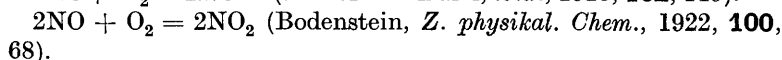
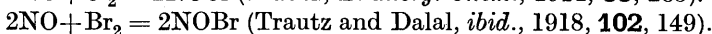
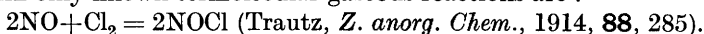


CII.—*The Interaction of Nitric Oxide and Hydrogen and the Molecular Statistics of Termolecular Gaseous Reactions.*

By CYRIL NORMAN HINSHELWOOD and THOMAS EDWARD GREEN.

THE only known termolecular gaseous reactions are :

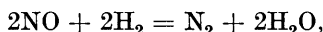


We have succeeded in measuring a homogeneous change between nitric oxide and hydrogen in the region of 1100° Abs. , which proceeds in accordance with the equation

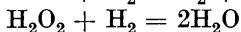
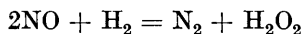
$$- d[\text{NO}]/dt = k[\text{NO}]^2[\text{H}_2] \quad . \quad . \quad . \quad (1)$$

and is thus termolecular.

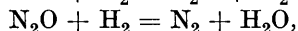
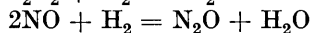
The ultimate result of the interaction being expressed by the equation



it must be supposed that the action takes place in stages thus,



or



the second stage in either of the alternatives being a rapid reaction subsequent to the main change of which the speed is measured.

There are reasons why this new reaction possesses considerable interest. These may be briefly outlined as follows.

The majority of known gaseous reactions are bimolecular. The application of the kinetic theory of gases leads to a simple explanation of these. The molecules which react are those which collide while they possess the "energy of activation," which can be found from the temperature coefficient of the reaction velocity. When the total number of collisions taking place in unit time is multiplied by $e^{-E/RT}$, a fraction representing the chance that the energy of the colliding molecules shall exceed the energy of activation, E , a number is obtained which is very nearly equal to the number of

molecules which actually undergo chemical transformation. Thus the possession of the energy of activation seems to be the only important factor in bimolecular reactions. Since the number of collisions depends on the molecular diameter, and since all molecular diameters are of the same order, 10^{-8} cm., the rate of a bimolecular change is chiefly determined by the value of $e^{-E/RT}$. We find, therefore, that different bimolecular reactions attain approximately equal rates at temperatures which make E/RT respectively the same for each (Hinshelwood and Hughes, J., 1924, **125**, 1841; Hinshelwood and Thornton, *Phil. Mag.*, 1925, **50**, 1135).

A bimolecular gaseous reaction which takes place with conveniently measurable velocity in the neighbourhood of 350° Abs. will have a heat of activation of about 20,000 calories, at 700° Abs. about 40,000 calories, and one which attains an equal speed at 1000° Abs. will have a value of about 60,000 calories. No exception is known to this rule, so that if we know the rate of a bimolecular reaction at a given temperature we can form a fairly accurate estimate of the heat of activation.

From the point of view of the molecular statistics of chemical change termolecular reactions are of special interest, since they depend on the rather rare event of a collision between three molecules. Bodenstein estimates the frequency of termolecular collisions to bear about the same proportion to the frequency of bimolecular collisions as the molecular diameter bears to the mean free path. At atmospheric pressure, the mean free path is of the order 10^{-5} cm., and since the molecular diameter is of the order 10^{-8} , ternary collisions should be about 1000 times less frequent than binary collisions. Thus if we have a bimolecular reaction and a termolecular reaction with equal heats of activation, the rate of the termolecular reaction should be at least 1000 times smaller than that of the bimolecular reaction at the same temperature. It will probably be more than 1000 times slower, since a considerable number of the ternary collisions are likely to be ineffective simply on account of unfavourable orientation of the molecules during impact. Taking this into consideration, it appears that the factor may be nearer 10,000.

Conversely, if a termolecular reaction and a bimolecular reaction were to take place at equal rates at the same temperature, then the heat of activation of the termolecular reaction would need to be the smaller by an amount ΔE , such that $e^{\Delta E/RT} = 1000$ to 10,000. Thus, other things being equal, the heats of activation of termolecular reactions ought to be about 5000 calories less at the ordinary temperature and about 15,000 calories less at 1000° Abs. than those of bimolecular reactions.

A bimolecular reaction which would take place at a rapid but measurable rate at the ordinary temperature would have a heat of activation of 12,000 to 15,000 calories, a termolecular reaction might therefore be expected to have one of 5000 to 10,000 calories. This would mean a very small temperature coefficient. Another factor enters, however, in this case, for Bodenstein found that the reaction $2\text{NO} + \text{O}_2 = 2\text{NO}_2$, instead of having a small positive temperature coefficient, had actually a very small negative temperature coefficient. This he attributed to the diminished "duration of collisions" at higher temperatures, which decreases the chance that two molecules shall still be within molecular distance of each other when a third approaches to complete a ternary collision. This factor is enough just to invert the small positive temperature coefficient which would otherwise be found. The other two termolecular reactions have in fact very small positive temperature coefficients. This new factor, therefore, is equivalent to the reduction of the apparent heat of activation by 5000 calories or so.

Trautz has an alternative explanation of Bodenstein's result. The reaction is supposed to be a bimolecular one between N_2O_2 and O_2 . But since $[\text{N}_2\text{O}_2]$ is proportional to $[\text{NO}]^2$, the reaction is kinetically termolecular. The negative temperature coefficient is due to the increasing dissociation of N_2O_2 at higher temperatures. The apparent heat of activation would thus be equal to the difference between that of the bimolecular reaction between N_2O_2 and O_2 and the heat of dissociation of N_2O_2 ; and actually this difference comes out to be a small negative quantity.

Whichever way of regarding the matter is preferred—and there is not really much difference between the transitory existence of N_2O_2 and a collision of finite duration between two molecules of NO —it is clearly of interest to examine the behaviour of a termolecular reaction which takes place at a much higher temperature, say in the neighbourhood of 1000°Abs . A bimolecular reaction which proceeded at a conveniently measurable speed at this temperature would have a heat of activation of approximately 60,000 calories. A termolecular reaction should therefore have one about 20,000 calories less.

The predicted heat of activation is thus about 40,000 calories. We find actually the heat of activation of the termolecular reaction between nitric oxide and hydrogen to be 44,000 calories. This result seems to show that termolecular reactions can be interpreted satisfactorily in terms of the simple kinetic theory, and to provide further evidence that the energy of activation is a quantity with a real physical meaning.

It is perhaps significant that the four termolecular reactions now

known all involve the participation of two molecules of nitric oxide. It may be simply coincidence, or it may be that the "duration of collision" is greater in encounters between molecules of nitric oxide than in encounters between other molecules, so that there is more chance of the third molecule arriving in time. Some may prefer to call this phenomenon, assuming it to be a real one, formation of N_2O_2 .

Preparation of the Gases.—The hydrogen used was electrolytic and was purified from oxygen by passage over a hot platinum wire; it was then dried with phosphoric oxide. The nitric oxide was prepared in a state of purity by the "nitrometer" reaction and stored in contact with concentrated sulphuric acid in the vessel in which it was made.

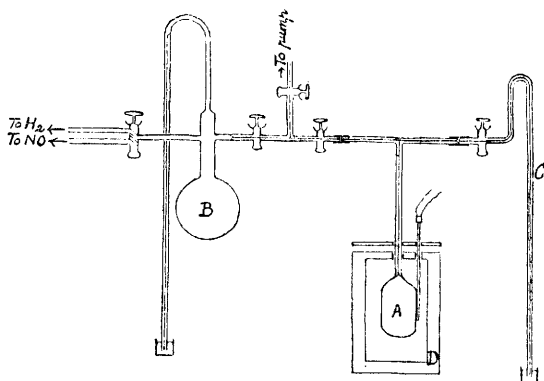
Apparatus and Method of Measurement.—Since the reaction is attended by a decrease in pressure, a simple manometric method can be employed. It is necessary, however, to prevent the condensation of the steam which is produced. This was done in the following way. The reaction vessels were of clear fused silica, 260 c.c. and 155 c.c. in capacity, respectively. The bulb was sealed to a long T-piece of fine silica capillary tube, which communicated with the manometer. The whole of this T-piece was heated to about 140° . Under these conditions, when the reaction took place in the heated bulb, no water vapour diffused through the length of capillary tube and condensed in the cooler part of the apparatus such as the capillary of the manometer itself. The silica capillary tube was joined to the glass parts of the apparatus by means of stout rubber joints. It was arranged that the silica and the glass made good contact beneath the joints, and careful observation showed that no disturbance of any kind arose from the presence of these. They were quite cold. The escape of hydrogen through the walls of the silica bulb at the temperature of the experiments was known from independent experiments to be negligible.

The arrangement of the apparatus is obvious from Fig. 1. *A* is the reaction bulb, heated in an electric furnace, the temperature of which was controlled by a thermo-couple and kept constant to about a degree by hand regulation of the heating current. The thermo-couple was standardised as described in previous papers (J., 1924, 125, 393). *B* is a reservoir in which the gases could be mixed before being allowed to stream into the reaction vessel. In some of the experiments it was omitted.

It was ascertained by direct experiment that the reaction tended asymptotically to the theoretical "end-point" and that diffusion of water vapour from the heated region did not occur during the time of an ordinary experiment.

Kinetics of the Reaction.—The main series of experiments were made at 826°C . This approaches the highest temperature at which experiments can be made accurately. The conclusions drawn about the nature of the reaction are as follows. It is almost entirely homogeneous at higher pressures, and is of the third order, its rate being proportional to the square of the pressure of the nitric oxide and to the first power of that of the hydrogen. At lower pressures, where the reaction is slower, it is less exactly of the third order, and, moreover, the straight line obtained by plotting the initial rate of reaction against the pressure of hydrogen does not pass exactly through the origin. These facts indicate that a certain amount of heterogeneous reaction takes place concurrently with

FIG. 1.



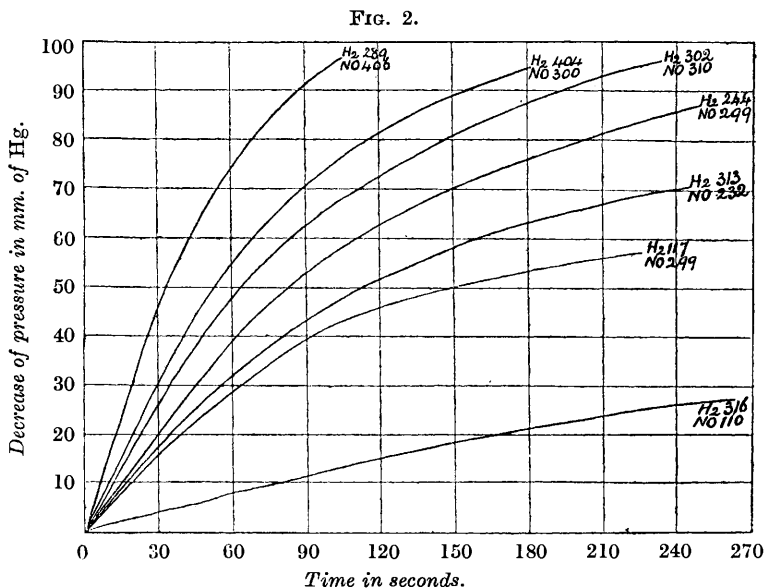
the homogeneous reaction. The heterogeneous change, as would be expected from the strong adsorption of hydrogen by silica, is probably almost independent of the hydrogen pressure. This assumption would explain also the failure of the reaction to follow the equation of a third-order reaction exactly at the lower pressures. These conclusions are confirmed by the addition of powdered silica to the reaction vessel to test for the existence of a surface reaction. There was found to be some, but it accounted for a small fraction only of the total change.

The results were very satisfactorily reproducible. For example, experiments 4, 5, and 31 of the whole series, which were made with the same pressures of nitric oxide and hydrogen, respectively, gave almost exactly superposable curves. This is in pleasing contrast with what is found when the reaction is one which takes place on the surface of the silica. A typical experiment is recorded below and others are shown in the curves of Fig. 2.

Temp. 826°. Initial pressure of NO = 406 mm. Initial pressure of H₂ = 289 mm., t is the time in seconds, and x the change of pressure in mm.

t	8	13	19	26	33	43	54	69	87	110	140	204	310	∞
x	10	20	30	40	50	60	70	80	90	100	110	120	127	144.5

The Order of the Reaction.—The following experiments were made with equimolecular amounts of nitric oxide and hydrogen. τ is the time in seconds required for half the reaction to complete itself,



Since the rate of reaction depends upon the square of the NO concentration but the first power only of the H₂ concentration, a high pressure of nitric oxide has much more effect than a high pressure of hydrogen.

a is the initial pressure in mm. of each gas, and n is the reaction order calculated from the equation $(a_1/a_2)^{n-1} = \tau_2/\tau_1$.

a_1 .	τ_1 .	a_2 .	τ_2 .	n .
354	81	202	224	2.81
340.5	102	288	140	2.89
340.5	102	243	176	2.62
375	95	251	180	2.60

The reason why n falls a little under 3.0 will be discussed below.

Influence of the Pressure of the Separate Gases.—(a) *Nitric oxide.* Experiments were made in which a fixed initial pressure of hydrogen was used and various initial pressures of nitric oxide. Curves were plotted on a large scale and the initial rate of reaction was found by drawing tangents. The following figures show that the rate is

proportional to the square of the nitric oxide concentration. The initial pressure of hydrogen was 400 mm. in each instance.

[NO]. (mm.).	[NO]. Relative.	[NO] ² . Relative.	Rate of reaction. (mm./100 sec.).	Rate of reaction. Relative.
359	2.38	5.57	150	6.00
300	1.98	4.12	103	3.92
152	1.00	1.00	25	1.00

A corresponding series of experiments made with a fixed initial pressure of hydrogen equal to 300 mm. gave the results

[NO]. (mm.).	[NO]. Relative.	[NO] ² . Relative.	Rate of reaction.	Rate of reaction. Relative.
400	1.73	3.00	174	3.86
310	1.34	1.80	92	2.05
232	1.00	1.00	45	1.00

(b) *Hydrogen*. In one series of experiments the initial pressure of nitric oxide was 400 mm.

[H ₂] (mm.).	[H ₂]. Relative.	Rate of reaction (mm./100 sec.).	Rate of reaction. Relative.
289	1.97	160	2.02
205	1.39	110	1.39
147	1.00	79	1.00

In the second series, the pressure of nitric oxide was 300 mm. [The reaction is slower in the ratio $(300/400)^2$ for equal hydrogen pressures.]

[H ₂]	404	302	244	147	117	104
Rate of reaction	103	85	72	59	52	45

These figures give a straight line when plotted, but the line does not pass exactly through the origin. The explanation of this lies in the fact that there is a small amount of surface reaction nearly independent of the pressure of hydrogen. This is what makes the experimentally determined order of reaction slightly less than 3.0. The effect is scarcely noticeable when there is a high pressure of nitric oxide, so that the speed of the gas reaction is great.

Influence of the Reaction Products.—We propose to investigate further the influence of inert gases on the rate of reaction. A preliminary investigation of the effect of the reaction products, steam and nitrogen, was made in the following way. Pairs of experiments were selected in which the nitric oxide and hydrogen were present in equimolecular proportions. A curve showing the amount of change at different times was first plotted from the results of the experiment in which the initial pressure was the greater. A point on this curve could be found at which the pressures of unchanged nitric oxide and hydrogen were the same as the initial pressures in the experiment with smaller initial pressures. This point was

used as the origin in plotting the results of the second experiment. The two curves proceeding from the new origin corresponded to reactions taking place under exactly the same conditions except that in one known amounts of the reaction products were present initially. In general, the curves nearly coincided; if anything, the products had a very slight accelerating influence, but it cannot be described as a first-order effect.

The Termolecular Velocity Coefficients.—The reaction follows the equation (1). If a is the initial pressure of nitric oxide and b that of hydrogen, this becomes

$$dx/dt = k(a - x)^2(b - x),$$

whence

$$kt = \frac{1}{(a - b)^2} \log \frac{b(a - x)}{a(b - x)} + \frac{1}{(a - b)} \left\{ \frac{1}{a} - \frac{1}{a - x} \right\}$$

It is convenient to record results in terms of the period of half-change, τ . If hydrogen is in excess, half-change corresponds to $x = a/2$. Thus

$$k = \frac{1}{\tau} \left\{ \frac{1}{(b - a)^2} \log \left(\frac{b}{2b - a} \right) + \frac{1}{a(b - a)} \right\}$$

When nitric oxide is in excess, half-change corresponds to $x = b/2$. Then

$$k = \frac{1}{\tau} \left\{ \frac{1}{(a - b)^2} \log \left(\frac{2a - b}{a} \right) + \frac{1}{(b - a)} \left(\frac{b}{a(2a - b)} \right) \right\}.$$

Finally, when the two gases are in equimolecular proportions, $k = 3/(2\tau a^2)$.

The following table shows the constancy of k when [NO] and [H₂] are varied considerably. The temperature was 826° C.

[NO].	[H ₂].	τ (secs.).	$k \times 10^7$.	[NO].	[H ₂].	τ (secs.).	$k \times 10^7$.
299	244	112	1.24	110	316	270	1.19
310	302	129	1.19	152	404	204	0.91
300	404	100	1.09	359	400	89	1.12
293	402	100	1.11	144	323.5	227	1.10
406	289	57	1.21	298	280	125	1.35
402	201	46	1.23	181	209.5	264	1.39
405	147	50	1.06	378	376	98	1.08
404	209	49	1.21	370	376	92	1.17
299	147	66	1.60	253	250	180	1.31
175.5	208.5	254	1.50	340.5	340.5	102	1.27
178	220	238	1.45	243	243	176	1.44
232	313	152	1.19	288	288	140	1.29

The increase in k at lower pressures is due to the existence of the small amount of heterogeneous reaction.

Influence of Surface.—The results already described lead us to suspect that a certain amount of surface reaction goes on concurrently with the gaseous change. A series of experiments was

made in a smaller silica bulb containing some powdered silica. A summary of these is given below. The temperature was 826° as before.

Av. value of k for expts. in which [NO] and [H ₂] were both greater than 300 mm.	1.18 × 10 ⁻⁷
Compare av. value for larger, empty bulb	1.17 × 10 ⁻⁷
Av. value of k for expts. in which [NO] and [H ₂] were both greater than 200 mm. but not greater than 300 mm. ...	1.66 × 10 ⁻⁷
Compare av. value for corresponding expts. with the empty bulb	1.30 × 10 ⁻⁷

This confirms our conclusions, and indicates that at pressures above 300 mm. of each gas the reaction is almost entirely homogeneous.

The smaller bulb was now packed nearly half full with powdered silica. Its catalytic activity towards the decomposition of ammonia—a typical heterogeneous reaction—was about twenty to thirty times greater than that of the larger, empty bulb used in the main series of experiments. At a pressure of 270 mm. of nitric oxide and of hydrogen, the value of k was now found to be 2.5 × 10⁻⁷, or about doubled, as compared with the twenty- to thirty-fold increase produced in the rate of decomposition of ammonia. The heterogeneous reaction must therefore be a small part of the whole change. These results can only be regarded as qualitative, since the catalysis of the ammonia decomposition is very erratic and cannot be taken as a strictly quantitative measure of the surface area. At temperatures about 100° lower, the surface reaction was relatively slightly more in evidence, but not very markedly so.

Influence of Temperature.—Three series of experiments were made, two series with the empty bulb, of which the second is the better, since the pressures were higher in all the experiments (greater than 300 mm.), and a third series in the smaller bulb packed with powdered silica. The object of the last series was to find how the proportion of surface reaction varied with temperature, and thus discover what error, if any, would be introduced into the value for the heat of activation determined from the experiments made in the empty bulb.

The first series extended over a range of seven temperatures from 652° to 834° C. The value of E was found to be 42,000 calories. The Arrhenius equation was used in the usual manner.

The results of the second series are given below.

t° C.	826°	788°	751°	711°	683°	631°
k' (av.)	476	275	130	59	25.3	5.3

k' is the velocity coefficient expressed, not as before with the concentrations in mm., but with these converted into gram-molecules per litre. The time is in seconds. By plotting $\log k$ against the reciprocal of $(t + 273)$ a value of E is found equal to 44,000

calories. This second value is the better. We adopt it rather than the average value 43,000.

The third series gave the results

t	827°	785°	745°	718°	684°
k'	1446	692	415	280	90

From these the value found for E is 39,000 calories. In these last experiments rather more than half the reaction was probably heterogeneous, yet the value of E was only changed from 44,000 to 39,000 calories. Hence we may conclude that the correction to be applied to the value 44,000 for the small fraction of surface reaction is negligible.

Conclusion.—We may therefore conclude that the reaction which takes place at 826° C. between nitric oxide and hydrogen is almost entirely in the gaseous phase, and that the velocity coefficient of the homogeneous reaction is within 10% of 1.0×10^{-7} when the concentrations are expressed in millimetres of mercury and the time in seconds. The heat of activation of the gaseous reaction is 44,000 calories. We consider that it is justifiable to use these values in considerations of the molecular statistics of the reaction. From this point of view the reaction possesses much interest. But the presence of some surface reaction makes it rather unsuitable for studies much more detailed than the general one we have described. We are now investigating the catalytic reaction at the surface of platinum.

Summary.

The interaction of nitric oxide and hydrogen in the region 1000° to 1100° Abs. is a termolecular reaction proceeding in accordance with the equation $-d[\text{NO}]/dt = k[\text{NO}]^2[\text{H}_2]$. At pressures above 300 mm. of each of the gases, it is almost entirely homogeneous, but there is a small amount of surface reaction which becomes relatively more important at lower pressures. The heat of activation of the gaseous reaction is 44,000 calories. The molecular statistics of termolecular gaseous reactions are discussed from the point of view of the theory of activation.

It is pointed out that all the termolecular gaseous reactions now known involve the participation of two molecules of nitric oxide.

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[Received, December 22nd, 1925.]