

THE THERMAL DECOMPOSITION OF LIGHT AND HEAVY AMMONIA AND PHOSPHINE ON TUNGSTEN.

BY RICHARD M. BARRER, PH.D., M.Sc.

Communicated by ERIC K. RIDEAL.

Received 1st November, 1935.

The decomposition of ammonia on tungsten filaments has been studied by various workers,¹ between 2 and 500 mm. pressure. The reaction has not been adequately examined at low pressures. Schwab's² work is confined mainly to the decomposition on platinum. The decomposition of phosphine on tungsten was studied by Melville and Roxburgh.³ Both these reactions were re-examined, using proto- and deuterio-molecules, mainly at low pressures. The determination of zero point energy differences on a number of tungsten catalysts was not however the only reason for pursuing the investigations. There exists a wide discrepancy in recorded energies of activation for the seemingly simple zero order ammonia decomposition. These energies range from 26 to 47 K. Cals. One can conclude either that the methods of measurement are inadequate, or that the activation energy varies in a random manner from one tungsten catalyst to another. The latter consideration seems unlikely in view of the stability of a polycrystalline tungsten filament when outgassed at 2000° C. We have therefore measured the energy of activation by the compensating filament method.⁴ This was done for both the phosphine and the ammonia reactions and trustworthy energies of activation were obtained. If a number of true energies of activation (*i.e.*, for the zero order reactions)

¹ Hinshelwood and Burk, *J.C.S.*, 1925, **127**, 1105; Kunsman, *J.A.C.S.*, 1928, **50**, 2100; Hailes, *Trans. Faraday Soc.*, 1931, **27**, 601; Motschan, *Perevesenseffr Roginsky Acta Physicochimica*, 1935, **2**, 203.

² Schwab., *Z. physik. Chem.*, 1927, **128**, 161.

³ *J.C.S.*, 1933, 586.

⁴ Forsythe and Worthing, *Astrophys. J.*, 1935, **61**, 146.

can be measured, absolute rates can be calculated, just as for homogeneous processes. The well-known characteristics of polycrystalline tungsten filaments⁵ enabled the calculations to be made for the two reactions here studied.

Experimental.

The reactions occurred on tungsten filaments of lengths 31 and 9 cms. and of 0.1 mm. diameter. Each filament during reaction formed one arm of a Wheatstone's bridge. The bridge was kept in balance, and the catalyst so maintained at constant temperature, by increasing the total current through the bridge as the reaction proceeded. From the properties of ideal filaments,⁶ the temperature could be calculated for a given filament current *in vacuo*. In the presence of the gas the current was increased until the resistance (and therefore temperature) of the filament was that already measured *in vacuo*. The cooling effect of the 1 mm. tungsten lead was allowed for by calculation as suggested by Langmuir, Maclane and Blodgett.⁷ This does not yet allow the true temperature coefficient to be measured however. The velocity on the short filament at temperature T_1 was next subtracted from the velocity on the long filament at T_1 . The resultant velocity was taken as representing the velocity on the middle section (22 cms.) of the long filament. This resultant velocity was used to determine energies of activation.

Light and heavy ammonias and phosphines were prepared from magnesium nitride, and calcium phosphide, previously outgassed, in an apparatus described elsewhere.⁸ The D-content of ammonia was estimated from vapour pressure measurements, and of phosphine from density measurements. 98 per cent. D_2O was used in preparing ND_3 and PD_3 . Ammonia and phosphine were purified by distilling several times between liquid air and solid carbon dioxide. Hydrogen was prepared electrolytically, and passed over palladium-coated copper at $350^\circ C.$ and phosphoric oxide. Cylinder nitrogen (99 per cent. pure) was passed over palladium-coated copper at $350^\circ C.$ and through a liquid air trap. The filaments were thoroughly outgassed (several hours at $2000^\circ C.$) before use, and were also outgassed between each experiment for 20 minutes at the same temperature. Under these severe conditions the catalytic activity was reasonably constant. After an experiment with ammonia a filament retained occluded gas, which with for an initial gas pressure 10^{-2} cm. was comparable in amount with this pressure. The phosphine decomposition gave negligible occlusion. This suggests that the occluded gas was nitrogen. For the phosphine decomposition a stoidiometric relation held between initial and final volumes as demanded by the equation $2PH_3 = 2P + 3H_2$, the phosphorous being deposited as the red variety on the glass walls. The ammonia decomposition was more complicated. More gas was obtained finally than the original pressure indicated. This was traced to a strong and relatively slow sorption⁹ by the walls of the reaction vessel. Typical of this sorption are the data here shown.

Ammonia was therefore admitted at a higher pressure than that at which the experiment was subsequently conducted, until the sorption was nearly completed. Some was then frozen out, a convenient pressure obtained, and after a further interval for desorption the run was commenced.

$Cms. \times 10^3$ Press. NH_3 .	Time (Mins.)
2	0
1.2	1
0.85	2.5
0.65	4.0
0.50	5.5
0.43	7.0

⁵ Becker, *Rev. Mod. Physics*, 1935, **7**, 95.

⁶ Langmuir, *Physic. Rev.*, 1916, **7**, 154; *ibid.*, 1916, **7**, 302.

⁷ *Ibid.*, 930, **35**, 478.

⁸ Barrer. This volume, p. 487.

⁹ Cf. Burt, *Trans. Faraday Soc.*, 1932, **28**, 179.

Kinetics of the Reactions.

The ammonia decomposition was studied between 6.1×10^{-4} cms. and 6.3×10^{-2} cms. pressure. The reaction is nearly of zero order, except at the highest temperatures (Table I.) and lowest pressures, on the 9 cm. filaments.

Similarly at the lower temperatures (ca 900° K.) at which measurable

TABLE I.

Time Mins.	Total Press. $\times 10^2$ cms.	$K = \frac{\Delta p}{\Delta t} \times 10^3$.
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Temp. 1060° K.

0	6.60	
1	7.15	0.55
2	7.64	0.49
3	8.24	0.60
4	8.60	0.36
5	9.18	0.58
6	9.68	0.50

Temp. 1174° K.

0	10.0	
1	15.26	5.26
2	18.85	3.59
3	21.30	2.45
4	22.55	1.25

TABLE II.

Initial Press. (cms. $\times 10^3$).	$\frac{(dp)}{(dt)_{init.}} \times 10^3 = k$ (t in mins.)
0.61	0.37
0.96	0.52
3.00	0.62
5.35	0.64
10.0	0.96
14.5	0.83
15.0	0.93
19.9	0.86
25.0	1.00
33.0	1.00
63.6	0.96

decomposition occurred on the longer 31 cm. filaments, a good approximation to zero order was again found (Fig. 1). A feature of the reaction was the occurrence of a zero order velocity constant at 6.1×10^{-4} cms. pressure of only 0.37 times the velocity constant at pressures of 10 to 60×10^3 cms. Also decomposition occurred with an initial pressure of 6.1×10^{-4} cms. until 7×10^{-3} cms. pressure obtained in the gas phase. Both these effects

were ascribed to sorption on the walls. The walls by giving off ammonia as that in the gas phase was decomposed, acted as a reservoir of ammonia which kept the gas phase and therefore filament surface concentrations nearly constant and so gave the appearance of a zero order reaction on the filament, which could yet be less rapid than the true zero order process at greater pressures. On this basis the relation between the initial value of dp/dt and

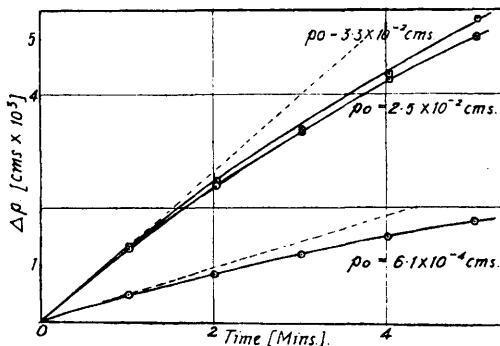


FIG. 1..

the pressure should be that of an isotherm, of which the initial curvature is controlled by the sorption isotherm of ammonia on glass, and of which the last portion is controlled by the saturation concentration at the tungsten surface. The relevant data, collected in Table II., and Fig. 2, show that this is indeed the case :

Over a sixteen-fold increase in pressure there was a 2.5-fold increase in velocity, and then above about 10^{-3} cms. the velocity remained constant.

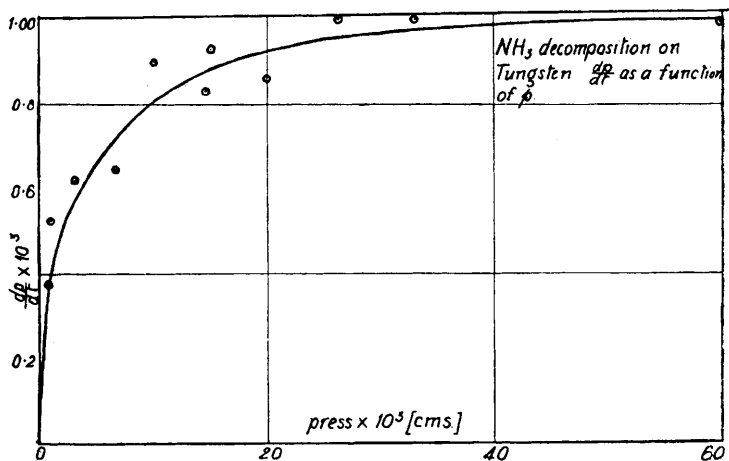


FIG. 2.

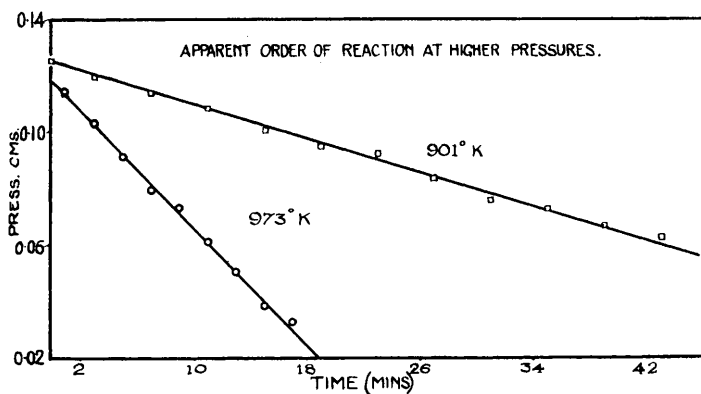


FIG. 3.

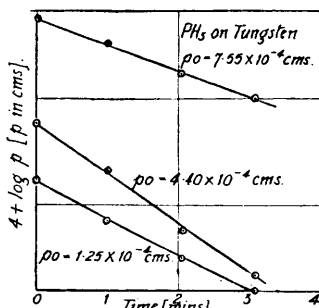


FIG. 3a.

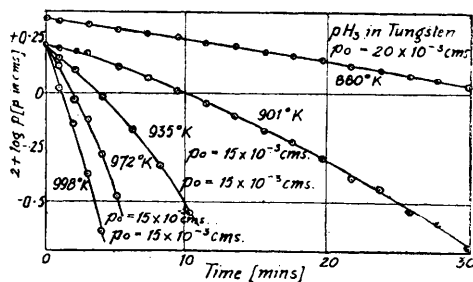


FIG. 3b.

The kinetics of phosphine decomposition were not complicated by sorption on the walls and enabled an interesting change in the order of the reaction with varying pressure to be followed.

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On a 31 cm. filament between 10^{-4} and 10^{-3} cms. pressure Fig. 3*a* shows that a first order reaction was obtained. On a 9 cm. filament at pressure

$(15 \text{ to } 20) \times 10^{-3}$ cms. pressure the plot of Log (press.) against time was definitely curved, showing a reaction of intermediate order (Fig. 3*b*). Finally at pressures of a few millimetres a zero order reaction was found (Fig. 3*c*). The kinetic equation for the reaction

TABLE III.

Time Mins.	Press. PH_3 (cms. $\times 10^3$).	k from Eqn. (1).	Time from Eqn. (2), (Mins.).
6	23.07	—	0
5	20.07	4.0	4.5
9	18.51	3.1	9.7
13	16.97	3.4	13.0
21	13.57	3.3	21.2
31	10.23	—	30.5
41	7.11	3.3	41.0
51	4.89	3.2	50.9
61	3.07	—	61.9

of intermediate order, at 860° K. was either

$$-dp/dt = kp^{\frac{1}{2}} \quad \dots \quad (1)$$

or, $-dp/dt = ap/1 + bp$ (with $a = 0.0227$ and $b = 26.60$). \dots (2)

as is shown by the data of Table III. The rate equation thus follows a Freundlich or a Langmuir isotherm.

The most interesting way to follow the transition from first to zero order is by measuring the half-life period as a function of pressure. At low pressures the half-life ($t_{\frac{1}{2}}$) should be independent of pressure, and at high pressures proportional to it. These predicted relations are realised in the data of Table IV.

The experiments establish that the real rate determining process is unimolecular with respect to phosphine. Fig. 4 shows the relation between the half-life period and the pressure at two different temperatures, on a 9 cm. filament.

Energetics of the Reactions.

The velocity of thermal decomposition of ammonia on 9 and 31 cm. filaments was measured over a range of temperatures. Excellent linear graphs of Log (k) against $\frac{1}{T}$ ($T = ^\circ\text{K.}$) were obtained. The slope for the 9 cm. filament is greater than for the 31 cm. filament, the *apparent* energies being respectively 52.3 and 43 K. Cals. The corresponding rate equations are:

$$\text{Log}_{10} \cdot K_2 = 7.409 - \frac{52,300}{2.303RT} \quad \dots \quad (1)$$

$$\text{Log}_{10} \cdot K_1 = 6.475 - \frac{43,000}{2.303RT} \quad \dots \quad (2)$$

TABLE IV.

Press $\times 10^3$ (cms.).	$t_{\frac{1}{2}}$ (mins.).	$\frac{t_{\frac{1}{2}}}{p} \times 10^3$.
9 cm. filament 972° K.		
127.9	10.4	0.000
32.7	4.05	0.124
17.4	2.90	0.167
10.2	2.26	0.222
4.39	1.81	0.413
1.63	1.62	1.00
0.83	1.30	1.58
0.44	1.10	2.50
0.189	1.10	5.82
31 cm. filament $^\circ$ K.		
81.5	8.88	0.109
74.5	8.80	0.118
16.6	4.60	0.277
9.9	3.30	0.330
9.8	3.35	0.328
9.5	3.40	0.368
5.0	2.40	0.480
4.0	2.10	0.520
1.74	2.25	1.29
0.76	2.20	2.92
0.44	1.60	3.64
0.245	1.30	5.30
0.123	1.50	12.20

From the linear graphs of $\text{Log } K$ against $1/T$, the value of $(K_1 - K_2)$ was obtained at two different temperatures. The integrated van't Hoff isochore

$$\text{Log}_e \frac{(K_1 - K_2)_{T_1}}{(K_1 - K_2)_{T_2}} = \frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

then gave the true value of E for the zero order reaction as 42.400 cal./gram. mol. for 22 cms. of the central zone of the 31 cm. filament. The true rate equation is then

$$\text{Log}_{10} (K_1 - K_2) = 6.35 - \frac{42,400}{2.303RT}$$

The energy of activation for the decomposition of phosphine was calculated from the relationship between the half-life period ($t_{1/2}$) and the

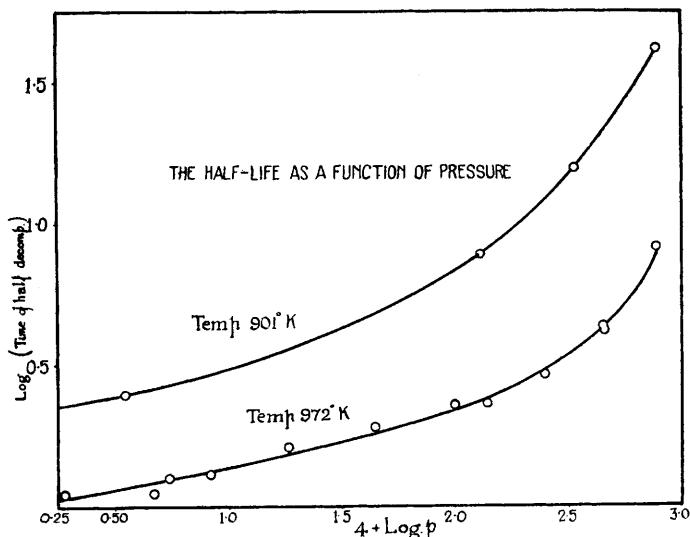


FIG. 4.

temperature, and also from the value of $d\phi/dt$ at constant pressure and at various temperatures. The temperature coefficient was not the same at all pressures for a given rise in temperature. The relationship between derived energies of activation E_1 and E_2 for the reaction proceeding as a first and an apparent zero order reaction respectively is $E_1 + \Delta H_s = E_2$ where ΔH_s is the heat of sorption of the phosphine on tungsten. The values of E as a function of pressure are given in Table V.

TABLE V.

9 cm. filament.

$T_1 = 901^\circ \text{ K.}$

$T_2 = 972^\circ \text{ K.}$

Press. (cms. $\times 10^3$).	$(t_{1/2})_{T_1}/(t_{1/2})_{T_2}$.	E (K. Cals.).	$(\frac{d\phi}{dt})_{T_1}/(\frac{d\phi}{dt})_{T_2}$.	E (K. Cals.).
0.23	—	—	3.0	26.6
0.47	2.74	24.6	—	—
8.00	—	—	3.7	32.0
14.00	3.60	31.3	—	—
18.00	—	—	3.6	31.3
34.00	3.86	33.0	—	—
127.00	3.99	34.2	—	—

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Similarly for a 31 cm. filament between 878·8° K. and 919·2° K. the following values were obtained :

<i>Press</i> (cms. 10 ³).	<i>E</i> (K. Cals).
0·41	26·5 (First Order Reactions)
9·0	31·5 (Intermediate Order)
80·0	32·5 (Approximate Zero Order)

From the differences in the extreme values of *E* of 10 and 6 K. Cals. for the 9 and 31 cm. filaments one can assume ΔH_s to be about 8 K. Cals. The rate equations are :

$$\text{Log} \left(\frac{dp}{dt} \right)_1 = 5\cdot69 - \frac{32,500}{2\cdot303RT},$$

and

$$\text{Log} \left(\frac{dp}{dt} \right)_2 = 5\cdot39 - \frac{32,500}{2\cdot303RT},$$

for the long and the short filaments respectively. From these relations when $\text{Log } dp/dt$ is plotted as a function of $1/T$ the true energy of activation may be derived, since

$$\frac{\partial}{\partial \frac{1}{T}} \left[\text{Log} \left\{ \left(\frac{dp}{dt} \right)_1 - \left(\frac{dp}{dt} \right)_2 \right\} \right] = \frac{E_{\text{true}}}{2\cdot303R}.$$

From the values of dp/dt at 800° and 900° K., and employing the integrated isochore one obtains.

$$\text{Log} \frac{0\cdot00273}{0\cdot000274} = \frac{E_{\text{true}}}{2\cdot303R} \left(\frac{1}{800} - \frac{1}{900} \right),$$

whence $E = 32,200$ Cals.

The Influence of Products upon the Velocity of Decomposition.

It has been shown that hydrogen has no effect upon the decomposition of phosphine.³ It has been stated by Schwab² that the ammonia decomposition is retarded by the resultants, whereas Hinshelwood Burk and Hailes¹ consider the reaction to be unretarded, in spite of a known strong sorption of hydrogen by clean tungsten,¹⁰ or of the possibility of nitriding of the filament. A new series of experiments was carried out on the influence of hydrogen, nitrogen and oxygen on the ammonia reaction. In an orienting experiment the filament was heated in ammonia at 1700° K. until the latter was decomposed. Residual hydrogen, nitrogen and ammonia were pumped off, but the filament was not outgassed, and retained occluded gases. A subsequent experiment at 984° K. gave the same velocity of decomposition as did the outgassed filament. The wire (0·1 mm diameter and 31 cms.

TABLE VI.

<i>Initial Pressure of Gas</i> 10 ³ (cms.)	<i>Reaction Velocity.</i>
Hydrogen.	
0	0·82
6·6	0·94
11·4	0·98
16·5	1·00
17·9	1·03
23·5	0·88
30·4	1·00
Nitrogen.	
0	0·75
13·6	0·78
28·7	0·91

long) gave off 0·25 c.c. of gas at N.T.P. when it was subsequently glowed at 2200° K. Thus occluded gas has no influence. Further investigation

¹⁰ Roberts, *Proc. Camb. Phil. Soc.*, 1934, **30**, 174.

was carried out by adding various initial pressures of hydrogen and nitrogen and observing the decomposition velocities. The results of Table VI. show that these gases had no observable influence.

Oxygen on the other hand produced definite retardation. Ammonia was admitted, and the run commenced at 975° K., the usual zero order reaction being obtained. The ammonia was frozen out, and the oxygen at 2×10^{-3} cms. pressure admitted to the filament at 600° K. and then pumped off. The original

experiment was then recommenced the value of dp/dt being first negligible and then increasing steadily towards the original value, apparently due to a process of clean-up of the oxygen film which restored the original catalytic surface. Finally the experiment was repeated with some gaseous oxygen present. dp/dt was now no longer positive (*i.e.*, an increase in total pressure with time) but negative.¹¹ The results are summarised in Fig. 5. It is of interest that the effect of oxygen is not permanent at 975° K.

FIG. 5.

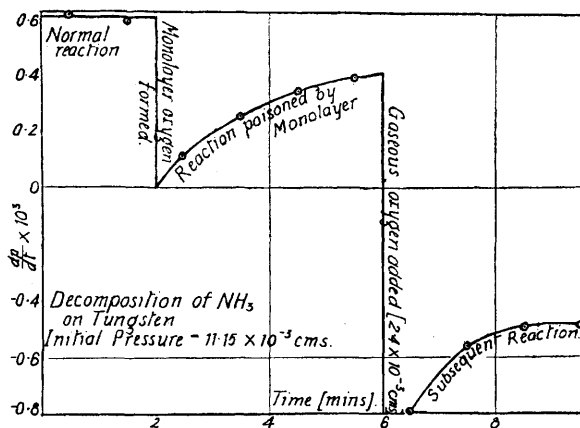


TABLE VII.

CATALYST A. 9 CM. FILAMENT. 0.1 MM. DIAM. TEMP. 1085° K.	$dp/dt \times 10^3$. (NH ₃ , 70% H, 30% D.)	$dp/dt \times 10^3$. (ND ₃ , 98% D.)
	0.72	0.51
	0.63	0.53
	0.70	0.54
	0.64	0.49
	—	0.52
	0.67	0.52

were prepared. These were decomposed on three catalysts A, B, C. The results of a number of the experiments are summarised in Tables VII., VIII., IX.

For the gases of the compositions of the Table VII., a difference in zero point energy ΔE of 550 cal./mol. will give the observed separation. Assuming a linear relation between D-content and ΔE , the ΔE for pure NH₃ and ND₃ is 800 cal./mol.

For catalyst B, $\Delta E = 790$ cal./gram. mol. for the pure gases ND₃, NH₃.

Relative Velocities of Decomposition of Proto- and Deutero-Molecules.

Three samples of ammonia of D-contents 98 per cent., 30 per cent. and 0 per cent.

were prepared. These were decomposed on three catalysts A, B, C. The results of a number of the experiments are summarised in Tables VII., VIII., IX.

TABLE VIII.

CATALYST B. 31 CM. FILAMENT. 0.1 MM. DIAM. TEMP. 956° K.	$dp/dt \times 10^3$. (NH ₃ , 100% H.)	$dp/dt \times 10^3$. (NH 98% D.)
	0.285	0.173
	0.370	0.250
	0.270	0.208
	0.312	0.210

¹¹ Pressures were measured with a Macleod gauge, so that water vapour pressures are not given adequately.

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For Catalyst C, $\Delta E = 890$ cal./gram. mol. for the pure gases. The values of ΔE agree with the experimental errors with each other, and the value 900 cal./gram. mol. given by Taylor and Jungers at much higher pressures.¹² It is of importance to note that ΔE is constant within the errors of experiment for a surface process wherein various tungsten catalysts were employed.

Experiments were made on similar lines with PH_3 and PD_3 . The separations encountered were smaller. Values of dp/dt were derived from pressure-time curves, and, as for ammonia, the relation

$$\text{Log} \left(\frac{dp}{dt} \right)_{\text{PH}_3} / \left(\frac{dp}{dt} \right)_{\text{PD}_3} = \frac{\Delta E}{RT}$$

was used to calculate ΔE . The results of numerous experiments on two different catalysts D and E are summarised in Tables X. and XI. Again both catalysts D and E gave the same separation ΔE of 550 cal./gram. mol. for pure PH_3 and PD_3 .

TABLE X.—CATALYST D. 9 CMS. LONG. 0.1 MM. DIAM. PH_3 AND PD_3 (98 PER CENT. D CONT.).

Press. $\times 10^2$.	$dp/dt \times 10^3$.		Ratio.	Temp. °K.	ΔE (Cals.).
	PH_3 .	PD_3 .			
12	0.238	—	1.42	860	600
	—	0.173			
	0.252	—			
9.5	—	0.400	1.38	901	590
	0.595	—			
	—	0.420			
	—	0.416			
	0.550	—			
8.5	—	0.420	1.32	936	520
	0.935	—			
	—	0.692			
	—	0.729			
9.5	2.53	—	1.25	973	490
	—	2.07			
	2.62	—			

Mean Value, $E = 550$ Cals.

¹² Taylor and Jungers, *J.A.C.S.*, 1935, **57**, 679.

TABLE XI.—CATALYST E. 3I CMS. LONG. 0.1 MM. DIAM. PH₃ AND PD₃ (80 PER CENT. D).

Press. $\times 10^3$ (cms.).	Ratio $\frac{dp}{dt}PH_3 / \frac{dp}{dt}PD_3$.	Temp. °K.	Mean E (Cals.) for 100 Per Cent. PD ₃ .
9	1.27, 1.27	873	490
7	1.24, 1.29		
5	1.23, 1.31		
9	1.42, 1.62, 1.34, 1.43	836	660
7	1.53, 1.47, 1.34, 1.57		
5	1.27, 1.32, 1.20, 1.43		
9	1.34, 1.25, 1.40	819	510
7	1.20, 1.27, 1.34		
5	1.20, 1.37, 1.36		

Mean Value, $\Delta E = 510$ Cals.

Discussion.

Since hydrogen has no influence upon the reaction rates for either phosphine or ammonia, it is improbable that the evaporation of a tungsten hydride layer is a rate determining step. Since, however, proto- and deutero-molecules do not decompose equally fast, in both reactions rearrangement of hydrogen bonds is involved. Thus evaporation of tungsten-nitride or a tungsten-phosphorus layer is not a rate controlling step. For the phosphine decomposition our experiments establish that the rate determining step is a true first order reaction; and the same is most probably true of the ammonia decomposition.

The simplest theory supposes that the energy is communicated by the underlying solid. Then:

$$\text{Rate} = No. (p \cdot \nu) \cdot e^{-E/RT} \quad (1)$$

Where $No.$ = the number of molecules adsorbed/cm.² and ν has the dimensions of a frequency, and is often identified with the characteristic frequency of the solid. The factor p allows for deactivation before reaction, and for the participation of many degrees of freedom in supplying the activation energy (*cf.* Eqn. (2)). More explicitly¹³ the equation becomes:

$$\text{Rate} = No. f(E_1, n) \frac{\alpha}{\beta} \cdot \nu \cdot e^{-E/RT} \quad (2)$$

Here $f(E_1, n)$ expresses the effect of n degrees of freedom on the rate, α is the rate at which the preactivated molecules become critically activated and decompose, supposing no deactivation occurred and β is the rate at which deactivation takes place. $f(E_1, n) \geq 1$; $\alpha/\beta \leq 1$. The transition state method¹⁴ gives the rate as:

$$No. C : F'_a / F_n \cdot KT/h \cdot e^{-E_0/RT} \quad (3)$$

¹³ Hinshelwood, *J.C.S.*, 1935.

¹⁴ Tolman "Statistical Mechanics; Chem. Cat. Co." 1927, Eyring, *J. Chem. Phys.*, 1935, 3, 107 *et al.*

C is the reciprocal of the number of times the activated state must be crossed before reaction occurs. F'_a and F_n are partition functions for the activated and normal states respectively. F'_a however does not include the partition function of the co-ordinate in which decomposition occurs. The partition function of this co-ordinate is included in the factor $KT/h \cdot e^{-E_0/RT}$. T has the maximum rates, at the temperature $\approx 1000^\circ \text{K.}$, according to (1), (2); and (3) respectively¹⁵ equal to

$$5 \times 10^{12} \cdot e^{-E/RT} \quad \text{and} \quad 2 \times 10^{13} \cdot e^{-E_0/RT},$$

where the E 's are not defined in quite the same way;

$$E = E_0 + \Sigma[f \cdot (\nu'T)] - RT,$$

if E is obtained from the expression $\partial/\partial T \cdot \log(\text{rate}) = E/RT^2$. In what follows we shall neglect $\Sigma[f(\nu'T)]$. Also ν in (2) is taken as equal to the lattice frequency of tungsten.

At saturation $N_0 = 7.0 \times 10^{14}$ mols./cm.² (one PH_3 or NH_3 molecule per two W atoms). The ratio 1.4 : 1 gives the ratio of real⁵ to apparent surface.

The rate constants at 1000°K. and at 900°K. for the ammonia and phosphine decompositions are respectively 1.34×10^{-3} cms./minutes and 2.73×10^{-3} cms./minute. Equation (1) gives a value of $p = 10^{-3}$ and 1.4×10^{-4} for the ammonia and phosphine decompositions respectively (assuming $\nu = 5 \times 10^{12}$). On the basis of equation (2) this is to be interpreted as a small ratio α/β . When $\nu = KT/h = 2 \times 10^{13}$, and $E = (E_0 - RT)$, as in the equation (3) the values of $p = C \cdot F'_a/F_n$ become 2×10^{-4} and 3×10^{-5} for the ammonia and phosphine decompositions respectively. A restriction on the validity of these calculations is the assumption of a uniform catalytic activity of the surface.¹⁶

It is interesting to collect the energies of activation recorded for each reaction in the series (see table on opposite page).

The most uncertain method of measuring filament temperature seems to be direct determination of resistance, which often gives much lower energies than do measurements by other means.

Summary.

1. The thermal catalytic decomposition of ammonia on tungsten filaments has been studied between 6×10^{-2} and 6×10^{-4} cms. pressure at temperatures between 950° and 1150°K. The thermal catalytic decomposition of phosphine has been studied between 10^{-1} and 2×10^{-4} cms. pressure, and from 800° to 970°K. On various tungsten catalysts the ammonia decomposition was over early stages a zero order reaction. Towards the end of decomposition, or at the lowest pressures the velocity fell as the ammonia pressure decreased. The kinetics of decomposition of phosphine could be followed from a first order reaction at pressure 10^{-4} to

¹⁵ This calculation assumes that F'_a/F_a has the value unity, and that $p = f(E_1, n) \frac{\alpha}{\beta}$ of equations (1) and (2) have the value unity. Often these quantities are less than unity, $f(E_1, n)$ can however be greater than unity.

¹⁶ Roberts work (*P.R.S.*, 1935, **152A**, 445) suggests that after strong outgassing ($> 2000^\circ \text{K.}$) and then exposure to residual gas from the walls of the apparatus, about 12 per cent. of the tungsten atoms only should remain denuded of oxygen under the conditions of our experiments. The remaining 88 per cent. very quickly takes up a stable atomic film of oxygen.

Worker.	Reaction.	Energy of Activation. (Cals.).	Temperature Measurement.
Hinshelwood and Burk	NH ₃ Decom- position	38.7 (zero order)	Resistance.
Taylor and Jungers	"	35.0 " "	"
Kunsman	"	47.3 " "	Optical Pyrometer
Hailes	"	26.31 " "	Resistance
Perevessenseff, Motscham and Roginsky	"	42.1 " "	Optical Pyrometer
Barrer	"	42.4 " "	Current-Temperature. Characteristics of ideal filaments and compensating fila- ment method.
Melville and Roxburgh	PH ₃ Decom- position	25 (Inter. Order)	Compensating fila- ment method
Barrer	"	25 (First order) 32.2 (Approx. zero order)	Compensating filament method.

5.0×10^{-3} cms., to an intermediate order reaction from 10^{-3} to 5×10^{-2} cms., and an approximate zero order reaction at pressures ca 10^{-1} cms.

2. The rate determining step in both reaction involves a rearrangement of a hydrogen bond, since separations were observed in zero-point energy of 800 to 900 Cals. in the case of proto- and deuterio-ammonia, and 550 Cals in the case of proto- and deuterio-phosphine. The rate determining step in the phosphine decomposition is unimolecular.

3. Hydrogen and nitrogen have no influence upon the velocity of catalytic decomposition of ammonia. Oxygen-treated catalysts are temporarily poisoned but recover their activity at least in part as the reaction proceeds. The presence of a little gaseous oxygen alters the nature of the decomposition at 1000° K.

4. Energies of activation were measured by a compensating filament method which eliminates the effect of end losses. The energy of activation for the zero order ammonia decomposition was 42.4 K. Cals, and for the first order phosphine decomposition 25 K. Cals. The zero order phosphine decomposition gave an energy of activation of 32.2 K. Cals. Calculations were made of the absolute rates, which were respectively $\frac{1}{10000}$ and $\frac{1}{7000}$ for the ammonia and the phosphine decompositions, of the rate given by

$$-dn/dt = N_0 \cdot \nu_0 e^{-E/RT}.$$

It is a pleasure to thank Professor E. K. Rideal, F.R.S., for his interest and advice, and the 1851 Exhibition Commissioners for an Overseas Scholarship.

*Laboratory of Colloid Science,
Cambridge.*