VAPOUR PRESSURE OF RHENIUM HEPTOXIDE, VAPOUR PRESSURE AND DISSOCIATION PRESSURE OF RHENIUM OCTOXIDE.

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As a rule the elements of the 7th group stand in closer relationship to the elements of the 8th group than to those of the 6th group. Rhenium also resembles osmium in many points. For example its oxides, rhenium heptoxide and rhenium octoxide, are volatile without decomposition as is the case in osmium tetroxide, while the oxides of tungsten are not so. In 1929 I. and W. Noddack published their laborious work on these two rhenium oxides. The present author reinvestigated the properties of these substances and found that some of them do not agree with their description. It has been found that rhenium heptoxide does not decompose at its boiling points, 363°C., and so its vapour pressure can be measured. It is true that rhenium octoxide already slightly dissociates into rhenium heptoxide and oxygen at ordinary temperature, but the partial pressure of oxygen is very small even at 220°C., and the vapour pressure of rhenium octoxide can therefore be measured, although accurate values can not be expected.

Experimental Part.

Considering the fact that the result of I. and W. Noddack was obtained by using only one gr. of the metal soon after its discovery, it may be somewhat uncertain. The author found that the results of the preliminary experiments did not well agree with their results as following.

1. The oxides prepared by Noddacks may be not perfectly anhydrous. As rhenium octoxide and heptoxide are both very hygroscopic according to the author's experiments, it would be insufficient to dry the oxygen by merely passing one sulphuric acid bottle, one calcium chloride tube and one phosphorus pentoxide tube as they used in their experiments. Noddacks found that the heptoxide melts at 220°C., a temperature which is very much lower than the author's value, 298°C. This fact indicates that the lower value obtained by them is probably due to the presence of water resulting from insufficient drying of the gas.

(1) I. and W. Noddack. Z. Anorg. Chem. 181, 1-37, (1929).

2. They stated that heptoxide easily changes to octoxide by heating in oxygen. The author found that this is not the case, the reaction $2Re_2O_8 \rightarrow 2Re_2O_7 + O_2$ being almost irreversible.

3. According to Noddacks heptoxide changes to blue lower oxide by heating above 300°C. in a vacuum. It does not, however, decompose at least at its boiling point, 363°C., in the author's experiment.

4. They described in page 11 that crude rhenium heptoxide prepared must be heated in N_2 at 170°C. for 10 minutes in order to convert mixed octoxide to heptoxide. For completing the reaction, however, it has been found desirable to keep in a reduced pressure at 180–190°C. for one or two hours.

5. They stated in page 13 that rhenium heptoxide have a large vapour tension even at 150°C., but the author found its tension at 150°C., was only 3.0 mm.

Vapour Pressure of Rhenium Heptoxide. *Dry of Oxygen.* Oxygen from a bomb was passed into one sulphuric acid washer, two calcium chloride tubes, 3 cm. in diameter and 80 cm. in length, and one empty 2 liter flask and then four phosphorus pentoxide tubes of the same size as the calcium chloride tubes. A spring manometer, one phosphorus pentoxide tube, and four sulphuric acid washers were next connected. All of these connections were made in glass. Velocity of oxygen was 30 c.c. or 40 c.c. per minute.

Apparatus and Preparation. The apparatus was shown in Fig. 1. After cleaning with hot HNO_3 solution of $K_2Cr_2O_7$, the entire system was evacuated to 0.0001 mm. for several hours. The sensibility of this spring manometer was 0.01 mm. 2 Gr. of rhenium was taken into a porcelain boat. At the beginning of heating, a small quantity of Re_2O_8

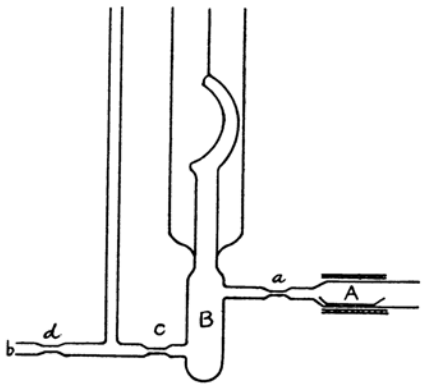

Fig. 1.

was formed, which adhered to the wall of the apparatus, but soon changed to yellow Re_2O_7 on heating with flame. When all of rhenium had sublimated, the apparatus was sealed at a and d. In order to convert octoxide, which might still have remained, into rhenium heptoxide, it was heated at 210°C. for 10 minutes and then at 190°C. for 2 hours, the manometer being immersed in a bath of liquid paraffine and evacuated to 0.0001 mm. It was then sealed at c. The detail of the method of the measurement using a spring manometer was already described in the previously published paper on osmium tetroxide.[2] The electric furnace used for heating was 15 cm. in internal diameter and 50 cm. in depth. It was 13 cm. long from the bottom of B to the top of the spring. The mercury reservoir of the thermometer was placed at the middle of this interval. The temperature fluctuation of the electric furnace was about ±2.0°C. in this interval. Three thermometers were used. Two of these had the range of 100–200°C. and of 200–300°C. respectively, and were graduated into hundredths of a degree. The other had the range of 300–360°C. and was graduated into tenths of a degree. Temperature was so regulated as to be within ±0.3°C. by adjusting the current by hand for about four hours. After each measurement temperature was lowered to the ordinary temperature, and no increase in pressure was observed. This shows that any dissociation did not occur. For reading pressure a cathetometer was used and necessary corrections were added to the data. The data up to 1/10 mm. or

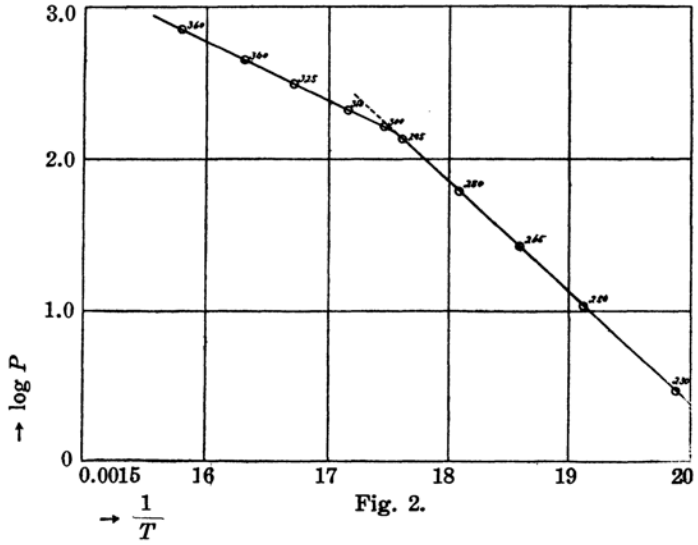

Fig. 2.

(2) This Bulletin, **6** (1931), 302–317.

1 mm. were adopted. Above 340°C. the needle moved a little left or right owing to irregularity of temperature. The vapour pressure soon reached its equilibrium. The relations of $\log P$ and $1/T$ is linear as shown in Fig. 2 and expressed by following August's formulas.

Sublimation:

$$\log P = -7217.95/T + 14.83866.$$

Vaporization:

$$\log P = -3920.13/T + 9.04668.$$

Table 1.

t°C	T°abs.	$1/T$	P mm.	$\log P$
230	503	0.0019881	3.0	0.47712
250	523	0.0019120	10.9	1.03473
265	538	0.0018587	26.5	1.42325
280	553	0.0018083	61.2	1.78675
295	568	0.0017606	135	2.13033
300	573	0.0017452	160	2.20412
310	583	0.0017153	210	2.32222
325	598	0.0016722	312	2.49415
340	613	0.0016313	449	2.65225
360	633	0.0015798	711	2.85187

Melting Point and Boiling Point. The melting point and the boiling point obtained from Fig. 2 are 297°C. and 363°C. respectively. The observed melting point was 297°C.

Heat of Sublimation. The mean heat of sublimation between 230°C. and 295°C. obtained by the above formula is 33050 cal. The mean heats of sublimation in more limited ranges are as follows.

Temperature range	Mean temperature	ΔH (cal.)
230—250	240	33710
250—265	257.5	33140
265—280	272.5	33020
280—295	287.5	32980

Extrapolating to 297°C. we obtain 32910 cal., which is the heat of sublimation at the melting point.

Heat of vaporization. The mean heat of vaporization between 300°C. and 360°C. obtained from the above formula is 17950 cal. The mean heats of vaporization in more limited ranges are as follows.

Temperature range	Mean temperature	ΔH (cal.)
300—310	305	18080
310—325	317.5	18260
325—340	332.5	17700
340—360	350	17750

The heats of vaporization at the melting point and at the boiling point obtained by extrapolation are 18300 cal. and 17400 cal. respectively.

Heat of fusion. 32910–18300 = 14610 cal.

Trouton's constant

$$\Delta H/T = 17400/636 = 27.4$$

According to vapour density measurement of Noddack, rhenium heptoxide has a composition of Re_2O_7 at 502°C.

Vapour Pressure and Dissociation Pressure of Rhenium Octoxide. *Apparatus and Preparation.* Oxygen was dried in the same way as in the case of heptoxide. Velocity of the gas was 100 c.c. or 110 c.c. per minute. The apparatus used was shown in Fig. 3. A, a spiral tube which was made by coiling twelve times a tube of 6 mm. in diameter, was 5.5 cm. in inner diameter and 9 cm. in height. After the apparatus was cleaned carefully, it was dried thoroughly by heating in a vacuum of 0.0001 mm. 2 Gr. of rhenium was taken. At the beginning of the reaction, rhenium octoxide was so rapidly formed that it escaped through four sulphuric acid washers, but with the scintering of the surface of rhenium its production became less and less until rhenium heptoxide began to deposit near the boat. After all of rhenium sublimated, heptoxide was driven into the spiral. Rhenium octoxide, which is white when pure, owing to the presence of rhenium heptoxide, adhered to the inside of the spiral in somewhat yellow fine powder. The apparatus was then sealed at a and b and kept in a vacuum of 0.0001 mm. at ordinary temperature for ten minutes after which it was sealed at c.

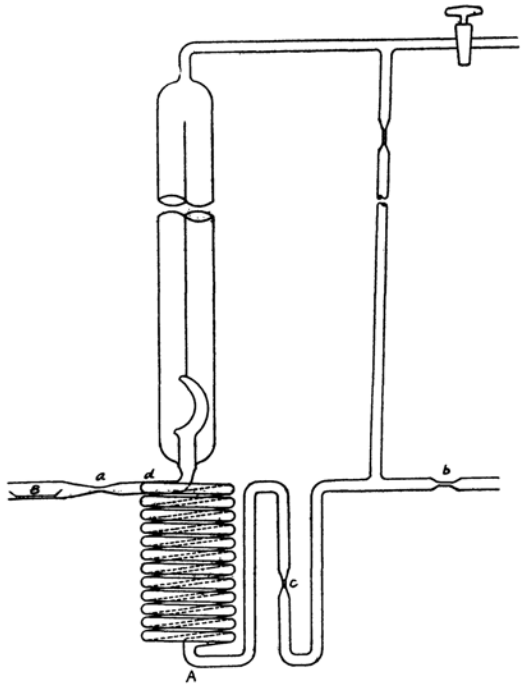

Fig. 3

Dissociation Pressure of Octoxide. For heating, the electric furnace previously described was used. The distance from the bottom of A to the top of the spring was 21 cm. The fluctuation of temperature was ±3°C. On heating at 100°C. pressure rose to 10.8 mm. after about 2 hours from the start and it remained constant for four hours. After cooling it became 3.24 mm. at 14.5°C., which did not change until the next day. The time required to reach the equilibrium pressure became more rapid with rise of temperature. Temperature was maintained constant for four hours in each experiment. Pressure was measured up to 220°C. The results are shown in Table 2. As these increases in pressure did not change during several days, it can be assumed that the reaction $2Re_2O_8 \rightarrow 2Re_2O_7 + O_2$ is perfectly irreversible at ordinary temperature. It was assumed that this increase in pressure indicates the dissociation pressures at each temperature, and the equilibrium pressures were calculated by adding necessary corrections. The values obtained in this manner are shown in the 3rd column in Table 2. The linear relations of $\log P$ and $1/T$ are shown in Fig. 4.

Table 2.

t°C	$1/T$	O_2 press. (mm.)	log P
100	0.0026810	4.19	0.62221
120	25445	4.73	0.67486
140	24213	5.39	0.73159
160	23095	6.01	0.77887
180	22075	6.63	0.82151
200	21142	7.30	0.86332
220	20284	7.84	0.89432

$$\log P = -416.08/T + 1.73877$$

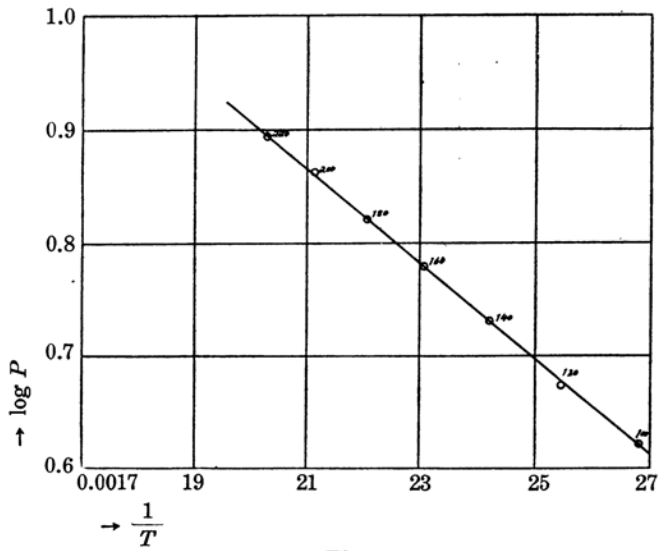

Fig. 4.

Vapour Pressure of Octoxide. The values obtained by substracting the dissociation pressure from the observed pressures were adopted as the vapour pressure of rhenium octoxide as shown in Table 3. In the apparatus used for the determination of dissociation pressure (Fig. 3) the greater part of the heptoxide was in d, and the octoxide, yellowish white in colour due to the presence of a small quantity of heptoxide, was spread all over the spiral. There was nothing in the spring. After heating to 100°C. a small quantity of white sublimate of rhenium octoxide

was observed in the spring. The quantity of this sublimate increased gradually until the temperature at 220°C. and the inside of the spring was covered with it. This pure white sublimate always existed at each temperature of measurement. It shows that there was an excess of octoxide in the spring at each time of the experiment. The reason why rhenium octoxide on cooling should have assembled in the spring may be due to its being surrounded by the outer tube of reduced pressure or inhomogeneity of temperature of the electric furnace. It was unnecessary to consider the influence of rhenium heptoxide, as octoxide was in pure state. The linear relations between the logarithm

Table 3.

t°C	$1/T$	P mm.	log P
100	0.0026810	6.6	0.81954
120	25445	11.7	1.06819
140	24213	18.7	1.27184
160	23095	25.6	1.40824
180	22075	31.8	1.50243
200	21142	39.2	1.59329
220	20284	46.6	1.66839

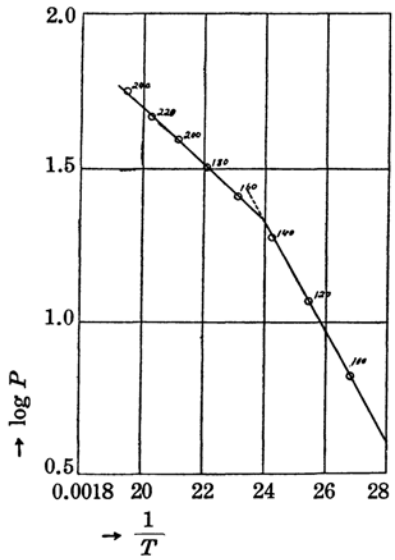

Fig. 5.

of the vapour pressure determined as mentioned above and $1/T$ are shown in Fig. 5. There is a knick at 145°C. It must be the melting point. But this relation can no longer exist above 240°C., owing to the sublimation of heptoxide. As this sublimated heptoxide dissolves in the melted octoxide in the spring it is not possible to calculate the vapour pressure of Re_2O_8.

Sublimation:

$$\log P = -1738.74/T + 5.48512$$

Vaporization:

$$\log P = -924.18/T + 3.54384$$

Heat of Sublimation. The mean heat of sublimation between 100°C. and 140°C. is 7960 cal. Those in more limited ranges are as follows.

Temperature range	Mean temperature	ΔH
100—120	110	8340
100—140	120	7970
120—140	130	7570

Extrapolating to 145°C. 7000 cal. is obtained.

Heat of Vaporization. The mean heat of vaporization between 160° and 220°C. is 4230 cal. Those in more limited temperature ranges are as follows.

Temperature range	Mean temperature	ΔH
160—200	180	4340
180—200	200	4240
160—220	180	4230

The mean heat of vaporization at the melting point obtained by extrapolation is 4500 cal.

Heat of fusion. 7000—4500 = 2500 cal.

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