heats of solution in the low concentration range. The equation indicates that the heat of solution is 5507 cal. per mole at infinite dilution, but it seems inadvisable to give much weight to this extrapolated value in view of the large rate of change of ΔH with m at very low concentrations. Heats of solution at concentrations less than 0.00035 m were below the limit of measurement of the calorimeter used.

The heats of formation of crystalline boric acid and of aqueous boric acid solutions at rounded concentrations are shown in Table II. These values were calculated using a value of −303 kcal. per mole for the heat of formation of boric oxide reported recently by the National Bureau of Standards as a result of measurements of the heat of dissociation of diborane.[12] This value is in agreement with one obtained by Nathan and Stegeman[2b] by direct combustion of boron. The following two reactions were also used in the calculations

$$B_2O_3(c) + 3H_2O(l) + 1000H_2O = 2(H_3BO_3 \cdot 500H_2O)$$
$$\Delta H_{298°K} = -3.48 \text{ kcal./mole}$$
$$H_3BO_3(c) + 1000H_2O = H_3BO_3 \cdot 500H_2O$$
$$\Delta H_{298°K} = 5.27 \text{ kcal./mole}$$

The heat effect of the first reaction was reported by Southard[13] and the value for the second reaction was obtained in this study. The uncertainty of the tabulated values is probably of the order of 1% due to a similar uncertainty in the value of the heat of formation of boric oxide. The uncertainty in the differences between the values, however, is probably no greater than 0.01 kcal.

TABLE II

HEATS OF FORMATION OF BORIC ACID AND OF AQUEOUS BORIC ACID SOLUTIONS

State		Heat of formation, kcal./mole
H_3BO_3	crystalline	−260.98
H_3BO_3 in	59.3 H_2O (satn.)	−255.76
H_3BO_3 in	100 H_2O	−255.74
H_3BO_3 in	200 H_2O	−255.72
H_3BO_3 in	500 H_2O	−255.71
H_3BO_3 in	5000 H_2O	−255.71
H_3BO_3 in	20000 H_2O	−255.70
H_3BO_3 in	50000 H_2O	−255.65
H_3BO_3 in	100000 H_2O	−255.59
H_3BO_3 in	150000 H_2O	−255.56

Summary

The heats of solution and dilution of orthoboric acid have been determined in the range of concentrations from saturation (0.936 m) to 0.00035 m. An equation was found to express the data.

The heats of formation of crystalline boric acid and of aqueous solutions of boric acid from saturation $H_3BO_3 \cdot 59.3\ H_2O$ to $H_3BO_3 \cdot 150{,}000\ H_2O$ have been calculated.

PITTSBURGH, PENNSYLVANIA RECEIVED FEBRUARY 3, 1950

[12] E. J. Prosen, W. H. Johnson and F. A. Yenchius, National Bureau of Standards Technical Report on Project NA-onr-8-49 (1948).

[13] J. C. Southard, THIS JOURNAL, **63**, 3147 (1941).

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

The Activity Coefficients of $LaCl_3$, $CaCl_2$, KCl, NaCl and HCl in Dilute Aqueous Solutions

BY THEODORE SHEDLOVSKY

In this laboratory the activity coefficients of $LaCl_3$,[1] $CaCl_2$,[2] KCl,[2] NaCl[3] and HCl[4] for dilute solutions in water at 25° have been obtained from measurements on the e. m. f. of concentration cells, together with transference numbers by the method of the moving boundary.

All these salts, except $LaCl_3$, gave results which were in accord with the Debye–Hückel theory for strong electrolytes.

The apparent abnormal behavior of $LaCl_3$ as previously reported is, however, not real, but has been found to be due to an error in the computations which consisted in evaluating the integral of $Ed\delta$ instead of the required δdE by graphical means.[1] The corrected computations lead to results, given below, which show that the activity coefficient values for this tri-univalent salt are also in complete accord with the Debye–Hückel theory in sufficiently dilute aqueous solutions. I am indebted to Dr. R. H. Stokes, of the University of Western Australia, for suggesting the probability of error in the original calculations.

Since the publication of the papers mentioned above, there has been a significant revision of the most probable values of some of the constants involved in the Debye–Hückel equation for activity coefficients.[5] Accordingly, the data for all the five electrolytes have been recomputed on the newer basis and the results are reported in the present communication.

The familiar Debye–Hückel equation for ionic activity coefficients, f_R, in sufficiently dilute solutions is

$$-\log f_R = A\sqrt{C}/(1 + B\sqrt{C}) \qquad (1)$$

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[1] T. Shedlovsky and D. A. MacInnes, THIS JOURNAL, **61**, 200 (1939).

[2] T. Shedlovsky and D. A. MacInnes, *ibid.*, **59**, 503 (1937).

[3] A. S. Brown and D. A. MacInnes, *ibid.*, **57**, 1356 (1935).

[4] T. Shedlovsky and D. A. MacInnes, *ibid.*, **58**, 1970 (1936).

[5] R. T. Birge, *Rev. Mod. Phys.*, **13**, 253 (1941), R. T. Birge, *Rep. Prog. Phys.*, **8**, 90 (1941).

f_R is a measure of deviations in thermodynamic behavior of the ions from Raoult's law, C is the concentration in moles of electrolyte per liter of solution.

$$A = \frac{2\lambda[\Sigma_i \nu_i Z_i/2]^{3/2}}{2.3026(\Sigma\nu_i)}$$

$$B = 2\lambda[\Sigma_i \nu_i Z_i^2/2]^{1/2}\, a \equiv \beta\mathring{a}$$

$$\alpha = \epsilon^2/DkT$$

$$\lambda^2 \equiv 2\pi N\alpha^3/1000$$

in which ν_i is the number of i ions of valence Z_i, a is the mean ionic diameter and $\mathring{a}$ its value in ångströms, D is the dielectric constant of the solvent, $k = 1.38047 \times 10^{-16}$ is the Boltzmann constant, $T = t + 273.16$ is the absolute temperature, $\epsilon = 4.8025 \times 10^{-10}$ is the electron's charge and $N = 6.0228 \times 10^{23}$ is Avogadro's number.

The dielectric constant of water, D, has been taken to be

$$D = 78.555[1 - 4.579 \times 10^{-3}(t - 25) + 1.19 \times 10^{-5} (t - 25)^2 - 2.8 \times 10^{-8} (t - 25)^3]$$

from the work of Wyman,[6] Drake, Pierce and Dow,[7] and Wyman and Ingalls.[8]

The "rational" activity coefficient f_R is related to the corresponding coefficients f and γ, which are for the concentration scales C (moles per liter) and m (moles per 1000 g. of H_2O), respectively, by the relation[2]

$$f_R = f(d - 0.001MC + 0.18\, \nu C)d_0 = \gamma(1 + 0.018\, \nu) \quad (2)$$

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.

The new computations for the five electrolytes have been made on the basis of f_R with equation (1) to which a term linear in C (for NaCl, HCl and $CaCl_2$) or in $C \log C$ (for KCl and $LaCl_3$) has been added to express analytically the experimental values within the limits of experimental error, that is, within a few units in the fourth place of the activity coefficients.

The use of the terms in C or $C \log C$ is empirical here, although a more detailed statistical mechanical analysis of the effect of interionic forces on activity coefficient than in the original treatment which led to equation 1 indicates that such higher terms should be present.[9,10]

New values of the constants A and β, required for the computations, are summarized in Table I. Columns 2 and 3 list the A and β values for uni-univalent electrolytes at several temperatures. Corresponding values for other valence type electrolytes may be obtained by multiplying these figures by the appropriate valence type factors at the right of the table.

The new values of f reported in the present communication differ, on the average, from those formerly published for $CaCl_2$, KCl, NaCl and HCl by about one unit in the third place. The average ionic diameters, $\mathring{a}$, obtained from the new equations also differ somewhat. The activity coefficient values, f, for all five electrolytes in water at 25° are given by the equation

$$-\log f = \frac{A\sqrt{C}}{1 + B\sqrt{C}} + DC + D'C \log C + \log (d - 0.001MC + 0.018\, \nu C)/d_0 \quad (3)$$

which is obtained from (1) and (2) with the addition of the higher terms. The values of the constants in this equation for the various solutes are given in Table II in which are also listed the average ionic diameters $\mathring{a}$ in ångströms. The concentration range of the measurements extended to $C = 0.10$ for HCl, NaCl and $CaCl_2$, to $C = 3.0$ for KCl and to $C = 0.033$ for $LaCl_3$.

Since the correctly computed f values for $LaCl_3$ have not been previously published they are given in Table III. Column 2 refers to the experimentally derived figures and column 3 to those computed by equation 3.

TABLE I

DEBYE–HÜCKEL CONSTANTS FOR ACTIVITY COEFFICIENTS IN WATER

t, °C.	A	β		Valence type factors for A	Valence type factors for β
0	0.48807	0.32403			
10	.49627	.32584	1–1	1	1
20	.50435	.32759	2–1	3.4621	1.7320
25	.50891	.32858	3–1	7.3485	2.4495
30	.51371	.32961	4–1	12.649	3.1623
40	.52435	.33187			
50	.53621	.33435			

TABLE II

CONSTANTS FOR EQUATION 3

	A	B	D	D'	$\mathring{a}$[11]
HCl	0.5089	1.45	−0.115	......	4.4
NaCl	0.5089	1.30	0.044	......	4.0
KCl	0.5089	1.51	.....	−0.0368	4.6
$CaCl_2$	1.7629	2.85	−0.139	......	5.0
$LaCl_3$	3.7397	5.50	.....	0.536	6.8

TABLE III

ACTIVITY COEFFICIENTS OF $LaCl_3$ IN WATER AT 25°

C, moles/liter	f (exp.)	f (calcd.)
0.0006070	0.8248	0.8270
.0016628	.7461	.7463
.0032179	.6823	.6822
.004885	.6386	.6383
.010936	.5495	.5495
.017188	.4991	.4995
.025257	.4574	.4578
.033333	.4289	.4288

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(6) J. W. Wyman, *Phys. Rev.*, **35**, 623 (1930).

(7) F. H. Drake, G. W. Pierce and M. T. Dow, *Phys. Rev.*, **35**, 613 (1930).

(8) J. W. Wyman and E. N. Ingalls, THIS JOURNAL, **60**, 1182 (1928).

(9) J. G. Kirkwood, private communication.

(10) V. K. LaMer and C. F. Mason, THIS JOURNAL, **49**, 420 (1927).

(11) It is interesting to note that these values are larger than the crystallographic ones by approximately one water molecule diameter (1.3 Å.) for HCl, NaCl and KCl, two for $CaCl_2$ and three for $LaCl_3$.

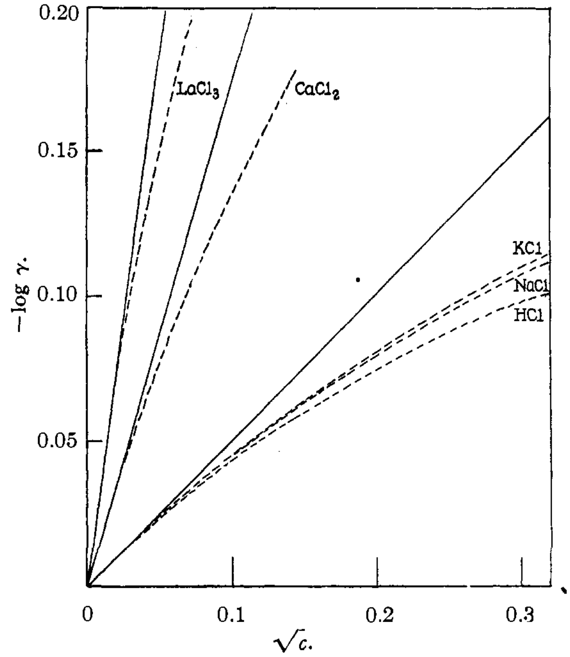

Fig. 1.

In Table IV values of γ, the activity coefficients on the molality (m) basis, which is most commonly used, are listed for the five electrolytes at round concentrations. They are obtained from the appropriate equations resulting from equations 3 and 2. In Fig. 1, the values of ($-\log \gamma$) as a function of $\sqrt{C}$ are shown by the broken curves. The solid lines are the corresponding theoretical slopes, A. It is evident, of course, that the curves for all these electrolytes approach the limiting slopes, in accord with theory. The average ionic diameters ($\mathring{a}$ values) for KCl, NaCl and HCl are 4.6, 4.0 and 4.4 ångströms, respectively, which would indicate that $\mathring{a}$ (Na^+) < $\mathring{a}$ (H_3O^+) < $\mathring{a}$ (K^+). The reason why the deviations of the curves for these chlorides from the limiting slope are not in this sequence is because the higher terms, in C and $C \log C$, which were used empirically to fit the data with equation 3, were different. However, the ion sizes obtained appear to be reasonable.[11]

TABLE IV

ACTIVITY COEFFICIENTS (γ) AT ROUND CONCENTRATIONS (m)

m (moles/ kg. H_2O)	γ HCl	NaCl	KCl	$CalC_2$	$LaCl_3$
0.001	0.9653	0.9651	0.9650	0.8893	0.7902
.002	.9525	.9519	.9516	.8519	.7294
.005	.9287	.9273	.9270	.7888	.6361
.01	.9049	.9022	.9015	.7314	.5597
.02	.8757	.8707	.8694	.6681	.4831
.05	.8301	.8192	.8164	.5825	.3881
.10	.7938	.7744	.7692	.5232	(.3252)

Summary

1. Activity coefficients for $LaCl_3$ in water at 25° obtained from measurements on the e. m. f. of concentration cells with transference are in accord with the Debye-Hückel theory.

2. New values are presented for activity coefficients of HCl, NaCl, KCl, $CaCl_2$ and $LaCl_3$, based on revised fundamental constants.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, HOWARD UNIVERSITY]

Liquid-Vapor Equilibrium in Microscopic Capillaries.[1] I. Aqueous System

BY J. L. SHERESHEFSKY AND CLARENCE P. CARTER

The capillary condensation theory of adsorption proposed by Zsigmondy[2] stimulated a number of investigations seeking to establish experimentally the validity of the Kelvin[3] equation, $\ln (P/P_0) = \pm 2\sigma V/RTr$, with respect to convex and concave surfaces of liquid bodies of microscopic size. In this equation σ is the surface tension and V is the molar volume of the liquid, r is the radius of curvature and RT has the usual significance. The positive sign applies to convex surfaces and the negative sign to concave surfaces.

Goodris and Kulikova[4] substantiate the Kelvin equation for water droplets several microns in diameter. Woodland and Mack[5] assume the presence of a halo of vapor about 0.5 to 0.6μ in thickness surrounding the microscopic n-butyl phthalate droplets in order to validate the Kelvin equation. This is substantiated by Shereshefsky and Steckler[6] who studied the evaporation of n-butyl droplets from 1.673 to 0.473 μ in radius, but find that without this assumption the surface tension decreases with increase in curvature.

For concave surfaces the data in the literature are very limited. The early work of one of the authors[7] shows that the lowering of the vapor pressure of water in a uniform capillary of 8.1 microns in diameter is 23 times greater than the Kelvin value. For capillaries of other sizes and

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[1] Based on a thesis submitted by Clarence P. Carter to the Graduate School of Howard University in partial fulfillment of the requirements for the degree of Master of Science.

[2] Zsigmondy, *Z. anorg. Chem.*, **71**, 356 (1911).

[3] Thomson, *Phil. Mag.*, [4] **42**, 448 (1871).

[4] Goodris and Kulikova, *J. Russ. Phys.-Chem. Soc.*, Phys. Part, **56**, 167 (1924).

[5] Woodland and Mack, THIS JOURNAL, **55**, 3149 (1933).

[6] Shereshefsky and Steckler, *J. Chem. Physics*, **4**, 108 (1936).

[7] Shereshefsky, THIS JOURNAL, **50**, 2966 (1928).