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*I hereby recommend that the thesis prepared under my supervision by* Masaru Nishibayashi

*entitled* The Density of Sodium and Sodium Hydroxide

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

*Approved by:*

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# THE DENSITY OF SODIUM AND SODIUM HYDROXIDE

A dissertation submitted to the
Graduate School of Arts and Sciences
of the University of Cincinnati

in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY

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by

Masaru Nishibayashi

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## ABSTRACT

A densitometer to be used for liquids at temperatures up to ca. 1000°C. and maintained in an inert atmosphere was constructed. The hydrostatic weighing method of Kohlrausch was chosen as the method most readily adaptable to the conditions imposed. This method utilizes the buoyancy principle of Archimedes. The plummet was suspended from one arm of an analytical balance and immersed in the sample contained in the densitometer tube. The apparent loss in weight of the plummet upon immersion was measured by a chainomatic balance. The entire apparatus was made gas-tight; observations and manipulations of the balance were made through gas-tight seals.

The densitometer was fabricated from grade "A" nickel and the density of sodium was determined from 254° to 860°C., and that of sodium hydroxide from 447° to 736°C. The following equations were obtained:

(1) $d_{Na} = 0.9378(\pm 0.0086) - 0.000268(\pm 0.000018)(t - 97.5)$

(2) $d_{NaOH} = 1.753(\pm 0.002) - 0.000565(\pm 0.000008)(t - 318.4)$

Using these equations, the deviation between observed and calculated values of density were found to vary an average of 0.93 per cent for sodium and 0.23 per cent for sodium hydroxide.

Hence, a densitometer with which the density of liquids,

e.g. molten metals and salts, can be determined over a wide range of temperature and in an inert atmosphere was constructed. This method and apparatus has the advantage that the entire range of temperatures can be covered with a single sample of material.

## INTRODUCTION

The purpose of this investigation was to construct a densitometer to measure the density of molten metals or salts accurately at temperatures up to 1000°C. Since sodium metal and sodium hydroxide were chosen as the materials for study, it was necessary to take into account the many difficulties that would arise in working with these materials and attempt to minimize these by virtue of a judicious choice of method for the density determination.

Density, d, is defined by the equation

$$d = \text{mass/volume} = m/V.$$

In the c.g.s. system of units, density is expressed in grams of mass per cubic centimeter. The density expressed in this manner is referred to as the "absolute density" with the symbol, $d^t$.

More commonly, a density measurement is expressed as the "relative density", $d_4^t$, or grams of weight per milliliter. This manner of expression is frequently called "density relative to water at 4°C." or "specific gravity relative to water at 4°C." since it gives the ratio of the absolute density at t°C. to the absolute density of water at 3.98°C.

In the present investigation using a relative method, the terms weight and mass were numerically interchangeable

since all of the weighings are taken at the same geographical location and hence, $W_1/W_2 = m_1/m_2$.

Another means of expressing the mass-volume relationship is "specific gravity", $d_t^t$, which is defined as the mass, m, of a substance at t°C. relative to the mass, $m_o$, of an equal volume of water at t°C.

$$d_t^t = (m/V)/(m_o/V)$$

In this investigation, all density values are given as the absolute density, $d^t$, expressed in grams per cubic centimeter of material.

Four means for determining densities of liquids (13) received consideration: (1) the pycnometer, (2) the dilatometer, (3) a modified balanced column method, and (4) the hydrostatic weighing method.

In choosing a suitable method for determining the density of sodium and sodium hydroxide at elevated temperatures, it is essential to keep in mind the corrosive character of the materials, the readily oxidizable nature of the sodium, and the wide temperature range over which the measurements were to be taken. Due to the corrosive nature of the test materials, methods involving visual measurements, such as the pycnometric or the dilatometric methods, were eliminated, since the materials of construction were of necessity opaque, metallic materials.

Previous investigators of the density of sodium, in most cases, used the dilatometric method. The Naval Research Laboratories (1), Hackspill (2), and Ramsey (3) have reported values obtained by the use of a quartz dilatometer. However, in these cases, the measurements were performed at relatively low temperatures near the melting point of sodium, i.e. 100° to 260°C., at which quartz is able to withstand the reducing action of the sodium. Since quartz is readily attacked by sodium at more elevated temperatures, data were not obtained by these investigators above the aforementioned temperatures. Hence, the use of a visual method of measurement was eliminated.

Schwartz (4) has used a modified method of Ciochina's balanced column method (5), dealing with the effect of variation of the pressures on the sample, to determine the density of molten cast irons. This method could be adapted for use with opaque materials of construction. However, this method, after careful consideration, was considered insufficiently precise for use in this investigation.

The density of sodium hydroxide has never been determined accurately. Meyer and Heck (6) determined the density of sodium hydroxide by a rather crude but ingenious method. They determined the volume of the pipe formed after the sodium hydroxide had been heated to the desired temperature and quenched suddenly. From the extent of the contraction

measured by the volume of the pipe, the total volume of the sample at the specified temperature was obtained. Since the original volume at the starting temperature and the weight of the sample were known, the density of the sample at the elevated temperature could be calculated.

However, the data obtained by this method, upon critical analysis, can not be considered reliable, since a brass cartridge was used to contain the sodium hydroxide. It is very probable that some corrosion of the brass occurred with the resulting contamination of the sample. Also, the investigators failed to mention any provisions that were made for the expansion of the brass container with the increasing temperature. This would be a source of error in that at the specified elevated temperature, the level of the sodium hydroxide would not be as high as it should be if the dimensions of the container remained constant. Observing the results of these investigators, it is found that their results are considerably higher than those obtained in this investigation. However, since this is the only data available in the literature, it is reported here as a matter of interest.

Hence, of the methods mentioned above, the hydrostatic weighing method of Kohlrausch was chosen as the method which would lend itself most readily to adaption under the conditions imposed. The most common instrument utilizing the

Archimedes principle (the upward buoyant force exerted on a body immersed in a liquid is equal to the weight of the liquid displaced) is the well-known Mohr-Westphal balance (7). Because this instrument, as such, was considered too inaccurate for the present work, a method was developed wherein a chainomatic analytical balance could be used as the weighing mechanism.

Suitable materials for the construction of the apparatus for use with sodium are certain of the stainless steels, type 303, 304, and 410, pure nickel, tungsten, molybdenum, and tantalum. It is common knowledge that sodium hydroxide is an extremely corrosive material and investigations by Wallace and Fleck (8) and more recently, the National Bureau of Standards (9), show that pure nickel is the most satisfactory material for withstanding attack by sodium hydroxide aside from silver and gold. Hence, from the consideration of the merits of nickel from the standpoint of availability and economy, the apparatus was fabricated from grade "A" nickel. The specifications for "A" nickel (15) are given below.

Composition limits

99% Ni minimum

| | | | |
|---|---|---|---|
| 0.25% Cu | maximum | 0.5 % Si | maximum |
| 0.5 % Fe | " | 0.2 % C | " |
| 0.35% Mn | " | 0.02% S | " |

## DESCRIPTION OF APPARATUS

The densitometer designed consisted essentially of a chainomatic analytical balance housed in a gastight steel case with a crucible extending from the base plate of the balance case. The plummet was suspended from the left arm of the balance by means of a 5 mil tungsten wire. An exterior view of the apparatus is shown in Figure I.

A Christian Becker chainomatic balance was rebuilt to be housed in a steel case 10 1/2 in. x 4 3/4 in. x 15 in. high (A, Fig. I). The steel case was made from 1/4 in. and 3/8 in. steel plates. The walls of the case were welded, soldered and caulked for gastightness. Flanges were welded to the walls of the case and drilled so that the tapped brass top and base plates could be screwed tightly to the case. Gastightness was insured by machining grooves in the brass plates and using Neoprene "O" rings as gaskets.

Two observation ports (B, Fig. I) were included in the case, one for the viewing of the pointer and scale, and the other for the observation of the vernier and dial of the chainweight mechanism. These observation ports were made from 1/2 in. Plexiglas, and gastightness insured by the use of "O" rings, and a brass cap (see Fig. III).

Since the overall dimensions of the balance case were reduced to minimize the mass of the case, it was necessary to revise the construction of the balance. Since the beam

arrest mechanism in the original balance extended below the base plate of the balance, it became necessary to raise the balance beam and post approximately 1 1/2 in. so that the beam arrest drive rod would extend through the front plate of the balance case through an "O" ring seal. This was accomplished by machining a supplementary brass stand (A, Fig.II) for the balance post. The stand was screwed to the base plate, and the balance post was screwed onto the stand.

In conjunction with the raising of the beam, it became necessary to raise the rider adjusting mechanism, The rider mechanism was also shortened to conform to the reduced dimensions of the balance case. Reconstruction of the chainweight mechanism was also required. The chainweight drive mechanism was revised so that the chainweight could be driven by means of a friction pulley system, with the drive rod extending from the front of the balance case through an "O" ring seal (C, Fig. I; B, Fig. II).

The rider adjusting rod protrudes from the side of the balance case through an "O" ring with the position of the rider ascertained from the length of the arm protruding (D, Fig. I). When direct observation of the rider was necessary, the rider could be observed from the upper observation port.

The densitometer tube was attached to the balance case by means of a brass flange brazed to the densitometer tube

(C, Fig. II). The flange was fitted with an "O" ring to obtain gastightness.

The densitometer tube (E, Fig. I; D, Fig. II) was a 21 in. length of 1 1/2 in. IPS "A" nickel pipe. Approximately 2 1/2 in. of the tube extended from the lower end of a Sobers vertical combustion furnace having a heating chamber two inches in diameter and seven inches long. Nine inches from the upper end of the tube, a side arm (E, Fig. II) was welded in an inclined position. The sample was injected into the densitometer tube through this side arm. The inner half of a 12/5 spherical joint was made an integral part of the side arm. During the injection process, a filter (F, Fig. I), fitted with the outer half of the 12/5 spherical joint was securely fastened to the side arm and the sample was injected into the tube without contamination. During the actual course of the run, a ground cap fitted to the spherical joint was tightly held in place by a nut.

The lower end of the tube was sealed by means of a tapered metal to metal seal. A nickel round was machined so that the plug would fit snugly in the tube, and the sealing was accomplished by the metal to metal valve seat seal. The plug (F, Fig. II) was 6 inches in overall length with the lower 2 1/2 inches extending from the bottom of the furnace. This plug also housed the thermocouple well (G, Fig. II; B, Fig. IV), a 3/8 inch hole being drilled the length of the

plug. The plug was held in place tightly by means of a nut (F, Fig. IV) which was screwed to the densitometer tube. A satisfactory vacuum could be drawn in this manner. However, should a slight leak have persisted after tightening of the nut, this leak was effectively sealed by the freezing of the sample around the valve seat by means of a cooling coil in intimate contact with the portion of the tube extending from the bottom of the furnace (D, Fig. IV). In this manner, a very good seal was obtained.

Cooling coils were also included in the upper portion of the tube (G, Fig. I). In order to prevent completely hot vapors from rising and condensing in the balance case, heat baffles were also included. These baffles were made from 20 gauge nickel sheet cut into two inch diameter circles and formed in a die so as to give the plates a slightly conical shape. Sample condensing on these plates was led to the walls of the tube and returned to the pool below with a minimum of splashing. The baffle plates were welded to the walls of a 1 1/4 in. nickel pipe. This was accomplished by cutting small holes in the pipe and welding the plates to the pipe through these holes. A 3/8 in. hole was drilled through the length of the baffle plates so that the suspension wire could hang freely from the balance.

The plummet to be immersed in the sample was hung from the left arm of the balance by means of a 5 mil tungsten wire

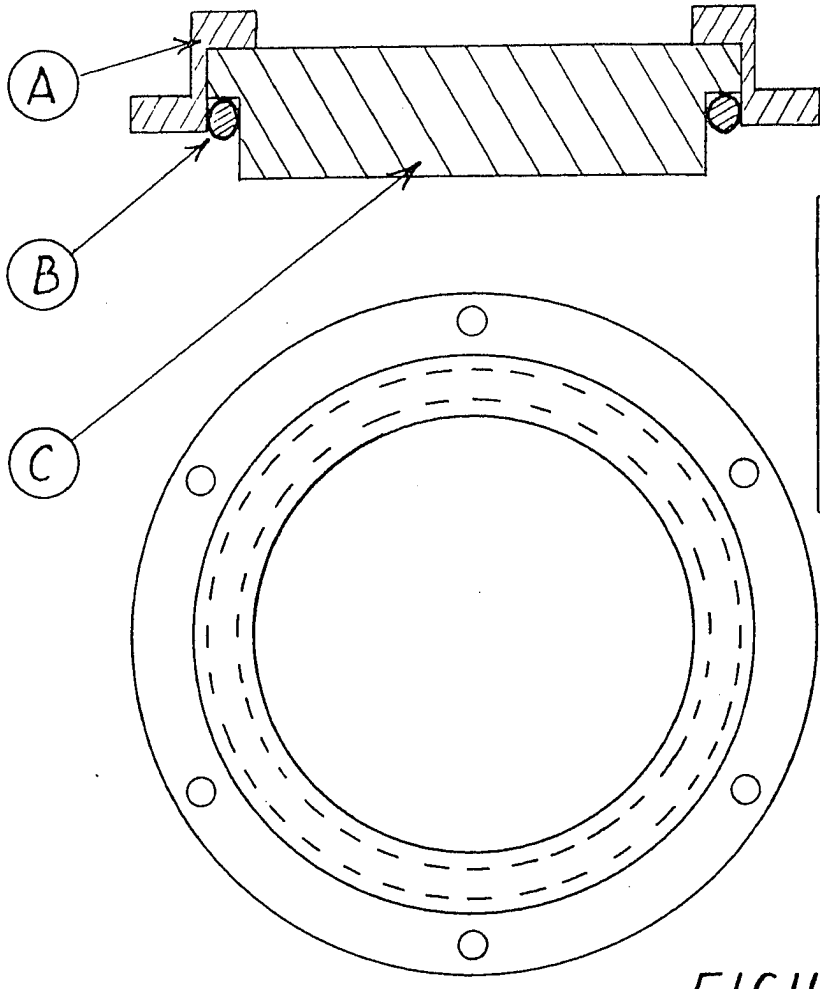
(H, Fig. II). As small a diameter wire as feasible was used for a suspension in order to avoid any errors that might arise due to the varying length of wire that is immersed in the sample as the temperature of the sample is raised with the consequent increase in the volume of the sample. The use of a 1 mil tungsten wire was attempted but was proven impractical due to the constant breaking of the wire.

The size of the plummet made of "A" nickel to be immersed in the sample was carefully calculated so that the apparent increasing weight of the plummet, due to the decreasing density of the sample with increasing temperature, could be compensated for by the use of the rider alone. A tare was hung from the right arm of the balance to compensate for the weight of the plummet at the lowest temperature to be investigated. Thus, the density of the sample could be obtained over the entire range of temperatures without the necessity of additional weights.

A copper tubing gas system was devised whereby an inert gas could be introduced or a vacuum drawn through a gas port provided in the top of the balance case (H, Fig. I). The gas port was located in the center of the balance case so that should a constant stream of gas be allowed to enter the system during the actual course of a run, the disturbance of the swinging of the balance by the gas would be kept to a minimum. Since the quantity of gas leaking from the system

was found to be negligible, no difficulty was encountered with erratic swinging of the balance due to the entry of the gas into the case.

Thus, it is possible, with this apparatus, to determine the density of one sample of material over an extremely wide range of temperatures in an inert atmosphere with the possibilities of contamination of the sample kept to a minimum.



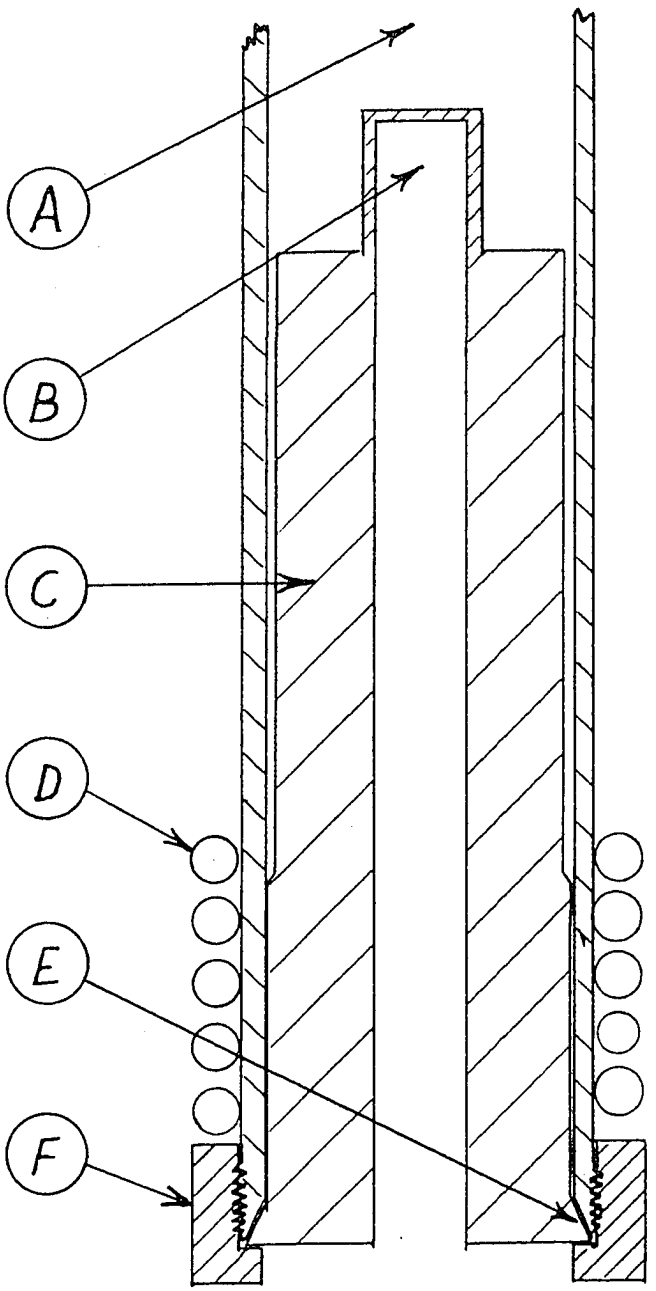

A Brass Cap
B "O" Ring
C Lucite Window

FIGURE III

DENSITOMETER

BALANCE CASE OBSERVATION PORT

Scale : 1" = 1"




A Densitometer tube
B Thermocouple well
C Plug
D Cooling Coil
E Tapered Seal
F Nut

FIGURE IV

DENSITOMETER THERMOCOUPLE WELL & PLUG ASSEMBLY

Scale: 1" = 1"

## EXPERIMENTAL PROCEDURE

### Calibration of plummet

The calibration of the plummet was accomplished by using boiled, distilled water as the standard material (see Table I). After calibration of the plummet, the volume was checked further by determining the density of anhydrous ethyl acetate (Eastman's white label grade). The value of the density (see Table II) obtained agreed with the literature value within 0.4 per cent.(10). During this calibration procedure, it was found that as fine a wire as feasible should be used in order to avoid noticeable variations of the volume immersed in the liquid. Therefore, the amount of sample introduced was also a factor to be considered, and a weighed amount of sample was introduced in each run.

After the calibration of the plummet, the density of the volume immersed, the nickel plummet plus a portion of the suspension wire, was calculated (see Table I) and future volumes were calculated from this value since the weight of the plummet varied after each run, due to the cleaning of the plummet with an abrasive after each run.

### Purification of sodium

Two methods of purifying sodium are customarily used. The first is the vacuum distillation of sodium using a suitable still. Triple distillation of the sodium is recognized as standard procedure and should the distillate be taken off

in fractions, sodium metal could be separated from other alkali metals as well as other contaminating oxides and salts that may be present.

The second method available is the filtration of reagent grade sodium through a sintered disk at low temperatures, not exceeding 110°C. (11). Provided the temperature is kept below the stated temperature, the oxides and contaminating salts are satisfactorily removed, and the only impurities remaining are any heavy metals or other alkali metals which were present in the original sodium. Since a good grade of sodium will be contaminated by a minimum of other metals, filtration of a reagent grade of sodium may be expected to be a satisfactory method of purification. It has been found that the filtration method of purification is as adequate a procedure as the triple distillation. Due to the adequacy and simplicity of the filtration, this method was selected as the method of purification.

Reagent grades of Merck and Mallinckrodt sodium were used. The purity of this sodium conforms to the specifications of the American Chemical Society which allow for the following maximum impurities:

| | | | |
|---|---|---|---|
| Chloride | .0015% | Sulfate | .002% |
| Nitrogen | .003 % | Heavy metals | .001% |
| Phosphate | .0005% | Iron | .001% |

Filtrations were made using both Pyrex and stainless steel sintered disks. The filtrations made in Pyrex were

advantageous in that it was possible to observe the shiny appearance of the filtered sodium. However, difficulties were encountered in the flaking and eventual disintegration of the sintered disk after a few filtrations. Hence, further filtrations were carried out in a stainless steel Buchner type funnel with a sintered stainless steel disk of coarse porosity. The funnel was adapted to contain a greater volume by welding a stainless steel extension to it. A brass flange was brazed to the filter extension and fitted with a brass cap and rubber gasket. A gas inlet was provided in this cap so that a vacuum could be drawn in the system or an overpressure applied to the sodium to force it through the filter and inject it into the densitometer tube.

The filter (F, Fig. I) was heated by wrapping the filter with asbestos and then nichrome ribbon, with several layers of asbestos wrapped around the heating element. Temperature control was obtained by means of a Powerstat variable transformer. Preliminary investigations as to the amount of current necessary to produce the desired temperature were made by immersing a thermometer in the sample and varying the current until the desired temperature was obtained. In this manner, overheating of the sample, which might consequently contaminate the sample, was avoided.

The lower end of the funnel was welded to the outer half of a stainless steel 12/5 spherical joint. During the

filtration process, this joint was attached securely to the inner half of the 12/5 spherical joint which had been made an integral part of the side arm of the densitometer tube.

After the filter was put in place and the weighed quantity of sodium placed in the filter, the system was evacuated and flushed with helium several times. With a helium pressure slightly greater than atmospheric on the system at all times, the sodium was heated. After allowing the sample to come to temperature, the sodium was forced into the pre-heated densitometer tube with a small over-pressure. In this manner, it was possible to avoid contamination of the sample should there be any leak in the system.

After the sample had been injected into the tube, the filter was then taken off while there was still a constant stream of helium over the sodium, and the ground cap was set in place and screwed tightly. This operation of removing the filter and replacing it with the cap took less than seven seconds; hence, the possibility of contamination of the sample at this juncture was kept at a minimum.

To further insure against contamination of the sample, the helium used was previously bubbled through molten sodium before entering the system so that any impurities in the helium which might contaminate the sodium would be eliminated before the helium reached the system. This was necessitated

because observable contamination of the shiny sodium was observed in the glass filter when unpurified helium was allowed in the system.

Temperature measurement

The temperature of the sample was measured and controlled by means of a chromel-alumel thermocouple in the thermocouple well made as an integral part of the lower plug, and the use of a Leeds and Northrup Speedomax recorder-proportional controller, or a Minneapolis-Honeywell Brown ELECTRONIK Continuous Balance Controlling Potentiometer.

The actual temperature of the sample was measured following all of the runs with sodium and sodium hydroxide by immersing a thermocouple directly in the densitometer tube and substituting tin for the sample material. This chromel-alumel thermocouple was calibrated at the melting point of potassium dichromate. The voltage output of the thermocouple was measured by a Leeds and Northrup Type K-1 potentiometer (see Table III). The results were plotted against the control temperature registered by the lower thermocouple on the Speedomax (Fig. V). The temperatures obtained from this graph were used in the final calculations of the densities.

Weighing procedure

The weighing operations were carried out in the usual balanced swings method. However, at temperatures below 353°C., the Curie point of nickel, it was necessary to turn

off the furnace during the weighings. If the weighings were attempted with the furnace on at these lower temperatures, the electrical, and consequent magnetic, field set up by the windings of the furnace caused considerable erratic behavior in the swinging of the balance with the on-off action of the controller. Hence, the weighings were made by approximately attaining balance equilibrium while the furnace was still on and then turning the furnace off for the final weighing. In this manner, the off time of the furnace was considerably shortened and consequently avoided significant temperature lowering of the sample.

At temperatures above the Curie point of nickel, it was found unnecessary to turn the furnace off to achieve the desired results, and therefore, there was no measurable change of temperature during the weighing operation.

At each temperature, a series of five or six weighings was performed; a reproducible weight was obtained for each temperature. The sample was allowed to remain at one temperature for at least one and one-half hours to insure a constant temperature throughout the sample.

With this method of weighing, weights to the nearest tenth of a milligram can be obtained. Although the balance was altered from the rated sensitivity of a Christian Becker chainomatic analytical balance (0.05 mg/div.), the balance remained sufficiently sensitive so that weighings could be

made accurately to the nearest tenth of a milligram.

Pressure system

The pressure on the system was controlled by a Regolator reducing valve and measured more accurately by a pressure gauge included in the copper tubing gas system.

Helium gas, 99.5 per cent pure, used during the sodium runs was bubbled through molten sodium prior to entry into the system; the hydrogen gas used for sodium hydroxide was passed through a catalytic Deoxo purifier to rid the gas of any oxygen that may be present.

An overpressure was always maintained in the system to prevent air from leaking into the system should any small leak persist. For sodium at the lower temperatures, 200° - 500°C., and for sodium hydroxide, the pressure on the system was maintained at 5 p.s.i. above atmospheric pressure. However, at temperatures at which the vapor pressure of sodium becomes appreciable, above 500°C., the pressure on the system was increased to 20 p.s.i. above atmospheric pressure in order to insure against boiling of the sample as the temperature was raised. With sodium hydroxide in the temperature range studied, this consideration was eliminated because of the high boiling point of sodium hydroxide.

Sodium Hydroxide

The density of molten sodium hydroxide was determined in the same general manner as that described for sodium.

No alterations in the apparatus were needed to accomplish these determinations.

The sodium hydroxide used as the test material was Mallinckrodt's analytical reagent grade sodium hydroxide which meets the specifications of the American Chemical Society, with the maximum limits of impurities listed as:

Sodium carbonate ($Na_2CO_3$) 2.5%

| | | | |
|---|---|---|---|
| $NH_4OH$ ppt. | 0.020% | Phosphate ($PO_4$) | 0.001% |
| Chloride (Cl) | 0.010% | Potassium (K) | 0.05 % |
| Heavy metals (as Ag) | 0.003% | Sulfate ($SO_4$) | 0.005% |
| Nitrogen Cmpds. (as (N) | 0.001% | Iron (Fe) | 0.001% |

with the minimum sodium hydroxide content 97.0 per cent.

A weighed quantity of sodium hydroxde was introduced to the densitometer tube in stick form and the tube was sealed up as quickly as possible in order to avoid, as much as possible, contamination of the sample by water and carbon dioxide. The hygroscopic nature of the sodium hydroxide did not pose as much of a problem as did the formation of the carbonate. At the temperatures at which the determinations were performed, it is presumed that any of the water present would be driven off. The lowest temperature at which the density was determined was 447°C., and hence, any water that might have been present would be driven off with the prolonged heating of the sample at these temperatures.

Much difficulty was encountered with a suitable atmosphere in which the determinations could be run. Using a helium atmosphere as for the sodium determinations, it was

observed that the nickel apparatus was oxidized in some manner with resulting blackening of the surfaces of the nickel and the coloring of the sodium hydroxide various shades of green, brown, gray, or black.

It was learned (12) that a water vapor atmosphere was effective in preventing the oxidation of the nickel and the dissolution of the nickel in the sodium hydroxide. Attempts were made with this method by blowing air saturated with water at a temperature of approximately 60°C., into the apparatus, but the results were the oxidation of the nickel surfaces and the coloring of the sodium hydroxide as in the case with helium. Hence, this method was abandoned.

Several experiments were run with the sodium hydroxide being contained in a brightly polished nickel crucible with a jet of steam playing on the surface of the molten caustic. This procedure seemed satisfactory in that the brightly polished nickel retained its near mirror surface.

With steam being used as an atmosphere, the resulting sodium hydroxide, hygroscopic in itself, was found to contain much water on cooling. However, should steam be used in the apparatus, the possibility of water condensing on the balance was considered. In order to avoid this possibility, a trial with a hydrogen gas atmosphere was made. In this case, as in the case with steam, the nickel was observed to remain polished and the sodium hydroxide extracted from

the crucible had undergone no noticeable discoloration. Hence, due to the adequacy of a hydrogen atmosphere and the avoidance of the possibility of water condensing in the cooler portions of the apparatus, a hydrogen atmosphere was maintained in the apparatus during the determinations.

The actual determinations were carried out in an identical manner to that used for sodium except that a nickel wire was used in place of the tungsten wire for the suspension. The runs for the sodium hydroxide were terminated in each case when the temperature was raised to above 750°C., due to breaking of the wire. This may have been due to the solution of the nickel wire in the sodium hydroxide, caused possibly by the presence of some impurities in the nickel wire used. However, prolonged heating at lower temperatures than this failed to break the wire; hence, it was assumed that the high temperatures plus the action of the sodium hydroxide was the cause, and the wire did not cause contamination of the sample at the lower temperatures.

Subsequent to a run, the plummet was dissolved free from the sodium hydroxide and it was found that it had not lost any weight over the course of three to four days of constant exposure to sodium hydroxide at temperatures of from 400° to 750°C. Therefore, the possibility of the solution of the nickel in the hydroxide may be discounted for the temperature range over which the density values are given.

Rather than a loss in weight being observed for the plummet, it was noticed that the plummet had gained some 0.008 grams during this time. Since this represents such a small part of the total weight of the plummet, it was considered negligible.

Therefore, from the consideration of all of these facts, it is assumed that the purity of the sodium hydroxide was nearly that of the maximum limits of impurity of the original analytical reagent grade sodium hydroxide used.

## EXPERIMENTAL DATA

The data necessary for the evaluation of the density of a sample were the following: (1) the apparent weights of the plummet upon immersion in the sample, (2) the exact weight of the tare, (3) the weight of the plummet before immersion in the sample, (4) the volume of the plummet at some specific temperature, (5) the coefficient of thermal expansion of the material of which the plummet was made, (6) the weights of any other material hung from either arm of the balance, and (7) the pressure under which the system was kept during the course of the run. Other factors which received consideration, i.e. the temperature of the balance case and the density and coefficient of expansion of the tares and weights were found to be insignificant.

The apparent weight of the plummet upon immersion in the sample was obtained by the method described in the preceding section. The other weights, as mentioned in (2), (3), and (6) above were obtained by weighing on an analytical balance. The volume of the plummet was obtained by calibration with substances of accurately known densities. From the volume so obtained the density of the plummet was calculated. Once the density of the plummet was known, its volume at any time could be obtained from a measurement of its weight. The pressure on the system, shown to be of no consequence in the discussion of data section, was noted

by means of a pressure gauge included in the gas system.

Data accumulated during this investigation are shown on the following pages.

TABLE I
Calibration of Plummet

| T | $W_1$ | $W_2$ | $W_3$ | $d_w$ | V |
|---|---|---|---|---|---|
| 23.8 | .4046 | 24.0708 | 2.6293 | .997345 | 2.63630 |
| 23.8 | .4048 | 24.0710 | 2.6291 | .997345 | 2.63610 |
| 23.8 | .4046 | 24.0708 | 2.6293 | .997345 | 2.63630 |
| 25.8 | .4057 | 24.0719 | 2.6282 | .996836 | 2.63654 |
| 25.6 | .4057 | 24.0719 | 2.6282 | .996888 | 2.63640 |
| 25.6 | .4057 | 24.0719 | 2.6282 | .996888 | 2.63640 |
| 26.3 | .4059 | 24.0721 | 2.6280 | .996703 | 2.63670 |
| 26.5 | .4061 | 24.0723 | 2.6278 | .996649 | 2.63664 |
| 28.0 | .4066 | 24.0728 | 2.6273 | .996232 | 2.63724 |
| 25.6 | .4058 | 24.0720 | 2.6281 | .996888 | 2.63630 |

Weight of plummet : 23.1914 gm

Total weight of left side : 24.0708 gm

T : temperature ($^{o}C$)

$W_1$ : observed weight (gm)

$W_2$ : total apparent weight (gm)

$W_3$ : apparent loss in weight (gm)

$d_w$ : density of water (gm/cc)

V : volume of plummet calculated (cc)

The volume of the nickel plummet was determined to be 2.6363 cc at 25°C. From this value, the density of the volume immersed (plummet plus portion of the suspension wire) was determined to be 8.79695 gm/cc. The volumes for the various weights of the plummet for the other runs was calculated from this density value.

TABLE II

Determination of Density of Ethyl Acetate

| T | $W_1$ | $W_2$ | $d_c$ | $d_t$ |
|---|---|---|---|---|
| 28.2 | .7249 | 2.3384 | .8870 | .8905 |
| 30.3 | .7292 | 2.3341 | .8853 | .8879 |
| 30.5 | .7293 | 2.3340 | .8853 | .8877 |
| 30.6 | .7308 | 2.3325 | .8847 | .8875 |

Weight of left side : 24.1002 gm

Weight of right side : 21.0369 plus $W_1$

Weight of plummet : 23.1914 gm

Volume of plummet @ 25°C : 2.6363 cc

T : temperature (°C)

$W_1$ : actual weighing (gm)

$W_2$ : apparent loss in weight of plummet (gm)

$d_c$ : calculated density (gm/cc)

$d_t$ : density calculated from equation of Wade and Merriman (10)

$$d_t = 0.92454 - 0.001168(t) - 0.00000195(t^2) + 0.00000002(t^3)$$

Agreement between $d_c$ and $d_t$ is well within 0.4 per cent.

TABLE III

Calibration of Temperatures

| $T_1$ | E | $E_{ave.}$ | $T_2$ |
|---|---|---|---|
| 250 | 11.475 | 11.453 | 282.5 |
| | 11.440 | | |
| | 11.445 | | |
| 300 | 13.856 | 13.917 | 341.0 |
| | 13.952 | | |
| | 13.952 | | |
| | 13.896 | | |
| | 13.931 | | |
| 350 | 16.230 | 16.203 | 391.3 |
| | 16.170 | | |
| | 16.227 | | |
| | 16.185 | | |
| 400 | 18.242 | 18.349 | 447.0 |
| | 18.340 | | |
| | 18.327 | | |
| | 18.330 | | |
| | 18.435 | | |
| | 18.420 | | |
| 450 | 20.800 | 20.800 | 503.0 |
| | 20.780 | | |
| | 20.818 | | |
| 500 | 22.630 | 22.619 | 546.5 |
| | 22.620 | | |
| | 22.605 | | |
| 550 | 24.830 | 24.805 | 598.0 |
| | 24.815 | | |
| | 24.783 | | |
| | 24.790 | | |
| 600 | 26.665 | 26.678 | 642.0 |
| | 26.695 | | |
| | 26.700 | | |
| | 26.652 | | |
| 650 | 28.730 | 28.732 | 690.5 |
| | 28.740 | | |
| | 28.724 | | |
| | 28.735 | | |
| 700 | 30.656 | 30.618 | 736.0 |
| | 30.643 | | |
| | 30.555 | | |

$T_1$ : control temperature measured by Speedomax (°C)
E : output of thermocouple immersed in sample (mv)
$E_{ave.}$ : average value of output of thermocouple (mv)
$T_2$ : temperature of the sample (°C)

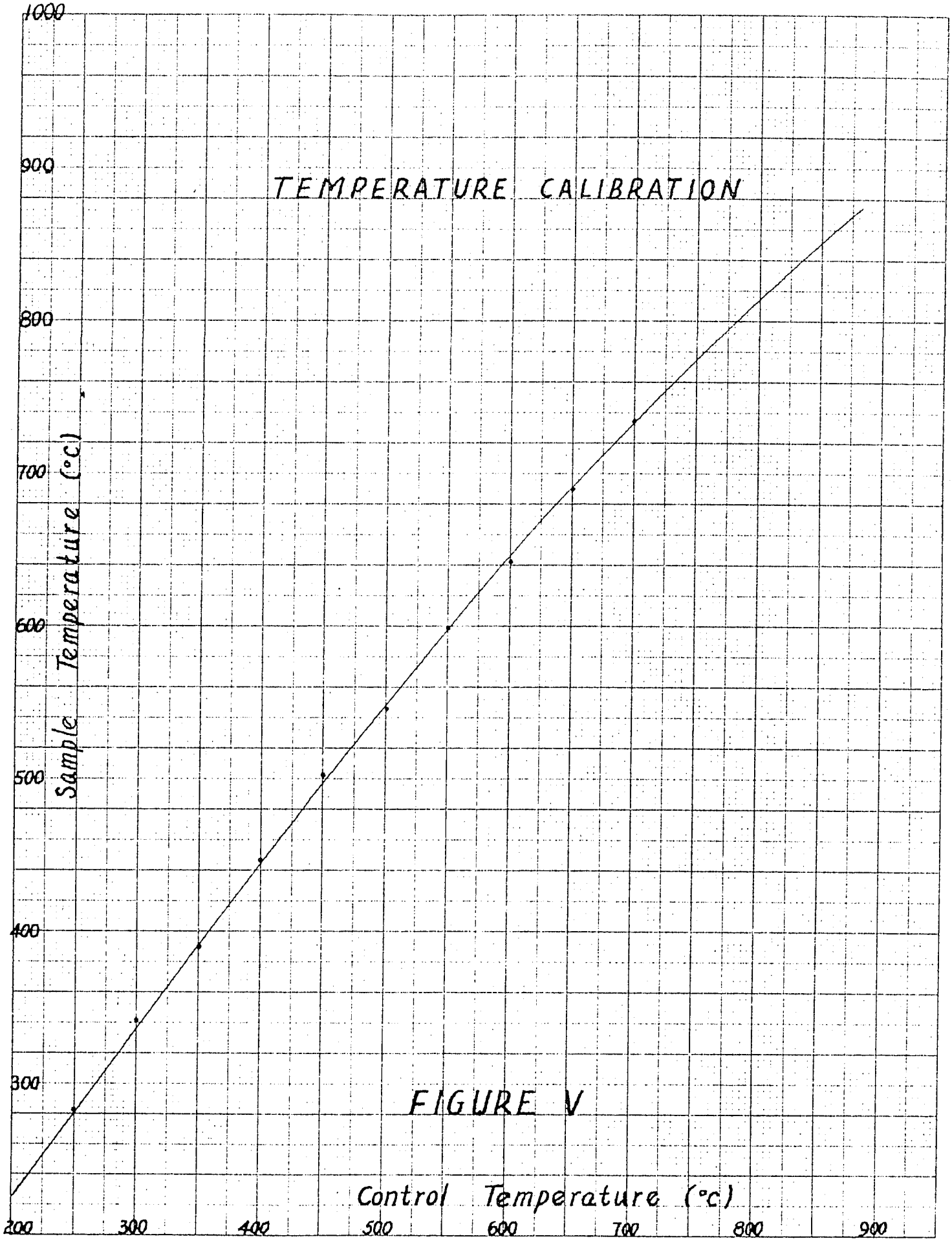



FIGURE V

TABLE IV
Run No. 1 Sodium

| $T_1$ | $T_c$ | $W_1$ | $W_2$ | $W_3$ | d |
|---|---|---|---|---|---|
| 255 | 288 | .8041 | 21.8410 | 2.3288 | .8734 |
| 303 | 344 | .8320 | 21.8689 | 2.3009 | .8602 |
| 301 | 342 | .8313 | 21.8682 | 2.3016 | .8606 |
| 352 | 396 | .8573 | 21.8942 | 2.2756 | .8484 |
| 350 | 394 | .8551 | 21.8920 | 2.2778 | .8493 |
| 410 | 458 | .8854 | 21.9223 | 2.2475 | .8350 |
| 414 | 461 | .8906 | 21.9275 | 2.2423 | .8329 |
| 405 | 451 | .8897 | 21.9266 | 2.2430 | .8336 |
| 457 | 506 | .9290 | 21.9659 | 2.2039 | .8167 |
| 457 | 506 | .9345 | 21.9714 | 2.1984 | .8146 |
| 550 | 595 | .9831 | 22.0200 | 2.1498 | .7929 |
| 550 | 595 | .9826 | 22.0195 | 2.1503 | .7931 |
| 610 | 652 | 1.0208 | 22.0577 | 2.1121 | .7767 |
| 609 | 651 | 1.0204 | 22.0573 | 2.1125 | .7769 |
| 658 | 697 | 1.0520 | 22.0889 | 2.0809 | .7635 |
| 660 | 699 | 1.0428 | 22.0797 | 2.0901 | .7668 |
| 660 | 699 | 1.0463 | 22.0832 | 2.0866 | .7655 |
| 683 | 720 | 1.0790 | 22.1159 | 2.0539 | .7527 |
| 683 | 720 | 1.0646 | 22.1015 | 2.0683 | .7580 |
| 682 | 719 | 1.0672 | 22.1041 | 2.0657 | .7571 |
| 683 | 720 | 1.0737 | 22.1106 | 2.0592 | .7546 |
| 688 | 725 | 1.0721 | 22.1090 | 2.0608 | .7550 |

Weight of plummet : 23.1609 gm

Total weight of left side : 24.1698 gm

Volume of plummet at 25°C. : 2.6328 cc

$T_1$ : control temperature (°C)

$T_c$ : corrected temperature (°C)

$W_1$ : observed weight (gm)

$W_2$ : total apparent weight (gm)

$W_3$ : apparent loss in weight (gm)

d : density (gm/cc)

TABLE V
Run No. 1 Sodium

| T | $d_o$ | $d_1$ | $d_c$ | $r_1$ | $r_c$ |
|---|---|---|---|---|---|
| 288 | .8734 | .8762 | .8868 | -.32 | -1.51 |
| 343 | .8604 | .8612 | .8720 | -.09 | -1.33 |
| 395 | .8489 | .8470 | .8581 | +.22 | -1.07 |
| 457 | .8338 | .8301 | .8415 | +.45 | - .92 |
| 506 | .8157 | .8167 | .8284 | -.12 | -1.53 |
| 595 | .7930 | .7924 | .8045 | +.08 | -1.43 |
| 652 | .7768 | .7769 | .7892 | -.01 | -1.57 |
| 698 | .7653 | .7643 | .7769 | +.13 | -1.49 |
| 721 | .7555 | .7581 | .7708 | -.34 | -1.98 |

T : temperature (°C)

$d_o$ : average observed density (gm/cc)

$d_1$ : calculated density from equation 1 (gm/cc)

$d_c$ : calculated density from combined equation (gm/cc)

$r_1$ : deviation between $d_1$ and $d_o$ (per cent)

$r_c$ : deviation between $d_c$ and $d_o$ (per cent)

Average $r_1$ : 0.20 per cent

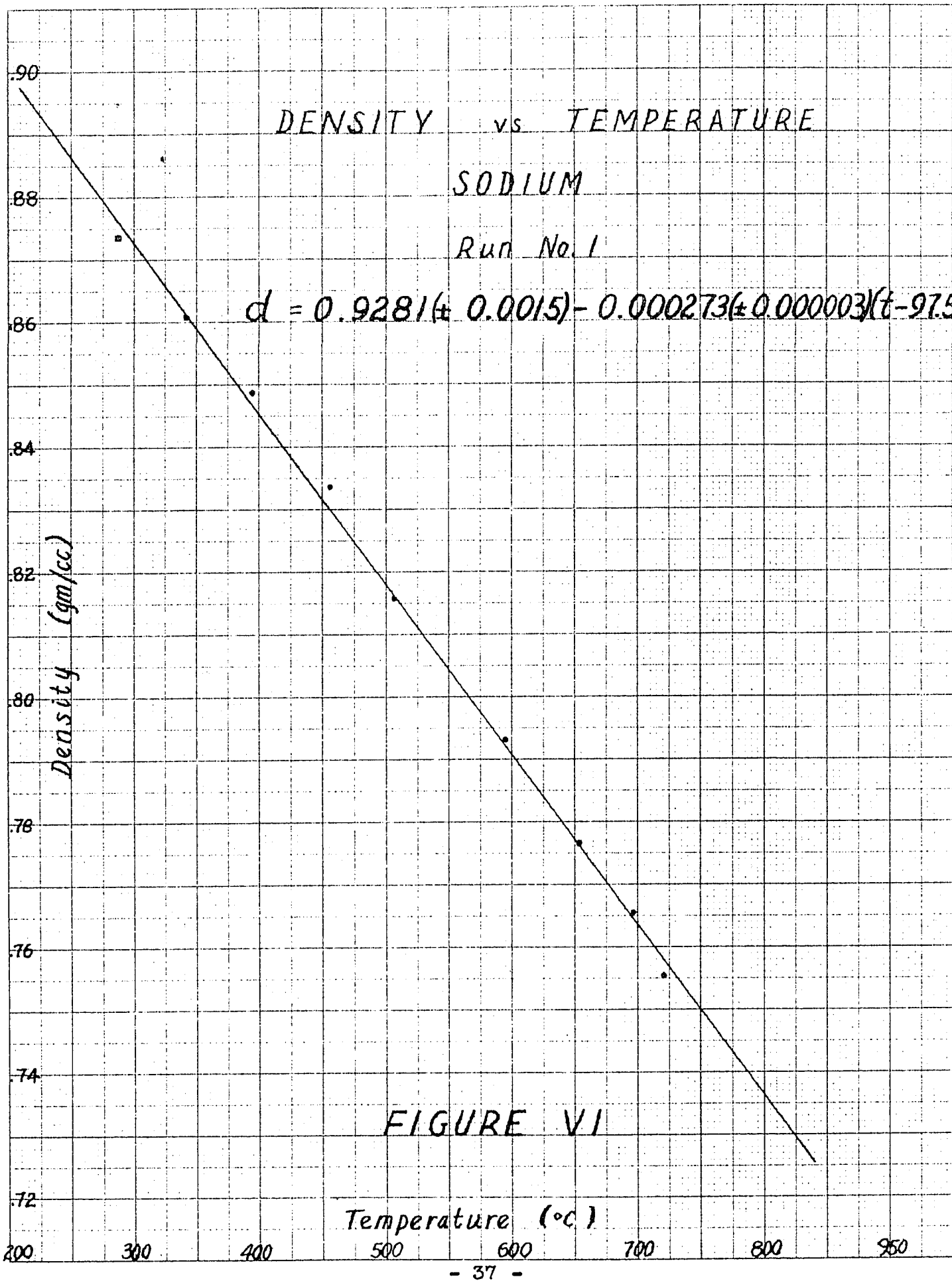



FIGURE VI

TABLE VI
Run No. 2 Sodium

| $T_1$ | $T_c$ | $W_1$ | $W_2$ | $W_3$ | d |
|---|---|---|---|---|---|
| 248 | 280 | .1098 | 21.8384 | 2.3814 | .8942 |
| 250 | 282 | .1113 | 21.8399 | 2.3799 | .8935 |
| 300 | 340 | .1390 | 21.8676 | 2.3522 | .8803 |
| 300 | 340 | .1397 | 21.8683 | 2.3515 | .8800 |
| 354 | 397 | .1775 | 21.9061 | 2.3137 | .8631 |
| 350 | 394 | .1765 | 21.9051 | 2.3147 | .8636 |
| 403 | 450 | .2095 | 21.9381 | 2.2817 | .8487 |
| 403 | 450 | .2096 | 21.9382 | 2.2816 | .8487 |
| 403 | 450 | .2103 | 21.9389 | 2.2809 | .8484 |
| 450 | 498 | .2365 | 21.9651 | 2.2547 | .8365 |
| 450 | 498 | .2347 | 21.9633 | 2.2565 | .8371 |
| 452 | 500 | .2365 | 21.9651 | 2.2547 | .8364 |
| 503 | 550 | .2669 | 21.9955 | 2.2243 | .8229 |
| 503 | 550 | .2739 | 22.0025 | 2.2173 | .8203 |
| 550 | 595 | .3040 | 22.0326 | 2.1872 | .8073 |
| 550 | 595 | .3049 | 22.0335 | 2.1863 | .8069 |
| 600 | 643 | .3413 | 22.0699 | 2.1499 | .7915 |
| 600 | 643 | .3408 | 22.0694 | 2.1504 | .7917 |
| 600 | 643 | .3401 | 22.0687 | 2.1511 | .7920 |
| 703 | 738 | .3825 | 22.1111 | 2.1087 | .7726 |
| 703 | 738 | .3869 | 22.1155 | 2.1043 | .7710 |
| 705 | 740 | .3889 | 22.1175 | 2.1023 | .7702 |
| 702 | 737 | .3788 | 22.1074 | 2.1124 | .7740 |
| 702 | 737 | .3756 | 22.1042 | 2.1156 | .7752 |
| 702 | 737 | .3975 | 22.1261 | 2.0937 | .7672 |
| 702 | 737 | .3820 | 22.1106 | 2.1092 | .7729 |
| 753 | 783 | .4335 | 22.1621 | 2.0577 | .7522 |
| 751 | 782 | .4034 | 22.1320 | 2.0878 | .7633 |
| 754 | 786 | .4076 | 22.1362 | 2.0836 | .7616 |
| 752 | 783 | .4175 | 22.1461 | 2.0737 | .7581 |
| 752 | 783 | .4102 | 22.1388 | 2.0810 | .7608 |
| 802 | 829 | .4340 | 22.1626 | 2.0572 | .7503 |
| 802 | 829 | .4382 | 22.1668 | 2.0530 | .7488 |
| 802 | 829 | .4392 | 22.1678 | 2.0520 | .7484 |
| 801 | 828 | .4399 | 22.1685 | 2.0513 | .7482 |
| 837 | 860 | .4594 | 22.1680 | 2.0518 | .7472 |

Weight of plummet : 23.1437 gm
Total weight of left side : 24.2198 gm
Volume of plummet @ 25°C. : 2.6309 cc

$T_1$ : control temperature (°C)
$T_c$ : corrected temperature (°C)
$W_1$ : observed weight (gm)
$W_2$ : total apparent weight (gm)
$W_3$ : apparent loss in weight (gm)
d : density (gm/cc)

TABLE VII
Run No. 2 Sodium

| T | $d_o$ | $d_2$ | $d_c$ | $r_2$ | $r_c$ |
|---|---|---|---|---|---|
| 281 | .8939 | .8932 | .8886 | +.08 | + .60 |
| 340 | .8802 | .8777 | .8728 | +.28 | + .85 |
| 396 | .8634 | .8629 | .8588 | +.06 | +1.01 |
| 450 | .8486 | .8486 | .8434 | .00 | + .85 |
| 499 | .8367 | .8357 | .8302 | +.12 | + .78 |
| 550 | .8216 | .8222 | .8166 | -.07 | + .61 |
| 595 | .8071 | .8103 | .8045 | -.39 | + .32 |
| 643 | .7917 | .7976 | .7917 | -.74 | .00 |
| 738 | .7719 | .7725 | .7662 | -.08 | + .74 |
| 783 | .7592 | .7607 | .7542 | -.20 | + .66 |
| 829 | .7489 | .7485 | .7418 | +.05 | + .96 |
| 860 | .7472 | .7403 | .7335 | +.93 | +1.87 |

T : temperature (°C)

$d_o$ : average observed density (gm/cc)

$d_2$ : calculated density from equation 2 (gm/cc)

$d_c$ : calculated density from combined equation (gm/cc)

$r_2$ : deviation between $d_2$ and $d_o$ (per cent)

$r_c$ : deviation between $d_c$ and $d_o$ (per cent)

Average $r_2$ : .25 per cent

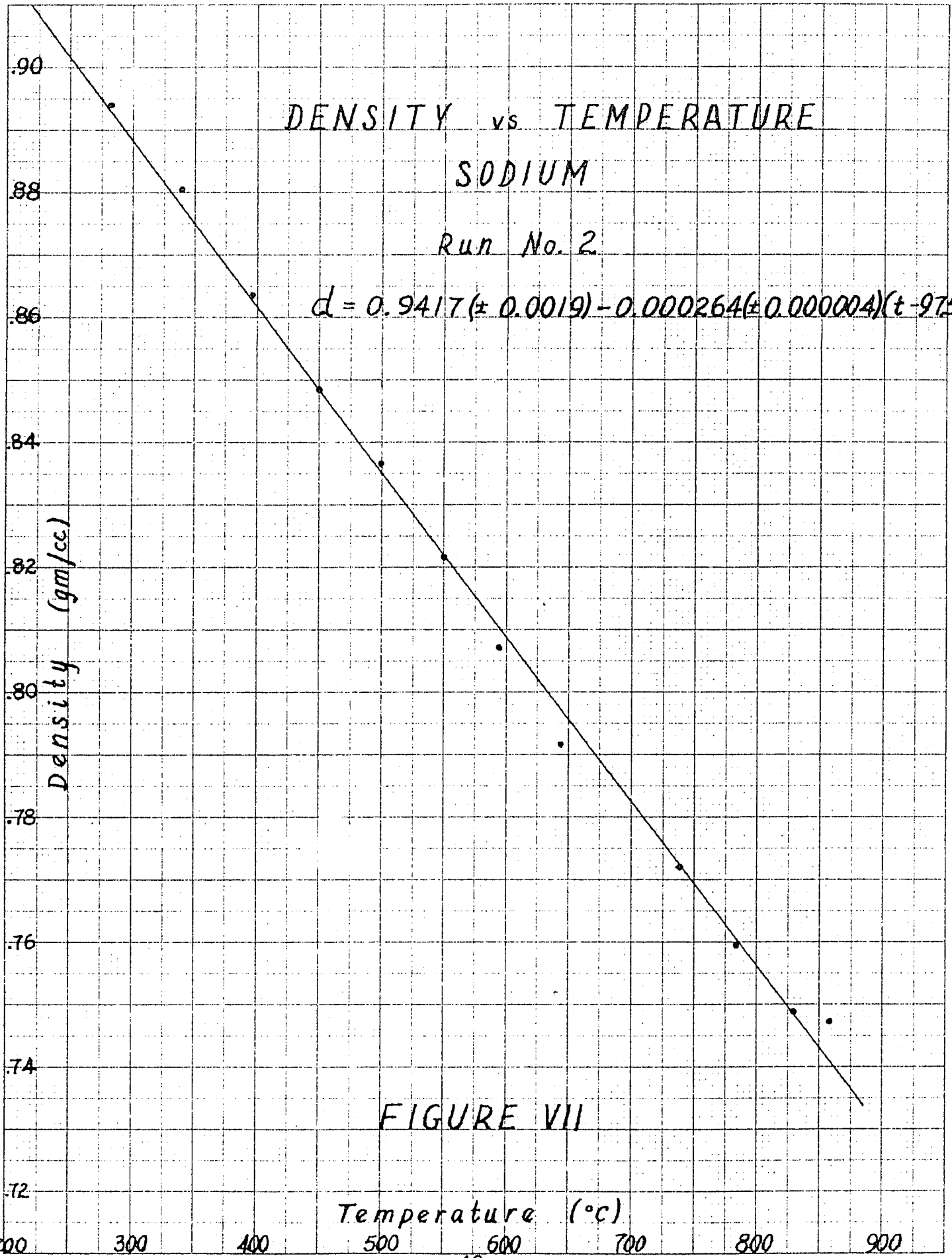



FIGURE VII

TABLE VIII
Run No. 3 Sodium

| $T_1$ | $T_c$ | $W_1$ | $W_2$ | $W_3$ | d |
|---|---|---|---|---|---|
| 226 | 253 | .0838 | 21.8124 | 2.3943 | .9009 |
| 225 | 252 | .0821 | 21.8107 | 2.3960 | .9016 |
| 228 | 256 | .0839 | 21.8125 | 2.3942 | .9007 |
| 251 | 284 | .0924 | 21.8210 | 2.3857 | .8961 |
| 250 | 283 | .0917 | 21.8203 | 2.3864 | .8964 |
| 253 | 286 | .0937 | 21.8223 | 2.3844 | .8955 |
| 252 | 285 | .0944 | 21.8230 | 2.3837 | .8953 |
| 250 | 283 | .0932 | 21.8218 | 2.3849 | .8959 |
| 300 | 339 | .1141 | 21.8427 | 2.3640 | .8853 |
| 350 | 393 | .1614 | 21.8900 | 2.3167 | .8650 |
| 350 | 393 | .1607 | 21.8893 | 2.3174 | .8652 |
| 350 | 393 | .1612 | 21.8898 | 2.3169 | .8650 |
| 400 | 447 | .1901 | 21.9187 | 2.2880 | .8517 |
| 402 | 449 | .1911 | 21.9197 | 2.2870 | .8512 |
| 400 | 447 | .1919 | 21.9205 | 2.2862 | .8510 |
| 400 | 447 | .1925 | 21.9211 | 2.2856 | .8508 |
| 450 | 498 | .2295 | 21.9581 | 2.2486 | .8347 |
| 503 | 549 | .2847 | 22.0133 | 2.1934 | .8120 |
| 502 | 548 | .2929 | 22.0215 | 2.1852 | .8090 |
| 503 | 549 | .2772 | 22.0058 | 2.2009 | .8148 |
| 503 | 549 | .2865 | 22.0151 | 2.1916 | .8113 |
| 503 | 549 | .2872 | 22.0158 | 2.1909 | .8111 |
| 552 | 597 | .3065 | 22.0351 | 2.1716 | .8019 |
| 552 | 597 | .3120 | 22.0406 | 2.1661 | .7999 |
| 552 | 597 | .3283 | 22.0569 | 2.1498 | .7938 |
| 604 | 647 | .3315 | 22.0601 | 2.1468 | .7907 |
| 604 | 647 | .3420 | 22.0706 | 2.1361 | .7868 |
| 604 | 647 | .3402 | 22.0688 | 2.1379 | .7874 |
| 604 | 647 | .3415 | 22.0701 | 2.1366 | .7870 |
| 650 | 689 | .3605 | 22.0891 | 2.1176 | .7783 |
| 652 | 691 | .3590 | 22.0876 | 2.1191 | .7788 |
| 700 | 737 | .3646 | 22.0932 | 2.1135 | .7749 |
| 700 | 737 | .3750 | 22.1036 | 2.1031 | .7711 |
| 700 | 737 | .3690 | 22.0976 | 2.1091 | .7733 |
| 700 | 737 | .3745 | 22.1031 | 2.1036 | .7713 |

Weight of plummet : 23.1302 gm
Total weight of left side : 24.2067 gm
Volume of plummet at 25°C. : 2.6293 cc

$T_1$ : control temperature (°C)
$T_c$ : corrected temperature (°C)
$W_1$ : observed weight (gm)
$W_2$ : total apparent weight (gm)
$W_3$ : apparent loss in weight (gm)
d : density (gm/cc)

TABLE IX
Run No. 3 Sodium

| T | $d_o$ | $d_3$ | $d_c$ | $r_3$ | $r_c$ |
|---|---|---|---|---|---|
| 254 | .9011 | .9039 | .8959 | -.31 | + .58 |
| 284 | .8958 | .8953 | .8878 | +.06 | + .90 |
| 339 | .8853 | .8795 | .8731 | +.66 | +1.40 |
| 393 | .8651 | .8639 | .8586 | +.14 | + .76 |
| 447 | .8512 | .8484 | .8442 | +.33 | + .83 |
| 498 | .8347 | .8338 | .8305 | +.11 | + .51 |
| 549 | .8116 | .8191 | .8168 | -.92 | - .64 |
| 597 | .7985 | .8053 | .8040 | -.84 | - .68 |
| 647 | .7880 | .7909 | .7906 | -.37 | - .33 |
| 690 | .7786 | .7786 | .7791 | .00 | - .06 |
| 737 | .7739 | .7650 | .7665 | +1.16 | + .97 |

T : temperature (°C)

$d_o$ : average observed density (gm/cc)

$d_3$ : calculated density from equation 3 (gm/cc)

$d_c$ : calculated density from combined equation (gm/cc)

$r_3$ : deviation between $d_3$ and $d_o$ (per cent)

$r_c$ : deviation between $d_c$ and $d_o$ (per cent)

Average $r_3$ : .45 per cent

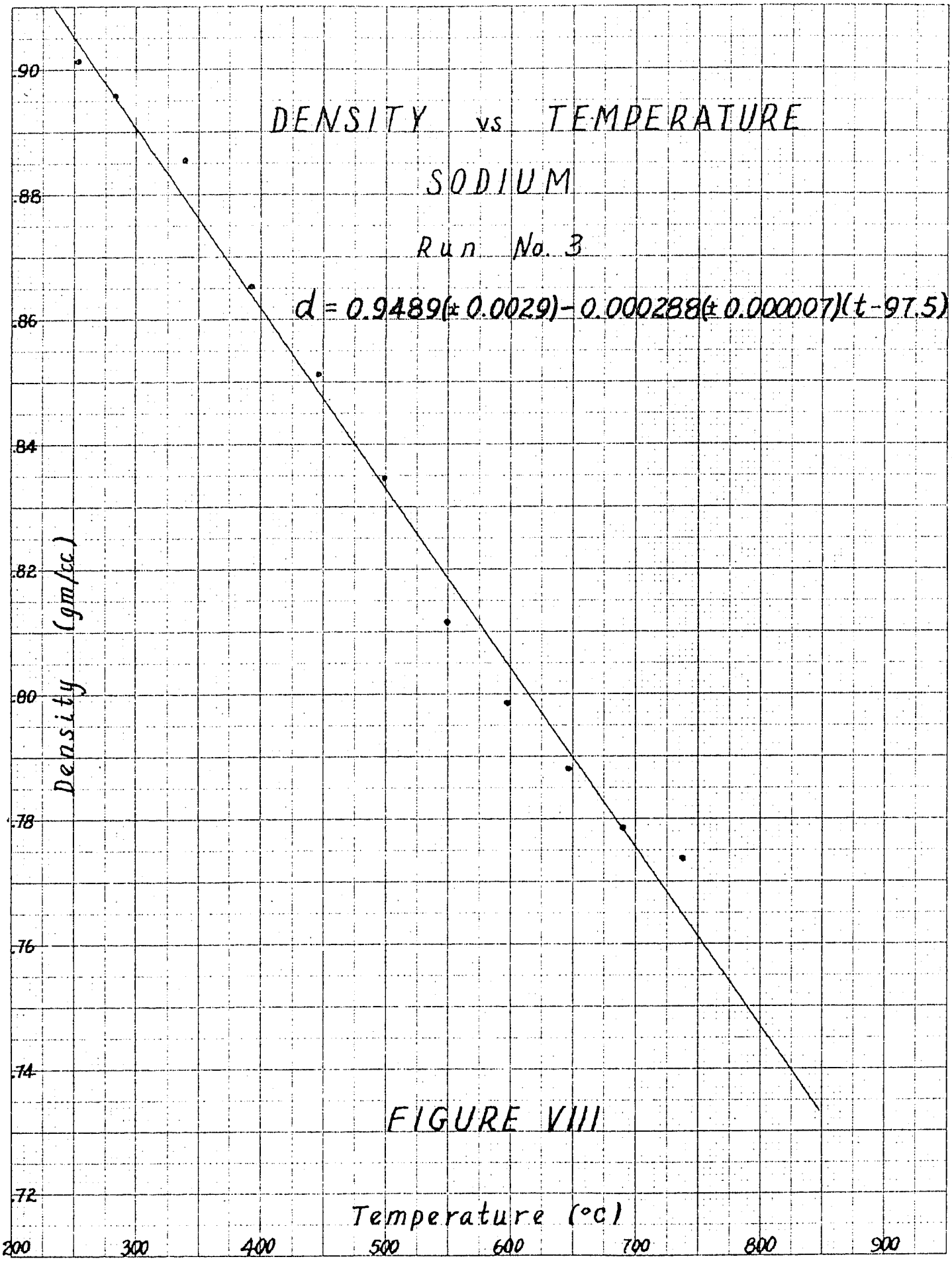



FIGURE VIII

TABLE X
Run No. 1
Sodium Hydroxide

| $T_1$ | $T_c$ | $W_1$ | $W_2$ | $W_3$ | d |
|---|---|---|---|---|---|
| 400 | 447 | .4513 | 21.4884 | 4.7026 | 1.6845 |
| | | .4534 | 21.4905 | 4.7005 | 1.6837 |
| | | .4529 | 21.4900 | 4.7010 | 1.6839 |
| 450 | 498 | .5257 | 21.5628 | 4.6282 | 1.6533 |
| | | .5274 | 21.5645 | 4.6265 | 1.6527 |
| | | .5267 | 21.5638 | 4.6272 | 1.6530 |
| 500 | 547 | .5914 | 21.6285 | 4.5625 | 1.6256 |
| | | .5900 | 21.6271 | 4.5639 | 1.6261 |
| | | .5900 | 21.6271 | 4.5639 | 1.6261 |
| 550 | 596 | .6449 | 21.6820 | 4.5090 | 1.6025 |
| | | .6444 | 21.6815 | 4.5095 | 1.6026 |
| | | .6446 | 21.6817 | 4.5093 | 1.6026 |
| 600 | 644 | .7050 | 21.7421 | 4.4489 | 1.5772 |
| | | .7042 | 21.7413 | 4.4497 | 1.5775 |
| | | .7045 | 21.7416 | 4.4494 | 1.5774 |
| | | .7056 | 21.7427 | 4.4483 | 1.5770 |
| | | .7064 | 21.7435 | 4.4475 | 1.5767 |
| | | .7068 | 21.7436 | 4.4471 | 1.5765 |
| | | .7065 | 21.7436 | 4.4474 | 1.5766 |
| 650 | 689 | .7894 | 21.8265 | 4.3645 | 1.5438 |
| | | .7883 | 21.8254 | 4.3656 | 1.5441 |
| | | .7874 | 21.8245 | 4.3665 | 1.5445 |
| | | .7890 | 21.8261 | 4.3649 | 1.5439 |
| 700 | 736 | .8485 | 21.8856 | 4.3054 | 1.5192 |
| | | .8504 | 21.8875 | 4.3035 | 1.5186 |
| | | .8523 | 21.8894 | 4.3016 | 1.5179 |
| | | .8529 | 21.8900 | 4.3010 | 1.5177 |
| | | .8539 | 21.8910 | 4.3000 | 1.5173 |
| | | .8548 | 21.8919 | 4.2991 | 1.5170 |

Weight of plummet : 24.0330 gm
Total Weight of left side : 26.1910 gm
Volume of plummet at 25°C. : 2.7321 cc

$T_1$ : control temperature (°C)

$T_c$ : corrected temperature (°C)

$W_1$ : observed weight (gm)

$W_2$ : total apparent weight (gm)

$W_3$ : apparent loss in weight (gm)

d : density (gm/cc)

TABLE XI
Run No. 1
Sodium Hydroxide

| T | $d_o$ | $d_1$ | $d_c$ | $r_1$ | $r_c$ |
|---|---|---|---|---|---|
| 447 | 1.6840 | 1.6841 | 1.6800 | +.01 | +.24 |
| 498 | 1.6530 | 1.6551 | 1.6511 | -.13 | +.12 |
| 547 | 1.6259 | 1.6273 | 1.6235 | -.09 | +.15 |
| 596 | 1.6026 | 1.5995 | 1.5958 | +.19 | +.40 |
| 644 | 1.5770 | 1.5722 | 1.5687 | +.31 | +.53 |
| 689 | 1.5441 | 1.5466 | 1.5433 | -.16 | +.05 |
| 736 | 1.5180 | 1.5199 | 1.5167 | -.13 | +.09 |

T : temperature ($^oC$)

$d_o$ : average observed density (gm/cc)

$d_1$ : calculated density from equation 1 (gm/cc)

$d_c$ : calculated density from combined equation (gm/cc)

$r_1$ : deviation between $d_1$ and $d_o$ (per cent)

$r_c$ : deviation between $d_c$ and $d_o$ (per cent)

Average $r_1$ : .17 per cent

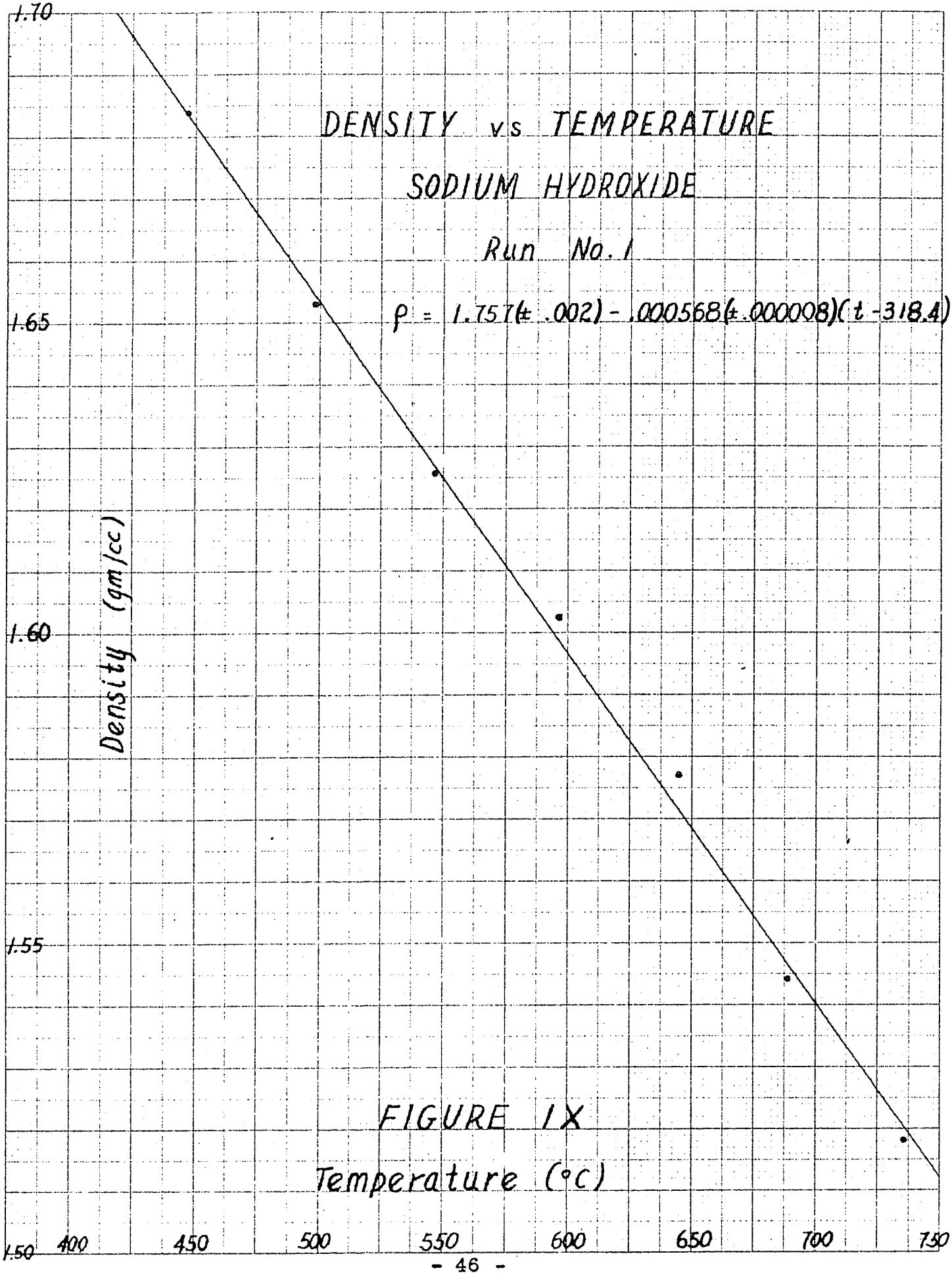



FIGURE IX

TABLE XII
Run No. 2
Sodium Hydroxide

| $T_1$ | $T_c$ | $W_1$ | $W_2$ | $W_3$ | d |
|---|---|---|---|---|---|
| 400 | 447 | .2377 | 21.2748 | 4.8591 | 1.6747 |
| | | .2373 | 21.2744 | 4.8595 | 1.6749 |
| | | .2368 | 21.2739 | 4.8600 | 1.6751 |
| 450 | 498 | .3027 | 21.3398 | 4.7941 | 1.6479 |
| | | .3020 | 21.3391 | 4.7948 | 1.6482 |
| | | .3037 | 21.3408 | 4.7931 | 1.6476 |
| | | .3038 | 21.3409 | 4.7930 | 1.6475 |
| 500 | 547 | .3691 | 21.4062 | 4.7277 | 1.6209 |
| | | .3697 | 21.4068 | 4.7271 | 1.6206 |
| | | .3696 | 21.4067 | 4.7272 | 1.6207 |
| | | .3696 | 21.4067 | 4.7272 | 1.6207 |
| 550 | 596 | .4443 | 21.4814 | 4.6525 | 1.5910 |
| | | .4452 | 21.4823 | 4.6516 | 1.5907 |
| | | .4452 | 21.4823 | 4.6516 | 1.5907 |
| 600 | 644 | .5091 | 21.5462 | 4.5877 | 1.5650 |
| | | .5094 | 21.5465 | 4.5874 | 1.5649 |
| | | .5098 | 21.5469 | 4.5870 | 1.5647 |
| | | .5097 | 21.5468 | 4.5871 | 1.5648 |
| 650 | 689 | .5697 | 21.6068 | 4.5271 | 1.5408 |
| | | .5706 | 21.6077 | 4.5262 | 1.5405 |
| | | .5718 | 21.6089 | 4.5250 | 1.5401 |
| | | .5728 | 21.6099 | 4.5240 | 1.5397 |
| | | .5716 | 21.6087 | 4.5252 | 1.5401 |
| 700 | 736 | .6377 | 21.6748 | 4.4591 | 1.5140 |
| | | .6384 | 21.6755 | 4.4584 | 1.5138 |
| | | .6414 | 21.6785 | 4.4554 | 1.5128 |
| | | .6415 | 21.6786 | 4.4553 | 1.5127 |

Weight of plummet : 24.9784 gm
Total weight of left side : 26.1339 gm
Volume of plummet at 25°C. : 2.8394 cc

$T_1$ : control temperature (°C)

$T_c$ : corrected temperature (°C)

$W_1$ : observed weight (gm)

$W_2$ : total apparent weight (gm)

$W_3$ : apparent loss in weight (gm)

d : density (gm/cc)

TABLE XIII
Run No. 2
Sodium Hydroxide

| T | $d_o$ | $d_2$ | $d_c$ | $r_2$ | $r_c$ |
|---|---|---|---|---|---|
| 447 | 1.6749 | 1.6757 | 1.6800 | -.05 | -.30 |
| 498 | 1.6478 | 1.6471 | 1.6511 | +.04 | -.20 |
| 547 | 1.6207 | 1.6195 | 1.6235 | +.07 | -.17 |
| 596 | 1.5908 | 1.5920 | 1.5958 | -.08 | -.31 |
| 644 | 1.5649 | 1.5651 | 1.5687 | -.01 | -.24 |
| 689 | 1.5402 | 1.5398 | 1.5433 | +.03 | -.20 |
| 736 | 1.5133 | 1.5134 | 1.5167 | -.01 | -.22 |

T : temperature (°C)

$d_o$ : average observed density (gm/cc)

$d_2$ : calculated density from equation 2 (gm/cc)

$d_c$ : calculated density from combined equation (gm/cc)

$r_2$ : deviation between $d_2$ and $d_o$ (per cent)

$r_c$ : deviation between $d_c$ and $d_o$ (per cent)

Average $r_2$ : .04 per cent

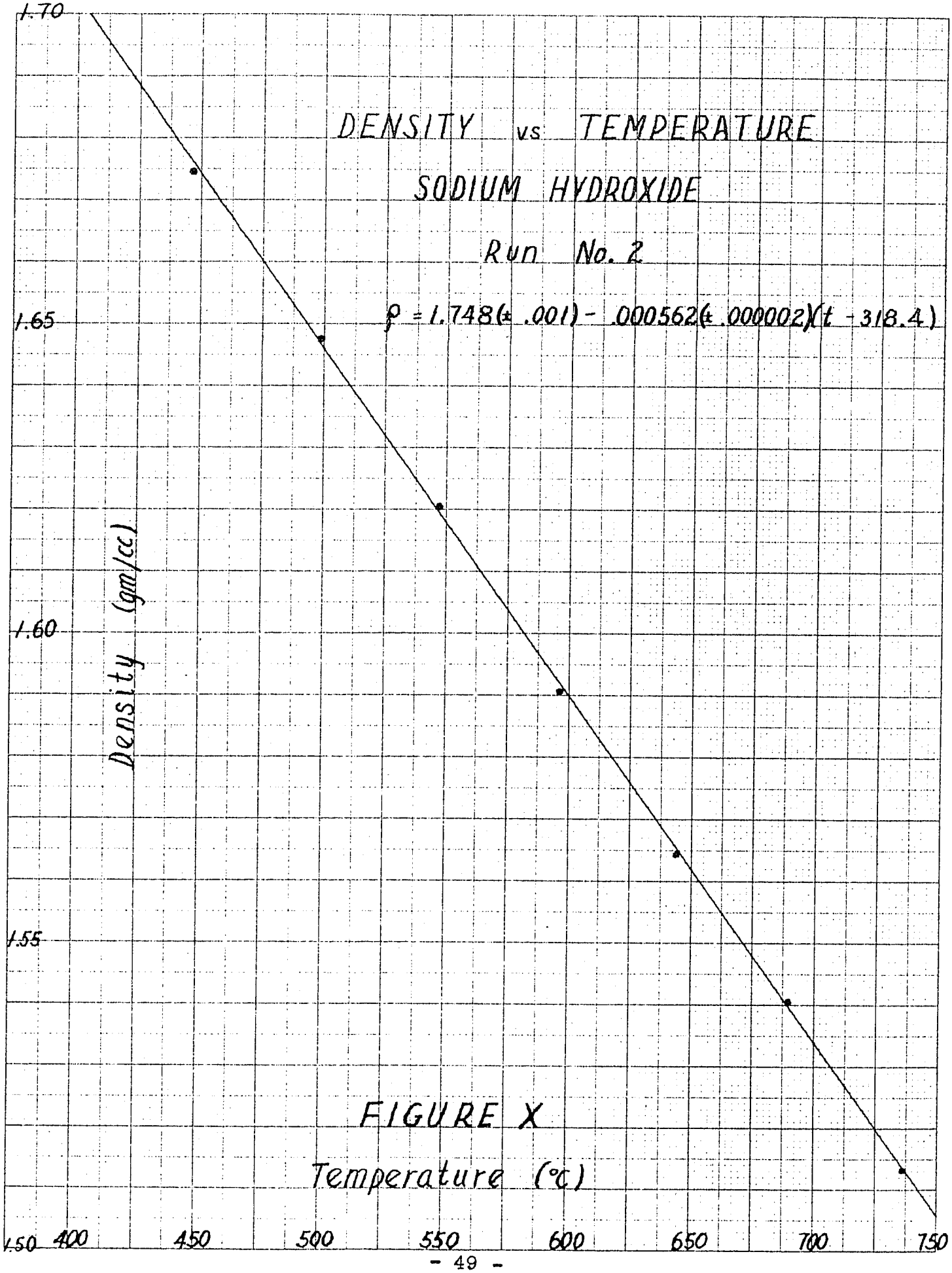



FIGURE X

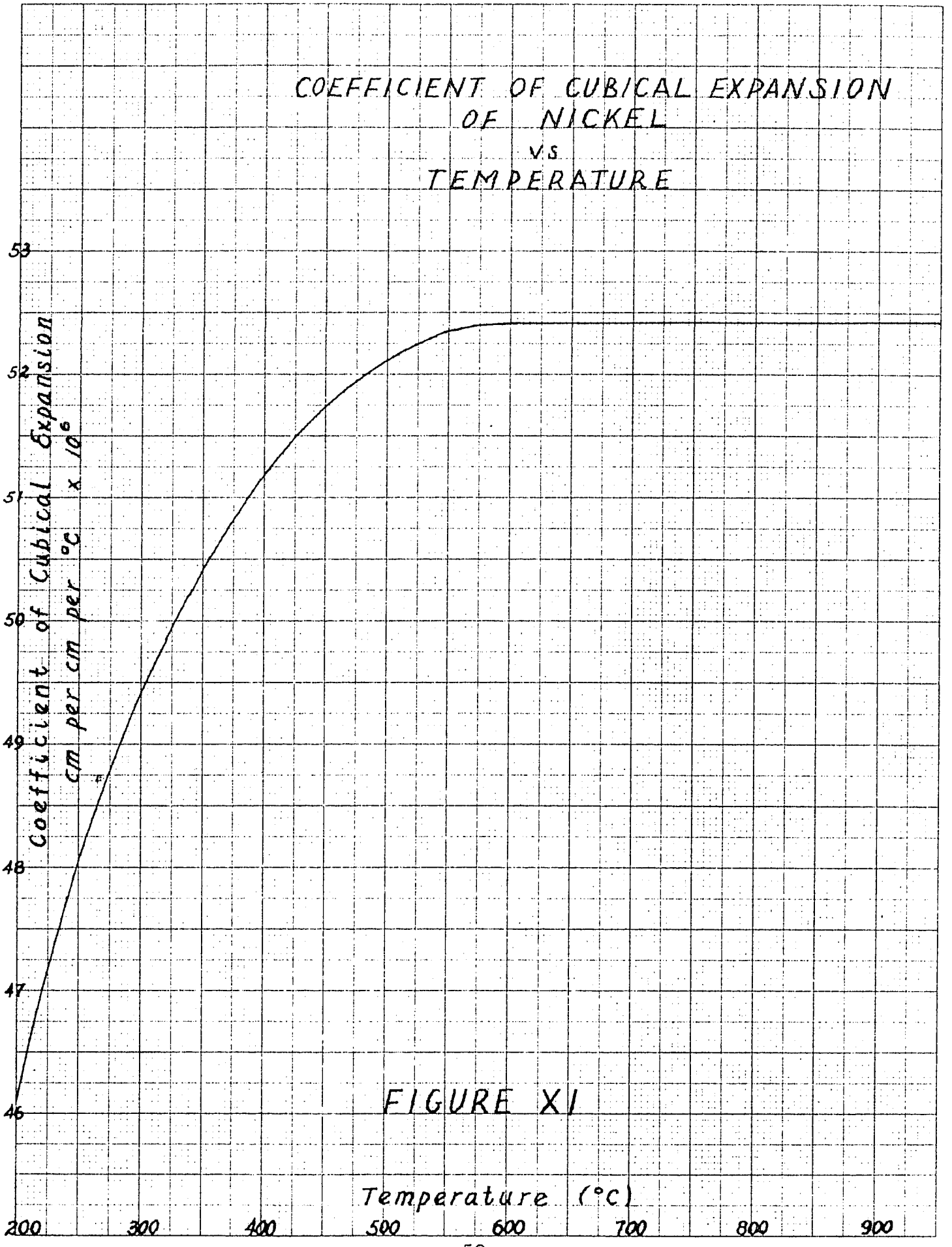



FIGURE XI

## SAMPLE CALCULATIONS

Data (from TABLE VI):

| | |
|---|---|
| Material | Sodium |
| Run No | 2 |
| Control temperature ($T_c$) | 503°C |
| Corrected temperature ($T_c$) | 550°C |
| Weight of plummet ($W_p$) | 23.1437 gm |
| Density of plummet ($d_p$) | 8.79695 gm/cc |
| Coefficient of cubical expansion ($\alpha$) | 52.25 x $10^{-6}$ cm/cm/°C |
| Total weight of left side ($W_l$) | 24.2198 gm |
| Tare ($W_t$) | 21.7286 gm |
| Observed weight ($W_o$) | .2669 gm |

Calculation of Volume:

Volume of plummet at 25°C. ($V_o$) = $W_p$ / $d_p$

$V_o = 23.1437 / 8.79695$

$V_o = 2.6309$ cc

Volume of plummet at 550°C. ($V_t$) = $V_o( 1 + \alpha (\Delta T))$

$V_t = 2.6309(1 + 52.25 \times 10^{-6}(550 - 25))$

$V_t = 2.7031$ cc

Calculation of Density:

Total weight of right side ($W_r$) = $W_t + W_o$

$W_r = 21.7286 + .2669$

$W_r = 21.9955$ gm

Apparent loss in weight ($W_a$) = $W_l - W_r$

$W_a = 24.2198 - 21.9955$

$W_a = 2.2243$ gm

Density of sodium at 550°C. (d) = $W_a$ / $V_t$

$d = 2.2243 / 2.7031$

$d = 0.8229$ gm/cc

## DISCUSSION OF DATA

### Observation of weights

The most common weighing errors outside of personal errors are due to inaccuracies in the values of the weights. However, in this method, these inaccuracies were of no consequence since the actual weights were not used in the operations; both the plummet and tare were weighed with the same set of weights and, therefore, any inaccuracies in the weights compensated for themselves.

Other possible sources of errors are:

(1) The two arms of the beam may not be of the same length;

(2) The temperature of the two arms of the balance may be different;

(3) The buoyancy due to the atmosphere present in the balance may affect the apparent weight.

Since most analytical balances are so accurately made, the error due to inequality of arms of the balance does not exceed one part in several thousand, and thus, this error may be overlooked.

As for the differences in temperature between the two arms of the balance, it is believed that this type of error may also be considered negligible. Any expansion of the balance arms that might be expected due to thermal expansion caused by the high temperature of the crucible may be discounted. A thermometer was hung in the balance case during

the actual course of a determination and it was found that the temperature in the balance case never got higher than approximately 35°C., even though the temperature in the crucible may have been as high as 750°C. The convection currents which may arise due to the hot crucible were thought to be kept to a minimum since any hot gases rising from the crucible had to pass through the cooling section at the upper end of the densitometer tube through a hole 3/8 inches in diameter, and it is believed that any gases passing through this section were cooled sufficiently so that the effect of any convection currents would be negligible. During the course of the runs, no erratic swinging of the balance that could be attributed to convection currents was noticed.

The buoyancy effect on the apparent weight of the objects weighed due to air or any other gases that may be used in the apparatus may be considered negligible. All of the objects, plummet, tare, etc., were weighed in air prior to insertion into the apparatus; and all of these weights were corrected to weights in vacuum and were found to be different from the weight in air by only 0.2 mg or 1 part in 100,000. When these weights were then corrected again to weights in a 15 p.s.i. atmosphere of helium, the weights were found to differ from those weights in air by only 0.1 mg or 1 part in 200,000. Therefore, it was considered suffi-

ciently accurate to use those weights obtained in air throughout all of the calculations.

Another source of error in the weighing procedure is the error introduced by the action of the surface tension of the sample on the wire. In order to reduce the possibilities of sizeable errors from this source, the suspension wire used was of as small a diameter as was feasible. In the case of molten sodium metal, where the surface tension is nearly 300 dynes per centimeter (15) at its melting point in a carbon dioxide atmosphere, the error introduced in the weighing is of the order of magnitude of some 0.05 per cent. This would be the maximum error produced by the surface tension effect, since as the temperature is increased, the surface tension of the sample is decreased. As for the case of sodium hydroxide, this error is also negligible since the surface tension of molten salts are much lower than those of the metals.

In the case of sodium, an actual calculation of this effect showed that a surface of less than 0.04 cm of wire would be exposed to the sodium and this would represent a force of some 12 dynes acting upward. This would be slightly greater than 1.2 mg of weight. Considering the total apparent loss in weight of the plummet upon immersion, 2.6 gm., this results in an error of 0.05 per cent as noted.

Probably the largest source of error in this method

would be the clinging of droplets of the sample to the suspension wire. This would increase the apparent weight of the bob with the result that the apparent loss in weight of the plummet would be less, and the resulting density value calculated would be less than the true value.

A trial run was made by observing the weights at 50 degree intervals as the temperature was increased from 250° to 550°C.; when the sample was cooled in 50 degree decrements from 550° to 250°, the data from the run just mentioned were not reproduced. It was observed that for the weighings made while increasing the temperature, the weight *vs.* temperature curve showed a constant slope; for the same measurements made while decreasing the temperature a straight line of lesser slope was obtained on the weight *vs.* temperature plot. From this, it was concluded that this increased weight observed was due to the adherence of sample to the suspension.

An attempt was made to heat the suspension wire electrically, but this proved to be of no avail. Much difficulty was encountered with the burning out of the suspension wire. This was attributed to (1) the shorting of the wire to the baffle plates when current was passed, and (2) the overheating of the wire in the hot zone due to the increased resistance of the wire. The first possibility was avoided by the insertion of a Pyrex glass bushing in the topmost baffle plate so that the suspension wire could hang freely through the

baffle plates. However, breaking of the wire persisted, presumably due to the second possibility mentioned above. Since direct observation of the suspension wire in the hot zone of the furnace was impossible, the actual cause of the breaking of the wire could not be established. Therefore, heating of the suspension wire electrically was eliminated for the many difficulties which it presented.

In order to minimize this effect of material clinging to the suspension, all determinations were made by constantly increasing the temperature so that the level of the sample would never be above that at which the determinations were being made. In this manner, the only amount of sample that could be adhering to the suspension would be from the dipping in and out of the sample of the wire as the balance is swinging. This could amount to not more than 1/2 inch at the maximum amplitude of the swing of the balance.

Another means by which the material could adhere to the wire is by the vaporization of the sample and the consequent condensation of the sample on the wire. The exact amount of the material that may cling to the wire in this manner could not be determined accurately.

Should as much as 10 mg or 0.15 cc of the sample adhere to the wire at 700°C., this would cause a deviation of only 4 parts in 800 or 0.5 per cent for the density of sodium. For sodium hydroxide, this deviation would be much less

since a slight weighing error would have less effect on the calculated density value since the density of sodium hydroxide is about twice that of sodium.

Although the extent of the error from this source cannot be determined accurately, it is observed that any weighing error becomes more noticeable as the temperature is increased, due to the decreasing density of the sample. From the consideration of the foregoing, it is believed safe to estimate the deviations due to weighing errors to be $\pm$ 1 per cent.

Variation of the volume immersed

Some error is introduced due to the variation of the length of wire that is immersed in the sample. Actually, some of the suspension wire in included in the total volume immersed during the calibration of the plummet and therefore, the error introduced is merely in the increased length of the wire immersed due to the rising level of the sample as the temperature is increased. The length of wire immersed is also increased due to the expansion of the wire with the increasing temperature.

However, the error introduced by this variation in the volume immersed is negligible, since the diameter of wire was judiciously chosen. If the length of wire immersed increases as much as two inches (an extreme case) over that length immersed during the calibration run, the increase in

the volume immersed is only slightly more than 0.0008 cc. This would represent a difference in volume of only 8 parts in 26,000 or less than 0.04 per cent variation in the volume immersed. Thus, the error caused from this source is considered negligible.

Coefficient of expansion

In this method it was necessary to calculate the increase in volume of the nickel plummet from coefficient of expansion data. The coefficient of linear expansion of "A" nickel was supplied by the International Nickel Co., Inc. (14) and the coefficient of cubical expansion was calculated from this by taking three times the linear coefficient. The validity of this procedure is shown by differentiating the volume expression with respect to temperature, and it is found that the coefficient of cubical expansion, $(1/V\ dV/dT)$, is equal to three times the linear coefficient if it is assumed that the linear coefficient of expansion for the radius is the same as that for the height of the cylinder.

Rather than use the average coefficients of expansion over a wide temperature range as is usually shown in tables, the coefficients were plotted against temperature and the coefficient of expansion at the desired temperature was taken from the graph (see Fig. XI). This eliminated the possibility of errors that would be introduced if any average value of

the coefficient of expansion were taken for a range of temperatures.

Temperature measurement and control

Using the method described previously on page 22, the temperature of the sample could be measured to within 3 degrees. This error is allowed on the basis of a check of the thermocouple by determining the melting point of potassium dichromate. The measured temperature of the melting point of $K_2Cr_2O_7$ was 399.0°C. as compared with the literature value of 397.5°C.

Allowing an error as much as 3 degrees in the temperature, it is found that the error in the density value would be approximately 0.1 per cent. Hence, a variation in the temperature of ca. 1 per cent would produce an error in the density of only 0.1 per cent for both sodium and sodium hydroxide.

It is believed that no error was introduced due to a temperature gradient through the sample. The sample was allowed to remain at one temperature for at least one and one-half hours prior to observing the weights. Constant temperature throughout the sample was also abetted by the stirring action of the plummet.

Sodium Hydroxide

The extremely corrosive nature of sodium hydroxide caused many difficulties during the initial stages of this

investigation.

The severe blackening of the nickel, which presumably provides a protective coating against further corrosion according to the literature (14, 15), did not prove to be effective against the severe conditions imposed during this investigation. It was found that the black coating on the nickel was not permanent but for the most part could be wiped off with the fingers. Hence, the black particles were suspended throughout the sodium hydroxide, imparting the gray to black appearance to the sample. It is known that even as small a quantity of metallic oxide impurities in sodium hydroxide as 0.05 per cent are enough to color sodium hydroxide deeply (8).

According to Wallace and Fleck, this black substance had the empirical formula of $Na_2Ni_5O_{13}$. However, more recent studies by the National Bureau of Standards (9) and the Naval Research Laboratories (16) have shown this black substance to be a nickelite compound or a double salt of sodium, $Na_2NiO_2$ or $Na_2O \cdot NiO$. The exact structure of this material has not been ascertained as yet. The formation of this material has been proposed to take place in the following manner:

(1) $2\ NaOH + Ni \rightleftharpoons Na_2NiO_2 + H_2$

As for the variation of the color of the NaOH subsequent to trials with other than a hydrogen atmosphere, the same phenomenon was observed by Wallace and Fleck. It was found

that the green color was obtained at temperatures ca. 350°C., with the brown color appearing at temperatures ca. 400-500°C. These colors were also found when 5 per cent $Na_2O_2$ was added to the sample and thus, it became apparent that any dissociation of NaOH to the oxide, or the presence of oxygen in the apparatus was the cause of the severe corrosion of the nickel.

Information was received that it was necessary to passify all of the nickel surfaces prior to exposure to the fused caustic (12). In order to pacify the nickel, chemical polishing to a near mirror surface is necessary.

Although the nickel was pacified in this manner, corrosion of the nickel was not prevented, and the surfaces were completely blackened. Since this black oxide coating is presumably a protective coating, subsequent trials were made, leaving the black oxide coating on the surfaces. However, the corrosion continued and gray to black sodium hydroxide was produced in each case.

Hence, the black oxide coating was removed by boiling the nickel in an extremely dilute hydrochloric acid solution, and then chemically polishing the surfaces with a commercial chemical polishing agent after each blackening.

Further evidence that oxygen or air was helpful in producing oxidation of the nickel was observed when two test pieces of polished nickel were immersed in the crucible at temperatures ca. 500°C. while a jet of steam was pointed at

the surface. One test piece was allowed to cool in air. The air-cooled piece commenced to darken as it cooled while the other retained its polish. A water quench of the hot test piece also prevented the blackening.

When a previously oxidized crucible was treated with the fused caustic in a steam atmosphere, it was found to clean up the nickel surfaces with the black particles being suspended throughout the caustic.

Hence, it became apparent that a reducing atmosphere was essential in avoiding the corrosion of the nickel. Also, from the observation of the proposed reaction, which satisfies all of the experimental data accumulated regarding the reaction, any pressure of hydrogen exceeding the equilibrium pressure of hydrogen in the reaction would be sufficient to inhibit the corrosion by this mechanism, so that the extent of the corrosion would be minimized.

Thus, the decision was made to use a hydrogen atmosphere to accomplish the two-fold purpose of (1) providing a reducing atmosphere and, (2) providing the necessary hydrogen overpressure to drive reaction (1) to the left. This use of hydrogen proved satisfactory with no detectable corrosion of the nickel.

Rectification of density data

The measured densities were plotted and found to fit a linear plot as expected for a density vs. temperature

relationship. Using the method of least squares on the densities measured over the entire temperature range, the following equations were obtained:

SODIUM

(1) Run No. 1

$$d = 0.9281(\pm 0.0015) - 0.000273(\pm 0.000003)(t - 97.5)$$

(2) Run No. 2

$$d = 0.9417(\pm 0.0019) - 0.000264(\pm 0.000004)(t - 97.5)$$

(3) Run No. 3

$$d = 0.9489(\pm 0.0029) - 0.000288(\pm 0.000007)(t - 97.5)$$

(4) Combined

$$d = 0.9378(\pm 0.0086) - 0.000268(\pm 0.000018)(t - 97.5)$$

SODIUM HYDROXIDE

(5) Run No. 1

$$d = 1.757(\pm 0.002) - 0.000568(\pm 0.000008)(t - 318.4)$$

(6) Run No. 2

$$d = 1.748(\pm 0.001) - 0.000562(\pm 0.000002)(t - 318.4)$$

(7) Combined

$$d = 1.753(\pm 0.002) - 0.000565(\pm 0.000008)(t - 318.4)$$

The densities calculated from these equations are listed in Tables V, VII, IX, XI, and XIII, as well as the average values of the observed densities for each temperature.

In calculating the above equations, the average value of the density was taken at each temperature and the method of least squares was applied. This was done in order to avoid overweighting the values measured at the higher temperatures where more determinations were required to obtain a good average value.

The per cent deviations between the observed values and the value calculated from the combined equation are shown in

Tables V, VII, IX, and Tables XI and XIII, for sodium and sodium hydroxide, respectively.

Using Equation (4) for sodium, the deviations between the observed and calculated values of the density varied as much as 1.98 per cent with the average deviation of 0.93 per cent. For sodium hydroxide, using Equation (7), the deviations varied as much as 0.53 per cent with the average deviation of 0.23 per cent.

## SUMMARY

The densities of molten sodium and sodium hydroxide were measured over the temperature range of 254° to 860°C., and 447° to 736°C., respectively. The determinations were made by Kohlrausch's hydrostatic weighing method utilizing the Archimedes principle. The apparatus used was a refinement of the commonly known Mohr-Westphal balance where a chainomatic analytical balance was used as the weighing mechanism for increased accuracy.

The equations,

$$d_{Na} = 0.9378(\pm 0.0086) - 0.000268(\pm 0.000018)(t - 97.5)$$

$$d_{NaOH} = 1.753(\pm 0.002) - 0.000565(\pm 0.000008)(t - 318.4)$$

were derived by the method of least squares from the data accumulated. The deviations between the observed and calculated values of the density varied between 0.00 to 1.98 per cent for sodium and 0.05 to 0.53 per cent for sodium hydroxide, with the average deviations being 0.93 per cent and 0.23 per cent for sodium and sodium hydroxide, respectively.

Although the densities reported are stated as being for sodium and sodium hydroxide, the values for sodium hydroxide should actually be considered as the density of analytical reagent grade sodium hydroxide. A better grade of sodium hydroxide is extremely difficult to obtain and is not readily available commercially. A method whereby pure sodium hydroxide can be produced by reacting pure sodium metal with water

vapor has been used by some investigators. However, the exact conditions for the reaction are not known publicly and hence, the obviously dangerous method was not attempted. Therefore, the density of reagent grade sodium hydroxide, with the main contaminant being the carbonate, is reported in this investigation.

The most important factors in the determining of the accuracy of the method are, (1) the accuracy with which the coefficient of expansion of the plummet material is known, and (2) the extent of the errors arising during the weighing operations.

The coefficient of expansion data was obtained directly from the International Nickel Co., Inc., and since the coefficients for each temperature were obtained from a plot of coefficients of expansion vs. temperature rather than use the average values for a range of temperatures as usually shown in tables, it is believed that the values used are well within the ±1 per cent accuracy claimed for this method.

Probably the determining factor in the accuracy with which the apparent loss in weight of the plummet can be determined is the extent of the adherence of material to the suspension wire. The extent to which droplets of the sample cling to the suspension wire can not be determined accurately. It can be estimated that the adverse effect due to this cause would be greater for materials of lower boiling points. This proved to be the case in this investigation as the values of

the density of sodium were less precise at the higher temperatures than the measurements for sodium hydroxide at the same temperatures.

Other factors, although of less importance than those mentioned above, in determining the accuracy of the method, are mentioned in the section on discussion of data.

The apparatus, as such, can be used in determining the densities of liquids, e.g. molten metals and salts, at high temperatures with an accuracy of approximately $\pm$ 1 per cent, with the advantage that the entire range of temperatures may be covered with a single sample of the test material.

# A P P E N D I X

## PHYSICAL PROPERTIES

### SODIUM

Melting point.... 97.5°C

Boiling point.... 880.0°C

Surface tension.. 295 dynes/cm at melting point in carbon dioxide atmosphere

Vapor pressures..

| | |
|---|---|
| 300°C | $1.385 \times 10^{-2}$ mm |
| 400°C | 1.2 mm |
| 500°C | 3.8 mm |
| 597°C | 24.9 mm |
| 701°C | 96.1 mm |
| 797°C | 254.0 mm |

Density.....

Rinck (17)
$d = 0.9385 - 0.000260(t - 96.5)$
range m.p. - 650°C

Hackspill (2)
$d = 0.9385 - 0.000275(t - 100)$
range 100 - 180°C

Naval Research Laboratories (1)
$d = 0.9275 - 0.000246(t - 100)$

National Distillers Chem. Corp. (18)
$d = 0.9287 - 0.0002393(t - 97.5)$

### SODIUM HYDROXIDE

Melting point.... 318.4°C

Boiling point.... 1390°C

Vapor pressure... $\log P_{mm} = 52.23(132) / T + 7.030$

Density.....

Meyer and Heck (6)
$d = 2.11 - 0.00063(t)$
range 340 - 440°C

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