# Solubilities of Sulfur and Sulfur Dioxide in Thionyl Chloride with and without 1.8 M $LiAlCl_4$

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**The solubilities of S and $SO_2$ in $SOCl_2$ containing 1.8 M $LiAlCl_4$ have been determined as a function of temperature. Sulfur solubility data have been obtained for temperatures between 0 and 55 °C, while the data for $SO_2$ solutions cover the range of temperatures between 0 and 60 °C. Over the temperature range considered here, the sulfur solubility increases with temperature in an approximately linear fashion. In contrast, the $SO_2$ solubility decreases with increasing temperature, and the relationship between molar solubility and temperature is an approximately parabolic one. Additionally, the effects of the presence of water or the products of the reaction between water and $SOCl_2$ upon the dissolution of sulfur in $SOCl_2$ have been examined. It has been found that neither hydrolysis product has a very significant effect upon the sulfur solubility, whereas $H_2O$ itself readily causes sulfur to precipitate from solution.**

## Introduction

Sulfur and sulfur dioxide are both produced during the normal discharge of the lithium|thionyl chloride primary battery, and both are soluble in the thionyl chloride electrolyte (*1–4*). However, once the solubility of the sulfur has been exceeded, it precipitates within the cathode and the separator (contributing to decreased cell capacity and efficiency) (*1*, *5*). Likewise, once the solubility of the sulfur dioxide has been exceeded, pressures beyond 1 atm will build up within the cell (*3*, *6*). It is thus important to know the extents to which these two substances can be dissolved in the battery electrolyte as a function of temperature.

The experimentally determined S and $SO_2$ solubilities in the standard electrolyte solution ($SOCl_2$ containing 1.8 M $LiAlCl_4$) and in pure $SOCl_2$ are reported and analyzed in this paper. Also discussed are the results of experiments performed to determine the way in which water affects the solubility of sulfur in thionyl chloride.

## Experimental Section

***A. Sulfur Solubility in Thionyl Chloride.*** The $SOCl_2$ was doubly distilled and stored under argon with Li chips until used. The rhombic sulfur was recrystallized from thionyl chloride and dried overnight in a 105 °C oven before use. The sulfur and thionyl chloride were transferred to a three-necked flask fitted with a reflux condenser and through which argon gas was slowly passed. An oil bath was used to heat the $SOCl_2$ to about 80 °C so as to effect the dissolution of the sulfur (forming a saturated or nearly saturated solution at this temperature). The solution was then cooled to a temperature between 0 and 45 °C and held at this temperature until enough sulfur had precipitated to yield a saturated solution at the lower temperature.

An argon-filled syringe was then used to rapidly transfer a measured volume of the solution to a preweighed flask. The $SOCl_2$ was then thoroughly evaporated, and the amount of sulfur contained within the saturated solution was obtained gravimetrically.

***B. Sulfur Solubility in $SOCl_2$ Containing 1.8 M $LiAlCl_4$.*** The electrolyte solution used was prepared by dissolving enough $LiAlCl_4$ in doubly distilled $SOCl_2$ to make a 1.8 M solution. The rhombic sulfur, supplied by Fisher, was recrystallized from thionyl chloride and dried in a 105 °C oven overnight before use. The sulfur and electrolyte solution were transferred to a three-necked flask fitted with a reflux condenser and through which dry argon gas was slowly passed. An oil bath was used to heat the electrolyte to about 80 °C so as to effect the dissolution of the sulfur (forming a saturated or nearly saturated solution at this temperature). The solution was then cooled to a temperature between 0 and 55 °C and held at this temperature until enough sulfur had precipitated to yield a saturated solution at the lower temperature.

An argon-filled syringe was then used to rapidly transfer a measured volume of the solution to a flask containing a preweighed, predried portion of carbon black. The $SOCl_2$ was evaporated and 25 mL of 3 M HCl was added to the flask. The contents of the flask were then refluxed to dissolve the $LiAlCl_4$, and the carbon–sulfur residue was collected by filtration through a preweighed glass filter paper. After thorough washing of the residue with distilled water, the filter paper (containing the carbon and sulfur) was placed in a weighing bottle and dried overnight at 105 °C. The sulfur concentration in the original electrolyte solution was then determined gravimetrically.

***C. Sulfur Dioxide Solubility in Thionyl Chloride.*** An Erlenmeyer flask was fitted with a side-arm bubbler through which $SO_2$ could be passed from a lecture bottle into $SOCl_2$ contained within the flask. The flask itself was contained within an oil or cold water bath by which the $SOCl_2$ was maintained at a preselected temperature between 0 and 60 °C. A glass-wool-packed water-jacketed condenser was employed to prevent the significant loss of $SOCl_2$ during its saturation with $SO_2$.

Initially, the flask was fitted with ground glass stoppers and weighed. Twice-distilled $SOCl_2$ was then transferred (under argon) into the flask. The flask was restoppered, and the volume of $SOCl_2$ was calculated from its density and the gain in weight of the flask upon the addition of the $SOCl_2$. The condenser was then connected to the flask, and the $SOCl_2$ was saturated with $SO_2$ as described above. The condenser was then removed, and the stoppered flask containing the $SO_2$-saturated $SOCl_2$ was weighed.

Another condenser was then connected to the flask, and dry argon was slowly bubbled into the $SOCl_2$, as it was heated to reflux the liquid, thus driving off the previously dissolved $SO_2$. Finally, the condenser was removed, the flask was again stoppered, and the amount of $SO_2$ previously contained in the saturated solution was determined gravimetrically.

***D. Sulfur Dioxide Solubility in $SOCl_2$ Containing 1.8 M $LiAlCl_4$.*** The experimental procedure employed in this case was identical with that used to determine the solubility of $SO_2$ in pure $SOCl_2$.

***E. Effect of Water upon the Solubility of Sulfur in Thionyl Chloride.*** Saturated sulfur–thionyl chloride solutions were prepared as previously described. They contained 24 mL of $SOCl_2$ and enough sulfur to make a 2 M solution. As the S–$SOCl_2$ solution began to cool (from the refluxing temperature to room temperature), 1 mL of an $H_2O$–$SOCl_2$ mixture was added with stirring. The $H_2O$–$SOCl_2$ mixture contained the amount of $H_2O$ needed to fix the final $H_2O$ "concentration" (assuming no reaction between the $H_2O$ and $SOCl_2$) at a predetermined value between $10^0$ and $10^5$ ppm. Then, the $SOCl_2$ solution was al-

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Table I. Solubility of Sulfur in Pure Thionyl Chloride

| $T$, °C | solubility, M | $T$, °C | solubility, M |
|---|---|---|---|
| 0 | 1.070 | 28.5 | 1.673 |
| 0 | 1.244 | 32 | 1.678 |
| 23.5 | 1.700 | 35 | 1.812 |
| 23.5 | 1.305 | 42 | 1.981 |
| 24.5 | 1.302 | 45 | 2.065 |
| 25 | 2.155 | 45 | 2.399 |
| 26 | 1.781 | | |

Table II. Solubility of Sulfur in Thionyl Chloride Containing 1.8 M $LiAlCl_4$

| $T$, °C | solubility, M | $T$, °C | solubility, M |
|---|---|---|---|
| 0 | 0.678 | 23 | 1.160 |
| 0 | 0.708 | 24 | 1.328 |
| 0 | 0.775 | 34 | 1.328 |
| 0 | 0.826 | 39 | 1.528 |
| 23 | 0.994 | 44 | 1.629 |
| 23 | 1.114 | 53 | 1.500 |

lowed to equilibrate at room temperature until only the equilibrium amount of sulfur remained in solution. The room-temperature solubility of sulfur was then determined as previously described.

## Results

***A. Sulfur Solubility in Thionyl Chloride.*** The experimentally determined solubility of sulfur (assumed to be present in monomeric form) in pure thionyl chloride is listed in Table I as a function of temperature. Assuming ideality, we relate the solubility of the sulfur (expressed as mole fraction, $x$) to the heat of fusion of the pure solute ($\Delta H_{fus}$), the temperature ($T$), and the melting point of the pure solvent ($T_0$) by the ideal law of solubility (*7*).

$$\ln x = -\frac{\Delta H_{fus}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{1}$$

($R$ is the ideal gas constant.) Thus, over a sufficiently narrow temperature range, a plot of $\ln x$ vs. $1/T$ should be approximately linear with a slope given by $\Delta H_{fus}/R$. Ths sulfur solubility data were treated in this way, on the assumption that the sulfur was present either as the monomer (S) or as the cyclic octamer ($S_8$).

Assuming the sulfur is present as the monomer, we express the relationship between the mole fraction of S and the temperature derived from a least-squares analysis of the data as

$$\ln x = -\frac{(7.94 \pm 1.96) \times 10^2}{T} + (0.403 \pm 0.657) \tag{2}$$

A heat of fusion equal to 1580 cal/gram formula weight is calculated from the slope of this least-squares line. This value is very far from the commonly accepted heat of fusion, 337 cal/gram formula weight (*8*).

Assuming the sulfur to be present as the cyclic octamer, we express the relationship between the mole fraction of $S_8$ and the temperature given by a least-squares analysis of the data as

$$\ln x = -\frac{(11.75 \pm 2.02) \times 10^2}{T} - (0.304 \pm 0.677) \tag{3}$$

A heat of fusion of cyclooctasulfur equal to 2338 cal/gram formula weight is calculated from the slope of this least-squares line, in acceptable agreement with the expected value, 2696 cal/gram formula weight. This agreement suggests that sulfur actually dissolves in $SOCl_2$ as the cyclic octamer. In order to make its application more convenient, the least-squares representation of the data has been plotted in Figure 1 expressed as the molar solubility of monomeric sulfur vs. the temperature.

***B. Sulfur Solubility in $SOCl_2$ Containing 1.8 M $LiAlCl_4$.*** The experimental data are listed in Table II as a function of temperature (the sulfur being assumed to be dissolved in monomeric form). Again assuming ideality, we analyzed the sulfur solubility data assuming that the sulfur was dissolved either as the monomer (S) or as the cyclic octamer ($S_8$). As before, the data were least-squares analyzed to yield the best-fit ln mole fraction vs. reciprocal temperature lines given by eq 4 for the case of monomeric sulfur and by eq 5 for the case of cyclooctasulfur.

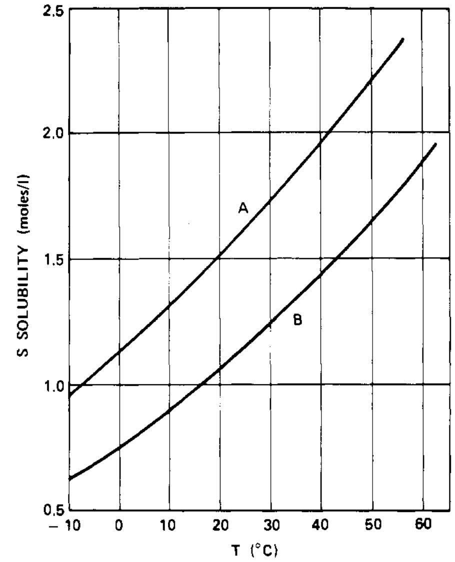

**Figure 1.** Solubility of S in $SOCl_2$: (A) without $LiAlCl_4$, (B) with 1.8 M $LiAlCl_4$.

Table III. Solubility of Sulfur Dioxide in Pure Thionyl Chloride

| $T$, °C | solubility, M | $T$, °C | solubility, M |
|---|---|---|---|
| 0.0 | 15.11 | 40.0 | 1.177 |
| 0.0 | 15.25 | 40.0 | 1.247 |
| 10.6 | 4.765 | 40.0 | 1.463 |
| 14.0 | 4.215 | 60.0 | 0.390 |
| 22.3 | 2.468 | 60.0 | 0.504 |
| 23.3 | 2.530 | 60.0 | 0.684 |
| 23.7 | 2.677 | | |

$$\ln x = -\frac{(13.20 \pm 1.20) \times 10^2}{T} + (1.829 \pm 0.409) \tag{4}$$

$$\ln x = -\frac{(13.88 \pm 1.27) \times 10^2}{T} + (0.057 \pm 0.432) \tag{5}$$

The heat of fusion calculated from eq 5 is 2758 cal/gram formula weight, in good agreement with the accepted heat of fusion of cyclooctasulfur, 2696 cal/gram formula weight (again suggesting that the sulfur dissolves as the cyclic octamer).

As before, the least-squares representation of the data (expressed as the molar solubility of monomeric sulfur vs. the temperature) has been plotted in Figure 1 to make its application more convenient.

***C. Sulfur Dioxide Solubility in Thionyl Chloride.*** The experimentally derived solubility of sulfur dioxide in pure thionyl chloride is listed in Table III as a function of temperature. If regularity is assumed, the solubility of $SO_2$ (expressed as mole fraction, $x$) is related to the heat of solution ($\Delta H_{sol}$) and the temperature ($T$) by an equation of the form (*9*)

$$\ln x = -\frac{\Delta H_{sol}}{R}\left(\frac{1}{T} - \alpha\right) \tag{6}$$

(Again, $R$ is the ideal gas constant and $\alpha$ is a proportionality constant.) Thus, over a sufficiently narrow temperature range, a plot of $\ln x$ vs. $1/T$ should be approximately linear. When the sulfur dioxide solubility data were treated in this way, the following

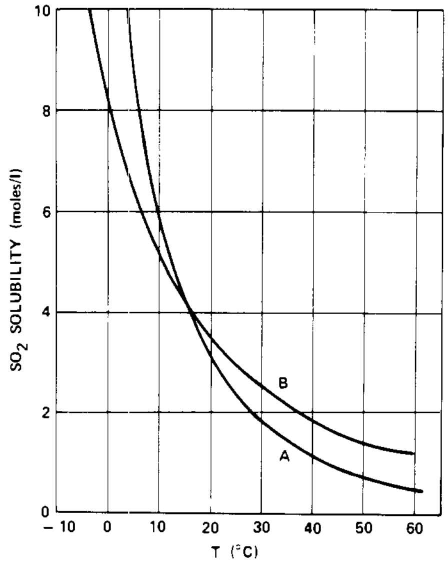

**Figure 2.** Solubility of $SO_2$ in $SOCl_2$: (A) without $LiAlCl_4$, (B) with 1.8 M $LiAlCl_4$.

Table IV. Solubility of Sulfur Dioxide in Thionyl Chloride Containing 1.8 M $LiAlCl_4$

| $T$, °C | solubility, M | $T$, °C | solubility, M |
|---|---|---|---|
| 0 | 8.658 | 34 | 2.504 |
| 0 | 8.681 | 40 | 1.793 |
| 11 | 3.940 | 43 | 1.900 |
| 11 | 4.237 | 44 | 1.412 |
| 13 | 4.195 | 50 | 1.341 |
| 23 | 4.095 | 56 | 0.915 |
| 24 | 3.923 | 58 | 1.660 |
| 30 | 2.467 | | |

least-squares expression for the relationship between the logarithm of the solubility and the reciprocal temperature resulted.

$$\ln x = \frac{(3.982 \pm 0.157) \times 10^3}{T} - (15.29 \pm 0.52) \qquad (7)$$

This line has been plotted in Figure 2, expressed as the molar solubility of $SO_2$ vs. temperature, in order to make its application more convenient.

***D. Sulfur Dioxide Solubility in $SOCl_2$ Containing 1.8 M $LiAlCl_4$.*** Table IV contains a listing of the experimental data as a function of the solution temperature. Again if regularity is assumed, the sulfur dioxide solubility data were analyzed to yield the best linear $\ln x$ vs. $1/T$ expression, given by

$$\ln x = \frac{(2.417 \pm 0.184) \times 10^3}{T} - (9.863 \pm 0.613) \qquad (8)$$

This line is also plotted in Figure 2, expressed as $SO_2$ molar solubility vs. temperature.

***E. Effect of Water upon the Solubility of Sulfur in Thionyl Chloride.*** The experimentally determined values for the room-temperature solubility of sulfur in pure $SOCl_2$ are listed in Table V as a function of the water "concentration" (assuming no reaction between the water and the thionyl chloride). The amount of water was increased from $10^0$ to $10^5$ ppm ($10^{-4}$ to $10^1$% $H_2O$). Surprisingly, the sulfur solubility only decreased by about one-third as the result of this $10^5$-fold increase in the amount of added $H_2O$ (from about 1.6 to about 1.1 M).

## Discussion

As shown in Figure 1, the addition of 1.8 M $LiAlCl_4$ to $SOCl_2$ reduces the sulfur solubility by about 30% over the entire temperature range considered here. In contrast, the effect of the addition of 1.8 M $LiAlCl_4$ upon the solubility of $SO_2$ depends strongly upon the temperature (see Figure 2). At 0 °C, the $SO_2$ solubility in the electrolyte is about 40% lower than it is in pure $SOCl_2$. However, at 60 °C, $SO_2$ is about 140% more soluble in the electrolyte than in the pure solvent. The solubilities are about equal at 15 °C.

Table V. Room-Temperature Sulfur Solubility vs. Amount of Added Water

| water "concn", ppm | sulfur solubility, M | water "concn", ppm | sulfur solubility, M |
|---|---|---|---|
| $1.0 \times 10^0$ | 1.522 | $5.0 \times 10^2$ | 1.237 |
| $1.0 \times 10^0$ | 1.542 | $1.0 \times 10^3$ | 1.493 |
| $2.5 \times 10^1$ | 1.597 | $5.0 \times 10^3$ | 1.392 |
| $5.0 \times 10^2$ | 1.134 | $1.0 \times 10^4$ | 0.959 |
| $5.0 \times 10^2$ | 1.284 | $1.0 \times 10^5$ | 1.289 |

A comparison of the solubilites of S and $SO_2$ either in pure $SOCl_2$ or in the $LiAlCl_4$ solution yields another useful generalization. At least over the range of temperatures considered here, the sulfur solubility increases with temperature in an approximately linear fashion. However, the $SO_2$ solubility decreases with increasing temperature, and the relationship between molar solubility and temperature is an approximately parabolic one. Thus, at lower temperatures, large changes in $SO_2$ solubility are brought about by relatively small changes in temperature, while at higher temperatures just the reverse is true. For instance, increasing the temperature from 0 to 10 °C results in a lowering of the $SO_2$ solubility in the 1.8 M $LiAlCl_4$ solution from about 8 to about 5 M. On the other hand, an increase in temperature from 25 to 35 °C only decreases the solubility from about 3.0 to about 2.2 M, and so forth.

An examination of the experimental data will indicate that the $SO_2$ measurements resulted in much more consistent data than did the S measurements, even though the temperature range employed in the $SO_2$ work was greater than that covered in the S experiments. Because all of the experimental work was done as carefully as was thought necessary to ensure reproducibility, these results were interpreted to suggest the presence of uncontrolled amounts of impurities in the chemicals themselves. The extent of dissolution of sulfur in the $SOCl_2$ would then be a function of the impurity concentration. The impurity most likely to be both generally present and detrimental to sulfur solution chemistry is, of course, water. Thus, some experiments were performed to gauge the effect of the presence of water upon the dissolution of sulfur in $SOCl_2$. Because water reacts with $SOCl_2$ to produce $SO_2$ and HCl, the effects of these two compounds upon the S solubility were also examined.

A 1 M S-$SOCl_2$ solution was prepared as previously described in the Experimental Section. The solution was cooled to room temperature without the precipitation of any sulfur. Then, dry HCl was bubbled through the solution for 20 min followed by a 1-h observation period. No precipitation of the S could be detected. Then, dry $SO_2$ gas was bubbled through the solution for 20 min followed by another 1-h observation period. Again, no precipitated S could be detected. Finally, the $SO_2$ gas was passed through a water-filled bubbler before contacting the sulfur solution. Sulfur was observed to precipitate as soon as the moist $SO_2$ reached the $SOCl_2$, the amount of precipitate increasing with the duration of the test.

The effect of moisture was checked in another way by simply varying the extent to which the rhombic sulfur was dried prior to its attempted dissolution in dry $SOCl_2$. In the first experiment, sufficient sulfur to make a 1 M solution was stored in the 105 °C oven overnight prior to contacting the refluxing $SOCl_2$. The S dissolved immediately and did not precipitate when the solution was cooled to room temperature. In the second experiment, the sulfur was kept in the 105 °C oven for only 30 min before contacting the refluxing $SOCl_2$. In this case, virtually none of the sulfur could be made to dissolve in the $SOCl_2$, even with prolonged heating. Finally, several drops of water were carefully added to the S–$SOCl_2$ solution previously prepared from the well-dried S. The immediate precipitation of S was observed where the $H_2O$ droplets contacted the $SOCl_2$.

Thus, neither hydrolysis product causes S to precipitate from $SOCl_2$ solution, whereas $H_2O$ itself apparently does have this effect. With this in mind, the results of the water addition experiment described above (section E) are immediately explained. Because the water was combined with a portion of $SOCl_2$ before it was added to the hot sulfur solution, what contacted the sulfur solution was primarily a solution of HCl and $SO_2$ in $SOCl_2$. Hence, the sulfur solubility was relatively unaffected.

Thus, while we have gained some understanding of how water and the products of the reaction between water and $SOCl_2$ affect the sulfur solubility, we have not been able to explain the scatter in the S solubility measurements themselves (since the experiments were performed with carefully dried chemicals and glassware). Nevertheless, that the averaged experimental results are reliable is certainly suggested by the good agreement between the accepted value of the $S_8$ heat of fusion and the values from the least-squares data analyses.

## Glossary

| | |
|---|---|
| $\Delta H_{fus}$ | heat of fusion, cal/gram formula weight |
| $\Delta H_{sol}$ | heat of solution, cal/mol |
| $R$ | ideal gas constant, cal/(deg mol) |
| $T$ | absolute temperature, K |
| $T_0$ | melting point, K |
| $x$ | mole fraction |
| $\alpha$ | proportionality constant |

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# Enthalpy of Solution of 32% Nitrogen Solutions at 25 °C

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**Measurements were made of the enthalpy of solutions at 25 °C of 50.36% ammonium nitrate solution in urea solutions. Measurements also were made of the enthalpies of dilution to near infinite dilution of urea–ammonium nitrate solutions. The results were combined with published values of the enthalpies of solution of ammonium nitrate and urea, respectively, in water to determine the enthalpy of producing certain fertilizer solutions from the compounds.**

The amount of energy required to avoid freezing during the preparation of 32% nitrogen solution from urea, ammonium nitrate, and water is important in the design of boilers for the process. No data are available for the enthalpy change involved.

The integral enthalpy of solution over the concentration range 0–9.7% nitrogen was determined by the scheme

$$NH_4NO_3 + xH_2O = NH_4NO_3 \cdot xH_2O \qquad (1)$$

$$CO(NH_2)_2 + yH_2O = CO(NH_2)_2 \cdot yH_2O \qquad (2)$$

$$NH_4NO_3 \cdot xH_2O + a[CO(NH_2)_2 \cdot yH_2O] = NH_4NO_3 \cdot aCO(NH_2)_2 \cdot (x + ay)H_2O \qquad (3)$$

$$(1) + a(2) + (3) = (4)$$

$$NH_4NO_3 + aCO(NH_2)_2 + (x + ay)H_2O = NH_4NO_3 \cdot aCO(NH_2)_2 \cdot (x + ay)H_2O \qquad (4)$$

where $a$ is the mole ratio of $CO(NH_2)_2$ to $NH_4NO_3$ in the 32% nitrogen solution.

Table I. Solutions Used in the Determination of Enthalpy of Solution of Ammonium Nitrate Solutions in Urea Solutions

| | | solution compn, % | |
|---|---|---|---|
| solution | % N | $CO(NH_2)_2$ | $NH_4NO_3$ |
| AN | 17.62 | | 50.36 |
| U5 | 2.36 | 5.06 | |
| U10 | 4.74 | 10.16 | |
| U15 | 7.02 | 15.05 | |

One ammonium nitrate solution and three urea solutions were prepared by dissolving the reagent-grade compounds in distilled water. The chemical analyses[2,3] and the percentages of ammonium nitrate and urea calculated from the analyses are listed in Table I.

The enthalpy of reaction 1, $\Delta H_1$ (4220 cal), was determined by substracting the enthalpy of formation of $NH_4NO_3$(c) from the enthalpy of formation of 50.36% $NH_4NO_3$ ($NH_4NO_3 \cdot 4.380H_2O$).[5] The enthalpy of reaction 2, $\Delta H_2$, for each urea solution was determined from the data of Egan and Luff.[1]

The ammonium nitrate solution was added to each urea solution in successive increments in the solution calorimeter and the differential enthalpy of solution, $d(\Delta H)/dm_s$, was determined in calories per mole at the average molality, $m_s$, of $NH_4NO_3 \cdot 4.380H_2O$ for each measurement.

The solution calorimeter and the method of measurement have been described[4] with the exception that the Wenner potentiometer and Aryton shunt were replaced by a Hewlett-Packard Model 3490A multimeter that measured the voltage drop across the calorimeter heater directly. The defined calorie was taken as 4.184 absolute J; and corrections were made for the