[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA.]

A COMPARISON OF THE ACTIVITIES OF TWO TYPICAL ELECTROLYTES.

BY G. A. LINHART.

In a paper on "The Free Energy of Chemical Substances,"[1] G. N. Lewis has outlined several methods of measuring relative activities of chemical substances in concentrated solution. These methods have been applied in the present investigation, which deals with activity measurements of hydrochloric acid and potassium chloride.

The hydrogen electrode has been recently studied by several investigators with the view of determining the thermodynamic or "corrected" degree of dissociation. All these investigators give approximately the same value for the e. m. f. of the 0.1 N hydrogen electrode, but at other concentrations, and especially below 0.1 N, the discrepancies are so large that it was impossible to decide what values to use in the calculations of the results of the present investigation. It, therefore, seemed desirable to repeat some of those measurements, and extend the investigation to include the concentration range from 0.01 N nearly to saturation at $25°$.

Experimental Results.

The improved hydrogen electrode and calomel electrode are fully described by Lewis, Brighton and Sebastian.[2] It may, however, be stated here that in order to obtain reproducible results in very concentrated solutions of hydrochloric acid, the platinum electrode used in the hydrogen cell was first gold plated and then firmly iridized, as recommended by Lewis in the paper already cited.

TABLE I.

Σ (HCl).	E (obs.).	[HCl].[3]	[H₂O].	[H₂].	E (calc. to H₂ at 1 atmos.).
0.01006	—0.5106	....			—0.5110
0.01006	—0.5104	....	23.8	736.2	—0.5108
0.1009	—0.3985	....			—0.3989
0.1009	—0.3986	....	23.7	736.1	—0.3990
1.029	—0.2774	....			—0.2778
1.029	—0.2776	....	22.9	737.1	—0.2780
2.25	—0.2228	....			—0.2231
2.25	—0.2228	....	21.5	738.5	—0.2231
6.75	—0.0970	....			—0.0972
6.75	—0.0970	(0.270)	14.0	745.7	—0.0972
10.0	—0.0300	....			—0.0302
10.0	—0.0301	3.66	9.4	747.0	—0.0303
16.0	+0.0692	....			+0.0662
16.0	+0.0693	156.6	3.9	599.5	+0.0663

[1] G. N. Lewis, THIS JOURNAL, **35,** 25 (1913).

[2] Lewis, Brighton and Sebastian, Ibid., **39,** 2245 (1917).

[3] See note at the end of this article.

In the table above are given the e. m. f. data of calomel electrodes against hydrogen electrodes. In each case two hydrogen electrodes and two calomel electrodes were used. In the first column are given the concentrations of hydrochloric acid expressed in mols per 1000 g. water; in the second, the e. m. f. data of each calomel electrode against the hydrogen electrodes, the concentration of the hydrochloric acid being the same throughout the cell; in the third, the partial vapor pressures of the hydrochloric acid; in the fourth, the partial vapor pressures of the water; in the fifth, the partial vapor pressures of the hydrogen; in the last column the e. m. f. values calculated to hydrogen at one atmosphere.

Discussion of Results.

The e. m. f. values given in the second column of Table I are those obtained at the end of twelve hours and twenty-four hours, during which period the maximum variations did not exceed a tenth of a millivolt. It
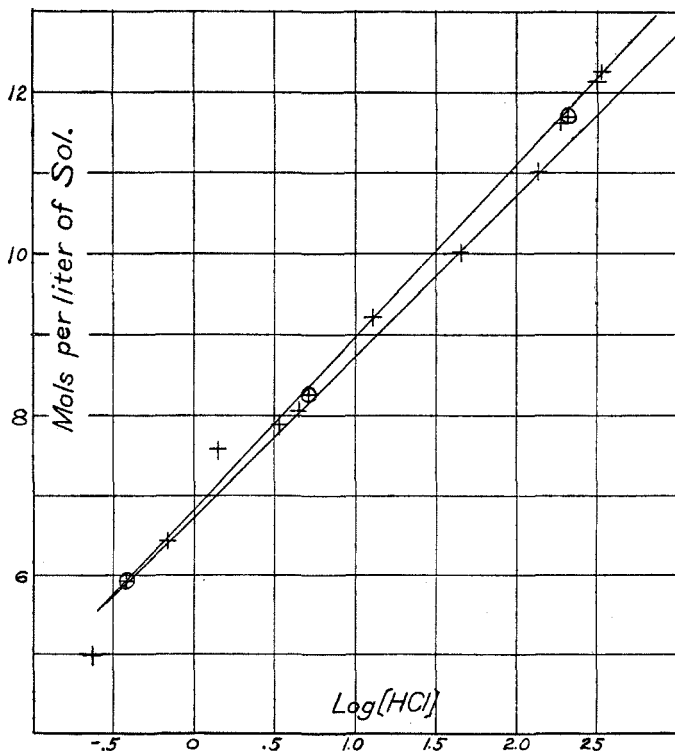
may be pointed out that if these e. m. f. values are plotted on a large scale against the logarithms of $\Sigma(HCl)$ the values given by Ellis[1] for the con-

[1] Ellis, THIS JOURNAL, 38, 752 (1916); see also Tolman and Ferguson, Ibid., 34, 232 (1912).

centration range 0.03332 M to 4.484 M, fall practically on the same line. The values given in the table for the e. m. f. obtained with 0.01006 M hydrochloric acid agree with those obtained in this laboratory by Lewis, Sebastian and Brighton.

Calculations of the Activity Products of $(H^+)(Cl^-)$ and the Equilibrium Constant $(H^+)(Cl^-)/[HCl]$.

In the calculations of the activity products of hydrogen and chloride ions from the e. m. f. values given in the second column of Table I, we must apply corrections for the partial vapor pressures, in the hydrogen cell, of the water and hydrochloric acid, respectively. For dilute solutions the partial vapor pressure of hydrochloric acid is negligible, and even at 10.0 M it is only about 3.66 mm., so that the vapor pressure of the water at each concentration may be calculated from the e. m. f. data given in the second column of Table I, by successive approximations with the aid of the thermodynamic equation

$$n_1 d \ln p = -f/RT\, n_2 dE,$$

where n_1 and n_2 denote the mols of H_2O and HCl, respectively; p, the partial vapor pressure of the water, and E the corresponding e. m. f. value. $f = 96,500$ coulombs, $R = 1.989$, $T = 298$. Integrating the above equation, we have,

$$2.3 \log p = 2.3 \log 23.8 + f/RT \int n_1/n_2 dE,$$

where 23.8 is the vapor pressure of pure water. The value for $n_1/n_2\ dE$ is evidently the area under the curve when n_1/n_2 is plotted against E. Subtracting now the values for the vapor pressures of the water and for those of hydrochloric acid from the barometric pressures gives the partial vapor pressures of the hydrogen in the cells.

Assuming now 0.93[1] as the "corrected" degree of dissociation of hydrochloric acid at 0.01 M, we may calculate the activity products of the chloride and hydrogen ions and the degree of dissociation of hydrochloric acid at the given concentrations by means of the equation

$$\Delta E = 0.059151 \log \frac{(H^+)(Cl^-)}{(0.93 \times 0.01006)^2},$$

where ΔE denotes the difference between the e. m. f. (of last column of Table I) at 0.01006 and at n M hydrochloric acid. In Table II are given the available vapor pressures of hydrochloric acid; the corresponding activity products of the hydrogen and chloride ions and the equilibrium constants; in Table III are given the thermodynamic or "corrected" degrees of dissociation of hydrochloric acid and potassium chloride, the latter calculated from existing e. m. f. data,[2] for comparison.

[1] In this laboratory the value 0.93 has been provisionally chosen for a number of uni-univalent electrolytes until more accurate data are obtained between 0.01 and 0.0001 M.

[2] Linhart, THIS JOURNAL, **39**, 618 (1917).

TABLE II.

Mols HCl per 1000 g. H₂O.	[HCl] 25° in mm.	$(H^+)(Cl^-)$.	$\dfrac{(H^+)(Cl^-)}{[HCl]}$.
6.75	(0.270)	862	(3200)
10.0	3.66	11720	3200
16.0	156.6	500800	3200

TABLE III.

Comparison of the Thermodynamic or "Corrected" Degree of Dissociation of HCl and KCl.

Σ (HCl).	$\dfrac{\sqrt{(H^+)(Cl^-)}}{\Sigma\,(HCl)}$.	$\dfrac{\sqrt{(K^+)(Cl^-)}}{\Sigma\,(KCl)}$.	Σ (KCl).
0.01006	0.93	0.93	0.010
0.10086	0.82	0.78	0.100
1.0293	0.85	0.60	1.031
2.2495	1.13	0.62	3.320
6.750	4.35	0.64	4.284
10.00	10.83	..	...
16.0	44.2	..	...

Finally, it is interesting to note that contrary to assertions frequently found in the literature,[1] the thermodynamic degrees of dissociation of HCl and KCl are not equal even in dilute solution, while in concentrated solution the divergence is enormous, as is evident from the values given in the table above.

NOTE.—Calculation of the Vapor Pressure of Aqueous Hydrochloric Acid at 25°. —There are at present no satisfactory vapor-pressure data of aqueous hydrochloric acid at 25°, but for 30° the results obtained by Dolezalek (Z. physik. Chem., 26, 334 (1898)), who used reliable methods, seem to be accurate considering the experimental difficulties encountered in such measurements. These vapor-pressure data do not extend below 5 molal, because below this concentration the vapor pressure is exceedingly small and therefore difficult to measure accurately. In Table IV, below, are given Dolezalek's original data as well as the interpolated values, enclosed in parentheses.

TABLE IV.

HCl in mols per l. of sol.	[HCl]₃₀° in mm.	log [HCl]₃₀°.
4.98	0.24	— 0.620
(5.93)	(0.404)	—(0.393)
6.43	0.69	—0.161
7.58	1.41	0.149
7.89	3.34	0.524
8.04	4.44	0.647
(8.27)	(5.24)	(0.719)
9.21	12.74	1.105
10.24	45.5	1.658
11.20	134.0	2.127
11.62	189.0	2.276
(11.69)	(210.0)	(2.32)
12.14	313.0	2.496
12.25	337.0	2.528

[1] Loomis, Essex and Meacham, THIS JOURNAL, 39, 1133 (1917); Loomis and Meacham, Ibid., 38, 2310 (1916).

If the values of column one are plotted against the logarithms of the vapor pressures, all points except the first and the third fall within two straight lines whose distance apart is within experimental error. In the original article Dolezalek expresses the concentration in mols per liter of solution. In order therefore to obtain from the curve the values for the vapor pressures for the corresponding concentrations of HCl given in Table I (16.0, 10.0 and 6.75 mols per 1000 g. of water) a liter of each of these solutions was weighed, and the concentration computed to mols per liter of solution. The vapor pressures corresponding to these concentrations are indicated by $\oplus$ on the curve. By means of these values and the heats of solution of HCl for the corresponding concentrations, the vapor pressures for 25°, were calculated by means of the equation

$$\ln \frac{[HCl]_2}{[HCl]_1} = \frac{\Delta H(T_2 - T_1)}{RT_2T_1},$$

where ΔH denotes the partial molal heat of vaporization of HCl at the given concentration n (mols HCl per 1000 g. H_2O). ΔH is numerically equal to the slope obtained by plotting against n the heat change Q,[1] when n mols of HCl gas are dissolved in 1000 g. H_2O. The results of these calculations are given in Table V.

TABLE V.

Mols HCl per 1000 g. H_2O.	$[HCl]30°$ mm.	$[HCl]25°$ mm.	ΔH cal.
6.75	(0.404)	(0.270)	14630
10.00	5.24	3.66	12930
16.0	210.0	156.6	10580

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A REVISION OF THE ATOMIC WEIGHT OF SAMARIUM.
THE ANALYSIS OF SAMARIUM CHLORIDE.

By O. J. STEWART AND C. JAMES.

Soon after the discovery of samarium by Boisbaudran, in 1878, Marignac[2] announced its atomic weight to be 149.4. This work was followed by that of Brauner,[3] who claimed to have prepared a purer material, giving the number 150.7. No details, however, were given.

Cleve's[4] systematic work, involving the synthesis of the sulfate from

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[1] The values for Q were taken from a paper by G. N. Lewis, THIS JOURNAL, 35, 11 (1913).

When the change in Q with n is so large as to necessitate a scale of about 1000 cal. to 1 mm. on the plotting paper, as in the present case, then dQ/dn may be resolved in such a manner as to render plotting more convenient. Thus, let $Q = nQ'$. Then $dQ/dn = d(nQ')/dn = dQ'/d \ln n + Q'$. The change in Q' is only 3940 cal. for the chosen range of concentration of the HCl (0.185 to 18.5 molal) while the change in Q for the same range is 244000 cal.

It will be noted also that if the values for log n are plotted as abscissae and those for Q' as ordinates, the values for Q' fall below the horizontal axis, so that the slopes $dQ'/d \ln n$, will be of opposite sign with respect to Q'.

[2] Arch. Sci. Phys. Nat., [3] 3, 435 (1880).

[3] J. Chem. Soc., 43, 287 (1883).

[4] Ibid., 43, 362 (1883).