XLVII.—*The Unimolecular Decomposition of Phosphine.*

By CYRIL NORMAN HINSHELWOOD and BRYAN TOPLEY.

AT the present time there remain unsolved problems of considerable interest in connexion with the velocity of unimolecular reactions. Perrin (*Ann. Phys.*, 1919, [ix], **11**, 5) suggested that since the velocity coefficient is not dependent on the concentration of the reacting substance, then in gaseous systems molecules cannot be brought into the reactive state by collisions, and activation must therefore be effected by absorption of radiation.   Lindemann (*Trans. Faraday Soc.*, 1922, **17**, 599) pointed out that the difficulty could also be met by supposing that a molecule, after acquiring by collision the "critical increment" of energy necessary for decomposition, did not necessarily decompose at once, but that on the average a certain time elapsed before an activated molecule decomposed, during which it might be deactivated by a further collision.   If the number of molecules entering and leaving the active state per second is large compared with the number undergoing chemical change, then the fraction of the total number of molecules which are at any moment in the active condition is maintained constant, although the total concentration be varied over a wide range.   At some sufficiently

small concentration, however, the frequency of collisions between molecules would become too small to maintain the supply of active molecules, and a falling off in the velocity coefficient would result.

In order to test this point experimentally, it is necessary to measure the reaction velocity of a homogeneous unimolecular gas reaction at extremely low pressures.   The decomposition of nitrogen pentoxide has been shown (Daniels and Johnston, *J. Amer. Chem. Soc.*, 1921, **43**, 53) to be homogeneous and to follow the unimolecular law, but it was subsequently found to be catalysed by the nitrogen peroxide formed. Recently, Trautz and Winkler (*J. pr. Chem.*, 1922, [ii], **104**, 53) have investigated the isomeric change of *cyclo*propane into propylene, and they claim to have realised experimentally conditions under which the reaction is uninfluenced by the surface of the containing vessel; but the results seem to be rather uncertain.   The only other reaction reported in the literature as being uncatalysed and unimolecular is the thermal decomposition of phosphine : $4PH_3 = P_4 + 6H_2$, studied by Trautz and Bhandarkar (*Z. anorg. Chem.*, 1919, **106**, 95), who concluded that under the conditions of their experiments (namely, in a 3-litre porcelain bulb) the extent of the reaction on the walls of the vessel was negligible at temperatures above 945° Abs., and accordingly that they were dealing with a homogeneous gas reaction.

This reaction is, moreover, of particular interest, since the experiments of Trautz and Bhandarkar have been widely discussed in connexion with the problem of unimolecular reaction velocity. Various forms of the radiation hypothesis have been tested by means of the results and abandoned (compare Langmuir, *J. Amer. Chem. Soc.*, 1920, **42**, 2190), taking Trautz and Bhandarkar's value for the temperature coefficient of the reaction velocity.   And indeed it appeared that there would not even be a sufficient number of collisions to activate molecules rapidly enough to account for the observed velocity (Langmuir, *loc. cit.*; Christiansen and Kramers, *Z. physikal. Chem.*, 1923, **104**, 451). Dushman (*J. Amer. Chem. Soc.*, 1921, **43**, 397), however, succeeded in bringing the results into line with his empirical equation for the velocity of a homogeneous unimolecular reaction.

The experiments on the decomposition of phosphine to be described in this paper were commenced with the object of discovering whether it is possible to realise experimentally the diminution in the velocity coefficient at very low pressures which Lindemann's suggestion leads one to expect.   Since, however, Trautz and Bhandarkar had not tested the unimolecular nature of the reaction by the most conclusive method of varying the initial pressure over a considerable range, and since their results were very variable, it did not seem quite

definitely established that the reaction was unimolecular even in the ordinary sense. Before working at pressures of 1/100 mm., therefore, experiments were made in which the initial pressure of phosphine was varied from 37 mm. to 707 mm. These showed satisfactorily that the velocity coefficients were not influenced by pressure over this range, thus far confirming the results of Trautz and Bhandarkar.

The experiments were made in a bulb of clear fused silica; it was an obvious precaution to repeat the measurements after introducing into the bulb a quantity of powdered fused silica the area of which had been determined. An increase in velocity was observed corresponding approximately to that expected from the increased surface, thus showing that the reaction under these conditions was almost entirely heterogeneous.

The volume of the bulb was 155 c.c. Trautz and Bhandarkar had used a porcelain bulb of 3 litres. It appeared at first sight that silica might be a very much more active catalyst than porcelain, and this together with the fact that the ratio Surface area/Volume was 2·6 times greater in our experiments than in those of Trautz and Bhandarkar seemed to be the obvious explanation of the discrepancy. But the absolute value of the velocity coefficient of the reaction in the silica bulb was approximately equal to that found by Trautz and Bhandarkar for the '' homogeneous '' reaction. In the silica bulb the heterogeneous reaction and the homogeneous reaction would be proceeding simultaneously, the velocity of the latter being uninfluenced by the nature of the bulb. But the reaction in the silica bulb being predominantly heterogeneous, the total reaction velocity would have to be very many times greater than that observed by Trautz and Bhandarkar if the reaction in the porcelain bulb were truly homogeneous.

In view of this difficulty a more extended investigation of the reaction at ordinary pressures was made, from which it was concluded : (a) that in a silica bulb the reaction, so far from being homogeneous at temperatures above 945° Abs., remains completely heterogeneous up to 1044° Abs. at least; (b) that since the observed velocities in the silica bulb were equal to or less than those obtained by Trautz and Bhandarkar at corresponding temperatures in a porcelain bulb, no homogeneous reaction proceeds in·either case.

It was also found by direct experiment that in fact porcelain is not less active catalytically than silica.

Trautz and Bhandarkar did not vary the surface area of porcelain, but based their conclusion as to the homogeneous nature of the reaction upon an apparent variation in the heat of activation, calculated from the temperature coefficient of the reaction, which seemed to indicate a transition from a wall reaction at lower temper-

atures to a pure gas reaction above 945° Abs.   It is very doubtful, however, whether their data really justify the conclusion that the heat of activation actually changes.   Moreover there is very considerable uncertainty in their value of the heat of activation at the higher temperatures, namely 86,700 calories, as may be seen by reference to Fig. 3.

We find : (a) that the heat of activation is constant over a range from 88 degrees above the highest temperature to considerably below the lowest temperature employed by Trautz and Bhandarkar; (b) that the value of this quantity is between 40,000 and 50,000 cals.

A comparison of these results with those of Trautz and Bhandarkar is given in Fig. 3.

The theoretical difficulties which the phosphine reaction had raised depended mainly on this very high value for the heat of activation, and on the assumption that the reaction occurred in the gaseous phase.   These difficulties can therefore no longer be regarded as real, and since there is now no reaction definitely known to be unimolecular and uncatalysed, discussion of the manner in which molecules become activated for such a reaction is perhaps not very fruitful; interest turns rather to the problem of why heterogeneous reactions preponderate.

Preparation of the Phosphine.—Pure phosphine was prepared in the usual way from phosphonium iodide and alkali, bubbled through 30 per cent. caustic soda solution, then passed through a spray trap of glass wool, and then through a long spiral immersed in a Dewar vessel containing a freezing mixture of ice and hydrochloric acid. The gas was further dried by phosphorus pentoxide, and stored over mercury in two gas-holders.   The generating apparatus was entirely of glass; after first filling with electrolytic hydrogen, it was evacuated to below 1 mm.; the evacuation was repeated after a preliminary filling with phosphine.

Apparatus.—The reaction vessel was a bulb of clear fused silica of 155 c.c. capacity, provided with a long, narrow neck, passing through the asbestos lid of the electric furnace in which the bulb was heated.   The neck terminated in a ground silica-to-glass joint with a mercury seal.   A short distance above the seal was a three-way tap, which connected the bulb either to a Gaede pump and McLeod gauge, or to a combination of gas pipettes which enabled the apparatus to be filled with phosphine at pressures from 1 atmosphere down to any fraction of a millimetre.   The whole system was evacuated up to the tap of the gas-holder by means of a Gaede pump before admitting phosphine.

It was originally intended to measure—at very low pressures— the amount of phosphine decomposed in a given time, by condensing

the phosphorus vapour and the undecomposed phosphine in a small bulb immersed in liquid air, and determining the residual hydrogen in a McLeod gauge. Since this portion of the apparatus was not required, it need not be described in greater detail. The portion of the apparatus used is shown in the diagram.

When the reaction bulb A had reached the steady temperature at which the experiment was to be carried out it was evacuated by means of the Gaede pump, and phosphine admitted from the pipette, B. The rate of decomposition was measured by the rate of fall of the mercury in the manometer, M. The time required for the establishment of thermal equilibrium between the inrushing gas and the bulb was determined by experiments with air and found to be less than three seconds. Very rapid rates of change could be measured in the following

FIG. 1.

way : the initial pressure of the phosphine admitted was so chosen, except in special cases, that both the initial and final pressure readings appeared on the scale of the capillary manometer, M, without manipulation of the wide reservoir, R. Readings were taken by two observers, one of whom turned the tap, C, on and off, and three seconds later began to call out manometer readings, the corresponding times being read off to the nearest half second by the second observer. The manometer was tapped vigorously during the whole course of the experiment. The actual rate of fall of mercury in the manometer was never so great that the inertia of the mercury influenced the readings, as was tested by blank experiments with air. By this means it was possible to get concordant results in successive experiments, even when the half-period of the reaction was as small as six seconds. The degree of concordance may be seen by reference to the detailed results given under series 3.

The Furnace.—The bulb was heated in an electric furnace, the
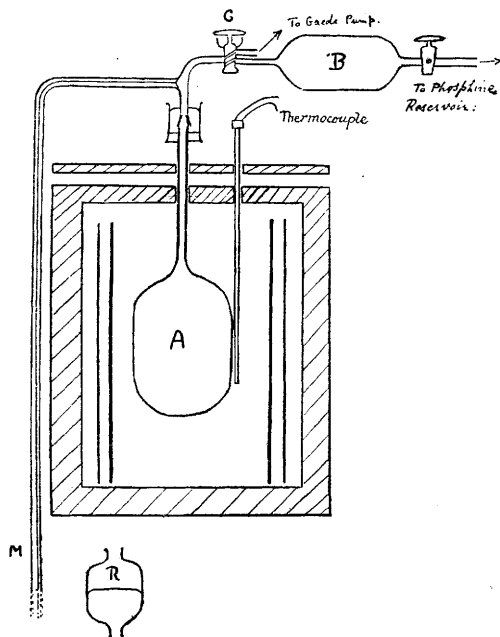
temperature being recorded by means of a thermocouple, placed
almost in contact with the bulb. The furnace was heated by a
current of 6 to 9 amps., which was regulated by hand to within
0·05 amp. by means of an ammeter and a rheostat with a shunt of
higher resistance to serve as a fine adjustment. The temperature
was kept constant to 1° for a period of one to two hours before
beginning a series of experiments at a given temperature, to eliminate
the possibility of a temperature lag.

In the preliminary experiments, it was found that the temperature
was not the same at different points along the length of the furnace.
In one series of experiments, therefore, the space between the walls
of the furnace and the bulb was packed with small iron nails; this,
whilst effective as a means of securing uniformity of temperature,
was subject to practical disadvantages, since the nails became, at
the bright red heat, solidly cemented together, and had subsequently
to be chipped out at considerable risk to the silica apparatus. The
bulb and thermocouple were surrounded, therefore, by two con-
centric cylinders of stout metal the conductivity of which ensured
a uniform temperature in the region of the bulb. This was tested
by moving the thermocouple.

Standardisation of the Thermocouple.—The temperature was
measured by a " Resilia " pyrometer, consisting of a base metal
thermocouple protected by a thin-walled silica tube, and a sensitive
voltmeter provided with a direct reading temperature scale, which
was checked by taking the boiling point of sulphur and the melting
point of pure antimony. In the region of temperature where the
experiments were carried out, a correction of $- 11°$ was added to
the scale readings. Taking into consideration both the errors of the
pyrometer scale and the small unavoidable temperature gradient
in the furnace, the relative temperatures should not be in error by
more than 2°, and the absolute temperatures should be correct
certainly to within 10°, and in all probability to within 5°.

The experiments were arranged in the following series :

Series 1.—Experiments on the variation of the initial pressure of
phosphine over a considerable range ($P =$ initial pressure of
phosphine in mm. and $t =$ half-period of the reaction in sec.).

Expt.	T (Abs.).	P.	t.	Expt.	T (Abs.).	P.	t.
1	953°	379	126	6	955°	360	19
2	957	171	102	7	955	160	16
3	951	79	84	8	955	80	21
4	954	37·5	83	9	956	37·5	16·5
5	957	707	84	10	956	352	19·5
				11	955	162	16

In the above set of experiments the
reaction bulb did not contain
any added silica powder.

In this set of experiments the bulb
contained a quantity of crushed
silica.

These figures establish quite definitely that, at any rate in the region of ordinary pressures, the velocity coefficient is not altered when the initial pressure of phosphine is varied over a 19-fold range, and therefore that the reaction obeys the unimolecular law. But this fact loses the interest it might otherwise have had owing to the circumstance that the reaction is found to be heterogeneous.

Series 2 (Expts. 36—88).—A series of velocity measurements made over a wide range of temperature; the bulb not containing any added silica powder. During this series the activity of the bulb showed considerable variation, the general trend indicating a certain deactivation of the catalytic surface of the bulb. The period of half decomposition is given as the most convenient measure of the rate of reaction. From its average value, t, in each case k is calculated from the relation $k = 1/t \log_e 2$.

Av. half-period (sec.)	119	63	29	41	8·1	23
Av. T (Abs.)	908°	933°	975°	972°	1,042°	1,009°
Av. $k \times 10^3$	5·83	11·0	24·1	16·9	85·6	29·9

Av. half-period (sec.)	15	570	9·9	7·5	262	63
Av. T (Abs.)	1,024°	882°	1,026°	1,029°	928°	963°
Av. $k \times 10^3$	45·3	1·22	70·0	92	2·65	11·0

Av. half-period (sec.)	21·5	123	88
Av. T (Abs.)	999°	939°	949°
Av. $k \times 10^3$	32·2	5·6	7·95

This series is regarded as of a preliminary character. After experiments at higher temperatures, the activity of the surface at lower temperatures was found to have fallen considerably. In series 3, 4, and 5, however, the surface appeared to have reached a fairly constant activity, at least during the course of each separate series.

Series 3.—A series similar to series 2, the bulb containing a quantity of crushed fused silica, the surface area of which was estimated to be approximately 1600 sq. cm. The surface area of the bulb was 213 sq. cm.

Expt.	T (Abs.).	Half-period (sec.)		Av. (sec.).	Av. T.	$k \times 10^3$.
90	958°	24	⎫			
91	956	20	⎬	22	956°	32
92	955	21	⎭			
93	1,007	6·5	⎫			
94	1,007	6·5	⎬	6·3	1,007°	110
95	1,007	6·0	⎭			
96	917	50	⎫			
97	917	55·5	⎬	52·5	917°	13·2
98	917	52	⎭			
99	856	280	⎫	288	858°	2·41
100	859	296	⎭			
101	894	120	⎫	117	894°	5·92
102	894	113	⎭			
103	979	14	⎫	14	979°	49
104	979	14	⎭			
105	828	560	⎫	580	828°	1·19
106	828	600	⎭			

P* 2

Series 4 (Expts. 107—115).—A further series, the bulb not containing any added silica powder.

Av. half-period (sec.)	131	9·3	35·5	26	63·5
Av. T (Abs.)	946°	1,044°	998°	1,018°	970°
Av. $k \times 10^3$	5·29	74	19·5	26·7	10·9

Series 5 (Expts. 127—141).—A series in which a quantity of silica powder of surface area approximately 3,140 sq. cm. was added.

Av. half-period (sec.)	22·2	9·8	6·3	78	36
Av. T (Abs.)	919°	963°	983°	864°	890°
Av. $k \times 10^3$	30·8	70·7	110	8·89	19·2

In a given series the bulb was not removed from the furnace between separate experiments ; the products of decomposition were pumped out, the phosphorus being condensed in a cold tube between the bulb and the Gaede pump. Several determinations were made at each given temperature. Between the separate series the bulb was removed, cleaned, and replaced in the same position in the furnace.

Experiments were satisfactorily reproducible (compare the values of the periods of half decomposition). The degree of constancy of $k \; [= 1/t \cdot \log_{10} p_\infty/(p_\infty - p)]$ through an experiment is seen in the following data, which are typical of the results obtained :

983° Abs.			828° Abs.		
t (sec.).	p (mm.).	$k \times 10^3$.	t (sec.).	p (mm.).	$k \times 10^3$.
2	30	59·6	73	20	0·700
6	60	47·3	173	40	0·63
12	90	46·1	302	60	0·55
19	110	48·5	465	80	0·549
28	120	36·4	662	100	0·532
55	125		906	120	0·527
			1,420	140	0·460
			1,517	155	0·565
			1,630	158	0·560

Fig. 1 shows that diffusion of phosphorus vapour and condensation in the cold tube could occur; but that diffusion was not sufficient to affect appreciably the value of the half period of the reaction is evident from the following considerations : first, there is not a very great diminution of the velocity coefficient in the course of an experiment; secondly, the actual rate of condensation of phosphorus could be observed by leaving the decomposition products in the bulb and observing the slow rate of diminution of pressure due to the diffusion and condensation of the phosphorus vapour. The pressure readings remained almost constant for a period equal to the duration of the experiment. The maximum effect that this source of error could have had on the results is discussed later.

Three series of results (Series 3, 4, and 5) are plotted in Fig. 2.

The lines are numbered in the order in which the series were done; the influence of surface is very evident; thus the effect of increasing the Surface/Volume ratio is shown by the following figures : the relative velocity coefficients are obtained from the graph and refer to the temperature 941° Abs.

Series.	Surface/Volume.	Relative rate of reaction.
4	1	1
3	8·6	4
5	15·7	9·8

The values of k should be proportional to the relative values of the Surface/Volume ratio; but in order to get the large surface of

FIG. 2.
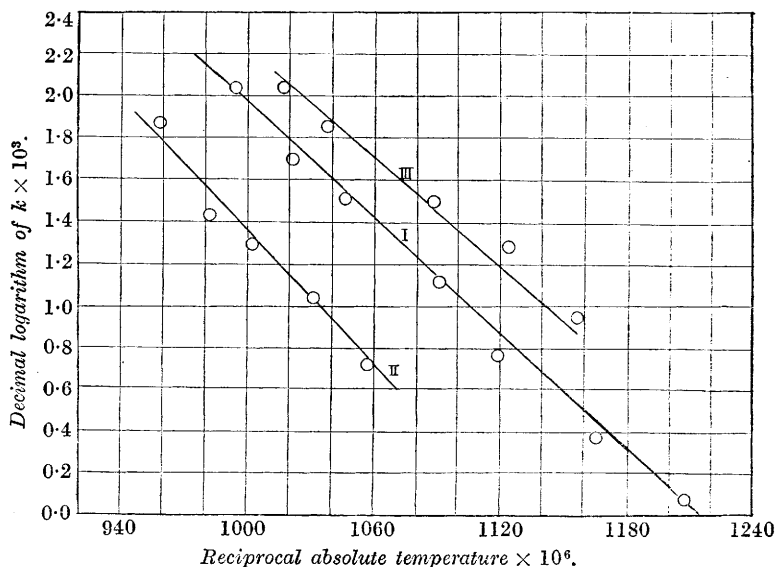
Influence of temperature and surface on the rate of thermal decomposition of phosphine.

I *and* III, *Bulb containing added silica powder.* II, *Silica bulb empty.*

silica employed in Series 3 and 5, the silica had of necessity to be added in the form of powder, the effective surface of which would be less than the total superficial area, owing to the fact that it lay in a heap at the bottom of the bulb. This is quite sufficient to account for the lack of direct proportionality observed. Though there can be no question here of a truly homogeneous reaction, it might be contended, nevertheless, that some part of the reaction takes place in the gaseous phase, and that in the region of temperature considered the transformation from wall-reaction to pure gas

reaction is in progress.   But if a gas reaction of high temperature coefficient had supervened to the extent of say 30 per cent. at 941° Abs., then at 991° Abs. (50° higher), it would preponderate overwhelmingly; this sort of transformation is what Trautz and Bhandarkar believed to be happening in their experiments.   But at 991° Abs. the velocity ratios are $1 : 3 \cdot 7 : 8 \cdot 3$, as compared with $1 : 4 \cdot 0 : 9 \cdot 8$ at 941° Abs.   These agree within the limits of experimental error, considering the variability of the surfaces. Hence there is no evidence for a transformation of the reaction from one type to the other.

Trautz and Bhandarkar did not vary their ratio Area/Volume, but based their conclusion that the reaction became homogeneous at higher temperatures upon a supposed increase in the temperature coefficient of the reaction.   It is maintained that a true gas reaction at this temperature would have a much higher temperature coefficient, or, more correctly, heat of activation than a reaction catalysed by the walls.   If we accept this view, it follows from our experiments that in a silica bulb there is no homogeneous reaction up to temperatures exceeding 1,040 Abs., and since the absolute values of the velocity coefficients in the silica bulb are less than those in the porcelain bulb of Trautz and Bhandarkar it seems to follow that the reaction under their conditions also is heterogeneous.   This argument would of course be invalid if the temperature coefficient of the catalysed reaction were nearly the same as that of the uncatalysed reaction.   The variability of catalytic surfaces makes it almost impossible to detect, by altering the ratio Surface/Volume, the progress of a reaction in the gaseous phase whose velocity is only, say, 10 per cent. of the total velocity.   We may therefore conclude that if general considerations about the temperature coefficient of gas reactions are valid, the phosphine reaction is completely heterogeneous; relying on the experimental data alone, it can be stated with absolute certainty only that it is predominantly heterogeneous over the whole range of temperature; but the assumption of a constant small homogeneous fraction is in the highest degree improbable.

With regard to the difficulty raised by the variability of the surface, this was largely eliminated in a given series by not dismantling the bulb at all, nor admitting air to the silica surface.   The capriciousness of these systems when such precautions are not taken is well illustrated by some experiments originally designed to test directly the catalytic activity of porcelain.

These experiments consisted in measuring the velocity of the reaction in the silica bulb under the following conditions :   (a) In the empty bulb, which had previously been cleaned.   (b) After

introducing a quantity of porcelain powder, of area 740 sq. cm. (c) After removing the crushed porcelain. (d) After replacing the porcelain powder.

All these experiments were done at sensibly the same temperature, namely, at 953° Abs., a temperature approximately equal to the highest used by Trautz and Bhandarkar.

	Expt.	T (Abs.)	Half-period (sec.).	Av. (sec.).	Av. T.	$k \times 10^3$.
(a)	142	953°	28	29	953°	23·9
	143	953	30			
(b)	144	952	15	11·4	953°	60·8
	145	953	12·5			
	146	953	10			
	147	953	8			
(c)	148	953	140	102	953°	6·79
	149	953	64			
(d)	150	956	15·0	8·2	956°	84·6
	151	956	4·5			
	152	956	5·0			

In experiments (a) and (c) the velocity coefficients should have been the same; actually the reaction proceeded about 3·5 times more slowly in the latter. This is attributed to the circumstance that in (a) the surface had been freshly cleaned, whilst on letting air into the apparatus before the experiments (b) and (c) the phosphorus which had condensed in the cold tube after (a) and (b) inflamed, and a certain amount of phosphorus oxide was carried into the reaction bulb, thus altering the nature of the surface exposed to the gas.

With regard to the effect of adding porcelain powder, it will be noticed that the reaction is strongly accelerated, and it would appear that porcelain is at least as active a catalyst as fused silica. Indeed, as regards the variability of catalytic surfaces, the results obtained by Trautz and Bhandarkar at the six highest temperatures would seem to afford a further illustration of this phenomenon. The data are tabulated below; considering the comparatively high degree of accuracy in their individual measurements, the wide variations would seem to be explicable only on the basis of a variable surface :

Temp. Abs. ...	956°	953°	948°	945°	942°	940°
$k \times 10^3$	22, 11, 22	15, 11	17, 10, 10, 11	8·5	17	13, 14

Referring once more to Fig. 2, the points in each series lie fairly satisfactorily on straight lines, thus showing that the value of the heat of activation is constant, again indicating that there is no change in the nature of the reaction as the temperature increases. The points through which line 1 is drawn cover a temperature range of

180°, and those through which line 2 is drawn extend to 88° above
the highest temperature employed by Trautz and Bhandarkar.

Calculation shows that a very small change in the slope of the
line makes a large change in the value of E, the heat of activation.
For this reason E was not calculated from the slope of the line
actually drawn through the points, but from all the experimental
values by applying the method of least squares to the formula
$\log k = A - E/RT$.   The values obtained were :

Series 2 (Preliminary)	$E = 46,700$ cals.
Series 4 (Line 2)	$E = 49,500$ cals.
Series 3 (Line 1)	$E = 41{\cdot}800$ cals.
[Series 5 (Line 3)	$E = 34,100$ cals.]

The points on line 3 were scarcely accurate enough for precise
calculation ; the small difference between the slope of this line and
that of the lines 1 and 2 shows how sensitive the value of E is to
small changes in the slope.

With regard to the possible source of error arising from the con-
densation of phosphorus during an experiment, if we make the most
unfavourable assumption and suppose that all the phosphorus con-
densed at the lowest temperatures used, and none at the highest,
the values of E would be 10 per cent. too small; having regard to the
actual conditions of the experiments, the errors in E arising from
this cause cannot amount to more than 4 per cent., and are probably
less.

In Fig. 3, a comparison is shown of the results of this investigation
with the results of Trautz and Bhandarkar.   All the experimental
points of Trautz and Bhandarkar are indicated by circles ; the curved
line is drawn through the interpolated values given by Trautz and
Bhandarkar, and from which they made their calculations.

The only evidence that the reaction changes in nature, becoming
homogeneous at the higher temperatures, depends essentially on the
increasing upward slope of this curve ; values for the heat of activ-
ation were calculated for each range of 3—5, and varied from
58,664 cals. between 918° and 923°, to 115,823 cals. between 953° and
956°.   The average value for the " homogeneous " reaction between
940° and 956° was 86,719 cals. There seems, however, no justification
for drawing this curved line rather than a straight line.   Indeed, over
the range where the reaction is supposed to become homogeneous,
namely above 940° Abs., the points lie evenly on either side of a
line parallel to the experimental line for the silica bulb which corre-
sponds to a heat of activation of about 49,599 cals.—although the
points are too scattered to permit any line to be drawn with con-
fidence.   Incidentally, the remarks previously made about the sensi-

tiveness of the value of E to small changes in the slope are significant in this connexion.   Since the accuracy of the individual experiments was high, the great variability of the results is in itself indicative of a changing catalytic surface.

FIG. 3.
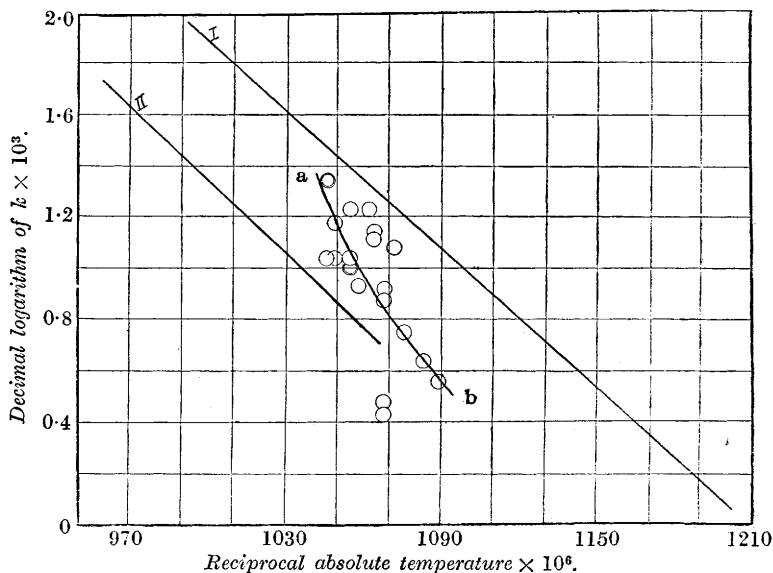
I, *Silica bulb + silica powder (C. N. H. and B. T.)*.
II, *Silica bulb (C. N. H. and B. T.)*.

The points enclosed by circles are the values of Trautz and Bhandarkar.   The line ab is the graph of their interpolated values.

Summary.

(1) The rate of decomposition of phosphine has been measured in a silica bulb, between 828° and 1,044° Abs.

(2) The velocity coefficient has been found to be uninfluenced by a 19-fold variation in the initial pressure of phosphine.

(3) In contradiction to the conclusions of Trautz and Bhandarkar, it is concluded that no homogeneous reaction makes its appearance up to 1,044° Abs.

(4) The heat of activation is constant and lies between 40,000 and 50,000 calories, and provides no evidence for the transformation of a heterogeneous " wall " reaction at lower temperatures into a homogeneous gas reaction at higher temperatures.

The theoretical difficulties in connexion with this supposed homogeneous reaction have therefore no reality.

Part of the cost of the apparatus used in this investigation was covered by grants from the Chemical Society and the Royal Society, to both of which bodies we would express our indebtedness. We have also to express our thanks to the Department of Scientific and Industrial Research for a grant to one of us (B. T.) during part of the time that this work has been in progress.

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