



**Apparent molar heat capacities of aqueous solutions of propylamine, 1,4-butanediamine, 1,6-hexanediamine, propylamine hydrochloride, propionamide, pyridine, and sodium benzenesulfonate at temperatures from 300 K to 525 K and a pressure of 28 MPa**

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The apparent molar heat capacities of dilute aqueous solutions of propylamine, 1,4-butanediamine, 1,6-hexanediamine, propylamine hydrochloride, propionamide, pyridine, and sodium benzenesulfonate were measured at  $300\text{ K} < T < 525\text{ K}$  and  $p = 28\text{ MPa}$ . Corrections for hydrolysis or dissociation reactions and relaxation effects were applied where necessary, and the results were extrapolated to infinite dilution to obtain  $C_p^\infty$ . After subtracting the heat capacity of a point mass, the remaining heat capacity was successfully divided into functional group contributions at all temperatures. Including the results of our previous papers on alcohols and diols and carboxylic acids and sodium carboxylates, the heat capacity contributions of the  $\text{CH}_2$ ,  $\text{CH}_3$ ,  $\text{OH}$ ,  $\text{COOH}$ ,  $(\text{COOH})_2$ ,  $\text{NH}_2$ ,  $\text{CONH}_2$ ,  $\text{COONa}$ , and  $\text{NH}_3\text{Cl}$  groups are now available, and these allow reasonably accurate predictions of the heat capacities of all aqueous compounds composed of these groups in this temperature range.

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**KEYWORDS:** apparent molar heat capacity; propylamine; 1,4-butanediamine; 1,6-hexanediamine; propylamine hydrochloride; propionamide; pyridine; sodium benzenesulfonate

## 1. Introduction

The thermodynamic properties of the aqueous solutions of organic species at elevated temperatures are of key importance in the understanding of a variety of

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natural phenomena, such as the transformation of natural hydrocarbon deposits at high temperatures, or the interaction of aqueous solutions with minerals. In addition, there are many industrial processes in which the knowledge of the properties of organic species dissolved in hot water is essential; for instance, boiler water chemistry, or wet oxidation at both moderate and supercritical temperatures. Recent papers from this laboratory<sup>(1-3)</sup> reported the apparent molar volumes of a variety of organic compounds,<sup>(3)</sup> and the heat capacities of alcohols and diols<sup>(1)</sup> and carboxylic acids and sodium carboxylates<sup>(2)</sup> in water at temperatures  $T$  to 525 K, and showed that group contribution methods were applicable from  $T = 300$  K to  $T = 525$  K for both these partial molar properties. This paper concludes the series on the heat capacities of aqueous solutions of organic compounds at high temperatures. We report here the heat capacities of several amines and other organic solutes and then explore the utility of dividing these heat capacities into functional group contributions. These heat capacities allow the accurate calculation of the chemical potentials of compounds built from these groups at temperatures to 525 K from chemical potentials and entropies at  $T = 298.15$  K.

TABLE 1. Apparent molar heat capacities  $C_{p,\phi}$  of propylamine(aq).  $C_{p,\phi} = C_{p,\phi}^{\text{exp}} + \Delta C_{p,\phi}$ ;  $\alpha$  denotes the degree of hydrolysis of the amine;  $\Delta C_{p,\phi}$  is the correction to  $C_{p,\phi}^{\text{exp}}$  due to hydrolysis and chemical relaxation;  $c_{p,s}/c_{p,w}$  is the ratio of massic heat capacities of solution and water, equation (1);  $m^\circ = 1 \text{ mol}\cdot\text{kg}^{-1}$

$T$ K	$p$ MPa	$m/m^\circ$	$c_{p,s}/c_{p,w}$	$C_{p,\phi}^{\text{exp}}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$\alpha$	$\Delta C_{p,\phi}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$C_{p,\phi}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>
302.92	28.01	0.3547	1.0069	324.5	0.0415	9.7	334.2
302.92	28.01	0.3547	1.0067	322.4	0.0415	9.6	332.0
302.92	28.00	0.3547	1.0071	326.9	0.0415	9.8	336.7
302.92	28.00	0.3547	1.0072	327.8	0.0415	9.9	337.7
302.92	28.07	0.6877	1.0139	329.2	0.0307	7.2	336.4
302.92	27.89	0.6877	1.0139	329.1	0.0307	7.2	336.3
302.92	27.89	0.6877	1.0138	328.8	0.0307	7.2	336.4
374.27	27.90	0.3547	1.0072	332.4	0.0287	2.1	334.5
374.27	27.90	0.3547	1.0067	325.7	0.0287	1.9	327.6
374.27	27.96	0.3547	1.0067	325.6	0.0287	1.9	327.5
374.27	27.96	0.3547	1.0069	328.9	0.0287	2.0	330.9
374.27	27.94	0.6877	1.0124	323.6	0.0211	1.3	324.9
374.27	27.94	0.6877	1.0121	321.8	0.0211	1.3	323.1
374.27	27.96	0.6877	1.0136	331.3	0.0211	1.5	332.8
374.27	27.96	0.6877	1.0133	329.6	0.0211	1.4	331.0
448.22	28.03	0.3547	1.0067	336.0	0.0147	-1.4	334.6
448.22	28.03	0.3547	1.0068	337.5	0.0147	-1.4	336.1
448.22	28.04	0.6877	1.0115	327.6	0.0108	-1.1	326.5
448.22	28.04	0.6877	1.0124	333.7	0.0108	-1.1	332.6
448.22	28.05	0.6877	1.0115	327.6	0.0108	-1.1	326.5
448.22	28.05	0.6877	1.0118	329.6	0.0108	-1.1	328.5
523.28	28.08	0.3547	1.0080	378.3	0.0060	-1.8	376.5
523.28	28.08	0.3547	1.0084	383.6	0.0060	-1.8	381.8
523.28	28.10	0.3547	1.0077	374.9	0.0060	-1.9	373.0
523.28	28.10	0.3547	1.0084	383.7	0.0060	-1.8	381.9
523.28	28.12	0.6877	1.0139	369.6	0.0044	-1.4	368.2
523.28	28.12	0.6877	1.0137	368.0	0.0044	-1.4	366.6
523.28	28.12	0.6877	1.0131	364.1	0.0044	-1.4	362.7
523.28	28.12	0.6877	1.0135	366.7	0.0044	-1.4	365.3

TABLE 2. Apparent molar heat capacities  $C_{p,\phi}$  of 1,4-butanediamine(aq).  $C_{p,\phi} = C_{p,\phi}^{\text{exp}} + \Delta C_{p,\phi}$ ;  $\alpha_1$  and  $\alpha_2$  denote the first and the second degree of hydrolysis of the amine, respectively;  $\Delta C_{p,\phi}$  is the correction to  $C_{p,\phi}^{\text{exp}}$  due to hydrolysis and chemical relaxation;  $c_{p,s}/c_{p,w}$  is the ratio of massic heat capacities of solution and water, equation (1);  $m^\circ = 1 \text{ mol}\cdot\text{kg}^{-1}$

$T$ K	$p$ MPa	$m/m^\circ$	$c_{p,s}/c_{p,w}$	$\frac{C_{p,\phi}^{\text{exp}}}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$	$\alpha_1$	$10^5\cdot\alpha_2$	$\frac{\Delta C_{p,\phi}}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$	$\frac{C_{p,\phi}}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$
303.00	28.03	0.4155	0.9952	313.6	0.0079	140	0.5	314.1
303.00	28.03	0.4155	0.9951	311.9	0.0079	140	0.5	312.4
303.00	28.03	0.4155	0.9953	314.3	0.0079	140	0.5	314.8
303.00	28.02	0.8608	0.9932	327.5	0.0056	77	0.6	328.1
303.00	28.02	0.8608	0.9931	326.7	0.0056	77	0.6	327.3
303.00	28.04	0.8608	0.9933	327.8	0.0056	77	0.6	328.4
303.00	28.04	0.8608	0.9933	327.7	0.0056	77	0.6	328.3
374.35	27.94	0.4155	0.9991	357.2	0.0058	7	0.5	357.7
374.35	27.94	0.4155	0.9999	366.0	0.0058	7	0.5	366.5
373.92	27.87	0.4155	0.9992	358.7	0.0058	7	0.5	359.2
373.92	27.87	0.4155	0.9990	356.2	0.0058	7	0.5	356.7
374.35	27.98	0.8608	1.0009	371.3	0.0041	4	0.4	371.7
374.35	27.98	0.8608	1.0007	370.2	0.0041	4	0.4	370.6
373.92	27.91	0.8608	1.0016	375.0	0.0041	4	0.4	375.4
373.92	27.91	0.8608	1.0013	373.4	0.0041	4	0.4	373.8
373.92	27.90	0.8608	1.0005	369.3	0.0041	4	0.4	369.7
373.92	27.90	0.8608	1.0003	368.3	0.0041	4	0.4	368.7
448.23	28.04	0.4155	1.0023	402.6	0.0032	0	-0.2	402.4
448.23	28.04	0.4155	1.0020	399.5	0.0032	0	-0.2	399.3
448.23	28.04	0.4155	1.0032	412.1	0.0032	0	-0.1	412.0
448.23	28.04	0.4155	1.0032	411.5	0.0032	0	-0.1	411.4
448.23	28.05	0.8608	1.0056	407.7	0.0022	0	-0.1	407.6
448.23	28.05	0.8608	1.0054	406.5	0.0022	0	-0.1	406.4
448.23	28.06	0.8608	1.0058	408.5	0.0022	0	-0.1	408.4
448.23	28.06	0.8608	1.0061	410.1	0.0022	0	-0.1	410.0
523.38	28.04	0.4155	1.0075	493.0	0.0014	0	-0.3	492.7
523.38	28.04	0.4155	1.0068	484.8	0.0014	0	-0.3	484.5
523.38	28.07	0.8608	1.0084	454.8	0.0010	0	-0.2	454.6
523.38	28.07	0.8608	1.0090	458.7	0.0010	0	-0.2	458.5
523.38	28.07	0.8608	1.0093	460.2	0.0010	0	-0.2	460.0
523.38	28.07	0.8608	1.0096	462.3	0.0010	0	-0.2	462.1

## 2. Experimental

Two stock aqueous solutions of propylamine, 1,4-butanediamine, 1,6-hexanediamine, propylamine hydrochloride, propionamide, pyridine, and sodium benzenesulfonate were prepared by mass from the solute and water.

Propylamine (Aldrich: mass fraction >0.99) was used directly without further purification. The two stock solutions were prepared by weighing the propylamine in a sealed syringe in order to reduce the error of the mass due to the high volatility of propylamine. The sample was then carefully transferred to a bottle containing a known mass of water. The 1,4-butanediamine (Aldrich: mass fraction >0.99) and 1,6-hexanediamine (Aldrich: mass fraction >0.98) were used without further purification. In order to determine the water content in the commercial samples, they were dissolved in methanol (Fluka: mass fraction >0.998, mass fraction of water

$<5 \cdot 10^{-5}$ ) and the resulting solutions were titrated with Karl-Fisher solution. Taking into account the water present due to the methanol in the solution, the water contents of the analysed sample of 1,4-butanediamine and 1,6-hexanediamine were mass fractions  $10^{-2} \cdot (3.02 \pm 0.03)$  and  $10^{-2} \cdot (2.3 \pm 0.2)$ , respectively. The concentrations of the aqueous solutions of 1,4-butanediamine and 1,6-hexanediamine were calculated, taking into account the water content of the samples. Propylamine hydrochloride (Aldrich: mass fraction  $>0.99$ ) was further purified by crystallization from (methanol + diethylether) solution. Propionamide (Aldrich: mass fraction  $>0.97$ ) was purified before use by sublimation. About 200 g of propionamide was placed in a round-bottomed flask with a long large neck connected at the top to a vacuum pump. The sample was heated in a thermostat at a temperature of 333 K. After 24 h, about 80 per cent of the original sample had sublimed on the surface of the upper neck. The sublimed sample was collected and used to prepare aqueous solutions. Pyridine (Fluka: mass fraction  $>0.998$ ) was used without further purification. Sodium benzenesulfonate solutions were

TABLE 3. Apparent molar heat capacities  $C_{p,\phi}^{\text{app}}$  of 1,6-hexanediamine(aq).  $C_{p,\phi} = C_{p,\phi}^{\text{exp}} + \Delta C_{p,\phi}$ ;  $\alpha_1$  and  $\alpha_2$  denote the first and the second degree of hydrolysis of the amine, respectively;  $\Delta C_{p,\phi}$  is the correction to  $C_{p,\phi}^{\text{exp}}$  due to hydrolysis and chemical relaxation;  $c_{p,s}/c_{p,w}$  is the ratio of massic heat capacities of solution and water, equation (1);  $m^\circ = 1 \text{ mol} \cdot \text{kg}^{-1}$

$\frac{T}{\text{K}}$	$\frac{p}{\text{MPa}}$	$m/m^\circ$	$c_{p,s}/c_{p,w}$	$\frac{C_{p,\phi}^{\text{exp}}}{\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}$	$\alpha_1$	$10^5 \cdot \alpha_2$	$\frac{\Delta C_{p,\phi}}{\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}$	$\frac{C_{p,\phi}}{\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}$
303.00	28.02	0.3610	1.0004	482.3	0.0177	33	5.0	487.3
303.00	27.98	0.3610	1.0006	485.2	0.0177	33	5.0	490.2
303.00	27.98	0.3610	1.0006	484.8	0.0177	33	5.0	489.8
303.00	28.03	0.6372	1.0006	481.9	0.0135	21	3.7	485.6
303.00	28.03	0.6372	1.0008	483.3	0.0135	21	3.7	487.0
303.00	28.02	0.6372	0.9997	475.6	0.0135	21	3.6	479.2
373.78	27.97	0.3610	1.0002	485.3	0.0122	16	0.6	485.9
373.78	27.97	0.3610	1.0005	489.2	0.0122	16	0.6	489.8
373.78	27.95	0.3610	1.0003	487.2	0.0122	16	0.6	487.8
373.78	27.95	0.3610	1.0002	485.6	0.0122	16	0.6	486.2
374.28	28.21	0.3610	1.0009	494.0	0.0122	16	0.7	494.7
374.28	28.21	0.3610	1.0010	495.5	0.0122	16	0.7	496.2
373.78	28.16	0.6372	1.0000	483.2	0.0092	10	0.4	483.6
373.78	28.16	0.6372	1.0004	486.3	0.0092	10	0.5	486.8
373.78	28.10	0.6372	0.9994	478.9	0.0092	10	0.4	479.3
374.35	28.00	0.6372	0.9997	481.2	0.0092	10	0.4	481.6
374.35	28.00	0.6372	1.0001	484.1	0.0092	10	0.4	484.5
448.23	28.06	0.3610	1.0020	522.2	0.0061	4	-0.8	521.4
448.23	28.06	0.3610	1.0017	519.2	0.0061	4	-0.8	518.4
448.23	28.04	0.3610	1.0024	527.4	0.0061	4	-0.8	526.6
448.23	28.04	0.3610	1.0022	524.4	0.0061	4	-0.8	523.6
448.23	28.02	0.6372	1.0032	520.7	0.0047	3	-0.6	520.1
448.23	28.02	0.6372	1.0035	522.8	0.0047	3	-0.6	522.2
448.23	28.04	0.6372	1.0034	522.6	0.0047	3	-0.6	522.0
448.23	28.04	0.6372	1.0032	520.4	0.0047	3	-0.6	519.8
523.38	28.04	0.3610	1.0046	597.9	0.0025	1	-0.9	597.0
523.38	28.04	0.3610	1.0058	613.3	0.0025	1	-0.9	612.4
523.38	28.05	0.6372	1.0060	583.0	0.0019	0	-0.6	582.4
523.38	28.05	0.6372	1.0063	585.0	0.0019	0	-0.6	584.4

TABLE 4. Apparent molar heat capacities  $C_{p,\phi}^{\text{exp}}$  of propylamine hydrochloride(aq).  $C_{p,\phi} = C_{p,\phi}^{\text{exp}} + \Delta C_{p,\phi}$ ;  $\alpha$  denotes the degree of dissociation of the propylammonium ion;  $\Delta C_{p,\phi}$  is the correction to  $C_{p,\phi}^{\text{exp}}$  due to dissociation and chemical relaxation;  $c_{p,s}/c_{p,w}$  is the ratio of massic heat capacities of solution and water, equation (1);  $m^\circ = 1 \text{ mol}\cdot\text{kg}^{-1}$

$T$ K	$p$ MPa	$m/m^\circ$	$c_{p,s}/c_{p,w}$	$\frac{C_{p,\phi}^{\text{exp}}}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$	$\alpha$	$\frac{\Delta C_{p,\phi}}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$	$\frac{C_{p,\phi}}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$
302.99	28.13	0.3881	0.9833	209.2	0.0006	0	209.2
302.99	28.13	0.3881	0.9829	205.1	0.0006	0	205.1
302.99	28.14	0.3881	0.9829	205.0	0.0006	0	205.0
302.99	28.14	0.3881	0.9827	202.3	0.0006	0	202.3
302.99	28.10	0.6876	0.9711	208.7	0.0003	0	208.7
302.99	28.10	0.6876	0.9716	212.0	0.0003	0	212.0
302.99	28.04	0.6876	0.9711	208.7	0.0003	0	208.7
302.99	28.04	0.6876	0.9719	213.6	0.0003	0	213.6
373.84	28.20	0.3881	0.9817	193.7	0.0006	0	193.7
373.84	28.20	0.3881	0.9824	201.7	0.0006	0	201.7
374.36	28.02	0.3881	0.9825	202.9	0.0006	0	202.9
374.36	28.02	0.3881	0.9821	198.4	0.0006	0	198.4
374.36	27.99	0.6876	0.9708	209.2	0.0003	0	209.2
374.36	27.99	0.6876	0.9703	205.8	0.0003	0	205.8
373.79	27.87	0.6876	0.9716	214.3	0.0003	0	214.3
373.79	27.87	0.6876	0.9719	216.3	0.0003	0	216.3
373.84	27.92	0.6876	0.9704	206.8	0.0003	0	206.8
373.84	27.92	0.6876	0.9702	205.5	0.0003	0	205.5
448.23	28.03	0.3881	0.9789	167.7	0.0007	-0.2	167.5
448.23	28.03	0.3881	0.9784	162.5	0.0007	-0.2	162.3
448.23	28.04	0.3881	0.9776	153.1	0.0007	-0.2	152.9
448.23	28.04	0.3881	0.9774	150.7	0.0007	-0.2	150.5
448.23	28.04	0.6876	0.9653	178.7	0.0004	-0.2	178.5
448.23	28.04	0.6876	0.9650	177.3	0.0004	-0.2	177.1
448.23	28.04	0.6876	0.9646	174.5	0.0004	-0.2	174.3
448.23	28.04	0.6876	0.9648	175.6	0.0004	-0.2	175.4
523.37	28.00	0.3881	0.9710	83.7	0.0014	-1.2	82.5
523.37	28.00	0.3881	0.9705	77.8	0.0014	-1.2	76.6
523.30	28.05	0.3881	0.9686	53.7	0.0014	-1.2	52.5
523.30	28.05	0.3881	0.9694	63.7	0.0014	-1.2	62.5
523.37	28.00	0.6876	0.9521	98.7	0.0011	-0.8	97.9
523.37	28.00	0.6876	0.9527	102.5	0.0011	-0.8	101.7
523.30	28.05	0.6876	0.9511	91.1	0.0011	-0.8	90.3
523.30	28.05	0.6876	0.9501	84.2	0.0011	-0.8	83.4

prepared using a sample (Fluka: mass fraction  $>0.99$ ) dried for 4 d in a vacuum oven at  $T = 323$  K.

The instrument and the experimental procedure used to measure the heat capacities of solutions have been described in detail by Carter and Wood,<sup>(4)</sup> with some modifications due to Sharygin.<sup>(5)</sup> The apparent molar heat capacities  $C_{p,\phi}^{\text{exp}}$  were calculated from:

$$C_{p,\phi}^{\text{exp}} = c_{p,w} \cdot \{(M + 1/m) \cdot (c_{p,s}/c_{p,w}) - 1/m\}, \quad (1)$$

where  $c_{p,s}$  and  $c_{p,w}$  are the massic heat capacities of solution and water, respectively;  $M$  is the molar mass of solute; and  $m$  is the molality of the solution. The ratio of

massic heat capacities  $c_{p,s}/c_{p,w}$  is related to the ratio of powers in the heater by the relation:

$$c_{p,s}/c_{p,w} = (\rho_w/\rho_s)_{\text{TSL}} \cdot \{1 + f \cdot (p_s - p_w)/p_w\}, \quad (2)$$

where  $(\rho_w/\rho_s)_{\text{TSL}}$  is the ratio of densities of water and solution at the temperature and pressure of the sample loop;  $f$  is the calibration factor for heat loss; and  $p_s$  and  $p_w$  are the powers that keep the temperature rise  $\Delta T_{\text{exp}}$  constant when water is replaced by the solution in the sample cell. The value of  $p_s$  that gives the same  $\Delta T_{\text{exp}}$  was found by calculation from a power that gave the same  $\Delta T_{\text{exp}}$  and the measured sensitivity of  $\Delta T$  to small changes in power.

The calibration factor for heat loss  $f$  {equation (2)} was determined by changing (with an auxiliary ISCO pump) the base flow rate in the sample cell in order to mimic a change in heat capacity. The resulting values of  $f$  for the present experiments have

TABLE 5. Apparent molar heat capacities  $C_{p,\phi} = C_{p,\phi}^{\text{exp}}$  of propionamide(aq).  $c_{p,s}/c_{p,w}$  is the ratio of massic heat capacities of solution and water, equation (1);  $m^\circ = 1 \text{ mol}\cdot\text{kg}^{-1}$

$T$ K	$p$ MPa	$m/m^\circ$	$c_{p,s}/c_{p,w}$	$C_{p,\phi}^{\text{exp}}$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
302.92	28.05	0.4000	0.9955	252.8
302.92	28.05	0.4000	0.9957	254.6
302.99	27.89	0.4000	0.9958	255.6
302.99	27.89	0.4000	0.9959	256.6
302.99	27.95	0.4000	0.9954	251.9
302.99	27.95	0.4000	0.9960	258.2
302.99	27.97	0.7808	0.9916	253.7
302.99	27.97	0.7808	0.9922	256.7
302.99	27.98	0.7808	0.9917	254.2
302.99	27.98	0.7808	0.9918	254.6
374.36	27.92	0.4000	0.9961	261.8
374.36	27.98	0.4000	0.9964	265.0
374.36	27.98	0.4000	0.9959	259.9
374.36	27.98	0.7808	0.9924	261.3
374.36	27.98	0.7808	0.9916	256.4
374.36	28.00	0.7808	0.9937	268.7
374.36	28.00	0.7808	0.9931	264.9
448.23	28.04	0.4000	0.9970	279.6
448.23	28.04	0.4000	0.9971	281.2
448.23	28.04	0.4000	0.9972	282.5
448.23	28.04	0.4000	0.9972	281.9
448.23	28.03	0.7808	0.9943	279.9
448.23	28.03	0.7808	0.9940	278.3
448.23	28.04	0.7808	0.9937	276.5
448.23	28.04	0.7808	0.9942	279.7
523.28	28.06	0.4000	0.9964	294.4
523.28	28.06	0.4000	0.9964	294.1
523.38	28.01	0.4000	0.9968	299.0
523.38	28.01	0.4000	0.9969	300.9
523.28	28.06	0.7808	0.9934	296.2
523.28	28.06	0.7808	0.9931	294.3
523.38	28.02	0.7808	0.9930	293.3
523.38	28.02	0.7808	0.9935	296.4

TABLE 6. Apparent molar heat capacities  $C_{p,\phi} = C_{p,\phi}^{\text{exp}}$  of pyridine(aq).  $c_{p,s}/c_{p,w}$  is the ratio of massic heat capacities of solution and water, equation (1);  $m^\circ = 1 \text{ mol}\cdot\text{kg}^{-1}$

$\frac{T}{\text{K}}$	$\frac{p}{\text{MPa}}$	$m/m^\circ$	$c_{p,s}/c_{p,w}$	$\frac{C_{p,\phi}^{\text{exp}}}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$
302.99	28.06	0.3965	0.9964	287.2
302.99	28.06	0.3965	0.9968	290.5
302.99	28.06	0.3965	0.9962	284.2
302.99	28.06	0.3965	0.9965	287.4
302.99	28.05	0.9269	0.9881	268.3
302.99	28.05	0.9269	0.9880	268.2
303.08	28.15	0.9269	0.9876	266.2
303.08	28.15	0.9269	0.9873	264.5
374.36	27.95	0.3965	0.9961	286.9
374.36	27.95	0.3965	0.9958	283.4
374.36	27.95	0.3965	0.9959	284.5
374.36	27.94	0.9269	0.9905	283.3
374.36	27.94	0.9269	0.9895	278.6
448.26	28.01	0.3965	0.9953	286.9
448.26	28.01	0.3965	0.9958	291.5
448.26	28.01	0.9269	0.9900	289.5
448.26	28.01	0.9269	0.9906	292.2
448.26	28.02	0.9269	0.9899	288.8
448.26	28.02	0.9269	0.9899	288.7
523.28	28.06	0.3965	0.9968	326.8
523.28	28.06	0.3965	0.9969	327.7
523.28	28.07	0.9269	0.9932	328.5
523.28	28.07	0.9269	0.9927	325.7

been reported by Inglese and Wood.<sup>(1)</sup> The temperature rise of the liquid in the sample cell  $\Delta T_{\text{exp}}$  was determined by measuring the temperatures after the sample cell heater, before and after turning on the heater. The temperature reported is  $T(\text{block}) + (1/2)\cdot\Delta T_{\text{exp}}$ .

The ratio of densities, at the temperature and pressure of the sample loop,  $(\rho_w/\rho_s)_{\text{TSL}}$ , was calculated for all solutes included in this study from the apparent molar volumes  $V_\phi$  determined by Criss and Wood<sup>(3)</sup> at  $m \approx 0.1 \text{ mol}\cdot\text{kg}^{-1}$ , by means of the equation:

$$(\rho_w/\rho_s)_{\text{TSL}} = (1 + m\cdot\rho_w\cdot V_\phi)/(1 + m\cdot M), \quad (3)$$

where  $M$  is the molar mass of the solute. Here,  $V_\phi$  was assumed constant in the investigated range of molalities for the purpose of this calculation. The obtained ratios of densities  $(\rho_w/\rho_s)_{\text{TSL}}$  at  $T = 298.15$  K and  $p = 28$  MPa for propylamine are 1.0046 ( $m = 0.3547 \text{ mol}\cdot\text{kg}^{-1}$ ) and 1.0089 ( $m = 0.6877 \text{ mol}\cdot\text{kg}^{-1}$ ); for 1,4-butanediamine, 1.0022 ( $m = 0.4155 \text{ mol}\cdot\text{kg}^{-1}$ ) and 1.0044 ( $m = 0.8608 \text{ mol}\cdot\text{kg}^{-1}$ ); for 1,6-hexanediamine, 1.0030 ( $m = 0.3610 \text{ mol}\cdot\text{kg}^{-1}$ ) and 1.0052 ( $m = 0.6372 \text{ mol}\cdot\text{kg}^{-1}$ ); for propylamine hydrochloride, 0.9975 ( $m = 0.3881 \text{ mol}\cdot\text{kg}^{-1}$ ) and 0.9958 ( $m = 0.6876 \text{ mol}\cdot\text{kg}^{-1}$ ); for propionamide, 0.9995 ( $m = 0.4000 \text{ mol}\cdot\text{kg}^{-1}$ ) and 0.9991 ( $m = 0.7808 \text{ mol}\cdot\text{kg}^{-1}$ ); for pyridine, 0.9994 ( $m = 0.3965 \text{ mol}\cdot\text{kg}^{-1}$ ) and 0.9988 ( $m = 0.9269 \text{ mol}\cdot\text{kg}^{-1}$ ); and for sodium benzenesulfonate, 0.9791 ( $m = 0.2957 \text{ mol}\cdot\text{kg}^{-1}$ ) and 0.9556 ( $m = 0.6684 \text{ mol}\cdot\text{kg}^{-1}$ ).

TABLE 7. Apparent molar heat capacities  $C_{p,\phi}^{\text{exp}} = C_{p,\phi}^{\text{exp}}$  of sodium benzenesulfonate(aq).  $c_{p,s}/c_{p,w}$  is the ratio of massic heat capacities of solution and water, equation (1);  $m^\circ = 1 \text{ mol}\cdot\text{kg}^{-1}$

$\frac{T}{\text{K}}$	$\frac{p}{\text{MPa}}$	$m/m^\circ$	$c_{p,s}/c_{p,w}$	$\frac{C_{p,\phi}^{\text{exp}}}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$
303.02	28.06	0.2957	0.9686	280.3
303.02	28.06	0.2957	0.9680	271.9
303.02	28.06	0.2957	0.9684	278.6
303.02	28.06	0.2957	0.9691	287.7
303.02	28.05	0.6684	0.9343	288.0
303.02	28.05	0.6684	0.9340	286.1
303.02	28.05	0.6684	0.9341	286.7
303.02	28.05	0.6684	0.9336	283.0
373.83	27.97	0.2957	0.9682	277.5
373.83	27.97	0.2957	0.9680	275.9
373.83	27.96	0.2957	0.9679	273.9
373.83	27.96	0.2957	0.9679	274.3
373.83	27.98	0.6684	0.9321	275.8
373.83	27.98	0.6684	0.9329	281.2
373.83	28.02	0.6684	0.9320	275.0
373.83	28.02	0.6684	0.9324	278.1
448.27	28.00	0.2957	0.9636	216.7
448.27	28.00	0.2957	0.9640	221.6
448.27	28.00	0.2957	0.9638	219.7
448.27	28.00	0.2957	0.9642	226.2
448.27	28.02	0.6684	0.9247	231.2
448.27	28.02	0.6684	0.9250	233.0
448.27	28.02	0.6684	0.9251	233.8
448.27	28.02	0.6684	0.9255	237.0
448.27	28.02	0.6684	0.9255	236.6
523.99	28.04	0.2957	0.9542	78.8
523.99	28.04	0.2957	0.9540	75.1
523.99	28.03	0.2957	0.9534	66.2
523.99	28.03	0.2957	0.9547	86.6
523.99	28.02	0.6684	0.9084	122.5
523.99	28.02	0.6684	0.9069	111.6
523.99	28.03	0.6684	0.9074	115.5
523.99	28.03	0.6684	0.9073	114.1

Although assuming  $V_\phi$  is not dependent on molality could cause a small error at higher molalities (perhaps  $6 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  at  $m = 0.7 \text{ mol}\cdot\text{kg}^{-1}$ , as estimated from the molality dependence of alcohols), the error is proportional to the molality, so it will not result in appreciable error in the extrapolated value of  $C_{p,2}^\circ$ .

At each temperature the calorimeter was tested by measuring the heat capacity of NaCl(aq) at  $m = 3.0007 \text{ mol}\cdot\text{kg}^{-1}$ . The experimental results obtained for this solution were in satisfactory agreement with the earlier measurements<sup>(1)</sup> and the literature results.<sup>(6)</sup>

### 3. Results

The ratio of specific heat capacities  $c_{p,s}/c_{p,w}$ , from equation (2), and the experimental apparent molar heat capacities  $C_{p,\phi}^{\text{exp}}$ , see equation (1), at constant pressure for



TABLE 8. Standard apparent molar heat capacities  $C_{p,2}^\infty$  of propylamine, 1,4-butanediamine, and 1,6-hexanediamine in aqueous solutions, where  $b$  is defined in equation (4), and  $\Delta$  is the difference between experimental  $C_{p,2}^\infty$  and that calculated from the functional group additivity scheme, equation (8)

$\frac{T}{\text{K}}$	$\frac{p}{\text{MPa}}$	$\frac{C_{p,2}^\infty}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$	$b$	$\frac{\Delta}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$
propylamine				
302.99	28.00	$334 \pm 7^a$	3	0
374.27	27.94	$332 \pm 12$	-7	-7
448.22	28.04	$343 \pm 12$	-21	-4
523.28	28.10	$392 \pm 10$	-38	10
1,4-butanediamine				
303.00	28.03	$300 \pm 3$	32	1
374.00	27.91	$349 \pm 9$	26	-5
448.23	28.05	$404 \pm 13$	4	-2
523.38	28.06	$516 \pm 17$	-67	-21
1,6-hexanediamine				
303.00	28.01	$496 \pm 14$	-19	-11
373.85	28.09	$499 \pm 10$	-25	-4
448.23	28.04	$524 \pm 9$	-5	9
523.38	28.04	$632 \pm 63$	-77	6

<sup>a</sup> The uncertainties are estimated 95 per cent confidence limits of  $C_{p,2}^\infty$  from the fit.

aqueous solutions of propylamine, 1,4-butanediamine, 1,6-hexanediamine, propylamine hydrochloride, propionamide, pyridine, and sodium benzenesulfonate are given in tables 1 to 7, respectively. Results obtained when the calorimeter occasionally exhibited a noisy baseline are not reported. Values of  $C_{p,\phi}^{\text{exp}}$  were calculated using initial and final baselines, and both are reported in tables 1 to 7. When the baseline shift was high ( $\geq 12 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  for a  $m = 0.4 \text{ mol}\cdot\text{kg}^{-1}$  solution), only values that agreed with the other measurements were reported.

Because the hydrolysis of the amines and dissociation of the propylammonium ion might make appreciable contributions to  $C_{p,\phi}^{\text{exp}}$  under the conditions of our measurements, we applied corrections due to these reactions and also due to the chemical relaxation effect.<sup>(7)</sup> Because of a lack of the data required for calculations, we could not make the corrections for sodium benzenesulfonate. Calculated corrections  $\Delta C_{p,\phi}$ , the degree of hydrolysis or dissociation  $\alpha$ , and the final corrected apparent molar heat capacity  $C_{p,\phi} = C_{p,\phi}^{\text{exp}} - \Delta C_{p,\phi}$  are reported in tables 1 to 4. The method of calculating the corrections was described in detail in the previous paper.<sup>(2)</sup> The data used to calculate the heat capacities of ions at infinite dilution at  $p = 28 \text{ MPa}$  were those of Sharygin<sup>(8)</sup> for HCl, Archer<sup>(6)</sup> for NaCl, and Simonson<sup>(9)</sup> for NaOH (corrected from the pressure  $p = 7 \text{ MPa}$ ). Reaction properties for all hydrolysis or dissociation reactions at standard temperature and pressure were calculated from the volumetric data of Høiland<sup>(10)</sup> ( $\Delta_r V_m^\infty$ ), from Robinson and Stokes<sup>(11)</sup> ( $\Delta_r H_m^\infty$  and  $\ln K$ ), and from Oloffson and Hepler<sup>(12)</sup> ( $\Delta_r H_m^\infty$  and  $\ln K$  for water dissociation). The corrections were never much larger than the estimated

TABLE 9. Standard apparent molar heat capacities  $C_{p,2}^\infty$  of propionamide, pyridine, propylamine hydrochloride, and sodium benzenesulfonate in aqueous solutions, where  $b$  is defined in equation (4), and  $\Delta$  is the difference between the experimental  $C_{p,2}^\infty$  and that calculated from the functional group additivity scheme, equation (8)

$\frac{T}{\text{K}}$	$\frac{p}{\text{MPa}}$	$\frac{C_{p,2}^\infty}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$	$b$	$\frac{\Delta}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$
propionamide				
302.98	27.95	255 $\pm$ 5 <sup>a</sup>	0	0
374.36	27.98	262 $\pm$ 15	1	7
448.23	28.04	284 $\pm$ 5	-7	-1
523.33	28.04	299 $\pm$ 8	-5	0
pyridine				
303.01	28.07	303 $\pm$ 6	-39	0
374.36	27.95	288 $\pm$ 9	-8	0
448.26	28.01	289 $\pm$ 8	1	0
523.28	28.06	327 $\pm$ 9	0	0
propylamine hydrochloride				
302.99	28.11	192 $\pm$ 3		0
373.79	27.99	176 $\pm$ 4		0
448.23	28.04	110 $\pm$ 11 <sup>b</sup>		-1
523.32	28.03	-71 $\pm$ 20 <sup>b</sup>		1
sodium benzenesulfonate				
303.02	28.06	267 $\pm$ 4		0
373.83	27.98	249 $\pm$ 4		1
448.27	28.01	174 $\pm$ 8 <sup>b</sup>		-2
523.99	28.03	-47 $\pm$ 16 <sup>b</sup>		1

<sup>a</sup> The uncertainties are estimated 95 per cent confidence limits of  $C_{p,2}^\infty$  from the fit.

<sup>b</sup> Due to the neglect of the second virial coefficient in the extrapolation, extra uncertainties ( $\pm 5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  at  $T = 448 \text{ K}$  and  $\pm 10 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  at  $T = 523 \text{ K}$ ) were added to the 95 per cent confidence limits.

experimental uncertainties; the largest corrections are 3 per cent at  $T = 303 \text{ K}$  (propylamine), and 1 per cent at  $T = 523 \text{ K}$  (propylamine hydrochloride).

The resulting apparent molar heat capacities for the amines were fitted with the equation:

$$C_{p,\phi} = C_{p,2}^\infty + b \cdot (1 - \alpha) \cdot (m/m^\circ), \quad (4)$$

with  $m^\circ = 1 \text{ mol}\cdot\text{kg}^{-1}$ , to obtain the values of the partial molar heat capacity at infinite dilution  $C_{p,2}^\infty$ , its estimated uncertainty, and the slope  $b$  (see table 8). The Pitzer ion-interaction treatment<sup>(13)</sup> with  $\beta_C^{(1)} = 0$  was used for the extrapolation of the heat capacities of propylamine hydrochloride and sodium benzenesulfonate:

$$C_{p,\phi} = C_{p,2}^\infty + (A_c/1.2) \cdot \ln\{1 + 1.2 \cdot (I/I^\circ)^{1/2}\} + 2RT \cdot \beta_C^{(0)} \cdot (1 - \alpha) \cdot (m/m^\circ), \quad (5)$$

where  $I = 1/2 \cdot \sum_i m_i \cdot z_i^2$  is the ionic strength ( $m_i$  and  $z_i$  are the actual molality and charge of ion  $i$ , respectively),  $A_c$  is the Debye-Hückel limiting slope (calculated here from Archer and Wang,<sup>(14)</sup> with properties of water given by Hill's<sup>(15)</sup> equation of state), and  $\beta_C^{(0)}$  is a constant. We have found previously<sup>(2)</sup> that the estimated

95 per cent confidence limits of  $\beta_C^{(0)}$  were always higher for the carboxylates than the value itself and the fits were almost undistinguishable with or without this parameter. The same was found for both salts included in this study; so  $\beta_C^{(0)} = 0$  was used in all extrapolations. The resulting  $C_{p,2}^\infty$  of propylamine hydrochloride and sodium benzenesulfonate and their estimated uncertainties are given in table 9. In the same table, the values of  $C_{p,2}^\infty$  for propionamide and pyridine may be found, for which the linear extrapolation, equation (4) with  $\alpha = 0$ , was used.

It has been shown in previous papers from this laboratory<sup>(1-3)</sup> that functional group methods work quite well for  $V_2^\infty$  and  $C_{p,2}^\infty$  at temperatures to 525 K. The functional group equation is:

$$C_{p,2}^\infty = v \cdot C_{p,\phi}(\text{std. state}) + \sum_j n_j \cdot C_j, \quad (6)$$

where  $v$  is the number of particles (1 for a non-electrolyte, 2 for a 1-1 electrolyte);  $C_{p,\phi}(\text{std. state})$  is the standard state heat capacity of a single particle; and  $C_j$  is the contribution to the heat capacity of the functional group  $j$ . The standard state heat capacity is the partial molar heat capacity produced by adding a point mass to a mass of 1 kg of solution at constant pressure.<sup>(16-18)</sup>

$$C_{p,\phi}(\text{std. state}) = 2 \cdot R \cdot T \cdot \alpha_w + R \cdot T^2 \cdot (\partial \alpha_w / \partial T)_p + (3/2) \cdot R, \quad (7)$$

where  $\alpha_w = (1/V_m) \cdot (\partial V_m / \partial T)_p$  for pure water. For convenience in calculating  $C_{p,\phi}(\text{std. state})$ , a table of  $\alpha_w$  values at  $p = 28$  MPa and  $300 \text{ K} < T < 525 \text{ K}$  is given by Ingles and Wood.<sup>(1)</sup> The form used for prediction of the temperature dependence of  $C_{p,2}^\infty$  was that introduced in a previous paper:<sup>(2)</sup>

$$C_{p,2}^\infty = C_{p,\phi}(\text{std. state}) + \sum_j n_j \cdot [a_j + b_j(T/\text{K}) + c_j / \{(T/\text{K}) - 800\}^2]. \quad (8)$$

Table 10 gives the functional group parameters resulting from a weighted least-squares fit of equation (8) to the calculated values of  $C_{p,2}^\infty$  from tables 8 and 9 (amines, propylamine hydrochloride, and propionamide) and from the previous

TABLE 10. Functional group parameters in equation (8)

Group $j$	$\frac{a_j}{\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}$	$\frac{b_j}{\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}$	$\frac{10^6 \cdot c_j}{\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}$
CH <sub>2</sub>	176.1	-0.369485	6.799465
CH <sub>3</sub>	331.1	-0.675805	11.621420
CONH <sub>2</sub>	-333.7	1.314136	-23.372452
COOH	-293.7	1.143762	-19.799139
(COOH) <sub>2</sub>	-292.2	1.396351	-24.249007
COONa	-448.2	2.232400	-86.467846
NH <sub>2</sub>	-288.3	0.936719	-9.370724
NH <sub>3</sub> Cl	-568.8	2.309475	-82.830479
OH	-202.4	0.801496	-14.341117
BzSO <sub>3</sub> Na	173.7	1.077675	-67.363069
Pyridine	378.7	-0.457771	10.599880

papers<sup>(1,2)</sup> (alcohols, diols, carboxylic acids, and carboxylates). The weights were  $(1/\sigma)^2$ , where  $\sigma$  is the estimated standard deviation of  $C_{p,2}^\infty$  from extrapolation. Because of a lack of data for related compounds, pyridine and sodium benzenesulfonate were evaluated separately, *i.e.*, one compound as one group. In the main fit, the average  $[\{C_{p,2}^\infty(\text{exp}) - C_{p,2}^\infty(\text{calc})\}/\sigma]$  was 0.78, and the maximum was 2.5. The average relative error was 2.0 per cent, which was mainly due to the high relative error in the sodium acetate measurement<sup>(2)</sup> at  $T = 448$  K. The reason for separate evaluation of the  $(\text{COOH})_2$  group and the evidence of steric, or near-neighbor effects, or both, were already discussed.<sup>(2)</sup> For diamines included in this work, these effects were found to be much less than the experimental uncertainties; the same holds true for diols reported in the previous paper.<sup>(1)</sup>

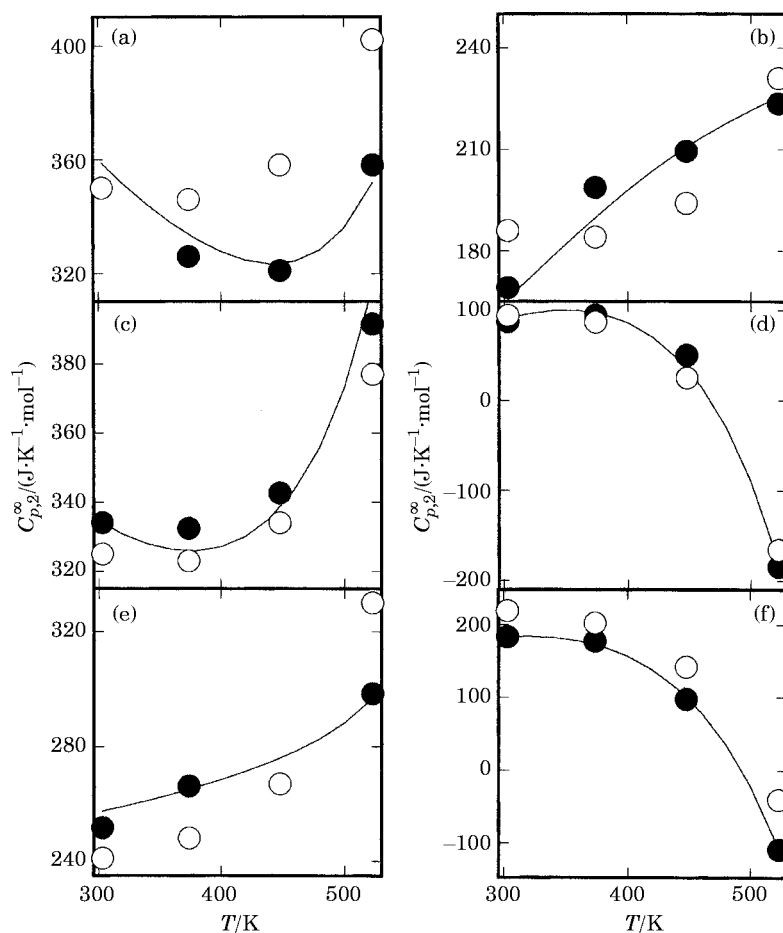


FIGURE 1. Comparison of  $C_{p,2}^\infty$  predictions with experimental data: ●, experimental results; ○, HKF equation of state;<sup>(21)</sup> —, predictions of the group contribution method, equation (8). (a), 1-propanol; (b), acetic acid; (c), propylamine; (d), sodium acetate; (e), propanoic acid; (f), sodium propanoate.

There are no direct experimental results at  $p = 28$  MPa with which to compare the measurements published in this series of papers. On the other hand, there are systematic predictions of the standard-state partial molar properties at elevated temperatures and pressures, based on the revised Helgeson–Kirkham–Flowers equation of state (Tanger and Helgeson,<sup>(19)</sup> Shock *et al.*<sup>(20)</sup>). Among almost 300 organic and inorganic species included in the SUPCRT92 software package,<sup>(21)</sup> six match our compounds: 1-propanol, propylamine, propanoic acid, acetic acid, sodium acetate, and sodium propanoate. The comparison, as summarized in figure 1, shows that the predictions are excellent, considering the narrow range of temperatures on which they were usually based.

Figure 2 displays the group contributions  $C_j$ , see equation (8), now available as a function of temperature for all functional groups, including three new ones ( $\text{CONH}_2$ ,  $\text{NH}_2$ , and  $\text{NH}_3\text{Cl}$ ). The new curves for  $\text{CH}_2$ ,  $\text{CH}_3$ ,  $\text{COOH}$ ,  $(\text{COOH})_2$ ,

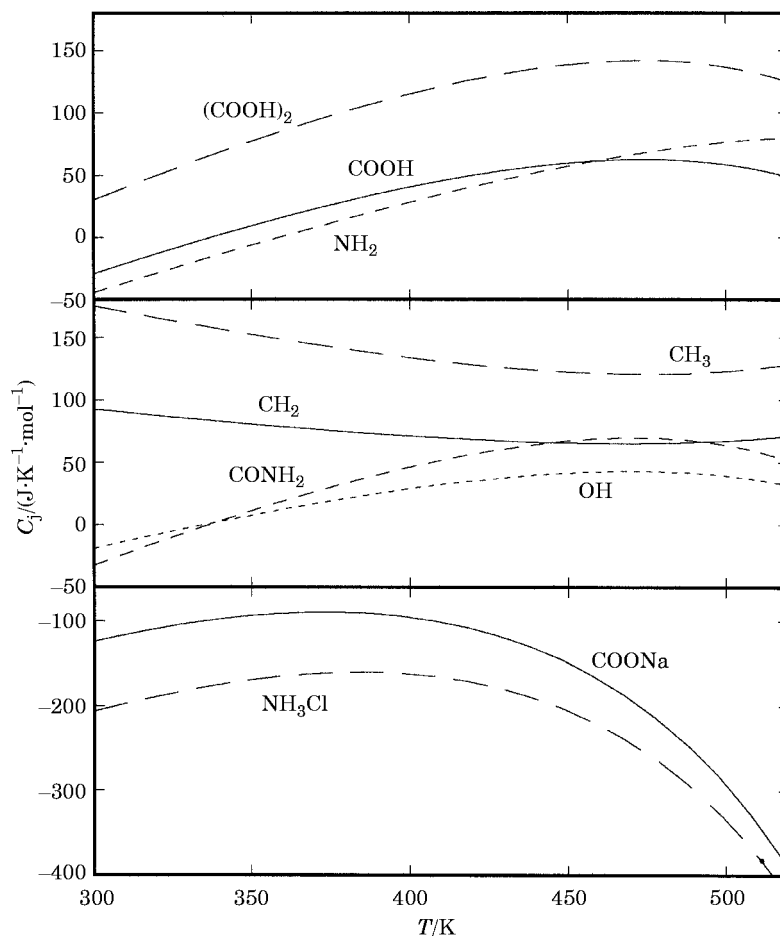


FIGURE 2. Functional group heat capacities  $C_j$  as a function of temperature.

COONa, and OH groups are not significantly different from those in the previous paper,<sup>(2)</sup> although there are differences in the coefficients of the fit. We may not be sure about actual uncertainties in functional group fits because there are not enough results for most groups, but some facts are encouraging: there is good consistency of functional groups found in several compounds (especially CH<sub>2</sub> and CH<sub>3</sub>) and the behavior of the temperature dependencies of the  $C_j$ s is always physically reasonable. As derived from the behavior of the limiting activity coefficient of the solute in the solvent critical region,<sup>(22)</sup> the partial molar heat capacity of the solute should approach infinity at the solvent critical point. As the temperature increases, the divergence is either positive, in the case when the solute molecules repel the solvent molecules or attract them weakly; or negative, when the solute attracts the solvent sufficiently strongly. These effects may be seen in the whole temperature range for our functional groups: for non-polar groups (CH<sub>2</sub>, CH<sub>3</sub>), the plot of  $C_j$  against  $T$  remains concave at all temperatures, and the slope is positive at the highest temperatures, while for polar groups {CONH<sub>2</sub>, NH<sub>2</sub>, COOH, (COOH)<sub>2</sub>, OH} the plot is convex at all temperatures, and the slope is negative at the highest temperatures, which indicates sufficiently strong attractive interactions. For the

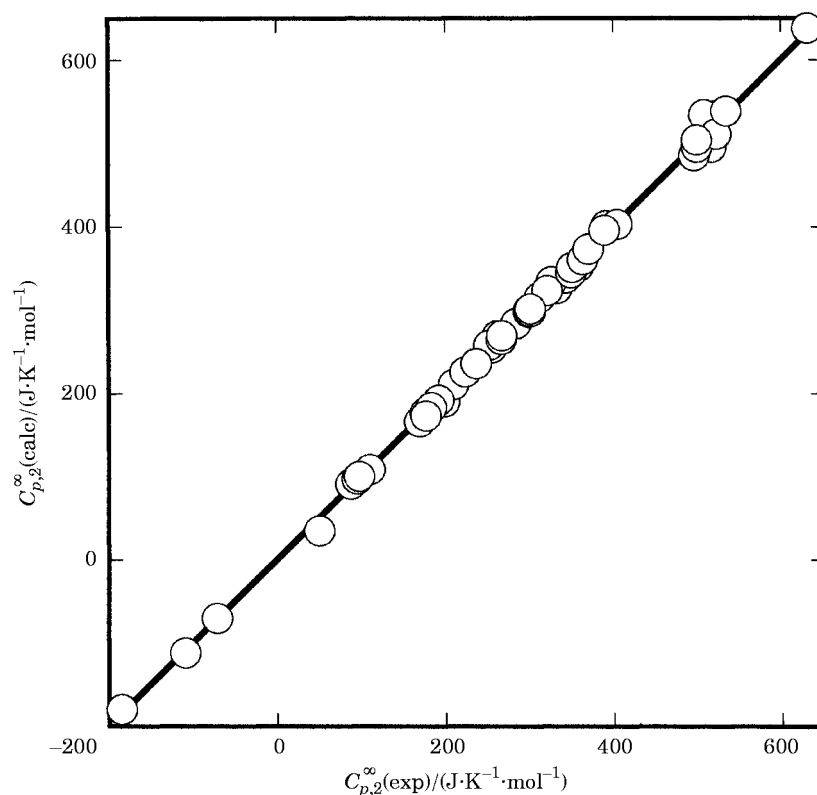


FIGURE 3.  $C_{p,2}^{\infty}$  calculated from functional group additivity, equation (8), plotted against experimental  $C_{p,2}^{\infty}$ .

COONa and  $\text{NH}_3\text{Cl}$  group (composed of the charged groups  $\text{Na}^+$ ,  $\text{COO}^-$ ,  $\text{NH}_3^+$ , and  $\text{Cl}^-$ ),  $(\partial^2 C_j / \partial T^2)_p$  is negative and large at all temperatures, and the slope at the highest temperatures is also negative and large, as expected from the strong long-range attractive forces between the charged groups and water.

Figure 3 (the plot of the calculated against experimental values of  $C_{p,2}^\infty$ ) gives an overall indication of the accuracy of our fit. Figure 3 indicates that reasonably accurate predictions of  $C_{p,2}^\infty$  at temperatures up to 525 K may be obtained with equation (8) for alcohols, polyols, mono- and polyfunctional carboxylic acids, sodium carboxylates, amines and polyamines, amides, and hydrochlorides. The reliability of the predictions should be slightly less than the precision of our fit, with somewhat larger uncertainty in the case of polyfunctional compounds and compounds with strong steric or near-neighbor effects.

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