PbO found, 64.44, 64.46, 64.55, calcd. for $Pb_3(IO_5)_2$, 64.68%. I_2O_7 found, 35.39, 35.39, 35.35, calcd., 35.34%.

When pure or impure triplumbous paraperiodate was heated above 130°, the formation of anhydrous meso salt caused a change in color to a dark brick red. The intensity of the color change and the amount of water lost were dependent upon the temperature and the time of heating. If the brick red salt was pulverized very finely, it became orange colored.

When the pure paraperiodate was converted into the anhydrous meso salt, the loss in weight corresponding to water was always too great, varying from 3.49 to 3.61% compared to the theoretical value of 3.38%; therefore the temperature of heating was varied from 130 to 275°, and the time from three minutes to six hours. Volumetric analyses of the heated samples showed that when the temperature was high enough to remove all the water there was a loss of oxygen with consequent formation of iodate.

It is believed that the salt before heating is the paraperiodate and not the mesoperiodate dihydrate for two reasons: (1) the water is retained up to 130°; (2) the anhydrous meso salt when kept under water for fifteen hours and again dried at 110° is found to have absorbed only 5% of the water lost.

Summary

1. Lead periodate was precipitated under varying conditions of acidity, temperature and concentration, only triplumbous paraperiodate, $Pb_3H_4(IO_6)_2$, being formed, although crystals of very different types and colors were obtained. It was pure only when precipitated from 0.006 to 0.1 *N* nitric acid or 0.9 *N* acetic acid solutions. This salt might also have the formula $Pb_3(IO_5)_2 \cdot 2H_2O$ but the para formula is more probable because the water is retained up to 130° and is not taken up by the anhydrous salt.

2. When the para salt was heated to 275° for fifteen minutes it was converted into triplumbous mesoperiodate, $Pb_3(IO_5)_2$, with slight reduction to iodate.

3. None of the other periodates of lead described in the literature could be prepared.

ANN ARBOR, MICHIGAN RECEIVED JANUARY 9, 1934

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, AUCKLAND UNIVERSITY COLLEGE, NEW ZEALAND]

The Activity Coefficients of the Alkali Chlorides and of Lithium Iodide in Aqueous Solution from Vapor Pressure Measurements

BY ROBERT A. ROBINSON AND DONALD A. SINCLAIR

Vapor pressure measurements should, in theory, provide a very accurate means of evaluating the activity coefficient of a salt in solution, but so far this method has hardly been used, mainly because of the elaborate and time-consuming technique required. The object of this paper is to show that after some improvements have been made in an isopiestic method previously described,[1] vapor pressure measurements will yield activity data with an accuracy comparable with that achieved in the e. m. f. and the freezing point methods.

Experimental Procedure

The apparatus consists of four silver dishes, gold-plated internally, 3.8 cm. square and 2 cm. deep, each dish weighing about 35 g. Into two of these dishes 2 cc. of potassium chloride solution is introduced while the other two contain a solution of another salt of approximately the same composition. The dishes are placed on a copper block, 2.5 cm. thick, in a desiccator which is evacuated at the beginning of an experiment and then rocked in a thermostat at 25°. Distillation occurs until the two solutions have the same vapor pressure, equilibrium being attained in twenty-four hours except with solutions 0.5 *M* and less in concentration, when periods up to three days may be required. The dishes are fitted with flap-lids, held open during an experiment by a wire bridge attached to the exit tube of the desiccator, so arranged that at the conclusion of an experiment the lids can be allowed to fall by rotating the exit tube through a small angle without opening the desiccator. This prevents contamination of the solutions by grease, dust or particles of mist on admitting air to the desiccator. From the changes in weight of the solution it is easy to find the concentrations of the isopiestic solutions, the error being not greater than 0.3%, which corresponds to 0.0005 mm. pressure in a 0.2 *M* solution. Several experiments in succession can be made with the same solutions.

To illustrate the accuracy attainable, two runs were made with potassium chloride solutions in each dish. The initial and final concentrations are given in Table I, from which it can be seen that although in the first experiment the initial concentrations differed widely, the final concentrations did not differ by more than one part in 2000, while in the second experiment the over-all variation was less than one part in 700. Our practice was, naturally, to commence with solutions having vapor pressures as nearly equal to one another as possible, so that the case illustrated by the first experiment is an extreme one designed to test the capability of the method.

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(1) *J. Phys. Chem.*, **37**, 395 (1933).

TABLE I

Experiment A

Dish	Initial concn., *M*	Concn. after 23 hours, *M*
1	4.085	2.179
2	3.102	2.179
3	1.733	2.178
4	0.823	2.178

Experiment B

Dish	Initial	Concentration, *M* After 1 day	After 2 days
1	0.25	0.2128	0.2155
2	.25	.2122	.2158
3	.22	.2094	.2155
4	.22	.2100	.2156

The materials employed were the purest obtainable and were in most cases purified further by recrystallization. In the case of the rubidium and cesium salts, however, we had insufficient of the respective hydroxides at our disposal to attempt further purification. The hydroxides were obtained from Kahlbaum and converted into chloride and analysis showed that the only impurities were other alkali metals, that the rubidium salt contained potassium chloride to the extent of 0.8%, while the cesium salt contained both potassium and rubidium chloride, and that the purity of the salt lay between 98.8 and 99.3% depending on the relative amounts of potassium and rubidium present. As the vapor pressure lowerings of these three chlorides are close to one another, the presence of 1% of one of the three cannot be of appreciable influence. The apparent equivalent weights were obtained by chlorine analysis and the presence of impurity thus allowed for.

Lowering of Vapor Pressure of Solutions of Potassium Chloride.—We believe that this method yields vapor pressures relative to those of potassium chloride solutions with an accuracy greater than has been attained in any absolute measurements, not excluding the very accurate work of Lovelace, Frazer and Sease[2] on potassium chloride solutions where the error was believed to be not greater than 0.001 mm. It is essential, therefore, to determine the vapor pressure–concentration curve of potassium chloride with as high a degree of accuracy as possible. We have calculated values of these vapor pressure lowerings, using data from different sources. While, unfortunately, the agreement is not all that could be desired, we believe that the standard values chosen are not far from the true values. To obtain these standard values the following methods have been used.

A. The data of Lovelace, Frazer and Sease yield the activity of the solvent, $a = p/p_0$, directly, p_0, the vapor pressure of water, being taken as 17.535 mm. at 20°. From a graph of these figures values at round concentrations were read and to these a small correction was applied to obtain the activity at 25°, by means of the equation[3]

$$\log a_{25} - \log a_{20} = -\overline{L}_1 y + (\overline{C}_p - \overline{C}_p^0)\, z \qquad (1)$$

the values of $\overline{L}_1$ and $(\overline{C}_p - \overline{C}_p^0)$ being those used by Saxton and Smith.[4] From the activity of the solvent it is easy to obtain the relative molar vapor pressure lowering, $R = (p_0 - p)/mp_0 = (1 - a)m$. The values so obtained are shown in Fig. 1. The plot of a against molality gives a curve with a "kink" in it about 0.6 *M*, an anomaly which Lovelace, Frazer and Sease could not smooth out in spite of numerous repetitions of the experiment in this region of concentration. As, however, the methods to be described below show no sign of such anomaly, the smoothest possible curve was drawn through the points representing solvent activities and consequently the curve in Fig. 1 does not show this "kink."

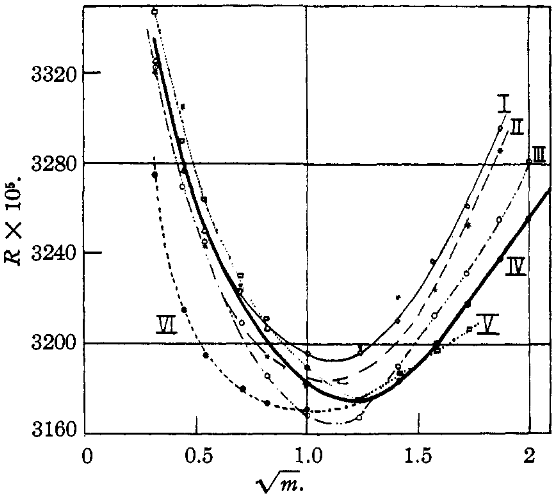

Fig. 1.—Values of *R* from different sources; I, e. m. f. data at 0°; II, b. p. data; III, e. m. f. data at 25°; IV, curve finally selected; V, f. p. data; VI, v. p. data.

B. The values of the molar depression of the freezing point, θ/m, were taken from the work of Jones and Bury,[5] Karagunis, Hawkinson and Damkohler,[6] Roloff,[7] Menzies[8] and Scatchard[9] and from a plot against molality values at round concentrations were selected and the activity of the solvent calculated by means of the equation[10]

$$\log a = -0.004211\theta - 0.0000022\theta^2 \qquad (2)$$

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[2] Lovelace, Frazer and Sease, THIS JOURNAL, **43**, 102 (1921).

[3] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 349.

[4] Saxton and Smith, THIS JOURNAL, **54**, 2626 (1932).

[5] Jones and Bury, *Phil. Mag.*, **3**, 1032 (1927).

[6] Karagunis, Hawkinson and Damkohler, *Z. physik. Chem.*, **150A**, 433 (1930).

[7] Roloff, *ibid.*, **18**, 578 (1895).

[8] Menzies, *Z. Elektrochem.*, **33**, 68 (1927).

[9] Scatchard, THIS JOURNAL, **55**, 4355 (1933).

[10] Lewis and Randall, "Thermodynamics," 1923, p. 284.

Thence a was corrected from the freezing point to 25° and another set of values of R obtained.

C. Similar calculations applied to the data of Saxton and Smith[4] on the elevation of the boiling point of potassium chloride solutions, using the equation

$$\log a = -0.015261\theta + 0.0000483\theta^2 \qquad (3)$$

yields a third set of figures.

D. The e. m. f. measurements of Harned[11] can be converted into values of molal vapor pressure lowerings by the equation

$$\ln a = -2/55.51 \left\{ m + \int_0^m m \, \mathrm{d} \ln \gamma \right\} \qquad (4)$$

$\int m \, \mathrm{d} \ln \gamma$ being obtained by a graphical integration.

E. Finally, the corresponding e. m. f. measurements of Smith[12] at 0° can be converted by equation (4) into solvent activities which can be converted to 25° by equation (1) and a further set of values of R obtained.

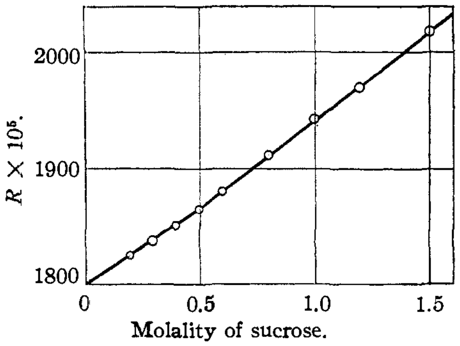

Fig. 2.—Values of R for sucrose.

These five sets of data are given in Table II and are shown in Fig. 1.

TABLE II

VALUES OF $R \times 10^5$ FOR SOLUTIONS OF POTASSIUM CHLORIDE

m	From v. p.	From f. p.	From b. p.	From e. m. f. at 25°	From e. m. f. at 0°	Value selected
0.1	3275	3347	3321	3323	3325	3332
.2	3215	3290	3305	3270	3277	3279
.3	3194	3264	3244	3245	3250	3253
.5	3180	3230	3223	3209	3222	3220
1.0	3173	3211	3194	3186	3206	3201
1.0	3170	3190	3182	3169	3196	3181
1.5	3176	3176	3198	3167	3197	3176
2.0	3184	3188	3221	3190	3211	3184
3.0	3218	3107	3253	3132	3262	3218
4.0	3256	..	3304	3181	..	3256

It can be seen that the agreement is moderately good but that some of the vapor pressure data are about 2% too low. In selecting the best values we have been guided by the following considerations. Suspicion must always be attached to values obtained from data at the freezing point or boiling point because, in spite of the accuracy of the data, error can be introduced by the temperature correction over such a range. The correction being larger in the case of the more concentrated solutions, such values of R in solutions of 1 M and over may not be very reliable. This also applies to the values of R obtained from the data of Smith at 0°. This objection does not apply to the direct determinations of Lovelace, Frazer and Sease, as the correction over a 5° temperature range is small. In this case it would seem that error is more likely to occur because of experimental difficulties with dilute solutions. The e. m. f. data of Harned should yield the most accurate values, although his data with concentrated solutions may be questioned because of the solubility of silver salts in concentrated alkali chloride solution. Nevertheless, we believe this fear to be groundless, except perhaps in very concentrated solutions, partly because of the agreement between Smith's results at 0° and freezing point data and partly because of the agreement of our results with other alkali chlorides and the corresponding e. m. f. measurements of Harned. In dilute solution (less than 1 M) all the methods except the direct vapor pressure measurements yield concordant results; on the other hand, the direct method functions more satisfactorily in concentrated solutions. In selecting our final values, therefore, we have taken the values of Lovelace, Frazer and Sease for solutions 1.5 M and more in concentration and combined them with the average value given by the freezing point and e. m. f. methods for solutions less concentrated. The boiling point data of Saxton and Smith have been eliminated, not because we believe their results to be erroneous, but because the two temperature corrections in equation (1) act against one another, leading to uncertainty as to the true result at 25°. We realize that these are somewhat arbitrarily selected values of R, but it appears to us to be the most satisfactory procedure until the discrepancy relating to the vapor pressure data at low concentrations is cleared up.

Confirmation of the Selected Values for the Vapor Pressure Lowering of Potassium Chloride Solutions from Data with Solutions of Sucrose.—

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[11] Harned, THIS JOURNAL, **51**, 416 (1929).

[12] Smith, *ibid.*, **55**, 3279 (1933).

Thirty-one experiments were carried out with solutions of the purest sucrose against solutions of potassium chloride, thirteen different sets of solutions being employed, with the following results.

TABLE III

CONCENTRATIONS OF ISOPIESTIC SOLUTIONS OF SUCROSE AND POTASSIUM CHLORIDE

m_1 = molality of potassium chloride, m_2 = molality of sucrose

m_1	m_2	m_1	m_2	m_1	m_2
0.1101	0.1997	0.3604	0.6198	0.6933	1.128
.1181	.2145	.3809	.6516	.7089	1.153
.1870	.3324	.3853	.6588	.7180	1.168
.2114	.3752	.4323	.7341	.7375	1.190
.2292	.4033	.5175	.8668	.7406	1.199
.2332	.4095	.5188	.8698	.7702	1.245
.3055	.5316	.5364	.8971	.8341	1.336
.3146	.5419	.5698	.9448	.8547	1.368
.3177	.5499	.5737	.9466	.8764	1.394
.3278	.5672	.6226	1.022	.9393	1.481
		.6677	1.090		

From these figures a graph was plotted (Fig. 3) of m_1/m_2 against m_2 and a series of values of m_1/m_2 read off at round concentrations of m_2, the values of $(p_0 - p)/p_0$ for potassium chloride being obtained from Fig. 1. This gives $(p_0 - p)/p_0$ for sucrose at corresponding values of m_2 shown in Table IV.

TABLE IV

VALUES OF $R \times 10^5$ FOR SUCROSE

m_2 =	0.2	0.3	0.4	0.5	0.6
$R \times 10^5$ =	1826	1839	1852	1866	1881
m_2 =		0.8	1.0	1.2	1.5
$R \times 10^6$ =		1912	1943	1971	2019

R varies almost linearly with m_2; it is therefore possible to extrapolate R back to $m_2 = 0$ and obtain a limiting value of R at infinite dilution of 0.01800 (Fig. 2), which compares well with the theoretical value of 0.018015, thus affording support for the values of R selected for potassium chloride.

Experimental Results

The following table gives the results obtained with solutions of alkali chlorides and of lithium iodide: m_1 is the concentration of potassium chloride and m_2 is the concentration of the isopiestic solution of the alkali halide.

TABLE V

LITHIUM CHLORIDE

Fifty-four determinations using sixteen solutions

m_1	m_2	m_1	m_2	m_1	m_2
0.1135	0.1114	0.6913	0.6333	1.914	1.594
.1369	.1342	.7044	.6449	1.930	1.609
.1627	.1586	.7335	.6704	1.946	1.621
.1666	.1632	.7767	.7063	2.065	1.711
.1831	.1782	.8948	.8079	2.232	1.827
.2120	.2056	.9160	.8254	2.335	1.904
.2276	.2203	1.004	.8978	2.360	1.916
.2580	.2485	1.052	.9385	2.372	1.925
.2870	.2754	1.087	.9647	2.393	1.939
.3306	.3149	1.109	.9795	2.761	2.187
.4700	.4422	1.118	.9872	3.024	2.373
.5043	.4735	1.168	1.028	3.684	2.798
.5056	.4736	1.256	1.097	3.717	2.816
.5913	.5491	1.382	1.200	3.812	2.867
.6009	.5582	1.420	1.227	3.859	2.897
.6113	.5666	1.814	1.530	4.259	3.159
.6521	.6027	1.900	1.590	4.474	3.283

SODIUM CHLORIDE

Thirty-five determinations using eight solutions

m_1	m_2	m_1	m_2	m_1	m_2
0.1064	0.1053	0.5576	0.5433	2.156	2.004
.1339	.1324	.5586	.5448	2.318	2.144
.1715	.1697	.6413	.6240	2.418	2.235
.1982	.1960	.7295	.7060	2.685	2.464
.2869	.2831	.7466	.7231	3.159	2.863
.2886	.2847	.7714	.7464	3.413	3.073
.3081	.3026	.8243	.7962	3.486	3.139
.3421	.3361	1.041	.9990	3.796	3.394
.4335	.4246	1.225	1.168	3.858	3.435
.4807	.4699	1.251	1.192	4.256	3.765
.5348	.5229	1.570	1.481	4.81	4.198
.5374	.5244	1.769	1.662		

RUBIDIUM CHLORIDE

Thirty-one determinations using nine solutions

m_1	m_2	m_1	m_2	m_1	m_2
0.4190	0.4226	1.281	1.297	2.619	2.675
.4287	.4320	1.316	1.333	2.766	2.825
.4483	.4512	1.358	1.376	2.954	3.013
.5030	.5059	1.552	1.577	3.136	3.064
.6462	.6538	1.840	1.871	3.616	3.716
1.074	1.088	1.946	1.984	3.682	3.784
1.082	1.096	1.947	1.987	4.060	4.162
1.151	1.168	2.070	2.114	4.198	4.321
1.173	1.190	2.281	2.326	4.289	4.425
1.260	1.276	2.372	2.417	4.81	4.962
		2.373	2.420		

CESIUM CHLORIDE

Twenty-eight determinations using six solutions

m_1	m_2	m_1	m_2	m_1	m_2
0.1216	0.1230	0.6445	0.6700	2.669	2.835
.1533	.1559	.6928	.7209	2.728	2.896
.2089	.2129	.8925	.9345	3.843	4.088
.2219	.2256	.9704	1.017	3.977	4.228
.3406	.3486	1.232	1.294	4.146	4.416
.4094	.4212	1.702	1.792	4.281	4.569
.4361	.4518	1.896	2.005	4.400	4.697
.4621	.4781	2.167	2.292	4.467	4.761
.5849	.6039	2.187	2.312	4.744	5.064
		2.674	2.830		

TABLE V (*Concluded*)

LITHIUM IODIDE

Thirty-two determinations using twelve solutions

m_1	m_2	m_1	m_2	m_1	m_2
0.1235	0.1197	1.160	0.9705	2.720	2.018
.1561	.1491	1.167	0.9782	2.854	2.089
.1714	.1630	1.238	1.026	2.909	2.127
.1976	.1866	1.334	1.098	2.974	2.170
.2034	.1910	1.616	1.294	3.245	2.327
.2055	.1941	1.757	1.392	3.596	2.529
.2646	.2485	1.825	1.443	3.942	2.710
.2819	.2627	2.079	1.613	4.183	2.832
.5751	.5176	2.536	1.906	4.198	2.845
.7848	.6877	2.625	1.956	4.522	3.012
.7964	.6852			4.81	3.152

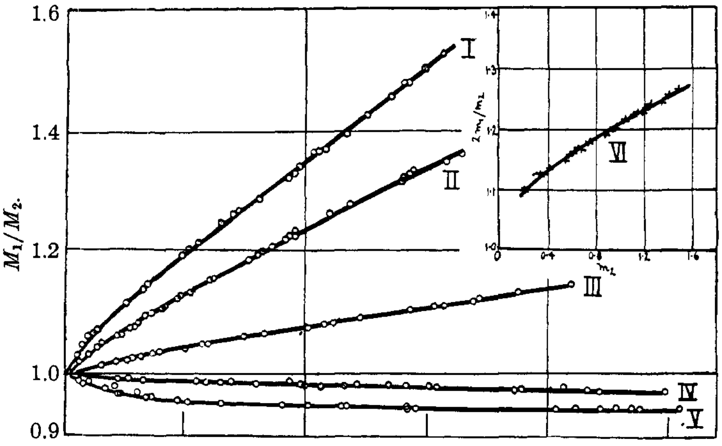

Fig. 3.—Isopiestic solutions of alkali halides: I, LiI; II, LiCl; III, NaCl; IV, RbCl; V, CsCl; VI, sucrose.

Figure 3 is a plot of m_1/m_2, against m_2, showing that there is no difficulty in drawing a smooth curve through the experimental points and enabling values of m_1/m_2 to be read at round concentrations.

Activity Coefficients of Alkali Chlorides and Lithium Iodide.—The activity coefficient of potassium chloride was obtained from the values of R given in the last column of Table II, using the graphical integration method of Randall and White.[13] It was desirable to obtain a value of the activity coefficient at 4.81 M; it was found possible to extrapolate the $R:m$ curve to 4.81 M for this purpose.

Having obtained activity coefficients corresponding to the vapor pressures of potassium chloride solutions, the activity coefficients of the other salts can be derived by a simplified method.

Let m_1, γ_1, be the molality and activity coefficient of potassium chloride and m_2, γ_2, the corresponding values for an isopiestic solution of another salt. Then, as the solvent activity in each solution is the same, we have

$$dm_1 + m_1 d \ln \gamma_1 = d\, m_2 + m_2\, d \ln \gamma_2 \qquad (5)$$

or

$$d\, m_1/m_2 + m_1 d \ln \gamma_1/m_2 = d \ln m_2 + d \ln \gamma_2$$

or

$$d \ln \gamma_2 = d \ln \gamma_1 + d \ln (m_1/m_2) + (m_1/m_2 - 1)\, d \ln (\gamma_1 m_1)$$

and since

$$d \ln (\gamma_1 m_1) = d \ln a_1 = 2d\sqrt{a_1}/\sqrt{a_1}$$

then

$$\ln \gamma_2 = \ln \gamma_1 + \ln (m_1/m_2) + 2 \int_0^{a_1} (m_1/m_2 - 1)\, d\sqrt{a_1}/\sqrt{a_1}$$

The values of m_1/m_2 are obtained from Fig. 3. The plot of $(m_1/m_2 - 1)/\sqrt{a_1}$ against $\sqrt{a_1}$ gives a curve which proceeds to zero when $\sqrt{a_1} = 0$ and it is easy to obtain a graphical integration. The type of curve obtained is shown in Fig. 4. The activity coefficients are given in Table V and compared with the values obtained for potassium, lithium and sodium chloride by Harned and for cesium chloride by Harned and Schupp.[14]

The agreement in the case of potassium chloride is very good, but this agreement has been forced to some extent by the fact that Harned's data were used as one set of data in determining the activity coefficients of solutions less than 1.5 M in concentration. The agreement in

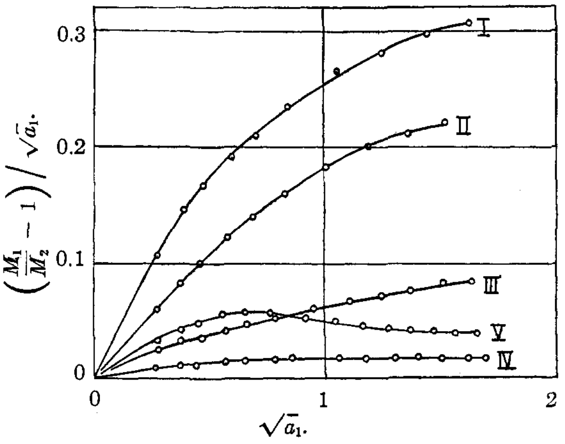

Fig. 4.—Evaluation of $\int \left(\frac{M_1}{M_2} - 1\right) \frac{d\sqrt{a_1}}{\sqrt{a_1}}$: I, LiI; II, LiCl; III, NaCl; IV, RbCl; V, CsCl.

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[13] Randall and White, THIS JOURNAL, **48**, 2514 (1926).

[14] Harned and Schupp, *ibid.*, **52**, 3886 (1930).

TABLE VI

ACTIVITY COEFFICIENTS OF ALKALI CHLORIDES AND LITHIUM IODIDE

m	γ_{KCl}[a]	γ_{KCl}[b]	γ_{NaCl}[a]	γ_{NaCl}[b]	γ_{LiCl}[a]	γ_{LiCl}[b]	γ_{RbCl}[a]	γ_{CsCl}[a]	γ_{CsCl}[c]	γ_{LiI}[a]
0.1	0.766	0.764	0.776	0.778	0.789	0.779	0.761	0.752	0.747	0.811
.2	.715	.712	.731	.732	.758	.756	.708	.690	.685	.794
.3	.684	..	.708	..	.745	..	.675	.650	..	.795
.5	.648	.644	.679	.678	.739	.725	.637	.602	.598	.806
.7	.624	..	.665	..	.751	..	.610	.571	.568	.835
1.0	.602	.597	.655	.656	.778	.757	.587	.541	.537	.903
1.5	.581	.576	.655	.658	.838	.819	.562	.512	.507	1.019
2.0	.572	.569	.669	.670	.927	.919	.549	.493	.488	1.190
2.5	.569	.568	.691	.690	1.039	1.040	.540	.483	.476	1.394
3.0	.570	.571	.716	.714	1.169	1.174	.538	.478	.467	1.697
3.5	.573	.571	.753	.749	..	1.358	.537	.474	..	...
4.0	.578	.581	.789	.779	..	1.554	.542	.472	..	...
4.5	..	..	..	..	..	..	..	..	..	...
4.81	.590	..	..	..	..	..	..	.472	..	...
5.0	..	..	..	..	..	..	.544	.474	..	...

[a] Values obtained in the present investigation. [b] Values obtained by Harned. [c] Values obtained by Harned and Schupp.

the concentrated solutions is determined by the agreement of Harned's data with the vapor pressure measurements of Lovelace, Frazer and Sease. In the case of the sodium chloride solutions, if the value at 4 *M* is omitted, the mean divergence between the two sets of results corresponds to 0.13 mv. with a maximum difference of 0.27 mv. at 3.5 *M*. At 4 *M*, however, there is a difference of 0.66 mv.

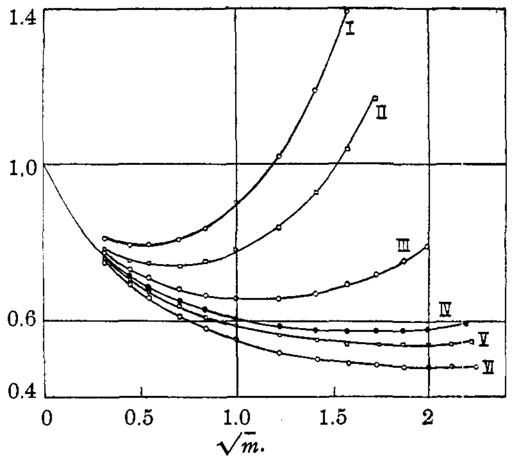

Fig. 5.—Activity coefficients: I, LiI; II, LiCl; III, NaCl; IV, KCl; V, RbCl; VI, CsCl.

With cesium chloride the following differences are found: 0.34, 0.37, 0.33, 0.27, 0.38, 0.51, 0.52, 0.75 and 1.19 mv., the differences being in the same direction throughout. A different selection of the value of $\gamma_{0.1}$ for Harned and Schupp's results would lead to excellent agreement except in the most concentrated solution.

In the case of lithium chloride the observed differences are 0.65, 0.14, 0.98, 1.41, 1.17, 0.45, −0.05 and 0.22 mv. As Harned regarded his results as having an accuracy of the order of ± 1 mv. we may consider the agreement as good as can be legitimately expected.

The authors are indebted to Dr. H. S. Harned, for his helpful criticism of this paper.

Summary

1. The vapor pressures of solutions of sucrose, lithium, sodium, rubidium and cesium chloride and lithium iodide relative to those of a solution of potassium chloride have been determined by an isopiestic method.

2. Values of the vapor pressures of potassium chloride solutions have been calculated from five sources and compared. A set of values has been selected as a standard and this has been shown to be consistent with the theoretical value for the vapor pressure lowering of sucrose in infinitely dilute solution.

3. A method is derived for obtaining the activity coefficients of salts and applied to the five alkali halides. Original values are given for the activity coefficients of rubidium chloride and lithium iodide. Satisfactory confirmation is obtained of the values previously found for potassium, sodium and lithium chloride by Harned and for cesium chloride by Harned and Schupp. This agreement indicates that the silver–silver chloride electrode behaves reversibly in chloride solutions.

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RECEIVED FEBRUARY 3, 1934