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I hereby recommend that the thesis prepared under my supervision by John Tinsley Rucker

entitled A Vector Analysis of Thermodynamic Surfaces

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

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A VECTOR ANALYSIS OF THERMODYNAMIC SURFACES

A dissertation submitted to the

Graduate School
of the University of Cincinnati

in partial fulfillment of the

requirements for the degree of

DOCTOR OF PHILOSOPHY

1941

by

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Cincinnati, Ohio
May 15, 1941

The Gentlemen of the Faculty
Graduate School of Arts and Sciences
University of Cincinnati
Cincinnati, Ohio

Gentlemen:

In partial fulfillment of the requirements for the degree of Doctor of Philosophy, I submit herewith a dissertation entitled A Vector Analysis of Thermodynamic Surfaces.

This research was undertaken primarily to demonstrate the ease with which the geometrical properties of plane diagrams and curved surfaces obtained by various combinations of the eight thermodynamic functions for a general one-component system can be deduced by means of vector and dyadic analysis. It was hoped also that the method might lead to some new thermodynamic theorems of general interest.

As a consequence, the facility of the vectorial method has been amply illustrated both by the elucidation of the geometry of the surfaces and by the use of these surfaces to develop certain thermodynamic relations. The aspiration to new results, however, has not been fully realized inasmuch as the propositions, for the most part, were well known previous to this investigation.

Respectfully submitted,
John T. Rucker
John T. Rucker

ACKNOWLEDGMENT

The writer wishes to express his gratefulness to Dr. Earl F. Farnau without whose encouraging assistance and stimulating counsel this work could never have been successfully completed. He was particularly kind in allowing the author free access to his personal files during the course of this research.

SYMBOLS

A: Specific work content, or "maximum work"

a: A constant of proportionality

c: Subscript denoting "circuit"; subscript denoting "critical point"; constant of proportionality

c_1, c_2, c_3: Positive constants

C_p: Specific heat at constant pressure

D: The discriminant of the quadratic form, q

$\bar{e}$: A unit vector

F: Specific free energy

$\bar{f}$: A vector

rot $\bar{f}$: The rotation, or curl, of $\bar{f}$

G: Any thermodynamic function

H: Specific enthalpy, or "heat content"

ijk: Right-handed set of unit vectors

i = 1, 2, 3---p: Indices

J: Jacobian

K: A constant

K_1, K_2: Principal curvatures; constants

L: A straight-line segment; perpendicular distance from tangent plane to surface; liquid state

m: Mass

$\bar{N}$: Normal

$\bar{n}$: Unit normal

o: Subscript denoting "triple-point"

P: Pressure

SYMBOLS - continued

P, Q: Two functions of x and y

q: A quadratic form

R: A point

$\bar{r}$: Position vector

S: Surface area; surface; solid state

s: Arc length

T: Thermodynamic temperature

$\bar{t}$: Position vector of a point in a tangent plane

$\bar{t}_o$: Position vector of a point in a tangent plane through the origin

$\bar{u}$: A vector denoting the difference between the position vectors of two points which represent co-existent states

V: Vapor state

v: Specific volume

x, y, z: Rectangular co-ordinates

[x, y, z]: A vector with components x, y, and z, respectively

x_y: $\frac{\partial x}{\partial y}$, the partial derivative of x with respect to y

x_{yy}: $\frac{\partial^2 x}{\partial y^2}$, the second partial derivative of x with respect to y

ΔQ: Heat absorbed in a change of thermodynamic state

ΔW: Work done in a change of thermodynamic state

δ: The variation of

ϵ: Specific internal energy

Φ, Ψ, Ω: Dyadics

Φ_2: The second invariant of Φ

SYMBOLS - continued

η: Specific entropy

θ: Angle

∇: $\bar{n}\frac{d}{dn}$, the gradient of

PART ONE

PLANE DIAGRAMS

I Definition of a Fundamental Equation

According to the First Law of Thermodynamics the increase in the internal energy of a body undergoing a change of state is given by the difference between the heat absorbed and the work done by the body; or, in any consistent set of units,

$$\Delta\epsilon = \Delta Q - \Delta W \tag{1}$$

But, by the Second Law of Thermodynamics, the heat received in the assigned change from state 1 to state 2 is given by the expression

$$\Delta Q = \int_{\eta_1}^{\eta_2} T \, d\eta \tag{2}$$

Also, if the work involved be limited to a pressure-volume effect,

$$\Delta W = \int_{V_1}^{V_2} P \, dv \tag{3}$$

The five thermodynamic functions, then, are subject to the general differential equation

$$d\epsilon = T \, d\eta - P \, dv \tag{4}$$

whence

$$T = \left(\frac{\partial \epsilon}{\partial \eta}\right)_v$$

and

$$P = -\left(\frac{\partial \epsilon}{\partial v}\right)_\eta$$

Since the state of a body is capable, at the most, of only two independent variations, there must exist three independent equations relating the five functions η, v, ϵ, P, T. Any finite equation (i.e., not a differential equation) between ϵ, η, and v considered together with the differential relations above will furnish the three independent equations. Hence, such an expression relating ϵ, η, and v may be regarded as a fundamental equation for the substance in question.

II Basic Idea of Two-dimensional Diagram

The state of the fluid like the position of a point in a plane is capable of two independent variations, and it may be assumed that these variations can occur continuously, or reversibly. It is therefore possible to associate in a continuous manner all the equilibrium states of the fluid with the points in a plane so that each point corresponds to one, and only one, state of the body. The five quantities v, P, T, η, ϵ thus become uniform scalar point functions in the plane. Moreover, it is apparent that this one-to-one correspondence between the states of the body and the points in a plane is attainable by an infinitely large number of different methods of association, the only restriction being that the conditions of continuity must be fulfilled.

Points corresponding to states of equal temperature

will form lines in the diagram, different lines being associated with different temperatures. These lines are called isothermals. Similarly, there may be traced isobaric (constant pressure), isometric (constant volume), isentropic (constant entropy), and isodynamic (constant energy) lines. The shape of any particular family of such lines will vary with the method of association used in forming the diagram.

Any finite and reversible change of state of the body will appear on the diagram as a line composed of points corresponding to all the intermediate states assumed by the body in passing from its initial to its final state. Such a line is called a path. The shape of a path likewise will vary with the rule of association used in forming the diagram.

III Properties of the General Diagram

Isothermals, isobarics, etc. may, in general, be called contour lines, or level lines. Let G denote any one of the thermodynamic functions, and $G=k_1$ and $G=k_2 (k_2>k_1)$ be two contours. $\bar{n}$ is a unit normal and $\bar{e}$ a unit vector in the direction RR' (Figure 1).

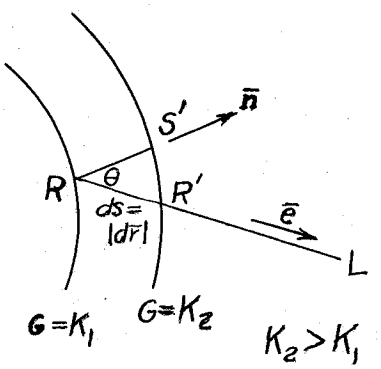

Figure 1

Then

$$\frac{dG}{ds} = \lim_{R' \to R} \frac{G(R') - G(R)}{RR'} = \lim_{R' \to R} \frac{G(s') - G(R)}{Rs'} \frac{Rs'}{RR'} \qquad (5)$$

$$= \left(\lim_{s' \to R} \frac{G(s') - G(R)}{Rs'} \right) \left(\lim_{R' \to R} \frac{Rs'}{RR'} \right) = \frac{dG}{dn} \cos \theta$$

$$= \frac{dG}{dn} \bar{n} \cdot \bar{e} = \bar{e} \cdot \nabla G \text{ where } \nabla G = \bar{n} \frac{dG}{dn} \sim \text{gradient of } G$$

The quantity $\frac{dG}{ds}$[1] is the directional derivative of G. Its value gives the magnitude of the rate of change of the function along any line L. Its maximum value is the magnitude of ∇G (since $\frac{dG}{ds} = \frac{dG}{dn} \cos \theta$). The gradient, ∇G, therefore, is a vector giving both the direction and magnitude of the maximum rate of increase of G at R. From the definition, it appears that ∇G is invariant to the choice of co-ordinate systems. For computation, however, ∇G may be referred to x-y co-ordinates as follows:

$$\bar{e} \cdot \nabla G = \frac{dG}{ds} = \frac{\partial G}{\partial x} \frac{dx}{ds} + \frac{\partial G}{\partial y} \frac{dy}{ds} = \bar{e} \cdot \left(\frac{\partial G}{\partial x} \nabla x + \frac{\partial G}{\partial y} \nabla y \right) = \bar{e} \cdot \left(\frac{\partial G}{\partial x} i + \frac{\partial G}{\partial y} j \right)$$

or $$\nabla G = \frac{\partial G}{\partial x} i + \frac{\partial G}{\partial y} j \qquad (6)$$

where i and j are unit vectors in the x and y directions, respectively. The differential of G may be defined conveniently in terms of ∇G and the differential of the position vector $\bar{r}$ of a point as follows:

$$dG = \frac{dG}{dn} \cos \theta \, ds = \frac{dG}{dn} \bar{n} \cdot d\bar{r} = \nabla G \cdot d\bar{r} \qquad (7)$$

---

[1] The symbol d is used because along any line L, the independent variables x and y as well as G are functions of s.

The rotation of any vector $\bar{f}$ may be defined symbolically in terms of the operator $\nabla(= i\frac{\partial}{\partial x} + j\frac{\partial}{\partial y})$ as follows:

$$\text{rot } \bar{f} \equiv \nabla \times \bar{f} = i \times \frac{\partial \bar{f}}{\partial x} + j \times \frac{\partial \bar{f}}{\partial y} \qquad (8)$$

in terms of x-y co-ordinate system.

The integral $\triangle W$ is not independent of the path followed by the body in undergoing a change of state; for if the work effect be written $\triangle W = \int_1^2 (Pdv + 0dP)$, then

$(\frac{\partial P}{\partial P})_v = 1 \neq (\frac{\partial 0}{\partial v})_P$. But the equality of these partial derivatives is a necessary condition for independence. Hence, $\triangle W$ is a line integral in the P-v diagram. It is, therefore, a line integral in any of the infinite number of possible diagrams attainable by different methods of association, all of which represent P as a uniform point function. Similarly, $\triangle Q$ is a line integral.

With any path representing a finite change of state of the body, then, there will be associated definite quantities of heat and work which may be computed by eqs. (2) and (3). Any path forming a closed circuit also will involve definite amounts of work and heat which by equation (1) must be equal. Such a path likewise will inclose a certain area on the diagram. It is desired to relate the work (and heat) of a circuit to the area inclosed.

If W_c denote the work of a circuit, then by eqs. (2)

and (7) and Green's Theorem:

$$W_c = \int_o P dv = \int_o P \nabla \mathbf{v} \cdot d\bar{r} = \iint \bar{k} \cdot \text{rot } (P \nabla v)\, dS \qquad (9)$$

in which k is a unit vector normal to the plane of the diagram[1]. It will be observed that equation (9) is formally independent of the particular law of association used in forming the diagram.

To facilitate interpretation the right member of equation (9) may be converted into its Cartesian equivalent. Let x and y denote in general any two thermodynamic functions. Let $\bar{f}$ denote the vector $P \nabla v$. Then

$$\bar{f} = P \nabla \mathbf{v} = P \frac{\partial v}{\partial x} i + P \frac{\partial v}{\partial y} j$$

$$\frac{\partial \bar{f}}{\partial y} = \left(\frac{\partial P}{\partial y} \frac{\partial v}{\partial x} + P \frac{\partial^2 v}{\partial x \partial y} \right) i + \left(\frac{\partial P}{\partial y} \frac{\partial v}{\partial y} + P \frac{\partial^2 v}{\partial y^2} \right) j$$

$$\frac{\partial \bar{f}}{\partial x} = \left(P \frac{\partial^2 v}{\partial x^2} + \frac{\partial P}{\partial x} \frac{\partial v}{\partial x} \right) i + \left(\frac{\partial P}{\partial x} \frac{\partial v}{\partial y} + P \frac{\partial^2 v}{\partial y \partial x} \right) j$$

By equation (8)

---

[1] Green's Theorem may be written $\int_o \bar{f} \cdot d\bar{r} = \iint \bar{k} \cdot \text{rot } \bar{f}\, dS$

in vector notation, if $\bar{f} = Pi + Qj$; $\bar{r} = xi + yj$; $\bar{k} = i \times j$. Then, this expression becomes $\int_o (P dx + Q dy) = \iint \left(\frac{\partial Q}{\partial x} - \frac{\partial P}{\partial y} \right) dx\, dy$

which is the usual form for Green's Theorem in the xy-plane.

$$\text{rot } \bar{f} = \left(\frac{\partial P}{\partial x}\frac{\partial v}{\partial y} - \frac{\partial P}{\partial y}\frac{\partial v}{\partial x}\right)\bar{k}$$

The vector $\bar{k}$ is chosen so that ijk form a right-handed set. The quantity $\left(\frac{\partial P}{\partial x}\frac{\partial v}{\partial y} - \frac{\partial P}{\partial y}\frac{\partial v}{\partial x}\right)$ is defined as the Jacobian of P and v with respect to x and y. If it be denoted by J, equation (9) becomes by substitution

$$W_c = \iint J \, dx \, dy \qquad (10)$$

In order that equation (10) be consistent with the definition of W, it is necessary that areas circumscribed in a clockwise direction be considered as negative.

The principle of dimensional homogeneity requires that the J of equation (10) have the dimensions of $\frac{\text{work}}{\text{area}}$[1], and, therefore, J may be regarded as the reciprocal of the scale of work (and heat[2]) in the diagram in question. It is evident that the scale in general will vary from point to point in a diagram. If x and y be identified respectively with v and P, the Jacobian assumes the value minus unity, and, thus, the P-v diagram exhibits work (and heat) to constant scale. Similarly, the T-η diagram is one of constant scale. Such plots are most convenient for ascertaining the

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[1] This may be seen also directly from the definition of J.

[2] By equation (1), $W_c = Q_c$ since $\epsilon_c = 0$. Hence, if W_c = constant x inclosed area, then Q_c = constant x inclosed area; and, therefore a diagram which exhibits work to constant scale must also exhibit heat to the same scale.

work (and heat) of a circuit graphically.

By starting with equation (3), a relation formally similar to equation (9) may be obtained for the heat of a circuit in terms of T and η. The reciprocal scale, J, then appears explicitly as the Jacobian of T and η with respect to x and y.

In the special case in which J vanishes, the work (and heat) of the circuit is zero by equation (10). But the vanishing of the Jacobian is a sufficient condition that a functional relation exist between P and v. Such a circuit, therefore, consists simply of an oscillation along a plane curve, and it circumscribes no area[1].

Equation (10) may be applied to an open path by forming a circuit consisting of the given path and suitable contour lines. The work (or heat) of the path is then obtained as the difference between the work (or heat) of the circuit and the work (or heat) of the portion of the circuit consisting of the contour lines, which latter quantities may be readily obtained by eq. (2)(or eq. (3)).

IV Contour Lines for an Ideal Gas in General

A gas may be considered ideal if it obeys the

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[1] This is true provided the functions are represented as uniform point functions.

equations

$$Pv = aT \tag{11}$$

$$\epsilon = cT \tag{12}$$

Here, the relation of "a" to the gas constant R is apparent, and "c" is evidently the specific heat taken at constant volume. From eqs. (4), (11), and (12), T and P may be eliminated and the fundamental equation for an ideal gas obtained by integration[1] as

$$\ln \epsilon = \frac{\eta}{c} - \frac{a}{c} \ln v \tag{13}$$

By suitable manipulations among equations (11), (12) and (13) the following relations may be evolved:

(T constant): $Pv = \text{const.}$ (14)

(P constant): $v = T \times \text{const.}$ (15)

(v constant): $P = T \times \text{const.}$ (16)

(η constant): $\ln \epsilon = \text{const.} - \frac{a}{c} \ln v$ (17)

(ϵ constant): $\eta - a \ln v = \text{const.}$ (18)

The vector equations of these contour lines are most easily obtained in terms of the Cartesian components of the position vector. Let x and y be the independent variables. Then the quantities P, v, T, η, ϵ are defined by sets of values of x and y. For example,

$P = P(x,y)$ and $v = v(x,y)$

whence,

---

[1] The constant of integration becomes zero if $\eta = 0$ in the state in which $\epsilon = v = 1$.

$$x = x(P,v)$$
$$y = y(P,v) \qquad \text{provided } J \neq 0.$$

But along a contour line, P and v are functionally related (the relation for the isothermal, for instance, is given explicitly by equation (14)), and, therefore, J necessarily vanishes. Along such a line, y becomes a function of the constant quantity and x, and, hence, the thermodynamic functions are there defined by values of x. The position vector of any point on a given contour line, then, is

$$\bar{r} = xi + yj$$

in which x is an independent variable and the form of the function $y = y(x)$ is determined from the particular one of the eqs. (14)-(18) in question.

V Arrangement of the Contour Lines about a Point

The order in which the isothermal, isobaric, isometric and isentropic of an ideal gas succeed each other around a point, as well as the sides of these lines on which the functions are increasing, appears from a consideration of the gradients of the respective functions. As ∇ is an invarient to co-ordinate systems, no generality is lost by identifying T and v with the rectangular co-ordinates x and y respectively. The following relations hold:

$$T = T$$
$$v = v$$

$$P = \frac{aT}{v}$$

$$\eta = c \ln c + c \ln T + a \ln v$$

Then, by equation (6):

$$\nabla T = i$$

$$\nabla v = j$$

$$\nabla P = \frac{a}{v} i - \frac{aT}{v^2} j$$

$$\nabla \eta = \frac{c}{T} i + \frac{a}{v} j$$

Since the quantities a, c, T, v are positive and finite except at the absolute zero of temperature, the gradients must fall as in Figure (2).

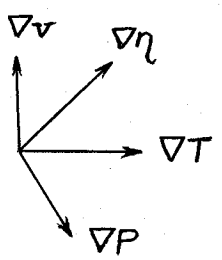

Figure 2

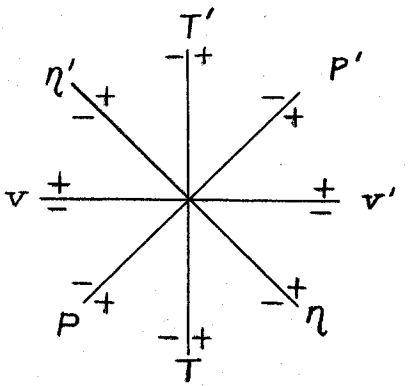

Figure 3

The corresponding contour lines then appear as in Figure (3) in which the + signs indicate the side of a line on which the function is increasing. The arrangement of Figure (3) (either as it appears, or inverted) must prevail in any diagram which represents P, v, T, η as uniform point functions.

In general, choosing v and T as the independent variables,

$$\nabla T = i$$

$$\nabla v = j$$

$$\nabla P = \left(\frac{\partial P}{\partial T}\right)_v \mathbf{i} + \left(\frac{\partial P}{\partial v}\right)_T \mathbf{j}$$

$$\nabla \eta = \left(\frac{\partial \eta}{\partial T}\right)_v \mathbf{i} + \left(\frac{\partial \eta}{\partial v}\right)_T \mathbf{j}$$

The position of the isobaric and isentropic will thus depend upon the values of the quantities $\left(\frac{\partial \eta}{\partial T}\right)_v$, $\left(\frac{\partial P}{\partial v}\right)_T$, and $\left(\frac{\partial P}{\partial T}\right)_v \left[=\left(\frac{\partial \eta}{\partial v}\right)_T\right]$ which in turn may be expected to vary with the substance in question and the type of equilibrium considered; i.e., stable or neutral, as well as with the position of the point in the diagram in certain cases.

VI Inter-relations among Special Diagrams

In determining the work and heat accompanying a change of state, it may be desirable to consider the deformation necessary to transform a given diagram into one of constant scale. Consider, for instance, the volume-entropy diagram. If each point be shifted vertically such a distance as to make the isobarics straight horizontal lines spaced at distances proportional to the differences in pressure between the lines, the diagram will become a volume-pressure diagram. This "shearing" may be accomplished by the action of a suitable, variable, planar dyadic upon the position vectors of the points in the volume-entropy diagram. Let Φ be such a dyadic and $\bar{r}$ the position vectors to be transformed into the position vectors $\bar{r}'$.

$$\bar{r} = v\mathbf{i} + \eta\mathbf{j}$$

$$\Phi^{1} = ii + \frac{P}{\eta}\, jj$$

$$\mathbf{r}' = \Phi \cdot \mathbf{r} = \Phi \cdot vi + \Phi \cdot \eta j$$

$$\Phi \cdot vi = vi$$

$$\Phi \cdot \eta j = Pj$$

$$\therefore \mathbf{r}' = vi + Pj$$

The transforms are evidently position vectors in the volume-pressure diagram.

Similarly, consider the transformation produced by the operator Ψ :

$$\Psi = \frac{T}{v}\, ii + jj$$

$$\mathbf{r}' = \Psi \cdot \mathbf{r} = Ti + \eta j$$

The volume-entropy diagram is thus converted into a temperature-entropy diagram, and the effect of Ψ is to slide all points horizontally so that isothermals become vertical

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[1] The dyadic Φ may be formulated in other ways in terms of the idemfactor, I. For example, $\Phi = I - \frac{1}{\eta}(\eta - P)jj$ effects the desired transformation. This formulation, while lacking somewhat in compactness, (i.e., it introduces an extraneous dyad, kk), possibly presents more clearly the actual mechanism of the transformation.

Along any isobaric, η may be computed from eqs. (11), (12), and (13) as a function of v and the constant pressure chosen; viz., for an ideal gas,

$$\eta = c \ln \frac{c}{a} P v^{\frac{a}{c}+1}$$

In terms of the variable factor v, the dyadic Φ then appears as

$$\Phi = I - \frac{1}{c} \ln^{-1} \frac{c}{a} P v^{\frac{a}{c}+1} \left(c \ln \frac{c}{a} P v^{\frac{a}{c}-1} - P\right) jj$$

straight lines spaced linearly with respect to the temperature.

The combined effect of the dyadics Φ and Ψ may be achieved with a single dyadic Ω as follows:

$$\Omega = \Phi \cdot \Psi = \left(ii + \frac{P}{\eta}\, jj\right) \cdot \left(\frac{T}{v}\, ii + jj\right) = \frac{T}{v}\, ii + \frac{P}{\eta}\, jj$$

$$\bar{r}' = \Omega \cdot \bar{r} = \left(\frac{T}{v}\, ii + \frac{P}{\eta}\, jj\right) \cdot \left(vi + \eta j\right)$$

$$\bar{r}' = Ti + Pj$$

The volume-entropy diagram is thus deformed into a temperature-pressure diagram. The scale of work and heat for this diagram, however, is not constant, the value of J being $-\left(\frac{\partial v}{\partial T}\right)_P$.

In general, any diagram formed by such a method that two thermodynamic functions can be identified with the co-ordinates of an orthogonal system may be transformed into any other such diagram through the operation of planar dyadics as illustrated above.

VII A Defect in Diagrams of Constant Scale

It may occur in a diagram of variable scale for certain substances that the reciprocal scale J change sign in passing from one region of the diagram to another. From the principle of continuity, two such regions must be separated by a line upon which J vanishes. Consider the mapping of points in such a diagram upon the v-P plane, a diagram of

constant scale. A sufficient condition that biunique (one-to-one) correspondence be obtained is that J be not zero. However, the sense of rotation will be preserved or reversed according as J is positive or negative; i.e., the region in which J is negative will be inverted in mapping on the v-P plane. In view of the continuity between the two regions, such an inversion is attainable only by "folding" the diagram along the line upon which J vanishes. In the v-P plane, therefore, this line may be regarded as a boundary of the diagram on one side of which no states of the body are represented and on the other side of which the points, for a certain distance, at least, are double-valued. Moreover, this behavior may be expected in any diagram of constant scale for such a substance, as is evident from the consideration that circuits described in the same direction in a diagram of variable scale may be associated with quantities of work of opposite sign; whereas, this is not possible in a constant scale diagram.

This defect need not hinder the application of the propositions previously developed under the assumption that the thermodynamic quantities are represented as uniform point functions, however, for such a constant scale diagram may be considered as two, distinct, superposed diagrams continuous only along the line of fold. Each such sheet will then be amenable to treatment by the relations developed.

A specific example of the general case discussed

above is furnished by water. In the v-η diagram

$$J=\frac{\partial(P,v)}{\partial(v,\eta)}=\left(\frac{\partial P}{\partial v}\right)_{\eta}\left(\frac{\partial v}{\partial \eta}\right)_{v}-\left(\frac{\partial P}{\partial \eta}\right)_{v}\left(\frac{\partial v}{\partial v}\right)_{\eta}=-\left(\frac{\partial P}{\partial \eta}\right)_{v}$$

It is apparent that the line of fold in this case is the line which represents states of maximum density for liquid water; for along this line J vanishes, and on opposite sides of it J assumes opposite signs.

PART TWO

THE ENTROPY-VOLUME-ENERGY SURFACE

I Graphical Representation

From an application of the First and Second Laws to a reversible change of state of a one-component body of unit mass there appears the fundamental differential equation

$$d\epsilon = T\, d\eta - P\, dv \qquad (1)$$

whence

$$T \equiv \epsilon_\eta \text{ and } P \equiv -\epsilon_v \qquad (2)$$

It is obvious that an Equation of State for the body relating ϵ, η, and v, considered together with the general differential equation, will suffice to evaluate the five variables ϵ, η, v, P, and T, as well as any other thermodynamic functions of state which may be defined in terms of them, for any assigned values of η and v. In terms of entropy and volume as the independent variables, such an Equation of State may be written in the form

$$\epsilon = \epsilon(\eta, v) \qquad (3)$$

in which ϵ is an analytic function for homogeneous (i.e., one-phase) states of the body[1].

Probably the simplest graphical representation of equation (3) may be obtained by identifying η, v, and ϵ respectively with the x, y, and z of a set of right-handed, orthogonal axes. Points representing homogeneous states then

---

[1] The equation for two-phase states is easily derived from this equation, as will be shown; a similar statement applies for three-phase states.

form an analytic surface which may be called, after Gibbs, the primitive surface. Multi-phase states of the body are shown by surfaces derived from the primitive surface in a manner to be described later. The general properties of the primitive and derived surfaces will be deduced from the first two laws of thermodynamics.

II Regarding the Independent Variables: η, v

The isometric and isentropic through a point p (η', v', ϵ') will evidently be the curves of intersection of the perpendicular planes $v = v'$ and $\eta = \eta'$ respectively with the surface. By equation (2) the temperature of the body is equal to the slope of the isometric, and the pressure is given by the negative of the slope of the isentropic. For various values of η' and v' there will be obtained two families of curves lying on the surface; and corresponding to any point of intersection p, there will be unique values of η and v. The values (η,v) may be regarded as curvilinear co-ordinates on the surface, and the corresponding isentropics and isometrics as parametric curves. The parametric equations of the surface then are

$$\begin{aligned} \eta &= \eta \\ v &= v \\ \epsilon &= \epsilon(\eta, v) \end{aligned} \qquad (4)$$

It is easily shown that the parametric curves are

not, in general, orthogonal. In terms of the usual constant unit vectors i, j, k, the position vector $\bar{r}$ of a point[1] p may be written as

$$\bar{r} = \eta i + v j + \epsilon k$$

or, more compactly, as

$$\bar{r} = [\eta, v, \epsilon] \tag{5}$$

The partial derivatives of $\bar{r}$ with respect to η and v will evidently be vectors tangent to the isometric and isentropic respectively. The condition of orthogonality, therefore, is that the dot product of these two tangent vectors vanish. Differentiating equation (5),

$$\bar{r}_\eta = [1, 0, \epsilon_\eta] \tag{6}$$

and

$$\bar{r}_v = [0, 1, \epsilon_v] \tag{7}$$

Hence, orthogonality requires that

$$\bar{r}_\eta \cdot \bar{r}_v = \epsilon_\eta \epsilon_v = -TP = 0 \tag{8}$$

But both T and P are, in general, positive, real quantities, and, therefore, equation (8) will not hold true. The condition is evidently equivalent geometrically to the property that the tangent vector to either the isentropic or the isometric be parallel to the η-v plane.

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[1] For brevity, a point p with position vector $\bar{r}$ will hereafter be referred to as "the point $\bar{r}$".

III Effect of Varying the Mass of the Body

The quantities ϵ, η, $\mathbf{v}$ of equations (4) refer to a body of unit mass. If a mass, m ($m > 0$), be considered, the parametric equations take the form

$$\begin{aligned} \eta' &= m\eta \\ \mathbf{v}' &= m\mathbf{v} \\ \epsilon' &= m\epsilon(\eta, \mathbf{v}) \end{aligned} \tag{9}$$

where the primed variables refer to a body of mass m. The equations (9) represent a family of surfaces the various members of which correspond to various values of m but over any one of which the value of m is constant. By eqs. (5) and (9),

$$\bar{r}' \equiv [\eta', \mathbf{v}', \epsilon'] = m\bar{r} \tag{10}$$

Thus any surface of the family may be derived from the surface of unit mass by means of a conical projection of the points of the latter in accordance with the transformation (10).

From (10)[1], by differentiation,

$$d\bar{r}' = m\, d\bar{r} \tag{11}$$

---

[1] Equation (10) may be written in the form: $\bar{r}' = m\bar{r} = mI \cdot \bar{r} = \Phi \cdot \bar{r}$ where

$$\Phi = mI = mii + mjj + mkk$$

Thus any surface of the family may be regarded as derivable from the surface of unit mass by means of a "pure strain" with constant and equal principal ratios of elongation. For such a transformation it is well known that the transforms of plane areas are given by the second invariant of Φ (a dyadic) and the magnification of volumes by the third invariant (a

Let ds denote the length of the linear element $d\bar{r}$ connecting adjacent points on the surface. Then

$$(ds')^2 = d\bar{r}' \cdot d\bar{r}' = m^2 d\bar{r} \cdot d\bar{r} = m^2 (ds)^2$$

or

$$\frac{ds'}{ds} = m \tag{12}$$

The linear extension ratio in a direction $d\bar{r}$ on the surface for the transformation (10) is equal to m. But the direction of $d\bar{r}$ is arbitrary; and, therefore, the magnification of an element of surface is given by m^2.

Differentiating equation (10) partially with respect to entropy,

$$\bar{r}'_\eta = m\bar{r}_\eta \tag{13}$$

Similarly, differentiating with respect to volume,

$$\bar{r}'_v = m\bar{r}_v \tag{14}$$

Since the two vectors $\bar{r}'_\eta$ and $\bar{r}'_v$ are tangent to the surface S', the unit normal $\bar{n}'$ to the surface must be perpendicular to their plane; or

$$\bar{n}' = \frac{\bar{r}'_\eta \times \bar{r}'_v}{|\bar{r}'_\eta \times \bar{r}'_v|} \tag{15}$$

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scalar). Let Φ_2 and Φ_3 denote these respective invariants. Then

$$\Phi_2 \equiv mj \times mkj \times k + mk \times mik \times i + mi \times mji \times j = m^2(ii + jj + kk) = m^2 I$$

and

$$\Phi_3 \equiv (mi \times mj \cdot mk)(i \times j \cdot k) = m^3$$

Hence, if $d\bar{S}$ be a vector denoting any plane area (e.g., the area of an element of surface)

$$d\bar{S}' = m^2 I \cdot d\bar{S} = m^2 d\bar{S}$$

and, similarly, if V denote an element of volume enclosed by the surface and the co-ordinate planes

$$V' = m^3 V$$

Thus, plane areas are magnified by m^2; volumes by m^3.

By eqs. (13)-(15),

$$\bar{n}' = \bar{n} \qquad (16)$$

The surfaces S and S' thus have equal unit normals at corresponding points (i.e., points with parallel position vectors). They are, therefore, similar.

From equation (10) it is clear that no two surfaces of the family may intersect or touch at corresponding points; and, hence, they may not touch or intersect at any point[1]. The surfaces, however, although similar and non-intersecting, will not necessarily be parallel; i.e., they will not possess common normals. The condition for parallelism as just defined is easily derived. Consider the surface of unit mass S and a consecutive surface S'. Let $\bar{r}_i$ (i=1, 2, 3,---p) denote points on S corresponding to $\bar{r}'_i$ on S'. Let $\bar{n}_i$ be the unit normal at $\bar{r}_i$. Assume that S is parallel to S'. At the point $\bar{r}_1$, there is a unit normal $\bar{n}_1$ which must be normal to S' at the point $\bar{r}'_2$ measured along the line of $\bar{n}_1$ from $\bar{r}_1$. Corresponding to the point $\bar{r}'_2$ is the point $\bar{r}_2$ on S with unit normal $\bar{n}_2$. By equation (10),

$$\bar{n}_1 = \bar{n}_2$$

The points $\bar{r}_1$ and $\bar{r}_2$ will be adjacent points on S since the surfaces S and S' are consecutive members of the family. Similarly, there may be located a point $\bar{r}_3$; etc. There is

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[1] Equation (10) applies to the primitive surfaces. Similarly, the derived surfaces may have no points in common. It is, however, possible that the primitive surface S' intersect the surface derived from the primitive surface S.

thus obtained on the surface a linear succession of points $\bar{r}_i$ for which

$$\bar{n}_i = \bar{n}_1 \qquad i = 1, 2, 3, \text{---}p \tag{17}$$

where $\bar{n}_i$ are common normals to S and S'.

Conversely, if equation (17) be assumed, it follows that the surfaces are parallel. Moreover, it is apparent that the reasoning may apply to any two consecutive surfaces of the family. Hence,

> The necessary and sufficient condition that the surfaces of the one-parameter family of equation (9) be parallel is that through each point of a surface there may be drawn at least one curve having the property that all unit normals to the surface from points on the curve are equal and common to all surfaces of the family.

Such a curve must evidently lie in a plane. Hence, in general, the condition that the energy surfaces be parallel requires that they be planar. As will appear later, three-phase states of the body are indeed represented on a plane surface; and, therefore, these planes must be parallel for all surfaces of the family[1].

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[1] Two special cases may arise which constitute exceptions to the statement that parallel surfaces must be plane.

First, it may occur that the points $\bar{r}_i$ (i=1, 2, 3, ---p) are co-incident. Such could be the case only if the unit normal $\bar{n}$ were linearly dependent upon the position vector $\bar{r}_i$; i.e.,

$$\bar{n}_i = k\bar{r}_i \qquad k \neq 0$$

This is the requirement that the surfaces be central spheres.

Second, it may happen that the linear succession $\bar{r}_i$ fall along a straight line. In this case, if plane surfaces be excepted, only one such line may pass through a given point; and, hence, the surface is a ruled surface. But along each ruling the unit normal is constant. The ruled surface is therefore a developable. Moreover, the restriction that

The various surfaces obtained by suitably representing the entropy, volume, and energy of one-component bodies alike except in mass have been shown to be similar to one another with linear dimensions proportional to the quantity of matter taken. It will be sufficient, therefore, to consider in greater detail only a single surface of the family. This may be chosen without loss of generality as the surface corresponding to a body of unit mass.

IV Effect of Changing Units

Let η, v, ϵ, T, P be expressed in any units consistent with the form of equation (1), and let the primed letters refer to the same quantities expressed in any arbitrary units. Suppose the entropy, volume, and energy of the body be measured in terms of such units that

$$\begin{aligned} \eta' &= c_1 \eta \\ v' &= c_2 v \\ \epsilon' &= c_3 \epsilon \end{aligned} \tag{18}$$

where c_1, c_2, and c_3 are positive constants. The fundamental differential equation (1) then becomes

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$\bar{n}_i$ be common to all surfaces of the family requires that the unit normals ($\bar{n}_i$) lie in the plane of the position vectors ($\bar{r}_i$); for, otherwise the surface must be plane. This is the condition that the developables be central, circular, coaxial cylinders.

As these are the only two exceptions possible to the requirement that any parallel surfaces defined by equation (9) be plane surfaces, it is apparent that the energy surfaces will not in general be parallel.

$$\frac{1}{c_3} d\epsilon' = \frac{T}{c_1} d\eta' - \frac{P}{c_2} dv' \qquad (19)$$

If the units of T and P be so selected that

$$T' = \frac{c_3}{c_1} T$$

and (20)

$$P' = \frac{c_3}{c_2} P$$

then

$$d\epsilon' = T' d\eta' - P' dv' \qquad (21)$$

It appears then that regardless of the units in which η, v, ϵ may be measured, it will be possible so to change the units of T and P that equation (1) is formally unaffected.

The effect on the thermodynamic surface of a change in the units of η, v, ϵ is also easily seen. The position vector to a point becomes

$$\bar{r}' = c_1\eta i + c_2 v j + c_3 \epsilon k \qquad (22)$$

The vector connecting any two points $\bar{r}'_1$ and $\bar{r}'_2$ on the surface is, therefore,

$$\bar{r}'_2 - \bar{r}'_1 = c_1(\eta_2 - \eta_1)i + c_2(v_2 - v_1)j + c_3(\epsilon_2 - \epsilon_1)k \qquad (23)$$

The η, v, and ϵ components of a vector joining two points thus are directly proportional to c_1, c_2, and c_3 respectively; and, therefore, they vary inversely as the magnitudes of the corresponding units employed.

To see how the area of an element of surface depends upon the units used to measure entropy, volume, and

energy, equation (22) may be written as

$$\bar{r}' = \bar{\Phi} \cdot \bar{r} \tag{24}$$

where

$$\bar{\Phi} = c_1 ii + c_2 jj + c_3 kk \tag{25}$$

Hence, the effect on the surface of the change of units given by equation (18) is the same as if the surface were subjected to the transformation (24). But in such a transformation, plane areas are magnified in accordance with the second invariant of $\bar{\Phi}$. Hence, if $d\bar{S}$ denote an element of area, its transform is defined by the equation

$$d\bar{S}' = \bar{\Phi}_2 \cdot dS \tag{26}$$

where

$$\bar{\Phi}_2 = c_2 c_3 ii + c_3 c_1 jj + c_1 c_2 kk \tag{27}$$

V Nature of the Derived Surface in General

The Equation of State (4) relates the entropy, volume and energy of a body of unit mass existing in a homogeneous state of equilibrium. Provided the body is in a state of thermodynamic equilibrium, however, it will have a definite entropy, volume, and energy irrespective of whether it be uniform or diverse in phase, and the pressure and temperature in either case will be uniform throughout. The entropy, volume, and energy of the body as a whole must be the sums of the entropies, volumes, and energies respectively of the parts of the body existing in different states at equilibrium.

This principle may be used to derive the surfaces of multi-phase states from the primitive surface.

Consider a p-phase state, and let $(\eta_i, v_i, \epsilon_i)$ denote the co-ordinates of the point on the primitive surface which represents the body when wholly in the state i. Let m_i be the part of the total mass existing in the $i^{\underline{th}}$ phase. Then the position vector of the point representing the p-phase body may be expressed by

$$\bar{r} = \left(\sum_{i=1}^{p} m_i \eta_i\right) i + \left(\sum_{i=1}^{p} m_i v_i\right) j + \left(\sum_{i=1}^{p} m_i \epsilon_i\right) k$$

$$= \sum_{i=1}^{p} \left\{ m_i (\eta_i i + v_i j + \epsilon_i k) \right\}$$

$$= \sum_{i=1}^{p} m_i \bar{r}_i$$

and, since the body is of unit mass, this may be written

$$\bar{r} = \frac{\sum_{i=1}^{p} m_i \bar{r}_i}{\sum_{i=1}^{p} m_i} \qquad (28)$$

Equation (28) expresses that the point $\bar{r}$ on the derived surface be the centroid of the points $\bar{r}_i$ on the primitive surface associated respectively with the scalars m_i (i=1, 2, 3,---p). In particular, for p=3, equation (28) expresses the necessary and sufficient condition that the

four points $\bar{r}$ and $\bar{r}_i$ be co-planar; and for p=2, it expresses the condition that the three points $\bar{r}$ and $\bar{r}_i$ be collinear.

For any given coexistent states i (i=1, 2, 3,---p), the point $\bar{r}$ is evidently a function of m_i which is continuously variable within the limits $0 \leq m_i \leq 1$, subject to the restriction that $\sum_{i=1}^{p} m_i = 1$. The point $\bar{r}$ is therefore a function of (p - 1) independent variables. Hence, two-phase states are represented by a curve (viz., a straight line); three-phase states by a surface (viz., a plane). Moreover, since states capable of coexistence must be of equal temperature and pressure, the continuum of points $\bar{r}$, as well as the points $\bar{r}_i$ (i=1, 2, 3,---p), must have parallel tangent planes; and, therefore, they have a common tangent plane. Hence, a necessary condition that points represent states capable of coexistence is that they possess a common tangent plane[1].

VI Gibbs' Criteria of Equilibrium and Stability

To determine the properties of the surface relating

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[1] It is immediately evident geometrically that the body may not be compounded of more than three phases capable of continued coexistence. For, if a four-phase state were possible, the point $\bar{r}$, being a function of three independent variables, would necessarily generate a volume; and, hence, the proposition just proved would lose meaning. Four distinct phases obviously may not be represented by co-planar points since any one of such points would be expressible as the centroid of the other three, suitably weighted.

to the various possible types of equilibria it is desirable to have a geometrical criterion for each type of equilibrium. Such conditions have been derived by Gibbs through an application of the First and Second Laws to a process by which the body is permitted to attain a state of equilibrium when surrounded by a medium of constant temperature and pressure. In terms of Gibbs' criteria, the following definitions may be laid down for thermodynamic equilibria.

The necessary and sufficient condition for <u>stable equilibrium</u> of the body when surrounded by the aforementioned medium of constant T and P is that

$$\delta(\epsilon - T\eta + Pv) > 0 \qquad (29)$$

where "δ refers to the variation produced by any variation in the state of the body, and (when different parts of the body are in different states) in the proportion in which the body is divided between the different states". The quantities ϵ, η, and v refer to the state of which the stability is in question.

The necessary and sufficient condition for <u>neutral equilibrium</u> is that

$$\delta(\epsilon - T\eta + Pv) = 0 \qquad (30)$$

It may be observed that neutral equilibrium is not to be considered as a particular case of stable equilibrium as defined above, for the word "necessary" would then make the definitions contradictory.

If the term "equilibrium" be used to include both

stable and neutral types, then the necessary and sufficient condition for equilibrium is that

$$\delta(\epsilon - T\eta + Pv) \geq 0 \qquad (31)$$

The equilibrium is said to be metastable if equation (31) holds for all continuous variations restricted to the neighborhood of the point representing the state in question but does not hold for variations not so restricted.

All states not satisfying equation (31) for continuous variations confined to an arbitrarily small neighborhood are unstable.

VII Vectorial Expression of Gibbs' Criteria

The geometrical interpretation of the criteria of equilibrium and stability presents itself when the analogous vectorial expressions are displayed.

If $\bar{N}$ denote the normal vector to the thermodynamic surface at a point $\bar{r}$, then

$$\bar{N} = \bar{r}_\eta \times \bar{r}_v = [-\epsilon_\eta, -\epsilon_v, 1] \qquad (32)$$

Let $\bar{t}$ be the position vector of any point in the tangent plane at $\bar{r}$. The vector $(\bar{t} - \bar{r})$ lies in the plane; and, hence, the equation of the tangent plane is

$$(\bar{t} - \bar{r}) \cdot \bar{N} = 0 \qquad (33)$$

By eqs. (32) and (33)

$$\epsilon - T\eta + Pv = -\eta\epsilon_\eta - v\epsilon_v + \epsilon = [\eta, v, \epsilon] \cdot [-\epsilon_\eta, -\epsilon_v, 1] = \bar{r} \cdot \bar{N} = \bar{t} \cdot \bar{N} \qquad (34)$$

For a plane through the origin parallel to the tangent plane at $\bar{r}$, equation (33) reduces to

$$\bar{t}_o \cdot \bar{N} = 0 \qquad (35)$$

where $\bar{t}_o$ is the position vector of any point in the plane. By eqs. (34) and (35),

$$\epsilon - T\eta + Pv = (\bar{t} - \bar{t}_o) \cdot \bar{N} \qquad (36)$$

The vectorial analogues of Gibbs' Criteria then appear as

$$\delta\left[(\bar{t} - \bar{t}_o) \cdot \bar{N}\right] > 0 \qquad (37)$$

$$\delta\left[(\bar{t} - \bar{t}_o) \cdot \bar{N}\right] = 0 \qquad (38)$$

$$\delta\left[(\bar{t} - \bar{t}_o) \cdot \bar{N}\right] \geq 0 \qquad (39)$$

If $\bar{n}$ denote the unit normal to the surface, then

$$\bar{N} = |\bar{N}|\,\bar{n} \qquad \bar{N} > 0 \qquad (40)$$

The necessary and sufficient conditions may be expressed in terms of the unit normal by equation (40) as follows:

Stable equilibrium -

$$\delta\left[(\bar{t} - \bar{t}_o) \cdot \bar{n}\right] > 0 \qquad (41)$$

Neutral equilibrium -

$$\delta\left[(\bar{t} - \bar{t}_o) \cdot \bar{n}\right] = 0 \qquad (42)$$

Equilibrium -

$$\delta\left[(\bar{t} - \bar{t}_o) \cdot \bar{n}\right] \geq 0 \qquad (43)$$

The vector $(\bar{t} - \bar{t}_o)$ has as its terminus a point in the tangent plane to the thermodynamic surface and as its origin a point in the plane through the origin of co-ordinates parallel to the tangent plane. The expression in brackets is the normal component of this vector. It therefore is the per-

pendicular distance of the point denoting the state of the body at a pressure P and a temperature T from the plane through the origin representing the same pressure and temperature; and the conditions of equilibrium state that this distance may not be diminished by any variations in the state of the body when surrounded by a medium of pressure P and temperature T, supposed constant.

Equation (42) may equally well be written

$$(\bar{\tau} - \bar{\tau}_0)\cdot\bar{n} = \text{constant} \qquad (44)$$

for all possible states in neutral equilibrium. But equation (44) is the equation of the tangent plane to the thermodynamic surface. Hence the sufficiency of the necessary condition for points representing states capable of continued co-existence[1]; viz., that they have a common tangent plane, is established.

VIII Geometrical Requirements of the Criteria

The position of the surface relative to the tangent plane may be inferred readily from the equilibrium conditions just stated. Suppose the body to be initially in equilibrium at the pressure and temperature of the medium. Its state will be represented by a point on the thermodynamic surface. By suitable variations in the entropy and vol-

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[1] See footnote (1) on page 30.

ume of the body it obviously will be possible to bring it to a state represented by any arbitrarily chosen point on the surface[1], and such a point by virtue of relation (43) may not lie below the tangent plane to the surface at the initial point. No part of the surface, therefore, may fall below the tangent plane to a point corresponding to a state of equilibrium.

The varied state may or may not be at the temperature and pressure of the medium. As it is represented by a point on the thermodynamic surface, however, its pressure and temperature in either event will be denoted by the inclination of the tangent plane at that point. Consider the case in which the varied state is at the temperature and pressure of the medium. The initial point and the varied point may have distinct but parallel tangent planes, or they may have identical tangent planes. If equation (42) hold for the initial point with respect to the variation considered, the tangent planes will be identical, and the equation must hold also for the varied point. The two states are then said to be in neutral equilibrium, for the relation between them is a reciprocal one, and there can be no tendency for the one to pass into the other. If, however, the inequality (41) hold for the initial point, the varied point will have a tangent

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[1] Certain points in the region of unstable states may not be actually realizable. If they be considered at least possible in theory, however, they must fall as indicated.

plane parallel to, but above, the tangent plane to the initial point. The varied point, therefore, will be unstable with respect to the initial point; and, hence, the state of the body must spontaneously revert to the initial state.

In the event the temperature and pressure of the varied state differ from the temperature and pressure of the initial state, equation (42) obviously does not apply. If the relation (41) hold for the initial state, the varied state evidently will be unstable with respect to the initial state; for the temperature and pressure of the body must revert to the temperature and pressure of the medium, and, as shown above, such processes will then ensue that return the body to its initial state. Points for which condition (41) holds are therefore said to represent states of stable equilibrium.

Thus far, only those varied states represented by points on the thermodynamic surface have been considered. It may occur that the varied state be denoted by a point not on the surface. Such a state cannot be one of equilibrium or of metastable equilibrium, for all such states are represented on the surface. It is, therefore, unstable, and by the criteria stated it must revert to a state denoted by a point on the thermodynamic surface whose tangent plane represents the temperature and pressure of the surrounding medium.

It remains to consider states of metastable equilibrium. If in the vicinity of the initial point the surface

does not fall below the tangent plane but does do so at other points not in this vicinity, it follows from what has been said that the initial point will represent a state of equilibrium with respect to varied states restricted to the neighborhood of the point, but of instability with respect to certain variations not so restricted. Such a point, therefore, is said to represent a state of metastable equilibrium.

IX Expression of Criteria for Infinitesimal Variations

In order to study more closely the nature of the surface in the neighborhood of a point, the conditions of equilibrium and stability may be thrown into a form more convenient than the relations (41)-(43). The change in energy of the body in going from a state η, v to a state $\eta + \delta\eta$, $v + \delta v$ is, by Taylor's Theorem,

$$\delta\epsilon = \epsilon_\eta \delta\eta + \epsilon_v \delta v + \tfrac{1}{2}\left[\epsilon_{\eta\eta}(\delta\eta)^2 + 2\epsilon_{\eta v}\delta v\delta\eta + \epsilon_{vv}(\delta v)^2\right] + \cdots \tag{45}$$

or, rearranging and denoting the quadratic form in brackets by q,

$$\delta\epsilon - T\delta\eta + P\delta v = \tfrac{1}{2}q + \cdots \tag{46}$$

If the varied state be sufficiently near the initial state, terms of order higher than the second in $\delta\eta$ and δv are negligible. Furthermore, since the body is considered surrounded by a medium of constant temperature T and pressure P, the left member of equation (46) is precisely the left mem-

bers of relations (29)-(31). Hence, for sufficiently small variations, the necessary and sufficient conditions may be expressed as follows:

For stable equilibrium -

$$q>0 \tag{47}$$

For neutral equilibrium -

$$q=0 \tag{48}$$

For equilibrium -

$$q\geqslant 0 \tag{49}$$

The behavior of a quadratic form is determined essentially by the value of its discriminant. If D denote the discriminant, by definition[1],

$$D=\epsilon_{\eta\eta}\epsilon_{vv} - (\epsilon_{\eta v})^2 \tag{50}$$

From the elementary theory of quadratic forms, certain deductions may be drawn from conditions (47)-(49) as to the signs of D and of the differential coefficients $\epsilon_{\eta\eta}$ and ϵ_{vv}. This information may be tabulated as follows:

Stable equilibrium -

$$q>0;\ D>0;\ \epsilon_{\eta\eta}>0;\ \epsilon_{vv}>0 \tag{51}$$

Neutral equilibrium -

$$q=0;\ D=0;\ \epsilon_{\eta\eta}=\epsilon_{vv}=\epsilon_{\eta v}=0 \tag{52}$$

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[1] If equation (50) be written in determinate form; i.e., $D=\begin{vmatrix}\epsilon_{\eta\eta} & \epsilon_{\eta v}\\ \epsilon_{\eta v} & \epsilon_{vv}\end{vmatrix}$, the discriminant will be recognized immediately as the Hessian of the function ϵ.

Equilibrium -

$q \geqslant 0$; $D = 0$ (53)

The following definitions and theorems are listed for convenience. It is assumed that both $\delta\eta$ and δv are not zero simultaneously; for then the quadratic form would disappear since there would be no variation in the state of the body.

(A) If q is of one sign only, the form is said to be definite. The necessary and sufficient condition that q be definite: $D > 0$. It is then positive definite if $\epsilon_{\eta\eta} > 0$ (so that $\epsilon_{vv} > 0$ also); otherwise, it is negative definite.

(B) If q assume values of different sign, the form is indefinite. The necessary and sufficient condition that q be indefinite: $D < 0$.

(C) If q vanish for certain variations but otherwise assume values of one sign only, the form is semi-definite. The necessary and sufficient condition that q be semi-definite: $D = 0$.

(D) If $\epsilon_{\eta\eta} = \epsilon_{vv} = \epsilon_{\eta v} = 0$, the statements above do not apply. It is evident that this is the necessary and sufficient condition that the form vanish for all variations.

X Geometrical Meaning of q

Let $\bar{r}$ be the position vector to a point A on the thermodynamic surface for which the parameter values are η, v. Then, by Taylor's Theorem, the position vector to a neighboring point B $(\eta + \delta\eta, v + \delta v)$ has the value

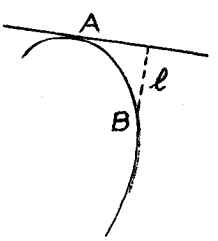

Figure 4

$$\bar{r} + \bar{r}_\eta \delta\eta + \bar{r}_v \delta v + \tfrac{1}{2}\left[\bar{r}_{\eta\eta}(\delta\eta)^2 + 2\bar{r}_{\eta v}\delta\eta\delta v + \bar{r}_{vv}(\delta v)^2\right] + \cdots$$

The length of the perpendicular distance from B to the tangent plane at A is the component of the vector $\overline{AB}$ in the direction of the normal at A. Denoting this length by ℓ,

$$\ell = \bar{n}\cdot(\bar{r}_\eta \delta\eta + \bar{r}_v \delta v) + \tfrac{1}{2}\bar{n}\cdot\left[\bar{r}_{\eta\eta}(\delta\eta)^2 + 2\bar{r}_{\eta v}\delta\eta\delta v + \bar{r}_{vv}(\delta v)^2\right] \quad \cdots \quad (54)$$

Since n is perpendicular to $\bar{r}_\eta$ and $\bar{r}_v$, terms of the first order vanish; and, hence, to terms of the second order,

$$\ell = \tfrac{1}{2}\bar{n}\cdot\left[\bar{r}_{\eta\eta}(\delta\eta)^2 + 2\bar{r}_{\eta v}\delta\eta\delta v + \bar{r}_{vv}(\delta v)^2\right] \quad (55)$$

From equation (5), by differentiation,

$$\bar{r}_{\eta\eta} = [0,\ 0,\ \epsilon_{\eta\eta}] \quad (56)$$

$$\bar{r}_{\eta v} = [0,\ 0,\ \epsilon_{\eta v}] \quad (57)$$

$$\bar{r}_{vv} = [0,\ 0,\ \epsilon_{vv}] \quad (58)$$

and, also,

$$\bar{n} = \frac{1}{|\bar{N}|}\bar{N} = \frac{1}{|\bar{N}|}\bar{r}_\eta \times \bar{r}_v = \frac{1}{|\bar{N}|}[-\epsilon_\eta,\ -\epsilon_v,\ 1] \quad (59)$$

By eqs. (55)-(59),

$$\ell = \frac{1}{2|\bar{N}|}\left[\epsilon_{\eta\eta}(\delta\eta)^2 + 2\epsilon_{\eta v}\delta\eta\delta v + \epsilon_{vv}(\delta v)^2\right]$$

or

$$\ell = \frac{1}{2|\bar{N}|}\, q \quad (60)$$

At a given point the quantity $|\bar{N}|$, of course, is a positive constant. The value of the quadratic form q, therefore, is directly proportional to the length ℓ which is the perpendicular distance from the tangent plane at a stationary point A of a varied point B on the surface. The value of q is thus intimately connected with the curvature of the surface in the immediate vicinity of the stationary point in

question.

XI Sign of q for Equilibrium States of One, Two, and Three Phases

(A) Three-phase States

By equation (28) all states of the body composed of three co-existent phases must be represented by co-planar points. Such points, therefore, satisfy equation (44); and, hence, constitute a field of neutral equilibrium for which the relations (52) hold; viz.,

$$\epsilon_{\eta\eta}=\epsilon_{vv}=\epsilon_{\eta v}=0;\ q\equiv 0;\ D\equiv 0 \qquad (61)$$

(B) Two-phase States

If, in equation (28), $\bar{r}_i$ $(i=1, 2)$ be constant, then any state $\bar{r}$ composed of the two states (or phases) denoted by $\bar{r}_1$ and $\bar{r}_2$ must be collinear with $\bar{r}_1$ and $\bar{r}_2$ by equation (28). Hence, all possible such two-phase states will be represented by a straight line. If the primitive states now be varied slightly and equilibrium maintained, a second series of two-phase states will be possible, and these will be represented by a second straight line. Thus all possible two-phase states will be shown by a series of straight lines. Moreover, the condition that $\bar{r}_i$ $(i=1, 2)$ be continuously variable requires that these lines be the generators of a ruled surface.

Consider one such ruling. It has been shown that points representing states capable of co-existence are char-

acterized by a common tangent plane (p. 34), and hence all points on the ruling satisfy equation (44). States shown by points along the line are, therefore, in neutral equilibrium, and for such states $q=0$. But no other point on the ruled surface may represent a state in equilibrium with these states, for it would then be possible to have the body composed of three co-existent phases; whereas, by premise, the discussion is limited to the field of two-phase states. Therefore, for any variation from a state represented by a point on the ruling to a point not on that ruling $q>0$, and the initial point denotes a state of stable equilibrium with respect to the varied point. Hence, this is a field of equilibrium states neutral toward variations at constant temperature and pressure and stable toward all others. The relations (53) must hold; viz.,

$$q \geqslant 0; \quad D=0 \tag{62}$$

The geometrical sifnificance of the vanishing of the discriminant is easily shown. Equation (62) may be written in the form

$$D \equiv \begin{vmatrix} \epsilon_{\eta\eta} & \epsilon_{\eta v} \\ \epsilon_{v\eta} & \epsilon_{vv} \end{vmatrix} \equiv J\left(\frac{\epsilon_\eta, \epsilon_v}{\eta, v}\right) = 0 \tag{63}$$

where J denotes the Jacobian. Hence, equation (63) expresses a necessary and sufficient condition that ϵ_η and ϵ_v be functionally related. But, in view of eqs. (6) and (7), this is equivalent to a functional relation between $\bar{r}_\eta$ and $\bar{r}_v$. The equation of the tangent plane to the surface, by virtue of

eqs. (33) and (59), is

$$(\bar{t} - \bar{r}) \cdot \bar{r}_\eta \times \bar{r}_v = 0 \qquad (64)$$

and the necessary and sufficient condition that this equation represent a one-parameter family of planes is that there exist a functional relation between $\bar{r}_\eta$ and $\bar{r}_v$. But the envelope of a one-parameter family of planes is by definition a developable surface. Hence, the necessary and sufficient condition that the surface be developable is

$$D = 0$$

(C) One-phase States

No succession of ppints in the field of homogeneous states may have a common tangent plane, for then these points would denote states which could exist in equilibrium in accordance with equation (28) contrary to the supposition that the field is constituted solely of points which represent states of one phase. Therefore, for any possible variations $q \neq 0$; and, hence, $q > 0$. These are thus states of stable equilibrium, and the relations (51) must hold; viz.,

$$q > 0;\ D > 0;\ \epsilon_{\eta\eta} > 0;\ \epsilon_{vv} > 0 \qquad (65)$$

(D) Metastable States

For variations restricted as previously defined, the foregoing considerations apply without change to those portions of the surface which correspond to states of metastable equilibrium. Points in this field, therefore, may represent states either homogeneous or diverse in phase.

XII Sign of q in the Region of Unstable States

It is true that, in general, "states" of instability lie outside the domain of definition of the thermodynamic functions, and, consequently, these quantities lose meaning when applied to such states. Unless there are to be gaps in the primitive surface, however, it is apparent that there will exist sets of values of η, ϵ, and v which satisfy equation (3), and which, therefore, determine points on a surface, but which fail to satisfy the conditions of equilibrium or of metastable equilibrium. Such portions of the thermodynamic surface may be defined arbitrarily as the field of unstable states, and the points so defined will correspond in accordance with the assumption of analyticity of $\epsilon(\eta, v)$, to unique sets of values (ϵ, η, v) and, consequently, to unique values of P and T. Obviously, not all of the triple infinitude of conceivable unstable states is included by this definition.

A sufficient condition that a point on the surface lie in the field of unstable states then is

$$\delta(\epsilon - T\eta + Pv) < 0$$

or (66)

$$\delta[(\bar{\tau} - \bar{\tau}_0)\cdot\bar{n}] < 0$$

where δ has the same significance as previously indicated. The state represented by such a point will exhibit instability with respect to all variations. In order that a state be un-

stable, however, it is not necessary that the inequality (66) hold true for all variations; it evidently is sufficient if it hold for any particular continuous variations. The following possibilities, therefore, may occur:

$$\delta<0;\ \delta\leqslant 0;\ \delta\gtrless 0;\ \delta\gtrless 0 \qquad (67)$$

where the variation "δ" is understood to refer to the quantity $(\epsilon - T\eta + Pv)$.

If $\delta<0$, then $q<0$ and by (A) (p. 39), the following relations may be written:

$$q<0;\ D>0;\ \epsilon_{\eta\eta}<0;\ \epsilon_{vv}<0 \qquad (68)$$

If $\delta\leqslant 0$, then $q\leqslant 0$, and the point must lie on a surface derived from points on the primitive surface by equation (28). Owing to the practical insignificance of even the primitive parts of the field of unstable states, however, it is not worthwhile to investigate in detail the derived portions of this field. It may be observed immediately, nevertheless, that this derived surface will be a developable of a similar nature to the developable found previously for two-phase equilibrium states with the exception that the latter was convex downward whereas this one must be convex upward.

Consider the condition $\delta\gtrless 0$. For sufficiently small variations this is equivalent to $q\gtrless 0$. But if q be positive for certain variations and negative for others, there will exist at least one variation for which q vanishes since ϵ is analytic. Therefore, the possibility of the case $\delta\gtrless 0$ may be denied.

If $\delta \gtrless 0$, then for sufficiently small variations $q \gtrless 0$. The quadratic form is said to be indefinite, and, hence, by (B) (p. 39), $D<0$.

But these are the only possible types of points which characterize unstable states on the primitive surface. Hence, regions which correspond to states unstable to all continuous variations are constituted of points for which

$$q<0;\ D>0;\ \epsilon_{\eta\eta}<0;\ \epsilon_{vv}<0 \qquad (69)$$

Regions which correspond to states stable with respect to certain continuous variations but unstable toward others are constituted of points for which

$$q \gtrless 0;\ D<0^{1} \qquad (70)$$

XIII Geometry of the Surface Near a Point

The geometry of a surface in the neighborhood of a point may be studied readily by considering the curve of intersection of the surface with a plane parallel to the tangent plane at the point and displaced from it an infinitesimal distance along the normal. To infinitesimals of the first order it is easily demonstrated that this curve is a conic section with semi-axes equal to $\sqrt{2h}\ K_1^{-\frac{1}{2}}$ and $\sqrt{2h}\ K_2^{-\frac{1}{2}}$ respectively,

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[1] The character of the succession of points constituting the boundary line between two such regions appears at once from the consideration that q and D are continuous functions; thus $q \leqslant 0;\ D=0$
See footnote (1), p. 56.

where K_1 and K_2 are the prinicipal curvatures at the point and h is the displacement of the plane from the point measured along the principal normal[1]. The corresponding conic section with semi-axes equal respectively to $K_1^{-\frac{1}{2}}$ and $K_2^{-\frac{1}{2}}$ is a similar curve. It is called the <u>indicatrix</u> at the point.

The equation of the indicatrix is expressible most simply perhaps in dyadic form. If the dyadic Φ be defined as

$$\Phi \equiv K_1 ii + K_2 jj \qquad (71)$$

then the equation of the indicatrix may be written[2]

$$r \cdot \Phi \cdot r = 1 \qquad (72)$$

It is of interest to consider the form of the indicatrix for

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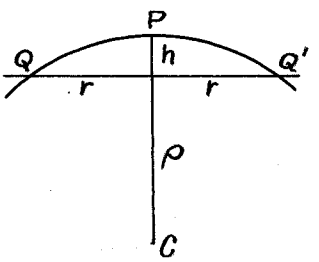
[1] The following derivation is from Weatherburn, "Differential Geometry", Cambridge Press, 1927, p. 74.

Let the plane QQ' be taken parallel to the tangent plane at P, and displaced from it a distance h in the direction of the unit normal $\bar{n}$. The figure shows a normal section cut by a plane QPQ'. If ρ is the radius of curvature of this section and 2r the length QQ', then



$$(\rho - h)^2 + r^2 = \rho^2$$

whence, to first order infinitesimals,

$$r^2 = 2h\rho$$

By Euler's Theorem on normal curvature, in which θ is the angle between the normal section and a principal direction,

$$\frac{1}{\rho} = K_n = K_1 \cos^2\theta + K_2 \sin^2\theta = \frac{2h}{r^2}$$

or

$$K_1 r^2 \cos^2\theta + K_2 r^2 \sin^2\theta = 2h$$

Writing $x = r \cos\theta$ and $y = r \sin\theta$ gives

$$\frac{x^2}{2h/K_1} + \frac{y^2}{2h/K_2} = 1$$

[2] If the unit vectors i and j be taken at the point in question as origin and parallel to the tangents to the lines of principal curvature, then equation (72) will represent a curve not only similar to but also similarly situated to the section of the surface cut by the plane parallel to the tangent plane.

various points on the thermodynamic surface.

(A) States Not Unstable

(1) Three-phase States

The field of three phase states has been shown to be plane (p. 30), and, therefore, $K_1 = K_2 = 0$. The dyadic Φ vanishes, and, hence, the indicatrix as defined by equation (31) does not exist.

(2) Two-phase States

The total curvature of a surface at a point is defined as the product of the principal curvatures, given by the equation[1]

$$K_1 K_2 = \frac{\epsilon_{\eta\eta}\epsilon_{vv} - (\epsilon_{\eta v})^2}{(1 + \epsilon_\eta^2 + \epsilon_v^2)^2} = \frac{D}{(1 + \epsilon_\eta^2 + \epsilon_v^2)^2} \qquad (73)$$

The sign of the total curvature is evidently the same as the sign of the discriminant D. In the field of two-phase states the discriminant is zero, and, consequently, either K_1 or K_2 vanishes. The dyadic Φ thus reduces to a single dyad, and the indicatrix, therefore, consists of a pair of parallel straight lines. Such a point is called parabolic. The portion of the thermodynamic surface corresponding to two-phase states is therefore a surface of parabolic points.

(3) One-phase States

In the field of homogeneous states the discriminant is positive, and, therefore, by equation (73), K_1 and K_2 are

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[1] See Weatherburn, loc. cit., p. 76.

of the same sign. Equation (72) thus represents an ellipse, and the points are said to be elliptical, or points of positive curvature. The surface in the neighborhood of such a point evidently lies entirely on one side of the tangent plane. The region of the thermodynamic surface representing homogeneous states, therefore, is a surface of elliptical points.

(B) Unstable States

That portion of the field of instability which is composed of points representing states stable toward certain continuous variations while unstable with respect to others was found to satisfy the relation $D<0$. For this region, therefore, by equation (73), the two principal curvatures differ in sign. The indicatrix is, by equation (72), then, a hyperbola. The points in the field are said to be hyperbolic points, or points of negative curvature. The two lines of principal curvature evidently lie on different sides of the tangent plane at a point of this type, and the hyperbola conjugate to that of equation (72) would be cut by a plane parallel to the plane cutting the curve of equation (72) but on the opposite side of the tangent plane from it. This is easily seen to be the case by writing the equation of the indicatrix of such a section; i.e.,

$$\bar{r}\cdot\Phi\cdot\bar{r}=-1 \qquad (74)$$

The equation of the asymptotes is clearly the same whether obtained from equation (72) or equation (74); viz.,

$$\bar{r} \cdot \Phi \cdot \bar{r} = 0 \qquad (75)$$

and, hence, the hyperbolas are conjugate.

Letting $\eta = r \cos \theta$ and $v = r \sin \theta$, equation (75) may be transformed into polar co-ordinates as

$$K_1 \cos^2\theta + K_2 \sin^2\theta = 0 \qquad (76)$$

But the left member of equation (76) is, by Euler's Theorem on normal curvature, precisely the normal curvature in the direction given by θ. Therefore, the normal curvature of the surface in the directions of the asymptotes is zero.

The region of states unstable toward all variations is composed of points characterized by a positive discriminant. For any such point the indicatrix has been shown to be an ellipse, and the surface, accordingly, must lie entirely on one side of the tangent plane. Since $\epsilon_{\eta\eta} < 0$ and $\epsilon_{vv} < 0$, such a point is a maximum. Both principal curvatures are negative[1], and the surface lies below the tangent plane, being convex upward. This region thus differs from the field of stable one-phase states which was shown to be constituted also of elliptical points; for in the latter both principal curvatures are positive, and the surface falls above the tangent plane, being convex downward.

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[1] The convention is here adopted that a line of principal curvature is positive if the unit normal to the surface points toward the concave side of the line; otherwise, it is negative. With this convention, equation (74) represents the indicatrix if $K_1 < 0$ and $K_2 < 0$; whereas, equation (72) is applicable in all other cases.

XIV General Features of the Thermodynamic Surface

The mutual relations between the various parts of the energy surface, whose properties have been investigated separately, may be made clearer perhaps by a discussion of the surface as a whole. Homogeneous states of the body are represented on the so-called primitive surface; multi-phase states on surfaces derived therefrom. Suppose the substance to be capable of existing in the three forms solid, liquid, and vapor. The derived surface of three-phase states then is a plane triangle whose vertices are three points on the primitive surface lying in the fields of solid, liquid, and vapor, respectively. The plane of the triangle is tangent to the primitive surface at these three points, and except for these points the primitive surface lies entirely above the plane.

Each edge of the triangle represents states of two-phase equilibria; viz., solid-liquid, liquid-vapor, vapor-solid, and points representing such equilibria must lie in a plane tangent to the primitive surface at two points. Suppose the triply tangent plane to leave the primitive surface at one point; say, solid, and roll on the surface while maintaining its double tangency. That part of the envelope of the rolling plane between the points of double tangency is the developable surface representing states of liquid-vapor equilibrium, and the primitive surface must everywhere fall above this envelope except along the two lines where they touch. The envelope is

developable in the sense that if the tangent plane be considered stationary and the surface imagined to roll over it, the two lines traced upon it would bound a plane surface.

Similarly, two other derived developables may be formed by letting the doubly tangent plane commence to roll from the other two edges of the three-phase triangle. Thus the plane triangle together with the three developables and the three sections of the primitive surface included between them form a continuous sheet which is the surface of dissipated energy. The surface of dissipated energy may nowhere fall below the tangent plane to it at any point.

The rolling doubly-tangent planes trace six lines on the primitive surface. These are the boundary lines between the developables and the primitive surface. The three sections of the primitive surface outside these lines represent homogeneous states of stable equilibrium of liquid, vapor, and solid respectively. Inside these lines on the primitive surface are the points which represent homogeneous states of metastability and instability. The tangent planes to such points cut the primitive surface at points removed from the point of contact. Included between any two regions of metastability, which are included between a pair of lines traced by the rolling doubly tangent plane, is a region of unstable states. The tangent plane to any point in this region either cuts the primitive surface at the point of contact or else lies above the surface in the vicinity of the

of the point of tangency. Thus any field representing homogeneous metastable states is bounded on one side by one of the aforementioned six lines and on the other side by a region of instability, and each such region of instability is included between two fields of metastable states; viz., solid and liquid, solid and vapor, or liquid and vapor.

The triply-tangent plane may not only roll on the primitive surface as a doubly-tangent plane by leaving one point of contact as previously described, but it may also commence by rotating in the opposite direction. The part of its envelope included between the points of double tangency is thus a continuation of one of the three developables mentioned above, but the tangent plane to it along any generator cuts the primitive surface at a point removed from the line of tangency. This part of the developable represents two-phase states of metastable equilibrium. It terminates in a region of instability.

The Clapeyron-Clausius Equation may be derived readily from a consideration of the geometry of the developable surfaces. Let the vector $\bar{u}$ denote the difference between the position vectors of any two points which represent states capable of co-existence. Then $\bar{u}$ lies in the common tangent plane to these points. Hence, if $\bar{N}$ be the normal to the tangent plane,

$$\bar{u}\cdot\bar{N}=0 \qquad (77)$$

Let the tangent plane turn about the line connecting the two

points as an instantaneous axis through an infinitesimal angle, and let the corresponding new value of $\bar{N}$ be $\bar{N}'$. Then

$$\bar{u} \cdot \bar{N}' = 0 \tag{78}$$

Combining these two equations by subtraction and denoting the infinitesimal vector $(\bar{N}' - \bar{N})$ by $d\bar{N}$ gives

$$\bar{u} \cdot d\bar{N} = 0 \tag{79}$$

Equation (79) is the vector equivalent of the Clapeyron-Clausius Equation.

The relation may be converted to the usual form by evaluating the vectors in terms of their components.

$$\bar{N} = \left[-\epsilon_\eta, -\epsilon_v, 1\right] = \left[-T, P, 1\right] \tag{80}$$

Differentiating,

$$d\bar{N} = \left[-dT, dP, 0\right] \tag{81}$$

$$\bar{u} = \left[\Delta\eta, \Delta v, \Delta\epsilon\right] \tag{82}$$

$$\therefore \bar{u} \cdot d\bar{N} = -\Delta\eta\, dT + \Delta v\, dP = 0 \tag{83}$$

Rearranging, and replacing $\Delta\eta$ by its equivalent $\frac{\ell}{T}$ where ℓ denotes the specific latent heat of the change of state at the temperature T, the equation becomes

$$\frac{dP}{dT} = \frac{\ell}{T\Delta v} \tag{84}$$

XV Boundary Points

It remains to consider the nature of the points on the primitive surface which constitute the boundaries between regions of stability and metastability, and of metastability

and instability, and, in particular, the critical point. The latter point is excluded in the following discussion.

It has been shown that for points in the fields of both stable and metastable homogeneous states the relations (65) hold; viz.,

$$q>0;\ D>0;\ \epsilon_{\eta\eta}>0;\ \epsilon_{vv}>0 \qquad (85)$$

and, therefore, these relations hold for points on the curve dividing these two fields. For these points, then, both principal curvatures are positive, the indicatrix is an ellipse, and the surface nowhere falls below the tangent plane but touches it at two points each of which lies on such a boundary curve.

The curve which lies between the fields of metastability and of instability, however, is somewhat different. On the metastable side of this curve, both principal curvatures are positive. On the unstable side, at least one of them is negative. On the curve, therefore, at least one of them is zero; i.e., the lines of that principal curvature which changes sign on crossing the curve have points of inflection on this curve. The tangent planes to the surface at such points then have contacts of the second order at least with the surface in the section of least curvature, and since these planes must be pierced by the lines of that curvature which changes sign, they must be cut by the surface. The points on the boundary curve consequently represent unstable states. Moreover, by equation (73), for these points

$$D=0^{1} \qquad (86)$$

XVI The Critical Point

The critical point may be defined as the limiting state at which the distinction between co-existent masses of liquid and vapor disappears. It is therefore the point at which the points of bi-tangency of the rolling tangent plane whose envelope is the derived surface of liquid-vapor equilibrium become identical. The two curves, joining at the critical point, which are the loci of the points of contact of this rolling tangent plane with the primitive surface con-

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[1] By (C) (p. 39), this is the necessary and sufficient condition that a point be characterized by a semi-definite quadratic form, and in view of the fact that one principal curvature is positive, the form must be positive for variations along that line of curvature, however small; and, therefore, $q \geqslant 0$ for the point. The equality sign evidently arises from the fact that the other line of principal curvature has a contact of the second order with the tangent plane at the point. With respect to variations sufficiently small so that infinitesimals of order higher than the second vanish, therefore, the condition of equilibrium is satisfied; viz.,

$$\delta(\epsilon - T\eta + Pv) \geqslant 0$$

But for sensible variations this condition is not satisfied, and the point represents an unstable state.

In the region of unstable states there may be traced a similar succession of points which constitute the boundary curve between that portion of the field which satisfies relations (69) and the part for which the conditions (70) hold (See footnote (1), p. 46). This curve also is the locus of points of inflection of a line of principal curvature. It differs from the curve discussed above, however, in that the other principal curvature is negative for all points on it. The relations $D=0$, $q \leqslant 0$ hold, and the states represented obviously are unstable.

stitute the saturation curve for the liquid. Likewise it appears from the definition of the critical point that the normal plane through any two points representing co-existent states, however slightly removed from the critical state, must cut the primitive surface in the region of unstable states. Hence the boundary curve between the region of metastable liquid states and the field of instability and the curve between the field of metastable vapor states and the region of instability join at the critical point. This curve may be called the spinodal curve; and the saturation curve will be designated the connodal curve. Both of these curves pass through the critical point, and, since they may not intersect, they are tangent to each other there[1].

By virtue of equation (86) and what has been said above, the value of D for any point on the spinodal curve arbitrarily close to the critical point is zero; and, therefore, since the function ϵ is analytic, for the critical point

$$D=0 \qquad (87)$$

Hence, by equation (73), at least one principal curvature becomes zero at the critical point. This accords with the fact that the critical state is represented by the point of coalescence of the two points of inflection of the lines of that

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[1] That both curves are continuous is evident from the fact that the critical state is a state of continuous transition from the liquid state to the vapor state; i.e., the property of continuity is inherent in the definition of the critical point.

principal curvature which changes sign on crossing the spinodal curve. The particular line through the critical point, therefore, has a third order contact with the tangent plane to the surface at that point. It is tangent to the spinodal curve (and, hence, to the connodal curve) but does not actually cut it. Its normal curvature is zero at the critical point, but positive elsewhere.

Since the critical point marks the merger of the points of bitangency of the rolling tangent plane, the surface may nowhere fall below the tangent plane at that point. The critical state, then, is not unstable; and, therefore, by equation (87) and (C) (p. 39),

$$q \geqslant 0^{1} \qquad (88)$$

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[1] In light of the discussion of the curvature of the surface at the critical point, it is clear that for infinitesimal variations the equality holds with respect to varied points along the line of that principal curvature which vanishes at the critical point. Along the other line of principal curvature, therefore, the inequality must hold. At the critical point, then, one principal curvature is positive; the other, zero.

By (D) (p. 39), this conclusion is valid only if the discriminant does not vanish identically, term by term. It appears unlikely that the discriminant should so vanish; but, on the other hand, there seems to be no theoretical basis for the denial of this possibility. Regarding it, therefore, as a trivial case, it may be stated at once that for such a point

$$D \equiv 0 \text{ term by term; } q \equiv 0 \text{ term by term; } \epsilon_{\eta\eta} = \epsilon_{vv} = \epsilon_{\eta v} = 0;$$
$$K_1 = K_2 = 0$$

Moreover, since that line of principal curvature which cuts the spinodal curve at the critical point cannot change the sign of its normal curvature there (for it would then cut the tangent plane, which property is not allowable since the critical state is not unstable) it must have a contact with the tangent plane of odd order exceeding unity. At such a point, therefore, the tangent plane to the surface osculates both lines of principal curvature.

It follows from relation (88) that

$$\epsilon_{\eta\eta} > 0; \quad \epsilon_{vv} > 0 \tag{89}$$

and from eqs. (87) and (89) that

$$\epsilon_{\eta v} \neq 0 \tag{90}$$

Experimentally, the value of the partial derivative $\epsilon_{\eta v}$ is found to be negative for the critical state. It will be observed, however, that none of the considerations so far adduced suffices to determine the sign of this quantity. It thus appears to be possible thermodynamically that substances exist having the property that $\epsilon_{\eta v}$ is positive for the critical state. It is known that certain compounds, said to exhibit anomalous thermodynamic behavior, do show this property in other states. Water, for example, behaves anomalously in the liquid states below 4° C. In accordance with experiment, however, the quantity $\epsilon_{\eta v}$ will be assigned a negative value. The following relations may then be written for the critical point:

$$q \geqslant 0; \quad D = 0; \quad \epsilon_{\eta\eta} > 0; \quad \epsilon_{vv} > 0; \quad \epsilon_{\eta v} < 0 \tag{91}$$

XVII Sequence of the Isentropic, Isometric, Isothermal, and Isobaric at the Critical Point

Consider the projection on the entropy-volume plane of the primitive surface in the neighborhood of the critical point. By equation (6), Part One, the gradients of the functions η, v, T, and P are as follows:

$$\nabla\eta = \mathbf{i} \tag{92}$$

$$\nabla v = \mathbf{j} \tag{93}$$

$$\nabla T = \left(\frac{\partial T}{\partial \eta}\right)_v \mathbf{i} + \left(\frac{\partial T}{\partial v}\right)_\eta \mathbf{j} = \epsilon_{\eta\eta}\mathbf{i} + \epsilon_{\eta v}\mathbf{j} \tag{94}$$

$$\nabla P = \left(\frac{\partial P}{\partial \eta}\right)_v \mathbf{i} + \left(\frac{\partial P}{\partial v}\right)_\eta \mathbf{j} = -\epsilon_{v\eta}\mathbf{i} - \epsilon_{vv}\mathbf{j} \tag{95}$$

From eqs. (87), (94), and (95), it appears that the gradients of T and P have the same direction (and sense); and, therefore, the isothermal and the isobaric are tangent at the critical point in the entropy-volume diagram. But the operator ∇ is formally invariant with respect to a transformation of co-ordinates. The property of tangency, consequently, must hold in any diagram whatever which represents states of the body uniquely. In particular, it follows that in any intensity-extensity diagram, constant intensity curves have horizontal tangents at the critical point.

By relations (91)-(95), the gradients must fall as indicated in Figure (5), and the corresponding iso-lines as in Figure (6), in which the side of a line on which the function is increasing is designated by a plus sign.

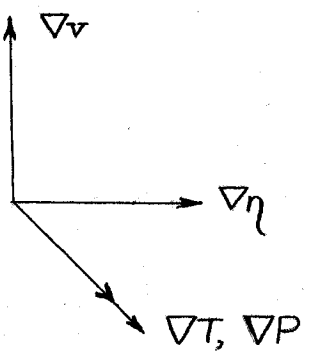


Figure 5

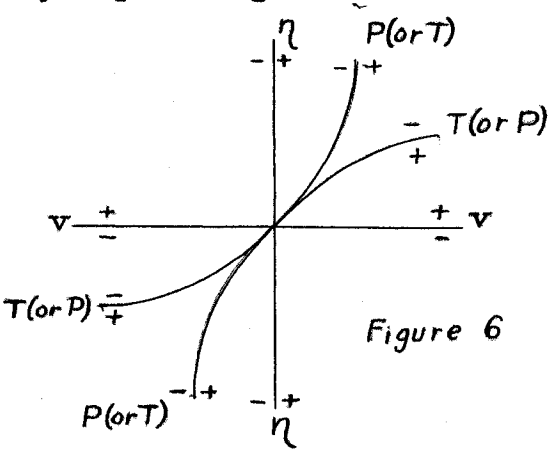


Figure 6

As the constant intensity curves are tangent at the critical point, the relative positions of these two lines are not ascertainable from a consideration of the gradients alone. The condition that the critical state is stable, however, requires that at constant pressure the temperature increase with heat received, and therefore with the entropy. The iso-lines at the critical point then may fall only in the order indicated in Figure (7), and this arrangement is independent of the particular method selected for forming the diagram.

Equation (87) holds not only for the critical point but also for any other point on the spinodal curve. The isothermal and isobaric through any point on this curve, therefore, are tangent to each other. But states represented on the spinodal curve are, in general, unstable, and, hence, the arrangement of Figure (7) may not hold; i.e., the order of succession of the isothermal and isobaric about a point on the unstable side of the spinodal curve is reversed. These two lines, therefore, although tangent to each other, may not intersect on the spinodal curve if they cross it. Thus, in general, the isothermal and the isobaric may have a simple tangency on the spinodal curve, but at the critical point they must have a contact of the second or higher even order.

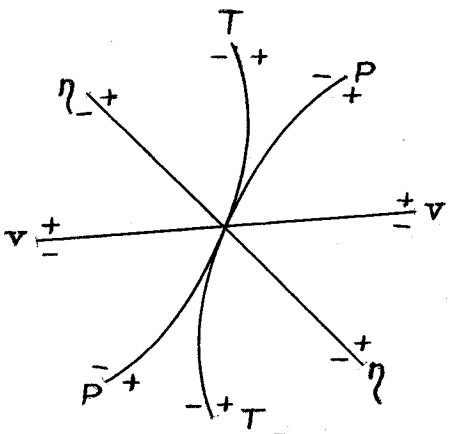


Figure 7

XVIII Slope of the Spinodal and Connodal Curves at the Critical Point

It has been shown that the isothermal and isobaric have an even order of tangency at the critical point, and, hence, they may not cross the spinodal curve. Therefore, the isothermal and isobaric are tangent to the spinodal curve at the critical point, and, consequently, they must be tangent to the connodal curve (p. 57). It follows that in any extensity-intensity diagram the connodal curve has a horizontal tangent at the critical point; i.e.,

$$\left(\frac{dP}{dv}\right)_c = \left(\frac{dT}{dv}\right)_c = \left(\frac{dP}{d\eta}\right)_c = \left(\frac{dT}{d\eta}\right)_c = 0 \qquad (96)$$

Thus, on the connodal curve, at the critical point P and T have extreme values. They evidently are maxima. The discriminant, D, on the other hand, is a minimum at the critical point where it vanishes, for at all other points on the connodal curve its value is positive. The following equations, therefore, hold:

$$dP = -\epsilon_{vv}dv - \epsilon_{v\eta}d\eta = 0 \qquad (97)$$

$$dT = \epsilon_{\eta v}dv + \epsilon_{\eta\eta}d\eta = 0 \qquad (98)$$

$$dD = D_v dv + D_\eta d\eta = 0 \qquad (99)$$

These are the "Equations of the Critical Point". From eqs. (97) and (98), it is seen that

$$\left(\frac{d\eta}{dv}\right)_c = -\frac{\epsilon_{vv}}{\epsilon_{\eta v}} = -\frac{\epsilon_{\eta v}}{\epsilon_{\eta\eta}} > 0$$

XIX The Geometry of Plane Diagrams in the Neighborhood of the Critical Point

At the critical point, the arrangement of the isolines shown in Figure (3) must hold, as must also eqs. (96)-(99). These relations are illustrated geometrically in the following diagrams.

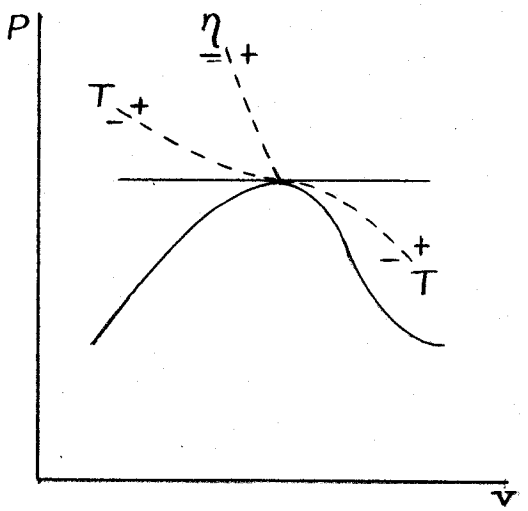


Figure 8

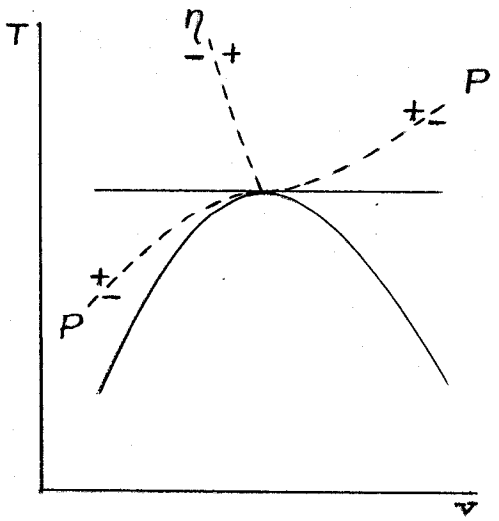


Figure 9

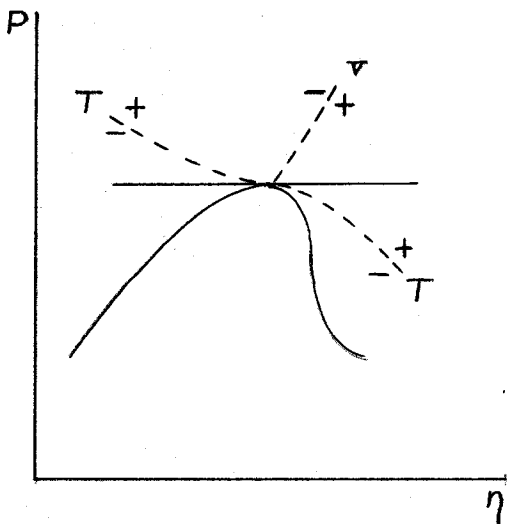


Figure 10

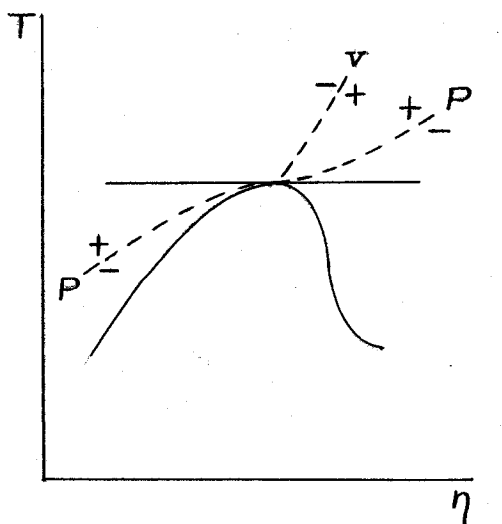
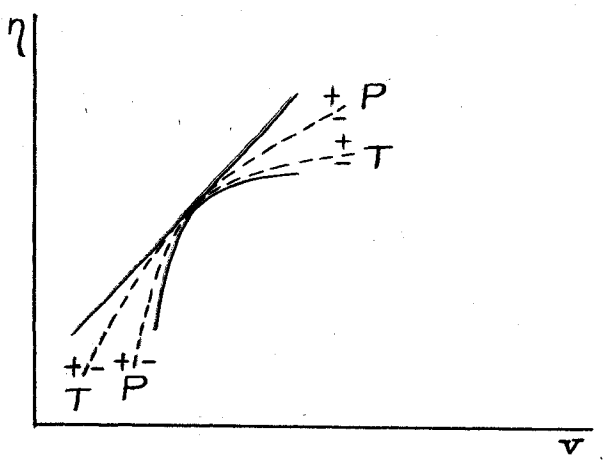


Figure 11

Figure 12



The following analytic expressions are immediately evident.

$$\left(\frac{\partial P}{\partial v}\right)_T = \left(\frac{\partial T}{\partial v}\right)_P = \left(\frac{\partial P}{\partial \eta}\right)_T = \left(\frac{\partial T}{\partial \eta}\right)_P = 0 \qquad (100)$$

$$\left(\frac{\partial \eta}{\partial v}\right)_P = \left(\frac{\partial \eta}{\partial v}\right)_T = \left(\frac{d\eta}{dv}\right)_c > 0 \qquad (101)$$

$$\left(\frac{\partial P}{\partial v}\right)_\eta < 0 \qquad (102)$$

$$\left(\frac{\partial T}{\partial v}\right)_\eta < 0 \qquad (103)$$

$$\left(\frac{\partial P}{\partial \eta}\right)_v > 0 \qquad (104)$$

$$\left(\frac{\partial T}{\partial \eta}\right)_v > 0 \qquad (105)$$

In particular, by virtue of eqs. (100),

$$C_P \equiv T\left(\frac{\partial \eta}{\partial T}\right)_P = \infty \qquad (106)$$

The only other diagram possible using the four quantities η, v, P, and T is the temperature-pressure diagram. But this diagram fails to show η and v as single-valued functions in regions of multi-phase states, and, therefore, the conclusions reached in Chapters XVII and XVIII from a consideration of gradients are not applicable. By eqs. (97) and (98), the differentials of P and T vanish at the critical

point. At a point infinitely little removed from the critical point, however, they are not zero; hence, by division,

$$\left(\frac{\partial P}{\partial T}\right)_v = -\frac{\epsilon_{\eta v}}{\epsilon_{\eta\eta}} \tag{107}$$

and

$$\left(\frac{\partial P}{\partial T}\right)_\eta = -\frac{\epsilon_{vv}}{\epsilon_{\eta v}} \tag{108}$$

These equations hold for a point in the field of stable, homogeneous states infinitely near the critical point, and, consequently, from continuity considerations, the value of the discriminant may be assumed to differ infinitely little from zero. Hence,

$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial P}{\partial T}\right)_\eta \tag{109}$$

Moreover, by the Clapeyron Equation, for the connodal curve at the critical point,

$$\left(\frac{dP}{dT}\right)_c = \left(\frac{d\eta}{dv}\right)_c = -\frac{\epsilon_{vv}}{\epsilon_{v\eta}} > 0$$

Hence,

$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial P}{\partial T}\right)_\eta = \left(\frac{dP}{dT}\right)_c > 0 \tag{110}$$

The isentropic, the isometric, and the connodal curve thus have a common tangency at the critical point. At a point sensibly removed from the critical point in the field of stable states, however, the discriminant is positive, and, hence,

$$\left(\frac{\partial P}{\partial T}\right)_\eta > \left(\frac{\partial P}{\partial T}\right)_v > 0$$

The isentropic, therefore, is steeper than the isometric in

this field. The T-P diagram, then, must appear as shown in Figure (13) for the critical neighborhood.

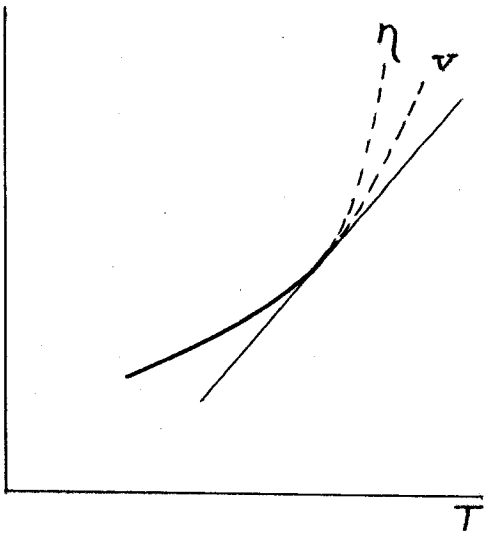


Figure 13

PART THREE

OTHER SURFACES

I Surfaces in General

The η-v-ϵ surface has been considered at some length. The geometrical criteria corresponding to Gibbs' Criteria of Equilibrium and Stability, however, may be expressed in a form more readily applicable to other surfaces than are the relations previously developed. For this purpose, equation (34) may be written as

$$\epsilon - T\eta + Pv = \bar{N}\cdot\bar{r} \qquad (111)$$

whence, by eqs. (37)-(39), the sign of the quantity $\bar{N}\cdot\delta\bar{r}$ is taken as the geometrical criterion of stability. The quantity $\delta\bar{r}$ is defined as

$$\delta\bar{r} = \bar{r}' - \bar{r} \qquad (112)$$

where $\bar{r}'$ and $\bar{r}$ denote two points on the surface, and the normal $\bar{N}$ is to be taken at the point $\bar{r}$.

The quantity $\bar{N}\cdot\delta\bar{r}$ will serve as a convenient criterion of the geometry of any thermodynamic surface. A positive value indicates that the vector $\delta\bar{r}$ lies on the same side of the tangent plane to the surface at the point $\bar{r}$ as does the normal $\bar{N}$. A negative value indicates that these two vectors lie in regions on opposite sides of the tangent plane. The quantity vanishes only if $\delta\bar{r}$ lies in the tangent plane. In view of equation (32) the vector $\bar{N}$ must always make an acute angle with the positive direction of the z-axis; i.e., $\bar{N}$ must fall on the "upper" side of the tangent plane. If the criterion is always positive, therefore, the surface lies above the

tangent plane; if negative, below; and if both positive and negative, the plane cuts the surface.

Consider the surface

$$z = z(x, y) \tag{113}$$

then

$$\bar{r} = xi + yj + zk \tag{114}$$

$$\delta\bar{r} = \delta x i + \delta y j + \delta z k \tag{115}$$

$$\bar{N} = \bar{r}_x \times \bar{r}_y = \left[1, 0, z_x\right] \times \left[0, 1, z_y\right] \tag{116}$$

and

$$\bar{N} \cdot \delta\bar{r} = \bar{r}_x \times \bar{r}_y \cdot \delta\bar{r} = \delta z - z_x \delta x - z_y \delta y \tag{117}$$

To evaluate the right member of equation (117), it is desirable to express the quantities appearing there in terms of η and v as independent variables. Thus

$$\begin{aligned} x &= x(v, \eta) \\ y &= y(v, \eta) \\ z &= z(v, \eta) \end{aligned} \tag{118}$$

whence

$$\begin{aligned} dx &= x_v dv + x_\eta d\eta \\ dy &= y_v dv + y_\eta d\eta \\ dz &= z_v dv + z_\eta d\eta \end{aligned} \tag{119}$$

From these equations

$$z_x = \frac{J(z, y)}{J(x, y)} \tag{120}$$

and

$$z_y = \frac{J(z, x)}{J(y, x)} \tag{121}$$

where J denotes the Jacobian of the quantities in parenthesis

with respect to η and **v**.

To study a surface in the neighborhood of a point, the function z may be expanded in Taylor's Series and the criterion expressed as a quadratic form for variations sufficiently small so that orders higher than the second of varied quantities are negligible. Thus

$$\bar{N}\cdot\delta\bar{r}=\tfrac{1}{2}\left[z_{xx}(\delta x)^2 + 2z_{xy}\delta x\delta y + z_{yy}(\delta y)^2\right]=\tfrac{1}{2}q \qquad (122)$$

The signs of the partial differential coefficients z_{xx} and z_{yy}, and of the discriminant D, generally may be ascertained readily from the sign of q.

The foregoing equations now will be applied to specific cases.

II The T-v-A Surface

The so-called maximum work function A is defined by the equation

$$A=\epsilon - T\eta \qquad (123)$$

If this function be identified with z and the functions T and v with x and y respectively, it is easy to see that the surface so obtained will be a fundamental surface in the sense that all the thermodynamic properties of the body are thereby determined.

For such a surface,

$$\delta z=\delta\epsilon - \delta(T\eta) \qquad (124)$$

$$\delta x=\delta T \qquad (125)$$

$$\delta y = \delta v \tag{126}$$

Also, by equation (120),

$$z_x = A_T = \frac{\begin{vmatrix} A_\eta & A_v \\ 0 & 1 \end{vmatrix}}{\begin{vmatrix} T_\eta & T_v \\ 0 & 1 \end{vmatrix}} = \frac{A_\eta}{T_\eta} = \frac{\epsilon_\eta - T - \eta T_\eta}{T_\eta} = -\eta \tag{127}$$

and, by equation (121),

$$z_y = A_v = \frac{\begin{vmatrix} A_\eta & A_v \\ T_\eta & T_v \end{vmatrix}}{\begin{vmatrix} T_\eta & T_v \\ 0 & 1 \end{vmatrix}} = \frac{A_\eta T_v - A_v T_\eta}{-T_\eta} =$$

$$\frac{T_v(\epsilon_\eta - T - \eta T_\eta) - T_\eta(\epsilon_v - \eta T_v)}{-T_\eta} = -P \tag{128}$$

Hence, by equation (117),

$$\bar{N}\cdot\delta\bar{r} = \delta\epsilon - (T\eta) + \eta\delta T + P\delta v$$

$$= \delta\epsilon - T\delta\eta + P\delta v - \delta T\delta\eta \tag{129}$$

For variations at constant temperature, the conditions that a state $\bar{r}$ be stable, neutral, or unstable appear at once from this equation.

To determine similar conditions for variations at constant volume, the equation above may be re-written in the form

$$\bar{N}\cdot\delta\bar{r} = \delta\epsilon - T'\delta\eta + P'\delta v - \delta P\delta v \tag{130}$$

or

$$\bar{N}\cdot\delta\bar{r} = -\left[(-\delta\epsilon) - T'(-\delta\eta) + P'(-\delta v)\right] - (-\delta P)(-\delta v) \tag{131}$$

From this equation there may be read immediately the conditions that, for constant volume, a state $\bar{r}'$ be stable, neutral, or unstable with respect to any state $\bar{r}$. The symbol δ, as always, means the primed quantity minus the unprimed.

The following relations, therefore, may now be written.

For stable homogeneous states:

T constant, $\bar{N}\cdot\delta\bar{r}>0$; stable state $\bar{r}$ (132)

$\therefore q>0$; $A_{vv}>0$ (133)

v constant, $\bar{N}\cdot\delta\bar{r}<0$; stable state $\bar{r}'$ (134)

$\therefore q<0$; $A_{TT}<0$ (135)

Hence, $D<0$ (136)

For two-phase states of neutral equilibrium:

T constant, $\bar{N}\cdot\delta\bar{r}=0$; state tested $\bar{r}$ (137)

$\therefore q\equiv 0$ term by term (138)

$A_{vv}=0$ (139)

v constant, $\bar{N}\cdot\delta\bar{r}<0$; state tested $\bar{r}'$ (140)

$\therefore q<0$; $A_{TT}<0$ (141)

η constant, $\bar{N}\cdot\delta\bar{r}>0$; state tested $\bar{r}$ (142)

$\therefore q>0$ (143)

Hence, $D<0$ (144)

For three-phase states of neutral equilibrium:

T is constant necessarily,

$\therefore \bar{N}\cdot\delta\bar{r}=0$ (145)

$q\equiv 0$ term by term (146)

$A_{vv}=0$ (147)

For unstable states:

In the region characterized by $\delta\epsilon - T\delta\eta + P\delta v < 0$,

T constant, $\bar{N}\cdot\delta\bar{r} < 0$; state tested $\bar{r}$ (148)

$\therefore q < 0$; $A_{vv} < 0$ (149)

v constant, $\bar{N}\cdot\delta\bar{r} > 0$; state tested $\bar{r}'$ (150)

$\therefore q > 0$; $A_{TT} < 0$ (151)

Hence, $D < 0$ (152)

In the region characterized by $\delta\epsilon - T\delta\eta + P\delta v \gtrless 0$,

$\epsilon_{vv} < 0$ $\left.\right\}$ $\bar{N}\cdot\delta\bar{r}$ 0 (153)

$\epsilon_{\eta\eta} > 0$ $\left.\right\}$ $\therefore q < 0$; $A_{vv} < 0$; $A_{TT} < 0$; $D > 0$ (154)

$\epsilon_{vv} > 0$ $\left.\right\}$ $\bar{N}\cdot\delta\bar{r} > 0$ (155)

$\epsilon_{\eta\eta} < 0$ $\left.\right\}$ $\therefore q > 0$; $A_{vv} > 0$; $A_{TT} > 0$; $D > 0$ (156)

In view of equation (132), the T-v-A surface must be such that in any isothermal, plane section every point falls above the tangent plane to a point representing a stable state; i.e., the fields of stable equilibrium must be concave upward in such a section. On the other hand, in any isometric plane section, by equation (134), a point is stable if it falls below the tangent plane to any other point on the surface. Hence, stable fields must be convex upward. It is apparent that fields of stable homogeneous states, then, are regions of hyperbolic points.

From eqs. (137) and (140), and considerations of continuity, it is seen that two-phase states correspond to ruled surfaces. Such surfaces are skew in light of equation (144). In isometric section, they are convex upward; curves

of constant entropy are concave upward. The generators lie in isothermal planes.

Three-phase, or invariant, states of neutral equilibrium must lie along the line of intersection of the plane of equation (145) and the isothermal plane which contains the three points representing respectively the three homogeneous states which are capable of co-existence. The slope of this line is given by equation (128).

The regions of instability, from relations (148)-(156), may contain hyperbolic points and elliptic points of both positive and negative curvature. Hyperbolic points correspond to elliptic points of negative curvature on the η-v-ϵ surface; whereas, elliptic points correspond to hyperbolic points on the latter surface. The explicit correspondence between the two types of elliptic points and the two kinds of hyperbolic points appears from relations (153)-(156).

It is now possible to present an integrated picture of the general features of the T-v-A surface. The surface lies completely in the first octant, and it may be assumed to be of indefinitely great extent. Letting the subscript zero denote quantities pertinent to three-phase equilibrium states, co-existent L_o-V_o-S_o states are shown on a straight line parallel to the v-A plane with a slope of $-P_o$. The three homogeneous states are represented by three points on this line. For normal substances, the extremity nearest the A-T plane is the point S_o, while the other extremity is the point V_o. In

between, is found the point L_o. The slopes of the tangent planes along this line are equal in the plane $T=T_o$. Their inclination with the negative direction of the temperature axis, however, increases progressively from S_o to V_o; i.e., the tangent plane rotates clockwise, as viewed from the point S_o, as it moves along the line from S_o to V_o.

The segment S_oL_o is a terminal generator of the stable portion of the skew surface of S-L equilibria; likewise, the segment L_oV_o is a terminal generator of the stable section of the ruled surface of L-V equilibria. The line $S_oL_oV_o$ is a terminal generator of the stable portion of the ruled S-V surface.

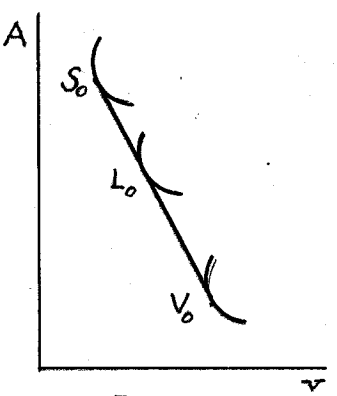


Figure 14

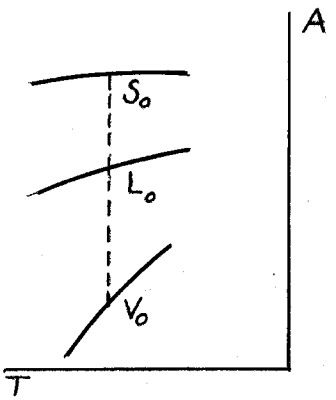


Figure 15

It is apparent that these three surfaces intersect along the line of invariant states. The form of the primitive surface is such that in the plane section $T=T_o$ projected on the v-A plane it falls everywhere above this line except at the three points S_o, L_o, and V_o where it touches the line. In the three planes $v=v_{V_o}$, $v=v_{L_o}$, and $v=v_{S_o}$ projected on the T-A plane, however, the primitive surface must be convex upward.

Let the body be in a state represented by the point L_o, and let the temperature increase slightly, the volume remaining fixed. For this change,

$$dA = A_T dT = -\eta dT \qquad dT > 0 \qquad (157)$$

If the entropy of the liquid state L_o exceed the entropy of the composite state $S_o - V_o$, represented by the co-ordinates of the point L_o, then it is evident that the value of A for the liquid state will diminish more rapidly with temperature than will the value for the composite state. Part of the primitive surface L, therefore, will protrude below the line SV in the plane

$$T = T_o + dT$$

That is, composite S-V states here become metastable, and the section of the surface of dissipated energy cut by the plane will consist of three sections of the primitive surface representing respectively stable states of solid, liquid, and vapor together with two tangent segments which correspond re-respectively to composite states of solid-liquid and liquid-vapor. On the other hand, a decrease in temperature will have the result that the portion of the primitive surface of liquid states will fall completely above the line SV in the section cut by the plane

$$T = T_o - dT$$

The liquid state thus becomes metastable with respect to the composite state S-V for temperatures less than T_o.

It is apparent from a consideration of the Clausius-Clapeyron Equation in connection with the P-T diagram for bodies in the neighborhood of the triple-point that substances which undergo a diminution in volume upon freezing may be

represented by surfaces like that described above. For anomalous substances, like water, which suffer expansion upon solidification, on the other hand, the order of the points S_o and L_o will be switched, and the effects of changing the temperature near the line of invariant states will be the reverse of those described. It follows that a necessary and sufficient condition that $v_{L_o} > v_{S_o}$ is that the entropy of the liquid state L_o exceed the entropy of the composite solid-vapor state S_o-V_o of the same volume. An evident alternative statement is that whenever it is possible to form a composite S_o-V_o state of the same volume as the liquid state L_o, the entropy of the liquid will exceed the entropy of the composite state; for the possibility of such formation hinges upon the truth of the inequality, $v_{L_o} > v_{S_o}$. Likewise, whenever it is possible to form a composite state L_o-V_o of the same volume as the solid state S_o (i.e., when $v_{S_o} > v_{L_o}$), the entropy of the composite state will exceed the entropy of the homogeneous state. The truth of this statement, however, is obvious, apart from any consideration of the T-v-A surface.

For temperatures less than T_o, the surface of dissipated energy, then, will normally consist of a ruled skew surface of S-V equilibria adjoining, on the side nearest the T-A plane, a portion of the primitive surface of solid states and, on the other side, a primitive field of vapor states. The stable part of this ruled surface terminates in the line of invariant states. For temperatures exceeding T_o, the sur-

face of dissipated energy is composed of the two, ruled, skew sheets representing respectively S-L and L-V equilibria and three sections of the primitive surface which correspond to stable states of solid, liquid, and vapor respectively. The two, ruled surfaces are included between the solid and vapor fields; whereas, the liquid field is included between the ruled surfaces. The point L_o is common to this liquid field and the three, skew surfaces of neutral states. The length of the generator of the skew surface of L-V equilibria diminishes as the temperature increases, the surface terminating in a generator of zero length at the critical temperature. The tangent plane to any point of the surface of dissipated energy cuts that surface at the point of contact.

Regions of metastable composite states appear as extensions of the three, ruled surfaces past the line of invariant states. Homogeneous metastable states are shown by sections of the primitive surface covered by the three, ruled sheets. Between any two such sections covered by a skew surface there must be included a region of instability. The curves bounding regions of instability must pass through points of inflection of at least one line of principal curvature; but it is not necessary, on the other hand, that all such points of inflection lie on the border line of a region of metastability, for such points may occur also within the fields of unstable states remote from the boundary line.

III The P-η-H Surface

The enthalpy function H is defined by the equation

$$H=\epsilon + Pv \tag{158}$$

A third fundamental surface may be obtained by identifying P with x, η with y, and H with z. It may be of interest to see what form the criteria take for this surface. Thus

$$\delta z=\delta\epsilon + \delta(Pv) \tag{159}$$

$$\delta x=\delta P \tag{160}$$

$$\delta y=\delta\eta \tag{161}$$

and, by eqs. (120) and (121),

$$z_x=H_P=\frac{\begin{vmatrix} H_\eta & H_v \\ 1 & 0 \end{vmatrix}}{\begin{vmatrix} P_\eta & P_v \\ 1 & 0 \end{vmatrix}}=\frac{H_v}{P_v}=\frac{\epsilon_v + P + vP_v}{P_v}=v \tag{162}$$

$$z_y=H_\eta=\frac{\begin{vmatrix} H_\eta & H_v \\ P_\eta & P_v \end{vmatrix}}{\begin{vmatrix} P_\eta & P_v \\ 1 & 0 \end{vmatrix}}=\frac{P_v(\epsilon_\eta + vP_\eta) - P_\eta(vP_v)}{P_v}=\epsilon_\eta=T \tag{163}$$

Hence, by equation (117),

$$\begin{aligned}\bar{N}\cdot\delta\bar{r}&=\delta\epsilon + \delta(Pv) - v\delta P - T\delta\eta \\ &=\delta\epsilon - T\delta\eta + P\delta v + \delta P\delta v\end{aligned} \tag{164}$$

whence the criteria for a state $\bar{r}$ may be obtained for variations at constant pressure by inspection.

To find the criteria for isentropic variations,

equation (164) may be put in the form

$$\bar{N}\cdot\delta\bar{r}=-\left[(-\delta\epsilon) - T'(-\delta\eta)\right] + P'(-\delta v) + (-\delta T)(-\delta\eta) \tag{165}$$

This equation furnishes a geometrical test of the type of equilibrium represented by a point $\bar{r}'$.

The following information is contained in the two foregoing equations.

For stable homogeneous states:

P constant, $\bar{N}\cdot\delta\bar{r}>0$; stable state $\bar{r}$ (166)

$\therefore q>0$; $H_{\eta\eta}>0$ (167)

η constant, $\bar{N}\cdot\delta\bar{r}<0$; stable state $\bar{r}'$ (168)

$\therefore q<0$; $H_{PP}<0$ (169)

$D<0$ (170)

For two-phase states of neutral equilibrium:

P constant, $\bar{N}\cdot\delta\bar{r}=0$; state tested $\bar{r}$ (171)

$\therefore q\equiv 0$ term by term (172)

$H_{\eta\eta}=0$ (173)

η constant, $\bar{N}\cdot\delta\bar{r}<0$; state tested $\bar{r}'$ (174)

$\therefore q<0$; $H_{PP}<0$ (175)

v constant, $\bar{N}\cdot\delta\bar{r}>0$; state tested $\bar{r}$ (176)

$\therefore q>0$ (177)

$D<0$ (178)

For three-phase states of neutral equilibrium:

P is constant necessarily,

$\therefore \bar{N}\cdot\delta\bar{r}=0$ (179)

$q\equiv 0$ term by term (180)

$$H_{\eta\eta}=0 \tag{181}$$

For unstable states:

In the region characterized by the relation $\delta\epsilon - T\delta\eta + P\delta v<0$,

P constant, $\bar{N}\cdot\delta\bar{r}<0$; state tested $\bar{r}$ (182)

$$\therefore q<0;\ H_{\eta\eta}<0 \tag{183}$$

η constant, $\bar{N}\cdot\delta\bar{r}>0$; state tested $\bar{r}'$ (184)

$$\therefore q>0;\ H_{PP}>0 \tag{185}$$

$$D<0 \tag{186}$$

In the region characterized by the inequality

$\delta\epsilon - T\delta\eta + P\delta v \gtrless 0$,

$$\left.\begin{matrix}\epsilon_{vv}<0\\ \epsilon_{\eta\eta}>0\end{matrix}\right\}\quad \bar{N}\cdot\delta\bar{r}>0 \tag{187}$$

$$\therefore q>0;\ H_{PP}>0;\ H_{\eta\eta}>0;\ D>0 \tag{188}$$

$$\left.\begin{matrix}\epsilon_{vv}>0\\ \epsilon_{\eta\eta}<0\end{matrix}\right\}\quad \bar{N}\cdot\delta\bar{r}<0 \tag{189}$$

$$\therefore q<0;\ H_{PP}<0;\ H_{\eta\eta}<0;\ D>0 \tag{190}$$

A comparison of the criteria above with those found for the T-v-A surface reveals the striking similarities in the geometry of the two surfaces. In order to avoid further repetition, therefore, a detailed geometric interpretation of the preceding relations will be omitted.

IV The P-T-F Surface

The free energy function F is defined by the equation

$$F=\epsilon + Pv - T\eta \tag{191}$$

A fourth fundamental surface is represented by equation (113)

if z be identified with F, x with P, and y with T. The geometric criteria may be formulated as before. Thus,

$$\delta z=\delta\epsilon + \delta(Pv) - \delta(T\eta) \tag{192}$$

$$\delta x=\delta P \tag{193}$$

$$\delta y=\delta T \tag{194}$$

and

$$z_x=F_P=\frac{\begin{vmatrix} F_\eta & F_v \\ T_\eta & T_v \end{vmatrix}}{\begin{vmatrix} P_\eta & P_v \\ T_\eta & T_v \end{vmatrix}}=\frac{T_vF_\eta - T_\eta F_v}{T_vP_\eta - T_\eta P_v}=$$

$$\frac{T_v(vP_\eta - \eta T_\eta) - T_\eta(vP_v - \eta T_v)}{T_vP_\eta - T_\eta P_v}=v \tag{195}$$

$$z_y=F_T=\frac{\begin{vmatrix} F_\eta & F_v \\ P_\eta & P_v \end{vmatrix}}{\begin{vmatrix} T_\eta & T_v \\ P_\eta & P_v \end{vmatrix}}=\frac{P_vF_\eta - P_\eta F_v}{P_vT_\eta - P_\eta T_v}=$$

$$\frac{P_v(vP_\eta - \eta T_\eta) - P_\eta(vP_v - \eta T_v)}{P_vT_\eta - P_\eta T_v}=-\eta \tag{196}$$

Hence,

$$\begin{aligned}\bar{N}\cdot\delta\bar{r} &= \delta\epsilon + \delta(Pv) - \delta(T\eta) - v\delta P + \eta\delta T \\ &= \delta\epsilon - T\delta\eta + P\delta v + \delta P\delta v - \delta T\delta\eta \\ &= \delta\epsilon - T'\delta\eta + P'\delta v \\ &= -\left[(-\delta\epsilon) - T'(-\delta\eta) + P'(-\delta v)\right]\end{aligned} \tag{197}$$

Equation (197) is in a form from which the conditions that a state $\bar{r}'$ be stable, neutral, or unstable with

respect to a state $\bar{r}$ may be read off immediately. The explicit information is as follows:

For stable homogeneous states:

$$\bar{N}\cdot\delta\bar{r}<0 \tag{198}$$

$$\therefore q<0;\ F_{PP}<0;\ F_{TT}<0;\ D>0 \tag{199}$$

For two-phase states of neutral equilibrium:

P (and, hence, T) constant, $\bar{N}\cdot\delta\bar{r}\equiv 0$; i.e., $\delta\bar{r}\equiv 0$ (200)

P, T variable, $\bar{N}\cdot\delta\bar{r}<0$ (201)

$$\therefore q<0 \tag{202}$$

For three-phase states of neutral equilibrium:

P, T constant necessarily, $\therefore\delta\bar{r}\equiv 0$ (203)

For unstable states:

In the regions for which $\delta\epsilon - T\delta\eta + P\delta v<0$,

$$\bar{N}\cdot\delta\bar{r}>0 \tag{204}$$

$$\therefore q>0;\ F_{PP}>0;\ F_{TT}>0;\ D>0 \tag{205}$$

In the regions for which $\delta\epsilon - T\delta\eta + P\delta v\gtrless 0$,

$$\bar{N}\cdot\delta\bar{r}\gtrless 0 \tag{206}$$

$$\therefore q\gtrless 0;\ D<0 \tag{207}$$

In light of the criteria above, the general geometric properties of the P-T-F surface may now be described. From equation (203) it is manifest that states of L_o-V_o-S_o equilibria are shown as a single point (the triple-point) on the surface; and it is further evident that this point must be common to the three primitive fields L, V, and S. The intersection of these three primitive sheets constitute the three curves of univariant equilibria (see relations (200)-

(202)) which emanate from the triple-point and which correspond respectively to composite states of solid-liquid, solid-vapor, and liquid-vapor. The surface of dissipated energy, then, consists simply of the stable sections of the three sheets described, together with the three curves of intersection mentioned as converging to the triple-point. In accordance with relation (198), any point on this surface falls below the tangent plane to any other point, and, consequently, from continuity considerations, each of the three constituent sheets is a region of elliptic points convex upward. The curves of intersection, therefore, also are convex upward.

It is apparent from what has been said that, if negative values of P and T be excluded, every point of any path circumscribed about the triple-point in the P-T plane may be considered as the projection, parallel to the F-axis, of a corresponding point on the surface of dissipated energy. It is possible, on the other hand, to describe such a path by the projection of points which, with the exception of three points of univariant equilibria, lie wholly in regions of metastability. For it is apparent that the three primitive sheets do not terminate with the curves of intersection previously mentioned; they extend continuously beyond these curves, and by condition (198), such extensions must fall in a region above the surface of dissipated energy. They are, therefore, representative of states which are unstable with respect to states of the same pressure and temperature shown

by points on the surface of dissipated energy. Provided condition (198) is satisfied for continuous variations in the neighborhood of a point, however, the state corresponding to that point will be stable toward such variations; i.e., provided the extensions are convex upward in both principal curvatures, they will represent regions of metastable states. Further extension into a field of instability, by relations (204) and (206), must involve a change in the sign of one, or both, principal curvatures. Metastable composite states correspond to points on the curves of intersection of the metastable extensions of the primitive sheets. Such curves obviously converge to the triple-point where they are continuous with the corresponding curves which lie on the surface of dissipated energy.

For given positive values of P and T, a line parallel to the F-axis will intersect each of the primitive sheets, and, therefore, there will be obtained, in general, three different values for the free energy. The smallest value will be that of the point on the surface of dissipated energy, and the other two points will represent metastable states unstable with respect to this state. The intermediate point, however, by condition (198), will be stable with respect to

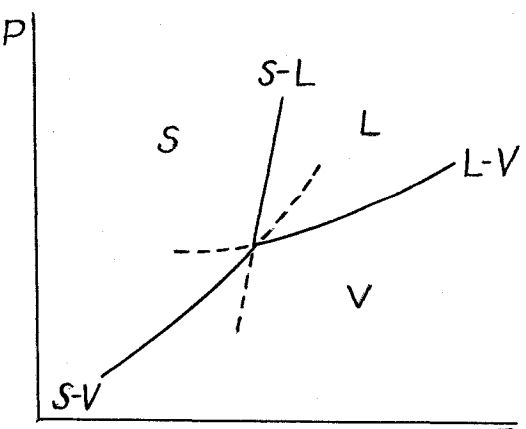


Figure 16

the point above it.

A projection of the P-T-F surface in the neighborhood of the triple-point on the T-P plane is shown in Figure (16). The dotted lines represent the metastable extensions of the curves of univariant equilibria. The critical point (not shown) lies at the terminus of the stable L-V curve remote from the triple-point.

V Interrelationships among the Surfaces

Certain interrelationships among the four primitive surfaces discussed derive from the fact that the quantities proportional to the slopes of the tangent planes to one surface are the independent variables for another. Thus considered, the surfaces fall naturally into two pairs, the ϵ and F surfaces obeying the rule, and also the A and H surfaces. Considerations of surface curvatures further emphasize this classification. When the ϵ surface is concave upward in both principal curvatures, the F surface is convex upward, and the A and H surfaces exhibit hyperbolic points. Where one principal curvature of the ϵ surface changes sign, the other surfaces exhibit a response, the points of the ϵ and F surfaces becoming hyperbolic and those of the A and H surfaces elliptic. Likewise, when the ϵ surface is convex upward in both curvatures, the F surface is concave upward, and the points of the A and H surfaces are again hyperbolic, both lines of

curvature having changed sign once.

Other similarities appear when expressions for each of the dependent variables ϵ, F, A, and H are formulated in terms of the quantities appearing in the equation of a given surface. These expressions are tabulated below for convenience in comparison.

Surface / Quantity	η-v-ϵ	P-T-F	T-v-A	P-η-H
ϵ	z	$\bar{r}_x \cdot \bar{r}_y \cdot \bar{r}$	$\bar{r} \times \bar{r}_x \cdot j$	$\bar{r} \times \bar{r}_x \cdot j$
F	$\bar{r}_x \times \bar{r}_y \cdot \bar{r}$	z	$i \cdot \bar{r}_y \times \bar{r}$	$i \cdot \bar{r}_y \times \bar{r}$
A	$\bar{r} \times \bar{r}_x \cdot j$	$\bar{r} \times \bar{r}_x \cdot j$	z	$\bar{r}_x \times \bar{r}_y \cdot \bar{r}$
H	$i \cdot \bar{r}_y \times \bar{r}$	$i \cdot \bar{r}_y \times \bar{r}$	$\bar{r}_x \times \bar{r}_y \cdot \bar{r}$	z

The quantities are expressed as scalar triple-products of triads of vectors chosen from the position vector, its derivatives, which are tangent vectors to the parametric curves, and the unit base vectors i and j. These expressions may easily be verified by expanding them in terms of the components and comparing the relations so obtained with the defining equations for the thermodynamic functions. The simplest geometric interpretation of the value of the scalar triple-product is that it expresses the volume of a parallelogram having the three vectors as concurrent edges[1].

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[1] Other expressions, of course, may equally well be chosen to represent the functions in question. The derivatives of the position vector may be replaced by the normal, for example. Thus

An inspection of the table reveals that the ϵ and F surfaces exhibit reciprocal properties insofar as the quantities ϵ and F are concerned; but they are similar inasmuch as the geometrical representation of the functions A and H are identical for the two respective surfaces. The A and H surfaces, likewise, are seen to exhibit reciprocal properties with respect to A and H, but similar properties with respect to ϵ and F.

$\overline{r}_x \times \overline{r}_y \cdot \overline{r} = \overline{N} \cdot \overline{r}$

Again,

$\overline{r} \times \overline{r}_x \cdot j = \overline{r} \cdot \overline{r}_x \times j = \overline{r} \cdot \overline{\Phi} \cdot \overline{r}_x$

where

$\overline{\Phi} = -I \times j$

The dyadic $\overline{\Phi}$ is a so-called perversor; i.e., it effects a rotation of the vector $\overline{r}_x$ about the j-axis through an angle of 90 degrees, followed by reflection in the origin. The scalar triple-products, however, are simpler and formally more consistent.

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