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# The Kinetics of the Homogeneous Thermal Decomposition of Ethyl Ether at Pressures up to Two Hundred Atmospheres

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(Received May 28, 1934)

A new and simple apparatus is described by means of which it is possible to investigate the kinetics of homogeneous gas reactions up to pressures of several hundred atmospheres. With this apparatus the decomposition of gaseous ethyl ether has been investigated at 426°C over the pressure range 2000 to 14,500 cm. The rate of reaction increases rapidly with pressure up to 10,000 cm and then

increases more slowly. The rate at 14,500 cm is approximately 50 times greater than the previously assumed value at infinite pressure. It is shown that by assuming that the number of degrees of freedom involved varies with the time between molecular collisions it is possible to explain these results. Further investigations are in progress.

## INTRODUCTION

A REACTION may be quite definitely designated as unimolecular, the rate constants of which show a characteristic behavior in that they tend to a constant value as high pressures are approached, but fall in value as one goes to low pressures. "As a matter of fact," to quote O. K. Rice,<sup>1</sup> "in many cases . . . this is a statement of theoretical expectation rather than an experimental fact, since the limiting high pressure rate has not been reached experimentally." It was therefore considered to be of interest to extend the range of experimental investigation to as high a pressure as possible.

According to the Hinshelwood theory<sup>2</sup> (theory I)<sup>3</sup> of homogeneous unimolecular reactions, on plotting  $1/k$  against  $1/P$  a straight line with an intercept at  $1/k_\infty$  should be obtained. The theories of Rice and Ramsperger<sup>4</sup> (theory II) and of Kassel<sup>5</sup> (theory III) demand a curved plot, the curvature being greatest when the number of squared terms involved is large. However, the latter two theories depend, for their complete verification, in by far the majority of cases, upon an extrapolation to the high pressure rate based upon theory I, i.e., a linear

extrapolation of  $1/k$  against  $1/P$  is used although this is almost certainly incorrect. It is therefore very desirable to approximate experimentally as closely as possible to the high pressure rate.

The localized energy theories (II and III) also predict different Arrhenius heats of activation at low and high pressures. While the difference in energies of activation may be too small to be evaluated experimentally in most cases, the general result predicted is that the rate should fall off more rapidly at higher temperatures as the pressure is lowered; this effect should be most pronounced with large values of  $n$ .

A further possibility attendant upon increasing the experimental pressure range has been pointed out by O. K. Rice.<sup>6</sup> Over an extended pressure range it may be possible to have several transitions from unimolecular to bimolecular rates in the case of a complex molecule. Fletcher and Hinshelwood<sup>7</sup> also bring forward evidence indicating the possibility of several activated states for a given molecule, these different activated states having different transformation probabilities.

There are, then a large number of inducements for extending the pressure range of kinetic measurements. Experiments at low pressures have yielded results of great importance, and high pressure rate measurements may reveal further material of theoretical value.

<sup>1</sup> Rice, J. A. C. S. **54**, 4558 (1932).

<sup>2</sup> Hinshelwood, Proc. Roy. Soc. **A113**, 230 (1926).

<sup>3</sup> This method of identification of current theories follows the usage of Rice and Ramsperger.

<sup>4</sup> Rice and Ramsperger, J. A. C. S. **49**, 1617 (1927).

<sup>5</sup> Kassel, J. Phys. Chem. **32**, 225 (1928).

<sup>6</sup> Rice, Zeits. f. physik. Chemie **B7**, 226 (1930).

<sup>7</sup> Fletcher and Hinshelwood, Proc. Roy. Soc. **A141**, 41 (1933).

At the time this investigation was initiated some work had already been done in what may be termed the high pressure range. Kistiakowsky<sup>8</sup> investigated the hydrogen iodide decomposition at concentrations up to seven moles per liter. Nagasako and Volmer<sup>9</sup> followed the effect of pressure on the kinetics of the decomposition of nitrous oxide up to 800 cm, the reaction being found to remain unimolecular as the pressure was increased. Newitt and Vernon<sup>10</sup> reported an investigation of the decomposition of diethyl ether at pressures up to 17 atmospheres, but aside from suggesting a chemical mechanism drew no theoretical conclusions from their work. Coffin and Geddes<sup>11</sup> have recently reported a study of the transition from paraldehyde to acetaldehyde over a range extending from a few millimeters to eighteen atmospheres; they find a rather unexpected decrease in rate with increased pressure.

#### APPARATUS

The apparatus finally devised is extremely simple in principle. A quantity of the reactant is introduced by distillation into a steel reaction vessel which is connected to a pressure measuring device by steel capillary tubing, the gas pressure being transmitted to the gauge through a liquid. The course of the reaction is then followed by observing the change of pressure with time.

The complete assembly is shown in Fig. 1, and the detailed construction of the reaction vessel in Fig. 2.

#### Reaction vessel

A cylindrical bar of "Stabrite" stainless steel 8 inches long and 1.5 inch external diameter was drilled to a depth of 7.5 inch, the bore being 0.75 inch in diameter. The upper end of the hole was widened to 1 inch diameter and tapped to take a stainless steel adapter. This adapter (part 5, Fig. 2), after being seated firmly was welded into place, particular care being taken to ensure the absence of slag holes in the weld. The emergent end of the adapter had a 0.25 inch bore and

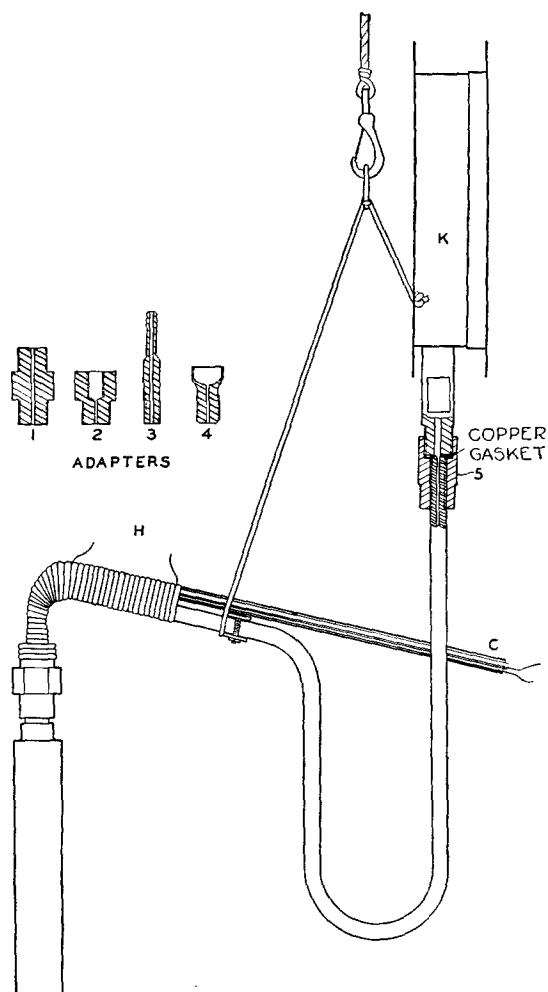


FIG. 1. Reaction vessel complete assembly.

was machined down to 0.5 inch diameter. The upper surface was scored with a circular 60° V-groove. The volume of the bomb was 47 cc.

The method of coupling the bomb to the tubing was a modified form of that employed by the Fixed Nitrogen Research Laboratory (U. S. Department of Agriculture).<sup>12</sup> A small collar of stainless steel was made to screw on the tubing end. A union nut of machine steel was then screwed down tightly on the adapter as indicated, drawing the tubing and adapter ends firmly together and thus compressing the inserted annealed copper gasket. The copper flowed into the V-groove on the adapter end, and into a

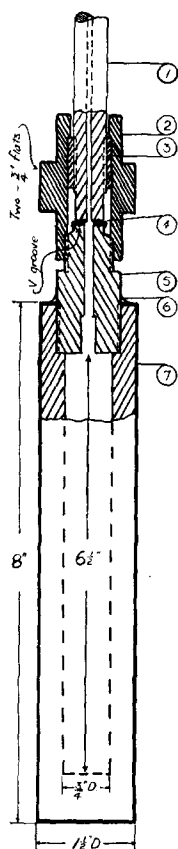
<sup>8</sup> Kistiakowsky, J. A. C. S. **50**, 2315 (1928).

<sup>9</sup> Nagasako and Volmer, *Zeits. f. physik. Chemie* **B10**, 414 (1930).

<sup>10</sup> Newitt and Vernon, *Proc. Roy. Soc.* **A135**, 307 (1932).

<sup>11</sup> Coffin and Geddes, *J. Chem. Phys.* **2**, 47 (1934).

<sup>12</sup> Curtis, *Fixed Nitrogen*, p. 267, New York, Chemical Catalog Co. (1932).



Number	Name of Part	Material
(1)	Tubing	Stainless Steel
(2)	Union Nut	Stainless Steel
(3)	Threaded Adapter	Stainless Steel
(4)	Gasket	Annealed Copper
(5)	Adapter	Stainless Steel
(6)	Weld	Stainless Steel
(7)	Bomb	Stainless Steel

FIG. 2. Details of reaction vessel.

similar groove scored on the tubing end, and so formed a gas-tight joint. No part of the union was then exposed to the gas pressure. Difficulty was encountered, due to lack of suitable equipment, in scoring the tubing end uniformly, and also in providing perfectly plane surfaces on the two ends to be brought together. It was found necessary on this account to exert exceptional force on an 18 inch spanner in order to effect a gas-tight joint.

### Tubing

The stainless steel tubing was made to specifications (by the Summerill Tubing Co.),

0.5 inch external diameter and a capillary bore of approximately 0.05 inch. The tubing was bent cold into the shape indicated in Fig. 1. The end of the tubing affixed to the bomb has been described; the other end which formed one arm of a U-bend was threaded to take an adapter, 5, made of machine steel with two 0.75 inch milled flats. This adapter was tapped so as to take any one of several adapting units or a Bourdon gauge.

At the end towards the bomb the tubing was wound with a small nichrome heating element. Insulated from this by a few turns of asbestos rope was placed a thermocouple junction enclosed in a Pyrex tube, *C*. The thermocouple and heating element were then tightly wrapped with several turns of asbestos rope as indicated at *H* in Fig. 1.

### Gauges

Bourdon gauges were used to follow the change of pressure during the reaction. Two Crosby, 8.5 inch dial, AIH gauges were employed: One was graduated in 20 lb. units from 0 to 1500 lbs./sq. inch, the other was graduated in 100 lb. units from 0 to 5000 lbs./sq. inch. When in use their tubes, made of rust resistant steel, were filled with butyl phthalate.

The gauges were guaranteed by the manufacturers to be accurate to within 1 percent of the maximum graduation at any part above the first 5 percent of the scale. In practice the first 15 percent of the scale was seldom used. In order to calculate rate constants only a series of differences in pressure over a comparatively short range were required. It was therefore considered justifiable to assume that the true difference between any two readings in a single run was equal to the difference indicated by the gauge within the limits set by other sources of experimental error. Since rate measurements checked well within the possible experimental error, it was not deemed necessary to recalibrate the gauges. As a matter of interest, however, the low pressure gauge was checked against the vapor pressure of carbon dioxide at 0°C and 20°C; the pressures indicated were 515 and 835 lbs./sq. inch, respectively, checking well with the accepted values ((I.C.T.) of 506 and 831 lbs./sq. inch.

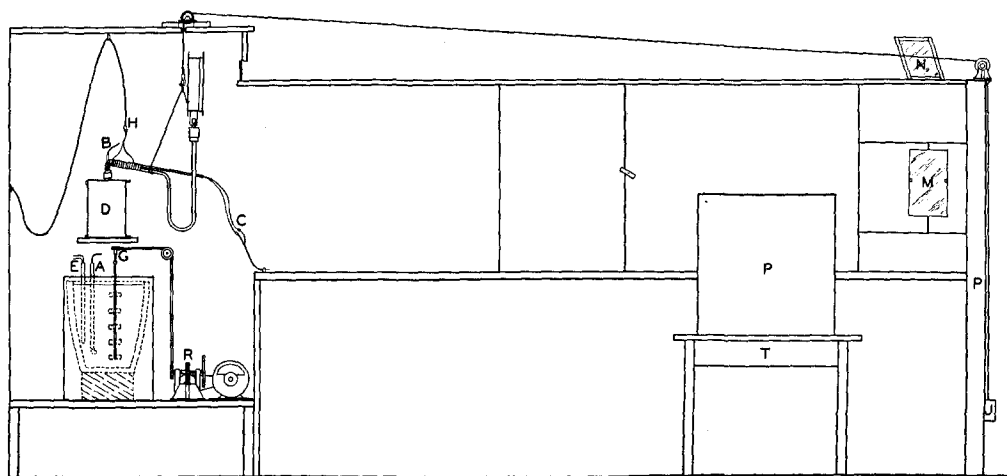


FIG. 3. Complete apparatus.

As has been frequently pointed out, Bourdon gauges tend to "creep" with long use, and periodic recalibration is necessary. During the period of this research, however, neither of the gauges was in operation for a total time exceeding 50 hours, and only seldom were they subjected to more than 75 percent of the maximum dial reading.

### Experimental procedure

The bomb assembly was connected with a glass filling system through a rubber stopper and a cup shaped metal adapter. The reaction vessel was then cooled in an acetone-carbon dioxide mixture, and purified ethyl ether was introduced by distillation. This was followed by a thread of mercury which filled the steel capillary tubing to the bend next the bomb. The U-bend was then cooled, freezing the mercury, and butyl phthalate run in above the mercury.

The bomb assembly was then removed from the filling unit, the gauge was screwed tightly into place, and the entire unit suspended as indicated in Fig. 3. The bomb was placed in the pre-heating furnace *D*, which was constructed from a hinged organic combustion furnace and fitted around the bomb. The bomb was preheated to a temperature about 50° below that at which reaction takes place at an appreciable rate. The heating element *H* was kept about 50° above the critical temperature of the reactant in order to prevent the formation of a liquid phase during

the reaction. The temperatures of the furnace *D* and the heater *H* were followed by a furnace pyrometer.

From this stage on all manipulations were made by the operator seated facing the plate glass mirror *M*, and protected by a stout housing of  $\frac{3}{4}$  inch planks fitted with laminated safety glass windows. During the pre-heating period the acetone-carbon dioxide mixture surrounding the U-bend warms up until the mercury in the capillary melts, allowing the pressure being built up in the bomb to register on the gauge. When the pressure reading has reached its maximum constant value, the air furnace is swung open. Simultaneously the counterweight *J* is gently given an upward impetus and a portion of the weight removed. The bomb sinks rapidly into a six liter bath of molten lead until only the union nut appears above the surface. Pressure readings are then taken at frequent time intervals by means of a telescope directed at *M*.

When the bomb is first introduced the temperature of the lead bath drops several degrees, but within a minute the temperature may be brought to the desired equilibrium value. On account of the high heat capacity of the lead, fluctuations in temperature are reduced to a minimum, a constancy of  $\pm 1^\circ\text{C}$  being maintained by manual control throughout a run. The temperature of the bath was measured by means of a chromel-alumel thermocouple and could be read to about  $0.2^\circ\text{C}$ .

When a run had progressed sufficiently to give all the desired information, the bomb assembly was withdrawn from the lead bath and allowed to cool in the air. The bomb was then cooled in an acetone-carbon dioxide mixture, and when the pressure had dropped to 600 lbs. per sq. inch or less the mercury in the U-bend was frozen and the gauge removed. If the products of the reaction were to be discarded, the bomb was inverted and, when the mercury melted, the gas pressure forced out the mercury and butyl phthalate in the capillary. If it was desired to collect the products of reaction for analysis they were allowed to enter an evacuated two liter flask through a steel needle valve. The bomb and capillary were then rinsed out with ether prior to making another run.

#### EXPERIMENTAL RESULTS

Pressure-time data for runs at various pressures are given in Table I and are plotted in Fig. 4.

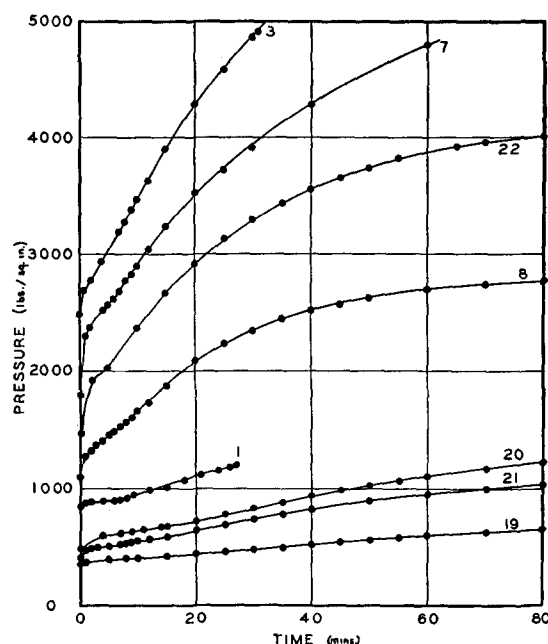


FIG. 4. Pressure-time curves.

TABLE I. Pressure-time data for runs at various pressures. I, time in minutes; II, pressure, lbs./sq. in.

A		B		C		D		E		F		G		H	
I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II
0	350	0	410	0	490	0	850	0	1100	0	1470	0	1800	0	2490
1	380	1	480	2.25	595	1	885	1	1280	2	1930	1	2300	1	2690
2	385	2	490	4	600	2	890	2	1325	3	1950	2	2390	1.5	2750
5	395	3	500	5.5	605	4	900	3	1370	5	2030	4	2520	2	2780
10	405	5	510	7	620	6	900	4	1405	10	2370	5	2570	2.75	2840
15	422	7	525	9	635	7	910	5	1455	15	2670	6	2620	4	2940
20	440	10	550	11	650	8	925	7	1530	20	2920	7	2680	5.75	3090
30	480	15	590	15	680	10	950	10	1660	25	3130	8	2780	7	3195
40	520	20	640	25	780	12	990	15	1890	30	3300	9	2830	8	3280
50	560	30	740	35	890	15	1000	20	2090	35	3440	10	2900	9	3380
60	595	40	822	50	1025	18	1075	30	2355	40	3560	12	3045	10	3470
80	660	70	998	70	1165	21	1100	40	2520	45	3660	15	3240	12	3630
100	715	100	1087	90	1265	24	1150	60	2690	50	3740	20	3535	15	3900
120	760	120	1130	110	1335	25	1175	80	2775	55	3830	25	3720	20	4290
180	845	∞	1320	130	1385	26	1200	100	2810	60	3865	30	3900	25	4590
∞	1020			150	1420			120	2865	65	3915	60	4795	30	4870
				170	1450			180	2920	70	3950			31	4910
				190	1470			225	2950	∞	4140				
				220	1500			∞	3140						

A. Initial pressure=26.9 atm.; reaction vessel C; temperature 426°C;  $k = 1.1 \times 10^{-4}$  sec.<sup>-1</sup>. B. Initial pressure=34.4 atm.; reaction vessel C; temperature 424.5°C;  $k = 2.5 \times 10^{-4}$  sec.<sup>-1</sup>;  $k_{426} = 2.7 \times 10^{-4}$  sec.<sup>-1</sup> (calc.). C. Initial pressure=40.8 atm.; reaction vessel C; temperature 424°C;  $k = 2.7 \times 10^{-4}$  sec.<sup>-1</sup>;  $k_{426} = 3.0 \times 10^{-4}$  sec.<sup>-1</sup> (calc.). D. Initial pressure=61 atm.; reaction vessel A; temperature 426.5°C;  $k = 4.0 \times 10^{-4}$  sec.<sup>-1</sup>;  $k_{426} = 3.9 \times 10^{-4}$  sec.<sup>-1</sup> (calc.).

E. Initial pressure=92 atm.; reaction vessel A; temperature 428°C;  $k = 7.1 \times 10^{-4}$  sec.<sup>-1</sup>;  $k_{426} = 6.4 \times 10^{-4}$  sec.<sup>-1</sup> (calc.). F. Initial pressure=121 atm.; reaction vessel C; temperature 426°C;  $k = 6.7 \times 10^{-4}$  sec.<sup>-1</sup>. G. Initial pressure=167 atm.; reaction vessel A; temperature 425°C;  $k = 6.3 \times 10^{-4}$  sec.<sup>-1</sup>;  $k_{426} = 6.7 \times 10^{-4}$  sec.<sup>-1</sup> (calc.). H. Initial pressure=190 atm.; reaction vessel A; temperature 424°C;  $k = 6.3 \times 10^{-4}$  sec.<sup>-1</sup>;  $k_{426} = 6.9 \times 10^{-4}$  sec.<sup>-1</sup> (calc.).

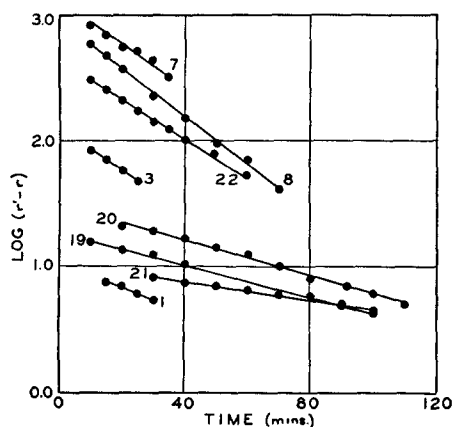


FIG. 5. Results plotted according to Guggenheim method.

The rate constants have been calculated directly from the pressure-time readings using the method of Guggenheim,<sup>13</sup> which is particularly suitable since it requires knowledge neither of the initial pressure nor of the initial time. The linearity of the curves in Fig. 5 shows the applicability of the method. The method has been applied to find the initial rate constant with reference to fractional pressure increase, rather than a rate constant which might be calculated therefrom by correcting for the number of moles of gas formed per mole of ether decomposed. The method by which the true rate constants are obtained from these values is described later. The experiments have varied slightly as to temperature, ranging from 424 to 428°C. In order to bring all to a common basis for comparison, the rate constants have been recalculated to 426°C by assuming an energy of activation of 53,000 calories per gram molecule. Since, at most, the correction is made for 2°C, the error that may be introduced is negligible even if the energy of activation assumed is erroneous in the region under investigation.

For the purpose of plotting rate against pressure an approximation to the initial pressure must be made. When the pressure readings of an individual run are plotted against time it is found that the curve (Fig. 6) obtained is divided into three more or less distinct portions. The first portion may be attributed to the thermal

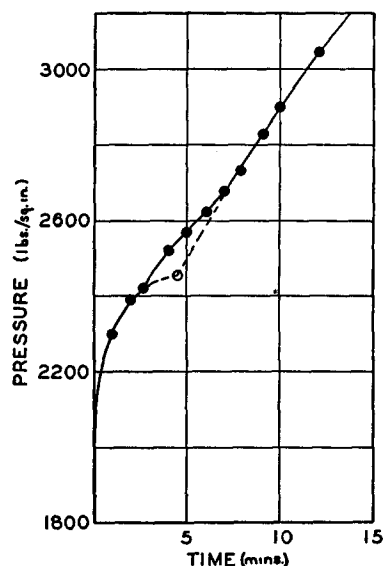


FIG. 6. Determination of initial pressure.

increase in pressure of the gas on passing from the pre-heating temperature to the temperature of the lead bath; this portion is characterized by a rapid increase of pressure which gradually decreases in rate. During the next few minutes the rate of increase of pressure picks up again, this being due to the reaction process starting while the superimposed thermal increase is drawing to a close. Finally the curve smooths out again and becomes a purely logarithmic rate curve. To determine the initial pressure a sufficiently accurate approximation may be made by extrapolating the pure reaction curve until it meets the extrapolated thermal expansion curve.

#### COMPARISON OF RESULTS AT HIGH AND LOW PRESSURES

The decomposition of diethyl ether was first studied by Hinshelwood.<sup>14</sup> His rate measurements have since been confirmed by Steacie<sup>15</sup> and by Kassel<sup>16</sup> within a range of one or two degrees in the absolute temperature scale. Hinshelwood represents the rate by the equation

<sup>14</sup> Hinshelwood, Proc. Roy. Soc. **A114**, 84 (1927).

<sup>15</sup> Steacie, J. Phys. Chem. **36**, 1562 (1932); J. Chem. Phys. **1**, 313 (1933).

<sup>16</sup> Kassel, J. A. C. S. **54**, 3641 (1932).

<sup>13</sup> Guggenheim, Phil. Mag. **7**, 538 (1926).

$$\ln k = 26.47 - 53,000/RT.$$

Kassel<sup>17</sup> finds, on recalculation of Hinshelwood's data, that the results may be more satisfactorily given by

$$\ln k = 26.35 - 53,000/RT.$$

O. K. Rice and Sickmann<sup>18</sup> have published a preliminary note on rate measurements at low pressures (0.15 to 490 mm), and find an activation energy of about 60,000 calories compared to Hinshelwood's 53,000. They also report tentatively the appearance of a second unimolecular reaction at these low pressures. Newitt and Vernon<sup>19</sup> have extended the measurements up to a pressure of about 17 atmospheres. Their results indicate an energy of activation approximately equal to that found by Hinshelwood.

Hinshelwood gives the following equation as representing the main reaction over the range 150 to 500 mm:



This would indicate a pressure increase of 250 percent, but Hinshelwood found the pressure increase in general to be about 188 percent; at lower pressures the increase may have been somewhat larger, approaching 210 percent, although the experimental accuracy was insufficient to establish this definitely.

Newitt and Vernon in the pressure range from 3 to 14 atmospheres found the pressure increase to be  $175 \pm 2$  percent. They interpret their results, in the light of analyses, as indicating a dual mechanism. The ether molecule is supposed to decompose in two ways:

- (1)  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5 = \text{HCHO} + \text{CH}_4 + \text{C}_2\text{H}_4$   
 $\text{HCHO} = \text{H}_2 + \text{CO}$   
 $\text{C}_2\text{H}_4 + \text{H}_2 = \text{C}_2\text{H}_6.$
- (2)  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5 = \text{CH}_3\text{CHO} + \text{C}_2\text{H}_6$   
 $\text{CH}_3\text{CHO} = \text{CH}_4 + \text{CO}.$

Analyses carried out at various stages during single runs indicate that the formation of acetaldehyde and ethane is favored at higher

pressures. There would seem to be no *a priori* reason for expecting this. In any case it seems probable that the variation of the products with pressure is due to secondary reactions rather than to a change in the primary step, since the activation energy does not vary with pressure.

### The products of the reaction

A comparison of the products obtained in the various investigations is given in Table II.

TABLE II. *The products of the reaction.*

Observer	Pressure, atm.	Temperature, °C	CO <sub>2</sub> , %	C <sub>2</sub> H <sub>4</sub> , %	CO, %	CH <sub>4</sub> , %	C <sub>2</sub> H <sub>6</sub> , %	H <sub>2</sub> , %
Hinshelwood	ca. 0.3	477	0.0	8.9	27.9	54.4	8.8	—
Newitt & Vernon	0.26	530	—	7.4	30.8	47.9	8.7	4.1
Newitt & Vernon	2.95 to 13.8	490	0.1	0.8	31.4	32.2	31.1	2.1
Newitt & Vernon	2.95 to 13.8	490	0.1	1.9	30.6	33.3	31.6	1.4
Stearie and Solomon	26.9	426	0.1	5.0	26.5	33.3	32.6	—
Stearie and Solomon	34.4	424	0.1	4.0	30.3	32.3	31.5	—

It will be seen from the above table that the general nature of the products does not change with changing pressure. The main change on going from low to high pressure is an increase in the amount of ethane at the expense of ethylene and methane. It should be noted that virtually all the change occurs in going from 0.3 to 3 atmospheres; above this pressure the products remain virtually the same.

### Homogeneity and pressure increase

A certain degree of difficulty arises in considering whether or not at high pressures we are dealing with the same reaction as at low pressures, and if, therefore, the data are comparable. We may rule out, on several grounds, the possibility of a concurrent heterogeneous reaction becoming prominent at high concentrations. Reaction vessels of two different sizes have been used and these have yielded identical results: The volume-surface ratio of Bomb A was 0.17 cc/cm<sup>2</sup>, and of bomb C 0.04 cc/cm<sup>2</sup>; i.e., the volume surface ratio has been varied over four-fold. In any case, a high concentration in the gaseous phase tends to make any heterogeneous process negligible. In addition, the mere fact that the rates found are comparable with those of Newitt and Vernon at intermediate pressures would indicate that no additional complicating factor of this nature is involved.

A further point to be considered is the fact

<sup>17</sup> Kassel, *Kinetics of Homogeneous Gas Reactions*, New York, 1932.

<sup>18</sup> Rice and Sickmann, J. A. C. S. **54**, 3778 (1932). We are indebted to Dr. Rice for permitting us to see his complete results before their publication.

<sup>19</sup> Newitt and Vernon, Proc. Roy. Soc. **A135**, 307 (1932).



that as the initial pressure is increased the percentage pressure increase at completion decreases, thus:

Hinshelwood	low pressures	(210%)
	2.5 cm to 48.7 cm	188%
Newitt and Vernon	200 to 1200 cm	175%
Steacie and Solomon	2040 cm	158%
	2600 cm	161%
	6800 cm	132%
	9700 cm	120%

However, it is possible to correct for this by assuming that a definite fraction of the total pressure increase indicates the same fractional decomposition, and all rate constants reported here have been calculated on that basis. In any case, even if this assumption is in error, it cannot throw the results out by a factor of more than 1.5. In order to reduce the results of the various investigations to a common basis the data have been treated as follows:

(a) *This investigation.* The apparent rate constants, listed in Table I, have been corrected to the true constants by allowing for the pressure increase at completion. The values of  $T_{20}$  (the time for 20 percent completion) have been calculated from the rate constants by using the relationship  $T_{20} = 0.223/k$ . The data are summarized in Table III. The second to last column

TABLE III. Summary of results.

Pressure, cm	$\frac{10^4}{P}$	$k \times 10^4$ (apparent), sec. <sup>-1</sup>	$k \times 10^4$ (true) sec. <sup>-1</sup>	Total % pressure increase	$T_{20}$ , min.
2040	4.90	1.1	0.70	158	53.1
2600	3.85	2.7	1.7	161	21.8
3100	3.23	3.0	1.9	(156)	19.5
4650	2.15	3.9	2.7	(145)	13.7
6800	1.47	6.4	4.9	132	7.6
9700	1.03	6.7	5.6	120	6.6
12,700	0.79	6.7	6.0	(112)	6.2
14,500	0.69	6.9	6.4	(108)	5.8

in Table III gives the total pressure increase at completion; the values in brackets were obtained by interpolation or extrapolation.

(b) *Hinshelwood.* Hinshelwood's data for 525°C were used. The data are given in the form of times for a 50 percent pressure increase. We may assume with Hinshelwood that this represents 26.6 percent reaction. The values are then multiplied by 0.722 to give  $T_{20}$ . Using 53,000 calories for the energy of activation, we then

multiply by 120.5 to obtain  $T_{20}$  at 426°C. It is true that the variation of rate with pressure will be slightly different at 426°C, but the error thus introduced is negligible.

(c) *Steacie.* Steacie's results at 478°C have been treated in the same way, again assuming that 188 percent pressure increase corresponds to complete reaction.

(d) *Rice and Sickman.* We have used Rice and Sickman's values at 478 and 462°C. Their results are given in the form of constants expressing the rate of pressure increase. These have been transformed as before assuming 188 percent increase at completion. In correcting to 426°C we have used 53,000 calories for the heat of activation instead of 60,000 as reported by them, in order to make the calculations of the various investigations consistent with one another.

(e) *Newitt and Vernon.* Results at 462 and 490°C have been used. The data have been recalculated on the basis of a pressure increase at completion of 175 percent as found by Newitt and Vernon.

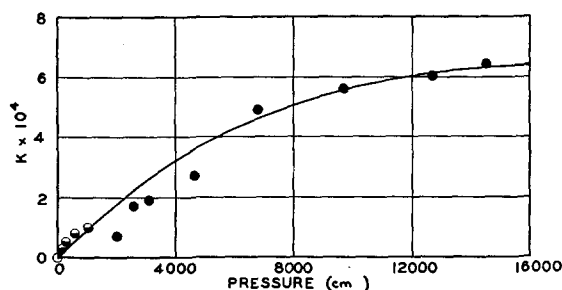


FIG. 7. Variation of rate constant with pressure. Black circles, Steacie and Solomon; black and white circles, Newitt and Vernon; open circles, Hinshelwood, Steacie, Kassel, Rice and Sickmann.

The data of all these investigations, recalculated as described above, are plotted in Figs. 7 and 8. It is evident, especially from Fig. 8, that it is absurd to extrapolate low pressure measurements in a linear fashion in order to obtain the rate at infinite pressure. Nevertheless even the proponents of theories II and III have had to resort to the simple Hinshelwood theory in obtaining  $k_{\infty}$  by a linear extrapolation of a  $1/k - 1/P$  plot. The value thus obtained with ethyl ether would indicate a rate about 50 times slower than that reported here at 14,500 cm.

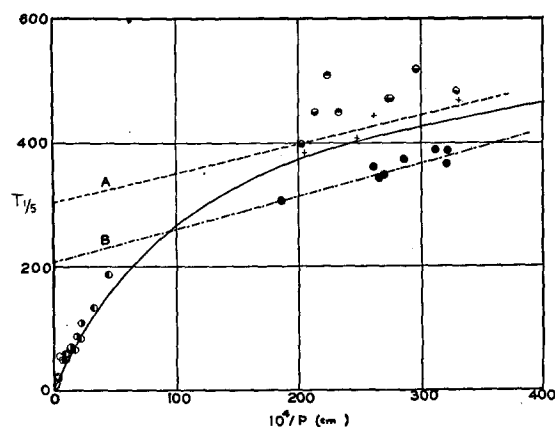


FIG. 8.  $T_{1/2}-1/P$  plot. Circles, lower half black, Rice and Sickmann, 478°C; circles, upper half black, Rice and Sickmann, 462°C; crosses, Hinshelwood, 525°C; black circles, Steacie, 478°C; circles, right half black, Newitt and Vernon, 462°C; circles, left half black, Newitt and Vernon, 490°C; open circles, Steacie and Solomon, 426°C; A, Kassel's extrapolation of Hinshelwood's data; B, extrapolation of Steacie's data.

It is obvious that although a certain amount of error may be introduced into the high pressure results on account of aberrations from the ideal gas law such errors can have no effect on the general result that the rate is much higher at high pressures than would have been predicted. It is also possible that a concurrent bimolecular reaction might occur at low pressures, but not come into prominence until high pressures were attained. This would account for the high pressure rate being greater than that previously predicted, but such an explanation is ruled out by the fact that at very high pressures the rate constant is tending to become essentially independent of the pressure in the manner characteristic of unimolecular reactions.

### DISCUSSION

Some interesting conclusions may be reached from a consideration of Fig. 7. The rate of reaction is still falling off at a pressure of 14,500 cm. If we assume that the rate would remain approximately constant at higher pressures, then as a rough approximation we may consider that at this pressure the rate of activation is just great enough to keep up the rate of reaction. We may therefore determine the number of squared terms involved.

At 699°K and 14,500 cm pressure the number

of molecules reacting per cc per second is  $1.16 \times 10^{18}$ , assuming that the ideal gas law holds. This value may be in error by 10 or 15 percent on account of gas law aberrations, but this error is negligible compared to that introduced by the uncertainty in the collision number at high pressures. The total number of collisions per second is approximately given by

$$\sqrt{2}\pi s^2 n^2 (3RT/M)^{1/2} \cdot 1/(1-nb),$$

where  $s$  is the molecular diameter,  $n$  is the number of molecules per cc ( $2.02 \times 10^{21}$ ), and  $b$  is four times the volume of the molecule, which is assumed to be spherical.<sup>20</sup> Taking  $s$  as  $5 \times 10^{-8}$  cm, the number of collisions per cc per second is  $1.41 \times 10^{33}$ . On the basis of the Hinshelwood theory, taking  $E$  as 53,000 calories, we have

$$\frac{e^{-(53,000 + (n/2-1)RT)/RT} \left[ \frac{53,000 + (n/2-1)RT}{RT} \right]^{n/2-1}}{|n/2-1|} = \frac{1.16 \times 10^{18}}{1.41 \times 10^{33}}.$$

Whence we obtain

$$\frac{(38.29 + n/2 - 1)^{n/2-1}}{e^{n/2-1} |n/2-1|} = 35.$$

If  $n=4$  the left-hand side equals 14, if  $n=6$  it is 109. It must be pointed out that Kistiakowsky<sup>21</sup> found that the collision formula correction factor,  $1/(1-nb)$ , failed at concentrations above 8500 cm. Above this pressure the number of collisions increases with great rapidity. This would tend to still further reduce the value of  $n$ . We are justified therefore in considering that the number of squared terms is not greater than 4.

Hinshelwood<sup>2</sup> has found in a similar manner that in order to account for the behavior of ethyl ether at ordinary pressures about 8 squared terms are necessary. We have now arrived at an apparent impasse: the observed rate at 20 cm cannot be accounted for unless  $n$  is greater than 8, but the fact that the rate is still falling off at 14,500 cm cannot be accounted for unless  $n$  is

<sup>20</sup> O. E. Meyer, *Kinetische Theorie der Gase*, Breslau (1899).

<sup>21</sup> Kistiakowsky, J. A. C. S. 50, 2315 (1928).

at least as small as 4. Also, the high pressure rate is much greater than would be expected on the basis of the application of theories II and III to the low pressure results.

The above calculation has been made on the basis of the simple Hinshelwood theory, and is of course only approximate. It would undoubtedly be more accurate to make a more elaborate calculation on the basis of theory II or III. Owing to the approximations involved, however, this would hardly be worth while. In any case the main point at issue would not be altered, namely, that any value of  $n$  which is consistent with the low pressure results is not applicable to those at high pressures, and *vice versa*.

The simplest assumption to make is that the number of degrees of freedom involved may be some function of the time between collisions. At very low pressures, where the time between collisions is comparatively large, eight squared terms are insufficient to maintain the rate and it falls off slowly as the pressure is decreased. At very high pressures, when the time between collisions is small, a much smaller value of  $n$  is required in order to maintain the rate. At still higher pressures, presumably,  $n$  will finally equal 2, the only vibrational degree of freedom involved being that in which the actual rupture of the molecule occurs. This would most probably be expected when the time between collisions is of the same order of magnitude as the time of vibration ( $10^{-13}$  to  $10^{-14}$  sec.). The time between collisions at 14,500 cm is about  $10^{-12}$  sec. (or possibly considerably smaller since the correction factor is becoming very uncertain). On this basis at very low pressures we would expect  $n$  to increase to a maximum until the number of degrees of freedom participating in the activation is given by the total number of oscillators in the molecule.

The mechanism for limiting the number of degrees of freedom would most probably be some form of atomic "insulators" suggested by O. K. Rice.<sup>22</sup> As the collision frequency increases less time is offered for the various degrees of freedom to come into play, and the insulators become more and more effective in limiting the critical energy to one oscillator.

In order to account for their results with

<sup>22</sup> Rice, *Zeits. f. physik. Chemie* **B7**, 226 (1930).

acetaldehyde, Fletcher and Hinshelwood<sup>7</sup> found it necessary to postulate the existence, over various pressure ranges, of a number of activated states, each associated with its own transition probability. By assuming a change with pressure in the value of  $n$ , we arrive at the same result, i.e., the rate-pressure curve should be made up of a series of segments smoothly joined and corresponding to various values of  $n$ . However, since we are dealing with a large number of molecules constituting a statistical assemblage, we may expect that rather than sharp breaks in the curve as  $n$  changes, the curve will represent a continuous and progressive change in  $n$ . It is difficult to see how Fletcher and Hinshelwood can justify the clear-cut angles between the various segments of the rate-pressure curves, in view of the accuracy of the experimental data. It would be far more logical to expect a gradual transition from one activated state to another.

Since the completion of this work a paper has appeared by Hunter<sup>23</sup> on the decomposition of nitrous oxide up to pressures of 40 atmospheres. He finds that the rate increases considerably with increasing pressure, and interprets his results in the manner proposed by Fletcher and Hinshelwood. He finds that about 4 squared terms are required to account for the observed rate at 40 atmospheres. The rate is still increasing at this pressure, and on the theory outlined here it would seem likely that  $n$  is tending towards 2 at high pressures. (Hunter's calculations are probably considerably in error, since he neglects to correct the collision frequency for aberrations from the ideal gas law. Such a correction, however, would not change the general conclusions to be drawn from his work.)

Further work on the decomposition of ethyl ether is in progress. It is planned to (a) investigate the reaction at lower pressures by the same method so as to tie in with the low pressure results, (b) extend the work to still higher pressures, and (c) follow the rate by analysis at the higher pressures so as to eliminate effects due to gas law aberrations. Until such work is done we have thought it desirable to defer any discussion of the exact form of the pressure-rate curve over the entire pressure range.

<sup>23</sup> Hunter, *Proc. Roy. Soc.* **A144**, 386 (1934).