[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, FISK UNIVERSITY]

The Ternary Systems Ferrous Chloride–Hydrogen Chloride–Water, Ferric Chloride–Ferrous Chloride–Water

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The isotherms of various temperatures of the system $FeCl_2$–HCl–H_2O have been established together with the solid phases. It was found that the behavior of ferrous chloride in concentrated hydrogen chloride solutions resembles more closely that of nickel chloride than that of cobalt chloride, although iron is adjacent to cobalt in the Periodic System. The 25° isotherm of the system $FeCl_2$–$FeCl_3$–H_2O was established and shows that no mixed chlorides of iron can be obtained by concentrating aqueous solutions of both salts.

A. Introduction

In connection with other investigations it was desirable to have data on the ternary systems $FeCl_2$–HCl–H_2O and $FeCl_3$–$FeCl_2$–H_2O. From known related systems such as $FeCl_3$–HCl–H_2O,[1] $NiCl_2$–HCl–H_2O,[2] or $CoCl_2$–HCl–H_2O,[3] no conclusion can be drawn in regard to the two systems dealt with in this paper. As Fischer and Seidel have shown, cobalt and nickel are entirely dissimilar in their behavior toward concentrated hydrochloric acid. While the former forms complex compounds with HCl, the latter does not. Likewise if the system $FeCl_3$–$FeCl_2$–H_2O followed the same pattern as the known system $FeCl_3$–HCl_2–H_2O, it should be possible to prepare mixed ferrous ferric chlorides from aqueous solutions, which has been found impossible, although claimed by others.

The binary systems ferrous chloride–water[4,5] and ferric chloride–water[6] have been investigated some time ago.

B. Experimental Part

The salts were purified in the usual manner by several recrystallizations, care being taken that the ferrous salts were free from ferric salts and the ferric salts did not contain any basic compounds. They were considered pure when the chlorine and the iron determinations agreed.

I.—In the case of the ternary system ferrous chloride–hydrogen chloride–water the 0, 20, 40, 60 and 100° isotherms were determined. Usually the experiments were carried out so that a surplus of ferrous chloride tetrahydrate was partially dissolved in air-free concentrated hydrochloric acid and stirred in a closed container for about two hours in a carbon dioxide atmosphere until no change in the concentrations could be found. A sample was pipetted off and titrated for ferrous ions with permanganate and for chlorine with silver nitrate in the customary manner. For the taking of a sample from a highly acidic solution without losses, particularly at the higher temperatures, the pipet previously described[5] was again found to be useful. The temperatures were kept constant in a thermostat with automatic temperature regulation. Solutions of various concentrations were

TABLE I

SYSTEM $FeCl_2$–HCl–H_2O

Point	$FeCl_2$, %	HCl, %	Solid phases
	Temperature, 0°		
A	33.2	0	$FeCl_2·6H_2O$
	32.1	0.6	$FeCl_2·6H_2O$
	17.2	10.8	$FeCl_2·6H_2O$
	12.1	15.6	$FeCl_2·6H_2O$
B[a]	11.2	17.0	$FeCl_2·6H_2O$ and $FeCl_2·4H_2O$
	10.45	17.4	$FeCl_2·4H_2O$
	7.95	19.3	$FeCl_2·4H_2O$
	7.21	19.9	$FeCl_2·4H_2O$
	4.34	24.1	$FeCl_2·4H_2O$
	3.53	25.55	$FeCl_2·4H_2O$
	2.13	29.9	$FeCl_2·4H_2O$
	2.08	30.2	$FeCl_2·4H_2O$
	1.70	31.4	$FeCl_2·4H_2O$
	Temperature, 20°		
C	38.5	0	$FeCl_2·4H_2O$
	28.7	6.1	$FeCl_2·4H_2O$
	19.4	12.0	$FeCl_2·4H_2O$
	18.1	13.5	$FeCl_2·4H_2O$
	12.8	17.9	$FeCl_2·4H_2O$
	6.23	24.85	$FeCl_2·4H_2O$
	4.35	30.0	$FeCl_2·4H_2O$
D	4.00	31.6	$FeCl_2·4H_2O$ and $FeCl_2·2H_2O$
	Temperature, 40°		
E	40.7	0	$FeCl_2·4H_2O$
	32.9	5.25	$FeCl_2·4H_2O$
	24.4	10.7	$FeCl_2·4H_2O$
	18.3	15.6	$FeCl_2·4H_2O$
	13.55	19.3	$FeCl_2·4H_2O$
	10.0	24.25	$FeCl_2·4H_2O$
	9.3	25.5	$FeCl_2·4H_2O$
	8.9	26.3	$FeCl_2·4H_2O$
F	8.8	26.75	$FeCl_2·4H_2O$ and $FeCl_2·2H_2O$
	5.8	29.85	$FeCl_2·2H_2O$
	4.4	32.8	$FeCl_2·2H_2O$
	Temperature, 60°		
G	43.9	0	$FeCl_2·4H_2O$
	36.65	5.2	$FeCl_2·4H_2O$
	25.7	13.85	$FeCl_2·4H_2O$
H	23.9	15.2	$FeCl_2·4H_2O$ and $FeCl_2·2H_2O$
	23.5	15.4	$FeCl_2·2H_2O$
	23.3	15.5	$FeCl_2·2H_2O$
	22.7	15.7	$FeCl_2·2H_2O$
	21.8	16.3	$FeCl_2·2H_2O$
	16.4	20.7	$FeCl_2·2H_2O$
	10.35	26.5	$FeCl_2·2H_2O$
	9.3	27.3	$FeCl_2·2H_2O$
	Temperature, 100°		
	48.7	0	$FeCl_2·2H_2O$
	46.4	1.3	$FeCl_2·2H_2O$
	39.9	5.3	$FeCl_2·2H_2O$
	31.05	11.05	$FeCl_2·2H_2O$
	28.4	13.0	$FeCl_2·2H_2O$

[a] The values of point B have been found by graphic interpolation.

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[1] B. Roozeboom and F. A. H. Schreinemakers, *Z. physik. Chem.*, **15**, 588 (1894).

[2] W. Fischer and W. Seidel, *Z. anorg. allgem. Chem.*, **247**, 333 (1941).

[3] W. Seidel and W. Fischer, *ibid.*, **247**, 367 (1941).

[4] G. Agde and F. Schimmel, *ibid.*, **173**, 111 (1928).

[5] F. Schimmel, *ibid.*, **176**, 285 (1928).

[6] B. Roozeboom, *Z. physik. Chem.*, **10**, 477 (1892).

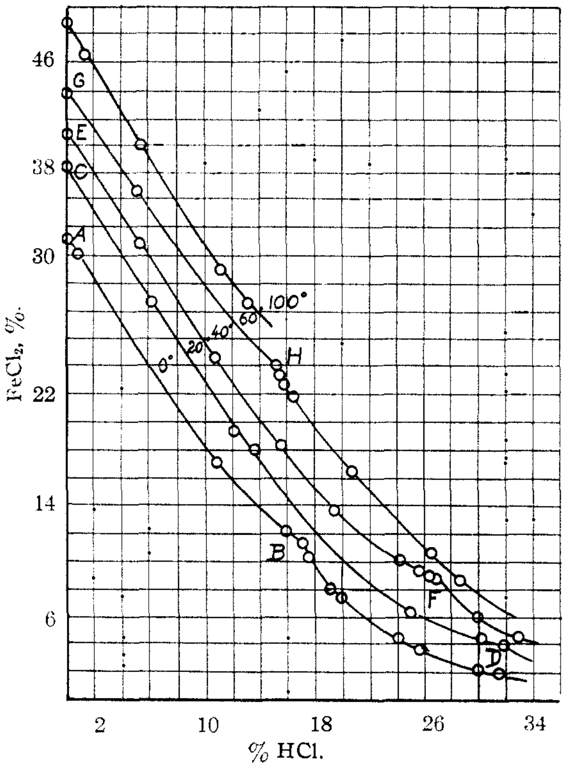

Fig. 1.—Isotherms of the system $FeCl_2$–HCl–H_2O.

obtained by diluting the strongly acidic solutions with air-free distilled water, so that the solubility equilibria were reached from undersaturation.

The data obtained are listed in Table I. Figure 1 gives a graphical representation of these numerical results, with the concentration of ferrous chloride as the ordinate and the concentration of hydrogen chloride as abscissa.

As expected, concentrations of hydrogen chloride have a dehydrating effect upon the ferrous chloride hydrates. While in aqueous solution the transition point of the hexahydrate to the tetrahydrate is at 12.3°, it is shifted to 0°, if the solution contains 17.0% of free hydrogen chloride. Similarly the transition point of the tetrahydrate to the dihydrate lies at 76.5° in aqueous solution, while the presence of 26.75% of HCl lowers it to 40° and of 15.2% HCl to 60°. The composition of the solid phase was determined by the wet-residue method.[7] The isotherms were followed approximately up to the saturation point of the solution with hydrogen chloride.

Because the last point, which could be conveniently determined on the 20°-isotherm due to near saturation of the solution with HCl, was the transition point D, a few analyses of the wet residue of points on this isotherm are given here:

Solution			Wet residue	
$FeCl_2$, %	HCl, %	Solid phase	$FeCl_2$, %	HCl, %
19.4	12.0	$FeCl_2 \cdot 4H_2O$	33.3	8.0
12.8	17.9	$FeCl_2 \cdot 4H_2O$	30.0	11.4
6.23	24.85	$FeCl_2 \cdot 4H_2O$	38.5	11.0
4.00	31.6	$FeCl_2 \cdot 4H_2O$ and $FeCl_2 \cdot 6H_2O$	41.2	13.4
4.00	31.6	$FeCl_2 \cdot 4H_2O$ and $FeCl_2 \cdot 6H_2O$	43.3	13.0

If the determination at the transition point is carried out so that the crystals of the solid phase are not too small, the dihydrate and the tetrahydrate which are present can be distinguished by their color.

The similar systems $CoCl_2$–HCl–H_2O and $NiCl_2$–HCl–H_2O are known at least at 0° from papers by W. Fischer and W. Seidel.[2,3,8] Some time ago these authors pointed out that the solubilities of the chlorides of similar elements are influenced by the presence of hydrogen chloride in an entirely different manner individually. Among other salt pairs they compared cobalt chloride and nickel chloride. With ferrous chloride included we may now make the following observations: ferrous, cobalt and nickel chlorides form the same hydrates in hydrochloric acid solution, namely, the hexa-, tetra- and dihydrate. The solubilities of the pure salts in water at 0° are of the same order. Addition of hydrogen chloride to their aqueous solutions lowers their solubility at first gradually. At the highest HCl concentrations the concentration of $NiCl_2$ has been lowered by more than two powers of ten, while the solubility of $CoCl_2$ increases after passing through a minimum, so that the final decrease in solubility is less than one power of ten. Ferrous chloride takes an intermediate position. Its final solubility at 0° is lower by about 1.5 half power of ten. The solubility curve at the highest HCl values is neither sloping down as in the case of nickel nor sloping upwards as in the case of cobalt, but has the tendency to run nearly horizontally. In other words, the tendency for complex formation with HCl increases in the order $NiCl_2$, $FeCl_2$ and $CoCl_2$.

II.—The system $FeCl_3$–$FeCl_2$–H_2O was investigated at 25°. The experimental procedure was the same as described above for the other ternary system. The values given in Table II were obtained.

TABLE II

Point	$FeCl_3$	$FeCl_2$	Solid phase
A	39.2	0	$FeCl_2 \cdot 4H_2O$
	35.9	4.1	$FeCl_2 \cdot 4H_2O$
	31.4	9.9	$FeCl_2 \cdot 4H_2O$
	22.8	19.46	$FeCl_2 \cdot 4H_2O$
	14.45	30.4	$FeCl_2 \cdot 4H_2O$
	8.3	39.8	$FeCl_2 \cdot 4H_2O$
	7.05	41.95	$FeCl_2 \cdot 4H_2O$
B	5.44	46.65	$FeCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6H_2O$
	3.96	47.01	$FeCl_3 \cdot 6H_2O$
	3.49	47.41	$FeCl_3 \cdot 6H_2O$
C	0	49.7	$FeCl_3 \cdot 6H_2O$

The isotherm is drawn in Fig. 2. The composition of the solid phases was determined by the wet-residue method as before. Only two phases exist in aqueous solution, namely, ferric chloride hexahydrate and ferrous chloride tetrahydrate. The formation of a mixed ferrous–ferric chloride as Chandra[9] and Lefort[10–14] have claimed and J. W. Retgers,[15] H. Remy

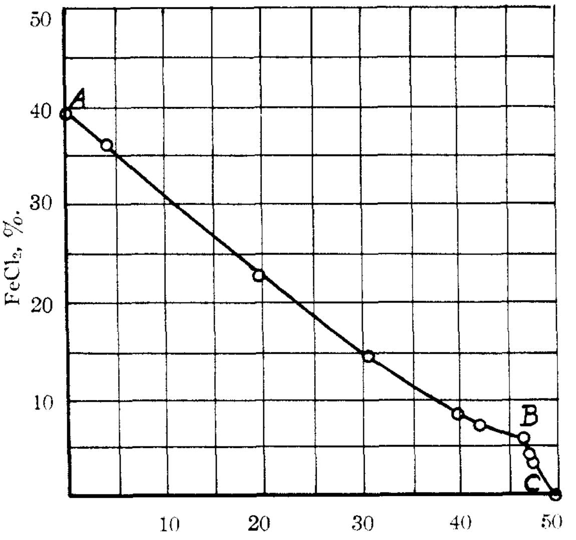

Fig. 2.—The system $FeCl_2$–$FeCl_3$–H_2O at 25°.

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(7) F. A. H. Schreinemakers, *Z. physik. Chem.*, **11**, 81 (1893).

(8) W. Fischer, *Z. anorg. allgem. Chem.*, **247**, 384 (1941).

(9) H. Chandra, Dissertation, Berlin, 1913.

(10) J. Lefort, *Compt. rend.*, **34**, 490 (1852).

(11) J. Lefort, *ibid.*, **69**, 179 (1869).

(12) J. Lefort, *J. Pharm. Chim.*, [4] **10**, 85 (1869).

(13) J. Lefort, *J. prakt. Chem.*, **108**, 191 (1869).

(14) J. Lefort, *Jahresberichte*, 267 (1869).

(15) J. W. Retgers, *Z. physik. Chem.*, **9**, 391 (1892).

and H. J. Rothe[16] and G. Neumann[17] have disclaimed, appears to be impossible through evaporation of neutral solutions.

C. **Acknowedgment.**—I wish to thank the Carnegie–Fisk Foundation for the support of this investigation.

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[16] H. Remy and H. J. Rothe, *J. prakt. Chem.*, [2] **114**, 144 (1926).

[17] G. Neumann, *Ann.*, **244**, 336 (1888).

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY]

Thermodynamics of Coprecipitation: Dilute Solid Solutions of AgBr in AgCl[1]

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The importance of the thermodynamic properties of dilute AgBr–AgCl solid solutions to the coprecipitation of small amounts of bromide ion by AgCl was evaluated by accurately measuring the "carrying" of 35.9 h Br^{82} activity. From the magnitude and temperature variation of the equilibrium distribution coefficient ($D = X_{AgBr}m_{Cl^-}/m_{Br^-}$) the *excess* free energy, entropy and enthalpy of solid solution formation in the Henry's law region ($X_{AgBr} = 10^{-4}$ to 10^{-2}) at 30° were found to be 287 cal. mole^{-1}, -1.4 e.u. and -139 cal. mole^{-1}, respectively. The observed enthalpy agreed with an estimate computed from Born–Mayer crystal lattice theory. The negative, excess entropy was attributed to a lowering of the vibrational randomness of a bromide ion when placed in a nearly pure AgCl lattice. Measurements on other systems revealed that interaction in the solid solution may sometimes be decisive in determining the "carrying-down" of traces by precipitates.

The process of coprecipitation whereby a substance soluble by itself is coseparated with an insoluble precipitate has been of general importance to radiochemical analysis, to the isolation of substances initially present in very low concentrations, such as radium and other radioactive species useful as tracers, and to conventional gravimetric analysis. The principles involved in most cases appear to be partly understood,[2a,b,3] although the difficulty of obtaining equilibrium, or reproducible and ideal conditions with non-equilibrium (*i.e.*, heterogeneous) type coprecipitations, has frequently prevented a demonstration of their applicability. When true equilibrium is established, the distribution of a microcomponent between crystals and a saturated solution is governed by the law of Berthelot–Nernst, provided the composition of both phases remains constant. A more general, exact quantitative description based on thermodynamic considerations may be applied, and it has been the object of our research to demonstrate this by accurate measurements of the "carrying down" of small quantities of bromide ion by silver chloride precipitates. From measurements of distribution coefficients and their temperature variations it was possible to estimate partial molar free energies, entropies and enthalpies of interaction for a bromide ion present at high dilution in a silver chloride crystal. These thermodynamic quantities are then interpreted on the basis of an "atomistic" picture which emphasizes the importance of structure in solid solutions for coprecipitation phenomena.

Theory

The distribution of an ion between a homogeneous solid solution and its equilibrium saturated aqueous solution may be regarded formally as an exchange reaction for which a mass law constant may be written (*viz.*, for the coprecipitation of bromide ion with insoluble silver chloride)

$$\mathrm{AgCl} + \mathrm{Br}^- \rightleftharpoons \mathrm{AgBr} + \mathrm{Cl}^-$$

and

$$K_a = (\mathrm{AgBr})(\mathrm{Cl}^-)/(\mathrm{AgCl})(\mathrm{Br}^-) \qquad (1)$$

where the parenthesized quantities denote thermodynamic activities, *a*. The relations of these activities to the compositions of the solid and fluid phases will be defined by the Gibbs chemical potentials. Compositions of the aqueous solutions will be given in molalities, *m*, and the reference state will be taken as the infinitely dilute solution (*i.e.*, pure solvent). Binary solid solution compositions will be expressed in mole fractions, *X*, and pure, crystalline silver chloride and bromide each will be taken as standard states. Choosing AgBr as solute (2) and AgCl as solvent (1) and denoting the fluid phase by primes, the chemical potential, $\bar{F}_2'$, of AgBr in an aqueous solution *in equilibrium with the solid solution* is

$$\bar{F}_2' = \bar{F}_2^{0\prime}(\mathrm{T.P}) + RT \ln a' \qquad (2)$$

and its potential in the solid solution will be

$$\bar{F}_2 = \bar{F}_2\,(\mathrm{T.P}) + RT \ln X_2 f_2 \qquad (3)$$

where f_2 is the activity coefficient.

Imposing the Gibbs equilibrium condition: $\bar{F}_2 = \bar{F}_2'$ leads to

$$\ln (X_2 f_2/a_2') = -(\bar{F}_2^0 - \bar{F}_2^{0\prime})/RT \qquad (4)$$

Similarly, for component (1)

$$\ln\ [(1 - X_2)f_1/a_1'] = -(\bar{F}_1^0 - \bar{F}_1^{0\prime})/RT \qquad (5)$$

Combining equations (4) and (5)

$$\ln [(X_2 f_2)a_1'/(1 - X_2)f_1 a_2'] = -[(\bar{F}_2^0 - \bar{F}_2^{0\prime}) - (\bar{F}_1^0 - \bar{F}_1^{0\prime})]/RT \qquad (6)$$

The right hand member of equation (6) may be simplified by the expressions for the chemical potentials of the pure components in equilibrium with their own saturated solutions, respectively

$$\bar{F}_{20}' = \bar{F}_2^{0\prime}(\mathrm{T,P}) + RT \ln a_{20}' = \bar{F}_{20} \equiv \bar{F}_2^0 \qquad (7a)$$

and

$$\bar{F}_{10}' = \bar{F}_1^{0\prime}(\mathrm{T,P}) + RT \ln a'_0 = \bar{F}_{10} \equiv \bar{F}_1^0 \qquad (7b)$$

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[1] Presented before Division of Physical and Inorganic Chemistry, 115th Meeting, American Chemical Society, March 27–April 1, 1949, San Francisco, California.

[2] (a) V. G. Khlopin, *Trav. Inst. Etat Radium, U.R.S.S.*, **4**, 34 (1938); (b) O. Hahn, "Applied Radiochemistry," Cornell Univ. Press, Ithaca, N. Y., 1933.

[3] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1943, Ch. VIII.