A THESIS ON

THE HEAT OF FUSION OF IODINE

and

THE USE OF LIQUID IODINE AS A SOLVENT IN DETERMINING MOLECULAR WEIGHTS

Respectfully submitted by

Kenneth H.Barnard

May 20th. 1912.

Under the direction of Dr.F.G.Keyes of the

Research Laboratory of Physical Chemistry.

Outline.

9/5-83

The Heat of Fusion of Iodine and the Use of Liquid Iodine as a Solvent in Determining Molecular Weights.

The following thesis is a record of attempts made to determine the molecular weight of potassium iodide when dissolved in liquid iodine by examining the resulting freezing point lowering; as well as an accurate determination of the latent heat of fusion of iodine itself. This work is closely connected with that of Dr. G.N.Lewis on the conductivity of potassium iodide in liquid iodine and his work may be summarized in the following interesting plot.

(Note. This plot may be found at the end of this thesis.)

It is evident that the conductivity changes with a change in the concentration of the potassium iodide and so a study of the condition of the potassium iodide in liquid iodine by an entirely different method such as that of freezing point determinations might lead to interesting results in the light of Dr.Lewis's work . The subject had a further interest for me because of its novelty and generality.

The first problem to be taken up is naturally that of purification of the iodine and the following methods have been considered:

a.) Rotating the iodine with conductivity water in a thermostat until a constant conductance is reached.

b.) Simple sublimation from potassium iodide.

c.) Stas method.

d.) A modified Stas method.

Ojection to (a) was that of the difficuly of drying the resulting iodine and the fact that only water soluble impurities would be removed.

(b) is good as far as it goes ,but is inadequate.

(c)The method which Stas employed in the purification of iodine for his atomic weight work consists in dissolving the iodine in a saturated aqueous potassium iodide solution,precipitating out the iodine by dilution with excess water;and the subsequent steam distillation of the filtered iodine and its filtration and drying.This process is rather long and is open to the same objection as that for (a).

(d) The method adopted was the precipitation of the relatively pure iodine from a potassium iodide solution as in (c) and then after filtering and drying with an air blast and over calcium chloride and phos-

phorus pentoxide,the iodine was put in a boat in a 3' glass tube,sealed at one end and connected to a good vacuum pump at the other,and the iodine was distilled in steps up the tube by careful electric heating. This vacuum distillation yielded perfectly dry and beautifully crystalline flakes of a very pure iodine and could be conducted on a relatively large scale. (that is 10 - 15 gms. at a time.)

The purity of the iodine was tested by determining its melting point in the apparatus which will be described later. The following point was obtained by means of a Beckman thermometer - 113°.4 C.

Over a 100 gms. of iodine were obtained by this method and this was used in the determinations of the freezing point lowerings.

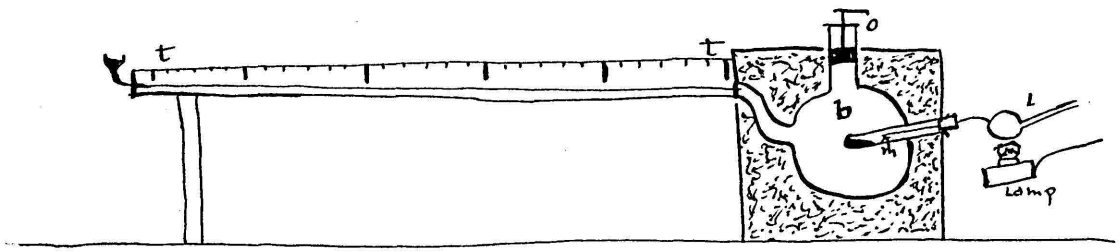
The principal work,as the title suggests,may be

divided in two parts (A) the Heat of Fusion of Iodine. (B) the Use of Liquid Iodine as a Solvent and these two subjects will now be separately considered.

A- The Heat of Fusion of Iodine.

Previous Work.

The specific heats of iodine and its latent heat have not been redetermined since the researches of Favre[1.] and Sibbermann in 1850. Their work was highly inaccurate as the following sketch and description of their apparatus and method will show.



b = mercury resevoir or calorimeter.

m= muffle where hot substance cools off.

l= pipette ,from which a weighed amount of the substance is introduced.

1.)Ann.de Chimie et de Phys. 37,465,1853.

t-t' capillary tube into which the mercury is forced by the heat .The length of the thread is read with a telescope and the temperature corresponding is determined from the calibration of the capillary.

o: plunger to vary the initial volume of the mercury.

The method of operation for the heat of evaporation for example was to heat the pipette to boiling point of the liquid under consideration and introduce the tip into the muffle and distill over 2 or 3 gms. of the liquid. As the vapor liquified inside the mercury calorimeter the heat given off drove the mercury out into the capillary and the amount of heat liberated was thus determined.

Evidently as the mercury is under pressure it cannot be stirred and neither can the liquid itself. The rate of cooling is indefinite and variable and loss of heat very likely. Thus the method,although quite

ingenious is not scientific,nor accurate .His value for the heat of fusion is 11.71 calories;and sp.heat of solid iodine is .05412.

Victor Regnault[1.] derives a formula for the specific heat of iodine by applying Newton's law to the rate of cooling of some water,first alone and then with a glass bomb with warmed iodine in it. As the work of Favre and Silbermann was intended to correct his values,little more need be said about Regnault's results except to give the numerical values he obtained,namely .0541 (±.0001) for the specific heat of solid iodine.

The values given above are those still found in the most recent edition of Landolt and Bornstein,although it seems rather strange that such important physical constants have not been redetermined more recently.

1.) Ann. de Chim. et de Phys. LXXlll ,p.5,and Pogg. Annalen; (44) 21,228, (1840).

work

The present calorimetric, was performed with a new calorimeter of Dr. Keyes design in which the usual losses and corrections were reduced or eliminated as far as possible. The method in brief is the usual one depending on the exchange of heat between the hot body and a definite amount of water in a calorimeter, but 2 exactly similar bombs are used with which parallel runs are made in a precisely similar manner, the only difference being that one bomb holds the iodine and the other is filled with that quantity of water which will give the same rise in temperature when dropped into the calorimeter.

The bomb with its charge is heated to the desired temperature in a constant temperature bath from which it is released and drops in a Dewar bulb or calorimeter proper, where the rise of temperature is noted with a Beckmann thermometer. As the following runs with the water bomb start at exactly the same temperature and are adjusted to give the same rise of temperature in the calorimeter, the specific

heats of the iodine and the water are inversely as the amounts of these two substances used.

The description of the apparatus itself is naturally somewhat detailed and for the sake of clearness will be divided in 4 parts as follows:-

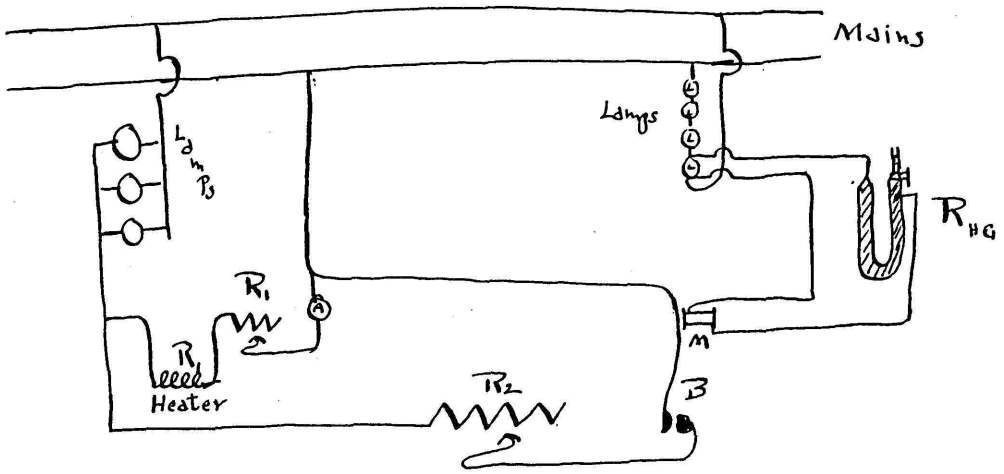
1). The upper constant temperature bath or thermostat.

2). Mechanism for dropping the bomb.

3). Calorimeter itself.

4). The bombs.

1). The upper constant temperature bath consists of the usual metal cylinder, well lagged on sides and bottom and heated electically by a resistance coil of 16 ohms. Oil is used as the circulating fluid and its temperature is maintained within $\pm 0^{\circ}.02$ C of the desired temperature by means of a mercury regulator, which actuates a circuit breaker in the main heating line. A simplified diagram of the electrical connections shows this -



where R_1 and R_2 are variable resistances

B = circuit breaker actuated by magnet M through the rise of mercury in the capillary of the regulator R_{HG}

A = ammeter and H = Heater in the oil bath.

By using two adjustable rheostats as indicated the amount of current through the heater may be fixed so that just enough current flows through the bath to heat it about 0.001° C per minute and when the shunt circuit is closed the effective heating is dropped to that value which will allow cooling at the rate of about 0.001° C per minute. In this way superheating or supercooling is avoided and the bath is kept at a constant temperature in spite of the viscosity of the oil and the consequent slower stirring.

2). Within the bath is a vertical brass cylinder opening outside of the bath at the bottom and terminating in a small open pipe at the top. It is within this cylinder that the bomb is heated while suspended by a fish line through the narrow pipe. The other end of the line is fastened to a trigger and is released at the start of the run. The lower end of the cylinder is closed by a cork,which is also pulled out at the commencement of the run. To ensure an equalization of temperature within the cylinder a slow current of dry air,first passing through coils in the thermostat, finally enters the base of the cylinder and passes up and out at the top.

Below theebath isa glass tube to guide the dropping bomb into the opening in the Dewar bulb and this guide tube swings in and out of position to allow the cork to snap out. The entire operation is controlled by one lever which causes things to happen in the following order; a slight downward movement snaps the cork out of the bottom of the hot cylin-

der,a continuation of this movement releases the guide tube which is pulled into position and in so doing releases the bomb which drops down into the calorimeter. A final upward movement of the lever closes the cover of the calorimeter which had been opened just previously and the whole operation can be done in one fifth of a second. The bomb is partially arrested in its fall by a system of springs and releases which bring it almost to a stop just before slipping into the calorimeter and thus avoids splashing the water or breaking the bomb.

3). The calorimeter is a Dewar bulb holding 500 cc. of water with the bomb and stirrer and thermometer. It is closed on top with a hard rubber cover and is surrounded by a water bath. The temperature of this is regulated by hand to a hundredth of a degree with the help of an electric heating coil and water cooling pipes . Its temperature is kept at some point within the range of the rise inside

the Dewar flask. It is stirred of course, by a small motor as are the other two stirrers.

4). The first bombs used were made of silver dimes, weighing about 90 gms. and fitted with heavy Ag plugs that screwed into the necks. Before filling, the bombs were made to weigh exactly alike and then one was filled with iodine and made tight by using a small gold washer under the plug. For the water bomb a little rubber washer was used. These two bombs worked nicely at 50° until a leak developed in the iodine bomb at the joints which were poorly soldered. A glass bomb was tried next but cracked on account of some strain in the glass. Two similar bombs were next made out of "HH" glass and thoroughly annealed by heating to 530° and letting cool down in the furnace for 20 hours. These bombs withstood the sudden temperature fall of 100° to 20° C and the shock of the drop in the calorimeter successfully. All the bombs were of a size sufficient to hold easily 100 gms. of solid iodine.

Actual experimentation began with the adjustment of the thermostat to 50° and determination of the proper heating and cooling values of the current through the heater, The thermometers were also compared with the standard; a Gerhardt graduated in 0°.1 and read to 0°.01 C with the following results; the zero of the Beckmann corresponds to 18°.19 C ,the thermometer in the lower water jacket has a connection of + 0°.09 ,the Götze thermometer used in the upper oil bath has at 50°.00 a correction of - 0°.11 C.

Runs were next made with the silver bomb filled with iodine and heated to 50°.00 for from 1.5 to 4 hours. The corrected rise for 3 runs was 0°.680; 0°.718; and 0°.730 as taken from plots of Beckmann readings vers time. It can be shown that the maximum rise would not exceed 0°.733 which is within the experimental error,but this value was not realized because the leak developed before the bomb could be heated more than 4 hours.

Runs were made with the silver water bomb at 50.00° which was heated till the rise checked to within 0.003° C or better. One hour was found to be long enough. As the weight of the water could not be at first adjusted to give the exact rise found with the iodine, the amount of water was varied to give values on either side of this temperature rise and the correct weight of the water found from a plot of temperature rise versus weight of water.

The results of the runs at 50° may be summarized by these figures; the weight of iodine = 109.84 gms.
the weight of water = 8.911 "

The data for the determination of this weight of water is as follows.

#Run;	Time of Heating	Rise	Wt. of Water.
#8	2 hours	0.693	8.647 gms.
#9	17 hours	0.690	8.650
#11	1.1 hrs.	0.823	9.539
#12	0.83	0.821	9.534

The variations in the weights of water may be due to the

difficulty in weighing a bomb with a large surface without a suitable counterpoise. It is evident that the rubber gasket was tight and also that the time was sufficient in every instance.

From the values the plotted value for the weight of water necessary for a rise of $0^{\circ}.730$ was found to be 8.911 gms. and therefore

$$\frac{\text{Wt. of water}}{\text{Wt. of iodine}} = \frac{\text{sp. heat iodine}}{\text{sp.heat of water}}$$

$$\text{or } \frac{8.911}{109.84} = \frac{x}{1}$$

$$x = 0.0813 \text{ calories per gm.}$$

The temperature of the upper bath was next shifted to 100° and the current readjusted to give the desired constancy. Runs were then made in the same manner as previously indicated, starting with the iodine bomb as before.

The results are briefly as follows:

#Run;	Time of Heating.	Rise,	Wt. of Iodine.
13	4	2.431	91.81 {Bomb broke in calorimeter.
14	42	1.779	105.53
16	15	Irregular on account of poor stirring.	
17	21	1.652	105.53
18	70	1.779	"

A lack of time prevented the complete results from being entered in this thesis, but there is sufficient data to enable one to obtain an idea of the precision of the method.

The weight of the bombs and their charges was known to within ±0.05 gms. in 100 gms or 0.05%

The weight of the water added to the calorimeter was constant within ±0.05 in 500 gms. or .01%

The temperature drop varied in the different runs possibly 0.1. in 30.0° or 0.3%

but could be corrected to ±0.03° C or 0.1%

The temperature rise in the Beckmann was probably with

±0.002 C in 0.700 or 0.3%

and much greater precision with larger rises.

It is probable therefore that the resulting calculations are inside of ± 0.5% and could be bettered by applying corrections which could be calculated from existing data. The error due to the lag of the Beckmann thermometer behind the true temperature rise is important, but has not been determined here. Such an error could be eliminated by the use of a platinum resistance thermometer which has practically no lag. It has also been assumed that the stirring was constant and hence the heat put into the calorimeter by the stirrer was constant. However, the heat capacity of the contents of the calorimeter is changed when the bomb drops in, but the change in heating from the stirrer due to this effect is small and cancels out almost when the water bomb is used compared with the iodine bomb. Similarly, if exactly the same rise were obtained

on the Beckmann with both bombs there could be no error due to variation in the bore of the Beckmann capillary. This exact parallelism of rise was closely enough attained to exclude this error however. Errors due to change in the rate of radiation were also negligible as the radiation loss was very small and the temperature of the water bath was kept constant to within $\pm 0.^{\circ}01$ C.

The results of the calorimeter work are unsatisfactory in one respect, namely that the value of the heat of fusion was not obtained, but there was obtained evidence of something more important than the rest of the thesis put together and that result is an indication of an allotropic form of iodine. As Dr. Keyes suggested, the high value of the specific heat as determined at 50°, indicates that there is being liberated heat due to some transformation of an unstable to a stable phase at a temperature between 50° and 20° C.

Even if this heat of reaction is distributed over the range of temperature from 9° - 98° as was done in Regnault's determination, the resulting value is still much higher than that of .0505 demanded by Dulong and Petit's law.

Further evidence of this is found in the long time required for the bomb to come to a thermal equilibrium, thus ,42 hours heating at 100 was just sufficient to give a constant value for the rise of the Beckmann, or in other words the apparent specific heat seems to be a ~~formation~~ function of the temperature. It is inconceivable that the conductivity of the solid iodine is low enough to explain this, for if such were the case it would be a far superior heat insulator to any now known. Therefore it seems evident that some allotropic form of iodine is formed in these experiments.

B.-The Use of Iodine as a Solvent.

Until very recently but little work has been done on the use of liquid iodine as a solvent in molecular weight determinations. An Italian,F.Olivaiř,found the value of the molal freezing point lowering constant,or ~~potas-~~ K ~~sium~~ to be 213 by dissolving the following iodides in an iodine melting at 113.4 C.;-As I_3 ,PbI_2 ,SnI_4 and HgI_2 . He also used as solutes various organic substances that did not react with molten iodine and got normal molecular weights in general. He found ,however,that sulpher formed S_8 in a solution of iodine;while Se is present as Se_2 and tellurium as TeI_2 .

Furthermore;with potassium iodide the molecular weight is near the normal value,but it first increases and then decreases with increasing concentration. Owing to the great hygroscopic power of CaI_2 and SiI_2 no satis-

1.) Chem.Zentralblatt,I,408;1910.

2.) " " II,136,1910.

factory results were obtained.

Beckmann[3] working on the same subject found a value of the constant K to be 210; while Timmerman[4] got a value of 253.5. These results indicate that they took for their heat of fusion that of one gram-atom and not that for one gram-molecule,as is done in the following mathematical treatment.

If we assume no association nor dissociation of the solute in the solution we can derive an equation which is exact,depending only on Raoult's law & the Gas law.This may be done in the following manner:-

If to a mixture of a solid in equilbrium with its liquid a solute be added which dissolves in the liquid but not in the solid,the temperature of the mixture will

3) Zeit. fur Anorg. Chem. 63,63; C.11 789.1909.

4) Journ. de Chim. Physique 4,170;C 11 197.1906.

fall & the vapor pressures p_s &p of solid & liquid respectively will be lowered. This lowering is due to two causes,(1)the effect of the solute& (2) the lowering of the temperature;or mathematically:-

$$dp= (\partial p/\partial N')_T dN' + (\partial p/\partial T)_{N'} dT \qquad 1)$$

where N' is the mol-fration of the solute or n'/n_o+n' .

The change in the vapor pressure of the solid is

$$dp = (\partial p/\partial T)\, dT \qquad 2)$$

but the solid & the solution are in equilibrium &

$$dp=dp_s \qquad 3)$$

By combining (1) & (2) & (3).

$$dp_s=dp=(\partial p_s/\partial T)_{N'} dT=(\partial p/\partial N')_T dN + (\partial p/\partial T)_{N'} dT$$

or
$$(\partial p_s/\partial T)_{N'} - (\partial p/\partial T)_{N'}= (\partial p/\partial N')\frac{dN'}{dT} \qquad 4)$$

but the influence of temperature on the vapor pressure of a liquid or solid can be shown[5] to be:-

5) Lewis,Proc.Amer. Acad.,37.53(1901)

$(\partial p_s/\partial T)_{N'} = L_s/VT$ & $(\partial p/\partial T)_{N'} = L/VT$

where L_s & L are respectively the molecular heats of vaporization of the liquid & solid under constant pressure, and V is the volume of the vapor at the temperature T.

By subtraction of one of these equations from the other, we obtain:-

$$(\partial p_s/\partial T)_{N'} - (\partial p/\partial T)_{N'} = \frac{L_s - L}{VT} = \frac{\Delta H}{VT}$$

where ΔH is the molecular heat of fusion into the solution at the temperature T.

by substitution in 4), we get;-

$$(\partial p/\partial N')_T \frac{dN'}{dT} = \frac{\Delta H}{VT} \qquad 5)$$

Now, from Raoult's law we know that

$$\frac{p_0 - p}{p_0} = \frac{n'}{n_0 + n'} = N' \quad \text{or} \quad p = p_0(1 - N')$$

Differrentiating this last with respect to N

$$\partial p/\partial N' = -p_0 = \frac{-p}{1 - N'} \qquad 6)$$

and by substituting 6) in 5)

$$\frac{dN'}{dT} = \frac{-\Delta H\ (1-N')}{pVT}$$

Simplifying, by introducing the Gas law, RT=PV ;& replacing T by $T_o + t$, where T_o is the freezing point of the solvent(absolute scale) we obtain;-

$$\frac{dN'}{dt} = \frac{-\Delta H(1 - N')}{R(T_o + t)^2}$$

In order to integrate this expression it is only necessary to express ΔH as a function of the temperature. Thus if ΔH_o is the molecular heat of fusion of I_2 at its melting point & ΔC_p the difference between the molecular heat capacities of the solid I_2 & the solution; then

$$\Delta H = \Delta H_o + \Delta C_p\, t$$

We can thus obtain the final differential equation:

$$\frac{dN'}{dt} = \frac{-(\Delta H_o + \Delta C_p\, t)(1 - N')}{R(T_o + t)^2}$$

This can be integrated in the usual way, noting that when t=o ,N=o; as t corresponds to $-\Delta t$, the freezing point lowering

with the following result:-

$$\ln(1-N') = \frac{\Delta C_p}{R}\ln\left(\frac{T_o + t}{T_o}\right) + \frac{(\Delta H_o - \Delta C_p T_o)t}{RT_o(T_o + t)}$$

This is perfectly exact & general and only involves those two assumptions that have been mentioned. For dilute solutions where N' is small we can get a more usefull form by expanding into a series, since when $N' = o, t = o$ & obtain

$$N = \frac{\Delta H}{RT_o^2}\left[\Delta t - 1/2\left(\frac{\Delta H_o}{RT} + \frac{\Delta C_p}{H} - \frac{2}{T_o}\right)\Delta t^2\right]$$

where Δt is written for $-t$, as has been indicated.

Using the following values for the constants:

$\Delta H_o = (11.7 * 254) = 2975$ calories per gram-mol.

$R = 1.99$ calories per degree

$T = 113 + 273 = 386$

c small & undetermined so neglect.

we obtain $$N' = \frac{2975}{1.99 * (386)^2}\left[t - \left(\frac{.01002 - .00518}{2}\right)\Delta t^2\right]$$

$$N' = o.o1oo2(\Delta t - o.oo242\Delta t)$$

& for small values of Δt

$$N' = o.o1oo2\Delta t$$

In the plot of results at the end of this thesis will be found this value of N plotted against assumed values of Δt, giving the straight theoretical line for dilute solutions.

In calculating and plotting the results from the experiments it was assumed that only an infinitesimal portion of the solid separated out when the freezing point was taken, as otherwise the actual concentration would not be known. Evidently as the theoretical line is based on the assumption that no disassociation or association took place we can find the amount of this change by comparing the theoretical and experimental results.

The present work undertaken consisted in merely adding to a pure liquid iodine solution, whose melting point was known on the Beckmann, known amounts of potassium iodide in the form of little pills and then determining the freezing point of the resulting solution.

The apparatus used for these determinations was of the customary Beckmann type, consisting of a sort of large glass test-tube about 3.5 cm. in diam. & 16 cm long fitted with a ground glass joint at the top for the cover, which was also a glass bulb but had two openings: a large central one for the Beckmann thermometer and a smaller one at the side for a platinum wire stirrer. The whole was supported by a wooden frame and fitted within an electrically heated thermostat, which also had pipes for water cooling. The current at 220 volts or 110 volts could be adjusted by a hand operated rheostat and was also

supplied to the motor which drove a stirrer within the bath. As the temperature was around 114° C, an oil pump was used as the circulating fluid and its viscosity was small at this temperature. The method of procedure was in general like this; the bath was brought up to a little above the melting point of the iodine solution and kept there until the iodine was completely melted,- in about an hour; then the temperature of the outside bath was quickly dropped a degree or two by the cautious use of the cooling water pipes and the gradual drop of the Beckmann noted every 30 seconds while stirring the interior contents of the tube with the platinum stirrer. After the freezing point was reached as indicated by a halt or even a rise of the Beckmann, the current was turned into the thermostat again and the process repeated till three consecutive concordant readings were obtained.

The preliminary experimental work consisted in the standardization of the Beckmann thermometer. This was done by direct comparison of the Beckmann with a good glass scale thermometer, #9766, which was first tested for its ice and steam point and a correction of 0.1° C was found at 100.0° C. Then in the oil bath in a series of eight trials, the zero reading of the Beckmann was found to correspond to 108.0 C (± 0.1 corrected) on the standard.

The freezing point of the pure iodine was next determined as previously indicated, both with stirring and without, and the following Beckmann readings obtained 5.400; 5.397; 5.391; 5.389 corresponding to a melting point of the pure iodine of 113.4° C.

The work for about a month and one half now consisted of adding the potassium iodide pills and getting the freezing points of the solutions. The potassium iodide itself was Kahlbaum's, tested for purity by conductivity

measurements and carefully dried in vacuum and kept in a desiccator. These pills could be added to the liquid iodine by lifting out the Beckmann slightly and dropping them in. As the iodine vapor is heavy little of it was lost while adding the pills. In general the freezing point was attempted soon after dropping in the pills,which of course dissolved quickly but it was found the freezing point suffered considerable variation,rising after a pill was added to a maximum and then gradually sinking to a lower constant value,which was taken as the true temperature between the solid solvent and the solution. This variation in the freezing point was rather troublesome,but could not be avoided. At times it seemed to depend on the length of time the iodine was heated and at other times on the amount of superheating,both of these tending to to give high and variable freezing points. This was especially noticeable in the first runs each morning when

both of these factors would be at a maximum. However, the most cautious heating and the most rapid determinations that could be made,4 or 5 in an hour,failed to eliminate these variations. On the other hand,overheating the iodine and rapid supercooling would sometimes yield excellent check results with other methods. The stirring had a slight influence if any,as it became almost mechanical and constant from long practice. It is also inconceivable that the Beckmann changed either by a distillation of the mercury up into the resevoir or by a gradual change in the volume of the glass bulb. Evidently if the glass took a few hours to expand fully,this would cause the temperature readings to fall off from a high value to a lower constant one. To eliminate this possible error,the thermometer was immersed in a steam bath when not in the hot iodine solution,but no difference in the phenomena was noticed as a result of this treatment.

The only other explanation was that of a chemical reaction between the potassium iodide and the iodine and some evidence of this was found in the more concentrated solutions, for on cooling them there was a marked a and rapid rise before the gradual fall that immediately preceeded the freezing point. This rise was of much larger proportions than that which is due to a slight supercooling at the freezing point.

Another difficulty, which was however easily overcome, was the accurate weighing of the iodine. Evidently the weight of solvent taken right before a series of runs will not remain constant during them on account of the constant distillation of the iodine from the solution to the upper cooler portion of the bulbs. By weighing the top and bottom portions of the apparatus separately, the weight of the sublimed iodine could be found and for a short period this loss was assumed proportional to the time of heating and by making this allowance, the true weight of available iodine that could act as a solvent was determined.

The experimental results, including over 200 separate determinations, are briefly summarized in the data sheet following and in the plot of results. The data is arranged in three columns, each line across representing the average best values for a single point. At the left is the freezing point lowering as read off the Beckmann, and following it is the concentration of the potassium iodide per 100 gms. of the liquid iodine, and also as mol. fractions of solute. It will be noticed that the molecular weight of iodine is used throughout and not the atomic.

In plotting this data a break in the curve will be noticed which 40 runs failed to smooth out. The only difference between that point and the one preceeding is that the first large potassium iodide pill was added there. From the plot, which is on a very greatly reduced scale, it is evident that in very dilute solutions the potassium iodide behaves normally, -i.e. follows the theoretical straight line, -but as the concentration increases the lowering of the temperature is not as large

as would be expected, or in other words the potassium iodide is associated. As a matter of interest the percentage of association has been calculated at the following values of Δt & N'

Δt	Mol. fraction KI added	Percent association.
0.1	.001	0%
0.5	.0064	21%
1.0	.017	35%
1.5	.0235	42%

These values are not very accurate but indicate the trend of the association.

The weight of the KI can be determined to within .0002 gms. in .0200 or more or about 1%

The weight of the iodine was determined to within 0.1 gms. in 100 or about 0.1%

The Beckmann reading was not excepted unless 3 readings checked with .002 or about 1%

So that the resultant precision was never better than one percent and may have been worse.

Summary.

To conclude, the results of this work are :—

1). That potassium iodide exists in liquid iodine in the normal state in very dilute solutions, but that association sets in as the concentration is increased.

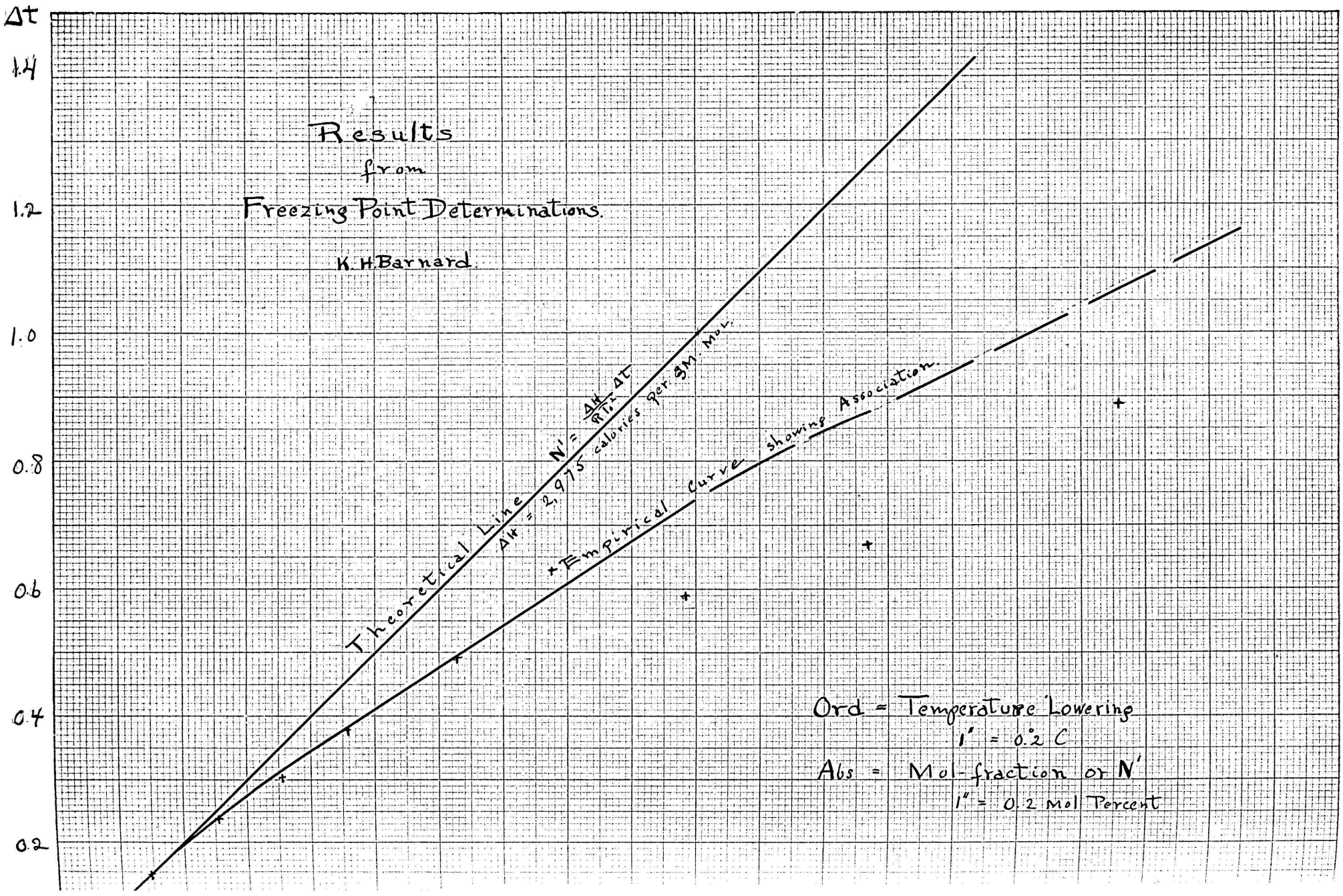
2). A precise general equation has been developed and integrated for the theoretical relation between the concentration of the solute and the freezing point lowering.

3). The calorimeter work shows an abnormally high specific heat for the solid iodine as well as a very slow approach to thermal equilibrium conditions, from which it is concluded that a possible alletropic form of iodine exists within the range of temperature investigated.

The following is a table of experimental data as prepared for final plot of results.

Δt	$\frac{\text{Gms. KI}}{\text{100 Gm. 1}}$	N'
.050	.0276	.000422
.060	.0463	.000708
.138	.0971	.001484
.239	.1680	.002564
.303	.2327	.00355
.379	.3016	.00459
.489	.413	.006285
.629	.511	.00775
.579	.651	.00988
.669	.841	.0127
.889	1.102	.01659
1.289	1.572	.02356
1.519	1.820	.0272
1.488	1.764	.0263
1.686	1.784	.0266
2.155	2.380	.0352

Where $N' = \frac{n'}{n_o + n'} = \frac{\text{Gms.KI}/166}{n' + 100/254}$

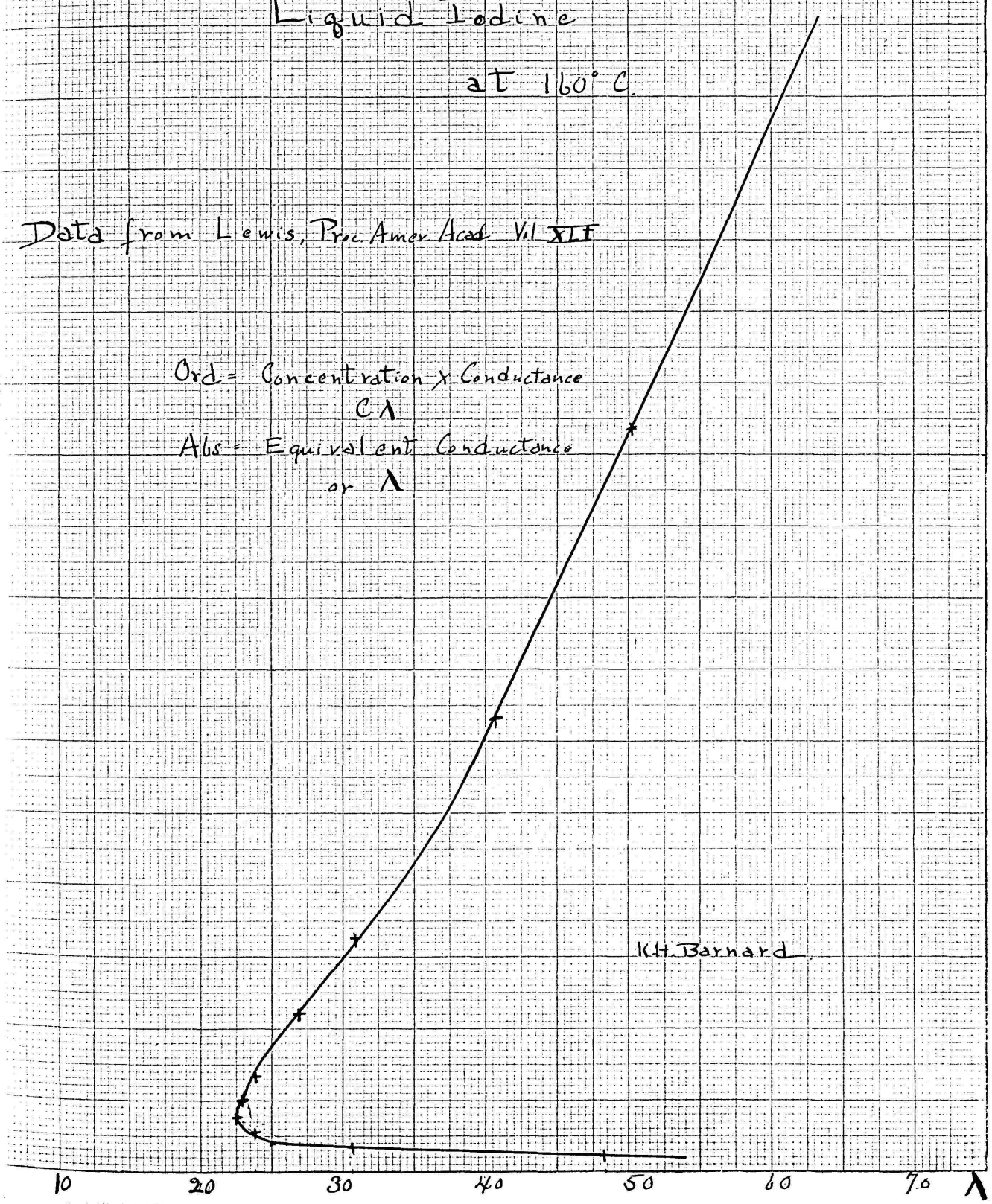

Δt
1.4
1.2
1.0
0.8
0.6
0.4
0.2
Results
from
Freezing Point Determinations.
K. H. Barnard.
Theoretical Line
ΔH = 2,975 calories per Gm. Mol.
N' = ΔH/RT₁T · Δt
+ Empirical Curve showing Association
Ord = Temperature Lowering
1" = 0.2 C
Abs = Mol-fraction or N'
1" = 0.2 Mol Percent

Conductivity of KI in Liquid Iodine at 160° C.

Data from Lewis, Proc. Amer. Acad. Vol XLI

Ord = Concentration × Conductance
$C\Lambda$

Abs = Equivalent Conductance
or Λ



The Photographs.

The accompanying photographs give a clearer idea of the calorimeter than any written description can. In them, can be clearly seen the constant temperature bath with its stirrer and 2 thermometers above, and below the water bath surrounding the Dewar flask. Between the two are the guide tube, thermometers, stop-watch, stirrers etc. , and at the left the lever that operates the whole.