4. The activation energies of bimolecular reactions of ethyl radicals with hydrogen or azomethane are calculated to be greater than 15 kilocalories.

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The Dissociation of Water in Lithium Bromide Solutions at 25°

BY JOHN E. VANCE

The dissociation of water has been determined by means of electromotive force measurements in several salt solutions. A complete list of references on the subject and a discussion of the method is available.[1]

To afford a comparison with lithium chloride a similar determination in lithium bromide solutions has been undertaken.

The electromotive forces of the cells $H_2 \mid LiOH(m_1), LiBr(m_2) \mid AgBr \mid Ag$ are connected with the desired function through the equation

$$\log K_\gamma = \log \frac{\gamma_H \gamma_{OH}}{a_{H_2O}} = \frac{E - E_0 + 0.05915 \log m_2/m_1}{0.05915} + \log K_w + \log \gamma_H \gamma_{Br} \quad (1)$$

where K_w is the equilibrium constant for the dissociation of water.

By measuring the above cell with a constant value of m_1 and several values of m_2, and by determining $\gamma_H \gamma_{Br}$ $(m = 0)$ in lithium bromide solutions of the same total ionic strength, we can evaluate K_γ if we know E_0 and K_w in pure water. E_0 has recently been determined to be 0.07172 v.,[2] and K_w has been found by electromotive force measurements to be 1.008×10^{-14}.[3] The associated functions $m_w = m_H = m_{OH}$, $\gamma_H \gamma_{OH}$, and $\gamma = \sqrt{\gamma_H \gamma_{OH}}$ can then be calculated if a_{H_2O} is obtainable.

Measurement of the Cells: $H_2 \mid LiOH(m_1), LiBr(m_2) \mid AgBr \mid Ag$.—The determinations were carried out in the usual type of cell. The silver bromide electrodes were protected from light and carbon dioxide was carefully excluded from the cells and solutions. Table I gives the results; column six the mean electromotive force.

In equation (3), rearranged to give

$$E - E_0 + 0.05915 \log m_2/m_1 = -0.05915 \log K_w a_{H_2O} - 0.05915 \log (\gamma_H \gamma_{Br}/\gamma_H \gamma_{OH}) \quad (1a)$$

it is seen that by plotting the left side against μ the function will extrapolate to $0.05915 \log K_w$ at infinite dilution. Use was made of this equation to obtain values of E at round concentrations. Column seven of Table I gives the value of the left side of equation (1a) as determined and column two of Table III gives the value at round concentrations.

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(1) Vance, THIS JOURNAL, **55**, 2729 (1933); Harned and Mason, *ibid.*, **54**, 3112 (1932).

(2) Harned and Hamer, *ibid.*, **55**, 4496 (1933).

(3) (a) Harned and Copson, *ibid.*, **55**, 2206 (1933); (b) Harned and Hamer, *ibid.*, **55**, 2194 (1933).

TABLE I

THE ELECTROMOTIVE FORCES OF THE CELLS: H_2 | LiOH (m_1), LiBr (m_2) | AgBr | Ag

m_1	m_2	μ	No. of cells	Δ(m. v.)	E	$[E - E_0 + 0.05915 \log m_1/m_2]$
0.009913	0.02002	0.02993	2	0.21	0.8801	0.8264
.009963	.04999	.05995	2	.20	.8563	.8260
.009990	.07479	.08478	2	.02	.8451	.8251
.009995	.09995	.1099	2	.32	.8372	.8246
.009969	.1976	.2076	2	.12	.8182	.8232
.009991	.3016	.3116	2	.18	.8058	.8216
.009973	.4020	.4120	2	.07	.7968	.8200
.009985	.4994	.5094	2	.15	.7900	.8188
.009908	.7480	.7579	2	.27	.7761	.8155
.01000	1.0007	1.0107	2	.07	.7651	.8117
.01000	1.4993	1.5093	2	.34	.7486	.8056

The Determination of the Activity Coefficient of Hydrobromic Acid in Lithium Bromide Solutions.—The cell H_2|HBr (0.01), LiBr(m)|AgBr|Ag was measured, and the electromotive forces so obtained were subtracted from the electromotive force of the cell: H_2 | HBr(0.01) | AgBr | Ag.

This process is equivalent to the direct measurement of the cell: Ag | AgBr | HBr(0.01), LiBr (m) | H_2 | HBr (0.01) | AgBr | Ag. The equation connecting the electromotive force of the last cell with the activity coefficient of the acid is

$$E = 0.1183 \log \frac{\gamma_{\mathrm{HBr}}}{0.906} \left[\frac{(0.01 + m)}{0.01}\right]^{1/2} \qquad (2)$$

where 0.906 is the activity coefficient of hydrobromic acid at a concentration of 0.01 m in its own solution. Values of $\gamma_{\mathrm{HBr}\,(0.01)}$ at round concentrations were obtained by plotting the values of $\gamma_{\mathrm{HBr}\,(0.01)}$ from equation (4) against $\mu^{1/2}$. Values of $\gamma_{\mathrm{H}}\gamma_{\mathrm{Br}\,(0.0)}$ are required by equations (1) and (1a), and can be found by making the usual short extrapolation of

TABLE II

THE ACTIVITY COEFFICIENT OF 0.01 MOLAL HYDROBROMIC ACID IN LITHIUM BROMIDE SOLUTIONS AT 25°

m	No. of cells	Δ(m. v.)	E	$\gamma_{\mathrm{HBr}\,(0.01)}$	m	No. of cells	Δ(m. v.)	E	$\gamma_{\mathrm{HBr}\,(0.01)}$
0.0	15	0.2	0.31343	0.906	0.7993	1	...	0.20488	0.833
.02500	3	.04	.28401	.859	.8997	1	...	.20089	.849
.04827	1	...	.27263	.830	.9010	1	...	.20058	.854
.07472	1	...	.26406	.814	.9996	2	0.0	.19720	.866
.1004	2	0.15	.25769	.806	1.1989	1	...	.19041	.903
.1994	1	...	.24270	.784	1.4008	1	...	.18354	.956
.2995	1	...	.23324	.776	1.5996	1	...	.17724	1.011
.4016	2	0.1	.22561	.780	1.7893	1	...	.17133	1.074
.5016	1	...	.21940	.790	1.9837	1	...	.16541	1.144
.5993	1	...	.21458	.795	2.2502	1	...	.15851	1.229
.6002	1	...	.21432	.798	2.2581	1	...	.15813	1.236
.7006	1	...	.20936	.815	2.4893	1	...	.15137	1.343

$\gamma_{\text{HBr (0.01)}}$,[4] to obtain $\gamma_{\text{HBr (0.0)}}$ and then by squaring $\gamma_{\text{HBr (0.0)}}$. Table II contains the values of the measured electromotive forces and of $\gamma_{\text{HBr (0.01)}}$. Column three of Table III gives the values of $\gamma_{\text{HBr (0.01)}}$ at round concentrations and column four the corresponding values of $\gamma_{\text{H}}\gamma_{\text{Br (0.0)}}$.

The Calculation of $a_{\text{H}_2\text{O}}$ in Lithium Bromide Solutions.—Values of $a_{\text{H}_2\text{O}}$ in these solutions were calculated from the activity coefficients of lithium bromide according to the method originated by Harned.[5] The values of γ_{LiBr} used were those given by Harned.[6] The activity coefficients of lithium bromide can be expressed by the equation

$$\log \gamma_{\text{LiBr}} = -\beta m\alpha' + \alpha m \qquad (3)$$

when the constants have the values $\beta = 0.271$, $\alpha' = 0.361$ and $\alpha = 0.177$. Values of $a_{\text{H}_2\text{O}}$ were subsequently calculated from the equation

$$\ln \frac{1}{a_{\text{H}_2\text{O}}} = \frac{m}{55.5}\left[\nu + \frac{2.303\ \alpha\nu m}{2} - \frac{2.303\ \beta\nu\alpha'}{\alpha' + 1} m^{\alpha'}\right] \qquad (4)$$

These values are given in column six of Table III.

TABLE III

CALCULATION OF K_γ FROM DATA IN TABLES I AND II, WITH VALUES OF m_{w}, $\gamma_{\text{H}}\gamma_{\text{OH}}$ AND $\sqrt{\gamma_{\text{H}}\gamma_{\text{OH}}}$ AT ROUND CONCENTRATIONS

μ	$[E - E_0 + 0.05915 \log m_2/m_1]$	$\gamma_{\text{HBr (0.01)}}$	$\gamma_{\text{H}}\gamma_{\text{Br}\ (m = 0)}$	K_γ	$a_{\text{H}_2\text{O}}$	$m_{\text{w}} \times 10^7$	$\gamma_{\text{H}}\gamma_{\text{OH}}$	γ
0.03	0.8267	0.865	0.747	0.712	0.999	1.19	0.711	0.844
.04	.8263	.851	.723	.679	.999	1.22	.678	.824
.05	.8261	.840	.702	.655	.998	1.24	.654	.809
.06	.8258	.830	.685	.632	.998	1.26	.631	.794
.075	.8254	.820	.669	.608	.997	1.29	.606	.779
.10	.8249	.808	.650	.579	.997	1.32	.577	.760
.15	.8240	.790	.621	.534	.995	1.37	.531	.729
.20	.8232	.780	.605	.504	.993	1.41	.500	.708
.40	.8202	.772	.593	.440	.986	1.51	.434	.659
.60	.8174	.798	.632	.420	.978	1.55	.411	.641
.80	.8147	.826	.679	.406	.971	1.58	.394	.627
1.00	.8120	.863	.740	.398	.963	1.59	.383	.619
1.25	.8088	.914	.830	.394	.952	1.60	.375	.612
1.50	.8057	.978	.950	.401	.942	1.59	.378	.615

Calculation of K_γ, m_{w}, $\gamma_{\text{H}}\gamma_{\text{OH}}$ and γ.—These functions can now be calculated from equation (1). The values of K_γ, m_{w}, $\gamma_{\text{H}}\gamma_{\text{OH}}$ and $\gamma = \sqrt{\gamma_{\text{H}}\gamma_{\text{OH}}}$ are given in columns five, seven, eight and nine, respectively, of Table III. The values for K_γ in these solutions are slightly but definitely lower than the values found in lithium chloride solutions.[3a]

Summary

1. The electromotive forces of the cells: $\text{H}_2 \mid \text{LiOH}\ (m_1), \text{LiBr}\ (m_2) \mid \text{AgBr} \mid \text{Ag}$, and of the cells: $\text{H}_2 \mid \text{LiBr}\ (m), \text{HBr}\ (0.01) \mid \text{AgBr} \mid \text{Ag}$, have

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(4) See, for example, Harned and Mason, THIS JOURNAL, 54, 3112 (1932).

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

(6) Harned, THIS JOURNAL, 51, 416 (1929).

been measured and the activity coefficient of 0.01 *m* hydrobromic acid determined in lithium bromide solutions.

2. From a combination of the data obtained from the two cells and from the known activity coefficients of lithium bromide, the dissociation of water in lithium bromide solutions has been calculated.

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Further Discussion of the Surface Tension of Film-Covered Liquids at Saturation

BY HENRY BROWN

The surface tension[1] σ_{13} registered at saturation vapor pressures by a liquid covered with a film is given by

$$\sigma_{13} = \sigma_{12} + \sigma_{23} \tag{1}$$

This equation must be interpreted differently for a film of monomolecular thickness from that for a film of such thickness that its interior possesses the properties of a phase in mass. In the latter case, two surfaces of discontinuity exist, and hence two surface tensions σ_{12} and σ_{23}, but in the former case the value σ_{13} cannot be interpreted in terms of σ_{12} and σ_{23}, *per se.* The lowering of the surface tension of the liquid by the molecules of the monomolecular film is to be explained by the closer packing of the film molecules as a two-dimensional phase[2] according to the familiar conceptions developed by Langmuir.

The amount of lowering of the surface tension by a given number of film molecules when packed in the form of a monomolecular film would be different from that when packed as a polymolecular film of the same area, and since in the former case all the film molecules would be in closer contact (in fact, they would be in direct contact) with the molecules of the supporting liquid, it follows that the monomolecular film would cause the greater lowering of the surface tension for the same number of molecules per unit area, *i. e.*, for the same value of the film density; hence the monomolecular film is of greater stability, and by condensation from the vapor probably never becomes a thicker film with an interior having,

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(1) Bartell, Case and Brown, THIS JOURNAL, **55**, 2769 (1933).

(2) For a two-dimensional phase, the fundamental thermodynamic equation would be

$$d\epsilon = t d\eta - f ds + \mu_1 dm_1 + \mu_2 dm_2 + \ldots \tag{2}$$

where in place of the $-p dv$ term of a three-dimensional phase (J. Willard Gibbs, equation 86), we have $-f ds$; the f is the two-dimensional outward pressure exerted by the molecules of the film in the plane of the film. The monomolecular film is to be considered as a part of the surface of discontinuity of the liquid, the fundamental equation of which (Gibbs, equation 501) contains a $+\sigma ds$ term instead of the $-f ds$ term above. These terms differ in sign because the natural tendency (to minimum potential energy) for the monomolecular film is to *expand* in area, whereas, for the surface of a liquid, to *contract.* It follows that the greater the value of f of the monomolecular film, the lower will be the value of σ.