decompose in very different parts, is considered additional evidence in support of theories of homogeneous unimolecular reactions.

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The Dissociation of Water in Strontium Chloride Solutions at 25°

BY JOHN E. VANCE

The electromotive forces of the cells

$$H_2 \mid Sr(OH)_2(m_1),\ SrCl_2(m_2) \mid AgCl \mid Ag$$

are given by the equation

$$E = E_0 - 0.05915 \log \gamma_H\gamma_{Cl}m_Hm_{Cl} \qquad (1)$$

Substituting the equilibrium constant for the dissociation of water

$$K_W = \frac{\gamma_H\gamma_{OH}}{a_{H_2O}}\, m_Hm_{OH} \qquad (2)$$

and rearranging, the equation

$$E - E_0 + 0.05915 \log \frac{m_2}{m_1} = -0.05915 \log K_Wa_{H_2O} - 0.05915 \log \frac{\gamma_H\gamma_{Cl}}{\gamma_H\gamma_{OH}} \qquad (3)$$

results. Knowing $E_0 = 0.22239$,[1] we can, by measuring the cell designated above with varying values of m_2 and a single suitable value of m_1, and by determining separately $\gamma_H\gamma_{Cl(m\,=\,0)}$ in strontium chloride solutions of the same total ionic strength, make an extrapolation, plotting the left side of equation (3) against μ and obtain a value for K_W at zero ionic strength.

Subsequently K_γ may be calculated by rearranging equation (3)

$$\log K_\gamma = \log \frac{\gamma_H\gamma_{OH}}{a_{H_2O}} = \frac{E - E_0 + 0.05915 \log m_2/m_1}{0.05915} + \log K_W + \log \gamma_H\gamma_{Cl} \qquad (3a)$$

Finally, values of $m_W = m_H = m_{OH}$, $\gamma_H\gamma_{OH}$, and $\gamma = \sqrt{\gamma_H\gamma_{OH}}$ may be obtained from equation (2) after values of a_{H_2O} are calculated from a suitable source.

This process or an essentially similar one has been used to determine K_W accurately and to find K_γ in several aqueous salt solutions of cesium,[1b] potassium, sodium,[2] lithium,[3] and barium chloride,[4] as well as of potassium and sodium bromide.[5]

Measurement of the Cells $H_2 \mid Sr(OH)_2(m_1), SrCl_2(m_2) \mid AgCl \mid Ag$.—The determinations were made in the customary manner in the usual type of

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[1] (a) Roberts, THIS JOURNAL, **52**, 3877 (1930); (b) Harned and Schupp, *ibid.*, **52**, 3892 (1930); (c) Harned and Ehlers, *ibid.*, **54**, 1350 (1932).

[2] Harned, *ibid.*, **47**, 930 (1925).

[3] Harned and Swindells, *ibid.*, **48**, 126 (1926); Harned and Copson, *ibid.*, **55**, 2206 (1933).

[4] Harned and Mason, *ibid.*, **54**, 3112 (1932).

[5] Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926).

cell. Every precaution was taken to prevent the presence of carbon dioxide. The results of the measurements are given in Table I. Column six contains the mean value of the electromotive forces and column seven the value of the left side of equation (3). To obtain values at convenient concentrations, the values in column seven were plotted against μ as indicated above. Since the cells were not measured in sufficiently dilute solutions to give an unambiguous value of K_W, use was made of the value of K_W recently determined by others in this Laboratory.[6] This value is 1.008×10^{-14}, and correspondingly the curve was extrapolated to a value of $0.05915 \log K_W = 0.08279$. The second column of Table III gives the values of $[E - E_0 + 0.05915 \log(m_2/m_1)]$ thus obtained.

TABLE I

THE ELECTROMOTIVE FORCES OF THE CELLS

$H_2 \mid Sr(OH)_2(m_1), SrCl_2(m_2) \mid AgCl \mid Ag$, at 25°

m_1	m_2	μ	No. of cells	Δ(m. v.)	E	$\left[E - E_0 + 0.05915 \log \frac{m_2}{m_1}\right]$
0.01369	0.02009	0.1013	2	0.3	1.0390	0.8265
.01309	.05010	.1896	2	.07	1.0131	.8252
.01329	.07481	.2643	2	.13	1.0022	.8242
.01329	.09993	.3397	2	.04	0.9939	.8234
.01312	.2013	.6433	2	.08	.9730	.8207
.01320	.2995	.9381	2	.10	.9609	.8187
.01338	.5003	1.5410	2	.16	.9435	.8141
.01343	.7461	2.2786	2	.20	.9284	.8092
.01323	.9988	3.0361	2	.4	.9154	.8041
.01332	1.4948	4.5244	2	.4	.8956	.7946
.01371	1.9810	5.9841	2	.15	.8803	.7856
.01344	2.4855	7.4968	1	. .	.8641	.7758

The Determination of $\gamma_H\gamma_{Cl(0.01)}$ in Strontium Chloride Solutions.—The cell

$$Ag \mid AgCl \mid HCl\ (0.01),\ SrCl_2(m) \mid H_2 \mid HCl\ (0.01) \mid AgCl \mid Ag$$

would serve to give the desired values of $\gamma_H\gamma_{Cl}$ through the relation

$$E = 0.1183 \log \frac{\gamma_{HCl}}{0.904} \left[\frac{(0.01 + 2m)}{0.01}\right]^{1/2} \qquad (4)$$

This double cell was not measured directly but the electromotive force was obtained by subtracting the electromotive force of the cell

$$H_2 \mid HCl\,(0.01),\ SrCl_2(m) \mid AgCl \mid Ag$$

from that of a similar cell containing 0.01 m hydrochloric acid alone. Table II gives the results, showing the electromotive forces of the single cell containing 0.01 m HCl and $SrCl_2(m)$ along with the activity coefficients calculated from equation (4) using the value 0.904 at 0.01 m as found by Randall and Young.[7]

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[6] Harned and Copson, THIS JOURNAL, **55**, 2206 (1933); Harned and Hamer, *ibid.*, **55**, 2194 (1933).

[7] Randall and Young, *ibid.*, **50**, 989 (1928).

These values of $\gamma_{HCl(0.01)}$ were plotted against $\mu^{1/2}$ and values of $\gamma_{HCl(0.01)}$ at round concentrations read off. These last values appear in column three of Table III. Equation (3a), however, requires values of $\gamma_H\gamma_{Cl(m=0)}$ in strontium chloride solutions. These were found by first obtaining values of $\gamma_{HCl(m=0)}$ from the usual short extrapolation of $\gamma_{HCl(0.01)}$,[4] and then by squaring the values of $\gamma_{HCl(m=0)}$. The results appear in column four of Table III.

TABLE II

THE ACTIVITY COEFFICIENT OF 0.01 MOLAL HYDROCHLORIC ACID IN STRONTIUM CHLORIDE SOLUTIONS AT 25°

m	No. of cells	Δ(m. v.)	E	HCl	m	No. of cells	Δ(m. v.)	E	HCl
0.00	15	0.11	0.46445	0.904	0.75	4	0.13	0.34166	0.801
.025	2	0	.42480	.797	1.00	4	.10	.32902	.888
.05	4	0.07	.41157	.761	1.25	4	.02	.31771	.994
.075	4	.08	.40319	.743	1.50	4	.26	.30666	1.121
.1	4	.16	.39702	.731	1.75	4	.16	.29569	1.286
.2	4	.21	.38163	.706	2.00	4	.31	.28574	1.460
.3	4	.10	.37110	.711	2.25	4	.12	.27532	1.686
.4	4	.01	.36301	.721	2.50	2	.15	.26529	1.944
.5	4	.23	.35628	.737	2.75	2	.21	.25513	2.260

The Calculation of a_{H_2O} in Strontium Chloride Solutions.—Values of a_{H_2O} in solutions of strontium chloride were calculated from the activity coefficients of strontium chloride by the method due to Harned.[8] The

TABLE III

CALCULATION OF K_γ FROM DATA IN TABLES I AND II, AND VALUES OF m_W, $\gamma_H\gamma_{OH}$, AND $\sqrt{\gamma_H\gamma_{OH}}$ AT ROUND CONCENTRATION

μ	$\left[E - E_0 + 0.05915 \log \frac{m_2}{m_1}\right]$	$\gamma_{HCl(0.01)}$	$\gamma_H\gamma_{Cl(m=0)}$	K_γ	a_{H_2O}	$m_W \times 10^7$	$\gamma_H\gamma_{OH}$	γ
0.01	0.8277	0.904	0.814	0.807	0.999	1.12	0.806	0.898
.05	.8271	.829	.686	.665	.999	1.23	.664	.814
.10	.8264	.795	.629	.593	.998	1.30	.592	.769
.20	.8250	.753	.566	.505	.997	1.41	.503	.709
.30	.8238	.731	.533	.454	.995	1.49	.452	.672
.40	.8228	.718	.514	.422	.994	1.55	.419	.647
.60	.8210	.708	.500	.382	.991	1.63	.379	.615
.80	.8193	.708	.500	.358	.988	1.68	.354	.595
1.00	.8178	.714	.508	.343	.985	1.72	.338	.581
1.50	.8143	.736	.540	.318	.972	1.78	.309	.555
2.00	.8111	.772	.593	.308	.967	1.81	.298	.547
3.00	.8046	.882	.774	.313	.949	1.79	.297	.546
4.00	.7982	1.028	1.053	.331	.923	1.74	.306	.553
5.00	.7917	1.214	1.469	.359	.894	1.68	.321	.567
6.00	.7853	1.458	2.120	.404	.863	1.58	.349	.590
7.00	.7789	1.774	3.136	.466	.829	1.47	.386	.621

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(8) See Taylor, "A Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1924, First Ed., Vol. II, pp. 751–753.

activity coefficients of strontium chloride used were those measured by Lucasse.[9] The equation

$$\log \gamma_{SrCl_2} = -\beta m\alpha' + \alpha m \tag{5}$$

expressed the experimental results when the constants $\beta = 0.776$, $\alpha' = 0.358$ and $\alpha = 0.420$ were used. Subsequently a_{H_2O} was calculated from the equation

$$\ln \frac{1}{a_{H_2O}} = \frac{m}{55.5}\left[\nu + \frac{2.303\ \alpha\nu m}{2} - \frac{2.303\nu\beta\alpha'}{\alpha' + 1} m^{\alpha'}\right] \tag{6}$$

The values of a_{H_2O} appear in column six of Table III.

Calculation of K_γ, m_W, $\gamma_H\gamma_{OH}$ and γ.—The requisite data are now at hand to calculate the desired values from equations (2) and (3a). The values of K_γ, m_W, $\gamma_H\gamma_{OH}$ and $\gamma = \sqrt{\gamma_H\gamma_{OH}}$ are given in columns five, seven, eight and nine, respectively, of Table III.

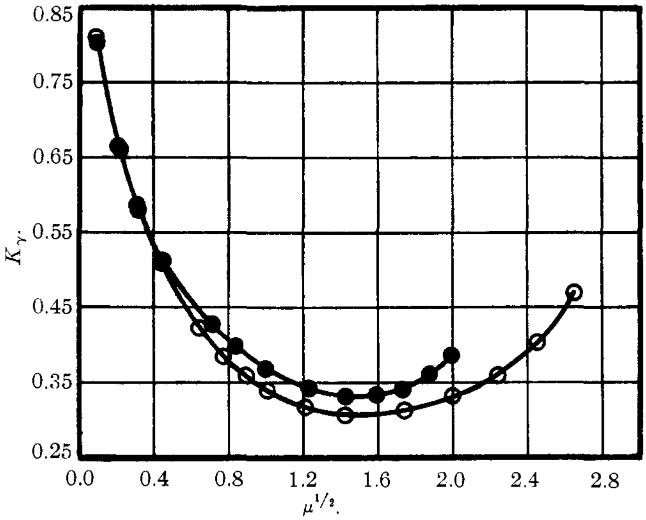

Fig. 1.—K_γ in $BaCl_2$ ●; K_γ in $SrCl_2$ ⊙.

Figure 1 affords a comparison of K_γ in barium chloride as determined by Harned and Mason,[4] and K_γ in strontium chloride.

The writer wishes to express his thanks to Professor H. S. Harned, who suggested the work.

Summary

1. The electromotive forces of the cells $H_2 | Sr(OH)_2\ (m_1),\ SrCl_2(m_2) | AgCl | Ag$ and of the cells $H_2 | SrCl_2(m),\ HCl\ (0.01) | AgCl | Ag$ have been determined and the activity coefficient of 0.01 *m* hydrochloric acid in strontium chloride found.

2. By a combination of the data thus obtained K_γ in strontium chloride solutions has been determined.

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[9] Lucasse, THIS JOURNAL, **47**, 743 (1925).

3. From these results and previous work of others the dissociation of water in strontium chloride solutions has been calculated.

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Thermal Data on Organic Compounds. XI. The Heat Capacities, Entropies and Free Energies of Ten Compounds Containing Oxygen or Nitrogen

BY GEORGE S. PARKS, HUGH M. HUFFMAN AND MARK BARMORE

The previous papers[1] of this series have dealt mainly with thermal data for hydrocarbons and for some aliphatic alcohols and acids. From these studies it has become evident that the entropy and free energy of an organic compound are related to its constitution in a simple additive manner, and we have been able to assign definite numerical values to the changes in these thermodynamic quantities, corresponding to the introduction of a CH_2 group into an aliphatic chain, to the substitution of a methyl or ethyl branch for a hydrogen atom, to the replacement of a hydrogen atom by an alcoholic hydroxyl group, etc. The work now seems to warrant greater diversification of the substances to be studied, and accordingly in the present investigation we have measured the heat capacities of the following ten organic compounds containing oxygen or nitrogen: urea, glycine, ethyl acetate, *n*-amyl alcohol, *tert*-amyl alcohol, isopropyl ether, phenol, aniline, benzoic acid and sucrose.

These data have then been utilized to calculate, by the third law of thermodynamics, the corresponding entropies and free energies.

Materials

Urea and Glycine.—These were C. P. Pfanstiehl products. The urea had a melting point of 132° and a water content guaranteed to be less than 0.05%. The glycine was guaranteed to be free of ammonia and chlorides and to have less than 0.15% water content and less than 0.08% ash.

Ethyl Acetate.—This was one of the very pure standard samples prepared in the laboratory of Professor Timmermans at the University of Brussels. It had a certified melting point of −83.6°, while we found −83.76° by a rough measurement with a thermocouple in the course of our fusion determinations.

***n*-Amyl Alcohol, *Tert*-amyl Alcohol, and Isopropyl Ether.**—These compounds were very carefully prepared for us by Dr. H. E. Buc of the Standard Oil Development Company. The *n*-amyl alcohol boiled at 137.9° at 760 mm. pressure. The *tert*-amyl alcohol boiled between 102.33 and 102.35° at 762 mm., and melted at −9.1°, which is 2.8° above the point given in the "International Critical Tables." The isopropyl ether boiled between 68.9 and 69.15°.

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(1) See, for instance, Parks, Kelley and Huffman, THIS JOURNAL, **51**, 1969 (1929); Huffman, Parks and Thomas, *ibid.*, **52**, 3241 (1930); Parks and Huffman, *ibid.*, **52**, 4381 (1930); and Huffman, Parks and Barmore, *ibid.*, **53**, 3876 (1931).