800°; this is what would be expected from the thermal decomposition of an ammonobasic iodide mixture. This experiment affords no evidence for the presence of a lower oxidation state of aluminum either in the original solid or in the heated solid.

McElroy, Kleinberg and Davidson[14] found that when aluminum ions, iodide ions and the ammoniated electron species were all present in the same solution, an insoluble ammonobasic iodide, $Al(NH_2)_2I \cdot Al(NH_2)_3 \cdot 2NH_3$,[15] was always formed. The components of the reaction systems described in this report differed from those of McElroy, Kleinberg and Davidson only in that alkali or alkaline earth metal ions were also present. Since these metal ions, as such, should have no direct effect upon the nature of aluminum products obtained, the two systems are essentially equivalent, and ammonobasic aluminum compounds should also be the result of the present experiments. In the reactions investigated in the present work, the excess of solvated electrons, which, of course, were accompanied by alkali or alkaline earth metal ions, allowed further reaction and the formation of products other than the one ammonobasic iodide obtained by McElroy and co-workers.

Finally a few words are necessary concerning the interpretation of the potentiometric titration data of Watt, Hall and Choppin.[2] If reduction of aluminum to lower oxidation states takes place, the species formed must react almost instantaneously with the solvent since it has not been possible to detect any reducing power in the reaction mixtures. With aluminum(II) as the specific example, this reaction would be $Al^{2+} + NH_3 = Al^{3+} + NH_2^- + {}^1/_2H_2$. If the aluminum(II) reacted immediately after its formation, the effective concentration of aluminum(II) in the system would remain essentially constant, and nearly equal to zero. Since aluminum(III) is regenerated from the lower state its effective concentration should also remain essentially constant until the accumulation of base (amide ion) would cause a change in the aluminum(III) species present. If the potentiometric data are to reflect reduction of aluminum(III) to aluminum(II), the change in potential must result from changes in the concentration ratio Al(III)/Al(II). Furthermore, the conversion to aluminum(II), and subsequently to aluminum(I), must take place to a major extent in order to change the ratios which cause a potential change. As pointed out above, however, the concentrations of both of these species would be expected to remain nearly constant. Therefore no change in potential would occur as the result of reduction and no break in the curve would be found. It would appear reasonable to expect that if lower valent species were present for a sufficient length of time to allow their detection by the rather slow process of potentiometric titration, they would also be detectable by the various means already mentioned.

Acknowledgment.—The authors are indebted to the Office of Naval Research for a grant in support of this investigation.

LAWRENCE, KANSAS

---

[14] A. D. McElroy, J. Kleinberg and A. W. Davidson, THIS JOURNAL, **72**, 5178 (1950).

[15] This compound is similar to the insoluble ammonobasic iodide isolated by Franklin (ref. 12) by reaction in liquid ammonia between potassium amide and aluminum iodide in the formula weight ratio 2.5:1.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OKLAHOMA A. AND M. COLLEGE]

Activities of Transition Metal Chlorides in Aqueous Hydrochloric Acid Mixtures. I. Nickel(II) Chloride and Cobalt(II) Chloride[1]

BY T. E. MOORE, E. A. GOOTMAN AND P. C. YATES

RECEIVED JULY 26, 1954

The activities of each of the components in ternary H_2O–HCl–$NiCl_2$ or $CoCl_2$ mixtures have been determined at 30° by measurement of the HCl and H_2O partial pressures and integration of the Gibbs–Duhem equation for 3 components. The measurements were made on series of solutions each having constant HCl concentration (from 4.69 and 8.86 m) and variable salt concentrations (from 0.5 m to saturation). The Stokes and Robinson treatment of the activity coefficients of concentrated binary solutions of electrolytes has been extended to ternary mixtures and the experimental results have been treated according to this extended theory. For $CoCl_2$–HCl mixtures where the theory does not hold, spectrophotometric evidence is presented for association of cobalt and chloride ions forming $CoCl_2$.

Recent studies of the solvent extraction of salts from aqueous solutions have shown that the distribution coefficients of many transition metal chlorides are greatly increased when the salts are dissolved in concentrated hydrochloric acid.[2] The literature, however, contains almost nothing of the thermodynamic properties of such acid–salt–water mixtures. As a part of a program of study of the factors affecting the 2-octanol extraction of certain transition metal halides, the activities of each of the components in the ternary systems $NiCl_2$–HCl–H_2O and $CoCl_2$–HCl–H_2O were determined over a wide range of acid and salt concentrations.

Since no satisfactorily reversible electrodes have been found for metals such as nickel or cobalt,[3] it was necessary to make use of the Gibbs–Duhem equation applied to a ternary system and to calculate the salt activity from experimental values of

---

[1] Presented in part at the 9th Southwest Regional meeting of the American Chemical Society, New Orleans, La., 1953. Supported under Contract AT(11-1)-71 No. 1 with the U. S. Atomic Energy Commission.

[2] H. M. Irving, *Quart. Rev.*, **5**, 200 (1951).

[3] W. M. Latimer, "Oxidation Potentials," 2nd edition, Prentice-Hall, Inc., New York, N. Y., 1952, p. 210.

the acid and water activities. The integration of the ternary Gibbs–Duhem equation has been discussed recently by Darken[4] and McKay,[5] who have developed relations for the integration from a knowledge of one of the partial molal quantities under isothermal isobaric conditions, but at all compositions. However, in this investigation it was convenient to measure the partial molal free energies of two of the components, *i.e.*, H_2O and HCl, and thereby greatly cut down the number of necessary experiments.

Theoretical

The Gibbs–Duhem equation for three components is

$$0 = n_1 \mathrm{d}\bar{F}_1 + n_2 \mathrm{d}\bar{F}_2 + n_3 \mathrm{d}\bar{F}_3 \qquad (1)$$

where n_1, n_2, n_3 are the moles of each component and $\bar{F}_1$, $\bar{F}_2$, $\bar{F}_3$ are the respective partial molal free energies. Using the usual definition of the activity $\bar{F}_j = \bar{F}_j^0 + RT \ln a_j$, differentiating with respect to n_3, and dividing through by n_1 gives

$$0 = \left(\frac{\partial \ln a_1}{\partial n_3}\right)_{n_1,n_2} \mathrm{d}n_3 + \frac{n_2}{n_1}\left(\frac{\partial \ln a_2}{\partial n_3}\right)_{n_1,n_2} \mathrm{d}n_3 + \frac{n_3}{n_1}\left(\frac{\partial \ln a_3}{\partial n_3}\right)_{n_1,n_2} \mathrm{d}n_3 \qquad (2)$$

Since for volatile components (assuming ideal behavior in the gas phase) $a_j = p_j/p_j^0$, eq. 2 becomes

$$\mathrm{d}\phi = \frac{-n_3}{n_1} \times \left(\frac{\partial \ln a_3}{\partial n_3}\right)_{n_1,n_2} \qquad (3)$$

where $\phi = \ln p_1 p_2^{k} - \ln p_1^0 p_2^{0k}$ and $k = n_2/n_1$. Integration of eq. 3 along lines of constant n_2/n_1 then permits evaluation of a_3 as a function of the mole ratio n_3/n_1. If component 1 is chosen as H_2O, component 2 as HCl and component 3 as the salt, the integration gives the salt activity as a function of its molality in solutions of fixed HCl molality.

Experimental

Apparatus.—The apparatus was a modification of that described by Bechtold and Newton[6] for the measurement of water vapor pressures by the comparative gas-transpiration technique. The principal modification was in the absorbers, which were filled with a mixture of anhydrous magnesium perchlorate and sodium hydroxide–impregnated asbestos. The latter occupied about the first $^2/_3$ of the absorption tube and the pure magnesium perchlorate the remaining $^1/_3$. Preliminary experiments demonstrated the complete absorption of both HCl and H_2O vapors in these absorbers.

Procedure.—The procedure followed was essentially that used by Bechtold and Newton[6] and the partial pressures of HCl and H_2O were calculated from the weight of absorbed gases as described in their paper. All runs were made at 30.00 ± 0.02° employing tank nitrogen as the carrier gas.

Before measurements were made on ternary systems, the apparatus was tested by determination of the water vapor pressures of H_2SO_4–H_2O standards and the partial pressures of HCl and H_2O in HCl–H_2O mixtures. Three H_2SO_4 standards (1.630, 3.195 and 4.713 *m*) were run, and the experimental results were compared with the water partial pressures calculated from the osmotic coefficients of Stokes.[7] Agreement within 0.1% was obtained with a precision of better than 0.1%.

Partial pressures of water found in the HCl–H_2O system agreed with the results reported by several independent methods; the experimental points fell on a smooth curve lying slightly above that determined from the values listed in the compilation by Zeisberg[8] and slightly below that calculated from the results of the electromotive force measurements of Akerlof and Teare.[9] Similarly the HCl partial pressures fell on a smooth curve drawn through the points given in the Zeisberg[8] compilation. Since these values supplement the literature values in regions where the vapor pressure curve is rising sharply, they are presented in Table I.

TABLE I

VAPOR PRESSURES OF HCl SOLUTIONS AT 30°

Molality	*P* (mm.)	Molality	*P* (mm.)
4.69	0.055	8.86	2.51
4.84	0.072	9.12	3.08
5.53	0.129	9.57	4.45
6.10	0.219	10.02	6.27
6.97	0.514	10.40	8.02
7.73	1.015	10.65	10.53
8.25	1.573		

Materials.—C.P. or Reagent grade chemicals were used throughout the investigation. The $NiCl_2$ label listed an assay of only 0.02% cobalt and the $CoCl_2$ 0.08% of nickel.

Mallinckrodt Analytical Reagent NaOH having 0.010% chloride as impurity was used in the preparation of the absorbers, and Merck reagent grade perchloric acid containing 0.001% chloride was employed in analysis of their contents. The asbestos (such as is ordinarily used in the preparation of Gooch filters) and the $Mg(ClO_4)_2$ also used in the absorbers were shown by test to be free of chloride.

Solutions.—Solutions of salt–HCl–H_2O were prepared either by adding the anhydrous salt (pulverized and redried at 130°) to HCl solutions of predetermined molality or by preparing a stock solution of the desired HCl molality but concentrated with respect to the salt and weighing portions of this stock into weighed amounts of HCl of the same molality. The compositions of the solutions were confirmed by analysis.

Saturated solutions were prepared by carefully adding at intervals small amounts of the anhydrous salt to the nearly saturated solution maintained at 30° in a water-bath. In this manner only a very small amount of the solid hydrate was formed in a large quantity of solution so that the acid molality was unaltered by its formation.

The composition of the solid phases at equilibrium with the different solutions was determined by the wet-residue method of Schreinemakers[10] in the ternary solutions and by separation and blotter drying of crystals prior to analysis in the binary solutions.

Analytical Procedures.—The weighed contents of the absorbers were dissolved in water and the absorbers rinsed repeatedly with water and 25% perchloric acid. After neutralization, the chloride was determined volumetrically by employing a potentiometric endpoint.[11] The absorbed water was calculated from the total weight increase and the HCl found upon analysis. Solutions having a relatively large chloride content were analyzed gravimetrically.

Nickel was determined either by electrolysis[12] or gravimetrically as bis-(dimethylglyoximo)-nickel.[13]

Cobalt was determined electrolytically[12] or gravimetrically as anhydrous $CoCl_2$ after evaporation of the acid solutions.

Calculation of Activities.—All activities were referred to the conventional standard states of the solutes in binary aqueous solutions; *i.e.*, to hypothetical 1 molal solutions having the same chemical potentials as at infinite dilution. This choice of standard states, rather than the alternative states in which each HCl–H_2O mixture is considered a mixed solvent containing the salt as solute, permitted comparisons between series of different HCl/H_2O mole ratios.

Since data were lacking on the activities of binary solu-

---

[4] L. S. Darken, THIS JOURNAL, **72**, 2909 (1950).

[5] H. A. C. McKay, *Trans. Faraday Soc.*, **49**, 237 (1953).

[6] M. F. Bechtold and R. F. Newton, THIS JOURNAL, **62**, 1390 (1940).

[7] R. H. Stokes, *Trans. Faraday Soc.*, **44**, 295 (1948).

[8] Zeisberg, *Chem. Met. Eng.*, **32**, 326 (1925).

[9] G. C. Akerlof and J. W. Teare, THIS JOURNAL, **59**, 1855 (1937).

[10] A. Findlay, "The Phase Rule and Its Applications," 8th Ed., Dover Publications, Inc., New York, N. Y., 1945, p. 271.

[11] I. M. Kolthoff and N. H. Furman, "Potentiometric Titrations," John Wiley and Sons, Inc., New York, N. Y., 1931, pp. 144–154.

[12] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Rev. ed., the Macmillan Co., New York, N. Y., 1953, p. 427.

[13] Ref. 12, p. 722.

tions of $NiCl_2$ at 30°, the data of Stokes[9] at 25° were used to evaluate the activity at the arbitrarily selected concentration of 1.5 molal. The corresponding activity at 30° was then computed from the data compiled by Rossini, *et al.*,[14] for the heat content of the solute by integration to obtain the activity at the higher temperature.[15] It was necessary to regard the partial molal heat content of $NiCl_2$ as constant from 25–30° since no data on the partial molal heat capacities were found in the literature.

Unfortunately no corresponding thermal data were available for $CoCl_2$, but since the literature[8] showed that the activity coefficients of $CoCl_2$ and $NiCl_2$ at 25° are extremely close up to concentrations of 1 molal and even up to 2 molal deviations are of the order of 2%, the assumption was made that the partial molal heat contents of the two salts were the same in a 2 molal solution. The $CoCl_2$ activities in the binary solutions at 30° were then calculated like those of $NiCl_2$ from the data of Robinson and Brown.[16]

The activities of $NiCl_2$ and $CoCl_2$ in saturated solutions at 30° in equilibrium with $NiCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$ were evaluated by extending the vapor pressure measurements on the binary solutions to saturation and integrating the Gibbs–Duhem equation for two components.

From the activity of the salts in saturated solutions the activities of the hexahydrates were calculated according to the relation

$$RT \log a(\text{salt} \cdot 6H_2O) = RT \log a(\text{salt}) + 6RT \log p_1/p_1^0 \quad (4)$$

where $a(\text{salt} \cdot 6H_2O)$ and $a(\text{salt})$ refer to the activities of the solid hydrate and the saturated solution, respectively. Here p_1/p_1^0 is the activity of water referred to pure water. The corresponding activity of $NiCl_2 \cdot 4H_2O$ was obtained from the data of Derbye and Yngve[17] for the equilibrium vapor pressure of the system $NiCl_2 \cdot 6H_2O \rightleftarrows NiCl_2 \cdot 4H_2O + 2H_2O$ and the activity of the hexahydrate.

The activity of $NiCl_2$ or $CoCl_2$ in any one of the salt-saturated ternary solutions was then calculated from the values of the activities of the solid hydrates and the measured water activities of the solutions. The activities of each of the reference states described are listed in Table II.

To obtain the salt activity in a ternary solution, eq. 3 was graphically integrated from a particular concentration to the saturated solution at constant HCl/H_2O mole ratio. The integrations were made on the ϕ curves constructed from large-scale plots of the experimental data by square counting combined with the use of a planimeter and were checked by Simpson's rule.[18] The estimated error in the integration was of the order of 1%. For purposes of the integration eq. 3 was rearranged to give

$$\log (a''_3/a'_3) = \frac{(\phi/r)' - (\phi/r)''}{2.303} - \int_{m'_3}^{m''_3} (\phi/r) \, d \log m_3 \quad (5)$$

where $r = n_3/n_1$. This function was found to be relatively insensitive to errors in plotting and integration.

Precision.—The HCl vapor pressure measurements in the ternary systems were made with an average deviation of ±0.01 mm. from the average of two or more experiments at each concentration. The corresponding deviation in the water vapor pressure measurements was ±0.04 mm. While no claim is made for extremely high accuracy in the values of the salt activities in the ternary systems, no comparable data are found in the literature.

A calculation of the temperature correction to be applied to the water activities at 25° to permit comparison with the 30° experimental activities in the binary salt solutions indicated that this should be within the probable experimental error in the 30° measurements. Comparison with the 25° isopiestic data of Robinson and Brown[16] on $CoCl_2$ solutions at 25° and of Robinson and Stokes[19] on $NiCl_2$ solutions showed that over the range of integration of the Gibbs–Duhem equation the 30° experimental values agreed within ±0.2% with the 25° values.

Discussion of Results

Although aqueous solutions of $NiCl_2$ and $CoCl_2$ are closely similar in their activity coefficients up to moderately high concentrations, the two salts are markedly different in HCl solutions. This is shown by the relative effects of the salts in lowering the H_2O activity and raising the HCl activity at equivalent concentrations. Figures 1 through 3 present the activity curves obtained for H_2O, HCl and $NiCl_2$ or $CoCl_2$ as a function of the salt concentration at constant HCl molality. Particularly striking is the enormous increase in the salt activity in the acid solutions relative to that in aqueous solution. The activity of 1 *m* $NiCl_2$, for example, in 6.86 *m* HCl is *ca.* 10^5 as great as it is in water. Qualitatively these results are consistent with a higher degree of ionic association for $CoCl_2$ than for $NiCl_2$. This might be expected to lower the HCl activity and raise the H_2O activity more in $CoCl_2$ solutions than in $NiCl_2$ solutions which presumably contain a larger number of highly hydrated ions.

I. **$NiCl_2$–HCl Mixtures.**—Efforts to relate empirically the activity coefficients of binary solutions of electrolytes to ionic hydration have met with considerable success through a relation developed by Stokes and Robinson.[20] These authors have shown that by a modification of the Debye–Hückel equation the ion–solvent interactions may be adcounted for up to ionic strengths of about 4. The possibility of relating the activities of mixed-electrolytes to their hydration in a similar fashion has also been treated by Robinson and Stokes.[21] The following is an extension of the Stokes and Robinson treatment applicable to mixtures of two or more electrolytes.

If h_2 and h_3 are the hydration numbers of HCl and $NiCl_2$, respectively, the moles of hydrated solute (primed quantities) per 1000 g. of "free" water are

$$m'_2 = m_2F \text{ and } m'_3 = m_3F \quad (6)$$

where $F = (55.51)/[55.51 - (h_2m_2 + h_3m_3)]$. Written in terms of molalities the Gibbs–Duhem equation (1) is

$$55.51 \, d \ln a_1 + m_2 \, d \ln a_2 + m_3 \, d \ln a_3 = 0 \quad (7)$$

which after allowing for the hydration of the solutes becomes

$$[55.51 - (h_2m_2 + h_3m_3)] \, d \ln a_1 + m_2 \, d \ln a'_2 + m_3 \, d \ln a'_3 = 0 \quad (8)$$

Combination of (7) and (8) gives the basic equation

$$-(h_2m_2 + h_3m_3) \, d \ln a_1 + m_2 (d \ln a_2 - d \ln a'_2) + m_3 (d \ln a_3 - d \ln a'_3) = 0 \quad (9)$$

For variations at constant n_1 and m_2, the introduc-

---

(14) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, 1950.

(15) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed., Reinhold Publ. Corp., New York, N. Y., 1950, chapter 8.

(16) R. A. Robinson and J. B. Brown, *Trans. Proc. Roy. Soc., New Zealand*, **77**, 1 (1948).

(17) I. H. Derbye and V. Yngve, This Journal, **38**, 1439 (1916).

(18) H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand and Co., Inc., New York, N. Y., 1943, p. 460.

(19) R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **36**, 1137 (1940).

(20) R. H. Stokes and R. A. Robinson, This Journal, **70**, 1870 (1948).

(21) R. A. Robinson and R. H. Stokes, *Ann. N. Y. Acad. Sci.*, **51**, 593 (1949).

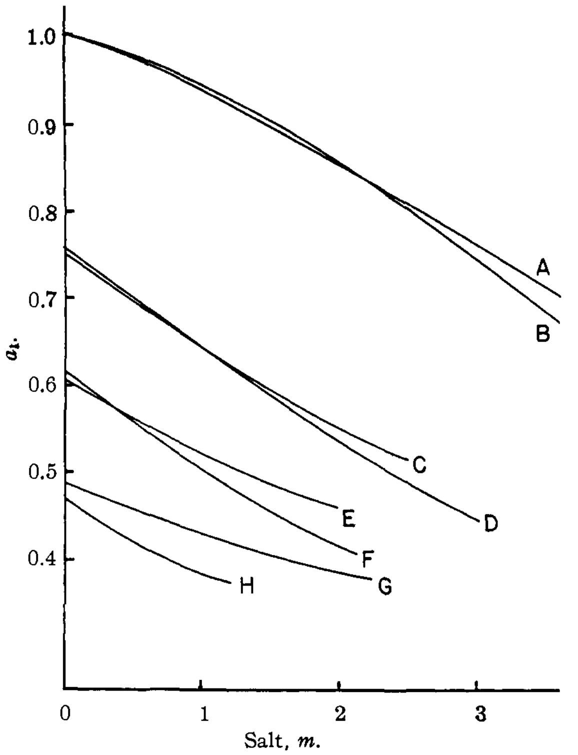

Fig. 1.—Water activities in HCl–salt mixtures: A, $CoCl_2$ alone; B, $NiCl_2$ alone; C, 4.84 *m* HCl + $CoCl_2$; D. 4.69 *m* HCl + $NiCl_2$; E, 6.97 *m* HCl + $CoCl_2$; F, 6.86 *m* HCl + $NiCl_2$; G, 8.86 *m* HCl + $CoCl_2$; H, 9.12 *m* HCl + $NiCl_2$.

tion of mean ionic activity coefficients and rearrangement of terms converts (9) into

$$\nu_2 m_2 \left[\frac{h_2}{\nu_2}\left(\frac{\partial \ln a_1}{\partial m_3}\right)_{n_1,m_2} dm_3 - \left(\frac{\partial \ln \gamma'_{\pm 2}/\gamma_{\pm 2}}{\partial m_3}\right)_{n_1,m_2} dm_3 - \left(\frac{\partial \ln F}{\partial m_3}\right)_{n_1,m_2} dm_3\right] + \nu_3 m_3 \left[\frac{h_3}{\nu_3}\left(\frac{\partial \ln a_1}{\partial m_3}\right)_{n_1,m_2} dm_3 - \left(\frac{\partial \ln \gamma'_{\pm 3}/\gamma_{\pm 3}}{\partial m_3}\right)_{n_1,m_2} dm_3 - \left(\frac{\partial \ln F}{\partial m_3}\right)_{n_1,m_2} dm_3\right] = 0 \quad (10)$$

Integration of the expressions within the brackets results in two equations which must then be simultaneously satisfied in m_2 and m_3

$$\frac{h_2}{\nu_2} \ln a_1 + \ln \gamma'_{\pm 2} - \ln \gamma_{\pm 2} - \ln F + C_2 \quad (11)$$

$$\frac{h_3}{\nu_3} \ln a_1 + \ln \gamma'_{\pm 3} - \ln \gamma_{\pm 3} - \ln F + C_3 \quad (12)$$

where C_2 and C_3 are constants to be determined from the experimental data. One recognizes from the symmetry of these equations that the arguments can be extended to the case of any number, *p*, of such hydrated solutes, leading to a set of *p* simultaneous equations of the type (11) or (12).

After introducing the usual Debye–Hückel expressions for the hydrated ions,[22] the final equations, corresponding to equation 9 of Stokes and Robinson, are

$$\frac{h_2}{\nu_2} \log a_1 + \log \gamma_{\pm 2} + \frac{0.3634\sqrt{\Gamma}}{1 + 0.2331 a_2^0\sqrt{\Gamma}} + \log \{1 - 0.018 [(h_2 - \nu_2)m_2 + (h_3 - \nu_3)m_3]\} + C_2 = 0 \quad (13)$$

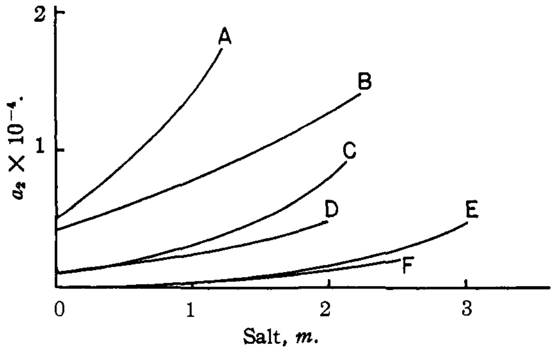

Fig. 2.—HCl activities in HCl–salt mixtures: A, 9.12 *m* HCl + $NiCl_2$; B, 8.86 *m* HCl + $CoCl_2$; C, 6.86 *m* HCl + $NiCl_2$; D, 6.97 *m* HCl + $CoCl_2$; E, 4.69 *m* HCl + $NiCl_2$; F, 4.84 *m* HCl + $CoCl_2$.

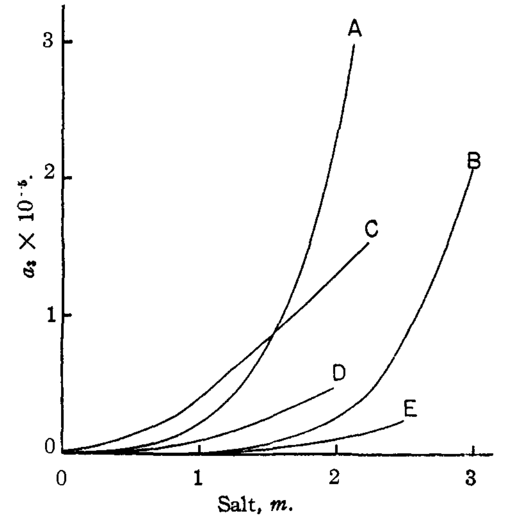

Fig. 3.—Salt activities in HCl–salt mixtures: A, 6.86 *m* HCl + $NiCl_2$; B, 4.69 *m* HCl + $NiCl_2$; C, 8.86 *m* HCl + $CoCl_2$; D, 6.97 *m* HCl + $CoCl_2$; E, 4.84 *m* HCl + $CoCl_2$.

$$\frac{h_3}{\nu_3} \log a_1 + \log \gamma_{\pm 3} + \frac{0.7268\sqrt{\Gamma}}{1 + 0.2331 a_3^0\sqrt{\Gamma}} + \log \{1 - 0.018 [(h_2 - \nu_2)m_2 + (h_3 - \nu_3)m_3]\} + C_3 = 0 \quad (14)$$

Here $\Gamma = \Sigma C_j Z_j^2$ where the C_j's are the volume ionic concentrations and Z_j's the ionic valences.

In order to test these relations, values of a_2^0 and a_3^0 were selected by reference to those listed in Tables II and III by Stokes and Robinson. These were both taken equal in the first approximation to 4.84. Subsequent calculations showed, however, that the choice of the a^0 values was not critical in determining the hydration parameters. From these values of a^0 and equations 13 and 14 the mean activity coefficients were calculated from the experimental water activities and the hydration parameters listed in Table III. Figure 4 presents the calculated values (solid curves) and the experimental values for comparison. The circles have diameters corresponding to 0.1 in $\gamma\pm$.

Although the agreement between the two sets of values is not completely satisfactory over the entire concentration range, it does serve to show the general applicability of this type of correlation to

---

[22] H. S. Harned and B. B. Owen, ref. 15, pp. 119–121.

TABLE II

ACTIVITY DATA AT 30°

	HCl molality = 0	4.69			6.86			0	4.84			6.97			8.86		
Salt m.	a_1 (H_2O)	a_1 (H_2O)	$\gamma_{\pm 2}$ (HCl)	$\gamma_{\pm 3}$ (Ni-Cl_2)	a_1 (H_2O)	$\gamma_{\pm 2}$ (HCl)	$\gamma_{\pm 3}$ (Ni-Cl_2)	a_1 (H_2O	a_1 (H_2O)	$\gamma_{\pm 2}$ (HCl)	$\gamma_{\pm 3}$ (Co-Cl_2)	a_1 (H_2O)	$\gamma_{\pm 2}$ (HCl)	$\gamma_{\pm 3}$ (Co-Cl_2)	a_1 (H_2O)	$\gamma_{\pm 2}$ (HCl)	$\gamma_{\pm 3}$ (Co-Cl_2)
0.5		0.701	2.73	2.71	0.553	5.46	5.03		0.693	2.77	2.44	0.560	5.19	4.47	0.456	8.17	6.54
0.6	0.972	.690	2.89	2.79	.542	5.75	5.30	0.963	.683	2.90	2.66	.552	5.38	4.55	.451	8.34	6.57
0.7		.679	3.06	2.87	.532	5.05	5.57		.672	3.02	2.84	.544	5.57	4.64	.446	8.51	6.62
0.8	.957	.668	3.25	2.99	.522	6.34	5.86	.950	.662	3.19	3.00	.536	5.75	4.74	.440	8.68	6.71
0.9		.656	3.44	3.12	.512	6.65	6.17		.651	3.33	3.12	.528	5.93	4.85	.435	8.84	6.84
1.0	.942	.645	3.64	3.28	.502	6.95	6.47	.936	.641	3.53	3.21	.521	6.10	4.87	.430	8.99	7.01
1.1		.634	3.85	3.45	.493	7.26	6.80		.631	3.70	3.28	.514	6.28	5.10	.425	9.14	7.15
1.2	.927	.623	4.07	3.64	.483	7.59	7.12	.921	.622	3.88	3.35	.507	6.45	5.23	.420	9.29	7.26
1.3		.611	4.29	3.84	.475	7.93	7.44		.613	4.08	3.41	.500	6.61	5.36	.415	9.45	7.33
1.4	.911	.599	4.52	4.05	.465	8.28	7.77	.907	.604	4.27	3.47	.493	6.77	5.47	.410	9.60	7.38
1.5		.589	4.76	4.29	.457	8.63	8.12		.595	4.46	3.55	.487	6.95	5.57	.406	9.76	7.41
1.6	.893	.578	5.02	4.53	.449	8.98	8.46	.891	.586	4.65	3.65	.480	7.13	5.66	.401	9.92	7.42
1.7		.567	5.28	4.79	.439	9.33	8.80		.577	4.83	3.75	.475	7.31	5.73	.397	10.12	7.42
1.8	.874	.557	5.54	5.04	.431	9.68	9.17	.874	.569	5.02	3.87	.469	7.49	5.79	.393	10.26	7.41
1.9		.546	5.82	5.30	.423	10.05	9.55		.561	5.20	3.99	.463	7.67	5.83	.389	10.42	7.39
$(^3)$1.98(sat.)												.459	7.77	5.85			
2.0	.854	.536	6.10	5.59	.416	10.42	9.92	.857	.552	5.39	4.13				.385	10.57	7.37
2.1		.525	6.40	5.90	.409	10.78	10.30		.544	5.57	4.27				.382	10.73	7.34
$(^3)$2.13(sat.)					.407	10.91	10.40										
2.2	.832	.515	6.72	6.20				.838	.536	5.76	4.39				.378	10.86	7.31
$(^3)$2.23(sat.)															.377	10.91	7.30
2.3		.506	7.05	6.48					.528	5.97	4.50						
2.4	.811	.497	7.38	6.79				.818	.520	6.20	4.59						
$(^3)$2.49(sat.)									.514	6.41	4.65						
2.5		.489	7.73	7.08													
2.6	.789	.479	8.08	7.38				.799									
2.7		.471	8.43	7.69													
2.8	.768	.463	8.77	8.00				.779									
2.9		.454	9.14	8.31													
$(^2)$3.0(sat.)	.746	.445	9.61	8.41				.761									
3.2	.725							.741									
3.4	.703							.720									
3.6	.682							.700									
3.8	.661							.680									
4.0	.639							.660									
4.2	.618							.642									
4.4	.596							.624									
$(^3)$4.56(sat.)								.610									
4.6	.574																
4.8	.559																
5.0	.533																
5.2	.516																
$(^1)$5.32(sat.)	.508																

Activities of equilibrium solid phases: $(^1)$ $NiCl_2 \cdot 6H_2O$, 1.039×10^5, $(^2)$ $NiCl_2 \cdot 4H_2O$, 8.14×10^3, $(^3)$ $CoCl_2 \cdot 6H_2O$, 4.43×10^2.

TABLE III

HYDRATION PARAMETERS

System	h_2	h_1
4.69 *m* HCl + $NiCl_2$	4.2	6.8
6.86 *m* HCl + $NiCl_2$	3.6	6.1
4.84 *m* HCl + $CoCl_2$	5.6	0^a
6.97 *m* HCl + $CoCl_2$	4.4	0^a
8.86 *m* HCl + $CoCl_2$	3.0	0^a

[a] h_3 arbitrarily set equal to 0.

electrolyte mixtures at rather high total ionic strengths (9 to 13). A part of the disagreement in the 4.69*m* values may well be attributed to experimental inaccuracies, particularly at the low salt concentrations.

The magnitudes of the hydration parameters also seem reasonable if interpreted as effective hydration numbers; they decrease with increasing acid concentration and are much smaller than those found by Stokes and Robinson for the same solutes in binary solutions at lower concentrations. Furthermore, it seems significant that if one considers the water activity to be proportional to the number of moles of "free" water per 55.51 moles of total water, the corresponding "bound" water varies almost linearly above 0.5 *m* $NiCl_2$ with salt concentration at constant acid molality. From this, one calculates the following values of the hydration parameters

$$h_2 = 3 \qquad h_3 = 5.5$$

These values are seen to be not greatly different from those obtained by the other method and tend to support the interpretation of the former as representing the degrees of hydration of the solutes.

It has been frequently found[23] that in solutions of HCl containing the chlorides of the higher-valence metals there is a linear variation in the values of log $\gamma\pm$(HCl) with acid or salt molality at constant ionic strength. The data obtained for $NiCl_2$–HCl mixtures in this investigation also appear to follow this type of variation as a first approximation over the range of ionic strengths from 6.86 to 13.26. The following empirical equations express the observed relations at constant ionic strength, from 6.86 to 13.26

$$\log \gamma_{\pm 2} = A + \alpha m_3 \qquad (15)$$

$$\log \gamma_{\pm 2} = B + \beta m_3 \qquad (16)$$

where α and β are independent of the ionic strength

---

[23] H. S. Harned and B. B. Owen, ref. 15, chapter 14.

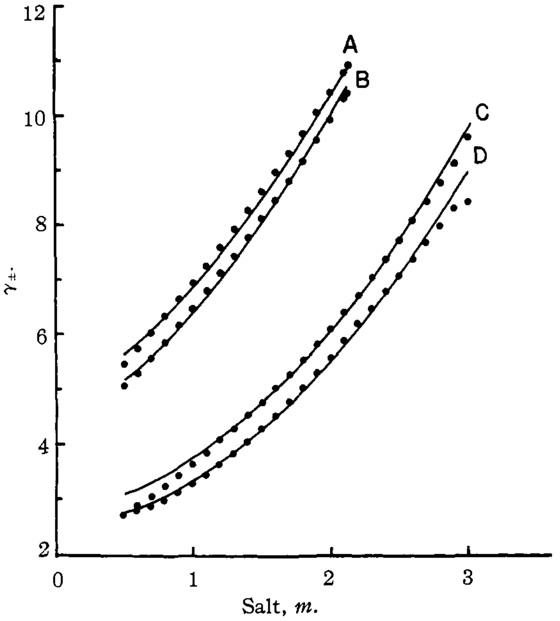

Fig. 4.—Comparison of theoretical (lines) and experimental (circles) activity coefficients of HCl and $NiCl_2$ in their mixtures: A, HCl in 6.86 *m* HCl + $NiCl_2$: B, $NiCl_2$ in 6.86 *m* HCl + $NiCl_2$; C, HCl in 4.69 *m* HCl + $NiCl_2$; D, $NiCl_2$ in 4.69 *m* HCl + $NiCl_2$.

and have the value −0.13 and 0.45, respectively. The constant *A* equals log $\gamma_{\pm 2}$ for pure HCl at the same ionic strength as in the mixture while *B* theoretically represents the value of log $\gamma_{\pm 2}$ for HCl at zero concentration in the presence of $NiCl_2$ at the same ionic strength as the mixture. The significance of *B* is obscure since pure $NiCl_2$ solutions do not exist at the high ionic strengths corresponding to the mixtures studied. Unfortunately each of the three HCl–$NiCl_2$ mixtures studied provided only a single point on each of the constant ionic strength curves, and the applicability of equation 16 could not be tested at the lowest salt concentrations.

II. $CoCl_2$–HCl Mixtures.—There is a large amount of experimental evidence in favor of the association of cobalt and chloride ions in mixtures with other chlorides such as HCl. Consequently, sets of relations such as equations 13 and 14 or 15 and 16 which were found descriptive of $NiCl_2$–HCl mixtures would not be expected to be entirely applicable to $CoCl_2$–HCl mixtures. For example the variation of log $\gamma\pm$(HCl) with HCl or $CoCl_2$ molality at constant ionic strength (equations 15 and 16) was found to be non-linear, and the variation of log $\gamma\pm(CoCl_2)$ with $CoCl_2$ molality cannot be represented accurately by (14). Consideration of equations 11 and 12, from which 13 and 14 were derived shows, however, that it would be still possible for the activity coefficients of HCl in mixtures with $CoCl_2$ to satisfy (13) without those of $CoCl_2$ satisfying the corresponding equation 14 if 12 is satisfied. This is because (12) contains no explicit expression for the activity coefficient of the hydrated solute. If $CoCl_2$ is incompletely dissociated in HCl solutions, the Debye–Hückel term in (14) will not accurately predict the activity coefficients of the hydrated form. The agreement between experimental and calculated values of $\gamma_{\pm 2}$ is shown in Fig. 5. Since there was no way of determining what values of the hydration parameters (Table III) would simultaneously satisfy (11) and (12) because of a lack of knowledge of the explicit form for ln $\gamma_{\pm 3}$ in (12), a degree of arbitrariness was unavoidably introduced in the choice of the parameters employed in the calculation of the HCl activity coefficients. Thus $h_3 = 0$ does not necessarily mean zero hydration of $CoCl_2$ in mixtures with HCl.

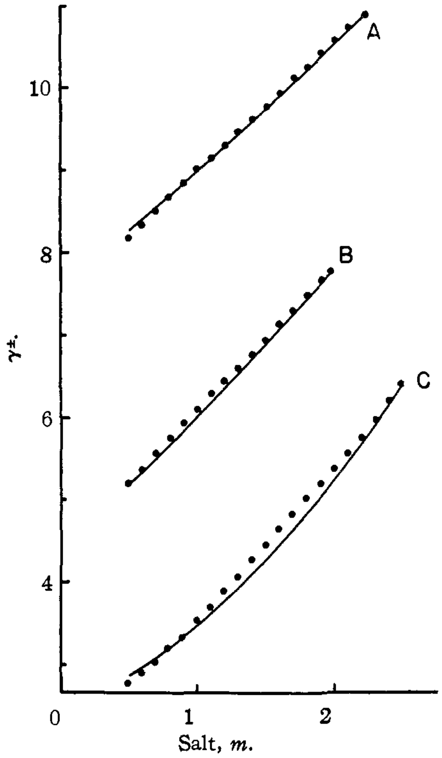

Fig. 5.—Comparison of theoretical (lines) and experimental (circles) activity coefficients in mixtures of HCl and $CoCl_2$: A, HCl in 8.86 *m* HCl + $CoCl_2$; B, HCl in 6.97 *m* HCl + $CoCl_2$; C, HCl in 4.84 *m* HCl + $CoCl_2$.

The changes in color from rose to blue observed in $CoCl_2$ solutions upon the addition of HCl or other chlorides have been variously ascribed to the dehydration of cobalt ions, to the formation of neutral molecules, and to the formation of chloro complex ions of cobalt. Recently Robinson and Brown[16] on the basis of their spectrophotometric and vapor pressure measurements concluded that the reaction causing the change in color was

$$Co(H_2O)_6^{++}(\text{rose}) + 2Cl^- \rightleftharpoons Co(H_2O)_4Cl_2(\text{blue}) + 2H_2O$$

By assuming that the activity coefficients of $CoCl_2$ at low concentrations in solutions of $CaCl_2$ at high concentrations were equal to those of the latter and that the activity coefficients of the undissociated blue complex were constant over the range of their experimental measurements, they were able to calculate values of the equilibrium constant which were reasonably constant. In the present investigation the series of solutions having the lowest HCl concentration (4.84 *m*) similarly showed the transition from rose color to blue as the $CoCl_2$ concentration increased. It was decided, therefore, to test Robinson and Brown's conclusions in relatively concentrated mixtures of HCl and $CoCl_2$.

The optical densities were measured by means of a Beckman DU spectrophotometer at 30° employing 1-cm. corex cells whose optical thickness had been decreased to 0.1 cm. by silica spacers. Because of the high optical densities involved, only a portion of the 4.84 *m* series of solutions could be studied. Following Robinson and Brown, the optical densities at wave lengths characteristic of the blue complex (λ *630, 660, 690* mμ) were assumed to be proportional to the activity of the complex. It was also assumed that the quantity of the complex corresponded to but a small fraction of the total $CoCl_2$ in solution. The latter assumption was supported by the constancy of the apparent extinction coefficients at wave lengths characteristic of the rose species (λ 480 mμ).

The results showed that the optical densities $(O.D.)_\lambda$ of the blue colored solutions were proportional to the activities of $CoCl_2$ except at the higher Cl/Co ratios where appreciable deviations of the apparent extinction coefficients from constancy at 480 mμ were observed. These results, therefore, provide evidence for the association reaction

$$Co^{++}(aq.) + 2Cl^-(aq.) \rightleftarrows CoCl_2(aq.)$$

rather than for the formation of higher chlorocomplexes. Table IV presents the values of the constant *k* defined by

$$k = a(CoCl_2)/(O.D.)_\lambda$$

TABLE IV

CONSTANTS FOR THE ASSOCIATION OF Co^{++} AND Cl^- IN 4.84 *m* HCl

$CoCl_2$, *m*	O.D. (λ = 630 mμ)	$k \times 10^{-2}$
0.5	1.95	1.38
0.6	2.82	1.49
0.7	4.03	1.66
0.8	5.37	1.63
0.9	7.08	1.86
1.0	9.33	1.68
1.1	12.3	1.66
1.2	15.1	1.54
1.3	19.1	1.51
1.4	21.9	1.56
1.5	24.7	1.66
1.6	28.5	1.75

Although both investigations indicate the presence of an undissociated complex, the results obtained here differ from those of Robinson and Brown, who found that the optical densities of the blue solutions were proportional not only to the assumed activities of $CoCl_2$ but also to the 4th power of the water activities. Although the experimental data of these authors do not support the mechanisms given by the equations on page 8 of their paper, their results can be accounted for on the basis of the reaction

$$Co^{++}(aq.) + 4H_2O + 2Cl^-(aq.) \longrightarrow Co(H_2O)_4Cl_2$$

It is possible that the cause for the differences in these two studies may arise from the differences in the systems under investigation or from the assumptions underlying the approximation to the $CoCl_2$ activities made by Robinson and Brown.

STILLWATER, OKLAHOMA

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Vaporization of TiN and ZrN[1]

BY MICHAEL HOCH, DAVID P. DINGLEDY AND HERRICK L. JOHNSTON

RECEIVED JULY 8, 1954

The vaporization of TiN and ZrN has been studied by the Knudsen effusion method between 1987–2241 and 2236–2466° K., respectively. Whereas TiN vaporizes to gaseous Ti and N_2, the heat of reaction being $\Delta H_0^0 = 191.20$ kcal., ZrN decomposes to solid Zr and N_2 with $\Delta H_0^0 = 79.53$ kcal./mole. From these data, the standard heat of formation for TiN is $\Delta H_{298}^0 = 79.4$ kcal./mole; and for ZrN, $\Delta H_{298}^0 = 80.43$ kcal./mole.

Introduction

No experimental data are available on the vaporization of TiN and ZrN. Kelley[2] calculated an equation for the free energy of formation of these two compounds by using the heats of formation obtained by Neumann, Kröger and Kunz[3] and estimated entropies.

In the present investigation the Knudsen effusion method was used to determine the vapor pressure above TiN and ZrN.

Materials.—The TiN was obtained from Metal Hydrides, Inc., Beverly, Mass. The composition, as given by the manufacturer, was Ti 77.5%. N 18.0%, corresponding to a Ti:N ratio of 1:0.794, impurities being mostly Ca, Mg, Si, 4.5%. During degassing, at 1750°, for 2.5 hr., a 500-mg. sample lost 25 mg., which corresponds approximately to the weight of the impurities present.

The ZrN was prepared by heating ZrH_2, obtained from Charles Hardy, Inc., N. Y., in a stream of nitrogen for 21 hr. at 1050°. From the weight gain, the ratio Zr:N was calculated to be 1:0.979. On degassing at 1500°, a 500-mg. sample lost 6 mg. No other purification was carried out on either material.

Apparatus and Experimental Procedure.—The same vacuum apparatus and identical Knudsen effusion cells made of tantalum were used as described previously.[4]

Experimental Results

Both nitrides could vaporize according to the following patterns: (1) undissociated, as TiN and ZrN, (2) dissociated, into gaseous metal and nitrogen or (3) dissociated, into solid metal and nitrogen.

---

[1] This work was supported in part by the Office of Naval Research under contract with The Ohio State Univerity Research Foundation.

[2] K. K. Kelley, "Contribution to the Data on Theoretical Metallurgy, VIII." U. S. Bureau of Mines, Bull. No. 407 (1937).

[3] B. Neumann, C. Kröger and H. Kunz, *Z. anorg. allgem. Chem.*, **218**, 379 (1934).

[4] M. Hoch and H. L. Johnston, THIS JOURNAL, **76**, 4833 (1954).