were made up in two concentrations, 0.05 and 0.1 M. Both sets of solutions were made, respectively, 0.05 and 0.1 M with nitric acid in order to prevent the precipitation of chromium hydroxide and to control the ionic strength. The same results were obtained with both series of solutions, indicating that if the solutions are prepared stoichiometrically without any regard for complex formation small changes in ionic strength do not affect the validity of the results for the mole ratios. The optical density is a measure of concentration because the color of the chromium nitrate solution follows Beer's law. It can also be shown, by applying the mathematical treatment of Gould and Vosburgh,[14] that hydrofluoric acid complexes which might be formed will not interfere.

Experimental Part

Data and Results.—Optical densities of these solutions were measured at various wave lengths, with the results shown in Fig. 2. The absorption maxima occur at approximately 430 mμ and 600 mμ. The results show a maximum at 0.5 which means the complex formed under these conditions is CrF^{++}. All Y values are negative because the extinction coefficient for the chromium(III) ion is greater than the extinction coefficient for the complex CrF^{++}. Under the conditions of this experiment no other complex is formed. If the complex CrF_2^+ had been formed, there would have been a shift in the absorp-

(14) R. K. Gould and W. C. Vosburgh, THIS JOURNAL, **64**, 1630 (1942).

tion maximum and the calculation of Y would have given a maximum at 0.67 at some of the wave lengths used. Since neither of these two conditions occurred it can be assumed that only the complex CrF^{++} existed in these solutions.

The absorption spectra of a solution prepared by dissolving chromium metal in hydrofluoric acid shows a shift in the absorption maximum to higher wave lengths. This type of shift is characteristic of increasing complexity of halide complexes. It can be stated that higher complexes than CrF^{++} may exist, but definite formulas cannot be given.

Similar experiments were carried out for copper(II), cobalt(II), and nickel(II). The results showed no complexing with fluoride ion under the conditions investigated. Iron(III) fluoride complexes have been worked out by Babko and Kleiner.[5] Vanadium(III) and titanium(III) do not lend themselves to this type of investigation because of oxy-complexes of these ions.

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Summary

The existence of the $MnF_6^=$ complex as well as a CrF^{++} complex has been demonstrated. It seems necessary to have tervalent ions of the iron type to give complexes with fluoride ions. No complexes of fluoride ions with the bivalent ions copper(II), cobalt(II), and nickel(II) are evident.

The Vapor Pressure of Inorganic Substances. II. B_2O_3[1]

BY RUDOLPH SPEISER, SAM NAIDITCH AND HERRICK L. JOHNSTON

The vapor pressure of B_2O_3 has been measured by Cole and Taylor[2] using a dynamic method. B_2O_3 was evaporated into a stream of dry nitrogen flowing over a crucible containing the B_2O_3. The loss in weight of the B_2O_3, at a given temperature, was determined for different rates of flow of the nitrogen. The rate of evaporation of B_2O_3 at zero rate of flow was then obtained by graphical extrapolation. Such a method of extrapolation is not fully reliable and generally leads to vapor pressures that are considerably too high. The Knudsen method of effusion through an orifice avoids this difficulty and yields more reliable data.

The most plausible molecular species of the boric oxides in the vapor phase are BO, B_2O_3, and B_4O_6. Spectroscopic evidence[3] indicates that a complex molecule such as B_2O_3 or B_4O_6 is present in flame spectra whereas the BO bands have only been observed when high energies of excitation

(2) S. S. Cole and N. W. Taylor, THIS JOURNAL, **28**, 82 (1935).

(3) W. Jevons, Proc. Roy. Soc. (London), **91A**, 120 (1914); R. S. Mulliken, Phys. Rev., **25**, 259 (1925).

were employed such as in the active nitrogen discharge tube and the carbon arc (i. e., at temperatures of 4000°K.). It seems likely, therefore, that at temperatures below 1800°K. dissociation of B_2O_3 or B_4O_6 (whatever the molecular species in the vapor phase) into O_2 and BO does not take place.

Experimental Method

Vapor pressures of B_2O_3 were measured by the method of Knudsen (rate of effusion through an orifice) with high temperatures produced by induction heating, as previously described.[4]

A platinum Knudsen cell was employed with an orifice $1/16$ in. in diameter. The area of the orifice was corrected for thermal expansion.

In several experiments a platinum target was used with the effusion cell, so that the weight of material deposited upon the target and the change in weight of the Knudsen cell were measured simultaneously. This procedure made it possible to determine experimentally whether a non-condensable gas such as oxygen is formed as

(4) R. B. Holden, R. Speiser and H. L. Johnston, THIS JOURNAL, **70**, 3897 (1948).

a result of thermal decomposition of boron oxide. In case there is dissociation, with formation of atomic or molecular oxygen, less than the expected amount of condensate (calculated from the geometry of the experimental arrangement) will deposit upon the target.

If the target is perpendicular to the axis joining the centers of the target and the orifice, it can be shown that the fraction of the total vapor effusing through the orifice and intercepted by the target is

$$f = \frac{1}{2}\left\{1 - \frac{a^2 + c^2 - b^2}{\sqrt{(a^2 + c^2 - b_2)^2 + 4c^2b^2}}\right\} \quad (1)$$

where a is the radius of the orifice, b the radius of the target, and c the distance between the target and Knudsen cell. (This equation has been derived upon the assumption that the cosine law of evaporation is obeyed.)

A further simplification of formula (1) can be made if a is much less than b, then

$$f = b^2/(c^2 + b^2) \quad (2)$$

Temperatures were measured by sighting a disappearing filament optical pyrometer (Leeds and Northrup, Model 8622) through the orifice into the interior of the cell which approximated

an excellent "hohlraum." The pyrometer was calibrated against a tungsten ribbon filament lamp standardized by the National Bureau of Standards. With practice, pyrometer readings could be reproduced to within 0.1 to 0.2%.

The pressure is calculated from rate of effusion data by the equation

$$p = m\sqrt{2\pi RT/M} \quad (3)$$

where p is the pressure given in atmospheres, R is the molar gas constant, T is the absolute temperature, m is the rate of effusion in grams per sq. cm. per sec., and M is the molecular weight of the vapor.

Preparation and Purity of B_2O_3.—The boric oxide was made by the dehydration of C. P. boric acid manufactured by the Coleman and Bell Co. The maximum impurities were listed as As, 0.0005%, Ca, 0.005%, Cl, 0.002%, Fe, 0.001%, Pb, etc. 0.001%, PO_4, 0.001%, and SO_4, 0.001%. The boric acid was first dehydrated at 400° for several hours and then heated at 900° for one hour in a high vacuum.

Results and Discussion of Data

Comparison of the value of f calculated from equation (2) and the ratio of weight gained by the target to the weight lost by the Knudsen cell for several temperatures (see Table I) proves that in the temperature range of the measurements, the dissociation of "B_2O_3" to sub-oxides and oxygen, and in particular BO and oxygen, is of no importance and need not be further considered.

In Table II, the experimental data and the

TABLE I

Temp., °K.	Condensate on target, mg.	Loss in weight of cell, mg.	Ratio of Column 2 and 3	f, calcd.
1331	0.60	4.57	13.129	13.193
1497	2.50	18.40	13.587	13.585
1505	4.35	34.63	12.560	12.600
1642	6.35	47.44	13.390	13.585

TABLE II

THE VAPOR PRESSURE OF B_2O_3 (OR B_4O_6)

Temp., °K.	Time, sec.	Weight evaporated, mg.	Evaporated, g./sec./sq. cm.	Press. atm. (as B_2O_3)	Press. atm. (as B_4O_6)
1331	27,683	4.71	7.851×10^{-6}	7.742×10^{-7}	5.474×10^{-7}
1331[a]	27,683	4.71	7.851×10^{-6}	7.742×10^{-7}	5.474×10^{-7}
1350	3,456	1.27	1.894×10^{-5}	1.881×10^{-6}	1.330×10^{-6}
1369	10,104	5.39	2.462×10^{-5}	2.462×10^{-6}	1.741×10^{-6}
1380	7,872	8.53	5.001×10^{-5}	5.021×10^{-6}	3.550×10^{-6}
1390	3,606	3.13	4.474×10^{-5}	4.509×10^{-6}	3.188×10^{-6}
1390	7,098	4.77	3.464×10^{-5}	3.491×10^{-6}	2.468×10^{-6}
1449	5,349	10.70	9.231×10^{-5}	9.499×10^{-6}	6.717×10^{-6}
1449[a]	5,349	11.60	1.001×10^{-4}	1.030×10^{-5}	7.280×10^{-6}
1476	4,555	13.43	1.520×10^{-4}	1.587×10^{-5}	1.116×10^{-5}
1490	1,818	8.39	2.374×10^{-4}	2.503×10^{-5}	1.770×10^{-5}
1490	3,564	13.22	1.917×10^{-4}	2.000×10^{-5}	1.415×10^{-5}
1497	3,446	18.40	2.752×10^{-4}	2.875×10^{-5}	2.033×10^{-5}
1497[a]	3,446	18.40	2.752×10^{-4}	2.875×10^{-5}	2.033×10^{-5}
1510	2,852	22.35	4.050×10^{-4}	4.254×10^{-5}	3.008×10^{-5}
1540	1,818	21.70	6.153×10^{-4}	6.526×10^{-5}	4.615×10^{-5}
1550	1,630	21.87	6.916×10^{-4}	7.360×10^{-5}	5.204×10^{-5}
1569	1,684	21.05	6.443×10^{-4}	6.900×10^{-5}	4.879×10^{-5}
1569[a]	1,684	25.62	7.020×10^{-4}	7.517×10^{-5}	5.316×10^{-5}
1631	769	31.79	2.131×10^{-3}	2.310×10^{-4}	1.634×10^{-4}
1642	875	47.47	2.795×10^{-3}	3.050×10^{-4}	2.157×10^{-4}
1642[a]	875	46.74	2.465×10^{-3}	2.700×10^{-4}	1.909×10^{-4}

[a] Determined by deposition on a platinum target.

vapor pressures calculated from equation (3) are listed, assuming that the molecular species in the vapor phase is either pure B_2O_3 or pure B_4O_6. The data are also plotted in Fig. 1 as B_2O_3.
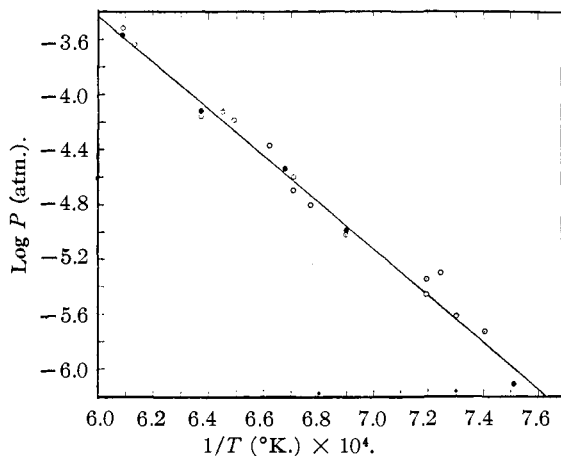

Fig. 1.—Vapor pressure of B_2O_3.

The slope of the log p vs. $1/T$ plot shown in the graph, yields a value of 77.6 kcal. as the mean value of the heat of evaporation of boric oxide over the temperature range 1330 to 1640°K.

Least squares fitting of the data to the Clausius–Clapeyron equation for the B_2O_3 molecule yields the expression

$$\log p \text{ (atm.)} = -(77600/4.575T) + 6.742 \quad (4)$$

and for the B_4O_6 molecule, the expression

$$\log p \text{ (atm.)} = -(77600/4.5757T) + 6.591 \quad (5)$$

Summary

The vapor pressure of boric oxide has been determined by measuring the rate of effusion through an orifice in a platinum Knudsen cell.

Experiments show that boric oxide is not decomposed into non-condensable products in the temperature range 1300 to 1650°K.

Since it is not known whether the molecular species in the vapor is B_2O_3 or B_4O_6, the vapor pressures are computed from the effusion data assuming the possibility of either structure.

The heat of evaporation as determined by application of the Clausius–Clapeyron equation is 77.6 kcal.

Spectroscopic Investigation of the Reaction between Aluminum and Aluminum Chloride

BY L. M. FOSTER, ALLEN S. RUSSELL AND C. NORMAN COCHRAN

Several proposals to produce or purify aluminum involve the "catalytic distillation" of the material from a charge of impure metal or aluminum bearing alloy in the presence of an aluminum halide. In an early process described by Willmore,[1] the aluminum bearing material was admixed or briquetted with aluminum fluoride and the mass was heated in vacuum, or an inert gas, to the vicinity of 1000° where appreciable distillation of pure aluminum was observed. The simultaneous sublimation of aluminum fluoride suggested that the aluminum and the halide had reacted at the high temperature to form a volatile lower fluoride of aluminum which on cooling disproportionated to metallic aluminum and aluminum trifluoride. Gross[2] proposed that the aluminum halide be volatilized in a separate boiler and passed over a bed of aluminum bearing material.

Fairly convincing evidence had been obtained in these Laboratories and elsewhere that the lower halide involved was the monohalide, AlX. An accurate determination of the composition of

the sublimed products obtained by heating an intimate mixture of aluminum fluoride and metallic aluminum was made by Klemm and Voss.[3] Repeated sublimation gave a product whose over-all composition closely approached that corresponding to AlF.

Perhaps the most convincing proof of the existence of aluminum monohalides in these reactions is the character of the absorption spectra of the reaction vapors. Rochester[4] had determined the absorption spectrum of AlF from thermal dissociation of aluminum fluoride, heated in a carbon resistance furnace to 1300–1700°. In 1940 Anderson,[5] in these Laboratories, observed the same partially developed spectrum of AlF from the heated vapors of briquetted aluminum, aluminum fluoride, magnesium fluoride and graphite, at about 1000°.

The spectrum of AlCl had been observed by excitation of aluminum chloride vapors in an electric discharge.[6] Analysis of the spectrum was

(1) C. B. Willmore, U. S. Patent 2,184,705 (1939).

(2) P. Gross, U. S. Patents 2,470,305 and 2,470,306 (1949) (see also Australian Patent Application 10,766 (1947) of the International Alloys Ltd.)

(3) W. Klemm and E. Voss, Z. anorg. allgem. Chem., 251, 233 (1943).

(4) G. D. Rochester, Phys. Rev., 56, 305 (1939).

(5) S. Anderson, unpublished work.

(6) W. Jevons, Proc. Roy. Soc. (London), A106, 174 (1924).