THERMODYNAMICS OF HYDRAZINE IN AQUEOUS SOLUTION AT 25°C.

by

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THERMODYNAMICS OF HYDRAZINE IN AQUEOUS SOLUTION AT 25°C.

INTRODUCTION

Following the discovery by A. W. Hofmann of the compound, which he called Hydrazobenzene, a large number of organic derivatives of a similar type were synthesized. The inorganic parent, $\text{N}_2\text{H}_4$, was not isolated until 1887 by T. Curtius, although it had been predicted and named in 1875 by E. Fischer. In 1892 R. Bach (7) determined the heat of solution of the sulfate, hydrate, and mono and dichloride at random temperatures lower than 25°C.

No further work was done of this type on hydrazine until 1934 when E. C. Gilbert and Alan E. Cobb (2) using an adiabatic calorimeter determined the specific heats at 20°C and 25°C of the mono and dichlorides and bromides, and of the perchlorate. They also determined the heats of solution at 25°C of the mono and dichlorate, mono bromide, perchlorate hemihydrate, and perchlorate (anhydrous). In 1935 E. C. Gilbert and V. C. Bushnell (3) determined the heats of solution of the sulfate, dibromide dihydrate, and the anhydrous dibromide. They also determined the specific heat of the sulfate at 25°C.

This thesis adds to this phase of the study of
hydrazine the heat of solution, and the heat of dilution of hydrazine hydrate and the heat capacity of its aqueous solutions.
EXPERIMENTAL

DESCRIPTION OF APPARATUS

The apparatus used for this study was the same as that set up by E. C. Gilbert and Alan W. Cobb (2) with the exception of a few important changes. It consisted essentially of an automatic adiabatic calorimeter. The reaction vessel of the calorimeter was a gold plated, copper container of about 0.9 liter capacity supported on bakelite pegs in a submarine jacket which was likewise gold plated on the inside. This assembly was submerged in a 12 liter, insulated, copper tank.

The calorimeter contents could be heated by a 35 ohm spade heater. An 18 volt storage battery was used as a source of energy. The IR drop across this heater could be measured by the use of two extra leads, one connected at each end of the actual heating resistance, a volt box, and a Type K potentiometer. The current could be measured by measuring the IR drop across a standard on ohm resistance in series with the heater - correction being made for the small current flowing through the volt box.

At all times the inner and outer baths were maintained at the same temperature for an adiabatic condition. A 17 junction copper-constantan thermocouple was placed with one arm in the inner solution, and one in the outside
surrounding water, and connected in series with a sensitive galvanometer. When the outer bath lost heat by conduction or evaporation a potential was developed in the thermo-couple swinging the galvanometer in such a way that a beam of light was reflected onto a photo-cell. This cell operated a set of relays allowing a current from the 110 volt A.C. source to heat the outer bath by secondary conduction. If the inner solution was being heated an additional circuit in parallel was used that heated the outer bath almost as rapidly as the inner solution was being heated. While temperature measurements were being taken the galvanometer was held at zero by manual control of the heating circuits rather than automatic. The maximum variation in the outer bath from the temperature of the inner solution was not more than $\pm 0.0025^\circ C$. on automatic control, and less than $\pm 0.0003^\circ C$. on manual control.

Both baths were well stirred by motor-driven propellers. The stirrer in the reaction vessel was rotated at a constant speed by a synchronous motor, thus giving a constant mechanical heat for any given solution per unit time. This heat was determined at the end of each run.

A Leeds and Northrup platinum resistance thermometer was used in the outer bath. It was connected to a Mueller type resistance bridge and a sensitive galvanometer. The resistance could be read exactly to 0.0001 ohm correspond-
ing to 0.001°C.

The most important modification lay in the design of the pipette for introduction of reagents into the calorimeter. Gilbert and Cobb used a 50 ml. glass pipette with the tip cut off at the bottom of the bulb, with a valve at the bottom that could be opened from the top admitting the salt to the solution. The pipette was filled through a hole on the side that could later be sealed. The chief disadvantages with this pipette were that there was only one small outlet at the bottom making the complete solution slow and somewhat of an uncertainty, the glass possessed poor heat conductivity delaying the thermal equilibrium; and specifically with the use of hydrazine there was too much exposure to air while filling, too large an air-space inside, and it could not be hermetically sealed.

With these faults in mind a new pipette was constructed. It was composed of a brass cylinder 2.25 x 0.75 inches fitted with valves both at the upper and lower end. The valves were connected with a valve stem which joined a bakelite rod above the solution level. The rod, and bakelite tube attached to the cylinder carriage, extended through a chimney several inches above the surface of the outside bath. The entire assembly was supported on the chimney (Fig. II). The metal parts in the reaction vessel were heavily gold plated. The valves could be opened and closed by a small nut
Fig. I

CYLINDER

- Bakelite Tube
- Filling hole

Fig. II

VALVE ASSEMBLY

- Bakelite Tube

TOP ASSEMBLY

- Bakelite Rod
- Threaded brass Collar pinned to valve-stem
- Nut
- No. 4 Rubber stopper
- Hydrogen inlet
- Nut threaded down to chimney
- Chimney
at the top of the valve stem. The pipette was filled through a small hole on the side that could be sealed with a glass bead and paraffin. When assembled this pipette had a capacity of about 12 cc., and was air tight. A hydrogen attachment could be fitted on the top of the pipette to displace the air in the reaction vessel with hydrogen; the air going out through the stirrer chimney, and the washed hydrogen entering between the valve stem and tube.

**TECHNIQUE**

For the particular determinations made in the present work many important changes were made in the technique previously employed. Liquids instead of solids were now being used, and the change of temperature was positive instead of negative. The two liquids used not only took up moisture from the air, but they also were oxidized by the oxygen of the air. To best explain the technique the procedure for a typical heat of dilution determination will be presented.

The pipette was cleaned and assembled, the valves sealed with paraffin. Five to ten milliliters of hydrazine hydrate were run into the pipette from a stock supply of 100% hydrazine hydrate in a weight burette. The filling hole of the pipette sealed with paraffin and a glass bead,
TABLE I.  DATA AND CALCULATIONS OF AN ACTUAL RUN

HEAT OF DILUTION OF $N_2H_4 \cdot H_2O$

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. of Burette before</td>
<td>101.73629 gm.</td>
<td></td>
</tr>
<tr>
<td>Wt. of Burette after</td>
<td>93.92564 gm.</td>
<td></td>
</tr>
<tr>
<td>Wt. of $N_2H_5OH$</td>
<td>7.81065 gm. cor. = 7.8189 gm.</td>
<td></td>
</tr>
<tr>
<td>Wt. of Can + Sol'n.</td>
<td>1093.47 gm.</td>
<td></td>
</tr>
<tr>
<td>Wt. of Can</td>
<td>188.09 gm.</td>
<td></td>
</tr>
<tr>
<td>Wt. of Sol'n.</td>
<td>907.38 gm. cor.  = 908.37 gm.</td>
<td></td>
</tr>
</tbody>
</table>

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ohm start</td>
<td>28.0101</td>
<td>cor. = 28.00497</td>
</tr>
<tr>
<td>Ohm end</td>
<td>28.0455</td>
<td>cor. = 28.04042</td>
</tr>
<tr>
<td>$\Delta$ohm</td>
<td>0.03550 cor. for heat of stirring = 0.03503</td>
<td></td>
</tr>
</tbody>
</table>

| Time                  | 10.3 min.        |                  |
|                       |                  |                  |
| $\Delta t$            | 0.3488°C         |                  |

HEAT OF STIRRING

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ohm start</td>
<td>28.0455</td>
<td></td>
</tr>
<tr>
<td>Ohm end</td>
<td>28.0461</td>
<td></td>
</tr>
<tr>
<td>$\Delta$ohm</td>
<td>0.0006</td>
<td></td>
</tr>
</tbody>
</table>

| Time                  | 13.0 min.        |                  |

CALCULATIONS

$$\Delta H = \left[ (916.19 \times 0.9898) + 28.43 \right] \frac{0.3488 \times 50.06}{7.81893} = \frac{-2086.6 \text{ cal. per mol}}{2088.6 \text{ cal. per mol}}$$

$$\sigma_h - \sigma^0_h = \left(2092.6 \times 0.1722\right) + \left[2088.6(0.3478 - 0.1722)\right] = \frac{-2090.6 \text{ cal. per mol}}{0.3478}$$
the pipette was mounted in the chimney on the top of the submarine jacket. The amount of hydrazine hydrate used was determined by the loss in weight of the weight-burette, corrected to vacuo.

Next the reaction vessel was filled with about 900 grams of especially deoxygenized water, or solution, and weighed to a 0.01 gram. The reaction vessel was quickly mounted in the submarine jacket; and the top, carrying the stirrer, heater, thermocouple, and pipette, attached by thumb-screws. The joints had been greased with stopcock grease to prevent leakage.

Having the submarine part assembled the hydrogen connection was put onto the top of the pipette, and a flow of washed hydrogen sent through the pipette support into the reaction vessel. Allowing sufficient time to remove the air the hydrogen was shut off, and the rubber stopper turned a quarter-turn to close the opening in the bakelite tube (see Fig. II). The submarine part was then submerged, and the electrical and mechanical connections made.

The stirrers were started, and the thermocouple and galvanometer, with a two ohm shunt, connected. After the temperature of the two baths were brought together the two ohm shunt was removed. The galvanometer, reflecting a beam of light focused at eight meters onto a meterstick, indicated the thermal head between the inner solution and
the outside bath. The zero point (the point of absolute adiabatic condition) was noted by momentarily opening the circuit. Carefully the temperature was raised to 25.00°C. (thermometer resistance equaled about 28.0104 ohms), the exact resistance of the thermometer read, and a stop watch started. The nut holding the valves shut was partially unscrewed, and the valve stem tapped to open the valves. The auxiliary circuit was then added to heat the outside bath. By alternately opening and closing the valves the galvanometer was held fairly close to its zero point. After 10-15 minutes had passed to allow a good thermal equilibrium to be established the zero point was rechecked, the temperature read, and the time noted. An additional 15-20 minute run was usually made at equilibrium to determine the heat of stirring. After a run the solution was sampled for analyses, put in a dark place and protected from air.

The iodate method of W. C. Bray and Cuy (1) was used for the analyses of the solutions. A five gram sample was acidified and diluted to 250 ml. Twenty-five milliliter aliquots were put into glass stoppered erlenmyer flasks of 250 ml. capacity. Approximately 10 ml. of 6 N sulfuric acid and exactly 25 ml. of 0.1 N potassium iodate were added. After standing for five minutes 10 ml. of 10% sodium iodide were added, and back-titrated to the starch end-point with sodium thiosulfate. The results were accurate to approxim-
ately one part in a thousand.

CALORIMETER CONSTANT

Modification in the apparatus required a redetermination of the calorimeter constant or "water value". From previous work the calorimeter, without the pipette, had a calorimeter K of 92 J. per °C. The new pipette weighed 38.7591 gms. with specific heat of approximately 0.092 cal. per gm. per °C. Its heat capacity, therefore, was 38.759 x 0.092 x 4.1333 = 14.92 J. per degree making a total of 107 J. per degree.

To determine the calorimeter K experimentally a weighed amount of water was put into the reaction vessel; the calorimeter assembled and brought to equilibrium. Immediately after the temperature was read the heating circuit was closed and carefully timed. The IR drop and I were determined frequently. Finally the heating circuit was opened and the operation continued as usual. The difference between the input per degree, and the apparent input per degree was the calorimeter constant.

\[
\left( \frac{V \times I \times \text{sec}}{\Delta t} \right) - (\text{Wt. } H_2O \times 4.1833 \times \text{Sp. Ht.}) = \text{Cal. K.}
\]

Three results were 111.9 per °C., 110.3 J. per °C., and 109.6 J. per °C. For the calorimeter K 108 J. per °C. was chosen. In one part of the work 3.7 gms. of paraf-
fin was added to the reaction vessel. Its heat capacity was 0.694 cal. per gm. per °C. (4) so 11 J. per °C. was added to the calorimeter K at that point.

CALIBRATION OF APPARATUS

Since this study was to deal with systems in which heat was evolved, whereas previous work had to do only with systems in which heat was absorbed, it seemed advisable to develop technique on some reaction other than that involving the expense of hydrazine. The reaction

$$\text{NaOH} + \text{HCl} = \text{NaCl} + \text{H}_2\text{O} + \text{Heat}$$

was chosen.

A saturated solution of sodium hydroxide from which the carbonate had settled was used as a stock reagent, but no attempt was made to remove other impurities such as potassium, lithium, sulfate, etc. The specific heat of NaCl was taken from data by Lipsett, Johnson and Maass (6). The heat of neutralization thus determined was 13680 cal. per mol NaOH. It now became necessary to calculated from data in the literature the true heat of neutralization under this particular set of conditions. The determination above was taken at 20°C. The sodium hydroxide used was NaOH·10H₂O, the hydrochloric acid was HCl·1000H₂O, and the resultant salt was NaCl·1011H₂O.
NaOH·10H2O + 90H2O = NaOH·100H2O \[ \Delta H = 127 \text{ cal.} \] (11)
NaOH·100H2O + HCl·100H2O = NaCl·201H2O \[ \Delta H = -13924 \text{ cal.} \] (9)
NaCl·201H2O + 800H2O = NaCl·1001H2O \[ \Delta H = 22 \text{ cal.} \] (6)
HCl·1000H2O = HCl·100H2O + 900H2O \[ \Delta H = 180 \text{ cal.} \] (10)
\[ \Delta H = -13595 \text{ cal.} \]

Since this work was carried out at 25°C. three heats of neutralization determinations were made at 25°C. giving 13286, 13300, and 13286 calories per mol. The average was 13291 calories per mol.

The calculated results were:
NaOH·10H2O + 90H2O = NaOH·100H2O \[ \Delta H = +12 \text{ cal.} \] (11)
NaOH·100H2O + HCl·100H2O = NaCl·201H2O \[ \Delta H = -13568 \text{ cal.} \] (12)
NaCl·201H2O + 800H2O = NaCl·1001H2O \[ \Delta H = +7 \text{ cal.} \] (6)
HCl·1000H2O = HCl·100H2O + 900H2O \[ \Delta H = +190 \text{ cal.} \] (10)

Total \[ \Delta H = -13360 \text{ cal.} \]

Since the sodium hydroxide used was not especially purified the above agreement was as good as might be expected.

PREPARATION OF MATERIALS

In the preparation of the substances used in this work great care was exercised to avoid the presence of heavy metals and oxygen. A slight trace of a heavy metal caused rapid decomposition. In all cases the water used was distilled in glass under vacuum, and stored in a 12 liter flask containing hydrogen. If this stock supply was not used
for several days it was boiled under vacuum several times, each time the flask being refilled with hydrogen.

Some of the hydrazine used was bought in 100 gm. lots from Schering-Kahlbaum A.G. Berlin. This supply ran about 103% hydrazine hydrate by analysis, so it was carefully diluted to exactly 100% and stored in a weight burette. Some of the dilute solutions were prepared as according to Charles D. Hurd and C. W. Bennett (5). A mixture of 75 parts water, 200 parts hydrazine sulfate, and 160 parts sodium hydroxide refluxed then distilled yields a solution of 40-45% hydrazine hydrate. Since hydrazine attacks tin and cork an all glass still was necessary to avoid formation of peroxides. The anhydrous hydrazine was prepared by fractional distillation of the prepared dilute solutions. The hydrazine was recovered from all solutions by adding sulfuric acid and recrystallizing as the sulfate.
CALCULATIONS AND RESULTS

The specific heats were run in such a way that
\[ \frac{t_1 + t_2}{2} = 25^\circ C. \]

All data are in 15° calories.

The apparent molal heat capacity of hydrazine hydrate can be calculated (2) by the formula

(1) \[ \phi_c = \left( \frac{1000 + M_2}{m} \right) S_2 - \frac{1000 S_1}{m} \]

where \( M_2 \) is the molecular weight of the solute, \( m \) is the molality, and \( S_2 \) is the specific heat of the solution.

Randall and Rossini (8) show that

(2) \[ C_p = m \phi_c + 55.508 \bar{C}_{p_1}^0 \]

where \( \bar{C}_{p_1}^0 \) is the molal heat capacity of the pure solvent.

(3) \[ 55.508 \bar{C}_{p_1}^0 = 1000 S_1 \]

where \( S_1 \) is the specific heat of the pure solvent. From equation two

(4) \[ \bar{C}_{p_1} = \left( C_p - m \bar{C}_{p_2} \right) \frac{55.508}{55.508} \]

From the slopes of tangents of a curve, where \( \phi_c \) is plotted against \( \gamma_m \), \( \bar{C}_{p_2} \) can be calculated as follows:

(5) \[ \bar{C}_{p_2} = \phi_c + \frac{\gamma_m}{2} \frac{d \phi}{d \gamma_m} \]

where \( \frac{d \phi}{d \gamma_m} \) is the slopes of the tangent.

The change in heat capacity of the solvent is
### TABLE II. HEAT CAPACITY DATA ON AQUEOUS HYDRAZINE HYDRATE AT 25° IN 15° CALORIES

<table>
<thead>
<tr>
<th>No</th>
<th>m</th>
<th>$\gamma_m$</th>
<th>$S_2$</th>
<th>$\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.9979</td>
<td></td>
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<tr>
<td>1</td>
<td>0.1310</td>
<td>0.3619</td>
<td>0.9944</td>
<td>22.9</td>
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<tr>
<td>2</td>
<td>0.1537</td>
<td>0.3921</td>
<td>0.9934</td>
<td>22.9</td>
</tr>
<tr>
<td>3</td>
<td>0.1559</td>
<td>0.3948</td>
<td>0.9938</td>
<td>23.0</td>
</tr>
<tr>
<td>4</td>
<td>0.2269</td>
<td>0.4763</td>
<td>0.9922</td>
<td>24.1</td>
</tr>
<tr>
<td>5</td>
<td>0.3731</td>
<td>0.6108</td>
<td>0.9892</td>
<td>25.8</td>
</tr>
<tr>
<td>6</td>
<td>0.3762</td>
<td>0.6134</td>
<td>0.9892</td>
<td>25.9</td>
</tr>
<tr>
<td>7</td>
<td>0.6949</td>
<td>0.8336</td>
<td>0.9834</td>
<td>29.0</td>
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<table>
<thead>
<tr>
<th>No</th>
<th>$C_p$</th>
<th>$\bar{C}_{p2}$</th>
<th>$\bar{C}_{p1}$</th>
<th>$\bar{C}<em>{p1} - \bar{C}</em>{p1}$</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>997.9</td>
<td>17.978</td>
<td>0.000</td>
<td></td>
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<tr>
<td>1</td>
<td>1000.9</td>
<td>24.93</td>
<td>17.973</td>
<td>-0.005</td>
</tr>
<tr>
<td>2</td>
<td>1001.4</td>
<td>25.53</td>
<td>17.970</td>
<td>-0.008</td>
</tr>
<tr>
<td>3</td>
<td>1001.5</td>
<td>25.65</td>
<td>17.970</td>
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<tr>
<td>4</td>
<td>1003.4</td>
<td>27.30</td>
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<td>-0.013</td>
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<td>5</td>
<td>1007.5</td>
<td>29.90</td>
<td>17.949</td>
<td>-0.029</td>
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<tr>
<td>6</td>
<td>1007.6</td>
<td>30.02</td>
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<td>-0.029</td>
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<tr>
<td>7</td>
<td>1018.0</td>
<td>34.60</td>
<td>17.908</td>
<td>-0.070</td>
</tr>
</tbody>
</table>
\( \bar{C}_p - \bar{C}_p^0 \). For water

\[ 55.508 \bar{C}_p^0 = 1000 \times 0.9979 \]

\[ = 997.9 \text{ calories} \]

\[ \bar{C}_p^0 = 17.978 \text{ calories per mol.} \]

With these equations \( C_p, \bar{C}_p, \bar{C}_p^0 \), and \( \bar{C}_p - \bar{C}_p^0 \) were calculated, and shown in Table II.

Having determined the heat capacities of hydrazine solutions it was possible, then, to determine the heat of dilution of the hydrate by adding small amounts to solutions of known concentration. The heat evolved was calculated from the following formula:

\[ (6) \Delta H = \left[ (\text{Wt. Sol'n x Sp. Ht.)} + \text{Cal. K} \right] \frac{M \Delta t}{\text{Wt. added}} \]

where \( M \) is the molecular weight.

The heat given off by the addition of enough hydrate to raise the concentration from zero to the concentration under consideration is known as the total or integral heat of dilution \( (\varnothing_h - \varnothing_h^0) \). It is calculated as follows:

If the concentration of a solution is raised from \( m' \) to \( m'' \) the total heat of dilution will consist of two parts: the heat evolved from \( m^0 \) to \( m' \), and the heat evolved from \( m' \) to \( m'' \). The first part would be

\[ (\varnothing_h - \varnothing_h^0) \frac{m'}{m''} \]
### TABLE III. DIFFERENTIAL AND INTEGRAL HEATS OF DILUTION AT 25° C. IN 15° CALORIES

<table>
<thead>
<tr>
<th>m'</th>
<th>m''</th>
<th>ΔH</th>
<th>$\phi_h - \phi_h^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>0.1295</td>
<td>-2095</td>
<td>-2095</td>
</tr>
<tr>
<td>0.0000</td>
<td>0.1722</td>
<td>-2093</td>
<td>-2093</td>
</tr>
<tr>
<td>0.1295</td>
<td>0.3101</td>
<td>-2087</td>
<td>-2091</td>
</tr>
<tr>
<td>0.1722</td>
<td>0.3478</td>
<td>-2089</td>
<td>-2091</td>
</tr>
<tr>
<td>0.3292</td>
<td>0.4320</td>
<td>-2076</td>
<td>-2086</td>
</tr>
<tr>
<td>0.3101</td>
<td>0.5184</td>
<td>-2068</td>
<td>-2079</td>
</tr>
<tr>
<td>0.3478</td>
<td>0.5476</td>
<td>-2065</td>
<td>-2081</td>
</tr>
<tr>
<td>0.4820</td>
<td>0.6616</td>
<td>-2067</td>
<td>-2080</td>
</tr>
<tr>
<td>0.5476</td>
<td>0.7480</td>
<td>-2031</td>
<td>-2068</td>
</tr>
<tr>
<td>0.646</td>
<td>0.874</td>
<td>-2067</td>
<td>(-2073)</td>
</tr>
</tbody>
</table>

### TABLE IV. PARTIAL MOLAL HEATS OF DILUTION OF SOLUTE AND SOLVENT AT 25° C. IN 15° CALORIES

<table>
<thead>
<tr>
<th>Molality</th>
<th>$\overline{H}_2 - H_2(L)$</th>
<th>$\overline{H}_1 - \overline{H}_1^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>-2094</td>
<td>-0.0003</td>
</tr>
<tr>
<td>0.2</td>
<td>-2087</td>
<td>-0.0149</td>
</tr>
<tr>
<td>0.3</td>
<td>-2062</td>
<td>-0.0447</td>
</tr>
<tr>
<td>0.5</td>
<td>-2066</td>
<td>-0.1634</td>
</tr>
<tr>
<td>0.7</td>
<td>-2049</td>
<td>-0.3497</td>
</tr>
</tbody>
</table>
and the second part

\[ \Delta H \times \frac{\Delta m}{m'} \].

Adding the two parts

\[
\phi_h - \phi_h^0 = (\phi_h - \phi_h^0) \cdot \frac{m'}{m''} + \left( \Delta H \times \frac{\Delta m}{m''} \right)
\]

\[
= \left( \phi_h - \phi_h^0 \right) \cdot \frac{m'}{m''} + \left( \Delta H \times \frac{\Delta m}{m''} \right)
\]

Rossini (13) shows that the change in the partial molal heats is

\[ H_2 - H_2(L) = (\phi_h - \phi_h^0) + \frac{\gamma_m}{2} \frac{d}{d\gamma_m} (\phi_h - \phi_h^0) \]

where \( H_2(L) \) is the heat content of the pure solute.

Also

\[ H_1 - H_1^0 = -\frac{m}{55.508} \times \frac{\gamma_m}{2} \frac{d}{d\gamma_m} (\phi_h - \phi_h^0) \]

where \( \frac{d}{d\gamma_m} (\phi_h - \phi_h^0) \) are the slopes of tangents from a curve where \( (\phi_h - \phi_h^0) \) is plotted against \( \gamma_m \).
SUMMARY

New thermodynamic data, including the specific heat, molal heat capacity, partial molal heat capacity of both solvent and solute, integral heat of dilution, and the relative partial molal heat of both solvent and solute, have been determined for hydrazine in aqueous solutions.

A more efficient pipette for introducing reagents into the reaction vessel of an adiabatic calorimeter has been described.
BIBLIOGRAPHY


