[Contribution from the Sterling Chemistry Laboratory of Yale University]

EQUILIBRIUM IN SYSTEMS COMPOSED OF SULFUR DIOXIDE AND SODIUM, POTASSIUM OR AMMONIUM THIOCYANATE

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In a previous investigation,[1] we have determined the composition of the solid phases and the vapor pressure relations in two-component systems composed of sulfur dioxide and an alkali (or ammonium) iodide. We give below the corresponding results obtained on systems containing thiocyanates instead of iodides. The methods, apparatus and procedure were the same in both investigations and were described in detail in the earlier one.

Sodium Thiocyanate and Sulfur Dioxide.—Sodium thiocyanate forms a bright yellow compound having the composition $NaCNS{\cdot}2SO_2$ when brought in contact with liquid sulfur dioxide. The compound is rather insoluble in the liquid, yielding a pale yellow solution. The composition of the compound was determined by allowing the saturated solution to evaporate at a pressure of one atmosphere of sulfur dioxide at two temperatures where the vapor pressure data given below showed that only the pure compound could exist in equilibrium. The following results were obtained.

NaCNS, g.	SO_2, g.	Ratio NaCNS : SO_2	Temp., °C.
5.316	8.11	1:1.93	−8.0
2.450	3.79	1:1.96	0.0

The observed vapor pressures of the two univariant systems are given in the table.

I		II	
$NaCNS{\cdot}2SO_2$–Solution–Vapor		$NaCNS{\cdot}2SO_2$–NaCNS–Vapor	
T, °C.	*P*, cm.	*T*, °C.	*P*, cm.
−21.40	44.5	−21.30	9.1
12.20	69.2	9.70	23.2
2.75	103.5	0.00	49.9
0.00	115.9	+7.00	79.8
		10.50	102.0

I: $\text{Log } p = 6.954 - \frac{1335.5}{T}$, $\Delta H = 6100$

II: $\text{Log } p = 9.396 - \frac{2290.4}{T}$, $\Delta H = 10{,}500$

The results are plotted in Fig. 1. Ephraim and Kornblum[2] reported that sodium thiocyanate does not absorb sulfur dioxide to form a compound at 0° and one atmosphere pressure. Our results show that the addition

[1] Foote and Fleischer, This Journal, **53**, 1752 (1931).

[2] Ephraim and Kornblum, *Ber.*, **49**, 2007 (1916).

product is stable under these conditions. It is not unlikely, however, that the absorption of the vapor is slow, as is often the case with solids. There is no difficulty in obtaining the compound by the method we have described.

Potassium Thiocyanate and Sulfur Dioxide.—Ephraim and Kornblum[2] investigated this system and recognized the fact that two compounds exist, to which they assigned the formulas $KCNS \cdot SO_2$ and $KCNS \cdot 0.5SO_2$. They did not, however, give the data on which these formulas are based. In the present investigation, it has been found that on standing for some hours in contact with liquid sulfur dioxide, potassium thiocyanate is converted, with apparent increase in volume, to a pale yellow compound which crystallizes in needles. The saturated solution has a bright yellow color though the compound is not readily soluble, as shown by the fact that the vapor pressure curve of the saturated solution lies only slightly below that of liquid sulfur dioxide.

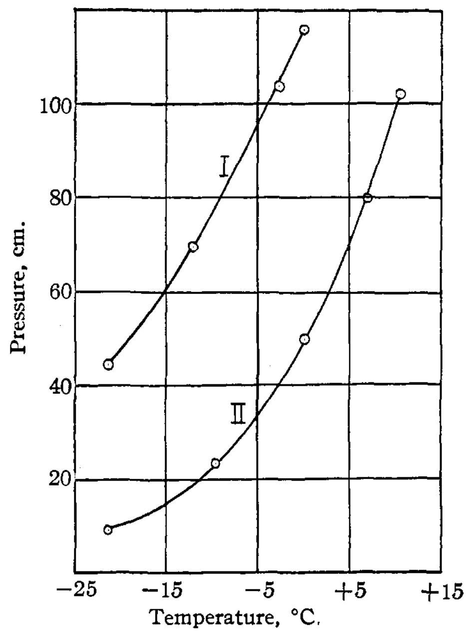

Fig. 1.—$NaCNS-SO_2$: Curves I and II represent, respectively, the systems $NaCNS \cdot 2SO_2$–solution–vapor and $NaCNS \cdot 2SO_2$–NaCNS–vapor.

The compound was prepared in pure condition by allowing the saturated solution, in contact with excess of solid, to evaporate at 0° and atmospheric pressure. The following results were obtained.

KCNS, g.	SO_2, g.	Ratio, KCNS : SO_2
3.225	4.155	1:1.95
4.875	6.438	1:2.00

The compound therefore has the formula $KCNS \cdot 2SO_2$. We found no indication of the 1:1 compound mentioned by Ephraim and Kornblum. Evaporation of sulfur dioxide from the compound at 20° and atmospheric pressure—conditions under which the vapor pressure measurements show that a lower compound is stable—left a bright yellow solid as residue. This reaction, however, takes place slowly. The following data were obtained after allowing the bulb containing the higher compound to stand several days at room temperature, the excess of sulfur dioxide escaping meanwhile at atmospheric pressure through the mercury bubbler.

KCNS, g.	SO_2, g.	Ratio, KCNS : SO_2
3.225	1.327	1:0.62
4.875	2.020	1:0.63

It is probable that the formula of this compound is $KCNS \cdot 0.5SO_2$ as stated by Ephraim and Kornblum, the high sulfur dioxide content of the residue being due to the slow rate of dissociation of the higher compound. The following tables contain the vapor pressure data of the three univariant systems.

I		II		III	
$KCNS \cdot 2SO_2$–Solution–Vapor		$KCNS \cdot 2SO_2$–$KCNS \cdot 0.5SO_2$–Vapor		$KCNS \cdot 0.5SO_2$–KCNS–Vapor	
T, °C.	*P*, cm.	*T*, °C.	*P*, cm.	*T*, °C.	*P*, cm.
−21.30	44.5	−10.00	18.3	0.00	2.85
14.50	61.9	0.00	37.1	12.00	7.0
7.50	84.2	+11.00	73.8	19.00	11.2
0.00	114.3	14.50	91.2	20.85	12.9
		16.60	102.9	24.00	15.4

$\text{Log } p = 6.825 - \frac{1301.5}{T}$ $\quad \Delta H = 5950$

$\text{Log } p = 9.353 - \frac{2126.4}{T}$ $\quad \Delta H = 9750$

$\text{Log } p = 9.475 - \frac{2461.6}{T}$ $\quad \Delta H = 11{,}270$

The results are plotted in Fig. 2.

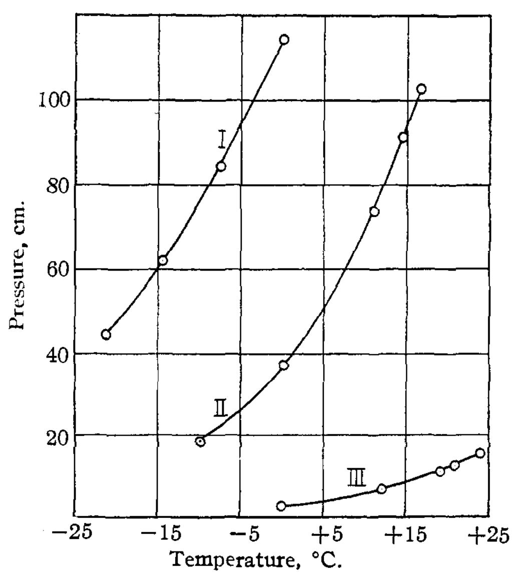

Fig. 2.—KCNS–SO_2: Curves I, II and III represent, respectively, the systems $KCNS \cdot 2SO_2$–solution–vapor, $KCNS \cdot 2SO_2$–$KCNS \cdot {}^1/_2SO_2$–vapor, and $KCNS \cdot {}^1/_2SO_2$–KCNS–vapor.

Ammonium Thiocyanate and Sulfur Dioxide.—This salt is more soluble than the potassium salt in liquid sulfur dioxide. The saturated solution has the color of an aqueous dichromate solution, quite different from the yellow color of the solutions of the sodium and potassium salts.

Isothermal evaporation of solution at a pressure somewhat below that of the saturated solution left a residue of transparent yellow cubes of composition corresponding to the formula $NH_4CNS \cdot SO_2$. The data are given in the table, together with the temperatures and pressures at which the evaporation was carried out.

NH_4CNS, g.	SO_2, g.	Ratio $NH_4CNS:SO_2$	T, °C.	P, cm.
5.812	4.460	1:1.02	−16	40
4.667	4.061	1:1.03	−10	50
4.012	3.534	1:1.05	− 2	77

The compound floats on the saturated solution and therefore has a lower density than the latter. The existence of lower compounds was disproved by the fact that at a constant temperature practically all the sulfur dioxide was removed at constant pressure. Furthermore, evaporation of the solution at +7° and atmospheric pressure left a residue containing only 0.03 mole of sulfur dioxide per mole of thiocyanate.

The compound decomposes to a liquid and a solid phase when warmed slightly, showing the existence of a transition temperature. This temperature was found to be +2.4° from the intersection of the vapor pressure curves of the three univariant systems given below. The solubility of $NH_4CNS \cdot SO_2$ in liquid sulfur dioxide increases with rising temperature, which is the case with all the other addition compounds investigated, while the solubility of NH_4CNS (above the transition point) decreases, as it does for all the other simple iodides and thiocyanates investigated.

Vapor Pressure Data of the Three Univariant Systems

I		II		III	
$NH_4CNS \cdot SO_2$–Solution–Vapor		$NH_4CNS \cdot SO_2$–NH_4CNS–Vapor		NH_4CN_2–Solution–Vapor	
T, °C.	P, cm.	T, °C.	P, cm.	T, °C.	P, cm.
−20.40	41.5	−20.90	20.1	+3.00	94.7
19.75	42.6	−12.60	35.2	4.00	98.7
16.50	48.0	− 7.50	49.6	4.50	100.7
13.20	55.3	− 4.60	59.9	5.70	105.7
7.70	68.1	0.00	80.1	6.40	108.5
5.90	72.4			7.20	112.4
3.50	78.9				
0.00	87.4				

$$\text{Log } p = 9.178 - \frac{1987.0}{T} \qquad \text{Log } p = 6.931 - \frac{1368.0}{T}$$

$$\Delta H = 9100 \qquad \Delta H = 6250$$

The results are plotted in Fig. 3.

Ephraim and Kornblum found no absorption of sulfur dioxide by ammonium thiocyanate at 0° and atmospheric pressure. Our data confirm this observation, since the dissociation pressure in system II above is greater than atmospheric at 0°.

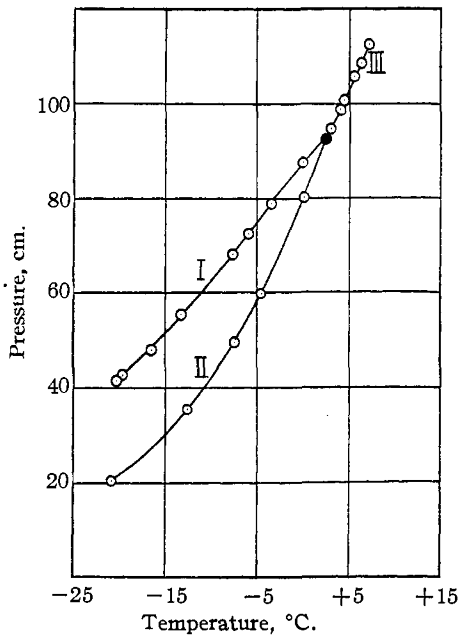

Fig. 3.—NH_4CNS–SO_2: Curves I, II and III represent, respectively, the systems $NH_4CNS \cdot SO_2$–solution–vapor, $NH_4CNS \cdot SO_2$–NH_4CNS–vapor, and NH_4CNS–solution–vapor. The black dot represents the invariant system.

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 −20 and +25° for the two-component systems of sulfur dioxide with sodium, potassium and ammonium thiocyanates. The investigation supplements a previous one on similar systems with alkali iodides.

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