4. It is shown that the distribution ratio, when calculated on a basis of unchanging solvents, increases sharply with the concentration of acid, even after corrections for dissociation of acid and association of water.

5. It is shown to be probable that the average state of association of water dissolved in ether is somewhat less than two.

CAMBRIDGE, MASSACHUSETTS.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY.]

CHEMICAL REACTIONS AT LOW PRESSURES. IV. THE CLEAN-UP OF NITROGEN BY A HEATED MOLYBDENUM FILAMENT.[1]

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In previous papers[2] it has been shown that a tungsten filament heated in a fairly high vacuum to a temperature at which vaporization occurs, causes a disappearance or clean-up of practically all the common gases except the inert gases such as argon. This phenomena has often been used in this laboratory to obtain a particularly high vacuum.[3]

It is well known that molybdenum at its melting point evaporates very rapidly, in fact much more rapidly than tungsten at its melting point. If then molybdenum vapor shows the same tendency as tungsten vapor to react with gases, the use of a heated molybdenum filament would seem to offer a still more promising method of obtaining a high vacuum. With this end in view, experiments were undertaken to study the clean-up of nitrogen by a heated molybdenum filament. It was soon found that this metal was much less suitable than tungsten for the purpose. Whereas with tungsten the clean-up is quite rapid at any temperature sufficiently high to produce perceptible volatilization of the metal, with molybdenum enough material may evaporate to darken the bulb considerably before any clean-up is observed. It was found, however, by raising the temperature of the filament still higher that rapid clean-up does occur, and that just as in the case of tungsten, the *rate of clean-up is independent of the pressure* of the gas. This fact seemed very peculiar, for the explanation that had previously been given for the case of tungsten, namely that the nitrogen combines quantitatively with the metallic vapor as fast as it is produced, certainly does not apply here.

The resistance of the filament in the experiments with molybdenum

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[1] Most of the experimental work described in this paper was carried out during 1913 and 1914. A very brief summary of the results was published in THIS JOURNAL, **37**, 1157 (1915).

[2] THIS JOURNAL, **34**, 1310 (1912); **35**, 105, 931 (1913); *Trans. Amer. Inst. Elec. Eng.*, **32**, 1895 (1913); *Z. anorg. Chem.*, **85**, 261 (1914).

[3] See for example Langmuir, *Physik. Z.*, **15**, 519 (1914).

increased very rapidly during the clean-up of the nitrogen. A simple calculation showed that about 15 atoms of molybdenum evaporated to one molecule of nitrogen cleaned up, whereas with tungsten the ratio was one atom of tungsten to one molecule of nitrogen.

Molybdenum, like tungsten, undoubtedly gives a monatomic vapor.[1] At the low pressure used in these experiments the molybdenum vapor must have diffused to the walls of the bulb before the atoms could have collided with each other so as to form larger aggregates. It can be readily shown from the principles of the kinetic theory that the number of collisions n which a gas molecule makes while travelling between two points separated by the distance L is approximately equal to

$$n = (L/\lambda)^2 \qquad (1)$$

where λ is the mean free path of the molecules. The pressure used in these experiments was usually not over 10 bars,[2] so that the value of λ must have been about one cm. Placing $L = 3$ cm., the diameter of the bulb, we find from (1) that the molybdenum atoms made about 9 collisions with nitrogen molecules before striking the bulb.

The partial pressure of molybdenum vapor must have been very small. The maximum pressure may be roughly estimated from the diffusion coefficient and the known rate at which the molybdenum was diffusing through the nitrogen. The greatest rate of evaporation was 4×10^{-6} g. per second. By comparison with other substances of similar molecular volume and molecular weight it is safe to conclude that the diffusion coefficient of molybdenum vapor through nitrogen at atmospheric pressure would not be less than 0.05 cm^2. per sec. From these data and the dimensions of the bulb, calculation shows that the partial vapor pressure of molybdenum in the bulb about one cm. from the filament could not have exceeded about 0.001 bar. This is 10,000 times less than the pressure of the nitrogen, so that a molybdenum atom leaving the filament has about 10,000 times greater chance of colliding with a nitrogen molecule than with another molybdenum atom. In other words, even at the highest pressures used, only about one out of a thousand molybdenum atoms could have collided with another such atom before striking the bulb. These considerations indicate that the nitrogen molecules cannot combine with 15 molybdenum atoms, but that only one out of about 15 molybdenum atoms combines with nitrogen to form a stable compound, presumably MoN_2.

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[1] Experiments made in 1915 have shown that when molybdenum is vaporized in carbon monoxide at low pressure each molybdenum atom combines with one molecule of carbon monoxide very much as tungsten combines with nitrogen. This is good experimental evidence that molybdenum vapor is monatomic.

[2] The bar is the C. G. S. unit of pressure, one dyne per sq. cm. It is very nearly equal to one-millionth of an atmosphere.

If this reaction can occur during any collision between a molybdenum atom and a nitrogen molecule the rate of clean-up should vary with the pressure. Since the mean free path is inversely proportional to the pressure, we see from Equation 1 that the number of collisions which a molybdenum atom makes before reaching the bulb is proportional to the square of the pressure. If each collision brought an equal chance of reaction, the rate of clean-up of nitrogen should be proportional to the square of the pressure, whereas experiment shows that down to pressures of about one bar the rate is entirely independent of the pressure. The fact that the rate is constant down to such low pressures thus indicates that the reaction occurs during the first collisions between the molybdenum atoms and the nitrogen molecules.

The question arises: what are the differences in the conditions between the first and subsequent collisions, which might make the reaction possible only during the first collision? One answer might evidently be that the velocity of the molybdenum atom fresh from the filament is higher than that of atoms which have already struck nitrogen molecules—that after the first collision the velocity has been reduced to so low a value that the reaction does not occur. On this hypothesis we should conclude that of all the molybdenum atoms leaving the filament, those with the highest velocities would be the ones which would react with the nitrogen; the ratio between the number of molybdenum and nitrogen molecules would thus vary with the temperature and would approach closer to unity when the filament temperature and the bulb temperature were raised. The velocity that must be considered in this reaction is the relative velocity of the molybdenum atoms with respect to the nitrogen molecules. Because of the low pressures the temperature of the nitrogen and the molybdenum vapor are not necessarily the same when they react; in fact the velocity of the nitrogen is determined by the bulb temperature while that of the molybdenum depends on the filament temperature. The relative velocity of the molybdenum atoms and nitrogen molecules can thus be increased either by raising the bulb temperature or the filament temperature.

To test out the above hypothesis that the higher relative velocities favor the reaction, some experiments were undertaken to measure the rate of clean-up while the bulb was maintained at 270°. The expectation was that the rate would be much increased. It was found, however, that the effect was in the opposite direction, the heating of the bulb causing the rate to fall to about $^1/_6$ of its previous value. This unexpected result indicates that the high velocity of the atoms direct from the filament is not a favorable condition for the reaction. What is it then which determines what fraction of the atoms reacts with the nitrogen, and if low relative velocity favors the reaction why do not the atoms react with the nitrogen even more easily on the subsequent collisions? To answer these questions it was decided to investigate the effect of bulb temperature and filament temperature in more detail and to find the relation between the rate of clean-up and the rate of evaporation under various conditions. In the preliminary experiment there was no provision for cooling the bulb in liquid air so a couple of special lamps were made up for this purpose.

In order to determine accurately the rate of evaporation of molybdenum at different temperatures some experiments were undertaken to measure the rate of loss of weight of filaments when run in a high vacuum at various temperatures. The results of these measurements have already been published.[1] It was found that the rate of evaporation m in vacuum (in g. per sq. cm. per second) could be expressed by the equation

$$\log_{10} m = 17.110 - (38600/T) - 1.76 \log T. \qquad (2)$$

By analogy with the clean-up of nitrogen by tungsten we may now calculate the rate of clean-up of nitrogen by molybdenum on the assumption that nitrogen combines with all the molybdenum to form a compound MoN_2. This evidently does not correspond to the facts but it enables us to determine the maximum theoretical rate of clean-up. One g. of molybdenum would combine with 250 cc. N_2 at 20° to form MoN_2. Hence the maximum theoretical rate of clean-up R_c would be $15.0 \times 10^6 \times m$ in cu. mm., per minute per sq. cm. From (2) we thus have R_c in cu. mm. per min. per sq. cm.

$$\log_{10} R_c = 24.286 - (38600/T) - 1.76 \log T. \qquad (3)$$

In order to compare the observed rates of clean-up R_o with those calculated by the above formula we shall have occasion to tabulate R_o/R_c. This ratio which we shall call ϵ denotes the fraction of the molybdenum atoms leaving the filament, which combine with the nitrogen to form MoN_2.

Experiments on the Clean-up of Nitrogen by Molybdenum Filaments.

The general plan adopted in the experiments was similar to that employed in the study of the clean-up of nitrogen by a tungsten filament. A lamp bulb containing two separate single-loop filaments was sealed onto a vacuum system, consisting of Töpler pump, McLeod gage, and apparatus for quantitatively analyzing small amounts of gas. Between the lamp and the rest of the system was a trap which was kept continually immersed in liquid air and which thus insured absence of mercury vapor and water vapor in the lamp. After exhaustion, the lamp was heated to 360° for an hour to drive moisture and carbon dioxide off the glass. The filament was aged for half an hour at high temperature. The lamp was then ready for an experiment on the clean-up of nitrogen.

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[1] Langmuir and Mackay, *Phys. Rev.*, 4, 377 (1914).

A definite pressure of nitrogen was introduced, usually about 5 to 15 bars, and a gage reading taken. The filament was then heated to the chosen temperature and readings on the gage were taken every minute. As the filament gradually evaporated the temperature was maintained approximately constant by keeping $v\,\sqrt[3]{A}$ constant[1] (v = volts, A = amperes).

Temperature of the Filaments.—The temperatures were found by the method, used in determining the rate of evaporation,[2] based upon the determination of the total candle-power per sq. cm. radiated by the filament. The emissivity of the molybdenum was taken to be 3% greater than that of tungsten. A careful comparison of this temperature scale with that based on the Holborn-Kurlbaum pyrometer was subsequently made,[3] and they were found to lie within 10° of each other over the range 1900–2500° K., which includes the range used in the present experiments. The formula actually used for determining the temperature of the molybdenum filaments is

$$T = 11230/(7.041 - \log_{10} H) \qquad (4)$$

where H is the intrinsic brilliancy of the molybdenum filament in international candles per sq. cm. of projected area. In the experiments on the rate of evaporation the candle-power per unit length of filament was directly determined and the temperature derived by the above formula; in this way a relation between current and temperature was obtained. The experiments on the rate of clean-up of nitrogen were made with pieces of wire from the same spool. Therefore, the temperature was determined from the *current* using the relation already obtained. From these temperatures a curve was prepared giving the relation between $v\,\sqrt[3]{A}$ and the temperature, whence the temperatures during the various experiments were determined.

Filaments and Bulbs.—Three separate lamps were used. In the preliminary experiment (Expt. 378) the bulb was about 6 cm. diameter and 10 cm. long and contained two loops of molybdenum wire of 0.0156 cm. diameter. Each loop consisted of 8.90 cm. of wire. The total surface of each loop was thus 0.436 sq. cm. The bulb of this lamp was sealed to the vacuum system by a tube of large diameter attached to the bottom of the lamp; it could therefore not conveniently be cooled by liquid air.

In both the second (Expt. 380) and the third (Expt. 381) experiments the bulb was made smaller and was connected to the system through a goose-neck tube attached to its upper part so that the whole bulb could

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[1] A discussion of this and other methods of determining temperatures and of holding them constant has been published. See Langmuir, *Phys. Rev.*, 7, 309 (1916).

[2] *Phys. Rev.*, 4, 380 (1914).

[3] Langmuir, *Ibid.*, 7, 325 (1916)

be placed in liquid air while still connected to the vacuum system. Some of the same wire as before was used for these filaments, but the length used for each loop was 7.45 cm., the surface thus being 0.365 sq. cm. per loop.

TABLE I.—EXPERIMENT 378.

Run.	T_F.	T_B.	t.	R_o.	R_C.	ϵ_o.	T_o.	ϵ_C.
1	2327	300	11	2.90	59	0.049	775	0.049
2	2260	300	8	1.62	20	0.081	760	0.061
3	2277	300	10	2.46	26.5	0.093	764	0.058
4	2110	300	48	0.13	1.37	0.095	727	0.102
5	2160	543	49	0.02	3.50	0.006	952	0.009
6	2168	300	14	0.25	4.02	0.062	740	0.082
7	2261	543	20	0.24	20.2	0.012	974	0.008
8	2200	300	29	0.65	7.1	0.092	747	0.074
9	2203	300	21	0.68	7.5	0.091	748	0.073
10	2204	300	22	0.73	7.7	0.095	748	0.073
11	2204	300	16	0.88	7.7	0.114	748	0.073
12	2186	300	14	0.74	5.6	0.132	744	0.077
13	2199	300	16	0.87	7.0	0.124.	747	0.074
14	2204	300	16	1.20	7.7	0.156	748	0.073
15	2230	300	20	1.71	12.0	0.143	753	0.067

Experiment 378.—A summary of the data obtained in this first or preliminary experiment is given in Table I. The first 3 runs were made with filament *a* and the remaining 12 runs with filament *b*. In the column headed T_F is given the temperature (absolute) of the filament during the run. This was maintained as nearly constant as possible by adjusting the current from time to a time to keep $v\,^3\sqrt{A}$ constant. The temperature of the bulb is given in the next column under T_B. The duration of the run in minutes is given under t. The observed rate of clean-up of nitrogen R_o is expressed in cu. mm. of nitrogen (at 20° C. and 760 mm. pressure) per minute, per sq. cm. of filament surface. The volume of nitrogen cleaned up was calculated from readings of the McLeod gage and the known volume of the apparatus; when the bulb was at temperatures other than room temperature it was assumed that the pressure of nitrogen in the bulb was equal to

$$p = p_g\sqrt{T_B/T_g}$$

where T_B is the temperature of the bulb, T_g that of the gage, and p_g is the pressure as indicated by the gage. At low pressures this relation must be used in calculating pressures and quantities of gas in systems having parts at different temperatures.[1] The column headed R_c contains the rates calculated from Equation 3, which gives the rate which would prevail if the molybdenum evaporates at the same rate as in a high vacuum and all the molybdenum vapor combines with nitrogen to form a compound MoN_2. The ratio of the observed to the calculated rates R_o/R_c

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[1] See Knudsen, *Ann. Phys.*, 31, 205 (1910).

is given under ϵ_0. The meaning of the data in the columns headed T_0 and ϵ_c will be explained later.

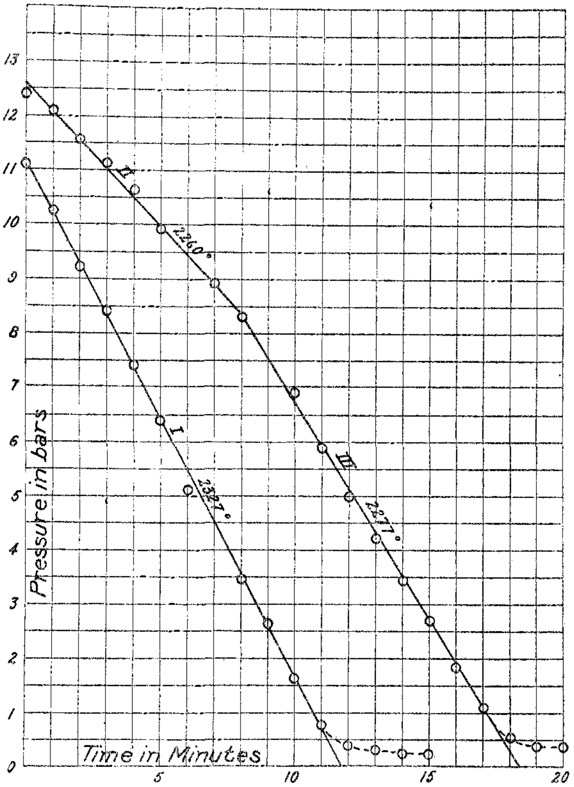

Fig. 1.

The first 3 runs showed distinctly that the rate of clean-up is independent of the pressure of nitrogen. Plots of these first runs are given in Fig. 1. It will be seen that while the pressure varies from 11 down to less than one bar the rate of clean-up remains unchanged. All the other runs of this as well as the later experiments gave plots that were characterized by the same straight line curve.

During these runs the changes in the "hot resistance" of the filament were recorded and from these the rates of evaporation were calculated and compared with those obtained from Equation 2.

Run.	T_F.	$10^6 m$ by (1).	$10^6 m$ by resistance.
1	2327	3.39	3.1
2	2260	1.32	1.8
3	2277	1.75	2.6

It is seen that the rates of evaporation found from these rough data are not greatly different from those found from the more accurate vacuum experiments. The agreement is sufficient to indicate that the rate of evaporation of the molybdenum is not materially decreased by the nitrogen and that the difference between R_0 and R_c is not due to a change in the rate of evaporation. In most of the other runs the rate of evaporation was also calculated from the resistance changes, but as the general results are similar to those already given they will not be discussed further.

Adsorption of Gases by the Deposit on the Bulb.—After the third run the bulb was heated to 324° C. for about an hour to see if the nitrogen which had been cleaned up was merely adsorbed by the finely divided molybdenum of the bulb and would be given up on heating. Until the bulb reached a temperature of about 200° no gas was given off, but on raising the temperature about 12 cu. mm. of gas was obtained (34 cu. mm. of N_2 had been cleaned up); subsequent analysis, however, showed that this gas was practically pure hydrogen.[1] On cooling the bulb to room temperature 9 cu. mm. of this hydrogen disappeared and of the remaining 3 cu. mm. all but 0.8 cu. mm. disappeared on applying a tuft of cotton dipped in liquid air to the outside of the bulb. On again heating the bulb (to 306°) all the hydrogen came off again and was pumped out. The bulb was then cooled to room temperature and 14.2 cu. mm. of nitrogen was admitted. Of this, 0.6 cu. mm. was immediately adsorbed by the deposit on the bulb. By applying liquid air as before to the bulb 13.3 cu. mm. of nitrogen was adsorbed leaving only 0.3 cu. mm. When the bulb warmed up again *all* of the nitrogen immediately returned. This nitrogen was then pumped out and 13.8 cu. mm. of hydrogen was admitted to the system. Within 15 minutes 7.7 cu. mm. of this had been taken up by the deposit on the bulb at room temperature (marked contrast to nitrogen). By pumping out the hydrogen 1.5 cu. mm. of this escaped again from the walls of the bulb. Evidently then hydrogen is dissolved at room temperature with comparative ease by the finely divided molybdenum, and reaches a certain equilibrium in which it is divided between the deposit and the space.

The hydrogen was again allowed to return to the system and the 1.5 cu. mm. was again taken up. The quantity of free hydrogen then remaining was 6.1 cu. mm. Of this only 2.6 cu. mm. was absorbed by cooling the bulb with liquid air.

The following summary of the results with nitrogen and hydrogen will make the behavior of these gases clearer:

Gas.	Initial quantity admitted.	Amount remaining.	
		At room temp.	At —180°.
N_2	14.2	13.6	0.3
H_2	13.8	6.1	3.5

In the case of nitrogen the phenomenon is clearly one of adsorption by a finely divided substance. Hydrogen, however, is not readily adsorbed, but at higher temperatures is apparently dissolved by the deposit. In both cases definite equilibrium is reached, but much more rapidly with nitrogen than with hydrogen.

An interesting case of solution or absorption of nitrogen in the deposit was observed after the fourth run. As a preliminary to the fifth run the bulb was heated to 306° after 16.7 cu. mm. of nitrogen had been admitted. When a temperature of about 240° was reached the nitrogen

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[1] This gas is usually obtained on heating a bulb in which a filament has been run at high temperature for a considerable time. See Langmuir, THIS JOURNAL, **34**, 1310 (1912); Freeman, *Ibid.*, **35**, 927 (1913).

began to disappear and in about 30 minutes, at 300°, 2.5 cu. mm. of nitrogen had been absorbed. To prevent further absorption the bulb was cooled to 270°, at which temperature the nitrogen practically ceased disappearing. This phenomenon will be discussed again in connection with Expt. 381.

In the fifth run of Expt. 378 the bulb was maintained at 270° and the rate of clean-up was extremely slow ($R_0 = 0.02$), only about 0.2 cu. mm. out of 14 disappearing in 49 minutes. This rate of clean-up is probably too low since a little hydrogen is usually evolved on heating a bulb containing a glowing filament and this evolution would partly mask the clean-up of the nitrogen. Although the bulb was also heated in the seventh run, this source of error was probably not serious since the rate of clean-up was much greater and the time of heating was shorter.

The next 3 runs (Nos. 8, 9, 10) were made for the purpose of studying the effect of pressure on the rate of clean-up. The pressures at the begining and end of each run were:

Run.	Initial pressure. Bars.	Final pressure Bars.
8	39.5	33.3
9	15.4	10.9
10	7.5	2.7

From Table I we see that the values of ϵ_0 for these three runs are practically identical. Evidently the rate of clean-up is entirely independent of the pressure of nitrogen even with pressures as high as 40 bars.

In the 11th to 15th runs different temperatures of the filament were tried. The results show a slight tendency for higher values of ϵ_0 at lower temperatures of the filament as the experiment is continued. This slow change is undoubtedly due to increasing error in the temperature determinations due to irregular evaporation of the filament.

Experiment 380.—All the runs of this experiment (see Table II) were made with the same single-loop filament and with the bulb kept immersed in liquid air. The experiment was terminated after the sixth run by an accident which broke the bulb. During the first two runs the quantity of gas in the system decreased from 31.2 to 24.8 cu. mm.—that is, 6.4 cu. mm. were cleaned up. On removing the liquid air from the bulb after the second run the quantity of gas rose from 24.8 to 27.5. Thus only 3.7 cu. mm. failed to reappear on allowing the bulb to warm up to room temperature. During the last 4 runs (3 to 6) the amount of nitrogen which cleaned up was 26.2 cu. mm.; of this 8.3 cu. mm. reappeared on removing the liquid air.

Experiment 381.—Table III gives a summary of the data obtained in Expt. 381, in which both the bulb temperature and the filament temperature were varied over rather wide ranges.

TABLE II.—EXPERIMENT 380.

Run.	T_F.	F_B.	t.	R_o.	R_C.	ϵ_o.	T_o.	ϵ_C.
1	2072	90	25	0.27	0.65	0.42	523	0.49
2	2109	90	20	0.52	1.35	0.39	531	0.43
3	2110	90	10	0.55	1.37	0.40	531	0.42
4	2168	90	11	1.32	4.02	0.33	543	0.34
5	2221	90	10	2.95	10.40	0.28	554	0.27
6	2170	90	8	1.22	4.18	0.29	544	0.33

TABLE III.—EXPERIMENT 381.

Run.	T_F.	T_B.	t.	R_o.	R_C.	ϵ_o.	T_o.	ϵ_C.
1	2111	90	28	0.57	1.40	0.40	532	0.42
2	2147	90	12	1.01	2.77	0.36	539	0.36
3	2171	90	22	1.35	3.58	0.38	544	0.33
4	2171	90	21	1.37	3.58	0.38	544	0.33
5	2137	90	13	0.90	2.30	0.39	537	0.38
6	2237	90	5	3.70	13.5	0.27	557	0.25
7	2246	300	12	0.97	15.7	0.062	758	0·064
8	2132	195	7	0.39	2.09	0.19	635	0.27
9	2241	195	10	2.15	14.5	0.15	658	0.18
10	2132	90	11	0.93	2.09	0.45	536	0.39
11	2246	90	3	4.40	15.7	0.28	559	0.24
12	2132	273	19	0.29	2.09	0.14	707	0.12
13	2246	273	10	2.30	15.7	0.15	731	0.084
14	2138	273	21	0.29	2.34	0.12	709	0.12
15	2260	273	7	1.53	19.8	0.078	734	0.080
16	2150	373	23	0.18	2.92	0.062	802	0.042
17	2262	373	13	0.78	20.5	0.038	826	0.030
18	2143	273	15	0.46	2.60	0.18	709	0.12
19	2265	273	4	2.38	21.7	0.11	735	0.078
20	2033	273	50	0.10	0.295	0.33	686	0.18
21	2369	273	2	5.81	113	0.051	757	0.057

A careful study was also made of the adsorption phenomena occurring when the bulb temperature was changed. The runs 1 to 13 were made with one loop of filament (*a*), while the runs 14–21 were made with the second loop (*b*).

Adsorption Effects.

Table IV gives data on the adsorption effects observed. It may be of interest to illustrate these effects by describing in detail the first few runs.

Before the first run, after exhausting and baking out the lamp, 31.3 cu. mm. of pure nitrogen was introduced into the system at a pressure of 29.4 bars. The bulb of the lamp was then immersed in liquid air but this caused no measurable adsorption of nitrogen. During the first 3 runs (see Table III) the amount of nitrogen in the system decreased from 31.3 cu. mm. to 10.6 cu. mm., that is, 20.7 cu. mm. were cleaned up. However, on removing the liquid air from the bulb at the end of the third run, 8.0 cm. mm. of nitrogen reappeared. The net clean-up was therefore 12.7 cu. mm. (see Col. A of Table IV). The rate of clean-up of nitrogen given under R_0 in Table III is that actually observed while the liquid air remained on the bulb and therefore does not represent the rate at which nitrogen is permanently cleaned up.

TABLE IV.

At end of run No.	A. Permanent adsorption.	B. Irreversible adsorption.	C. Reversible adsorption.	D. N_2 equivalent of Mo deposit.	Ratio C : D.
3	12.7	6.3	1.1	59	0.019
4	24.1	2.9	2.5	118	0.021
6	37.6	0.7	3.6	181	0.020
7	41.8	—	5.0	255	0.020
9	49.9	—	5.8	311	0.019
11	65.9	0.5	8.8	362	0.024
13	76.6	—	13.2	443	0.030
21	99.8	—	..	...	...

The quantity of gas in the system, as we have seen, had risen from 10.6 to 18.6 cu. mm. by removal of the liquid air. Upon replacing the liquid air only 1.7 cu. mm. of nitrogen was adsorbed and the pressure in the bulb after this adsorption was 7.3 bars. Again removing the liquid air the 1.7 cu. mm. was given off again. This could be repeated as often as desired. Evidently this effect was a typical adsorption phenomenon, the nitrogen being adsorbed by the finely divided molybdenum deposit, when cooled by liquid air, exactly as it would have been by charcoal.

From the known rate of evaporation of the molybdenum and the time the filament had been heated, the amount of molybdenum evaporated could be calculated. The nitrogen stoichiometrically equivalent to this evaporated molybdenum was found on the assumption that nitrogen and molybdenum can form a compound MoN_2. This for the first 3 runs was 59 cu. mm. (See Column D of Table IV.)

Since the quantity of adsorbed gas varies with the pressure it was desirable to reduce the observations in different runs to a common basis. At the end of the experiment, after the 21st run, some tests were made to see how the adsorption varied with the pressure. With the bulb in liquid air it was found that

$$q = cp^{0.18}$$

where q is the amount of gas adsorbed at the pressure p.

Making use of this approximate relation we can now express our results on the adsorption in terms of the constant c. The column headed C in Table IV gives the values of c obtained after various runs. The figures given denote the quantity of nitrogen in cu. mm. that is adsorbed by the deposit when the pressure is one bar.

It is seen that the amounts of gas thus reversibly adsorbed are very small compared to the chemical equivalent of the molybdenum deposited. During the first 13 runs the ratio C : D remains practically constant so that we may say that the finely divided molybdenum adsorbs from nitrogen at one bar pressure about $^1/_{50}\%$ of its chemical equivalent.

It is also seen that the amount of nitrogen that can be adsorbed reversibly (Column C) is only 10–20% of the nitrogen permanently cleaned up.

On removing the liquid air from the bulb after a run, the amount of nitrogen liberated is always somewhat greater than the amount adsorbed again upon replacing the liquid air. Thus, after the third run, 8.0 cu. mm. was liberated, and only 1.7 cu. mm. was readsorbed. The difference 6.3 cu. mm. (Column B, Table IV) may be considered to have been irreversibly adsorbed (more strictly irreversibly released). It will be noted that the quantity thus irreversibly adsorbed decreases in subsequent runs. In Runs 7–9 and 13 where the bulb was not cooled in liquid air there was no gas thus adsorbed.

With the bulb cooled by a mixture of solid carbon dioxide and acetone (Runs 8 and 9) the adsorption effects were hardly appreciable, only about 0.4 cu. mm. of nitrogen being reversibly adsorbed at a pressure of 10 bars.

Runs 14–21 were all made with the bulb at 0° or higher, since the special Dewar flask used for the liquid air runs had been broken. The trap immediately below the lamp was, however, kept cooled by liquid air during the whole experiment up to the end of the 21st run. At this time a failure of the liquid air supply made it impossible to maintain the trap at low temperature. When the liquid air around the trap evaporated the pressure in the system rose from 0.4 to 50 bars, corresponding to 52.4 cu. mm. of gas. It was thought that this was probably carbon dioxide and moisture which had been driven off the bulb by the heating and during the 16th and 17th runs.[1] The quantity was, however, unusually large. A couple of days later, when liquid air was again placed around the trap, the pressure fell only to 49 bars, showing that the gas was not either carbon dioxide or water vapor. An analysis showed the gas to be nearly pure *hydrogen*. Upon exhausting the lamp and heating it to 300° for about an hour a further quantity of 32.7 cu. mm. of hydrogen was evolved.

The accidental removal of liquid air from the trap thus caused a liberation of about 85 cu. mm. of hydrogen. The liberation of from 2 to 9 cu. mm. of hydrogen from a liquid air trap on the removal of liquid air is usually observed after a filament has been heated for a considerable time in a gas containing hydrogen. This phenomenon has been studied in detail and an account of some of the earlier observations has been published.[2]

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[1] The gases derived from the original baking out of the bulb had not been condensed in the trap below the lamp but had been adsorbed in phosphorus pentoxide or pumped out previously to the first run.

[2] Langmuir, "A Chemically Active Modification of Hydrogen," THIS JOURNAL, 34, 1310 (1912.)

The large evolution of hydrogen in this experiment, especially the evolution on heating the bulb after the accidental removal of the liquid air, indicates that the hydrogen was produced by the decomposition of water vapor from the trap by the finely divided molybdenum deposited on the bulb.

The deposit on the bulb thus had very unusual properties. It adsorbed nitrogen instantly when cooled by liquid air very much as charcoal would do. It dissolved hydrogen slowly at room temperature and gave it up again slowly at higher temperatures, but at liquid air temperature it adsorbed only little hydrogen. At temperatures of 300° or more it was able to combine with nitrogen. At room temperatures it decomposed water vapor and produced hydrogen.

It must be pointed out that these properties are not characteristic of all molybdenum deposits. When a filament of molybdenum (or tungsten) is vaporized in a very high vacuum (pressure less than 0.1 bar), the deposit is a dense and coherent metallic deposit which adsorbs only negligible amounts of gases even when cooled by liquid air. A deposit formed in this way adheres to the glass so strongly that it can be rubbed or scraped off only with difficulty. On the other hand, the deposits formed when a molybdenum or tungsten filament is vaporized in nitrogen at pressures above about one bar appears less metallic and can be easily rubbed off the glass with the finger. The same difference has been observed with palladium deposits; when the metal evaporates in a very high vacuum the film formed shows no greater tendency to absorb hydrogen than the massive metal, but deposits formed in the presence of gases have very great activity.

Experiments on the Clean-up of Nitrogen by Tungsten Filaments.—The experiments previously made with tungsten and nitrogen (*loc. cit.*) had shown that with the bulb at room temperature ϵ was constant under all conditions and was equal to unity. Whether or not ϵ was still unity at very high or low bulb temperatures remained to be determined. Analogy with the molybdenum results at least suggested that at high bulb temperatures ϵ would become less than unity.

A series of experiments (Expt. 394) was undertaken to investigate this point. Four different bulb temperatures were tried—190°, 20°, 200° and 300°—and the results showed conclusively that the rate of clean-up of nitrogen by a tungsten filament was not perceptibly affected by a change in bulb temperature. Even with the bulb at 300°, the value of ϵ remains unity.

Subsequent Experiments with Molybdenum and Nitrogen.

Experiment 461.—In August, 1915, in connection with an experiment made for another purpose it was observed that no clean-up of nitrogen occurred when a molybdenum filament was heated in nitrogen at low pressure in a spherical bulb of 20 cm. diameter which had not been baked out. Filament temperatures as high as 2330° were employed, and pressures of nitrogen of 1.3 and 9 bars. At this temperature in a bulb at room temperature the rate of clean-up R_0 should have been 2.7 cu. mm. per min. per sq. cm. judging from Run 1 of Table I. Actually, however, the quantity of gas increased from 40.8 to 41.6 cu. mm. during an 8-minute run, corresponding to $R_0 = -0.2$. In another run, with the filament at 2250°, the quantity of gas changed from 6.1 to 5.8 in 3 minutes and then rose in 11 minutes more to 6.6 cu. mm. During these runs the resistance changes showed that the filament lost weight at the usual rate. The failure of the nitrogen to clean-up in this experiment must have been due either to the large size bulb (20 cm.) or to the fact that the bulb had not been baked out to drive off moisture. The bulb was, however, provided with an appendix 2.5 cm. in diameter and 12 cm. long which had been kept immersed in liquid air for several hours before the clean-up was attempted. The system, as a whole, had been dried out for about two weeks by another appendix immersed in liquid air. The pressures of water vapor remaining were certainly extremely low, probably less than 0.001 bar.

Immediately after these runs, carbon monoxide was tried with the bulb at room temperature and the filament at 2115° and at 2250°. The rates of clean-up R_0 were 1.3 and 18.0, respectively, while the values of R_c by Equation 3 for these temperatures were 1.5 and 17.0, respectively. The values of ϵ are thus 0.87 and 1.06. Thus within the experimental error the results indicate that every atom of molybdenum vapor combines with a molecule of carbon monoxide even under conditions which prevent any clean-up of nitrogen by the molybdenum vapor.

Experiment 465.—This experiment was undertaken to determine whether the presence of minute pressures of water vapor was responsible for the failure of the nitrogen to clean up in the previous experiment. It was also planned to find out if the bulb size influenced the rate of clean-up.

Two bulbs, each containing two filaments, were sealed to the vacuum system. The larger bulb was cylindrical in form, was about 12 cm. long and 8 cm. in diameter and contained one tungsten and one molybdenum filament. The small bulb was 8 cm. long and 3 cm. diameter and contained two molybdenum filaments. The bulbs were well exhausted and dried at room temperature for 24 hours by an appendix immersed in liquid air. The filaments were aged for one hour just below their vaporizing temperatures, and all evolution of gas from them had ceased.

The small bulb was immersed in liquid air and one of the molybdenum filaments was heated to 2120° for 8 minutes. The rate of clean-up R_0 was 0.44, corresponding to $\epsilon_0 = 0.27$. This is somewhat lower than the value $\epsilon_c = 0.41$ obtained from Equation 14, which is based on the results of the earlier experiments. The rate of clean-up in this case was independent of the pressure as before. Upon removing the liquid air from the bulb an amount of gas was released which exceeded the amount that had been cleaned up. This suggested that at room temperature water vapor from the unbaked bulb reacted with the deposit on the bulb generating hydrogen.

With the small bulb at room temperature two runs were made at filament temperatures of 2120° and 2227°. In both cases there was an evolution instead of a clean-up; at the lower temperature 0.8 cm. mm. in 11 minutes and at the higher 6.1 cu. mm. in 10 minutes. The remaining gas (20.5 cu. mm.) was found to contain 7.8 cu. mm. of hydrogen.

The bulbs were now baked out for an hour by direct heating with a large Bunsen flame which does not permit as thorough heating as the usual heating in an oven at 360°. There was still some evolution of gas observed when the filament in the small bulb was heated in nitrogen to 2220°, but when about one cm. of the lower portion of the bulb was immersed in liquid air (most of the bulb at room temperature) there was a linear clean-up of nitrogen corresponding to $\epsilon_0 = 0.074$ with a filament temperature of 2220°. This agrees well with the value $\epsilon_c = 0.069$ from the earlier experiments.

With the entire bulb in liquid air ϵ_0 rose to 0.25, while with the level of liquid air up to the middle of the filament ϵ_0 was 0.21. The value of ϵ_c corresponding to $T_F = 2220°$ and $T_B = 90°$ is 0.27, in good agreement with the above.

Removing the liquid air entirely and heating the filament to 2220° gave a value of $\epsilon_0 = 0.039$ as against $\epsilon_c = 0.069$.

These results indicate that the presence of even very minute amounts of water vapor prevent the clean-up of nitrogen by a molybdenum filament. The results show clearly, however, that in this experiment the effect of bulb temperature is only partly due to a change of the water vapor pressure. In the earlier experiments where the conditions were much better for the removal of water vapor, the results were probably not influenced appreciably by this effect.

With the large bulb of Expt. 465 at room temperature a run was made with the molybdenum filament at 2220°. During the first 20 minutes there was an evolution but after 25 minutes the clean-up was steady and corresponded to $\epsilon_0 = 0.037$, which is practically the same as the last run in the small bulb.

A run was then made with the tungsten filament in the large bulb. The bulb was at room temperature and the filament was at 2750°. The rate of clean-up of nitrogen was uniform and was equal to $R_0 = 2.1$. Taking the data on the rate of evaporation of tungsten[1] we obtain the

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[1] Langmuir, *Phys. Rev.*, **2**, 330 (1913).

value $\epsilon_0 = 1.24$. If, however, the temperature of the filament were 2764° instead of 2750°, the value of ϵ_0 would be exactly unity.

Immediately after this run with tungsten, another run was made with the molybdenum filament at 2220°. The evolution of gas was again observed, although it was less than before. The clean-up of nitrogen by tungsten vapor is therefore not affected by the presence of low pressures of water vapor as the clean-up by molybdenum is.

The evolution of hydrogen observed with molybdenum also does not occur with tungsten, or at least occurs to a very much less degree. It seems that the molybdenum-nitrogen deposit is much more readily acted on by moisture than the deposit of WN_2 produced by the tungsten filament.

The results of Expt. 465 indicate that the rate of clean-up of nitrogen by molybdenum is not dependent to any marked degree on the size of the bulb, as long as proper care is taken to exclude water vapor.

Summary of Results on the Rate of Clean-up of Nitrogen by Molybdenum.

The results of the experiments may be summarized as follows (see Tables I, II and III):

I. At high temperatures molybdenum evaporates in low pressures of nitrogen at substantially the same rate as in vacuum. The molybdenum is therefore not preceptibly attacked by nitrogen at any temperature.

II. The amount of nitrogen cleaned-up is always much less than would be required to convert the evaporated molybdenum into the compound MoN_2.

III. *The rate of clean-up of nitrogen is entirely independent of the pressure* of the nitrogen between wide limits (1 to 40 bars or more).

IV. The rate of clean-up increases greatly if the bulb is cooled in liquid air or solid carbon dioxide and decreases if the bulb is heated.

V. The rate of clean-up increases with the filament temperature much more slowly than the rate of evaporation of molybdenum.

If we define ϵ as the ratio of the number of molecules of nitrogen cleaned-up to the number of atoms of molybdenum evaporated in the same time, then we can state the last four conclusions even more briefly, thus:

II. ϵ is always much less than unity.

III. ϵ is independent of the pressure.

IV. ϵ decreases as the bulb temperature is raised.

V. ϵ decreases as the filament temperature is raised.

Mechanism of the Clean-up of Nitrogen.

In attempting to determine from the experimental data the probable mechanism by which the nitrogen is cleaned-up, let us analyze the problem before us. The disappearance of the nitrogen must be due to a reaction taking place between it and the molybdenum.[1] This reaction may occur in one or more of the following places: 1. At the surface of the filament. 2. In the space between the filament and the bulb. 3. On the inner surface of the bulb, or in the deposit on the bulb. Let us examine into the possibilities of the reaction occurring in these places.

1. **Reaction on the Filament.**—If the gas reacts with the solid filament at its surface to form a volatile product the rate of loss of weight by the filament should be different from what it would be in vacuum. Furthermore, in general, the rate of clean-up of the gas should increase with the gas pressure. The reaction between oxygen and tungsten, molybdenum or carbon are typical cases of this behavior. In each instance the loss of weight of the filament greatly exceeds the normal loss by evaporation and the oxygen disappears at a rate which decreases markedly as the pressure falls.

Among all the direct reactions between gases and filaments which have been studied there has been only one in which the rate of clean-up has been independent of the pressure. This was the clean-up of carbon monoxide by a tungsten filament in a bulb cooled to temperatures below —40°.[2] In this case the gas attacked the filament forming a monomolecular surface layer which distilled off at a constant rate. The filament lost weight about 5 times as fast as if heated in vacuum to the same temperature. The rate was independent of the gas pressure and bulb temperature over wide ranges.

Since the loss of weight of molybdenum in nitrogen is the same as in vacuum and since the rate of clean-up of nitrogen is independent of the pressure it is evident that the nitrogen does not react directly with the filament.

2. **Reaction in the Space around the Filament.**—At the low pressures employed in these experiments the molybdenum atoms evaporating from the filament travel on the average, a distance of at least several millimeters before striking nitrogen molecules. This mean free path varies inversely as the pressure, but by Equation 1 the number of collisions that the atoms make before reaching the bulb should be approximately proportional to the square of the pressure. At pressures above two or three bars relatively few atoms reach the bulb without having collided with at least one nitrogen molecule.

We may consider the following possibilities:

Case 1.—If a molybdenum atom always combines with the first nitrogen molecule with which it collides and if the compound formed does not

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[1] In accordance with the writer's theory (see THIS JOURNAL, 40, 1361 (1918)) adsorption must be looked upon as a chemical phenomenon and the adsorption of nitrogen by a deposit of molybdenum should be regarded as a chemical reaction.

[2] THIS JOURNAL, 38, 2277 (1916).

decompose again, then the rate of clean-up would be independent of the pressure of nitrogen at all pressures high enough to prevent the atoms from reaching the bulb before striking nitrogen molecules. This means that ϵ should be equal to unity as has been observed in the case of the $W + N_2$, $W + CO$, $Mo + CO$, $Pt + O_2$ reactions.

Case 2.—If the reaction takes place on the first collision but a portion of the compound formed decomposes on striking the bulb then the rate of clean-up will be independent of the pressure, although the value of ϵ will be less than unity.

Case 3.—If the first collision between the molybdenum atom and the nitrogen does not always result in combination, then in general the molybdenum atoms will have other opportunities for combining during their subsequent collisions with nitrogen molecules. The conditions during these subsequent collisions are not the same as during the first collision because the molybdenum atom gradually loses kinetic energy by collisions with molecules of lower temperature. Apart from the loss of translational velocity a collision which does not result in combination, should, however, not change the molybdenum atoms. This loss of translational velocity must increase or decrease the tendency of the molecules to combine on the subsequent collision. Two cases arise.

Case 3*a*.—The reaction takes place much less readily because of the loss of velocity. If this decrease is sufficient, the amount of reaction due to all the subsequent collisions will be negligible. The rate of clean-up will then be independent of the pressure and ϵ will be less than unity. If the filament temperature be lowered, however, the translational velocity of the molybdenum atoms decreases and the value of ϵ should decrease, while an increase of temperature should increase ϵ. This is not in accordance with the experiments.

Case 3*b*.—The reaction takes place more readily because of the loss of velocity. In this case a large amount of clean-up should result from the subsequent collisions. At higher pressures the number of collisions would be sufficient for the reaction to be complete so that $\epsilon = 1$, but at low pressures the rate of clean-up should increase approximately with the square of the pressure since the number of opportunities for reaction (collisions) increases with the square of the pressure.

Considering now the actual experimental results we see that Cases 3*a* and 3*b* do not agree with the facts. The value of ϵ was found to increase as the filament temperature is lowered. This indicates that the reaction is favored by low relative velocity of the molybdenum atoms and nitrogen molecules. This excludes Case 3*a*. But since ϵ is not equal to unity or does not vary with the pressure Case 3*b* cannot apply. Case 1 is excluded for the same reason.

We are thus forced to Case 2 as the probable mechanism. The molybdenum and nitrogen combine on the first collision and travel to the bulb together as molecules of the composition MoN_2. When these strike the bulb a portion of the nitrogen is given off again. The amount of nitrogen released is independent of the pressure of the nitrogen but naturally varies with the bulb temperature.

There is still a difficulty in the fact that ϵ varies markedly with the filament temperature. If the combination takes place on the first collision and yet the amount of nitrogen subsequently released depends on the filament temperature, this can only mean that the nature of the compound formed depends on the filament temperature. In other words, the molecules formed by the combination must differ according to the relative velocities with which the molybdenum atoms and nitrogen molecules collide. The lower the relative velocity, the more stable is the compound formed, so that a smaller proportion of it decomposes when it subsequently deposits on the bulb. This conclusion is confirmed by the fact that when the deposits on the bulb were heated from liquid air temperature a part of the nitrogen was given off readily but another part (the larger part) could not be driven off by heating in vacuum to 360°. In fact, at these higher temperatures nitrogen combined spontaneously with the finely divided molybdenum to form a very stable compound.

The compound formed when tungsten vapor reacts with nitrogen is characterized by its brown color in thin films and by the evolution of ammonia when it is brought into contact with moisture. There can be little doubt that this compound should be represented by the formula $N \equiv W \equiv N$. It is a typical compound of the first order according to Werner's nomenclature. It is probable that the stable forms of the molybdenum-nitrogen compounds have the analogous structure $N \equiv Mo \equiv N$.

The latent heat of vaporization of molybdenum is very high, 162,000 calories per g. molecule. This measures the energy required to separate the atoms from each other. It is over twice as great as the energy required to separate hydrogen and oxygen in water. After the separation this energy probably resides in the electro-magnetic stray field around the atoms. The field of force around such molybdenum atoms should therefore be unusually intense.

In the case of solid bodies these forces even when much weaker than the forces around molybdenum atoms cause adsorption of gases in the form of monomolecular layers[1] involving only secondary valence forces. With molybdenum vapor where the forces are much more intense it is therefore to be expected that even if the atoms do not combine with gas molecules to form compounds of the first order, they should at least combine with them by secondary valence forces to form a compound repre-

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[1] See Langmuir, THIS JOURNAL, 38, 2267 (1916).

sented by the formula Mo:N_2. In other words, we may describe the phenomenon as an adsorption of gas molecules by each other.[1]

The energy liberated by this combination tends to cause the atoms or molecules to separate again, or at least tends to prevent them from forming such intimate union as if the internal energy of the newly formed molecule were less. The lower the relative velocities of the molecules before collision the more stable will be the combination. Strutt[2] found that atomic nitrogen recombines to form molecules much more rapidly at low temperatures than at high, and he reasons that a high translational velocity of the reacting atoms or molecules should in general hinder rather than hasten the reaction. He considers that rotational velocity of the molecules, on the other hand, favors the reaction and that this fact in the vast majority of reactions greatly outweighs that of translational velocity.

Another striking example of a reaction which takes place more rapidly at lower temperatures is the reaction between carbon monoxide and a heated tungsten filament. With the bulb at temperatures below —40° the carbon monoxide attacks the filament to form the first order compound WCO, while with the bulb at room temperature the filament is not attacked, although the tungsten vapor combines with the carbon monoxide. The filament loses weight in presence of this gas about five times faster when the bulb is cooled than when it is warm.

The tendency to form more stable compounds when the translational velocity is low is thus proved in these two cases and it is probable that in the nitrogen-molybdenum reaction a similar relation holds.

Let us now examine the mechanism of the reaction occurring during the collision of a molybdenum atom with a nitrogen molecule.

[1] There is much evidence that this phenomenon of adsorption of gases by gases or formation of double molecules is not an unusual occurrence. When tungsten is vaporized in hydrogen at low pressures while the bulb is cooled in liquid air, hydrogen is cleaned-up in a way which indicates that the hydrogen molecules combine with the tungsten atoms before they strike the bulb. The experiments of Duane and Wendt, *Phys. Rev.*, 10, 116 (1917), indicate that when atomic hydrogen is produced in hydrogen at atmospheric pressure the atoms are immediately adsorbed on to molecules, producing H_3. This is exactly the behavior that would be expected from the properties of atomic hydrogen previously pointed out by the writer, THIS JOURNAL, 34, 1310 (1912). The departure of the properties of gases from the simple gas laws as the critical temperature and pressure are approached must also be largely, if not entirely, caused by the adsorption of gas molecules by each other. Otherwise it is not possible to explain the continuous transition from the gaseous to the liquid state. In fact, the writer inclines to the opinion that all gas molecules combine or are adsorbed onto each other in every collision, but that because of their inability to give up the liberated energy the molecules ordinarily "evaporate" from each other so soon that the time during which they remain thus "adsorbed" is negligible. In other words, no sharp distinctions should be drawn between so-called elastic collisions of molecules and cases of mutual adsorption of gas molecules such as those cited above.

[2] *Proc. Roy. Soc.*, 87, 302 (1912).

The temperature of the filament can be of importance only in so far as it determines the average translational velocity of the molybdenum atoms. The temperature of the bulb, however, not only determines the translational velocity of the nitrogen molecules, but also their rotational velocity. The reaction between the molybdenum and nitrogen depends on the *relative velocities* of the reacting atoms and molecules, and may depend on the *internal* energy of the nitrogen molecule. The molybdenum atoms should not have any rotational energy.

To test this theory against the experimental data we need to calculate the average relative velocity of the molybdenum atoms and nitrogen molecules at the moment of their collision and to see how this relative velocity depends on the temperature of the filament and bulb, respectively. The question arises, does ϵ, the real reaction velocity, depend simply on the relative velocity of the molecules which collide, or does it also depend on the temperature of the bulb?

Let T in Fig. 2 represent a point at which two molecules collide; let v_1 and v_2 be the respective velocities of the two molecules and let these vectors be represented by the lines PT and OT. The angle θ is the angle between these vectors. The relative velocity of the molecules v is given by the line OP and is equal to

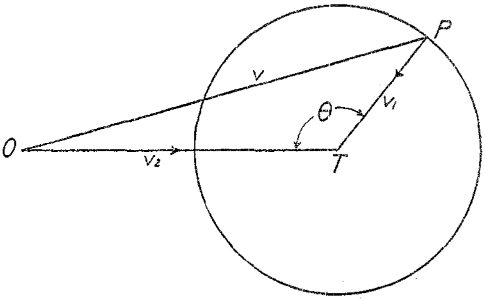

Fig. 2.

$$v = \sqrt{v_1^2 + v_2^2 - 2v_1v_2 \cos \theta}. \tag{5}$$

Molecules are much more likely to collide if they are moving towards one another than if moving in the same general direction. In fact, the chance of a collision is directly proportional to the relative velocity v. The average relative velocity V of the two molecules is thus found from the expression

$$V = \frac{\int v^2 ds}{\int v ds} \tag{6}$$

where ds is an element of the surface of the sphere (of radius v_1) described about the point T.

Substituting the value of v from Equation 5 and integrating over the whole surface of the sphere gives

For $v_2 > v_1$:

$$V = (v_1^2 + v_2^2)/(v_2 + {}^1/_3 v_1^2/v_2) \tag{7}$$

For $v_1 > v_2$:

$$V = (v_1^2 + v_2^2)/(v_1 + {}^1/_3 v_2^2/v_1) \tag{8}$$

This gives approximately the average relative velocity of the two molecules at the moment of collision in terms of the average translational velocities of the two kinds of molecules.

The average velocities of the gas molecules are related to the temperatures by the equations

$$v_1 = k\sqrt{T_1/M_1}, \qquad v_2 = k\sqrt{T_2/M_2} \tag{9}$$

where T_1, T_2 are the temperatures of the gases and M_1 and M_2 are their molecular weights; k is a constant.

If we let the subscript 1 apply to nitrogen and 2 apply to molybdenum, then $M_1 = 28$; $M_2 = 96$. When T_2 is 2000° or more and T_1 is 580° or less, v_2 is greater than v_1. Hence under all the conditions used in these experiments we should apply Equation 7 rather than 8.

Substituting (9) in (7) gives

$$V = k\left(\frac{T_1}{M_1} + \frac{T_2}{M_2}\right) \div \left(\sqrt{\frac{T_2}{M_2}} + {}^1/_3\,\frac{T_1}{M_1}\sqrt{\frac{M_2}{T_2}}\right). \tag{10}$$

Instead of calculating the relative velocities V it will be more convenient to calculate the "equivalent temperature." In the above case we have considered that the two gases are at different temperatures and that the relative velocity V depends on both temperatures. If the two gases are brought to the same temperature T_o and then this temperature is varied until the relative velocity V has the same value as before, then T_o will serve as a measure of this relative velocity.

To calculate T_o we place $T_1 = T_2 = T_o$. In this case, however, v_1 is greater than v_2 and we cannot use Equation 10. We therefore substitute these and the values of v_1 and v_2 from (9) in Equation 8. This gives

$$V = k\sqrt{T_o}\left(\frac{1}{M_1} + \frac{1}{M_2}\right) \div \left(\frac{1}{\sqrt{M_1}} + {}^1/_3\,\frac{\sqrt{M_1}}{M_2}\right). \tag{11}$$

Eliminating V from (10) and (11) gives

$$T_o = (M_1/M_2)\, T_2\, \frac{(1 + {}^1/_3\, M_1/M_2)^2(1 + M_2T_1/M_1T_2)^2}{(1 + M_1/M_2)^2(1 + {}^1/_3\, M_2T_1/M_1T_2)^2}. \tag{12}$$

Substituting $M_1 = 28$; $M_2 = 96$ yields

$$T_o = 0.2105\, T_2\left(\frac{1 + 3.428\, T_1/T_2}{1 + 1.143\, T_1/T_2}\right)^2. \tag{13}$$

This "equivalent temperature" (T_o) is the temperature which a mixture of nitrogen and molybdenum vapor should have in order to give the same average relative velocity at collision as that which exists under the conditions of the experiments.

The values of T_o calculated by Equation 13 for each of the runs recorded in Tables I, II and III are tabulated in the next to the last columns of these tables. The temperature T_o is always intermediate between

T_F and T_B and really gives a properly weighted mean of these two temperatures.

We are now in a position to answer the question previously raised as to whether ϵ depends simply on the relative velocity V (or on $T_\circ$), or whether it also depends on T_B. To determine this all the experimental values of log ϵ_0 were plotted against $1/T_\circ$. It was found that the values lay much more nearly on a continuous curve than if log ϵ_0 were plotted against either $1/T_B$ or $1/T_F$, but there was a very distinct tendency for higher values of ϵ to occur at the higher bulb temperatures. The following semi-empirical formula agreed fairly well with the experimental data

$$\log_{10} \frac{\epsilon}{1 - \epsilon} = \frac{4000}{T_\circ} - \frac{156}{T_B} - 5.93. \qquad (14)$$

Values of ϵ calculated by this equation from the corresponding values of $T_\circ$ and T_B are given in the last columns of Table I, II and III under the heading ϵ_c. It is seen that the agreement is reasonably good. In the last few runs of Table I the calculated values of ϵ are much less than the observed. It has already been noted, however, that these values of ϵ_0 were much too high, probably because of irregularities in the filament temperature.

These results show that reaction velocity ϵ is much increased as the relative velocity V (or $T_\circ$) decreases. The lowering of the bulb temperature increases ϵ only because it lowers the relative velocity of the molecules. The increase in ϵ, however, is not as great as is to be expected by the lowering of the relative velocity. In other words, the results show that while a high translational velocity hinders the reaction a high *rotational* velocity of the nitrogen molecules hasten the reaction. The results are thus entirely in accord with Strutt's conclusions from his work on atomic nitrogen.

It should be noted that there is nothing in these results to indicate that if the reaction velocity between molybdenum and nitrogen were studied under more usual conditions any negative temperature coefficient would be observed. The very large positive temperature coefficient of the rate of evaporation of the molybdenum would completely mask the small negative coefficient of the reaction between the molybdenum vapor and the nitrogen.

3. **Reaction on the Bulb.**—The theory developed in the preceding pages according to which the reaction occurs during the first collision between the molybdenum atoms and the nitrogen molecules seems to furnish a satisfactory explanation of the observed phenomena. Would it also be possible to explain the results by a reaction between the molybdenum vapor and adsorbed nitrogen on the bulb?

It has been previously noted[1] that the linear relationship in the clean-up of nitrogen by a tungsten filament in a bulb cooled by liquid air held down to pressures so low that the tungsten atoms could not have collided with nitrogen atoms on their way to the bulb. The explanation offered was that the tungsten atoms combined with nitrogen molecules adsorbed on the bulb. There is some evidence of the same kind in the clean-up of nitrogen by molybdenum.

Is it possible that the molybdenum atoms do not combine at all with the nitrogen until after they have struck the bulb and that the nitrogen is then simply adsorbed by the finely divided deposit? This hypothesis would account for the greater clean-up as the bulb temperature is lowered and would indicate why ϵ is small compared to unity.

On the other hand, it does not seem capable of explaining why ϵ_0 decreases as the filament temperature is raised, nor why the rate of clean-up is always independent of the pressure above a few bars' pressure.

For these reasons as well as for the inherent improbability that atoms of molybdenum vapor would be more inert towards nitrogen than is solid molybdenum, this hypothesis must be discarded. But there is every reason to believe that combination with adsorbed nitrogen does occur when the pressures are so low that many molybdenum atoms strike the bulb before striking molecules of nitrogen. We still have to consider the phenomenon of the release of part of the nitrogen when the molybdenum-nitrogen molecules strike the bulb.

That part of the nitrogen which stays in the deposit on the bulb even when it is heated to 360° is probably a compound NMoN. The molybdenum atoms having their primary valences saturated have very little tendency to react with each other. Molecules represented by Mo : N_2 however would behave differently on striking the bulb. The molybdenum atoms are not saturated chemically and the very large forces normally acting between adjacent molybdenum atoms can come into play. These forces must greatly exceed those acting between molybdenum atoms and nitrogen molecules. Under these conditions the molybdenum atoms combine with each other and the forces holding the nitrogen are further decreased so that a large part of the nitrogen held by secondary valence forces escapes. At low bulb temperatures very weak restraining forces are sufficient to keep the nitrogen from evaporating, but at temperatures as high as room temperature nearly all the nitrogen escapes except that held by primary valence forces.

As the nitrogen molecules leave, the molybdenum atoms are enabled to approach each other so as to form more points of contact. This sintering process takes place even when the temperature is raised from liquid air temperature to room temperature. Thus when the bulb is

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[1] THIS JOURNAL, 37, 1157 (1915).

cooled again by liquid air the deposit does not absorb all of the nitrogen evolved when it first warmed up. This explains the irreversible adsorption given in Col. B of Table IV.

According to this viewpoint the deposit is built up of molybdenum atoms one by one in such a way that each atom makes contact with probably only two or three others. In a crystal of tungsten and probably also of molybdenum the atoms are arranged in a simple cubic lattice,[1] each atom being surrounded by six equidistant ones. Thus the structure allows the primary valence forces of the hexavalent atoms to manifest themselves. The very great strength, high melting point, and low vapor pressures of these metals are probably largely the result of this structure.

When these metals form spongy deposits by vaporization in presence of gases, the atoms are undoubtedly held to each other in chains and branches of great complexity by primary valence forces. The stability of such deposits at ordinary temperature is excellent proof that the forces holding the atoms together are very directive in character. Thus if two tungsten atoms come into contact with a third the first two are not able at ordinary temperatures to alter their positions on the surface of the third so that they can come into contact with each other. As the temperature is raised, however, the thermal agitation makes it easier for the two atoms to change their relative positions slightly so that their chance of coming into contact increases. If atoms once come into contact the attractive forces become so great that they cannot separate again.[2] Sintering processes are thus irreversible.

The high chemical activity of the molybdenum deposits on the bulb are thus understandable. The deposit consists of atoms many of which are in contact with only one or two other atoms. The strong forces of these atoms are therefore far from being saturated. It is not surprising that such atoms should react with water vapor at room temperature.

The slow absorption of hydrogen by these deposits at room temperature is probably similar in nature to the penetration of hydrogen into iron, palladium or platinum. It is probable that the hydrogen penetrates these metals in the form of positive ions which are nothing but the nuclei of hydrogen atoms and are thus smaller than electrons. These "positive

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[1] P. Debye, *Phys. Z.*, 18, 483 (1917).

[2] This theory of sintering seems to be of very wide application. Finely divided tungsten and molybdenum sinter markedly at temperatures as low as 1200°—thousands of degrees below their melting point. Impurities seem to hinder rather than help this action. The theory has often been advanced that sintering of clays, porcelains, etc., depends on the presence of small amounts of easily fusible materials and that pure substances would not sinter. As a matter of fact, exceptionally pure lime, magnesia, etc., in a fine state of division, sinter readily many hundreds of degrees below their melting point.

electrons,"[1] probably take positions between the metal atoms rather than outside of them. The slowness of the action is probably due to the time required for the dissociation of the molecular hydrogen into atomic before the ionization occcurs.

The adsorption of nitrogen by the deposit when this is cooled by liquid air is a typical adsorption phenomenon and need not be further discussed here.[2]

The irreversible absorption of nitrogen by the deposit at temperatures above 300° is probably a direct combination of nitrogen with the most unsaturated of the molybdenum atoms to form the stable compound NMoN. It is likely that some of these molybdenum atoms are nearly as reactive as those in the molybdenum vapor. The experiments on the nitrogen clean-up have shown that the reaction takes place most readily at low temperatures. It is not improbable that at 600° K. the reaction occurs between the nitrogen and the deposit on the bulb, especially as this temperature is close to the equivalent temperatures T_0, at which reaction occurred most readily (see T_0 in Tables I, II and III).

The proposed theory of clean-up of nitrogen by a molybdenum filament thus accounts satisfactorily not only for the observed rates of clean-up under various conditions, but also explains in large measure the peculiar properties of the deposit collecting on the bulb.

Summary.

Molybdenum filaments were heated to temperatures ranging from 2000° to 2400° K. in nitrogen at pressures of 40 bars or less (0.03 mm. of mercury), great care being taken to exclude water vapor.

The filaments lost weight at the same rate as if heated in vacuum. Evidently the nitrogen did not attack the filaments. The nitrogen disappeared at a rate independent of the pressure at all pressures above about one bar.

The amount of nitrogen cleaned-up is much less than the chemical equivalent of the molybdenum evaporated.

If we denote by ϵ the ratio of the number of molecules of nitrogen cleaned-up to the number of atoms of molybdenum evaporated in the same time, the results show that ϵ decreases as the filament temperature or bulb temperature is raised. The highest values of ϵ were about 0.4 while the lowest were about 0.01.

With very minute pressures of water vapor such as result even in presence of drying agents from failure to bake out the bulb, no clean-up of nitrogen occurs. Under these same conditions, however, molybdenum will clean-up carbon monoxide, and tungsten will clean-up nitrogen or

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[1] According to Rutherford.

[2] The general theory of this kind of adsorption has been treated in This Journal, 40, 1361 (1918).

carbon monoxide. In each of these cases ϵ is unity. From the fact that ϵ is independent of the pressure but varies with the bulb temperature and filament temperature it is necessary to conclude that the reaction takes place in the space around the filament, that each collision between molybdenum atoms and nitrogen molecules results in combination, but that at least two products are formed. These probably are: a first order compound of the formula NMoN and a second order compound $Mo:N_2$. The proportion of these two depends on the relative velocity of the molecules at the moment of collision and also on the internal energy of the nitrogen molecules. The first compound is very stable and cannot be decomposed on the bulb by heating to 360°. Its formation is favored by low relative translational velocity of the colliding molecules and by high internal or rotational velocity in the nitrogen molecule. All those collisions which do not yield the first order compound give the second order compound. This is so unstable that it decomposes practically completely on striking the bulb, because of the much greater attractive forces between pairs of molybdenum atoms than between these and nitrogen molecules.

The experiments show that the deposit which collects on the bulb has remarkable properties as follows:

1. It is spongy and can be easily rubbed off by the finger on opening the bulb, while deposits formed in high vacuum are dense and can hardly be scratched off with a knife.
2. The deposit formed with the bulb at liquid air temperature gives up some nitrogen on being warmed to room temperature, but only a part of this nitrogen is absorbed again on cooling the bulb. The larger part of the nitrogen in the deposit is not liberated by heating in vacuum at 360° C.
3. The deposit readily adsorbs up to about $^1/_{30}$ of its chemical equivalent of nitrogen when cooled by liquid air. This adsorption takes place very rapidly. It does not readily adsorb hydrogen under these conditions.
4. At room temperature and above, the deposit slowly absorbs or dissolves large quantities of hydrogen which it slowly gives up again at 300° in a good vacuum.
5. When heated in nitrogen to 270° or more the deposit combines with nitrogen and this is not given off again by heating in vacuum to 360°.
6. The deposit reacts rapidly with water vapor at room temperature producing hydrogen, much of which remains dissolved in the deposit until liberated by heating.

The theory of the mechanism of the reaction accounts satisfactorily for all these phenomena.

The larger part of the experimental portion of this investigation was carried out by Mr. S. P. Sweetser.

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HYDROGEN OVERVOLTAGE.

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Hydrogen overvoltage will be defined, for the purpose of this paper, as the difference of potential that exists between a reversible hydrogen electrode and an electrode, in the same solution, at which molecular hydrogen, H_2, is being formed from hydrogen ions. A reversible hydrogen electrode is, of course, one at which the reaction

$$2H^+ + 2\epsilon = H_2 \qquad (1)$$

(ϵ = electron) has reached equilibrium. This equilibrium is attained, and maintained during the passage of very small currents, only on electrodes covered with a dispersed "noble" metal, such as platinum, palladium, or iridium. If a stronger current is passed across such a metal-electrolyte boundary, or if other electrodes are used, the reaction does not take place under equilibrium conditions, and an overvoltage appears.

A number of theories have been advanced to account for overvoltage. The one proposed by Nernst,[1] discussed by Lewis and Jackson,[2] and lately championed by Bennett and Thompson,[3] assumes that Reaction 1 occurs in the two stages

$$2H^+ + 2\epsilon = 2H_1 \quad (2), \qquad \text{and} \qquad 2H_1 = H_2, \qquad (3)$$

that Reaction 3 is slower than Reaction 2 and that the excess potential is due to an accumulation, above the equilibrium concentration, of H_1. Möller,[4] on the other hand, finds a relation between the overvoltage of an electrode, and its "randwinkel," *i. e.*, the angle between the surface of an electrode and the edge of a large bubble attached to it. Newbury,[5] in his later papers, considers that hydrogen overvoltage is principally due to the formation, during electrolysis, of metallic hydrides with higher solution tensions than that of hydrogen. However, it is not our purpose to review all of the theories of overvoltage. It is noteworthy, nevertheless, that none of the published theories, with the exception of that of Möller, attempts an explanation of the great influence the physical condition of the electrode may have on the overvoltage. For instance, a polished platinum electrode may show an overvoltage as high as 0.1 volt,

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[1] *Ber.*, **30**, 1547 (1897).

[2] *Z. physik. Chem.*, **56**, 193 (1906).

[3] *Trans. Am. Electrochem. Soc.*, **29**, 24 (1916) and *J. Phys. Chem.*, **20**, 296 (1916).

[4] *Z. physik. Chem.*, **65**, 226 (1909).

[5] *J. Chem. Soc.*, **109**, 1359 (1916).