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The Activated Adsorption of Nitrogen on a Finely Divided Tungsten Powder

BY RAYMOND T. DAVIS, JR.[1,2]

Two recent papers from this Laboratory have reported the results of hydrogen adsorption measurements on two finely divided tungsten powders.[3] The results of the study were unique from both an experimental and theoretical viewpoint. The present investigation was undertaken to determine the detailed nature of nitrogen adsorption on tungsten powder under conditions similar to those employed in the study of hydrogen adsorption. As tungsten is a fairly active synthetic ammonia catalyst, it is of interest to know both the nitrogen and hydrogen adsorption characteristics for this metal.

Experimental

Tungsten Powder.—Tungsten powder obtained from Dr. W. D. Coolidge of the General Electric Co. and marked Y-9799 was used in the investigation This was identical with one of the powders used by Frankenburg.[3] Low temperature nitrogen adsorption measurements, when plotted by the BET method,[4] give a surface area of 2.81 m.^{2}/g. During the reduction and outgassing of the powder, some sintering occurs such that after this pretreatment the surface corresponds to 2.00 m.^{2}/g., a value which was reproduced with several powder samples after their pretreatment.

Gases.—The purification of the hydrogen used in the reduction of the tungsten powder has been described in the earlier paper.[3] The nitrogen for adsorption purposes was prepared by the thermal decomposition of sodium azide. The sodium azide was obtained from A. D. MacKay Co., New York, N. Y., and contained 1% sodium oxide as impurity. The nitrogen evolved at 350° was passed through a cold trap at −195° and was collected in an evacuated bulb. The gas contained none of the rare gases as impurity and was better than 99.9% pure.

Apparatus.—The construction and calibration of the apparatus has been described in the previous paper.[3] A palladium tube has been added to the original apparatus during the present work. Figure 1 shows the modified apparatus. By means of stopcocks Z and Q, the palladium tube H may be evacuated while being heated by the external heater N. Gases from the system proper may be expanded into the evacuated palladium tube by closing stopcock Z and opening stopcock U. When the palladium

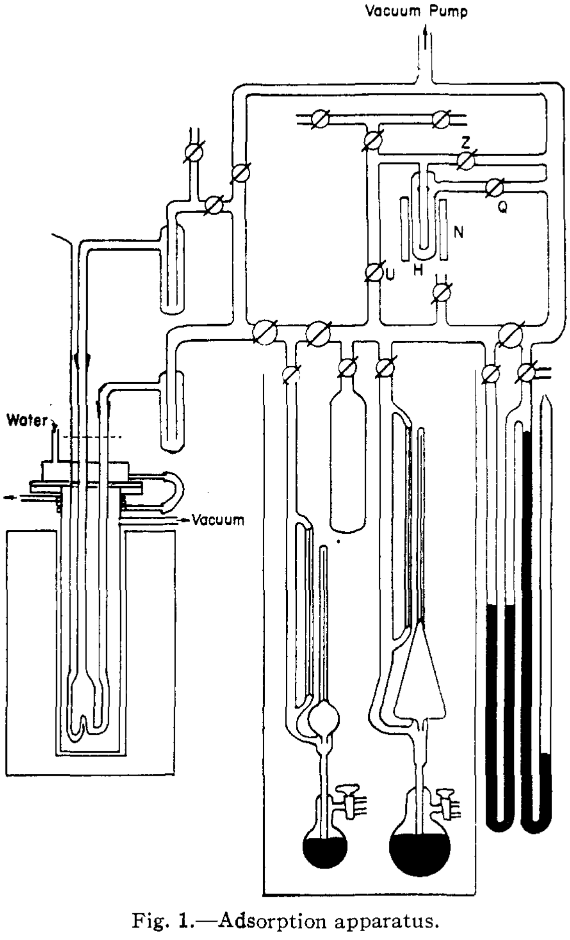

Fig. 1.—Adsorption apparatus.

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[1] Present address: Mellon Institute of Industrial Research, Pittsburgh, Pa.

[2] The material for this paper was obtained from the author's thesis which was submitted to the faculty of Johns Hopkins University as a partial requirement for the degree of Doctor of Philosophy.

[3] Frankenburg, THIS JOURNAL, **66**, 1827 (1944); **66**, 1838 (1944).

[4] Brunauer, Emmett and Teller, *ibid.*, **60**, 309 (1938).

tube is heated to 400° any hydrogen present in the gases may be detected because of its diffusion through the tube and a subsequent decrease of the gas pressure in the system as read by the McLeod gages. By this method, it was possible to detect the presence of hydrogen in a total sample of gas as small as 0.0002 cc. (S. T. P.) when the pressure of the gas in the system is of the order of 10^{-4} mm., provided the hydrogen content is greater than 5%.

Reduction and Outgassing of the Powder.—A weighed amount of tungsten powder, approximately 15 g. was placed in the adsorption vessel. The technique of reducing and outgassing the powder, as described in the previous paper[3] was followed. Careful checks were kept on the gas evolution of the powder during its outgassing until experience showed that the powder was in a reproducible state and had adsorptive properties identical to those of previous samples.

Adsorption Technique.—The adsorption technique employed by Frankenburg[3] was used. All gas inlets were made at 750° except when rate experiments were being made. With any given amount of gas in the system, measurements were made at temperatures above those at which the equilibrium pressure was too small to be measured and above those at which the time required for equilibration was excessively long. Experience showed that 400° was the lowest temperature at which equilibrium measurements could satisfactorily be made.

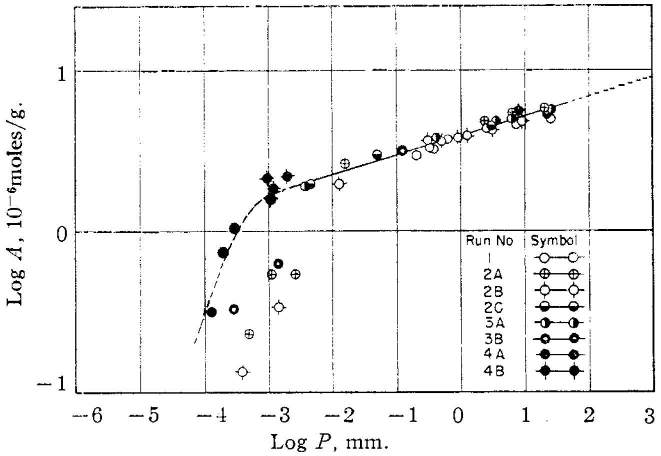

Fig. 2.—Adsorption of nitrogen on tungsten powder 9799 at 750°. The numeral of the run number refers to the powder sample, while the letter refers to the particular run on that sample of powder. Runs 4A and 4B were made after the palladium tube was added to the apparatus.

Rate of Adsorption Measurements.—Two methods were employed. The first consisted of admitting to the adsorption vessel an inlet of gas at some fixed temperature and then following the adsorption process as a function of time. When the adsorption rate became exceedingly low, the temperature was then quickly raised by 100° and the rate of the adsorption process followed at this higher temperature. In the second method a large amount of gas was admitted to the adsorption vessel and the rate of adsorption followed as a function of time. The amount of gas admitted was of such a size that the total pressure during the adsorption process did not change by more than about 10%.

Results

Equilibria.—The results of the adsorption equilibrium measurements are shown in Figs. 2 and 3. Figure 2 shows the adsorption isotherm for the single temperature 750° showing all of the experimental points taken with various runs and different samples of the same powder. Figure 3 shows the adsorption isotherms obtained at the various temperatures studied. The adsorption isotherms are very close to each other at higher pressures. Hence, the experimental points of the various isotherms are very densely crowded in this range. We omitted for this reason, the experimental points in Fig. 3. In order to obtain Fig. 3, the experimental points were entered in a large scale diagram and the best curves were drawn through the experimental points. Because of the wide pressure range covered,

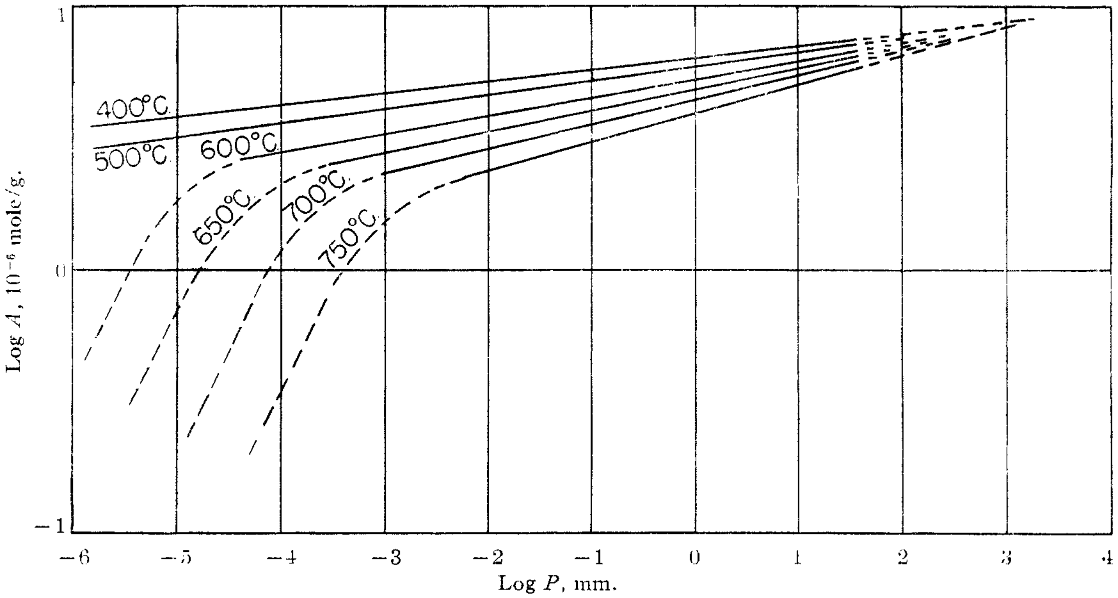

Fig. 3.—The adsorption isotherms of nitrogen on tungsten powder 9799.

10^{-6} to 35 mm., it was necessary to plot the equilibrium pressure values on a logarithmic scale. It was found advantageous to plot the amounts adsorbed also on a logarithmic scale. Hereafter in this paper the adsorption isotherms when referred to will be those plotted on a log-log scale. The dashed portions of the isotherms in the high pressure regions represent an extrapolation of the data. The dashed portions in the very low pressure region represent data which have a much lower accuracy, on account of the large limits of error in this range. They indicate, however, the correct order of magnitude of the equilibrium pressures.

Rates.—Table I gives the per cent. of equilibrium reached in one and thirty minutes at various temperatures along with the accompanying pressure changes occurring during the adsorption process when a sample of gas was admitted to the freshly outgassed powder. Because of the exceedingly slow rate of adsorption below 400°, no adsorption equilibrium measurements were made below this temperature.

After one of the nitrogen adsorption runs, the powder was outgassed in the normal manner and then hydrogen adsorption measurements were made on its surface. Values in perfect agreement with those obtained by Frankenburg[3] were obtained. This seems to indicate that the powder had been thoroughly outgassed of all adsorbed nitrogen and that it was in an identical condition to the powder used in the hydrogen adsorption studies. There exists, however, the possibility that the hydrogen adsorption might not be influenced by any adsorbed nitrogen. Effects of this kind were found by Brunauer and Emmett[5] for the case of hydrogen adsorption at 100° on certain iron synthetic ammonia catalysts which had been subjected, previously, to a chemisorption of nitrogen.

The results of the rate of adsorption measurements are plotted in Figs. 4, 5, 6 and 7. Figures 4 and 5 represent the results of the experiments in which the temperature was suddenly increased by 100° during the adsorption process. Figure 6 represents the amount of adsorbed gas at constant temperatures plotted as a function of time. The adsorption data in Fig. 6 are plotted in Fig. 7 as a

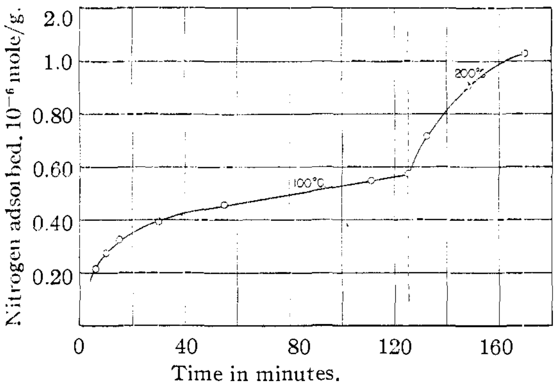

Fig. 4.—The variation of the rate of nitrogen adsorption when the temperature is changed from 100 to 200°.

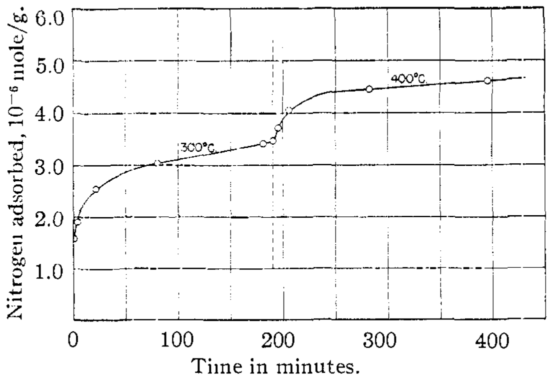

Fig. 5.—The variation of the rate of nitrogen adsorption when the temperature is changed from 300 to 400°.

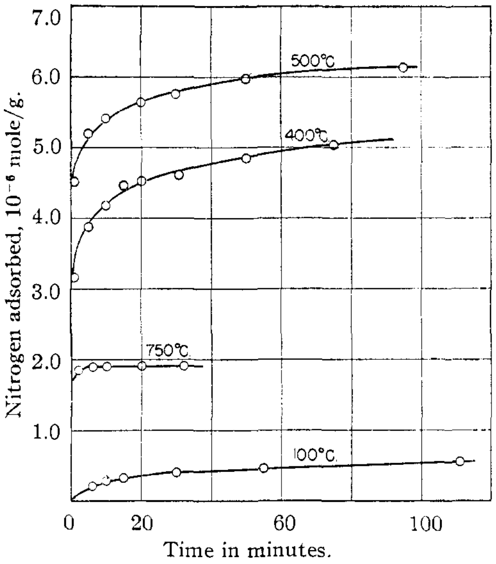

Fig. 6.—The variation of the rate of nitrogen adsorption with temperature.

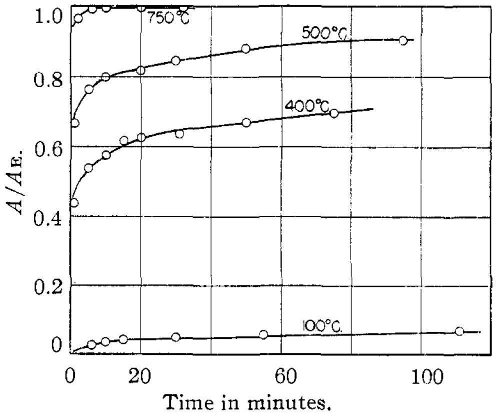

Fig. 7.—The variation of the rate of adsorption equilibration with temperature.

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[5] Brunauer and Emmett, THIS JOURNAL, **62**, 1733 (1940).

function of A/A_E where A is the amount of gas adsorbed during the time t minutes and A_E is the amount of gas adsorbed after equilibrium has been reached at the temperature studied.

Discussion of Results

Table I and Figs. 4 to 7 illustrate the slowness of the adsorption process and indicate that we deal with an activated adsorption. This seems to be in complete disagreement with the results of Roberts[6] and Van Cleave,[7] both of whom measured the N_2 adsorption on a tungsten wire by means of the technique developed by Roberts[8] for the determination of the accommodation coefficients and hydrogen adsorption on tungsten wires.

TABLE I

TIMES REQUIRED FOR EQUILIBRATION OF NITROGEN ON TUNGSTEN AT VARIOUS TEMPERATURES

Temp., °C.	% of equilibrium in 1 min.	in 30 min.	Pressure change during time of observation, mm.
100	1	5	0.9 to 0.5
400	45	64	27 to 24
500	66	85	27 to 24
750	95	99.9	0.04 to 0.004

They report a rapid nitrogen adsorption at room temperature and a "complete saturation" of the surface at a nitrogen pressure of less than 1 mm. pressure. Our data indicate an extremely slow adsorption at 100° with less than 5% of the surface covered at the end of thirty minutes at a similar pressure. It is difficult to explain this discrepancy. Robert's and Van Cleave's method is, in our opinion, not sufficiently sensitive to detect more than the initial uptake of a small amount of nitrogen. In addition, the surfaces of the adsorbent wires were possibly larger than those calculated from geometric data due to a surface roughness.[9] It should also be pointed out that their method is an indirect one based on heat of adsorption measurements. Finally, it is also conceivable, although not probable, that there is a distinct difference between the adsorption phenomena occurring at a plane surface of a tungsten wire and that occurring on the surface of a tungsten powder.

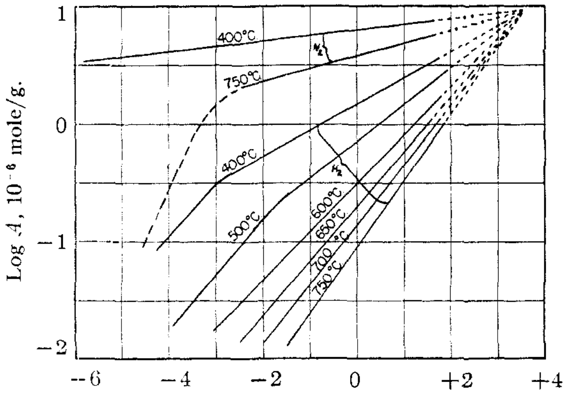

Fig. 8.—The adsorption isotherms of nitrogen and hydrogen on tungsten powder 9799.

Messner and Frankenburg[10] have made a few measurements of the adsorbing capacity of a tungsten powder for nitrogen. Their results indicated an activated adsorption. Another fact to be mentioned here is the slowness of the adsorption of nitrogen on tungsten as indicated by the work of Joris and Taylor[11] who measured the rate of the nitrogen isotope exchange $N_2^{15} + N_2^{14} \rightarrow 2N^{14}N^{15}$ on a tungsten powder surface. The exchange process was so slow that below 450° it could not be detected.

The isotherms in Fig. 3 show several interesting features which we shall now consider separately. Essentially they are of the same type found by Frankenburg[3] for hydrogen on tungsten. Figure 8 shows the nitrogen and corresponding hydrogen isotherms on the same plot.[12] The hydrogen adsorption values vary over a much larger range than the nitrogen values. Furthermore, the change of the isotherm slopes with change in temperature is more pronounced.

Isotherm Intersections.—It should be noted that the isotherms in Figs. 3 and 8 intersect each other at a single point if they are extrapolated in a linear fashion. This point of intersection is, within the limits of error of the experiments, identical for both the hydrogen and nitrogen adsorption on the same tungsten powder. For reasons already pointed out,[12] it cannot be decided whether or not this point corresponds to the actual saturation of the surface or whether there is a "true saturation value" which, for the hydrogen system, has been estimated as being approximately 100% higher than s. The apparent saturation value s for the nitrogen system corresponds to $\log A = 0.96$, $\log P = 3.3$. A calculation of the surface covering based on this value leads to the result that, in this state of adsorption, one nitrogen molecule is adsorbed for every four tungsten atoms on the surface of the metal. It is very possible that the "true saturation value" for the

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(6) Roberts, *Nature*, **137**, 659 (1936).

(7) Van Cleave, *Trans. Faraday Soc.*, **34**, 1174 (1938).

(8) Roberts, *Proc. Roy. Soc.* (London), **152A**, 445 (1935).

(9) See footnotes 26 and 28 of Frankenburg, ref. 3.

(10) Messner and Frankenburg, *Z. physik. Chem.*, Bodenstein Festband, 593-607 (1931).

(11) Joris and Taylor, *J. Chem. Phys.*, **7**, 893 (1939).

(12) It should be noted that, as before, the dotted portions of the isotherms represent extrapolated portions of the isotherms. The isotherms in the high pressure region were extrapolated linearly. The point of intersection of the isotherms corresponds only to an apparent saturation value and not to the "true saturation value" which is discussed in the second paper of Frankenburg.[3] Any attempts at trying to find the "true saturation value" by analysis of the experimental values of the nitrogen isotherms are necessarily futile because of the extremely slight slope of the isotherms in the case of nitrogen adsorption. Hence, in this paper, the term "saturation value" implies the point of intersection of the extrapolated isotherms and will be represented in all equations by "s" to differentiate it from the "true saturation value" "S" which has been estimated for hydrogen adsorption in the previous papers.[3]

nitrogen system is the same as that of the hydrogen system in which case the surface covering was estimated to correspond to one nitrogen molecule for every two atoms on the surface. The very flat nature of the nitrogen isotherms permit, however, no safe conclusion on this point.

Isotherm Shape.—All of the isotherms in Fig. 3 are, in very good approximation over this entire length, either single straight lines (below 600°) or straight lines in the high and medium pressure regions curving toward the pressure axis in the low pressure regions (above 600°). The curved portions of the isotherms, as previously mentioned, are less well defined for reasons to be discussed later. Frankenburg[3] has shown that the straight line portions of the isotherms may be represented by the equation

$$\log P_A = -\alpha \log (s/A) + \log P_S \qquad (1)$$

where P_A is the pressure at equilibrium when the amount A is adsorbed, P_S is the pressure when the saturation amount S is adsorbed, and α is d log P/d log A which we shall define as the slope[13] of the isotherm. In the previous paper[3] it was shown that as the slopes of these isotherms are greater than 2, the isotherms cannot correspond to the simplified Langmuir equation for either molecular or atomic adsorption.

Curved Portion of Isotherms.—In the extremely low pressure region it was observed that the isotherms for 600° and higher temperatures tend to depart from a straight line and slope toward the pressure axis. The reason for the inexactness of the data in this region is as follows:

In performing the adsorption measurements, it was noticed early in the investigation that when A was small several strange effects appeared. First, the equilibrium pressure in this region was higher by several orders of magnitude than could be expected if the straight line portions of the isotherms were extrapolated to values of log A lower than 0.40. It should be recalled that the hydrogen isotherms were all straight lines to log A = 0.50-2. It was further discovered that if the system was allowed to stand a number of hours at the higher temperatures (650° or above), there was a gradual increase in the pressure, as much as by one order of magnitude. At first these discrepancies were attributed to the slow but steady gas evolution and also possible slight inaccuracies in the McLeod gage in the low pressure region. It was suggested, however, that the increase in pressure might be caused by the evolution of traces of adsorbed hydrogen left on the surface of the tungsten from the reduction which was being desorbed because of the high heat of the nitrogen adsorption. To check this, the palladium tube was added to the system. By its use it was found that the irregular pressure increase was actually due to hydrogen evolution. By the constant diffusion of this evolved hydrogen through the palladium tube, constant pressure could be maintained in the system.[14] The equilibrium pressures obtained by this method still did not fall in line with the extrapolated straight line portions of the isotherms. It is thus necessary to assume that the isotherms curve toward the pressure axis at some point. From a study of the heat of adsorption of the process it seems necessary that at some value of the amount adsorbed, the isotherms should tend to curve toward the pressure axis and become parallel to each other. The experimental data indicate that this occurs at about log A = 0.35. Even the isotherms at 400 and 500° may curve toward the pressure axis at values of log A lower than this value, but such an effect could not be detected experimentally due to the impossibility of measuring pressures below 10^{-6} mm. with our apparatus. A similar curvature was found in the tungsten–hydrogen system but it occurred at much lower log A values. The slope of the isotherms in the very low pressure range is approximately 2 which, as Frankenburg has pointed out, is indicative of atomic adsorption. This further confirms the postulate presented in the previous papers that in the low pressure, low covering region, the gas is adsorbed as atoms, and in the higher pressure region as "loosened" molecules.

Thermodynamics of the Nitrogen–Tungsten System

Heat of Adsorption.—From any two isotherms made at different temperatures, the heat of adsorption may be calculated by the integrated Clausius–Clapeyron equation

$$\log P_2 - \log P_1 = Q(T_2 - T_1)/2.303RT_2T_1 \qquad (2)$$

where P_2 and P_1 are equilibrium pressures for the amount A adsorbed at the temperatures T_2 and T_1, and Q is the differential heat of adsorption when the amount A is adsorbed. From the equation (2) it is seen that on a log P *vs.* log A isotherm plot, the linear distance along the log P axis between the two isotherms at constant "A" is directly proportional to the heat of adsorption. Thus, at the point of intersection of the isotherms, the heat of adsorption is zero. In the low covering range where the isotherms are in all probability parallel to each other, the heat of adsorption is a constant. For the straight line portions of the isotherms between low coverings and saturation, the heat of adsorption decreases as a function of the amount adsorbed. The relationship between the straight line portions of the isotherms and the heat of adsorption can be derived mathematically and shown to be

$$Q = \phi \log (s/A) \text{ where } \phi = 2.303\, RT_1T_2(\alpha_1 - \alpha_2)/(T_2 - T_1) \qquad (3)$$

and α is the slope of the isotherm as already de-

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[13] d log P/d log A is actually the reciprocal of the "mathematical slope" d log A/d log P.

[14] The amount of hydrogen adsorbed is so small that it occupies only a very small fraction of the surface, possibly 1/10,000 part or less and the gas evolution is so small that it cannot be detected at pressures above 10^{-8} mm.

fined. Thus Q, the differential heat of adsorption, decreases as a logarithmic function of the fraction s/A. In Table II are listed the values of the isotherm slopes α and also the calculated ϕ values for the various temperature intervals.

TABLE II

SLOPE (d LOG P/d LOG A) OF THE ADSORPTION ISOTHERMS AT VARIOUS TEMPERATURES AND THE CALCULATED VALUES OF ϕ

Temp., °C.	Slope α	ϕ, kcal./mole
750	9.28	
		137.0
700	10.79	
		138.9
650	12.48	
		139.7
600	14.37	
		119.5
500	18.25	
		105.0
400	22.55	

It seems best to neglect the values of ϕ calculated for the temperature intervals lower than 600° as it is possible that the isotherms at these lower temperatures do not represent complete equilibria because of the extremely long times required for equilibration. The value of ϕ is relatively constant over the temperature range 600 to 750° and between the limits log A 0.35 and 0.96. It should be pointed out again that the slopes of the isotherms are very slight; α is very large, and a very small change in the slopes will make a large change in the value of ϕ calculated above.

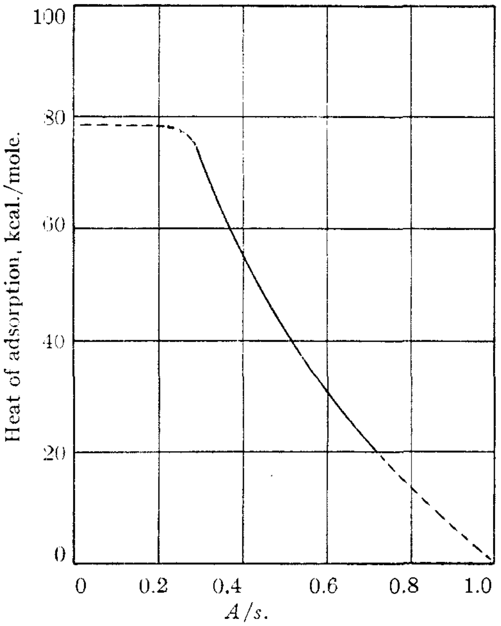

Fig. 9.—The variation of the differential heat of adsorption of nitrogen on tungsten powder 9799 as a function of A/s.

The relationship for the heats of adsorption mentioned above holds only for the straight line portions of the isotherms. Using the approximate curves for the curved portions of the isotherms a value of Q = 70.0 to 80.0 kcal./mole seems to be best. This is a constant heat of adsorption apparently independent of temperature and surface coverings lower than log A = 0.35. This heat represents an upper limiting value of the heat of adsorption. Indeed, some limit is to be expected for, if the isotherms continued as straight lines, it would indicate the absurd value of infinity for the heat of adsorption for an infinitely small surface covering.

The variation of the heat of adsorption with the fraction of surface covering is plotted in Fig. 9. The dotted portions represent the values calculated from the extrapolated portions of the isotherms.

Activation Energy.—From the rate of adsorption experiments it is possible to calculate the energy of activation of the adsorption process. If the rate of adsorption is assumed to follow the equation

$$dA/dt = ke^{-E/RT} \qquad (4)$$

then for two different temperatures T_1 and T_2 where the rates are $(dA/dt)_1$ and $(dA/dt)_2$

$$E = \frac{2.303T_1T_2}{(T_2 - T_1)} R \log [(dA/dt)_2/(dA/dt)_1] \qquad (5)$$

Or it may also be used in the form

$$E = \frac{2.303T_1T_2R}{(T_2 - T_1)} \log (t_1/t_2) \qquad (6)$$

where t_1 and t_2 are the times required for A moles of gas to be adsorbed at the respective temperatures. These equations should be applied only for equal fractions of the surface being covered, as the activation energy may well vary with the surface covering. In Table III are listed in column 6 the various values of E calculated by means of equation 5, together with the rate data taken from Figs. 4, 5 and 6. Obviously, the activation energy is a function of the fraction of the surface covered.

It is of interest at this point to see how well the equations which have been developed by Eyring,[15] for the rates of adsorption will fit the experimental data. Rate equations for four different types of adsorption have been proposed, namely: 1, immobile adsorbed layer, adsorption on single sites

$$dA/dt = C_gC_s(1 - \theta)\frac{\sigma}{\sigma\ddagger}\frac{h^4e^{-E/RT}}{8\pi^2I(2\pi MRT)^{3/2}} \qquad (7)$$

2, immobile adsorbed layer, adsorption on dual sites

$$dA/dt = \frac{1}{2}sC_gC_s(1 - \theta)\frac{\sigma}{\sigma\ddagger}\frac{h^4e^{-E/RT}}{8\pi^2I(2\pi MRT)^{3/2}} \qquad (8)$$

3, mobile monolayer

$$dA/dt = (1 - \theta)\frac{Pe^{-E/RT}}{(2\pi MRT)^{1/2}} \qquad (9)$$

4, immobile adsorbed layer, adsorption with dissociation resulting from the jump of one or both

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[15] Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 350, 351 and 358.

TABLE III

ACTIVATION ENERGY OF ADSORPTION AS A FUNCTION OF SURFACE COVERING

T, °K.	P, mm.	A in 10^{-5} mole/g.	$(1 - A/s)$	dA/dt mols/sec. sq. cm.	Energy of activation in kcal./mole Eq. 5	Eq. 7	Eq. 8	Eq. 9
373	0.6	0.572	0.942	0.855×10^9	10.00	12.22	12.68	14.03
473	0.6	0.572	.942	14.7×10^9		12.33	13.35	15.03
573	1.0	3.45	.655	1.5×10^9	23.10	17.45	18.93	20.93
673	1.0	3.45	.655	30.3×10^9		16.05	17.40	20.41
673	25.0	5.00	.500	4.94×10^9	25.00	22.40	23.90	26.80
773	25.0	5.00	.500	55.0×10^9		21.80	23.40	27.10
773	24.0	5.64	.434	6.06×10^9		24.90	26.60	30.10

of the atoms constituting the molecule from one site to another.

$$\mathrm{d}A/\mathrm{d}t = C_{\mathrm{g}}^{1/2}C_{\mathrm{s}}\frac{kT}{h}\frac{\sigma^{1/2}}{\sigma\ddagger}\frac{(1-\theta)(h^{5/2})e^{-E/RT}}{[8\pi^2 I(2\pi MRT)^{3/2}kT]^{1/2}} \quad (10)^{16}$$

Using the dA/dt values determined from the curves in Figs. 4, 5 and 6, and assuming that $\sigma = 2$ and $\sigma\ddagger = 1$, and $C_s = 1.2 \times 10^{15}$, the number of tungsten atoms on the surface, these values together with the other constants can be substituted in the above equations and the energy of activation necessary to satisfy the equation is calculated. These calculated values are listed in Table III. The calculated values using equations 7, 8 and 9 are all close to one another and agree rather well with those calculated by equation 5 over a temperature range. The values calculated using equation 10 are about 20 kcal. too high. Since they are completely out of line they are not tabulated. It is not possible to come to any conclusion as to which equation best fits the experimental data because of the slight variation in the calculated values. However, the variation of E with surface covering as calculated by equations 5, 7, 8 and 9 is plotted in Fig. 10. It will be noticed that E varies in a different manner when calculated by equation 5 than when calculated by equations 7, 8 and 9. It is also of interest that the differences in E as calculated by equation 5 and by those calculated by equations 7, 8 and 9 will make a difference in the adsorption rate of less than a factor of 10.

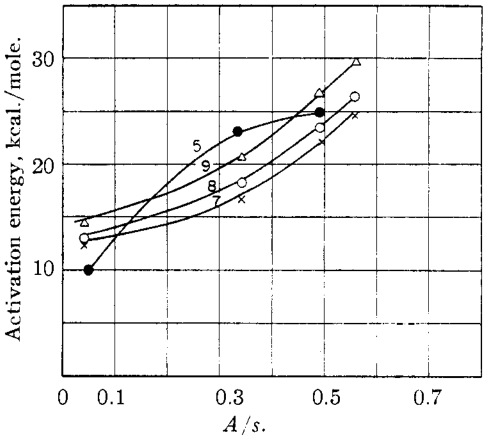

Fig. 10.—The variation of the energy of activation of the adsorption of nitrogen on tungsten powder 9799 as a function of A/s.

Energy of Desorption.—Since both the heat of adsorption and the activation energy of adsorption are known, the heat of desorption for the adsorbed nitrogen from the tungsten surface can be derived by means of the equation $E_{\mathrm{d}} = Q + E_{\mathrm{a}}$. This energy value can then be used in the equation

$$-\mathrm{d}N/\mathrm{d}t = C_{\mathrm{s}}\frac{\theta kTe^{-E_{\mathrm{d}}/RT}}{h} \quad (11)$$

where the nomenclature is the same as used in the rate equations. Using this equation and the calculated desorption energy for the desorption of the last 25% of the surface covered, the rate is insufficient to account for the experimental fact that after pumping for approximately fifty hours at 750° reproducible adsorption values are obtained with powders which had had one or more sets of nitrogen measurements made on their surface. Moreover, as has already been men-

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(16) The nomenclature used in the above equation is
C_g = concentration of gas molecules/cm.^{3}
C_s = concentration of adsorption sites on bare surface/cm.^{2} (See note below)
θ = fraction of surface covered A/s
σ = symmetry factor for gas molecule = 2
$\sigma\ddagger$ = symmetry factor for adsorbed molecule = 1
s = number of adjacent sites = 6
I = moment of inertia of gas molecule = 13.7×10^{-40} g. cm.^{2}
M = molecular weight of gas molecule
k = Boltzmann number
R = gas law constant calories/deg.
h = Planck constant
T = absolute temperature
E = energy of activation
dA/dt = rate of adsorption in molecules adsorbed/sec. cm.^{2}
P = Pressure of gas in mm. Hg.

Note: $C_s = 12 \times 10^{14}$/sq. cm. (average number of tungsten atoms/sq. cm.) was used in the above calculations. If, as the adsorption data indicate, there is only 1 N_2 molecule adsorbed for every 4 W atoms on the surface then $C_s/4$ should be used. However, Frankenburg[3] came to the conclusion that there is 1 H_2 molecule adsorbed for every 2 W atoms on the surface, in which case $C_s/2$ should be used. In any case the calculated energy of activation would be increased by a factor 2.303RT log 4 or 2.303RT log 2 which, for the maximum temperature studied, amounts to approximately 1,000 or 2,000 cal./mole or a maximum uncertainty of less than 8% which, considering the uncertainties involved in other terms, may be ignored.

TABLE IV

EQUILIBRIUM PRESSURES OF HYDROGEN–TUNGSTEN AND NITROGEN–TUNGSTEN SYSTEMS AT EQUAL TEMPERATURES AND HEATS OF ADSORPTION

	Amount Ads.[a] 10^{-6} Mole/g.		Equilibrium pressures at						Equilibrium pressures at 600°		
			600°		650°		500°				
Q kcal./mole	H_2	N_2	H_2, mm.	N_2, mm.	H_2, mm.	N_2, mm.	H_2, mm.	N_2, mm.	Q kcal./mole	H_2, mm.	N_2, mm.[b]
50.0	0.1	4.00	0.06	0.02	0.20	0.09	0.002	0.0008	50.0	0.06	0.07
40.0	0.25	4.70	0.60	0.20	2.0	0.6	0.03	0.02	40.0	0.6	0.7
30.0	0.63	5.50	6.0	1.0	11.0	5.0	0.60	0.3	30.0	6.0	7.0
25.0	1.00	6.00	17.8	7.0	31.0	16.0	3.0	2.0	25.0	18.0	25.0
20.0	1.58	6.60	50.0	28.0	80.0	50.0	12.0	9.0	20.0	50.0	100.0

[a] For nitrogen $s = 9.2 \times 10^{-6}$ mole/g.; for hydrogen $s = 10.0 \times 10^{-6}$ mole/g. [b] Calculated on the basis of $s = 10.0 \times 10^{-6}$ mole/g. for nitrogen.

tioned, the hydrogen adsorptions measured after a nitrogen run were identical with those obtained by Frankenburg for the same powder. Frankenburg and Messner,[10] and Van Cleave[7] have both reported that they were able to pump off the adsorbed nitrogen at 750° in reasonable lengths of time.

The reasons why the desorption rate calculations do not fit into the experimental picture are most likely connected with certain entropy changes which occur and have not been taken into account. It is hoped that in a later paper these factors can be presented and also those involved in the adsorption process.

It seems well to point out some of the similarities which exist between the hydrogen–tungsten and nitrogen–tungsten systems.

1. The experimentally determined isotherms have the same shape in both cases.
2. An extrapolation of the experimentally determined isotherms results in their intersection at a point which is approximately the same, both in pressure and adsorption magnitude for both systems.
3. The decrease in the heat of adsorption is a similar function of the covering of the tungsten surface in both systems.
4. Within the limits of experimental errors the slopes of the nitrogen isotherms are related to the slopes of the hydrogen isotherms by the relation $\alpha_{N_2} = 5.9\alpha_{H_2}$ at the same temperature.
5. At equivalent heats of adsorption the equilibrium pressures which exist at the same temperatures for the two systems are nearly equal. There are some discrepancies but they are small considering the wide range of equilibrium pressures covered. The various values obtained for the two systems at identical heats of adsorption and temperature are given in Table IV. The last column of this Table shows that slight changes in the accepted saturation value s can lead to a very good agreement for the equilibrium pressures obtained for both systems at coverings with identical heats of adsorption.

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Summary

1. The adsorption of nitrogen on a tungsten powder has been measured over the pressure range 10^{-6} to 35 mm. pressure and at temperatures between 400 and 750°.
2. The adsorption isotherms on a log–log plot consist of a curved portion in the low covering region and of straight lines in the high covering range.
3. At saturation there is one molecule of nitrogen adsorbed for every four tungsten atoms on the surface.
4. The heat of adsorption is constant at about 75.0 kcal./mole in the low covering range and decreases according to the relation $Q = 139.0 \log s/A$ kcal./mole in the higher covering range.
5. The activation energy involved in the adsorption is approximately 10.0 to 25.0 kcal./mole and varies with the surface covering.
6. Application of the Eyring rate equations for adsorption gives results in agreement with the experimentally determined activation energies.
7. The usual calculation of the rate of desorption is not in agreement with the experimental facts.
8. There is a close relationship between the hydrogen–tungsten and the nitrogen–tungsten systems.

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