origin of the difference between their results and ours is not clear. It should be noted that the presence of side reactions could lead, with their analytical method, to substantial errors.

From considerations of a statistical mechanical nature, Aston, Isserow, Szasz and Kennedy[11] have calculated the equilibrium constants for the dehydrogenation of *i*-propyl alcohol and compared these with those of Parks and Kelley.[2] These statistically calculated values of log K_p and those calculated from equation (3) are, respectively, at 355.5, 450 and 500°K.: −2.09, −2.14, −0.38, −0.36, +0.28, +0.32.

Summary

1. Equilibrium constants for the reactions of *i*-propyl and *s*-butyl alcohols to form the corresponding ketones and hydrogen have been measured in the temperature range of 416 to 491°K. The degree of dissociation of the latter alcohol is very slightly the greater of the two.

2. The equilibrium constants in terms of partial pressures are independent of pressure at pressures between one-third and one atmosphere.

EVANSTON, ILL. RECEIVED AUGUST 10, 1944

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Coördination Compounds of Boron Trichloride. II.[1] Systems with Sulfur Dioxide and Hydrogen Sulfide

BY DONALD RAY MARTIN

Since the boron atom of boron trichloride has only six electrons, it acts as an acceptor in the formation of coördination compounds.[1] The donor atoms of these compounds have been found to be limited to the non-metals nitrogen, phosphorus, arsenic, oxygen, sulfur, fluorine and chlorine.

In studying the formation of coördination compounds of a gas like boron trichloride, the method of thermal analysis offers many advantages. The object of this investigation was to extend the knowledge of the coördination compounds of boron trichloride with gaseous sulfur compounds by means of thermal analysis.

Apparatus and Procedure

The apparatus and procedure used for this investigation were very similar to those previously described[2,3,4] except for four modifications. First, the fractionating column using liquid air as the head refrigerant was modified to give better control of the fractionation as suggested by Booth and McNabney.[5]

Second, in order to have more positive action in the opening and closing of the automatic stopcock on the fractionating column, the 20-ohm telegraph sounder described by Booth and Bozarth[6] was modified as shown in Fig. 1. The compressed air bleed-off line is connected to the bicycle tire valve V which is attached to the sounder base D by a brass adapter C. When electrical contact is made by the mercury in the control manometer of the fractionating column, the sounder is actuated causing its arm A to be lowered toward the base D. As a result the iron pin P drops thus allowing the bicycle tire valve stem to close. All of the compressed air is then forced into the automatic stopcock mechanism. Due to the strength of the spring in the bicycle tire valve stem, the sounder spring S has to be located at a greater distance from the fulcrum than on an unmodified sounder. This is achieved by attaching brass strips E and F.

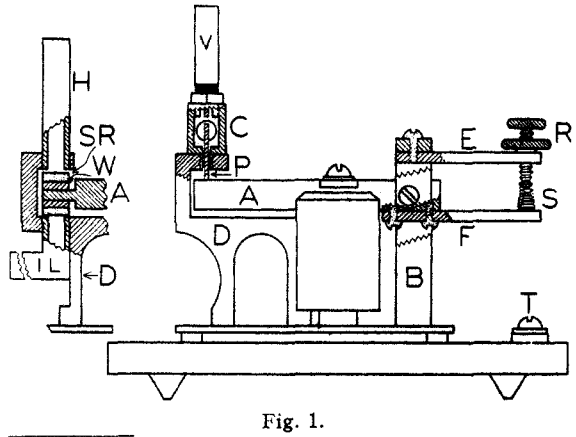

Fig. 1.

The modified sounder is unsatisfactory as the control valve for the injection of liquid air into the head of the fractionating column because the narrow opening through the bicycle tire valve V affords too much resistance to the escaping air thus producing a pressure of sufficient magnitude to cause the injection of liquid air. This difficulty was obviated by modifying the sounder as shown by the section at the left in Fig. 1. The liquid air injector is connected to the brass tubing IL which is soldered into the special brass base D. This replaces the regular base differing from it in being one-half inch in width. This affords room for the brass tubing which is $^5/_{32}$ inch in diameter. The exit tube from the head of the fractionating column is connected to the brass tubing H. The arm A of the sounder is modified as shown to accommodate the valve seats made from brass washers W and sponge-rubber pads SR. With this arrangement one of the valves is always open while the other is closed with the result that liquid air can be injected only when the sounder is actuated by the control manometer.

The third modification deals with the use of cooled acetone as the refrigerant for the head of the fractionating column. As previously described,[6] the acetone is circulated by a small centrifugal pump from a pint size Dewar

(1) D. R. Martin, *Chem. Rev.*, **34**, 461–473 (1944).

(2) H. S. Booth and D. R. Martin, THIS JOURNAL, **64**, 2198–2205 (1942).

(3) H. S. Booth and D. R. Martin, *Chem. Rev.*, **33**, 57–88 (1943).

(4) A. F. O. Germann and H. S. Booth, *J. Phys. Chem.*, **30**, 369–377 (1926).

(5) H. S. Booth and Ralph McNabney, *Ind. Eng. Chem., Anal. Ed.*, **16**, 131–133 (1944).

(6) H. S. Booth and A. R. Bozarth, *Ind. Eng. Chem.*, **29**, 470–475 (1937).

flask reservoir through a coil of 0.25-inch diameter copper tubing immersed in an acetone–Dry Ice-bath, thence to the head of the fractionating column and finally is returned to the reservoir. This procedure affords excellent heat transfer in the coil of copper tubing but has the disadvantage that the acetone freezes due to moisture from the atmosphere which enters at the reservoir. On a humid day it is difficult to distill for four hours without experiencing this trouble. By eliminating the coil of copper tubing and cooling the brass reservoir R (Fig. 2), this difficulty is eliminated. The reservoir was made by soldering a cap on a suitable length of $2^1/_2$ in. brass tubing. The centrifugal pump L connected to the motor M is placed in the reservoir R which in turn is placed on a cotton pad P in a half-gallon size Dewar flask D. The head H of the vacuum-jacketed fractionating column VJ is insulated with a special-thick cork refrigeration pipe insulation C. Acetone may be used in this manner for several days of distillation.

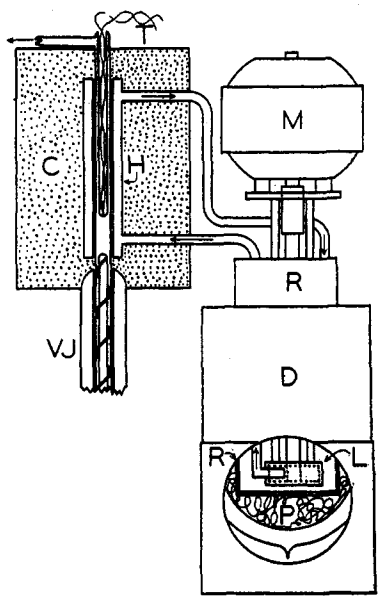

Fig. 2.

The other modification concerns the receptacles for the cracked ice used to hold the calibrated flasks at constant temperature during the establishment of the mole fractions. Previously,[2,3,4] inverted bell jars were used. However, in the course of a thermal analysis it is necessary that the temperature of the flasks be held at 0° for many hours, which procedure requires frequent siphoning of water from the receptacles. Otherwise the flasks are buoyed up until the pressure becomes sufficiently great to break the glass manifold. Replacement of the inverted bell jars by the suitably supported upper halves of inverted five gallon glass bottles, fitted with a glass drainage tube in a one-hole rubber stopper, proved beneficial. Experience has shown that the glass drainage tube should be at least 14 mm. in diameter.

In the establishment of the mole fractions the pressure of BCl_3 in the calibrated flask was never permitted to exceed 450 mm. inasmuch as its vapor pressure is 477 mm. at 0°.[6a]

The System Sulfur Dioxide–Boron Trichloride

Inasmuch as only five compounds of sulfur have been reported[1] to form coördination compounds with boron trichloride, and since the evidence for the existence of some of these compounds is questionable, it was decided to study the coördinating ability of the sulfur atom in two common compounds, *i. e.*, sulfur dioxide and hydrogen sulfide.

Quill[7] and Whittenberg[8] have reported that boron trichloride and sulfur dioxide react to form a yellow liquid which becomes crystalline upon exposure to air. They propose the formula $SO_2 \cdot BCl_3$ for this compound although no analysis was made. The compound $SO_2 \cdot BF_3$ has been reported by Booth and Martin.[2]

The boron trichloride used in this thermal analysis was prepared by the reaction of boron trifluoride with aluminum chloride.[9] It was purified by fractional distillation.

The sulfur dioxide was obtained from the Ansul Chemical Company and was purified by fractional distillation.

The freezing point of purified boron trichloride was found to be $-108.3 \pm 0.4°$ and that of purified sulfur dioxide $-76.0 \pm 0.4°$. Sulfur dioxide and boron-trichloride were found to be almost completely immiscible at the low temperatures of their freezing points. From the data in Table I, shown graphically in Fig. 3, it is evident that

TABLE I

DATA FOR THE SYSTEM SULFUR DIOXIDE–BORON TRICHLORIDE

Mole fraction, BCl_3	Freezing point, −°C. BCl_3 in SO_2	SO_2 in BCl_3	Mole fraction, BCl_3	Freezing point, −°C. BCl_3 in SO_2	SO_2 in BCl_3
0.000	76.0		0.401	78.1	108.1
.021	76.8		.493	78.0	
.038	77.1		.598	78.2	107.3
.099	78.0		.705	78.0	106.7
.198	78.0		.797	78.1	108.3
.296	78.0		.938	78.2	
			1.000		108.3

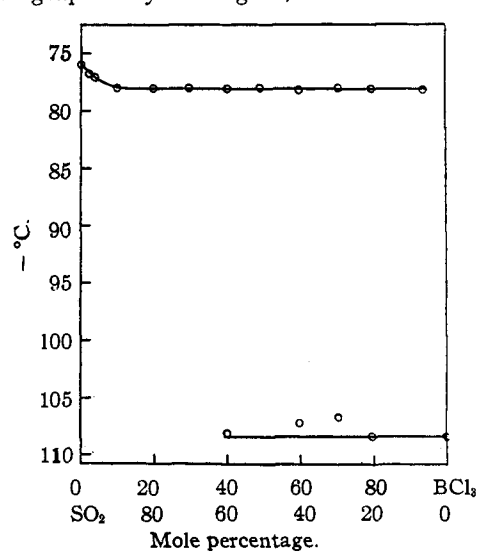

Fig. 3.

(6a) A. Stock and O. Preiss, *Ber.*, **47**, 3109-3113 (1914).

(7) L. L. Quill, *Trans. Illinois State Acad. Sci.*, **23**, 333–338 (1931).

(8) L. E. Whittenberg, B.S. Thesis, University of Illinois, Urbana Illinois, 1930.

(9) E. L. Gamble, P. Gilmont and J. F. Stiff, THIS JOURNAL, **62**, 1257–1258 (1940).

TABLE II

Compound	Dipole moment, $\mu \cdot 10^{18}$, e.s.u.	Boiling point, °C.	Molal volume, cc./mole 25°C.	Molal volume, cc./mole −40°C.	Internal pressure $a^{1/2}/V$ cal.$^{1/2}$/cc. at 25°C.	Internal pressure $a^{1/2}/V$ cal.$^{1/2}$/cc. at −40°C.	$(a^{1/2}/V)_{SO_2} - (a^{1/2}/V)_{XCl}$ at 25°C.	$(a^{1/2}/V)_{SO_2} - (a^{1/2}/V)_{XCl}$ at −40°C.
$SiCl_4$	0	59.6	115.3	105.0[a]	7.57	8.33	2.81	3.30
BCl_3	0[b]	12.5[c]	88.9[d]	79.3[d]	7.93	9.02	2.45	2.61
CCl_4	0	76.5	97.1	90.0[e]	8.54	9.21	1.84	2.42
SO_2	1.61[f]	−10.0[g]	46.8[h]	41.8[h]	10.38	11.63	..	..

[a] Calculated from data of P. L. Robinson and H. C. Smith, *J. Chem. Soc.* (London), 2162–2182 (1926). [b] H. Ulich and W. Nespital, *Z. Elektrochem.*, **37**, 559–563 (1931). [c] A. Stock and O. Preiss, *Ber.*, **47**, 3109–3113 (1914). [d] Calculated from data of H. V. A. Briscoe, P. L. Robinson and H. C. Smith, *J. Chem. Soc.* (London), 282–290 (1927). [e] Calculated from data of J. Timmermans and F. Martin, *J. chim. phys.*, **23**, 745–787 (1926). [f] C. T. Zahn, *Phys. Rev.*, **27**, 455–459 (1926). [g] W. F. Giauque and C. C. Stephenson, THIS JOURNAL, **60**, 1389–1394 (1938). [h] Calculated from data of A. Lange, *Z. angew. Chem.*, **12**, 275–277 (1899).

sulfur dioxide is practically insoluble in boron trichloride while the latter is soluble in sulfur dioxide to the extent of 9.9 ± 0.2 mole per cent. at −78.0 ± 0.4°. The second breaks in the cooling curves were very difficult to obtain accurately due to the fact that boron trichloride is less dense than sulfur dioxide at these temperatures and the sulfur dioxide having a higher freezing point solidified first at the base of the thermocouple well, thus stopping the stirring action in the freezing point cell. The remaining liquid boron trichloride was approximately 4 cm. above the thermocouple junction with the result that its freezing point was difficult to determine.

This immiscibility is interesting when compared with the statement of Schattenstein and Wiktorow[10] that sulfur dioxide and boron trichloride are miscible in all proportions. These authors did not report the temperature of their observation.

It is of interest to note that the chlorides of the neighboring non-metallic elements of boron in the periodic table, *e. g.*, carbon tetrachloride and silicon tretrachloride, are miscible with sulfur dioxide at temperatures near its boiling point, but are immiscible at lower temperatures.[11,12] This phenomenon may be explained on the basis of differences in the solute and solvent molecules with respect to internal pressures and polarities. The greater these differences, the greater will be the deviation from the properties of an ideal solution in the direction of smaller solubility.[13] These deviations usually become greater as the temperature is lowered.[14] These facts are borne out as shown in Table II in which the above-mentioned non-metallic chlorides and boron trichloride are compared with sulfur dioxide with respect to their dipole moments, $\mu \cdot 10^{18}$, and their internal pressures, expressed as energy density in the term $a^{1/2}/V$ as calculated by Hildebrand.[13] Inasmuch as boron trichloride has an internal pressure which is between the values for silicon tetrachloride and carbon tetrachloride, it would be expected that it too would be immiscible at low temperatures.

There was found no evidence for the existence of the compound $SO_2 \cdot BCl_3$. The compound $SO_2 \cdot BF_3$ is somewhat dissociated above its melting point and since it has been shown that boron trichloride less readily forms coördination compounds than boron trifluoride,[1] it is not surprising that $SO_2 \cdot BCl_3$ does not exist.

In the disposition of the contents of the freezing point cell upon the conclusion of a thermal analysis, the mixture of sulfur dioxide and boron trichloride came in contact with a small quantity of water. A yellow colored liquid was produced which is probably of the same composition as the yellow liquid previously reported.[7,8] Evidently it owes its existence to the presence of water. All of the anhydrous mixtures prepared in this thermal analysis were water-white.

The System Hydrogen Sulfide–Boron Trichloride

Since the sulfur atom attached to oxygen atoms in sulfur dioxide fails to coördinate with the boron atom of boron trichloride, it was of interest to see whether the sulfur atom attached to hydrogen atoms in hydrogen sulfide can coördinate with the boron atom of boron trichloride. Inasmuch as the compounds $H_2S \cdot BF_3$[4] and 12 $H_2S \cdot BCl_3$[15] have been reported, it was of interest to see whether the compound $H_2S \cdot BCl_3$ exists.

The boron trichloride used for this investigation was prepared and purified as described above. The hydrogen sulfide was obtained from the Ohio Chemical Company and was purified by fractional distillation.

The purified boron trichloride was found to freeze at −107.9 ± 0.4° and the purified hydrogen sulfide at −85.4 ± 0.4°. The data in Table III depicted in the phase rule diagram in Fig. 4 indicate a maximum freezing point at 50.0 ± 0.2 mole per cent. boron trichloride corresponding to the compound $H_2S \cdot BCl_3$, the freezing point of which is −35.3 ± 0.4°. Eutectic points were found on each side of this maximum. One exists at 2.0 ± 0.2 mole per cent. boron trichloride and

(10) A. I. Schattenstein and M. M. Wiktorow, *Acta Physiochim.* U. R. S. S., **7**, 883–898 (1937); *J. Phys. Chem.* (U. S. S. R.), **11**, 18–27 (1938).

(11) P. A. Bond and H. T. Beach, THIS JOURNAL, **48**, 348–356 (1926).

(12) P. A. Bond and W. R. Stephens, *ibid.*, **51**, 2910–2922 (1929).

(13) J. H. Hildebrand, "Solubility of Non-electrolytes," 2nd. ed., Reinhold Publishing Corporation, New York, N. Y., 1936, pp. 95–106.

(14) J. H. Hildebrand, *ibid.*, p. 53.

(15) A. W. Ralston and J. A. Wilkinson, THIS JOURNAL, **50**, 258–264 (1928).

$-93.9 \pm 0.4°$, while the other exists at 99.9 ± 0.2 mole per cent. boron trichloride and $-108.8 \pm 0.4°$. No evidence was found for the existence of the compound $12H_2S \cdot BCl_3$ melting at $-47.0°$.[15] A point corresponding to that percentage composition and melting at $-47.0°$ would almost fall upon the curve in the phase rule diagram.

TABLE III

DATA FOR THE SYSTEM HYDROGEN SULFIDE–BORON TRICHLORIDE

Mole fraction of BCl_3	Freezing point, −°C.	Eutectic temp., −°C.	Mole fraction of BCl_3	Freezing point, −°C.	Eutectic temp., −°C.
0.000	85.4		0.300	38.9	
.004	88.9		.324	38.3	
.009	90.7		.391	36.1	
.016	91.6		.424	35.9	
.046	56.1	93.9	.500	35.3	
.047	62.6		.597	35.8	
.097	48.1	93.9	.695	39.4	
.101	47.1		.800	44.4	
.148	45.0		.901	52.4	
.203	43.7		.980	78.0	108.8
.252	41.2		.998	107.8	108.8
.298	38.7		1.000	107.9	

Considerable difficulty was experienced in obtaining reproducible freezing point values on the compound sides of the eutectics. This was especially true on the boron trichloride side of the maximum. If a freezing point were determined for a mixture of hydrogen sulfide and boron trichloride which had been held at $-78°$ for several hours, a value was obtained which could not be reproduced. Subsequent melting and freezing produced a slightly lower freezing point value. This procedure was repeated until a minimum value was obtained. These minimum values were duplicated with different samples of boron trichloride and hydrogen sulfide (open and solid circles in Fig. 4).

These minimum values were obtained in much less time by holding the components in the liquid state at a temperature about 20° above their freezing points for about ten minutes. The first freezing point taken immediately thereafter was usually the minimum value for that mole fraction. There seemed to be no correlation between the length of time the sample was held in the solid state and the value of the first freezing point taken immediately thereafter, whereas it appears that the length of time the sample is held above its freezing point is related to the time required to obtain the minimum freezing point value.

There seems to be no adequate explanation of this phenomenon. If one assumes the existence of the equilibrium

$$H_2S \cdot BCl_3 \underset{(2)}{\overset{(1)}{\rightleftharpoons}} H_2S + BCl_3$$

it appears from experimental results that reaction (2) proceeds at the lower temperatures and is slower than reaction (1) which is proceeding at temperatures above the freezing points. At the higher temperatures, the quantity of $H_2S \cdot BCl_3$ would become smaller and the quantities of hydrogen sulfide and boron trichloride correspondingly larger with the result that the quantity of solute present increases while the quantity of solvent decreases, thus causing a lowering of the freezing point. This effect is less pronounced on the hydrogen sulfide side of the maximum. Perhaps this is due to a difference in the behavior of the solutes hydrogen sulfide and boron trichloride in the liquid solvent $H_2S \cdot BCl_3$.

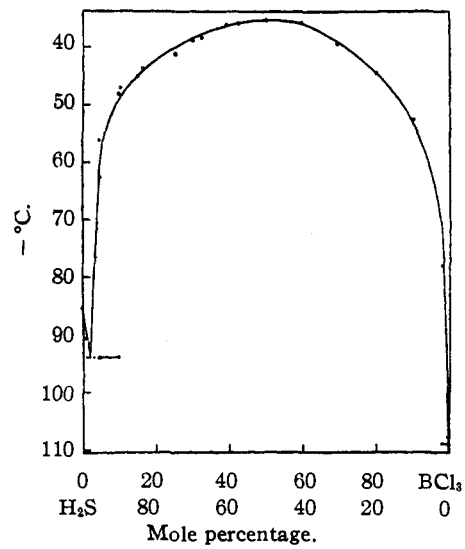

Fig. 4.—O = first analysis; ● = second analysis.

Summary

1. Sulfur dioxide was found to be immiscible with boron trichloride at low temperatures. These compounds have been reported miscible in all proportions but the temperature of observation was not given.[10]

2. Boron trichloride was found to be soluble in sulfur dioxide to the extent of 9.9 ± 0.2 mole per cent. at $-78.0 \pm 0.4°$.

3. The immiscibility of sulfur dioxide and boron trichloride at low temperatures is attributed to the large differences in the internal pressures and in the dipole moments of these two gases. Boron trichloride, silicon tetrachloride and carbon tetrachloride are compared with respect to their miscibility with sulfur dioxide at temperatures near its boiling point, and also with respect to their immiscibility with sulfur dioxide at lower temperatures.

4. No evidence for the compound $SO_2 \cdot BCl_3$ previously postulated[7,8] was found.

5. The compound $H_2S \cdot BCl_3$ with a freezing point of $-35.3 \pm 0.4°$ was found. This study revealed no evidence for the compound $12H_2S \cdot BCl_3$ previously reported.[15]

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