was contained in a platinum–rhodium capsule which was sealed gas tight by gold soldering. The heat content of the capsule was determined by separate measurements. The experimental results are listed in Table II and are plotted in Fig. 2.

The substance behaved satisfactorily up to about 550°K. Above that temperature the results are somewhat discordant and become progressively too high. This is attributed to beginning of thermal decomposition of the substance, which is confirmed by the fact that the gas pressure within the platinum–rhodium capsule became large enough to cause rupture at 610°K. All values in parentheses in Table II show decomposition effects. Between 298.16 and 550°K., the results are represented to within an average deviation of 0.8% by the equation

$$H_T - H_{298.16} = 45.42T + 12.90 \times 10^5T^{-1} - 17{,}869$$

The corresponding molal heat-capacity equation is

$$C_p = 45.42 - 12.90 \times 10^5T^{-2}$$

These equations, however, should not not be employed for extrapolation to higher temperatures.

Table III gives smooth values of the high-temperature heat content and corresponding entropy increments above 298.16°K.

TABLE III

HEAT CONTENT AND ENTROPY INCREMENTS FOR AMMONIUM VANADATE ABOVE 298.16°K.

T, °K.	$H^\circ_T - H^\circ_{298.16}$, cal./mole	$S^\circ_T - S^\circ_{298.16}$, cal./deg./mole
350	1730	5.35
400	3580	10.29
450	5480	14.76
500	7420	18.85
550	9390	22.61

Summary

The low temperature heat capacity of ammonium vanadate was measured throughout the temperature range 51.4 to 298.16°K. The entropy is $S^\circ_{298.16} = 33.6 \pm 0.3$ cal./deg./mole.

The high temperature heat content of ammonium vanadate was measured throughout the temperature range 298.16 to 550°K. Thermal decomposition precluded obtaining satisfactory results at higher temperatures. Heat content and entropy increments above 298.16°K. are tabulated.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Thermodynamic Data on the Cadmium Chloride Complexes Determined from the Solubility of Cadmium Ferricyanide

BY EDWARD L. KING[1]

In this paper data on the solubility of cadmium ferricyanide in solutions containing chloride ion will be presented. It is possible to interpret these data in terms of the formation of the cadmium chloride complexes: $CdCl^+$, $CdCl_2$ and $CdCl_3^-$. These complexes have been studied previously by I. Leden[2] and others.[3] The solubility measurements have been carried out at several temperatures making it possible to calculate heats of formation and entropies of the several complex species as well as the several equilibrium constants.

Experimental Work

Preparation of Solutions Used in These Experiments.—All solutions were prepared using doubly distilled water, the second distillation being from an alkaline permanganate solution. Analytical reagent grade chemicals were used in all cases without further purification. In the preparation of the sodium perchlorate solution, equivalent amounts of perchloric acid and sodium carbonate were mixed.

Preparation of the Cadmium Ferricyanide.—The solid used in the solubility measurements was prepared by precipitating cadmium ferricyanide at room temperature from a freshly prepared dilute solution of potassium ferricyanide by the addition of cadmium nitrate solution. The solid separates as a very finely divided yellow material. Analyses of the material used in the solubility measurements as well as several other samples of solid precipitated in the presence of a low (less than 0.1 *M*) excess of potassium ferricyanide or in the presence of an excess of cadmium nitrate were performed. The solid was decomposed by heating with concentrated sulfuric acid. The iron and cadmium were then separated by isopropyl ether extraction of iron as described by Swift.[4] The iron was analyzed iodometrically[5] and cadmium was determined gravimetically by conversion to the sulfate. The ratio of cadmium to iron in the five different samples analyzed ranged from 1.47 to 1.52 with an average of 1.49. Thus the finely divided yellow solid is $Cd_3\{Fe(CN)_6\}_2 \cdot xH_2O$. The degree of hydration of the solid was not determined as in no case was the solid dried and weighed; only the ratio of cadmium to iron was determined.

Solubility Measurements.—Before using the $Cd_3\{Fe(CN)_6\}_2 \cdot xH_2O$ in a solubility determination, it was washed several times with a dilute solution of sodium perchlorate. Then each portion was washed with a solution of the composition to be used in the solubility experiment. The solubility equilibrium is established very rapidly; in no experiment was a slowness detected even though in the experiments at 47.5° samples were removed after two minutes stirring. In several experiments equilibrium was approached from the supersaturated side as well as from the other side. Because of the high rate of solution, it was possible to carry out the measurements in open vessels; no errors due to evaporation would be expected. The

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[1] Present address: Department of Chemistry, University of Wisconsin, Madison, Wisconsin.

[2] Leden, *Z. physik. Chem.*, **188A**, 160 (1941).

[3] Reference 2 contains a comprehensive review.

[4] E. H. Swift, "A System of Chemical Analysis," Prentice Hall, New York, N. Y., 1946, pp. 291-298.

[5] E. H. Swift. *op. cit.*, pp. 298-300.

solid was stirred with the solution in 40 ml. test-tubes with a mechanical stirrer in a thermostat. At two or three different times, aliquots of solution and suspended solid were removed, delivered into a centrifuge cone and centrifuged to remove the suspended solid, which otherwise settled exceedingly slowly upon standing. By using 15 ml. centrifuge cones which were centered in the cups for 50-ml. cones by use of a rubber stopper with the appropriate sized hole, it was possible to jacket the cone with the thermostat media. Only in the case of the experiments at 47.5° was real trouble experienced during centrifugation in keeping the solution at the approximate temperature of the experiment. In these experiments at 47.5°, hot air was blown into the centrifuge (International Clinical model) through the small hole in the lid. Even with this device, the solution temperature would drop several degrees during the centrifugation. Because the saturated solution at 47.5° will be supersaturated at room temperature, a measured aliquot of the solution from the centrifugation was diluted for analysis.

The concentration of dissolved cadmium ferricyanide was determined by measurement of the ferricyanide concentration by means of light absorption. The absorption at several wave lengths in the region 4200 to 4600 Å. was determined with a Beckman Quartz Spectrophotometer. This proved to be a convenient method of analysis at the concentrations under consideration.

Experimental Results and Discussion

In practically all experiments two or three portions of saturated solution were removed at various times. The average variation in the concentrations in the successive aliquots in a given experiment was 1.7% for the experiments at 0.0° and 25.0°, while in the experiments at 47.5° it was 3%. The greater variation in the experiments at 47.5° is due no doubt to the temperature variations during centrifuging. The results of the solubility experiments are presented in Table I and also in Fig. 1.

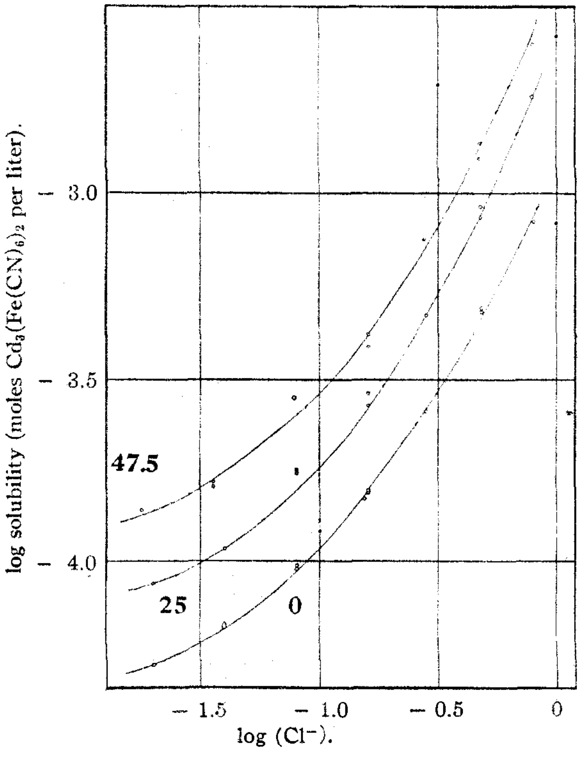

Fig. 1.—Solubility of $Cd_3(Fe(CN)_6)_2 \cdot xH_2O$ in solutions containing chloride ion at 0, 25 and 47.5°.

The Equilibria which are Consistent with Solubility Data.—The equations for the net reactions occurring when $Cd_3(Fe(CN)_6)_2 \cdot xH_2O$ dissolves in a solution containing chloride ion are

$$^1/_3Cd_3(Fe(CN)_6)_2 \cdot xH_2O + nCl^- = CdCl_n^{+2-n} + {^2/_3}Fe(CN)_6^{\equiv} + x/3H_2O \quad (1)$$

$n = 0, 1, 2, 3$

The equilibrium constants for these reactions are

$$K_n = (CdCl_n^{+2-n})(Fe(CN)_6^{\equiv})^{2/3}/(Cl^-)^n$$

The equilibrium constants for the reactions of cadmium ion to form the several complex species

$$Cd^{++} + nCl^- = CdCl_n^{+2-n} \quad (2)$$

TABLE I

SOLUBILITY OF $Cd_3(Fe(CN)_6)_2 \cdot xH_2O$

All solutions: 2.96 M Na^+; 0.04 M H^+; $\{3.00 - (Cl^-)\}$ M ClO_4^-

Total concentration of Cl⁻, mole/liter	Observed solubility,[c] moles $Cd_3(Fe(CN)_6)_2$ per liter × 10^5 0.0°C.	25.0°C.	47.5°C.[b]
0.000	4.0, 3.75	6.8. 6.5	9.9, 9.4
.018			13.8
.020	5.15	8.65	
.036			16.0, 16.5
.040	6.6, 6.7	10.8, 10.8	
.080	9.5, 9.7	17.8, 17.4	26.8
.154	14.8[a]		
.160	15.6, 15.4	28.9, 26.8	38.7, 41.7
.280	25.9	46.9	75
.480	49, 48	8[illegible], 92	124, 137
.800	84	182	251

[a] In this experiment $(H^+) = 0.15\ M$, $(Na^+) = 2.85\ M$. [b] In all experiments at 47.5° $(H^+) = 0.02\ M$, $(Na^+) = 2.98\ M$. [c] When two figures are given they are the results of two independent experiments.

are related to the K's for the solubility reactions in the following manner

$$\beta_n = \frac{(CdCl_n^{+2-n})}{(Cd^{++})(Cl^-)^n} = \frac{K_n}{K_0}$$

It is seen that K_0 is the cube root of the solubility product constant for $Cd_3(Fe(CN)_6)_2 \cdot xH_2O$.

The solubility experiments were all carried out at constant ionic strength made up of sodium ion, hydrogen ion, perchlorate ion and chloride ion. In the solutions in which the solid is most soluble, the increased ionic strength due to the ferricyanide ion and the various complexes is of the order of one per cent. of the total. The approximation has been made that the activity coefficients of the various species are not affected at constant ionic strength when the medium is varied from 3.0 M ClO_4^- to 2.20 M ClO_4^-, 0.80 M Cl^-. Thus the equilibrium constants presented will all be concentration equilibrium constants for a solution of ionic strength of 3.00.

The Value of K_0, the Cube Root of the Solubility Product Constant for $Cd_3(Fe(CN)_6)_2 \cdot xH_2O$.—The values of K_0 at the several temperatures can be determined from the results of single experiments at each temperature. This is the measurement of the solubility in the absence of chloride ion. It is seen that $K_0 = S^{5/3} \times 3 \times (2)^{2/3} = 4.76\ S^{5/3}$ where S is the solubility of $Cd_3(Fe(CN)_6)_2 \cdot xH_2O$. Using the values of the solubility of 3.85×10^{-5}, 6.65×10^{-5} and 9.7×10^{-5} mole per liter, values of K_0 calculated are 2.1×10^{-7}, 5.2×10^{-7} and 9.7×10^{-7} at 0°, 25° and 47.5°, respectively.

In the interpretation of the data on the solubility in the presence of chloride ion it is necessary to know that at the concentration of ferricyanide present, no soluble cadmium ferricyanide complexes exist. This was checked in a simple experiment. A solution of 9.1×10^{-4} *M* cadmium nitrate in 2.69 *M* sodium perchlorate–0.04 *M* perchloric acid was added with rapid stirring to a solution of the composition: 3.8×10^{-3} *M* potassium ferricyanide, 2.96 *M* sodium perchlorate and 0.04 *M* perchloric acid. At a point in the addition of the cadmium solution when the concentration of cadmium was less than 6×10^{-5} *M*, precipitation had already occurred. This leads to an upper limit of K_0 of 1.4×10^{-6} at 25°. This is 2.7-fold higher than calculated from the solubility of the pure salt but would still lead to the result that no more than one per cent. of the cadmium (II) dissolved in a solution of 0.80 *M* chloride ion is present as a ferricyanide complex.

From the values of the equilibrium constants at the three temperatures, it is possible to calculate the heat of solution of $Cd_3\{Fe(CN)_6\}_2 \cdot xH_2O$ in a solution of ionic strength 3.0. When log K_0 is plotted *vs.* $1/T$, an approximately straight line results with a slope which corresponds to a ΔH of solution of 17.2 ± 0.7 kcal. per formula weight of $Cd_3(Fe(CN)_6)_2 \cdot xH_2O$.

The Dependence of the Solubility upon Hydrogen Ion Concentration.—In eq. (1) for the net reaction which occurs when cadmium ferricyanide dissolves in a solution containing chloride ion, neither the cadmium chloride complex ion nor ferricyanide ion are shown with attached hydrogen ion. One would expect $CdCl_nH^{+3-n}$ to be a strong acid since hydrochloric acid is strong and the presence of the metal ion would cause an acid strengthening. Kolthoff and Tomsicek[6] have presented data which indicate that ferricyanide ion exists as such at hydrogen ion concentrations as high as 6×10^{-3} *M*. In one of the solubility measurements run at 0°, the hydrogen ion concentration was 0.15 *M* instead of 0.04 *M* (see Table I and Fig. 1). It is seen that this experimental point is on the same smooth curve as are the other data. If the species of ferricyanide present in a solution of this hydrogen ion concentration range were $HFe(CN)_6^{=}$, a 3.7-fold change in hydrogen ion concentration would give rise to a change in solubility by a factor of 1.7. Therefore, these data indicate that at a hydrogen ion concentration as high as 0.15 *M*, ferricyanide exists as $Fe(CN)_6^{\equiv}$.

The Values of the Several Equilibrium Constants.—It is possible to calculate the various equilibrium constants by a variety of methods. The method which best uses all of the data in the chloride ion concentration range in which the appropriate constant is most relevant is the method of Leden[2] and Connick.[7] A few obvious modifications of the method of Leden make it suitable for the treatment of these solubility data.

It was found necessary to assume the presence in solution of the species Cd^{++}, $CdCl^+$, $CdCl_2$ and $CdCl_3^-$ in order to explain the solubility data. It was not necessary to assume the presence of $CdCl_4^=$ The values of K_n, the equilibrium constants for reactions (1), are given in Table II. The curves in Fig. 1 are calculated using these equilibrium constants and the solubility product constants discussed earlier. Included in Table II are the values of K_n at 25° calculated from Leden's values[2] of β_n and the value of $K_0 = 5.2 \times 10^{-7}$.

TABLE II

EQUILIBRIUM CONSTANTS FOR REACTIONS

$1/3\ Cd_3\{Fe(CN)_6\}_2 \cdot x\ H_2O + n\ Cl^- = CdCl_n^{+2-n} + 2/3\ Fe(CN)_6^{\equiv} + x/3\ H_2O$

Temperature, °C.	$K_1 \times 10^5$	$K_2 \times 10^5$	$K_3 \times 10^6$
0.0	0.57 ± 0.04	3.7 ± 0.3	1.6 ± 0.3
25.0 (this work)	1.3 ± 0.15	8.0 ± 1	13 ± 3.0
(Leden)	2.0	8.8	13.5
47.5	3.5 ± 0.5	13.0 ± 3.0	28 ± 4

It should be noted that in the case of the bromide and iodide complexes of cadmium, complexes which involve four halide ions are observed.[2] The chloride complexes appear to be less stable to an extent such that at 0.8 *M* Cl^-, the species $CdCl_4^=$ is not present at appreciable concentrations.

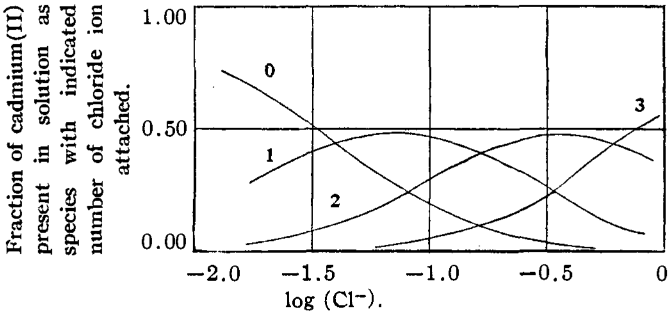

Fig. 2.—Distribution of cadmium (II) among the various complex species at 25°.

The overlapping of the chloride ion concentration ranges in which the various complexes are most important is clearly shown in Fig. 2. In systems where such an overlapping occurs, it is possible to fit the experimental data, unless they

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[6] Kolthoff and Tomsicek, *J. Phys. Chem.*, **39**, 955 (1935).

[7] R. E. Connick, private communication.

are exceedingly accurate, with an appreciable range of values for each equilibrium constant. This accounts for the rather large uncertainty shown in values in Table II.

The Heats of Formation and Entropies of the Several Complexes.—It is possible to obtain heats of formation of the complex species $CdCl^+$, $CdCl_2$ and $CdCl_3^-$ from the ions Cd^{++} and Cl^- by considering the values of β_n as a function of temperature. These data are plotted in Fig. 3. The vertical lines in this figure indicate the ranges of values of β_1, β_2 and β_3 which are consistent with the experimental inaccuracies. Heats of reaction (2) at 25° have been calculated from the slope of these curves. These values are given in the first column of Table III. It is seen that all of the complexes except $CdCl_2$ are formed endothermically. Their stability is due to the entropy increase which occurs upon their formation. Unlike association reactions in the gas phase which are associated with a decrease in entropy, these association reactions of ions in solution are accompanied by an increase in entropy. This is due to the greater freedom of motion of the solvent molecules in the field of the complex compared to their freedom in the field of the several reacting ionic species.

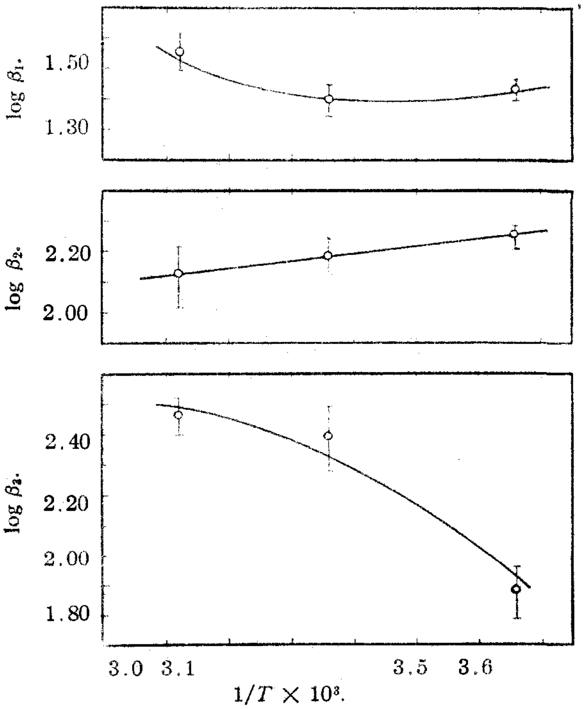

Fig. 3.—Values of β_n at various temperatures.

The entropies of the several complex species can be calculated from the ΔS of the reactions for their formation and the known entropies of cadmium and chloride ions. The entropies of these two ions are given by Latimer, Pitzer and Smith[8] as -16.4 for Cd^{++} and $+13.5$ for Cl^-. The results of these calculations are given in the last column of Table III. In these calculations the entropies used are for the hypothetical one molal solution while the entropy change is for a hypothetical one molal solution in which the ionic strength is 3.0. The use of the two sets of quantities without correction to the same standard state is the best one can do in view of lack of data regarding the effect of ionic strength changes on the entropy.

TABLE III

VALUES OF HEAT, FREE ENERGY AND ENTROPY CHANGES FOR THE REACTIONS: $Cd^{++} + nCl^- = CdCl_n^{+2-n}$

Reaction for the formation of	$\Delta H/T$, cal./mole deg.	$-\Delta F/T$, cal./mole deg.	ΔS cal./mole deg.	S complex
$CdCl^+$	2.1	6.4	8.5	5.6
$CdCl_2$	−3.7	10.1	6.4	17.0
$CdCl_3^-$	15.5	11.0	26.5	50.7

The entropy of the species $CdCl_3^-$ is quite large. That it is probably larger than one would expect is realized if the entropy change for the reaction

$$CdCl_2 + Cl^- = CdCl_3^-$$

is considered. This entropy change is +20.2 entropy units. If the entropy change arises largely from the change in the polarization of water by ionic charges, it might be expected to be small. However Frank and Evans[9] have pointed out that other factors play an important role in determining entropies of dissolved species.

It is very desirable to have more data on the entropies of complex ions in solution such that correlations could be made.

Summary

The solubility of $Cd_3(Fe(CN)_6)_2 \cdot xH_2O$ has been determined in aqueous solution containing various concentrations of chloride ion at 0.0°, 25.0° and 47.5°. These data have been interpreted on the basis of there being present in solution the species: Cd^{++}, $CdCl^+$, $CdCl_2$ and $CdCl_3^-$. The complex species $CdCl_4^=$ is not appreciably stable in solutions in which the chloride ion concentration is 0.8 M.

The ΔH of solution of $Cd_3(Fe(CN)_6)_2 \cdot xH_2O$ has been found to be 17.2 ± 0.7 kcal. per formula weight.

The heats and entropies of formation of the several complex species have been calculated by considering the variation of the various equilibrium constants with temperature.

CAMBRIDGE, MASS. RECEIVED JULY 14, 1948

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(8) Latimer, Pitzer and Smith, THIS JOURNAL, **60**, 1829 (1938).

(9) Henry S. Frank and Marjorie W. Evans, *J. Chem. Phys.*, **13**, 522 (1945).