of known strength of potassium chloride at 25°, have been reported.

2. From these the activity coefficients of alkaline bromides and iodides have been computed at concentrations of from 0.1 to 4 *M*.

3. Activity coefficients determined by this method are found to be in good agreement with the best electromotive force and freezing point data.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, AUCKLAND UNIVERSITY COLLEGE]

The Activity Coefficients of Alkali Nitrates, Acetates and *p*-Toluenesulfonates in Aqueous Solution from Vapor Pressure Measurements

BY ROBERT A. ROBINSON

The isopiestic method of determining the vapor pressure of a solution (and thence the activity coefficient of the solute), previously described[1] with reference to the alkali halides has now been applied to other alkali salts. Measurements have been made on the nitrates of lithium, sodium and potassium which are of interest because of the very low activity coefficient of the latter salt[2] and on the corresponding *p*-toluenesulfonates, the potassium salt of which Sinclair[3] has found to resemble potassium nitrate in respect of its vapor pressure lowering.

Harned and Robinson[4] have found that the plots of the activity coefficient of acetic acid in solutions of lithium, sodium and potassium chloride against salt concentration are in the order K>Na>Li, exhibiting a reversal of the order characteristic of hydrochloric acid in these alkali chloride solutions, namely, Li>Na>K. Scatchard and Prentiss[5] have recently shown by measurements of the freezing point of alkali acetate solutions that the order of the activity coefficient curves is also the reverse of that which obtains for the alkali halides. To confirm this important observation at another temperature a series of measurements have been made on three alkali acetates.

Experimental Results

The experimental procedure as well as the derivation of the activity coefficient have already been described. The three nitrates and lithium and sodium acetates were recrystallized several times. Potassium acetate was made by neutralization of the carbonate with the calculated amount of acetic acid and subsequent crystallization. The toluenesulfonates were made by simi-

TABLE I

ISOPIESTIC SOLUTIONS OF POTASSIUM CHLORIDE AND SOME ALKALI SALTS

m_1 = concentration of potassium chloride. m_2 = concentration of alkali salt in the isopiestic solution.

m_1	m_2	m_1	m_2	m_1	m_2
		Lithium Acetate			
0.1263	0.1252	1.232	1.145	2.839	2.499
.1621	.1598	1.241	1.147	2.896	2.545
.2118	.2082	1.565	1.431	3.113	2.719
.3397	.3319	1.741	1.579	3.253	2.828
.5922	.5678	1.793	1.622	3.821	3.294
.7327	.6951	2.015	1.815	4.067	3.501
.8090	.7665	2.365	2.107	4.480	3.840
1.017	.9490	2.479	2.199	4.516	3.869
1.103	1.028	2.527	2.239	4.810	4.091
		2.565	2.272		
		Sodium Acetate			
0.1263	0.1238	1.461	1.279	2.691	2.247
.1621	.1586	1.594	1.390	2.735	2.281
.2118	.2050	1.741	1.510	2.866	2.373
.3397	.3266	1.793	1.548	2.896	2.397
.5922	.5516	1.819	1.570	2.998	2.474
.7327	.6733	2.015	1.721	3.113	2.559
.8090	.7408	2.287	1.930	3.375	2.754
1.017	.9164	2.365	2.003	3.583	2.909
1.103	.9873	2.409	2.030	4.480	3.572
1.232	1.100	2.479	2.088	4.516	3.593
1.241	1.102	2.565	2.150	4.810	3.813
1.453	1.278	2.671	2.231		
		Potassium Acetate			
0.1263	0.1230	1.017	0.9012	2.244	1.855
.1621	.1575	1.103	.9766	2.365	1.947
.1872	.1821	1.232	1.085	2.479	2.035
.2118	.2037	1.241	1.088	2.896	2.336
.3397	.3233	1.435	1.236	3.113	2.487
.3593	.3417	1.442	1.245	3.568	2.810
.5185	.4830	1.741	1.480	3.630	2.854
.5922	.5496	1.793	1.518	3.983	3.099
.8090	.7326	2.015	1.685	4.480	3.458
.9231	.8295	2.060	1.716	4.516	3.475

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(1) (a) Robinson and Sinclair, THIS JOURNAL, **56**, 1830 (1934); (b) Robinson, *ibid.*, **57**, 1161 (1935).

(2) Scatchard, Prentiss and Jones, *ibid.*, **54**, 2690 (1932).

(3) Sinclair, *J. Phys. Chem.*, **37**, 495 (1933).

(4) Harned and Robinson, THIS JOURNAL, **50**, 3157 (1928).

(5) Scatchard and Prentiss, *ibid.*, **56**, 807 (1934).

TABLE I (*Concluded*)

m_1	m_2	m_1	m_2	m_1	m_2
		Lithium Nitrate			
0.1064	0.1053	1.211	1.084	2.731	2.276
.1545	.1515	1.265	1.131	2.809	2.335
.2697	.2627	1.430	1.260	2.893	2.397
.3816	.3656	1.456	1.284	3.087	2.550
.4919	.4655	1.577	1.385	3.130	2.577
.5120	.4846	1.591	1.392	3.257	2.673
.6345	.5925	1.647	1.440	3.415	2.791
.7695	.7093	1.977	1.701	3.524	2.870
.9991	.9070	1.989	1.712	4.095	3.279
1.082	.9780	2.287	1.933	4.228	3.378
1.109	1.003	2.378	2.009	4.616	3.658
1.111	1.003	2.665	2.230	4.81	3.805
		2.712	2.264		
		Sodium Nitrate			
0.1040	0.1052	1.419	1.529	3.257	3.840
.2036	.2059	1.456	1.569	3.272	3.863
.2052	.2077	1.543	1.674	3.391	4.038
.3365	.3431	1.647	1.798	3.434	4.087
.4307	.4428	1.687	1.845	3.585	4.315
.5090	.5236	1.868	2.060	3.698	4.467
.5732	.5935	2.304	2.596	3.888	4.735
.7063	.7357	2.418	2.738	4.076	5.000
.8404	.8774	2.482	2.814	4.095	5.016
.8724	.9159	2.560	2.912	4.134	5.072
1.109	1.175	2.595	2.956	4.228	5.194
1.111	1.181	2.731	3.127	4.431	5.505
1.132	1.205	2.734	3.138	4.516	5.628
1.211	1.293	2.809	3.237	4.542	5.671
1.235	1.317	3.000	3.506	4.616	5.759
1.342	1.441	3.130	3.672	4.81	6.025
		3.167	3.719		
		Potassium Nitrate			
0.0999	0.1023	0.8072	0.9513	1.477	1.993
.1454	.1504	.8389	.9936	1.538	2.127
.2031	.2126	.8724	1.039	1.543	2.127
.2158	.2264	1.023	1.251	1.591	2.199
.2467	.2617	1.028	1.267	1.629	2.284
.2585	.2747	1.055	1.298	1.687	2.387
.2661	.2831	1.061	1.318	1.759	2.542
.3350	.3620	1.109	1.387	1.868	2.762
.3524	.3812	1.132	1.423	1.990	3.011
.4358	.4775	1.211	1.539	2.066	3.190
.4978	.5533	1.255	1.612	2.084	3.248
.5590	.6262	1.371	1.819	2.136	3.322
.6442	.7338	1.419	1.893	2.188	3.469
.6736	.7699	1.430	1.917	2.247	3.578
.7540	.8806	1.456	1.954	2.304	3.740
		Lithium *p*-Toluenesulfonate			
0.1052	0.1050	1.240	1.237	2.107	2.155
.2083	.2079	1.389	1.383	2.618	2.676
.2844	.2823	1.420	1.419	2.887	2.972
.3340	.3323	1.463	1.471	3.355	3.427
.4944	.4885	1.543	1.547	3.451	3.524
.5550	.5500	1.630	1.639	3.839	3.899
.7120	.7056	1.687	1.707	4.483	4.513
.7217	.7174	1.858	1.894	4.810	4.819
1.132	1.123	1.950	1.988	4.810	4.822
		Sodium *p*-Toluenesulfonate			
0.1520	0.1526	1.477	1.641	2.244	2.702
.3030	.3071	1.497	1.679	2.290	2.791
.3965	.4044	1.508	1.690	2.431	2.990
.4729	.4829	1.612	1.818	2.547	3.144
.6786	.6997	1.726	1.981	2.582	3.209
.6992	.7243	1.779	2.057	2.702	3.400
.8869	.9337	1.922	2.272	2.800	3.521
1.078	1.154	2.025	2.428	3.201	4.106
1.079	1.157	2.066	2.477	3.229	4.152
1.324	1.454	2.215	2.677	3.344	4.299
1.427	1.577	2.229	2.688		
		Potassium *p*-Toluenesulfonate			
0.1540	0.1547	0.4941	0.5186	1.056	1.231
.1722	.1737	.4978	.5230	1.218	1.473
.2487	.2533	.5732	.6077	1.401	1.757
.2695	.2752	.6124	.6536	1.624	2.128
.4099	.4253	.6240	.6671	1.879	2.598
.4241	.4396	.6476	.6971	1.942	2.716
.4465	.4637	.7125	.7757	2.102	3.028
.4572	.4765	.8044	.8851	2.375	3.579
.4771	.4969	.8754	.9779	2.516	3.870
		.9170	1.032		

lar neutralization of the corresponding carbonates and were also recrystallized. All measurements were made at 25°. For the data for potassium *p*-toluenesulfonate I am indebted to Mr. D. A. Sinclair, M.Sc.[6]

The activity coefficients calculated from these results are given in Table II and the plot of log γ against the square root of the concentration is illustrated in Fig. 1.

Discussion

The activity coefficients of the alkali nitrates may be compared with those given in Landolt–Börnstein's "Tabellen"[7] for 25° corrected from the freezing point data and also with the activity coefficients obtained by Scatchard and Prentiss corrected to 25° in a similar manner. Over the range where the data are comparable these activity coefficients are recorded in Table III.

There is disagreement as to the initial value to be assigned to the activity coefficient at 0.1 *M* concentration but if this is obviated by referring all activity coefficients to the same standard at 0.1 *M* concentration, the agreement at higher concentrations is very satisfactory.

There are no other determinations on the *p*-toluenesulfonates to render a comparison possible. Two peculiarities are apparent in the curves for these salts: in the first place the large dispersion between the three nitrates is not re-

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(6) Thesis, University of New Zealand, 1933.

(7) Fifth edition, Zweiter Ergänzungsband, 1931, p. 1112.

TABLE II

ACTIVITY COEFFICIENTS OF ALKALI ACETATES, NITRATES AND *p*-TOLUENESULFONATES

m	$LiC_2H_3O_2$	$NaC_2H_3O_2$	$KC_2H_3O_2$	$LiNO_3$	$NaNO_3$	KNO_3	$LiC_7H_7SO_3$	$NaC_7H_7SO_3$	$KC_7H_7SO_3$
0.1	0.779	0.788	0.793	0.785	0.755	0.730	0.770	0.761	0.757
.2	.737	.752	.764	.748	.699	.656	.726	.705	.698
.3	.715	.738	.749	.734	.661	.605	.695	.669	.659
.5	.695	.735	.748	.725	.613	.540	.661	.622	.605
.7	.688	.738	.752	.728	.581	.492	.639	.590	.560
1.0	.687	.754	.776	.743	.546	.439	.619	.549	.507
1.5	.706	.796	.836	.780	.507	.376	.593	.500	.436
2.0	.731	.851	.906	.837	.479	.326	.572	.458	.385
2.5	.766	.916	.989	.899	.455	.292	.563	.426	.348
3.0	.804	.989	1.082	.969	.436	.265	.561	.401	.317
3.5	.844	1.066	1.182	1.048	.421	.243	.564	.383	.293
4.0	.889	..	..	..	.408	..	.571	.367	..
4.5	..	..	..	..	.396	..	.582	..	..
5.0	..	..	..	..	.386	..	..	..	..
5.5	..	..	..	..	.378	..	..	..	..
6.0	..	..	..	..	.372	..	..	..	..

produced in the toluenesulfonates in spite of the similarity of the two curves for the potassium salts. Second, the curves of log γ against $\sqrt{m}$ for sodium and potassium *p*-toluenesulfonates exhibit a slight but definite concavity toward the concentration axis in the region of 0.7 *M*. This has not been found with any other salt and does not occur with lithium toluenesulfonate although the curve for the latter salt is much flatter between 0.3 and 2 *M* than the curves for other salts of comparable activity coefficients.

The three alkali acetates exhibit a very small dispersion between the three salts. A direct comparison with the results of Scatchard and Prentiss is not possible in the absence of data for the partial molal heat contents and specific heats but from the equation

$$\frac{2RT^2}{25}\{\log \gamma^{25}_m/\gamma^0_m - \log \gamma^{25}_{0.1}/\gamma^0_{0.1}\} = -(\bar{L}_m - \bar{L}_{0.1})$$

where γ^0, γ^{25} are the activity coefficients at 0 and 25°, respectively, for the concentrations 0.1 *M* and *m*, an approximate value can be obtained for the relative partial molal heat of dilution $(\bar{L}_m - \bar{L}_{0.1})$ of the solute averaged over the temperature range 0 to 25°. In the absence of specific heat data further comparison is not possible.

These values, which can only be regarded as approximate, nevertheless give reasonably smooth curves except in the case of the sodium salt.

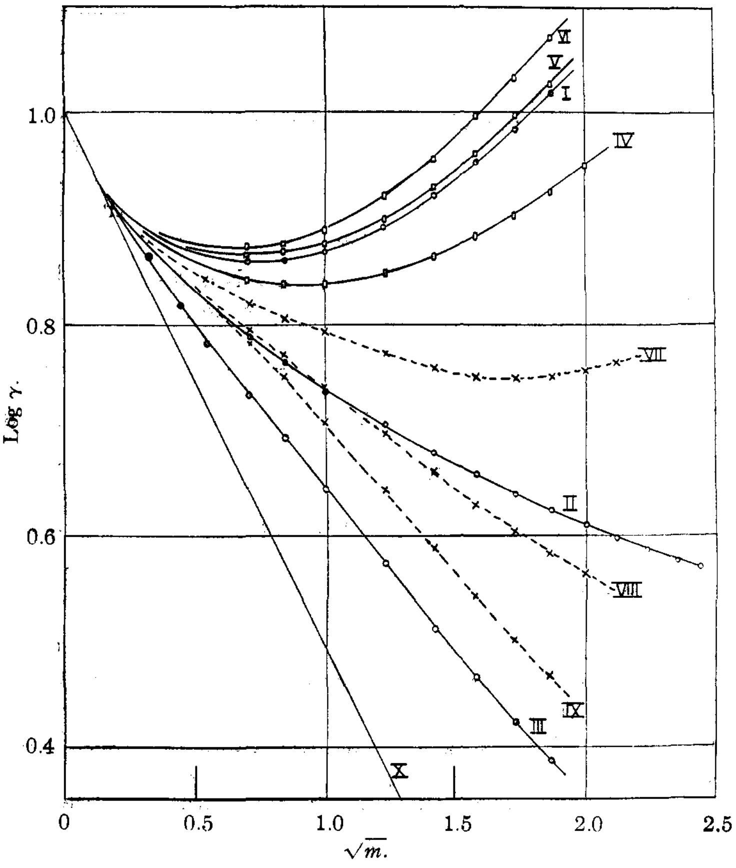

Fig. 1.—Activity coefficients of alkali salts: I, $LiNO_3$; II, $NaNO_3$; III, KNO_3; IV, Li acetate; V, Na acetate; VI, K acetate; VII, Li *p*-toluenesulfonate; VIII, Na *p*-toluenesulfonate; IX, K *p*-toluenesulfonate; X, limiting Debye–Hückel slope.

While it is dangerous to generalize from such scanty data, there are indications that the heat of

TABLE III

COMPARISON OF ACTIVITY COEFFICIENTS OF ALKALI NITRATES

F = f. pt. data in Landolt–Börnstein. S = data of Scatchard and Prentiss. R = present results.

m	F	S	R
	$LiNO_3$		
0.1	0.794	0.800	0.785
.2	.753	.763	.748
.3	.736	.748	.734
	$NaNO_3$		
0.1	0.754	0.770	0.755
.2	.704	.712	.699
.3	..	.680	.661
.5	.624	.634	.613
.7	..	.598	.581
1.0	.553	.555	.546
	KNO_3		
0.1	0.724	0.730	0.730
.2	.653	.658	.656
.3	..	.609	.605
.4	.543	.544	.540
.5	..	.497	.492
.6	.449	.443	.439

TABLE IV

AVERAGE MOLAL HEAT OF DILUTION OF ALKALI ACETATE SOLUTIONS, IN CAL. PER MOLE OF SALT

m	0.2	0.3	0.5	0.7	1.0
$LiC_2H_3O_2$	116	221	364	505	744
$NaC_2H_3O_2$	125	155	92	120	134
$KC_2H_3O_2$	48	149	185	334	424

dilution decreases in the order Li > K > Na, resembling in this respect the alkali hydroxides.

The osmotic coefficients of these nine salts at 1 *M* concentration are as follows

	Li		Na		K
NO_3	0.977	←	0.836	←	0.744
$C_7H_7SO_3$	.889	←	.833	←	.786
$C_2H_3O_2$	.944	→	.985	→	.995

I wish to tender my thanks to Dr. H. S. Harned for his encouragement and his advice in the compilation of this and the preceding paper.

Summary

1. Measurements of the concentrations of aqueous solutions of alkali nitrates, acetates and *p*-toluenesulfonates isopiestic with solutions of known strength of potassium chloride at 25° have been made.

2. From these the activity coefficients of the salts have been computed. The values of this quantity derived from these measurements agree with the activity coefficients computed from freezing point measurements in the case of the nitrates. In the case of solutions of the other salts, direct comparison with freezing point data could not be made. However, from the freezing point data and the vapor pressure data at 25°, the relative partial molal heat content of the acetates has been estimated.

AUCKLAND, NEW ZEALAND RECEIVED MARCH 21, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF COLLOID SCIENCE, THE UNIVERSITY]

The Primary Decomposition of Hydrocarbon Vapors on Carbon Filaments

BY LEONARD BELCHETZ[1] AND ERIC K. RIDEAL

It is now certain that radicals are involved in the cracking as well as in the combustion of hydrocarbon vapors, but the nature of those produced in the primary decomposition cannot be regarded as firmly established. Neither is it known whether the products vary when the decomposition is effected at different hot catalytic surfaces. This communication deals with the decomposition of methane and ethane on carbon filaments.

In a preliminary note[2] experimental evidence was advanced in support of the views that of the two most probable reactions in the decomposition of methane at a hot platinum surface

$$\text{(a)}\quad CH_4 + M \longrightarrow CH_3 + H + M$$
$$\text{(b)}\quad CH_4 + M \longrightarrow CH_2 + H_2 + M$$

the second reaction occurs exclusively.[3]

In the case of ethane, it is generally considered that ethylene and hydrogen are primary products. Rice,[4] however, has suggested that a break of a C–C bond first occurs with the production of methyl radicals, which are able to initiate chains.

The very careful work of Travers and Hockin[5]

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(1) Emmanuel College External Research Scholar and H. B. Webb Gift Research Scholar (South Africa).

(2) Leonard Belchetz, *Trans. Faraday Soc.*, **30**, 170 (1934).

(3) From the theoretical considerations of Lennard-Jones [*ibid.*, **30**, 70 (1934)] Mullikan [*J. Chem. Phys.*, **1**, 500 (1933)] and Van Vleck [*ibid.*, **2**, 20 (1934)], this also appears to be the case for the homogeneous decomposition. For an alternative view, see Rice [*Trans. Faraday Soc.*, **30**, 152 (1934)] and Rice and Dooley [THIS JOURNAL, **56**, 2747 (1934)].

(4) Rice, THIS JOURNAL, **53**, 1959 (1931); **55**, 3035 (1933).

(5) Travers and Hockin, *Proc. Roy. Soc.* (London), **A136**, 1 (1932).