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Thermodynamic Quantities for the Interaction of H^+ and Na^+ with $C_2H_3O_2^-$ and Cl^- in Aqueous Solution from 275 to 320°C

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The aqueous reactions,

$$H^+ + Cl^- = HCl, H^+ + Ac^- = HAc,$$
$$\text{and } Na^+ + Ac^- = NaAc\ (Ac = C_2H_3O_2^-)$$

were studied as a function of ionic strength at 275, 300, and 320°C using a flow calorimetric technique. Log K, ΔH and ΔS values were determined from the fits of the calculated and experimental heats while ΔCp values were calculated from the variation of ΔH values with temperature. The log K and ΔH values for the first two reactions agree well with literature values at these temperatures. No previous results have been reported for the third reaction. The use of equations containing identical numbers of positive and identical numbers of negative charges on both sides of the equal sign (isocoulombic reaction principle) was applied to the log K values determined in this study. The resulting plots of log K for the isocoulombic reactions vs. 1/T were approximately linear, which demonstrates that the ΔCp values for these reactions are approximately zero.

KEY WORDS: Equilibrium constant; enthalpy change; entropy change; heat capacity change; capacity change; flow calorimetry; high temperature; hydrochloric acid; acetic acid; sodium acetate; isocoulombic reaction.

1. INTRODUCTION

The need for experimental data involving interactions among the dissolved substances in high temperature aqueous solutions has been pointed out.(1,2) These data are especially needed in the electric power

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industry where they could be used to gain an understanding of corrosion in steam generators. The interaction of SO_4^{2-} with H^+ and Na^+ from 150 to 320°C has been studied.(3) In the current paper, the reactions of two more anions of interest in high temperature chemistry, Cl^- and Ac^-, with H^+ and Na^+ are studied. The source of Cl^- in steam generators of power plants is most likely condenser leakage of natural cooling water which contains significant amounts of Na^+, SO_4^{2-}, and Cl^-. Acetate ion (Ac^-) enters the system when the synthetic resins, used to remove harmful ions from the condensate, leach over time. All of these ions can concentrate with time to produce concentrated electrolyte solutions which are corrosive to the construction materials of the system.

Many studies of aqueous electrolyte solutions and the determination of log K and ΔH values for solute-solute interactions have been made near room temperature and pressure. However, corresponding thermodynamic values are scarce for electrolyte systems at elevated temperatures. Work which has been done using electrolytes at high temperature includes the systems: sodium chloride,(4-6) potassium chloride,(7) sulfate complexes,(3,8,9) phosphoric acid,(10,11) boric acid,(12) silicic acid,(13) and hydrochloric acid.(14-17)

Various experimental methods have been used to study chemical equilibria in high temperature aqueous solutions. Some of these investigations have resulted in log K values for reactions (1) and (2).

$$H^+ + Cl^- = HCl(aq) \tag{1}$$

$$H^+ + Ac^- = HAc(aq) \tag{2}$$

$$Na^+ + Ac^- = NaAc(aq) \tag{3}$$

Experimental values for reaction (3) are not available above 150°C. Other investigators(18,19) have estimated log K values for reactions (1) and (2) at high temperatures from experimental data taken at lower temperatures.

The log K values for reaction (1) have been determined as a function of temperature from 250 to 360°C. Experimental determinations of log K values for reaction (1) have been reported above 250°C using both electrical conductance(20,21) and solubility of silver chloride in hydrochloric acid(15) measurements. Noyes(20) reported evidence of HCl formation in aqueous solution from electrical conductance studies at 260 and 306°C. These data have been re-evaluated by Wright *et al.*(22) and used to estimate log K values. Pearson *et al.*(21) have determined log K values for the formation of aqueous hydrochloric acid by means of electrical conductance measurements from 300 to 383°C. Solubility measurements of silver chloride in aqueous hydrochloric acid solution from 100 to 350°C were made by Ruaya and Seward.(15) Frantz and Marshall(17) made electrical conductance studies of HCl solutions from 100 to 700°C and reported log *K* values for HCl formation from 400 to 700°C. Helgeson(18) calculated log *K* values for HCl(aq) formation from low temperature entropy and enthalpy data. Few log *K* values near room temperature(23,24) have been reported for reaction (1).

Log *K* values for reaction (2) have been determined from electrical conductance measurements from 25 to 350°C by several workers.(20,25-29) Conductance measurements by Noyes have been re-evaluated to give log *K* values at 100, 156, 218 and 306°C.(27) Fisher and Barnes(27) used their own data and data from previous studies(20,25,29) to fit a smooth curve and obtain the "best values" for the ionization of acetic acid from 25 to 350°C. The ionization constant of HAc has also been calculated from low temperature data.(19)

In the present study, log *K*, ΔH, and ΔS values were determined for reactions (1), (2), and (3) as a function of ionic strength (I) at 275, 300, and 320°C. The determination of ΔH as a function of temperature makes possible an accurate estimate of ΔC_p for reactions (1), (2), and (3). Next, the complete data set taken as a function of I and temperature was used to calculate a consistent set of log *K* and ΔH values over the temperature range 275 to 320°C. This procedure is considered more accurate than that involving the determination of ΔH and ΔC_p values from the variation of log *K* with temperature because one less differentiation with respect to temperature is required. The isocoulombic reaction principle was found to be useful to estimate high temperature log *K* values from low temperature log *K* data.(3) The isocoulombic reactions studied were those formed by the combination of reactions (1), (2), and (3) with those for the ionization of water and for the first dissociation of phosphoric acid.

2. EXPERMENTAL

2.1. Materials

The reagents used were MCB Reagent Grade H_2SO_4, Mallinckrodt Reagent Grade HCl, Mallinckrodt Reagent Grade $NaHSO_4$, Baker Analyzed Reagent NaAc, and Fisher Reagent Grade NaCl. The water was deionized and distilled.

Table I. Calorimetric Data Obtained by Mixing NaAc Solution with H_2O, NaAc Solution with HCl Solution, and HCl Solution with H_2O[a]

Flow of Stream		Heat of Reaction	Heat of Dilution		Flow of Stream		Heat of Reaction	Heat of Dilution	
A	B		A	B	A	B		A	B
275 °C					300 °C				
Stream A: 1.0661m NaAc; Stream B: 1.0164m HCl;					Stream A: 1.0711m NaAc; Stream B: 1.0210m HCl				
		a=1	a=1	a=1.0437			a=1	a=1	a=1.0439
		b=1	b=1.0179	b=1			b=1	b=1.0180	b=1
0.4655	0.1810	3.1685	-1.2674	-2.1869	0.4654	0.1809	2.0556	-1.8392	-3.3591
0.4655	0.2504	4.6612	-1.6800	-2.5973	0.4654	0.2504	3.1574	-2.4865	-3.9009
0.4655	0.2709	5.1843	-1.8199	-2.6782	0.4654	0.2709	3.5949	-2.6931	-4.0517
0.4655	0.3154	6.0564	-2.0765	-2.8479	0.4654	0.3153	4.2564	-3.0577	-4.2766
0.4655	0.3430	6.7032	-2.2000	-2.9960	0.4654	0.3429	4.7139	-3.2510	-4.4356
0.4655	0.3846	7.7326	-2.3984	-3.1459	0.4654	0.3846	5.4416	-3.5660	-4.6505
0.4655	0.4152	8.4061	-2.5305	-3.2649	0.4654	0.4151	5.9779	-3.7906	-4.7764
0.4655	0.4589	9.4782	-2.6495	-3.3618	0.4654	0.4589	6.7584	-4.0194	-4.8918
0.4655	0.4883	9.9263	-2.7502	-3.4364	0.4654	0.4882	7.2041	-4.1753	-5.0427
0.4655	0.5313	9.8222	-2.8688	-3.4726	0.4654	0.5313	7.1492	-4.3999	-5.0948
0.4655	0.5600	9.7432	-2.9989	-3.5382	0.4654	0.5599	7.2269	-4.5829	-5.1902
0.4655	0.6026	9.7459	-3.1036	-3.6440	0.4654	0.6025	7.1680	-4.7760	-5.3161
0.4655	0.6747	9.6867	-3.3573	-3.7062	0.4654	0.6747	7.0078	-5.2677	-5.4360
Stream A: 0.5175m NaAc; Stream B: 0.4999m HCl;					Stream A: 0.4982m NaAc; Stream B: 0.4677m HCl				
		a=1	a=1	a=1.0202			a=1	a=1	a=1.0194
		b=1	b=1.0082	b=1			b=1	b=1.0076	b=1
0.4762	0.1827	2.4695	-0.4919	-0.8887	0.4766	0.1828	1.9544	-0.8036	-1.4497
0.4762	0.2529	3.5318	-0.6435	-1.0500	0.4766	0.2530	2.8937	-1.0462	-1.6765
0.4762	0.2736	3.9537	-0.6785	-1.1178	0.4766	0.2737	3.2965	-1.1600	-1.7557
0.4762	0.3184	4.6448	-0.7689	-1.1741	0.4766	0.3186	3.8576	-1.2838	-1.8597
0.4762	0.3463	5.0923	-0.8248	-1.2155	0.4766	0.3465	4.2618	-1.4499	-1.9396
0.4762	0.3884	5.7829	-0.9661	-1.2952	0.4766	0.3886	4.8223	-1.6314	-2.0535
0.4762	0.4192	6.2196	-1.0316	-1.3168	0.4766	0.4195	5.2274	-1.7651	-2.1206
0.4762	0.4634	6.9877	-1.0306	-1.3723	0.4766	0.4636	5.8936	-1.7847	-2.1594
0.4762	0.4930	7.3141	-1.0610	-1.3551	0.4766	0.4933	6.2506	-1.8674	-2.1804
0.4762	0.5365	7.2778	-1.1024	-1.4062	0.4766	0.5368	6.7843	-2.0300	-2.2417
0.4762	0.5654	7.2690	-1.1916	-1.4385	0.4766	0.5658	6.8431	-2.1377	-2.2766
0.4762	0.6084	7.2970	-1.2465	-1.4341	0.4766	0.6088	6.8288	-2.2549	-2.3880
0.4762	0.6813	7.2622	-1.3272	-1.4868	0.4766	0.6817	6.7321	-2.4372	-2.4208
Stream A: 0.2574m NaAc; Stream B: 0.2502m HCl;					Stream A: 0.2625m NaAc; Stream B: 0.2715m HCl				
		a=1	a=1	a=1.0093			a=1	a=1	a=1.0095
		b=1	b=1.0035	b=1			b=1	b=1.0039	b=1
0.4814	0.1836	1.6409	-0.1380	-0.3133	0.4813	0.1835	1.7145	-0.3157	-0.7940
0.4814	0.2540	2.3697	-0.1971	-0.3504	0.4813	0.2539	2.4369	-0.4334	-0.9154
0.4814	0.2748	2.6688	-0.1974	-0.3473	0.4813	0.2747	2.7636	-0.4765	-0.9682
0.4814	0.3199	3.0735	-0.2266	-0.3792	0.4813	0.3198	3.2076	-0.5745	-1.0452

Table I. Concluded.

Flow of Stream		Heat of Reaction	Heat of Dilution		Flow of Stream		Heat of Reaction	Heat of Dilution	
A	B		A	B	A	B		A	B
0.4814	0.3479	3.3510	-0.2582	-0.4117	0.4813	0.3478	3.5051	-0.5992	-1.0951
0.4814	0.3902	3.7622	-0.3234	-0.4280	0.4813	0.3900	3.9576	-0.7183	-1.1594
0.4814	0.4212	4.0384	-0.3360	-0.5113	0.4813	0.4210	4.2464	-0.7473	-1.1948
0.4814	0.4655	4.5547	-0.3239	-0.4383	0.4813	0.4653	4.6262	-0.7855	-1.2010
0.4814	0.4953	4.7440	-0.3659	-0.4327	0.4813	0.4951	4.6870	-0.8281	-1.2516
0.4814	0.5390	4.7188	-0.3869	-0.4352	0.4813	0.5388	4.5734	-0.8784	-1.2407
0.4814	0.5681	4.6776	-0.3469	-0.4622	0.4813	0.5678	4.5765	-0.8220	-1.2634
0.4814	0.6113	4.7129	-0.3880	-0.4865	0.4813	0.6110	4.5298	-0.8922	-1.2745
0.4814	0.6844	4.7480	-0.3612	-0.5408	0.4813	0.6842	4.4939	-0.9424	-1.3528
		320 °C					320 °C		
Stream A: 0.5115m NaAc; Stream B: 0.4824m HCl;					Stream A: 0.2530m NaAc; Stream B: 0.2370m HCl				
		a=1	a=1	a=1.0199			a=1	a=1	a=1.0091
		b=1	b=1.0079	b=1			b=1	b=1.0033	b=1
0.4723	0.1796	0.9937	-1.1732	-2.1696	0.4774	0.1804	1.0982	-0.5412	-1.1274
0.4723	0.2501	1.5009	-1.5800	-2.5374	0.4774	0.2513	1.6574	-0.7688	-1.3304
0.4723	0.2744	1.7210	-1.7355	-2.6627	0.4774	0.2757	1.8681	-0.8245	-1.4146
0.4723	0.3163	2.0392	-1.9568	-2.7950	0.4774	0.3178	2.1783	-0.9609	-1.5008
0.4723	0.3456	2.2900	-2.0597	-2.8705	0.4774	0.3472	2.4179	-1.0176	-1.5397
0.4723	0.3881	2.6218	-2.2750	-3.0157	0.4774	0.3899	2.7183	-1.1491	-1.6396
0.4723	0.4181	2.8898	-2.4004	-3.0567	0.4774	0.4200	2.9565	-1.1839	-1.6642
0.4723	0.4612	3.2884	-2.5594	-3.1219	0.4774	0.4633	3.3278	-1.2406	-1.6778
0.4723	0.4870	3.5627	-2.6308	-3.1605	0.4774	0.4893	3.5455	-1.2823	-1.7082
0.4723	0.5303	3.5653	-2.8399	-3.2627	0.4774	0.5327	3.5531	-1.3976	-1.7754
0.4723	0.5610	3.5996	-2.9290	-3.2831	0.4774	0.5636	3.5595	-1.4266	-1.7701
0.4723	0.6038	3.5402	-3.1204	-3.3697	0.4774	0.6066	3.4754	-1.5385	-1.8453
0.4723	0.6750	3.5204	-3.3522	-3.4626	0.4774	0.6780	3.4546	-1.6552	-1.8778

[a] Units: flow,g H_2O-min^{-1}; heats, J-min^{-1}. To determine the mass flow rate of stream A in g H_2O-min^{-1} multiply flow A by *a*. To determine the mass flow rate of stream B in g H_2O-min^{-1} multiply flow B by *b*. Example: Flow A for the first data point at 275°C for the heat of dilution of B is (0.4655×1.0437) g H_2O-min^{-1}.

2.2. Procedure

The construction and operation of the flow calorimeter used in the study have been described together with the mathematical procedures used to reduce the raw data.(3,30,31) Several modifications in design and operation were made(31,32) to ensure that the inlet streams were raised to the proper temperature and to increase control over the process. First, the area of heat exchange between the exit stream and the two inlet

Table II. Calorimetric Data Obtained by Mixing NaAc Solution with H_2O, NaAc Solution with $NaHSO_4$ Solution, and $NaHSO_4$ Solution with H_2O^a

Flow of Stream A	Flow of Stream B	Heat of Reaction	Heat of Dilution A	Heat of Dilution B	Flow of Stream A	Flow of Stream B	Heat of Reaction	Heat of Dilution A	Heat of Dilution B
		275 °C					300 °C		
Stream A: 1.0661*m* NaAc; Stream B: 1.0522*m* $NaHSO_4$;					Stream A: 1.0711*m* NaAc; Stream B: 1.0557*m* $NaHSO_4$				
		a=1 *b*=1	*a*=1 *b*=1.0330	*a*=1.0437 *b*=1			*a*=1 *b*=1	*a*=1 *b*=1.0331	*a*=1.0439 *b*=1
0.4655	0.1783	-3.3959	-1.2674	-1.5928	0.4654	0.1783	-2.4416	-1.8392	-2.6820
0.4655	0.2468	-4.5734	-1.6800	-1.8864	0.4654	0.2468	-3.2216	-2.4865	-3.1751
0.4655	0.2670	-5.0196	-1.8199	-1.9806	0.4654	0.2669	-3.4888	-2.6931	-3.3234
0.4655	0.3108	-5.6597	-2.0765	-2.1259	0.4654	0.3107	-3.8478	-3.0577	-3.5492
0.4655	0.3380	-6.0868	-2.2000	-2.2253	0.4654	0.3379	-4.1679	-3.2510	-3.7080
0.4655	0.3790	-6.6450	-2.3984	-2.3687	0.4654	0.3790	-4.4872	-3.5660	-3.8903
0.4655	0.4091	-6.9132	-2.5305	-2.4718	0.4654	0.4091	-4.6741	-3.7906	-3.9874
0.4655	0.4522	-7.2354	-2.6495	-2.4914	0.4654	0.4522	-4.8507	-4.0194	-4.0872
0.4655	0.4812	-7.3921	-2.7502	-2.5405	0.4654	0.4811	-4.9413	-4.1753	-4.2000
0.4655	0.5236	-7.6540	-2.8688	-2.6288	0.4654	0.5235	-5.0767	-4.3999	-4.2901
0.4655	0.5518	-7.7042	-2.9989	-2.6486	0.4654	0.5518	-5.2354	-4.5829	-4.3505
0.4655	0.5938	-7.8180	-3.1036	-2.7096	0.4654	0.5937	-5.2094	-4.7760	-4.4282
0.4655	0.6649	-7.8931	-3.3573	-2.7538	0.4654	0.6648	-5.2961	-5.2677	-4.6008
Stream A: 0.5175*m* NaAc; Stream B: 0.5126*m* $NaHSO_4$;					Stream A: 0.4982*m* NaAc; Stream B: 0.5157*m* $NaHSO_4$				
		a=1 *b*=1	*a*=1 *b*=1.0143	*a*=1.0202 *b*=1			*a*=1 *b*=1	*a*=1 *b*=1.0144	*a*=1.0194 *b*=1
0.4762	0.1816	-1.5212	-0.4919	-0.6315	0.4766	0.1816	-0.9836	-0.8036	-0.9979
0.4762	0.2513	-2.0658	-0.6435	-0.7227	0.4766	0.2513	-1.2912	-1.0462	-1.2183
0.4762	0.2719	-2.2567	-0.6785	-0.7239	0.4766	0.2719	-1.3721	-1.1600	-1.3110
0.4762	0.3165	-2.5669	-0.7689	-0.7845	0.4766	0.3165	-1.5460	-1.2838	-1.4357
0.4762	0.3442	-2.7574	-0.8248	-0.8150	0.4766	0.3442	-1.6469	-1.4499	-1.6126
0.4762	0.3860	-2.9912	-0.9661	-0.9128	0.4766	0.3860	-1.8415	-1.6314	-1.5979
0.4762	0.4167	-3.1177	-1.0316	-0.9306	0.4766	0.4166	-1.9030	-1.7651	-1.6334
0.4762	0.4605	-3.2412	-1.0306	-0.8477	0.4766	0.4605	-2.0118	-1.7847	-1.7380
0.4762	0.4900	-3.3298	-1.0610	-0.9303	0.4766	0.4900	-2.0073	-1.8674	-1.7540
0.4762	0.5332	-3.4089	-1.1024	-0.9042	0.4766	0.5332	-2.0278	-2.0300	-1.7667
0.4762	0.5620	-3.4562	-1.1916	-0.9812	0.4766	0.5619	-2.0969	-2.1377	-1.7992
0.4762	0.6047	-3.4979	-1.2465	-0.9269	0.4766	0.6047	-2.0742	-2.2549	-1.8049
0.4762	0.6771	-3.5396	-1.3272	-1.0251	0.4766	0.6771	-2.2147	-2.4372	-1.8029
Stream A: 0.2574*m* NaAc; Stream B: 0.2568*m* $NaHSO_4$;					Stream A: 0.2625*m* NaAc; Stream B: 0.2545*m* $NaHSO_4$				
		a=1 *b*=1	*a*=1 *b*=1.0063	*a*=1.0093 *b*=1			*a*=1 *b*=1	*a*=1 *b*=1.0062	*a*=1.0095 *b*=1
0.4814	0.1831	-0.7128	-0.1380	-0.1953	0.4813	0.1831	-0.3801	-0.3157	-0.4498
0.4814	0.2533	-0.9544	-0.1971	-0.2159	0.4813	0.2534	-0.5301	-0.4334	-0.5095
0.4814	0.2741	-1.0641	-0.1974	-0.2119	0.4813	0.2741	-0.5820	-0.4765	-0.5339
0.4814	0.3190	-1.2144	-0.2266	-0.2332	0.4813	0.3190	-0.6504	-0.5745	-0.5773
0.4814	0.3469	-1.2974	-0.2582	-0.2677	0.4813	0.3470	-0.7043	-0.5992	-0.6327

Table II. Concluded.

Flow of Stream A	Flow of Stream B	Heat of Reaction	Heat of Dilution A	Heat of Dilution B	Flow of Stream A	Flow of Stream B	Heat of Reaction	Heat of Dilution A	Heat of Dilution B
0.4814	0.3891	-1.4418	-0.3234	-0.2984	0.4813	0.3891	-0.7626	-0.7183	-0.6873
0.4814	0.4200	-1.4837	-0.3360	-0.3143	0.4813	0.4200	-0.7875	-0.7473	-0.7789
0.4814	0.4642	-1.5054	-0.3239	-0.2719	0.4813	0.4642	-0.8426	-0.7855	-0.6961
0.4814	0.4939	-1.5234	-0.3659	-0.2810	0.4813	0.4940	-0.8491	-0.8281	-0.7508
0.4814	0.5375	-1.5808	-0.3869	-0.2905	0.4813	0.5375	-0.9296	-0.8784	-0.8109
0.4814	0.5665	-1.5778	-0.3469	-0.2584	0.4813	0.5665	-0.9295	-0.8220	-0.8031
0.4814	0.6095	-1.6091	-0.3880	-0.3338	0.4813	0.6096	-0.9740	-0.8922	-0.8786
0.4814	0.6825	-1.6230	-0.3612	-0.3141	0.4813	0.6826	-0.9692	-0.9424	-1.0012
		320 °C					320 °C		
Stream A: 0.5115*m* NaAc; Stream B: 0.5027*m* $NaHSO_4$;					Stream A: 0.2530*m* NaAc; Stream B: 0.2517*m* $NaHSO_4$				
		a=1	*a*=1	*a*=1.0199			*a*=1	*a*=1	*a*=1.0091
		b=1	*b*=1.0140	*b*=1			*b*=1	*b*=1.0061	*b*=1
0.4723	0.1785	-0.2937	-1.1732	-1.7056	0.4774	0.1799	-0.0162	-0.5412	-0.7810
0.4723	0.2486	-0.3226	-1.5800	-2.0485	0.4774	0.2505	0.0144	-0.7688	-0.9224
0.4723	0.2728	-0.3192	-1.7355	-2.1658	0.4774	0.2749	0.0441	-0.8245	-0.9765
0.4723	0.3144	-0.3374	-1.9568	-2.3150	0.4774	0.3169	0.0517	-0.9609	-1.0569
0.4723	0.3435	-0.3218	-2.0597	-2.4096	0.4774	0.3462	0.0594	-1.0176	-1.0842
0.4723	0.3858	-0.3397	-2.2750	-2.5195	0.4774	0.3888	0.0515	-1.1491	-1.1632
0.4723	0.4156	-0.3517	-2.4004	-2.5910	0.4774	0.4188	0.0703	-1.1839	-1.1894
0.4723	0.4584	-0.2820	-2.5594	-2.6508	0.4774	0.4620	0.1275	-1.2406	-1.2081
0.4723	0.4841	-0.2778	-2.6308	-2.6698	0.4774	0.4879	0.1520	-1.2823	-1.2042
0.4723	0.5271	-0.2776	-2.8399	-2.7664	0.4774	0.5312	0.1561	-1.3976	-1.2651
0.4723	0.5576	-0.2572	-2.9290	-2.7878	0.4774	0.5620	0.1816	-1.4266	-1.2649
0.4723	0.6002	-0.2392	-3.1204	-2.8585	0.4774	0.6049	0.1747	-1.5385	-1.3324
0.4723	0.6709	-0.2165	-3.3522	-2.9626	0.4774	0.6761	0.2020	-1.6552	-1.3562

[a] See Table I, footnote *a*.

streams was increased. This was done by tightly wrapping the exit and inlet tubing together for a distance of 20 cm with silver wire. Second , a heater was added length-wise along the three tubes. The heater was particularly important at the higher flow rates because heat exchange alone could not heat the incoming solutions to the desired temperature. When only one inlet stream was flowing, temperature control required the preheater to be on 50% of the time; when both inlet streams were flowing, the preheater was on 90 to 100% of the time. The addition of the preheater allowed heating of the inlet streams at either low or high flow rates from room temperature to within 8°C of the system temperature. The rest of the heating of the inlet streams occurred by heat exchange. A Hart Scientific Model 3701 controller together with the preheater was

Table III Calorimetric Data Obtained by Mixing H_2SO_4 Solution with H_2O, H_2SO_4 Solution with NaCl Solution, and NaCl Solution with H_2O^a

Flow of Stream		Heat of	Heat of Dilution		Flow of Stream		Heat of	Heat of Dilution	
A	B	Reaction	A	B	A	B	Reaction	A	B
		320 °C					320 °C		
Stream A: 0.5053*m* NaCl; Stream B: 0.5187*m* H_2SO_4;					Stream A: 0.2515*m* NaCl; Stream B: 0.2546*m* H_2SO_4				
		a=1	*a*=1	*a*=1.0077			*a*=1	*a*=1	*a*=1.0031
		b=1	*b*=1.0166	*b*=1			*b*=1	*b*=1.0074	*b*=1
0.4781	0.1781	2.6007	-1.2635	-2.0554	0.4802	0.1797	1.3541	-0.5307	-0.9396
0.4781	0.2480	3.4329	-1.6882	-2.4238	0.4802	0.2502	1.7484	-0.6831	-1.1050
0.4781	0.2721	3.7644	-1.8318	-2.5365	0.4802	0.2746	1.9024	-0.7455	-1.1471
0.4781	0.3136	4.0814	-2.0701	-2.6983	0.4802	0.3165	2.0795	-0.8481	-1.2304
0.4781	0.3427	4.3358	-2.1965	-2.7833	0.4802	0.3458	2.1756	-0.8841	-1.2625
0.4781	0.3848	4.5998	-2.4259	-2.8930	0.4802	0.3883	2.3030	-0.9991	-1.3510
0.4781	0.4145	4.7827	-2.5517	-2.9629	0.4802	0.4183	2.4214	-1.0416	-1.3847
0.4781	0.4573	5.0483	-2.6921	-3.0333	0.4802	0.4615	2.5785	-1.0834	-1.4114
0.4781	0.4829	5.2347	-2.7720	-3.0736	0.4802	0.4873	2.6450	-1.1265	-1.4171
0.4781	0.5257	5.4038	-2.9617	-3.1812	0.4802	0.5305	2.7262	-1.2051	-1.4912
0.4781	0.5562	5.5702	-3.0542	-3.1992	0.4802	0.5613	2.8521	-1.1905	-1.4737
0.4781	0.5987	5.7021	-3.2325	-3.3016	0.4802	0.6041	2.9041	-1.3042	-1.5401
0.4781	0.6692	6.0008	-3.4573	-3.3985	0.4802	0.6753	3.0708	-1.3619	-1.5970

[a] See Table I, footnote a.

used to control the temperature of the inlet streams as they exited the preheater. The control thermistor on the preheater was contained in silver foil to increase heat transfer and was attached with silver wire to the tubing containing the inlet streams after they exited the preheater. Good thermal contact is needed between the sensor and the tantalum tubing containing the solutions. If there is not enough thermal mass or if the thermistor is not in good thermal contact with the tubing, then the temperature of the inlet streams oscillates. Third, a temperature controller was added to maintain the outer shield at a constant temperature ensuring that the characteristics of the passive heat leak path remained constant. In the previous design,(3) the outer shield did not have a separate temperature controller. Instead, a constant amount of heat was supplied to the shield resulting in a drift in the temperature of the outer shield during the 10 hour period of the run. Fourth, the time allowed for the system to reach chemical equilibrium and steady-state was increased. These four modifications increased the reproducibility of the data over that achieved using the previous equipment configuration.(3)

The raw flow calorimetric heat of reaction and heat of dilution data are given in Tables I through III. Details of the data reduction method are available.(31)

The solutions were made by dissolving appropriate amounts of the reagents in water. Before use in the calorimeter, the solutions were sparged with argon(14) for 20 minutes to remove excess dissolved oxygen. This was done to reduce embrittlement of the tantalum by the oxygen. All solutions were standardized at 25°C after the argon treatment.

The total enthalpy changes upon mixing equimolal aqueous solutions of NaAc with HCl, NaAc with $NaHSO_4$, and NaCl with H_2SO_4 were measured at 275°C and 10.3 MPa, 300°C and 10.3 MPa, and 320°C and 12.8 MPa. Also, the total enthalpy changes upon mixing equimolal aqueous solutions of NaCl with H_2SO_4 were measured at 320°C and 12.8 MPa. The nominal concentrations of the solutions used were 0.25, 0.50, and 1.0 *m* at 275 and 300°C and 0.25 and 0.50 *m* at 320°C. The heats of dilution of the solutions were measured by mixing each with water as has been described.(3)

2.3. Calculations

Log *K* and ΔH values valid in aqueous solution were determined earlier for reactions (4), (5), and (6)

$$H^+ + SO_4^{2-} = HSO_4^- \tag{4}$$

$$Na^+ + SO_4^{2-} = NaSO_4^- \tag{5}$$

$$H^+ + HSO_4^- = H_2SO_4(aq) \tag{6}$$

by fitting the measured calorimetric heats obtained when mixing aqueous solutions of Na_2SO_4 and H_2SO_4 with each other and with water from 150 to 320°C.(3) With log *K* and ΔH values for reactions (4), (5) and (6) known, the log *K* and ΔH values for reactions (1), (2), and (3) were obtained by fitting the experimental overall heat of reaction data for the systems NaAc + HCl, NaAc + $NaHSO_4$ and NaCl + H_2SO_4 and the heat of dilution data obtained by mixing a solution of each component with water. The procedure described earlier(3) was used to determine log *K* and ΔH values from calorimetric data. Activity coefficients, γ_i, based on the Liu-Lindsay model(4) were calculated and were used to extrapolate log *K* values at the I values of the experiments to the log *K* values at I=0. The Liu-Lindsay model based on NaCl data to 300°C includes three assumptions. First, at high temperatures the activity coefficients of all 1:1 electrolytes approach each other and can be assumed to be a function only of I, temperature, species charge, and dielectric constant. Second, sodium chloride is an acceptable model for all 1:1 electrolytes, especially at high temperature. Third, γ for multiply-charged species can be approximated by the following equation

$$\gamma_{z=n} = (\gamma_{z=1})^{n^2} \tag{7}$$

where n is the charge of the ion.

The complete data set as a function of temperature and I for all three systems studied was used to determine the log K and ΔH values. The final values produced the minimum difference between the calculated and experimental heats when all temperatures, concentrations and systems were considered. A cross-checking of log K and ΔH values was possible because each reaction of interest occurred in two of the three systems studied. The fact that these values work for the reactions in different chemical systems provides confidence in the physical meaning of the values. The average estimated uncertainties for the log K and ΔH values are 0.04 log K units and 2.0 kJ-mol^{-1}, respectively.

It is difficult to predict which reactions occur at high temperatures. Some complexed species which are highly dissociated at room temperature may be highly associated at elevated temperatures, while others may be only slightly associated. The selection of the correct reactions requires that all possible association reactions of the species in solution be considered. Initially, only the reactions for which good evidence is given in the literature were included in data reduction. These reactions included the formation of HCl(aq)(14) and HAc(aq).(27) Other possible reactions were tested by including them in the data reduction. If their addition did not improve the fit, then they were neglected and presumed unimportant to the overall heat.

The possible 1:1 associated species in a NaAc-HCl mixture are NaAc(aq), NaCl(aq), HAc(aq) and HCl(aq). Significant amounts of Na^+, Ac^-, Cl^-, and H^+ are also present. Of the ion paired species, NaAc(aq), HAc(aq), and HCl(aq) were used to fit the data. When NaCl was included the fit of the data improved only slightly and the calculated log K values for NaCl association were much too high to be reasonable. The possible associated monomeric species in the NaAc-$NaHSO_4$ mixture are NaAc(aq), HAc(aq), $NaSO_4^-$, HSO_4^-, Na_2SO_4(aq), H_2SO_4(aq), and $NaHSO_4$(aq). It was concluded earlier(3) that Na_2SO_4(aq) and $NaHSO_4$(aq) were not significant in the H_2SO_4 + Na_2SO_4 system, and for this reason were not included when reducing the calorimetric data to log K and ΔH values. Therefore, NaAc(aq), HAc(aq), HSO_4^-, $NaSO_4^-$ and H_2SO_4(aq) were the associated species used in the analysis of this system. The possible associated monomeric species in the NaCl-H_2SO_4 mixture are NaCl(aq), HCl(aq), $NaSO_4^-$, HSO_4^-, Na_2SO_4(aq), H_2SO_4(aq), and $NaHSO_4$(aq). Reactions for the formation of HCl(aq), HSO_4^-, $NaSO_4^-$, and H_2SO_4(aq) were included in the analysis while reactions for the other associated species were neglected because they did not improve the fit.

3. RESULTS AND DISCUSSION

Log K, ΔH, ΔS and ΔC_p values for reactions (1), (2), and (3) determined as a function of temperature and valid at I=0 are given in Tables IV, V and VI, respectively, together with those determined by others and those extrapolated by us and others from low temperature K values. It was assumed that ΔH values for reactions (1), (2), and (3) could be fitted to an equation of the form

$$\Delta H = a + bT + cT^2 + d/T \tag{8}$$

Applying the van't Hoff equation to Eq. (8) results in an expression for K of the form

$$R \ln K = -a/T + b \ln T + cT - \tfrac{1}{2}\, d/T^2 + e \tag{9}$$

where e is the constant of integration determined by selecting a reference temperature. The reference temperature of 523 K was chosen because reliable data for HCl were not available at lower temperatures and it was desired to have the same reference temperature for all three reactions. The coefficients in Eqs. (8) and (9) were determined by fitting both the log K and ΔH values at 275, 300, and 320°C. Expressions giving ΔS and ΔC_p as a function of temperature were derived from Eqs. (8) and (9).

In Table VII, equations are given expressing log K, ΔH, ΔS and ΔC_p values (valid at I=0) for reactions (1), (2), and (3) as a function of temperature. Agreement of the calculated and experimental heats for the NaAc + HCl system in Figure 1 are seen to be good. Similar agreement was found for the dilution heats of NaAc and HCl. A sharp break in each curve in Figure 1 at the equivalence point (0.96 g water-min^{-1}) is seen in both the experimental and calculated heats. At a constant concentration, the observed overall heat of reaction Q decreases with increasing temperature, particularly between 300 and 320°C. This trend may be due to the increasing contribution of the negative heats of dilution on the overall heat for the reaction at higher temperatures. In ad-

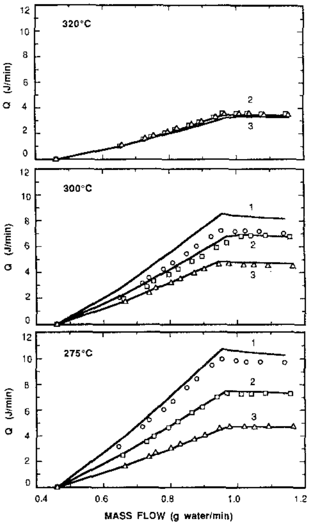

Fig. 1 Plots of calculated and experimental heats versus flow rates for the system NaAc + HCl at 275, 300, and 320°C. Experimental data and calculated values are represented by symbols (cir = 1.0 *m*, squ = 0.5 *m*, and tri = 0.25 *m*) and by solid lines, respectively.

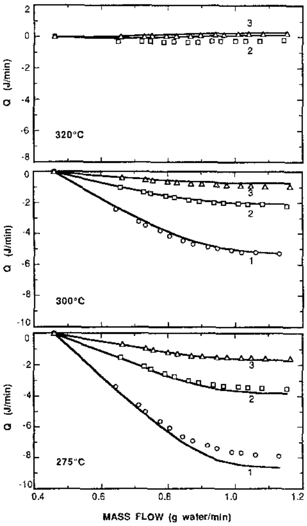

Fig. 2 Plots of calculated and experimental heats versus flow rates for the system NaAc + $NaHSO_4$ at 275, 300, and 320°C. Experimental data and calculated values are represented by symbols (cir = 1.0, squ = 0.5 *m*, and tri = 0.25 *m*) and by solid lines, respectively.

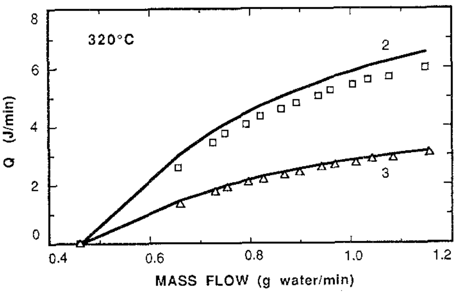

Fig. 3 Plots of calculated and experimental heats versus flow rates for the system NaCl + H_2SO_4 at 320°C. Experimental data and calculated values are represented by symbols (cir = 1.0, squ = 0.5 *m*, and tri = 0.25 *m*) and by solid lines, respectively.

dition, the difference between curves 2 and 3 decreases with increasing temperature, and at 320°C the curves fall on the same line. This suggests that over this temperature range the negative dilution heats increase at a greater rate than the positive reaction heats. In Figure 2, heats calculated using log K and ΔH values for reactions (2), (3), (4), and (5) for the NaAc + $NaHSO_4$ system are compared to those determined experimentally. As temperature increases, the observed heat of reaction becomes less negative until at 320°C the net heat of reaction for NaAc + $NaHSO_4$ is approximately zero. The log K and ΔH values for reactions (1), (4), (5), and (6) used to fit the calorimetric data for the systems Na_2SO_4 + H_2SO_4, NaAc + HCl, and NaAc + $NaHSO_4$ gave a good fit for the NaCl + H_2SO_4 system at 320°C as shown in Figure 3. This provides an excellent cross-check for the log K and ΔH values obtained. Some of the lack of agreement between the calculated and experimental heats may be due to the activity coefficient model used. Lindsay(34) has compared the high temperature activity coefficients for NaCl with those for other electrolytes and found that the agreement is reasonably good for 1:1 electrolytes but somewhat poorer for 1:2 and 2:1 electrolytes. At higher concentrations, the ability to predict γ values for divalent ions is decreased.

3.1. Formation of HCl, HAc, and NaAc

The log K values for HCl formation given in Table IV are represented graphically in Fig. 4. Extrapolating the data of Frantz and Marshall(17) at constant density to lower temperatures, log K values were estimated by us at 275, 300 and 320°C. These estimated values are given in Table IV. The log K values calculated in this study lie at the

Table IV. Log K, ΔH, ΔS and ΔC_p Values as a Function of Temperature for the Aqueous Reaction $H^+ + Cl^- = HCl$.[a]

°C	Pressure	Log K	ΔH	ΔS	ΔC_p	Method[b]	Ref.
250		0.49	80.7		1200	SOL	15
		0.3-0.53				PT	33
		0.67				EST	18
275	10.3	0.37	103	195	1222	CAL	This Study
		0.937	116			SOL	15
		0.20				COND	c
		0.955				EST	18
300	10.3	0.87	141	263	1844	CAL	This Study
		1.51	163.00		2100	SOL	15
		0.90					c
		1.24				COND	20
320	12.8	1.37	184	336	2431	CAL	This Study
		2.078	209.00			SOL	15
		1.55					c
360		3.26				COND	20

[a] Values from this study are valid at $I = 0$. Units: pressure, MPa; ΔS and ΔC_p, J-mol^{-1}-K^{-1}; ΔH, kJ-mol^{-1}. [b] CAL = Calorimetry, COND = Conductance, EST = Estimated from low temperature data, PT = Potentiometry, SOL = Solubility. [c] Extrapolation from data in reference 17.

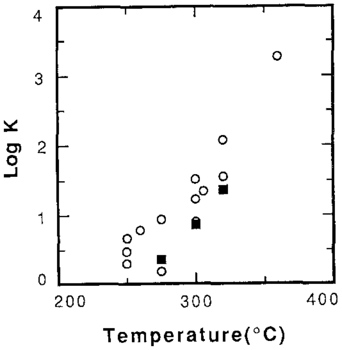

Fig. 4 Plot of log K for $H^+ + Cl^- = HCl(aq)$ as a function of temperature. The solid squares are the results obtained in the present study, all other points are taken from references listed in Table IV.

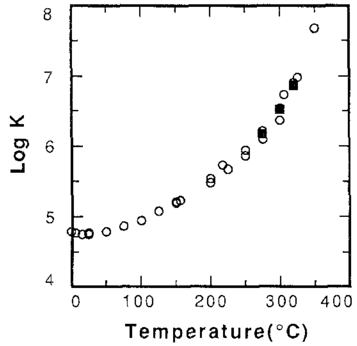

Fig. 5 Plot of log K for $H^+ + Ac^- = HAc(aq)$ as a function of temperature. The solid squares are the results obtained in the present study, all other points are taken from references listed in Table V.

lower end of the log K range for each temperature and the ΔH values in Table IV are similarly lower than those reported by Ruaya and Seward. Methods used by other workers to determine log K values include electrical conductance, solubility and potentiometry. The earlier ΔH values were estimated by Ruaya and Seward(15) from the variation of log K with temperature. Calorimetric methods allow the direct measurement of overall heats of reaction from which both log K and ΔH values can be determined. For this reason, log K and ΔH values determined from calorimetric measurements should be considered more accurate.

In Table V, thermodynamic values obtained in the present study for reaction (2) are compared with previous data. The log K and ΔH values determined in the present study agree well with previous literature values (see Figure 5).

The log K values for reaction (3), given in Table VI, are much smaller than log K values for the interaction of hydrogen ion with acetate ion. This same trend exists for the ΔH values. To the best of our knowledge, these are the only data available for the formation of sodium acetate at elevated temperatures. The values for reaction (3) are less certain than are those for reactions (1) and (2) because reaction (3) proceeds to a lesser extent and contributes less to the overall heat than do either of the other reactions. Because the calculated heats are relatively insensitive to the log K and ΔH values used for NaAc formation, it is difficult to refine these values.

3.2. Explanation of Large Positive ΔH and ΔS values

The signs of ΔH and ΔS for reactions (1), (2), and (3) would be

Table V. Log K, ΔH, ΔS and ΔC_p Values as a Function of Temperature for the Aqueous Reaction $H^+ + Ac^- = HAc$.[a]

°C	Pressure	Log K	ΔH	ΔS	ΔC_p	Method[b]	Ref.
25		4.756				COND	27
		4.76				EST	19
150		5.22				COND	27
		5.19				EST	19
156		5.24				COND	20
200		5.54				COND	27
		5.51				COND	25
		5.50				EST	19
218		5.74				COND	20
225		5.67				EST	19
250		5.95				COND	27
		5.86				EST	19
275	10.3	6.18	70	245	862	CAL	This Study
		6.21	67.62[c]			COND	26
		6.10					27
300	10.3	6.52	97	293	1320	CAL	This Study
		6.54	99.77[c]			COND	27
		6.36					28
		6.32				EST	19
306		6.74				COND	20
320	12.8	6.86	127	346	1748	CAL	This Study
		6.90	117.78[c]			COND	27
350		7.68				COND	27

[a] [b] See Table IV for footnotes. [c] ΔH values determined from log K vs T data

Table VI. Log K, ΔH, ΔS and ΔC_p Values as a Function of Temperature for the Aqueous Reaction $Na^+ + Ac^- = NaAc$.[a]

°C	Pressure	Log K	ΔH	ΔS	ΔC_p	Method[b]	Ref.
275	10.3	0.033	59	108	237	CAL	This Study
300	10.3	0.290	65	119	252	CAL	This Study
320	12.8	0.498	70	128	280	CAL	This Study

[a] [b] See Table IV for footnotes.

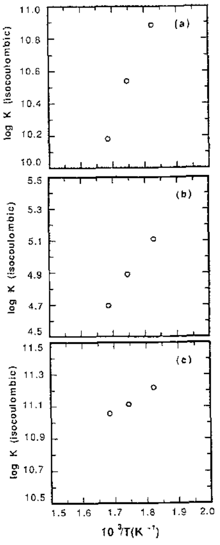

Fig. 6 Plots of log K *vs.* $10^3/T$ for the isocoulombic reactions (a) $HCl + OH^- = H_2O + Cl^-$, (b) $HAc + OH^- = H_2O + Ac^-$ and (c) $NaAc + OH^- + H^+ = H_2O + Na^+ + Ac^-$.

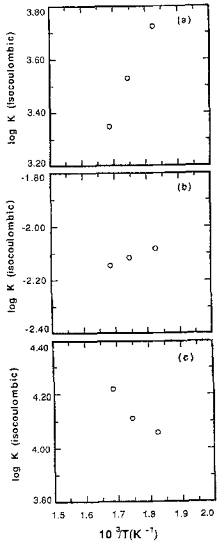

Fig. 7 Plots of log K *vs.* $10^3/T$ for the isocoulombic reactions (a) $HCl + H_2PO_4^- = H_3PO_4 + Cl^-$, (b) $HAc + H_2PO_4^- = H_3PO_4 + Ac^-$ and (c)$NaAc + H_2PO_4^- + H^+ = H_3PO_4 + Na^+ + Ac^-$.

Table VII. Equations[a] for Log K, ΔH, ΔS, and ΔC_p for Reactions (1), (2) and (3) as a Function of Temperature (275 to 320°C) at I=0

$H^+ + Cl^- = HCl$

$$\text{Log } K = 15{,}875.833 - 5{,}485.412 \log T - 1{,}137{,}150/T + 1.68062\,T + 90{,}687{,}000/T^2 \quad (10)$$

$$\Delta H = 21{,}770.280 - 45.6079085\,T + 0.032174901\,T^2 - 3{,}472{,}333.8/T \quad (11)$$

$$\Delta S = 258{,}328.8 - 105{,}016.1 \log T + 64.3498\,T - 1{,}736{,}170{,}000/T^2 \quad (12)$$

$$\Delta C_p = -45{,}608 + 64.35\,T + 3{,}472{,}300{,}000/T^2 \quad (13)$$

$H^+ + Ac^- = HAc$

$$\text{Log } K = 11{,}416.87 - 3{,}944.675 \log T - 814{,}398/T + 1.2115\,T + 64{,}605{,}000/T^2 \quad (14)$$

$$\Delta H = 15{,}591.34 - 32.79761\,T + 0.02319374\,T^2 - 2{,}473{,}661/T \quad (15)$$

$$\Delta S = 185{,}773.93 - 75{,}519.29 \log T + 46.3875\,T - 1{,}236{,}830{,}000/T^2 \quad (16)$$

$$\Delta C_p = -32{,}797.6 + 46.3875\,T + 2{,}473{,}660{,}000/T^2 \quad (17)$$

$Na^+ + Ac^- = NaAc$

$$\text{Log } K = 1{,}990.245 - 674.305 \log T - 162{,}234/T + 0.18712\,T + 15{,}034{,}000/T^2 \quad (18)$$

$$\Delta H = 3{,}105.91 - 5.60644\,T + 0.00358241\,T^2 - 575{,}650/T \quad (19)$$

$$\Delta S = 32{,}496 - 12{,}909.3 \log T + 7.1648\,T - 287{,}830{,}000/T^2 \quad (20)$$

$$\Delta C_p = -5{,}606.4 + 7.1648\,T + 575{,}650{,}000/T^2 \quad (21)$$

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[a] Temperatures in equations are in K, concentrations are in molality units, ΔH values are in kJ-mol^{-1}, and ΔS and ΔC_p values are in J-mol^{-1}-K^{-1}.

expected to be negative in the gas phase. In aqueous solution, the signs of ΔH and ΔS are positive and the magnitudes of both of these quantities increase dramatically as temperature increases. When solvation effects are considered within the framework of the water model proposed by Frank and Wen(35) and discussed previously,(3) the large positive values for ΔH and ΔS can be explained. When ion association occurs, water molecules are released from the primary and secondary hydration spheres to the bulk phase. Considerable energy is required to restore the newly released water molecules to the rotational, vibrational, and translational freedom which exists in the bulk water. The absorption of the required energy from the surroundings results in the large positive ΔH values for ion association reactions in water at high temperatures. Large positive ΔS values result from ion association because many water molecules are released from the ordered structure of the primary and secondary hydration spheres to the highly disordered state of the bulk liquid. At these high temperatures, ion association is an entropy driven process. The variation of log K with temperature is not as large as those of ΔH and ΔS. This is due to the compensating effects of ΔH and $-T\Delta S$.

Thermodynamic values obtained in this study for the formation of HCl, HAc, and NaAc from their constituent ions are given in Tables IV, V, and VI. Higher ΔH and ΔS values are expected for the formation of HCl(aq) than for HAc(aq) because the charge density is greater for Cl^- than for Ac^-. Thus, the water molecules held in the primary hydration sphere are more tightly bound to the Cl^-. Hence, when these water molecules are released from the primary hydration sphere to the bulk water upon ion association higher ΔH and ΔS values will result.

3.3. Evaluation of the Isocoulombic Reaction Principle

The isocoulombic reaction principle was used to test the log K values determined in this study. Log K values for reactions (1), (2), and (3) were combined with data for the ionization of water(36) to form isocoulombic reactions (22), (23), and (24).

$$HCl + OH^- = H_2O + Cl^- \tag{22}$$

$$HAc + OH^- = H_2O + Ac^- \tag{23}$$

$$NaAc + OH^- + H^+ = H_2O + Na^+ + Ac^- \tag{24}$$

Also, the log K data for reactions (1), (2), and (3) were combined with data for the first ionization of phosphoric acid(10,37) to form isocoulombic reactions (25), (26) and (27).

$$HCl + H_2PO_4^- = H_3PO_4 + Cl^- \tag{25}$$

$$HAc + H_2PO_4^- = H_3PO_4 + Ac^- \tag{26}$$

$$NaAc + H^+ + H_2PO_4^- = H_3PO_4 + Na^+ + Ac^- \tag{27}$$

The results are plotted in Figures 6 and 7 as log K for the isocoulombic reaction *vs.* $1/T$.

The approximate linear relationships for the plots in Figures 6 and 7 demonstrate that the isocoulombic principle is valid for reactions (22-27) over the temperature range studied. Log K values for the first dissociation of H_3PO_4(10,37) were not available above 300°C. Both errors in extrapolation of the H_3PO_4 data to 320°C and the uncertainty in the NaAc values may explain the curvature in the data for the isocoulombic reaction (27) shown in Figure 7c.

If the isocoulombic reaction principle can be used successfully to predict log K values at elevated temperatures from low temperature data, then the inverse should also be possible, *i.e.*, log K at high temperatures can be used to predict low temperature log *K* values. This method would be useful for species which are associated to a measurable extent at high temperature but only to a limited extent at room temperature, such as HCl. For example, log *K* values for HCl(aq) formation at 25°C could be estimated from log *K* values determined experimentally over a temperature range where appreciable HCl formation occurs. A log *K* value for HCl association at 25°C of -3.8 was obtained by fitting the log *K* values for the isocoulombic reaction (22) at 275, 300, and 320°C to a straight line and then extrapolating to 25°C. This value is considerably larger than those calculated from partial vapor pressure data by Marsh and McElroy(24) (-6.2) and by Robinson(23) (-5.9).

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[3] This Report is available from Research Reports Center, P.O. Box 50490, Palo Alto, CA 94303.