that even the highly enhanced mobility of the solution in that region would probably not make high temperature crystallization advantageous as compared with possible lower temperature crystallization. It is quite possible, of course, that at temperatures and pressures beyond the range of the present experiments, the solubility may increase to a value at which an excellent yield of crystals may be obtained. In this respect, it is encouraging that lithium fluoride at the higher solvent densities and calcium fluoride show increasing solubilities above the critical point.

Acknowledgment.—The generosity of the Harshaw Chemical Company, which made this investigation possible by the endowment of a fellowship and by supplying experimental materials, is gratefully acknowledged.

Summary

A technique for the measurement of solubilities at high temperatures and pressures has been developed, in which filtration of the saturated solution is effected by quenching the high-pressure vessel. The solubilities of four sparingly soluble salts, calcium, barium, and lithium fluorides and strontium sulfate, formerly known only at low temperatures, were measured up to or past the critical temperature of water. The previously investigated solubilities of calcium and sodium sulfates at high temperatures were checked and extended.

The dependence of the solubility of lithium fluoride in water above its critical point on the density of the solvent was measured at several temperatures.

The very low solubilities of the salts investigated in the region of the critical point make it seem unlikely that the recrystallization from their pure aqueous solutions of these salts will be a practical method for the making of synthetic crystals of optical quality unless at appreciably higher temperature and pressure.

The precision of the results obtained compares well with other measurements in the same region, most of which required far more complex apparatus.

RECEIVED NOVEMBER 9, 1949

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS UNIVERSITY]

Some Fluoride Complexes of Certain Bivalent and Tervalent Metal Ions in Aqueous Solution[1]

BY EDWARD R. SCHEFFER[2] AND ELLWOOD M. HAMMAKER

The purpose of this investigation was to determine the formulas for some fluoride complexes with metal ions in aqueous solution. Although complex fluoride compounds have been studied,[3-8] the evidence for the existence of the complex ions is based mainly on the formation of solid compounds and on the behavior of the other halides, as pointed out by Ephraim[4] on the existence of $CrF(H_2O)_5^{++}$ and $CrF_2(H_2O)_4^+$, similar to the ions $CrCl(H_2O)_5^{++}$ and $CrCl_2(H_2O)_4^+$. The complex $FeF_6^{\equiv}$ is mentioned in most analytical texts. The literature shows a complex formed between manganese(III) and fluoride ion; however, if a specific complex is mentioned, it is $MnF_5H_2O^{=}$[9] and not $MnF_6^{\equiv}$ as would seem logical considering the similarity between manganese(III) and iron(III).

In this investigation spectrophotometric methods were used to attain the evidence of complexing. There were limitations because of the presence of fluoride ions, which will combine with hydrogen ion to give hydrofluoric acid especially in solutions with a *p*H below 4. Hence, plastic optical cells were used in place of glass. Since all plastic materials absorb light in the ultraviolet as well as the near infrared only ions which give a color in the visible range were considered. Therefore, ions which are colored in the completely hydrated form offer the best starting point. Chromium(III), manganese(III), copper(II), cobalt II, nickel(II), vanadium(III) and titanium(III) are some of the possibilities which are colored and have been shown to complex. They were used to investigate the possibilities of complexing with fluoride ion.

Manganese(III) Fluoride Complexes

Of the various spectrophotometric methods presented in the literature the limiting density method developed by Bent and French[10] was used

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[1] Part of a thesis submitted by Edward R. Scheffer to Rutgers University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Present address: National Lead Company, Titanium Division, Sayreville, New Jersey.

[3] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, N. Y., 1922-1937.

[4] F. Ephraim, "Inorganic Chemistry," 4th ed. (translation Thorne and Roberts) Interscience Publishers, Inc., New York, N. Y., 1946.

[5] A. K. Babko and K. E. Kleiner, *J. Gen. Chem.* (*U. S. S. R.*), **17**, 1259 (1947).

[6] R. J. MacWalter and S. Barrett, *J. Chem. Soc.*, 517 (1934).

[7] "Gmelins Handbuch der anorganischen Chemie," No. 5, Verlag Chemie G. m. b. H., Leipzig, 1926.

[8] R. Weinland, "Einfuhrung in die Chemie der Komplex-Verbindungen," F. Enke, Stuttgart, 1924.

[9] The water molecules which are coördinated with the ions have been omitted from the formulas except where the discussion is clarified by including them.

[10] H. E. Bent and C. L. French, THIS JOURNAL, **63**, 568 (1941).

with certain modifications and found to be satisfactory. Bent and French worked with sufficiently dilute solutions so that they could assume the complex was mostly in the dissociated form; thus, they assumed that the concentration of one ion could be maintained practically constant, and that the concentration of the other ion was essentially equal to the total concentration in the solution including that in the complex. If, instead of making these assumptions, the actual concentration of each ion in the solution can be measured, the method can be applied to higher concentrations than those normally used in this method. The reaction involved is

$$MnF_x^{(3-x)} \rightleftarrows Mn^{+++} + xF^- \qquad (1)$$

The equilibrium constant for the reaction is

$$K = (Mn^{+++})(F^-)^x/(MnF_x^{(3-x)}) \qquad (2)$$

If the log of both sides of the equation is taken and the expression rearranged

$$\log (MnF_x^{(3-x)}) - \log (Mn^{+++}) = x \log (F^-) - \log K \qquad (3)$$

This is the equation for a straight line whose slope "x" is the number of fluoride ions combined with one manganese(III) ion to give the complex. It is necessary to measure the concentration of the $MnF_x^{(3-x)}$ ion, the manganese(III) ion, and the fluoride ion to solve for "x."

Ivett and DeVries[11] have shown that the lead amalgam–lead fluoride electrode can be used to measure fluoride ion concentration in solution. Using a calomel reference electrode the fluoride ion activity is expressed as

$$\log (F^-) = \frac{E^0_{PbF_2} - E_{Hg} - E}{59.1} \text{ at } 25° \qquad (4)$$

All e. m. f. values are expressed in millivolts. Since $E^0_{PbF_2}$ and E_{Hg} are constants that will only displace the curve without changing the slope, they can be incorporated into an over-all constant.

$$\log (F^-) = (-E/59.1) + C \qquad (5)$$

Since the color of the solution is due to the complex, optical density measurements may be used to obtain values proportional to the $MnF_x^{(3-x)}$ concentration.

The manganese(III) ion concentration can be measured if the solution is saturated with manganese(II) fluoride since the oxidation–reduction potential and solubility product equations apply. The oxidation–reduction potential of the solution is expressed by the three equations.

$$E_{redox} = E^0_{4,2} + \frac{59.1}{2} \log \frac{(MnO_2)(H^+)^4}{(Mn^{++})(H_2O)^2} \qquad (6)$$

$$E_{redox} = E^0_{4,3} + 59.1 \log \frac{(MnO_2)(H^+)^4}{(Mn^{+++})(H_2O)^2} \qquad (7)$$

$$E_{redox} = E^0_{3,2} + 59.1 \log \frac{(Mn^{+++})}{(Mn^{++})} \qquad (8)$$

Although any one of these equations is true for the oxidation–reduction potential, equation 8 is most suitable for use. If $K_{SP}/(F^-)^2$ is substituted for (Mn^{++}) in equation 8, then

$$E_{redox} = E^0_{3,2} + 59.1 \log (Mn^{+++}) - 59.1 \log K_{SP} + 118.2 \log (F^-) \qquad (9)$$

Into 9 substitute 5 for $\log (F^-)$

$$E_{redox} = E^0_{3,2} + 59.1 \log (Mn^{+++}) - 59.1 \log K_{SP} - 2E + C_1 \qquad (10)$$

Rearranging and solving for $\log (Mn^{+++})$

$$\log (Mn^{+++}) = (-E^0_{3,2} + 59.1 \log K_{SP} + 2E + E_{redox} - C_1)/59.1 \qquad (11)$$

$E^0_{3,2}, C_1$, and $\log K_{sp}$ are constants

$$\log (Mn^{+++}) = (2E + E_{redox})/59.1 + C_2 \qquad (12)$$

This shows that a value proportional to the manganese(III) ion concentration can be determined by measuring the oxidation–reduction potential and fluoride ion concentration of the solution. Substituting optical density, d, for the concentration of the complex and substituting equations 5 and 12 into 3

$$\log d - \frac{2E}{59.1} - \frac{E_{redox}}{59.1} = \frac{-xE}{59.1} - \log C_3 \qquad (13)$$

and rearranging

$$\log d - \frac{E_{redox}}{59.1} = \frac{(2-x)E}{59.1} - \log C_3 \qquad (14)$$

The constant C_3 contains all the values which have been assumed to be constant throughout the measurements; it is not the equilibrium constant.

If $\log d - E_{redox}/59.1$ is plotted against $E/59.1$ the slope of the straight line is equal to $(2 - x)$, and "x" can be determined. If equations 6 and 7 are used to express the manganese ion concentration, equations are obtained involving pH values which cannot be measured accurately in these solutions.

Experimental

Materials and Apparatus.—Lead amalgam was prepared as recommended by Jahn-Held and Jellinek.[12] Lead fluoride was prepared by adding Merck reagent grade lead acetate dissolved in conductivity water to a concentrated solution of C. P. ammonium fluoride. All chemicals used were of C. P. grade.

The lead fluoride electrodes were prepared from 4-inch lengths of $^1/_8$-inch cellulose acetate butyrate tubing which were placed in hot water and bent to form a J. The lead amalgam was placed (at about 100° to ensure one phase) into the tube filling the lower portion of the J and the rest of the short end was filled with lead fluoride. A platinum wire was inserted into the long arm, and the arm was filled with paraffin. A saturated calomel electrode was used as the reference electrode. Platinum foil electrodes were used for measuring potentials.

Lucite was found to possess the necessary optical properties and also to be inert to the concentrations of hydrofluoric acid used. Lucite sheet $^1/_{16}$-inch thick was cut to construct absorption cells which were approximately 1 cm. square. To cancel the effects of small inequalities of construction the same cell was used for all blanks and another for all samples. For concentrated solutions a cell having a light path $^1/_{16}$ of an inch was constructed. All glass equipment that came in contact with hydrofluoric acid was coated with paraffin.

The e. m. f. measurements were made using a Leeds and

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[11] R. W. Ivett and T. DeVries, THIS JOURNAL, 63, 2821 (1941).

[12] W. Jahn-Held and K. Jellinek, *Z. Elektrochem.*, 42, 401 (1936).

Northrup KI type potentiometer and an enclosed lamp and scale galvanometer. The absorption spectra were obtained using a Beckman spectrophotometer model DU.

Procedure.—Solid manganese(II) fluoride and manganese dioxide were put into 125-ml. Erlenmeyer flasks in sufficient amounts to have the solutions saturated with respect to each substance. Distilled water and from 0.5 to 5.0 ml. of 48% hydrofluoric acid were added to give a total volume of approximately 90 ml. Equilibrium was established within twenty-four to thirty-six hours, after which the solutions were transferred to paraffined paper cups. A lead fluoride electrode was placed in the solution, and the cell was sealed by paraffining another paper cup on top of the first cup. These cells were allowed to stand overnight to allow equilibrium to be reached between the solution and the electrode. Each lead fluoride electrode was previously calibrated against one electrode picked as standard and the appropriate corrections made. A cell using a saturated calomel electrode and a lead fluoride electrode was found to be more satisfactory than a system of concentration cells.

Data and Results.—The maximum of absorption appeared at 460 mμ for the $MnF_x^{(3-x)}$ complex under the conditions investigated. All measurements were made at this wave length and at room temperature. Figure 1 illustrates the type of points obtained and shows a slope of −4. The data gave an average slope of −4.1 calculated by the method of least squares. However, the value must be a whole number; therefore, −4 is the value used. From equation 14 the slope is equal to $(2 - x)$, whereby $x = 6$. Thus, under the conditions used in this experiment the number of fluoride ions complexing with one manganese(III) ion is six, making the complex $MnF_6^{=}$.

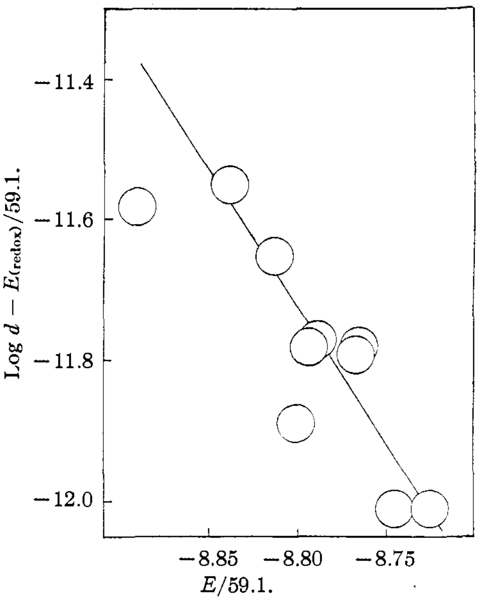

Fig. 1.—Graphical determination of "x" using equation 14. The diameter of the circles is indicative of the accuracy of the measurements.

As further evidence that the $MnF_x^{(3-x)}$ complex is an anion rather than a cation, a modified transference cell was used. The evidence showed that the complex has at least four fluoride ions complexing with the manganese(III) ion to give a complex which is an anion. The use of less concentrated solutions showed some evidence for the possibility of lower complexes; however, the solutions were not stable enough to allow accurate measurements under these conditions.

Since the literature shows that only K_2MnF_5 can be obtained, how can the complex $MnF_6^{=}$ be explained? It has been pointed out by Pauling and others that most fluoride ion complexes, especially those of the tervalent metals, have predominately ionic bonds. This means that the manganese(III) ion will have one electron in each of four 3 d orbitals. If this is the case, the magnetic susceptibility should be the same for the complex as for the free manganese(III) ion. Grey[13] measured the magnetic susceptibility of some manganese compounds including K_2MnF_5. His results showed that the observed atomic moment for manganese(III) in K_2MnF_5 is lower than the value for manganese(III) ion. His explanation is a secondary bond formation between cations thereby depleting the unpaired electrons on the manganese(III) ion and lowering the magnetic moment. In solutions the distance between cations is large enough so that secondary bonds do not occur. The manganese(III) ion behaves normally giving $MnF_6^{=}$ in solution and MnF_5^{-} in solids.

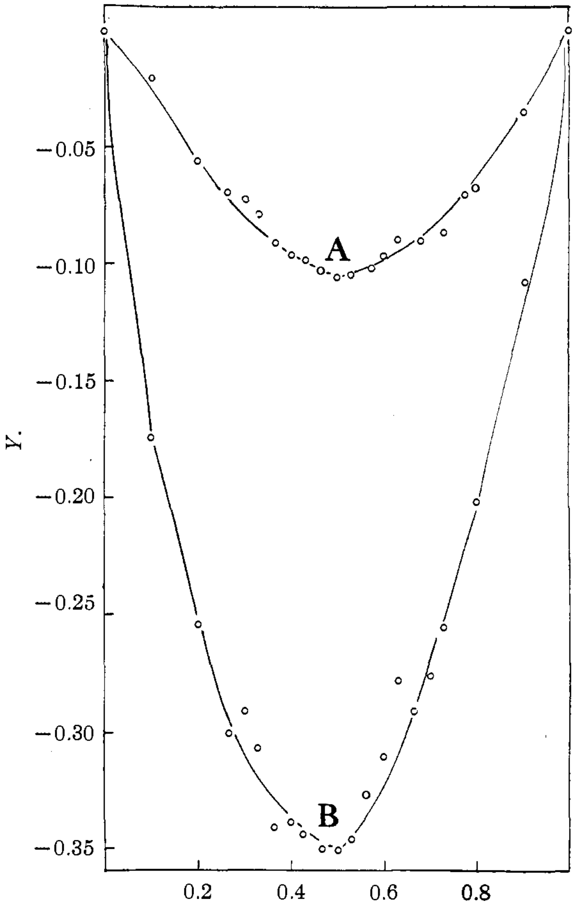

Fig. 2.—Continuous variations method for $CrF_x^{(3-x)}$ complexes; A, 580 mμ; B, 430 mμ.

Chromium(III) Fluoride Complexes

The application of the limiting density method to these complexes is not possible because the solution of the equations involves *p*H measurements. However, since it is possible to make up standard solutions of chromium(III) ions the continuous variations method can be applied. Chromium(III) nitrate and sodium fluoride were used to prepare the standard solutions which

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[13] J. T. Grey, THIS JOURNAL, **68**, 605 (1946).

were made up in two concentrations, 0.05 and 0.1 *M*. Both sets of solutions were made, respectively, 0.05 and 0.1 *M* with nitric acid in order to prevent the precipitation of chromium hydroxide and to control the ionic strength. The same results were obtained with both series of solutions, indicating that if the solutions are prepared stoichiometrically without any regard for complex formation small changes in ionic strength do not affect the validity of the results for the mole ratios. The optical density is a measure of concentration because the color of the chromium nitrate solution follows Beer's law. It can also be shown, by applying the mathematical treatment of Gould and Vosburgh,[14] that hydrofluoric acid complexes which might be formed will not interfere.

Experimental Part

Data and Results.—Optical densities of these solutions were measured at various wave lengths, with the results shown in Fig. 2. The absorption maxima occur at approximately 430 mμ and 600 mμ. The results show a maximum at 0.5 which means the complex formed under these conditions is CrF^{++}. All *Y* values are negative because the extinction coefficient for the chromium(III) ion is greater than the extinction coefficient for the complex CrF^{++}. Under the conditions of this experiment no other complex is formed. If the complex CrF_2^{+} had been formed, there would have been a shift in the absorption maximum and the calculation of *Y* would have given a maximum at 0.67 at some of the wave lengths used. Since neither of these two conditions occurred it can be assumed that only the complex CrF^{++} existed in these solutions.

The absorption spectra of a solution prepared by dissolving chromium metal in hydrofluoric acid shows a shift in the absorption maximum to higher wave lengths. This type of shift is characteristic of increasing complexity of halide complexes. It can be stated that higher complexes than CrF^{++} may exist, but definite formulas cannot be given.

Similar experiments were carried out for copper(II), cobalt(II), and nickel(II). The results showed no complexing with fluoride ion under the conditions investigated. Iron(III) fluoride complexes have been worked out by Babko and Kleiner.[5] Vanadium(III) and titanium(III) do not lend themselves to this type of investigation because of oxy-complexes of these ions.

Acknowledgment.—The authors wish to thank the Rutgers Research Council which provided the fellowship that made this research possible.

Summary

The existence of the $MnF_6^{=}$ complex as well as a CrF^{++} complex has been demonstrated. It seems necessary to have tervalent ions of the iron type to give complexes with fluoride ions. No complexes of fluoride ions with the bivalent ions copper(II), cobalt(II), and nickel(II) are evident.

NEW BRUNSWICK, NEW JERSEY RECEIVED JUNE 11, 1949

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[14] R. K. Gould and W. C. Vosburgh, THIS JOURNAL, **64**, 1630 (1942).

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

The Vapor Pressure of Inorganic Substances. II. B_2O_3[1]

BY RUDOLPH SPEISER, SAM NAIDITCH AND HERRICK L. JOHNSTON

The vapor pressure of B_2O_3 has been measured by Cole and Taylor[2] using a dynamic method. B_2O_3 was evaporated into a stream of dry nitrogen flowing over a crucible containing the B_2O_3. The loss in weight of the B_2O_3, at a given temperature, was determined for different rates of flow of the nitrogen. The rate of evaporation of B_2O_3 at zero rate of flow was then obtained by graphical extrapolation. Such a method of extrapolation is not fully reliable and generally leads to vapor pressures that are considerably too high. The Knudsen method of effusion through an orifice avoids this difficulty and yields more reliable data.

The most plausible molecular species of the boric oxides in the vapor phase are BO, B_2O_3, and B_4O_6. Spectroscopic evidence[3] indicates that a complex molecule such as B_2O_3 or B_4O_6 is present in flame spectra whereas the BO bands have only been observed when high energies of excitation were employed such as in the active nitrogen discharge tube and the carbon arc (*i. e.*, at temperatures of 4000°K.). It seems likely, therefore, that at temperatures below 1800°K. dissociation of B_2O_3 or B_4O_6 (whatever the molecular species in the vapor phase) into O_2 and BO does not take place.

Experimental Method

Vapor pressures of B_2O_3 were measured by the method of Knudsen (rate of effusion through an orifice) with high temperatures produced by induction heating, as previously described.[4]

A platinum Knudsen cell was employed with an orifice $^1/_{16}$ in. in diameter. The area of the orifice was corrected for thermal expansion.

In several experiments a platinum target was used with the effusion cell, so that the weight of material deposited upon the target and the change in weight of the Knudsen cell were measured simultaneously. This procedure made it possible to determine experimentally whether a non-condensable gas such as oxygen is formed as

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[1] This work was carried out under contract between the Office of Naval Research and The Ohio State University Research Foundation.

[2] S. S. Cole and N. W. Taylor, THIS JOURNAL, **28**, 82 (1935).

[3] W. Jevons, *Proc. Roy. Soc.* (*London*), **91A**, 120 (1914); R. S. Mulliken, *Phys. Rev.*, **25**, 259 (1925).

[4] R. B. Holden, R. Speiser and H. L. Johnston, THIS JOURNAL, **70**, 3897 (1948).