

tures⁶ "the attachment of water molecules through their oxygen atoms to the metallic surface, and the subsequent elimination of hydrogen from two bound molecules in accordance with the (bond activation) mechanism of Horiuti and Szabo."

A fuller discussion of mechanisms will be left to the following paper.⁸

Summary

Quantitative data were secured on the extent of isotopic separation which occurs in the following respective reactions which liberate hydrogen or gaseous hydrides: Li, Na, K, Ca, CaC₂ and Al₄C with water; Mg, Zn, Fe, Mn, Al and FeS with aqueous sulfuric acid; and aluminum with aqueous sodium hydroxide. With a few exceptions the runs were made at or near room temperature. The hydrogen and hydrides were burned in a flame, with a slight excess of tank oxygen, and

the water of combustion carefully purified and analyzed for its hydrogen isotope proportions by the free submerged float method. Correction was applied for the O¹⁸ abnormality of the tank oxygen, which was separately determined.

The data were quite reproducible, for a given set of reagents, and confirm the applicability of the quantitative relationship $d \ln [H] = \alpha d \ln [D]$, in which [H] and [D] are instantaneous values of the amounts of protium and deuterium, respectively, in the liquid phase, and α is the "isotopic separation factor," different for each reaction. The form of this relationship is identical with that which pertains to the isotopic separations by electrolysis.

A discussion of regularities observed in the results, and their bearing on some phases of the reaction mechanism is included.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

Iodine Monochloride. IV. The System Potassium Chloride-Iodine Monochloride¹

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This paper describes a series of studies in which existing vapor pressure data of iodine monochloride have been extended, the system potassium chloride-iodine monochloride has been formulated, and earlier work with the polyhalides potassium dichloriodide, KCl·ICl or KICl₂, and potassium dibromiodide, KBr·IBr or KIBr₂, has been reviewed.

1. The Vapor Pressure of Iodine Monochloride.—The vapor pressure of iodine monochloride was measured by Cornog and Karges,³ who used the static method of Smith and Menzies⁴ for measurements within the temperature range 35 to 70°. A modified form of the dynamic method of Pearce and Snow⁵ was used to measure all of the vapor pressure data included in this paper. The vapor pressure of iodine monochloride was measured between the temperatures -15 and 50°. This served both to validate the method and to extend existing data. The iodine monochloride used in these measurements froze at 27.3°. Measurements were made in a thermostat in which temperatures were constant within $\pm 0.02^\circ$. Vapor pressure measurements were reproducible within ± 0.1 mm. at

low pressures and ± 0.3 mm. at higher pressures. The vapor pressure data for iodine monochloride are shown in Table I and are graphically represented in Fig. 1.

TABLE I
VAPOR PRESSURE OF SOLID AND LIQUID IODINE MONOCHLORIDE

1 Temp., °C.	2 V. p. liq. ICl, mm.	3 V. p. solid ICl, mm.	4 V. p. liq. ICl by Cornog and Karges, mm.
-15		1.2	
-10		2.0	
-5		3.1	
0		4.6	
5		6.8	
10	12	9.9	
15	16.3	14.3	
20	21.9	20.4	
25	29.3	28.3	
27.3	33.2	33.2	
30	38.4		
35	50.2		48.0
40	64.4		62.5
45	84.5		81.0
50	107.1		103.6

(1) A summary of a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in the Department of Chemistry, in the Graduate College of the State University of Iowa, May, 1942.

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(3) Cornog and Karges, *THIS JOURNAL*, **54**, 1882 (1932).

(4) Smith and Menzies, *ibid.*, **32**, 1427 (1910).

(5) Pearce and Snow, *J. Phys. Chem.*, **31**, 231 (1927).

Each value in columns 2 and 3, Table I, is the average of from two to six observations. Comparison of the values shown in columns 2 and 4, Table I, shows reasonable agreement between current and previous observations. In the course of these experiments considerable time and ef-

fort was expended in attempts to measure the vapor pressures of the labile beta form of iodine monochloride. While the labile form was readily obtained, transformation to the stable form was too rapid to permit vapor pressure measurements by this method.

The data in Table I may be used to calculate the heats of vaporization, sublimation and fusion of iodine monochloride by use of the Clausius-Clapeyron equation. By this means the heat of vaporization of iodine monochloride was found to be 9950 cal./mole, the heat of sublimation was 11,800 cal./mole. By difference the heat of fusion was found to be 1850 cal./mole.

2. **Potassium Dichloriodide, $KCl \cdot ICl$ or $KICl_2$.**—Some earlier workers^{6,7,8} have applied this name and formula to a compound, perhaps the hydrate, having a much lower melting point than the product obtained in this Laboratory. The hydrate is discussed in Part 7. Anhydrous potassium dichloriodide is formed when equal molecular quantities of potassium chloride and iodine monochloride are joined in a glass-stoppered bottle and maintained at or somewhat above room temperature for several weeks. The initial mixture, nearly black in color, slowly changes to the bright orange-yellow characteristic of this compound. This compound melts sharply at 195° in a closed glass tube, and is so stable that a specimen was kept in a glass-stoppered bottle for more than one year with less than 1% loss in weight. The dissociation pressure of potassium dichloriodide was measured by use of the method mentioned in Section 1 (see Table II).

TABLE II
THE DISSOCIATION PRESSURE OF POTASSIUM DICHLORIODIDE

1 Temperature, °C.	2 Dissociation pressure, mm.
25	0.20
35	.40
40	.55
45	.70
50	1.00
55	1.35
60	1.80

The probable limit of accuracy of the figures in column 2 is 0.05 mm.

3. **Potassium Trichlorodiiodide, $KCl \cdot 2ICl$ or KI_2Cl_3 .**—This compound has not been reported previously. It is the stable solid phase formed when solutions of potassium chloride in iodine monochloride are brought to crystallization at temperatures below 45°. The needle-like crystals are nearly black when viewed in masses but are ruby-red in thin sections. In a closed tube these crystals melt at 45° but when exposed to the air at room temperature they decompose rapidly into potassium dichloriodide crystals and iodine monochloride vapor. The composition of these crystals was determined by (a) determining the loss of weight on heating and (b) determining the iodine monochloride content. The latter was accomplished by converting the iodine monochloride in the crystals to free iodine by means of potassium iodide and titrating the free

(6) Wells and Wheeler, *Z. anorg. Chem.*, **1**, 442 (1892).

(7) Ephraim, *Ber.*, **80**, 1069 (1917).

(8) Cremer and Duncan, *J. Chem. Soc.*, 1857 (1931).

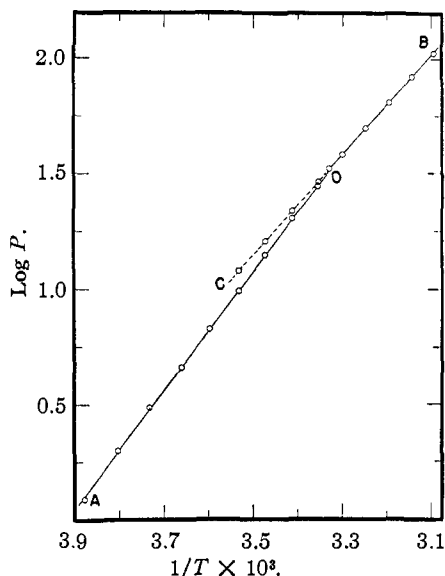


Fig. 1.—Vapor pressure of iodine monochloride: Point O is 27.3° the m. p. of ICl , AO vapor pressure solid ICl , OB is the vapor pressure of liquid ICl above the m. p., OC is the vapor pressure of undercooled ICl .

iodine with sodium thiosulfate solution. These data are shown in Table III.

TABLE III

(a) Loss of weight on heating	Run 1	Run 2
Sample taken, g.	0.954	0.351
Wt. KCl obtained, g.	.1726	.064
Calcd. wt. $KCl \cdot 2ICl$.924	.343
(b) By $Na_2S_2O_3$ titration		
Wt. of sample, g.	0.200	
Vol. 0.0966 N $Na_2S_2O_3$, ml.	21.67	
Equiv. of oxidizing halogen	0.00209	
Calcd. equiv. of oxidizing halogen	.00200	

Inspection of Table III part (a) shows that the "Sample taken" is greater than the "Calculated weight of $KCl \cdot 2ICl$ " by 3% in Run 1 and by 2% in Run 2. This discrepancy is probably caused by the fact that the potassium dichloriodide crystals are very fine needles and were crystallized from iodine monochloride solution, some of which adhered to the crystals and was lost when the crystals were heated.

The method mentioned in Section 1 was used to get the dissociation pressure data shown in Table IV, which are represented graphically in Fig. 2.

In Fig. 2 the line OB represents the vapor pressure of the univariant system potassium trichlorodiiodide-potassium dichloriodide-vapor. The line OA represents the univariant system potassium trichlorodiiodide-solution-vapor. The point O (45°) represents the invariant system potassium trichlorodiiodide-potassium dichloriodide-solution-vapor. Below 45° potassium trichlorodiiodide is the stable phase in equilibrium, while above 45° potassium dichloriodide (*cf.* Section 4) is the stable phase in equilibrium with saturated solutions. The apparent melting that occurs when potassium trichlorodiiodide is heated to 45° in a closed tube is, in reality, the decomposition of

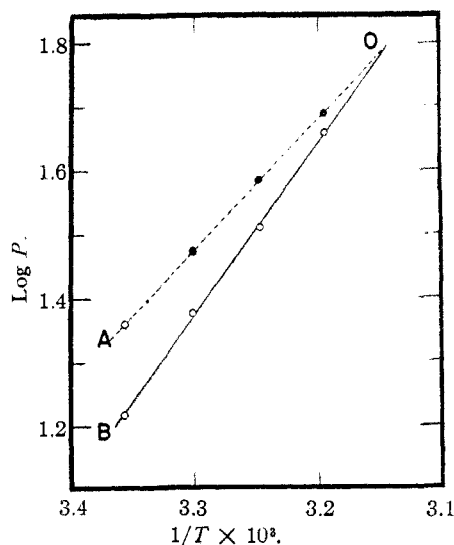


Fig. 2.—The line OB, dissociation pressure of KI_2Cl_3 , intersects the dotted line, vapor pressure of saturated KI_2Cl_3 solution, at 45° the melting point of KI_2Cl_3 .

solid potassium trichlorodiodide into solid potassium dichlorodiodide and saturated solution of potassium dichlorodiodide in iodine monochloride. Cremer and Duncan⁹ have suggested similar ideas regarding the melting points of polyhalide compounds.

TABLE IV

DISSOCIATION PRESSURE OF POTASSIUM TRICHLORODI-
IODIDE

1 Temp., °C.	2 Dissociation pressure KI_2Cl_3 , mm.	3 V. p. satd. soln. KI_2Cl_3 in ICl , mm.
15	8.3	...
25	16.5	23.05
30	23.8	29.8 ^a
35	32.5	38.5 ^a
40	45.6	48.5 ^a

^a Calculated by assuming that vapor pressure lowering is proportional both to the quantity of dissolved potassium chloride and to the vapor pressure lowering at 25° and by applying this assumption to the experimental data in Tables I, V and VI.

4. **The Potassium Trichlorodiodide-Potassium Dichlorodiodide Transition Temperature.**—The location of this transition temperature was learned by getting the solubility curves of the tri and pentahalide compounds and observing where the two curves intersected (see Table V and Fig. 3). Each solubility datum in Table V was obtained by saturating iodine monochloride, contained in a flask, with potassium chloride at a temperature well above that at which solubility was later measured. The flask containing the saturated solution was plugged with glass wool and placed in a thermostat in which the temperature variation did not exceed $\pm 0.02^\circ$. Equilibrium between the solid and the solution was assumed to exist when the potassium chloride content of successive portions of saturated solution removed at twenty-four to forty-eight hour intervals were in

(9) Cremer and Duncan, *J. Chem. Soc.*, 2251 (1931).

TABLE V
SOLUBILITY OF POTASSIUM CHLORIDE IN IODINE MONO-
CHLORIDE

1 Temp., °C.	2 G. KCl dissolved in 100 g. ICl Solid phase $KCl \cdot 2ICl$	3 Solid phase $KCl \cdot ICl$
15	4.70	
20	4.90	
25	5.20	
30	5.55	
35	5.95	
40	6.45	6.80
45		6.95
50		7.20
55		7.40
60		7.70
65		8.05

agreement. The glass wool plugs served as filters in removing such portions. The potassium chloride content of portions thus removed was determined by weighing the portion, removing iodine chloride by heating and weighing the potassium chloride residue. Separate experiments were performed to establish the identity of the solid phases by methods previously described by Cornog and Olson¹⁰ (see Table V and Fig. 3).

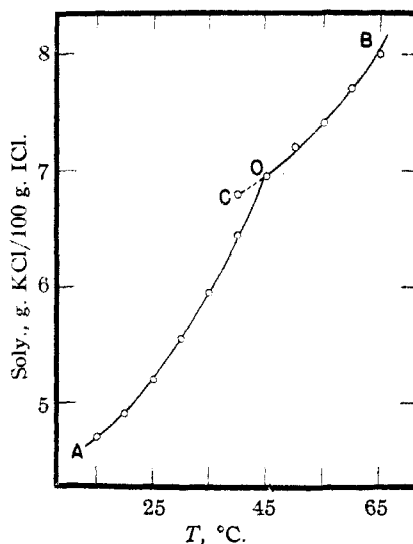


Fig. 3.—The solubility of potassium chloride in iodine monochloride: $KCl \cdot 2ICl$ is the stable solid phase represented by AO. The point O (45°) is the transition temperature between $KCl \cdot 2ICl$ and $KCl \cdot ICl$. The line CO represents metastable and OB, stable, $KCl \cdot ICl$.

5. **The Vapor Pressure of Solutions of Potassium Chloride in Iodine Monochloride.**—The general procedure described in Part I was used to obtain the vapor pressure of solutions of potassium chloride in iodine monochloride as recorded in Table VI and graphically represented in Fig. 4.

The calculations used in getting the figures in column 5 Table VI and the dotted line in Fig. 4 are based on the assumption that the dissolved potassium chloride, or the derived solute, is dissociated into two ions, each of which

(10) Cornog and Olson, *THIS JOURNAL*, 62, 3328 (1940).

TABLE VI

THE VAPOR PRESSURE OF SOLUTIONS OF POTASSIUM CHLORIDE IN IODINE MONOCHLORIDE AT 25°

1 Mole fraction KCl	2 P, mm.	3 ${}^a P_0 - P$, mm.	4 $(P_0 - P)/P_0$	5 $(P_0 - P)/P_0$ calcd.
0.005	29.00	0.30	0.010	0.0099
.02	28.30	1.00	.034	.0392
.04	27.25	2.05	.070	.0769
.05	26.45	2.85	.097	.0952
.06	25.85	3.45	.118	.1131
.0875	24.05	5.25	.197	.1608
.1015 ^b	23.05	6.25	.213	.1843

^a $P_0 = 29.3$ (Table I). ^b Saturated.

acts as a perfect solute. At the lower concentrations, the observed vapor pressure lowering is less than, and at higher concentrations, greater than the calculated values.

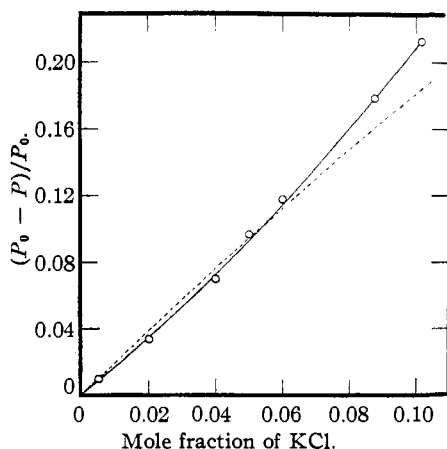


Fig. 4.—The vapor pressure of KCl-ICl solutions. The solid line represents experimentally determined values of vapor pressure lowerings. The dotted line represents calculated vapor pressure lowerings assuming dissociation of the solute into two different ions.

Although these data are probably insufficient in quantity and precision to warrant calculations of activities, they serve as the basis of the tentative conclusion that potassium chloride, or its derivative, is ionized in iodine monochloride. Further, since the crystalline material separating from the solution at 25° is represented by the formula KI_2Cl_3 , the tentative inference is drawn that the ions in solution are probably represented by the formula K^+ and $I_2Cl_3^-$. The data in Table VI are also used in plotting curve AB Fig. 5, Section 6.

6. **The System Potassium Chloride-Iodine Monochloride.**—The vapor pressure data in the preceding sections have been used to construct the vapor pressure-composition diagram of the system potassium chloride-iodine monochloride at 25° as shown in Fig. 5.

The similarity in general outline between Fig. 5 and corresponding diagrams for hydrate systems is obvious.

7. **Potassium Dichloroiodide Monohydrate, $KCl \cdot ICl \cdot H_2O$.**—This compound is obtained when the product mentioned in Section 2 is recrystallized from water solution. The hydrated crystals thus obtained are much like potassium dichromate in general appearance and melt at 43°

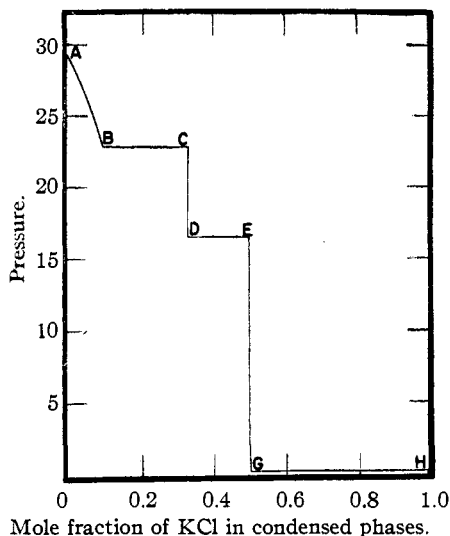


Fig. 5.—Vapor pressure-composition diagram of the system KCl-ICl at 25°: AB represents the vapor pressure of unsaturated solutions of KCl in ICl. At B solid KI_2Cl_3 begins to form and continues to C where the liquid phase disappears. DE represents the KI_2Cl_3 - $KICl_2$ equilibrium at constant pressure. At E only $KICl_2$ is present. GH represents the $KICl_2$ -KCl equilibrium at constant pressure. At H only KCl is present.

in a closed tube. The composition of the hydrated crystals was estimated by heating weighed portions in an oven at 110° to constant weight. These data follow.

	1	2
Weight of sample taken, g.	3.572	2.342
Weight of KCl residue, g.	1.045	0.686
Calcd. corresponding wt. $KICl_2$	3.321	2.180
Calcd. corresponding wt. $KICl_2 \cdot H_2O$	3.573	2.346

An indication of the water content of the hydrated crystals was given by the weight of the residue obtained when crystals were dried in a desiccator over phosphorus pentoxide.

Weight of sample, g.	1.570
Weight of residue from drying with P_2O_5	1.452
Weight of sample calcd. from wt. residue	1.562

The melting point of the material changed from 43° before drying to approximately 195° after drying. A small quantity of iodine monochloride was doubtless lost in drying.

The dissociation pressure of the monohydrate, Table VII, was measured in such a way as to distinguish between the partial pressures of water and of iodine monochloride.

The segregation and estimation of the partial pressures of water vapor and iodine monochloride vapor which together made up the dissociation pressure of the monohydrate, was accomplished by passing the vapor from dissociation through two absorbers arranged in series. The first absorber, containing phosphoric anhydride, retained water vapor but passed iodine monochloride vapor, while the second absorber contained soda lime and retained iodine monochloride vapor.

TABLE VII
THE DISSOCIATION PRESSURE OF $\text{KCl}\cdot\text{ICl}\cdot\text{H}_2\text{O}$

1	2	3	4	5
Temp., °C.	P_{ICl} , mm.	$P_{\text{H}_2\text{O}}$, mm.	$P = P_{\text{ICl}} + P_{\text{H}_2\text{O}}$, mm.	Interpolated Cremer and Duncan dissociation pressure, mm.
25	0.1	9.9	10.0	9.2
30	.2	15.0	15.2	14.2
35	.4	20.6	21.0	20.6
40	.7	29.6	30.3	29.5

The data in column 2 show that the partial pressure of iodine monochloride in the hydrated compound is virtually the same as the dissociation pressure of anhydrous potassium dichloroiodide (see Part 2). Comparison of columns 2 and 3 indicates that the dissociation pressure of the hydrate is due almost entirely to the partial pressure of water vapor. Comparison of columns 4 and 5 indicates that the substance measured by Cremer and Duncan¹¹ was probably the hydrate.

The preparative methods described by Ephraim⁷ were repeated in this Laboratory. The compound thus obtained was identical in properties with the monohydrate described above.

8. **Potassium Dibromiodide, $\text{KBr}\cdot\text{IBr}$ or KIBr_2 , and Potassium Dibromiodide Monohydrate, $\text{KBr}\cdot\text{IBr}\cdot\text{H}_2\text{O}$ or $\text{KIBr}_2\cdot\text{H}_2\text{O}$.**—Potassium dibromiodide was prepared by Cremer and Duncan¹ by exposing "dry" potassium iodide to bromine vapors in a desiccator for three days. The product thus obtained melted at 58–60° and was converted to potassium dichloroiodide by chlorination. When this work was repeated in this Laboratory, several weeks were required for potassium iodide to absorb the theoretically required quantity of bromine, the resulting potassium dibromiodide melted in a closed tube at 180° and the rate of conversion to the dichloroiodide by chlorination was so slow as to render the method impractical. Upon recrystallizing the potassium dibromiodide of melting point 180° from water solution, the resulting crystals melted at 58° in a closed tube. The composition of the material crystallized from water solution is indicated by the following data.

A. Loss of weight on heating crystals ($\text{KIBr}_2\cdot\text{H}_2\text{O}$)	
Weight of sample taken, g.	0.961
Weight of KBr residue, g.	.332
Calculated weight assuming KIBr_2	.910
Calculated weight assuming $\text{KIBr}_2\cdot\text{H}_2\text{O}$.960
B. Loss of weight $\text{KIBr}_2\cdot\text{H}_2\text{O}$ by drying over P_2O_5	
Weight of sample taken, g.	3.290

(11) Cremer and Duncan, *J. Chem. Soc.*, 2245 (1931).

Weight of residue after drying with P_2O_5	3.104
Weight of sample computed from wt. of residue assuming $\text{KIBr}_2\cdot\text{H}_2\text{O}$	3.280

These data and the melting point data together indicate that the low melting substance is potassium dibromiodide monohydrate while the high melting substance is potassium dibromiodide.

Potassium dibromiodide of melting point 180° is expeditiously prepared by joining equivalent quantities of potassium iodide and bromine in a glass-stoppered bottle, at room temperature. The initially nearly black mixture begins to assume the bright red color of potassium dibromiodide in a day or two and the reaction goes to completion in about a week.

Summary

1. A dynamic method has been used to measure the vapor pressure of iodine monochloride between –15 and 50°. These data have been used to compute the heats of fusion, vaporization and sublimation of iodine monochloride.

2. Potassium dichloroiodide has been prepared by the direct union of iodine monochloride and potassium chloride. The dissociation pressure of this compound has been measured.

3. A new compound, potassium trichloroiodide, has been prepared by direct union of iodine monochloride and potassium chloride at temperatures below 45°. The dissociation pressure of the compound has been measured.

4. Solubility curves for potassium dichloroiodide and potassium trichloroiodide in iodine monochloride have been plotted and the transition temperature between these compounds has been established at 45° from the intersection of these curves.

5. The vapor pressure–composition relations for the system potassium chloride–iodine monochloride have been formulated.

6. Methods for preparing both the anhydrous and hydrated forms of potassium dichloroiodide and potassium dibromiodide have been described. The melting points of all four different compounds have been determined.

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