

## Heats of Solution

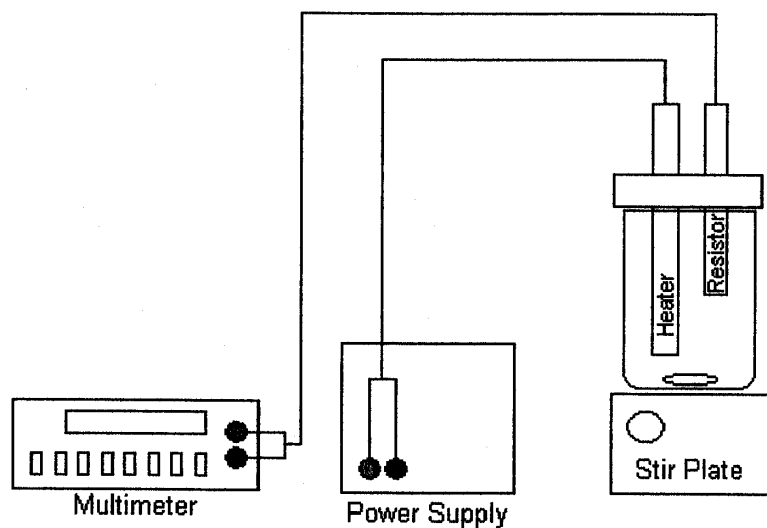
### Abstract:

A Dewar flask containing both a heater and a resistor was used to measure determine the heat of solution of aqueous  $\text{KNO}_3$ . By gathering data on changes in resistance and the time it took for these changes to occur and applying them to a set of equations, values for  $\Delta H_i$ , the enthalpy of a specific solution,  $\Delta H_{int}$ , the integral heat of solution for a trial, and  $\Delta H_\infty$ , the enthalpy of a solution at infinite dilution, which have many applications in thermodynamic calculations.

*give results.*

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## Apparatus



**Figure 1:** Apparatus for Determination of Heat of Solution

### Theory:

In a solution with a given concentration,  $\Delta H_{\text{Int}}$ , the integral heat of solution, is the heat absorbed when one mole of solute is dissolved isothermally in enough solvent to form a final solution with a new concentration, "m". This is the enthalpy change as pressure and temperature are held constant. This can be found using the equation:

$$\Delta H_{\text{Int}} = (\Sigma \Delta H_I) / (\Sigma n_I) \quad (1).$$

In the previous equation, the  $\Delta H_I$  is the heat of solution for each separate trial, and can be found using the equation:

$$\Delta H_I = C_p(T_o - T_I) \quad (2). \quad \checkmark$$

The heat capacity of the system must also be found and is done using:

$$C_p = (V_H^2 * t / R_H) / (T_2' - T_1') \quad (3). \quad \checkmark$$

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The temperature is found is by the relationship

$$R = R_{\infty} e^{(B/T)} \quad (4).$$

The B value of the system is 3859.2 and the  $R_{\infty}$  value is 0.005360  $\Omega$ .

### Experimental Method

The apparatus was set up as shown in Figure 1, with the multimeter set to AC voltage, and to measure Ohms ( $\Omega$ ) in the 0 to 20k $\Omega$  range. With the power supply turned off, the resistance of the power supply and the banana plugs was measured, and recorded. Before reconnecting the system, the power supply was turned on and the potential generated was measured using the multimeter using the voltage setting. The system was then restored to its initial setup, as shown in Figure 1, with the power supply on, but the heater off. The water in the Dewar flask was allowed to reach an equilibrium resistance, as measured by the multimeter, and this initial resistance,  $R_0$ , was recorded. A measured amount of potassium nitrate ( $\sim 4.0\text{g}$ ) was then added to the Dewar flask, and a timer was started. Time to reach a minimum resistance was recorded, after which the heater was turned on, and the time for the resistance to return to  $R_0$  was recorded. The process was repeated five times, without emptying the Dewar flask. Subsequent amounts of potassium nitrated were added to the solution, and  $R_0$  values were taken for each trial.

1.0 / 1.0

## Results

The results for  $\Delta H_i$ , (J/mol) and  $\Delta H_{int}$ , (J/mol) which vary with molality, are located in *Table 1*. These values were used to calculate  $\Delta H_\infty$ , which is the y-intercept of

Chart 2.  
Figure

$$C_{P_{ave}} = 1353.332 \text{ J/mol} \pm 33.76 \text{ J/mol}$$

$$\Delta H_\infty = 40999 \text{ J/mol} \pm 1292.81 \text{ J/mol}$$

$$\Delta H_\infty(\text{literature}) = 34894.56 \text{ J/mol}$$

See *Appendix 1* for all charts, and *Appendix 2* example calculations, and *Appendix 3* for raw data.

## Conclusion:

$$C_{P_{ave}} = 1353.332 \text{ J/mol} \pm 33.76 \text{ J/mol}$$

$$\Delta H_\infty = 40999 \text{ J/mol} \pm 1292.81 \text{ J/mol}$$

$$\Delta H_\infty(\text{literature}) = 34894.56 \text{ J/mol}$$

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Through the inverse relationship between resistance and temperature shown in *Equation 4*, it is shown that after adding the salt to solution and thus increasing resistance, the temperature drops. Reheating the solution to its original temperature leads to a value for the amount of heat required to raise this solution 1K, which is the solution's  $\Delta H_i$  value, depicted in *Equation 2*. The CP value in equation is the aver

The integral heat of solution,  $\Delta H_{\text{Int}}$ , as described in the theory section, is the enthalpy change for a change in state at constant pressure and temperature, and can be calculated using *Equation 1*. In <sup>Figure</sup> ~~Chart~~ 1, the results of the calculation for  $\Delta H_{\text{Int}}$  are plotted against the molality of the solution. The purpose of this plot is to prove the results are linear, which, with an  $R^2$  value of 0.979, is true.

<sup>Figure</sup> ~~Chart~~ 2 is similar to <sup>Figure</sup> ~~Chart~~ 1, except that  $\Delta H_{\text{Int}}$  is plotted against the square root of molality. Linear results are also shown here, with an  $R^2$  value of 0.9989, but more importantly, the y-intercept of 40999 J/mol is the heat of solution at infinite dilution, or  $\Delta H_{\infty}$ . Note that despite the results agreeing with each other, the difference between derived value of  $\Delta H_{\infty}$  and the literature value is significant. This is due to an error in trial ✓ okay.

2. After adding the potassium nitrate to the Dewar flask, the stir bar became jammed, and the salt did not dissolve at the same rate as in previous and subsequent trials. Results for this trial were not taken, but the heating process was still done, to prepare for the next trial. After calculations were done, however, it was realized that the equations for many of the desired values called for summations of results. Having six different values for molality and only 5 values for other sums created incorrect results. To remedy this, trial 1 was counted twice. While this gives a better result, it is still not correct.

The other source in of error in this experiment was in trial 1. When reheating, the solution was heated beyond the original temperature. This created problems in calculating  $C_p$ , and all results dependent on  $C_p$ . Overheating the solution yielded a  $C_p$  value that was too small, as can be seen in application of *Equation 3*. The  $(T_2 - T_1)$  term will be too large. This translates into  $\Delta H_i$  that are also lower than should be observed, as

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Discussion

can be determined from *Equation 2*. This error will cascade through all the calculations, and ultimately contribute to the error observed in  $\Delta H_{\infty}$ .

A source of error that was not a factor in this analysis, but must still be mentioned is that after heating back to equilibrium temperature, cooling of the solution may occur. This is due to any salt that did not completely dissolve in the initial addition. When the solution is cooled from the dissolving of the  $\text{KNO}_3$ , the solubility in water goes down due to the lower temperature. After heating, the solubility goes back up, and any undissolved salt will dissolve, thus cooling the solution again. Therefore, the final temperature must be taken immediately, to ensure the value is correct.

# Appendix 1

Figure  
Chart 1:  $\Delta H_{int}$  vs Molality

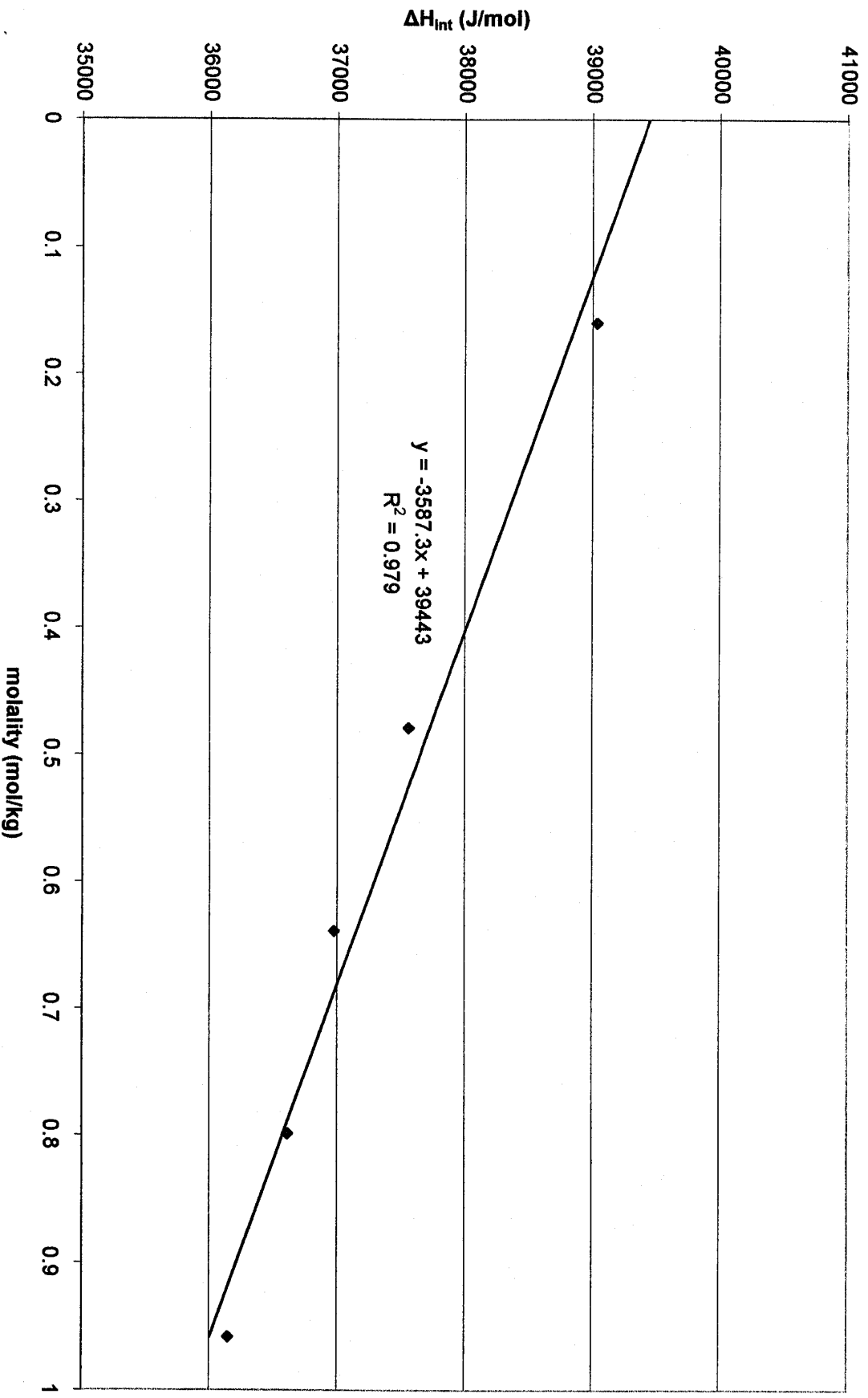
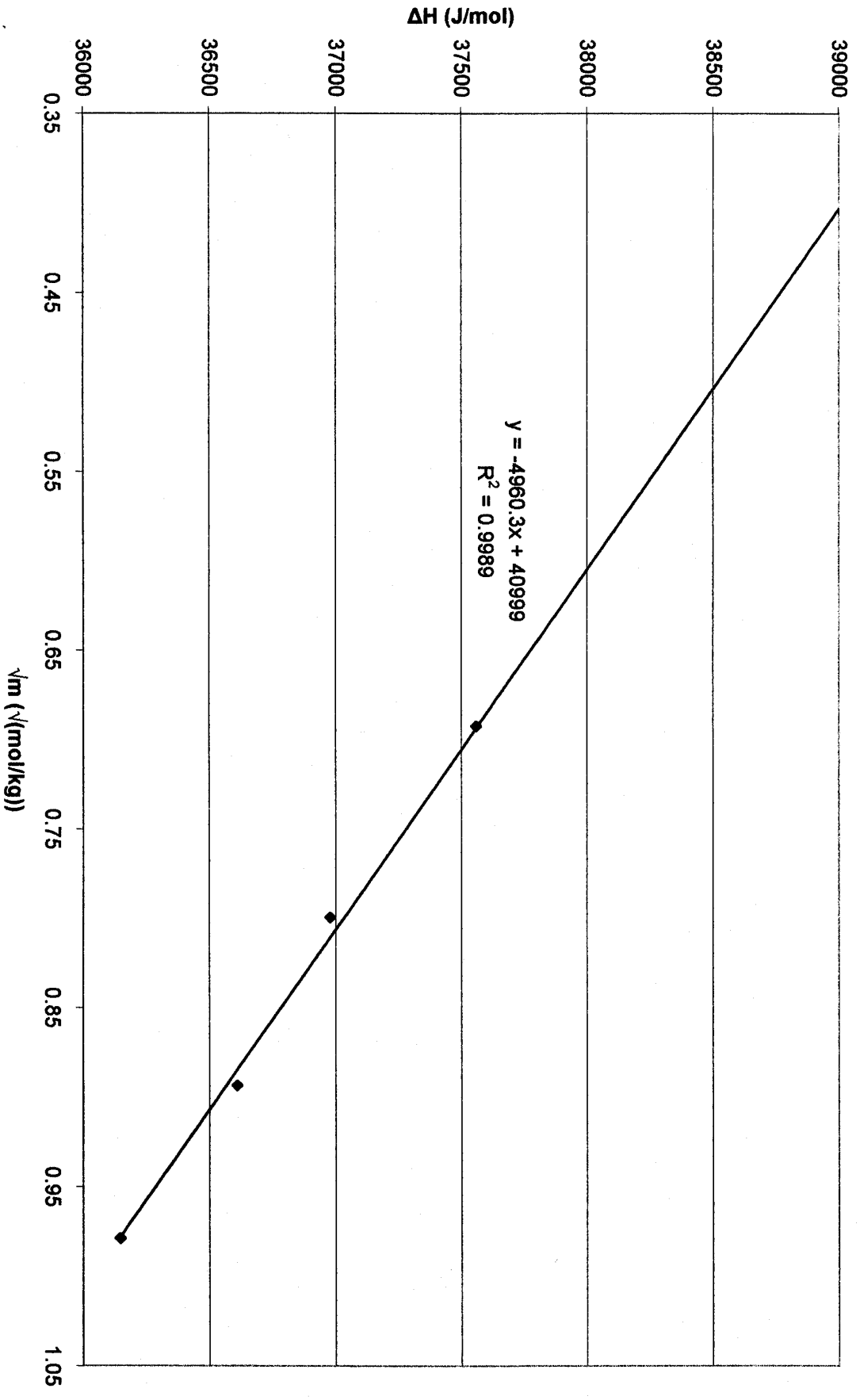




Figure  
Chart 2:  $\Delta H_{int}$  vs  $\nu_m$

graph 10/10



## **Appendix 2**

## Calculations

$$R_{total} = R_{\infty} e^{(B/T)}$$

$$(2.024 + 10.3) = (.005360\Omega) \times e^{(3859.2K/T)}$$
$$T = 300.404K$$

$$C_P = \frac{\left\{ \frac{V_H t}{R_H} \right\}}{T_0 - T_1}$$

$V_H$ =heater voltage,  $t$ =heating time, and  $R_H$ =heater resistance

$$C_P = \frac{\left\{ \frac{(9.88^2 \times 157)}{10.2} \right\}}{(300.0406 - 298.8974)}$$
$$C_P = 1316.594 J/mol$$

$$\Delta H_i = C_{P(ave)}(T_0 - T_1)$$

$$\Delta H_i = 1353.332 \times (300.0406 - 298.8974)$$

$$\Delta H_i = 1544.42 J \cdot K/mol$$

$$\Delta H_{Int} = \frac{(\sum \Delta H_i)}{m(\sum n_i)} \quad m = \text{molality, and } n_i = \text{number of moles salt added}$$

$$\Delta H_{Int} = \frac{1544.42}{4.0006/101.1032}$$

$$\Delta H_{Int} = 39030.6 J/mol$$

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data analysis

$$\bar{x} = \frac{\sum_{i=1}^n x_i}{n}$$

$$\bar{x} = \frac{10.2 + 10.2 + 10.2 + 10.1 + 10.3 + 10.3}{6}$$

$$\bar{x} = 10.21667V$$

$$S_x = \sqrt{\frac{\sum (x - \bar{x})^2}{n-1}}$$

$$S_x = \sqrt{\frac{3 \times (10.2 - 10.21)^2 + (10.1 - 10.21)^2 + 2 \times (10.3 - 10.21)^2}{6-1}}$$

$$S_x = 0.0753$$

$$RSD = \frac{S_x}{\bar{x}}$$

$$RSD = \frac{.0753}{10.21667}$$

$$RSD = 0.007368$$

$$95\%CI = \frac{S_x \times t_{student}}{\sqrt{n}}$$

$$95\%CI = \frac{.0753 \times 2.571}{\sqrt{6}}$$

$$95\%CI = 0.079011$$

found

error analysis 1.0/1.0

## **Appendix 3**

Table 1

Trial	V <sub>source</sub> (volts)	R <sub>source</sub> (Ω)	mass, KNO <sub>3</sub> g	m, sol (mol/kg)	sqrt(m)	t <sub>0</sub> (sec)	t <sub>1</sub> (sec)	R <sub>0</sub> (Ω)	T <sub>0</sub> (K)	R <sub>1</sub> (Ω)	T <sub>1</sub> (K)	C <sub>p</sub> J/(mol*K)	ΔHi J/mol	ΔHint J/mol
1	9.88	10.2	4.0006	0.1597	0.399684	70	157	2066.2	300.04	2170.2	298.9	1316.594	1544.42	39030.6
2	9.92	10.2	4.0000	0.3195	0.565218	-	-	-	-	-	-	-	-	-
3	9.97	10.2	3.9999	0.4792	0.692236	71	154	1994.2	300.87	2088.2	299.8	1394.078	1456.89	37560.1
4	9.97	10.1	4.0008	0.6389	0.799341	65	139	1978.1	301.06	2067.1	300	1328.042	1394.04	36977.1
5	9.97	10.3	4.0002	0.7987	0.893688	70	144	1963.3	301.24	2051.3	300.2	1352.509	1390.53	36610.7
6	9.97	10.3	4.0010	0.9584	0.979	68	141	1950.3	301.39	2034.3	300.4	1375.439	1338.86	36147.6
Ave	9.9467	10.21667				68.8	147					1353.332		
Std dev	0.0383	0.075277				2.387	8.031					32.16724		
RSD	0.0039	0.007368				0.035	0.055					0.023769		
95% CI	0.0402	0.079011				2.506	8.43					33.76294		

ΔH<sub>∞</sub> (J/mol)  
39416

Std dev 2211.89819

ΔH<sub>∞</sub> (lit) (J/mol)  
34894.56