[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

The Determination of Activity Coefficients from the Potentials of Concentration Cells with Transference. III. Potassium Chloride. IV. Calcium Chloride

BY THEODORE SHEDLOVSKY AND DUNCAN A. MACINNES

In the two previous papers in this series[1,2] it was shown that accurate activity coefficients can be obtained from the results of potential measurements on concentration cells with transference of the form

$$\text{Ag; AgCl, MCl}\,(C_1)\text{:MCl}(C_2)\text{, AgCl; Ag} \qquad \text{(A)}$$

in which M represents a positive ion constituent. The computations involved the use of the equation

$$-E = \frac{2RT}{F}\int_{C_1}^{C_2} t\,\mathrm{d}\log Cf \qquad (1)$$

in which E is the potential of a cell of type A, t is the transference number of the positive ion, C is the concentration in gram moles per liter of solution and f the activity coefficient. The papers mentioned describe the determination of the activity coefficients of sodium chloride and of hydrochloric acid, respectively, up to concentrations of 0.1 normal, the upper limit being determined by the available accurate transference data. We have continued the measurements to include solutions of potassium chloride and calcium chloride. The first of these was chosen because it is a commonly used type and reference salt, and also because precise determinations of the transference numbers of potassium chloride have been made over a wide range of concentrations. Longsworth[3] has obtained transference data for that substance over the concentration range 0.001 to 1.0 N, by the moving boundary method, and MacInnes and Dole[4] have used the Hittorf method over the range 0.2 to 3.0 N. The two methods gave closely agreeing values, the greater precision, however, being obtained with the moving boundary method.

Calcium chloride has been added to the series because it is an example of a salt of a higher valence type. For a bi-univalent electrolyte equation (1) must be modified to

$$-E = \frac{3RT}{2F}\int_{C_1}^{C_2} t\,\mathrm{d}\log Cf \qquad (2)$$

The value of the coefficient 3/2 may be explained readily by the fact that the passage of 2 faradays of current through a calcium chloride concentration cell "without transference" is accompanied by the transport of three gram moles of ions, *i. e.*, one of calcium and two of chloride. Accurate transference numbers for calcium chloride have been obtained recently by Longsworth[5] in the concentration range C = 0.005 to 0.1 N.

The experimental procedure employed in determining the potentials of the concentration cells followed closely that described for cells containing hydrochloric acid.[2] The potassium chloride was of the best obtainable grade, and was given a further purification by precipitation with hydrogen chloride gas, and repeated crystallization from conductivity water. The calcium chloride was from the same sample as was used by Shedlovsky and Brown[6] in their conductance measurements. The solutions were made up by weight dilution from known stock solutions and their concentrations confirmed by accurate conductance determinations.[6,7] The two silver–silver chloride electrodes in the concentration cell never differed from each other by more than 0.02 mv. and the effect of this small difference of potential was eliminated, within a few microvolts, by duplicate measurements with the positions of the two solutions in the cell reversed. From the experimental data values of activity coefficient ratios have been computed by the method described in the first paper of this series.[8]

Activity coefficients may be stated in terms of concentrations, C (moles per liter), m (moles per 1000 g. of solvent), mole fractions, n and other concentration scales which will not concern us here. They are connected by the relation

$$a_c : a_m : a_n = fC : \gamma m : f_r n \qquad (3)$$

in which a_c, a_m and a_n are activities on the scale represented by the subscripts, and f, γ and f_r

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(1) Brown and MacInnes, THIS JOURNAL, **57**, 1356 (1935).

(2) Shedlovsky and MacInnes, *ibid.*, **58**, 1970 (1936).

(3) Longsworth, *ibid.*, **54**, 2741 (1932); MacInnes and Longsworth, *Chem. Rev.*, **11**, 210 (1932).

(4) MacInnes and Dole, THIS JOURNAL, **53**, 1357 (1931).

(5) Longsworth, *ibid.*, **57**, 1185 (1935).

(6) Shedlovsky and Brown, *ibid.*, **56**, 1066 (1934).

(7) Shedlovsky, Brown and MacInnes, *Trans. Electrochem. Soc.*, **66**, 165 (1934).

(8) In that paper,[1] equation (11) should read

$$-\Delta\log f = -\frac{E}{118.29\,t_1} - (\log C_2 - \log C_1) - \frac{1}{t_1}\int^2 \Delta t\,\mathrm{d}\log C + \frac{1}{t_1}\int_1^2 \Delta t\ \mathrm{d}(\Delta\log f)$$

are the corresponding activity coefficients. Since it is assumed that these activity coefficients approach unity at infinite dilution they are measures of deviations from ideal solutions defined in three different ways. The activity coefficient f_r has been called "rational" because it measures departures from Raoult's law.[9] The relations between f, γ and f_r are the following

$$f_r = f(d - 0.001MC + 0.018\nu C)/d_0 = \gamma(1 + 0.018\nu m) \tag{4}$$

in which ν is the number of ions into which the solute dissociates, M is the molecular weight of the solute and d and d_0 are the densities of the solution and solvent.

To obtain the activity coefficients, f, from values of $-\Delta\log f$ computed directly from the data it was necessary to evaluate the activity coefficient of the reference solution. To this end use was made of the Debye–Hückel equation in the form

$$-\log f = \Delta\log f - A = \alpha\sqrt{C}/(1 + \beta\sqrt{C}) + \log\frac{(d - 0.001MC + 0.018\nu C)}{d_0} \tag{5}$$

in which α is 0.5056 for a uni-univalent and 1.7515 for a bi-univalent electrolyte, respectively, at 25° and β involves the distance of closest approach of the ions. The last term of this equation is of negligible magnitude in dilute solutions.[10] To obtain a value of A a plot was made of $(\Delta\log f - \alpha\sqrt{C})$ against $(A - \Delta\log f)\sqrt{C}$, and the value of A adjusted until it agreed with the intercept of the plot, as described in more detail in the previous papers. With this value of A, $\log f$ values may be obtained directly from $\Delta\log f$, as indicated in equation (5).

Results and Discussion

(a) Potassium Chloride.—The results of the series of measurements on the potentials of potassium chloride concentration cells are given in Table I. The first column of the table contains the concentrations C_2 in moles per liter at 25°. The reference solution C_1 was 0.1 mole per liter. The second and third columns contain the corresponding potentials, E, in millivolts, and the transference numbers, t. The fourth column lists values of $-\Delta\log f$. From these figures the activity coefficients f, given in the next column, were obtained with the aid of the value of A determined as described above. The value of β in equation (5) was found to be 1.350, corresponding to a distance of closest approach of 4.13 Å.[11] Using this constant and equation (5), the activity coefficients "f computed" in column 6 were calculated. It will be seen that the agreement between the experimental and computed activity coefficients extends to about $C = 0.2$. This concentration is considerably higher than the usual upper limit of validity of this equation. In the cases of sodium chloride and hydrochloric acid it is about $C = 0.04$.

For higher concentrations Hückel[9] has proposed the equation

$$-\log f_r = \alpha\sqrt{C}/(1 + \beta\sqrt{C}) - DC \tag{6}$$

in which D is a constant. A careful analysis, to be published elsewhere, has proved that an equation of this type will not fit our data above $C = 0.5$. However, the equation

$$-\log f = \alpha\sqrt{C}/(1 + \beta\sqrt{C}) - DC\log C + \log[(d - 0.0386C)/d_0] \tag{7}$$

was found to agree surprisingly closely with the experimental results throughout the concentration range studied, *i. e.*, $C = 0.005$ to 3.0, as can be seen by comparing the figures in columns 5 and 7 of Table I. The values of β and D in this equation were found to be 1.50 and 0.0365, respectively.

It has, however, been usual to express activity coefficients in terms of γ values, *i. e.*, a_m/m, in which m represents moles per 1000 g. of water. The relation between f and γ is given in equation (4). Thus, equation (7), which was obtained from the data in Table I, can also be put in the form

$$-\log\gamma = \frac{0.5056\sqrt{C}}{1 + 1.50\sqrt{C}} - 0.0365C\log C + \log(1 + 0.036m) \tag{7a}$$

For reference, values of γ at round concentrations for potassium chloride at 25° are given in Table II.

(b) Calcium Chloride.—The results of measurements and computations on solutions of calcium chloride are given in Table III, which is

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(9) Hückel, *Physik. Z.*, **26**, 93 (1925).

(10) In the previous papers of this series this term was not included. For sodium chloride and hydrochloric acid it is negligible, within the experimental error, up to $C = 0.1$, the upper limit of the measurements.

(11) The last term in equation (5) was computed with the aid of the relation

$$d = 0.99707 + 0.04805C - 0.00230C^{3/2}$$

for the density, d, at 25°, of potassium chloride solutions, from the data given in the "International Critical Tables." For the density, d, at 25°, of calcium chloride solutions the corresponding equation is

$$d = 0.99707 + 0.0924C - 0.0042C^{3/2}$$

from the measurements of Shedlovsky and Brown.[6]

TABLE I

THE POTENTIALS OF THE CONCENTRATION CELL: Ag; AgCl, KCl (0.1): KCl (C_2), AgCl; Ag AT 25° AND THE COMPUTATION OF THE ACTIVITY COEFFICIENTS OF POTASSIUM CHLORIDE IN AQUEOUS SOLUTION

Concn. moles per liter at 25°, C_2	E. m. f. mv., E	Trans. no., t	Log activity coeff. ratio, $-\Delta \log f$	Activity coefficients: f exptl.	f, computed equation (5)	f, computed equation (7)
0.0050080	70.765	0.4904	0.0797	0.9273	0.9276	0.9273
.010003	54.025	.4903	.0679	.9024	.9024	.9022
.010053	53.895	.4903	.0679	.9024	.9023	.9022
.020002	37.489	.4901	.0521	.8702	.8701	.8704
.020003	37.483	.4901	.0521	.8702	.8701	.8704
.030000	27.890	.4900	.0416	.8494	.8490	.8497
.030285	27.688	.4900	.0410	.8482	.8485	.8493
.040000	21.170	.4899	.0326	.8320	.8321	.8318
.050106	15.905	.4899	.0256	.8187	.8183	.8179
.059995	11.731	.4899	.0194	.8071	.8067	.8062
.080004	5.113	.4898	.0086	.7872	.7874	.7872
.10000	0.000	.4898	.0000	.7718	.7719	.7720
.20000	−15.757	.4894	− .0289	.7221	.7216	.7226
.50000	−36.453	.4888	− .0692	.6581	.6537	.6594
.9974	−52.442	.4882	− .0924	.6239	.6051	.6234
1.0000	−52.508	.4882	− .0923	.6238	.6049	.6233
3.0000	−80.417	.4857	− .0856	.6337	.5376	.6333

TABLE II

ACTIVITY COEFFICIENTS, γ, AT ROUND MOLAL CONCENTRATIONS FOR POTASSIUM CHLORIDE AT 25°

m = moles/1000 g. H_2O in vacuum	C = moles/liter	$\gamma_{\text{comp.}}$
0.005	0.004985	0.9275
.01	.009968	.9021
.05	.04979	.8172
.10	.09943	.7701
.20	.19830	.7191
.50	.4916	.6516
1.00	.9692	.6069
2.00	1.8827	.5781
3.00	2.7419	.5741
3.55	3.1526	.5765
4.00	3.5514	.5806

TABLE III

THE POTENTIALS OF THE CONCENTRATION CELL: Ag; AgCl, $CaCl_2$ (0.05): $CaCl_2$ (C_2), AgCl; Ag AT 25° AND THE COMPUTATION OF THE ACTIVITY COEFFICIENTS OF CALCIUM CHLORIDE IN AQUEOUS SOLUTION

Concn. moles per liter at 25°, C_2	E. m. f. mv., E	Trans. no., t	Log activity coeff. ratio, $-\Delta \log f$	Activity coefficients: f exptl.	f computed equation (5)	f computed equation (8)
0.0018153	47.545	0.4310	0.1679	0.8588	0.8586	0.8586
.0060915	29.263	.4254	.1230	.7745	.7746	.7743
.0095837	22.697	.4224	.1009	.7361	.7364	.7361
.024167	9.751	.4143	.0479	.6514	.6510	.6513
.037526	3.819	.4096	.0191	.6097	.6085	.6099
.050000	0.000	.4060	.0000	.5834	.5810	.5836
.096540	− 8.607	.3958	− .0438	.5275	.5198	.5276

mostly self-explanatory. For this salt the reference concentration was C_1 = 0.05 mole per liter and the computation yielded the value for β of 2.98. This value for β corresponds to a distance of closest approach of 5.27 Å. The sixth column of the table gives values of f computed, using these constants and the appropriate value of α in equation (5). It will be seen that the observed and computed values of the activity coefficient f agree to C = 0.03. It is of great interest to find that the Debye–Hückel theory in its simple form holds for this "unsymmetrical" type of electrolyte. The distance of closest approach is large enough so that the higher terms of the theory[12] are negligible. Agreement between the observed and computed values is observed throughout the range of the measurements with the equation

$$-\log f = \frac{1.7515\sqrt{C}}{1 + 2.814\sqrt{C}} - 0.147C + \log(1.0029d - 0.057C) \quad (8)$$

as can be seen by comparing the fifth and seventh columns of Table III. Values of γ for solutions of calcium chloride at 25° can be obtained from the equation

$$-\log \gamma = \frac{1.7515\sqrt{C}}{1 + 2.814\sqrt{C}} - 0.147C + \log(1 + 0.054m) \quad (8a)$$

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[12] La Mer, Gronwall and Greiff, *J. Phys. Chem.*, **35**, 2245 (1931).

Summary

The activity coefficients in aqueous solution at 25° of potassium chloride from $C = 0.005$ to 3.00 moles per liter, and of calcium chloride from $C = 0.002$ to 0.1 have been determined from measurements of potentials of concentration cells with transference, and accurate transference numbers.

It has been found that the simple Debye–Hückel equation $-\log f_r = \alpha\sqrt{C}/(1 + \beta\sqrt{C})$ fits the data, with high precision to $C = 0.2$ for potassium chloride and to $C = 0.03$ for calcium chloride, with distances of closest approach of 4.1 and 5.2Å., respectively.

The equation

$$-\log f_r = \frac{0.5056\sqrt{C}}{1 + 1.50\sqrt{C}} - 0.0365C\log C$$

holds for potassium chloride up to $C = 3.00$, and the expression

$$-\log f_r = \frac{1.7515\sqrt{C}}{1 + 2.814\sqrt{C}} - 0.147C$$

fits the data for calcium chloride up to $C = 0.1$.

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[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

A Revision of the Atomic Weight of Carbon. II

BY GREGORY P. BAXTER AND ARTHUR H. HALE

Quantitative combustion of hydrocarbons has been continued during the past year and the results confirm the conclusion already reported[1] that the atomic weight of carbon is not far from 12.010.

Only minor changes were made in the combustion apparatus and analytical technique. The ring seal of the second bulb in the water absorption system was eliminated in order that complete equalization of pressure might be more easily secured during weighing. Furthermore, the air in this system was saturated with water during the first weighing, so that no correction was necessary on this score. In some of the analyses (71, 74, 78, 79, 80), a somewhat smaller but similar system was used for absorbing the carbon dioxide, in order to increase the accuracy of weighing.

During the earlier work preliminary experiments had shown that the "blank" corrections were very small. These and later experiments, carried out by passing air and oxygen through the empty combustion tube while it was heated as in the combustions, produced the changes in weight (positive) given in the following tables.

AIR

	Duration of run, hours	H_2O, mg.	CO_2, mg.
	44	0.26	0.38
	64	.52	.62
Total	108	.78	1.00
Gain per hour		.0072	0.0093

OXYGEN

At the close of each run the tubes were swept out with air, and a correction made for the period during which air was used.

	Duration of run, hours	H_2O, mg.	CO_2, mg.
	44	0.76	0.01
	71	.68	1.17
	69	.53	0.90
	80	.73	.81
Total	264	2.70	2.89
Gain per hour		0.0102	0.0109

On the basis of these results in each of the new experiments as well as in those already reported a negative correction based on these blanks has been applied. This correction usually amounted to about 0.1 mg. each for both water and carbon dioxide.

Purification of Hydrocarbons

Pyrene.—Although our earlier attempts to purify pyrene had apparently been unsuccessful, further efforts were made as follows. One specimen after crystallization from pure benzene was first melted in vacuum with freshly fused potassium hydroxide and then distilled from the potassium hydroxide. After another crystallization the sample was melted in nitrogen at low pressure in contact with metallic sodium, and then distilled from the sodium. Crystallization from benzene, distillation at low pressure and another crystallization followed.

Another sample was kept melted, in nitrogen at low pressure, over metallic mercury for twenty hours. This was followed by crystallization from benzene, treatment with sodium as described above, another crystallization, distillation at low pressure and a final crystallization.

The benzene used in these experiments and in the puri-

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[1] Baxter and Hale, THIS JOURNAL, **58**, 510 (1936).