

PHASE STUDIES ON THE REACTION



BY

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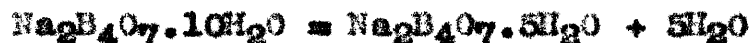
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PHASE STUDIES ON THE REACTION



For many years an experiment has been carried out in the Advanced Physical Chemistry course of this school dealing with the heat of hydration of the deca hydrate of borax. Data was lacking whereby thermodynamic calculations could be made. By knowing the vapor pressure variation with temperature of the deca hydrate, the necessary data could be obtained. Finding but one value in the International Critical Tables for this pressure, this work was undertaken.

HISTORICAL PART

The dissociation pressure of hydrates was first recognized as a definite physical phenomenon in the latter part of the 19th century. Before 1875 the work done was of little value owing to the vague ideas concerning the nature of the phenomenon. Between 1875 and 1881 several independent investigators established the fundamental fact that at a definite temperature a mixture of two hydrates is necessary to produce a definite pressure of water vapor. From this time on the work

developed rapidly. Investigators used the vapor pressure idea for substantiating some thermodynamic laws, for humidity control, and for the construction of phase diagrams.

Borax occurs rather widely distributed over the earth in natural waters, old lake beds, etc. The early Greeks and Romans were well acquainted with some of its properties and used it to the best of their knowledge. In 1829 Payen (1) discovered and proved the composition of the penta hydrate or octahedral borax. After this time considerable work was done on determining whether other hydrates were formed or not. At the present time this subject of the existing hydrates of borax between the penta hydrate and the anhydrous salt is only partially solved.

The methods used in measuring dissociation pressures may be divided into three classes: static, dynamic and indirect. These will be discussed briefly under these headings.

STATIC METHODS

The static method was, of course, the first used. The early equipment consisted only of a barometer tube into which the sample was placed. The depression of the column was taken as the dissociation pressure. Debray (2), Lescoeur (3), Wiedemann (4) and Pareau (5) were among the early investigators to use this method. The chief error in these early experiments was that no attempt could be made to

eliminate adsorbed and occluded air from the specimen. Among the successful attempts to eliminate this difficulty are recorded the work of Frowein (6) who developed the Frowein Tensimeter, and modifications by Andreas (7), Schottky (8) and Menzies (9). Other methods of static character have been developed by Johnston (10), Bolte (11), and Frazer and Lovelace (12). All of these men adopted means of first boiling out the system and then allowing a confining liquid to reach equilibrium with the water vapor generated by the hydrate system on one side with a known pressure on the other side.

DYNAMIC METHODS

The first dynamic method was a diffusion method developed by Mueller and Erzbach (13). In this method, the rate at which water escaped from two identical flasks, one of which contained the hydrate, while the other contained pure water, both being placed in a desiccator, was taken as indicating the relation between the two vapor pressures.

Tammann (14) in 1897 introduced the air flow method. This consists of passing a known volume of dry air through the mixture of the hydrates and weighing the water absorbed by the air. Then

$$\text{Vapor pressure} = \frac{\text{gas. of H}_2\text{O absorbed} \times RT}{18 \times \text{vol. of air}}$$

This method has been brought to a high degree of refinement by Baxter and Lansing (15), Hightberger (16), and others.

This method has not been used on salts which are known to approach equilibrium slowly. This is a very slow method.

Johnston (17) in 1908 devised the isoteniscope method. This consists of trapping a liquid in a bulb, allowing it to boil for a time to remove gases and volatile impurities, and then permitting the temperature to fall until the pressure on each side of the trapping liquid is the same. The pressure read immediately gives the vapor pressure at the observed temperature. This method easily eliminates gases and is rapid. Smith and Menzies (18), and Derby and Yngve (19) have used this method on pure liquids with much success.

INDIRECT METHODS

Any indirect method does not measure the vapor pressure directly, but brings the hydrate system into equilibrium with a substance of known vapor pressure. The most common type is to balance the system in a desiccator with sulfuric acid. By varying the concentration of the sulfuric acid, its vapor pressure is varied. When equilibrium is obtained, an analysis of the acid will give the vapor pressure of the system. Mueller and Arzbach, and Tamann (14) and others have used this method successfully. Linebarger (20) first suggested obtaining equilibrium by shaking the hydrates with an excess of a liquid in which they are insoluble, but in which water is somewhat soluble. R. E. Wilson (21) and Noyes and Westbrook (22) have used this

method along with a conductimetric method of analysis.

THEORETICAL DISCUSSION

If some hydrated salts are exposed to the atmosphere a few will seem to crumble and deteriorate, others will remain apparently unchanged, while others may even form saturated solutions. The first and last transformations are of interest in the present research. In the first case, the salt loses its water of crystallization. In doing this, the loss does not take place all at once, but gradually. As the transformation proceeds, either a lower hydrate or the anhydrous salt is formed. This causes two hydrates (or one hydrate and the anhydrous salt) to be present. Considering now the transformation into the saturated solution, the hydrate takes on sufficient water to cause a part of it to go into solution. Left for a longer time, the entire mass will dissolve. Before this happens, there are present a salt hydrate and a saturated

solution of this hydrate. These characteristics of hydrated salts are dependent upon their vapor pressure.

Willard Gibbs (23) in 1878 gave to science his development of the Phase Rule. This has been expressed mathematically by $P + F = C + 2$

where P = number of phases present

F = degrees of freedom

C = number of components

In the light of this equation, let us examine the first system of hydrated salts just described. The phases present consist of the two hydrates and the vapor, making 3. The components are the anhydrous salt and water, making 2.

Substituting these values into the above equation we obtain

on solving for F $F = 2 + 2 - 3$

$$F = 1$$

This means there is only one independent variable. If the temperature is varied arbitrarily, all other variables, pressure, etc., will vary dependently. Thus the vapor pressure of a hydrate system is a function of the temperature.

The use of isothermal dehydration is a very effective tool in establishing which hydrates are in equilibrium. When a hydrate is dehydrated ever so slightly, the equilibrium is established because a second solid phase is at once formed. As long as these two phases are present and the temperature remains constant, the pressure will remain constant. If we plot the amount of water lost from a known weight of a hydrate as the abscissa and the pressure as the ordinate, we

should get a series of horizontal lines showing constant pressure separated by a series of vertical lines, each pressure line being lower than its predecessor. The drops mean that the last trace of the higher hydrate has disappeared and that a new system has been formed. By knowing the amount and which hydrate is present at the start, it is simple to calculate the existing hydrates of any salt.

Consider now the derivation of the Van't Hoff isochor equation upon which some very interesting calculations depend (24). It has been shown that

$$Tds = dE + pdV \quad (1)$$

By differentiating this equation with respect to volume at constant temperature we obtain for any isothermal process

$$p = T \left(\frac{\partial s}{\partial v} \right)_T - \left(\frac{\partial E}{\partial v} \right)_T \quad (2)$$

If we differentiate again with respect to temperature keeping the volume constant, we obtain

$$\left(\frac{\partial p}{\partial T} \right)_v = T \left(\frac{\partial^2 s}{\partial v \partial T} \right) + \left(\frac{\partial s}{\partial v} \right)_T - \left(\frac{\partial^2 E}{\partial v \partial T} \right) \quad (3)$$

Now, since the volume is constant

$$ds = c_v \frac{dT}{T} \quad (4)$$

which on rearranging gives

$$\frac{ds}{dT} = \frac{c_v}{T} \quad (5)$$

By differentiating (5) with respect to volume we obtain

$$\left(\frac{\partial^2 s}{\partial v \partial T} \right) = \frac{1}{T} \left(\frac{\partial c_v}{\partial v} \right)_T \quad (6)$$

It can be shown also that

$$\left(\frac{\partial E}{\partial T} \right)_v = c_v \quad (7)$$

which on differentiating with respect to T and V gives

$$\frac{\partial^2 E}{\partial T \partial V} = \left(\frac{\partial c_v}{\partial V} \right)_T \quad (8)$$

Then by substituting equations 6 and 8 in (3) we obtain

$$\left(\frac{\partial P}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T \quad (9)$$

In respect to the process of vaporization, the pressure p is independent of the volume. Also, we may replace the infinitesimal $\left(\frac{\partial S}{\partial V} \right)_T$ by the expression $\frac{\Delta S}{\Delta V}$ which refers to one mol of the substance in question. Hence, for the vaporization of any substance we have the relation

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} \quad (10)$$

Since the process is reversible

$$\Delta S = \frac{\Delta H}{T} \quad (11)$$

Substituting 11 in 10 we get $\frac{dp}{dT} = \frac{\Delta H}{T \Delta V}$ (12)

but $\Delta V = V_g - v_l$ (13)

The molal volume of a gas is very large in comparison to the molal volume of its liquid, and therefore may be disregarded without causing any appreciable error.

Equation (12) now becomes

$$\frac{dp}{dT} = \frac{\Delta H}{T V_g} \quad (14)$$

but $pV = RT$ (15)

$$v = RT/p \quad (16)$$

Since for pressures of less than one atmosphere (the pressures in this research were around 1/7 th of an atmosphere and less) practically all gases obey Boyles' Law quite closely, equation (16) may be substituted in equation (14) for V_g without destroying the validity of the equation. We obtain

$$\frac{dP}{dT} = \frac{\Delta H}{RT^2} \quad (17)$$

If now we can determine the variation of the vapor pressure with temperature, we have an equation by means of which we can calculate ΔH over a range of temperature. Solving equation (17) for ΔH we obtain

$$\Delta H = RT^2 \frac{dP}{dT} \quad (18)$$

The term activity has been defined by Lewis and Randall as

$$F_A = RT \ln a_A + C_A \quad (19)$$

From this we can obtain the change of free energy in going from a state where A has an activity of a to a state where A has an activity of a' by the equation

$$\Delta F_A = RT \ln a'/a \quad (20)$$

Consider any reaction



in which all substances are in a state such that their activity is a . Then

$$F_A = RT \ln a_A \quad (22)$$

$$F_B = RT \ln a_B \quad (23)$$

and so forth. Then

$$\Delta F_a = RT \ln \frac{a_c^c a_D^d}{a_A^a a_B^b} \quad (24)$$

Consider the same reaction occurring in a state such that all substances have an activity of a' . Then, similarly

$$\Delta F_{a'} = RT \ln \frac{a_C^c a_D^d}{a_A^a a_B^b} \quad (25)$$

The change in free energy for the reaction taking place at two different activities will then be

$$\Delta F_a - \Delta F_{a'} = \Delta F = RT \ln \frac{a_c^c a_D^d}{a_A^a a_B^b} - RT \ln \frac{a_c'^c a_D'^d}{a_A'^a a_B'^b} \quad (26)$$

Now if we consider the reaction as carried out in the first stage with an activity of a as the reference point, or, as we say all substances are in their standard state, their activities will be unity and equation (26) will become

$$\Delta F = -RT \ln \frac{a_c^c a_D^d}{a_A^a a_B^b} \quad (27)$$

Let us now look at a concrete example, the reaction involved in this research. It is



In this equation the two hydrates are solids and are therefore in their standard states, their activities being unity. For this reaction, equation (27) will reduce to

$$\Delta F = -RT \ln a_{\text{H}_2\text{O}}^5 \quad (29)$$

If we consider the reaction taking place with the evolution of only one mol of water vapor, then

$$\Delta F = -RT \ln a_{H_2O} \quad (30)$$

Since we are operating at less than one atmosphere, as stated before, the activity of the water vapor may be considered identical with the equilibrium pressure of equation (28) since activity is equal to the ratio of the fugacities. This ratio for practically all gases at or below one atmosphere is unity. Equation (30) now becomes

$$\Delta F = - RT \ln p \quad (31)$$

From our vapor pressure measurements can now be calculated two important thermodynamic functions, ΔH and ΔF for the reaction. Knowing these two quantities it is possible to calculate the entropy change of the reaction by

$$\Delta S = \frac{\Delta H - \Delta F}{T} \quad (32)$$

Also, ΔE , the heat absorbed when the reaction occurs at constant volume can be calculated from

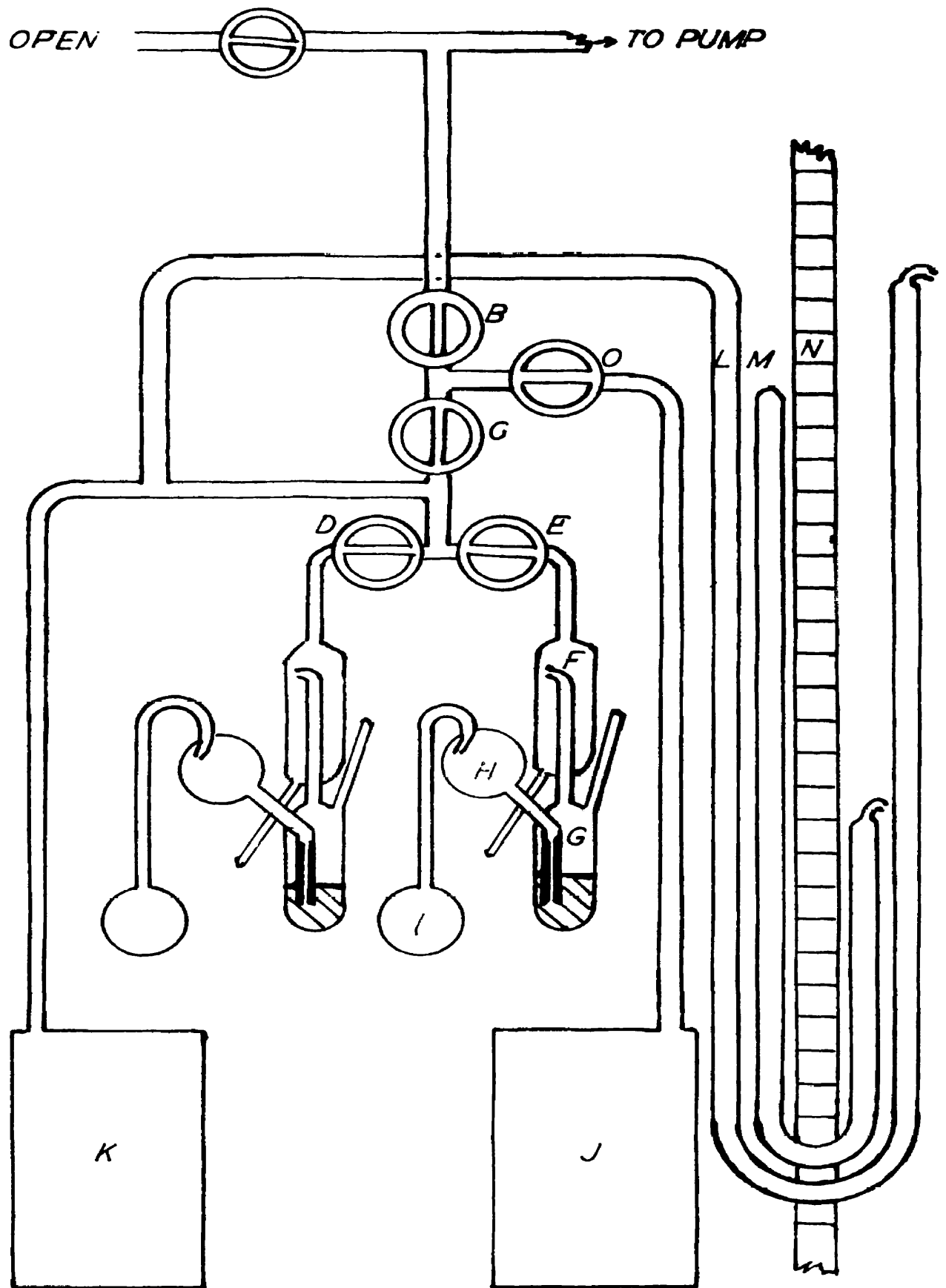
$$\Delta E = \Delta H - \Delta nRT \quad (33)$$

where Δn is the change in the number of mols of gas during the reaction. If we can find the rate of change of ΔE with temperature we have a value which is equivalent to ΔC_v , the change of heat capacity of the reaction at constant volume. Similarly, the rate of change of ΔH with temperature will give values of ΔC_p . These can both be obtained by plotting the desired function against temperature and taking tangents to the curve at various points.

METHOD AND APPARATUS

For the work at hand we desired a range of temperature of from 25°C to about 80°C. Previous work by Hignberger (16), carried out in this laboratory, had demonstrated that the air flow method was not satisfactory for temperatures of 50°C and above. Therefore, another method had to be obtained. A method that was rapid, allowed for the elimination of absorbed air, and one giving pressure readings good to at least one tenth of a millimeter over the range was desired. After searching the literature the isoteniscope method used by Smith and Mensies (18) seemed to fit our purpose. The method as carried out by these men involved a constant pressure and a variable temperature. It was considered better for this problem to maintain a constant temperature and operate by varying the pressure. With this in view the apparatus was set up as shown diagrammatically in the accompanying sketch - Fig. I. The glass parts of the apparatus were made of pyrex. Bulbs F and G were about 25 mm. in dia. Into G was sealed a capillary tube of 1 mm. bore. Before sealing this in, a line was etched around it near the middle. Bulb H was used as a trap to prevent the confining liquid in G from being drawn back into the sample, which was contained in bulb I. Bulb F served as a trap to prevent condensed water vapor from flowing back into the

FIG 1.
ISOTENISCOPE



confining liquid and changing its volume. These made up the isoteniscope bulbs. Two of these were made as nearly alike as was convenient and connected to stop cocks D and E. This provided for checking the data on a separate piece of equipment which was nearly identical with the first. K was in the system continuously for the purpose of increasing the capacity of the system, thereby increasing the sensitivity. K was a 55 lb. ether drum. J was a similar drum which was completely evacuated and used for fine adjustment by sucking out small portions of air from the rest of the system. K was connected to an open mercury manometer L. L and a mercury barometer M were mounted on the brass scale of a Cenco College Grade Boyles' Law apparatus N. On the scale was mounted a spring slider carrying a mirror which had a black hair line on it. The slider also carried a vernier for reading to tenths of a millimeter. The open ends of both the manometer and barometer were protected from dirt by turned down tips. The manometer and barometer were constructed from the same bore pyrex tubing, the latter being thoroughly boiled out after filling.

Both of the isoteniscope bulbs were immersed in a water bath of about 12 gals. capacity nearly to stop cocks D and E. The bath was well stirred. It was heated with two Anlaco Lomag heaters. One of these heaters was connected through a mercury thermoregulator and an Anlaco Super Sensitive Relay to the 110 volt power supply. The

other was connected through a variable rheostat directly to the power line. This latter one was used as a continuous heater keeping the temperature a few degrees below the desired point. The bath temperature was read by means of a calibrated 5 junction thermocouple, made from Driver Harris No. 24 cotton covered wire labeled Ideal and Comet. The potential was read on a Leeds and Northrup student double range potentiometer. For higher temperatures than about 50°C the bath was covered with a layer of melted paraffin to decrease the heat losses by evaporation.

The method used in making the determinations was as follows: Into bulb G was placed dibutyl phthalate until the capillary rise coincided with the etched line on the capillary. This method of filling insured atmospheric pressure both on the capillary and on the body of the liquid which insured pressure equilibrium when the liquid was later adjusted to this same mark. Dibutyl phthalate was chosen as a confining liquid because of its low specific gravity (about 1.01) and because of its very low vapor pressure. At room temperature its vapor pressure is less than that of mercury. Its rate of increase is a little more than that of mercury. The extension tube was then sealed off. The bulb was then immersed in water, with provision for all surfaces of the phthalate to be at atmospheric pressure, at 25°C. The temperature was then raised to the boiling point of water. The meniscus was observed with a cathetometer to find out if any change occurred in the relation of the

meniscus to the etched line on the capillary on change of temperature. The construction of the apparatus was such that the meniscus always coincided with the etched line over the temperature range employed. Some deca and penta hydrates of borax (it was later found that the penta was not needed) were ground together and placed in bulb I which was then sealed in place. With the bath temperature adjusted and the bulbs in thermal equilibrium with the bath, the entire system was evacuated until, with the pump turned off, a continuous stream of bubbles flowed out of the capillary in G. This allowed all of the air to be washed out of bulbs I and H. After some time - perhaps an hour or longer - of boiling out, air was admitted into the system through B, C, E with O closed. If too much air was admitted, O was opened and a little drawn out, J having been previously completely evacuated. In this manner the pressure in K was adjusted so that the height of the liquid in the capillary of G again coincided with the etched line. After being sure that I was at thermal and pressure equilibrium - determined by whether there was any movement of the meniscus in the capillary on standing some time - the pressure in I, which was the vapor pressure of the hydrate system, was equal to the manometric pressure. By reading both the manometer and the barometer at the same time on the same scale, all corrections except temperature were eliminated as negligible, and the difference between the two gave the value of the vapor pressure.

MATERIALS USED

The borax used was the finest sodium tetraborate decahydrate obtainable from Mallinckrodt Chemical Company. This was further purified by recrystallization from water at 50°C. The penta hydrate was prepared by recrystallization of the same stock material at the temperature of boiling of its saturated solution. Both were analyzed by fusion in a platinum crucible and found to be the pure hydrates. They were stored in well stoppered bottles from which they were taken and ground as needed.

The dibutyl phthalate used as a confining liquid was obtained from the Eastman Kodak Company and used as received. It had a boiling point range of from 203° to 208°C at 20 mm. pressure.

The mercury used in the manometer and barometer was washed 5 times through a solution of $\text{HNO}_3 + \text{HgNO}_3$. This washed material was then distilled in a current of air according to Hulett and Minchin (25). The distilled product was filtered through a pin hole directly into the desired tube.

THE DATA

In order that the temperature of the bath could be accurately read, the thermocouple had to be calibrated. The most sensitive method of calibration is one in which a very large change in a property occurs for a very small change of temperature. The variation of the property with temperature must be known to a high degree of precision. It was decided that the vapor pressure of pure water was the most sensitive property available for our use. The variation of this property of water with temperature has been very carefully worked out. It gave the degree of sensitivity desired for the calibration of the thermocouple. This was done by placing twice distilled water in the bulb of the isoteniscope. The thermocouple - the junctions being immersed in dibutyl phthalate - was placed directly beside the bulb being used. The vapor pressure was read as described previously, and the potentiometer was read. All readings were checked on each bulb. The pressure readings could be checked to ± 0.05 mm., and the potentiometer readings could be checked to ± 0.002 m.v. Similar data was then obtained on the other bulb. It was observed that the thermometer in the bath had a variation of $\pm 0.02^{\circ}\text{C}$. Some of this variation was probably due to drafts on the long stem of the thermometer. Since the sample was encased in glass and not stirred, and since on standing under continual

observation at equilibrium the meniscus in the apparatus did not show change, it was considered that the thermometer variation did not show the variation in the sample, and that the sample did not vary in temperature nearly as much, but was at the mean temperature of the bath. This condition should be true for the thermocouple too. To find what variation there was in the thermocouple, the standard cell was checked upon and a reading of the thermocouple was made every three minutes over a period of an hour. This was done at all points in the calibration. Each of the readings has in it the possibility of error in the actual temperature of the bath and also error in setting the instrument. A typical example of these readings is given in Table I.

Table I
Variation in bath temperature at 66.3°C

Millivolts	Deviation from Mean	M.V.	Deviation from Mean
12.879	-.0053	12.886	+.0017
12.884	-.0003	12.886	+.0017
12.884	-.0003	12.886	+.0017
12.886	+.0017	12.884	-.0003
12.884	-.0003	12.885	+.0007
12.884	-.0003	12.884	-.0003
12.888	+.0037	12.884	-.0003
12.888	+.0007	12.882	-.0023
12.885	+.0007	12.885	+.0007
12.883	-.0013	12.883	-.0013

The average of the deviations is ± 0.001 which is less than can be read on the potentiometer. As stated before, this

instrument could be read to ± 0.002 for certainty. In view of this, then, it is quite safe to say the variation of the bath is $\pm 0.01^{\circ}\text{C}$. Having now 2 pressures and 2 millivolt readings on each bulb, the pressures were corrected to mercury at 0°C . The 4 readings were then averaged, as were the potentiometer readings. By use of the vapor pressure tables for water in the International Critical Tables the temperature corresponding to the averaged pressure was obtained. This was done for bath temperatures between 25°C and 66°C . These values gave precise temperatures for the calibration of the thermocouple. Calibration data is given in Table 2.

Table 2

Calibration of Thermocouple

Temperature in $^{\circ}\text{C}$	Thermocouple readings in Millivolts
24.90 $^{\circ}\text{C}$	4.552 mv.
35.01	6.534
45.30	8.561
56.84	10.672
66.59	12.877

Because of the size of paper required to graph this data with the same precision as the readings, it was thought advisable to use an equation instead. The data was then used in obtaining the following equation:

$$t^{\circ}\text{C} = 1.065 + 5.318V - 0.018V^2 \quad (34)$$

The thermocouple was then tested for hysteresis and none was found.

Having now calibrated the temperature measuring equipment, the bulbs of the isoteniscope were charged with a mixture of the ground deca and penta hydrates of $\text{Na}_2\text{B}_4\text{O}_7$. In obtaining this data the same procedure was followed: the bulb was boiled out and allowed to come to thermal and pressure equilibrium. When two successive readings checked on the same bulb to ± 0.05 mm. and the potentiometer readings checked to ± 0.002 mv. the second bulb was used and checked in the same manner. Averaging the four corrected pressures (corrected to mercury at 0°C) and the four millivolt readings, the temperature was obtained by equation (34). The data for this hydrate system is given in Table 3.

Table 3

P-T Variation of the Hydrate System

Temperature in $^\circ\text{C}$	Pressure in mm. of Hg at 0°C .
29.876 $^\circ$	20.99 mm.
46.090	61.76
52.167	90.02
59.523	138.66

For the benefit of future calculations this data was put into an equation which took the form of

$$p = - 43.603 + 4.26445t - 0.120899t^2 + 0.00169174t^3 \quad (35)$$

where t is $^\circ\text{C}$ and p is mm. of Hg at 0°C . This data is plotted in Fig. 2. The work by D. P. Hightberger (loc.cit.) by the air flow method and the early work in this thesis

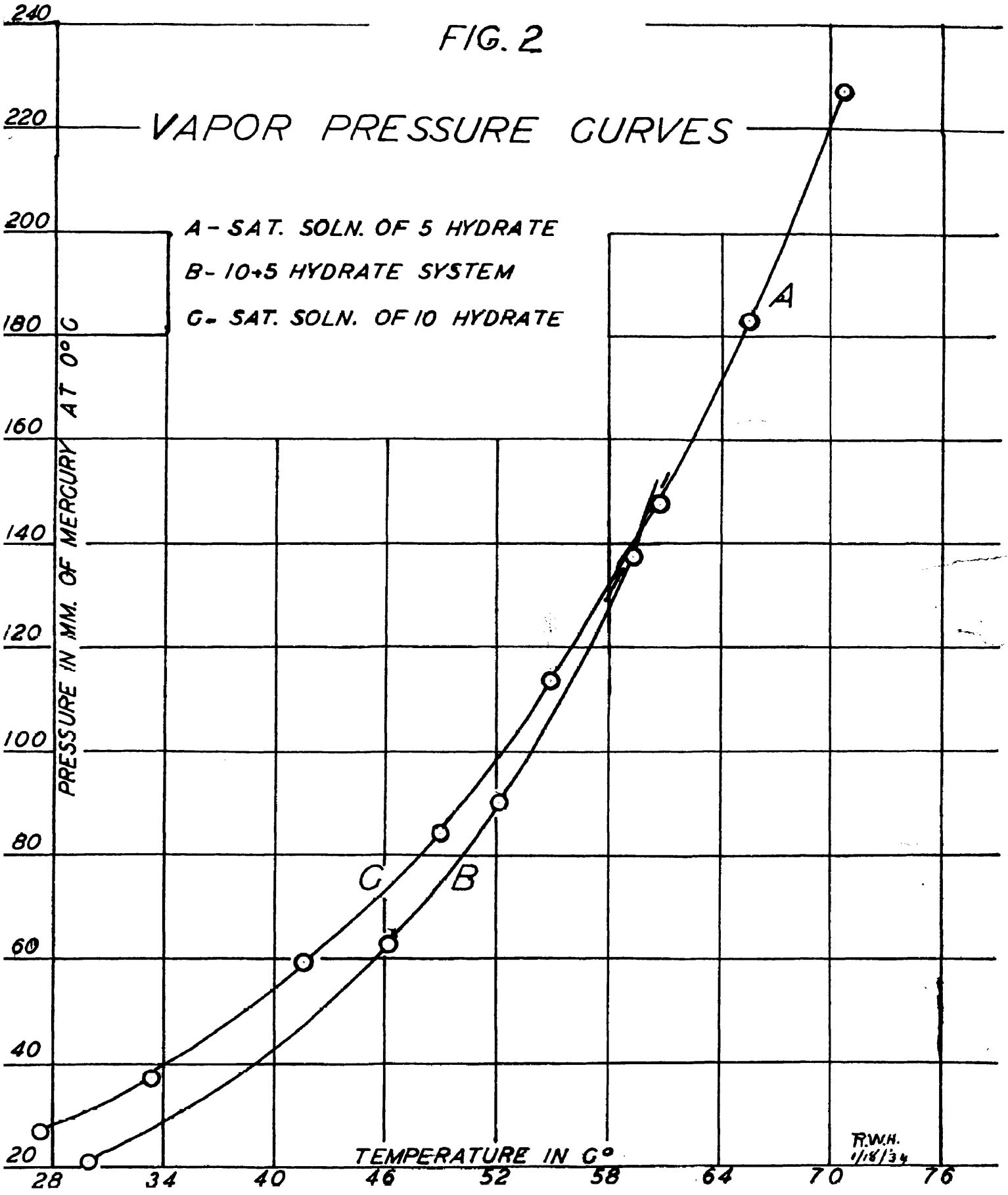
FIG. 2

VAPOR PRESSURE CURVES

A - SAT. SOLN. OF 5 HYDRATE

B - 10+5 HYDRATE SYSTEM

C - SAT. SOLN. OF 10 HYDRATE



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by the isoteniscope method wherein both cases thermometers were used for measuring temperature were in agreement within experimental error. This last data, using a thermocouple, gave a curve slightly higher but parallel to the previous work.

In order to be sure that the deca hydrate of borax and the penta hydrate were in equilibrium with each other, the apparatus was modified slightly and an isothermal dehydration of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ was carried out. In place of one of the sample bulbs was placed a ground glass joint, one end of which carried a small bottle which could be placed on the balance and weighed. A weighed sample of the deca hydrate of borax was placed in this bottle. This was then placed on the isoteniscope and boiled out for a considerable time. A pressure reading was taken in the usual way after equilibrium had been reached and the bottle taken off after the pressure in it had been brought back to atmospheric, capped and weighed. The temperature at which this was carried out was 45.459°C . After many such readings the loss of H_2O was plotted against the pressure. Several runs of this type were made. Minor changes had to be made in the apparatus to overcome experimental difficulties which developed. At very low pressures the dibutyl phthalate invariably bubbled over into the sample bottle causing the loss of the run. Because of the lack of time, this study was not carried much beyond the first break in the curve. The time required for the sample to come to

equilibrium at this very low pressure was exceedingly long. Since the pressure is so very low at this rather high temperature, it seems unlikely that any hydrate of borax exists below the penta hydrate. In other words, the penta hydrate exists in equilibrium with the anhydrous salt. The data is given in Table 4 and is plotted in FIG. 5.

Table 4

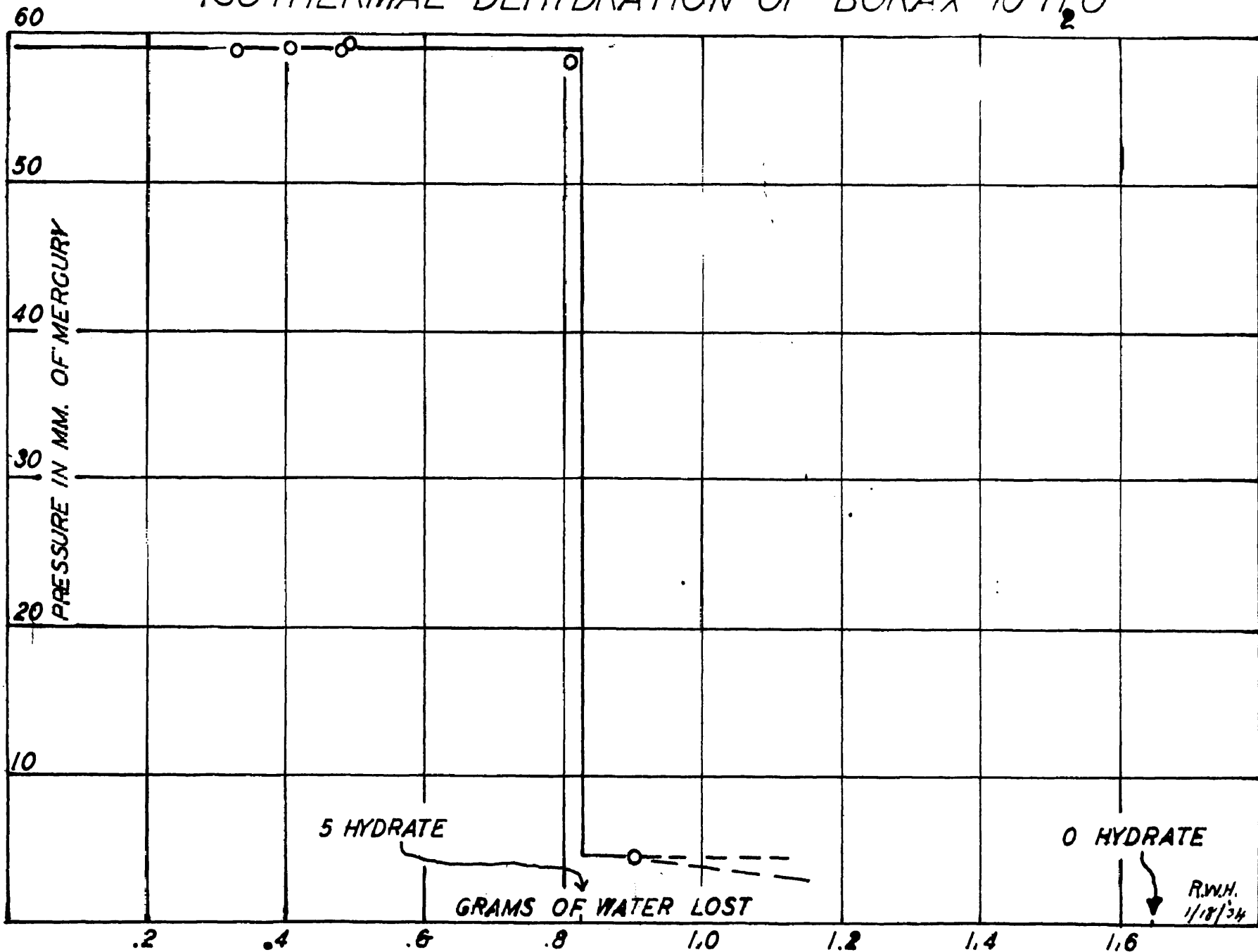
Isothermal Dehydration of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
at 45.489°C .

Grams of H_2O Lost	Pressure in mm. of Hg at 0°C
0.333	58.7
0.408	58.8
0.480	58.8
0.490	59.4
0.808	59.1
0.901	4.5
?	4.5
?	4.3

A very careful consideration of all possible buoyancy corrections led to the conclusion that this weight correction was negligible for this work.

In previous work it was observed that if the temperature of the penta - deca hydrate system rose to above 61°C the sample became sticky indicating liquid formation. Knowing this it was decided to run the vapor pressure curve of the saturated solution of the penta hydrate. This curve should intersect the curve for the penta - deca hydrate system at the transition point of the system. This curve was obtained with the same

FIG. 3
ISOTHERMAL DEHYDRATION OF BORAX 10 H₂O



technique and apparatus as was used for the curve of the hydrate system. To be sure of the solution being saturated, a saturated solution was made up in a beaker at a temperature higher than that at which the run was to be made and allowed to crystallize in the bath at the highest temperature desired in the run. This point was determined first. Each successive lower temperature was taken in order. This insured the liquid being at all times in equilibrium with the solid hydrate and saved time in waiting for saturation to be reached. This data is given in Table 5 and is plotted on Fig. 2.

Table 5

P-T Relation of Saturated Solution of Penta Hydrate of Borax

Temperature in C°	P in mm. of Hg at 0°C
60.875°	147.94 mm.
65.729	163.49
70.779	227.51

Thermodynamics requires that the saturated solution curve of the deca hydrate shall intersect the saturated solution curve of the penta at the same point at which this latter curve intersects the dissociation curve of the penta hydrate - deca hydrate system. To check up on this point, the vapor pressure curve of the saturated solution of the deca hydrate of borax was determined in the same manner as before. This data is given in Table 6 and is plotted on

Fig. 2.

Table 6

P-T Data of Saturated Solution of 10
Hydrate of Borax

Temperature in C°	P in mm. of Hg. at 0° C
27.349°	26.93 mm
33.436	37.38
41.788	59.34
48.791	84.53
55.117	113.96
59.180	137.75

By plotting these curves on especially large paper all were found to intersect at $60.3^{\circ} \pm 0.2^{\circ}\text{C}$. This is the transition point of the deca hydrate into the penta hydrate.

CALCULATIONS AND ERRORS

In the theory of this paper was derived an equation (13) by means of which ΔH could be calculated.

The equation is
$$\Delta H = \frac{\frac{dp}{dt} RT^2}{p} \quad (13)$$

By differentiating equation (35) with respect to t we obtain

$$dp/dt = 4.26445 - 0.241798t + 0.00507528t^2 \quad (36)$$

Also, by equation (35) we can calculate the vapor pressure for any desired temperature. With these values it is an easy matter to calculate ΔH for the reaction



This was done, the data being given in Table 7 and being plotted in Fig. 4. A glance at this curve shows it to be very unusual. A detailed discussion of all experimental errors and their propagation will follow. The one errorless factor was necessarily considered to be the vapor pressure tables of pure water in the International Critical Tables which were used for calibration. These had to be considered as absolute. In the calibration of the thermocouple, the error of ± 0.05 ma. in reading the manometer and the error of ± 0.002 mv. in reading the potentiometer give an accumulative error in the temperature. This accumulated error can be calculated by the equation

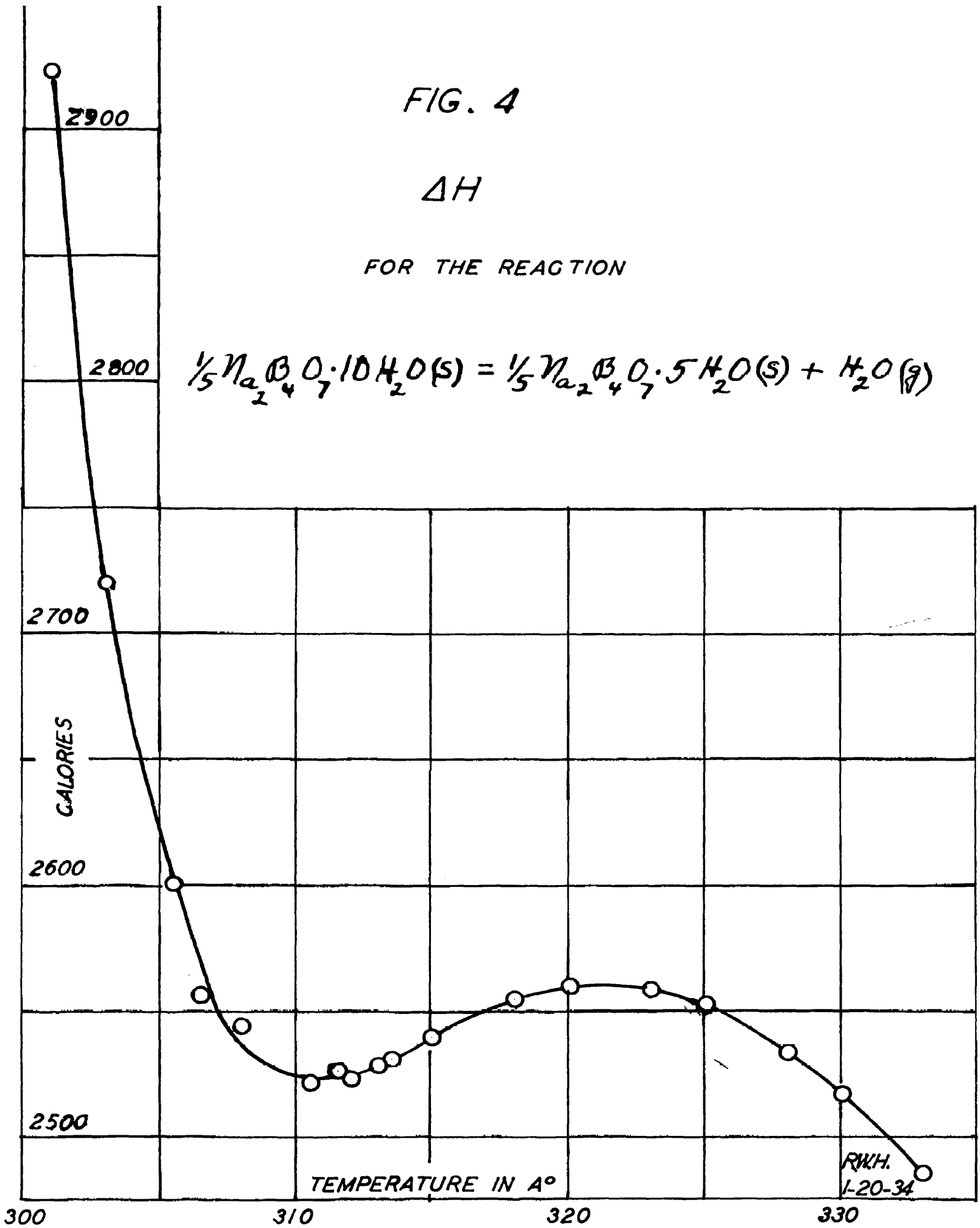
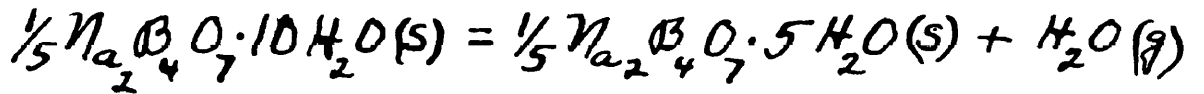
$$\text{Final error in } t = \sqrt{(\frac{dt}{dv})^2 (\text{error in } v)^2 + (\text{error in reading } p)^2} \quad (38)$$

or

FIG. 4

ΔH

FOR THE REACTION



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$$\Delta = \sqrt{\left(\frac{dt}{dv}\right)^2 (.002)^2 + (.06)^2} \quad (39)$$

This gives an average error in t of $\pm 0.013^\circ$ over the range used. Next, there is an error in the pressure due to the error in t and also due to the error in reading the manometer. This accumulated error in pressure can be calculated by an equation of the same form as was used above (38). These values are:

at 30°C the error in $p = \pm 0.043$ mm.
 at 45°C the error in $p = \pm 0.051$
 at 60°C the error in $p = \pm 0.090$

The error in dp/dt was calculated similarly for the same range of temperatures. These errors range from ± 0.001 to ± 0.007 . Considering all of these errors, and considering the constant H to be errorless (the error in the absolute temperature T was found to be negligible) the fractional error in ΔH can be calculated by the equation

$$\frac{\Delta}{\Delta H} = \sqrt{\left(\frac{\Delta}{P}\right)^2 + \left(\frac{\Delta dp}{dt}\right)^2} \quad (40)$$

where Δ is the error in each function just mentioned above. Calculating these fractional errors and transforming them into absolute errors, we find the error in ΔH for reaction (37) as written to be

Error in ΔH at $30^\circ\text{C} = \pm 6$ cal
 Error in ΔH at $45^\circ\text{C} = \pm 3$ cal
 Error in ΔH at $60^\circ\text{C} = \pm 2$ cal

In calculating these errors every opportunity was used

to increase rather than decrease the error. Upon examination of these errors and of the curve it is plain that even if the error as calculated were to be tripled, it would not account for the variation in the curve. If this curve were due to the experimental error, it would hardly be possible to draw a smooth curve through all of the points. As it is, all of the points lie on a smooth curve with the exception of one or two which are accounted for by the calculated error.

In calculations of not too great precision ΔH is ordinarily considered to be constant over a small range of temperature. For more precise calculations, its variation for many substances and reaction is found to be gradual. The equation for expressing this variation is obtained by integrating the equation

$$\left(\frac{d\Delta H}{dt}\right)_p = \Delta C_p \quad (41)$$

Suppose we consider the reaction



Let the variation of the specific heat with temperature of each constituent of reaction (42) be represented by

$$C_{pA} = l_1 + m_1T + n_1T^2 + o_1T^3 + \text{-----} \quad (43)$$

$$C_{pB} = l_2 + m_2T + n_2T^2 + o_2T^3 + \text{-----} \quad (44)$$

$$C_{pC} = l_3 + m_3T + n_3T^2 + o_3T^3 + \text{-----} \quad (45)$$

$$C_{pD} = l_4 + m_4T + n_4T^2 + o_4T^3 + \text{-----} \quad (46)$$

The total change in heat capacity for the reaction (42) is then

$$\Delta C_p = C_{pC} + C_{pD} - C_{pA} - C_{pB} \quad (47)$$

Putting equations (43) to (46) inclusive in their proper places and combining all like terms we obtain

$$\Delta C_p = \Delta l + \Delta nT + \Delta nT^2 + \Delta eT^3 \quad (48)$$

By substituting equation (48) in equation (41) for ΔC_p and integrating, placing the term ΔH_0 in place of the constant of integration (meaning that this is the value of ΔH if the reaction could be carried out at 0°A) we obtain

$$\Delta H = \Delta H_0 + \Delta lT + \frac{1}{2} \Delta nT^2 + \frac{1}{3} \Delta nT^3 + \frac{1}{4} \Delta eT^4 \quad (49)$$

This equation should fit the experimental curve. There must be some phenomenon causing this variation in the heat capacities of the solids which in turn causes the variation in ΔH . It was thought that there might be a change of crystal structure at about 35°C, where the break in the curve occurs. In an endeavor to confirm this, borax was crystallized on microscope slides at 45°C and 20°C. Photomicrographs were made of each, and each was examined under a polarizing microscope. These examinations, since the rate of crystallization had to be considered effecting the outward appearance of the crystal, did not show any difference between the two crystals. It was then decided that the difference might not be of sufficient magnitude to be shown by these methods, so some X-ray

pictures - by the powder method - were taken. The samples, as before, were crystallized at 45°C and 20°C, ground up and mixed with Duro cement. After a technique had been acquired, two sufficiently good pictures were obtained. After the necessary calculations had been carried out, all the lines on each film checked each other within the limits of error of the experiment. This showed the two crystals to be of the same structure so far as the atoms reflected the X-rays. The only other influencing factor not yet considered was the variation in the specific heat of the constituents. This variation for water is very well known. However, for the two hydrates, nothing reliable could be found. It seems most probable that the combination of the heat capacities of the solid constituents of this reaction would account for the variation in this function. This phase of the work is being carried on in this laboratory in order to try to find the reason for the shape of this curve. It should be pointed out, however, that the work with the microscope and the X-ray was more or less crude. It is possible that expert technicians with these two tools might be able with more refined apparatus to show some difference between crystals made at these two temperatures. In all previous work, authors of papers have used the method of plotting $\log p$ against $1/T$ to obtain ΔH . By multiplying the slope of the above

mentioned curve by $2.3026 p/RT^2$ the value of ΔH is obtained. This method is not nearly as accurate as the one used in this paper. In the first place, if a large range is required it is impossible to obtain large enough graph paper so that the plot may be made with the same degree of precision as the data. Secondly, the methods of obtaining tangents to nearly straight lines are very inaccurate. If one can obtain a precision of ± 200 calories by the above method one is lucky. The above data was plotted in this way and an essentially straight line was obtained. The value of ΔH by this method was about the mean of the calculated values - 2573 cal. Calculations in earlier work by this tangent method showed similar variations which were attributed to errors in the method. After carefully considering all possible errors, the curve appears to be authentic and to indicate a phenomenon not yet known is operating in the system.

By equation (31) the value of ΔF for the reaction was calculated. This is given in Table 7 and is plotted in Fig. 5.

By means of equation (32), ΔS was calculated. This data is given in Table 7 and is plotted in Fig. 6. This curve is quite peculiar also, the break being at about the same temperature as the break in the ΔH curve. The same

explanation will no doubt apply to both curves.

By means of equation (33) ΔE was calculated. This data is tabulated in Table 7 and plotted in Fig. 7. As to be expected, this curve resembles the ΔH curve.

By reading the slopes of the ΔH and ΔE curves with a tangent meter values of ΔC_p and ΔC_v were obtained. These values are tabulated in Table 8 and plotted in Fig. 8.

Table 7

Values for the Reaction



No.	t °C	T °A	P in mm.	P in atm.	ΔH calcs.	ΔF calcs	ΔE calcs	ΔS calcs/deg.
1	33.0	301.1	18.15	.02300	+2923	+2934	+2325	2.29
2	30.0	303.1	21.20	.02789	2719	2156	2116	1.85
3	32.5	305.6	25.22	.03318	2600	2068	1994	1.74
4	33.5	306.6	27.18	.03576	2556	2029	1948	1.62
5	35.0	308.1	30.09	.03958	2524	1977	1913	1.62
6	37.5	310.6	35.49	.04668	2521	1891	1905	2.03
7	38.5	311.6	37.92	.04984	2526	1857	1907	2.15
8	39.0	312.1	39.17	.05154	2523	1839	1904	2.19
9	40.0	313.1	41.81	.05501	2528	1804	1906	2.31
10	40.5	313.6	43.18	.05813	2530	1773	1908	2.41
11	42.0	315.1	47.57	.06260	2539	1735	1913	2.55
12	45.0	318.1	57.64	.07583	2554	1630	1922	2.90
13	47.0	320.1	65.40	.08695	2559	1560	1924	3.12
14	50.0	323.1	73.34	.10373	2558	1455	1917	3.41
15	52.0	325.1	89.11	.11724	2552	1383	1906	3.59
16	55.0	328.1	106.69	.14037	2553	1280	1882	3.82
17	57.0	330.1	119.97	.15785	2516	1211	1861	3.95
18	60.0	333.1	142.45	.18742	2484	1108	1824	4.13

Table 8

Variation for the Reaction



$T^\circ\text{A}$	ΔC_p calz.	ΔC_v calz
302		-104.00
304	-52.80	- 59.20
306	-36.80	- 46.40
308	-10.40	- 10.72
310	+ 0.96	- 2.92
312	+ 3.56	+ 1.12
314	+ 6.60	+ 3.28
316	+ 8.88	+ 4.64
318	+ 8.52	+ 1.92
320	+ 1.68	- 0.64
322	- 1.04	- 2.64
324	- 3.28	- 5.36
326	- 5.20	- 7.36
328	- 7.12	- 9.44
330	- 9.12	- 11.36
332	-11.68	- 12.96

FIG. 5

ΔF

FOR THE REACTION

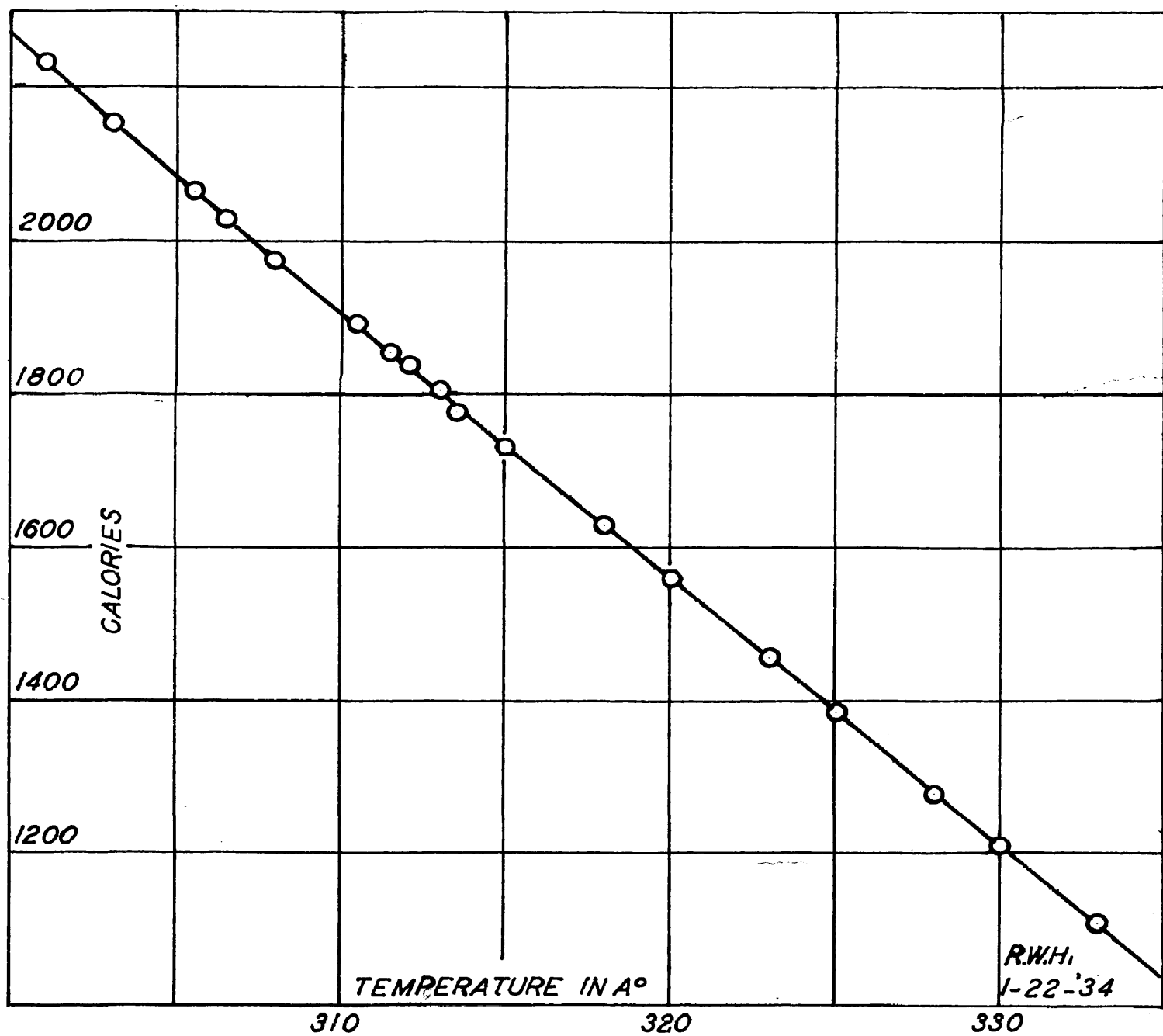
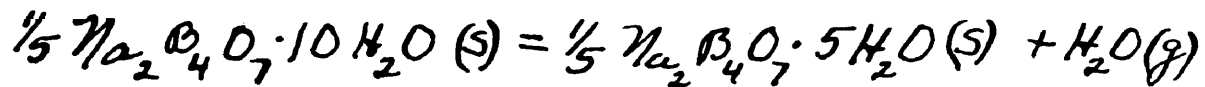


FIG. 6

ΔS

FOR THE REACTION

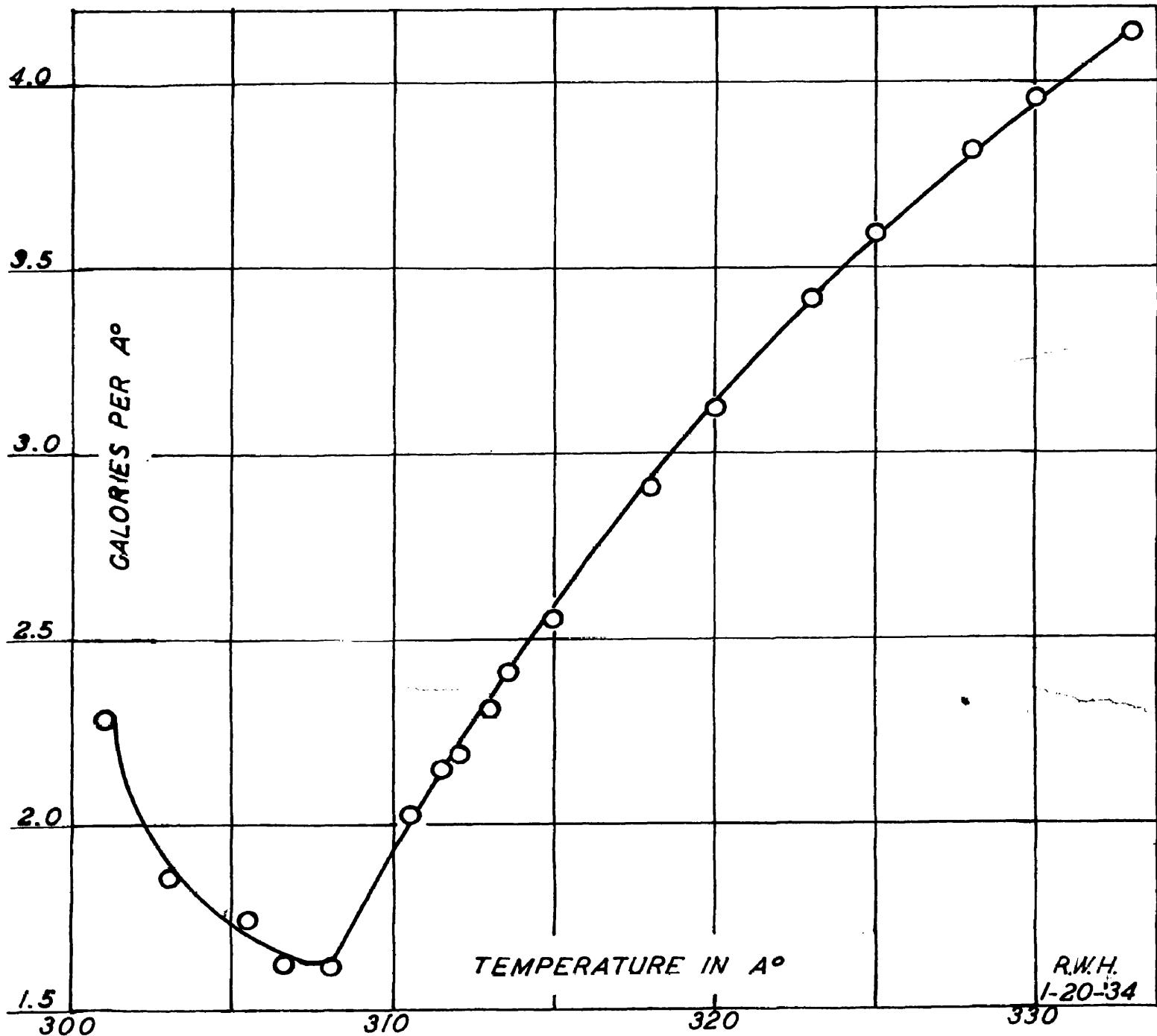
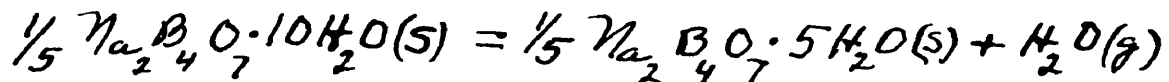


FIG. 7

ΔE

FOR THE REACTION

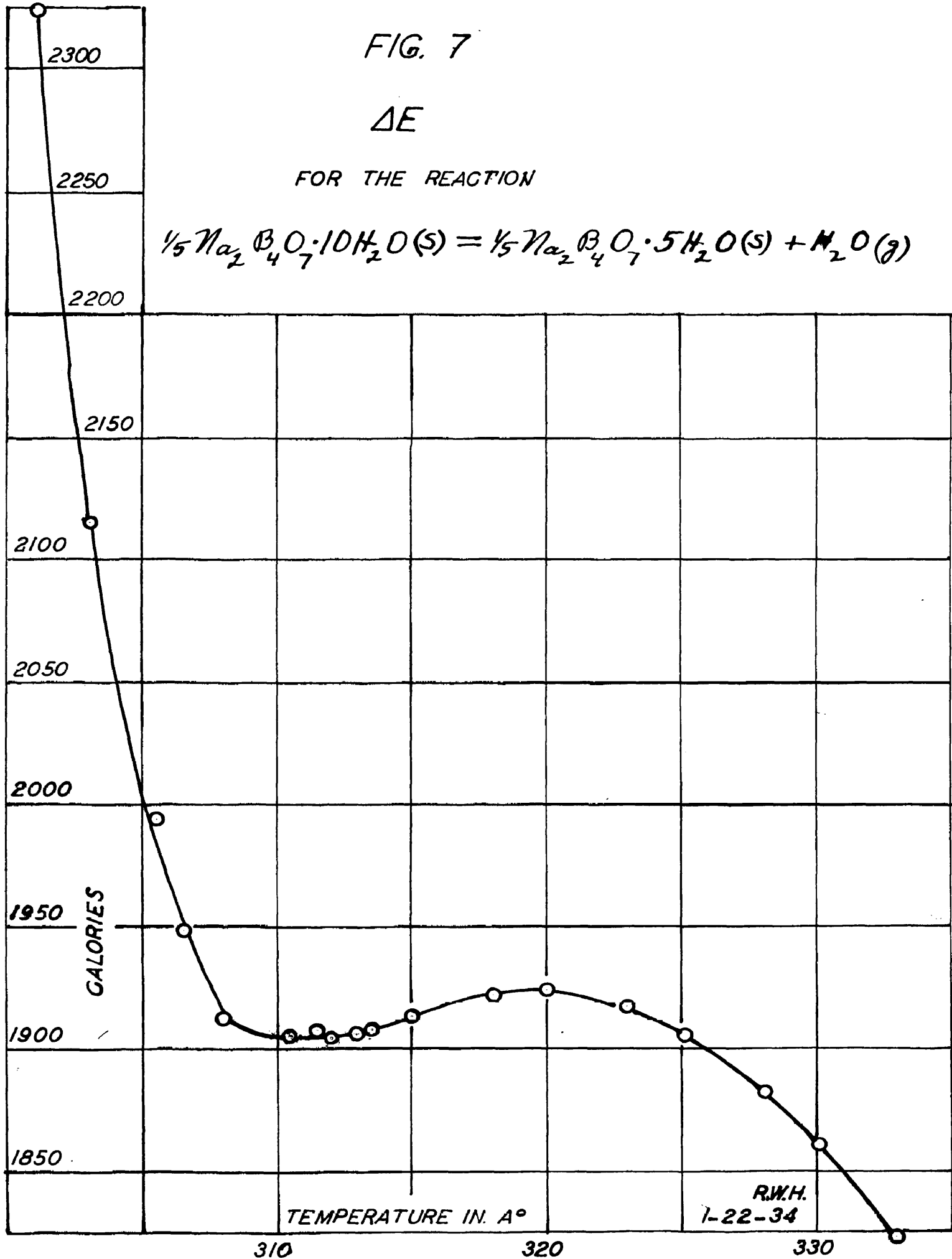
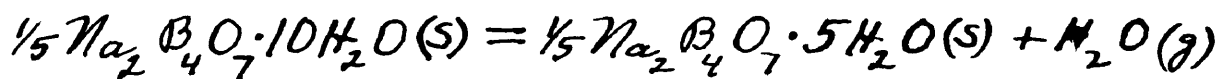
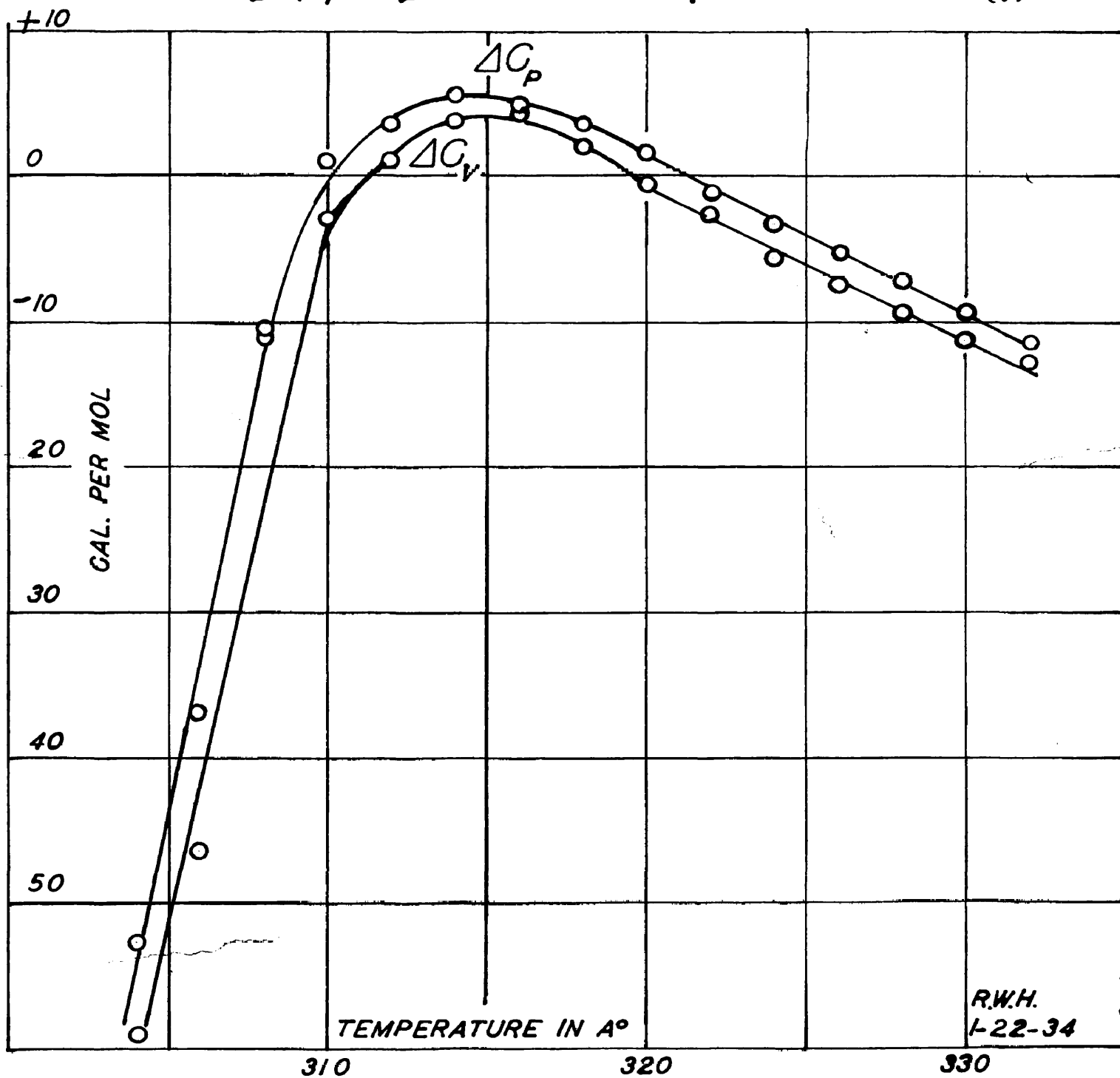


FIG. 8

ΔC_p & ΔC_v
FOR THE REACTION



SUMMARY

1. The vapor pressure variation with temperature of the system deca hydrate of borax in equilibrium with the penta hydrate of borax has been studied between 30°C and 60°C. It is represented by the equation

$$p = - 43.603 + 4.26445t - 0.120399t^2 + 0.00169174t^3$$

2. The vapor pressure variation with temperature of a saturated solution of the penta hydrate of borax has been studied between 60°C and 70°C.
3. The vapor pressure variation with temperature of a saturated solution of the deca hydrate of borax has been studied between 30°C and 60°C.
4. The intersection of the three vapor pressure curves, and consequently the transition point of the deca hydrate was obtained and found to be 60.3°C \pm 0.2°.
5. The thermodynamic values of ΔH , ΔF , ΔE , ΔS , ΔC_p , ΔC_v have been calculated for the reaction
$$\frac{1}{5} Na_2B_4O_7 \cdot 10H_2O(s) = \frac{1}{5} Na_2B_4O_7 \cdot 5H_2O(s) + H_2O(g)$$
6. A peculiar variation in the ΔH curve for the reaction was obtained which has not yet been accounted for, but more work is being carried out in this laboratory in an attempt to find the explanation.

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