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**EQUILIBRIUM IN SYSTEMS COMPOSED OF SULFUR DIOXIDE  
AND AMMONIUM OR AN ALKALI IODIDE<sup>1</sup>**

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Systems composed of sulfur dioxide and an alkali iodide have been investigated chiefly by Walden and Centnerzwer,<sup>2</sup> Ephraim and Kornblum,<sup>3</sup> and De Forcrand and Tabouris.<sup>4</sup> All the investigators mentioned have obtained solid addition products of the two components, but there is much disagreement as to their composition, due partly to the fact that the existing equilibrium conditions have not been sufficiently studied. The pressure-temperature data in the various systems are also incomplete and many results which are comparable do not agree closely.

We have determined the composition of the solid phases and the vapor pressure relations in the two component systems consisting of sulfur dioxide with sodium, potassium, rubidium, cesium and ammonium iodides between the maximum limits of  $-25$  and  $+25^{\circ}$ . The invariant points within this temperature range have also been determined. At room temperature, a slow reaction takes place between the components which results in the liberation of iodine. The reaction only becomes noticeable after several days, and it is not sufficiently rapid to offer difficulty in determining vapor pressures.

**Method, Apparatus and Procedure**

In two component systems like those under consideration, composed of a volatile and a non-volatile component, the equilibria involved, as well as the composition of existing compounds, can be readily studied through the medium of the vapor pressure relations, which are entirely analogous in principle to those in a system composed of a salt and water. A complete vapor pressure-composition isotherm of a system formed of sulfur dioxide and a salt with which it forms an addition product exhibits a sharp change in pressure at the composition of the pure compound, while constant vapor pressures are exhibited by the univariant systems on either side of the pure compound regardless of the relative amounts of the phases present. The determination of the vapor pressures of these univariant systems as a function of temperature fixes the limits of pressure and temperature between which the compounds formed are stable. The intersection of the

<sup>1</sup> An abstract of a dissertation presented by Joseph Fleischer to the Graduate School, Yale University, 1930, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> Walden and Centnerzwer, *Z. physik. Chem.*, **39**, 513 (1902); **42**, 432 (1903).

<sup>3</sup> Ephraim and Kornblum, *Ber.*, **49**, 2007 (1916).

<sup>4</sup> De Forcrand and Tabouris, *Compt. rend.*, **168**, 1253 (1919); **169**, 162 (1920).

vapor pressure curves fixes the invariant points existing in the temperature range studied. If no addition products form, the vapor pressure relations are correspondingly simplified.

The measurements were carried out with an apparatus, the essential features of which are illustrated in Fig. 1 (not drawn to scale). The volume of the bulb was 29.3 cc. Tubes A, B, and C were each provided with a well-ground, mercury sealed stopcock. Tube A was attached to a manometer through a fused joint. The manometer was of the open type and was therefore used in conjunction with a calibrated barometer. The final pressures were rounded off to the nearest millimeter after the usual corrections. Tube B was connected with a two-liter suction flask which served as a vacuum reservoir. By means of a three-way stopcock, the reservoir could be connected with a pump, shut off, or opened to the air. Tube C connected with the supply of sulfur dioxide, which was dried by means of concentrated sulfuric acid.

A silvered Dewar flask of two liters' capacity served as a thermostat. Temperatures somewhat below  $0^{\circ}$  were obtained by mixtures of ice and sodium chloride. The lowest temperatures were produced by the additional use of ammonium chloride. The variation in temperature could be kept within about  $0.1^{\circ}$  for the time necessary for the systems to reach equilibrium. The thermometer used had been calibrated with considerable care.

The salts were dried at  $100^{\circ}$  either in a vacuum or in a stream of dry air free from carbon dioxide. When necessary, the salts were purified by customary methods and in every case the purity was checked by analysis.

The experimental procedure was, in general, as follows. A weighed quantity of salt was introduced into the bulb, the stopper sealed in and the bulb and contents weighed. The bulb was then attached to the apparatus, the joint being sealed with mercury. The entire apparatus was then alternately evacuated and filled with sulfur dioxide to remove air. Twenty to thirty grams of sulfur dioxide was then allowed to condense in the bulb at a temperature of about  $-20^{\circ}$ .

Before making any measurements, it was essential to insure the complete conversion of the original salt into its highest addition product. With salts rather insoluble in liquid sulfur dioxide, this was accomplished by allowing the finely ground iodide to stand for twelve hours or more in the presence of an excess of liquid. In all cases where the solubility allowed, the solid was brought completely into solution by removing the bulb from the bath and warming. The addition product was then crystallized from the solution by cooling and, if necessary, by evaporating a portion of the solvent. A vapor pressure-composition isotherm was usually carried out on this material at a temperature approximating  $-20^{\circ}$  with the object of determining the univariant systems of three phases and the composition of any addition products. A temperature constant within several tenths of a degree was sufficient for this purpose. After the vapor pressure of

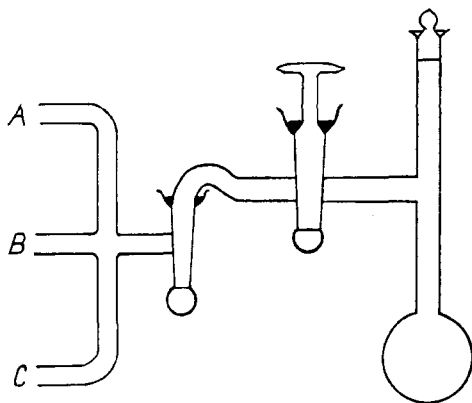


Fig. 1.—The bulb at the right connects through mercury-sealed stopcock and detachable ground-glass joint with the tubes A, B and C.

the saturated solution was determined, sulfur dioxide was allowed to evaporate at a pressure of some thirty or forty millimeters below this value until the material in the bulb was in equilibrium with this pressure, as indicated by the absence of any trend in the meniscus of the manometer when the system was closed. This procedure left a homogeneous solid in the bulb which was of necessity the highest addition product which could form at the temperature of the isotherm or at a higher temperature, and its composition could be calculated after weighing the bulb and making the proper small correction for the weight of sulfur dioxide present as vapor in the bulb at known temperature and pressure. If a second addition product existed, its composition was next determined in a similar manner.

The behavior of a compound as it warmed to room temperature in the bulb gave helpful information concerning the relations existing in the system. Decomposition into a liquid and a solid indicated the existence of a transition temperature between the temperature of the bath and that of the room; melting to a clear liquid indicated a congruent melting point; while the absence of any change showed that no invariant point existed in this temperature range.

In determining the vapor pressure curves of the three-phase univariant systems, the pressure reached the equilibrium value rapidly whenever a liquid phase were present if the bulb were shaken thoroughly. In such a case, the presence of the solid phase could be confirmed both visually and by checking for constant vapor pressure after withdrawing a portion of the sulfur dioxide. Such mixtures were allowed to stand for at least a half hour at constant temperature before the pressure was measured. In cases where two solids were present, instead of solid and liquid, equilibrium pressures were established rather slowly, more so when approached from higher pressures than from lower. The determinations were therefore made by averaging the value obtained from an initially lower pressure on standing for several hours with that reached from an initially higher value, a procedure which, on duplicating, proved to give satisfactory results.

When the vapor pressure curves had been determined for a system, it was frequently possible to determine the composition of a compound in the following simple manner which was applicable whenever the temperature could be adjusted to a value such that atmospheric pressure was intermediate between the vapor pressures of the saturated solution of the compound and that of the next lower univariant system. The bulb containing the saturated solution was immersed in a bath at such a temperature, and sulfur dioxide allowed to evaporate until the contents of the bulb were in equilibrium with a pressure of one atmosphere of sulfur dioxide; this could occur only when the liquid had disappeared. The evaporation was conveniently carried out by bubbling the gas through a thin layer of mercury serving as a trap, contained in a small vessel open to the air. By means of this contrivance, only the sulfur dioxide exerting a pressure greater than one atmosphere could escape and the point where

evaporation was complete was indicated by cessation of bubbling. The composition of the compound could then be determined by weighing the bulb. Similarly, the composition of a lower addition product could be determined by repeating the same process at a higher temperature, where atmospheric pressure was intermediate between the pressure of the two univariant systems which limit the formation of the lower compound.

The vapor pressure data, with a few exceptions, were found to satisfy equations of the form

$$\log p = \frac{A}{T} + B$$

The exceptions all consisted of the saturated solutions of the compounds the solubility of which increased with temperature sufficiently to cause a divergence from the usual curve of vapor pressure. The heat of vaporization per mole of sulfur dioxide was calculated for the normal cases by the relation  $\Delta H = 2.303 AR$ , where  $R$  is the gas constant in calories, and  $A$  is the constant in the equation above.

**Sodium Iodide and Sulfur Dioxide.**—This system was first studied by Ephraim and Kornblum<sup>3</sup> and later by De Forcrand and Tabouris.<sup>4</sup> The former described two compounds, one yellow and the other red, to which they assigned the formulas  $\text{NaI}\cdot 4\text{SO}_2$  and  $\text{NaI}\cdot 2\text{SO}_2$ , respectively. The latter found but one compound to which they gave the formula  $\text{NaI}\cdot 3\text{SO}_2$ .

In the present investigation it was found that on standing in contact with liquid sulfur dioxide below  $0^\circ$ , sodium iodide is converted to a bright yellow solid,  $\text{NaI}\cdot 4\text{SO}_2$ . The compound is rather insoluble in the liquid, to which it imparts, however, a pale red color. On evaporating the solvent, the compound crystallizes in the form of transparent pale yellow cubes. If heated in a closed system above a transition temperature of  $1.4^\circ$ , the compound melts incongruently and forms a bright red compound, whose composition as shown below corresponds to the rather unusual formula  $3\text{NaI}\cdot 8\text{SO}_2$ . The reverse change takes place readily on cooling below the transition point.

The composition of both compounds was determined as previously described, by evaporating sulfur dioxide at atmospheric pressure from the saturated solutions at temperatures where the vapor pressure data given below showed that only the pure compounds were stable. The temperature adopted for the higher compound was  $-8^\circ$ , and for the lower,  $+8^\circ$ .

The following results were obtained:

NaI·4SO <sub>2</sub>			3NaI·8SO <sub>2</sub>		
NaI, g.	SO <sub>2</sub> , g.	Ratio NaI:SO <sub>2</sub>	NaI, g.	SO <sub>2</sub> , g.	Ratio NaI:SO <sub>2</sub>
3.698	6.377	1:4.04	3.698	4.268	3:8.10
6.933	11.759	1:3.97	4.898	5.638	3:8.07
4.989	8.616	1:4.04	8.725	9.907	3:7.98
			9.778	11.248	3:8.07
			4.989	5.704	3:7.94

The compound to which we have assigned the unusual formula  $3\text{NaI}\cdot 8\text{SO}_2$  is undoubtedly the red compound to which the formula  $\text{NaI}\cdot 3\text{SO}_2$  was assigned by De Forcrand and Tabouris, and  $\text{NaI}\cdot 2\text{SO}_2$  by Ephraim and Kornblum. The former investigators prepared the compound by starting with a saturated solution at a low temperature and allowing the excess sulfur dioxide to evaporate at  $0^\circ$  and atmospheric pressure. While this method should, in principle, yield the lower compound ultimately in pure condition, it involves the primary formation of the higher 1:4 compound, followed by its subsequent decomposition, and the latter process is slow. The writers repeated this experiment of De Forcrand and Tabouris at  $0^\circ$  and after two hours the escape of sulfur dioxide nearly ceased and the empirical composition of the residue corresponded to  $\text{NaI}\cdot 2.96\text{SO}_2$ . On raising the temperature to  $+3^\circ$ , which is just above the transition point ( $1.4^\circ$ ), the excess of sulfur dioxide was converted to liquid and escaped in a few minutes, leaving a residue corresponding closely to the 3:8 ratio. Ephraim and Kornblum obtained the same red compound by passing sulfur dioxide over the iodide at  $0^\circ$  and atmospheric pressure, a procedure which should yield the pure compound. The experimental data reported by them (5.86 g. of sulfur dioxide absorbed by 5.15 g. of sodium iodide) yield the formula  $3\text{NaI}\cdot 7.98\text{SO}_2$ , almost exactly the 3:8 ratio, and indicate that the pure compound was obtained, but that the results were misinterpreted, as the formula  $\text{NaI}\cdot 2\text{SO}_2$  was assigned.

The following vapor pressure data were obtained on the three univariant systems. Here and in all subsequent cases pressure is given in centimeters of mercury. Whenever applicable, the equation for calculating the vapor pressures is given, as well as  $\Delta H$ .

I. $\text{NaI}\cdot 4\text{SO}_2$ - Solution-Vapor		II. $\text{NaI}\cdot 4\text{SO}_2$ - $3\text{NaI}\cdot 8\text{SO}_2$ -Vapor		III. $3\text{NaI}\cdot 8\text{SO}_2$ - NaI-Vapor	
$T, ^\circ\text{C.}$	$p, \text{cm.}$	$T, ^\circ\text{C.}$	$p, \text{cm.}$	$T, ^\circ\text{C.}$	$p, \text{cm.}$
-20.20	47.2	-18.65	29.9	-24.35	4.4
15.75	58.4	14.15	42.4	-10.90	13.3
13.10	65.8	9.20	60.1	0.0	28.6
10.70	72.8	7.00	70.0	9.90	55.9
7.50	84.0	4.00	85.2	18.40	96.4
5.10	92.9	0.0	111.9	19.40	102.4
3.20	100.8				
0.0	115.8				

$\text{Log } p = 6.944 - \frac{1332.9}{T}$	$\text{Log } p = 9.776 - \frac{2110.3}{T}$	$\text{Log } p = 8.811 - \frac{2281.7}{T}$
$\Delta H = 6100 \text{ cal.}$	$\Delta H = 9650 \text{ cal.}$	$\Delta H = 10,450 \text{ cal.}$

The vapor pressure curves of systems I and II above intersect at  $+1.4^\circ$ , a transition point where the four phases in equilibrium are the two addition products, solution and vapor. This temperature was also determined directly by immersing a bulb containing the compound  $\text{NaI}\cdot 4\text{SO}_2$  with its

saturated solution in a bath of slowly rising temperature contained in a transparent Dewar flask and observing the temperature at which the red 3:8 compound first appeared. This temperature was found to be  $+1.5^\circ$ , in close agreement with the result obtained from the vapor pressure curves.

Above the transition point, another univariant system exists, but the pressures were too high to be determined with safety in our apparatus. It consists of the phases  $3\text{NaI}\cdot 8\text{SO}_2$ -solution-vapor.

The vapor pressure curves of the three systems are shown in Fig. 2.

**Potassium Iodide and Sulfur Dioxide.**—Walden and Centnerzwer<sup>2</sup> have investigated the freezing point diagram of this system over a wide range of temperature and have described the compounds  $\text{KI}\cdot 4\text{SO}_2$  and  $\text{KI}\cdot 14\text{SO}_2$ . The latter compound only exists at very low temperatures, below the range we have investigated. Pechard<sup>5</sup> and Fox<sup>6</sup> claim the existence of the compound  $\text{KI}\cdot \text{SO}_2$ , and Kistiakowsky,<sup>7</sup> the compound  $2\text{KI}\cdot \text{SO}_2$ . We have found no evidence that either of these compounds exists.

Isothermal evaporation of unsaturated solutions at pressures slightly below those of the saturated solutions between  $-20$  and  $-5^\circ$  left residues corresponding to the formula  $\text{KI}\cdot 4\text{SO}_2$ , thus confirming Walden and Centnerzwer's formula. The following results were obtained

KI, g.	SO <sub>2</sub> , g.	Ratio KI:SO <sub>2</sub>	Temp., °C.
5.491	8.419	1:3.98	-18.3
5.159	7.951	1:3.99	-15.0
7.113	11.003	1:4.01	-12.0
6.680	10.352	1:4.02	-7.6

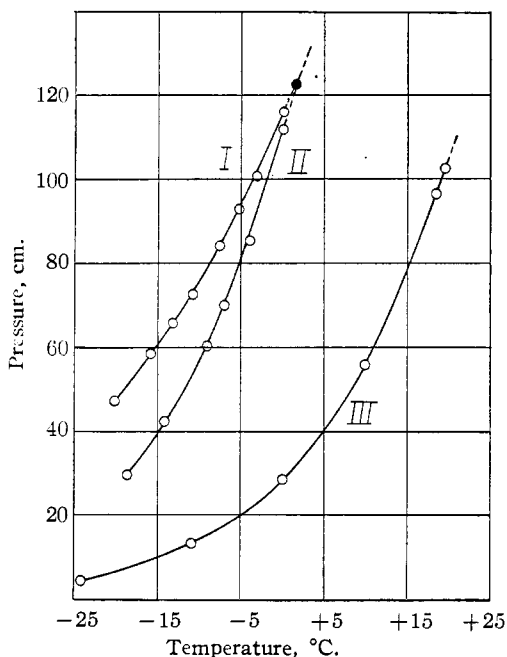


Fig. 2.— $\text{NaI}\text{-SO}_2$ . Curves I, II and III represent, respectively, the systems  $\text{NaI}\cdot 4\text{SO}_2$ -solution-vapor;  $\text{NaI}\cdot 4\text{SO}_2$ - $3\text{NaI}\cdot 8\text{SO}_2$ -vapor; and  $3\text{NaI}\cdot 8\text{SO}_2$ - $\text{NaI}$ -vapor. The black dot represents the invariant system of four phases.

<sup>5</sup> Pechard, *Compt. rend.*, **130**, 1188 (1900).

<sup>6</sup> Fox, *Z. physik. Chem.*, **41**, 458 (1902).

<sup>7</sup> Kistiakowsky, *J. Russ. Phys.-Chem. Soc.*, **34**, 24 (1902).

The compound has a pale red color and crystallizes in cubes. The saturated solution has a pale yellow color at  $-20^{\circ}$ , but due to the rapidly increasing solubility, the color deepens and the viscosity increases as the

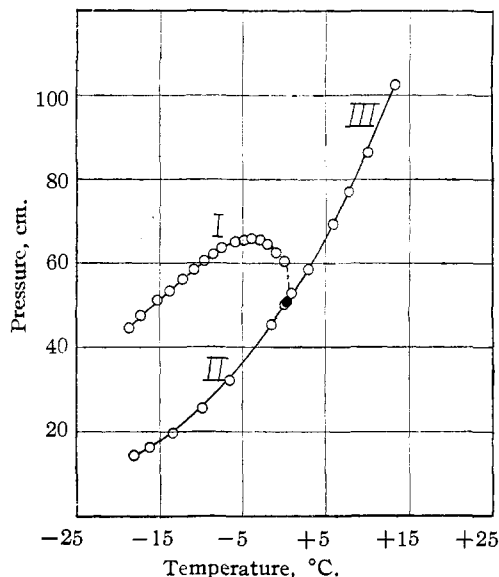


Fig. 3.—KI-SO<sub>2</sub>. Curves I, II and III represent, respectively, the systems KI·4SO<sub>2</sub>-solution-vapor, KI·4SO<sub>2</sub>-KI-vapor, and KI-solution-vapor. The black dot represents the invariant system of four phases.

temperature rises. Withdrawal of sulfur dioxide from the compound at  $0^{\circ}$  results in the appearance of white potassium iodide, the pressure remaining constant until the sulfur dioxide is almost completely removed, thus showing the non-existence of compounds containing less sulfur dioxide. The vapor pressure curves of the three univariant systems are given in the following table and are plotted in the diagram (Fig. 3).

The three curves intersect at about  $+0.2^{\circ}$ , which is the invariant point where the two solid phases, liquid and vapor, coexist. Walden and Centner-zwer<sup>2</sup> also determined this temperature ( $+0.26^{\circ}$ ) and considered it a transition point rather

I. KI·4SO<sub>2</sub>-  
Solution-Vapor

T, °C.	p, cm.
-18.7	44.9
17.05	47.8
15.25	51.2
13.90	53.5
12.25	56.3
10.80	58.7
9.60	60.8
8.50	62.5
7.55	63.7
5.85	65.2
4.80	65.8
4.05	66.1
2.95	65.7
2.00	64.8
1.00	62.7
0.00	60.6

II. KI·4SO<sub>2</sub>-  
KI-Vapor

T, °C.	p, cm.
-18.20	14.3
16.05	16.3
13.30	19.9
9.85	25.7
6.50	32.3
1.50	45.7
0.00	50.2

$$\text{Log } p = 9.534 - \frac{2139.3}{T}$$

$$\Delta H = 9800$$

III. KI-Solution-  
Vapor

T, °C.	p, cm.
0.95	53.1
2.85	58.9
5.85	69.4
7.80	77.0
10.00	86.4
13.30	102.4

$$\text{Log } p = 8.345 - \frac{1814.3}{T}$$

$$\Delta H = 8300$$

than a eutectic, so that the melting point was incongruent. We found the pure compound, however, melted congruently to a clear liquid and the form of the vapor pressure curve (Fig. 3, I) also indicates that the pure compound melts slightly above the invariant point, which is therefore a eutectic rather than a transition point. In either case, the composition of the liquid at the invariant point is very close indeed to that of the compound  $\text{KI}\cdot 4\text{SO}_2$ .

**Rubidium Iodide and Sulfur Dioxide.**—Rubidium iodide dissolves readily in liquid sulfur dioxide to give an orange-red solution. On evaporating this solution at  $0^\circ$  and atmospheric pressure, using the mercury bubbler, a solid residue of transparent yellow needles remained, the composition of which corresponded to the formula  $\text{RbI}\cdot 3\text{SO}_2$ .

RbI, g.	$\text{SO}_2$ , g.	Ratio RbI: $\text{SO}_2$
4.376	4.045	1:3.06
4.971	4.577	1:3.05
4.608	4.217	1:3.03
5.125	4.719	1:3.05

Removal of sulfur dioxide from the solid compound caused the appearance of white rubidium iodide, and the pressure remained constant until the sulfur dioxide was almost completely removed; therefore, no lower compound exists. At room temperature the compound decomposed to a very viscous orange-brown liquid and solid rubidium iodide, indicating the existence of a transition temperature.

The vapor pressures of the univariant systems are shown in the following tables and Fig. 4. The vapor pressure curve of the saturated solution of the compound in liquid sulfur dioxide could not be determined over the entire range, as, at the higher temperatures, the pressures became too high for the apparatus, but the curve must display a maximum as indicated. The intersection of

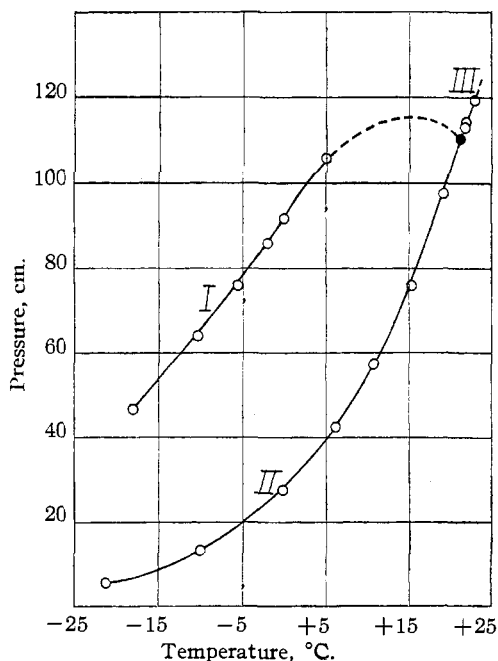


Fig. 4.— $\text{RbI}-\text{SO}_2$ . Curves I, II and III represent, respectively, the systems  $\text{RbI}\cdot 3\text{SO}_2$ -solution-vapor;  $\text{RbI}:3\text{SO}_2$ - $\text{RbI}$ -vapor and  $\text{RbI}$ -solution-vapor. The black dot represents the invariant system of four phases.



Curves II and III places the transition temperature at  $+21.3^{\circ}$ ; Curve I must meet the other curves at this point.

I. RbI·3SO <sub>2</sub> - Solution-Vapor		II. RbI·3SO <sub>2</sub> - RbI-Vapor		III. RbI-Solution -Vapor	
T, °C.	p, cm.	T, °C.	p, cm.	T, °C.	p, cm.
-18.10	46.8	-21.30	5.5	+21.75	113.0
10.30	64.0	10.00	13.4	22.0	114.1
5.60	76.0	0.00	27.35	23.0	119.4
2.00	85.7	+6.30	42.6		
0.0	91.5	10.90	57.2		
+5.00	105.9	15.30	75.8		
		19.20	97.4		

$$\text{Log } p = 9.836 - \frac{2294.0}{T}$$

$$\Delta H = 10,500$$

De Forcrand and Tabouris<sup>4</sup> found the same composition for the compound that we have found. Their result for the vapor pressure of the saturated solution at  $0^{\circ}$  is 82 cm., a value almost 10 cm. below ours, which was repeatedly checked on different samples of salt. Ephraim and Kornblum<sup>3</sup> state that rubidium iodide absorbed 4.4 moles of sulfur dioxide per mole of salt at  $0^{\circ}$ —an inexplicable result—and therefore assigned the formula RbI·4SO<sub>2</sub> to the compound.

**Cesium Iodide and Sulfur Dioxide.**—Cesium iodide dissolves readily in liquid sulfur dioxide, giving a pale red solution. Evaporation of the latter at  $0^{\circ}$  and atmospheric pressure left a residue of pale yellow needles of composition corresponding to the formula CsI·3SO<sub>2</sub>, confirming the formula of De Forcrand and Tabouris.<sup>4</sup> Ephraim and Kornblum<sup>3</sup> assigned the formula CsI·4SO<sub>2</sub> to this compound.

The following results were obtained

CsI, g.	SO <sub>2</sub> , g.	Ratio CsI:SO <sub>2</sub>
5.144	3.946	1:3.05
4.844	3.693	1:3.03

Removal of sulfur dioxide from the compound resulted in the appearance of white cesium iodide and the pressure remained constant until the sulfur dioxide was nearly all removed, showing the absence of lower compounds.

The increasing solubility of the compound in liquid sulfur dioxide with rising temperature causes the vapor pressure curve of the saturated solution to diverge considerably from that of pure sulfur dioxide, although its form can be expressed by an equation of the usual type over the temperature range studied. At somewhat higher temperatures, the curvature probably reverses and the curves of the two univariant systems intersect. Following are the results of the vapor pressure determinations. The results are plotted in Fig. 5.

I. CsI·3SO<sub>2</sub>-Solution-Vapor

T, °C.	p, cm.
-21.60	42.7
18.45	48.8
16.30	53.9
11.50	65.8
8.10	75.5
4.25	87.1
0.0	102.5

$$\text{Log } p = 6.440 - \frac{1209.7}{T}$$

$$\Delta H = 5550$$

II. CsI·3SO<sub>2</sub>-CsI-Vapor

T, °C.	p, cm.
-19.60	6.3
15.90	8.5
10.90	12.3
5.25	18.4
0.0	26.65
+ 7.50	43.8
12.40	60.3
17.10	80.8
20.25	98.2

$$\text{Log } p = 9.629 - \frac{2240.6}{T}$$

$$\Delta H = 10,250$$

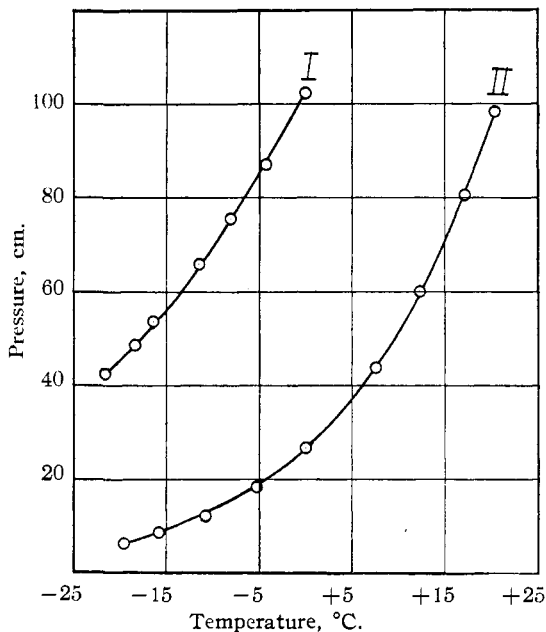


Fig. 5.—CsI-SO<sub>2</sub>. Curves I and II represent, respectively, the systems CsI·3SO<sub>2</sub>-solution-vapor and CsI·3SO<sub>2</sub>-CsI-vapor

**Ammonium Iodide and Sulfur Dioxide.**—There appear to be no data in the literature on this system. Ammonium iodide dissolves readily in liquid sulfur dioxide forming a red solution. Evaporation of sulfur dioxide from unsaturated solutions to a pressure somewhat below that of the

NH <sub>4</sub> I, g.	SO <sub>2</sub> , g.	Ratio NH <sub>4</sub> I:SO <sub>2</sub>	Temp., °C.
4.883	6.647	1:3.08	-22
3.383	4.636	1:3.10	-19
5.980	8.160	1:3.09	-20

saturated solution, at three temperatures, left in each case a residue of yellow needles having the composition corresponding to  $\text{NH}_4\text{I}\cdot 3\text{SO}_2$ .

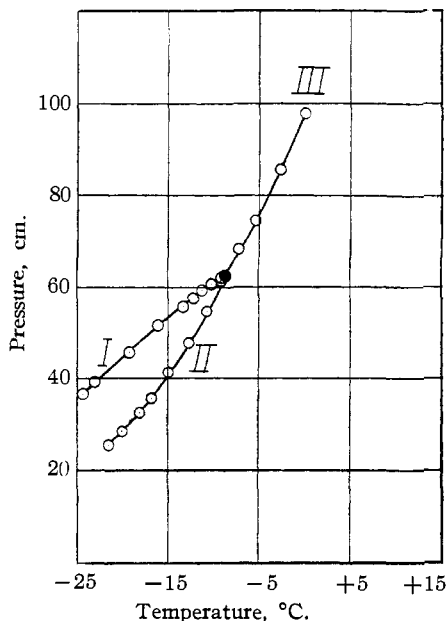


Fig. 6.— $\text{NH}_4\text{I}\text{-SO}_2$ . Curves I, II and III represent, respectively, the systems  $\text{NH}_4\text{I}\cdot 3\text{SO}_2$ -solution-vapor;  $\text{NH}_4\text{I}\cdot 3\text{SO}_2$ - $\text{NH}_4\text{I}$ -vapor; and  $\text{NH}_4\text{I}$ -solution-vapor: To avoid confusion, the results in the metastable region of curve III are omitted. The black dot represents the invariant system of four phases.

The existence of lower compounds was disproved by the fact that withdrawal of sulfur dioxide from the compound caused the appearance of white ammonium iodide and the pressure remained constant until sulfur dioxide was almost completely removed.

The existence of a transition temperature was indicated by the fact that on removal from the freezing bath, the compound  $\text{NH}_4\text{I}\cdot 3\text{SO}_2$  decomposed to yield a liquid and a solid. The intersection of the vapor pressure curves of the three univariant systems placed the transition temperature at  $-8.8^\circ$ . At this temperature, the phases in equilibrium are  $\text{NH}_4\text{I}\cdot 3\text{SO}_2$ - $\text{NH}_4\text{I}$ -solution-vapor.

The vapor pressure data are given below and plotted in Fig. 6. It was possible to obtain some measurements on the system  $\text{NH}_4\text{I}$ -solution-vapor at temperatures below the transition point, a region in which the system is

I.  $\text{NH}_4\text{I}\cdot 3\text{SO}_2$ -Solution-Vapor

$T, ^\circ\text{C.}$	$p, \text{cm.}$
-24.40	36.5
23.05	39.0
19.35	45.6
16.10	51.3
13.45	55.6
12.25	57.6
11.25	59.1
10.20	60.6
9.00	62.0

II.  $\text{NH}_4\text{I}\cdot 3\text{SO}_2$ - $\text{NH}_4\text{I}$ -Vapor

$T, ^\circ\text{C.}$	$p, \text{cm.}$
-21.50	25.5
20.00	28.2
18.05	32.6
16.80	35.7
14.90	41.1
12.70	47.6
10.80	54.5
9.15	61.2

III.  $\text{NH}_4\text{I}$ -Solution-Vapor

$T, ^\circ\text{C.}$	$p, \text{cm.}$
-13.85 <sup>a</sup>	48.2
12.35 <sup>a</sup>	52.3
10.45 <sup>a</sup>	57.4
7.20	68.1
5.45	74.3
2.65	85.5
0.0	97.6

$$\text{Log } p = 9.537 - \frac{2045.8}{T}$$

$$\Delta H = 9350$$

$$\text{Log } p = 7.781 - \frac{1581.6}{T}$$

$$\Delta H = 7250$$

<sup>a</sup> Metastable system.

metastable. As in the case of all the simple alkali iodides (as distinct from the addition products) the solubility of ammonium iodide in sulfur dioxide decreases with rising temperature.

### Summary

The composition of the solid addition products and the vapor pressure curves limiting the stability of these compounds have been determined between the maximum limits of  $-25$  and  $+25^{\circ}$  for the 2-component systems of sulfur dioxide with sodium, potassium, rubidium, cesium and ammonium iodides.

NEW HAVEN, CONNECTICUT

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

## THE KINETICS OF THE DECOMPOSITION OF AMMONIA ON COPPER

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The decomposition of ammonia on the surfaces of certain metals has been studied by Hinshelwood and Burk, Schwab and Kunsman.<sup>2</sup> In each case the metal in the form of a hot filament has been used to decompose the ammonia. In order to obtain a true conception of a heterogeneous reaction a knowledge of the following is necessary: (1) the heats of adsorption of the gases involved in the reaction; (2) the amount of each gas adsorbed, as a function of its pressure; (3) the rates of adsorption of the gases; and (4) the law expressing the relation between the velocity of reaction and the pressures of the gases above the surfaces.<sup>3</sup> Except at low pressures, the use of a filament as a surface precludes any attempts to make measurements on the first three quantities. The object of the present work has been to study the kinetics of the decomposition of ammonia on copper, using enough of the metal to make later measurements on the first three factors possible.

Elöd and Banholzer<sup>4</sup> have studied the decomposition of ammonia on copper and iron by a dynamic method. Their results on copper agree with those given here and can now be interpreted in a quantitative way.

### Experimental

About fifty experiments on the decomposition of ammonia on forty grams of granular copper (see below) were performed in a static system.

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<sup>2</sup> (a) Hinshelwood and Burk, *J. Chem. Soc.*, **127**, 1105 (1925); (b) Schwab, *Z. physik. Chem.*, **128**, 161 (1927); (c) Schwab and Schmidt, *ibid.*, **B3**, 337 (1929); (d) Kunsman, *THIS JOURNAL*, **50**, 2100 (1928); **51**, 688 (1929).

<sup>3</sup> Hinshelwood, "Kinetics of Chemical Changes in Gaseous Systems," Oxford University Press, 1929.

<sup>4</sup> Elöd and Banholzer, *Z. Elektrochem.*, **32**, 555 (1926).