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The Thermodynamic Constants of Iodine Trichloride

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Introduction

The univariant system $ICl_3(s)$, $ICl(l)$, $I_2(g)$, $Cl_2(g)$, $ICl(g)$ was first studied by Stortenbecker[1] during his classic investigation of equilibria in mixtures of iodine and chlorine. For purposes of free energy calculations his results are not sufficiently accurate or complete, although from the point of view of the phase rule they leave nothing to be desired. In this paper are presented the results of more careful measurements on the dissociation of solid iodine trichloride at 25.0 and 35.0°, together with the results of free energy, heat content and entropy calculations.

Since the system under consideration is, according to the phase rule, univariant, then at a fixed temperature the partial pressures of iodine, chlorine and iodine monochloride above the two-phase mixture of liquid iodine monochloride and solid iodine trichloride are also fixed. Iodine trichloride has been shown by Stortenbecker not to exist in the vapor phase. Moreover, at the temperatures of interest, chlorine is always present in excess in the vapor phase, and since the degree of dissociation of gaseous iodine monochloride is small,[2] all of the iodine may be considered to be present as iodine monochloride. For the present purposes the chemical equation can therefore be written as

$$ICl_3(s) = ICl(g) + Cl_2(g)$$

Experimental

The iodine and chlorine used were of the best grades obtainable. The iodine was not purified further. The chlorine, which contained very little hydrogen chloride, was dried with anhydrous calcium chloride and then condensed into glass bulbs provided with easily breakable tips.

To determine the composition of the vapor phase a mixture of iodine and chlorine ($Cl_2/I_2 = 1.7$) in a two-liter evacuated flask was allowed to remain in a thermostat for several days. The samples of the vapor were collected in 100-cc. evacuated bulbs which were attached to the large flask in such a way that a magnetically operated plunger could effect a connection between them. In this manner the halogens were prevented from coming in contact with anything other than glass. The bulbs were sealed off and opened under a known volume of standard potassium iodide solution. The resulting solution was diluted to just 250 cc. and aliquot portions were taken for analysis. One portion was acidified slightly with hydrochloric acid and titrated with standard thiosulfate. This served to determine the total halogen present. A second portion was treated with an equal volume of concentrated hydrochloric acid and was titrated with standard permanganate, carbon tetrachloride serving to show the end-point. This titration makes possible the determination of the free chlorine present in the sample. The difference between the total halogen and the free chlorine gives the amount of iodine monochloride in the sample. All analyses were made in duplicate.

The pressure measurements were also carried out in an all-glass apparatus. A glass click gage was used in connection with a mercury manometer to determine the pressures. The 100-cc. bulb which was to contain the equilibrium mixture was first filled with 10 g. of iodine and then evacuated. By means of a magnetically operated plunger, a tube containing five grams of chlorine was broken and the chlorine allowed to distil into the bulb. The apparatus was again evacuated while the bulb was immersed in liquid air and then sealed off. The pressure measurements were made while the bulb and click gage were submerged in a water thermostat. From time to time portions of the vapor were condensed into side-arms by means of liquid air and the side-arms sealed off. It was not until the removal of several portions caused no appreciable changes in the equilibrium pressures that the measurements were regarded as representing the true vapor pressure of the system being studied. Equilibrium was approached from both the high and low temperature sides.

Results of the Experiments and Calculations

In Table I are presented representative results of the measurements.

From these results the values for the equilibrium constant $K = P_{ICl}P_{Cl_2}$ for reaction (1) were

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[1] Stortenbecker, *Z. physik. Chem.*, **3**, 15 (1899).

[2] Blair and Yost, THIS JOURNAL, **55**, 4489 (1933).

TABLE I

RESULTS OF THE EQUILIBRIUM MEASUREMENTS

Temp., 24.8°		Temp., 34.8°	
Press., mm.	Mol. ratio,[a] Cl_2/ICl	Press., mm.	Mol. ratio,[a] Cl_2/ICl
49.5	0.885	100.6	1.345
49.4	.893	100.5	1.281
49.4	.896	100.5	1.317
49.1	.878	99.5	1.312
49.1		99.4	1.272
49.3		99.9	1.334
		99.7	
Mean 49.3 ± 0.2 mm.		99.7	
Mean 0.888 ± 0.005		99.9	
		100.2	
		100.4	
		Mean 100.0 ± 0.3 mm.	
		Mean 1.320 ± 0.026	

[a] The mole ratios do not refer to the same mixtures on which pressure measurements were made.

calculated and their logarithms plotted against $1/T$. The value of K at 25.0° is 1.09×10^{-3}, and that at 35.0° is 4.36×10^{-3}, when the pressures are expressed in atmospheres.

The value of ΔH for reaction (1) was calculated to be 25,300 cal. for the temperature range of the experiments, and the free energy change, $\Delta F^\circ = -RT \ln K$, at 25° is $\Delta F^\circ_{298} = 4040$ cal.

The results just presented were combined with the thermodynamic data for iodine monochloride[2] and the following equations derived.

$$ICl(g) + Cl_2(g) = ICl_3(s) \qquad (2)$$
$$\Delta H = -25{,}300 \text{ cal.} \quad \Delta F^\circ_{298} = -4040 \text{ cal.}$$
$$^1/_2Cl_2(g) + {^1/_2}I_2(s) = ICl(g) \qquad (3)$$
$$\Delta H = 4158 \text{ cal.} \quad \Delta F^\circ_{298} = -1370 \text{ cal.}$$

Hence

$$^1/_2I_2(s) + {^3/_2}Cl_2(g) = ICl_3(s) \qquad (4)$$
$$\Delta H = -21{,}150 \text{ cal.} \quad \Delta F^\circ_{298} = -5410 \text{ cal.}$$

The standard virtual entropy of $ICl_3(s)$ at 25° is 41.1 cal./deg. when the entropies of $Cl_2(g)$[3] and $ICl(g)$[2] at 25° and one atmosphere are taken to be 53.31 cal./deg. and 59.15 cal./deg., respectively.

The value of 21,150 cal. for the heat of formation of iodine trichloride from the elements is higher than that found calorimetrically by Berthelot,[4] namely, 16,300 cal. Inasmuch as Berthelot himself called attention to the unsatisfactory nature of his experiments, it is believed that the value derived from the equilibrium measurements is to be regarded as the reliable one.

Summary

Measurements have been made on the pressure and composition of the vapor from the univariant system $ICl_3(s)$, $ICl(l)$, $ICl(g)$, $Cl_2(g)$ at 25 and 35°. The equilibrium constants, $K = P_{ICl}P_{Cl_2}$, at 25 and 35° are 1.09×10^{-3} and 4.36×10^{-3}, respectively, when pressures are expressed in atmospheres. The free energy and heat content of solid iodine trichloride at 25° are $\Delta F^\circ_{298} = -5410$ cal. and $\Delta H = -21{,}150$ cal., respectively. The standard virtual entropy of $ICl_3(s)$ at 25° is 41.1 cal./deg.

[3] Giauque and Overstreet, THIS JOURNAL, **54**, 1731 (1932).

[4] Berthelot, *Ann. chim. phys.*, **21**, 370 (1880); "I. C. T.," Vol. V, p. 177.

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The Dissociation of Sulfur Monochloride Vapor

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Introduction

Aside from the observation of Thorpe[1] that sulfur monochloride dissociates slightly at the boiling point (138°), no studies on the stability of the vapor have been reported. In an effort to determine the nature and extent of the dissociation as a function of the temperature and composition of the vapor, a thorough investigation of it under equilibrium conditions was made. The results of the experiments are presented in this paper together with a discussion of the thermodynamic quantities calculated from the data.

Preparation of Materials and Method of Experimentation

Sulfur.—A high quality of sulfur was resublimed at atmospheric pressure.

Chlorine.—Chlorine from a tank was first passed through a saturated solution of potassium permanganate, and then through concentrated sulfuric acid; finally it was condensed into glass capsules equipped with easily breakable tips. The capsules were weighed before and after filling so that the weight of the chlorine in them was accurately known.

Sulfur Monochloride.—Equivalent quantities of sulfur and chlorine were mixed in an evacuated bulb equipped with side-arms having fragile tips. The mixture was heated to 120° for twelve hours and, on cooling, the golden-yellow liquid formed was allowed to run into the side-arms

[1] Thorpe, *J. Chem. Soc.*, **37**, 356 (1880).