

THE THERMOCHEMISTRY OF HYDRAZINE
(1) CONSTRUCTION OF AN AUTOMATIC ADIABATIC CALORIMETER
(2) DETERMINATION OF SPECIFIC HEAT CAPACITIES

by

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INTRODUCTION

A knowledge of the heat and energy quantities involved in chemical reactions is the foundation of Chemical Thermodynamics. The great importance of thermo-chemical data was recognized in the second half of the 19th century by Thomsen, a Danish chemist, and Berthelot in France, whose investigations, particularly those of the former (1), for a period of many years were largely devoted to the thermochemical field. Their results are in many cases the only thermal data available for important chemical systems, despite the fact that numerous remarkable improvements in technique have been developed within the last fifteen years.

T. W. Richards and his students at Harvard (2-12) are largely responsible for the recent improvements in thermochemical technique, and particularly are they noted for their investigations in the field of aqueous solutions.

The very important work of Lewis and Randall on theoretical chemical thermodynamics (13) has provided a unified method of treating, correlating and applying thermochemical data to the solution of many problems. The developments in both the practical and the theoretical branch of the subject have lead to stimulated research activity for the purpose of remeasuring and extending the work of Thomsen, Berthelot and other early workers. Aside from the strictly thermodynamic treatment, certain theoretical relationships have been developed during the last six to eight years as corollaries of the newer theories of solutions that demand precise heat data.

The foundation upon which is built the structure of thermo-

chemistry has been shown to be specific heats. The accurate observation of heats of reaction, heats of solution and dilution are obviously of small value unless the necessary heat capacities are known with equal accuracy. The specific heats of aqueous solutions, especially, have been a subject of active investigation for many years, but the advent of the modern calorimetry of the past ten years has rendered the previously recorded data on this subject obsolete.

A critical search of chemical literature has shown that thermodynamic data on hydrazine ($\text{NH}_2\text{-NH}_2$), a homolog of ammonia, was almost completely lacking. Salts of hydrazine, as well as the parent substance, have been investigated over a period of years at Oregon State College with the object of eventually completing a systematic study of all their important physical and chemical properties.

The work presented in this thesis represents the first part of a study on the thermodynamic properties of hydrazine compounds. In the future it is planned to complete a thorough investigation on the thermochemical properties of these substances; and for much of the study, the apparatus herein described will be used.

THE THERMOCHEMISTRY OF HYDRAZINE

(1) CONSTRUCTION OF AN AUTOMATIC ADIABATIC CALORIMETER

(2) DETERMINATION OF SPECIFIC HEAT CAPACITIES

PURPOSE

The purpose of this investigation was three-fold:

1. To present the design of an automatic adiabatic calorimeter suitable for use in an accurate investigation of many thermochemical properties of aqueous solutions of hydrazine derivatives.
2. To present specific heat data obtained with this calorimeter on various salts of hydrazine.
3. To give a correlation of the data obtained following the latest and best methods that have been developed.

APPARATUS

There are available three types of apparatus suitable for a study of heat capacities at ordinary temperatures. First is the classical calorimeter that operates with an outer bath at a fixed temperature while an insulated, submerged vessel is being heated by a measured amount of electrical energy. The temperature rise for the heating is taken and a correction is applied for heat leakage between the inner container and the outer bath. By knowing the weight of solution and the calorimeter equivalent it is possible to evaluate the specific heat. With the exception of the errors involved in the heat leakage factor, the method is excellent. But it is quite impossible to reduce the variability of the heat leakage below a certain value by any

refinement in apparatus.

To minimize this factor, Richards and students (2-12) were led to eliminate all thermal head between the outer bath and the calorimeter. This second design is known as the adiabatic calorimeter. Its chief value lies in the elimination of practically all thermal head and consequently all heat leakage. The apparatus and its operation is otherwise essentially similar to the ordinary calorimeter.

A third important method for very accurate measurement of heat capacities is that recently applied by Richards and Gucker (5). The apparatus, designed after Pflaundler's modification of Joule's "Twin Calorimeter", consists of two identical calorimeters immersed in an adiabatic bath. Its accuracy is within one part per 10,000, a considerable improvement over other types. The "Twin Calorimeter", however, is applicable only for specific heat determinations, whereas the usual adiabatic calorimeter is equally useful for measuring nearly all thermochemical properties in aqueous solutions.

The apparatus built was an improved modification of Richard's adiabatic calorimeter in which the adiabatic control was made automatic. The design followed that of Williams and Daniels (14) and that of Urban (15) with several modifications. The choice of the particular apparatus was based upon the best accuracy compatible with its use as an instrument adaptable for measuring heats of solution, dilution and reaction as well as heat capacities of aqueous solutions. Arrangements were made whereby a slight modification would allow the measurement of any of the above heat quantities.

The apparatus constructed for use in this research is shown in Figure 1. The principles laid down by White (16) and Barry (17) were

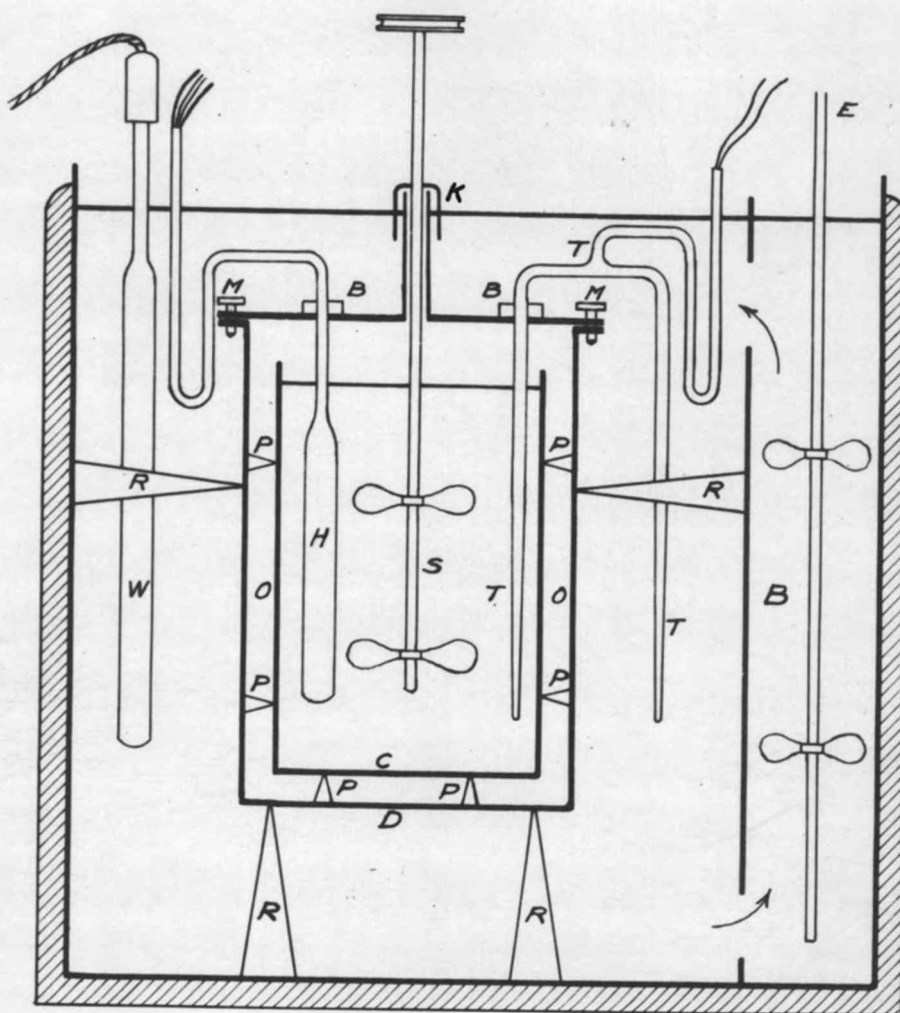


Figure 1
The Calorimeter

applied in the design. The outer copper can of 12 liter capacity, which was lagged with an insulating material, acted as a bath in which to immerse the calorimeter. Tube B welded into the can served to provide more efficient circulation by stirrer E. The assembled calorimeter rested on three large Bakelite pegs R, which were screwed into the bottom of the outer bath. Four additional pegs, acting as supports, projected from the side of the container.

The solution, whose properties are to be measured was contained in the heavily gold-plated cylindrical container C, of 0.9 liter capacity. The vessel C was inclosed in a submarine jacket D, and supported in place by small Bakelite pegs P, that served both as thermal insulation and to maintain an air gap O, of 11 mm. The interior of the jacket was polished and heavily gold-plated to prevent corrosion. The cover on the submarine jacket was ridged about the edge and ground to fit a groove in the rim (~~Fig. 1~~). The cover was held tightly in place by three thumb screws M, located equidistantly around the rim. The groove was coated with special stopcock grease and was never known to leak when properly assembled.

The gold-plated stirrer for the inner can was operated through a central shaft from above. The upper part of the stirrer shaft is of Bakelite to reduce heat leakage to the outside. The water seal K, at the surface of the outer bath stopped air circulation along the stirrer tube and reduced evaporation losses to a minimum. The stirring rate was maintained exactly constant at 230 revolutions per minute by a large synchronous motor. At this rate the heat of stirring was approximately 0.0002° centigrade per minute. The exact value was

obtained for each determination.

There was an additional tube (not shown in the figure) through the cover of the submarine jacket for a breaker rod of four prongs. Along the side of the inner vessel C, were located four clips, each of which could hold a small glass bulb. At a suitable time the rod could be turned, allowing a prong to break one of the bulbs which would introduce new material into the vessel. Further turning of the rod would cause the breaking of another bulb, and by rotating the breaker rod in the other direction, the two remaining bulbs could be broken similarly. Consequently, it is possible to study other heat quantities previously mentioned in a stepwise manner by following the temperature change produced.

It was necessary to provide a thermel to record any differences in temperature between the calorimeter and the outer bath. A glass enclosed thermel T, was constructed according to White (18) and consisted of 17 copper-constantan junctions (No. 34 D.S.C. Copper and No. 30 D.S.C. Constantan) embedded in naphthalene to lessen thermal lag. The junctions were equally spaced over a distance of several centimeters to obtain an average temperature effect from the top to the bottom of the calorimeter. The leads were connected to a Leeds and Northrup H. S. galvanometer having a standard sensitivity of 10 mm per microvolt. The scale was placed at a distance of four meters from the galvanometer so that each centimeter corresponded to a temperature difference of 0.0008° centigrade. One arm of the thermel projected through a conical stuffing box B, into the inner container with the other remaining in the outer bath.

A heater H, for the inner vessel projected through the second stuffing box and was of a type described by Urban (15). Two heaters were constructed of 35 and 40 ohms. They were made by wrapping No. 32 bare constantan wire in a bifilar manner on a thin mica strip. Two thin mica sheets placed over the coil acted as insulation and protection for the element. Thin copper foil was soldered over the element as a sheath and was coated with Bakelite laquer and baked for several hours at 110° centigrade. In no case was there any contamination of the solutions with copper noted. Leads of No. 30 copper were silver soldered onto the constantan heater wire and several turns of this were placed in the heater to minimize heat leakage along the leads. The No. 30 leads were in turn soldered to a set of potential leads of No. 30 copper and to a set of current leads of No. 26 copper wire. The top of the copper sheath was soldered to a piece of 5 mm glass tubing which had been platinized. The glass tubing served both as a support and as a protection for the lead wires which were extended for a distance of 20 centimeters in the bath to minimize heat leakage to the room.

The electrical system (Fig. 2) for accurately measuring the energy input was similar to Williams and Daniels (14) and to Ewing, Rogers, Miller and McGovern (20). Three large storage batteries B, in series supplied current which passed through heater H and a standard one ohm resistance, O. A volt box V, having a ratio of 26.009:1 was connected in parallel with the heater. A Leeds and Northrup type K potentiometer connected through switch S_2 to the one ohm standard resistance or to the volt box served for the measurement of the current and



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the voltage across the heater. A galvanometer of sensitivity of 0.05 microamperes per mm at one meter scale distance with a critical damping resistance of 300 ohms was used with the potentiometer. For a period of twenty minutes before starting an experiment, switch S₁ is thrown to allow current to pass through the polarizing resistance D. This enabled the batteries to reach a steady potential. The resistance of D was the same as that of the heater circuit. During an actual experiment, readings were taken on the potentiometer at definite intervals and were averaged to give the most probable value for the heater resistance and the current flowing. The fluctuations in the heater current were very small and seldom amounted to more than one part per 5,000 during any one determination. The standard cell, the standard one ohm resistance and the volt box were carefully calibrated with standards certified by the Bureau of Standards.

A Leeds and Northrup platinum resistance thermometer in the outer bath indicated the temperature before and after each experiment. The inner calorimeter temperature was exactly equal to that indicated by the platinum thermometer when the thermel galvanometer registered no deflection. This location of the rather bulky thermometer in the outer bath was recommended by Williams and Daniels (14) to eliminate a large source of error due to heat leakage along the thermometer stem. The platinum thermometer was connected to a Mueller type resistance bridge. A Leeds and Northrup galvanometer of 0.5 microvolt per mm sensitivity with a damping resistance of 50 ohms was used in connection with the bridge. An increased sensitivity was obtained by placing the scale at a distance of four meters from the mirror. With reasonable care,

changes of 0.0005° centigrade could be measured.

The thermometer was calibrated by reference to three fixed points, the boiling point of water, the freezing point of water, and the transition point of sodium sulfate decahydrate. It was also calibrated for us by the Gray Instrument Company, Philadelphia.

In this research, provision was made to heat or to cool the outer bath as desired. Electrolytic heating was used because, first it eliminated the necessity of providing a heater and, second, it heated more uniformly throughout the bath. The bath was made conducting by adding small amounts of disodium phosphate to distilled water until the desired conductivity was reached. The conductance was satisfactorily maintained by adding distilled water to the outer bath occasionally to replace evaporation losses. Figure 2 shows the plan for heating control of the outer bath. Ordinary 110 volt alternating current was used. One side of the line connected directly to the large copper can; the other side was branched to allow the main part of the current to flow through switch T and 45 ohm variable resistance R, to the submarine jacket of the calorimeter. The shunted circuit acted as a control mechanism for the exact regulation of bath heating. The current passed through a 250 watt lamp, which acted as a resistance, a switch S, and thence through a relay for automatic control, or shunted around the relay to the bath in which case control was maintained manually with variable resistance, R_2 (765 ohms).

The success of the adiabatic method is based upon the advantage that a negligible amount of heat will leak in or out of the calorimeter vessel during a determination. To accomplish this it is necessary to

maintain the temperature of the outer bath at the temperature of the inner calorimeter at all times. One of the greatest problems of adiabatic calorimetry is the maintenance of this adiabatic condition of zero temperature gradient between the calorimeter and the outer bath.

The automatic adiabatic control for this purpose deserves special mention because of its simplicity and general reliability. A Weston Photronic cell connected directly to a micro-relay and activated by a light beam reflected from the thermel galvanometer mirror served as the essential features of the system. The design is similar to that of Ewing et al (19). In Figure 2 a concentrated light source, L, of 200 watts was reflected from the galvanometer mirror O, to the Photronic cell at P. At the galvanometer's zero point, which indicated no temperature gradient in the apparatus, light reflected from the mirror illuminated part of the cell. If the outer bath became cool, the light beam shifted slightly to the right and illuminated more of the cell. This caused the cell to develop an E.M.F. sufficient to operate a very sensitive micro-relay which in turn caused the larger relay to close the auxiliary heating circuit. The outer bath then heated at an increased rate until the light beam shifted toward the edge of the cell at which the relays broke contact. Then cooling would take place until again the cell was energized. Best operation was obtained with the cell at a distance of one meter from the galvanometer. The time lag in this system was very small with the greater part occurring in the thermel. The adiabatic condition was maintained usually to about $\pm 0.0016^{\circ}$ centigrade with rarely a difference of $\pm 0.0025^{\circ}$ centigrade. Before and

after a determination it was advisable to shift switch S to manual control so that a closer control could be maintained at the time a temperature reading was taken. Readings were taken only when the thermel galvanometer registered zero for a period of several seconds. During the period preceding and following an experiment, adiabatic control was maintained with switch T open and S closed, and at the start T is closed and R, adjusted until the branch circuit will adequately take care of any fluctuations in heating rate that are necessary to give accurate control.

A cooling system was necessary for operation at temperatures below 20° centigrade. A system was devised which was almost free from large lags which are present in a usual cooling coil. When cooling was desired, needle valve N was opened a proper amount. Then electrolyte flowed from bottle B, set above the apparatus and through a copper coil immersed in ice and water and thence through A, to drop into the outer bath. There was very little change in height of liquid in the bottle so that with a given setting of N a very steady flow issued from A. The stream was adjusted for a slight cooling effect, and the adiabatic condition was then maintained by the auxiliary heating circuit as before. Provision was made to collect overflow which was returned to bottle B after each experiment. This method of producing a cooling effect obviated all lag except possibly that due to imperfect mixing.

OPERATION

The outer bath was cooled usually to about 17° centigrade before the start of a series of determinations. The cooled solution to

be tested was weighed into the inner vessel and immediately assembled in the submarine jacket. After completely assembling the apparatus, the inner solution was brought up to the temperature of the outer bath by the heater. Upon reaching the adiabatic condition a temperature reading was taken. Current was then passed through the heating coil in the solution for a definite period of time (usually about twenty-two minutes). The exact time was recorded by a calibrated stop-watch. By means of the automatic control the outer bath was heated at such a rate as to maintain an adiabatic condition at all times during the determination. Then a second temperature reading was taken after a period of seven to eight minutes had elapsed following the discontinuance of the heating. This period allowed the apparatus to reach thermal equilibrium. Following this temperature reading the heating current was turned on for a repetition of the procedure. Usually three separate determinations over a total interval of 9° centigrade could be made with one assembling of the apparatus. The heat of stirring was determined for each solution by noting the rise in temperature over a measured time interval during which the heat input was zero, and a correction was applied which depended upon the total time between temperature readings. Knowing the input of electrical energy, the temperature rise, the calorimeter equivalent and the weight of solution, it was possible to calculate the specific heat of the solution. As an illustration the details of a typical experiment are given in Table I.

TABLE I

Calculation of a Typical Run - 0.5 M $\text{N}_2\text{H}_5\text{Cl}$

| <u>Heating Period</u> | <u>No. 1</u> | <u>No. 2</u> | <u>No. 3</u> |
|--|--------------|--------------|--------------|
| Time of heating - sec. | 1320.2 | 1320.4 | 1320.1 |
| Total elapsed time - sec. | 1680. | 1620. | 1710. |
| Temperature at start ° centigrade | 17.2795 | 20.5750 | 23.8743 |
| Temperature at end ° centigrade | 20.5750 | 23.8688 | 27.1618 |
| Correction - heat of stirring ° centigrade | 0.0053 | 0.0051 | 0.0054 |
| Corrected temperature rise ° centigrade | 3.2902 | 3.2887 | 3.2821 |
| Mean value - heater current - amperes | 0.52008 | 0.52012 | 0.51996 |
| Mean potential across heater - volts | 0.71221 | 0.71224 | 0.71195 |
| 26.009 | | | |
| Total heat input per 1° rise-joules | 3865.6 | 3868.4 | 3872.5 |
| Calorimeter equivalent - joules | 97.0 | 97.0 | 97.0 |
| Corrected vacuo weight of solution - grams | 937.53 | 937.53 | 937.53 |
| Calculated specific heat - joules/degree | 4.0197 | 4.0226 | 4.0269 |
| Calculated specific heat - calories (15°) | 0.9609 | 0.9616 | 0.9626 |
| Mean temperature of run ° centigrade | 18.93 | 22.22 | 25.02 |

The mean value for heater current was obtained by averaging the potentiometer readings across the one ohm standard resistance and subtracting a correction for current that flowed through the volt box, which usually amounted to about 0.017 ampere. The potentiometer reading across the volt box was multiplied by 26.009 to give the true potential drop across the heater. The calculation to give heat input per 1° rise follows for run No. 1.

$$\frac{0.52008 \times (0.7122 \times 26.009) \times 1320.2}{3.2902} = 3865.6 \text{ joules/degree}$$

Several blank determinations using water in the inner container were made in order to evaluate the calorimeter equivalent. From the weight of water, the specific heat of water, and the conversion factor of calories into joules, the expected energy input in joules to cause 1° rise could be calculated and subtracted from the measured electrical input. The difference would be the energy in joules to heat the inner calorimeter apparatus 1° which is called the calorimeter equivalent. The value is the difference between two large numbers and may be determined accurately only to one per cent, which is sufficiently precise for its subsequent use. Its value over a long period of time checked to be 97.0. For the specific heat of water the values 0.9988 at 20° and 0.9979 at 25° were adopted from the International Critical Tables (21). The factor 4.1833, recently published by Southard and Brickwedde of the U. S. Bureau of Standards was used as the value in joules for one calorie (15°).

For run No. 1 the actual heat input to the solution would then be $3865.6 - 97.0 = 3768.6$ joules per degree. The heat input per gram or the specific heat would be $\frac{3768.6}{937.53} = 4.0197$ joules per degree

or 0.96088 calories (15°) per degree.

It is evident that the value calculated in this manner are averages over a range of 3.0° to 3.5° . At the end of the experiment weighed samples of the solutions were analyzed for hydrazine content by the iodic acid method of Bray and Cuy (22).

SUMMARY OF RESULTS

The specific heats obtained in the manner described were plotted on an appropriate scale against temperature, and the interpolated values in calories (15°) per gram of solution are given in the following table.

TABLE II

| <u>Salt</u> | <u>Molality</u> | <u>20°</u> | <u>25°</u> |
|---------------|-----------------|------------|------------|
| $N_2H_6Cl_2$ | 1.000 | .8955 | .8969 |
| $N_2H_6Cl_2$ | 0.500 | .9387 | .9396 |
| $N_2H_6Cl_2$ | 0.200 | .9713 | .9723 |
| $N_2H_6Cl_2$ | 0.100 | .9840 | .9847 |
| $N_2H_6Br_2$ | 1.000 | .8291 | .8297 |
| $N_2H_6Br_2$ | 0.500 | .9007 | .9012 |
| $N_2H_6Br_2$ | 0.200 | .9536 | .9541 |
| $N_2H_6Br_2$ | 0.100 | .9751 | .9756 |
| N_2H_5Cl | 1.000 | .9281 | .9294 |
| N_2H_5Cl | 0.500 | .9611 | .9620 |
| N_2H_5Cl | 0.200 | .9822 | .9826 |
| N_2H_5Cl | 0.100 | .9894 | .9900 |
| N_2H_5Br | 1.000 | .8935 | .8939 |
| N_2H_5Br | 0.500 | .9409 | .9412 |
| N_2H_5Br | 0.200 | .9728 | .9735 |
| N_2H_5Br | 0.100 | .9842 | .9852 |
| $N_2H_5ClO_4$ | 1.000 | .9043 | .9056 |
| $N_2H_5ClO_4$ | 0.500 | .9451 | .9453 |
| $N_2H_5ClO_4$ | 0.200 | .9748 | .9749 |
| $N_2H_5ClO_4$ | 0.100 | .9862 | .9856 |
| KCl | 1.000 | | .9120 |
| KCl | 0.500 | | .9517 |
| *KCl | 1.000 | | .9118 |
| *KCl | 0.500 | | .9518 |

* Values taken from Randall and Rossini (23)

The values of K_{Cl} were determined as a check on the integrity of the apparatus and the accuracy of the calibrations. It is interesting to note that the determination on 0.5 M K Cl was made at the beginning of the work and that on the 1.0 M approximately one year later. Comparison of our results with the highly accurate data of Randall and Rossini shows a very satisfactory agreement.

ACCURACY OF RESULTS

Errors in the measurement of current and potential through the heater were very small and may be neglected in this discussion. The synchronous motor connected through reducing gears to the inner stirrer maintained the rate of stirring perfectly constant, so that error due to variation in heat of stirring is negligible. With the maintenance of adiabatic control, heat leakage can be calculated to be no appreciable source of error.

The probable accuracy of the results as influenced by factors other than the above may be estimated as follows (27). In the individual determinations of heat input Q , a known current I , was passed through the heater with a potential drop of E . The heat evolved EIt caused a rise in temperature ΔT . The heat input per degree would be:

$$C = \frac{Q}{\Delta T} = \frac{EIt}{\Delta T}$$

The error in Q is:

$$\Delta Q = E I \Delta t + E t \Delta I + I t \Delta E$$

Since I and E can be measured with great precision, the last two terms are negligible, and the expression reduces to $\Delta Q = E I \Delta t$

In an actual run

$$\Delta Q = (0.7122 \times 26.009) \times 0.5201 \times 0.4 = 3.86$$

making a generous assumption of 0.4 seconds probable error in the opening and closing of the heater switch and assuming a probable accuracy of 0.001 in the determination of temperature rise, the probable error in C will be

$$\Delta C = \sqrt{\left(\frac{\Delta Q}{\Delta T}\right)^2 + \left[\frac{Q}{(\Delta T)^2} \Delta(\Delta T)\right]^2} = \sqrt{\left(\frac{3.86}{3.30}\right)^2 + \left[\frac{12800}{(3.30)^2} (0.001)\right]^2}$$

$$\Delta C = \pm 2.7 \text{ joules}$$

This would mean an error of 2.7 joules per 3,870 or 0.7 joules per 1000 in the heat input for 1° rise. With other errors assumed negligible this same value will express the probable error in the specific heat values.

The solutions were weighed to 10 mg. and the salts to 1 mg. with appropriate vacuum corrections. Difficulty in preparing and maintaining the salts in strictly anhydrous condition required that the concentration of all solutions be checked by titration. The accuracy of these titrations is of the same order as that of the heat determinations. Errors in the concentration would be reflected in the apparent molal heat capacity.

Judging by the self-consistency of our results when treated graphically, it is believed that, in general, the accuracy of this work is within the calculated limits.

THERMODYNAMIC CALCULATIONS

The calculated thermodynamic quantities involved in this paper include the partial molal heat capacity of the solute \bar{C}_{p_2} , the

partial molal heat capacity of the solvent \bar{C}_p , and the apparent molal heat capacity ϕ . In order to define partial molal heat capacity let us consider a solution containing n_1 mols of X_1 , n_2 mols of X_2 etc. If the heat capacity of the solution as a whole is C_p and the partial molal heat capacity of X_1 is \bar{C}_p , the latter may be defined by the equation,

$$(1) \frac{\partial C_p}{\partial n_1} = \bar{C}_p, \quad \text{Also similarly } \frac{\partial C_p}{\partial n_2} = \bar{C}_{p_2}$$

It may be defined physically as the rate of change of the heat capacity with the amount of X_1 .

The apparent molal heat capacity is related to the partial molal heat capacity and is useful as the first step toward the calculation of the latter. It may be defined in relation to aqueous solutions as the heat capacity of a solution containing 1000 grams of water, minus the heat capacity of 1000 grams of water, all divided by the molality.

It may be represented by the following equation:

$$(2) \quad \phi = \frac{(1000 + mM_2)S_2 - 1000S_1}{m}$$

- m - molality of solute
- M_2 - molecular weight of solute
- S_2 - specific heat of solute at the given temperature
- S_1 - specific heat of water at the given temperature.

Following the theoretical treatment of Randall and Rossini (23) certain relationships will herein be derived. The heat capacity of solution $C_p = (1000 + mM_2)S_2$ and also $55.508 \times \bar{C}_p^\circ = 1000 \times S_1$ may be used to derive the following equation:

$$(3) \quad \phi = \frac{C_p - 55.508 \bar{C}_p^\circ}{m}$$

$\bar{C}_{p_i}^{\circ}$ is the heat capacity of pure water. Differentiating with respect to $m^{\frac{1}{2}}$ we find

$$(4) \frac{d\Phi}{dm^{\frac{1}{2}}} = \frac{m \frac{dC_p}{dm^{\frac{1}{2}}} - (C_p - 55.508 \bar{C}_{p_i}^{\circ}) \cdot 2m^{\frac{1}{2}}}{m^2}$$

now $C_p - 55.508 \bar{C}_{p_i}^{\circ} = m\Phi$ from (3)

and $\frac{dC_p}{dm^{\frac{1}{2}}} = \frac{dC_p}{dm} \cdot 2m^{\frac{1}{2}}$

substituting in equation (4)

$$\frac{d\Phi}{dm^{\frac{1}{2}}} = \frac{2m^{\frac{3}{2}} \frac{dC_p}{dm} - m^{\frac{3}{2}} \cdot 2\Phi}{m^2}$$

$$\frac{1}{2} \cdot m^{\frac{1}{2}} \frac{d\Phi}{dm^{\frac{1}{2}}} = \frac{dC_p}{dm} - \Phi$$

$$\frac{dC_p}{dm} = \bar{C}_{p_2}$$

so

$$(5) \quad \bar{C}_{p_2} = \Phi + \frac{1}{2} m^{\frac{1}{2}} \frac{d\Phi}{dm^{\frac{1}{2}}}$$

When Φ and \bar{C}_{p_2} are known \bar{C}_p may be calculated as follows. By definition

$$(6) \quad C_p = m \bar{C}_{p_2} + 55.508 \bar{C}_{p_i}^{\circ}$$

then

$$\bar{C}_{p_i}^{\circ} = \frac{C_p - m \bar{C}_{p_2}}{55.508}$$

from equation (3)

$$C_p = m\Phi + 55.508 \bar{C}_{p_i}^{\circ}$$

hence combining

$$(7) \quad C_p = \frac{m\Phi + 55.508 \bar{C}_{p_i}^{\circ} - m \bar{C}_{p_2}}{55.508} = \frac{m}{55.508} (\Phi - \bar{C}_{p_2}) + \bar{C}_{p_i}^{\circ}$$

Applying equation (5)

$$(8) \quad \bar{C}_{p_i} - \bar{C}_{p_i}^{\circ} = \frac{m^{3/2}}{55.508} \frac{d\Phi}{dm^{1/2}}$$

From the foregoing there is shown a correlation between Φ , \bar{C}_{p_i} , and $\bar{C}_{p_i}^{\circ}$ from which the latter three quantities may be calculated from a knowledge of the specific heat of the solution and that of water at the given temperature.

Randall and Ramage (24) have shown that a plot of \bar{C}_{p_i} against $m^{1/2}$ gives approximately a straight line for all concentrations. More recent treatment has shown, especially in later work of Randall and Rossini (23) that a plot of Φ against $m^{1/2}$ gives approximately a straight line for all salts investigated in aqueous solutions. If this be assumed true, inspection of equation (8) will show that $\bar{C}_{p_i} - \bar{C}_{p_i}^{\circ}$ or \bar{C}_{p_i} plotted against $m^{3/2}$ will give a straight line. This has also been noted by several investigators. The application of this method of treatment has been useful in determining the consistency of data and in studying solutions for which limited data have been obtained. In Table III a tabulation of the quantities Φ , \bar{C}_{p_i} , $\bar{C}_{p_i} - \bar{C}_{p_i}^{\circ}$, and $\bar{C}_{p_i}^{\circ}$ is given for the various solutions herein studied.

TABLE III

A. Data at 25° centigrade

| Salt | Molality | Specific Heat | Φ | $\bar{C}_{p_1} - \bar{C}_{p_1^0}$ | \bar{C}_{p_1} | \bar{C}_{p_2} |
|--|----------|---------------|--------|-----------------------------------|-----------------|-----------------|
| N ₂ H ₆ Cl ₂ | 1.0000 | .8969 | - 6.8 | -0.326 | 17.690 | 11.3 |
| N ₂ H ₆ Cl ₂ | 0.4750 | .9420 | -18.8 | -0.107 | 17.909 | - 6.5 |
| N ₂ H ₆ Cl ₂ | 0.2000 | .9723 | -26.2 | -0.0292 | 17.987 | -18.9 |
| N ₂ H ₆ Cl ₂ | 0.1845 | .9746 | -24.3 | -0.0260 | 17.990 | -21.9 |
| N ₂ H ₆ Cl ₂ | 0.1000 | .9847 | -29.0 | -0.01032 | 18.005 | -26.0 |
| N ₂ H ₆ Br ₂ | 0.9959 | .8307 | - 6.8 | -0.351 | 17.665 | 13.0 |
| N ₂ H ₆ Br ₂ | 0.5000 | .9012 | -18.4 | -0.1245 | 17.891 | - 4.7 |
| N ₂ H ₆ Br ₂ | 0.2000 | .9541 | -34.2 | -0.0315 | 17.984 | -21.0 |
| N ₂ H ₆ Br ₂ | 0.09952 | .9758 | -34.0 | -0.0111 | 18.005 | -29.1 |
| N ₂ H ₆ Br ₂ | 0.1691 | .9621 | -25.4 | -0.0240 | 17.992 | -23.1 |
| N ₂ H ₅ Cl | .9935 | .9319 | - 2.5 | -0.111 | 17.905 | 3.7 |
| N ₂ H ₅ Cl | .4979 | .9621 | - 6.0 | -0.0400 | 17.976 | - 1.8 |
| N ₂ H ₅ Cl | .2008 | .9826 | - 9.5 | -0.01006 | 18.006 | - 6.7 |
| N ₂ H ₅ Cl | .1000 | .9900 | -12.0 | -0.00356 | 18.012 | - 9.0 |
| N ₂ H ₅ Br | .9375 | .8993 | - 3.4 | -0.138 | 17.878 | 3.8 |
| N ₂ H ₅ Br | .4961 | .9415 | - 7.2 | -0.0464 | 17.970 | - 2.0 |
| N ₂ H ₅ Br | .1964 | .9740 | -11.8 | -0.01176 | 18.004 | - 7.8 |
| N ₂ H ₅ Br | .0997 | .9854 | -15.0 | -0.00415 | 18.012 | -10.7 |
| N ₂ H ₅ ClO ₄ | .9088 | .9120 | 26.5 | -0.195 | 17.821 | 38.7 |
| N ₂ H ₅ ClO ₄ | .4994 | .9453 | 20.1 | -0.0796 | 17.936 | 29.0 |
| N ₂ H ₅ ClO ₄ | .2009 | .9749 | 14.0 | -0.0201 | 17.996 | 19.3 |
| N ₂ H ₅ ClO ₄ | .1001 | .9856 | 9.5 | -0.00712 | 17.009 | 14.0 |

Specific heat given in 15°calories, other data in 25°calories

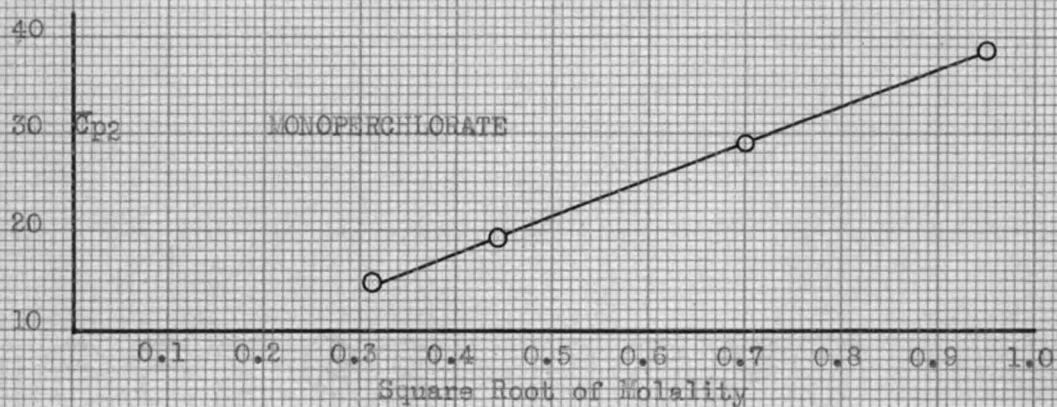
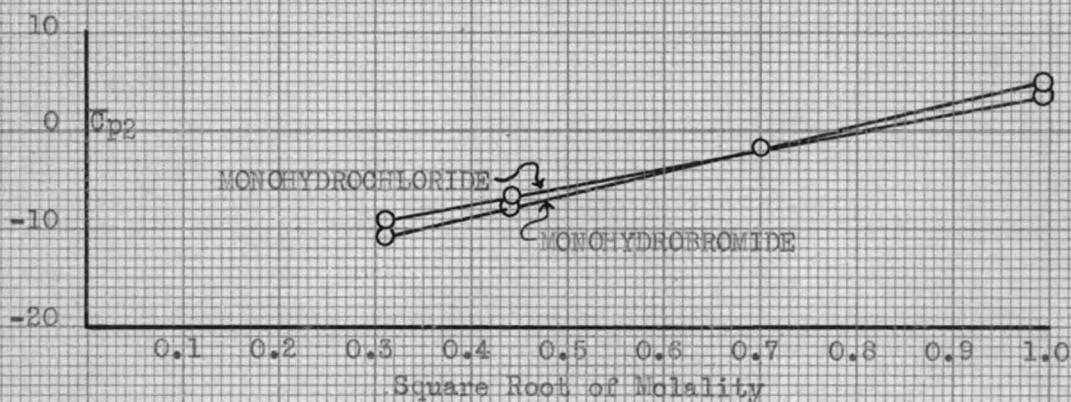
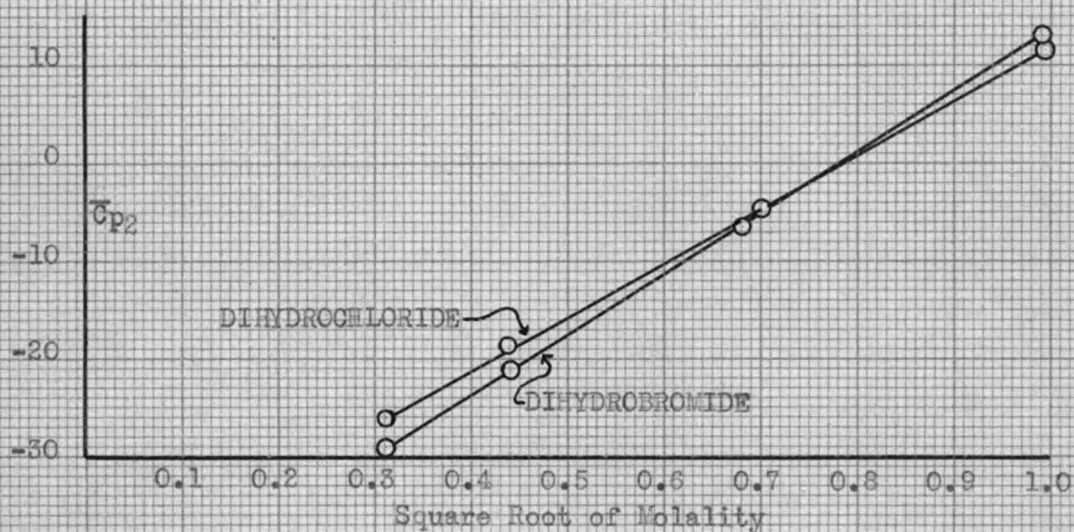
Conversion factor used was 0.9979

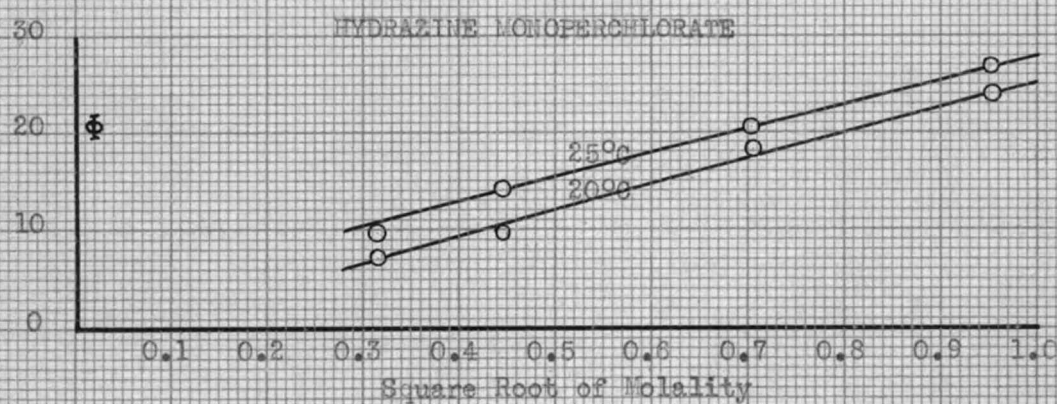
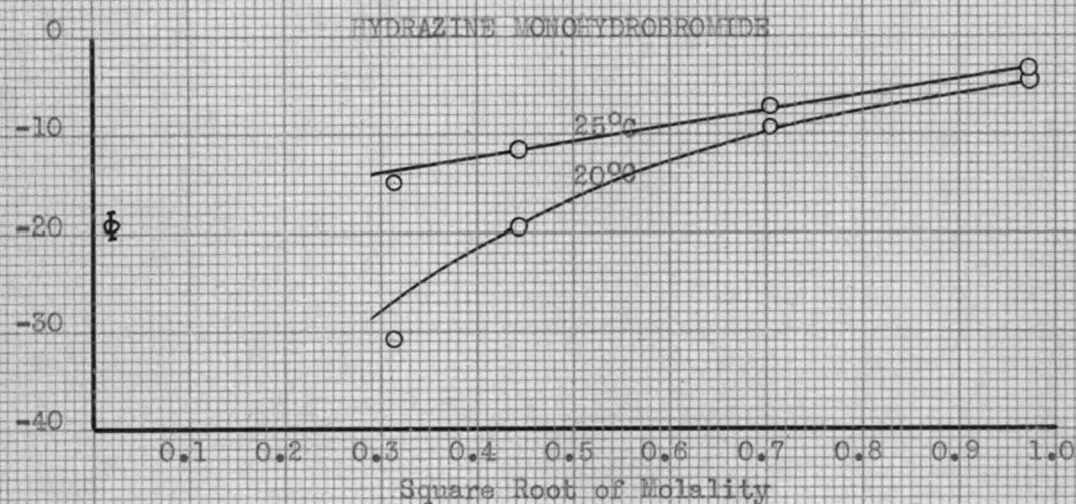
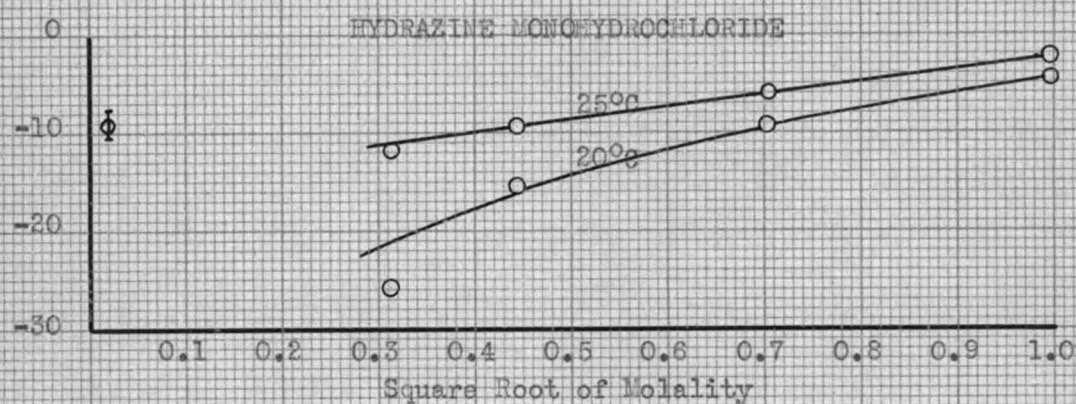
TABLE III

B. Data at 20° centigrade

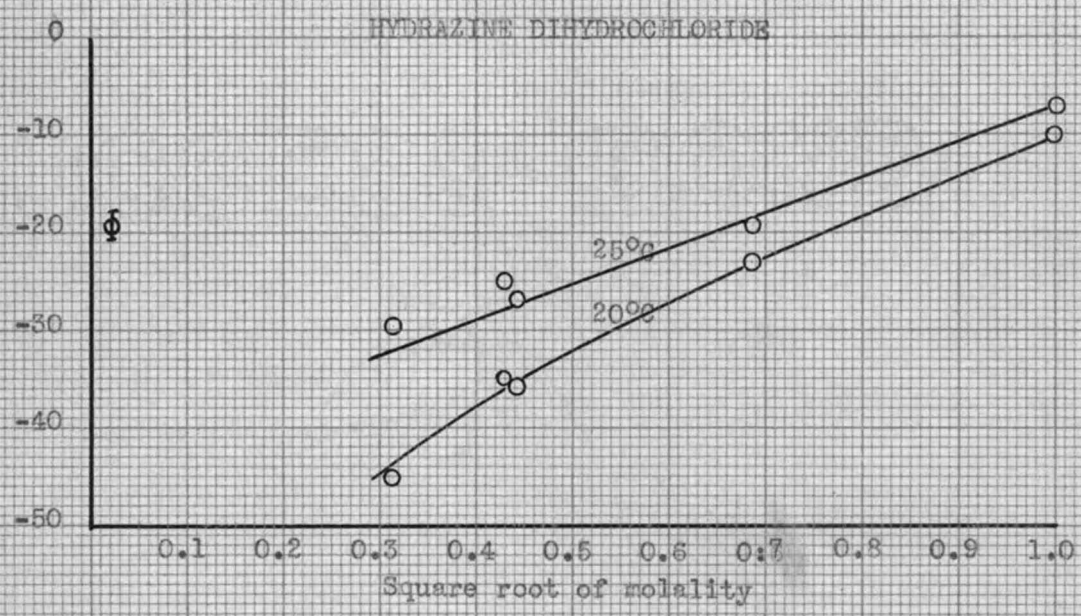
| Salt | Molality | Specific Heat | Φ |
|------------------|----------|---------------|--------|
| $N_2H_6Cl_2$ | 1.0000 | .8955 | - 9.4 |
| $N_2H_6Cl_2$ | 0.4750 | .9411 | -22.5 |
| $N_2H_6Cl_2$ | 0.2000 | .9713 | -35.3 |
| $N_2H_6Cl_2$ | 0.1845 | .9736 | -34.2 |
| $N_2H_6Cl_2$ | 0.1000 | .9840 | -44.5 |
| $N_2H_6Br_2$ | 0.9959 | .8307 | -8.3 |
| $N_2H_6Br_2$ | 0.5000 | .9012 | -21.3 |
| $N_2H_6Br_2$ | 0.2000 | .9541 | -40.9 |
| $N_2H_6Br_2$ | 0.0992 | .9758 | -46.0 |
| $N_2H_6Br_2$ | 0.1691 | .9621 | -32.0 |
| N_2H_5Cl | 0.9935 | .9306 | - 4.8 |
| N_2H_5Cl | 0.4979 | .9612 | - 9.5 |
| N_2H_5Cl | 0.2008 | .9822 | -15.4 |
| N_2H_5Cl | 0.1000 | .9894 | -26.0 |
| N_2H_5Br | 0.9375 | .8989 | - 4.8 |
| N_2H_5Br | 0.4961 | .9412 | - 9.5 |
| N_2H_5Br | 0.1964 | .9733 | -19.7 |
| N_2H_5Br | 0.0997 | .9846 | -31.0 |
| $N_2H_5Cl \ O_4$ | 0.9088 | .9107 | 23.9 |
| $N_2H_5Cl \ O_4$ | 0.4994 | .9451 | 18.0 |
| $N_2H_5Cl \ O_4$ | 0.2009 | .9748 | 9.3 |
| $N_2H_5Cl \ O_4$ | 0.1001 | .9862 | 7.0 |

PARTIAL MOLAL HEAT CAPACITIES AT 25°C.

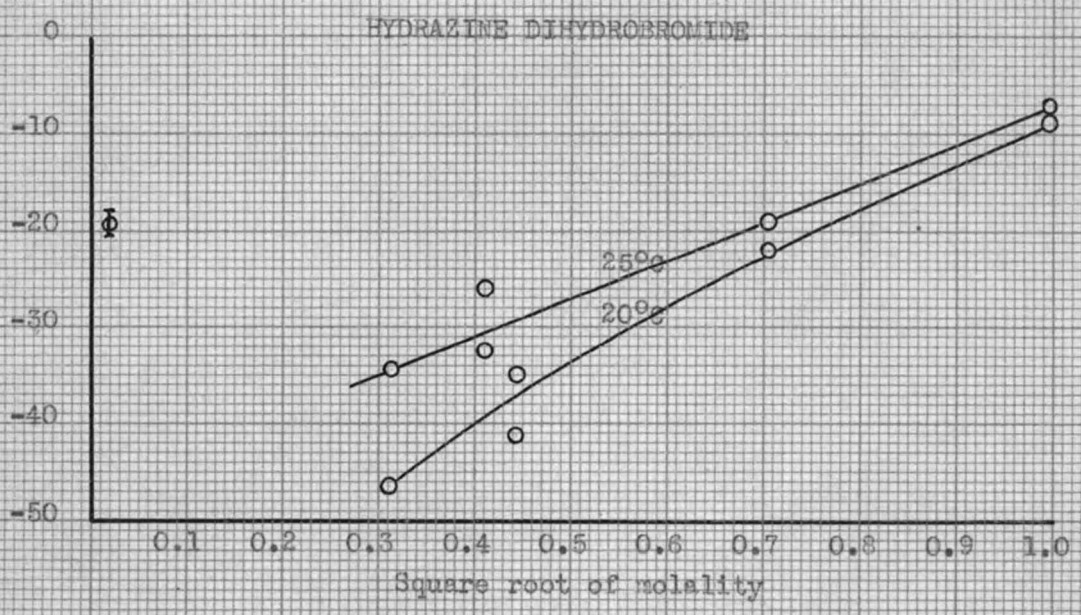




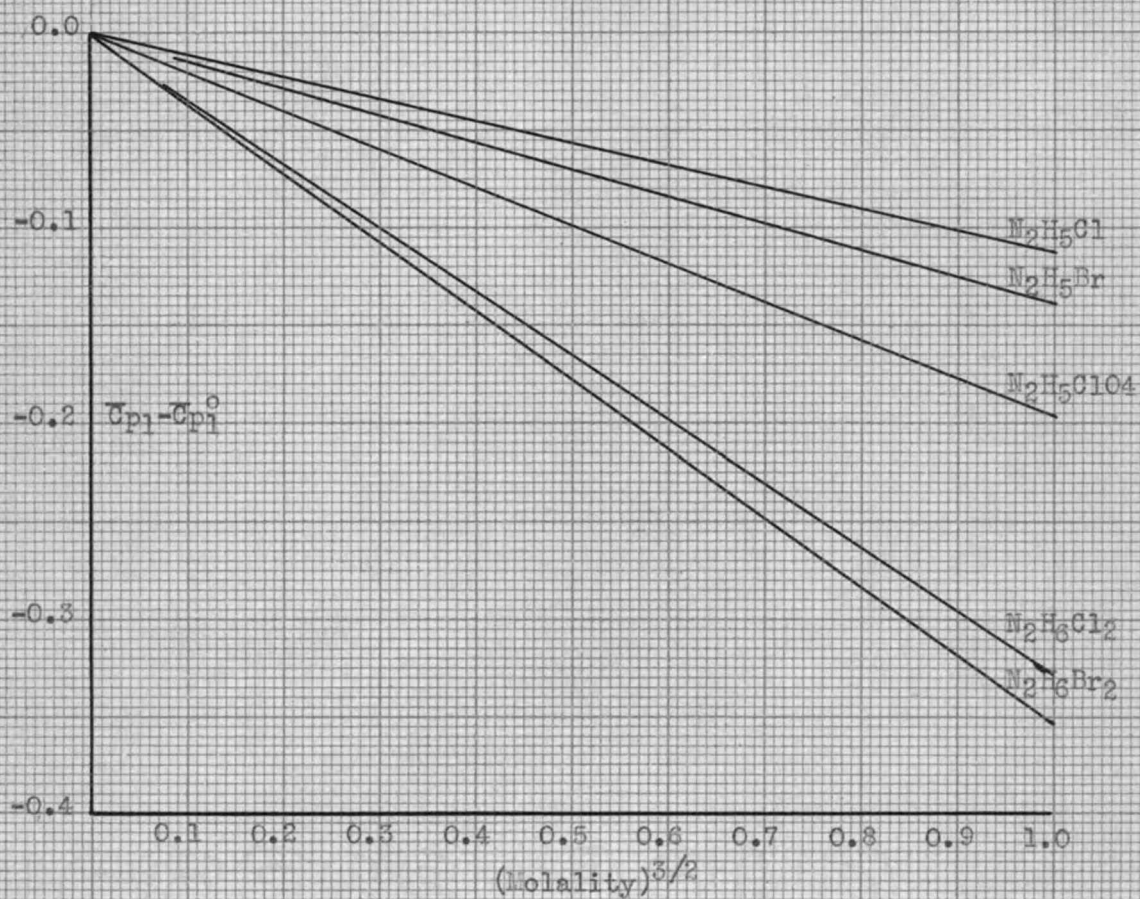
HYDRAZINE DIHYDROCHLORIDE



HYDRAZINE DIHYDROBROMIDE



CHANGE IN HEAT CAPACITY OF WATER WITH CONCENTRATION
OF ADDED SALT



The function Φ is but little affected by errors in measurement of specific^{heat} at concentrations above 0.5 molal, but at lower concentrations of the order of 0.2 and 0.1 molal, or less, Φ is very sensitive to error in specific heat. With the present apparatus it is quite useless to make calculations of Φ at concentrations lower than 0.1 molal because variations within the limit of probable error obscure any possible relationships.

At 20° the experimental results particularly for the monohydrochloride and monohydrobromide show a deviation from the expected straight line relationship between Φ and $m^{\frac{1}{2}}$. The deviation seems definitely to be outside the experimental error, particularly since the perchlorate shows no abnormality in this same respect. The question of this deviation can best be settled by the use of the still more precise method of the twin calorimeter. Most of the data shows excellent consistency with the rather empirical relationship that Φ is a linear function of $m^{\frac{1}{2}}$.

Recently Gucker and Schminke (25) have pointed out that, for several salts in the range below 0.2 molal, the apparent molal heat capacity shows a sudden increase which had not been noted before. This throws some doubt on the validity of extrapolation to infinite dilution, which has been done in many cases. There is at present no explanation for a deviation of this kind. If this abnormality is substantiated, there must either be a revision of older theory or the development of new theory to fit experimental facts of this nature. The limiting law of Debye-Huckel["] for very dilute solutions has been applied to a discussion of heat capacities (25). A development from this discussion

has shown that, for solutions in which the theory of Debye-Hückel can be applied, \bar{C}_p is a linear function of $m^{\frac{1}{2}}$. But best agreement occurs in concentrations far beyond the range to which this theory may be applied. The theory shows for a uni-univalent salt the slope of \bar{C}_p against $m^{\frac{1}{2}}$ in the dilute region should approximate 6 whereas most experimental results of other investigators show an average of 18 or 20. The monohydrochloride and monohydrobromide showed slopes of approximately 18-20 which is fair agreement, but the perchlorate gives a value of 36 that exceeds 30, the steepest one of Randall and Rossini(23). For other salt types the slopes are greater, and in general exceed that predicted by theory, by three-fold. Again, however, our experimental results for the dihydrochloride and bromide agree in slope with that observed for other bi-univalent salts. The reason for this discrepancy between theoretical and calculated slopes has not been found nor has any correlation of slopes with other properties been discovered.

SUMMARY

There have been presented in this thesis:

1. Details of construction and operation of an automatic adiabatic calorimeter designed to measure heats of solution, heats of dilution, heats of reaction and specific heats.
2. Experimental results on the specific heats of a series of solutions of hydrazine salts.
3. Calculations of important thermodynamic quantities based on these experimental results.
4. Comparisons of the results of this investigation with theoretical expectations and with the results of others.

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