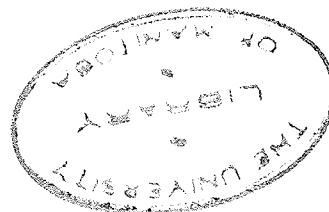


THE BOILING POINTS AND VAPOUR PRESSURES
OF CONCENTRATED SOLUTIONS
OF AMMONIUM NITRATE AND OF SILVER NITRATE
AT VARIOUS PRESSURES

Being a Thesis Submitted to the
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By

Jack Bert Fishman



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ABSTRACT

The boiling points of solutions of ammonium nitrate and silver nitrate from zero concentration to approximately ninety percent concentration, were determined at pressures of 701.6 mm., 597.2 mm., and 701.6 mm., 614.2 mm., respectively. A two stage barostat was constructed to regulate the pressure. A Scatchard still and a student Cotrell apparatus were used as the boiling point apparatuses.

By an application of the Clausius-Clapeyron equation, it was hoped to detect any evidence of layer hydration of ions, as postulated by Stokes and Robinson. It was found that the method of boiling points did not give the required accuracy. Within the limits of experimental error, no evidence of hydration was found.

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THEORETICAL INTRODUCTION

1. Ionic Hydration

The concept of ionic hydration first began to emerge in the early nineteen hundreds.⁴⁷ In spite of some theoretical and much experimental work, the significance of ionic hydration is not yet fully understood.

The diversity of phenomena studied in an attempt to clarify ionic hydration gives an indication of the important influence of ion-solvent interaction. Among the phenomena studied are freezing and boiling points, refractivity, vapour pressure, surface tension, density, compressibility of ionic solutions, transport of ions, and solubilities of non-electrolytes in the presence of electrolytes. It is evident that clarification of the problem of ionic hydration would be one of the major steps in clarifying the whole theory of solutions of strong electrolytes.

In the earliest concept of ionic hydration, ions were regarded as being chemically bound to a specific number of water molecules in solution. S. Aschkenazi¹ gave some experimental results involving conductivity and cryoscopic constants which seemed to support this concept, but the existence of definite hydrates in solution was never verified. K. Fajans²¹, from a consideration of the polarizability of water molecules, postulated that the ion-solvent

interaction was mostly Coulombic in nature and not covalent.

M. Born⁷ showed that for univalent electrolytes, a simplified form of Fajans concept gave good agreement with experimental results.

The Fajans-Born concept seems to hold for the simple ions of group 1A and 11A of the Periodic Table and also for the halogens. For more complicated ions, such as those in group VIII, it would appear that covalent linkage between the ions and the water molecules would take place. There exists little quantitative evidence with which to substantiate this. The Fajans-Born model for simple ions pictures the ions as holding, quite firmly, a definite number of water molecules which it will carry along with it at all times. There will also be a further interaction with the water molecules outside the firmly held sheath. Since the polarizability of the ions is dependent on the ionic radius and on the ionic charge, the smaller the ionic radius, the more water molecules will the ion bind, and the greater the ionic charge, the more water will be bound. This is consistent with experimental results.

F. A. Lindemann³¹ suggested that there was no permanent hydration of ions in solution and that the transport of water observed during electrolysis was due to momentum transfer from the ion to the water molecule upon collision. This would explain the experimental observations that smaller ions transport more water and would also

explain the dependence of the temperature coefficient of conductance upon the ion size. There is, however, no independent evidence supporting this theory.

A picture for hydration of ions in highly concentrated solutions has been postulated by R. H. Stokes and R. A. Robinson⁴¹. From their work on the gels formed by highly concentrated solutions of calcium nitrate they assume that this highly concentrated region could be looked upon as an adsorbent-adsorbate system. They also assume that the ion-ion forces at this stage are negligible. The ion-solvent forces are predominant. The solution would contain ions in various stages of hydration. Some ions would be incompletely hydrated, others would have a complete monomolecular hydration shell surrounding the ion, and still others would have two, three or more hydration layers around the ion. In the latter case, the second and higher layers would be successively less strongly bound. Since this model bore a strong resemblance to the adsorption isotherm derived by S. Brunauer, P. H. Emmet, and E. Teller¹⁰, Stokes and Robinson wrote their equation as

$$\frac{ma_w}{55.51(1 - a_w)} = \frac{1}{cr} + \frac{c - 1}{cr} a_w \quad (1)$$

where a_w is the activity of the water, m is the molality, r is the number of molecules of water in a monomolecular hydration layer

when this layer was complete, and c is a constant related to the heat of adsorption of the molecule in the layer. Stokes and Robinson got a surprising accuracy of fit for this equation from about 12-25M for a number of salts. Although Stokes and Robinson arrived at values of c and r in a purely empirical manner, the accuracy of their results would indicate that it would be profitable to obtain more experimental and theoretical results on the basis of their theory.

Recently, O. Ya Samoilov³⁷, from a consideration of the defects of Stokes law applied to ions in solution, has postulated that there is no such thing as definite hydration numbers: all that can be said is that the time of stay of water molecules around an ion is either larger or smaller than the time of stay of water molecules around one another. One can only speak of indefinite "coordination number" for the amounts of water molecules around the ion.

Two difficulties confront the formulation of an acceptable theory of ionic hydration. One is the lack of knowledge of the type of binding taking place between the ions and the water molecules. The second is the inability of experimental work to indicate if there is any such thing as a definite hydration number for the various ions. Until such time as these two problems are solved, the entire question of concentrated solutions of strong electrolytes will remain unresolved.

2. Experimental

The most common method of estimating ionic hydration is the moving boundary method. Buchbock¹¹ and Washburn⁴⁸ were the first to employ this method successfully. The Hittorf method of obtaining transference numbers neglected the fact that not only the ions are transported during passage of current, but also any water that might be firmly held by the ions. Thus the Hittorf transference numbers obtained by referring the change of electrolyte concentration to the water would not be the "true transference numbers." Buchbock and Washburn added a second solute to the solution, which was not an electrolyte. They assumed that this reference solute did not move during electrolysis. They were then able to refer the change in electrolyte concentration to the reference solute and obtain "true transference numbers." If the true transference number is known, it is then possible to calculate the number of moles of water carried per equivalent of cation and anion, using the equation

$$\Delta n = \tau_c N_w^c - \tau_a N_w^a \quad (2)$$

where Δn is the change in the number of moles of water in a given electrode portion, τ_c is the true transference number of the cation, τ_a is the true transference number of the anion, and N_w^c and N_w^a are the number of moles of water carried per equivalent of cation and anion respectively. Since both N_w^c and N_w^a are not known, it is necessary to assume one of them. Assumptions that have been made

are that large organic ions are not hydrated, ³⁵, NO_3^- ⁸ and I^- ¹⁵ are not hydrated. The most reasonable method divides amount of water transported in the ratio of ionic sizes. P.Z. Fischer and T.E. Koval²² have shown, however, that raffinose, the inert solute employed by Washburn, is transported during electrolysis. L.G. Longworth³² has shown that the displacement per faraday of ions varies with the nature of the non-electrolyte used. Thus there is a great deal of uncertainty concerning the significance of the hydration numbers obtained by this method.

In an attempt to overcome the necessity of adding a non-electrolyte, H. Remy³⁴ measured the volume change during electrolysis by means of a calibrated capillary. The central part of the solution was held fixed by use of a gelatin plug. This separated the anode and cathode compartments. The volume change as measured by the capillaries, then indicates the solvation of the anion and cation. It was found however that the gelatin had a large effect on the results obtained.¹⁸

Baborovsky² modified Remy's method by having the anode and cathode compartments separated by a thin diaphragm of parchment paper impregnated with collodion. The effect of water transport by the ions was determined by weighing the anode and cathode compartments before and after electrolysis. The accuracy of this

method is doubtful due to electroosmosis taking place. Volume change due to heating and reaction at the electrodes is also ignored. These errors are also present in the diffusion method of Janders²⁰ and the dialysis method of Brintzinger⁹.

H. Ulich⁴⁴ has calculated ionic hydration from ionic mobility by assuming there is stable hydration, i.e., tightly adhering water envelopes are formed, and that Stokes law of hydrodynamic friction holds for small ions. From his mobility measurements he calculates the radii of the migrating ions, and by a comparison with the radius of the ionic body proper, he is able to determine the degree of hydration of the individual ionic species. The molecular volume of the ion proper is given by $(N 4/3\pi r_o^3)$ where r_o , the ionic radius, is taken from a table of lattice measurements. $(N 4/3\pi r^3)$ calculated from Stokes law gives the molecular volume of the migrating ion. Subtracting these two quantities, Ulich obtains the space V_s occupied by the water envelope. Dividing this by the molar volume of pure water, the hydration number is obtained. Since there is probably a high pressure in the vicinity of the ions, this hydration number is too low and can be considered a lower limit. Assuming that in the vicinity of the ions the solvent volume is reduced to half its original value, Ulich calculates an upper limit of hydration. The final value is taken as an average of the two limits. Ulich's results for hydration numbers are doubtful. There is some doubt as to whether

Stokes law applies to ions in solution^{37, 28}. Also the change in water volume around an ion is unknown. The advantage of the method is that individual ionic hydration numbers are obtained directly.

E. Rouyer³⁶ and co-workers employed a cryoscopic method of determining hydration numbers. By observing the cryoscopic or ebullioscopic constants of a non electrolyte in electrolytic solution and in pure water, they arrive at the formula

$$x = 100 \frac{(k' - k)}{k'} \quad (3)$$

where x is the percent of water of hydration of the electrolyte, k is the cryoscopic constant of the non electrolyte in water, k' is the cryoscopic constant of the non-electrolyte in electrolytic solution. Among the non electrolytes used were ether, acetone, paraldehyde, and resorcinol. This method is open to criticism since the results are dependent on the non electrolyte used. Acetone and paraldehyde show unreasonable results while resorcinol behaves satisfactorily. The theory by which the results are evaluated is extremely inadequate.

B.H. Van Ruyven⁴⁶ has employed a vapour pressure method to estimate hydration numbers. He assumes that there is a definite number of water molecules bound to each ion and that there exists a degree of ionization for strong electrolytes. From Raoult's law and the Arrhenius equation of electrolytic dissociation he arrives

at the equation

$$\alpha_p = \frac{1000(S-S_2) \ 18 \ N_w S_2}{18 \ N_w S_2} \quad (4)$$

where α_p is the degree of ionization calculated from vapour pressure measurements, S is the vapour pressure of solvent, S_2 the vapour pressure of the electrolyte, and N_w is the concentration in grammolecules of solute per 1000 grams of solvent. Van Ruyven now assumes that the discrepancies in equation (4) with rising concentration are due to the fact that the amount of "free" water present is lowered because of the binding of water molecules to the ions. This would mean that N_w should be larger than the calculated value. He then rewrites equation (4) as

$$\alpha_{px} = \frac{1000(S - S_2) \ 18 \ N_w S_2}{18 \ N_w S_2 \ 18xN_w(S-S_2)} \quad (5)$$

where α_{px} is the degree of ionization of electrolyte binding x molecules of water and x is the number of water molecules bound to the ions. By inserting the proper value of x into equation (5) the discrepancy is removed and the hydration number assumed correct. Although Van Ruyven assumes a fixed hydration number, the high values he reports would seem to indicate his measurements include more than just the firmly held water molecules. His theoretical approach to the problem is also open to a great deal of criticism.

Another method of determining the degree of hydration utilizes

the "salting" out effect²⁹. The change in solubility of a non electrolyte upon the addition of an electrolyte is used to obtain a measure of the hydration on the assumption that the decrease in solubility on the addition of the electrolyte is due to a reduction in the activity coefficient of the water. This method takes no account of the effect of the non electrolyte on the dielectric properties of the solvent²⁰. Values calculated from this method are found to be dependant on the nature of the non electrolyte²⁹ and therefore cannot be considered to give valid results.

N. Bjerrum⁵ utilized the activity of water in a given solution to calculate hydration numbers. His theoretical approach is a great improvement on that of Van Ruyven. Bjerrum also states that the water removed from solution by the ions should be taken into account. He says that the concentration should be expressed as a mole fraction, $x = \frac{n}{n+n'}$, where n is the number of moles of solute, n' is the number of moles of solvent, and x is the mole fraction. If the ions are hydrated then x will be larger than without hydration. If the activity is defined by e.m.f. measurements, then what is being obtained is the activity of water free ions. If the ion holds mH_2O , then the activity of the water free ion A should be multiplied by the activity of water raised to the m th power. Therefore we get

$$a = A(p/p_o)^m \quad (6)$$

$$F_a c (p/p_o)^m = 55.5 f_a \quad (7)$$

$$F'_a c (p/p_o)^{m'} = \frac{c}{55.5+2c - (m' + m'')c} 55.5 f'_a \quad (8)$$

$$F''_a c (p/p_o)^{m''} = \frac{c}{55.5+2c - (m' + m'')c} 55.5 f''_a \quad (9)$$

where F_a, F'_a, F''_a are the apparent activity coefficients of the salt, the anion, and the cation respectively, f_a, f'_a, f''_a , are the corresponding true activity coefficients, and m' and m'' are the moles of water carried by the anion and cation respectively.

Introducing the relationships

$$F_a = \sqrt{F'_a F''_a}$$

$$f_a = \sqrt{f'_a f''_a}$$

$$m = m' + m''$$

into equations (8) and (9), converting the equations to logarithmic form and adding, we get

$$\ln F_a = \ln f_a - \frac{2m - 2c}{55.5} \quad (10)$$

This argument makes the assumption that the relationship $\ln f_a = -K^3 \sqrt{c}$ holds for strong electrolytes as well as weak. F_a can be obtained from standard activity measurements and m chosen to give equation (10) the proper fit. E. Schreiner³⁹ has used this method to find the hydration numbers of several ions.

Stokes and Robinson⁴¹ have arrived at the same results as Bjerrum using an improved approach. They begin by assuming that the Debye-Hückel equation is basically correct.

$$\ln f = \frac{-A \sqrt{c}}{1 + B a^0 c} \quad (11)$$

where f is the activity coefficient, A and B are constants, and a^0 the mean distance of closest approach of the ions. Equation (11) predicts an activity coefficient which is a decreasing function of the concentration, but at concentrations above about 0.1m the equation breaks down badly. It is found experimentally that the activity coefficient decreases to a minimum and then rises more or less rapidly with increasing concentration. Stokes and Robinson postulate that this behaviour is due to the binding of water molecules to the ions thus reducing the amount of free water in solution. They let n equal the number of bound water molecules. Then in a solution of molality m , there are nm molecules of bound water to (55.5 nm) molecules of free water. The true molality m' then is

$$m' = \frac{55.5 m}{55.5 - nm} = \frac{m}{1 - 0.018 nm} \quad (12)$$

If a' is the activity of the hydrated solute and a the activity of water, we obtain from the Gibbs-Duhem relationship,

$$d \ln a' = - \frac{(55.5)}{m} d \ln a_w \quad (13)$$

Introducing the mean molal activity coefficients γ and γ' , we get

$$d \ln \gamma' = -(55.5/\nu m') d \ln a_w - d \ln m' \quad (14)$$

where ν is the number of ions formed, and

$$d \ln \gamma = -(55.5/\nu m) d \ln a_w - d \ln m \quad (15)$$

Substituting for m' from (12) and integrating between molalities zero and m we get

$$\ln \gamma' = \ln \gamma + (n/\nu) \ln a_w + \ln (1 - 0.018 nm) \quad (16)$$

Stokes and Robinson are concerned, however, with the mean rational activity coefficient, f' , of the hydrated solute. This is related to γ' by the equation

$$\ln f' = \ln \gamma' + \ln (1 + 0.018 \nu m') \quad (17)$$

Combining (16) and (17) and simplifying by means of (12) we get

$$\ln \gamma = \ln f' - (n/\nu) \ln a_w - \ln (1 - 0.018(n-\nu)m) \quad (18)$$

Replacing the term $\ln f'$ by the Debye-Hückel expression we arrive at

$$\ln \gamma = \frac{A \sqrt{\mu}}{1 + B a^0 \sqrt{\mu}} - \frac{n}{\nu} \ln a_w - \ln (1 - 0.018(n-\nu)m) \quad (19)$$

where $\sqrt{\mu}$ is the ionic strength; a^0 and n were chosen to give the best fit. Stokes and Robinson found equation (19) gave very accurate results up to the point where the product of nm exceeded 10 or 15. They explained its failure above this limit by assuming that at high concentrations there will not be a sufficient number of water molecules to go around between the ions. The ions would then be

in competition for the water molecules and n would become a decreasing function of concentration.

J. D. Bernal and R. H. Fowler⁴ indicated that measurements of the partial molar volume of electrolytes at infinite dilution, would give satisfactory hydration numbers. Darmois¹⁸ applied this method to a number of electrolytic solutions, but since this method involves the use of Stokes equation in a similar way to Ulich⁴⁴, the validity of the results are open to the same objections.

Darmois¹⁷ and M. Cordier¹⁶ have also calculated hydration numbers by measuring the specific rotation of a metallo-organic complex in pure water and then in an electrolytic solution. The complex used by Cordier was a molybdenum tartrate. The hydrolysis of the complex in progressively diluted solutions of pure water was measured by reading of the specific rotation. This was repeated with an electrolyte in the solution. The specific rotations for the solutions containing the electrolyte were found to be higher. This is attributed to the hydration of the ions. Knowing the density of the solutions and comparing the specific rotations, it was possible to calculate the hydration number. These results are in doubt since the influence of the complex on hydration was ignored.

Y. Yasunaga and T. Sasaki⁴⁹ have calculated hydration numbers using an ultrasonic interferometer²³. They assume that both the

solute ions and the hydrated water are incompressible and that the decrease in compressibility of water - caused by the addition of an electrolyte - is due to hydrate formation. Their results are consistent with those obtained from mobility measurements.

The multiplicity of methods used is found to give widely varying results. Table (1) gives some hydration numbers of the sodium ion arrived at by different methods.

The diversity of the results makes any interpretation quite difficult. J. O'M. Bockris⁶ suggests that the hydration numbers less than ten give a measure of the primary hydration while those greater than ten give a measure of the total number of water molecules affected. It is improbable that any definite conclusion can be reached until more work is done on this subject and until the experimental techniques are extended to the higher concentrations.

TABLE (I)

Values of the Hydration Numbers of the Sodium Ion
by Various Experimental Methods.

WORKER	METHOD	HYDRATION NUMBER
Washburn ⁴⁸	Moving Boundry	2-10*
Ulich ⁴⁴	Ionic Mobility	4
Brintzinger ⁹	Dialysis	17
Baborovsky ³	Water Transport	8-9
Ulich ⁴⁵	Entropy Calculation	3.5
Reisenfeld & Reinhold ³³	Mobility	71
Bernal and Fowler ⁴	Density	8
Cordier ¹⁶	Specific Rotation	690-22#
Darmois ¹⁸	Stokes Law	1
Sutra ⁴²	Molar Volume	2.1

* Depending on hydration number of Cl varying from 0 to 6

Varying with concentration from 0.05M - 2M

STATEMENT OF SPECIFIC PROBLEM

Although there is no coherent theory of hydration, certain conclusions have been reached. Most workers will agree that ions in solution are hydrated. There also seems to be every indication that the number of water molecules affected extends beyond the immediate vicinity of the ions.

The hydration theories of Bjerrum⁵ and Stokes and Robinson⁴¹ are, in the opinion of this author, the soundest advanced, from a purely theoretical point of view, and their conclusions will be accepted.

It is then seen that as the concentration of an electrolytic solution is increased, there will be fewer and fewer molecules of water left to go around among the ions. At extremely high concentrations the ions should be in strong competition for the few remaining water molecules. This is assuming that no other forces come into play which would nullify the role played by ion-solvent interaction. On the picture given by Stokes and Robinson, it is seen that it would become progressively more difficult to strip away the successive layers of water surrounding the ions. When one arrives at the most strongly bound inner layer, one would expect to find it necessary to overcome very strong forces before this inner hydrate layer could be removed.

It was thought that the application of the Clausius-Clapeyron equation to the boiling points of progressively more concentrated electrolytic solutions at various pressures would provide a method of estimating the difficulty of removing water molecules from the ions.

The Clausius-Clapeyron equation may be written as

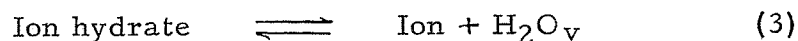
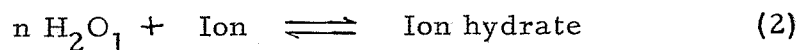
$$\ln p = -\Delta H/R \cdot 1/T + C \quad (1)$$

where C is a constant of integration, ΔH is the molar heat of vapourization, T the absolute temperature and p the pressure.

A plot of $\ln p$ against $1/T$ for a small temperature gradient should give a straight line of slope equal to $-\Delta H/R$. Knowing the slope it is then possible to determine ΔH .

Although the approximations involved in arriving at (1) introduce an element of error into this equation, it is felt that at the relatively low pressures employed, the error is negligible.

We can write the following equations for the reactions taking place.



where the subscripts l and v refer to the liquid and vapour phase respectively. We will call ΔH_1 , ΔH_2 , ΔH_3 , the heats of reaction for equations (2), (3), and (4) respectively. ΔH_3 , the heat of

vaporization of pure water can be obtained, from a handbook, over the entire temperature gradient, ΔH_2 , the heat of vaporization of water from electrolytic solution, is determined experimentally by means of equation (1). Therefore, ΔH_1 , the heat of ionic hydration, is calculated from (2), (3) and (4) by the relationship

$$\Delta H_1 = \Delta H_3 - \Delta H_2 \quad (8)$$

If there is no ion-solvent interaction present, then one would expect ΔH_1 to be zero. If the ion is hydrated, however, one would expect that ΔH_1 would show negative heats of hydration, corresponding to a lowering of the energy of the system⁴³. If there is more than one layer of bound water, as postulated by Stokes and Robinson, then the negative value of ΔH_1 should rise progressively as the number of water molecules in solution becomes less and less, up to the point where there is just enough water to go around among the ions.

Very little experimental work has been done on the boiling points of concentrated solutions of electrolytes. Van Ruyven⁴⁶ has listed the change of boiling points with concentration of several electrolytes but none of the concentrations run above 2-3M. A.N. Campbell and E.M. Kartzmark¹⁴ have found the boiling points at 760 mm. of ammonium nitrate and silver nitrate up to about a strength of solution of 90%. The method employed for the concentration of strength 20% and higher was not adequate to give the degree of accuracy desired for this work.

The present work was carried out with solutions of ammonium nitrate and silver nitrate.

EXPERIMENTAL PROCEDURE

1. Description of apparatus

(a) General

The apparatus is shown in figure (1). It consists essentially of a crude barostat, a sensitive barostat, and a boiling point apparatus. By means of the barostats it was possible to set the pressure of the system at any desired value and to maintain this pressure within very narrow limits. The boiling point apparatus used for the majority of the readings was a student Cotrell apparatus while the remaining readings were taken with the Scatchard equilibrium still.

(b) Pressure control

Constant pressure was maintained by means of the apparatus described by A.N. Campbell and W.J. Dulmage¹². The pressure control consists of two stages. In the first stage an air pump kept a crude barostat about 20 mm. of mercury lower than the desired pressure. The second stage consists of a sensitive barostat set at the desired pressure.

The pressure in the crude barostat was set by adding or removing mercury from the barostat. The pressure in the sensitive barostat was set by means of a third arm which acted as a mercury reservoir. By opening the stopcock connecting the reservoir to the rest of the

barostat mercury could be added, and by creating a vacuum in the reservoir mercury could be removed.

The tungsten needle contacts in the crude barostat operated a magnetic relay which activated the air pump. The contacts in the sensitive barostat operated an electronic relay of the type described by E. J. Serfass⁴⁰. This relay activated a fixed solenoid, described by D. J. LeRoy³⁰, which connected the sensitive barostat to the crude barostat. When the circuit was closed air was sucked from the sensitive to the crude barostat and when the circuit was open, the flow of air was stopped.

In order to obviate flutter and fluctuations in the sensitive barostat and so ensure a constant pressure, two devices were used. One was to introduce two leaks into the system. The leak connecting the two barostats was a fine capillary glass tube and the leak connected to the atmosphere was a fine needle valve. The needle valve was adjusted so as to give a balance between the air leaking into the sensitive barostat from the atmosphere and the air leaking out through the capillary. This kept the sensitive barostat at a steady state and kept the electronic relay operating at a high rate. The second device was the use of four large carboys in the system as buffers to reduce the sudden changes in pressure brought about by the operation of the air pump.

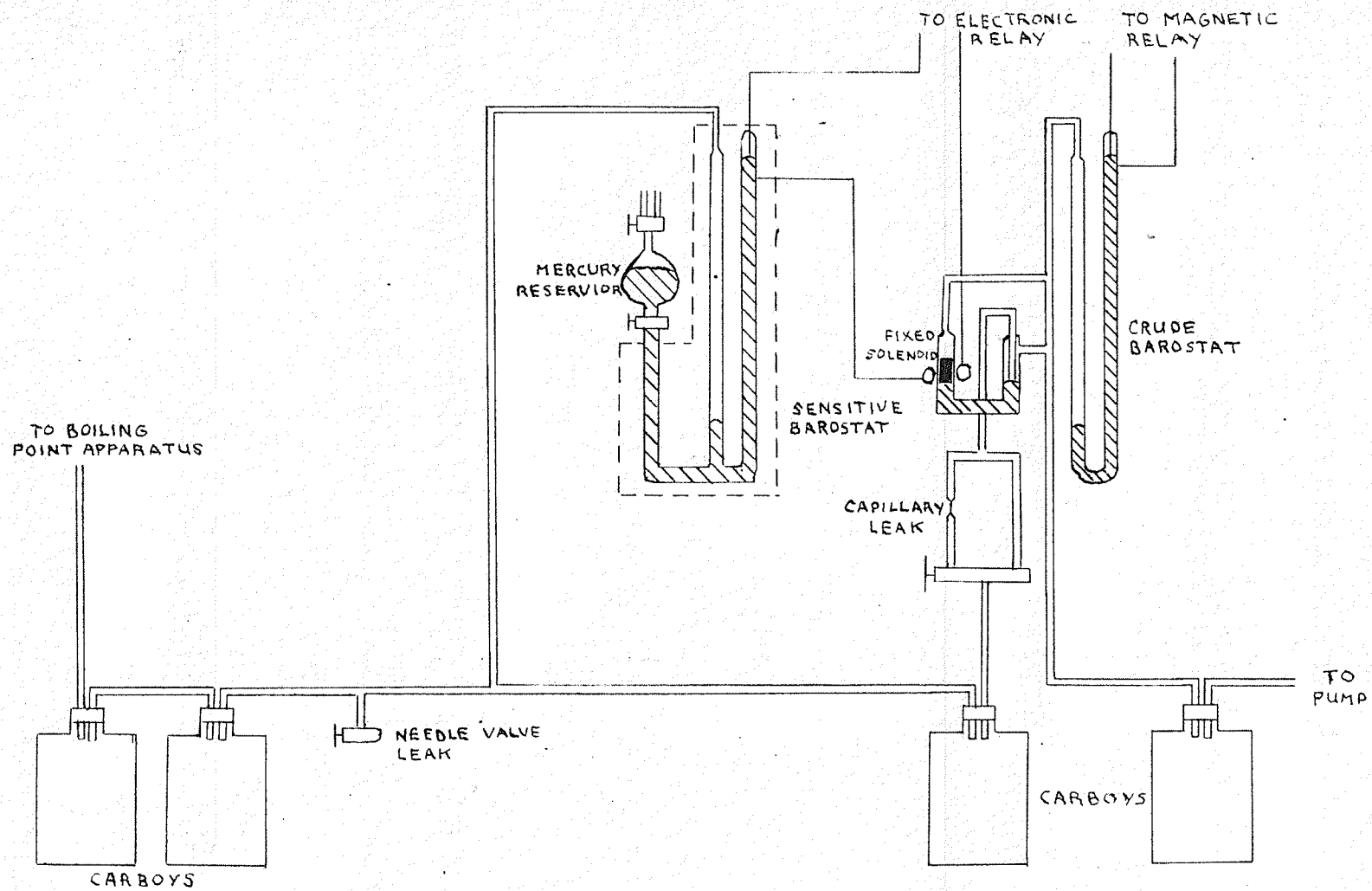


FIG. (1)

The pressure in the crude barostat was determined by means of a travelling cathometer. The pressure in the fine barostat was determined by means of the travelling cathometer and checked by determining the boiling point of pure water in the Scatchard equilibrium still. The pressure was ascertained from the boiling point by means of steam tables.

Both barostats were constructed of 15 mm. diameter Pyrex tubing. The tungsten needles used as contacts were sharpened to a fine point by stroking the red hot needles along a block of sodium nitrite. The mercury in the barostats was boiled three times to eliminate all air and moisture. The sensitive barostat was thermostated at 30°C. A 40 watt bulb was used as a heater while a fan insured good air circulation. A two-way stopcock was used as a bypass around the capillary leak so that the system could be taken down to the desired pressure rapidly. All connections were made with pressure tubing and the system was made leakproof. The barostats were checked for leaks with a Tesla coil.

With the system at equilibrium, the boiling point of pure water was found to remain constant to within $\pm 0.002^\circ$ over a period of several days. No flutter could be observed on the mercury surface of the sensitive barostat.

(c) Boiling point apparatus

The determination of the boiling points for pure water and for the solutions of under 25% concentration was made by means of the Scatchard³⁸ equilibrium still. The still consists of a double boiler, a Cotrell type pump and a hold up trap. The advantage of the Scatchard still is that superheating, reflux condensation, lack of equilibrium, and entrainment of vapour, are eliminated. For solutions stronger than 25% this still was unsatisfactory. Pronounced bumping started to take place and a steady temperature reading could not be made. Also, at very high concentrations the electrolyte crystallized in the cooler lower portion of the hold up trap thereby plugging up the still. The still was heated by means of a nichrome wire heating coil placed beneath the outer boiler. The coil was regulated by a Variac set so that steady boiling took place. The thermometer well was partially filled with mercury to reduce loss of heat due to radiation. Two hours of steady boiling were allowed before readings were taken to allow the still to reach equilibrium.

For the solutions stronger than 25%, a student Cotrell boiling point apparatus was used. Although not as accurate as the Scatchard still, it was the only other boiling point apparatus available. Platinum scrap was employed to prevent bumping. The still was heated by means of a heating pad controlled by a Variac.

(d) Temperature

Except for the highly concentrated ammonium nitrate solutions, 70-90% by weight, Beckman thermometers were used for all readings. For the highly concentrated ammonium nitrate solutions, a mercury in glass thermometer was used. All thermometers were calibrated at regular intervals against an N.R.C. platinum resistance thermometer. Each solution was boiled at least two hours and temperature readings taken at regular intervals. Due to the deficiencies of the student Cotrell apparatus and the difficulty of controlling bumping at the higher concentrations, the temperature accuracy is only about $\pm 0.03^\circ$.

2. Preparation of materials

(a) Ammonium Nitrate

The ammonium nitrate was obtained from the Consolidated Mining and Smelting Company. Although it was a commercial product, the analysis supplied at time of delivery showed it to be very pure. It was thought sufficient to recrystallize it twice from water. The experimental procedure made it unnecessary to take account of the moisture in the ammonium nitrate and the silver nitrate.

(b) Silver nitrate

The silver nitrate was obtained from the Johnson, Matthey and Mallock Company. The purity was such that further purification was unnecessary. The silver nitrate was kept in a dark cabinet to prevent decomposition due to light.

(c) Potassium chloride

Pure potassium chloride was required to make up the standard solutions for the calibration of the conductance cells. A good reagent grade salt was fused in a platinum dish to expel all moisture and stored in a desiccator.

(d) Water

The water used in making solutions was a good quality distilled water. Its specific conductance was in the order of 1.7×10^{-6} mhos. Since all the solutions were of high conductance, there was no need for highly purified conductivity water.

3. Method of Analysis

The work of A. N. Campbell and E. M. Kartzmark¹³ on the conductance of silver nitrate and ammonium nitrate at 25°C. and the availability of a conductance bridge made it most convenient to analyse the solutions by means of specific conductance measurements.

A Leeds and Northrup Campbell-Shackleton shielded ratio box together with the associated A. C. resistance boxes, variable capacitors, and an audio-frequency oscillator were arranged in an exact duplicate of that suggested by the Leeds and Northrup Company in their catalogue EN-95. Since the solutions were highly conducting, a simple telephone headpiece was used as a detector. The apparatus had been set up previously by A. P. Grey²⁴.

The conductance cells employed were of the type recommended by Jones and Bollinger²⁷. Although the behaviour of cells with high cell constants have not been reported in the literature, the work of A.P. Grey²⁴ would seem to justify their use. The platinum electrodes were coated with a light layer of platinum black by the electrolysis of a solution of platinic chloride in the cell. The cell constants were determined with 0.1N and 0.01N potassium chloride. Three cells were used during the investigation with cell constants of 210.57, 1270.1 and 2885.1. The cell constants were checked at regular intervals and no variation was found.

Since the variation of conductance with temperature is in the order of 2% per degree, the cells were suspended in a carefully controlled thermostat at 25.00°C. The thermostat consisted of an insulated 20 liter pyrex container. The bath fluid was paraffin oil as recommended by Davies¹⁹. The heating element was an 100 watt light bulb. Stirring was done with a propellor type mechanical stirrer having two propellers on the shaft. No temperature differences could be detected, with a Beckmann thermometer, between various parts of the bath.

4. Experimental procedure

With the barostats set at the desired pressure, solution which

had been made up to the desired concentration by a rough weighing, was introduced into the boiling point apparatus. In the case of the Scatchard still, approximately 100 ml. of solution was placed in the inner boiler, 40 ml. in the outer boiler, and the trap was filled to its capacity with distilled water. For the student Cotrell apparatus, 115 ml. of solution was added.

The solutions were boiled for at least one hour before readings were taken in order to allow the solutions to attain equilibrium with their vapour. The solutions analysed in each case were the equilibrium solutions.

After recording the boiling point readings for at least two hours, boiling was discontinued, the boiling point apparatus clamped off from the barostats, and the solution was pipetted out with a 25 ml. pipette and transferred to a ground glass stoppered container. For the case where the solution crystallized at room temperature the procedure was modified. To prevent crystallization the solution was removed by means of a heated pipette and transferred to a weighing bottle whose weight had been determined.

The solution was then transferred to the conductance cell and the specific conductance determined. In the case of solutions which had crystallized at room temperature, the solutions were diluted until the salt was completely dissolved.

Using the data of A. N. Campbell and E. M. Kartzmark¹³, it was then possible to find the corresponding concentration in weight percent. Since the extent of dilution of the highly concentrated solutions was known, it was possible to calculate their original concentration.

After each reading the cell was removed and cleaned by repeated rinsings with warm water. The cell was then dried with alcohol and ether and flushed out by passing clean dry air through it for about 10 minutes. This procedure produced no change in the cell constant.

EXPERIMENTAL RESULTS

(1) Silver Nitrate

TABLE (1)

Concentrations and Boiling Points of AgNO_3

at a Pressure of 701.6 mm. of Mercury

TEMPERATURE (°A)	CONCENTRATION (Weight %)	TEMPERATURE (°A)	CONCENTRATION (Weight %)
370.93	0	379.07	75.15
371.17	3.82	383.77	83.18
371.26	6.28	385.16	84.53
371.74	14.75	385.76	85.45
371.81	16.20	386.36	85.57
372.26	24.98	388.12	87.74
372.43	35.01	390.26	88.78
372.89	37.31	391.51	89.47
373.53	44.68	392.26	89.79
374.87	53.31	392.32	89.87
375.91	61.67	393.34	89.92
378.20	72.31		

TABLE (2)

Concentrations and Boiling Points of AgNO_3

at a Pressure of 597.2 mm. of Mercury

TEMPERATURE (°A)	CONCENTRATION (Weight %)	TEMPERATURE (°A)	CONCENTRATION (Weight %)
366.55	0	373.44	72.09
367.05	9.17	375.07	76.85
367.58	18.99	375.86	78.70
367.90	25.84	376.67	80.12
369.29	47.69	377.91	81.51
369.70	48.71	379.00	83.37
369.71	52.36	380.52	85.12
369.77	50.30	381.38	85.95
370.88	62.51	383.32	87.56
372.34	66.43	384.76	88.53
372.61	69.26		

396

GRAPH (1)

BOILING POINTS OF SILVER NITRATE

AT 701.6 mm. AND 597.2 mm.

392

388

384

TEMPERATURE (°A)

380

376

372

368

364

360

701.6 mm.

597.2 mm.

CONCENTRATION (WEIGHT %)

10

20

30

40

50

60

70

80

90

100

TABLE (3)

Boiling Points of AgNO_3 Obtained
from Graph (1) at Concentration Intervals of 5%

CONCENTRATION	PRESSURE 701.6 mm.	PRESSURE 597.2 mm.
	TEMPERATURE (°A)	TEMPERATURE (°A)
0	370.94	366.54
5	371.15	366.81
10	371.44	367.07
15	371.69	367.36
20	371.97	367.64
25	372.24	367.94
30	372.48	368.15
35	372.75	368.54
40	373.02	368.95
45	373.56	369.33
50	374.26	369.61
55	375.00	370.06
60	375.64	370.78
65	376.45	371.51
70	377.48	372.77
75	378.97	374.35
80	381.61	376.62
85	385.46	380.41
88	388.7	383.9

TABLE (4)

Values of ΔH_2 from Graph (2) for AgNO_3

CONCENTRATION (Weight %)	SLOPE ($-\Delta H/R$)	ΔH_2 (k. cal./mole)
0	-2167	9.9
5	-2194	10.0
10	-2181	10.0
15	-2208	10.1
20	-2208	10.1
25	-2229	10.2
30	-2215	10.1
35	-2288	10.5
40	-2365	10.8
45	-2280	10.4
50	-2077	9.5
55	-1966	9.0
60	-2006	9.2
65	-1983	9.1
70	-2090	9.6
75	-2147	9.8
80	-2017	9.3
85	-2035	9.3
88	-2181	10.0

GRAPH (2)

LOG P vs. 1/T FOR SILVER NITRATE

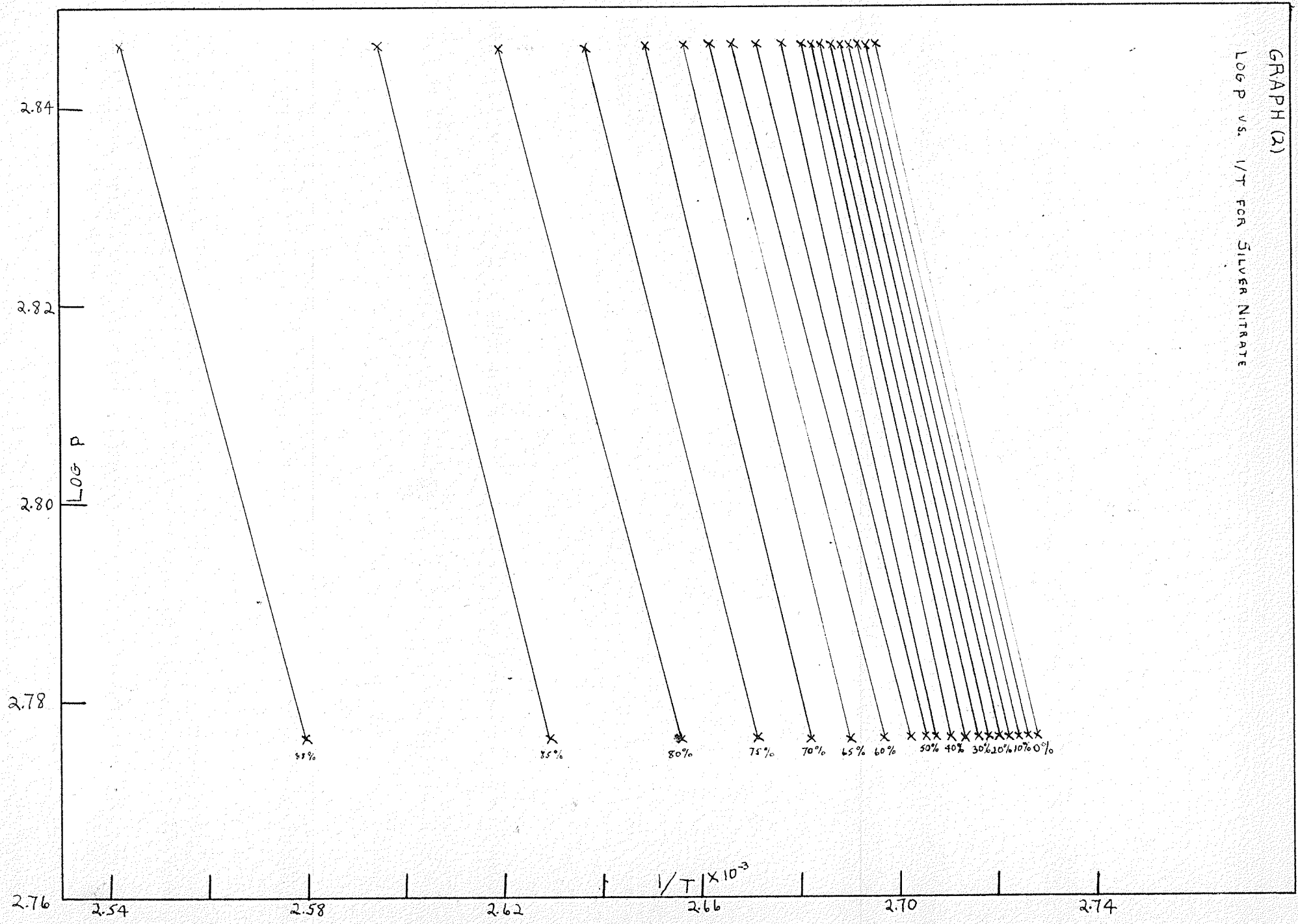


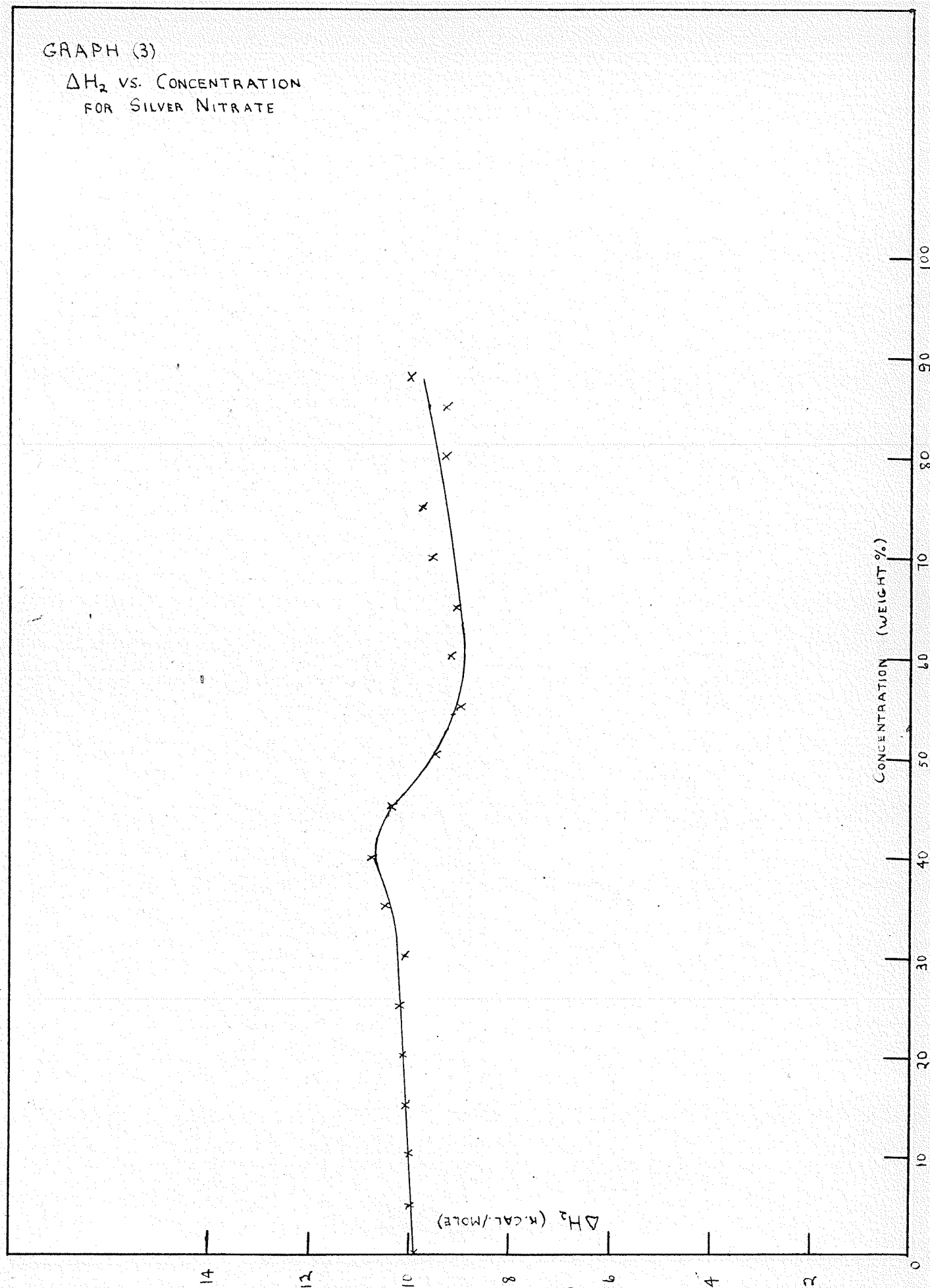
TABLE (5)

Values of ΔH_1 for AgNO_3 calculated from Equation (8)
Assuming $\Delta H_3 = 9.9 \text{ k. cal./mole}$

CONCENTRATION (Weight %)	ΔH_2 (k. cal./mole)	ΔH_1 (k. cal./mole)
0	9.9	0
5	10.0	-0.1
10	10.0	-0.1
15	10.1	-0.2
20	10.1	-0.2
25	10.2	-0.3
30	10.1	-0.2
35	10.5	-0.6
40	10.8	-0.9
45	10.4	-0.5
50	9.5	0.4
55	9.0	0.9
60	9.2	0.7
65	9.1	0.8
70	9.6	0.3
75	9.8	0.1
80	9.3	0.6
85	9.3	0.6
88	10.0	-0.1

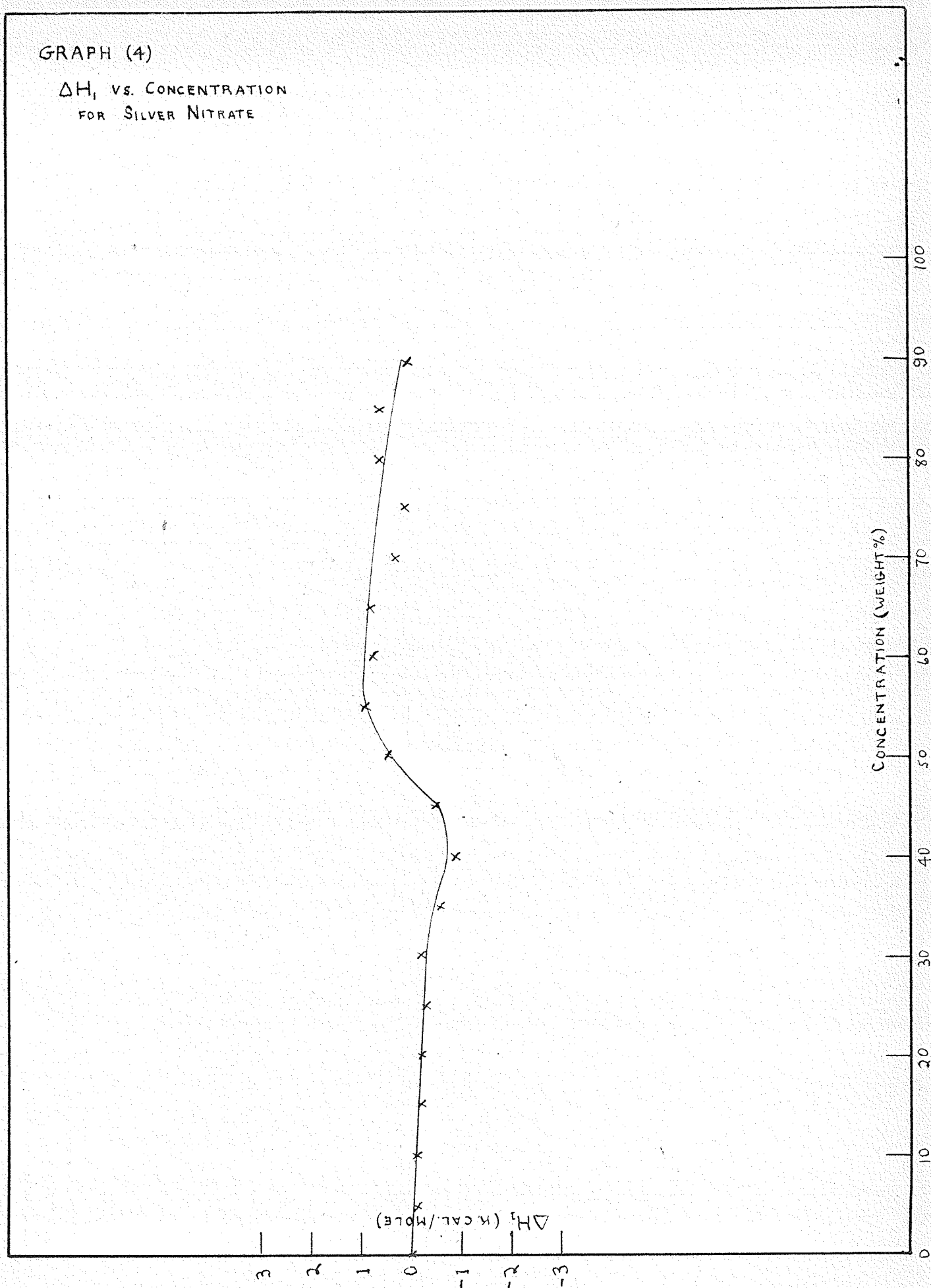
GRAPH (3)

ΔH_2 VS. CONCENTRATION
FOR SILVER NITRATE



GRAPH (4)

ΔH_i vs. CONCENTRATION
FOR SILVER NITRATE



(2) Ammonium Nitrate

TABLE (6)

Concentrations and Boiling Points of NH_4NO_3

at a Pressure of 701.6 mm. of Mercury

TEMPERATURE (°A)	CONCENTRATION (Weight %)	TEMPERATURE (°A)	CONCENTRATION (Weight %)
370.94	0	383.71	59.00
371.87	6.18	384.35	60.28
371.93	7.40	385.28	62.58
372.29	10.35	390.5	69.99
372.54	12.04	396.3	76.57
373.47	18.81	400.0	79.71
373.98	22.85	407.0	84.97
375.26	29.94	417.1	89.61
379.90	50.28	417.3	89.77



TABLE (7)

Concentrations and Boiling Points of NH_4NO_3

at a Pressure of 614.2 mm. of Mercury

TEMPERATURE (°A)	CONCENTRATION (Weight %)	TEMPERATURE (°A)	CONCENTRATION (Weight %)
367.31	0	380.91	61.73
368.07	6.83	385.73	68.23
368.74	13.02	387.25	70.65
369.62	19.77	389.79	72.24
370.24	23.48	395.51	80.98
372.07	32.03	398.76	83.13
373.58	38.70	406.56	87.23
374.84	44.05	410.6	88.84
376.33	48.25	416.3	90.51
377.86	54.85		

GRAPH (5)
Boiling Points of Ammonium Nitrate
at 701.6 mm. and 614.2 mm.

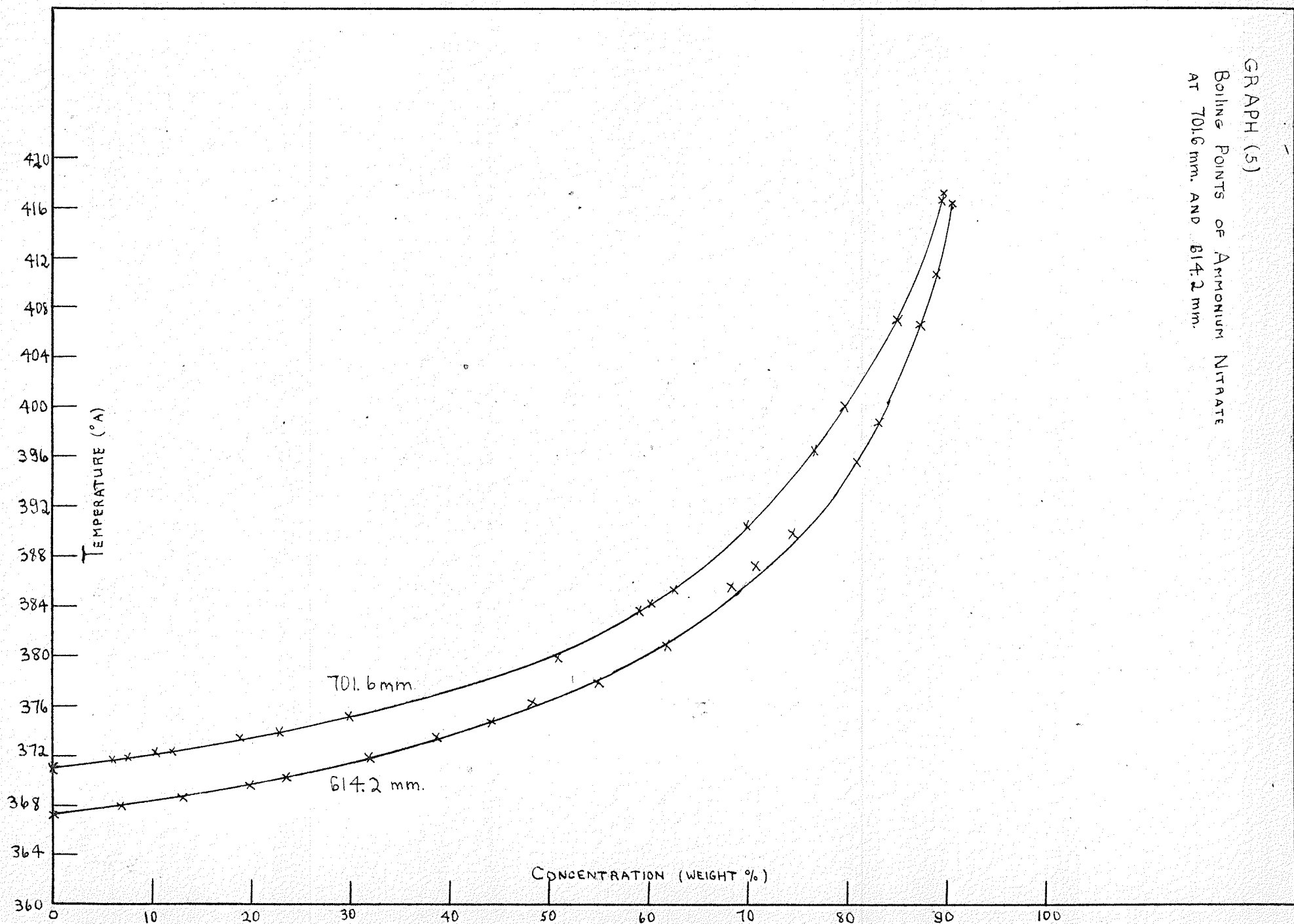


TABLE (8)

Boiling Points of NH_4NO_3 Obtained
from Graph (5) at Concentration Intervals of 5%

CONCENTRATION	PRESSURE (701.6mm)	PRESSURE (614.2mm)
	TEMPERATURE($^{\circ}\text{A}$)	TEMPERATURE($^{\circ}\text{A}$)
0	370.94	367.31
5	371.68	367.67
10	372.27	368.37
15	372.94	368.91
20	373.61	369.64
25	374.40	370.55
30	375.27	371.50
35	376.17	372.63
40	377.26	373.88
45	378.49	375.35
50	379.85	376.95
55	381.74	378.76
60	384.21	381.07
65	387.03	383.79
70	390.50	386.78
75	394.76	390.29
80	400.34	394.77
85	407.19	402.28
90	417.67	414.27

GRAPH (6)

Log P vs. $1/T$ FOR AMMONIUM NITRATE

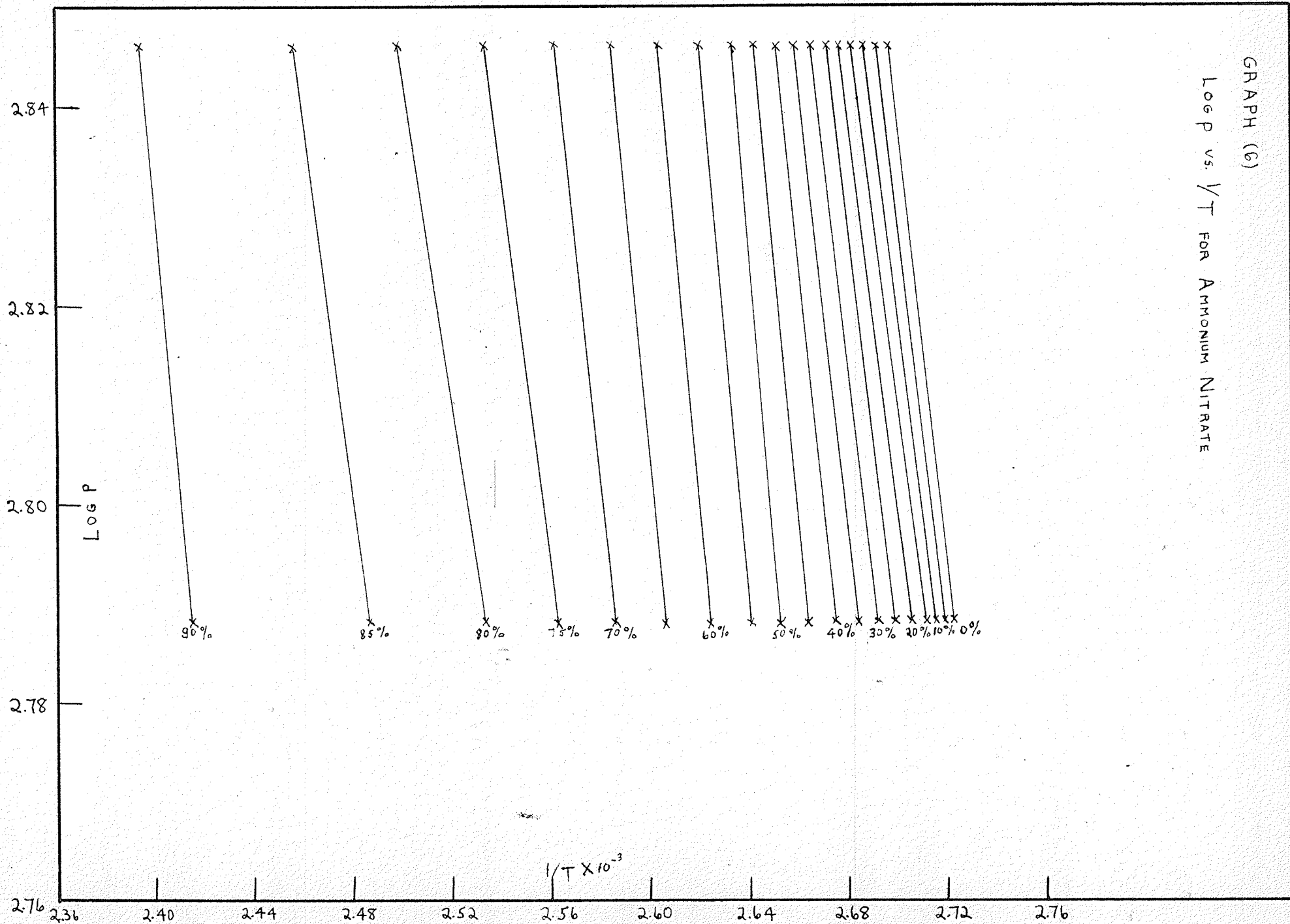


TABLE (9)

Values of ΔH_2 from Graph (6) for NH_4NO_3

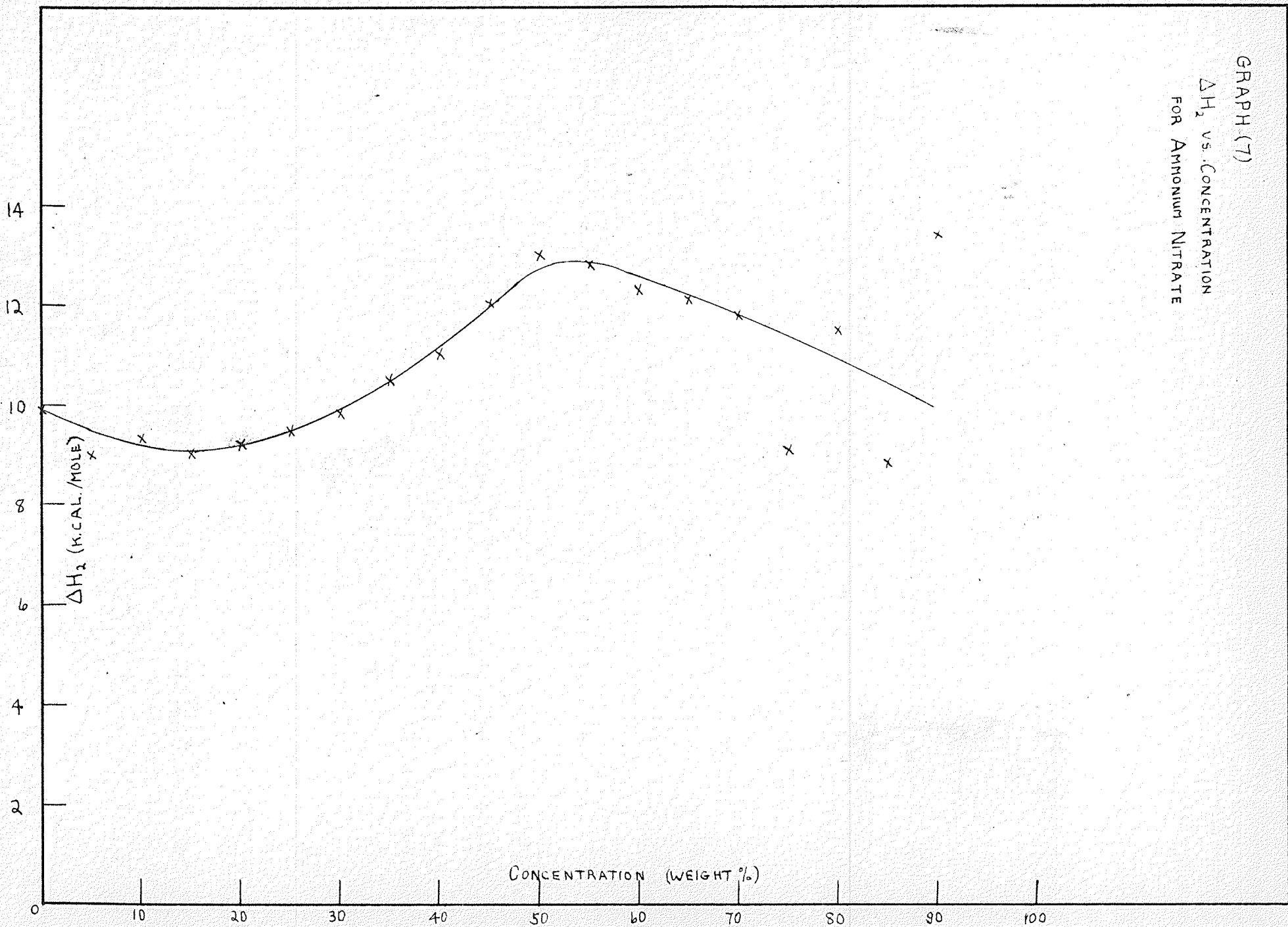
CONCENTRATION (Weight %)	SLOPE ($-\Delta H/R$)	ΔH_2 (k. cal./mole)
0	-2173	9.9
5	-1973	9.0
10	-2028	9.3
15	-1973	9.0
20	-2007	9.2
25	-2079	9.5
30	-2133	9.8
35	-2294	10.5
40	-2408	11.0
45	-2615	12.0
50	-2847	13.0
55	-2806	12.8
60	-2688	12.3
65	-2651	12.1
70	-2350	10.8
75	-1993	9.1
80	-2294	10.5
85	-1933	8.8
90	-2934	13.4

TABLE (10)

Values of ΔH_1 for NH_4NO_3 Calculated from Equation (8)
Assuming $\Delta H_3 = 9.9$ k. cal./mole

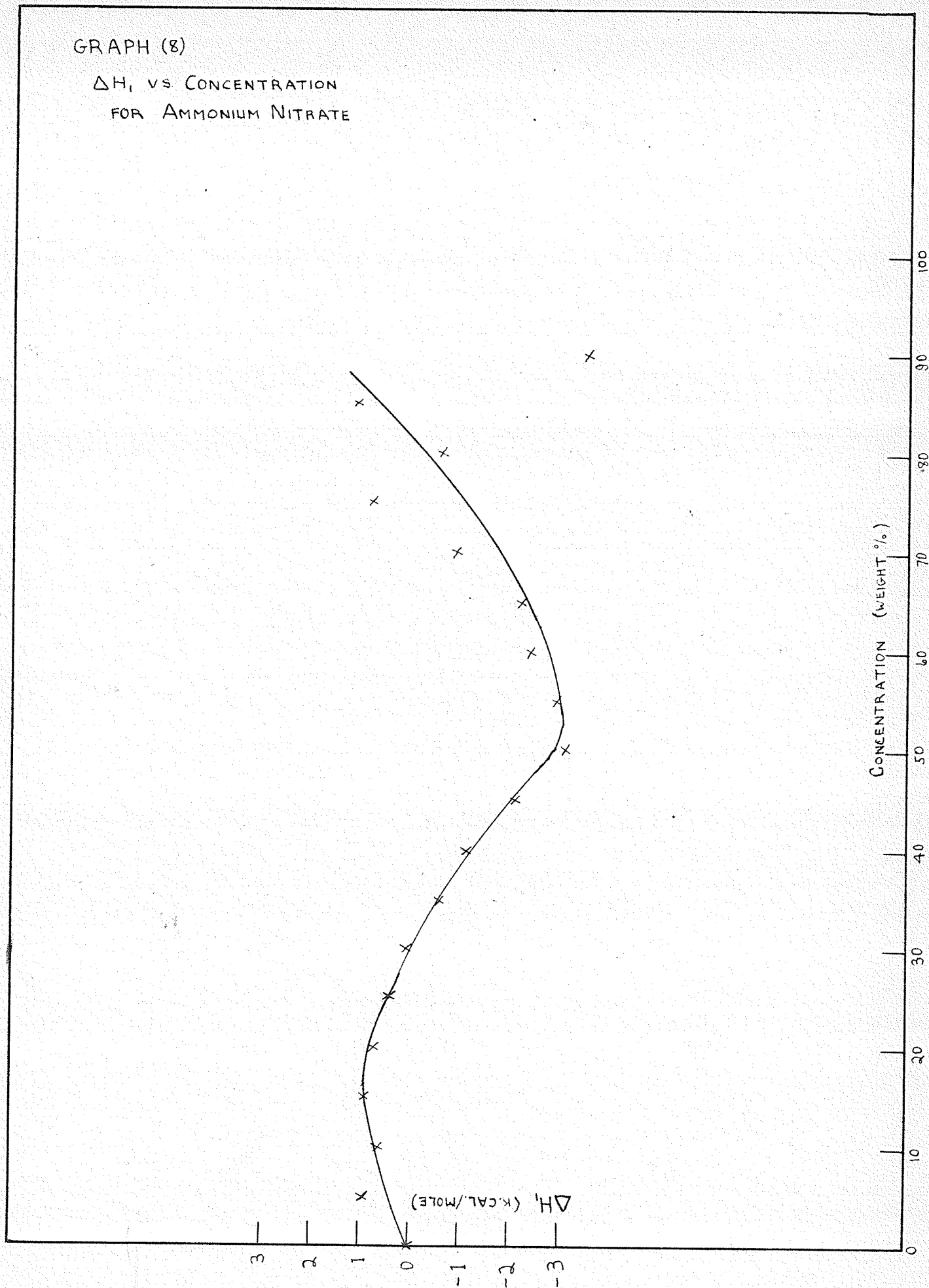
CONCENTRATION (Weight %)	ΔH_2 k. cal./mole	ΔH_1 k. cal./mole
0	9.9	0
5	9.0	0.9
10	9.3	0.6
15	9.0	0.9
20	9.2	0.7
25	9.5	0.4
30	9.8	0.1
35	10.5	-0.6
40	11.0	-1.1
45	12.0	-2.1
50	13.0	-3.1
55	12.8	-2.9
60	12.3	-2.4
65	12.1	-2.2
70	10.8	-0.9
75	9.1	0.8
80	10.5	-0.6
85	8.8	1.1
90	13.4	-3.5

GRAPH (7)
 ΔH_2 vs. CONCENTRATION
FOR AMMONIUM NITRATE



GRAPH (8)

ΔH_f vs CONCENTRATION
FOR AMMONIUM NITRATE



DISCUSSION OF RESULTS

Although it was planned originally to continue the experiment at several other pressures, it was seen from the results to date that the method employed was not of sufficient accuracy. Even with dilute solutions of strong electrolytes it is most difficult to obtain boiling points which are accurate enough to be used for activity coefficient measurements²⁶, and since the boiling point accuracy needed in this experiment is comparable with that required for activity coefficient determinations, and since the concentrations employed in this experiment are quite high, it is the opinion of this author that no worthwhile data can be obtained by the boiling point method.

What is required is an accurate method of determining vapour pressures of very concentrated solutions of strong electrolytes. One method is the isopiestic method as employed by Stokes and Robinson⁴¹. The fact that many concentrated salt solutions form gels, will allow determinations to be made up to very highly concentrated solutions. A second method which is capable of giving the accuracy desired up to very highly concentrated solutions, is a modified isoteniscope method. By having the electrolytic solution in one temperature variable bath, and a solvent whose vapour pressure is accurately known in another temperature variable bath, it should be

possible to obtain the vapour pressure of the electrolytic solution, at any temperature and concentration, by means of a differential manometer.

It is interesting to note that, with an error of $\pm .03^\circ$ in the temperature determinations and an error of $\pm .05\%$ in the composition determination, giving a total experimental error of 28%, the difference from zero of ΔH_1 , the heat of hydration, is no greater than the experimental error. Therefore, no hydration effect was noticed in this experiment.

Although the deviation of ΔH_1 from zero falls inside the limits of the experimental error, an examination of Graph (4) and of Graph (8) would seem to indicate that some regularity exists and that the curves might be significant. Although the experimental error on each boiling point determined was 28%, the method of plotting the data on a smoothed curve would most certainly lower the overall error considerably. A quantitative estimation of the deviation could not be obtained since the least squares method failed to yield an accurate analytical equation for the boiling point curves. It seems probable, however, that the deviation is low enough to make the results significant.

In the case of silver nitrate, Graph (4) deviates only very slightly from a straight line plot, showing very little hydration effect. This is in accord with experimental findings which indicate that both the silver ion and the nitrate ion are unhydrated in solution⁸. The rise in ΔH_1 at a concentration of about 45% could be due to the formation of a quasi lattice structure in the solution. The fact that silver nitrate solutions above this concentration formed gels at room temperature would

seem to support this view. For the remainder of Graph (4), ΔH_1 appears to remain constant.

For ammonium nitrate, Graph (8), the situation is roughly similar. Ammonium nitrate shows a greater hydration effect which is in accord with experimental findings⁴⁶.

One must also bear in mind a second possible explanation for the negative results obtained. It is possible that the phenomena being looked for does not exist and that the treatment of Stokes and Robinson⁴¹ is wrong. A more accurate study of this problem would undoubtedly clear up this point.

Although the main purpose of this research was not realized, it is to be hoped that the boiling point data obtained will prove useful in later work.

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