perature and a hydrogen pressure of two atmospheres. The catalytic activity is quite reproducible despite considerable variation in the cobalt content of the ammonia-insoluble product. These catalysts are largely deactivated by treatment with ammonium bromide (an acid) in liquid ammonia and it is of interest to note that the quantity of hydrogen thereby liberated is in good agreement with that obtained by thermal desorption. These catalysts are also somewhat deactivated by *extensive* washing with, or long periods of storage under, absolute ethanol, although as shown in Fig. 1 (Run 21) their activity is substantially uninfluenced by limited exposure to ethanol. Preliminary studies of the kinetics of the hydrogenation reaction indicate that it is first order with respect to the concentration of allyl alcohol. The significance of this fact, as well as the surface area data, will be considered in later papers concerned with other transitional metal catalysts formed by the reduction of salts in liquid ammonia.

AUSTIN, TEXAS RECEIVED OCTOBER 9, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING AT THE UNIVERSITY OF WASHINGTON]

The Thermal Dissociation of Some Chromium(III) Iodides

BY LYMAN L. HANDY AND N. W. GREGORY

Equilibrium pressures of iodine above CrI_3, $CrICl_2$ and $CrIBr_2$ have been measured. Thermodynamic properties of the last two are similar to those anticipated for a solid solution of CrI_3 and CrX_3 as suggested by structural properties. However, no definite conclusion has been drawn concerning the character of the mixed halide phases.

The structural characteristics of $CrICl_2$ and $CrIBr_2$ (prepared by reaction of iodine with $CrCl_2$ and $CrBr_2$, respectively) are similar to those which would be anticipated for a solid solution of the parent compounds CrI_3 and CrX_3.[1] In view of the reversible nature of the reaction between iodine and the chromium(II) halides, it was considered of interest to investigate the thermodynamic properties of the mixed halide phases by a study of the thermal decomposition equilibria. The data obtained are compared with results previously reported for CrI_3[2] and $CrCl_3$.[3,4] The thermal dissociation of CrI_3 has been reinvestigated by a different method which is found to give the thermodynamic constants confirming earlier results within experimental error.

Experimental

Preparation and identification of the materials have been discussed previously.[1,2] Two methods were used to measure iodine pressures: the Knudsen effusion technique,[5,2] and a static method of employing a thin Pyrex glass diaphragm gage.[6,7] A comparison of results from the two methods (by extrapolation) suggests that a rate problem is encountered in the effusion apparatus (*i.e.*, the sample is unable to maintain the equilibrium pressure with pinhole diameters of the order of 1 mm.) which leads to apparent equilibrium pressures (steady state pressures) lower than the true values. In the case of CrI_3 the results were not sufficiently different to affect thermodynamic quantities appreciably beyond experimental error. This was not true for the mixed halides, however. Diaphragm gage pressures were used exclusively for the data reported in this paper.

The manometer described previously[7] was modified slightly for experiments with CrI_3 and $CrIBr_2$. Some of the temperatures at which measurements were made for these two compounds were above the softening point of Pyrex. Hence a quartz bottom was attached to the apparatus and the temperature of the sample maintained at higher values than the diaphragm. For the majority of runs, the diaphragm was held at 200°. The pressure has been assumed constant within experimental uncertainty (± 2 mm.) throughout the apparatus (although there will obviously be continuous circulation). The validity of this assumption was substantiated by variation of the temperature of the diaphragm portion of the system while the sample temperature was held constant. The equilibrium pressure was not observed to change. The $CrICl_2$ system was studied with the entire apparatus at a uniform temperature.

Equilibrium pressures were also verified by an isopiestic method. With the sample at a given temperature, the pressure of iodine was determined by measuring the temperature of a cool portion of the tube (in a thermostat) at the point where iodine crystals began to grow, and conversely the temperature at which iodine crystals at this point evaporate. This method was not capable of great precision but taken with known vapor pressures of iodine gave results compatible with those obtained with the diaphragm gage.

Data for all compounds were checked with several independently prepared samples, including one series in each case where the material was formed in the apparatus by direct reaction of iodine with the chromium(II) salt. The relative amounts of chromium(III) and chromium(II) phases were also varied without significant effects on the equilibrium constant for the decomposition. These results indicate that the chromium(III) mixed halide phases maintain an essentially constant composition throughout the decomposition and hence behave effectively as a single component in so far as the phase rule is concerned.

It has been assumed that iodine is the only component present at significant concentrations in the gas phase. Appreciable amounts of chlorine or bromine would not be anticipated from thermodynamic considerations, and this view is supported by the nature of the thermal decomposition products. Doerner[3] finds the chloride system to be complicated at high temperatures by the presence of $CrCl_4$ in the vapor phase. However, the concentration of this substance is not significant at 400°, the highest temperature involved in the study of the $CrICl_2$ system. One would expect $CrBr_4$ and CrI_4 to be considerably less stable than $CrCl_4$ and have assumed neither to be present in significant amounts in the bromide or iodide systems. Absence of volatile compounds of chromium is also indicated by the lack of transport of chromium from the hot regions by sublimation.

Results and Discussion

The data for the three iodides are shown graphically in Fig. 1. The experimental points are given and the lines drawn correspond to the equations below as determined by a least squares fit of the data.

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(1) L. L. Handy and N. W. Gregory, THIS JOURNAL, **74**, 891 (1952).

(2) L. L. Handy and N. W. Gregory, *ibid.*, **72**, 5049 (1950).

(3) H. A. Doerner, *Bur. Mines T. P.*, **577**, U. S. Govt. Pt. Off. (1937).

(4) C. G. Maier, *Bur. Mines Bull.*, **436**, U. S. Govt. Pt. Off. (1942).

(5) M. Knudsen, *Ann. Physik*, **28**, 1002 (1909).

(6) F. Daniels, THIS JOURNAL, **50**, 1115 (1928).

(7) N. W. Gregory and B. A. Thackrey, *ibid.*, **72**, 3176 (1950).

Iodine pressures above solid	Temperature interval, °K.	log $P_{mm.}$ =
CrI_3	763–937	$-(8649/T)+12.04$
$CrIBr_2$	716–902	$-(5987/T)+9.38$
$CrICl_2$	581–746	$-(5601/T)+10.40$

The mean deviations of log P(calcd.) and log P(expt.) are 0.015, 0.015 and 0.011, respectively.

For purposes of comparison, the data have been changed to 25° using a very approximate value of ΔC_p of -1.0 for the decomposition reactions in each case. This value was estimated by a consideration of behavior expected on a classical basis and the discussion of the chloride system given by Maier.[4] Thermodynamic data are summarized in Table I.

TABLE I

THERMODYNAMIC CONSTANTS FOR SOME CHROMIUM(III) IODIDES FOR THE REACTION $CrIX_{2(s)} = CrX_{2(s)} + {}^1/_2\,I_{2(g)}$

Decomposition of	ΔH°_0, kcal.	$\Delta\alpha$, cal./deg.	I	ΔH°_{298}, kcal.	ΔF°_{298}, kcal.	ΔS°_{298}, e.u.
CrI_3	20.65	2.3	28.6	20.4	13.7	21.9
	(20.7)	(1.15)	(24.2)	(20.6)	(14.4)	(20.8)
$CrIBr_2$	14.53	2.3	22.6	14.2	9.5	15.9
$CrICl_2$	13.57	2.3	24.7	13.2	7.8	18.1

The constants are for the equation $\Delta F^\circ = \Delta H_0^\circ - \Delta\alpha\, T \log T - IT$.

The values in parentheses in Table I are those previously reported for CrI_3 (a slightly different value for ΔC_p was used) as determined by the effusion method.[2] The estimated uncertainty in ΔH° as determined by the slopes (exclusive of uncertainty in ΔC_p) is not expected to exceed 0.5 kcal. Maier's data[4] for decomposition of $CrCl_3$ to $CrCl_2$ and chlorine lead to values of 35.0, 27.7, and 24.4 for the enthalpy, free energy and entropy changes, respectively, at 25°.

The mixed halide phases possess interesting properties. Iodine converts the CrX_2 lattice (X = Cl or Br) into a chromium(III) lattice which has structural properties similar to that expected for a solid solution of CrX_3 and CrI_3.[1] Decomposition of this phase proceeds reversibly, eliminating iodine and reforming CrX_2. Whereas the simplest interpretation may be given in terms of the straightforward reactions written in Table I, it is also possible to associate this behavior with that anticipated for a solid solution of CrX_3 and CrI_3. In the latter case the decomposition reaction corresponds to an over-all process of the form

$$^2/_3\,CrX_3 + {}^1/_3\,CrI_3 = CrX_2 + {}^1/_2\,I_2$$

In either event the greater stability (greater negative free energy of formation) expected for $CrCl_2$ or $CrBr_2$ as compared with CrI_2 leads one to anticipate (as observed) that the equilibrium iodine pressures above the mixed halide phases will be larger than those over pure CrI_3 and that the energy required for decomposition will be smaller than for CrI_3. The magnitude of this effect may be modified by the change in activity of CrI_3 in the solution hypothesis.

Unfortunately, sufficient data are not available to permit a quantitative comparison of the thermodynamic properties of the mixed halide phases with those expected for a solid solution of CrX_3 and CrY_3 of corresponding composition. The bromide system has not been investigated, and the free energy and heats of formation of CrI_2 and CrI_3 are not known. Values of the latter may be calculated from the data above if $CrICl_2$ is assumed to be an "ideal mixed halide" phase, pictured as a crystal in which the halide ions are mixed randomly. The thermodynamic properties of such a mixture would be expected to correspond to a linear interpolation of the values of $CrCl_3$ and CrI_3, with inclusion of a mixing contribution for the free energy and entropy. The entropy of solid solutions of silver chloride and silver bromide has been found to agree with this interpretation.[8]

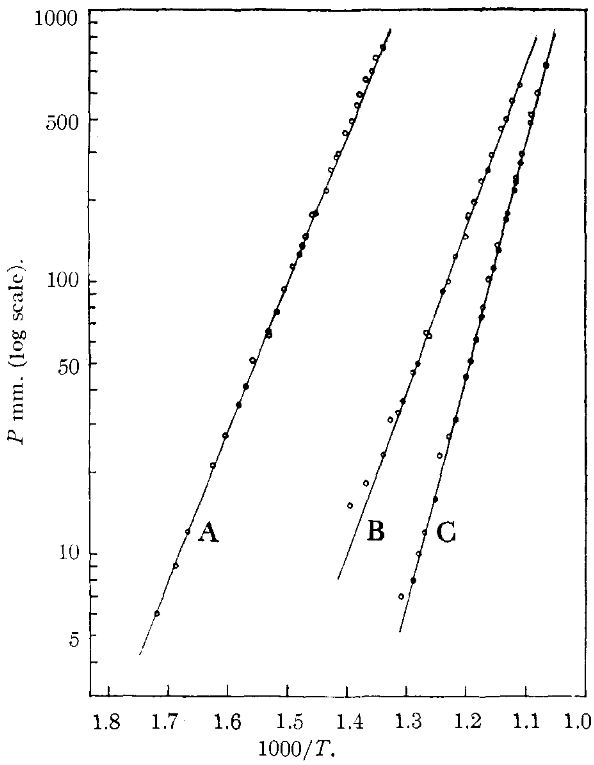

Fig. 1.—Equilibrium pressures of I_2 above $CrICl_2$–$CrCl_2$, $CrIBr_2$–$CrBr_2$ and CrI_2–CrI_2: A, $CrICl_2$; B, $CrIBr_2$; C, CrI_3.

If such an assumption is made in this case, the experimental entropy and heat of formation of $CrICl_2$ may be used to determine corresponding values for CrI_3. Taking Kelley's entropies[9] and Maier's heats of formation[4] for $CrCl_3$ and $CrCl_2$, values of $S^\circ = 49$ and $\Delta H^\circ = -66.6$ are obtained for CrI_3 by means of the equations

	$CrICl_{2(s)}$ =	$CrCl_{2(s)}$ +	$^1/_2\,I_{2(g)}$	Experimental results
ΔH°:	-110.2	-97	0	$\Delta H^\circ = 13.2$ kcal.
S°:	40.8	27.7	$^1/_2\,(62.29)$	$\Delta S^\circ = 18.1$ e.u.

and (assuming)

	$^2/_3\,CrCl_{3(s)}$ +	$^1/_3\,CrI_{3(s)}$ =	$CrICl_{2(s)}$	Values if ideal solid solution of halide ions
ΔH°:	$^2/_3\,(-132)$	?	-110.2	$\Delta H = 0$
S°:	$^2/_3\,(31)$	?	40.8	$\Delta S^\circ = 3.8$

Using additional data from the CrI_3–CrI_2 system, corresponding results for CrI_2 are 40 e.u. and -46 kcal., respectively.

The heats of formation for the pure iodides determined on this basis are appreciably lower than expected.[2] The entropies are somewhat larger

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(8) E. D. Eastman and R. T. Milner, *J. Chem. Phys.*, **1**, 445 (1933).

(9) K. K. Kelley, *U. S. Bur. Mines Bull.*, 434 (1942).

than predicted by Latimer's method[10] (47.7 for CrI_3; 37.4 for CrI_2) but in view of the approximations involved and the neglect of probable non-ideal characteristics they cannot be considered inconsistent with the solution hypothesis.

It is apparent that one may not draw a definite conclusion concerning the character of the solid mixed halide phases at this time. Thermodynamic properties are generally consistent with those one would anticipate for either random or ordered arrangement of halide ions. The relationship between chromium iodide and the iodide mixed halides investigated in this work bears a close resemblance to that observed between $FeBr_3$ and $FeBrCl_2$, formed by bromination of $FeCl_2$.[11]

The difference in entropy between CrI_3 and CrI_2 noted above corresponds fairly well with the estimation method proposed by Latimer.[10] It is also of interest that the change in entropy on thermal dissociation of $CrICl_2$ reverses the downward trend noticed in $CrIBr_2$ as compared with CrI_3. This may possibly be associated with the observation that $CrCl_2$ possesses a different crystal structure than $CrBr_2$ and CrI_2[12] since the structures of the chromium(III) phases are very similar. The difference in entropy between $CrCl_3$ and $CrCl_2$ (3.3 e.u.) is also observed to be small when compared with the difference between CrI_3 and CrI_2 (9.3 e.u.).

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[10] W. M. Latimer, THIS JOURNAL, **73**, 1480 (1951).

[11] N. W. Gregory, *ibid.*, **73**, 5433 (1951).

[12] L. L. Handy and N. W. Gregory, *J. Chem. Phys.*, **19**, 1314 (1951).

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[CONTRIBUTION NO. 174 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Solubility of Silver Chloride and the Formation of Complexes in Chloride Solution[1]

BY J. HAWORTH JONTE AND DON S. MARTIN, JR.

A radioassay technique has been used to determine the concentration of silver in various chloride solutions in contact with silver chloride at temperatures of 15.0, 25.0 and 35.0°. A minimum in silver concentration of about 5×10^{-7} *M* was found at 25° for a chloride activity of 2×10^{-3}. The data have been interpreted in terms of equilibria which involve the species Ag^+, AgCl(aq), $AgCl_2^-$ and AgCl(s). Equilibrium constants and thermodynamic quantities for the reactions involving these species have been calculated.

Introduction

Recently in this Laboratory radioactive assays have been utilized to measure the solubility of some rare earth oxalates.[2] From such experiments it was possible to evaluate equilibrium constants describing precipitation and complex formation. It has not been possible to apply other methods for the study of these equilibria. The present work, in which similar techniques were used to measure silver concentrations in various chloride solutions, was undertaken since some results of the radioassays could be tested directly with the solubility product determined by exceedingly accurate potentiometric means. Chloride concentrations could be adjusted only down to about 5×10^{-5} *M*. Actually, the region was small for which a solubility product law was valid because of the formation of complexes. The existence of chloro complexes of silver is well recognized since the solubility of silver chloride increases in concentrated chloride solutions. Forbes[3a] and Forbes and Cole[3b] have provided extensive quantitative data demonstrating this effect. They measured the concentration of silver in chloride solutions of various concentrations which produced a barely detectable turbidity. The results in this paper include a region of chloride concentration which has not been studied previously.

Experimental

Procedures and precautions for the determination of solubilities by radioactive assays have been included in the description of the measurements with the rare earth oxalates.

The radioactive silver was obtained from the Oak Ridge National Laboratory as a high specific activity sample with 0.088 millicuries/mg. The standard silver solutions were prepared by first electroplating the radioactive silver onto platinum. The weighed deposits were dissolved in a minimum quantity of dilute nitric acid. Small amounts of perchloric acid were added and the solutions repeatedly evaporated nearly to dryness so that the dense fumes of perchloric acid were evident. Finally, the residues were dissolved in the redistilled water and diluted in volumetric flasks. All equilibrium solution counting assays were compared with an evaporated aliquot from one of the standard silver solutions. A specific activity of 5×10^6 counts min.^{-1} $(\text{mg. Ag})^{-1}$ was obtained for first shelf geometry.

Sodium chloride solutions were prepared from reagent grade salt and standardized by conventional procedures.

All water used had been redistilled from alkaline permanganate.

Equilibrium mixtures were prepared by the mixing of standard solutions of silver in perchloric acid and of sodium chloride. The solutions were diluted to 200 ml. and stored in glass stoppered Pyrex flasks. Equilibrium for various mixtures was approached from both directions by first heating or cooling the flasks at least 10° above or below the equilibrium temperature and then shaking them in a thermostat which maintained the desired constant temperature to within ±0.05°. Samples were withdrawn after a period of at least a week in the thermostat and the total silver concentration of the solution determined by radioassays. Assays were repeated at least twice after intervals of several days to verify that concentrations were not changing. Mixtures which had been previously heated and cooled came to the same final concentration. The chloride ion concentration was calculated by subtracting the amount precipitated as silver chloride from that added as sodium chloride in the standard solution. In the most dilute chloride solution about 80% was precipitated; in many of the solutions only

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[1] Work performed in the Ames Laboratory of the Atomic Energy Commission.

[2] (a) C. E. Crouthamel and D. S. Martin, Jr., THIS JOURNAL, **72**, 1382 (1950); (b) **73**, 569 (1951).

[3] (a) G. S. Forbes, *ibid.*, **33**, 1937 (1911); (b) G. S. Forbes and H. I. Cole, *ibid.*, **43**, 2492 (1921).