron's equation (18). From Clausius' treatment, however, these relations are seen to be valid only because, when the temperatures, between which the cycle operates, differ only infinitesimally, the work developed, or heat expended, is an infinitesimal of higher order than the heat absorbed, i.e. in this case, Carnot's assumption that all of the heat is transferred from the higher to the lower temperature is mathematically correct (since in the process of infinite summation (integration) whereby these relations are placed in a form applicable in practice, infinitesimals of the second order absolutely vanish). Further, Clausius' exposition reveals, as already pointed out, that the left-hand member of (IV), also (IV'), is not a genuine partial derivative, but simply the limiting value of the ratio $\delta Q / \delta v$ for a particular path, namely, an isothermal one; hence, contrary to the viewpoint of Clapeyron and Holtzmann, these equations yield no general

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expressions for Q.

Combination of the analytical expressions of the Principle of Equivalence with those of Carnot's Theorem led Clausius to additional consequences which further served to confirm the validity of his premises. Dividing equation (IIa) , the analytical expression of the Principle of Equivalence for perfect gases by dv, the temperature being held constant, there results $(\frac{dQ}{dv}) = (\frac{dU}{dv})_t + AR\frac{\alpha + t}{v}$. This, when combined with (III), the expression of Carnot's Theorem for perfect gases, gives $\frac{RC}{v} = (\frac{dU}{dv})_t + AR\frac{\alpha + t}{v}$, or $(\frac{dU}{dv})_t = \left[C - A(\alpha + t)\right]\frac{R}{v}$. Integrating with respect to v, $U = \left[C - A(\alpha + t)\right] R \log v + \phi(t)$, or

$$dU = \left[(dC/dt - A)\, R \log v + B\right] dt + \left[C - A(\alpha + t)\right]\frac{R}{v}\, dv$$

where B is a function of t. Substituting this value of Du in (IIa), we finally obtain

$$dQ = \left[B + R((\frac{RC}{dt}) - A)\log v\right] dt + \frac{RC}{v}\, dv, \qquad \text{(IIc)}$$

this being the general analytical expression of the combination of the two fundamental principles in the theory of heat for perfect gases.

If we introduce the hypothesis that the work developed in isothermal expansion is equivalent to the heat absorbed, we may use (IIb) to conclude that

$$(\frac{dQ}{dv}) = \frac{RA(\alpha + t)}{v}\ , \qquad (19')$$

and this, combined with (IV) yields the important result

$$C = A(\alpha + t), \qquad (2o)$$

thus relating Carnot's funciton to the mechanical equivalent of heat, the coefficient of thermal expansion for perfect gases, and the temperature on the Centigrade scale.

Helmholtz (cf. p.273) had already obtained this equation in a slightly different form by a method of questionable validity, namely, by comparison of equations obtained by Holtzmann and Clapeyron; and Helmholtz had shown

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that values of C calculated from this expression agreed with those determined from the Clausium-Clapeyron equation. Further, the above expression for C was consistent with Thomson's view that the Centigrade temperature was an "absolute scale."

Substituting the above expression for C in the Clausius-Clapeyron equation (V), the latter becomes

$$r = A(\mathcal{L} + t)(s - \sigma)\left(\frac{dp}{dt}\right)_v . \qquad \text{(Va)}$$

Integrating this under the assumptions that r = constant, $s - \sigma = s$, and that the vapor obeys the perfect gas law, $pv = R(\mathcal{L} + t)$, Clausius obtained the well-known expression

$$\log (p/p_1) = \frac{r(t - 100)}{AR(\mathcal{L} + 100)(\mathcal{L} + t)}, \qquad (21)$$

where p_1 is the vapor pressure at 100°C. This formula agreed with an empirical formula already advanced by Young in 1820, namely $\log p = A + B/t$, where A and B are constants, and, very approximately, with one which Rankine in 1849 had found to express the results of experiments, namely, $\log p = \mathcal{L} - \beta/\theta^n - \gamma/\omega^2$, $\mathcal{L}$, β, and γ being characteristic constants.

By writing equation (Va) in the form

$$\frac{\mathcal{L} r}{(\mathcal{L} + t)^2 \frac{1}{p}\left(\frac{dp}{dt}\right)_v} = Ap\frac{\alpha}{\mathcal{L} + t}(s - \sigma), \qquad (22)$$

Clausius was led to an experimental test of the amount of deviation of saturated vapors from the perfect gas law. For, since the specific volume of the liquid is very small in comparison with that of the vapor, the right-hand member of the above equation should nearly equal to a constant, namely, $AR\mathcal{L}$, provided the vapor is a perfect gas. The actual value of this member, in the case of saturated steam, for a series of temperatures, Clausius calculated by employing Regnault's data to evaluate the left-hand member of

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the above equation, thus arriving at the empirical law, expressing the behavior of the saturated vapor, of the general form:

$$Ap(s - \sigma)\frac{\mathcal{L}}{\mathcal{L} + t} = m - ne^{kt}, \qquad (23)$$

where m,n, and k are constants.

We have seen that the analytical expression of the Principle of Equivalence for saturated vapor, together with Regnault's modification of Watt's Law, led Clausius to the conclusions that the specific heat of saturated water vapor is less than 0.305. Introduction of Carnot's Theorem showed this to be actually negative. For combination of equations (III) and (Va) gives

$$\frac{dt}{dt} + c - h\frac{r}{\mathcal{L} + t}, \qquad (23')$$

and substitution of Regnault's data for saturated water vapor into this equation gave negative values for h. h was also found to be negative for carbon bisulfide, chloroform, carbon tetrachloride, and acetone, but was positive for ether. In all cases, h increased with the temperature.

James Thomson's prediction of the lowering of the freezing point of water by pressure had been confused by the retention of the caloric theory (cf. p. 275). Clausius showed this to follow rigorously from the Clausius-Clapeyron equation (Va) written in the form

$$\frac{dt}{dp} = \frac{A(\mathcal{L} + t)(s - \sigma)}{r}, \qquad (24)$$

i.e. $\frac{dt}{dp}$ is negative because $s < \sigma$. Of course, the application of this formula to the equilibrium , solid-liquid, really assumes such a Carnot Cycle as first suggested by James Thomson, I.e. one employing a solid-liquid system as working body.

In a similar way, Clausius regarded equation (III), developed for saturated vapor, as also applicable to the equilibrium, ice-liquid water. If $\left(\frac{dp}{dt}\right)_v$ be eliminated from (III) by substitution from the Clausius-Clapeyron

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(Va), we obtain

$$\frac{dr}{dt} = h - c - \frac{r}{\alpha + t} \qquad (25)$$

where h-c now represents the difference between the specific heats of water and ice. For ice, Clausius found, by substitution of Regnault's data, $\frac{dr}{dt} = 0.81$.

Finally, Clausius showed that his equations for the Principle of Equivalence lead naturally to a calculation of the mechanical equivalent of heat by the method already employed by Mayer. For placing $c = c'/\gamma$, equation (10a) may be written $1/A = kR/(\gamma - 1)c'$. Using the available data on air, Clausius found $1/A = 370$.

On the other hand, the Clausius-Clapeyron equation, solved for 1/A, is

$$1/A = \frac{(\alpha + t)\frac{dp}{dt}}{r}(s - \sigma)$$

which led Clausius to the value $1/A = 437$, which was in much better agreement with Joule's results. The unreliability of the heat capacity data for air was thus indicated.

Clausius' 1850 memoir, whose contents we have just outlined, must certainly be regarded one of the very greatest in the history of thermodynamics. To be sure, practically every one of the particular results obtained by Clausius had already been known, either as an empirical law or as a prediction from the caloric theory or the hypothesis of molecular vortices. The merit of Clausius lies in his demonstration that all of these results rest essentially on two fundamental principles, the Principle of Equivalence and the axiom respecting the impossibility of heat flowing from lower to higher temperatures--which, to be sure, must be supplemented by a knowledge of the specific behavior of physical properties in order to place the general relations in a form capable of experimental verification. This peculiar

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service has justly accorded to Clausius the title, "systematizer of thermodynamics."

At the same time, we must admit that, by the middle of the nineteenth century, the time was obviously ripe for a new development in the theory of heat. The facts were pointing with increasing vigor to the necessity for the acceptance of the Principle of Equivalence and the consequent introduction of a new axiom to serve as proof of Carnot's Theorem. Clausius' 1850 paper was thus as much a product of historical necessity as of his own genius: he was less of a pioneer than Carnot. Indeed, that same historical necessity, combined with necessary insight, was simultaneously and, according to the best evidence, independently leading to essentially the same development in England. The reference, of course, is to the great work of William Thomson, whose position in the history of thermodynamics, relative to that of Clausius, is perhaps best described by Mach's statement that, deprived of the services of either of these investigarors, the development of thermodynamics would still have very probably followed along the same general course which, in fact, it did follow.

C. Thomson and the Postulate of Restricted Conversion.

We have already observed how Thomson, in his "Account of Carnot's Theory", published in 1849, pointed out certain fundamental objections to Carnot's Principle of the Conservation of Caloric. In a letter written to Joule in October, 1850, and published in November of the same year, Thomson appears to have at last given way to these objections and subscribed to the Principle of Equivalence. In this letter, which in the author's collected papers (56) bears the title, "On a Remarkable Property of Steam Connected with the Theory of the Steam Engine," Thomson employed the Principle of Equivalence to explain how Rankine's and Clausius' prediction of the negative heat capacity of

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saturated steam is consistent with the non-scalding property of steam which issues from a high-pressaure boiler into the atmosphere.

This negative heat capacity, says Thomson, requires only that the reversible, adiabatic expansion of saturated steam shall entail the precipitation of a portion of the latter. On the contrary, if, as in the case in question, the saturated steam rushes suddenly from a high pressure and temperature t to atmospheric pressure, the external work is practically zero and the steam contains practically the same "total heat" as before. More specifically, that portion of the "total heat" which , in reversible expansion, is converted into external work, remains, in the case in question, in the gas as freictional heat. It is this extra heat which prevents precipitation and consequent heating.[46]

Only four months after the publication of the letter just cited, Thomson presented his comprehensive exposition of the principles of thermodynamics in the paper, "On the Dynamical Theory of Heat, with Numerical Results Deduced From Mr. Joule 's Equivalent of a Thermal Unit, and M. Regnault's Observations on Steam" (56, Art. XLVIII). Like Clausius, Thomson proceeded from the conviction of the validity of the kinetic theory of heat, Davy's experiment on the melting of ice by friction served, said Thomson, to establish the "dynamical theory of heat," i.e. the hypothesis that heat consists of a motion excited among the particles of bodies and is not due to the presence of an imponderable fluid. This theory had been further confirmed by the experiments of Mayer, and especially Joule. The first formal statement of the Principle of Equivalence of Heat and Work, Thomson attributed to Robert Mayer.[47]

Thomson devoted the first part of his paper to the exposition of the foundations of the theory of the motive power of heat. With Clausius, he

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regarded this whole theory to be founded on the Principle of Equivalence and Carnot's Theorem--two propositions which he expressed separately as follows:

"I. When equal quantities of mechanical effect are produced by any means whatever from purely thermal sources, or lost in purely thermal effects, equal quantities of heat are put out of existence or are generated."

"II. If an engine be such that when it is worked backwards, the physical and mechanical agencies in every part of its motions are all reversed, it produces as much mechanical effect as can be produced by any thermodynamic engine, with the same temperatures of source and refrigerator, from a given quantity of heat."

Thomson credited these propositions to Joule, and to Carnot and Clasuius, respectively. Like the other adherents of the kinetic theory of heat, he considered the first proposition (Principle of Equivalence) to be grounded in the Principle of the Conservation of Vis Viva of pure mechanics, although we shall see that this assumption was not allowed to influence the form of his thermodynamic equations.[48] The second proposition (Carnot's Theorem) Thomson grounded on a new axiom which, he thought, would be generally admitted and which, according to his own testimony, he arrived at before knowing of the proof of Carnot's Theorem advanced by Clausius in his 1850 memoir.

This fundamental axiom Thomson worded as follows: "It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects." Starting with this proposition, which is practically identical to the conclusion arrived at by Carnot sometime before

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his death(cf. p.377) and which Thomson regarded as logically equivalent to Clausius' axiom respecting the impossibility of heat flowing "of itself" from a lower to a higher temperature, Thomson derived Carnot's Theorem by irrefutable logic.[49]

Let B be a reversible engine absorbing heat Q_1 at t_1, and developing heat Q_2' at t_2 and developing work W'. Suppose that, in violation of Carnot's Theorem, there exists another engine A which also absorbs heat Q_1 at t_1 and works between t_1 and t_2, but develops the smaller quantity of heat $Q_2 = Q_2' - h$ at t_2 and develops the larger quantity of work $W = W' + h$, where h is a positive quantity. Suppose that after the engine A has operated to yield the work W and to withdraw the heat Q_1 from the reservoir at t_1, the latter be restored to t_1 by working the reversible engine B backwards (cf. Figure 14). By hypothesis, B, in this operation,will absorb the work $W' = W - h$ and the heat $Q_2' = Q_2 + h$ at t_2. The net result of this double operation would be the conversion of the heat at t_2 into the equivalent quantity of work without any other change. Moreover, the argument is not invalidated by the assumption that all surrounding objects are at the same temperature t_1 of the source, so that the supposed process could consist of the "cooling" of (i.e. withdrawal of heat from) the refrigerator below the temperature of the coldest of the surrounding objects. Since this volume violates the fundamental axiom, the truth of the latter is sufficient for Carnot's Theorem.

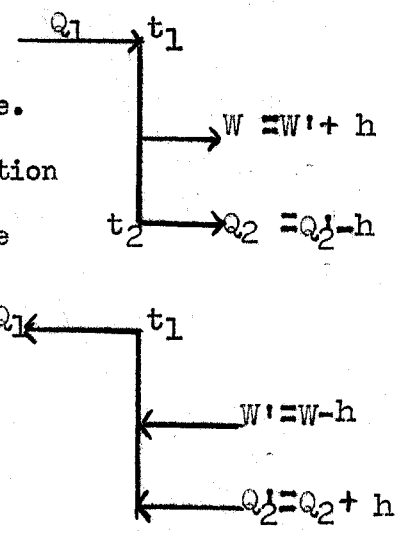

Figure 14

A complete theory of the motive power of heat, said Thomson, would consist in the application of the Principle of Equivalence and Carnot's Theorem to the two known methods of producing work from heat, namely, the electrical method and the method depending on the alterations of volume

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of a body effected through changes of temperature. With respect to the first method, Joule's experiments have demonstrated the applicability of the Principle of Equivalence. The application of Carnot's Theorem to these thermo-electrical phenomena, Thomson stated, probably cannot be attained "without certain limitations."[50]

Both principles may, however, be rigorously applied to the phenomenon of the development of work by means of the alternate volume changes of a body effected through changes of temperature; and it is the development and application of the principles for this case to which Thomson devoted the present paper. As Thomson admitted, this application of the Principle of Equivalence had already been made by Rankine and Clausius, and the correct application of Carnot's Theorem had been shown by Clausius to consist of Carnot's and Clapeyron's unmodified investigation for the case of an engine working betweeen temperatures, infinitely close. If the great Englishman's paper nevertheless constitutes far more than a mere repetition of Clausius' 1850 paper, this is not only because it contains a detailed analytical treatment of the efficiency of the heat engine but also because, as we shall see, Thomson's whole argument is presented in clearer and more general terms.[51]

The greater generality of Thomson's treatment, as compared with that of Clausius, derived mainly from two circumstances: (1) whereas Clausius was content simply to express the two fundamental principles in the special forms which they assumed for perfect gases and saturated vapors, respectively, Thomson set up general equations from which those for perfect gases and saturated vapors followed as particular cases; (2) whereas most of Clausius' equations depended on the validity of the hypothesis relating to the thermal properties of gases, whereby he evaluated Carnot's function, Thomson retained

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the latter, in the majority of his expressions, as an unknown function.

An important factor, contributing to the greater clarity and elegance of Thomson's development, is found in the fact that he derived his expression for the First Law by straight-forward mathematical analysis, thus dispensing, in this case with the somewhat awkward cycles employed by Clausius, following Clapeyron. His results are thus independent of any assumptions regarding the geometrical properties of infinitesimal figures on the p--v diagram--assumptions the establishment of whose validity, strictly speaking, required somewhat involved reasoning.

The general analytical expression of the Principle of Equivalence, Thomson derived in the following manner. Let v, p, and t denote, respectively, the volume, pressure, and temperature of a body whose state is determined by the values of the variables v and t.[52] In an infinitesimal change of state in which the independent variables receive increments dv and dt, the external work will be pdv. Wisely avoiding Clausius' introduction of a separate symbol for that ambiguous quantity, "the total heat of the body," Thomson simply wrote for the heat absorbed, $Mdv + Ndt$, so that the mechanical measure of the total external effect produced becomes

$$(p-JM)dv - JNdt$$

where J is the mechanical equivalent of a unit of heat. For any finite, reversible change, this external effect will be

$$\int\left[(p-JM)dv-JNdt\right] ,$$

the integration being extended along the path corresponding to the series of values assumed by v and t during the change of state. But, for a cyclical process, the Principle of Equivalence requires that this total external effect be zero, which, in turn, requires that the above line

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integral be independent of the path. The necessary and sufficient condition for this, hence the analytical expression of the Principle of Equivalence, is

$$\frac{\partial (p-JM)}{\partial t} = \frac{\partial (-JM)}{\partial v} \qquad (1)$$

Or, since J is an absolute constant,

$$\left(\frac{\partial p}{\partial t}\right)_v = J\left[\left(\frac{\partial M}{\partial t}\right)_v - \left(\frac{\partial M}{\partial v}\right)_t\right] \qquad (2)$$

This expression is seen to be the generalization of Clausius' equation (II) for gases and equation (III) for saturated vapors.[53]

To obtain the analytical expression of Carnot's Theorem, Thomson, like Clausius, resorted to Carnot's device of the infinitesimal cycle. Thomson's derivation is nevertheless more direct than that of Clausius, since the Englishman placed the theorem in the form that the ratio of the work developed to the heat absorbed at the higher temperature is independent of the working body, whereas, following Carnot, Clausius had dealt with the ratio of the work developed to the heat transferred to the lower temperature. The necessity of proving that, in the case of a cycle whose temperature limits are infinitely close, the latter ratio is equal to the former, was hence avoided by Thomson.

Thus suppose the infinitesimal Carnot cycle to operate between the temperature t and $t-\tau$. The work developed is $\left(\frac{\partial p}{\partial t}\right)_v \tau \, dv$ and the heat absorbed at t is Mdv. Hence, the ratio

$$\frac{\left(\frac{\partial p}{\partial t}\right)_v \tau \, dv}{Mdv} \quad \text{or} \quad \frac{\left(\frac{\partial p}{\partial t}\right)_v}{M} \tau$$

must be equal to a function of τ and t which is the same for all bodies. Or, since τ is involved only as a factor, we have, as the analytical expression of Carnot's Theorem,

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$$\frac{\left(\frac{\partial p}{\partial t}\right)_v}{M} = \mu \qquad (3)$$

where μ is a function of t, which is the same for all bodies.

According to Carnot's unmodified theory, the work obtained through the operation of an ideal heat engine is compensated solely by the fall of a definite quantity of heat from the temperature of the source to the temperature of the refrigerator. For an engine absorbing H units of heat and operating between temperatures infinitely close, the work obtained is μ dt: and when the temperatures S, of the source, and t, of the refrigerator, differ by a finite amount, the work, according to Carnot, is

$$H \int_t^S \mu dt, \qquad (4)$$

i.e. given a table of values of μ for different temperatures, the maximum work obtainable from a Carnot cycle absorbing heat H at S and working between S and t, is given, approximately, by the product of H(S-t) into the sum of the values of μ for each of the temperatures, S-1,..., t + 1, and t., divided by the number of such values.

In Part II of his paper, Thomson showed clearly just how these considerations are modified by the introduction of the Principle of Equivalence. To do this, Thomson supposed the given Carnot cycle operating between the temperatures S and t, differing by a finite amount, to be replaced by an infinite sequence of cycles, each operating between temperatures infinitely close, such that the souce of the first is the given source, the refrigerator of the first is the source of the second, the refrigerator of the second is the source of the third, and so on. [54] In any given time, each of these cycles will, according to the Principle of Equivalence, deposit in its refrigerator just as much less heat than was received from its source as is equivalent to the work done. Let t + dt and t denote the temperature limits of such a cycle; and q + dq and q, the quantities of heat which, in a given time are absorbed at t + dt and

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ejected at t, respectively. Then the work developed by the cycle in the given time will be Jdq. As is evident from the derivation of equation (3), this work must also equal to $q\mu dt$. Hence $Jdq = q\mu dt$. Denoting, by H, the heat supplied from the original source at S, and, by R, that ejected to the last refrigerator at T (this being practically the same as the amount of heat supplied to the source at T $+dt$), we obtain, by integration,

$$\log H/R = 1/J \int_T^S \mu dt, \tag{5}$$

or

$$R = He^{-\frac{1}{J}\int_T^S \mu dT}, \tag{6}$$

The total work produced is therefore

$$W = J(H-R) = JH(1-e^{-\frac{1}{J}\int_T^S \mu dt}). \tag{7}$$

To compare this with the expression for W obtained from Carnot's theory, Thomson expanded the exponential by Taylor's Series, obtaining

$$W = (1- \frac{\Theta}{1\cdot 2} + \frac{\Theta^2}{1\cdot 2\cdot 3} -\ldots) H\int_T^S \mu\, dt \tag{8}$$

where $\Theta = 1/J\int_T^S \mu\, dt$. Equation (8) shows that the work always falls short of that given by equation (4) of Carnot's theory, but approaches the latter as the temperature difference between source and refrigerator becomes progressively smaller--a result which had also been evident from Clausius' reasoning. Finally, equation (7) shows that Carnot's statement that greater economy should result by extending the difference between the temperatures of source and refrigerator, still holds, since as S and T differ by a progressively larger amount, the exponential in (7) becomes smaller, and the efficiency becomes correspondingly larger.

Thomson devoted Part III of his paper to the establishment of general relations between the physical properties of all bodies (whose states are determined by v and t) by means of the fundamental equations

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a general expression for M, the latent heat of expansion at constant temperature, not obtained by Clausius.

Replacing M in (10') by its value from (3), Thomson obtained a general expression for that famous quantity, the difference of heat capacities, in the form

$$K-N = \frac{\left(\frac{dp}{dt}\right)_v^2}{\left(\frac{dp}{dv}\right)_t \mu} \qquad (11)$$

For perfect gases, this becomes

$$K-N = \frac{\alpha^2 pv}{\mu (1+\alpha t)^2} \qquad (12)$$

As Thomson noted, if, in accordance with the assumption of the equivalence of external work to the latent heat of isothermal expansion, we also assume Clausius' equation (20), namely

$$\mu = 1/C = J \frac{\alpha}{1+\alpha t}, \qquad (13)$$

then equation (12) reduces to Clausius' equation (7).

From the relations (3) and (11), Thomson deduced a general expression for the change in temperature of a body on (reversible) adiabatic alteration of its volume--a problem already unsuccessfully attacked by Holtzmann. To make the results more convenient for application to liquid and solid media, he first converted equations (3) and (11) into the equivalent ones,

$$M = (1/\mu) \varkappa \underline{e} \qquad (14)$$

and

$$K-N = v \frac{\varkappa \underline{e}^2}{\mu} \qquad (15)$$

by means of the relations

$$\varkappa = -v \left(\frac{dp}{dv}\right)_t$$

and

$$\underline{e} = 1/\varkappa \left(\frac{dp}{dt}\right)_v,$$

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$$\left(\frac{\partial M}{\partial t}\right)_v - \left(\frac{\partial H}{\partial v}\right)_t = 1/J \left(\frac{\partial p}{\partial t}\right)_v \qquad (2)$$

and

$$M = (1/\mu) \left(\frac{\partial p}{\partial t}\right)_v , \qquad (3)$$

expressing the Principle of Equivalence and Carnot's Theorem, respectively. Most of the relations thus obtained by Thomson are generalizations of those already deduced by Clausius for perfect gases and saturated vapors, but some are entirely new.

By elimination of M from the relations (2) and (3), Thomson obtained a general expression for the volume coefficient of a body's heat capacity at constant volume, namely

$$\left(\frac{\partial N}{\partial v}\right)_t = \frac{\gamma}{\gamma t} (1/\mu) \left(\frac{\partial p}{\partial t}\right) - (1/J)\left(\frac{\partial p}{\partial t}\right) . \qquad (9)$$

For perfect gases, for which $pv = R(1 + \alpha t)$, (9) assumes the special form

$$\left(\frac{dN}{dv}\right)_t = \frac{\partial\left\{\frac{\alpha p}{\mu(1+\alpha t)} - \frac{p}{J}\right\}}{\partial t} \qquad (10)$$

On the other hand, if, in (9), we place $(1/\mu)\left(\frac{dp}{dt}\right) = \left(\frac{dQ}{dv}\right)$, $1/J = A$, $p = (R/v)(a + t)$, and assume, with Clausius, that $\left(\frac{dN}{dv}\right)_t = 0$, there results Clausius' equation (19') for perfect gases.

In the case where heat absorption occurs at constant pressure, we have

$$Kdt = Mdv + Ndt$$

where K is the heat capacity at constant pressure. Solving this expression for M, and transforming the result by means of the condition for constant pressure, namely,

$$0 = \frac{\partial p}{\partial v} dv + \frac{\partial p}{\partial t} dt,$$

there results

$$M = - \frac{\left(\frac{dp}{dv}\right)_t}{\left(\frac{db}{dt}\right)_v} (K-N), \qquad (10)$$

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κ and $\underline{e}$ denoting the "reciprocal of the compressibility" and the "coefficient of expansion with heat," respectively. Now the rise in temperature, θ , experienced by a body on adiabatic compression from $v + dv$ to v, must evidently equal to the ratio of the heat, which would have been evolved if the temperature had remained constant, to the heat capacity at constant volume. Then, by (14) and (15), θ is given by

$$\theta = \frac{M dv}{N} = (1/N) \quad \frac{\kappa \underline{e}}{\mu} dv \qquad (16)$$

$$= \frac{\kappa \underline{e}}{\mu K - v \kappa \underline{e}^2} dv \qquad (17)$$

In these relations κ is essentially positive, whereas the sign of $\underline{e}$ is the same as that of $(\frac{dp}{dt})_v$. From (16), Thomson was thus able to deduce that for a body, such as water between its freezing point and its maximum density, which tends to contract with rise in temperature $(\frac{dp}{dt} < 0)$, a small adiabatic compression will cause not a rise, but a fall in temperature. Equation (17), Thomson thought could be written in the approximate form

$$\theta = \frac{\kappa \underline{e}}{\mu K}, \qquad (18)$$

since, for solids and liquids, $v \kappa \underline{e}^2$ should be very small compared to μK.

Thomson next applied the fundamental relations (2) and (3) to a one-component system, consisting of a mass x of one phase and a mass $(1-x)$ of another phase containing less latent heat than the first. To fix the ideas, Thomson supposed the two phases to be a liquid and its saturated vapor, respectively, although he pointed out that the considerations apply equally well to the equilibrium of a solid and a liquid, or a solid and a gas.

If v denote the volume of the whole system and σ and s, the volumes

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of unit weight of liquid and vapor, respectively, we shall have

$$\sigma(1-x) + sx = v. \tag{19}$$

If r be the latent heat of unit weight of the vapor, c the specific heat of the liquid, and h the specific heat of saturated vapor, we shall have

$$Mdv = r\frac{\partial x}{\partial v}dv \tag{20}$$

and

$$Ndt = c(1-x)dt + hxdt + r\frac{\partial x}{\partial t}dt. \tag{21}$$

Also, by (19), we have

$$(s-\sigma)\frac{\partial x}{\partial v} = 1 \tag{22}$$

and

$$(s-\sigma)\frac{\partial x}{\partial t} + (1-x)\frac{\partial \sigma}{\partial t} + x\frac{\partial \sigma}{\partial t} = 0. \tag{23}$$

Equations (20) and (22) give

$$M = \frac{r}{s-\sigma} \tag{24}$$

whereas (21) and (23) yield

$$N = C(1-x) \quad hx - r\frac{(1-x)\frac{\partial \sigma}{\partial t} + x\frac{\partial \sigma}{\partial t}}{s-\sigma} \tag{25}$$

Having evaluated M and N for this case, the forms which the two fundamental principles assume are readily deducible . Substituting the value of M in (3), Carnot's Theorem assumes the form

$$\mu = \frac{(s-\sigma)\frac{dp}{dt}}{r}, \tag{26}$$

the differential coefficient being written as a total derivative since, as Thomson observed, p is uniquely determined by t alone in the case under consideration. Thomson's equation (26) is, of course, the famous Clapeyron-Clausius equation already obtained in the same form by Clapeyron (cf. his equation (18) and Clausius (cf. his equation (V)).

To deduce the form which the Principle of Equivalence assumes in the case in question, we need to evaluate the coefficients $(\frac{dM}{dv})_t$ and $(\frac{dN}{t})_v$. From (24),

$$(\frac{dM}{dv})_t = \frac{1}{s-\sigma}\frac{\partial r}{\partial t} - \frac{r}{(s-\sigma)^2}\frac{\partial (s-\sigma)}{\partial t}$$

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and, from (25),

$$\left(\frac{dN}{dt}\right)_v = \left(h-c-r\,\frac{\frac{\partial s}{\partial t}-\frac{\partial \sigma}{\partial t}}{s-\sigma}\right)\frac{\partial x}{\partial v}$$

$$= \left[\frac{h-c}{s-\sigma} - \frac{r}{(s-\sigma)^2}\right]\frac{\partial (s-\sigma)}{\partial t}.$$

By substituting of these expressions in equation (2), we obtain, as the analytical expression of the Principle of Equivalence for this case,

$$\frac{\frac{\partial r}{\partial t} + c - h}{s-\sigma} = (1/J)\,\frac{dp}{dt}, \qquad (27)$$

this being identical to Clausius' equation (III) which the latter obtained by a graphical method.

Eliminating $\frac{dp}{dt}$ from (26) and (27), Thomson obtained for the analytical expression of the combination of the two fundamental theorems for this case, the relation

$$\frac{\partial r}{\partial t} + c-h = \frac{r\mu}{J}. \qquad (28)$$

If we introduce Clausius' hypothesis expressed by Thomson's equation (13), Thomson's relation (28) becomes identical to the German's equation (23').

Clausius had already pointed out that if μ were known, equation (26) could be employed to calculate the amount by which the freezing point of water should be lowered by increasing the pressure. In fact, by taking for his value of μ that calculated from the formula

$$\mu = \frac{J\alpha}{1+\alpha t}, \qquad (29)$$

which corresponds to the hypothesis that the work done in isothermal compression of a perfect gas is equivalent to the heat developed, Clausius obtained the result that the freezing point of water is lowered by 0.00733° on increasing the pressure by one atmosphere. On the other hand, if μ be calculated from equation (26) by introduction of Regnault's data on steam, along with the assumption that its density conforms to the perfect gas law, and if this value of μ be used in the calculation of the freezing

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point depression, the latter is found to be 0.0075. Thomson's experimental determination of the depression had not been sufficiently precise to provide any basis for preference between these values and hence did not settle the question of whether "Mayer's Hypothesis," represented by the relation (29), was false or whether, on the other hand, the discrepancy was due to the departure of saturated vapor from perfect behavior.

Again, if h, the specific heat of saturated vapor, be calculated from (28), the result depends, of course, on the value employed for μ. Clausius, adopting the hypothesis (29), had obtained one series of values for the specific heat of saturated steam, and Thomson, using values of obtained from Regnault's data on steam in the manner already described, now obtains another series. Although the two series of values are fairly close, their divergence is hardly negligible, as the following table, taken from Thomson's paper, shows:

t	- h (according to Thomson)	-h (according to Clausius)
0	1.863	1.916
50	1.479	1.465
100	1.174	1.133
150	0.951	0.879
200	0.780	0.676

Here again, the sufficiently precise determination of the values of h would have established one or the other of the two series of values of as correct; however, no experimental data for h were available.

To be sure, Clausius had deduced a formula (eqn.(23), p. 310) in which the density of saturated steam was represented as deviating very considerably from the perfect gas law. However, as Thomson points out, Clausius' derivation of this formula depended on the assumed truth of "Mayer's Hypothesis"; hence, the formula contributed nothing to the solution of the problem (of the calculation of μ.

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In Part IV (published in April, 1851) of his paper, Thomson turned to the critical examination of "Mayer's Hypothesis." To begin with, Thomson showed that, because the formulae for the heat of isothermal expansion, obtained from Carnot's unmodified theory, are valid, the relation (4) of his "Account of Carnot's Theory" (cf. p.) between the work W done in the isothermal compression of a perfect gas and the heat developed, namely,

$$H = \frac{\mathcal{L}}{\mu (1+\alpha t)} W, \qquad (30)$$

still holds,

By assuming the coefficient of W in (30) to be simply J, Joule had obtained values of the mechanical equivalent in good agreement with values obtained by other methods. Also his free expansion experiments had further indicated the heat H of (30) to be truly the equivalent of W. Hence, as early as 1848, he had suggested to Thomson the formula (29) for μ, since this would reduce (30) to the desired relationship, $H = W/J$.

However, as Thomson pointed out, Joule's experiments really serve to establish the validity of "Mayer's Hypothesis" (29) only at the temperature at which they were carried out, namely 50^0 —60^0 F. The question of the general validity of formula (29), which Clausius had assumed without any specific justification (cf. p. 386), thus still remained unanswered for want of experimental data.

Accurate measurements of the work done and the heat developed in the isothermal compression of a gas are difficult to carry out, and, because of the smallness of the heat capacities of gases, compared to that of their containers, the same may be said of measurements of the free expansion effect. Hence, it is most significant that Thomson now proposed a new experimental method for the determination of the validity of "Mayer's

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Hypothesis"--a method permitting of much greater rapidity and accuracy than the two already used by Joule. This new method is the one based on the now famous "Joule-Thomson experiment."

Imagine, said Thomson, a long tube (figure 15) equipped with a porous plug P and pistons A and B. Suppose that, by gradual motion of the piston A, gas at the uniform pressure p_1 and temperature t be forced through the plug P and subsequently allowed to expand and force back the piston B at the lower pressure p_2. In the portion of the tube containing the plug and including the region immediately to the right of it, the pressure of the gas will not be uniform; beyond this region, however, the gas will have acquired the uniform pressure p_2.

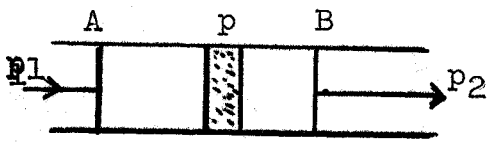

Figure 15

We wish to find an expression for H, the heat evolved from that portion of the tube containing the plug and the remainder of the tube, in order that, when a volume v_1 of the gas (measured at the in-going pressure p_1) is forced through the apparatus, the temperature of the plug and the remainder of the tube shall remain at t. If the frictional effects resulting from the passage of the gas through the plug had not been present and the gas had been simply subject to isothermal expansion from p_1, v_1 to p_2, v_2, heat would have been supplied equal to

$$\int_{v_1}^{v_2} M dv$$

or, by (3)

$$1/\mu \int_{v_1}^{v_2} \left(\frac{dp}{dt}\right)_v dv.$$

The net work done by the pistons on the gas, hence dissipated as frictional heat, is

$$W = \int_{v_1}^{v_2} p dv + p_1 v_1 - p_2 v_2 .$$

The net heat evolved H must equal to the excess of the heat equivalent to

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This work over that previously found to be absorbed when the mechanical effect is all external, i.e. when the expansion is reversible, Then

$$H = 1/J\left[\int_{v_1}^{v_2} pdv + p_1v_1 - p_2v_2\right] - 1/\mu \int_{v_1}^{v_2} \left(\frac{dp}{dt}\right)_v dv. \qquad (30')$$

For perfect gases, $p_1v_1 = p_2v_2$, and

$$W = \int_{v_1}^{v_2} pdv = p_0v_0 (1+\alpha t) \int_{v_1}^{v_2} \frac{dv}{v} = p_0v_0(1+\alpha t) \log v_2/ v_1, \qquad (31')$$

so that $$\int_{v_1}^{v_2} \left(\frac{dp}{dt}\right)_v dv = \frac{d}{dt}\int_{v_1}^{v_2} pdv = \left(\frac{dW}{dt}\right)_v = \alpha p_0v_0 \log v_2/v_1 = \frac{\alpha}{1+\alpha t} W.$$

Hence, the expression for the heat evolved becomes simply

$$H = \left(1/J - \frac{\alpha}{\mu (1+\alpha t)}\right) W. \qquad (31)$$

Therefore, if the gas conforms to "Mayer's Hypothesis," expressed by (29), (31) requires that

$$H = 0, \qquad (32)$$

i.e. if the whole process be carried out <u>adiabatically</u>, the temperature of the gas after passing through the plug and attaining the uniform pressure p_2, will again be t. In any case, so long as the gas is perfect, (30') and (31) give

$$\mu = \frac{\frac{J\alpha}{1+\alpha t}}{1 - J\left(H/p_2v_2 \log p_1/p_2\right)}, \qquad (33)$$

I.e. the method may be employed for the calculation of μ whether "Mayer's Hypothesis" be true or not.

The concept of energy or "force", as a substance whose identity persists throughout the manifold variety of phenomenal change, played, as we know, an all-important part in the thought of the precursors and founders of the First Law of Thermodynamics. Clausius, in his analytical formulation of the Principle of Equivalence for perfect gases, had introduced a definite mathematical symbol for this concept (his U function, cf. p.299), but had made no further use of it. The credit for introducing this function into all of the general equations of thermodynamics and for pointing out the advantages resulting from this introduction goes to Thomson. This noteworthy contribution constituted Part V of his 1851 paper and was entitled

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" On the Quantities of Mechanical Energy contained in a Fluid in Different States, as to Temperature and Density."

"The mechanical energy of a body in a given state," Thomson defined as the "mechanical value (equivalent) of the effects the body would produce in passing from the state in which it is given, to a standard (reference) state, or the mechanical value of the whole agency that would be required to bring the body from the standard state to the state in which it is given." That the "mechanical energy" so defined has a definite value independent of the manner in which the change from standard to given state is effected, is a consequence of the Principle of Equivalenee.

As before Thomson confined his treatment to the case of a body whose state is determined by the volume v and temperature t. For an infinitesimal change of state the mechanical value of the heat absorbed is $J(Mdv + Ndt)$ and the work done is pdv. The Principle of Equivalence requires that the net mechanical value of heat absorbed and work done be equal to the differential of a function of v and t, namely, of the mechanical energy E. Hence

$$dE = J(Mdv + Ndt) - pdv \qquad (34)$$

is the expression of the Principle of Equivalence. This is tantamount to the equations

$$\left(\frac{dE}{dv}\right)_t = JM - p \qquad (35) \qquad \text{and} \qquad \left(\frac{dE}{dt}\right)_v = JN . \qquad (36)$$

By making use of the fundamental relation, $\frac{d^2E}{dv\,dt} = \frac{d^2E}{dt\,dv}$, E may be eliminatwd between (35) and (36) to yield

$$\left(\frac{dp}{dt}\right)_v = J\left[\left(\frac{dM}{dt}\right)_v - \left(\frac{dN}{dv}\right)_t\right], \qquad (37)$$

which is Thomson's original expression of the Principle of Equivalence.[55]

"The value of J being known," says Thomson, "equations (35) and (36) may be used for determining the mechanical energy of a particular fluid mass

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in different states , from special experimental data regarding its pressure and thermal capacities, but not necessarily comprehending the values of each of these elements for all states of the fluid. The theory of the integration of functions of two independent variables will, when any set of data are proposed, make it manifest whether or not they are sufficient, and will point out the methods, according to the forms in which the data are furnished, to be followed for determining the value of E for every value of v."

In some cases, the data may be such that the expression for E may be written down without resort to integration. Thus let the standard state for water be the liquid state at 0°C. Then the value of E for a unit weight of fluid mass consisting of liquid water and saturated vapor at the temperature t and total volume v is equal to the mechanical value of the heat required to raise the unit weight of liquid from 0° to t plus that of the heat required to convert the weight $\frac{v - \sigma}{s - \sigma}$ of it into vapor, diminished by the work of expansion at the pressure p from σ to v. Therefore

$$E = J(ct + r\frac{(v - \sigma)}{(s - \sigma)} - p(v - \sigma). \qquad (38)$$

The relations (24) and (25) for M and N are obtainable from (35 and (36) by differentiation of (38).[56]

The fundamental equation (3) , expressing Carnot's Theorem, when combined with (35) yields the result:

$$(\frac{dE}{dv})_t = \frac{J}{\mu}(\frac{dp}{dt})_v - p. \qquad (39)$$

Integration of (39) yields the expression for E involving an arbitrary function of t. Supposing the law of pressures, hence $(\frac{dp}{dt})_v$, also J and μ to be known, this arbitrary function may be evaluated from a knowledge of E for all temperatures at a given constant volume, or what is the same thing, from a knowledge of the heat capacity of the body at constant volume for a particular

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volume and all temperatures. Hence, we may conclude that, given values of J and μ, the "mechanical energy" of a fluid body in any state may be calculated from determinations of its pressure for all temperatures and volumes and its heat capacity for a particular volume and all temperatures.

To illustrate, Thomson employed equation (39) to obtain an expression for the energy E of a perfect gas. Let us take as the standard state of zero energy that for which the pressure, volume, and temperature have the values p_o, v_o, t_o, respectively. From the perfect gas law, $p = \frac{p_o v_o}{v}(1+\alpha t)$, we have $\left(\frac{dp}{dt}\right)_v = \frac{p_o v_o \alpha}{v}$. Whence

$$\int_{v_o}^{v}\left(\frac{J}{\mu}\frac{dp}{dt} - p\right)dv = p_o v_o\left[\frac{J\alpha}{\mu} - (1+\alpha t)\right]\log(v/v_o).$$

If we denote by N_o the value of the heat capacity at the constant volume v_o regardless of the temperature, the expression for the energy of the gas in the state (v,t) will then be

$$E = p_o v_o\left[\frac{J\alpha}{\mu} - (1+\alpha t)\right]\log(v/v_o) + J\int_o^t N_o dt. \qquad (40)$$

Suppose now that we have obtained by the above methods a table of values of E for all values of v and t, i.e. for all states of a body. Let us see how such a table might be employed, along with auxiliary data, for the calculation of the pressure p, the heat capacity at constant volume N, and the heat capacity at constant pressure K. Regarding (39) as a differential equation for p with respect to t, integration gives for the value of p in the state (v, t),

$$p = e^{\frac{1}{J}\int_o^t \mu dt}\int_o^t \mu\frac{dE}{dv}e^{-\frac{1}{J}\int_o^t \mu dt}dt + \psi(v)\,e^{\frac{1}{J}\int \mu dt} \qquad (41)$$

where the constant $\psi(v)$ may be determined from a knowledge of the pressure for all volumes and a particular temperature. Also, from (36), we have

$$N = \frac{1}{J}\left(\frac{dE}{dt}\right)_v. \qquad (42)$$

Again, if we eliminate μ from (12), by means of (3), there results

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$$K = N + \frac{\left(\frac{dp}{dt}\right)_v}{-\left(\frac{dp}{dv}\right)_t} M$$

which , by viftue of (35) and (42), becomes

$$K = \frac{1}{J}\left(\frac{dE}{dt}\right)_v + \frac{1}{J}\left[\left(\left(\frac{dE}{dv}\right)_t + p\right)\frac{\left(\frac{dp}{dt}\right)_v}{\left(\frac{dp}{dv}\right)_t}\right] . \qquad (43)$$

From equations (41), (42), and (43), we infer that, if, besides our table of energy values, we know the pressure for all volumes and a particular temperature, we have sufficient data for the calculation of the pressure and the two heat capacities in all states. Thus Thomson was led to remark that "it is not improbable that such a table (of values of E), and a similar one for the pressure, may be found to be the most convenient expression for results of complete observations on the compressibility , the law of expansion by heat, and the thermal capacities of a vapor or gas."

As further illustration of the use of the above general expressions for p, N, and K, Thomson applied them to a perfect gas. Substitution of the expression (40) for the energy of a perfect gas into (41) gives

$$p = \frac{p_o v_o}{v}(1+\alpha t) + \chi(v) e^{\left(\frac{1}{J}\int \mu\, dt\right)}, \qquad (44)$$

i.e. a fluid whose pressure is expressed by (44) has the same expression for its energy as one obeying the perfect gas law. If we evaluate the coefficients $\left(\frac{dE}{dv}\right)_t$ and $\left(\frac{dE}{dt}\right)_v$ by differentiation of (40), substitution converts (42) and (43) into

$$N = N_o + \left[\frac{1}{J} p_o v_o \log (v/v_o)\right] \frac{d\left(\frac{J\alpha}{\mu} - (1+\alpha t)\right)}{dt} \qquad (45)$$

and

$$K = N_o + \left(\frac{1}{J} p_o v_o \log v/v_o\right) \frac{d\left(\frac{J\alpha}{\mu} - (1+\alpha t)\right)}{dt} + \frac{\alpha^2 p_o v_o}{\mu (1+\alpha t)} . \qquad (46)$$

Equation (45) shows that , unless "Mayer's Hypothesis" (29) holds, the heat capacity at constant volume of the same gas at the same temperature varies with the density, said variation being proportional to the decrement in the

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logarithm of the density. Equation (46) combined with (45) shows the relation

$$K = N_o + \frac{\alpha^2 p_o v_o}{\mu(1+\alpha t)} \qquad (47)$$

to be independent of "Mayer's Hypothesis." (Here N_o is the value of N for $v = v_o$, and $t = t$.)

Finally, by the introduction of the energy function Thomson showed that the theory of the "Joule-Thomson experiment " admits of a more precise and comprehensive treatment. Suppose a unit weight of gas before entering the plug (cf. Figure 15) occupies the volume v_1 and has the pressure p_1 and the temperature t_1, and that, after having passed through the plug, the corresponding vaues of these variables are v_2, p_2, and t_2. If Q be the heat emitted from the tube by the passage of this unit weight of gas through the plug, and S the mechanical equivalent of any sound produced, the net mechanical value of all external effects is $JQ + S + p_2v_2 - p_1v_1$. This must equal to the decrease in the energy of the fluid, so that

$$E(v_2, t_2) = E(v_1, t_1) - (JQ + S + p_2v_2 - p_1v_1). \qquad (48)$$

Regarding the sound effect as negligible and supposing the tube to be thermally insulated from the surroundings, this reduces to

$$E(v_2, t_2) = E(v_1, t_1) - (p_2v_2 - p_1v_1). \qquad (49)$$

If the temperatures on the two sides of the plug are found to be the same ($t_1 = t_2$), the perfect gas law then requires that $p_2v_2 = p_1v_1$, so that (49) becomes simply

$$E(v_2, t) = E(v_1, t), \qquad (50)$$

i.e. "Mayer's Hypothesis," in conjunction with the perfect gas law, is seen to require that the energy of a gas be independent of its volume.[57]

The actual experimental investigation of the behavior of air, carbon dioxide, and hydrogen when subjected to the "Joule-Thomson experiment" was carried out by Joule and Thomson together, the results being comprised in a

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series of papers entitled, "On the Thermal Effects of Fluids in Motion", published from 1852 to 1862 (56 , p. 333). In the case of air and carbon dioxide the gas was found to be decidedly cooler after passing adiabatically through the plug. Moreover, the cooling effect was found to increase in proportion to the difference in pressure on the two sides of the plug. Also, for a given pressure difference, the cooling effect was found to decrease as the temperature increased. At 15°C. the cooling effect amounted to 1.15°C. for carbon dioxide and 0.26°C. for air , for each atmosphere difference in pressure. In the case of hydrogen, the temperature difference was so small as to render it uncertain; in the earlier investigations the results seemed to indicate a very small cooling effect, but later experiments, reported in 1862, pointed to the conclusion that this gas, on passage through the plug, is actually heated by a small amount. (56, p. 423)

In the theoretical portion of the paper, which obviously must have been written by Thomson, the conclusions to be drawn from these data are presented in a masterly fashion. Let p_1, v_1, and t denote the pressure, volume and temperature of unit weight of gas before passing through the plug. After passing through the plug, the pressure falls to say p_2. Let v_2 denote the volume which unit weight of gas would occupy at the pressure p_2, if the temperature had remained at t. The external work done on the pistons by this unit weight of gas would be $p_2v_2 - p_1v_1$. Denoting by w the whole work done by the gas, the work dissipated as frictional heat in passing through the plug must equal to $w - (p_2v_2 - p_1v_1)$. Let H denote the latent heat of expansion, i.e. the heat which would have been absorbed in isothermal expansion from p_1, v_1 to p_2,v_2. The cooling effect (per unit difference in pressure) occurring when the process is conducted adiabatically corresponds to the heat $K\,\delta\,(p_1 - p_2)$ which would have to be supplied to keep the temperature constant (K being the specific heat

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of the gas) and must equal to the excess of the latent heat of reversible expansion over the heat generated by friction. Hence

$$K\delta(p_1 - p_2) = H\,(1/J)(w - (p_2v_2 - p_1v_1)). \quad (51)$$

This relation clearly shows that if "Mayer's Hypothesis" , $H = w/J$, holds (i.e. if the energy of the gas is independent of its volume) and the perfect gas law, $p_2 v_2 = p_1 v_1$, is true, then the thermal effect δ must be zero. The converse proposition, however, does not follow, i.e. the vanishing of δ might result from the fact that the deviation from "Mayer's Hypothesis" exactly balanced the deviation from the perfect gas law. Again, the above equations point clearly to the possibility of a heat ing effect, as was later found in the case of hydrogen.

The data of the Joule-Thomson experiments served to evaluate the left-hand member of the above equation, whereas Regnault's investigations on the compressibility of gases gave the value of $p_2v_2 - p_1v_1$. Joule and Thomson were thus able to calculate that at 15°C. the mechanical equivalent of the heat evolved by the isothermal compression of hydrogen exceeded only by 1/630 that of the work done;[58] in the case of air the heat exceeded by 1/174 the work, whereas, for carbon dioxide, the heat exceeded the work by 1/32. Thus, of these gases, hydrogen conformed most closely to "Mayer's Hypothesis." Since , in the case of air and carbon dioxide, the data revealed that both the cooling effect, as well as the deviation from the perfect gas law, increases with decreasing temperature, it was concluded that these gases approach conformity with "Mayer's Hypothesis" as the temperature is raised.

The all-important result of these investigations was the conclusion that the formula (29) , namely, $\mu = J\frac{\alpha}{1+\alpha t}$, is almost exactly correct for hydrogen(since both its cooling effect and its deviation from the perfect gas law are small), and is very approximately true for air. However, as

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already observed, values of μ calculated from this relation deviated considerably from values calculated from the Clausius-Clapeyron equation on the assumption that the density of saturated steam is calculable from that of the superheated vapor by means of the perfect gas law. The inevitable deduction was that saturated steam deviated very considerably from perfect behavior, a conclusion already drawn by Clausius from insufficient evidence (cf. p. 309). Substituting values of μ calculated from "Mayer's Hypothesis" into the Clausius-Clapeyron equation and regarding the density of the saturated steam as the unknown, Joule and Thomson were thus led to a new formula for the latter quantity.

We have seen that, even before he abandoned the caloric theory, Thomson recognized that Carnot's Theory provided the basis for a temperature scale independent of the specific properties of any particular substance. His failure, during the next six years, to revert to this subject of "absolute temperature," we may attribute to the prevalent uncertainty regarding the correct values of μ. Now that the Joule-Thomson experiments had largely removed this uncertainty, the time was ripe for a resumption of this line of thought.

Accordingly, in Part II (published in June, 1854) of Joule and Thomson's paper, "On the Thermal Effects of Fluids in Motion," we find several sections, obviously the work of Thomson, devoted to the definition and methods of determination of such a temperature scale.

According to Carnot's unmodified theory, the work developed by a Carnot cycle, absorbing unit heat at t° and working between t° and $(t-1)^{\circ}$, is compensated solely by the transfer of the unit of heat from t° to $(t-1)^{\circ}$;

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and the value of μ (t), the ratio of the work developed to the heat transferred, is the same for all working bodies. It thus appeared possible, by introducing a universal temperature scale T for which dW/dT = constant, to make the work value of a unit of heat per unit fall of temperature independent of the temperature. Thus it was this independence which Thomson, while still under the influence of the caloric theory, considered to be an essential characteristic of an "absolute temperature" scale. (cf. p. 274)

In Carnot's theory as modified by the Principle of Equivalence the function μ(t) is still a quantity which is the same for all bodies. Hence, if the values of μ or any function of it are taken as temperature numbers, the resultant scale will be absolute in the sense that it is independent of the specific properties of any particular substance, although it will not necessarily be absolute in the sense that the work developed by a Carnot cycle absorbing unit heat at the absolute temperature T^{o} and operating between T^{o} and $(T-1)^{o}$ shall be independent of T.[59] It is convenient to define T, the absolute temperature, by the linear realtion,

$$T = J/\mu , \qquad (52)$$

since, for a gas conforming to "Mayer's Hypothesis" (29), the absolute temperature then reduces to

$$T = 1/\alpha + t, \qquad (53)$$

i.e. the absolute temperature then differs from the Centigrade scale of the perfect gas thermometer only by a constant, namely, the reciprocal of the thermal coefficient of expansion measured according to the latter scale, of a gas conforming to "Mayer's Hypothesis."

If we apply the definition (53), along with Mayer's Hypothesis (29), to the expression (6) relating the heat H absorbed from the source (at S°C.) to the heat R given up at T°C. by a Carnot cycle, there results an alternative

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definition of the absolute temperature. For with these substitutions, (6) becomes

$$\frac{R}{H} = \frac{1+\alpha T}{1+\alpha S} = \frac{TR}{T_S} \qquad (54)$$

T_R and T_S denoting the absolute temperatures of refrigerator and source, respectively. Thomson thus arrived at the conclusion that any temperature scale is an absolute scale if it conforms to the following condition: "If any substance whatever, subjected to a perfectly reversible cycle of operations, takes in heat only in a locality kept at a uniform temperature, the temperature of these localities are proportional to the quantities of heat taken in or emitted at them in a complete cycle of operations."

If we wish to proceed independently of "Mayer's Hypothesis," we may, by means of the definition (52), replace μ by T in all of the general equations of thermodynamics, whereupon the latter become equations for T in terms of the measurable properties of bodies, just as they were formerly regarded as determining μ. Thus equations (9) and (11), by means of the relation (52), become, respectively,

$$JK-JN = \frac{T\left(\frac{dp}{dT}\right)^2}{-\frac{dp}{dv}} \qquad (55)$$

and

$$\frac{d(JN)}{dv} = T\left(\frac{d^2p}{dT^2}\right). \qquad (56)$$

Also the relation (30') for the Joule-Thomson thermal effect becomes

$$H = 1/J\left[\int_{v_1}^{v_2}\left(T\frac{dp}{dT} - p\right)dv + (p_2v_2 - p_1v_1)\right]. \qquad (55')$$

Any of these relations determine T as a function of p except for an arbitrary constant of integration. The assignment of a value to this constant corresponds to the choice of the unit of absolute temperature. Thomson observed that the choice may be made in either of two ways: (1) we may

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assign a definite numerical value to the absolute temperature of a reference state; (2) we may assign a definite number of absolute degrees to the interval between two reference states.

5. THE ENTROPY CONCEPT AND THE DISSIPATION LAW.

A. The Generalization of Carnot's Theorem.

A most important consequence of the absolute temperature concept was the fact that its introduction rendered possible a new analytical formulation of the Second Law of Thermodynamics. Thomson himself was the first to see this. In the introduction to his paper,"Thermo-Electric Currents" (published in May, 1854 as Part VI of "The Dynamical Theory of Heat"), he advanced the following statement of the Second Law: "If every part of the action (of a cyclic process), and all its effects, be perfectly reversible, and if all the localities of the system by which heat is either emitted or taken in, be at one or the other of two temperatures, the aggregate amount of heat taken in or emitted at the higher temperature must exceed the amount emitted or taken in at the lower temperature always in the same ratio when these temperatures are the same, whatever be the particular substance or arrangement of the material system and whatever be the particular nature of the operations to which it is subject." This proposition is, of course, no more than Carnot's Theorem stated in terms of the ratio of the quantity of heat exchanged at one temperature to that exchanged at the other temperature, instead of in terms of the ratio of the work developed to one of these quantities of heat. The importance of the new form of statement is that it may be readily expressed, analytically, in terms of the absolute temperatures of source and refrigerator; in fact, by (54), the ratio of the heat absorbed at the higher temperature to that developed at the lower temperature equals simply to the ratio of the respective temperatures, expressed on the absolute scale.

Thomson now made the important observation that if Q_1 denote the

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heat absorbed at T_1 and Q_2, that absorbed at the lower temperature T_2, equation (54) may be expressed in the form,

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0. \qquad (56')$$

In generalizing equation (56') so as to make it applicable to a reversible cycle exchanging heat at any finite number of temperatures, Thomson cleared the way for the formulation of the entropy concept. The above statement of the Second Law (Carnot's Theorem), said Thomson, is equivalent to the proposition that "if a material system experience ... a complete cycle of operations of a perfectly reversible kind, the quantities of heat which it takes in at different temperatures are subject to a linear equation, of which the coefficients are the corresponding values of an absolute function of the temperature." If absolute temperature be defined as the quotient of the mechanical equivalent of heat by Carnot's function μ, the "absolute function of the temperature" referred to is simply the reciprocal of the absolute temperature, as is evident from (56'), which is the expression of the theorem for the case where the heat exchanges occur only at two temperatures. If the quantities of heat, $Q_1, Q_2, Q_3 \cdots Q_{n-1}, Q_n$ be absorbed at the absolute temperatures of $T_1, T_2, T_3, \cdots, T_{n-1}, Tn$, the analytical expression of the above proposition is hence:

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} + \cdots + \frac{Q_{n-1}}{T_{n-1}} + \frac{Q_n}{T_n} = 0. \qquad (57)$$

To establish this theorem, Thomson imagined the given reversible cycle to be supplemented by a sequence of n-2 cycles, the first of which develops the heat Q_1 at T_1 and absorbs the corresponding

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quantity $\frac{T_2}{T_1} Q_1$ at T_2; the second develops the heat $T_2 \frac{Q_1}{T_1} + Q_2$ at T_2 and absorbs the corresponding quantity $T_2(\frac{Q_1}{T_1} + \frac{Q_2}{T_2})$ at T_3; the third develops the heat $T_3(\frac{Q_1}{T_1} + \frac{Q_2}{T_2}) + Q_3$ at T_3 and absorbs the heat $T_4(\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3})$ at T_4; and so on, the last developing the heat $T_{n-2}(\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \cdots + \frac{Q_{n-3}}{T_{n-3}}) + Q_{n-2}$ at T_{n-2} and absorbing the heat $T_{n-1}(\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \cdots + \frac{Q_{n-2}}{T_{n-2}})$ at T_{n-1}. The net result of this whole supplementary sequence of cycles is the development of the heat Q_1 at T_1, Q_2 at T_2, $\cdots$ Q_{n-2} at T_{n-2}, and the absorption of the heat $T_{n-1}(\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \cdots + \frac{Q_{n-2}}{T_{n-2}})$ at T_{n-1}. The supplementary sequence, when conjoined with the given cycle absorbing heat Q_1 at T_1, Q_2 at T_2, $\cdots$, Q_{n-1} at T_{n-1}, Q_n at T_n, constitutes a complex reversible cycle which incurs no net absorption or development of heat at the temperatures T_1, T_2, $\cdots$, T_{n-3}, T_{n-2} but gives rise to the absorption $T_{n-1}(\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \cdots + \frac{Q_{n-2}}{T_{n-2}})$ at Q_{n-1} at T_{n-1} and the absorption Q_n at T_n. Then by (56'),

$$\frac{Q_n}{T_n} + \frac{T_{n-1}(\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \cdots + \frac{Q_{n-2}}{T_{n-2}}) + Q_{n-1}}{T_{n-1}} = 0,$$

which is seen to reduce to (57), so that the proposition is proved.

This last form of the second fundamental principle in the theory of heat was obtained in another way by Clausius and led, with him, to the concept of entropy and the establishment of a precise analytical expression of the fact of irreversibility. At this point, we should observe that, although, in accordance with convention, we have, in the course of our exposition, referred to certain statements and analytical expressions as the "Second Law," still these really embody only two of the three general

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ideas embraced by the term, "Second Law," taken in its broadest meaning (cf. p.226). That is to say, the fact of irreversibility is not contained in these expressions and statements--at least, never explicitly.

By the way of introduction to Clausius' formulation of the entropy concept, let us briefly review the history of the notions of reversibility and irreversibility. Carnot, the father of these concepts, was led to them by a process of idealization whereby he conceived of the most perfect method of operating a heat engine. He thus arrived at his condition of reversibility, namely, that all changes of temperature of the body undergoing change should be due to changes of volume.

From Carnot's statements of the theorems relating to the heat absorbed or developed by gases on change of volume without change of temperature, it was clear that these applied only to reversible processes; that is, as long as the temperature of a body remains uniform and constant, temperature changes due to causes other than volume changes obviously cannot occur, and the process is reversible. Clapeyron, also Holtzmann, in attempting to extend Carnot's results to non-isothermal processes, was less careful in stipulating the condition of reversibility. Thus, not only did Clapeyron regard his equation (14) as applicable to the heat absorbed or developed by a perfect gas in a non-isothermal, reversible change of state, but also, by failing to mention the condition of reversibility, he implied that it also holds for irreversible changes of state. Again, in his statement of the theorem expressed by his equation (25) (cf. p.265), he also failed to prescribe the reversibility condition.

As a matter of fact, these omissions may very well have been deliberate; at any rate, they could have been justified by reference to the Principle of Conservation of Caloric. For, according to the latter, the heat

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exchanged by a body with its surroundings in any change of state is uniquely determined by the body's initial and final states and hence is the same regardless of whether the path is reversible or irreversible.

With the rejection of the caloric hypothesis and the adoption of the Principle of Equivalence of Heat and Work, the reversibility concept assumed a more secure position in the general theory of thermodynamics. Thus in Clausius' great memoir of 1850, also in Thomson's classical paper of 1851, all analytical expressions for finite heat and work effects were regarded as applicable to reversible processes only. On the other hand, the circumstance that the Energy Principle and Carnot's Theorem came to be employed more and more for the deduction of general relations between the physical properties of a body in any of its equilibrium states--relations whose validity are quite independent of the nature of the path connecting the equilibrium states--this circumstance caused the fact of irreversibility to fall more and more into the background. This explains why the general principle of the dissipation of energy was not formulated in these early papers of Clausius and Thomson. To be sure, the fact of irreversibility was mentioned in Thomson's paper in connection with the failure of heat engines to attain their maximum efficiency. However, the realization that this fact of irreversibility is the basis for a general, physical principle, according to which physical processes proceed in a definite direction--this realization still remained to be expressed.[60]

B. The Dissipation of Mechanical Energy.

It first found expression in a short paper by Thomson, published in 1852 and entitled "On a Universal Tendency in Nature to the Dissipation of Mechanical Energy" (56). He observed that, as a consequence of his fundamental axiom respecting the impossibility of an unsupplemented

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conversion of heat into work, processes involving the frictional production of heat and the diffusion of heat by conduction or radiation can never be completely reversed. Since such processes do, in fact, occur, the following conclusions are immanent:

"(1) There is at present in the material world a universal tendency to the dissipation of mechanical energy."

"(2) Any restoration of mechanical energy without more than an equivalent of dissipation, is impossible in inanimate material processes, and is probably never effected by means of organized matter, either endowed with vegetable life or subjected to the will of an animated creature."

"(3) Within a finite period of time past, the earth must have been, and within a finite period of time to come the earth must again be, unfit for the habitation of man as at present constituted, unless operations have been, or are to be performed, which are impossible under the laws to which the known operations going on at present in the material world are subject."

A general and precise analytical formulation of this "universal tendency to the dissipation of mechanical energy" was afforded by the concept of entropy introduced by Clausius. The complete formulation of this concept was very nearly attained in the latter's 1854 paper, entitled "On a Modified Form of the Second Fundamental Theorem in the Mechanical Theory of Heat." Unlike his first paper, in which the principle of thermodynamics were developed only for the special cases of perfect gases and saturated vapors, Clausius now attempted to develop equations applicable to any body whose state is determined by the variables v and t.

After expressing the First Law in the general form,

$$dQ = dU + Apdv \qquad (1)$$

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and showing, as Thomson had already done, that this is mathematically equivalent to the form:

$$\frac{\partial}{\partial t}\left(\frac{dQ}{dv}\right) - \frac{\partial}{\partial v}\left(\frac{dQ}{dt}\right) = A\frac{\partial p}{\partial t}, \qquad (2)$$

Clausius turned to the consideration of the Second Law. The point of view from which he now regarded the problem of the analytical formulation of the latter centered around a new meaning of the term, "equivalence." In the phrase, "Principle of Equivalence of Work and Heat," by which Clausius had denoted the Energy Principle, the "equivalence" referred to was not, strictly speaking, a mutual relation. Thus, a change consisting of the development of heat was said to be "equivalent" to one consisting of the development of a corresponding quantity of work, although the former could not bring about the same effects as the latter, even in the limiting (reversible) case; in the same sense, a calorie of heat at one temperature was said to be "equivalent" to a calorie at another temperature, in spite of the fact that these two "quantities of heat" were incapable of developing the same quantity of work.

On the other hand, Clausius now used the term "equivalence" in connection with the Second Law, to denote only a relationship which may be regarded as strictly mutual, without violation of the fundamental axiom that heat cannot pass from a lower to a higher temperature without any other change occurring. Two changes are equivalent in this latter sense only if each is actually capable of reversing or annihilating the other in the limiting (reversible) case.

In order "to discover the law according to which the transformations must be expressed as mathematical magnitudes, in order that their equivalence may be evident from the equality of their values," Clausius

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considered a reversible cycle of a new type, which is represented on the p—v diagram of Figure 16. As in the classical Carnot cycle, the working body is expanded isothermally along bc, absorbing the heat Q_1 from a body K_1 at the temperature t_1, and then expanded adiabatically along cd until its temperature falls to t_2. Now, however, isothermal compression along de causes the development of the heat Q_1, this being absorbed by a body K_2 at t_2. Adiabatic compression along ef elevates the working body's temperature to t. Then isothermal expansion along fa entails the absorption of the heat Q from a body K at t. Finally, adiabatic expansion along ab returns the working body to its initial state.

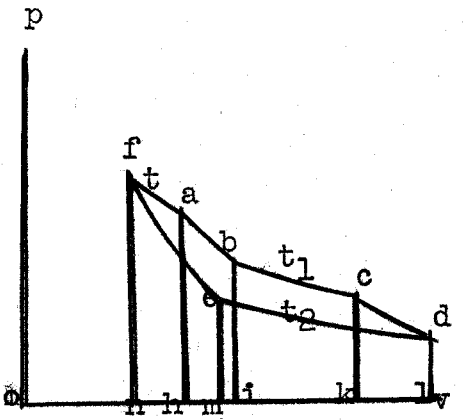

Figure 16

The cyclic process just described entails two changes: the passage of the heat Q_1 from K_1 at t_1 to K_2 at t_2; and the conversion of the heat Q at t into the work W, whose magnitude is given by the area of the closed figure described on the p—v diagram. By reversing the whole process, the reversal of the first change may be regarded as annihilating the second change. In other words, the change consisting of the conversion of the work W into the heat Q at t is equivalent to the change consisting of the passage of the heat Q_1 from t_1 to t_2. Clausius arbitrarily assigned positive equivalence-values to these last mentioned changes, their opposites thus acquiring negative values.

What are the general expressions for the equivalence-values of these transformations? With respect to the equivalence-value of the transformation consisting of the conversion of the work W into the heat Q at t, Clausius thought it obvious that this must be proportional to Q itself and,

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other than this, can depend only on t. He therefore wrote the equivalence-value of this change in the form

$$Q \cdot f(t) \ . \tag{3}$$

Similarly, he stated that, besides being proportional to Q_1, the equivalence value of the transformation consisting of the passage of the heat Q_1 from t_1 to t_2, can depend only on t_1 and t_2; and he therefore wrote its equivalence value in the form

$$Q_1 \cdot F(t_1, t_2). \tag{4}$$

Here $F(t_1, t_2)$ is some function of t_1 and t_2 which must conform to the relation

$$F(t_1, t_2) = -F(t_2, t_1), \tag{5}$$

since the passage of heatt Q_1 from t_2 to t_1 is a change which reverses the change consisting of the passage of heat Q_1 from t_1 to t_2 and must therefore have an equivalence-value equal and opposite to that of the latter.

The equivalence-value of the transfer of heat Q_1 from t_1 to t_2 being equal to that of the conversion of the work W into the heat Q at t, we have

$$-Q\, f(t) + Q_1\, F(t_1, t_2) = 0, \tag{6}$$

i.e. the sum of the equivalence-values of the two changes constituting the cyclic process of Figure 16 equals to zero.

Imagine a reversible cyclic process consisting of the reversal of the process described in connection with Figure 16 except that, instead of the heat Q being absrobed by K at t, the heat Q' is absorbed by K' at t'. The equation analogous to (6), connecting the equivalence values of this process, will be

$$Q'\, f(t') + Q_1\, F(t_2, t_1) = 0. \tag{7}$$

Adding (6) and (7) and applying (5) we obtain the relation,

$$-Qf(t) + Q'\, f(t') = 0. \tag{8}$$

Finally, suppose the two cyclic processes corresponding to equations

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(6) and (7) to be performed together so as to constitute a single double-process. In this latter, the exchanges of heat between t_1 and t_2 will no longer enter into consideration as they precisely cancel each other. There will remain only the development of the heat Q by K at t, the absorption of the heat Q' by K' at t', and the development, or absorption of a certain quantity of work corresponding to the difference Q' - Q. Thus suppose $t' > t$. Then the net result of the double-process must be the passage of the heat Q from K at t to K' at t' and the conversion of work into heat Q' - Q at t'. The equation analogous to (6) and (7), connecting the equivalence values of these two changes which constitute the double-process, will be

$$(Q' - Q)\, f(t') + Q\, F(t,t') = 0.$$

Eliminating Q' from this equation by means of (8), there results the fundamental relation :

$$F(t,t') = f(t') - f(t). \qquad (9)$$

Placing

$$f(t) = 1/T \qquad (10)$$

where T is some function of t, Clausius stated, as a result of (9), the "Theorem of the Equivalence of Transformations:" "If two transformations which, without necessitating any other permanent change, can mutually replace one another, be called equivalent, then the generation of the heat Q at the temperature t from work has the equivalence-vlaue Q/T, and the passage of the heat Q from the temperature t_1 to the temperature t_2 has the equivalence-value $Q(\frac{1}{T_2} - \frac{1}{T_1})$ where T is a function of the temperature independent of the nature of the process whereby the transformation is affected."

Thus, so far as its equivalence-value is concerned, a transformation consisting of the transfer of heat Q from t_1 to t_2 may be thought of as

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replaced by a double transformation consisting of the conversion of the heat Q at t_1 into work and the conversion of work into the heat Q at t_2. The task of computing the total equivalence-value of a cyclical process is hence greatly simplified. "For instead of examining what part of a given quantity of heat, during the cyclical process, has arisen from work, and whence the other part has come, every such quantity received may be brought into calculation as if it had been generated by work, and every quantity lost by a reservoir of heat, as if it had been converted into work." Thus, suppose that, in the course of a cyclical process, the reservoirs K_1, K_2, K_3, ... maintained at the temperatures t_1, t_2, t_3, ... receive the respective quantities of heat Q_1, Q_2, Q_3, ... Then the total equivalence-value N of all the transformations is given by

$$N = \frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} + \frac{Q_4}{T_4} + \cdots \qquad (11)$$

In the case where the temperature of emission varies continuously, this expression becomes

$$N = \int \frac{dQ}{T}, \qquad (12)$$

the number of reservoirs becoming correspondingly infinite.

Clausius next showed that for any reversible cyclical process, the equivalence-values as defined by (12) must equal to zero. For suppose $N \neq 0$ and the transformations occasioned by the cyclical operation to be divided into two groups, the first comprising transformations the algebraic sum of whose equivalence-values is zero, and the second comprising transformations whose equivalence-values all have the same sign. Supposing it to be possible to segregate the transformations of the first group into pairs, such that the equivalence-value of each pair is zero, it may be shown that all of these transformations may be cancelled by a finite or infinite number of simple cyclical processes of the type represented by

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Figure 16.[61] Hence the transformations of the second group would remain without any other change. If these transformations are negative, i.e. if they consist of transformations of heat into work and of heat from lower to higher temperatures, then of the two kinds, the transformations of the first kind may be replaced by those of the second, so that there would remain only transformations of heat from lower to higher temperatures, thus violating the fundamental axiom. Again, if the transformations of the second group were all positive, they could all be made negative by reversing the direction of the operations, and the same argument would again apply. We must conclude that the hypothetical second group comprising transformations of the same sign is really non-existent (assuming the validity of the fundamental axiom), i.e. all of the transformations are included in the first group whose equivalence-values have an algebraic sum equal to zero. The theorem is thus proved, and Clausius was led to write

$$N = \int \frac{dQ}{T} = 0 \qquad (13)$$

as the analytical expression of the Second Law for reversible cyclical processes.

According to the derivation of (13), T is the value of this function for the temperature t of the reservoir from which the heat dQ is received. However, as Clausius observed, since, in a reversible process, the temperatures of two bodies between which heat is exchanged can differ only infinitesimally, T may also be regarded as the value of this function for the temperature t which prevails over the body undergoing the reversible cyclical process at the time when the heat dQ is received. Thus interpreted, the integral in (13) refers only to changes occurring in the working body itself, i.e. to the elements of heat absorbed by the body and the temperature at which the absorptions occur.

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This interpretation of (13) permits the derivation, from it, of analytical results already obtained by different methods. Thus, since

$$dQ = \frac{dQ}{dt}dt + \frac{dQ}{dv}dv,$$

it follows from (13), says Clausius, that

$$\frac{dQ}{T} = \frac{1}{T}\frac{dQ}{dt}dt + \frac{1}{T}\frac{dQ}{dv}dv \qquad (14)$$

must be an exact differential. Whence

$$\frac{\partial}{\partial t}\left(\frac{1}{T}\frac{dQ}{dv}\right) = \frac{\partial}{\partial v}\left(\frac{1}{T}\frac{dQ}{dt}\right) \qquad (15)$$

or

$$\frac{dQ}{dv}\frac{\partial T}{\partial t} = T\left[\frac{\partial}{\partial t}\left(\frac{dQ}{dv}\right) - \frac{\partial}{\partial v}\left(\frac{dQ}{dt}\right)\right].^{62} \qquad (16)$$

Combining equation (16) with equation (2), expressing the First Law, there results

$$\frac{dQ}{dv}\cdot\frac{dT}{dt} = AT\frac{\partial p}{\partial t}, \qquad (17)$$

which, by virtue of the relation,

$$\frac{\partial p}{\partial t} = \frac{\partial p}{\partial T}\frac{dT}{dt},$$

may be written

$$\frac{dQ}{dv} = AT\frac{\partial p}{\partial T} \qquad (18)$$

Equation (18) is evidently the Clausius-Clapeyron equation which had formerly been expressed in the form

$$\frac{dQ}{dv} = C\frac{\partial p}{\partial t} = C\frac{\partial p}{\partial T}\frac{dT}{dt}. \qquad (19)$$

by comparison of (18) and (19), we obtain a relation between Carnot's function C and the new T function, namely,

$$\frac{dT}{dt} = \frac{AT}{C} \qquad (20)$$

Finally, Clausius showed that by the introduction of "Mayer's Hypothesis" that the work of reversible expansion of a perfect gas is equivalent to the heat absorbed, the T function may be identified with Thomson's absolute temperature. Expressed in general terms, this hypothesis is

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$$\frac{dQ}{dv}\,dv = Apdv$$

or

$$\frac{dQ}{dv} = Ap.$$

Substitution in (17) gives

$$\frac{\frac{dT}{dt}}{T} = \frac{\frac{\partial p}{\partial t}}{p}.$$

Eliminating p from this equation by means of the perfect gas law, $pv = (a + t)R$, we find $\frac{dT}{T} = \frac{dt}{a + t}$

or $$T = (a + t).\ \text{const.} \qquad (21)$$

The arbitrary constant of integration may be placed equal to unity without altering the relative equivalence-values; whence T reduces to the absolute temperature.[63]

C. Equivalence Values and Entropy.

Toward the close of his memoir, Clausius devoted several paragraphs to the consideration of irreversible processes. He there proved that the net equivalence-value, as defined by (12), of transformations occasioned by an irreversible process, can only be positive. To establish this, it is only necessary to recall the general lines of proof that the equivalence-value is zero when the cycle is reversible. To prove the latter, the transformations occurring were supposed divided into two groups, the first comprising transformations the algebraic sum of whose equivalence-values was zero, the second comprising transformations whose equivalence-values possessed the same sign. After showing that the transformations of the first group could be completely cancelled, it was demonstrated that the transformations of the second group could be neither negative nor positive. For if they were negative, they would lead to a contradiction of the fundamental axiom respecting the impossibility of heat passing "of itself"

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from a lower to a higher temperature, whereas, if they were positive, they could be completely reversed to form negative changes, again contradicting the fundamental axiom. This whole proof evidently applies to the irreversible cycle under consideration with the single exception that the proof that the transformations of the second group cannot be positive, no longer holds. For since these positive transformations are not reversible, they may not be replaced by the corresponding negative ones with the resultant contradiction. Thus, for the irreversible cycle, we can only prove that the equivalence-value is not negative. Since the zero equivalence-value has already been shown to apply to the reversible cycle, it appears feasible to suppose that the equivalence-value of the irreversible cycle must be positive. Since all cyclic transformations are actually irreversible, Clausius was led to formulate the "universal tendency to dissipation of mechanical energy" (Thomson), in the law: "The algebraical sum of all transformations occurring in a cyclical process can only be positive." A transformation which remains at the conclusion of an irreversible cyclic process and whose equivalence-value can only be positive, Clausius calls an "uncompensated transformation."

Near the close of his paper, Clausius also referred to irreversible, non-cyclical processes as uncompensated changes, although he did not explain how the equivalence-values of such changes are to be calculated. Not until 1862, in a paper, "On the Application of the Theorem of the Equivalence of Transformations to Interior Work," did Clausius undertake to give analytical formulation to the irreversibility of non-cyclical processes.

In all of Clausius' papers so far discussed, the kinetic theory of heat or, as Clausius called it, "the mechanical theory of heat," was consistently advocated, without, however, allowing it to exert any formal influence on the equations of thermodynamics. Unfortunately, this is not

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the case with the 1862 paper just referred to. For, like Rankine (cf.p.289) he now regarded the heat absorbed by a body, $-dQ$, as generally capable of resolution into the increase in sensible heat, d_H, and the work done (interior and exterior), AdL. He thus wrote the Energy Principle in the form:

$$-dQ = dH + AdL \qquad (22)$$

In an attempt to extend the equivalence-value idea to non-cyclical processes, Clausius introduced a new concept, namely, the "disgregation" of a body. The latter he defined as a quantity which measures the decrease in the molecular forces of a body. Thus, said Clausius, heat is converted into work in non-cyclical processes only at the expense of an increase in disgregation of the working body (associated with its increase in volume).

To obtain a quantitative definition of disgregation, Clausius postulated a new axiom: "The mechanical work which can be done (reversibly) by heat during any change of the arrangement of a body is proportional to the temperature at which this change occurs." [64]

"Since the increase of disgregation," said Clausius, "is the action by means of which heat performs work... we will fix the magnitude of the disgregation so that, at any given temperature, the increase of disgregation shall be proportional to the work which the heat can thereby perform... Also for the same disgregation at different temperatures, the corresponding work must (by the above axiom)be proportional to the absolute temperature." Hence, Clausius wrote, as the defining equation for the disgregation, the relation:

$$dZ = AdL/T \qquad (23)$$

Eliminating AdL from (22) and (23) and integrating the result for a finite, reversible change, Clausius obtained, as the combined analytical expression of the Energy Principle and the above axiom, the equation:

$$\int \frac{dQ + dH}{T} + \int dZ = 0. \qquad (24)$$

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Regarding as given, the result that

$$\int \frac{dQ}{T} = 0, \qquad (25)$$

for a reversible, cyclical process, Clausius showed that, since $\int dZ = 0$ for such a process, equation (24) requires that

$$\int \frac{dH}{T} = 0 \qquad (26)$$

for a reversible cyclic process, Clausius laid great weight on equation (26), which he considered to be equivalent to the proposition that "the quantity of heat actually present in a body depends only on its temperature, and not on the arrangement of its constituent particles."[65]

Clausius now approached the problem of the determination of equivalence-values. Three types of changes need to be considered: (1) transformations of work into heat; (2) transfers of heat from a higher to a lower temperature: (3) transformations incurring an increase in the disgregation of a body. In keeping with the custom of his 1854 paper, he elects to assign positive values to these transformations when occurring in the directions just specified.

Imagine, now, that the same change of arrangement (change of disgregation) occurs reversibly at two different temperatures. The quantity of heat Q which is thereby converted into work will not be the same in the two cases but, according to the fundamental proposition, will vary directly as the absolute temperature. In order that two transformations of heat into work, which supplement the same change of arrangement, we may have the same equivalence-value, the equivalence-value of such a transformation must be placed equal to $\frac{Q}{T}$. const.

where the constant may be chosen equal to unity. Clausius thus attempted to employ his new axiom as a questionable justification of the somewhat arbitrary step taken in his 1854 paper.

With respect to changes of the second kind (transfers of heat

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between different temperatures), Clausius had already shown that these could always be considered as replaced by several transformations of the first kind, and this view was still maintained in the present, 1862 paper.

As for transformations involving changes of disgregation, it is natural to assign to such a transformation an equivalence-value equal and opposite to that of the transformation of heat into work which supplements the given transformation. But in any case, the total equivalence-value of the transformation of heat into work (internal and external) is $-A\int\frac{dL}{T}$. Hence the equivalence-value of the change of disgregation thereby incurred is

$$Z - Z_0 = A\int\frac{dL}{T}. \qquad (27)$$

Equation (24) now assumes a new importance. For since dQ denotes the element of heat developed by a body and dH, the increase of the body's own heat, the term $\int\frac{dQ + dH}{T}$ is regarded as representing the total equivalence-value of all transformations of the first and second kinds. The term $\int dZ$ represents the total equivalence-value of all changes of disgregation. Hence, equation (24) asserts that the algebraic sum of all equivalence-values occasioned by a reversible process, equals to zero.

Without giving any clear explanation, Clausius stated that, in irreversible changes, the equivalence-value of the change of disgregation will be greater than its value for reversible changes, i.e. for irreversible changes $dZ > \frac{AdL}{T}$. Applying this to (22), we obtain, in place of (24) the relation

$$\int\frac{dQ + dH}{T} + \int dZ > 0, \qquad (28)$$

i.e. the equivalence-value of an actual (irreversible) transformation can only be positive.

In its rather hazy logic and its excess of vague concepts and arbitrary propositions, this paper of Clausius resembles Rankine's papers on energetics. In particular, Clausius' treatment would seem to indicate

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that the Theorem of Equivalence of Transformations, in its entirety, is based not on one, but on two axioms, namely, the original axiom respecting the impossibility of heat passing from a lower to a higher temperature and the new axiom respecting the proportionality of the work (interior and exterior) -value of heat to the absolute temperature. This manner of treatment was defended by Clausius in 1863 in a paper, "On an Axiom in the Mechanical Theory of Heat." There, he also stated that the axiom postulating the unique determination of a body's "actual heat" by its temperature, together with either of the two axioms just mentioned, may be taken as the fundamental starting point for the Second Law.

Not until 1865, in a paper entitled "On Several Convenient Forms of the Fundamental Equations of the Mechanical Theory of Heat," did Clausius return to the fertile series of ideas which, in his 1854 paper, had so nearly led him to the formulation of the entropy concept. In the 1854 paper, Clausius had already noted that dQ/T must be an exact differential, and he now introduced a definite symbol for the property of the body which is thereby determined; that is, he wrote

$$dS = dQ/T. \qquad (29)$$

For a reversible process in which the body is carried from a standard state where S has the value S_o to a new state where its value is S, the latter must be given by

$$S = S_o + \int \frac{dQ}{T}, \qquad (30)$$

the line-integral being taken along any reversible path connecting initial and final states.

The concepts of sensible heat (H) and disgregation (Z), which played such an important part in the 1862 paper, now appear to play only an accessory role: they are invoked merely to explain the "physical meaning" of the new S function. For, writing equation (24) in the form

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$$\int \frac{dQ}{T} = \int \frac{dH}{T} + \int dZ, \qquad (31)$$

The change in S is seen to represent the sum of the transformation-value of the heat contained in the body ($\int \frac{dH}{T}$) and the transformation-value of the change of arrangement or disgregation ($\int dZ$). Hence, Clausius stated that S might be called the "transformational content of the body." However, he preferred to call it by the name, entropy, after the Greek word for transformation.

Of the greatest significance, was Clausius' employment of the entropy concept in the formulation of the equivalence-values (transformation-values) of irreversible processes. The definition (12) of the equivalence-value of a cyclical process, was retained except that dQ was now reckoned as the element of heat absorbed by the body, so that (12) became

$$N = - \int \frac{dQ}{T}, \qquad (32)$$

Suppose now that a body has suffered an irreversible change of state. If the body be returned to its initial state, reversibly, the equivalence-value of the whole cyclical process is given by

$$N = - \int \frac{dQ}{T} - \int_r \frac{dQ}{T}, \qquad (33)$$

the second integral referring to the reversible, return path.[66]
By definition,

$$\int_r \frac{dQ}{T} = S_o - S, \qquad (34)$$

S_o and S denoting the value of the entropy in the initial and final states, respectively. Substituting in the expression for N, there results

$$N = S - S_o - \int \frac{dQ}{T}. \qquad (35)$$

Here N is the equivalence-value of the whole cyclical transformation; but, since the equivalence-value of all transformations occurring in connection with the reversible return path must be zero (cf. p. 351), the magnitude of N must really represent the equivalence-value of the original irreversible transformation.

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Although Clausius did not point it out, the great significance of equation (35) lies in the fact that, in it, the equivalence-value of a non-cyclical transformation is expressed in terms of measurable quantities and independently of the hazy concepts of sensible heat, internal work, and disgregation. Further, the whole development rests only on the axiom respecting the impossibility of the uncompensated transfer of heat from a lower to a higher temperature.

At the conclusion of his memoir, Clausius stated that the two laws of thermodynamics, when applied to the universe, assume the forms:"(1) The energy of the universe is constant; (2) The entropy of the universe tends to a maximum." Clausius did not state how he obtained the second proposition, which he regarded as a precise formulation of the universal tendency to dissipation of energy, pointed out thirteen years earlier by Thomson.[67]

In an 1866 appendix, entitled "On the Determination of the Energy and Entropy of a Body," Clausius showed how the entropy function could be profitably employed in the general equations of thermodynamics. Writing the First Law in the form,

$$dQ = dU + dw, \tag{36}$$

and the Second Law (for reversible processes) in the form

$$dQ = TdS, \tag{37}$$

he obtains, on combining these, the fundamental relation

$$TdS = dU + dw. \tag{38}$$

Supposing the state of the body to be determined by the values of the variables x and y, (38) may be written in the form:

$$T\frac{\partial S}{\partial x}dx + T\frac{\partial S}{\partial y} = \left(\frac{\partial U}{\partial x} + \frac{dw}{dx}\right)dx \left(\frac{\partial U}{\partial y} + \frac{dw}{dy}\right)dy.$$

This relation being true for all values of dx, dy, we must have

$$T\frac{\partial S}{\partial x} = \frac{\partial U}{\partial x} + \frac{dw}{dx} \tag{39}$$

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and

$$T\frac{\partial S}{\partial y} = \frac{\partial U}{\partial y} + \frac{dw}{dy} . \tag{40}$$

Differentiating (40) with respect to x and subtracting the result from that obtained by the differentiation of (39) with respect to y, we obtain

$$\frac{\partial T}{\partial y}\frac{\partial S}{\partial x} - \frac{\partial T}{\partial x}\frac{\partial S}{\partial y} = \frac{\partial}{\partial y}\left(\frac{dw}{dx}\right) - \frac{\partial}{\partial x}\left(\frac{dw}{dy}\right). \tag{41}$$

If we write $T = y$, then $\frac{\partial T}{\partial y} = 1$, $\frac{\partial T}{\partial x} = 0$, so (41) simplifies to

$$\frac{\partial S}{\partial x} = \frac{\partial}{\partial T}\left(\frac{dw}{dx}\right) - \frac{\partial}{\partial x}\left(\frac{dw}{dt}\right), \tag{42}$$

whence,

$$S = \int\left[\frac{\partial}{\partial y}\left(\frac{dw}{dx}\right) - \frac{\partial}{\partial x}\left(\frac{dw}{dT}\right)\right]dx + \phi(T), \tag{43}$$

$\phi(T)$ being an arbitrary function of T.

Again taking T and x as independent variables, (37) may be placed in the form:

$$\frac{\partial S}{\partial T}\,dT + \frac{\partial S}{\partial x}dx = \frac{1}{T}\,\frac{dQ}{dT}\,dT\,\frac{1}{T} + \left(\frac{dQ}{dx}\right)dx .$$

Equating like coefficients of dT, there results

$$\frac{\partial S}{\partial T} = \frac{1}{T}\left(\frac{dQ}{dT}\right). \tag{44}$$

Combining (42) and (44), we have, as the complete differential equation for S,

$$dS = \frac{1}{T}\left(\frac{dQ}{dT}\right) + \left[\frac{\partial}{\partial T}\left(\frac{dw}{dx}\right) - \frac{\partial}{\partial x}\left(\frac{dw}{dT}\right)\right]dx. \tag{45}$$

In (45), w denotes the external work. If the only work is that of a uniform and normally directly directed pressure, we have $dw = Apdv$, and (45) becomes

$$dS = \frac{1}{T}\left(\frac{dQ}{dT}\right)dT + A\left(\frac{\partial p}{\partial T}\,\frac{\partial v}{\partial x} - \frac{\partial p}{\partial x}\,\frac{\partial v}{\partial T}\right)dx. \tag{46}$$

Again, if the body is a pure substance in two states of aggregation, T determines p and $\frac{\partial p}{\partial x} = 0$, so that, for this case, (45) is

$$dS = \frac{1}{T}\,\frac{dQ}{dT}\,dT + A\,\frac{\partial p}{\partial T}\,\frac{\partial v}{\partial x}\,dx. \tag{47}$$

Finally, if we place $x = v$, we have

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$$dS = \frac{1}{T}\left(\frac{dQ}{dT}\right) dT + A\frac{\partial p}{\partial T} dv.^{68} \qquad (48)$$

D. Objections to the Second Law.

With the formulation of the entropy concept by virtue of which the ideas embraced by the Second Law admitted of precise analytical representation, Clausius completed (except for minor improvements in the proofs) that imposing structure known as classical thermodynamics. To be sure, the Second Law, as it was finally formulated by Thomson and Clausius, was not accepted without question. In fact, numerous objections were offered, and these had to be met squarely, in order that the new science of thermodynamics might acquire a position of security and prestige.

Typical of a whole group of objections was one propposed by Hirn in 1863. In Figure 17 A and B are two non-conducting cylinders of equal cross-section connected at the bottom by a narrow tube which is in thermal communication with a constant temperature reservoir at the temperature t_1. The cylinders are equipped with frictionless, non-conducting pistons whose rods are provided with teeth which fit into the teeth of a wheel in the manner shown. In this way, the motion of the pistons is always subject to the condition that the total space included under the pistons and in the narrow tube must remain invariable. Imagine now that at the commencement of the operation to be described, the piston of cylinder B is at the bottom of said cylinder, that of A being consequently at its highest position. Let A contain a certain quantity of gas at the temperature $t_0 < t_1$; and, by descent of A's piston and

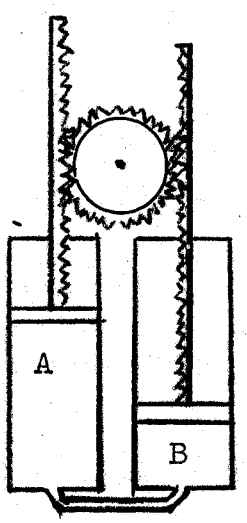

Figure 17

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consequent ascent of B's, let the air be gradually driven from A into B. The first small portion of gas entering B, having acquired the temperature t_1 of the reservoir, must expand, thereby causing a slight increase in the pressure and temperature of the gas remaining in A. Thereafter, every succeeding quantity of gas passing through the tube contributes by its expansion not only to the compression of the gas remaining in A but also to that already in B. Since the quantities of gas, upon their entrance into B, all have the temperature t_1, their subsequent temperatures after compression must exceed t_1. Thus at the end of the operation the small element of gas immediately under the piston will have the highest temperature, it having been compressed the greatest number of times; the temperatures of the underlying elements will decrease as we proceed toward the bottom of B, that of the lowest element having the temperature t_1.

Thus this operation has effected the transfer of a certain quantity of heat from the temperature t_1 to a higher temperature, namely, the final mean temperature of the gas. According to Hirn, nothing else has happened. For the gas has its initial volume; and no work has been done, since the pressure of the gas was uniform throughout the operation. Hence, said Hirn, Clausius' axiom respecting the impossibility of heat passing of itself from a lower to a higher temperature has been violated.

In his 1863 paper, "On an Axiom in the Mechanical Theory of Heat," Clausius had no difficulty in removing Hirn's objection. He simply pointed out that the heating of the gas to t_1, by passage through the tube, entails a passage of heat from a higher to a lower temperature. This process occurs simultaneously with the passage of heat from t_1 to the higher temperature of the gas in B. Therefore the fundamental axiom is not violated.

Of more importance than Clausius' specific reply to Hirn's objection was

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his general attitude toward the fundamental axiom as this attitude found expression in the same 1863 paper. This axiom, asserting, as it does, the impossibility of effecting the unsupplemented transfer of heat from a lower to a higher temperature by any contrivance whatsoever, is far too general to be considered a priori self-evident as it had been by Zeuner in his Grundzuge der mechanischen Warmetheorie published in 1860. Rather, said Clausius, its validity can arise only from its continued agreement with experience. Thus, far from belittling Hirn's objection, he stated that "it was fully justified from a scientific point of view," i.e. it is not unreasonable to suppose that cases exist which violate the axiom.

An altogether different type of objection to Clausius' axiom, hence the logically implicated one of Thomson, had been advanced in 1851 by Rankine (cf. p.). The latter had professed to derive Carnot's Theorem analytically from the hypothesis of molecular vortices, so that the introduction of a Second Law appeared to him (Rankine) unnecessary. In addition to a more specific objection relating to Rankine's interpretation of the concept of "real specific heat," Clausius pointed out that the circumstance that the Englishman's treatment "depends on a peculiar hypothesis concerning the constitution of molecules, and on their mode of motion, is sufficient to produce the conviction that complicated considerations must necessarily arise of a nature to raise doubts as to the degree of its trustworthiness."

The general tendency to the dissipation of energy, apparently incurred by the Second Law and first enunciated by Thomson, seemed irreconcilable with the common view that cosmic processes conform to principles of growth, periodicity , and spontaneous self-maintenance. An early attempt at reconciliation was contained in Rankine's 1852 paper, "On the Reconcentration of the Mechanical Energy of the Universe" (47). Supposing that interstellar space has bounds

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beyond which there is only empty space, Rankine suggested that, on reaching these bounds, radiant heat would be totally reflected and subsequently reconcentrated at foci. Any chemical compounds present at these foci would be resolved into their elements. Such a reproduction of chemical energy would evidently tend to off-set the dissipation of energy incurred by the Second Law.

However, even if one would accept the highly problematic assumption of a perfectly empty space, the above hypothesis of Rankine's must still be rejected because, in supposing heat to pass from the low temperatures of interstellar space to the warmer bodies of the solar system, it involves a flat contradiction of the Second Law, as was pointed out in 1863 by Clausius in a paper, "On the Concentration of Rays of Heat and Light, and on the Limits of Its Action."(67)

E. Applications to Thermo-Electricity and Phase Equilibria.

The First Law of Thermodynamics or the Principle of the Conservation of Energy was regarded from its very inception as an all-embracing postulate applicable to every branch of physical science. The Second Law, on the contrary, developed in connection with the relatively special problem of the "motive power of heat," and seemed at first to be of much narrower scope. However, since the phenomena of mechanics are interrelated with those of electricity, magnetism, and chemistry, it soon appeared that the Second Law should be applicable to the relations of the latter, as well of the former, to thermal phenomena. This general significance of the Second Law was further accentuated by the realization that all of the energies tend to pass, directly or indirectly, into heat.

Thermo-electricity was one of the first of the extra-mechanical phenomena to which the principles of thermodynamics were successfully applied. The classical treatment of the subject appeared in 1854 as a continuation

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(Part VI) of Thomson's great paper, "On the Dynamical Theory of Heat." (56), p.

Thomson's treatment of thermo-electricity is a topic of special significance in the history of thermodynamics because it raised for the first time the fundamental question: May the Second Law ($\int \frac{dQ}{T} = 0$) be applied to a portion of a process, supposed reversible, when the given process also involves irreversible portions which are inextricably connected in time and space with the hypothetical reversible portion? In other words, Is there any sense in speaking of a process as "partially reversible?" This question came to be raised in the following way. If a thermocouple, the temperatures of whose junctions differ by a finite amount, is allowed to operate freely, a finite current will flow with the simultaneous production of an irreversible heating effect whose magnitude by Joule's Law is proportional to the square of the current strength. However, if an engine whose inductive electromotive force differs only infinitesimally from that of the thermocouple be introduced into the circuit, the intensity of the current, hence the irreversible heating effect due to it , will become vanishingly small. By a very slight variation of the inductive electromotive of the engine, the direction of the current is reversed, the electric work developed per unit of time is changed in sign, and the heat exchanges occurring at the junctions and throughout the circuit, inconnection with the electrical work, are likewise reversed. Thus, under such conditions, the thermocouple would appear to operate reversibly. However, this overlooks the circumstance that, due to the temperature gradient, irreversible heat conduction is occurring throughout the circuit. Moreover, whereas the thermal effects associated with the production of the hypothetical reversible electromotive force are only infinitesimal in extent, the irreversible effects involved

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in heat conduction are quite finite.

Hence, in applying the Second Law ($\int \frac{dQ}{T} = 0$) to the supposedly reversible thermal effects associated with the electrical work for a vanishingly small current and neglecting the obviously irreversible effects entailed by conduction, Thomson took a step whose legitimacy, as he himself observed, could only be established by the agreement of the theoretical deductions with experiment. If the deductions so obtained should not be confirmed by experience, it is not the Second Law, said Thomson, but the hypothesis of the latter's applicability to the case in question which must be rejected.[69]

Thomson developed his theory in a perfectly general manner so as to be applicable to a thermo-element consisting of any number of metals arranged in series and with their junctions at different temperatures. We shall limit ourselves to an exposition of the theory for the special case of an element consisting of two metals only, whose junctions are at the absolute temperatures T and T'. Let $\Pi(T)$ and $-\Pi(T')$ denote, respectively, the quantities of heat absorbed at these junctions per second by a current of unit strength. Let $i\sigma_1 dT$, $i\sigma_2 dT$ denote the amounts of heat evolved in each of the two metals per second by a current of infinitely small strength, i, passing from a locality at temperature $T+dT$ to a locality at temperature T.[70]

In the operation of the couple the production of electrical energy does not incur a change of state of the couple itself. Hence the First Law of Thermodynamics requires that the net heat absorbed per unit of time per unit of current shall be equivalent to the electrical work produced, i.e. to the electromotive force E of the couple. Hence

$$E = J \left(\Pi(T) - \Pi(T') - \int_{T}^{T'} \sigma_1 \, dT - \int_{T'}^{T} \sigma_2 \, dT \right)$$

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or $$E = J\left(\Pi(T) - \Pi(T') + \int_{T'}^{T}(\sigma_1 - \sigma_2)\,dT\right). \qquad (1)$$

Also, under the hypothesis of reversibility, the Second Law $\int \frac{dQ}{T} = 0$, gives

$$\frac{\Pi(T)}{T} - \frac{\Pi(T')}{T'} + \int_{T'}^{T}\frac{\sigma_1 - \sigma_2}{T}\,dT = 0\,. \qquad (2)$$

Differentiation of equation (2) with respect to T yields

$$\frac{d\left(\frac{\Pi}{T}\right)}{dT} + \frac{\sigma_1 - \sigma_2}{T} = 0 \qquad (3)$$

or $$\sigma_1 - \sigma_2 = \frac{\Pi}{T} - \frac{d\Pi}{dT}\,. \qquad (3')$$

Combination of (1) and (3') leads to an expression for the thermoelectromotive force solely in terms of the Peltier evolution of heat at the junctions, namely,

$$E = J\int_{T',T}^{T}\frac{\Pi}{T}\,dT. \qquad (4)$$

All of these relations were found to be in good agreement with experiment, and the hypothesis of "partial reversibility" was thus verified.[71]

The theory just outlined relates only to the thermoelectric properties of linear conductors, i.e. to the ideal case in which the current through a point is supposed to flow all in one direction. Thomson devoted the latter part of his paper to the general treatment of thermoelectric currents in anisotropic crystals of finite dimensions. In the following year, 1855, in a paper on thermoelasticity (56, p. 291), he brought the theory of elasticity into relation with the new science of thermodynamics. This was followed in 1860 by the treatment of thermo-magnetic properties of matter. About the same time Thomson presented the first thermodynamic treatment of surface phenomena (58), a subject later treated exhaustively by Gibbs (59).

Of epoch-making significance was Willard Gibbs' extension of classical thermodynamics to the complicated phenomena of chemical equilibrium. In classical thermodynamics consideration had been limited to bodies of a pure substance existing either in a single or in two states of aggregation. In his famous paper, "On the Equilibrium of Heterogeneous Substances", published in installments between 1875 and 1878 (59), Gibbs undertook the

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thermodynamic treatment of a body composed of any number of separate homogeneous parts (phases) and constituted of any number of pure substances (components) of which the amount of any one in every homogeneous part is subject to variation by virtue of the possibility of mutual exchange of matter with the contiguous parts. Gibbs' method of attacking this problem was obviously modeled after the methods of classical mechanics; that is, just as, given a certain number of fundamental concepts, the whole analytical theory of classical mechanics had been shown to be deducible from a single postulate, expressing the condition for mechanical equilibrium, so Gibbs sought to deduce the various relations connecting the properties of a body and its constituent phases from a single postulate expressing the condition for thermodynamic equilibrium.

Such a criterion Gibbs found in Clausius' statement of the Second Law, namely, that every spontaneous change occurring in an isolated system must be accompanied by an increase of the entropy of the system. For it follows, conversely, from this that if no change occurs (i.e. if the system is in equilibrium), every virtual displacement of the system from the given state must be associated either with a decrease in entropy (stable equilibrium) or a vanishing in the variation of this quantity (neutral equilibrium). Further, the requirement that the system shall remain isolated is evidently expressible by the condition of constant energy. Hence Gibbs was led to write as the general condition for thermodynamic equilibrium in an isolated system, $(\delta S)_E \leqq 0$, a relation which he showed to be equivalent to the condition that every variation of the energy, subject to constant entropy, should either vanish or be positive, i.e. $(\delta E)_S \geqq 0$. In the particular case of a body subject to no force other than a uniform and normally directed pressure, Gibbs showed that these relations were equivalent to the condition that all possible sets of

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variations δE, δV, δS of the energy, volume, and entropy of the body should satisfy the relation $\delta E + p\,\delta V - T\,\delta S \geq 0$. In order that this general criterion should yield relations involving the properties of the individual phases, Gibbs found it necessary to generalize the concept of energy as it had been employed by Thomson and Clausius. Heretofore, the energy had been defined only for a body, i.e. for a physical object subject to no exchanges of matter with its environment. Thomson and Clausius had treated the energy of such a body as a uniform continuous function of the variables determining the body's state. Gibbs showed that, retaining the general notion of energy as the algebraic sum of the heat and work absorbed in passing from a reference state to a given state, the "energy of a phase" might similarly be regarded as a uniform, continuous function of the variables which determine its state. e.g. the temperature and volume of the phase and the masses of its constituents.

Clausius had referred to the entropy as a property of a body but had always regarded it as a dependent variable. Gibbs' choice of the entropy as an independent variable constituted an important innovation, entailing an altogether new point of view. Thus he regarded the energy of a phase as a function of its entropy, volume, and the masses of its constituents, and he showed it to be a homogeneous function of the first degree in each of these variables.[72]

The extended analytical results which Gibbs obtained with the above considerations as a starting point, and the subsequent application of them to the many and varied problems of physical chemistry--these are topics whose exposition must lie beyond the scope of the present history, which is concerned mainly with the rise of classical thermodynamics. However, we cannot refrain from pointing out the revolutionary point of view which is

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involved in Gibbs' method. In the first place,it is evident that Gibbs' treatment of chemical equilibrium includes, as a special case, the simple physical equilibria treated in classical thermodynamics. Further, in the later portions of his paper, Gibbs applied the general criterion of equilibrium to cases where the phases composing the system were subject to electrical, magnetic, gravitational, and capillary forces. Gibbs' paper, "On the Equilibrium of Heterogeneous Substances," is thus for more than simply an application of classical thermodynamics to special problems: it is essentially a new system of thermodynamics in which, starting with the concepts of energy and entropy as given, the whole of special theory may be elaborated, including the theory of those relatively simply systems upon the basis of whose behavior the concepts of energy and entropy were, historically, formulated, and excluding only the mechanistic hypotheses of explanatory physics as well as those branches of theory concerned with the time-rate of physico-chemical processes.[73]

With this brief reference to the significance of Gibbs' work, we must conclude our exposition of the history of the Second Law of Thermodynamics. Beginning as a special principle relating to the efficiency of heat engines, we have seen it develop and expand until, as expressed in terms of the entropy, it took its place, along with the First Law, as a postulate of the most general import. The resultant system of classical thermodynamics, if we take into account the modifications required of it by the theory of relativity, may still be regarded as the most valuable possession of physical science as well as the most trustworthy guide in future research.

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FOOTNOTES

(IV. THE DEVELOPMENT OF THE ENTROPY CONCEPT
and the SECOND LAW OF THERMODYNAMICS)

1 This teleological view of the world was the dominant element in the influential philosophical systems of Plato and Aristotle, whose notions of substance are, however, so completely foreign to physical realism as to render a discussion of their ideas irrelevant to our exposition.

2 Thus the "kinetic view" of nature (18) served to supplement, rather than replace, the astronomical view; i.e. taken together, they formed a more perfect mechanistic explanation of phenomena. The same may be said of the "atomic view," which developed in the early part of the nineteenth century in connection with the new science of chemistry: Dalton's atoms could serve as the centers of emanation for the Newtonian forces. Further, we should note that the astronomical view, through the efforts of Coulomb, Poisson, Ampere, and Weber (1846), performed a great service in organizing the newly discovered relationships between electricity and magnetism into the science of electrodynamics.

3 The first attempt to make the mechanistic hypothesis consistent with the Second Law was that of Rankine in 1851 who thought he could deduce Carnot's Theorem that the efficiency of a heat engine is independent of the working body, from the hypothesis that heat consists of a steady whirling motion of "atomic atmospheres." The first satisfactory treatment of the problem, in which the theory of probability was brought into service to account for irreversibility, came much later through the efforts of Boltzmann (1866), Clausius (1871), Helmholtz (1884), and Gibbs (1902).

4 Joule knew of Carnot's work but, like the others, failed to appreciate its significance. Mayer, as late as 1851, wrote: "Motion

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is latent heat; heat is latent motion." A suggestion of the notion of available energy occurred, however, in a letter to Griesinger (1844), in which Mayer stated that, in order to get one grain of food-stuff converted to work, the animal body must perhaps convert as much as 1-1/2 grains into heat, which is used in warming the air by respiration and vaporizing the water in the breath. Analogous considerations apply, he said, to the vapor machine. (cf. 32. p. 58)

5 The following improvements were introduced by Watt: (1) the separate condenser, i.e. the steam was condensed outside of the cylinder; (2) the expansive working of the steam, i.e. the steam supply was cut off before the end of the stroke and the steam already introduced allowed to expand; (3) the double-acting cylinder, i.e. steam was admitted, alternately, on both sides of the piston; (4) the employment of steam pressures exceeding atmospheric pressure.

6 Carnot's "motive power" is synonymous with out"work." Like Poncelet, he takes as its measure the product of a weight into the height which it is raised.

7 "The phenomenon of the production of motion by heat has not been considered in a sufficiently general way. It has been treated only in connection with machines whose nature and mode of action do not admit of a full investigation of it. In such machines, the phenomenon is ..., in a measure, imperfect and incomplete; it thus becomes difficult to recognize its principles and study its laws. To examine the principle of the production of motion by heat in all its generality, it must be conceived independently of any mechanism or of any particular agent; it is necessary to establish proofs applicable not only to steam engines but to

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all other heat engines, irrespective of the working substance and the manner in which it acts.

"The machines which are not worked by heat... can be studied in their last details by the principles of mechanics...Such a theory is evidently lacking for heat engines. We shall never possess it until the laws of physics are so extended and generalized as to make known in advance all the effects of heat acting in a definite way on any body whatsoever."(50,p. 6)

[8] To be sure, Carnot's description of this ideal process was somewhat vague. Although he surely was aware that the production of steam at constant temperature could occur only if the steam were allowed to expand so as to maintain a constant pressure, still he did not speak of any such expansion in connection with the first stage of his process. Instead, he seemed to imply that all of the useful work arises from the second, supposedly adiabatic stage. As a matter of fact, to make Carnot's process intelligible, we must assume that the first stage takes place in connection with the second stage, i.e. that the production of the steam is accompanied by its simultaneous admission into the cylinder where it undergoes isothermal expansion, followed by adiabatic expansion to the temperature of the condenser. Remarks occurring elsewhere in his paper indicated that Carnot was really quite clear on these points. His carelessness in describing the above process, we may attribute to the fact that he shortly supplanted it by a completely satisfactory one, employing a gas as working fluid (the classical Carnot cycle).

In the actual steam engine, the exhausted steam was condensed either by allowing it to mix with the cooling water or by ejection into the atmosphere. Carnot's genius for abstraction was revealed in his ideal supposition that the working body is cooled while preserving its identity and, finally, as we shall see, returned to its initial state.

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9 "The general and philosophical acceptation of the words perpetual motion should comprehend not only motion capable of indefinite continuance after it has been started, but also the action of an apparatus, of a set of bodies, capable of creating motive power in an unlimited quantity, and of setting in motion successively all the bodies of nature, if they are originally at rest, and of destroying in them the principle of inertia, and finally capable of furnishing in itself all the forces necessary to move the entire universe, to prolong and to constantly accelerate its motion." (50)

10 The value of γ, the ratio of specific heats at a given pressure and density, is obtained from the velocity of sound by employment of Laplace's classical formula (cf. p.). This, when substituted into the expression for β (cf. p.), yields, for $\vartheta = 1^{\circ}C.$, the result $\beta = \frac{\alpha}{(1+\alpha t)(\gamma - 1)}$, where α is the thermal coefficient of expansion. Thus Poisson could obtain β from the velocity of sound.

11 Such an assumption did not involve a contradiction with Carnot's law that "when the volume of a gas increases in geometrical progression, its specific heat increases in arithmetical progression," since Carnot had assumed the correctness of Delaroche and Berard's data in proving the law.

12 Writing U for the heat required to raise the given body of air from zero to t at constant unit volume, he defined s by the equation $s = e + U = T\log v + U$. Differentiating it with respect to t, he obtained $ds/dt = T' \log v + U'$ and then erroneously called ds/dt the specific heat at constant volume. (50, p.40). Hence he regarded the last equation as the analytical expression of the law respecting the variation of specific heat with density. This same incorrect expression permitted him to deduce the linearity of the function F (t) by assuming the specific heat to be independent of the density.

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13 We must suppose that the observation of this fundamental difficulty completely escaped Carnot, since he never mentioned it in his paper. For it is hardly feasible to suppose that the theoretical possibility of the absolute destruction of motive power would not have seemed objectionable to him. Aside from its violation of the general notion of substance, it is also out of accord with the mechanistic view of the world which Carnot tentatively advanced in the very paragraph in which he expounded the idea of a generalized excluded perpetual motion. That is to say, according to the mechanistic view, the absolute destruction of motive power would contradict the Principle of the Conservation of Living Force--a principle which Carnot must certainly have accepted.

14 As a matter of fact, this step was suggested by Carnot even in his paper of 1824: he remarked, in several places, that the caloric theory was in need of careful re-examination as it appeared to violate a number of experimental facts. From his notes, first published by his brother in 1878, we learn that, sometime before his death in 1832, he definitely discarded the caloric theory in favor of the kinetic theory of heat and even obtained a value of the mechanical equivalent of heat. "Heat," he said, "is the result of motion. Therefore it can be produced by the consumption of motive power and can produce this power."

Furthermore, it became perfectly clear to Carnot that the admission of the principle of the equivalence of heat and work must require that the proof of Carnot's Theorem be based on a new postulate, independent of the Energy Principle. For he said (in his notes), "When one creates motive power by the passage of the heat of the body A to the body B, is this quantity of heat the same regardless of the body employed to realize the motive power? Is there a means of consuming more heat in the production

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of motive power and of causing less to be imparted to B? Could one consume all of the heat, imparting none to B? If that were possible, one could create motive power without the consumption of fuel and by simple destruction of the heat of the body."

The fact of the impossibility of directly converting heat into work, while admitted by Carnot, nevertheless puzzled him. For he said,"It is difficult to say why, in the development of motive power through heat, a cold body is necessary, why one may not produce motion by consumption of the heat of the hot body."

Indeed, this stubborn fact was later taken by Thomson as the Second Law of Thermodynamics. Thus the point of view which Carnot reached before his death differed from the classical view, as formulated by Thomson, only in this: the fact, which to Carnot appeared novel and in need of explanation, Thomson accepted as an irreducible axiom.

These quotations must suffice to convince us that, had it not been for Carnot's untimely death in 1832, classical thermodynamics would very probably have been perfected twenty years before it actually was.

15 Gay-Lussac and Welter (1822), repeating the experiment of Clement and Desormes at a series of pressures and temperatures, found γ to be independent of temperature and pressure. Poisson (1823), along with Laplace, had assumed this to be generally true. Poisson had also assumed that the quantity of heat contained in a gas increases in proportion to its expansion at constant pressure.

16 "Now it is easy to show that this quadrilateral figure (abcd) is a paralellogram: this results from the infinitely small values assigned to the variations of the volume and pressure: let us conceive that perpendiculars are erected upon each point of the plane upon which the quadrilateral figure abcd is traced, and that on each of them, commencing at their foot, are described two quantities T and Q, the first equal to the temperature,

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20 Clapeyron's use of $\frac{dp}{dt}$ in place of $(\frac{dp}{dt})_v$ is unobjectionable, in this instance, since the vapor pressure of a liquid is completely determined by the temperature alone.

21 This same type of cycle, though of finite extent, had already been employed by Carnot. (cf. p.251)

22 "We have first raised the temperature of the body subjected to experiment by the quantity dT without changing its primitive volume v; afterwards, when it had become v + dv, we have lowered its temperature by the same quantity dT without varying its primitive volume v + dv. Now it may easily be seen that this double operation can be effected without loss of heat; let us suppose that n being a number indefinitely great, the interval of temperature dT be divided into a number n of new intervals $\frac{dT}{n}$, and that we have n + 1 sources of heat maintained at the temperatures T, $T + \frac{dT}{n}$, $T + \frac{2dT}{n}$, ..., $T + \frac{(n-1)\,dT}{n}$, T + dT.

"To raise the temperature of the body upon which we are operating from T to T + dT, we bring it successively into contact with the second, the third, and the (n + 1)th of these sources, until it has acquired the temperature of each of them. When, on the contrary, the volume v of the body being increased by dv, we wish to give it the temperature T, we bring it successively into contact with the nth, the (n-1)th, and the first of these sources, until it has acquired the temperature of each of them. We then return to these sources the heat that has been borrowed from each of them in the first part of the operation; for it is not necessary to attend to the differences of an order of inferior magnitude, arising from changes that may have been produced in the specific caloric of the body, in consequence of the variations of v and Q.

"Nothing therefore will have been lost or gained by any of these

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the second equal to the absolute quantity of heat possessed by the gas, when the volume and pressure have the values assigned to them by the abscissa v and the ordinate p which correspond to each point.

"The lines ab and cd belong to the projections of two curves of equality of temperature, passing through two points infinitely near, taken upon the surface of temperatures: ab and cd are therefore parallel: ad and bc will be also projections from two curves, for which Q = constant, and which would also pass through two points infinitely near, taken upon the surface Q = f (p,v); these two elements are therefore also parallel. The quadrilateral figure abcd is therefore a parallelogram....." (52, p.357)

17 Like many of the early writers, Clapeyron used the same notation for partial and total derivatives and differentials, eg. he wrote for $(\frac{dQ}{dv})$ simply $\frac{dQ}{dv}$. For clarity, we employ the modern notation. We shall see later that, from the stand-point of the First Law, these quantities are not genuine partial derivatives.

18 By comparison of equation (12) with Carnot's expression for du (cf.p.252), we see that the relation of Carnot's function F (t) to Clapeyron's function C (t) is given by $\frac{dF}{dt} = \frac{1}{C}$.

19 We have already observed (cf. p.) how Dulong (1829 (54) determined γ for a series of gases by measuring the velocity of sound (indirectly from the pitch of sound) in them and then applying Laplace's classical formula for sound velocity. From the values of C_p obtained by Delaroche and Berard (cf. p.125), he was then able to calculate the values of C_v. In this way, Dulong found that the temperature changes, experienced by the gases for the same compression, were inversely proportional to their specific heats at constant volume, from which he concluded that "equal volumes of all gases under the same conditions evolve on compression the same quantity of heat."

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sources, excepting always the source of which the temperature is $T + dT$, which will have lost the heat necessary to elevate the temperature of the body...from $T + \frac{(n-1)\,dT}{n}$ to $T + dT$, and the source maintained at the temperature T, which will have acquired the heat necessary to reduce the temperature of the same body from $T + (\frac{dT}{n})$ to T. If we suppose n to be infinitely great, these quantities of heat may be neglected."(52,p.365)

23 Like equation (13), for the heat effect of the isothermal expansion of a perfect gas, and equation (18) for the isothermal latent heat of vaporization, equation (25) is also valid and for the same reason: in an isothermal process, the caloric-theory assumption that the heat absorbed is determined by the state variables, p and v, is true. Substituting $DQ=TdS$ and $C = T$, equation (25) assumes its more general, modern form,

$$(\frac{dS}{dp})_T = -(\frac{dv}{dT})_p$$

24 This expression for dQ, like the one for Q from which it was obtained, is incorrect. Thus the expression for c_p, the coefficient of dt, is incorrect, i.e. c_p for a perfect gas is not a function of p. Fortunately, however, this incorrect expression for c_p is not used in the calculation. On the other hand, the coefficient of d_p, which is used, is correct. Hence, that the calculation of 1/C is correct, is no more than a happy accident.

25 Actually Holtzmann used the density ρ in place of v, as independent variable. For ease of comparison with Clapeyron's results, we shall retain v as independent variable.

26 Besides the dependence of this argument on the principle of the conservation of caloric, it also neglects the volume change, hence the work effect occasioned by the melting of the ice in the third stage of the process. However, once the correct conclusion respecting the depression of the freezing point be granted, James Thomson's analytical expression for it, which follows, is also correct.

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27 However, as Thomson candidly observed, Joule's experiments had not revealed any definite dependence of this ratio on the temperature, whereas according to (4), it would appear to decrease gradually with temperature since μ does. This discrepancy, along with the lack of temperature change on free expansion, caused Joule to suggest, in a letter written to Thomson in December, 1848, and reported in the latter's 1851 paper on "The Dynamical Theory of Heat, etc.", that the value of μ could be expressed by the formula $\mu = J\frac{\alpha}{1+\alpha t}$, J being the mechanical equivalent of heat. For this substitution reduces (4) to $W = JQ$. This formula for μ had already been deduced by Helmholtz by a questionable method (cf. p.273), and was later adopted by Clausius. Thomson was the first to thoroughly discuss the probability of its validity. (cf. p.327)

28 To be sure, Carnot's theory led to erroneous formulae when applied to adiabatic expansion and to the specific heats of gases (cf. p.249). With repsect to the former, however, it appears from Holtzmann's paper (1845), that the available data were not sufficiently accurate to reveal the discrepancies. Hence, so far as most of its consequences were concerned, Carnot's theory seemed valid. It was the contradiction with experience (e.g. Joule's experiments) of the method of proof of its fundamental theorem (Carnot's Theorem), rather than the discrepancies in the results of this theorem, that finally entailed the abandonment of the caloric postulate.

29 That the heat absorbed by the condenser of a heat engine, whose frictional heat is rendered sufficiently small, is actually less than that developed by the fire-box was not demonstrated experimentally until the work of Hirn in 1857. (17, p. 46)

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30 As a matter of fact, Watt's experiments had seemed to establish that the heat required to convert a given mass of water at 0°C. into saturated vapor at the pressure p was independent of p. This conclusion was known as "Watt's Law" and was widely accepted until Regnault's researches demonstrated its falsity. "Watt's Law," in conjunction with the caloric chpothesis, requires that the heat capacity of saturated vapor be zero, a result which, as we shall see, both Rankine and Clausius discredited on theoretical grounds.

31 Rankine continued to support such a view for many years. In 1865, long after the kinetic theory of gases was generally employed to explain the properties of gases, Rankine attempted to prove that "the Second Law of Thermodynamics follows from the supposition that sensible heat consists in any kind of steady molecular motion within limited spaces," but that an unsteady motion, such as the hypothetical vibratory motion of Bernoulli's kinetic theory of gases, was inconsistent with the Second Law. (cf. his paper, "On the Second Law of Thermodynamics." (47)

32 When the actual energy in question is heat, and the potential energy is work, Rankine's "Second Law" takes the form: "If the total actual heat of a homogeneous and uniformly hot substance be conceived to be divided into any number of equal parts, the effects of those parts in causing work to be performed are equal." Maxwell(47, xxix)has declared the meaning of this statement to be "inscrutable," since "total actual heat" has no meaning and, even if it had, we could not imagine it divided into equal parts so that we could study their actions separately.

33 Although one can never be too sure of the meaning which Rankine intended to convey by these general expressions, we may nevertheless hazard a guess as to the probable interpretation of (2) in a special case. Thus suppose an increment of heat d.Q, when added to a gas incurs both an

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increase of its temperature as well as a development of work by expansion. The increase of sensible heat would then be dQ, the term LdQ would represent the heat effect required to produce the volume change (i.e. the heat effect over and avove that causing the rise of temperature and the production of work), and the term $Q\frac{dP}{dQ}dV$ would supposedly represent the work done. The division of the heat element into such factors does not correspond to any physical operation. Also, Rankine's expression for the work done is hardly intelligible. Finally, his employment of Q as independent variable is reminiscent of the caloric theory, which he formerly rejected.

34 Rankine's equation (9') is really meaningless since the "actual heat energy" Q of a body is nowhere defined in terms of measurable operations. Helm's attempt (32, p.113) to show that equation (9') follows from the principles of modern thermodynamics is consequently unfortunate.

35 Rankine's A Manual of the Steam Engine and other Prime Movers (London, 1859) was the first text-book of thermodynamics.

Rankine's contributions to graphical thermodynamics are to be found in his paper, "On the Geometric Representations of the Expansive Action of Heat, and the Theory of Thermodynamic Engines" (1854) (47). He was the first to represent the heat added to a body in isothermal expansion AB, by the area, on the p—v diagram, formed by the isothermal line AB and the adiabatics AM and BN, indefinitely extended (cf. Fig. 11')

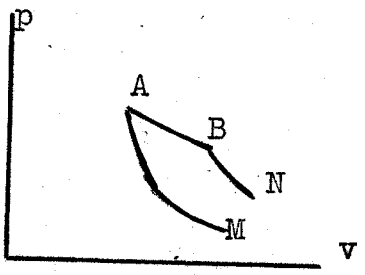

Figure 11'

36 "In our times, ever more facts point to the conclusion that heat is not a substance, but consists in a motion of the smallest parts of bodies. If this be correct, the general law of mechanics must also apply to heat—which law states that an existing motion may transform itself into work in such a manner that the loss in vis viva is proportional to the work gained."

37 This mechanistic viewpoint, as we shall see, played no formal part in the principles of thermodynamics as Clausius developed them in the

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present 1850 paper. Thus, he made no attempt to introduce, into his equations, separate terms for those portions of the absorbed heat corresponding to the increase of sensible heat and the internal work expended, respectively. This distinguishes Clausius from Rankine who employed such terms freely in his exposition of "energetics," thus exposing himself to the charge of vagueness. For there is no physical operation which may be employed to measure the "internal work;" and "sensible heat," as distinguished from "internal work," could be consistently defined only in terms of an absolute temperature scale, which, however, is not given. A curious contrast thus presents itself between the Englishman and the German: Rankine, while professing to expound the energetic view of thermodynamics, introduced species of energy, having no meaning except in terms of hypotheses relating to the structure of matter and the ultimate nature of heat; Clausius, while freely admitting such hypotheses, actually presented his theory in such a form as to be completely independent of them. To be sure, several of Clausius' later papers were considerably less fortunate in this respect.

38 In an 1864 footnote, Clausius insisted that, although Q is not a function of the state variables v,t, still the coefficients $(\frac{dQ}{dv})$ and $(\frac{dQ}{dt})$ are, i.e. for a given assignment of values to dt and dv, the element of heat which, neglecting higher order infinitesimals, may be represented by

$$dQ = (\frac{dQ}{dt})dt + (\frac{dQ}{dv})\,dv$$

is determined, so that $(\frac{dQ}{dt})$ and $(\frac{dQ}{dv})$ are also determined.

Clausius' notation is here rather confusing and was avoided by Thomson and many subsequent writers. For the employment of the symbols dQ, $(\frac{dQ}{dt})$, and $(\frac{dQ}{dv})$ really assumes that a definite path in the v,t plane has been specified; otherwise, these symbols have no meaning. Thus $(\frac{dQ}{dt})$ must mean,

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in general, the rate at which Q varies with respect to t, not while v is held constant but while v varies with t in accordance with the prescribed path. In other words, as Tunell observes, dt and dv in the above equation are not independent infinitesimals and $(\frac{dQ}{dt})$ and $(\frac{dQ}{dv})$ are not partial but total derivatives. Tunell nevertheless defends Clausius' notation on the ground that dQ may be regarded as the differential of a single parameter which by virtue of the prescribed path determines the independent variables v and t. Thus Q and likewise $(\frac{dQ}{dv})$ and $(\frac{dQ}{dt})$ are functions of the variables , the length of the prescribed curve in the v,t plane measured from a reference state v_o, t_o. Of course, in the particular case where the prescribed path is an isotherm, Q becomes a function of v only and $(\frac{dQ}{dv})$ becomes an ordinary derivative; as is also the case with $(\frac{dQ}{dt})$ when the prescribed path is perpendicular to the v axis.

Exactly similar considerations apply to W, the work done, also to $(\frac{dW}{dv})$ and $(\frac{dW}{dt})$.

Thus Clausius retained the notation of Clapeyron, giving to it, however, an entirely different meaning.

[39] In an appendix added in 1864 Clausius described the above transformation in detail. Placing $(\frac{dQ}{dt}) = M$, he obtained (II) in the form

$$\frac{\partial}{\partial t}(\frac{dQ}{dv}) = \frac{\partial M}{\partial v} + \frac{AR}{v}. \qquad (a)$$

Integration with respect to t, holding v constant, gives

$$(\frac{dQ}{dv}) = \int \frac{\partial M}{\partial v} dt + AR\frac{t}{v} + \phi(v). \qquad (b)$$

Substituting this value of $(\frac{dQ}{dv})$ in the "complete" expression, $dQ = (\frac{dQ}{dv})dv + (\frac{dQ}{dt})dt$, Clausius obtained

$$dQ = Mdt + \left(\int \frac{\partial M}{\partial v} dt + \phi(v) + AR\frac{t}{v}\right) dv. \qquad (c)$$

Since the expression

$$Mdt + \left[\int \frac{\partial M}{\partial v} dt + \phi(v)\right] dv$$

is exact, (c) may be written

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$$dQ = dS + AR\frac{t}{v}\,dv \qquad (d)$$

where S is an arbitrary function of v and t, corresponding to the arbitrariness of and M. If we write (d) in the form

$$dQ = d(S - ARa \log v) + AR\frac{a+t}{v}\,dv$$

and place $(S - ARa \log v) = U$,

we have the desired equation (IIa), namely,

$$dQ = dU + AR\frac{a+t}{v}\,dv. \qquad (e)$$

Clausius observed that the more general equation

$$\frac{\partial}{\partial t}\left(\frac{dQ}{dv}\right) - \frac{\partial}{\partial v}\left(\frac{dQ}{dt}\right) = A\left(\frac{dp}{dt}\right) \qquad (f)$$

may be similarly transformed into

$$dQ = dU + Apdv. \qquad (g)$$

He also noted that dQ, strictly speaking, is not given by Mdt + Ndv where $M = \frac{dQ}{dt}$, $N = \left(\frac{dQ}{dv}\right)$, but by

$$Mdt + Ndv + \tfrac{1}{2}\left\{\left(\frac{dM}{dt}\right)(dt)^2 + \left[\left(\frac{dM}{dv}\right) + \left(\frac{dN}{dt}\right)\right] dtdv + \left(\frac{dN}{dv}\right)(dv)^2 + \cdots\right.$$

40 We may recall that this proposition was first made the basis for the calculation of the mechanical equivalent of heat by Mayer in 1842. Mayer, unlike Seguin and Holtzmann, justified the assumption by reference to the free-expansion experiment of Gay-Lussac, later repeated by Joule. Clausius cited, as evidence for the probability of the assumption, the regularity in the deportment of gases without making specific reference to the free-expansion experiment: this regularity, he said, indicates that the attraction between the particles, hence the internal work, may be neglected.

41 Clausius specifically observed that the left-hand members of (5) and (6) are not bona fide partial derivatives since Q is not a function of the

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independent variables v and t, or p and t. Instead, they represent the limiting values of the ratios of increments under prescribed conditions.

42 Carnot and Clapeyron had concluded from Carnot's Theorem that this difference was a function of the temperature, and Holtzmann concluded that it depended on the pressure as well.

43 Carnot had concluded that γ is constant if β, the compression coefficient, is constant. (cf. p.246)

44 As the condition that a Carnot Cycle shall yield the maximum work, Clausius simply cited the one already given by Carnot, namely, that bodies of different temperatures shall never be allowed to come into contact. The fact that reversibility implies infinite slowness is still to be realized, or, at least, expressed.

45 "By repetition of these two alternating processes one could, without expenditure of work or any other change, convey as much heat as one wished from a cold body to a warmer one, and this contradicts the well-known behavior of heat which everywhere strives to equalize temperature differences and, accordingly, to pass from warmer to colder bodies."

46 The whole explanation is very concisely expressed in Thomson's 1851 paper: "The explanation of this apparent difficulty...is, that the steam in rushing through the orifice produces mechanical effect which is immediately wasted in fluid friction, and consequently reconverted into heat; so that the issuing steam at the atmospheric pressure would have to part with as much heat to convert it into water at the temperature 100° as it would have had to part with to have been condensed at the high pressure and then cooled down to 100°, which for a pound of steam initially saturated at the temperature t is, by Regnault's modification of Watt's Law, to 0.305(t-100)

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more heat than a pound of saturated steam at 100° would have to part with to be reduced to the same state; and the issuing steam must therefore be above 100° in temperature, and dry." (56, p. 209)

47 The experiment of Mayer, which Thomson referred to, is the one in which the "father of energetics" succeeded in raising the temperature of a body of water from 12° to 13°C. by shaking it. (May, 1942)

In a footnote, Thomson stated that he had not become acquainted with Helmholtz's 1847 paper until January, 1851--too late to profit by its contents in writing the present paper. This calls to mind that Carnot's original paper was also inaccessible to Thomson until late in the year 1848; also, Clausius had never seen it when he wrote his great memoir of 1850.

48 In a footnote, Thomson referred again to his original objection to the Principle of Equivalence, namely, that the actual disappearance of heat had never yet been experimentally demonstrated. This objection still stands, he said, and its removal would be "a very great step in the experimental verification of the dynamical theory of heat." Nevertheless he thought that the direct production of frictional heat, together with the fact that Joule's experiments conform with numerous deductions from the Principle of Equivalence, was sufficient evidence in favor of the latter's acceptance.

49 The form of Thomson's axiom was undoubtedly suggested by Carnot's statement (cf. p.237) that, in order to utilize the motive power of heat, a colder body is always necessary. For then, if the source of the heat, which we desire to convert into work, is itself the coldest body, no colder body is available to function as condenser and the production of work is impossible.

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The modern form of Thomson's axiom is stated thus: "A change of state consisting of a development of heat connot supplement a change of state consisting of an absorption of work." This appears to embrace Thomson's statement as a special case. The explanation of the peculiar form of Thomson's statement is to be found in the meaning which he ascribed to the phrase, "derive mechanical effect from any portion of matter:" although he understood, by this phrase, that the working body was supposedly returned to its initial state, he did not interpret it as excluding the possibility that part of the heat of the "portion of matter" might be passed on to a colder body. This explains the necessity for the reference to "the coldest of the surrounding objects," i.e. this reference excludes the possibility that heat may pass from a higher to a lower temperature.

Finally, Thomson's phrase, "by cooling it below the temperature of the coldest of the surrounding objects," is confusing, since the axiom is applied to bodies (infinite heat reservoirs) supposed capable of developing and absorbing heat without change of temperature. The phrase would have better been replaced by the words, "by withdrawal of heat from it at a temperature equal to, or below that of the coldest of the surrounding bodies."

[50] This phrase no doubt referred to the unavoidable, irreversible flow of heat from a higher to a lower temperature, accompanying the production of thermoelectricity. (cf. p.366)

[51] One important exception must be pointed out. Many writers, following Thomsom, have considered the latter's above-quoted axiom respecting the impossibility of obtaining work by a mere development of heat as logically equivalent to Clausius' axiom respecting the impossibility of heat flowing from a lower to a higher temperature. Actually, Clausius' axiom is the more general, and it, but not Thomson's axiom, is sufficient for the

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establishment of Carnot's Theorem. However, out of fairness to Thomson, we must admit that the refined point of view from which the German's axiom appears more general was evidently as foreign to Clausius as to Thomson.

52 Thomson was evidently not aware that bodies existed whose states were not determined by these variables, e.g. a body of liquid water, ice, and water vapor in equilibrium at the triple point. His treatment was therefore not as general as he supposed.

53 Thomson employed the same notation for partial derivatives as for total derivatives. Thus he wrote the left-hand member of (2) simply as $\frac{dp}{dt}$. Following our previous practice, we shall use the modern notation.

54 This device was first employed by Carnot. (cf. p. 241)

55 As Thomson observed, this expression might be employed to calculate J from the pressure and thermal capacities of fluids. Actually, because such data are not known with sufficient accuracy, J must be determined directly by experiment.

56 As before, σ denotes the specific volume of the liquid; s, that of the vapor; r, the latent heat of unti weight of the vapor; and c, the specific heat of the liquid. Regnault's researches had evaluated c, r, and p as definite functions of t from 0° to 230°C. The direct determination of s was carried out in 1860 by Fairbairn and Tate and showed that s could not be accurately calculated from the density of superheated vapor under the assumption that the latter continued to conform to the perfect gas law right up to the condensation point.

Note that the expression (28) neglects the small amount of work occasioned by the volume change on heating the liquid at constant pressure from 0° to t°

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57 If, instead of supposing the process to be adiabatic, we suppose the gas returned to its initial temperature t, equation (48) becomes, on neglecting S,

$$E(v_2, t) = E(v_1, t) - JQ.$$

Substituting the values of E from (40), the above expression reduces to

$$Q = \left[\left(\frac{1}{J} - \frac{\alpha}{\mu(1+\alpha t)}\right)\right] p_1 v_1 \cdot \log v_2/v_1$$

which is identical to the relation (31) already obtained by Thomson.

58 The experiments reported in 1862 indicated this heat to be slightly less than that equivalent to the work done.

59 As a matter of fact, by virtue of Thomson's choice of J/μ as the absolute temperature, the work developed by a Carnot cycle absorbing unit heat at the absolute temperature T° and operating between T° and $(T-1)^\circ$ is not independent of T but equal to its reciprocal, as is evident from equation (54) written in the form $(H-R)/H = (T_S - T_R)/T_S$.

60 It may be objected that Thomson's axiom respecting the impossibility of an unsupplemented conversion of heat into work, or Clausius' axiom respecting the impossibility of an unsupplemented transfer of heat from a lower to a higher temperature, expresses the fact of irreversibility. Rigorously, however, these axioms are negative propositions which do not state what processes actually occur in nature. These axioms express the fundamental fact of irreversibility only in case it be given that the processes, whose reversal the axioms declare to be impossible, actually occur in nature.

61 In a footnote added in 1864 Clausius demonstrated how this may be done. Three possibilities arise. In the first case, a pair of transformations may consist of two transformations of the same kind, e.g. the

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conversion of the heat Q at t into work and the transfer of the heat Q_1 from t_1 to t_2. These transformations, the sum of whose equivalence-values is zero by hypothesis, may be cancelled by reversing the cycle of Figure 16. Again, the pair may consist of two transformations of the first kind, e.g. a conversion of heat Q' at t' into work and the generation of the heat Q at t by work. Suppose a cycle to transform heat Q at t into work (thus cancelling the second transformation of the pari) and transfer heat Q_1 from t_1 to t_2. Then let a cyclical process of the opposite kind transfer heat Q_1 from t_2 back to t_1 and transform work into a quantity of heat at t'. This conversion of work into heat must be equivalent, aside from its sign, to the given conversion of heat into work, since they are both equivalent to the same heat transfer. Hence the heat absorbed at t' must be Q' and the first transformation of the pair is also cancelled. Finally, the pair of transformations may consist of two transformations of the second kind, e. g. one consisting of a transfer of heat Q_1 from t_1 to t_2, the other of a transfer of heat Q_1' from t_2' to t_1', where by hypothesis, $Q_1\left(\frac{1}{T_2} - \frac{1}{T_1}\right) + Q_1'\left(\frac{1}{T_1'} - \frac{1}{T_2'}\right) = 0$. Conceive of two cyclical processes in one of which Q_1 is carried from t_2 to t_1 (thus cancelling the first member of the pari) and heat Q at t generated by work, while in the second, heat Q is converted into work and a quantity of heat transferred from t_1' to t_2'. This transfer of heat from t_1' to t_2' must be equivalent, aside from its sign, to the given heat transfer from t_2' to t_1', since the two transfers are both equivalent to the production of heat Q at t. Hence the heat transferred from t_1' to t_2' must be Q_1' so that the second member of the pari is also cancelled.

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62 If we introduce Thomson's symbols, $T = J/\mu$, $\frac{\partial T}{\partial t} = 1$, $\frac{\partial}{\partial T} = \frac{\partial}{\partial t}$, $\frac{dQ}{dv} = M$, $\frac{dQ}{dt} = N$, equation (16) reduces to $M = \left(\frac{\partial M}{\partial t} - \frac{\partial N}{\partial v}\right)\frac{J}{\mu}$. This last equation becomes identical to Thomson's expression of the Second Law, namely, $M = \frac{(\partial p/\partial t)}{\mu}$, only if $\frac{\partial p}{\partial t} = J\left(\frac{\partial M}{\partial t} - \frac{\partial N}{\partial v}\right)$, which is Thomson's expression for the First Law. It thus appears that Clausius' equation(16), hence his equation (13), really involves the First Law as well as the second. This might have been predicted from the circumstance that the notion of equivalence of work and heat (in the sense of the First Law) was assumed in its derivation.

63 Later, in his book, Die mechanische Warmetheorie (60), Clausius proposed an alternative method for the derivation of (13)—a method which has become very popular with subsequent authors of texts on the subject. Regarding the absolute temperature as given, he first shows that if there were employed, as working body in a Carnot cycle, a gas conforming to "Mayer's Hypothesis" and the relation $pv = RT$, the efficiency of the cycle would equal to the ratio $\frac{T_1 - T_2}{T_1}$, T_1 and T_2 denoting the absolute temperatures of upper and lower isotherms, respectively. Denoting by Q_1 and Q_2 the quantities of heat absorbed at T_1 and T_2, respectively, this result may be placed in the form

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \qquad (1)$$

By Carnot's Theorem, this same relation must hold, regardless of what working body is employed in the cycle.

To generalize the above result, Clausius resorted to a graphical method. Let the closed curve C in the p—v diagram of Figure 16 represent any reversible cyclic process whatsoever. Let there be represented on

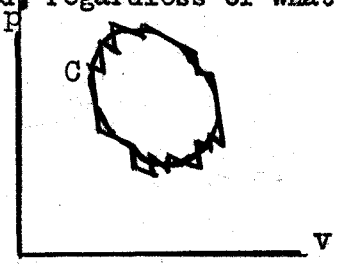

Figure 16

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this p—v diagram a series of n Carnot cycles, conforming to the following conditions: (1) each of their isotherms shall intersect the curve C; (2) the line representing the adiabatic expansion of the ith cycle shall coincide with that representing the adiabatic compression of the (i + 1)th cycle; (3) the line representing the adiabatic compression of the first cycle shall be tangent to the curve C near its left-hand extremity, in such a manner that none of the Curve C shall extend to the left of this line, and the line representing the adiabatic expansion of the nth cycle shall be tangent to the curve C near its right-hand extremity, in such a manner that none of the cruve C shall extend to the right of this line. (This last condition was assumed although not stated by Clausius.)

Taken together, these n Carnot cycles are equivalent to the compound cycle represented by the closed zig-zag line on the diagram. For, in the operation of the n Carnot cycles, the work effects associated with those portions of the intermediate adiabatics, represented by dotted lines, vanish, since each of these portions is traversed twice and in opposite directions. Therefore the net work of the n Carnot cycles, like that of the compound cycle, is given by the area of the closed zig-zag figure. Also, the heat effects of the series of Carnot cycles are the same as those of the compound cycle, since the series of Carnot cycles and the compound cycle have their isothermal portions in common. Then by (1) we have, for the compound cycle,

$$\sum_i \frac{Q_i}{T_i} = 0. \qquad (2)$$

Finally, Clausius tacitly assumed that, between any two isotherms on the p—v plane, there exists a continuous series of intermediate isotherms, and that between any two adiabatics, there exists a continuous series of intermediate adiabatics. Then, by increasing indefinitely the number n of

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Carnot cycles composing the compound cycle , subject to the condition that the line representing the adiabatic compression of the first cycle, as well as that representing the adiabatic expansion of the nth, shall not suffer change of position but only diminution in length, the closed zig-zag line, representing the compound cycle, may be made to approach the closed curve C, representing the original cycle, and, in the limit, will coincide with it. Hence, by (2), we shall have, for the original cycle,

$$\int \frac{dQ}{T} = 0 \qquad (3)$$

64 The obscure character of this axiom is evident from the fact that the "mechanical work" referred to is supposed to include internal or molecular work as well as external work, and the "heat" referred to is the sensible heat contained in the body. Thus, neither of the terms "mechanical work" and "heat" corresponded to any physical operation. Nor was any attempt made to define the "absolute temperature."

65 Since H was originally defined as heat, as measured by the thermometer, it is difficult to avoid the conclusion that the above proposition is a tautology.

Clausius interpreted the proposition to mean that the "real heat capacity" of a body should be a constant independent of the state of aggregation and the temperature. The difference in apparent specific heats of a body at different temperatures in the same state of aggregation, and at the same temperature in different states of aggregation, he attributes to differences in the internal work. Rankine, on the contrary, had attributed different "real specific heats" to a body in different states of aggregation.

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66 Although Clausius did not point it out explicitly, it is evident that in the first integral of the right-hand member of (33), T must be the temperature of the reservoir from which the heat dQ is absorbed. For since the process is irreversible, the "temperature" of the body itself is undefined, i.e. its temperature is not uniform.

67 If we suppose the body, whose entropy changes by $S-S_0$, to comprise all the bodies which suffer change, the term $\int \frac{dQ}{T}$ vanishes and there results simply $N = S-S_0$. Then, if N be assumed to be positive for all actual processes, an assertion frequently made by Clausius, we should obtain the result that every change in an isolated system is accompanied by an increase in the entropy of the system.

However, the much-quoted statement of Clausius asserts much more than this. It is not completely acceptable today, and was even less so when Clausius promulgated it. In the first place, no strictly scientific statement can be made about the "entropy of the universe," since the universe cannot be an object of experimental investigation. Even if we understand by "universe" the aggregate of those bodies which we may subject to experimental measurements, the "entropy of the universe" is still an ambiguous expression, since it tacitly assumes that between all of the states of these bodies there exist, or may exist, series of actual processes of such a nature that they serve to define reversible paths between the said states. For, otherwise, the entropies of the bodies cannot be defined for these states. But many states exist for which such an assumption appears ungrounded, e.g. the initial and final states of a complicated chemical reaction. Finally, even if we regard Clausius' statement as applicable only to those bodies for whose states the entropy is unambiguously defined, still he had no right to assert that the entropy of an isolated system of such bodies approaches a maximum. For the experimental evidence constituting the Third Law and supplying us with a legitimate concept of an

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absolute zero of temperature, was still lacking in Clausius' day. The German's unwarranted assumption of such a state of maximum entropy was probably suggested by his naive belief in a lowest attainable temperature, also perhaps by Thomson's 1852 statement that the universe appears to be tending toward a condition in which it will be unfit for human habitation.

68 In the 1865 memoir, Clausius noted that for a gas conforming to $pv = RT$, (48) gives for the entropy

$$S = S_0 + c\log T/T_0 + AR \log v/v_0, \qquad (49)$$

c being the specific heat at constant volume.

69 As Thomson noted, if substances existed which were good conductors of electricity and, at the same time, very poor conductors of heat, then irreversible conduction of heat occurring in a thermo-element constructed of such substances might become negligibly small, so that the Second Law might be unambiguously applied to the reversible thermal effects connected with the thermo-electric current. Actually, since such substances do not exist, the construction of such an ideal couple cannot even be approximated.

70 σ_1 and σ_2, which Thomson called "the specific heats of electricity in the different metals," can only be functions of the temperature; otherwise, as will become evident from the succeeding equations, an electric current could be generated by a mere application of heat to a homogeneous conductor maintained at a uniform temperature.

71 If the "specific heats of electricity" were equal to zero, equations (3) and (4) would become, respectively, $\frac{\Pi}{T} = \text{const.}$

and $$E = J\frac{\Pi}{T}(T-T').$$

In an earlier 1851 paper (56, p. 316), Thomson actually obtained these relations (in terms of Carnot's function μ) by assuming that the only

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reversible thermal effects were those occurring at the junctions. Similar relations had also been obtained by Helmholtz (cf. p. 209) and Clausius. Thomson soon found that they did not agree with experiment. He was thus led to suppose that additional thermal effects, occurring in the homogeneous metals themselves, were involved in the production of the current; the σ functions were hence defined and intoduced into the equations. The actual production of a temperature gradient by the flow of an electric current in a homogeneous conductor, as well as the converse phenomenon of pyroelectricity, was later demonstrated experimentally. (56, p. 460)

72 Unlike the "energy of a phase," the "entropy of a phase" is not a new concept, i.e. it is defined simply as the value of the integral $\int (dQ/T)$ for a reversible process in which the given masses of constituents are brought from their respective reference states to the states obtaining in the given phase-state.

73 Perhaps, we should also exclude the theory of the behavior of so-called stationary systems, i.e. those subject of a constant temperature gradient. However, attempts, whose legitimacy must still be considered problematical, have recently been made to extend thermodynamics to the treatment of such systems.

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APPENDIX

THE TEMPERATURE CONCEPT[1]

by

Martin K. Barnett

Introduction

In the classical development of thermodynamics--a development which still serves as model for the conventional presentation of the subject--the temperature concept occupies a position of strategic significance. For upon the assumption of the existence of an "arbitrary temperature scale" rests both the possibility of defining the concept of heat (and, subsequently, the generalized notion of energy) and of formulating the second law of thermodynamics. A critical analysis of the general validity of this assumption should therefore be a worthwhile undertaking.

Statement of Problem

Our task is to develop a method for ordering any given number of bodies, existing in certain states, into a "temperature series;" each body will then occupy a position in the series which is unambigously determined as either identical with, "less than," or "greater than" that of every other body in the series. Once the existence of such a series is established, an "arbitrary temperature scale" may readily be derived and its nature determined.

By the "state" of a body we mean to embrace all macroscopic aspects of the body's existence, capable of description in terms of established physical properties, other than the position and velocity of the body as a whole in space and its gravitational potential with reference to the earth. Further, only bodies existing in states satisfying the following criteria will be

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subject to classification: (1) each state property of the body maintains a constant value with the passage of time; (2) concurrent changes of state in neighboring bodies are not essential to the preservation of the state of the given body. The first criterion excludes bodies the states of which are chaotic or subject to regular and continual variation, while the second rules out bodies in the well-known "steady states."[2]

Method Adopted

The method here adopted for ordering bodies into a "temperature series" is an operational one and was first suggested by Langevin (3). It requires that every body to be classified shall be conjoined, in turn, with each of the other bodies under prescribed conditions, "the temperature series" then being derived from the nature of the reciprocal changes which ensue.

Each conjointment must begin with both bodies in their initial states; otherwise the classification deduced will not pertain to those initial states. Therefore, conduction to the place of conjointment must not alter the state of the body; or, if it does, the state must be restored before conjointment occurs.

Conjointment Conditions

Let A denote a body with which each of the other bodies, denoted by the general term K, is to be conjoined, in turn. So far as influences external to A and K are concerned, the conjointment conditions are simply expressed: A and K shall constitute an isolated system except for those external force fields indispensalbe to the preservation of their initial states. Care must be exerted that external fields associated with the initial state of one body do not, upon conjointment, alter the initial state of the other.

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With respect to certain types of possible mutual influences, the statement of the conditions of conjointment of A and K requires the introduction of the notion of "independent systems," a conception which we borrow from Duhem (1). Suppose that a certain set of values of the quantities $x_1, x_2, \ldots x_n$, finite in number, adequately[3] represent a given state of a system without being redundant; that is, the value of no one of these quantities is determined, by virtue of its definition, by assigning values to any or all of the remaining quantities. Thus, if our system is a homogeneous body, no more than two of the three quantities--mass, volume, and density--may be included among the quantities representing the state.

Not every arbitrary set of values assigned to the $x_1, x_2, \ldots x_n$ will represent another state of the same system. For these values are subject to certain general restrictions or "equations of condition." The latter are distinguished from the more specific experimental laws, which we ignore for the present, by the fact that they are immediate consequences of the definitions of the x_i and the general conditions of existence of the system. In fact, they may properly be regarded as the mathematical expression of these conditions. For example, if our system is an isolated, electrically charged body, the very definition of electrical charge requires that the elements of charge associated with the various mass elements of the body vary only in a manner which will maintain a constant value for their sum.

Let us suppose such restrictions, representing the so-called "constitution" of the system, are expressible in the form:

$$f_1(x_1, x_2, \ldots x_n) = C_1$$
$$f_2(x_1, x_2, \ldots x_n) = C_2$$
$$\ldots\ldots\ldots\ldots\ldots$$
$$f_m(x_1, x_2, \ldots x_n) = C_m$$

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where C_1, C_2, ... C_m are constants. Then only $p = n - m$ of the quantities x_1, x_2, ... x_n may be independently varied without violation of expression 1.

Assume a system S isolated except for those external force fields indispensable to the preservation of its state. Let this state be represented by the quantities x_1, x_2, ... x_n, subject to the constitutional liaisons (1). Suppose that it is possible to divide S into two sub-systems S_1 and S_2 and that the properties x_1, x_2, ... x_n, are divisible into two sub-groups corresponding to S_1 and S_2. Then S_1 and S_2 will each have a set of liaisons similar to (1). If the properties and liaisons associated with S_1 may be defined and evaluated without any reference to S_2 or its properties and liaisons, and similarly, if the properties and liaisons associated with S_2 may be defined and evaluated without any reference to S_1 or its properties and liaisons, -- then S_1 and S_2 are said to constitute a pair of "independent systems." They are said to be "independent of one another." In this case, the region of theoretically possible states (i.e., not contradicting the constitutional liaisons) of S_1, as well as that of S_2, is the same as it would be if S_1 and S_2 were isolated from one another.

With respect to certain types of possible mutual influences, the conditions of conjointment of A and K may now be stated: A and K, without being isolated from one another, shall constitute a pair of independent systems. The satisfaction of this condition corresponds to the exclusion of all mutual actions due to mechanical pressures, chemical action, and electrical conduction.

Thus, suppose that A and K have a portion of their surfaces in common and that this portion is deformable; that is, A and K are subject to mutual mechanical pressures effective in producing changes of form. The contour

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of that portion of A's surface which is common to K may be regarded as determined by the surface coordinates of K over this common region, and vice versa. The two systems are evidently dependent. They may be rendered independent in this respect by postulating that the common surface shall be perfectly rigid. For, then, the possible configurations of A and K at any instant are the same as if A and K were isolated from one another.

The existence of chemical action between A and K implies the possibility of transfer of matter across a spatial surface regarded as the separating boundry. The principle of conservation of mass provides a liaison for each chemical element. While A and K are isolated from one another, each such liaison for A is expressible by an equation in no way involving K, and vice versa. But when A and K are subject to mutual chemical action, the liaison can only express that the mass of a given element associated with A equals a constant minus the mass associated with K, and vice versa. The systems are dependent; but they can be rendered independent, in this respect, by postulating a separating membrane impermeable to matter.

Similarly, if independent, A and K may not influence one another by electrical conduction. For if such conduction were possible, the liaison expressing the principle of conservation of charge would take the form

$$q_1 + q_2 = \text{constant}$$

The charge associated with A would depend on the charge associated with K. To render the system independent in this respect, we must postulate a separating shield incapable of conducting electricity.

The possibility of mutual influences associated with electrical or magnetic induction and gravitation remain to be considered. The independence postulate evidently does not suffice here: such effects must be ruled out by specific statement. Because the gravitational field of the earth greatly overshadows that of terrestrial bodies, any mutual gravitational action of

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A and K may generally be neglected. Mutual actions associated with electrical or magnetic fields may usually be rendered negligible by imposition of separating shields of suitable properties. Such shields, like those assuring independence, must not serve to isolate A from K.[4]

Conditions Peculiar to A

Suppose that the state of A is adequately represented by the properties $x_1, x_2, \ldots x_n$ and that there are m liaisons expressing A's "constitution." Suppose further, that r relations are required to represent additional experimental laws connecting the x_i. This leaves $n - (m + r)$ properties which are independently variable.

We now require that $n - (m + r + 1)$ of the properties x_i of A shall be held constant during the conjointment of A with K. This stipulation will insure that any change of state of A will necessarily involve uniquely determined changes in each of the remaining $q (= m + r + 1)$ properties of A.

Duration of Conjointment

The duration of conjointment of A and K must be sufficient and just sufficient to produce detectable changes in the properties of A. This requirement is intended to decrease the probability that a property of A will change in more than one direction, i.e., will pass through maxima or minima, during a single conjointment.

After conjoining A and K in this way, we withdraw K and restore it to its original state. We next examine the body A with suitable instruments to determine how the conjointment with K has affected the variable properties of A. We then return A to its initial state.

We suppose the above series of operations to be repeated with each of the bodies being classified; that is, we conjoin, in turn, each of the other bodies with A under the prescribed conditions, and take note of the changes

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which each body produces in the variable properties of A. (These "variable properties" of A will remain constant in number but may be chosen differently in going from one conjointment to another.)

Formation of Temperature Classes

Some of the bodies will be found to produce no change in A (and likewise themselves suffer no change). Also, if any two of these bodies be conjoined with one another, no changes will ensue. These bodies, A', A", A''', ... we shall put in the same "temperature class" with A.

Consider the bodies which did produce a change in the variable properties of A (and, in so doing, suffered changes themselves). If we note how each of these bodies affected a particular property x_1 of A, the bodies will, in general, fall into classes, the one class comprising those bodies which produced an increase of x_1 of A, the other comprising those bodies which produced a decrease in x_1 of A. If we repeat the classification, using as a basis, in turn, the effect on the other variable properties of A, we find that, usually, each such classification divides the bodies in the same way, i.e., the bodies which cause an increase in x_1 are the ones and only ones which cause an increase, or decrease, in any other property x_i of A, and the bodies which cause a decrease in x_1 are the ones and only ones which cause a decrease, or increase, in any other property x_i. With a few properties discrepancies may appear. Thus, with respect to a property x_i of A, all other bodies may fall into one class, i.e., they all cause a decrease, or they all cause an increase, in x_i. The effect on such properties as x_i we neglect as long as other properties of A divide the bodies into two classes.

In this way, the original group of bodies is divided into three classes, the first class comprising A and all other bodies, A', A", ..., which produced no change in A; the second class, G_1, comprising those bodies which caused an increase in the properties x_r of A and a decrease in the properties

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x_s of A; the third class G_2 comprising those bodies which caused a decrease in the properties x_r of A and an increase in the properties x_s of A. The result is expressed symbolically as follows:

$$G_1$$
$$A,A',A'',\ldots$$
$$G_2$$

We now choose an object B in G_2 and compare it, in turn, with each of all the other bodies in the same manner that we compared A with each of the other bodies. Again we find that, neglecting the effect on those properties of B which behave like x_i, above described, all bodies will fall into three classes with respect to B: the first class will comprise those bodies B', B'',... which produce no change in B; the second will consist of bodies which cause an increase in the properties x_r of B and a decrease in the properties x_s of B[5] and will comprise all the bodies of G_1, the bodies A,A',A'', ..., and a part of the bodies of G_2 denoted by G'_2; the third class, denoted by G''_2, will consist of bodies which cause a decrease in the properties x_r of B and an increase in the properties x_s of B and will comprise the remainder of the bodies of G_2. Then the classification, at this point, may be symbolized by

$$G_1$$
$$A,A',A'', \ldots$$
$$G'_2$$
$$B,B',B'', \ldots$$
$$G''_2$$

Continuing this process, we finally segregate the bodies into a series of groups or classes such that a body experiences no change when conjoined, in the prescribed manner, with any other body in the same class. Having oriented the series of classes so that the class containing a body of melting ice is below the class containing a body of boiling water, we shall say that bodies in the same class

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that bodies in the same class have the same "temperature," and that a given body has a temperature greater than that of any body in a class below the given body's class, and a temperature less than that of any body in a class above a given body's class.

Thus, by means of Langevin's classification, the given bodies have been allocated[1] to definite positions in a "temperature series." The temperature of each body is determined as either equal to, greater than, or less than that of every other body. Further, experience teaches that between any two temperature classes in Langevin's classification there exist in nature as many distinct classes as we care to specify, or at least, as many as the delicacy of our instruments permits us to distinguish. We are therefore justified in saying that the temperature classes constitute a one-dimensional continuum.

The temperature series is not a thermometric scale as ordinarily understood. Rather, it constitutes an order criterion to which every special thermometric scale must conform.

Deduction of Test-Body Method

However, the test-body method of practical thermometry is logically a special case of Langevin's procedure. To show this, assume a body T the state of which is determined throughout a given region by a certain number of independently variable quantities and suppose that all but one of these be held constant. Then the possible states of T will constitute a continuous, one-dimensional set bounded, let us say, by states T_1 and T_n. We suppose that each of the states is classifiable in the sense of Langevin and that no one occupies the same temperature class as any other. Suppose also that each of these states is reproducible, i.e., that T always assumes the same state when conjoined with a reference body the temperature class of which is fixed and lies between those of T_1 and Tn. Further, assume that if T, in

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any one of these states, be conjoined with any classifiable body under the conjointment conditions of Langevin's method until no further change occurs, the latter will undergo no more than a negligible change of state.

Let us now choose n of these states of T, including the limiting states T_1 and T_n, and attempt to order them by the Langevin procedure. For this purpose, imagine the n states replaced by n distinct bodies identical to T in its given states. This artifice is permissible, since any number of bodies identical to T will generally be available.

Now the most fundamental condition the satisfaction of which makes possible the employment of T as a thermometric body is the following: throughout the process of classification of the n states of T (regarded as n distinct bodies), one or more of T's properties will be found always in the x_r group or always in the x_s group, and this shall remain true regardless of how many states we choose to consider between the two fixed end states, T_1 and T_n.

Thus, suppose that in testing T_4, we find that T_1, T_2, and T_3 cause the property x of T_4 to increase, while the ramainder of the bodies (states of T) cause x to decrease. Then Langevin's classification gives

$$T_1, T_2, T_3$$
$$T_4$$
$$T_5 \cdots T_i \cdots T_n$$

In testing T_5, let us say we find that T_1, T_2, T_3, and T_4 cause the same property x of T_5 to increase, while $T_6 \cdots T_i \cdots T_n$ cause it to decrease. Then we have the segregation into four classes

$$T_1, T_2, T_3$$
$$T_4$$
$$T_5$$
$$T_6, \cdots T_i \cdots T_n$$

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Continuing in this manner, we arrive finally at the result:

T_1

T_2

T_3

.

.

.

T_i

.

.

.

T_n

where T_{i-1}, when conjoined with T_i, causes x of T_i to increase, while T_{i+1}, when conjoined with T_i, causes x of T_i to decrease. According to our fundamental assumption, this will still be true, if, while holding the end-states fixed, we allow the total number of states, n, to be increased without limit.

Now, because T_{i-1} and T_i are different states of the same body, after conjointment of sufficient duration, we must have $x_{i-1} = x_i$. In this process of equalization, x_{i-1} has decreased initially, and x_i has increased initially. However, since by indefinite increase of n the states T_{i-1} and T_i are brought infinitely close, the initial decrease of x_{i-1}, however small it may be, may be regarded as sufficient to bring x_{i-1} to its equilibrium value. Similar considerations apply to x_i.

Thus x_{i-1} and x_i, initially unequal, have become equal, and in this process x_{i-1} has only decreased and x_i has only increased. Hence $x_{i-1} > x_i$.

Evidently, the continuous, one-dimensional series of states of T are in one-to-one correspondence with the property x of the body T as it assumes these states successively. The value of x, or any continuous, single-valued

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function of x, may be taken as indicative of the temperature of T as well as that of any body in equilibrium with T under the prescribed conditions of conjointment. T is called a "thermometer," and the range of values of x constitutes a "temperature scale."[6]

Qualitative Nature of Temperature

The temperature number, as we have defined it, is no more than a symbol denoting the position of a body in the temperature series. As such, it has no quantitative significance. As Maxwell (2) put it, "we have a right to say that the temperatures of freezing and boiling (water) differ by 180° Fahrenheit; but we have as yet no right to say that this difference is the same as that between the temperatures 300° and 480° on the same scale. Still less can one assert that a temperature of 244° is equal to the sum of the temperatures of freezing (32°) and boiling (212°)."

To be sure, the thermometric property x of the test-body T is a quantity. But the properties of a symbol system cannot be assumeed to be those of the objects symbolized. Thus the representation of temperature by the volume of a test-body does not imply that temperature partakes of the nature of volume.

Yet classical thermodynamics begins with the assumption, not only that unambiguous temperature symbols exist, but also that these symbols are quantitative: temperature is regarded as a real variable. Only the agreement of the resulting theory with experiment can justify such an assumption.

Role of Zeroth Law of Thermodynamics

The fact that "two bodies, each in thermal equilibrium with a third body, are themselfes in equilibrium," sometimes called the "zeroth law of thermodynamics," plays, as we have seen, a fundamental role in the definition of temperature equality. For, if it were not for this fact, changes could be produced in a group of conjoined bodies, initially in thermal equilibrium, merely by changing their positions relative to one another. This would deny

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the possibility of assigning to a body in a given state a fixed temperature of universal validity. The essentially biological concept of "organization" would then have a significance for thermodynamics which, in fact, it does not have.

However, the "zeroth law" provides no criterion whereby bodies of different temperature classes may be ordered with respect to one another.

Residual Character of Temperature

Our definition of temperature is a negative one in the sense that temperature equality or inequality is associated with the presence or absence, respectively, of a residual effect which persists after all other effects, assumed to have been already definied, have been eliminated by establishment of suitable conditions. This negative or residual character is not peculiar to temperature but is shared by the other"intensity factors" of physics each of which is defined in terms of a particular residue corresponding to a particular set of eliminating conditions.

Logical Significance of Langevin's Method

An "arbitrary temperature scale" is frequently established simply by identifying temperature with the value assumed by a particular property of a chosen test-body without resort to more fundamental considerations. Thus, in a region in which the volume at constant pressure of a one-phase body is in one-to-one correspondence with the possible states of the body, the values of this property are often defined as temperature numbers. Although, over the limited region where comparison is possible, such a method gives the same order as Langevin's procedure, the former is objectionable because it attaches a degree of arbitrariness to temperature which is not inherent in the concept. Such a procedure is analogous to the popular practice of basing the analytical formulation of the second law of thermodynamics on the behavior of a particular gaseous body.

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The existence of a temperature series is not contingent upon the existence of any particular body nor even upon the existence of a particular type of body. Rather it arises out of the mutual relations existing between all classifiable bodies. This fundamental, as contrasted with arbitrary, nature of temperature is emphasized by Langevin's method. The latter reveals the temperature series as a logical consequence of the directional nature of the initial reciprocal changes exhibited by all classifiable bodies when properly conjoined. If a body satisfies the two criteria of classifiable bodies and if the conjointment conditions are realizable, the order criterion provided by Langevin's method will allocate the body to a definite position in the temperature series, except in the scarcely conceivable case where every property of the body as well as that of every other body in the same temperature class is of the x_i type, i.e., exhibits a maximum or minimum in this temperature class.

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Footnotes

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[2] The idea of "temperature at a point," employed in the theory of heat conduction, corresponds experimentally to determining the mean temperature of a small region about the point. Such a small region, when isolated, undergoes no appreciable change of state and is thus not excluded by the second criterion.

[3] It may be argued that dynamic as well as static considerations contribute to the criterion of "adequate" representation of the state of a system. Thus, a group of properties may be regarded as "adequately" representing the system mainly because changes of state of the system may be described in terms of changes in the properties. However, in a formal exposition of the subject, it is unnecessary to concern oursleves with the ultimate origin of our knowledge respecting "adequate" representation; we may view the properties x_1, x_2, ... x_n as chosen independently of experimental laws.

[4] The problem of the experimental realization of conjointment conditions belongs to the special physical sciences. We merely state here that such realization is indispensable to the definition of temperature.

[5] "x_r" and "x_s" do not necessarily donote the same groups of properties as were previously designated by these symbols.

[6] At first thought, the radiation pyrometer may not seem to follow this logical scheme. The discrepancy is removed, however, when we recall that the radiation law holds only for ideal "black bodies." Radiation pyrometry is therefore made generally applicable only by adopting such a "black body" as a test-body and intensity of radiation as its thermometric property.

References

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(3) Perrin,Jean: Les principes, traite de chimie physique,p.56. Gauthier-Villars, Paris (1903).

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