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HEAT OF SOLUTION OF KCl IN WATER AT 303.15 K

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ABSTRACT

The enthalpies of solution of KCl in water at 303.15 K have been measured in a heat-flux calorimeter as a function of molality. The covered range is 0.01 to 0.06 mol/kg. The enthalpy of solution at infinite dilution is obtained using values for the enthalpy of dilution, L_ϕ . The proposed value is $\Delta H^\circ(303.15) = 16426$ J/mol.

INTRODUCTION

In order to increase the thermodynamic information about aqueous solutions of alkali-metal chlorides, particularly of experimental enthalpies of solution, we present experimental results of aqueous solutions of KCl as a function of molality at 303.15 K. In the literature few measurements of this type are encountered although the solution of KCl has been proposed as a reference reaction for solution calorimetry (ref.1).

EXPERIMENTAL

The heat-flux calorimeter used is a Tian-Calvet standard type described in detail in a previous work (ref.2). The temperature controller used regulates to better than ±0.001 K. The stability of the calorimetric system is ±0.005 K over 12 h. An electrical calibration is carried out before and after each measurement. The calorimetric energy equivalent is about 43 mV/w, the value is accurate to 0.05 per cent in each determination.

Materials

The water used is double distilled. All weightings were obtained with a sensivity of 10 micrograms. Solid sample is pro analysi Merck of 99.5 mass per cent. All weightings were obtained with a

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sensivity of 1 microgram. The particle size is $\geq$200 μm for the 80 per cent of sample. It is heated during four hours in a furnace at (773±5)K. The removal of occluded moisture is about 0.2 per cent. Because of KCl is not hygroscopic (ref.2), it presents no significant changes due to atmospheric moisture. Once the calorimetric cell is inserted in the calorimeter block a total time of 12 h is required in order to reach thermal equilibrium. During this time, the vaporization test shows that the solvent looses about 0.1 per cent of it mass. Thus the uncertainty of molality values is 0.1 per cent.

RESULTS AND DISCUSSION

The results of enthalpies of aqueous solutions of KCl at 303.15 K are shown in Table 1.

In this table, w_s and w_w are the solute and solvent mass, respectively. E is the energy absorbed in each solution. T_{mean} is the solvent temperature in each measurement (T_{mean} represents the average temperature between determinations before and after each solution. The maximum temperature shift is lower than 0.005 K). $\Delta H_m(T_{mean})$ is the molar enthalpy of solution at T_{mean}. $\Delta H_m(303.15)$ is the molar enthalpy of solution adjusted to 303.15 K. The solvent condensation effect has been considered.

The adjustment to 303.15 K is formed as follows (ref.3):

$$\Delta H_m(303.15) = \Delta H_m(T_{mean}) + C_{p,m}\ (303.15 - T_{mean}) \qquad (1)$$

where $C_{p,m} = C_{\phi,m} - C_p$.

$C_{\phi,m}$ is the apparent molar heat capacity of the dissolved salt at the given molality and C_p is the molar capacity of the salt before solution. Literature values of C_p (ref.4) and $C_{\phi,m}$ (ref.5) were employed.

The error due to condensation of solvent is given approximately by (ref.6):

$$\delta H = -\ (2\ x\ p^{*}V^{g}/RT)\cdot\Delta H_m(1,g) \qquad (2)$$

where x denotes the mole fraction of the solute after dissolution, p* the vapour pressure of the pure solvent and $\Delta H_m(1,g)$ the molar enthalpy of evaporation of the pure solvent. The correction of the solvent condensation effect, for our experimental conditions, is negligeable (≈0.08 J•mol^{-1}).

In order to analyse our experimental results, the enthalpy of solution at infinite dilution is calculated. Values for the enthalpy of dilution, L_ϕ, are generally used for corrections to infinite dilution. The expressions for L_ϕ, used in this work, are as follows (ref.7) and (ref.8), respectively:

$$L_\phi^{(1)}(m) = A_{DH}^{L}\, m^{\frac{1}{2}}\left[(1+m^{\frac{1}{2}})^{-1} - \frac{1}{m^{\frac{1}{2}}}(1 + m^{\frac{1}{2}} - \frac{1}{1+m^{\frac{1}{2}}} - 2\ln(1+m^{\frac{1}{2}}))\right] + B\, m + C\, m^{\frac{3}{2}} \qquad (3)$$

$$L_\phi^{(2)}(m) = \frac{A_{DH}^{L}}{1.8}\ln(1 + 1.2\, m^{\frac{1}{2}}) - 2\, R\, T^2 \frac{\partial \beta^{(0)}}{\partial T}\, m - R\, T^2 \frac{\partial \beta^{(1)}}{\partial T}\left[1 - (1 + 2\, m^{\frac{1}{2}})\, e^{-2m^{\frac{1}{2}}}\right] \qquad (4)$$

where A_{DH}^{L} is the Debye-Hückel constant for the apparent molar enthalpy. Literature values of A_{DH}^{L} (ref.9), B and C (ref.7), $\partial\beta^{(0)}/\partial T$ and $\partial\beta^{(1)}/\partial T$ (ref.8) were employed.

The results for the enthalpy of solution at infinite dilution are given in Table 2. The value difference is 0.6 per cent. Because of the values for the apparent molar enthalpy corresponding to expression (3) were obtained by direct experimental measurements, we estimate that the value of enthalpy of solution at infinite dilution obtained by means of $L_\phi^{(1)}(m)$ is more certain, so that the value of ΔH°(303.15) proposed is 16426 J/mol.

Holmes and Mesmer (ref.8) have proposed the following equation for the enthalpy of solution at infinite dilution as a function of temperature:

$$\Delta H^\circ(T) = q_1 + q_2\, T + q_3\, T^2 + q_4\, T^3 + q_5 \ln(T-270) \qquad (5)$$

The value of the enthalpy of solution at infinite dilution for aqueous solutions of KCl at 303.15 K proposed in this work agrees with that obtained using the expression (5) within 0.05 per cent. The results are shown in Table 3.

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TABLE 1

w_s	w_w	m	ε	T_{mean}	$\Delta H_m(T_{mean})$	$\Delta H_m(303.15)$
g	g	$mol \cdot kg^{-1}$	J	K	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$
0.014380	34.55783	0.005273	3.22	303.200	16694.2	16702.6
0.014975	34.62611	0.005801	3.37	303.212	16762.0	16771.6
0.027280	34.58705	0.01058	6.13	303.217	16750.6	16761.1
0.028870	34.46242	0.01124	6.37	303.220	16459.0	16469.9
0.035105	34.57030	0.01362	7.87	303.205	16705.8	16714.2
0.036749	34.52155	0.01428	8.34	303.172	16918.3	16921.6
0.037145	34.52204	0.01443	8.39	303.253	16832.9	16848.8
0.041168	34.44552	0.01603	9.33	303.127	16900.5	16896.7
0.046745	34.34229	0.01826	10.55	303.125	16827.4	16823.2
0.048160	34.52155	0.01871	10.71	303.223	16576.1	16587.4
0.052450	34.62405	0.02032	11.78	303.097	16744.1	16735.7
0.057008	34.51774	0.02215	12.80	303.088	16742.5	16732.9
0.065785	34.67330	0.02548	14.63	303.267	16553.9	16571.9
0.065795	34.39352	0.02566	14.85	303.182	16828.3	16832.5
0.071218	34.63407	0.02758	16.02	303.258	16774.3	16790.6
0.080938	34.69156	0.03131	18.17	303.203	16739.0	16747.4
0.089428	34.57057	0.03470	20.03	303.048	16831.0	16815.1
0.091168	34.66643	0.03528	20.27	303.259	16578.8	16591.4
0.091575	34.52204	0.03558	20.56	303.256	16736.8	16753.1
0.105933	34.55922	0.04112	23.60	303.028	16818.9	16837.7
0.155390	34.69156	0.06008	34.89	303.206	16739.0	16747.4

TABLE 2

Expression	$\Delta H^\circ(303.15)$
	$J\ mol^{-1}$
(3)	16426
(4)	16518

TABLE 3

Expression	$\Delta H^\circ(303.15)$
	$J\ mol^{-1}$
(3)	16426
(5)	16418

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