Enthalpies of Dilution and Excess Molar Enthalpies of an Aqueous Solution of Sulfuric Acid

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The enthalpies of dilution of the binary system $H_2SO_4 + H_2O$ have been measured at the temperatures of (283.15, 293.15, 313.15, and 333.15) K using two different calorimeters. The excess molar enthalpies, H^E, of the system $H_2SO_4 + H_2O$ are obtained from the enthalpies of dilution data. The enthalpies of dilution and the H^E data are reported and compared to literature values.

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1. Introduction

Since the measurement of Favre and Quaillard,[1] many scientists have measured the enthalpies of dilution in order to study the thermodynamic properties of sulfuric acid. Giauque et al.[2] have reported a very comprehensive data set for the entire mole fraction range of the system $H_2SO_4 + H_2O$. Wu and Young[3] made very precise measurements for this system, but the mole fraction range was limited to extremely low mole fractions of H_2SO_4.

Most previous measurements were made before the 1950s when modern calorimeters were not developed and measurements were performed at ambient temperature or at 293.15 K.[1,4−6]

In this work, a Calvet calorimeter (Seteram C80) and an isothermal flow calorimeter (Hart Scientific model 4250) are used to measure the enthalpy of dilution of the system $H_2SO_4 + H_2O$ at higher temperatures. Because the isothermal flow calorimeter works continuously and almost automatically, it is very convenient to measure a set of data. However, the isothermal flow calorimeter has a long contact time between the measuring fluid and its tubes especially when the flow rate is low. This long contact time can cause serious errors through corrosion at high temperature when the measuring fluid is a strong acid. For these cases, a Calvet calorimeter with a specially designed mixing vessel was used to measure the enthalpy of dilution of the system $H_2SO_4 + H_2O$.

2. Definition of Calorimetric Quantities

The enthalpy of dilution, $\Delta_{dil}H_m$, is defined as the enthalpy change per 1 mol of solute when a solution of a composition x_i is diluted to a concentration x_f. The enthalpy of dilution is negative for exothermic mixing. There are two special cases of enthalpy of dilution: if $x_i = 1$, it is called the enthalpy of solution $\Delta_{sol}H_m$. The other case occurs for $x_f = 0$, whereby the relative apparent molar enthalpy, L_ϕ, is defined. The relative apparent molar enthalpy is positive for exothermic mixing.

In Figure 1, the characteristic curves of the above-defined calorimetric quantities are represented schematically.

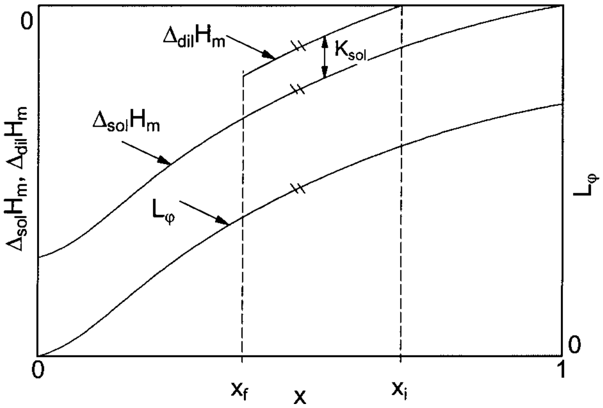

Figure 1. Characteristic curves of the enthalpy of dilution, the enthalpy of solution, and the relative apparent molar enthalpy.

According to the definition, the relationship between the enthalpy of dilution, the enthalpy of solution, and the relative apparent molar enthalpy is given by eq 1. This

$$\Delta_{dil}H_m(x_i \rightarrow x_f) = L_\phi(x_f) - L_\phi(x_i) = \Delta_{sol}H_m(x_f) - \Delta_{sol}H_m(x_i) \qquad (1)$$

relation can be used to check the consistency of the calorimetric measurements. The consistency of the measurements with different initial concentrations can be checked by vertical shifting of the individual curves. The curves must be transferable into one another thereby. Another advantage of this relation is that the enthalpies of dilution data sets, which have different initial concentrations, can be linked to one another. $\Delta_{sol}H_m(x_f)$ can be measured directly by diluting pure solute with solvent, but it can also be determined by adding a constant value K_{sol}, which corresponds to $\Delta_{sol}H_m(x_i)$, to $\Delta_{dil}H_m(x_i \rightarrow x_f)$. K_{sol} can be determined by minimizing the deviation between $\Delta_{sol}H_m(x_f)$ and $\Delta_{dil}H_m(x_i \rightarrow x_f) + K_{sol}$. Through this method, the absolute uncertainty of the enthalpy of solution, $\delta\Delta_{sol}H_m(x_f)$, can be kept smaller than that of directly measured values by diluting pure solute. The uncertainty of $\Delta_{sol}H_m(x_f)$ can be determined as eq 2 by vertical shifting. However, practically one should substitute δK_{sol}

$$\delta\Delta_{sol}H_m(x_f) = \delta\Delta_{dil}H_m(x_i \rightarrow x_f) + \delta\Delta_{sol}H_m(x_i) \qquad (2)$$

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10.1021/je0000221 CCC: $20.00

Table 1. Concentration of the Prepared H_2SO_4 Solutions before Dilution and the Temperatures of the Measurement

$100w$	$100\delta w$	T/K
100.0	0.30	293.15,[a] 313.15,[a] 333.15[a]
96.43	0.08	293.15,[b] 313.15,[a] 313.15,[b] 333.15[a]
40.03	0.15	283.15,[b] 293.15,[b] 313.15[b]
6.47	0.01	293.15[b]

[a] Measured with a Calvet calorimeter. [b] Measured with an isothermal flow calorimeter.

for $\delta\Delta_{sol}H_m(x_i)$.

$$\delta\Delta_{sol}H_m(x_f) = \delta\Delta_{dil}H_m(x_i \rightarrow x_f) + \delta K_s \tag{3}$$

$\delta\Delta_{sol}H_m(x_i)$ is estimated from one data point. Because K_{sol} is determined by optimizing two data sets, much more reliable values of δK_{sol} can be estimated compared to $\delta\Delta_{sol}H_m(x_i)$. δK_{sol} can be thought of as $\delta\Delta_{sol}H_m(x_i)$, of which the random factors are minimized.

After $\Delta_{sol}H_m$ is determined through the method of vertical shifting, it can be converted into an excess molar enthalpy, H^E, with eq 4 for binary mixtures.

$$H^E(x) = x\Delta_{sol}H_m(x) \tag{4}$$

The relation between the apparent molar enthalpy and the apparent molar heat capacity, $C_{p,\phi}$, is given by eq 5

$$C_{p,\phi} = C^o_{p,m} + \partial L_\phi/\partial T \tag{5}$$

where $C^o_{p,m}$ is the standard state value for the solute.

3. Experimental Section

Chemicals. The concentration of aqueous sulfuric acid, 95−97 mass % (p.a.), supplied by Merck was determined by acid−base titration with a 0.1 M sodium hydroxide standard solution (Fluka) using a piston buret, which has a resolution of 0.01 mL. Phenolphthalein (Merck, Art. 7233) was used as the indicator. After the titration, sulfuric acid was diluted with three times distilled water in order to prepare aqueous solutions of various strengths. The mole fractions of the solutions were determined from the mass of sulfuric acid, 96.43 mass %, and water with a balance (Sauter type 404/18), which has a resolution of 0.1 mg.

The 100 mass % H_2SO_4 was produced by dissolving SO_3 vapor (Aldrich, 99%) into 96.43 mass % H_2SO_4. First, solid SO_3 was melted in a thermal bath at 333.13 K and degassed with vacuum pump, and then the valve was opened in order to allow the SO_3 vapor to be absorbed into the 96.43 mass % H_2SO_4. After the concentration was determined by acid−base titration, 100 mass % H_2SO_4 was poured into five sample bottles and kept in a chamber, through which low-pressure dry N_2 gas was blown, to protect the sample from atmospheric moisture. Each sample was used for 10 measurements, and after the measurements, the concentration of the sample was determined again by acid−base titration. No change in the concentration was detected within the accuracy of the acid−base titration of 0.3 mass %.

In Table 1, the initial concentrations of the solutions, their uncertainties, and the temperatures of the measurements are listed.

Calorimeters. The enthalpies of dilution were determined using a Calvet calorimeter (Seteram C80) and an isothermal flow calorimeter (Hart Scientific model 4250).

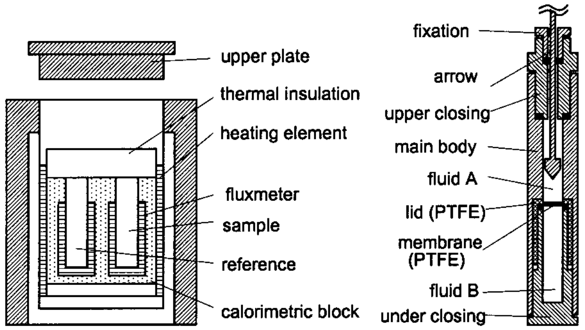

Figure 2. Scheme of the Calvet calorimeter and the mixing vessel.

The isothermal flow calorimeter was equipped with two precise syringe pumps. To protect the pumps from strong acid, a quartz cylinder with a PTEF piston was placed between the solvent pump and the calorimeter. All of the tubes in the calorimeter were made of Hastelloy C4 to avoid corrosion. The density data for aqueous sulfuric acid solutions, which are needed to determine the concentration of the solution after the dilution, were taken from Domke and Bein.[7] Details of the apparatus and the experimental procedure of the isothermal flow calorimeter were described by Rütten et al.[8]

The scheme of the Calvet calorimeter and the mixing vessel is shown in Figure 2. A precise description of the apparatus is given in the production information of Seteram.[9] To avoid corrosion, the body and the closings of the mixing vessel were made of Hastelloy C4, which has an excellent resistance against strong acids. Even so, the direct contact of 100 mass % H_2SO_4 to the body of the vessel causes a significant effect to the measurement. To minimize this effect, a membrane sheet was placed between the upper (fluid A) and the lower (fluid B) portions of the vessel. Before mixing, the 100 mass % H_2SO_4 was placed between the membrane and the lid so that there was no direct contact between the sulfuric acid and the Hastelloy C4 body. When thermal equilibrium was reached, the arrow tears the membrane and the two liquids were mixed. During the measurement, the output voltage of the fluxmeter, U, is recorded as a function of the time. The output voltage is proportional to the temporal energy flow after

$$\dot{Q} = -K_E U \tag{6}$$

The proportionality factor K_E/(mW μV^{-1}) is temperature-dependent and must be determined for each temperature with a electrically heated calibration vessel. The surface under the U curve was determined with an OTT compensation polarplanimeter.

Accuracy of the Measurement. The accuracy of the isothermal flow calorimeter was discussed by Rütten et al.[8] Only the calculation method for the uncertainty of the Calvet calorimeter is discussed here.

The temperature of the calorimetric block was measured with a PT 100 resistance thermometer. The deviation of the temperature in the stabilized phase, i.e., before mixing and at the end of the measurement, was within ±0.1 K. The maximum temperature increase during the measurements was not larger than 0.3 K.

The number of moles of H_2SO_4 used in the measurement is estimated as

$$n_{H_2SO_4} = n_{H_2SO_4,i} = n_{H_2SO_4,f} = \frac{w_{sol} m_{sol}}{M_{H_2SO_4}} \tag{7}$$

where w_{sol} is the mass fraction of the solution, m_{sol} the mass of the solution, and $M_{H_2SO_4}$ the molecular weight of H_2SO_4. The subscript i stands for the state before mixing and f for the state after mixing. The uncertainty of $n_{H_2SO_4}$ occurring from the uncertainty of the initial concentration and the accuracy of the balance (Sauter type 404/18), $\delta n^{m}_{H_2SO_4}$, is

$$\delta n^{m}_{H_2SO_4} = \left|\frac{m_{sol}}{M_{H_2SO_4}}\delta w_{sol}\right| + \left|\frac{w_{sol}}{M_{H_2SO_4}}\delta m_{sol}\right| \tag{8}$$

Because there are vapor spaces in the mixing vessel, $n_{H_2SO_4}$ and n_{H_2O} are influenced by the evaporation of the liquids. These uncertainties are calculated with eq 9.

$$(\delta n^{v}_{H_2SO_4})_i = p_{H_2SO_4,i}V_A/RT$$

$$(\delta n^{v}_{H_2SO_4})_i = p_{H_2O,i}V_A/RT$$

$$(\delta n^{v}_{H_2SO_4})_f = p_{H_2SO_4,f}(V_A + V_B)/RT$$

$$(\delta n^{v}_{H_2SO_4})_f = p_{H_2O,f}(V_A + V_B)/RT \tag{9}$$

In eq 9, $p_{H_2SO_4}$ and p_{H_2O} are the partial pressures, which depend on temperature and composition. V_A is the vapor space above the solution and V_B the vapor space above the solvent. The vapor phase is assumed as an ideal gas. The change in the liquid volume by mixing is neglected.

$(\delta n^{v}_{H_2SO_4})_i$, $(\delta n^{v}_{H_2O})_i$, $(\delta n^{v}_{H_2SO_4})_f$, and $(\delta n^{v}_{H_2O})_f$ vary depending upon the temperature, vapor space, initial concentration, and final concentration and are calculated with the help of the phase equilibrium data from Bolsaitis and Elliott.[10] The absolute uncertainty in $n_{H_2SO_4}$ after dilution, $(\delta n_{H_2SO_4})_f$, is determined by eq 10.

$$(\delta n_{H_2SO_4})_f = \delta n^{m}_{H_2SO_4} + (\delta n^{v}_{H_2SO_4})_f \tag{10}$$

The amount of energy, Q, measured with the Calvet calorimeter is calculated as

$$Q = -\frac{U_{max}AK_E}{\beta a v} \tag{11}$$

where U_{max} is the maximal voltage which corresponds to the entire paper width of the recorder, A the surface under the U curve, β the measuring range factor, v the line feed rate, a the height of the recorder excursion corresponding to the maximal voltage U_{max}, and K_E the calorimetric sensitivity of the Calvet calorimeter.

The maximal absolute uncertainty of the calorimeter δQ^{cal} is

$$\delta Q^{cal} = \left\{\left|\frac{\delta U_{max}}{U_{max}}\right| + \left|\frac{\delta A}{A}\right| + \left|\frac{\delta\beta}{\beta}\right| + \left|\frac{\delta a}{a}\right| + \left|\frac{\delta v}{v}\right| + \left|\frac{\delta K_E}{K_E}\right|\right\}|Q| \tag{12}$$

δU_{max}, $\delta\beta$, δv, and δa, which are due to the recorder, are assumed to be zero. δA is the uncertainty, which results from inaccurate measurement of the surface A. δA is 20 mm^2. K_E is temperature-dependent and is determined for each measuring temperature with a calibration vessel, which is constructed in the same form as the mixing vessel of Figure 2. The calibration vessel is equipped with a platinum wire heater, which can produce a constant amount of energy and is filled with silicon oil. The accuracy of K_E is within 0.2%.

Table 2. Enthalpies of Dilution of the System xH_2SO_4 + $(1 - x)H_2O$

x_f	$\Delta_{dil}H_m$/ (J mol^{-1})	$\delta\Delta_{dil}H_m$/ (J mol^{-1})	x_f	$\Delta_{dil}H_m$/ (J mol^{-1})	$\delta\Delta_{dil}H_m$/ (J mol^{-1})
$x_i = 1.092 \times 10^{-1}$, $T = 283.15$ K^{b}					
8.897×10^{-2}	−2554	33	1.966×10^{-2}	−8172	96
7.502×10^{-2}	−4198	57	1.271×10^{-2}	−8688	112
5.714×10^{-2}	−6002	75	1.271×10^{-2}	−8655	111
4.615×10^{-2}	−6969	85	1.080×10^{-2}	−8873	113
4.615×10^{-2}	−6819	83	1.080×10^{-2}	−9099	116
3.115×10^{-2}	−7828	93	8.818×10^{-3}	−8976	114
3.115×10^{-2}	−7639	91	8.818×10^{-3}	−9203	117
1.966×10^{-2}	−8375	98	6.039×10^{-3}	−9494	132
$x_i = 1.254 \times 10^{-2}$, $T = 293.15$ K,^{b} $K_{sol} = -73.0$ kJ mol^{-1}					
1.089×10^{-2}	−66.6	3	1.461×10^{-3}	−3563	76
9.625×10^{-2}	−120	5	1.461×10^{-3}	−3513	75
8.326×10^{-2}	−315	9	1.128×10^{-3}	−4268	89
6.234×10^{-3}	−5834	17	1.128×10^{-3}	−4290	90
4.149×10^{-3}	−1279	30	9.191×10^{-4}	−4908	102
3.554×10^{-3}	−1608	38	9.191×10^{-4}	−4929	102
2.486×10^{-3}	−2270	49	5.907×10^{-4}	−6406	133
2.070×10^{-3}	−2723	60	4.002×10^{-4}	−7860	166
1.774×10^{-3}	−3061	65	1.461×10^{-3}	−3563	76
$x_i = 1.092 \times 10^{-1}$, $T = 293.15$ K,^{b} $K_{sol} = -63.9$ kJ mol^{-1}					
2.473×10^{-2}	−8001	106	1.080×10^{-2}	−9174	112
1.966×10^{-2}	−8354	99	8.818×10^{-3}	−9596	116
1.271×10^{-2}	−8980	110	6.039×10^{-3}	−9756	123
$x_i = 8.322 \times 10^{-1}$, $T = 293.15$ K,^{b} $K_{sol} = -6.10$ kJ mol^{-1}					
6.627×10^{-1}	−9297	73	2.339×10^{-1}	−43122	411
6.627×10^{-1}	−9232	72	1.634×10^{-1}	−50711	395
6.627×10^{-1}	−9314	77	1.634×10^{-1}	−51600	402
4.114×10^{-1}	−28213	220	1.634×10^{-1}	−51245	414
4.114×10^{-1}	−28235	220	1.088×10^{-1}	−57439	447
4.114×10^{-1}	−27902	225	1.088×10^{-1}	−57931	459
3.283×10^{-1}	−34988	274	1.088×10^{-1}	−57761	464
3.283×10^{-1}	−34745	272	7.407×10^{-2}	−63128	507
3.283×10^{-1}	−34618	286	7.407×10^{-2}	−62621	514
2.339×10^{-1}	−44599	348	4.401×10^{-2}	−64771	531
2.339×10^{-1}	−42855	334			
$x_i = 1.000$, $T = 293.15$ K^{a}					
8.293×10^{-1}	−6227	165	5.540×10^{-1}	−20790	482
7.240×10^{-1}	−11336	307	5.430×10^{-1}	−23320	625
5.757×10^{-1}	−20185	590			
$x_i =1.092 \times 10^{-1}$, $T = 313.15$ K,^{b} $K_{sol} = -64.2$ kJ mol^{-1}					
1.966×10^{-2}	−8455	99	1.271×10^{-2}	−9023	111
1.966×10^{-2}	−8634	92	1.271×10^{-2}	−9095	100
1.966×10^{-2}	−8700	92	1.271×10^{-2}	−9172	101
1.271×10^{-2}	−9239	113	1.080×10^{-2}	−9495	116
$x_i = 8.322 \times 10^{-1}$, $T = 313.15$ K,^{b} $K_{sol} = -6.40$ kJ mol^{-1}					
7.112×10^{-1}	−6205	78	2.340×10^{-1}	−43540	550
6.627×10^{-1}	−9230	116	1.635×10^{-1}	−51492	651
5.507×10^{-1}	−16912	214	1.635×10^{-1}	−51082	645
4.115×10^{-1}	−27416	347	1.088×10^{-1}	−57942	732
3.284×10^{-1}	−34732	439	1.088×10^{-1}	−57080	721
2.340×10^{-1}	−43315	548	4.403×10^{-2}	−64744	820
$x_i = 8.322 \times 10^{-1}$, $T = 313.15$ K,^{a} $K_{sol} = -6.40$ kJ mol^{-1}					
3.917×10^{-1}	−29515	655	7.391×10^{-2}	−61498	645
3.309×10^{-1}	−34300	630	7.194×10^{-2}	−60970	843
2.117×10^{-1}	−45613	679	3.738×10^{-2}	−64451	721
1.478×10^{-1}	−52892	707	1.394×10^{-2}	−66524	679
1.470×10^{-1}	−52888	764	8.264×10^{-3}	−67611	701
1.447×10^{-1}	−53173	795	5.731×10^{-3}	−68953	701
9.832×10^{-2}	−58433	1085	5.615×10^{-3}	−69192	719
9.530×10^{-2}	−59452	729			
$x_i = 1.000$, $T = 313.15$ K^{a}					
8.797×10^{-1}	−5001	164	5.778×10^{-1}	−20990	581
7.516×10^{-1}	−10615	266			
$x_i = 8.322 \times 10^{-1}$, $T = 333.15$ K,^{a} $K_{sol} = -6.70$ kJ mol^{-1}					
6.568×10^{-1}	−9518	302	1.157×10^{-1}	−56327	829
5.805×10^{-1}	−14666	423	7.128×10^{-2}	−62442	750
4.214×10^{-1}	−25220	688	4.184×10^{-2}	−65051	599
2.858×10^{-1}	−39324	917	1.925×10^{-2}	−66660	515
2.765×10^{-1}	−40367	940	9.737×10^{-3}	−68342	483
1.987×10^{-1}	−49094	1117	5.368×10^{-3}	−68731	464
1.695×10^{-1}	−52053	976	2.574×10^{-3}	−68700	579
1.433×10^{-1}	−54995	929			
$x_i = 1.000$, $T = 333.15$ K^{a}					
7.876×10^{-1}	−9295	218	3.610×10^{-1}	−38437	923
5.674×10^{-1}	−21620	521			

[a] Measured with Calvet calorimeter. [b] Measured with isothermal flow calorimeter.

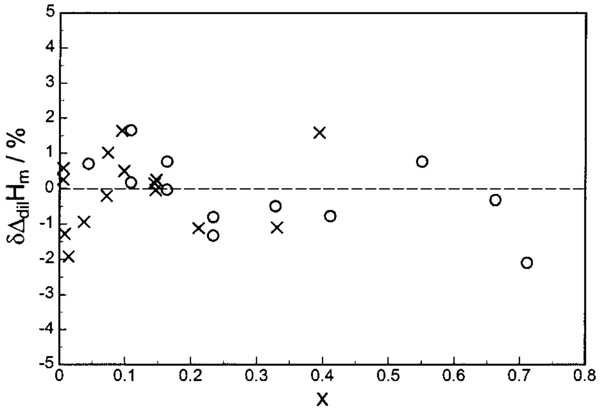

Figure 3. Deviations measured from the fitted (eq 17) enthalpies of dilution of 96.43 mass % H_2SO_4 at 313.15 K: ×, measured with a Calvet calorimeter; ○, measured with an isothermal flow calorimeter.

The uncertainty due to vaporization of the liquids, δQ^v, is calculated from eq 13. In eq 13, $\Delta_{vap}H_{m,H_2SO_4}$ and

$$\delta Q^v = -\max\left[\frac{(\delta n^v_{H_2SO_4})_f}{n_{H_2SO_4,f} - (\delta n^v_{H_2SO_4})_f}, \frac{(\delta n^v_{H_2O})_f}{n_{H_2O,f} - (\delta n^v_{H_2O})_f}\right]Q + \{(\delta n^v_{H_2SO_4})_f - (\delta n^v_{H_2SO_4})_i\}\Delta_{vap}H_{m,H_2SO_4} + \{(\delta n^v_{H_2O})_f - (\delta n^v_{H_2O})_i\}\Delta_{vap}H_{m,H_2O} \quad (13)$$

$\Delta_{vap}H_{m,H_2O}$ are molar enthalpies of vaporization of sulfuric acid and water, respectively. The maximal absolute uncertainty, δQ, is determined with eq 14.

$$\delta Q = \delta Q^{cal} + \delta Q^v \quad (14)$$

The enthalpies of dilution are determined according to the definition as

$$\Delta_{dil}H_m = Q/n_{H_2SO_4} \quad (15)$$

and the maximal absolute uncertainty, $\delta\Delta_{dil}H_m$, of the measurement is estimated from eq 16.

$$\delta\Delta_{dil}H_m = \left|\frac{1}{n_{H_2SO_4}}\delta Q\right| + \left|\frac{Q}{(n_{H_2SO_4})^2}(\delta n_{H_2SO_4})_f\right| \quad (16)$$

$\delta\Delta_{dil}H_m$ is estimated for each data point and listed in Table 2.

Because the measurement takes place at constant volume instead of constant pressure, the measured energy is actually the internal energy change of the mixing vessel, which has a constant volume. As the mixing vessel is filled at ambient temperature and pressure, the pressure of the vessel will rise with the measuring temperature, which reaches up to 333.15 K. However, the uncertainties arising from these two sources are about the order of 10^{-3} smaller than other sources of uncertainties specified above. Therefore, these sources are neglected by the estimation of $\delta\Delta_{dil}H_m$.

Enthalpies of Dilution Measurement. To be sure that both calorimeters deliver the same results, the enthalpy of dilution of 96.43 mass % H_2SO_4 was measured with the two calorimeters at 313.15 K. In Figure 3, the deviations between the measured and fitted enthalpies of dilution, $\delta\Delta_{dil}H_m$, are plotted against the mole fraction of sulfuric acid, x. The fitted function is given as eq 17. Figure 3 indicates that both calorimeters give the same result within the uncertainty of the measurement of 2%. The enthalpies

$$\Delta_{dil}H_m/(\text{J mol}^{-1}) = a_1 + a_2x + a_3x^2 \quad (17)$$

$$a_1 = -69\,463.4, \quad a_2 = 119\,363.7, \quad a_3 = -43\,032.4$$

of dilution of aqueous solutions of sulfuric acid are listed in Table 2. In the table, x_i is the mole fraction of the sulfuric acid before dilution and x_f the mole fraction after dilution. The calculated maximum uncertainty and the value of K_{sol} for each series of $\Delta_{dil}H_m$ measurements are also listed.

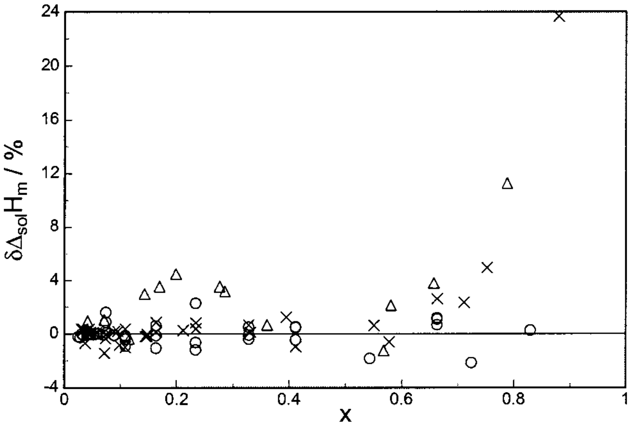

Figure 4. Deviations measured from the fitted (eq 18) enthalpies of solution of the system $xH_2SO_4 + (1 - x)H_2O$ for mole fractions of $0.024 < x < 0.83$ measured (○) at 293.15 K, (×) at 313.15 K, and (Δ) at 333.15 K.

Enthalpy of Solution and Excess Molar Enthalpy. The deviations between the measured $\Delta_{sol}H_m$ of the system $H_2SO_4 + H_2O$ at temperatures (293.15, 313.15, and 333.15) K and the fitted $\Delta_{sol}H_m$ at 293.15 K are presented in Figures 4 and 5. The fitted equations are given as eqs 18 and 19 according to the concentration range.

$$\Delta_{sol}H_m/(\text{J mol}^{-1}) = (1 - x)\{b_1 + b_2y + b_3y^2 + b_4y^3 + b_5y^4 + b_6y^5 + b_7y^6\} \quad (18)$$

$$y = 1 - 2x$$

$$b_1 = -54\,218, \quad b_2 = -24\,701, \quad b_3 = 18\,505, \quad b_4 = 12\,354, \quad b_5 = -57\,981, \quad b_6 = -25\,415, \quad b_7 = 59\,051$$

$$0.024 < x < 0.83$$

$$\Delta_{sol}H_m/(\text{J mol}^{-1}) = (1 - x)\left\{\frac{c_1}{x + c_2} + c_3\right\} \quad (19)$$

$$c_1 = -5.1823, \quad c_2 = 0.000\,299\,25, \quad c_3 = -73\,626$$

$$0.0004 < x < 0.024$$

In Figures 6 and 7, some of the literature values[1,2,4–6] are compared with the results of this work. The molar excess enthalpies of the system $H_2SO_4 + H_2O$ are calculated from $\Delta_{sol}H_m$ and listed in Table 3. The enthalpy of dilution data of Rütten et al.[8] are also included by the evaluation of H^E of the system $H_2SO_4 + H_2O$.

4. Discussion

In Figures 4 and 5, it is shown that there exists only a small temperature dependence of $\Delta_{sol}H_m$ up to the mole fraction of $x = 0.7$. However, in the high mole fractions,

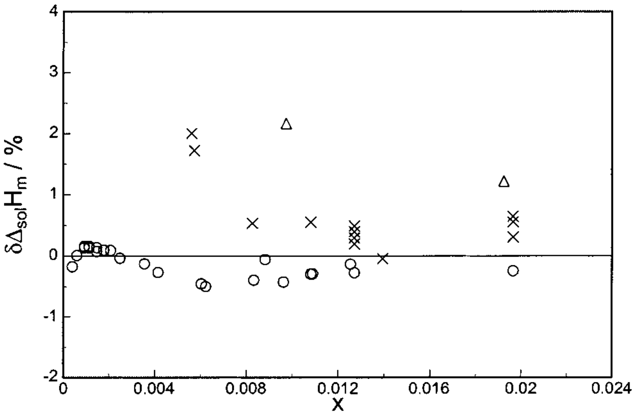

Figure 5. Deviations measured from the fitted (eq 19) enthalpies of solution of the system $xH_2SO_4 + (1 - x)H_2O$ for mole fractions of $0.0004 < x < 0.024$ measured (○) at 293.15 K, (×) at 313.15 K, and (Δ) at 333.15 K.

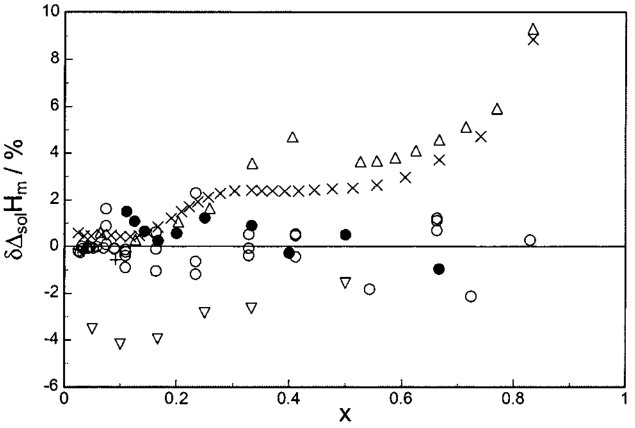

Figure 6. Deviations measured from the fitted (eq 18) enthalpies of solution of the system $xH_2SO_4 + (1 - x)H_2O$ for mole fractions of $0.024 < x < 0.83$: ○, this work at 293.15 K; ●, Favre and Quaillard;[1] ×, Giauque et al.[2] at 298.15 K; +, Becker and Roth[4] at ≈293.15 K; Δ, Brönsted;[5] ∇, Thomsen[6] at ≈293.15 K.

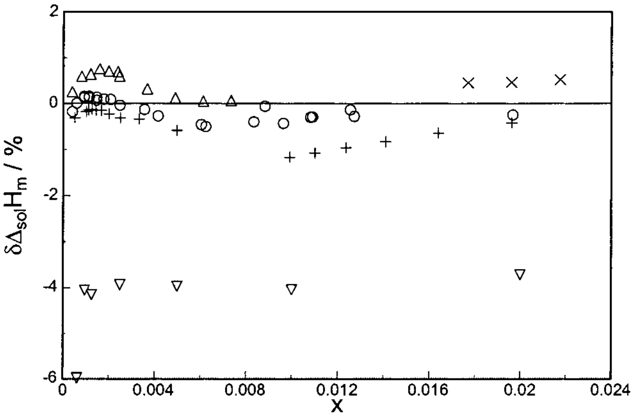

Figure 7. Deviations measured from the fitted (eq 19) enthalpies of solution of the system $xH_2SO_4 + (1 - x)H_2O$ for mole fractions of $0.0004 < x < 0.024$: ○, this work at 293.15 K; ×, Giauque et al.[2] at 298.15 K; +, Becker and Roth[4] at ≈293.15 K; Δ, Brönsted;[5] ∇, Thomsen[6] at ≈293.15 K.

especially over the azeotropic point, the temperature dependence of $\Delta_{sol}H_m$ grows very rapidly. The $\Delta_{sol}H_m$ of 333.15 K deviates 3.8% from that of 293.15 K at $x = 0.66$ but 11.3% at $x = 0.79$. This is probably the influence of the decomposition reaction of sulfuric acid as mentioned by Kunzler and Giauque.[11]

Table 3. Excess Molar Enthalpy of the System $xH_2SO_4 + (1 - x)H_2O$

x	H^E/(J mol^{-1})	x	H^E/(J mol^{-1})
	$T = 293.15$ K		
0.8294	−5164	0.0511	−3589
0.7240	−8207	0.0462	−3263
0.6626	−10203	0.0440	−3119
0.6626	−10160	0.0403	−2867
0.6626	−10214	0.0333	−2384
0.5757	−11620	0.0312	−2235
0.5540	−11518	0.0284	−2035
0.5430	−12664	0.0247	−1778
0.4113	−14112	0.0197	−1421
0.4113	−13984	0.0127	−926
0.4113	−14122	0.0109	−796
0.3283	−13408	0.0108	−789
0.3283	−13367	0.0096	−704
0.3283	−13488	0.0088	−648
0.2339	−11449	0.0083	−611
0.2339	−11511	0.0062	−459
0.2339	−11856	0.0060	−445
0.1634	−9282	0.0041	−308
0.1634	−9369	0.0036	−265
0.1634	−9437	0.0025	−187
0.1088	−6910	0.0021	−157
0.1088	−6945	0.0018	−135
0.1088	−6964	0.0015	−112
0.0890	−5909	0.0015	−112
0.0890	−5907	0.0011	−87
0.0751	−5108	0.0011	−87
0.0741	−5128	0.0009	−72
0.0741	−5091	0.0009	−72
0.0696	−4770	0.0006	−47
0.0572	−3989	0.0004	−32
	$T = 313.15$ K		
0.8797	−4400	0.0719	−4846
0.7516	−7978	0.0696	−4777
0.7110	−8963	0.0572	−3993
0.6627	−10359	0.0511	−3596
0.5778	−12128	0.0462	−3267
0.5506	−12836	0.0462	−3269
0.4114	−13913	0.0440	−3133
0.3948	−14181	0.0440	−3133
0.3309	−13468	0.0403	−2876
0.3284	−13508	0.0403	−2872
0.2340	−11633	0.0374	−2649
0.2340	−11685	0.0333	−2391
0.2117	−11011	0.0333	−2395
0.1635	−9397	0.0312	−2242
0.1635	−9464	0.0312	−2243
0.1478	−8762	0.0197	−1433
0.1470	−8717	0.0197	−1432
0.1447	−8618	0.0197	−1428
0.1088	−6908	0.0139	−1017
0.1088	−7002	0.0127	−933
0.0983	−6374	0.0127	−933
0.0953	−6274	0.0127	−931
0.0890	−5923	0.0127	−932
0.0890	−5925	0.0108	−796
0.0750	−5103	0.0083	−612
0.0750	−5103	0.0057	−432
0.0739	−5019	0.0056	−424
	$T = 333.15$ K		
0.7877	−7321	0.1987	−11088
0.6568	−10652	0.1695	−9957
0.5805	−12404	0.1433	−8841
0.5674	−12268	0.1157	−7293
0.4215	−13454	0.0713	−4927
0.3610	−13876	0.0418	−3002
0.2858	−13154	0.0193	−1413
0.2765	−13015	0.0097	−731

Figures 6 and 7 show a very interesting result. Even though the measured values coincide with one another in the low mole fractions within $\Delta_{sol}H_m$ of 1%, the measured values deviate significantly from one another in the middle and high mole fractions. Only the $\Delta_{sol}H_m$ values of Thomsen[6] deviate about 4% from that of other literature values[1,2,4,5] in the low mole fractions. Brönsted[5] supposed that the measurements of Thomsen[6] were performed with 99 mass % H_2SO_4.

The measured values of this work agree very well with that of Favre and Quaillard[1] within the uncertainty of the calorimeters of ±2%. Brönsted[5] also tried to explain the deviations of $\Delta_{sol}H_m$ of Favre and Quaillard[1] from that of his work with the accuracy of the calorimeters used. However, as shown in Figure 4, the systematic deviations of $\Delta_{sol}H_m$ of Giauque et al.[2] and Brönsted[5] from that of Favre and Quaillard[1] and this work in Figure 6 can be explained with the strong temperature dependence of $\Delta_{sol}H_m$ of the system $H_2SO_4 + H_2O$ in the high mole fractions. Favre and Quaillard[1] and Brönsted[5] did not report the temperatures of their measurements. However, according to this work, it can be expected that the measurements were made at near 293.15 K by Favre and Quaillard[1] and near 298.15 K by Brönsted.[5]

Comparison of this work with other previous measurements shows that more accurate experimental work is required on the caloric quantities of sulfuric acid in the concentration range of $0.1 < x < 1$.

To evaluate the limiting enthalpy of solution, $\Delta_{sol}H_m^{\infty}$, of sulfuric acid, the data set of Wu and Young[3] is compared with the results of this work at low concentrations. As the measurements of Wu and Young[3] are made at 298.15 K, the values of Wu and Young[3] are recalculated for 293.15 K with the apparent molar heat capacities, $C_{p,\phi}$, reported by Clegg et al.[12] The values of $C_{p,\phi}$ are assumed to be constant over the small temperature range. The evaluated $\Delta_{sol}H_m^{\infty}$ of sulfuric acid at 293.15 K, determined by the method of vertical shifting mentioned above, is -93.02 kJ mol^{-1}. This value can be compared with that of Wagman et al.[13] of -95.28 kJ mol^{-1} at 298.15 K.

When the results of this work are extrapolated with the data set of Wu and Young[3] without the correction with $C_{p,\phi}$, the value of -94.52 kJ mol^{-1} is obtained. The effect of the correction with $C_{p,\phi}$ is only 1.6% of the estimated $\Delta_{sol}H_m^{\infty}$.

Becker and Roth[4] have also estimated $\Delta_{sol}H_m^{\infty}$. Their measurements were performed at 293.15 K, but they extrapolated their data with the measurements of Lange et al.,[14] which are measured at 298.15 K. They reported a value of -94.43 kJ mol^{-1} for $\Delta_{sol}H_m^{\infty}$, which is comparable to the uncorrected value of this work of -94.52 kJ mol^{-1}.

Acknowledgment

This work was supported by the Deutsche Forschungsgemeinschaft (DFG).

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Received for review January 20, 2000. Accepted October 16, 2000.

JE0000221