STUDIES ON THE PROPERTIES OF DIASPORE(1) AND BAUXITE.

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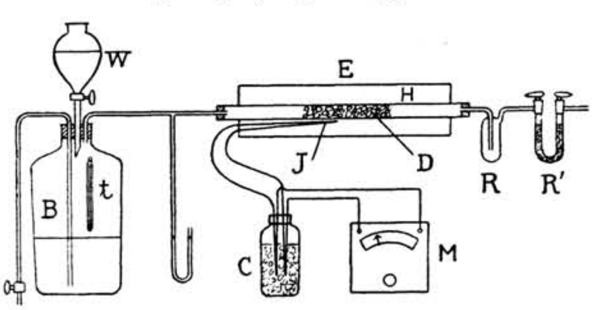
Both of the minerals, diaspore and bauxite, can be decomposed to alumina and water by heating. But no investigation regarding vapour pressures of decomposition at various temperatures and heats of decomposition as well has yet been made. In order to determine the vapour pressures of decomposition of these minerals, the following experiments were carried out by employing an apparatus based on the dynamical method.



W: funnel
B: bottle of large capacity
t: thermometer
E: electric furnace
H: hard glass tube
D: powdered diaspore
J: thermo-junction
C: cold junction
M: millivoltmeter
R: receiver
R′: $CaCl_2$ tube

Fig. 1.

As soon as the temperature of the powdered diaspore or bauxite which have been packed in the tube H becomes constant (T in absolute scale), two receivers R and R′ are attached to the one end of the tube H and a certain quantity of water is allowed to drop down from the funnel W into the bottle B in such a slow velocity that the air replaced by the dropping water flows out, practically maintaining the equilibrium with the powdered material. After a definite quantity of water (v c.c.) was dropped, the water collected in R and R′ is weighed (g gr.). Room temperature (t°C) and barometric pressure (P mm. Hg.) are also observed. Then the vapour pressure of decomposition (π in mm. Hg.) at T can easily be calculated from these observed values.

The volume in c.c. of dry air passed at the temperature t°C. and under P mm. pressure is expressed by $\frac{(P-p)v}{P}$, where p denotes the vapour tension of water at t°C. If n be the number of gram molecules of g gr. of water

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(1) The more detailed report is found in *Bulletin of the Institute of Physical and Chemical Research* (in Japanese), 5 (1926), 17.

and w the volume of g gr. of water vapour at $t°$ and under P mm. pressure, then

$$n=\frac{g}{18.016} \quad \cdots\cdots(1)$$

and

$$Pw=nR(273+t) \quad \cdots\cdots(2)$$

Hence

$$w=\frac{gR(273+t)}{18.016\,P} \quad \cdots\cdots(3)$$

The total volume V is equal to, at $t°$ and under P mm., the sum of the volume of the dry air passed and that of the water vapour, thus

$$V=\frac{(P-p)v}{P}+w \quad \cdots\cdots(4)$$

And there is the relation

$$\frac{\pi}{760}=\frac{w}{V} \quad \cdots\cdots(5)$$

So we have

$$\pi=\frac{760\,w}{\dfrac{(P-p)v}{P}+w}=\frac{760\times 3464\,g(273+t)}{(P-p)v+3464\,g(273+t)} \quad \cdots\cdots(6)$$

where 3464 is the numerical value of the constant R/18.016. As P, t, v and g are experimentally measurable values and p can be known from some table, the value of vapour pressure (π) at T can be calculated by equation (6).

Materials. The composition of diaspore used for the experiments⁽¹⁾ is expressed as AlO(OH) from the result of X-ray analysis by J. Böhm.⁽²⁾ The formula of bauxite will be expressed as $Al_2O_3 \cdot 2H_2O$ or $Al_2O(OH)_4$ as can be seen from Table 1, which has been obtained by authors.

TABLE 1.

Analysis of bauxite.

	SiO_2	Al_2O_3	Fe_2O_3	H_2O	Sum
Weight percentage.	5.4	62.0	10.7	22.0	100.1
Ratio of no. of gram mol.	1.335	9.06	1.00	18.2	

Decomposition Pressures of Diaspore and Bauxite. Experimental data and the calculated values therefrom of vapour pressures of diaspore and bauxite are shown in Tables 2 and 3.

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(1) The diaspore from Kanakura mine at Nagano province, Japan.

(2) J. Böhm, *Z. anorg. Chem.*, **149** (1925), 203.

TABLE 2. Diaspore.

Vol. of water dropped (v) c.c.	Barom. press. (P) mm. Hg.	Room temp. (t) °C.	Wt. of water collected (g) gr.	Vap. press. of diaspore at T (π) mm. Hg.	$\log \pi$	Abs. temp. (T)	$1/T \times 10^6$
750	771	19.5	0.0211	27.7	1.436	698	1432
300	752	27	0.0330	103.0	2.0128	721	1387
750	771	19.5	0.0610	74.7	1.873	723	1383
3500	761	20	0.38	98.2	1.992	728	1374
500	770.7	19.5	0.1616	229.7	2.361	743	1346
1000	761	18.5	0.42	275.5	2.440	746	1341
500	770.7	19.5	0.3788	384	2.584	758	1320
250	752	27	0.2731	463	2.666	759	1317
200	752	27	0.5837	613	2.788	768	1301
200	752	27	0.9015	658	2.818	772	1295
180	761.3	19.5	1.31	690	2.839	773	1294
500	761	20	2.04	645	2.810	773	1294
——	760	——	——	760	2.881	775.5	1290

TABLE 3. Bauxite.

Vol. of water dropped (v) c.c.	Barom. press. (P) mm. Hg.	Room temp. (t) °C.	Wt. of water collected (g) gr.	Vap. press. of bauxite at T (π) mm. Hg.	$\log \pi$	Abs. temp. (T)	$1/T \times 10^5$
700	758	21.5	0.1180	146	2.1644	503	199
300	765	20	0.0701	182	2.2601	517	194
400	746	27.5	0.1132	220	2.3424	526	190
400	746	27.5	0.1550	274	2.4378	546	183
300	753.5	29.2	0.1957	370	2.5682	548	182
200	761	18	0.5762	606	2.7825	570	175
450	755	21.5	0.9715	569	2.7551	573	174.5
300	746	27.5	0.6002	565	2.7520	577	173.5
200	760	22.5	0.3010	611	2.7860	581	172
300	755	21.5	2.0801	689	2.8382	598	167
200	746	27.5	1.5740	696	2.8426	604	165.5
300	753.5	29.2	2.2052	697	2.8432	606	165
300	754.5	27.5	0.1961	367	2.5647	628	159
300	746	28.8	0.1151	272	2.4346	631	158.5
200	756	27.0	0.0775	271	2.4330	648	154
200	754.5	27.5	0.2362	479	2.6803	655	153
300	746	28.8	0.1778	350	2.5441	656	152.5
200	756	27.0	0.2720	500	2.6990	677	148
200	746	28.8	0.2282	475	2.6767	690	145
200	754.5	27.5	0.3857	558	2.7466	690	145
200	756	27.0	0.3805	557	2.7459	701	143
200	754.5	27.5	0.1808	430	2.6336	720	139
200	756	27.0	0.2104	456	2.6590	723	138
200	746	28.8	0.2530	493	2.6928	730	137
200	756	27.0	0.4284	574	2.7589	756	132
200	746	28.8	0.4326	576	2.7604	791	126.5

In the case of diaspore, there exists a linear relation between $\log \pi$ and $1/T$ as shown in Fig. 2, and this agrees with the well known formula of Clapeyron and Clausius. From the curve of Fig. 2, the temperature at which the vapour pressure becomes **760 mm.** is found to be **502.5°C.** In the case of bauxite, there are found two distinct parts in the curve of $\log \pi$ and $1/T$ as shown in Fig. 3. The first part of the curve is straight while the second part is somewhat irregular. This requires a more precise experiment for it seems that this irregularity will be due to the slight deviation of equilibrium which may be occured between moist air and bauxite remained. It can hardly be considered that an impurities such as iron hydroxide give rise to such an irregularity, because the analysis of the bauxite shows that all of the water is exists in combination with alumina.

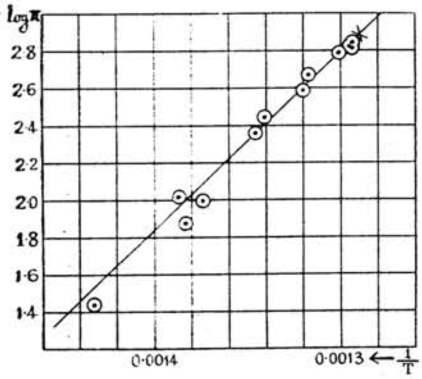

Fig. 2.

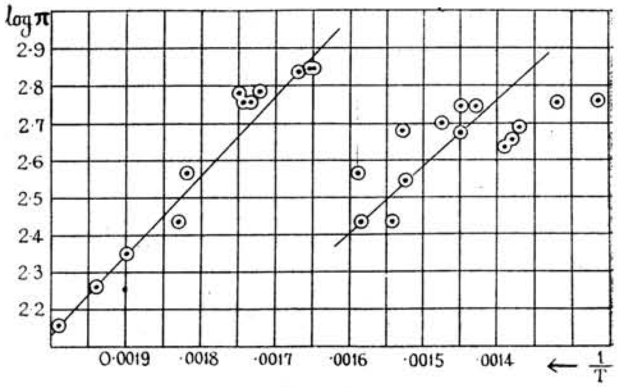

Fig. 3.

From this fact it may be concluded that the two parts of the curves came out from the decomposition of the hydrated alumina. The dehydrating decomposition in two stages was already found in some compounds having the water of crystallisation, but in hydroxide bauxite may be the first case ever known in such decomposition.

Heat of Decomposition. Diaspore and bauxite are decomposed by heating according to the following equations.

$$2AlO{\cdot}OH \text{ (or } Al_2O_3{\cdot}H_2O) \longrightarrow Al_2O_3 + H_2O - Q$$
$$Al_2O\,(OH)_4 \text{ (or } Al_2O_3{\cdot}2H_2O) \longrightarrow Al_2O_2\,(OH)_2 \text{ (or } Al_2O_3{\cdot}H_2O) + H_2O - Q_1$$
$$Al_2O_2\,(OH)_2 \text{ (or } Al_2O_3{\cdot}H_2O) \longrightarrow Al_2O_3 + H_2O - Q_2$$

The values of the heat of decomposition in these cases (Q, Q_1 and Q_2) can be calculated by the following equation using two pairs of experimental data.

$$\log \frac{\pi_2}{\pi_1} = 0.4343 \frac{Q}{1.985} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

The calculated values are shown in Table 4.

TABLE 4.

	log π	$1/T$	Temp.	Heat of decomp.
Diaspore	2.8451	0.001294	500	$Q = 42300$ cal./mol.
	2.3671	0.001346	470	
Bauxite	2.8382	0.001672	325	$Q_1 = 10100$,,
	2.2601	0.001934	244	
Bauxite	2.6767	0.001449	417	$Q_2 = 8100$,,
	2.4346	0.001585	358	

Specific Heat of Diaspore. Specific heat of diaspore was determined by an ordinary calorimetric method. This value is necessary to calculate the total energy required to decompose the diaspore in ordinary temperature. It is found from the results of experiment that the mean specific heat of diaspore, in calories, is expressed by the following empirical equation in the range from 100°C to 400°C.

$$c = 0.2085 + 0.000127\,t.$$

Summary.

(1) It was found that the vapour pressures of decomposition of diaspore could be calculated by the following equation in the range from 400° to 500°.

$$\mathrm{Log}\,\pi = 14.820 - 9255.1/T.$$

(2) In the case of bauxite, the curve of decomposition pressure was found to be consisted of two parts. The first part can be expressed by the equation

$$\log \pi = 6.5277 - 2206.5/T,$$

in the range from 200° to 340°, and the second roughly by

$$\log \pi = 5.2566 - 1780/T$$

in the range from 350° to 450°.

(3) The heats of decomposition of diaspore and bauxite were calculated by the integrated equation of Clapeyron and Clausius.

(4) The specific heat of diaspore was determined by the calorimetric investigation and found to be

$$c = 0.2085 + 0.000127\,t.$$

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