

## Isopiestic studies of aqueous solutions at elevated temperatures

### II. NaCl + KCl mixtures<sup>a</sup>

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Isopiestic studies have been made on aqueous solutions of the mixed electrolyte NaCl + KCl over the temperature range 383 to 474 K. Sodium chloride served as the isopiestic standard for the calculation of osmotic coefficients. The molality range covered in this study corresponded to about 0.6 to 6 mol kg<sup>-1</sup> for NaCl. The system of equations developed by Pitzer was fitted to each set of osmotic coefficients with a standard deviation of fit (in the osmotic coefficient) ranging from 0.0025 to 0.0044. Only one mixing parameter (in addition to the pure-electrolyte parameters) was necessary to describe the results adequately. Activity coefficients for NaCl and KCl in the mixed electrolyte system were calculated from the equations. The activity coefficients showed a monotonic decrease with increasing temperature and became much less dependent on molality at the higher molalities. The activity coefficient of NaCl is much more dependent on composition than that of KCl. The trace activity coefficients of NaCl and KCl are very nearly equal over this temperature range. The ability to describe the NaCl + KCl system with only one mixing parameter in Pitzer's equation is equivalent to Harned's rule. Excess Gibbs free energies calculated from the mixing parameter were, to a very good approximation, independent of temperature.

### 1. Introduction

Essentially all of the naturally occurring aqueous electrolyte solutions are of mixed electrolytes containing two or more solutes. In recent years there has been increased interest, both theoretical and practical, in the properties of aqueous solutions of mixed electrolytes. However, with the exception of some e.m.f. measurements,<sup>(1)</sup> practically all of the previous investigations have been conducted at, or near, 298.15 K. A continuing interest in the properties of aqueous solutions at elevated temperatures plus the availability of a proven high-temperature isopiestic facility<sup>(2,3)</sup> prompted the present study.

Liu and Lindsay<sup>(4)</sup> have made extensive vapor-pressure measurements on NaCl solutions at high temperatures. Their results have been incorporated into the evaluation of Silvester and Pitzer<sup>(5)</sup> to provide a comprehensive set of equations which describe the thermodynamic properties of NaCl solutions over a wide range of temperature. Our previous work<sup>(2)</sup> provides the osmotic and activity coefficient for

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aqueous KCl solutions up to 474 K. Wood<sup>(6)</sup> has made extensive calculations of the thermodynamics of  $\text{NaCl} + \text{KCl} + \text{H}_2\text{O}$  from 273 to 473 K. For the properties of pure KCl solutions, Wood relied heavily on the isopiestic results of Soldano and co-workers,<sup>(7-10)</sup> which are in serious disagreement with our recent results<sup>(2)</sup> for KCl solutions. For  $\text{NaCl} + \text{KCl} + \text{H}_2\text{O}$  at 298.15 K, the precise isopiestic measurements of Robinson<sup>(11)</sup> are available. It thus seems appropriate that our first study of aqueous solutions of mixed electrolytes should concern  $\text{NaCl} + \text{KCl}$ , the most common mixture for which there are pure-component data at high temperatures.

## 2. Experimental

Sodium and potassium chlorides were the same "ultrapure" grade used previously.<sup>(2)</sup> Stock solutions were prepared by mass from the dry salts. To obtain the desired mixture an appropriate quantity of each stock solution was weighed (from a weight buret) into a titanium solution cup. These solutions were then allowed to evaporate to dryness in a desiccator containing anhydrous calcium sulfate. (Because of a problem with creeping, a few of the mixtures were prepared by direct weighing of the dry "ultrapure" salts into a titanium solution cup using a semi-micro balance.) Duplicate solution cups containing pure NaCl served as the isopiestic standards.

The series I measurements (see table 1) were taken concurrently with the previously reported results<sup>(2)</sup> where the experimental details may be found. Two modifications to the apparatus were made prior to the series II measurements. The first was a change in the heating arrangement for the air bath in an attempt to reduce the temperature gradient across the copper block.<sup>(2)</sup> The concentrated "calrod" heaters<sup>(2)</sup> previously used for the air bath were replaced with 0.3175 cm thick copper sheets having heaters mounted uniformly on one side. Six of these copper sheets formed an approximately cubic air bath for the isopiestic vessel which was heated on all sides. This arrangement, plus using larger fan blades, also resulted in greatly improved circulation inside the air bath. The new heating arrangement also eliminated the need for "trim" heaters,<sup>(2)</sup> but unfortunately this modification did not eliminate the temperature gradient across the copper block. However, there was some modest improvement (see Results).

Secondly, the existing electromagnetic coil for the balance was replaced with one having fewer turns (about 0.3 of the original number). The reduction in turns resulted from using Teflon insulation rather than the original fragile ceramic. This required a larger balancing current in the coil but also gave an increased sensitivity (by a factor of 3) in terms of potential per unit mass. A principal advantage is that the new coil is not nearly so subject to electrical short-circuits.

The experimental procedure was essentially the same as that used previously.<sup>(2)</sup> Briefly, the experiment consists of allowing solutions, contained in titanium cups, to attain equilibrium while sitting on a massive copper block inside a closed pressure vessel at constant temperature. Molalities were determined by weighing the solution cups, *in situ*, with an electromagnetic balance which was calibrated with a set of standard weights interspersed with the solution cups. Water could be added, or removed, through a 0.16 cm o.d. stainless-steel capillary tube.

## 3. Results and discussion

The experimentally determined isopiestic molalities are listed in table 1. (In order to avoid round-off error and for consistency one more significant figure than warranted, in most cases, is used in table 1.) Results for two of the samples in series I (those with mole fractions of KCl equal to 0.10034 and 0.42006) were omitted from consideration

TABLE 1. Isopiestic molalities  $m$  of aqueous solutions of  $(1 - y)\text{NaCl} + y\text{KCl}$ 

$y$ :	0	0.10475	0.10034	0.20654	0.19461	0.39886	0.42006
$m/\text{mol kg}^{-1}$							
Series I, 382.76 K							
	6.0572	6.1576	6.1672	6.2492	6.2513	6.4471	6.4751
	6.1195	6.2205	6.2314	6.3254	6.3217	6.5190	6.5474
	6.1607	6.2649	6.2685	6.3646	6.3627	6.5594	6.5948
	6.1897	6.2926	6.2962	6.4036	6.3890	6.5914	6.6230
	6.2020	6.3068	6.3100	6.4061	6.4112	6.6015	6.6374
	6.2314	6.3379	6.3508	6.4394	6.4456	6.6383	6.6777
	5.2837	5.3609	5.3720	5.4498	5.4360	5.5851	5.6206
	5.3169	5.3950	5.4042	5.4809	5.4719	5.6254	5.6563
	5.3425	5.4227	5.4367	5.5108	5.5025	5.6553	5.6878
	5.3726	5.4525	5.4645	5.5429	5.5325	5.6848	5.7208
	5.3990	5.4794	5.4920	5.5710	5.5611	5.7147	5.7515
	4.4488	4.5046	4.5143	4.5676	4.5602	4.6733	4.7003
	4.4691	4.5298	4.5371	4.5933	4.5845	4.6961	4.7243
	3.4507	3.4875	3.4916	3.5356	3.5197	3.5938	3.6120
	3.4707	3.5073	3.5109	3.5520	3.5391	3.6144	3.6322
	2.7018	2.7258	2.7290	2.7574	2.7422	2.7942	2.8047
	2.7044	2.7272	2.7330	2.7570	2.7470	2.7956	2.8096
	1.8400	1.8469	1.8511	1.8638		1.8813	1.8913
	1.4724	1.4861	1.4797	1.4937		1.5039	1.5092
	1.6161	1.6253	1.6216	1.6423		1.6512	1.6570
	1.1676	1.1736	1.1745	1.1785	1.1774	1.1869	1.1912
	1.1698	1.1754	1.1775	1.1802	1.1802	1.1889	1.1942
Series I, 413.47 K							
	5.6252	5.7062	5.7067	5.7893	5.7790	5.9273	5.9648
	5.6341	5.7160	5.7203	5.7965	5.7930	5.9376	5.9770
	5.9211	6.0107	6.0138	6.0982	6.0900	6.2505	6.2907
	5.1428	5.2122	5.2272	5.2801	5.2863	5.4017	5.4469
	5.1458	5.2137	5.2312	5.2802	5.2886	5.4034	5.4506
	5.2210	5.2900	5.3092	5.3577	5.3692	5.4859	5.5341
	4.0954	4.1400	4.1545	4.1839	4.1928	4.2717	4.3038
	4.2966	4.3529		4.3936	4.4039	4.5018	
	3.5153	3.5587		3.5864	3.5876	3.6610	
	4.2992	4.3597		4.3955	4.3977	4.5086	
	2.8752	2.9081		2.9224	2.9244	2.9803	
	2.9543	2.9887		3.0042	3.0056	3.0641	
	2.1023	2.1233		2.1277	2.1305	2.1617	
	2.1373	2.1500		2.1581	2.1735	2.1965	
	2.1770	2.1902		2.1987	2.2140	2.2382	
	1.1684	1.1702		1.1721	1.1775	1.1854	
	1.1795	1.1832		1.1850	1.1865	1.1976	
	1.2539	1.2570		1.2596	1.2613	1.2726	
	1.2515	1.2548		1.2574	1.2590	1.2708	

TABLE 1—continued

y: 0	0.10475	0.20654	0.19461	0.39886	0	0.10475	0.20654	0.19461	0.39886
$m/\text{mol kg}^{-1}$									
Series I, 445.25 K									
6.9600	7.0749	7.1673	7.1546	7.3776	7.2121	7.3350	7.4230	7.4130	7.6472
7.2337	7.3607	7.4510	7.4378	7.6724	6.0856	6.1823	6.2494	6.2382	6.4191
6.7824	6.8936	6.9757	6.9630	7.1770	5.4277	5.5054	5.5605	5.5519	5.7063
5.6197	5.7030	5.7584	5.7431	5.9050	5.0007	5.0718	5.1176	5.1015	5.2443
5.3042	5.3772	5.4306	5.4213	5.5692	3.7511	3.7919	3.8209	3.8090	3.8998
2.8560	2.8833	2.9003	2.8882	2.9514	2.9826	3.0113	3.0294	3.0183	3.0851
1.9242	1.9375	1.9459	1.9327	1.9733	1.9930	2.0073	2.0161	2.0032	2.0450
1.1715	1.1694	1.1740	1.1712	1.1870	1.2010	1.1983	1.2020	1.2019	1.2162
1.2307	1.2289	1.2326	1.2324	1.2472	1.2628	1.2600	1.2636	1.2642	1.2801
1.2652	1.2642	1.2682	1.2671	1.2829	1.3407	1.3397	1.3440	1.3426	1.3601
Series I, 474.12 K									
4.3545	4.4019	4.4328	4.4276	4.5289	4.4907	4.5379	4.5736	4.5641	4.6703
4.5397	4.5888	4.6246	4.6174	4.7228	6.8684	6.9630	7.0348	7.0200	7.2147
5.9246	5.9993	6.0568	6.0486	6.2002	5.9940	6.0680	6.1317	6.1165	6.2748
5.0236	5.0818	5.1259	5.1130	5.2366	5.0720	5.1303	5.1792	5.1632	5.2854
3.9171	3.9569	3.9839	3.9817	4.0592	3.9193	3.9632	3.9893	3.9900	4.0663
3.0032	3.0250	3.0471	3.0346	3.0936	3.0188	3.0408	3.0618	3.0479	3.1070
1.8895	1.8982	1.9066	1.8950	1.9262	1.9009	1.9097	1.9190	1.9065	1.9383
1.0440	1.0362	1.0399	1.0413	1.0494	1.0397	1.0322	1.0354	1.0365	1.0448
1.0409	1.0330	1.0365	1.0375	1.0460					

y: 0	0.60051	0.79886	0.79754	0	0.60051	0.79886	0.79754
$m/\text{mol kg}^{-1}$							
Series II, 382.76 K							
3.9309	4.2062	4.2829	4.2830	4.1095	4.4050	4.4931	4.4911
5.7000	6.2246	6.3740	6.3763	5.7096	6.2367	6.3859	6.3822
5.8288	6.3724	6.5300	6.5289	5.9617	6.5312	6.6901	6.6928
4.8109	5.2007	5.3149	5.3160	4.9693	5.3826	5.5036	5.5038
4.3171	4.6390	4.7338	4.7358	4.5001	4.8477	4.9492	4.9510
3.1887	3.3756	3.4342	3.4352	3.3119	3.5126	3.5748	3.5760
3.3461	3.5507	3.6149	3.6148	2.1162	2.2028	2.2360	2.2364
2.2005	2.2943	2.3286	2.3292	1.0840	1.1058	1.1212	1.1209
1.0911	1.1127	1.1291	1.1285	1.1105	1.1324	1.1499	1.1491
1.1181	1.1402	1.1580	1.1574	1.1383	1.1611	1.1795	1.1787
1.1457	1.1694	1.1875	1.1873	1.1680	1.1937	1.2113	1.2119
0.5891	0.5995	0.6021	0.6003	0.5895	0.5997	0.6025	0.6007
0.5904	0.6001	0.6034	0.6017	0.5908	0.6003	0.6039	0.6022
0.5932	0.6014	0.6062	0.6044				

TABLE 1—*continued*

<i>y</i> :	0	0.60051	0.79886	0.79754	0	0.60051	0.79886	0.79754
Series II, 413.47 K								
5.6551	6.1201	6.2492	6.2590	6.3352	6.8930	7.0494	7.0541	
6.5393	7.1277	7.2912	7.2928	3.6493	3.8641	3.9364	3.9380	
3.7879	4.0169	4.0933	4.0946	4.2107	4.4887	4.5749	4.5769	
4.3425	4.6364	4.7262	4.7289	4.8597	5.2176	5.3244	5.3257	
5.0296	5.4092	5.5198	5.5229	2.4570	2.5547	2.6035	2.6046	
2.5373	2.6444	2.6916	2.6926	2.7910	2.9219	2.9728	2.9746	
2.8878	3.0274	3.0798	3.0815	3.1788	3.3466	3.4058	3.4063	
1.0959	1.1138	1.1304	1.1290	1.1371	1.1590	1.1769	1.1725	
1.1822	1.2041	1.2237	1.2221	1.1860	1.2089	1.2276	1.2265	
1.2236	1.2475	1.2680	1.2668	0.5676	0.5725		0.5758	
0.5679	0.5744		0.5762	0.5701	0.5750		0.5768	
0.5690	0.5741		0.5776	0.5695	0.5745		0.5781	
0.6208	0.6238		0.6315	0.6253	0.6294		0.6353	
1.5993	1.6478	1.6707	1.6653	1.6003	1.6494	1.6716	1.6662	
1.5974	1.6465	1.6685	1.6631	2.2216	2.3099	2.3465	2.3410	
2.9637	3.1160	3.1658	3.1610	2.9696	3.1231	3.1720	3.1677	
2.9902	3.1456	3.1949	3.1911					
Series II, 445.25 K								
3.0313	3.1734	3.2217	3.2172	3.0925	3.2405	3.2892	3.2856	
3.2397	3.3999	3.4518	3.4485	2.2657	2.3516	2.3835	2.3768	
2.2659	2.3518	2.3835	2.3772	2.2674	2.3536	2.3853	2.3789	
3.5649	3.7557	3.8146	3.8084	3.5682	3.7583	3.8180	3.8118	
3.5705	3.7613	3.8203	3.8143	4.5727	4.8610	4.9461	4.9499	
4.5711	4.8613	4.9454	4.9376	4.5644	4.8526	4.9375	4.9312	
5.6069	6.0085	6.1203	6.1160	5.5928	5.9928	6.1058	6.0990	
5.5484	5.9434	6.0543	6.0473	0.5827	0.5906	0.5937	0.5930	
0.5829	0.5911	0.5940	0.5933	0.5827	0.5909	0.5936	0.5931	
0.5831	0.5914	0.5940	0.5936	0.5835	0.5919	0.5944	0.5941	
0.9236	0.9420	0.9477	0.9479	0.9240	0.9423	0.9480	0.9482	
0.9244	0.9428	0.9486	0.9487	1.4937	1.5364	1.5498	1.5486	
1.4937	1.5367	1.5498	1.5487					
Series II, 474.12 K								
3.1441	3.2829	3.3266	3.3221	3.1543	3.2948	3.3374	3.3329	
3.2429	3.3907	3.4347	3.4300	5.5508	5.9028	5.9932	5.9875	
5.5656	5.9170	6.0111	6.0057	6.7154	7.1826	7.2938	7.2954	
6.7060	7.1704	7.2846	7.2818	4.2332	4.4635	4.5260	4.5220	
4.1696	4.3947	4.4556	4.4516	2.0860	2.1562	2.1798	2.1738	
2.0801	2.1493	2.1739	2.1660	2.0791	2.1492	2.1721	2.1671	
2.0812	2.1513	2.1746	2.1692	1.0357	1.0592	1.0633	1.0632	
1.0364	1.0599	1.0641	1.0639	0.6037	0.6144	0.6153	0.6146	
0.6026	0.6135	0.6139	0.6136					

after the solutions were inadvertently allowed to go to dryness at 413.47 K. At the conclusion of series I it was confirmed that salt had crept out of these two cups as the solutions went to dryness. The remaining voids in table 1 represent those few occasions when, for some unknown reason, a result was obviously erroneous.

Results were experimentally limited on the dilute end by a small temperature gradient across the copper block. Results from series I obviously had the same gradient

(about 0.02 K) and limitation (about  $1 \text{ mol kg}^{-1}$  of NaCl) as the previous work.<sup>(2)</sup> The improved temperature control for series II resulted in a lower temperature gradient (less than 0.01 K) but this still limited the results to about  $0.6 \text{ mol kg}^{-1}$  of NaCl. The most dilute solutions in table 1 were corrected for this gradient by rotating the samples through  $\pi$  after they had equilibrated. Re-equilibration resulted in a new set of molalities which differed by as much as 2 per cent from those obtained before rotation of the solutions. The corrected molalities listed in table 1 for the dilute solutions are the averages of the two molalities obtained on either side of the temperature gradient. These corrected molalities are estimated to be uncertain by not more than 0.4 per cent.

Osmotic coefficients  $\phi$  were calculated from the isopiestic molalities in table 1 by means of the relation:

$$\phi_x = \left\{ \sum_i (m_i)_s / \sum_i (m_i)_x \right\} \phi_s = R \phi_s, \quad (1)$$

where  $m_i$  is the molality of ion  $i$ .  $R$  is the isopiestic ratio and is frequently used in place of isopiestic molalities to report isopiestic results. Subscripts  $s$  and  $x$  refer, respectively, to the standard solution and the solution whose properties are unknown. Osmotic coefficients of the standard solutions (sodium chloride in the present case) were calculated from the equation given by Silvester and Pitzer.<sup>(5)</sup>

The resulting osmotic coefficients for these mixtures (and also for pure NaCl and KCl) at the four experimental temperatures are shown in figures 1 to 4 as a function of the total molality. (In the interest of clarity only about half of the experimental

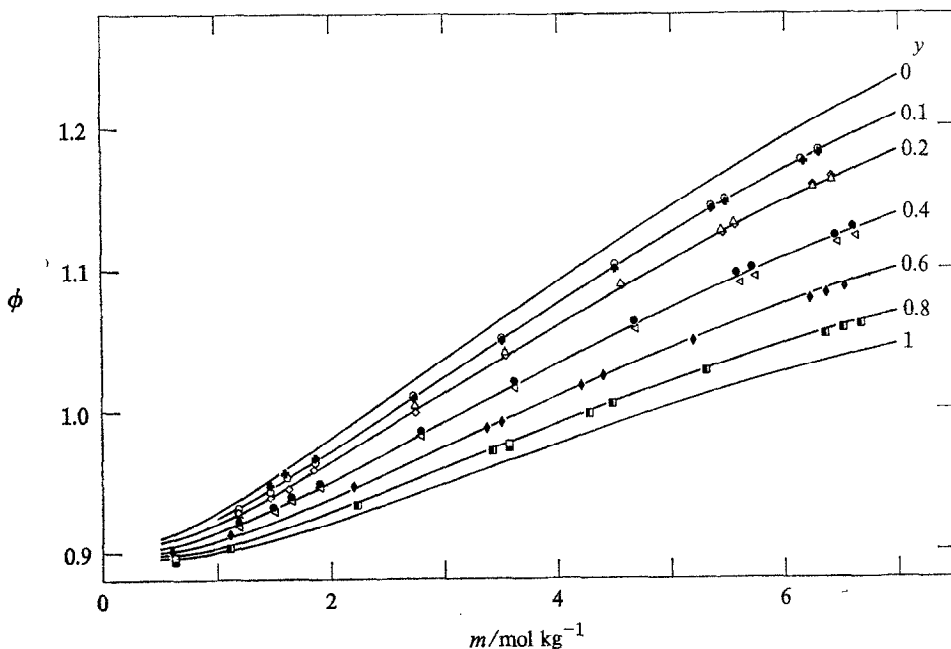


FIGURE 1. Osmotic coefficients of aqueous solutions of  $(1-y)\text{NaCl} + y\text{KCl}$  at 382.76 K as a function of total molality  $m$ .  $\circ$ ,  $y = 0.10475$ ;  $+$ ,  $y = 0.10034$ ;  $\diamond$ ,  $y = 0.20654$ ;  $\triangle$ ,  $y = 0.19461$ ;  $\bullet$ ,  $y = 0.39886$ ;  $\triangleleft$ ,  $y = 0.42006$ ;  $\blacklozenge$ ,  $y = 0.60051$ ;  $\blacksquare$ ,  $y = 0.79886$ ;  $\square$ ,  $y = 0.79754$ .

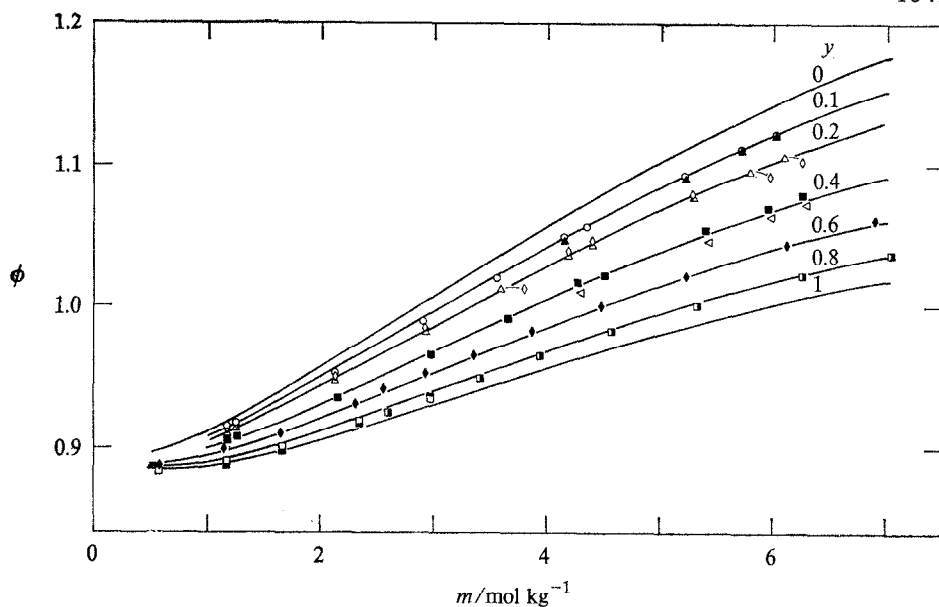


FIGURE 2. Osmotic coefficients of aqueous solutions of  $(1-y)\text{NaCl} + y\text{KCl}$  at 413.47 K as a function of total molality  $m$ .  $\circ$ ,  $y = 0.10475$ ;  $\blacktriangle$ ,  $y = 0.10034$ ;  $\diamond$ ,  $y = 0.20654$ ;  $\triangle$ ,  $y = 0.19461$ ;  $\bullet$ ,  $y = 0.39886$ ;  $\nabla$ ,  $y = 0.42006$ ;  $\blacklozenge$ ,  $y = 0.60051$ ;  $\blacksquare$ ,  $y = 0.79886$ ;  $\square$ ,  $y = 0.79754$ .

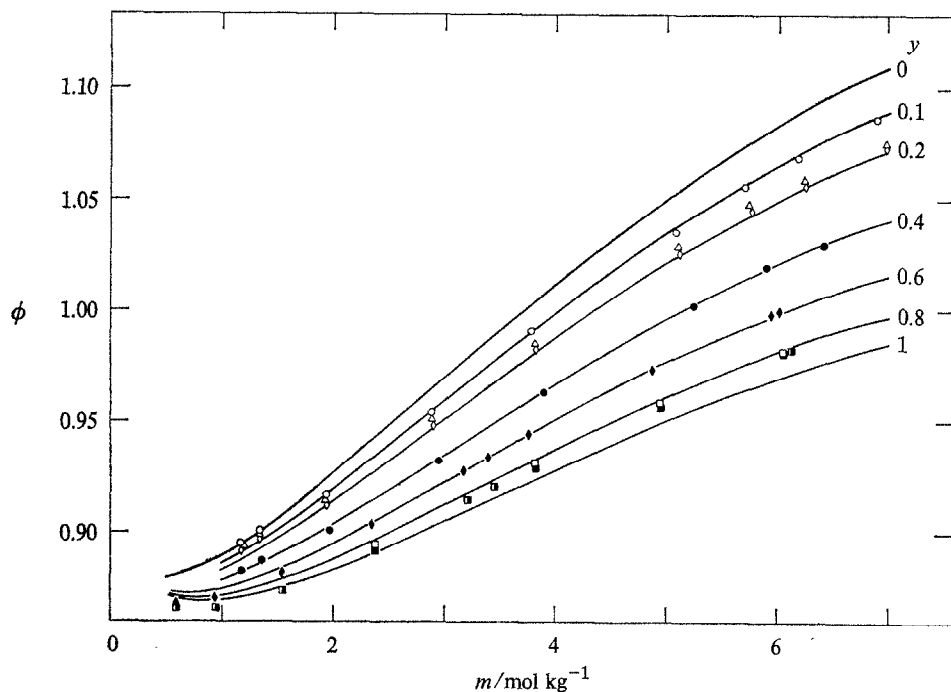


FIGURE 3. Osmotic coefficients of aqueous solutions of  $(1-y)\text{NaCl} + y\text{KCl}$  at 445.25 K as a function of total molality  $m$ .  $\circ$ ,  $y = 0.10475$ ;  $\diamond$ ,  $y = 0.20654$ ;  $\triangle$ ,  $y = 0.19461$ ;  $\bullet$ ,  $y = 0.39886$ ;  $\nabla$ ,  $y = 0.42006$ ;  $\blacklozenge$ ,  $y = 0.60051$ ;  $\blacksquare$ ,  $y = 0.79886$ ;  $\square$ ,  $y = 0.79754$ .

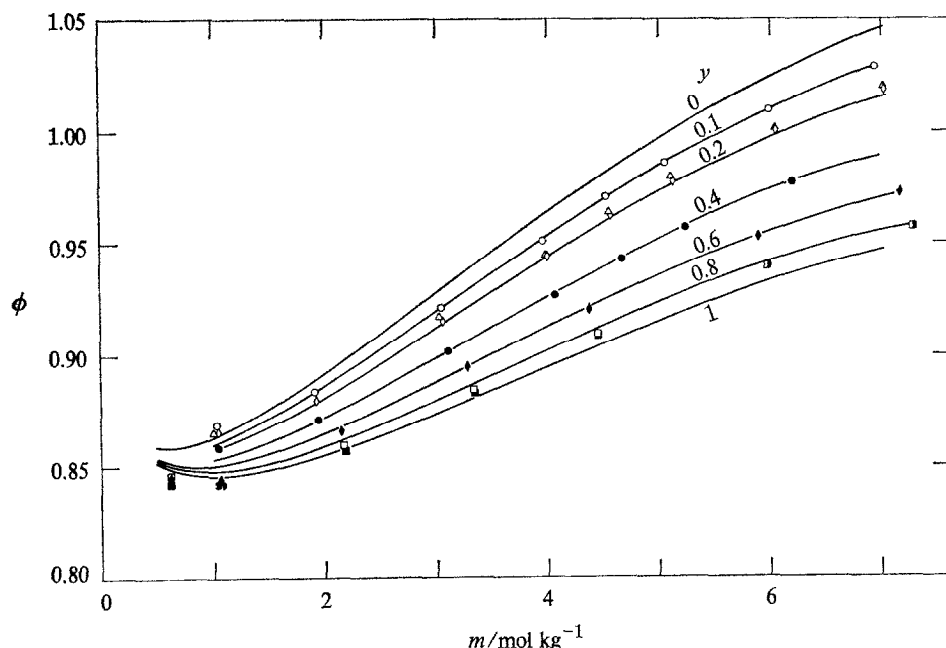


FIGURE 4. Osmotic coefficients of aqueous solutions of  $(1-y)\text{NaCl} + y\text{KCl}$  at 474.12 K as a function of total molality  $m$ .  $\circ$ ,  $y = 0.10475$ ;  $\diamond$ ,  $y = 0.20654$ ;  $\triangle$ ,  $y = 0.19461$ ;  $\bullet$ ,  $y = 0.39886$ ;  $\triangleleft$ ,  $y = 0.42006$ ;  $\blacklozenge$ ,  $y = 0.60051$ ;  $\blacksquare$ ,  $y = 0.79886$ ;  $\square$ ,  $y = 0.79754$ .

points are plotted in figures 1 to 4.) The osmotic coefficients of pure NaCl and KCl solutions were taken from Silvester and Pitzer<sup>(5)</sup> and from our previous work,<sup>(2)</sup> respectively. Lines drawn in figures 1 to 4 for the nominal mole fractions of KCl shown were calculated from an equation developed by Pitzer.<sup>(12)</sup> Parameters for this equation were obtained from a least-squares fit to the experimental results at each temperature. We estimate that, with the possible exception of the most dilute solutions, our results are consistent to about 0.002 in  $R$ . The absolute accuracy of the osmotic coefficients cannot, of course, be better than the reliability of  $\phi_s$ . (Silvester and Pitzer<sup>(5)</sup> give the standard deviation of fit of their equations to the osmotic coefficients of NaCl as 0.005.) A significant feature of the isopiestic method is that, if better standard data become available, the results can easily be recalculated from the isopiestic molalities.

Several trends are evident from the results presented in figures 1 to 4. The osmotic coefficients of these solutions uniformly decrease as the temperature increases. (This behavior is true for this temperature range only as the osmotic coefficients of NaCl and KCl solutions pass through a maximum below 373 K.<sup>(2,13)</sup>) In addition, the osmotic coefficients become somewhat less dependent on molality as the temperature increases. The addition of a small amount of KCl to a pure NaCl solution has a much larger effect on the osmotic coefficient than does the corresponding addition of a small amount of NaCl to a pure KCl solution. The deviation of the experimental points from the calculated lines is somewhat worse at the lower molalities (as expected because of the temperature gradient across the copper block).



Pitzer<sup>(12)</sup> has developed a set of equations that have been successfully used to describe the thermodynamic properties of a variety of aqueous electrolyte solutions at 298.15 K.<sup>(14)</sup> These equations have also been applied to aqueous NaCl solutions over the temperature range of 273 to 573 K,<sup>(5)</sup> and to numerous electrolyte mixtures at 298.15 K.<sup>(15)</sup> As before,<sup>(2)</sup> we have chosen to use Pitzer's equations to describe these experimental results. His equation for the osmotic coefficient  $\phi$  of a mixture of two 1—1 electrolytes (MX and NX) having a common anion X is

$$\phi - 1 = -A\{m^{1/2}/(1 + bm^{1/2})\} + m\{(1-y)B_{MX}^\phi + yB_{NX}^\phi + y(1-y)\Theta_{MN}\} \\ + m^2\{(1-y)C_{MX}^\phi + yC_{NX}^\phi + y(1-y)\Psi_{MNX}\}, \quad (2)$$

where  $B^\phi$  is defined as

$$B^\phi = \beta^{(0)} + \beta^{(1)}\exp(-\alpha m^{1/2}). \quad (3)$$

$A$  is the Debye-Hückel coefficient (calculated as in reference 5),  $m$  the total molality,  $y$  the mole fraction  $m(NX)/\{m(MX) + m(NX)\}$ , and  $b$  and  $\alpha$  are constants whose values are somewhat arbitrarily fixed. Following Pitzer<sup>(12)</sup> we have set  $b$  and  $\alpha$  equal to 1.2 and 2.0 kg<sup>1/2</sup> mol<sup>-1/2</sup>, respectively.  $\beta^{(0)}$ ,  $\beta^{(1)}$ , and  $C^\phi$  are parameters which are obtained from studies of the pure electrolytes only. The pure-electrolyte parameters for KCl were taken from our previous work<sup>(2)</sup> while those for NaCl were calculated from the equations of Silvester and Pitzer.<sup>(5)</sup>  $\Theta$  and  $\Psi$  are the mixing parameters which are determined from a least-squares fit of equation (2) to experimental results for mixed-electrolyte solutions. Following Pitzer and Kim,<sup>(15)</sup> we have assumed that  $\Theta$  is independent of molality. This independence is explicit in equation (2) while the original form contains terms that allow  $\Theta$  to vary with molality.

A general least-squares computer program<sup>(16)</sup> was used to obtain values of the mixing parameters from a fit of equation (2) to the osmotic coefficients obtained from table 1. Three cases were examined: case I,  $\Theta = 0$ ,  $\Psi = 0$ ; case II,  $\Theta \neq 0$ ,  $\Psi = 0$ ; and case III,  $\Theta \neq 0$ ,  $\Psi \neq 0$ . The resulting parameters (where applicable) are

TABLE 2. Mixing parameters for NaCl + KCl mixtures

Case I		Case II		$\frac{\Theta_{NaK}}{\text{kg mol}^{-1}}$	Case III	$\sigma(\phi)$
$T/K$	$\sigma(\phi)$	$\frac{\Theta_{NaK}}{\text{kg mol}^{-1}}$	$\sigma(\phi)$		$\frac{\Psi_{NaKCl}}{\text{kg}^2 \text{mol}^{-2}}$	
298.15	0.0116	-0.0187	0.0006	-0.0154	-0.00078	0.0004
382.76	0.0108	-0.0132	0.0025	-0.0136	0.00007	0.0025
413.47	0.0091	-0.0121	0.0030	-0.0147	0.00052	0.0029
445.25	0.0094	-0.0116	0.0040	-0.0155	0.00068	0.0040
474.12	0.0088	-0.0101	0.0044	-0.0130	0.00054	0.0044

listed in table 2 along with the standard deviation of fit  $\sigma(\phi)$  for each case. Parameters listed for 298.15 K were obtained from a fit of equation (2) to the precise isopiestic data of Robinson.<sup>(11)</sup> The results of Robinson<sup>(11)</sup> have also been treated by Pitzer and Kim<sup>(15)</sup> who obtained somewhat different parameters from those listed in table 2. A probable reason for the difference is that, in order to be consistent, we used Silvester

and Pitzer's<sup>(5)</sup> formulation to generate osmotic coefficients for the standard NaCl solutions at 298.15 K.

One important result in table 2 is that one can fit all of the osmotic coefficients to about 1 per cent using only the pure-electrolyte parameters (case I). This case is analogous to the simple method of Lietzke and Stoughton<sup>(17)</sup> for predicting the osmotic coefficient of mixtures. It is obvious that Robinson's results<sup>(11)</sup> give a better fit to equation (2) than our results and that the fit becomes somewhat worse as the temperature increases. Omission of the dilute solutions improved the standard deviation but did not significantly alter the parameters  $\Theta$  and  $\Psi$ . Therefore all of our results were used in determining the values listed in table 2. It is obvious that, with the possible exception of the results at 298.15 K, there is no improvement in the fit from including  $\Psi$ . It is clear from equation (2) that the maximum effect of  $\Theta$  (and  $\Psi$ , if used) occurs at high molalities and  $\gamma = 0.5$ . Even under these conditions the contribution to  $\phi$  of  $\Psi$  is only about 0.006 while that of  $\Theta$  is about 0.02. We do not believe that the inclusion of  $\Psi$  can be justified by these osmotic coefficients.

The mixing parameter  $\Theta$  has the simple temperature dependence shown in figure 5. This simplicity can be contrasted with that found by Silvester and Pitzer<sup>(5)</sup> for the temperature dependence of the pure-electrolyte parameters  $\beta^{(0)}$ ,  $\beta^{(1)}$ , and  $C^\phi$  for NaCl solutions as well as that observed for KCl,  $\text{MgCl}_2$ , and  $\text{CaCl}_2$ .<sup>(2)</sup> Error bars in figure 5 are the standard errors assigned from a least-squares fit to the experimental results assuming only random errors. The line in figure 5 represents the indicated equation which was obtained from a least-squares fit to the  $\Theta$  values. The resulting standard deviation of fit  $\sigma(\Theta)$  is 0.00022.

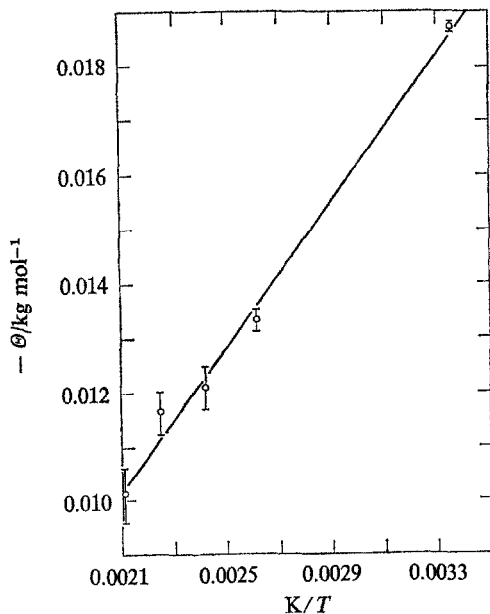


FIGURE 5. The mixing parameter  $\Theta$  for NaCl + KCl mixtures as a function of temperature. The line is calculated from  $\Theta/\text{kg mol}^{-1} = -6.726 \text{ K}/T + 0.0039$ .

Pitzer's equation<sup>(12)</sup> for the activity coefficient  $\gamma_{MX}$  of solute MX that corresponds to equation (2) is

$$\ln \gamma_{MX} = -A\{m^{1/2}/(1+bm^{1/2}) + (2/b)\ln(1+bm^{1/2})\} + m\{B_{MX}^{\phi} + y(B_{NX}^{\phi} - B_{MX}^{\phi} + \Theta_{MN})\} + m^2\{3C_{MX}^{\phi}/2 + y(C_{NX}^{\phi} - C_{MX}^{\phi} + \Psi_{MNX}/2) + y(1-y)\Psi_{MNX}/2\}, \quad (4)$$

where  $B^{\gamma}$  is defined as

$$B^{\gamma} = 2\beta^{(0)} + (2\beta^{(1)}/\alpha^2 m)\{1 - \exp(-\alpha m^{1/2})(1 + \alpha m^{1/2} - \alpha^2 m/2)\}, \quad (5)$$

and the other symbols are the same as in equation (2). The analogous equation for  $\gamma_{NX}$  can be obtained by transposing subscripts and replacing  $y$  with  $(1-y)$ . Thus, using the parameters in table 2 that were derived from osmotic coefficients, one can calculate the corresponding activity coefficients. One should keep in mind that the validity of such calculated activity coefficients depends on how accurately equation (2) describes the osmotic coefficients in dilute solutions for which we have no experimental results.

Calculated activity coefficients for the electrolyte mixtures are shown in figures 6 to 9 for temperatures of 383.15, 413.15, 443.15, and 473.15 K, respectively. The

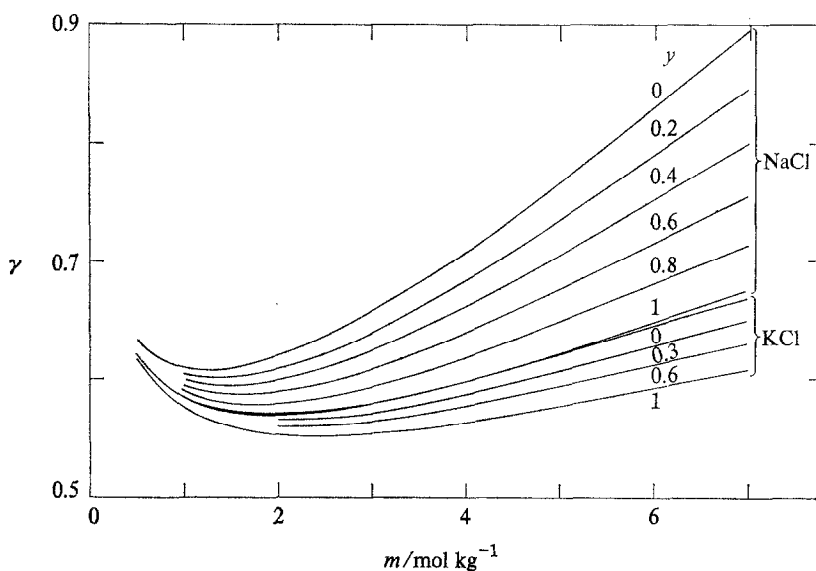


FIGURE 6. Activity coefficients  $\gamma$  of NaCl and KCl in aqueous solutions of  $(1-y)\text{NaCl} + y\text{KCl}$  at 383.15 K as a function of total molality  $m$ .

parameters for equation (4) were adjusted graphically to these rounded temperatures. The adjustments were very minor and were made easily with the required accuracy. There are three main temperature-dependent characteristics of the results shown in these four figures. First there is the monotonic decrease in the activity coefficient as the temperature is increased. Secondly, dependence of the activity coefficient on molality, particularly at the higher molalities, decreases as the temperature increases.

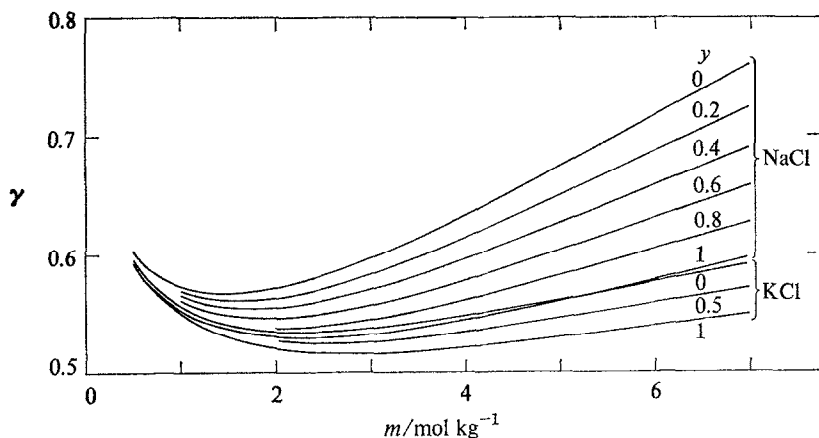


FIGURE 7. Activity coefficients  $\gamma$  of NaCl and KCl in aqueous solutions of  $(1 - y)\text{NaCl} + y\text{KCl}$  at 413.15 K as a function of total molality  $m$ .

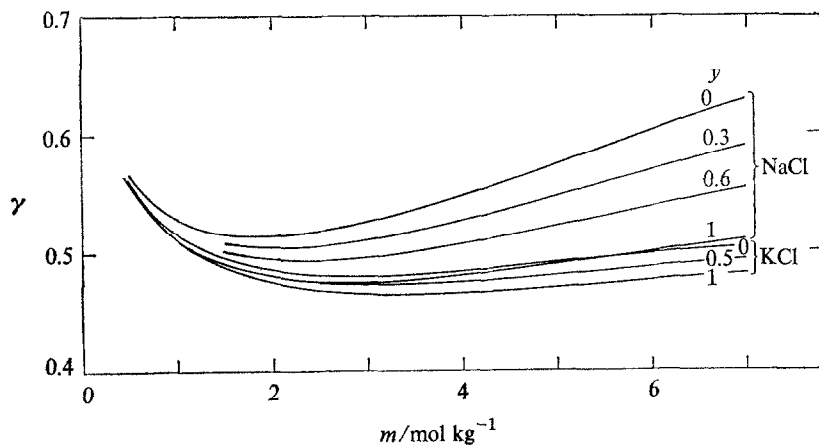


FIGURE 8. Activity coefficients  $\gamma$  of NaCl and KCl in aqueous solutions of  $(1 - y)\text{NaCl} + y\text{KCl}$  at 443.15 K as a function of total molality  $m$ .

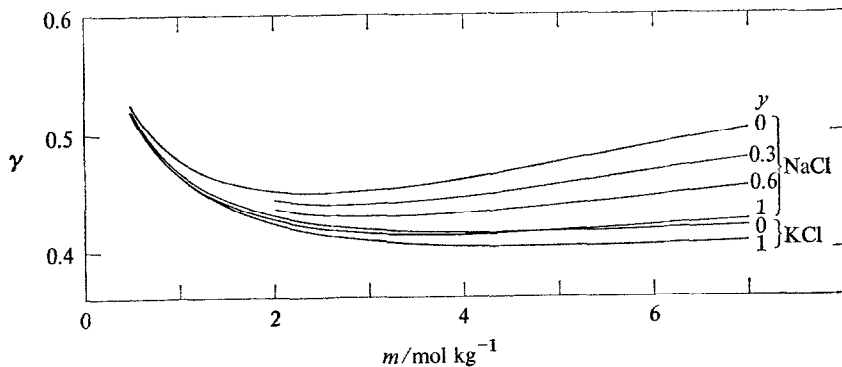


FIGURE 9. Activity coefficients  $\gamma$  of NaCl and KCl in aqueous solutions of  $(1 - y)\text{NaCl} + y\text{KCl}$  at 473.15 K as a function of total molality  $m$ .

Thirdly, the minimum in the activity curves shifts to higher molalities as the temperature increases. These characteristics are, of course, limited to the temperature range covered in figures 6 to 9. In the temperature range covered by figures 6 to 9, the activity coefficient of NaCl is affected much more by the addition of KCl than the converse. Also at these temperatures, the trace activity coefficients of NaCl and KCl are very nearly equal, *i.e.* the activity coefficient of infinitely dilute NaCl in a KCl solution is approximately equal to the activity coefficient of infinitely dilute KCl in a NaCl solution of the same molality. These latter two features are also true at 298.15 K.<sup>(11)</sup>

Harned's rule has been found to be very useful for describing mixed electrolyte systems.<sup>(18)</sup> For a mixture of two 1—1 electrolytes at constant total molality  $m$ , Harned's rule can be written as

$$\ln \gamma_1 = \ln \gamma_1^\circ + A_{12}m_2 = \ln \gamma_1^\circ + A_{12}ym, \quad (6)$$

where the subscripts refer to the two electrolytes,  $y$  is the mole fraction of electrolyte 2,  $\gamma_1^\circ$  is the activity coefficient of pure 1 at molality  $m$ , and  $A_{12}$  is a constant at constant total molality but has been found to be a function of molality. An analogous equation can be written for the second electrolyte but in general  $A_{21}$  is not equal to  $A_{12}$ . It can be shown from equations (4) and (5) that, by setting the mixing parameter  $\Psi = 0$ , we are forcing the present system to obey Harned's rule with

$$A_{12} = \beta_2^{(0)} - \beta_1^{(0)} + (\beta_2^{(1)} - \beta_1^{(1)})\exp(-\alpha m^{1/2}) + (C_2^\phi - C_1^\phi)m + \Theta_{12}. \quad (7)$$

An analogous equation can be written for the second electrolyte from which it may be deduced that, since  $\Theta_{12} = \Theta_{21}$ ,

$$A_{21} = -A_{12} + 2\Theta_{12}. \quad (8)$$

Figures 10 and 11 are Harned-type plots for the activity coefficients of NaCl and KCl, respectively, in their mixed solutions at a constant molality of 4 mol kg<sup>-1</sup>. Included in these two figures are Wood's calculations<sup>(6)</sup> and Robinson's description<sup>(11)</sup> of his own results at 298.15 K. Wood's calculations were based on an expression for  $\ln \gamma^\circ$  (a Debye-Hückel term plus a term linear in the ionic strength) and Harned's rule with an  $A$  parameter independent of molality. Thus it is not surprising that there are significant differences between his calculations and our results (figure 10). We suggest that, in the case of KCl (figure 11), the gross differences between our work and that of Wood reflects his reliance on the isopiestic results of Soldano *et al.*<sup>(7,10)</sup> Robinson<sup>(11)</sup> found that, while his KCl results could be adequately represented with a simple Harned's rule, a small additional term (quadratic in the molality) was required to represent the NaCl data accurately. This term accounts for the slight curvature seen in his results in figure 10. It would not do justice to Robinson's results to imply that our simplified treatment of them gives an equally accurate representation. However, we do think that our treatment, which is consistent for the five temperatures, is adequate for most purposes. In the interest of clarity we have not included Pitzer and Kim's<sup>(15)</sup> treatment of Robinson's results. They retained the mixing parameter  $\Psi$  which gives rise to a quadratic term in equation (6). As a consequence their results are somewhat closer than ours to those of Robinson at zero molality fractions. At high molality fractions there is no significant difference between the three treatments.

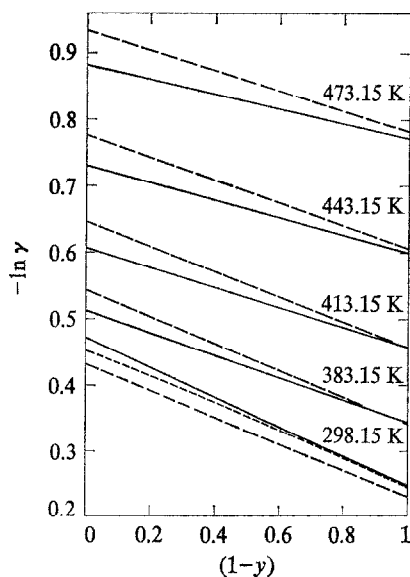


FIGURE 10. Harned plots of the activity coefficient  $\gamma$  of NaCl in aqueous  $(1 - y)\text{NaCl} + y\text{KCl}$  mixtures at constant total molality ( $4 \text{ mol kg}^{-1}$ ) at the indicated temperatures as a function of  $(1 - y)$ . —, this work; ---, Wood;<sup>(6)</sup> - · - ·, Robinson.<sup>(11)</sup>

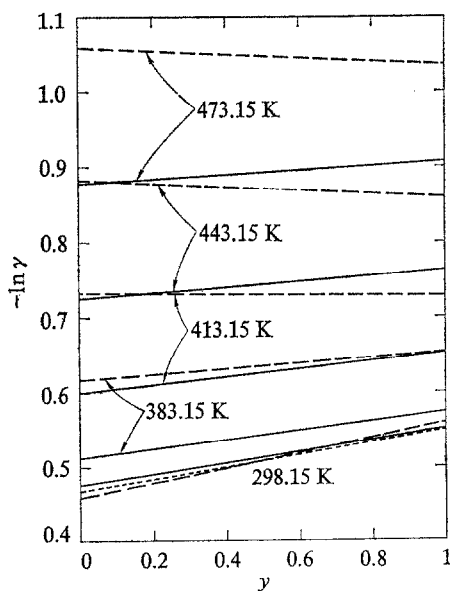


FIGURE 11. Harned plots of the activity coefficient  $\gamma$  of KCl in aqueous  $(1 - y)\text{NaCl} + y\text{KCl}$  mixtures at constant total molality ( $4 \text{ mol kg}^{-1}$ ) at the indicated temperatures as a function of  $y$ . —, this work; ---, Wood;<sup>(6)</sup> - · - ·, Robinson.<sup>(11)</sup>

For a two-component (excluding the water) system, Pitzer's treatment requires symmetric equations for the two electrolytes. It is interesting that Robinson<sup>(11)</sup> found experimentally that this was not necessary for the NaCl+KCl system at 298.15 K.

In their study of aqueous mixtures of alkali-metal halides Covington, Lilley, and Robinson<sup>(19)</sup> used a deviation function  $\Delta$ , defined as

$$\Delta = 2\phi - 2(1-y)\phi_1^\circ - 2y\phi_2^\circ, \quad (9)$$

where the subscripts refer to the two electrolytes,  $y$  is the molality fraction of electrolyte 2,  $\phi^\circ$  is the osmotic coefficient of the pure electrolyte at the same molality as the mixed solution, and  $\phi$  is the osmotic coefficient of the mixed solution. To represent the departure from ideality ( $\Delta = 0$ ), they used

$$\Delta = y(1-y)(b_1m + b_2m^2), \quad (10)$$

where  $b_1$  and  $b_2$  are constants for a given electrolyte pair. If equation (10) is valid, then it can be shown<sup>(18)</sup> that the excess Gibbs free energy  $G^E$  of a solution is given by

$$G^E = y(1-y)m^2RT(b_1 + b_2m/2), \quad (11)$$

where  $R$  is the gas constant and  $T$  is the temperature. Covington, Lilley, and Robinson, used (11) to calculate  $G^E$  for several electrolyte pairs. From equations (2) and (4), and the definition of  $G^E$  it can be shown that in the present case

$$G^E = 2y(1-y)m^2RT(\Theta + m\Psi/2). \quad (12)$$

Since we have set  $\Psi = 0$ ,  $G^E$  is given by the simple expression:

$$G^E = 2y(1-y)RT\Theta. \quad (13)$$

Excess Gibbs free energies calculated using equation (13) are given in table 3. As can be seen in table 3, the values obtained from our treatment of Robinson's results<sup>(11)</sup> are in reasonable agreement with those given by Covington, Lilley, and Robinson.<sup>(19)</sup> To a very good approximation  $G^E$  is independent of temperature.

TABLE 3. Excess Gibbs free energies  $G^E$  for 0.5NaCl + 0.5KCl as a function of total molality  $m$

$m/\text{mol kg}^{-1}$ $T/\text{K}$	1	2	3	4	5	6
	$G^E/\text{J kg}^{-1}$					
298.15 <sup>a</sup>	-17	-71	-167	-310		
298.15 <sup>b</sup>	-23	-92	-207	-368		
383.15	-22	-86	-194	-346	-540	-778
413.5	-21	-84	-190	-338	-528	-760
443.15	-21	-82	-185	-330	-515	-742
473.15	-20	-80	-181	-322	-503	-724

<sup>a</sup> From reference 19.

<sup>b</sup> Our treatment of Robinson's results.<sup>(11)</sup>

Subsequent papers will deal with the charge asymmetric mixture NaCl + CaCl<sub>2</sub>, the temperature dependence of the parameters  $\beta^{(0)}$ ,  $\beta^{(1)}$ ,  $C^\phi$ , and  $\Theta$ , and the application of these results to hydrothermal solutions.

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