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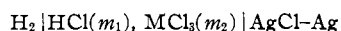
### The Activity Coefficient of Hydrochloric Acid in Concentrated Aqueous Higher Valence Type Chloride Solutions at 25°. III. The System Hydrochloric Acid–Aluminum Chloride

BY HERBERT S. HARNED AND ROBERT GARY

RECEIVED APRIL 1, 1955

The activity coefficient of hydrochloric acid in solutions of aluminum chloride has been determined at 1, 3, 5 total ionic strengths by measurements of the electromotive forces of suitable cells. The rule of the linear variation of the logarithm of the activity coefficient of the acid at constant total ionic strength is closely obeyed. The thermodynamics of the system is developed by the use of the Gibbs–Duhem and cross-differentiation equations.

Electromotive force measurements of cells of the type



have been made by Harned and Mason<sup>1,2</sup> and Mason and Kellam<sup>3</sup> on systems containing aluminum and cerium chlorides, respectively. Following the procedure adopted by us<sup>4</sup> in studying the cells containing barium and strontium chlorides, a precise and extensive series of results have been obtained which form the basis for a thorough exposition of the thermodynamics of the system hydrochloric acid–aluminum chloride–water at high ionic strengths.

**Experimental Data.**—Table I contains the observed electromotive forces of the cells designated. Each result is the mean of three measurements which agreed to within 0.05 mv.

**Activity Coefficients and the Linear Variation of their Logarithms at 1, 3, 5 Constant Ionic Strengths.**—Table II contains the activity coefficients of hydrochloric acid computed by the equation

$$E = E^\circ - 0.1183 \log \sqrt{\gamma_1^2 m_1 (m_1 + 3m_2)} \quad (1)$$

As in our earlier calculations,<sup>4</sup> the value of 0.22246 absolute volt for  $E^\circ$  was used. The molalities of the acid and salt are represented by  $m_1$  and  $m_2$ , respectively. The numerical equations given at the top

(1) H. S. Harned and C. M. Mason, *THIS JOURNAL*, **53**, 3377 (1931).

(2) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, p. 458.

(3) C. M. Mason and D. B. Kellam, *J. Phys. Chem.*, **38**, 689 (1934).

(4) H. S. Harned and R. Gary, *THIS JOURNAL*, **76**, 5924 (1954); **77**, 1994 (1955).

TABLE I

ELECTROMOTIVE FORCES IN ABSOLUTE VOLTS OF THE CELLS:  
 $\text{H}_2$  (1 ATM.) |  $\text{HCl}$  ( $\mu_1 = m_1$ ),  $\text{AlCl}_3$  ( $\mu_2$ ) |  $\text{AgCl}-\text{Ag}$  AT 25° AT  
1, 3, 5 TOTAL IONIC STRENGTHS

$m_1$	$\mu = 1$	$E$	$m_1$	$\mu = 3$	$E$	$m_1$	$\mu = 5$	$E$
1.0	0.23322		3.0	0.15813		5.0	0.09519	
0.9	.23799		2.7	.15841		4.5	.10290	
.8	.24321		2.4	.16484		4.0	.11108	
.7	.24869		2.1	.17183		3.5	.11968	
.6	.25499		1.8	.17959		3.0	.12897	
.5	.26207		1.5	.18810		2.5	.13901	
.4	.27024		1.2	.19794		2.0	.15036	
.3	.28039		0.9	.....		1.5	.16334	
.2	.29349		0.6	.22429		1.0	.17988	
.1	.31433		0.3	.24688		0.5	.20383	

of the table were used to test the validity of the linear variation rule. Since 0.1% in  $\gamma_1$  correspond to about 0.05 mv., the magnitudes of the deviations,  $\Delta\gamma_1$ , indicate that the linear equations represent the observed results within narrow limits. A possible exception occurs with the results at 5 total ionic strength and low acid concentration where the observed results seem to fall below the calculated ones. At 1  $\mu$  the formula used by Harned and Mason<sup>1</sup> was:  $\log \gamma_1 = -0.0900 - 0.0605 \mu$  which agrees closely with the equation employed by us.

**Thermodynamic Considerations.**—Following the procedure adopted in our earlier communications,<sup>4</sup> the assumption is made that the linear variation rule holds within narrow limits for the activity co-

TABLE II  
OBSERVED AND CALCULATED ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID

$\Delta\gamma_1 = \gamma_1(\text{obs.}) - \gamma_1(\text{calcd.})$

Eq. used for calcn.  $\begin{cases} \mu = 1; \log \gamma_1 = -0.09091 - 0.0614 \mu_2 \\ \mu = 3; \log \gamma_1 = 0.11915 - .0629 \mu_2 \\ \mu = 5; \log \gamma_1 = 0.37676 - .0631 \mu_2 \end{cases}$

$\mu = 1$			$\mu = 3$			$\mu = 5$		
$m_1$	$\gamma_1$	$\Delta\gamma_1$	$m_1$	$\gamma_1$	$\Delta\gamma_1$	$m_1$	$\gamma_1$	$\Delta\gamma_1$
1.0	0.8111	-0.0003	3.0	1.318	+0.002	5.0	2.380	-0.001
0.9	.7994	.0000	2.7	1.254	-.006	4.5	2.216	+.002
.8	.7870	-.0012	2.4	1.205	-.001	4.0	2.059	.000
.7	.7781	+.0010	2.1	1.157	+.002	3.5	1.916	+.002
.6	.7664	+.0002	1.8	1.108	+.002	3.0	1.780	.000
.5	.7555	.0000	1.5	1.062	+.003	2.5	1.657	+.002
.4	.7458	+.0009	1.2	1.015	+.001	2.0	1.537	-.002
.3	.7335	-.0009	0.9	.....	.....	1.5	1.431	.000
.2	.7246	+.0005	.6	0.9286	-.0008	1.0	1.322	-.009
.1	.7135	-.0005	.3	.8872	-.0026	0.5	1.225	-.013

efficients of both electrolytic components. Thus

$$\log \gamma_1 = \log \gamma_{1(0)} - \alpha_{12}\mu_2 \quad (2)$$

$$\log \gamma_2 = \log \gamma_{2(0)} - \alpha_{21}\mu_1 \quad (3)$$

$$\mu = \mu_1 + \mu_2 \quad (4)$$

In these expressions  $\gamma_{1(0)}$ ,  $\gamma_{2(0)}$  are the activity coefficients of the acid and salt in water,  $\gamma_1$ ,  $\gamma_2$  their activity coefficients in the mixtures,  $\mu_1$  and  $\mu_2$ , their concentrations expressed as ionic strengths and  $\alpha_{12}$  and  $\alpha_{21}$  are constants at each total ion strength.

If the constant  $\alpha_{12}$  is known and equations 2 and 3 are valid, then  $\alpha_{21}$  may be computed by the equation

$$\frac{\alpha_{21}}{z_{2+}z_{2-}} = \frac{\alpha_{12}}{z_{1+}z_{1-}} - \frac{2}{2.3\mu} \left[ \left( \frac{\phi_1}{z_{1+}z_{1-}} - \frac{\phi_2}{z_{2+}z_{2-}} \right) - \left( \frac{1}{z_{1+}z_{1-}} - \frac{1}{z_{2+}z_{2-}} \right) \right] \quad (5)$$

where  $z_{1+}$ ,  $z_{1-}$ ,  $z_{2+}$ ,  $z_{2-}$  are the valences of the ions and  $\phi_1$  and  $\phi_2$  are the osmotic coefficients of the two electrolytes in the pure solvent. If the subscripts one and two represent hydrochloric acid and aluminum chloride, respectively, then  $z_{2+} = 3$ ,  $z_{2-} = z_{1+} = z_{1-} = 1$  and this equation reduces to

$$\frac{\alpha_{21}}{S} = \alpha_{12} - \frac{0.868}{\mu} \left( \phi_1 - \frac{\phi_2}{3} - 0.667 \right) \quad (6)$$

From the knowledge of  $\alpha_{12}$  and  $\alpha_{21}$ , the osmotic coefficient,  $\phi_x$ , in the mixture may be computed by the equation

$$\left( \frac{\nu_1}{j} \alpha_{12} + \frac{\nu_2}{k} \alpha_{21} \right) \frac{x^2}{2} + \left( \frac{\nu_1}{2.3j\mu} - \frac{\nu_2}{2.3k\mu} - \frac{\nu_2}{k} \alpha_{21} \right) x = \frac{2}{2.3\mu} \frac{\phi_2}{z_{1+}z_{2-}} + \frac{2\phi_x}{2.3\mu} \left( \frac{x}{z_{1+}z_{1-}} + \frac{(1-x)}{z_{2+}z_{2-}} \right) \quad (7)$$

where  $\nu_1$  and  $\nu_2$  are the number of ions into which the electrolytes dissociate and the valence factors  $j$  and  $k$  are defined by the relations  $\mu_1 = jm_1$ ,  $\mu_2 = km_2$ . The activity of water and subsequently the water vapor pressure can be obtained by the equation

$$\log a_{w(x)} = \frac{2\mu\phi_x}{(2.3)55.5} \left( \frac{x}{z_{1+}z_{1-}} + \frac{(1-x)}{z_{2+}z_{2-}} \right) \quad (8)^5$$

Table III contains the measured values of  $\alpha_{12}$  and values of  $\alpha_{21}$  calculated by equation 6. The osmotic coefficients,  $\phi_1$  and  $\phi_2$ , were obtained from plots

(5) A typographical error in sign occurs in these last two equations as printed in our earlier communication (ref. 4). The minus sign should be plus in the right hand parentheses in both these equations. This error does not affect any of the calculations.

of the data of Stokes<sup>6</sup> and Robinson and Stokes.<sup>7</sup> In the second part of the table, similar quantities for the system hydrochloric acid-cerium chloride-water obtained from the data of Mason and Kellam<sup>8</sup> are recorded. The values of  $\alpha_{12}$  for the cerium chloride mixtures were obtained from measurements of the activity coefficient of the acid at 0.01  $M$  in the cerium chloride solutions and, consequently, are not the result of as comprehensive a study as the present one.

TABLE III  
DATA EMPLOYED IN EQUATIONS

	$\phi_1$	$\phi_2$	$\alpha_{12}$	$\alpha_{21}$	$S = 12\alpha_{12} + 4\alpha_{21}$
(1) HCl-AlCl <sub>3</sub> -H <sub>2</sub> O <sup>8</sup>					
$\mu = 1$	1.039	0.831	0.0614	-0.0636	0.482
$\mu = 2$	1.118	0.905	.062	-.099	.348
$\mu = 3$	1.348	1.007	.0629	-.1113	.310
$\mu = 5$	1.680	1.272	.0631	-.1179	.286
(2) HCl-CeCl <sub>3</sub> -H <sub>2</sub> O					
$\mu = 1$	1.039	0.795	0.0870	-.0177	0.973
$\mu = 2$	1.188	.847	.0908	-.0426	.919
$\mu = 3$	1.348	.914	.0918	-.0510	.898

We have shown that equation 2 expresses within narrow limits the variation of the logarithm of activity coefficient of hydrochloric acid at constant total ionic strength. Since no experimental method is available for determining the activity coefficient of aluminum chloride in these mixtures, we have assumed that its variation is expressed by equation 3. Following a procedure suggested by Glueckauf<sup>9</sup> which involves fundamental cross differentiation equations, we have shown that, if both equations 2 and 3 are valid, the quantity  $S = \nu_1 k \alpha_{12} + \nu_2 j \alpha_{21}$  must be a constant, independent of the total ionic strength,  $\mu$ . For systems containing a uniunivalent and a triunivalent electrolyte,  $S = 12\alpha_{12} + 4\alpha_{21}$ . Values of  $S$  are recorded in the last column of Table III.

The behavior of  $S$  for these acid-triunivalent salt mixtures follows the pattern found for the acid-bi-

(6) R. H. Stokes, *Trans. Faraday Soc.*, **44**, 295 (1948).

(7) R. A. Robinson and R. H. Stokes, *ibid.*, **45**, 612 (1949).

(8) The result at  $2\mu$  was computed from the data of Harned and Mason (reference 1).

(9) E. Glueckauf, H. A. C. McKay and A. R. Mathieson, *J. Chem. Soc. S.* 299 (1949); *Trans. Faraday Soc.*, **47**, 428 (1931).

univalent chloride systems.  $S$  appears to decrease rapidly in the more dilute solutions and to approach constancy at the higher concentrations. When the sensitivity of this test is taken into account, it appears that equations 2 and 3 yield a close approximation to the actual behaviors of these mixtures.

For purposes of future comparison, we record in Table IV the hypothetical osmotic coefficients of

TABLE IV  
OSMOTIC COEFFICIENTS AND VAPOR PRESSURES AT 25° OF  
THE SYSTEM HCl-AlCl<sub>3</sub>-H<sub>2</sub>O

$m$	$\mu = 1$			$\mu = 3$			$\mu = 5$		
	$\phi_x$	$p$	$\phi_x$	$m_1$	$\phi_x$	$p$	$m_1$	$\phi_x$	$p$
1.0	1.039	22.88	3.0	1.348	20.54	5.0	1.680	17.55	
0.9	1.026	22.96	2.7	1.327	20.79	4.5	1.651	18.00	
.8	1.013	23.02	2.4	1.306	21.03	4.0	1.622	18.44	
.7	1.000	23.09	2.1	1.282	21.27	3.6	1.592	18.89	
.6	0.985	23.15	1.8	1.257	21.51	3.0	1.560	19.33	
.5	.968	23.22	1.5	1.230	21.75	2.5	1.526	19.78	
.4	.950	23.28	1.2	1.199	21.99	2.0	1.488	20.23	
.3	.929	23.34	0.9	1.164	22.22	1.5	1.447	20.67	
.2	.904	23.48	.6	1.123	22.46	1.0	1.399	21.12	
.1	.872	23.49	.3	1.072	22.69	0.5	1.343	21.57	
.0	.831	23.52	.0	1.006	22.91	0.1	1.272	22.01	

[CONTRIBUTION FROM NOYES LABORATORY, DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF ILLINOIS]

## Mechanism of Complex Electrode Reactions

BY K. B. OLDHAM

RECEIVED FEBRUARY 21, 1955

Several possible mechanisms may be envisaged to explain any complex electrode reaction. By assuming a single step to be rate determining, any postulated mechanism may be reduced to an "equivalent reaction pair," which embodies all the kinetic properties of the mechanism. Account is taken of concentration polarization by including transport processes in the treatment. The procedure is easily extended to cover cases of mixed rate determination. From the equivalent reaction pair, current-voltage relationships can be derived in which it is possible to recognize regions of specific control. The converse operation, the determination of the reaction mechanism from current-voltage curves, is subject to severe limitation. The most direct method, examination of the regions of specific control, is applicable only for intermediate values of the rate constant. Under favorable conditions, experimental data will enable the equivalent reaction pair to be constructed, from which possible mechanisms may be inferred. Mechanisms yielding the same equivalent pair are kinetically indistinguishable.

Analysis of conditions at an electrode surface is greatly simplified if one variable, time, can be ignored; hence steady-state conditions only will be treated here. A steady-state electrode system is one in which the activities of all substances present, both at the electrode surface and in the bulk, do not vary appreciably with time, at any potential within the experimental range. Constancy of current is a necessary, though not a sufficient, criterion of steady-state conditions.

The term "electrode reaction" will here denote those processes intimately concerned in the transfer of electrons between an electrode and substances in solution. An electrode reaction may thus involve, in addition to the actual electron transfer, many other reactions, all occurring within a few molecular diameters of the electrode surface. It is convenient to consider the volume in which electrode reactions occur as a zone in which concentrations are uniform and to refer to the activities of substances in this reaction zone as activities "at" the electrode surface. It must be borne in mind that the reaction zone is also occupied by the electrical double layer, but no further mention will be made of this layer on the assumption that any effect of it

the mixtures and the water vapor pressure of the solutions as calculated by equations 7 and 8.

### Conclusions

(1) Equation 2 represents within narrow limits the variation of the logarithm of the activity coefficient of hydrochloric acid in aluminum chloride solutions. The values of  $\alpha_{12}$  change little with ionic strength in these solutions. A like behavior is found for hydrochloric acid-cerium chloride-water systems.

(2) The calculated values of the quantity  $\alpha_{21}$ , vary with ionic strength, and consequently  $S = 12\alpha_{12} + 4\alpha_{21}$  is found to decrease with increasing concentration. The magnitude of this decrease indicates that in these concentrated solutions, small deviations from results calculated by equation 3 will occur.

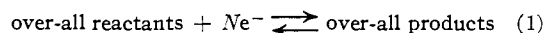
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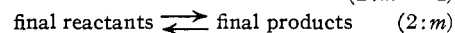
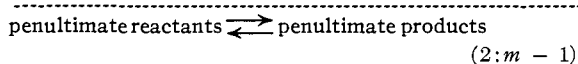
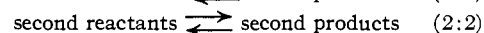
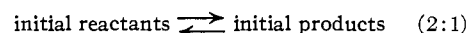
will be nullified by an excess of indifferent electrolyte, the presence of which will be assumed throughout.

### Reaction Rates

Any electrode reaction can be represented by a pair of opposed reactions



expressing the over-all stoichiometry of the reaction. Only for very simple electrode reactions, such as  $Tl^+ + e^- \rightleftharpoons Tl$ , however, can it be hoped that (1) will depict the mechanism of the process. For a more complex reaction the most likely mechanism is a sequence of a number, say  $m$ , of pairs of opposed reactions



all proceeding at the electrode surface. The possibility of parallel reaction paths is considered in an