HOMOGENEOUS
AND
HETEROGENEOUS
GAS REACTIONS

THESIS

A COMPARISON OF THE KINETICS OF HOMOGENEOUS AND HETEROGENEOUS GAS REACTIONS

H. A. Reeve, M. Sc.

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INTRODUCTION

Chemical kinetics is one of the most recent branches of physical chemistry. It has however, amply justified its existence by throwing light on two of the major problems of chemistry. Such problems for example as: the mechanism of reactions and the nature of chemical change, and to some extent the much discussed and investigated question of affinity, the latter prior to the last decade having been studied largely by investigations of systems in their initial and final states, with little or no consideration of the path by which they reached such states. In addition, much of what we now know concerning the mechanism and use of catalysts, from both the theoretical and practical aspects, is due to investigations carried out in the field of reaction velocities, and to mention only one more instance, our knowledge of the nature of surfaces and their very considerable importance in promoting chemical reaction, has been inestimably added to by the work of various investigators in this phase of physical chemistry.

Before proceeding to discuss the object of this work in more detail, it will be as well to consider in a summarized form the ideas held at present as to the nature of chemical change in gaseous systems, its mechanism, and so forth. (1). (2).

The majority of gas reactions proceed with a finite velocity, i.e. a certain fraction of the molecules react every second. If the molecules are all in the same condition, calculation will show that reaction should either be instantaneous or should not occur at all. Thus the logical deduction to make is that the molecules which react must be in an exceptional condition. While we cannot trace the behaviour of a single molecule, with the aid of the kinetic theory and statistical mechanics we can make calculations of the number of molecules which react, the number of collisions, and the fraction of the total number of molecules which possess energy in excess of a given amount. A little consideration will show that thermodynamics will not be of much help, since in this latter case we are concerned chiefly with initial and final states, while chemical kinetics is concerned with reactions during their occurrence.

While it is possible to define the order of a chemical reaction in general terms, by far the best means of doing so is a mathematical formulation.

thus for a:

Unimolecular reaction

let $a =$ the initial concentration,

$a - x =$ the concentration after a time t.

$$\text{then } \frac{dx}{dt} = K \ (a-x)$$

$$\text{hence } Kt = \ln \frac{a}{(a-x)}$$

thus the time to half-value, $T_{\frac{1}{2}}$, is given by

$$T_{\frac{1}{2}} = \frac{1}{K} \ln 2,$$

or in other words, the characteristic or a unimolecular reaction, from the point of view of a definition, is that the time to a given fractional change shall be independent of the initial concentration, within certain limits, which will be presently discussed.

For a bimolecular reaction

Suppose, for simplicity, that the initial concentrations are equal,

$$\text{then } \frac{dx}{dt} = K \ (a - x)^2$$

$$\text{or } Kt = \frac{X}{a(a - x)}$$

$$\text{and } T_{\frac{1}{2}} = \frac{a/ 2}{K.a.a/ 2} = \frac{1}{Ka}$$

or, for a bimolecular reaction, the time to a given fraction change is inversely proportional to the initial concentration.

Thus, in general, for an:

Nth order reaction

$$- \frac{dc}{dt} = Kc^n$$

or $T_{\frac{1}{2}}$ is proportional to $\frac{1}{a^{n} - 1}$

With gases the concentration is obviously proportional to the pressure.

The Arrhenius Equation (1)

This expression may be derived as follows: suppose we consider a balanced reaction, then the change in the equilibrium constant, with change of temperature, is given by a well known expression:

$$\frac{d\ \ln K}{dT} = Q/RT^2$$

where K, is the mass law constant, Q, is the heat of reaction, and k_1, and k_2, are the velocity constants of the direct and the opposing reactions respectively:

therefore $\ln K = \ln K_1 - \ln K_2$,

and hence $\frac{d\ \ln K_1}{dT} - \frac{d\ \ln K_2}{dT} = Q/RT^2$

thus $$\frac{d\ \ln K_1}{dT} = A_1/RT^2 + B$$

$$\frac{d\ \ln K_2}{dT} = A_2/RT^2 + B$$

where $A_1 - A_2 = Q$.

this is as far as we can get by thermodynamics, but Arrhenius,(3) found on empirical grounds, that $B = 0$, therefore for an irreversible reaction;

$$\frac{d\ \ln K}{dT} = A/RT^2$$

where K is the velocity constant, or

$$\ln K = C - A/RT,$$

thus, the logarithm of K, plotted against 1/T gives a straight line. A is expressed in terms of energy, and R being equal to 1.98 calories, then A will be given in terms of calories per gram molecule. Arrhenius postulated the existence of active molecules (3), making the supposition that these were formed endothermically from ordinary molecules. Thus the rapid increase in the rate of reaction with rise in temperature, could be explained on the basis of the shifting equilibrium for the change:

$$\text{normal} + Q = \text{active}$$

in the ordinary way, which may be expressed thermodynamically as

$$\frac{d\ \ln K}{dT} = A/RT^2.$$

Since A is the surplus heat necessary to the formation of an active molecule from one possessing the normal amount of energy, it has therefore been appropriately called the heat of activation.

The first explanation to spring to mind would be that some form of tautomeric change was operative. This idea, however, in the light of what is at present known is untenable, except in a few instances, and the active molecules are now regarded as those which possess exceptionally large amounts of energy, the heat of activation, as mentioned before, being regarded as the excess over the normal amount possessed by the average molecule.

This is the theory of activation in its most general form. No assumptions are made regarding the manner in which the added energy acts or is acquired. Most modern work on reaction velocities is concerned with ascertaining how the additional energy is acquired by the molecules.

The Arrhenius equation for the temperature coefficient has been found to hold for all known reactions, except in those cases where the reaction under observation is a composite one, which is made up of two different reactions having different temperature coefficients.

Bimolecular Reactions.

Since these are in some respects the simplest, we will briefly consider them first. Many examples of this type have been comprehensively studied by various investigators. Some of the best known are notably the union of hydrogen and iodine (4), the thermal decomposition of hydrogen iodide (4), of nitrous oxide (6) (7), and others. Generally speaking, the results agree with the bimolecular equation and the temperature coefficient is in agreement with the Arrhenius equation.

Now on the basis of the following assumptions:

(a) That the exceptional state apparently necessary to reaction is merely the acquisition of a certain amount of energy.

(b) That a collision of a certain degree of violence is necessary to reaction, or in other words a collision between two molecules possessing energy in excess of a certain critical amount.

It can be shown that it is possible to calculate the heat of activation in two totally different ways. For example, in the first instance, from the ratio of the number of effective collisions, (i.e. the rate of reaction as measured experimentally) to the total number of collisions, as calculated from the kinetic theory, we can calculate E, from the relationship;

$$\frac{\text{number of effective collisions}}{\text{total number of collisions}} = e^{-E/RT}$$

where E is the energy of activation. In the second case, by an independent method, involving the measurement of reaction velocities over a temperature range, i.e. a determination of the temperature coefficient, we can also calculate E, from the expression;

$$\frac{d \ln K}{dT} = E/RT^2$$

where K is the velocity constant, expressed in any units, e.g. we can use the reciprocal of the time to any given fractional amount of reaction instead of the actual velocity constant.

When this was done for the thermal decomposition of hydrogen iodide, the two modes of calculation gave the following values;

E, from temperature coefficient	43,900 cals. / gr. mol.
E, " ratio of collisions	44,000 " / " "

Other bimolecular reactions give good agreement, for example as mentioned above, the union of hydrogen and iodine and the thermal decomposition of nitrous oxide.

The Nature of the Energy of Activation.

We will next consider the significance of the energy of activation. There are a number of various internal circumstances which might cause chemical reaction. Among these are collision, rotation, vibration, and absorption and emission of radiant energy. The main facts upon which the theory of activation is based are;

(1) In a reaction, the molecules which undergo change are apparently in an exceptional state.

(2) The attainment of this state is much favored by rise in temperature.

When applying these ideas to bimolecular reactions the most natural assumption to make is that kinetic energy is what counts when collision occurs. There is however the possibility that all forms of energy may be pooled at the moment of impact. This does not matter much however since all forms of energy obey the same distribution law. For the present we will consider merely the energy E, of whatever kind it may be.

The number of collisions per second between activated molecules is

$$= \sqrt{2}\,\pi s^2 u n^2 . e^{-E/RT}$$

the maximum number that can react therefore is

$$= 2\sqrt{2}\,\pi s^2 u n^2 . e^{-E/RT}$$

There must however be some cases in which molecules rebound owing to ineffective collisions. Hence the number reacting is

$$P \ . \ 2\sqrt{2}\pi s^2 u \ n^2 . \ e^{-E/RT}$$

where P is a factor to take care of the above. The only possibility of testing the theory depends on P being approximately equal to 1. It has been shown that this is very nearly the case but it is impossible to obtain any exact information regarding P unless E can be measured with a degree of precision which is quite unattainable at present. However, " the real significance of the energy of activation is shown by a comparison of different bimolecular reactions. Since all molecular diameters and velocities are approximately the same, the rate of reaction at a given temperature is primarily determined by the magnitude of the factor $e^{-E/RT}$. Thus the higher the value of E the higher thould be the temperature at which the reaction can obtain a given speed. This conclusion is strikingly verified, as shown by the following table." Hinshelwood.

Reaction	E from collisions	E from Arrhenius	Temp. at which all have same speed.
2 N_2O	55,500	58,500	956°
2 HI	45,400	44,000	760°
2 NO_2	33,500	32,000	575°
2 Cl_2O	22,000	21,000	384°

There are two possibilities regarding the mechanism of reaction;

(1) The molecules become activated by collision and react at once, or

(2) The molecules become activated independently and react when they meet. In the first case kinetic energy would seem to be the

more important, and in the second case vibrational energy.

If we assume that practically all collisions are fruitful in which the sum of the kinetic enefgies of translation exceed E, we have,

No. of molecules reacting $n_1 = P_1 Z e^{-E/RT}$
if vibration is the cause $n_2 = P_2 Z e^{-E/RT}$
if radiation is the cause $n_3 = P_3 Z e^{-E/RT}$

where $Z = 2\sqrt{2}\pi s^2 u\, n^2 .\ e^{-E/RT}$

if all forms of energy operate at once,

$$n = n_1 + n_2 + n_3 = (P_1 + P_2 + P_3).Z\ e^{-E/RT}$$

but P_1, P_2, P_3, are all approximately equal to 1 and therefore to each other, or say P.

Hence $n = 3\ P\ Z\ e^{-E/RT}$

or if there are S ways in which activation can occur, (That is if S forms of energy participate),

$$n = S\ P\ Z\ e^{-E/RT}$$

since P is nearly equal to 1, then approximately

$$n = S\ Z\ e^{-E/RT}$$

Hence from the ratio of the effective to the total number of collisions we should be able to calculate the number of forms of energy which are effective in causing activation. Unfortunately, E enters in an exponential manner, and hence the accuracy with which we can determine E depends on the accuracy with which we can determine not K the velocity constant, but log K.

Hence any errors involved in the measurement of K will be greatly magnified in calculating E from the experimental results. For various reasons reaction velocity measurements are not susceptible of a high degree of accuracy, and hence the values of E are only approximate. Suppose we see if we can distinguish experimentally between $S = 1$ and $S = 3$ in the above equation. At $400^{\circ}K$, E is about 20,000 calories, for reactions proceeding at a measureable rate. A variation in S from 1 to 3 would change E by about 1000 calories, which is of the order of the experimental error. Hence it is at the present time impossible to determine how many forms of energy are operative in producing activation.

Rate of Reaction and Rate of Activation.

If the molecules are activated by the actual collision in which they are transformed, there is no distinction between the two. If, however, the molecules are activated independently, such as by the absorption of radiation, then active molecules must exist in definite concentration and have a definite average life terminated in bimolecular reactions by collision. Hence the rate of reaction can only be given by $Z. e^{-E/RT}$ if the concentration of active molecules can be maintained at a fraction $e^{-E/RT}$ of the whole in spite of the loss of active molecules by reaction. This can only be the case if the rate of activation is fast compared with the rate of reaction. This is not of great importance with bimolecular reactions but is of great importance with unimolecular reactions.

Summary for Bimolecular Reactions.

1. The rate is given by:

$$\frac{\text{no. of molecules reacting}}{\text{no. entering collisions}} = e^{-E/RT}$$

2. The rate can be accounted for on the assumption of activation by collision, i.e. the kinetic energy of translation is turned into vibration.
3. It can also be explained by the assumption of activation beforehand, either by collisions or by absorption of radiation.
4. It is impossible to tell which form of energy is operative in activation.
5. The most likely hypothesis seems to be activation by collision with all forms of energy pooled at the moment of impact.

UNIMOLECULAR REACTIONS.

By definition a unimolecular reaction is one in which the rate of change is proportional to the first power of the concentration of the reactant. Therefore the fraction of the molecules which undergo change in unit time is independent of the concentration, hence it is independent of the number of collisions. Thus, regardless of whether previous collisions have anything to do with reaction or not, the actual change is a process which is undergone by an isolated molecule.

It is necessary, therefore to explain (1) why unimolecular reactions are so rare, and (2) how the molecules become activated (on account of the high temperature coefficient activation seems to be necessary.) In the main, four theories have been advanced to explain unimolecular reactions, namely;

(a) The radiation theory.
(b) The hypothesis of Christiansen and Kramers.
(c) The hypothesis of Lindemann.
(d) Hinshelwood's modification of Lindemann's hypothesis.

We shall now consider these briefly.

The radiation theory.

From the fact that the rate is independent of the pressure, Perrin argued that it should be possible to expand the gas to infinite dilution without changing the rate of reaction. Hence an isolated molecule could become activated, which presumably leaves radiation as the only possible mechanism of activation. He assumed that in the activation of molecules a narrow band of infra red frequencies are operative.

Now it can be shown that for the frequency which is effective in activation, Nhv should be equal to E the energy of activation, where N is Avogadro's number, h is Plank's constant and v is the frequency. Hence knowing the heat of activation, the frequency which is effective in activation, should be given by, $v = E/Nh$. Hence we should find an absorption band at this frequency.

Furthermore, if the velocity constant is proportional to the radiation density, we have:

$$k = \text{constant}.\ e^{-hv/kT}$$

whence

$$\frac{d\ln k}{dT} = \frac{hv}{kT^2} = \frac{Nhv}{NkT^2} = \frac{E}{RT^2}.$$

Hence the Arrhenius equation will still hold.

The simple theory falls down immediately since there are in general no absorption bands in the calculated region, and since in most cases there is far too little energy in this region to account for the energy of activation.

The hypothesis of Christiansen and Kramers.

They suggest that as the products of the reaction possess the heat of activation plus the heat of reaction, they can immediately activate fresh molecules of the reactant and thus set up long reaction chains. They assume that each molecule of product immediately activates a molecule of reactant. Hence each activated molecule removed from the system is immediately replaced by a fresh one. Since, then, the number of activated molecules is thus a constant fraction of the total concentration of molecules of reactant, the reaction is, to all intents and purpose, unimolecular. As the products of the reaction accumulate, or if an inert gas is added, a large proportion of the activated molecules must be deactivated by collision with the inert molecules. Hence the reaction must tend to become bimolecular.

To overcome this difficulty they assume that the activated reaction products can only give their energy to molecules of reactant. While this seems somewhat unlikely, as a general case, certain reactions are known, however, which can be very adequately explained on this basis.

The hypothesis of Lindemann.

The basis of Lindemann's hypothesis is the assumption that a molecule may receive the energy of activation by collision and then react before it collides with another molecule, or in other words a time lag between activation and reaction. If the average time between activation and reaction is large compared with the time between collisions, most activated molecules will lose their energy before they have a chance to react, i.e.,

$$\begin{array}{ccc} \text{normal molecules} & = & \text{activated molecules} \\ & & \Vert \\ & & \text{products of reaction.} \end{array}$$

The right to left reaction is much faster than the up and down. A stationary state is thus reached, in which a constant fraction of the molecules, equal to $e^{-E/RT}$ are activated and will react if they pass through their next phase of minimum stability before their next collision. A small fraction only react, and the majority are deactivated. Hence the reaction has little effect on the concentration of the active molecules. The fraction $e^{-E/RT}$ is independent of pressure and since the number of molecules reacting per unit time is a small fraction of this, therefore the latter quantity is independent of concentration and all the conditions of a unimolecular reaction are satisfied.

Furthermore Lindemann's hypothesis will account for the independence of pressure over large ranges and the falling off at low pressures of the unimolecular velocity constant, an experimental fact common to practically all unimolecular reactions in the gaseous state. It explains the latter point as follows; if the pressure is sufficiently low, the time between collisions and the time between activation and reaction become comparable. Hence the removal of activated molecules by reaction will diminish the concentration of active molecules, and hence a point must be reached, at a sufficiently low pressure when the unimolecular velocity constant begins to fall off. In certain unimolecular reactions, however, notably the decomposition of nitrogen pentoxide, Lindemann's hypothesis will not account for the observed facts, and Hinshelwood has put forward a modification of the hypothesis to bring it more into line with such cases. Before considering this modification, however, we will examine some of the data relative to unimolecular reactions.

Experimental Data.

Nitrogen pentoxide. (1), (32) . Completely homogeneous.

$$2\ N_2O_5 = 2\ N_2O_4 + O_2$$

According to the radiation theory, light of about 1.16 mu should be effective. Exposure of the reaction vessel to light of this frequency has no effect. The reaction is unimolecular down to pressures of about 0.01 mm. Even at this low pressure there are still about 10^8 collisions for every molecule which reacts.

Acetone Unimolecular over a wide pressure range. (8).

Racemization of pinene, also unimolecular over a wide pressure range. (9).

Propionic aldehyde, constant falls off below 80 mm. (10).

Dimethyl ether, " " " " 350 mm. (11).

Diethyl ether, " " " " 150 mm. (12).

Azomethane, " " " at low pressures. (13).

Azoisopropane, " " " below about 0.25 mm. (14).

Ethylidene Diacetate, investigated over pressure range of 11 - 46 cms. of mercury. (15)

Butylidene Diacetate, pressure range; 5 - 56 cms. (16)

Ethylidene Dipropionate, " " 5 - 56 cms.

Gaseous decomposition of Paraldehyde, pressure range, 1.18 - 52 cms. (17).

Ethylene Oxide, pressure range, 2.4 - 90.5 cms. (18).

Methylisopropyldiimide, " " 0.0058 - 13.12 cms. (19).

Methyl Ethyl Ether, " " 2.6 - 24 cms. (20).

Methyl Propyl Ether, " " 2.2 - 33.6 cms. (20).

Nitrous Oxide, " " 8.1 - 800 cms. (21).

Ethylamine, " " 5 - 40 cms. (22).

Dimethyltriazene, " " 0.019 - 8.0 cms. (23).

Trichloromethyl chloroformate, pressure range, 0.4 - 1.7 cms. (24).

We will now consider in some detail, the mechanism of activation in unimolecular reactions, there are three possibilities:

(1) activation by collision,
(2) activation by radiation,
(3) activation by both simultaneously.

(1) Activation by collision.

If activation is by collision, there are two questions to be answered, (1) how the velocity constant of a unimolecular reaction remains independent of pressure, (2) whether the number of collisions taking place in the gas is great enough to activate molecules fast enough to account for the observed rate of reaction, even at the lowest pressure observed experimentally.

The hypotheses of Lindemann and of Christiansen and Kramers will both explain the first point, although the reaction chain theory necessitates rather arbitrary assumptions. In addition it could only apply to exothermic reactions, while the decomposition of nitrogen pentoxide is apparently endothermic. Lindemann's theory is weakened by the fact that this reaction shows no falling off at 0.01 mm. This however is not vital as it may fall off at still lower pressures, and in any case the experimental evidence is somewhat conflicting on this point.

The second point raises much more serious objections to Lindemann's hypothesis. The collisions by which activated molecules are produced are not numerous enough to account for the observed rate at ordinary pressures, and are therefore still less so at 0.01 mm. According to the hypothesis, the rate of activation has not merely to be equal to the rate of reaction but many times greater. The insufficiency of the number of collisions can be shown as follows; assume that no reaction is taking place in the gas. Of N molecules present let N_1 possess energy greater than E. These are the active molecules, and

$$N_1 = N e^{-E/RT}$$

Let Z_1 be the number of molecules which enter the active state in unit time, assuming activation by collision.

At equilibrium $Z_1 = Z_2$

where Z_2 is the number that leave the active state in unit time, also by collision.

Active molecules are very exceptional ones, hence nearly every collision undergone by an active molecule results in its deactivation. Hence Z_2 is approximately equal to the number of collisions undergone by active molecules in unit time. Therefore:

$$Z_2 = \text{total no. of collisions} \times \frac{\text{number of active molecules}}{\text{total number of molecules}}$$

$$= \sqrt{2}\,\pi\, s^2\, u\, n^2 \cdot \frac{N e^{-E/RT}}{N}$$

omitting the very few collisions in which both molecules have a high energy. The above expression also equals Z_1, since $Z_1 = Z_2$. If the system is disturbed by the loss of active molecules by reaction, Z_1 is the maximum rate at which they can be reformed. Hence it is the maximum rate of reaction.

In order to have Lindemann's hypothesis hold, it would be necessary to lower the observed activation energy of nitrogen pentoxide by about 6000 calories. This is quite outside the experimental error. In the case of the decomposition of acetone also, the number of molecules reacting is about 10^5 times the number given by $Z.e^{-E/RT}$.

Hinshelwood's Modification.

Lindemann's hypothesis, however, can be modified as follows to bring it into line with the observed facts: the use of the expression $e^{-E/RT}$ for the fraction of molecules with energy greater than E, depends on the assumption that the energy of activation is confined to a few degrees of freedom. This appears to be justified in bimolecular reactions. Almost all the molecules which undergo unimolecular reactions are very complicated, so we can extend the energy of activation to more degrees of freedom. An activated molecule can be regarded as one which possesses energy E made up in any of the ways which a large number of degrees of freedom make possible.

The chance that a molecule contains in n energy terms an amount of energy greater than E is no longer $e^{-E/RT}$,but

$$\frac{e^{-E/RT} \quad (E/RT)^{1/2n - 1}}{\text{factorial } (1/2n - 1)}$$

E is no longer given by the Arrhenius equation but a correction has to be added which equals (1/2n - 1) RT .

Suppose that equilibrium is established in the gas and ignore the chemical change. Then the number of molecules, N_1, of which the energy rises above the limit E in unit time, is equal to the number, N_2, the energy of which falls below E. Since the number of molecules which possess the energy E is small, practically all the activated molecules which suffer collisions will lose the energy of activation. Hence N_2 is very nearly equal to the number of collisions multiplied by the fraction of molecules with energy greater than E , i.e.,

$$\frac{Z . e^{-E/RT} (E/RT)^{1/2n - 1}}{\text{factorial} (1/2n - 1)}$$

Hence N_1 is also very nearly equal to this. If n is large, this is much larger than the simple expression and the discrepancies mentioned above can easily be wiped out.

In order that this should be true it is necessary that only complex molecules should undergo unimolecular reactions. This seems to be true. Bimolecular reactions are often undergone by fairly simple molecules, but unimolecular reactions only occur with complicated molecules.

In most unimolecular reactions which have been investigated, the velocity constant has been found to fall off at low pressures. Where the falling off of the constant occurs, we can calculate the number of energy terms needed. This works out at 12 for propionic aldehyde, 8 for diethyl ether, 11 for dimethyl ether. These values seem reasonable considering the complexity of these molecules. It has been observed that hydrogen prevents the falling off in the velocity constant with the ethers, which seems to support the hypothesis.

(2) Activation by radiation.

As mentioned before, if we calculate the frequency which should be effective in activation, we find generally that the molecules which should be activated by this frequency show no absorption spectra in the expected region, and that in any case, the amount of energy is not sufficient to account for the observed rates of reaction. Furthermore, attempts which have been made to assume a band of frequencies operative in activation, only complicate matters further and make experimental verification impossible or at least extremely difficult, at the present state of knowledge and experimental technique. This of course, does not preclude the possibility of activation by radiation in reactions as yet not studied or in reactions taking place at very elevated temperatures, for to do so would be to disregard all the facts of photochemistry, however, for the present purpose, the possibility of activation by radiation does not greatly concern us.

The Occurrence of Unimolecular Reactions.

One of the most notable features of unimolecular reactions is their scarcity where simple molecules are involved. Probably the main reason for this is that many unimolecular changes would lead to the production of free atoms, thus for example N_2O, and Cl_2O, might decompose as follows:

$$N_2O = N_2 + O$$
$$Cl_2O = Cl_2 + O$$

These reactions would be highly endothermic, since the heat of dissociation of oxygen is about 150,000 calories. Of course the excess energy would be regained by the system by the subsequent recombination of the atomic oxygen, but the unimolecular change would necessitate the momentary concentration of very large amounts of energy in the molecule, thus such unimolecular reactions would always be associated with large heats of activation, and for this reason the corresponding bimolecular change occurs in preference. The observed cases of unimolecular reactions always involve complicated molecules. The one partial exception to this is the decomposition of nitrogen pentoxide.

This reaction, however, seems to be exceptional in a number of ways, for example, while all the other observed unimolecular changes fit in well with the modified Lindemann hypothesis, it needs considerable straining to make the nitrogen pentoxide decomposition agree.

To sum up then, the best known of the various hypotheses advanced to explain the mechanism of unimolecular reactions, Perrin's hypothesis has been discredited in its original form, Christiansen and Kramer's may occur to some extent but it is unlikely as a general explanation, Lindemann's hypothesis is a very reasonable one, but cannot account for a fast enough rate, while Hinshelwood's modification is the best advanced at present. Hence throughout this thesis Hinshelwood's form of theory will be followed. Rice and Ramsperger's theory (25) is based on the same general premises. It is however, more complicated and probably more accurate, but it is doubtful if there is enough exact experimental evidence to justify its use in preference to the simpler theory of Hinshelwood.

HETEROGENEOUS REACTIONS.

Inasmuch as this thesis deals with a comparison of homogeneous and heterogeneous reactions from the point of view of a possible effect on the heat of activation, we will not discuss here the various theories extant as to the mode of action of surfaces in promoting chemical change.

Some fundamental concepts, however, should be kept in mind. In the first place, as follows from the definition of a heterogeneous change, in order to take part in a heterogeneous reaction, a molecule must be adsorbed, however short its life on the surface may be. But on the other hand, as is pointed out by Hinshelwood, adsorption alone is not a sufficient condition for reaction, and something quite analogous to the activation energy of homogeneous changes would seem to be necessary.

It would therefore seem to be of considerable interest to compare the rates of homogeneous and heterogeneous gas reactions, with a view to determining what effect the surface may have on the heat of activation. In this connection, ,the Hinshelwood-Polanyi equation gives expressions embodying a relationship between the true and apparent heats of activation, for the simple case of one reacting gas, when (a) the reaction is unretarded by the products, and (b) when such retardation takes place. (26).

For the first case of no retardation, if Q is the true heat of activation, E the apparent heat of activation, and L is the energy of desorption of the reacting gas, then it may be shown that:

$$E = Q - L.$$

i.e., the apparent heat of activation is less than the true value by an amount L, where L is defined as above.

In the second case of retardation by the product or products, an expression :

$$E = Q + L' - L$$

is obtained, Where E, Q, and L, have the same meaning as before and L' is the energy of desorption of the product. Thus the existence of an appreciable retarding effect may increase the apparent heat of activation.

However, attempts made to investigate a change which occurs both homogeneously and heterogeneously generally encounter the following difficulty; as has been pointed out by Hinshelwood, for example, there is a general tendency for such reactions to become unimolecular on the surface of a catalyst, the heat of activation falling to about one-half of its former value. This change in the characteristics of the reaction is accompanied by a modification of the reaction path.

The homogeneous decomposition of hydrogen iodide, for example, proceeds as indicated by the equation:

$$2\ HI = H_2 + I_2$$

the possible homogeneous unimolecular decomposition:

$$HI = H + I$$

followed by a subsequent recombination of the atoms, is ruled out since the formation of atomic hydrogen would be a highly endothermic process. The momentary concentration of a large amount of energy in the molecule would thus be necessary, and hence a very large heat of activation would be associated with the reaction. The presence of a metal surface, however, renders such a change possible since the atomic hydrogen and iodine formed can be held on the surface in an adsorbed condition, and later the atoms evaporate in pairs as molecular hydrogen and iodine.

The heat of activation of the homogeneous bimolecular decomposition is 44,000 calories per gram molecule. (27).

In order that two molecules may decompose, they must therefore have a combined energy in excess of 44,000 calories.

For the heterogeneous unimolecular decomposition on the surface of gold the heat of activation is 25,000 calories (28). Hence one molecule in order to decompose must have an energy in excess of 25,000 calories. The lowering of the activation energy is therefore accompanied by a change in the mechanism of the reaction, in the one case only a single molecule being activated, while in the other case two molecules must be activated simultaneously. In consequence the effect of the catalyst on the magnitude of the activation energy is left unanswered.

It therefore seemed of interest to compare the homogeneous and heterogeneous reactions in the case of a substance which decomposes homogeneously in a unimolecular manner, and with this in mind, the thermal decomposition of methyl ether on the surface of platinum was investigated, as another addition to a series of investigations carried out recently, on acetone (29), ethyl ether (30), and propionaldehyde (31). Here also the results have been such as to leave unanswered the question of the influence of the catalyst on the activation energy. Results have been obtained, however, which give rise to interesting speculations concerning the transfer of energy between gas molecules and solid surfaces.

EXPERIMENTAL METHODS.

Methods of investigating Heterogeneous Gas Reactions.

There are two main methods of investigating heterogeneous gas reactions.

(a) The catalyst is contained in a bulb in finely divided form. The reactant, or reactants, is admitted to the bulb, or passed through it continuously, and the reaction is followed by the pressure change which accompanies it or by analysis. This method is the simpler of the two, and is the more usual when the course of the reaction , yield, etc., is of primary importance. On account of the lack of definite knowledge of the surface, etc., it is not a suitable method of investigating the molecular statistics of the reaction.

Recently a modified form of flow method has been investigated by the author, (33), (34). It permits of the velocity of reaction being measured by pressure readings, rather than by tedious analytical methods, as would be used in the unmodified form of flow method mentioned above. It is applicable to both homogeneous and heterogeneous reactions. In principle the method consists of passing the reactants through a flow meter, then through a heated reaction chamber, and finally through a second flow meter. The ratio of the two flow meter readings, corrected for the change in viscosities of the gases, gives a direct measure of the extent to which the reaction has progressed. The method is somewhat limited in its applications, due chiefly to the necessity of very great accuracy in calibration, etc., and also due to the complicated nature of the hydrodynamics of the system, a drawback common to all flow methods.

(b) The catalyst consists of a fine filament stretched axially through the reaction vessel. The vessel containing the gas is kept at or near room temperature, while the filament is heated electrically to the desired temperature. This method is by far the most suitable when an accurate knowledge of the molecular statistics of the reaction is desired, and is the one used in this work. In this method the solid material can function in two ways, either by adsorbing the reactant and permitting a catalytic reaction, or else by merely acting as a source of energy. In the latter case the question of energy transfer between gas molecules and the solid surface will be of paramount importance.

Apparatus. The apparatus was similar with the exception of the electrical set-up, to that used by Steacie and Campbell (30) Steacie and Morton (31), for the investigation of the thermal decomposition of ethyl ether and propionaldehyde, respectively. It was made up as follows; (see fig. 1.)

A is the reaction bulb, in which is sealed axially a platinum filament B. A was connected by fairly large bore capillary tubing (ca. 1 mm. dia.) to the manometer C, the left arm of which was of the same tubing. This tubing was wound with nichrome wire, and electrically heated to about 50°C., to ensure that no condensation of condensable products, possibly formed during the reaction occurred. D is a bulb containing the reactant, methyl ether, which was kept immersed in a solid carbon-dioxide-acetone mixture, in a Dewar flask. E is a storage vesses for hydrogen. G is a pump by means of which the unchanged reactant and products could be removed from A, and stored in H for subsequent analysis. F is a trap which could be immersed in a freezing mixture, to condense out any unchanged ether, if so desired. I and J, are two bulbs of about 100 c.c., and 300 c.c., capacity, respectively, whose function was as follows; by making the diameter of the mercury surface in I large, a change in level of 800 mm., in C will cause a change in level in I of less than a mm., so that pressures will be given directly by a single reading of C, without any correction. I and J, were also added to enable runs to be made with initial pressures up to 800 mm., for this reason.

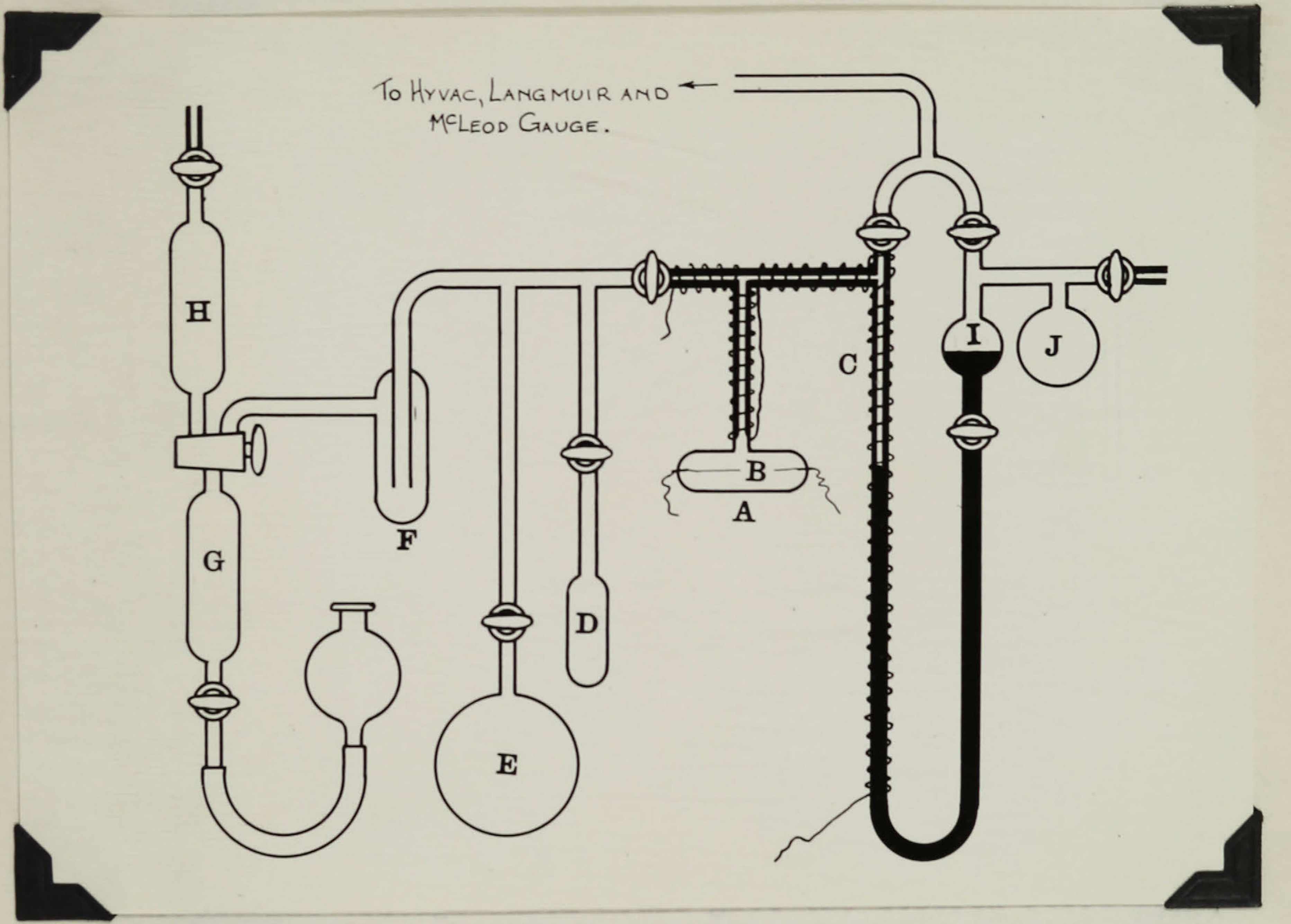

Fig. 1.

If the initial pressure is say, 500 mm., and the total length of C is about 800 mm., the reaction can only be carried to a final pressure of 800 mm., or a percentage pressure increase of about 60%, however, if after observing the initial pressure, air is admitted to I and J, until the level in C, is brought back to zero, then runs with initial pressures up to 800 mm., can be carried to 100% pressure increase conveniently. J was added to ensure that the small pressure increase in I and J, caused by the change of level in I, would be so small as to be completely negligible.

A was immersed in a bath of glycoline oil, which also contained a stirrer and electric heater, and the whole was kept at 45 ^{o}C.

In the previous investigations mentioned, the resistance of the filament B, was obtained by means of simultaneous readings of current and voltage, which meant that during the course of a run, as the resistance changed, a new value of the current and voltage which would give the desired resistance had to be calculated, and then the current had to be changed by means of a rheostat, this resulted in considerable inconvenience at moderately and very fast runs, as readings were made at the same time of the pressure and time.

Hence in the present investigation, the following procedure was adopted; (see fig. 2.) B was made one arm of Wheatstone bridge, the other arms consisting of a resistance K, of approximately the same order, (this is described in more detail

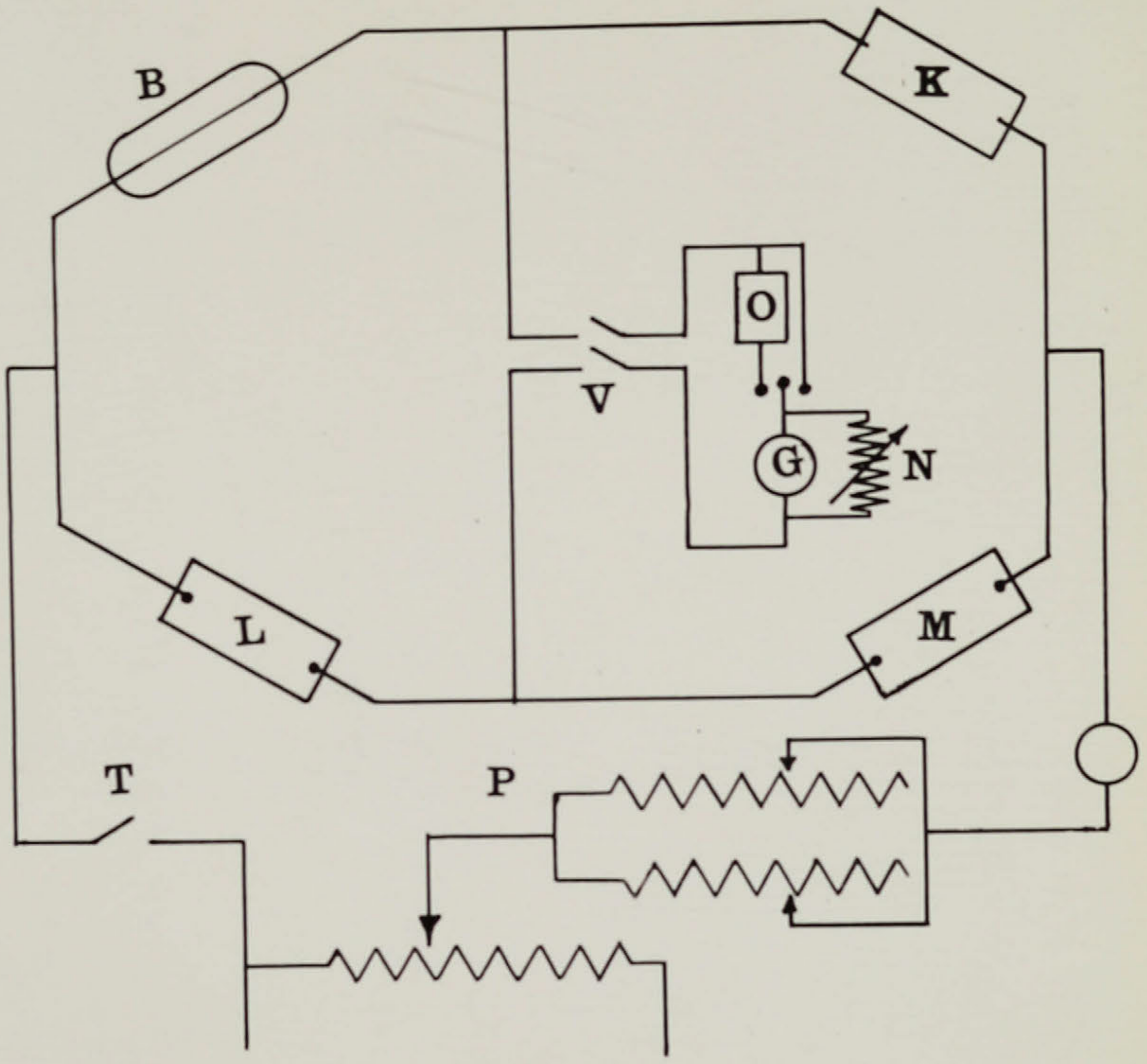

Fig. 2.

below) and two more L and M, of standard high resistance. M was fixed at 10,000 ohms and L was a variable precision resistance of 1/10 to 100,000 ohms. The galvanometer G, was a Leeds and Northrup precision instrument, it was connected in parallel with a variable resistance N, of 1 to 10,000 ohms, and in series with another high resistance of 20,000 ohms. By making N small, the initial rough adjustment could be made without throwing the galvanometer off scale, and then by increasing N, the more accurate adjustment desired could be attained. The voltage on the bridge could be changed by means of the rheostat system P, which in turn was connected across the 110 volts, d.c., line.

The resistance K. This was made approximately of the same order as that of the filament. It was important that it be capable of carrying considerable current (max., about 4 amps.,) without appreciable heating. Hence in the case of the fine filaments (about 0.05 mm., diameter) a 20 ohms nichrome wire rheostat was used. For the larger filaments (about 0.10 mm. diameter) this resistance was constructed in the following manner; about 250 ft., of insulated bell wire was wound on the outside of a battery jar, (dimensions 10 ins. dia., and 10 ins., deep) with guides of wood at each end to prevent the wire slipping off. In both cases, of cousse, the resistance was accurately measured by means of a Wheatstone bridge, and these resistances were kept in a well-stirred bath of glycoline oil.

The additional electrical arrangements included a heater for the oil bath containing the reaction bulb, controlled by a rheostat, and the nichrome wiring on the manometer and connecting tubing, also in series with a resistance, both being connected across the 110 volts d.c., supply.

Reaction Bulb and Filament.

A bulb of the shape and dimensions shown in fig. 3 was used. Considerable difficulty was experienced in the construction and sealing into the bulb of these filaments, particularly in the case of the very fine filaments. The most successful and convenient procedure adopted was as follows; a short length of platinum leading in wire, (0. 75 mm. diameter) was held with one end in the flame of a gas-oxygen blow torch, until a small globule of molten platinum had formed, this was withdrawn quickly from the flame, and while it was still molten, one end of the filament was thrust quickly into it, in this manner a good elcetrical contact was obtained. This procedure was repeated with the other end of the filament, and we then had the filament with its short lengths of lead in wire attached. The bulb was then clamped in a vertical position and through the two holes A and B, the filament was lowered into position in the bulb, with a short length of the lead in wire projecting at each end. A and B had previously been partially filled with lead sealing in glass, and by sticking a glob of this glass on one of the leads, the filament could thus be supported in position. With the finer filaments which could barely support the weight of the leads, great care had to be exercised. A blow torch flame was then played on the upper end until the glass became molten and a good joint

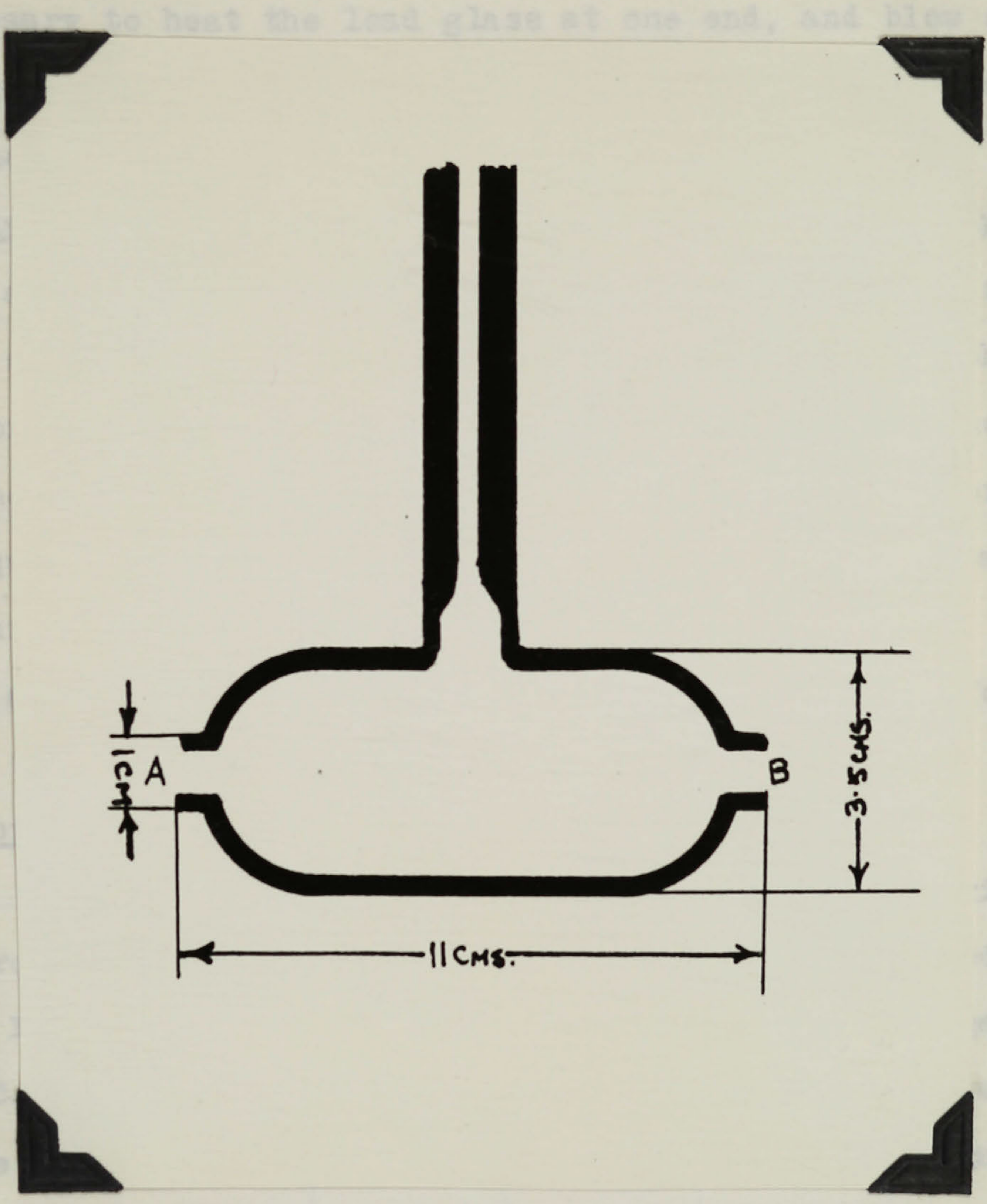

Fig. 3.

was obtained. The lower end was then filled in with lead glass, and to straighten and tighten the filament, it was merely necessary to heat the lead glass at one end, and blow so that the glass pulled the lead wire with it and thus tightened the filament.

Reactant. The methyl ether used was made from sulphuric acid and methyl alcohol. The gas was bubbled through sulphuric acid saturated with methyl ether, passed through phosphorus pentoxide tubes and fractionally distilled. During the course of the experiment, as mentioned previously, it was stored as a liquid in a bulb immersed in a solid carbon-dioxide-acetone mixture.

(I am indebted to Mr. J.S.Tapp of this laboratory for supplying the methyl ether used.)

Calibration.

The resistance of the filament at various temperatures was obtained. These temperatures were measured by means of a Leeds and Northrup optical pyrometer, over a range from 700°C., to 1100°C., at 50° intervals. A temperature-resistance curve was then plotted. On extrapolation this curve gave good agreement with the experimentally determined resistance of the filament at room temperature. Such a curve is given in fig. 4.

Even if the absolute values of the temperature of the filament are slightly in error, this will be unimportant for the present purpose provided that the relative temperatures are in good agreement.

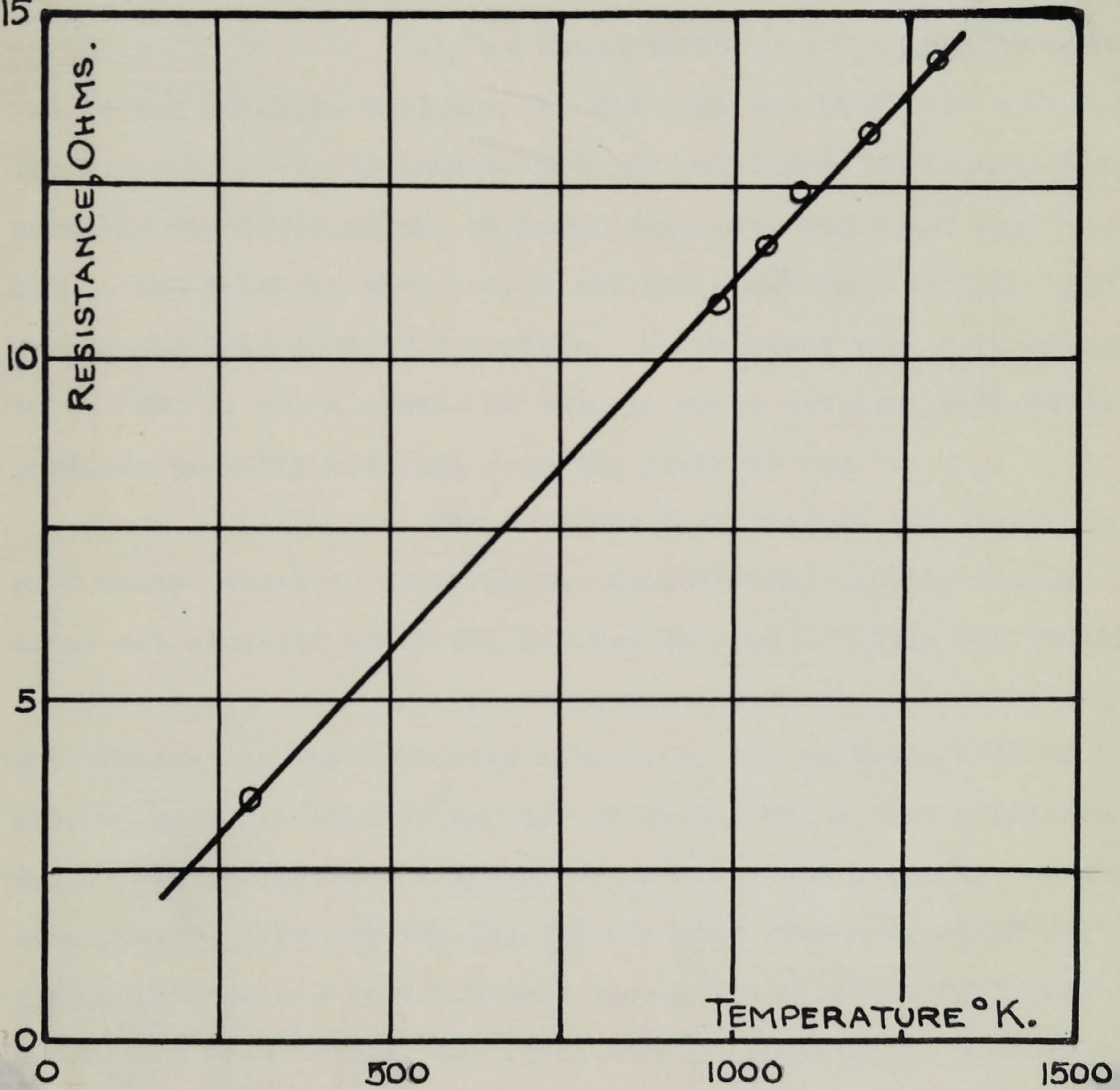

Fig. 4.

Experimental Procedure. Before each run, the oil bath and the nichrome wiring were brought to the desired temperatures of 45 C°. and 50°C. respectively, and the current so adjusted that these values remained constant to within 0.2° .

Air at atmospheric pressure was then admitted to the reaction bulb and the filament was heated to 1300°K. for a few minutes, to ensure that any substance, such as carbon, possibly deposited on the filament from previous runs, was burned off. The bulb was then pumped out for about half an hour, and during the last part of this time, the filament was again brought up to 1300°K. for a minute or two, to drive off any reactant or products possibly adsorbed form the previous run.

The bulb was then flushed out three times with methyl ether at about 30 mm. pressure and finally methyl ether was admitted until the desired initial pressure was obtained.

The temperature desired during the run was obtained in the following manner. L, the variable 1/10 to 100,000 ohms resistance, was set at such a value that a balance would give the desired filament resistance, and hence the desired temperature. The setting for the rheostat system P, which would give a balance was approximately known from previous runs, and it was set at this value. The resistance N, in parallel with the galvanometer was set at about 40 ohms, the switches V and T both being open.

The stop-clock was then started and as the second hand passed the zero mark, T was closed and immediately afterwards V. P was then quickly so adjusted as to balance the galvanometer, and N was increased to 800 - 1,000 ohms to give the desired sensitivity. This could all be done in the first 5 seconds of the run. Pressure readings were then made at intervals of from 30 seconds to 1 minute, for the first 5 minutes, depending on the rapidity of decomposition. The manometer column was tapped vigorously with a piece of heavy rubber tubing during each reading to prevent " sticking " of the mercury. With the very fast runs, i.e. those in which a percentage pressure increase of 100% resulted in less than 6 minutes, the assistance of another person was required.

Except in cases where the final pressure was desired, runs were usually concluded at a percentage pressure increase of somewhat over 100%.

When the switch T, was opened at the conclusion of a run, the pressure in the reaction bulb immediately dropped and in the cases of runs at pressures less than 450 mm. became constant within a minute. This "cold" pressure was noted and was used to calculate the initial "hot" pressure.

Inasmuch as a very considerable quantity of heat is dissipated during the course of a run, before each run, the resistance in series with the bath heater was increased to such a value that the bath temperature remained constant throughout the run.

With runs at initial pressures in excess of 500 mm., before starting, air was admitted to I and J (fig. 1) until the mercury level in C was brought back to zero.

Limitations of Filament Diameter.

While it is somewhat of an advantage to use a filament having as high a resistance as possible, due to the fact that the end correction then becomes very small, it was found in practice however, that there is a limitation to the filament diameter if one is to have a filament which will show constant characteristics, and not change with each succeeding run, at the temperatures used in this work.

An attempt was made to use a platinum filament having a diameter of 0.01 mm. Now, while a certain amount of preliminary aging is to be expected, in this case the aging effect showed no sign of ceasing, and the times to fractional pressure increases of 50% and 100%, instead of being nearly equal in the pressure range in which no falling off occurs, practically doubled in the course of three runs. Thus for the runs given below, performed in the order given, in which, had the filament been showing constant characteristics, the times given would have been equal or nearly so, there is odviously a progressive change going on:

Temperature.	pressure	time to fractional pressure increase	
1250°K.	722 mm.	(50%) 109 secs.	(100%) 255 secs.
	617 mm.	147 "	357 "
	522 mm.	202 "	495 "

That this is not due to " falling off " with decreasing pressure is shown by the data obtained for the following runs :

Temperature.	pressure	time to fractional pressure increase			
1150°K.	405 mm.	(50%)	584 secs.	(100%)	1448 secs.
	721 mm.		702 "		1680 "
	716 mm.		798 "		-----
	622 mm.		1290 "		3150 ".

If this effect was due to falling off, the times to 50% and 100% pressure increase, at the pressures of 721 mm. and 716 mm. should be shorter than those for the run at 405 mm.

CALCULATIONS.

For this purpose we will consider some data taken from a typical run.

Temperature 1150°K. Pressure 314 mm.

Time	Pressure hot	Pressure cold	Pressure corrected hot	Pressure increase	Per cent. increase
0	314	264	314	0	0
1	328		328	14	4.5
2	342		342	28	8.9
5	381		381	67	21.3
-	---		---	---	---
-	---		---	---	---
-	---		---	---	---
60	789	663	789	475	151.3

The first experimental reading was the "cold" pressure, namely, 264 mm. The "hot" pressure at the end of the run was 789 mm., this corresponds to a "cold" pressure of 663 mm. The initial "hot" pressure is given by multiplying the initial "cold" pressure by the ratio $\frac{789}{663}$, thus:

$$= 264 \times \frac{789}{663}$$

$$= 314 \text{ mm.}$$

This, of course, is based on the assumption that the "cold" to "hot" pressure ratio is the same at the conclusion of the run as it was initially. While this is not strictly true, due to the changing thermal conductivity as the reaction proceeds, nevertheless the error is very small, as is shown by extrapolation, for pressures of 450 mm., or less. For pressures above about 450 mm., the initial "hot" pressure was obtained by extrapolation of the first five or six pressure readings.

The remainder of the calculations, giving pressure increase and per cent., increase are, of course, merely ordinary arithmetic.

To obtain T_{25}, T_{50}, and T_{100}, the per cent., increase in pressure was plotted against time and the values were taken from the curve.

Heat of Activation.

If the times to fractional pressure increases are plotted against the reciprocal of the absolute temperature, as in figs., 8 and 9, the slope of the line thus obtained will give the heat of activation as follows:

$$\begin{array}{ll} \text{Log}_{10} \text{ of t when } 1/T = 800 \times 10^6 = & 0.07 \\ \text{Log}_{10} \text{ of t when } 1/T = 900 \times 10^6 = & \underline{1.56} \\ & \underline{1.49} \end{array}$$

therefore slope $= \dfrac{1.49 \times 10^6}{100}$

converting to natural logarithms:

$$\text{slope} = \frac{1.49 \times 10^6 \times 2.3026}{100}$$

from relationship: $\ln k = C - E/RT$

$$\text{slope} = E/R$$

therefore:

$$E = R \times \text{slope} = \frac{1.98 \times 1.49 \times 10^6 \times 2.3026}{100}$$

$= 68{,}000$ calories per gram molecule.

EXPERIMENTAL RESULTS.

The Course of the reaction.

Hinshelwood and Askey (11) found that the homogeneous decomposition of methyl ether was mainly as represented by the equation:

$$CH_3O\,CH_3 = (\,CH_4 + HCHO\,) = CH_4 + H_2 + CO$$

Thus in a typical analysis of the products they found 32.0% carbon monoxide, 33.5% hydrogen, and 34.5% methane.

That in the present investigation, the reaction, in the main, is the same as the above is shown by the following analyses at 100% pressure increase or 53.8% reaction.

Temperature °K.	Percentage				
	unchanged methyl ether	carbon monoxide	methane	hydrogen	unsatd. hydrocbs.
1150°	19.5	23.3	29.5	26.5	-----
	19.6	23.5	30.2	26.7	-----
	20.1	24.2	28.7	27.0	------
b 1200°	19.0	26.9	31.0	22.6	------
1250°	19.5	24.2	30.6	24.5	1.86

Hinshelwood's and Askey's analyses at 106% pressure increase or an apparent decomposition of 53% are as follows:

unchanged methyl ether	carbon monoxide	methane	hydrogen
21.0	22.5	30.7	25.8

Analyses at 50% pressure increase or 26.9 percent reaction gave the following values:

Temperature °K.	Percentage.			
	unchanged methyl ether	carbon monoxide	methane	hydrogen
1150°	48.0	14.0	19.6	19.3
	48.3	12.7	22.3	17.6
1200°	48.9	14.1	19.8	16.1
1250°	49.0	14.0	23.0	13.9

Those obtained in the homogeneous reaction, at 54% pressure increase or an apparent decomposition of 27% are:

unchanged methyl ether	carbon monoxide	methane	hydrogen
44.4	15.4	22.0	18.2

Furthermore, in the homogeneous decomposition, in agreement with the foregoing equation, pressure increases at completion of 200% were obtained. In the present investigation corrected values of 186 ± 2% were invariably obtained. That this somewhat lower value was obtained is undoubtedly due to the condensation of a small amount of paraformaldehyde on the walls of the reaction vessel, and the fact that there existed a small " dead space " outside the reaction bulb proper. As stated above, the value 186 2% is a corrected value, for apparent pressure increases of 186% to above 200% were occasionally obtained, particularly at the higher temperatures, this however was undoubtedly due to a secondary decomposition, possibly that of the methane formed. This is shown by the following analyses when the reaction was carried to pressure increases of 226% and 189%, respectively, at the temperatures given below:

Temperature °K.	Percentage.			
	carbon monoxide	methane	hydrogen	unsatd. hydrocbs.
1250°K.	36.1	23.5	38.3	2.1
1200°K.	33.7	28.0	37.0	1.2

The method of determining the true pressure increase due to the primary reaction, is shown graphically in fig. 5 (32). To test this, analyses were made when the reaction had reached a pressure increase of 176%, (this gives a corrected value of 186%). Of course, it is to be expected that some undecomposed methyl ether will still be present, for the secondary reaction occurs simultaneously with the primary decomposition during the last stages of the latter, however, the analyses given below show that an apparent pressure increase of 176%, or a corrected value of 186% represents completion, with sufficient accuracy for the present purpose.

Temperature °K.	Pressure increase	carbon monoxide	methane	hydrogen	unchanged methyl ether
1200°	176%	33.3%	29.8%	35.6%	2.2%
1150°	176%	30.9	32.1	34.2	2.9

The presence of small amounts of unsaturated derivatives were noted in each case.

The analyses given above, therefore, particularly those for the initial stages of 53.8% and 26.9% reaction, show that in the main, the reaction is the same as that in the homogeneous decomposition, and furthermore that it is justifiable to use the pressure increase as a criterion of the extent to which the reaction has progressed.

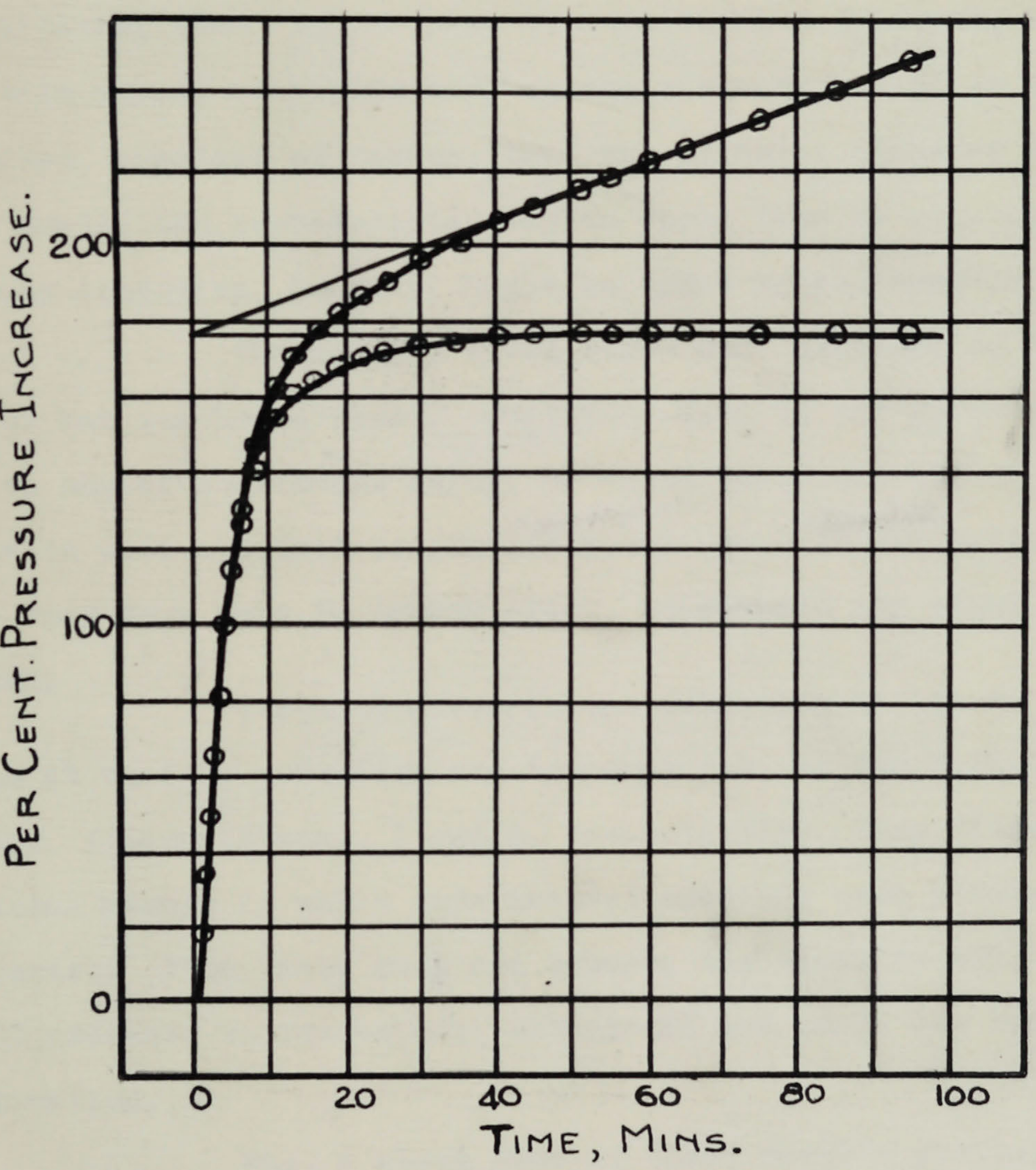

Fig. 5.

Curve A, Experimental.

Curve B, Corrected.

Experimental Results.

During the course of the investigation a number of different filaments were used. In general these filaments showed considerable differences, on account of differing diameter, surface conditions, etc. In the case of a particular filament, after a certain amount of preliminary aging, a steady condition was finally reached, provided of course, that the filament diameter was not too small, and reproducible results could then be obtained. This steady condition, however, might be upset by too drastic heating.

The results given below were obtained on filaments which had reached a steady condition, data is not given for those which showed continuous aging, or which burnt out before sufficient results were obtained to justify their use. In any paticular series the runs were made in random order, to obviate any error due to aging.

The data given in the following tables is for several runs at various pressures and temperatures, on two filaments, designated, filaments nos., 1 and 2, respectively. They illustrate the general manner in which experimental readings were obtained and recorded. From these runs and others, the times to 25%, 50% and 100% pressure increases were calculated and hence the heat of activation.

Fig. 6 shows some of these results plotted, giving typical pressure-time curves. For a few of these runs, K_m, the constant for a unimolecular reaction has been calculated, and is given in the last column. The mathematical handling of these results is given under " Calculations."

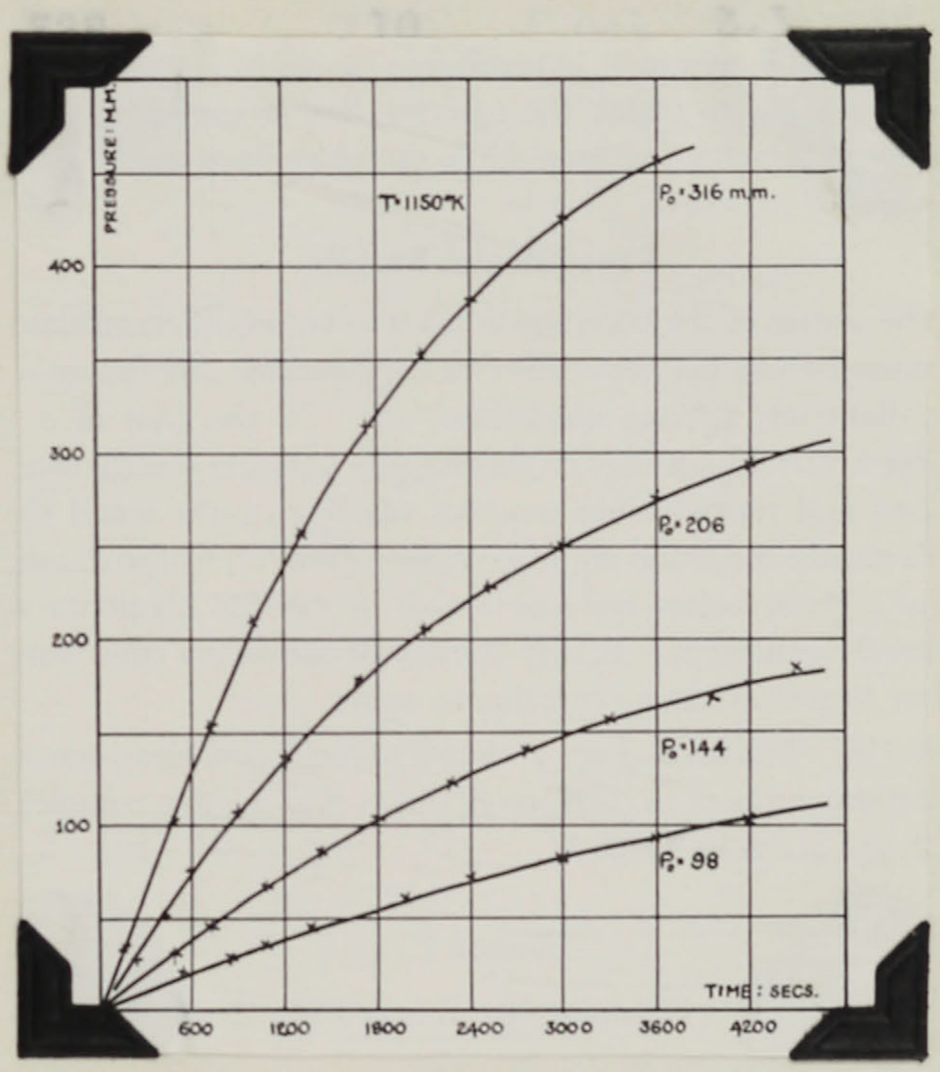

Fig. 6.

Pressure - Time Curves.

TABLE. 1.

Filament No. 1. Temperature 1100°K.

Time mins.	Pressure	Pressure increase.	Per cent increase.
0	318	0	0.0
3	328	10	3.1
6	336	18	5.7
12	355	37	11.6
21	385	67	21.1
30	414	96	30.2
41	447	129	40.5
50	474	156	49.0
60	500	182	57.3
70	525	207	65.2
80	548	230	72.4
90	570	252	79.2
100	588	270	85.0
110	606	288	90.5
120	623	305	96.0

T_{50} 51 mins. T_{100} 127 mins.

TABLE 2.

Filament No. 1   Temperature $1100^{\circ}K$.

Time mins.	Press. mm.	Press. incr.	Per cent incr.	Per cent decomp.	$\frac{a}{a - x}$	$\lg \frac{a}{a - x}$	K_m
0	432	0	0.0	0.00	1.000	0.00000	-------
2	444	12	2.8	1.51	1.015	0.00647	0.00324
6	464	32	7.4	3.98	1.041	0.01745	0.00291
12	495	63	14.6	7.85	1.085	0.03543	0.00295
20	539	107	24.8	13.32	1.153	0.06183	0.00309
30	594	162	37.5	20.18	1.252	0.09760	0.00325
40	645	213	49.4	26.52	1.360	0.13354	0.00334
45	665	233	54.0	29.00	1.410	0.14922	0.00332
50	690	258	59.8	32.15	1.473	0.16820	0.00336
55	715	283	65.5	35.20	1.543	0.18837	0.00342
60	733	301	69.7	37.50	1.600	0.20412	0.00349
65	753	321	74.3	39.90	1.662	0.22063	0.00339
70	772	340	78.7	42.30	1.732	0.23855	0.00341
75	790	358	83.0	44.60	1.807	0.25696	0.00343

T_{50} 40.5 mins. T_{100} 94 mins.

TABLE 3.

Filament No. 1   Temperature 1100°K.

Time mins.	Pressure mm.	Pressure increase	Per cent increase.
0	211	0	0.0
3	217	6	2.8
7	223	12	5.7
12	231	20	9.5
20	244	33	15.6
30	261	50	23.7
40	278	67	31.8
50	294	83	39.4
61	311	100	47.5
70	323	112	53.1
81	338	127	60.2
90	350	139	66.0
96	357	146	69.1

T_{50} 65 mins. T_{100} -------

TABLE 4.

Filament No. 1 Temperature 1150°K.

Time mins.	Press. mm.	Press. incr.	Per cent. incr.	Per cent. decomp.	$\frac{a}{a-x}$	$\lg \frac{a}{a-x}$	K_m
0	206	0	0.0	0.00	1.000	0.00000	-------
1	214	8	3.9	2.10	1.022	0.00945	0.00945
2	221	15	7.3	3.93	1.040	0.01703	0.00852
4	235	29	14.1	7.58	1.083	0.03463	0.00865
7	257	51	24.8	13.33	1.153	0.06183	0.00885
10	280	74	35.9	19.30	1.240	0.09342	0.00934
15	313	107	52.0	28.00	1.390	0.14301	0.00955
20	342	136	66.0	35.50	1.550	0.19033	0.00952
28	383	177	86.0	46.20	1.860	0.26951	0.00963
35	411	205	99.5	53.50	2.150	0.33244	0.00950
42	434	228	111.0	59.70	2.480	0.39445	0.00940
50	457	251	122.0	65.50	2.900	0.46240	0.00925
60	482	276	134.0	72.00	3.570	0.55267	0.00921
70	499	293	142.0	76.40	4.240	0.62737	0.00897
80	515	309	150.0	80.60	5.150	0.71181	0.00890
90	525	319	155.0	83.40	6.020	0.77960	0.00866
105	538	332	161.0	86.50	7.410	0.86982	0.00828

T_{50} 14.3 mins. T_{100} 35.3 mins.

TABLE 5.

Filament No. 1 . Temperature. 1150°K.

Time mins.	Pressure mm.	Pressure. increase,	Per cent. increase.
0	432	0	0.0
1	455	23	5.3
2	473	41	9.5
3	493	61	14.1
5	534	102	23.6
8	598	166	38.4
12	674	242	56.0
14	708	276	63.8
17	756	324	75.0
19	784	352	81.5
21	809	377	87.1

T_{50} 10.7 mins. T_{100} 25.4 mins.

TABLE 6.

Filament No. 1. **Temperature 1150°K.**

Time mins.	Pressure mm.	Pressure. increase.	Per cent. increase.
0	431	0	0.0
1	454	23	5.3
2	474	43	10.0
3.5	507	76	17.6
4	519	88	20.4
5.5	554	123	28.6
8.	610	179	41.5
11.5	683	252	58.5
14	729	298	69.0
17	780	349	81.0
19	806	375	87.0

T_{50} 10 mins. T_{100} 23 mins.

TABLE 7.

Filament No. 1. Temperature 1150°K.

Time mins.	Pressure mm.	Pressure. increase.	Per cent. increase.
0	433	0	0.0
1	451	18	4.2
2	471	38	8.8
3	489	56	12.9
5	531	98	22.6
8	594	161	37.2
12	670	237	54.8
14	705	272	62.9
17	754	321	74.2
19	783	350	81.0
21	809	376	87.0

T_{50} 10.7 mins. T_{100} 25.4 mins.

TABLE 8.

Filament No. 1. **Temperature 1150°K.**

Time mins.	Pressure mm.	Pressure. increase.	Per cent. increase.
0	98	0	0.0
1	102	4	4.1
3	111	13	13.3
5	115	17	17.4
9	120	22	22.6
14	127	29	29.8
23	143	45	46.2
33	158	60	61.5
40	169	71	73.0
50	180	82	84.0
60	191	93	95.5
70	201	103	106.0
80	210	112	115.0

T_{50} 25.5 mins. T_{100} 64.4 mins.

TABLE 9.

Filament No. 1. Temperature 1150°K.

Time mins.	Pressure mm.	Pressure increase	Per cent. increase
0	144	0	0.0
1	150	6	4.2
5	168	24	16.7
8	175	31	21.6
12	190	46	32.0
18	211	67	46.7
24	230	86	60.0
30	247	103	71.8
38	266	122	85.0
46	284	140	97.5
55	301	157	109.5
66	312	168	117.0
75	329	185	129.0
85	340	196	136.5
90	345	201	140.0
96	351	207	144.0

T_{50} 19.3 mins. T_{100} 48.4 mins.

TABLE 10.

Filament No. 1. Temperature 1150°K.

Time mins.	Pressure mm.	Pressure increase	Per cent. increase
0	316	0	0.0
3	351	35	11.1
8	418	102	32.3
12	469	153	48.4
17	526	210	66.5
22	574	258	81.5
29	630	314	99.3
35	669	353	111.5
40	698	382	121.0
50	741	425	134.3
60	772	456	144.0

T_{50} 12 mins. T_{100} 29 mins.

TABLE 11.

Filament No. 1. **Temperature 1200°K.**

Time mins.	Pressure mm.	Pressure increase	Per cent. increase
0	314	0	0.0
1	366	52	16.6
1.5	387	73	23.2
2	409	95	30.3
3	450	136	43.4
4	488	174	55.5
5	524	210	67.0
7	587	273	87.0
9	638	324	103.0
11	681	367	117.0
13.5	722	408	130.0
16	754	440	140.0
19	777	463	147.5
22	796	482	153.5
25	810	496	158.0

T_{50} 3.8 mins T_{100} 8.6 mins.

TABLE 12.

Filament No. 1. Temperature 1200°K.

Time mins.	Press. mm.	Press. incr.	Per cent. incr.	Per cent. decomp.	$\frac{a}{a-x}$	lg $\frac{a}{a-x}$	K_m
0	242	0	0.0	0.0	1.000	0.00000	---------
0.5	252	10	4.1	2.2	1.023	0.00988	0.01976
1.5	283	41	17.0	9.1	1.100	0.04139	0.0278
2	296	54	22.3	12.0	1.136	0.05538	0.0277
3	329	87	35.9	19.3	1.240	0.09342	0.0311
4	360	118	48.8	26.2	1.355	0.13194	0.0330
5	387	145	60.0	32.2	1.475	0.16879	0.0338
6	414	172	71.1	38.5	1.630	0.21219	0.0371
8	460	218	90.0	48.3	1.930	0.28556	0.0357
11	515	273	113.0	60.7	2.540	0.40483	0.0368
14	560	318	131.5	70.7	3.420	0.53403	0.0381
18	591	349	144.2	77.5	4.450	0.64836	0.0360
23	621	379	156.6	84.1	6.300	0.79934	0.0347
30	643	401	166.0	89.2	9.250	0.96614	0.0322
40	658	416	172.0				
55	668	426	176.0				
70	670	428	177.0				

T_{50} 4.1 mins. T_{100} 9.2 mins.

TABLE 13.

Filament No. 1. Temperature 1200°K.

Time mins.	Press. mm.	Press. incr.	Per cent. incr.	Per cent. decomp.	$\frac{a}{a - x}$	$\lg \frac{a}{a - x}$	K_m
0.0	400	0	0.0	0.0	1.000	0.00000	0.------
0.5	481	81	20.3	10.9	1.122	0.04999	0.09998
1.0	510	110	27.5	14.8	1.174	0.06967	0.06967
1.5	539	139	34.8	18.7	1.230	0.08991	0.06000
2.0	567	167	41.8	22.5	1.290	0.11059	0.05529
3.0	623	223	55.8	30.0	1.429	0.15503	0.05168
4.0	672	272	68.0	36.6	1.577	0.19783	0.04948
5.0	717	317	79.3	42.6	1.742	0.24105	0.04821
6.0	760	360	90.0	48.4	1.938	0.28735	0.04789
6.5	770	370	92.5	49.7	1.988	0.29842	0.04600

T_{50} 2.6 mins. T_{100} 7.3 mins.

TABLE 14.

Filament No.1. Temperature 1273°K.

Time mins.	Press. mm.	Press. incr.	Per cent. incr.	Per cent. decomp.	$\frac{a}{a-x}$	lg $\frac{a}{a-x}$	K_m
0.00	298	0	0.0	0.0	1.000	0.00000	-------
0.18	355	57	19.1	10.3	1.115	0.04727	0.262
0.42	405	107	35.9	19.3	1.239	0.09307	0.222
0.63	455	157	52.7	28.3	1.395	0.14457	0.230
0.87	505	207	69.5	37.4	1.597	0.20330	0.234
1.13	555	257	86.3	46.4	1.866	0.27091	0.240
1.43	605	307	103.0	55.4	2.242	0.35064	0.245
1.80	655	357	120.0	64.5	2.817	0.44979	0.250
2.28	705	407	136.5	73.4	3.759	0.57507	0.252
3.00	755	457	153.5	82.5	5.714	0.75694	0.252
4.67	805	507	170.0	91.4	11.628	1.06551	0.228

T_{50} 0.65 mins. T_{100} 1.42 mins.

TABLE 15.

Filament No. 1.. Temperature 1273°K.

Time mins.	Pressure mm.	Pressure increase	Per cent. increase
0	215	0	0.0
1	318	103	48.0
2	407	192	89.5
3	470	255	118.6
4	513	298	138.5
5	542	327	152.0
6	560	345	160.5
7	573	358	166.5
8	580	365	170.0
9	586	371	173.0
10	590	375	174.5
11	592	377	175.5
12	596	381	177.0
13	597	382	178.0
14	599	384	178.6
15	601	386	179.5
16	603	388	180.6
17	605	390	181.3

T_{50} 1.12 mins. T_{100} 2.33 mins.

TABLE 16.

Filament No. 1. Temperature 1273°K.

Time mins.	Press. mm.	Press. incr.	Per cent. incr.	Per cent. decomp.	$\frac{a}{a-x}$	lg $\frac{a}{a-x}$	K_m
0.00	396	0	0.0	0.0	1.000	0.00000	-------
0.25	505	109	27.7	14.9	1.175	0.07004	0.280
0.33	555	159	40.3	21.7	1.277	0.10619	0.319
0.50	605	209	52.8	28.40	1.397	0.14520	0.290
0.63	655	259	65.5	35.2	1.543	0.18837	0.298
0.80	705	309	78.0	41.9	1.721	0.23578	0.295
0.98	755	359	90.7	48.7	1.949	0.28981	0.296
1.18	805	409	103.0	55.4	2.242	0.35064	0.298

T_{50} 0.47 mins. T_{100} 1.15 mins.

TABLE 17.

Filament No. 1. Temperature 1273°K.

Time mins.	Pressure mm.	Pressure increase	Per cent. increase
0.00	212	0	0.0
0.47	255	43	20.3
1.05	305	93	43.9
2.00	373	161	76.0
3.00	428	216	102.0
4.00	471	259	122.0
5.00	501	289	136.0
6.50	531	319	150.5
7.00	539	327	154.0
8.00	550	338	159.2
10.00	563	351	165.5

T_{50} 1.23 mins. T_{100} 2.92 mins.

TABLE 18.

Filament No. 2. Temperature 1100°K.

Time mins.	Pressure	Pressure increase	Percent increase.
0	693	0	0.0
1	698	5	0.7
6	720	27	3.9
13	753	60	8.7
21	792	99	14.3
35	863	170	24.5
47	923	230	33.2
60	982	289	41.7
69	1020	327	47.2
78	1051	358	51.6
94	1114	421	60.9
105	1153	460	66.5
130	1213	520	75.0
151	1262	569	82.0
170	1301	608	87.8
194	1331	638	92,0
213	1361	668	96.5
226	1376	683	98.5

T_{50} 74 mins. T_{100} 236 mins.

TABLE. 19

Filament No. 2.   Temperature 1100 °K.

Time mins.	Press. mm.	Press. incr.	Per cent. incr.	Per cent. decomp.	$\frac{a}{a-x}$	$\lg\frac{a}{a-x}$	K_m
0	586	0	0.0	0.00	1.000	0.0000	-------
1	589	3	0.5	0.27	1.003	0.00130	0.00130
3	595	9	1.5	0.80	1.008	0.00346	0.00115
8	612	26	4.4	2.36	1.025	0.01072	0.00134
15	639	53	9.1	4,90	1.052	0.02202	0.00147
25	680	94	16.0	8.60	1.094	0.03902	0.00156
35	722	136	23.2	12.50	1.143	0.05805	0.00166
45	764	178	30.4	16.33	1.197	0.07809	0.00174
60	825	239	40.8	21.93	1.283	0.10823	0.00180
75	883	297	50.7	27.25	1.377	0.13893	0.00185
90	932	346	59.0	31.70	1.464	0.16554	0.00184
105	976	390	66.5	35.80	1.558	0.19257	0.00183
120	1011	425	72.5	39.00	1.639	0.21458	0.00179
135	1042	456	78.0	41.92	1.726	0.23704	0.00176
150	1070	484	82.5	44.30	1.795	0.25406	0.00169
165	1095	509	86.8	46.65	1.878	0.27370	0.00166

T_{50} 74 mins. T_{100} 216 min.

TABLE. 20

Filament No. 2. Temperature 1150°K.

Time mins.	Press. mm.	Press. incr.	Per cent. incr.	Per cent. decomp.	$\frac{a}{a-x}$	lg $\frac{a}{a-x}$	K_m
0	577	0	0.0	0.00	1.000	0.00000	--------
1	593	16	2.8	1.50	1.015	0.00647	0.00647
1.5	600	23	4.0	2.15	1.022	0.00945	0.00630
2	607	30	5.2	2.80	1.029	0.01242	0.00621
5	655	78	13.5	7.25	1.078	0.03262	0.00653
8	705	128	22.2	11.92	1.135	0.05500	0.00688
12	773	196	34.0	18.30	1.224	0.08778	0.00731
14	806	229	39.7	21.33	1.271	0.10415	0.00745
18	867	290	50.3	27.00	1.370	0.13672	0.00760
22	925	348	60.3	32.40	1.479	0.16997	0.00773
25	964	387	67.1	36.05	1.564	0.19424	0.00777
30	1012	435	75.5	40.55	1.682	0.22583	0.00752
34	1068	491	85.2	45.75	1.844	0.26576	0.00780
38	1108	531	92.0	49.50	1.980	0.29667	0.00780
42	1145	568	98.5	52.90	2.123	0.32695	0.00780
46	1176	599	103.8	55.75	2.260	0.35411	0.00770

T_{50} 17.8 mins. T_{100} 43 mins.

TABLE 21.

Filament No. 2   Temperature 1150^{0}K.

Time mins.	Pressure mm.	Pressure increase.	Per cent. increase.
0	698	0	0.0
2	729	31	4.5
4	765	67	9.6
7	823	125	17.9
9	861	163	23.4
12	920	222	31.8
15	976	278	39.8
17	1012	314	45.0
20	1064	366	52.5
23	1111	413	59.3
27	1169	471	67.5
31	1221	523	75.0
35	1269	571	82.0
39	1311	613	88.0
44	1361	663	95.0
45	1371	673	96.5
47	1388	690	99.0
48	1398	700	100.5
49	1408	710	102.0

T_{50} 18.5 mins. T_{100} 47 mins.

TABLE. 22.

Filament No. 2 Temperature 1200°K.

Time mins.	Press. mm.	Press. incr.	Per cent. incr.	Per cent. decomp.	$\frac{a}{a-x}$	$\lg\frac{a}{a-x}$	K_m
0.00	581	0	0.0	0.00	1.000	0.00000	0.------
1.17	647	66	11.4	6.13	1.065	0.02735	0.0234
2.07	697	116	20.0	10.75	1.121	0.04961	0.0240
2.90	747	166	28.6	15.40	1.182	0.07262	0.0250
3.78	797	216	37.2	20.00	1.250	0.09691	0.0256
4.72	847	266	45.7	24.60	1.326	0.12254	0.0260
5.68	897	316	54.4	29.20	1.412	0.14983	0.0264
6.69	947	366	63.0	33.80	1.511	0.17926	0.0268
7.81	997	416	71.5	38.40	1.623	0.21032	0.0269
9.00	1047	466	80.2	43.10	1.758	0.24502	0.0272
10.30	1097	516	88.8	47.70	1.912	0.28149	0.0273
11.70	1147	566	97.5	52.40	2.101	0.32243	0.0275
13.33	1197	616	106.0	57.00	2.326	0.36661	0.0275

T_{50} 5.20 mins. T_{100} 12.17 mins.

TABLE 23.

Filament No. 2. **Temperature 1200°K.**

Time mins.	Pressure mm.	Pressure increase.	Per cent. increase.
0.00	688	0	0.0
0.05	691	3	0.4
0.87	741	53	7.7
1.63	791	103	15.0
2.44	841	153	22.2
3.16	891	203	29.5
3.97	941	253	36.8
4.77	991	303	44.1
5.50	1041	353	51.3
6.36	1091	403	58.6
7.28	1141	453	65.9
8.28	1191	503	73.1
9.30	1241	553	80.5
10.41	1291	603	87.6
11.62	1341	653	95.0
12.97	1391	703	102.2

T_{50} 5.33 mins, T_{100} 12.5 mins.

TABLE 24.

Filament No. 2 Temperature 1250°K.

Time mins.	Press. mm.	Press. incr.	Per cent. incr.	Per cent. decomp.	$\frac{a}{a - x}$	lg $\frac{a}{a - x}$	K_m
0.00	683	0	0.0	0.00	1.000	0.00000	-------
0.28	737	54	7.0	4.25	1.044	0.01870	0.0660
0.55	787	104	15.2	8.17	1.089	0.03703	0.0674
0.80	837	154	22.6	12.15	1.138	0.05614	0.0703
1.10	889	204	29.9	16.10	1.192	0.07628	0.0693
1.35	937	254	37.2	20.00	1.250	0.09691	0.0717
1.65	987	304	44.5	23.90	1.314	0.11860	0.0718
1.97	1037	354	51.9	27.90	1.387	0.14208	0.0720
2.23	1087	404	59.1	31.80	1.466	0.16613	0.0744
2.53	1137	454	66.5	35.80	1.558	0.19257	0.0760
2.90	1187	504	73.8	39.70	1.658	0.21958	0.0757
3.25	1237	554	81.1	43.60	1.773	0.24871	0.0765
3.67	1287	604	88.5	47.50	1.905	0.27989	0.0763
4.07	1337	654	95.8	51.50	2.062	0.31429	0.0773
4.53	1387	704	103.0	55.40	2.242	0.35064	0.0773

T_{50} 1.87 mins. T_{100} 4.33 mins.

TABLE 25.

Filament No. 2. Temperature 1250°K.

Time mins.	Pressure mm.	Pressure increase.	Per cent. increase.
0.00	577	0	0.0
0.08	593	16	2.8
0.58	693	116	20.2
1.18	793	216	37.4
1.79	893	316	54.8
2.50	993	416	72.3
3.27	1093	516	89.5
4,25	1193	616	107.0

T_{50} 1.60 mins. T_{100} 3.84 mins.

An examination of the tabulated velocity constants will show that in the early stages of the reaction, the constants rise, and finally become constant within the experimental error. Exactly the same behaviour was noted in the case of the homogeneous reaction, and the reason is as follows. During the early part of the reaction, due to the existence of consecutive reactions, the secondary reaction or decomposition of formaldehyde does not become as fast as the primary decomposition until a small amount of formaldehyde has accumulated, the decomposition then attains its normal rate for the existing pressure and temperature.

Effect of Pressure.

The effect of pressure on the reaction is shown more concisely by the summary in Table 26, and graphically by the curve given in fig. 7. As in the homogeneous reaction the velocity constants fall off at pressures below 300 - 400 mm.

The same remarkable influence of hydrogen in keeping up the normal rate, at pressures below which falling off would occur in the absence of hydrogen, was noted. Some data are given below.

Filament No. 3.

Partial pressures mm.				
Methyl ether	Hydrogen	T_{25} mins.	T_{50} mins.	T_{100} mins.
46	229	4.5	8.7	16.8
123	485	5.0	9.4	19.4
154	619	4.7	9.1	19.6
192	795	3.7	7.6	19.2
498	0	5.5	10.5	-----

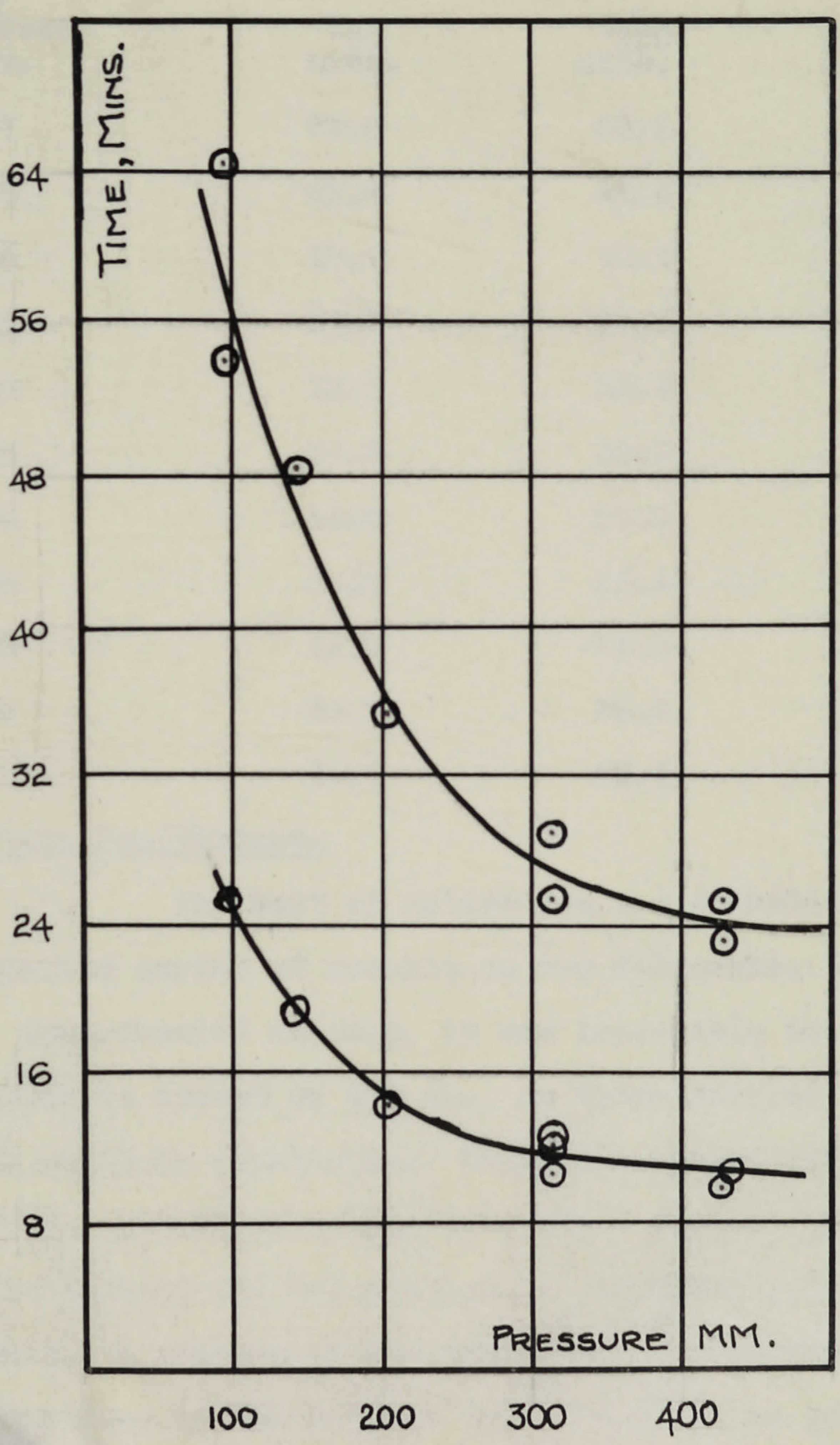

Fig. 7.

TABLE 26.

Filament No. 1. Temperature 1150°K.

Pressure mm.	T_{50} mins.	T_{100} mins.
97	23.0	53.6
98	25.5	64.4
144	19.3	48.4
206	14.3	35.3
314	10.6	25.4
315	12.6	30.0
316	12.0	29.0
318	12.0	28.3
430	10.0	23.0
432	10.7	25.4
433	10.7	25.4

The Temperature Coefficient.

The heat of activation was calculated from two entirely separate series of results on two filaments. In the first series, for experimental reasons, it was impossible to use initial pressures much in excess of 400 mm., so these results in themselves would not be entirely conclusive. Hence the second series of runs were made, with initial pressures from 600 - 800 mm. At these pressures the falling off was negligible and hence this objection cannot be made. A summary of the times used in calculating the heat of activation, in the case of both filaments is given below. Figs. 8 and 9 show a plot of T_{25}, T_{50}, and T_{100} against the reciprocal of the absolute temperature.

TABLE 27.

Pressures about 400 mm. Filament No. 1.

Temperature °K.	T_{50} mins.	T_{100} mins.
1100°	40.5	94.0
1150°	10.0	23.0
1200°	2.6	7.3
1273°	0.55	1.3

TABLE 28.

Pressures about 200 mm. Filament No. 1.

Temperature °K.	T_{50} mins.	T_{100} mins.
1100°	65.0	-------
1150°	14.3	35.3
1200°	3.8	8.6
1273°	1.1	2.33

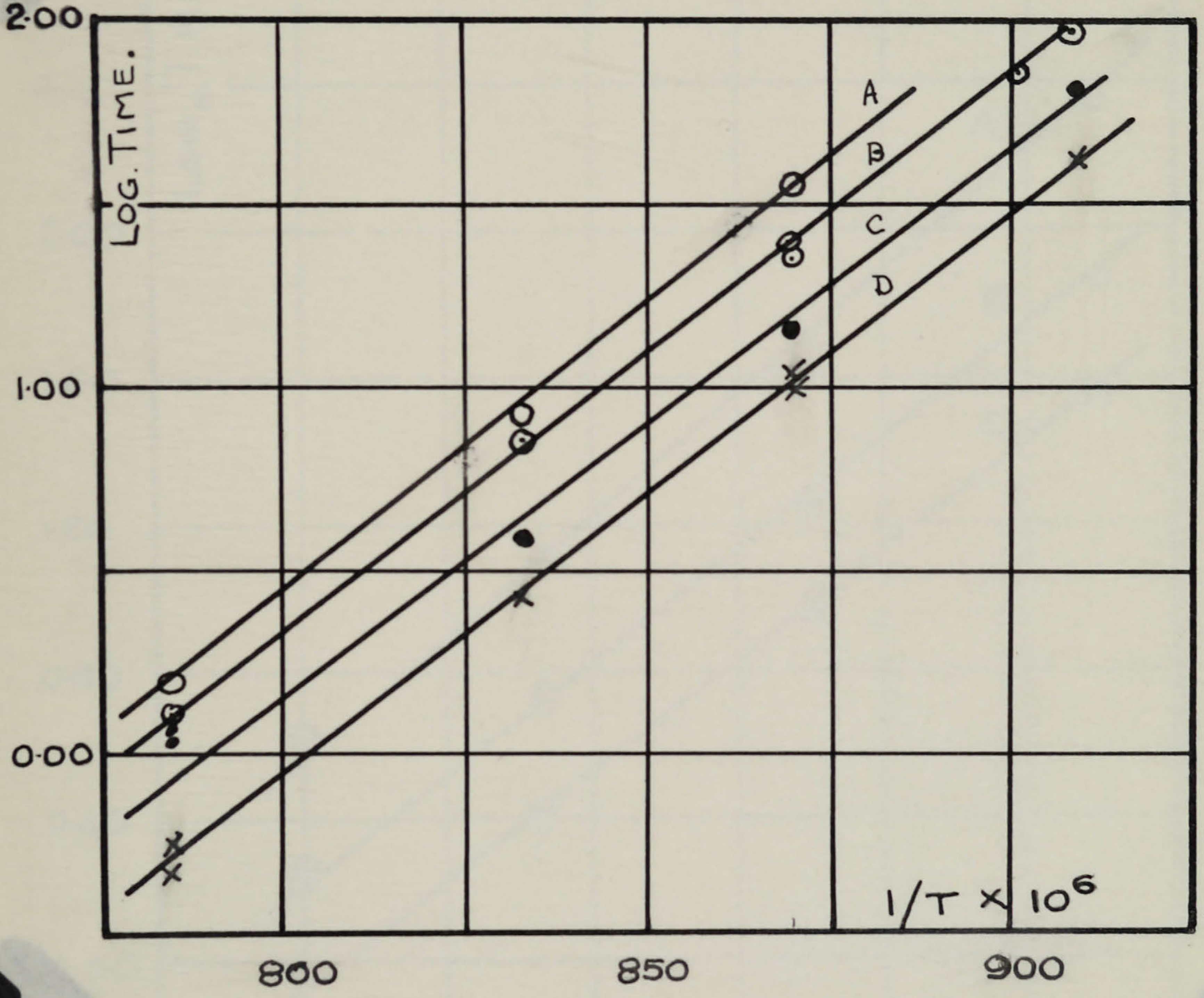

Fig. 8.

Curve A. T_{100} , 200 mm.

" B. T_{100} , 400 mm.

" C. T_{50} , 200 mm.

" D. T_{50} , 400 mm.

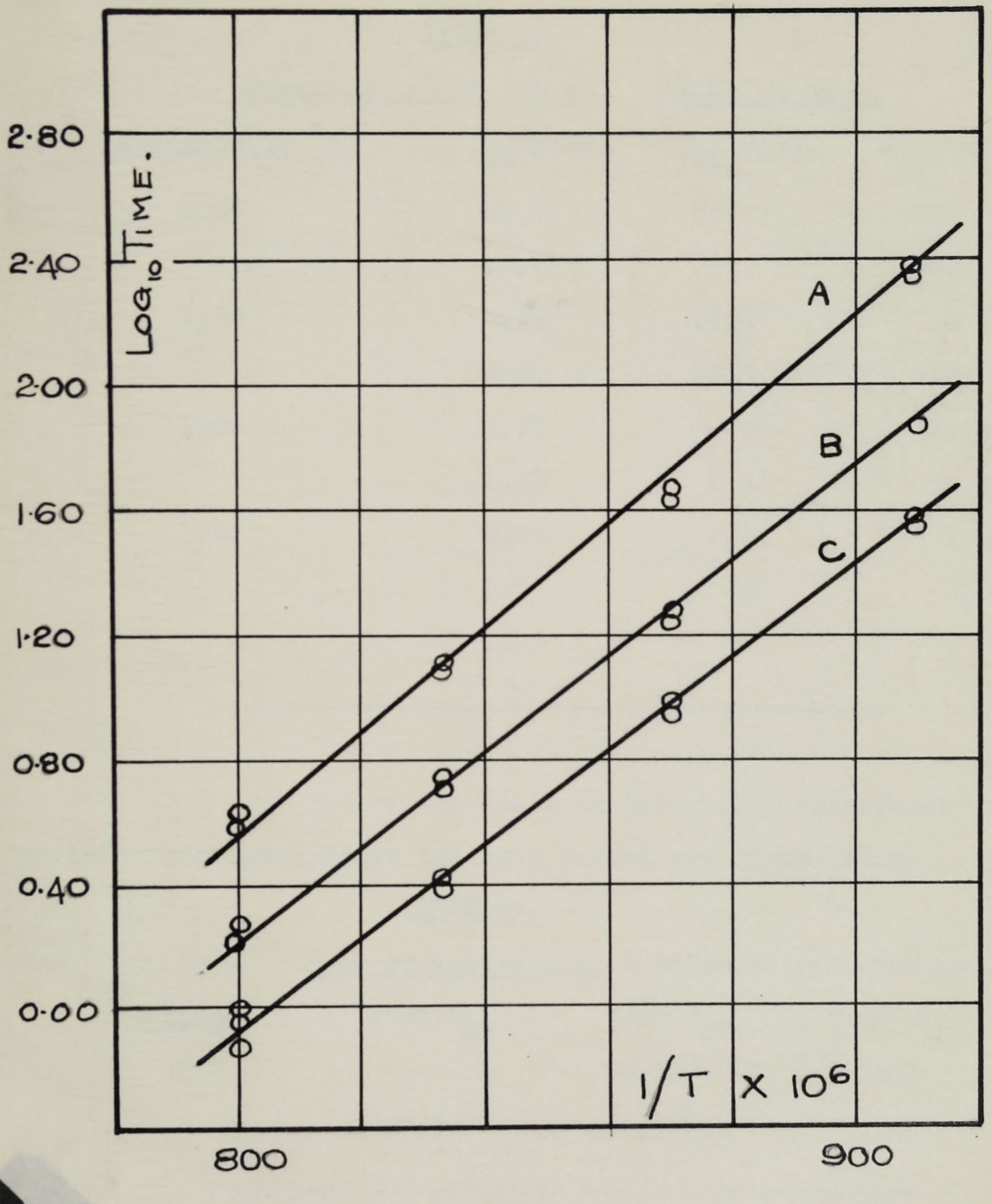

Fig. 9.

Curve A ----from T_{100}

Curve B ----from T_{50}

Curve C ----from T_{25}

TABLE 28.

Pressures about 700 mm. Filament No.2.

Temperatures °K.	T_{25} mins.	T_{50} mins.	T_{100} mins.
1100	37.5	74	216
	37.0	74	236
1150	8.75	17.8	43
	9.25	18.5	47
1200	2.53	5.20	12.2
	2.58	5.33	12.5
1250	0.92	1.60	3.84
	0.97	1.87	4.33
	0.73		

The heats of activation calculated for various fractional times for both series are given below.

TABLE 29.

Heat of Activation. (Calories per gram mol.)

Series	from T_{25}	from T_{50}	from T_{100}
1.	-------	68,500	70,100
2.	68,300	69,500	72,200

On account of the complications due to the intermediate formation of formaldehyde, previously mentioned, the best valuesof the heat of activationwill be obtained by extrapolation of the above values to initial rates. This is done in fig. 10. The

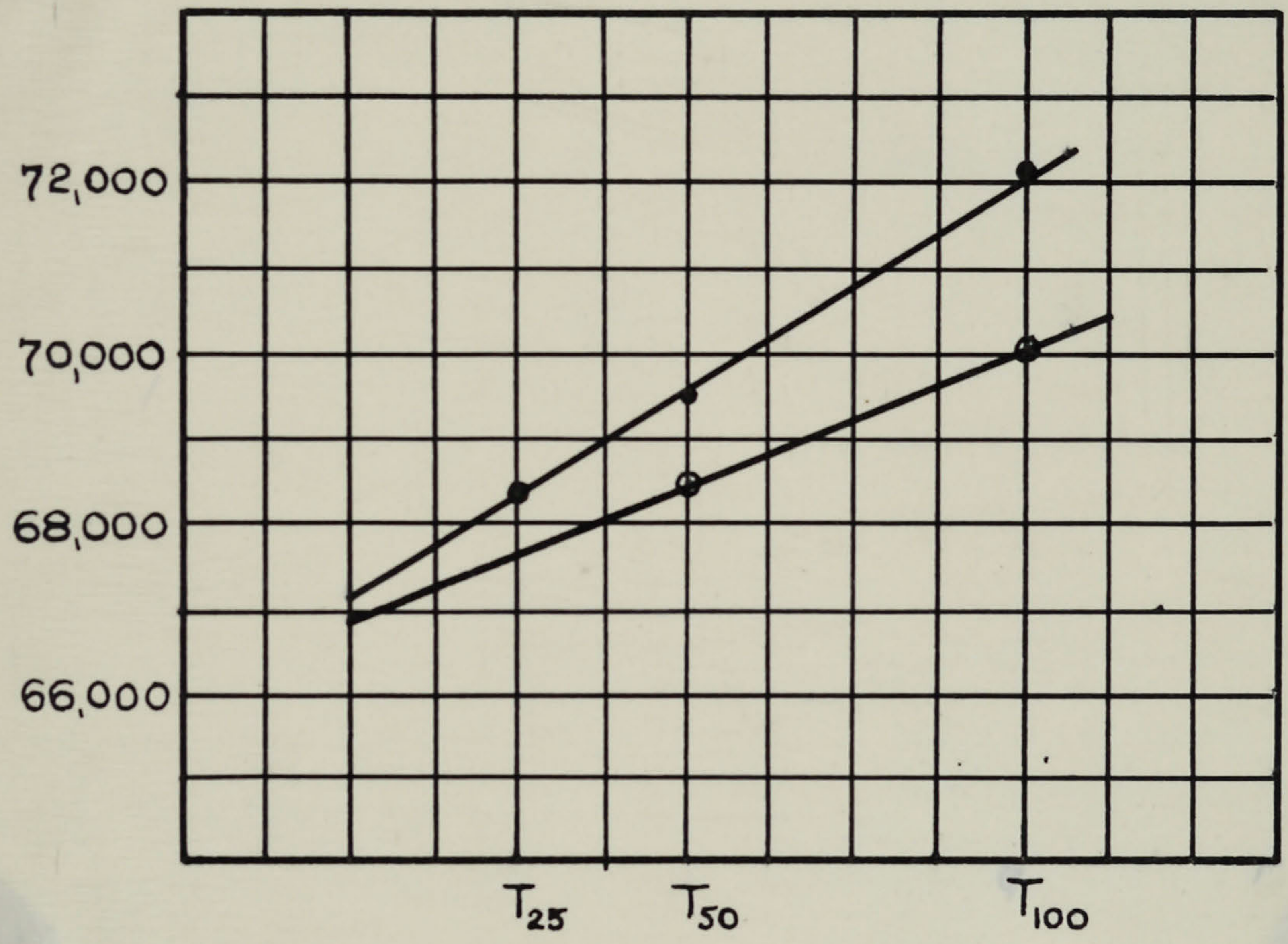

Fig. 10.

values obtained in this way, for the two series are 66,900 and 67,100, the mean value of the heat of activation is therefore 67,000 as compared with 58,500 found by Hinshelwood and Askey for the homogeneous reaction.

A COMPARISON OF SOME HOMOGENEOUS AND HETEROGENEOUS GAS REACTIONS.

The unimolecular decompositions of the following substances have been investigated both homogeneously, and heterogeneously in contact with hot filaments. The heats of activation are summarized in Table 30.

TABLE 30.

Substance.	Heat of Activation.	
	Homogeneous.	Filament.
Acetone	68,500 (8)	68,400 (29)
Ethyl Ether	53,000 (28)	52,000 (30)
		57,000 (35)
Propionaldehyde	55,000 (10)	96,500 (31)
Methyl Ether	58,500 (11)	67,000 (36)

It will be seen that in the first two cases the heats of activation agree within the experimental error, while in the last two, the heat of activation of the filament reaction is higher than that of the homogeneous reaction. This point will be discussed later in detail. We will now consider more fully the individual reactions.

(1) The thermal decomposition of Ethyl Ether on the surface of Platinum.

This was investigated by Steacie and Campbell (30). The heat of activation of the reaction was found to be 52,000 calories per gram molecule. This agrees within the experimental error with the value of 53,000 calories found by Hinshelwood for the homogeneous reaction (28).

The velocity constants of the surface reaction were found to fall off at low pressures as in the homogeneous reaction. There would seem to be two possible explanations:

(a) Molecules are activated by collisions with the filament.

(b) The filament serves as a source of energy, the surrounding gas layer being maintained at a high temperature. Activation takes place in the hot gas layer by ordinary molecular collisions.

The second explanation seems by far the most likely, since it is difficult to see why the velocity constants should fall off at low pressures if collision with the filament were a necessary preliminary to reaction. That this is the correct explanation may be proved conclusively by an examination of the statistics of the reaction.

Some typical data are:

Temperature	973°K.
Pressure...........................	400 mm.
Volume of reaction vessel..........	125 c.c.
Filament length....................	15 cms.
Filament diameter..................	0.15 mm.
Bulb temperature...................	323°K.

26.6 per cent decomposition in 150 seconds.

The number of molecules reacting.

From the above data this is found to be 2.67×10^{18} molecules per second.

The number of molecules hitting the filament.

According to Knudsen's equation we have

$$m = \sqrt{\frac{M}{2\pi RT}}\, p,$$

where m is the mass of gas striling the solid surface per second, M is the molecular weight, R is the gas constant in ergs per gram molecule, T is the absolute temperature, and p the pressure in bars Evaluating the constants, and putting the pressure in atmospheres, we have

$$m = 44.2\sqrt{\frac{M}{T}}\ P.$$

The value of T to be used is somewhat uncertain. Since we are only interested in the order of magnitude of the results, it is not of much importance, and the simplest assumption to make is that the temperature of the colliding molecules is that of the filament. In any case, an error of even 200° in T will not introduce more than a 10 per cent. error into the result.

Hence we have

$$m = 44.2\sqrt{\frac{74}{973}} \cdot \frac{400}{760}$$

$$= 6.42 \text{ grams per sec. per sq. cm.}$$

Hence the number of molecules striking the filament is

$$= \frac{6.42}{74} \times 6.06 \times 10^{23} \text{ molecules per sec. per sq. cm.}$$

The surface area of the filament is 0.0706 sq. cm. Hence the number of molecules hitting the filament is 3.72×10^{22} molecules per second.

The fraction of the molecules possessing the energy of activation.

Using Hinshelwood's form of theory, this will be given by

$$\frac{e^{-E/RT}\left(\frac{E}{RT}\right)^{n/2-1}}{\lfloor\underline{n/2 - 1}}$$

From Hinshelwood's data for the homogeneous reaction we have

E, the energy of activation = 53,000 + (n/2 - 1)RT

n, the number of degrees of freedom = 8

Hence the fraction of the molecules at 973°K. possessing the energy of activation is

$$\frac{e^{-\frac{53{,}000 \quad 3\times 2\times 973}{2\times 973}}\left(\frac{53{,}000 \quad 3\times 2\times 973}{2\times 973}\right)^{3}}{3\times 2}$$

$= 3.86 \times 10^{-10}$

Hence the total number of activated molecules produced by collisions with the filament only

$= 3.86 \times 10^{-10} \times 3.72 \times 10^{22}$ molecules per sec.

$= 1.44 \times 10^{13}$ molecules per second.

Hence about 2×10^{5} molecules react for every one which obtains the necessary energy from the filament by direct collision. It may therefore be concluded that the reaction is occurring in a layer of hot gas surrounding the filament. The effective dimensions of this layer may be calculated approximately as follows:

The total number of molecules entering into collisions in a gas per c.c. per sec. is given by $2\sqrt{2}\pi s^{2} u\, n^{2}$, where s is the molecular diameter, u the root mean square velocity, and n the number of molecules per c.c. The total number of activated molecules produced in the hot layer of gas per c.c. per sec. is therefore given by

$$\frac{2\sqrt{2}\pi s^2 u n^2 e^{-E/RT}\left(\frac{E}{RT}\right)^{n/2 - 1}}{\underline{\left| n/2 - 1 \right.}}$$

In order to evaluate this expression it is necessary to assign a value to s, the molecular diameter. Kinetic theory considerations indicate a value of about 10×10^{-8} cms. It is known, however, that molecules with a high energy content can transfer energy by resonance, and in general in dealing with energy transfer effective diameters much larger than kinetic theory diameters must be used. It will therefore be useful to evaluate the above expression with $s = 10 \times 10^{-8}$ cms., and also with $s = 100 \times 10^{-8}$. In the first case we obtain 2.88×10^{20}, and in the second case 2.88×10^{22} molecules per c.c., per second.

The number of molecules reacting per second is 2.67×10^{18}. Hence the effective volume of the space in which reaction occurs is $\frac{2.67 \times 10^{18}}{2.88 \times 10^{20}}$ c.c., or $\frac{2.67 \times 10^{18}}{2.88 \times 10^{22}}$ c.c., depending on the value of s chosen. Whence the effective thickness of the annular space surrounding the filament in which reaction occurs is either 0.055 or 0.001 mm.

It is well known that practically the entire temperature drop in the gas surrounding a filament of this typre takes place in a " skin " about 0.5 mm., thick by conduction. The last few degrees drop is much more gradual, and the heat transfer takes place mainly by convection. The total temperature drop here is 650°. If we assume that 600° of this occurs in such a layer, and that $s = 10 \times 10^{-8}$ cms., then the reaction is occuring in a zone surrounding the wire which contains a temperature gradient of about 60°; a value of $s = 100 \times 10^{-8}$ would give about 1°. Values between these extremes are quite reasonable ones, since (a) the velocity of a reaction falls off so rapidly with decreasing temperature that a drop of 10 to 20 degrees will cause the reaction to proceed at a rate negligible compared with that at a higher temperature, and (b) such an error in the value of the mean temperature of the reaction zone would introduce comparatively little error into the calculated heat of activation (which involves the difference of the reciprocals of the absolute temperatures).

It may therefore be concluded that the dynamics of the reaction are completely explained on the assumption that it occurs in a hot gas layer surrounding the filament.

The above reaction has also been investigated by Taylor and Schwartz on the surface of platinum and tungsten (35). Data are not given as to the dimensions of the filament and bulb. An approximate calculation, however, yields results very similar to those given above, the indications being that about 10^5 molecules react for every one that obtains the necessary energy directly from the filament.

(2) The Decomposition of Acetone on Platinum.

Taylor investigated this reaction (29) and found a heat of activation of 68,400 calories, as compared with 68,500 found by Hinshelwood and Hutchison for the homogeneous reaction(8). The homogeneous reaction was not investigated at low pressures, no falling off in the velocity constants was observed, and hence the value of the number of degrees of freedom effective in activation is unknown. Approximate calculations, however, indicate that again about 10^5 molecules react for each one which obtains the necessary energy directly from the filament.

It may therefore be concluded that in these cases the filament serves merely to maintain the surrounding gas at a temperature high enough to cause an appreciable rate of reaction. The reaction is confined to a thin layer, and the mean temperature of this layer does not differ from that of the filament by a large enough amount to introduce any appreciable error into the calculation of the heat of activation. As will be seen, however, the two following cases give results of quite a different mature.

(3) The Decomposition of Propionaldehyde on Platinum.

Steacie and Morton (31) found a heat of activation of 96,500 calories, compared with 55,000 calories for the homogeneous reaction (10).

If calculations are made as with methyl ether, we obtain for 1166°K. and 294 mm., initial pressure:

Number of molecules reacting $= 4.61 \times 10^{18}$ molecules per second.

Number colliding with the filament $= 2.81 \times 10^{22}$ molecules per sec.

If we assume that the observed heat of activation is an apparent one, and that the real energy necessary is that given by the homogeneous heat of activation, we have from Hinshelwood's and Thompson's data:

$$E = 55,000 + (n/2 - 1)RT$$

$$n = 12$$

Whence the fraction of the molecules possessing the energy of activation is given by

$$\frac{e^{-\frac{55,000 \quad 5 \times 2 \times 1166}{2 \times 1166}} \left(\frac{55,000 \quad 5 \times 2 \times 1166}{2 \times 1166}\right)^5}{\lfloor\underline{5}}$$

$= 6.03 \times 10^{-8}$

Hence the number of activated molecules produced by direct collisions with the filament is

$= 6.03 \times 10^{-8} \times 2.81 \times 10^{22} = 1.69 \times 10^{15}$.

Hence about 2500 molecules react for every one which gets the necessary energy from the filament. Proceeding as with ethyl ether , and putting $s = 10 \times 10^{-8}$ cms., we obtain 0.005 mm., for the thickness of the effective volume surrounding the filament in which reaction occurs. This is a reasonable value for such a layer.

We are still left with the necessity of explaining why the observed temperature coefficient leads to a heat of activation of 96,500 calories. This value cannot possibly be the true heat of activation. If it were the true heat of activation, the fraction of the molecules activated would be given by

$$\frac{e^{-\frac{96,500 \quad 5 \times 2 \times 1166}{2 \times 1166}} \left(\frac{96,500 \quad 5 \times 2 \times 1166}{2 \times 1166}\right)^5}{\lfloor\underline{5}}$$

$= 1.15 \times 10^{-14}$

Calculation shows that if the entire bulb were at 1166°K., and the true heat of activation were 96,500 calories, the rate would still be 167 times slower than the observed value.

(4) The Decomposition of Methyl Ether on Platinum.

As stated previously an apparent heat of activation of 67,000 calories was found , as compared with 58,500 for the homogeneous reaction. Proceeding as with ethyl ether, from the following data:

Filament temperature .... 1150°K.
Pressure .... 316 mm.
Volume of reaction vessel .... 100 c.c.
Filament length .... 10 cms.
Filament diameter .... 0.06 mm.
Bath temperature .... 318°K.
Rate of decomposition .... 0.033% per sec.

Whence we obtain:

The number of molecules reacting.

$= 3.19 \times 10^{17}$ molecules per second.

The number of molecules hitting the filament.

As with ethyl ether, the simplest assumption to make is that the temperature of the colliding molecule is that of the filament. Thus from Knudsen's equation we obtain:

mass of gas striking filament

= 3.68 grams per sec. per sq. cm.,

hence the number of molecules striking the filament is

$= 4.85 \times 10^{22}$ molecules per sec. per sq cm.,

the surface area of the filament is 0.188 sq. cm., hence the number of molecules striking the filament is

$= \underline{9.12 \times 10^{21} \text{ per second}}$

The fraction of the molecules at 1150°K. possessing the energy of activation.

Using Hinshelwood's form of theory, this will be given by

$$\frac{e^{-\frac{58{,}500 \quad 5 \times 2 \times 1150}{2 \times 1150}} \left(\frac{58{,}500 \quad 5 \times 2 \times 1150}{2 \times 1150}\right)^{5}}{5 \times 4 \times 3 \times 2}$$

assuming that the heat of activation found by Hinshelwood and Askey for the homogeneous reaction is the true one, and n = ca. 12. The above expression is

$= 1.36 \times 10^{-8}$

Hence the total number of activated molecules, produced by collisions with the filament only is

$= 9.12 \times 10^{21} \times 1.36 \times 10^{-8}$

$= \underline{1.24 \times 10^{14}\ \text{molecules per second.}}$

Hence about 2600 molecules react for every one which obtains the necessary energy from the filament by direct collision. It may therefore be concluded, as with the previous cases discussed, that the reaction is occuring in a layer of hot gas surrounding the filament. Proceeding as with ethyl ether, and assuming that $s = 20 \times 10^{-8}$ cm.,
the number of activated molecules produced by collisions in the gas at 1150°K. is

$= 3.54 \times 10^{22}$ molecules per c.c. per second.

the number of molecules reacting is

$= 3.19 \times 10^{17}$

hence the effective volume of the space in which reaction occurs is

$$= \frac{3.19 \times 10^{17}}{3.54 \times 10^{22}} = 9.00 \times 10^{-6}\ \text{c.c.}$$

Whence the effective thickness of the region surrounding the filament in which reaction occurs is

$$= 4.73 \times 10^{-4} \text{ mm.}$$

This volume is obtained by equating the number of molecules activated to the number reacting, therefore it will be a minimum value. It will, however, be approximately correct, since the calculations have been made for a pressure at which the velocity constants have fallen off to an appreciable extent.

As was stated for the ethyl ether decomposition, it is well known that practically the entire temperature drop in the gas surrounding a filament of this type takes place in a "skin" 0.5 mm., thick by conduction. The last few degrees drop is much more gradual, and the heat transfer takes place mainly by convection. The total temperature drop here is 832°. If we assume that 750° of this occurs in such a layer, then the reaction is occuring in a zone surrounding the wire which includes a temperature gradient of about 1°. The volume, however, is a minimum value, as explained before. We may therefore conclude that the zone in which reaction occurs does not include a great enough temperature gradient to introduce any appreciable error into the calculated value of the temperature coefficient of the reaction, provided that the filament is in thermal equilibrium with the gas.

Thus with methyl ether, as with ethyl ether, acetone, and propionaldehyde it is necessary to assume that the reaction occurs in a hot gas layer surrounding the filament.

We may therefore consider that the dynamics of the decomposition of ethyl ether and of acetone are completely explained. In the case of propionaldehyde and of methyl ether, however, it is still necessary to explain the fact that the temperature coefficients are higher than those of the homogeneous reactions. The heats of activation calculated for the filament reactions cannot be the true ones. Thus as pointed out for propionaldehyde calculation shows that if the true value of E were 96,500 calories, then even if the whole reaction vessel were at the temperature of the filament the rate would still be 167 times slower than the observed value

The only possible explanation of the high temperature coefficients of these reactions would seem to involve the transfer of energy between the filament and incident gas molecules.

Energy Transfer between Gas Molecules and the Filament.

To quote Langmuir (38): " Kundt and Warburg (37) , in a study of the viscosity of gases at low pressures, showed, both experimentally and theoretically, that there is a certain apparent slipping of the gas along the surface. In gases at atmospheric pressure this effect is very small, but it varies inversely proportional to the pressure and thus becomes very important at low pressures. The thickness of the layer in which this slipping occurs is approximately equal to the mean free path of the gas molecules. Kundt and Warburg predicted, from the analogy between viscosity and heat conduction, that a corresponding discontinuity in temperature at the surface of a solid body would be observed in the case of heat conduction through gases at low pressure.

Over twenty years later Smoluchowski (39),(40),(41), actually observed and studied this temperature drop and developed the theory of it. The temperature drop occurred within a layer about equal in thickness to the free path of the molecules. Smoluchowski found that in some gases, paticularly hydrogen, the amount of heat given up to the gas by a solid body was only a fraction of that which should be delivered if each molecule striking the surface reached thermal equilibrium with the solid before leaving it.

Smoluchowski developed the theory of this effect along the lines of two alternative hypotheses, which he denotes by A and B. Hypothesis A is equivalent to that made more recently by Knudsen (42). It assumes, when molecules of a temperature T_1 strike a surface at a higher temperature T_2, that the molecules leaving the surface have a temperature T which is intermediate between T_2 and T_1 and that the relation holds:

$$T - T_1 = \alpha(T_2 - T_1)$$

where α is a number less than unity and is called by Knudsen the "accommodation coefficient."

Hypothesis B is similar to that originally used by Maxwell (43) in dealing with the slip of gases. It assumes that, of all the molecules striking the surface, a fraction f, reaches thermal equilibrium with it, while the fraction 1 - f is reflected without change of temperature (or rather velocity).

The two methods give analogous, but quantitatively slightly different results."

More recently, by means of heat conductivity measurements at low pressures, Soddy and Berry (44) came to the conclusion that α for gases of high molecular weight was always in the neighborhood of unity. Langmuir's theory (45) indicates that all or nearly all the molecules hitting a solid condense and re-evaporate. The accommodation coefficients are therefore virtually unity and almost all the molecules leave in thermal equilibrium with the filament. This conclusion has been supported by a number of investigations. (46),(47),(48),(49),(50).

Recently, however, it has been shown that in certain cases molecular or atomic beams may be reflected specularly from solid surfaces without any transfer of energy. (51),(52),(53).

It therefore seems plausible to assume that energy transfer between complex gas molecules and solids may be highly specific, and that in certain cases the accommodation coefficients may be quite low. This is especially so in the case of molecules which decompose unimolecularly, since such molecules are notoriously specific in action insofar as the transfer of energy is concerned, (54), (55),(56). There is also some experimental justification for such an assumption. Rice and Byck (57) bombarded a platinum target with a molecular beam of dimethyl mercury. They found no decomposition at a temperature at which there should have been about 6 per cent. decomposition if equipartition had been reached.

The mechanism of the foregoing reactions may therefore be explained on the following basis. With acetone and ethyl ether the molecules are mostly adsorbed on collision. They evaporate after a very short mean life on the surface, and therefore leave in thermal equilibrium with the surface. The inner side of the gas layer next to the filament is therefore at a temperature which does not differ appreciably from the temperature of the filament. No appreciable error is therefore introduced into the calculation of the heat of activation of the reaction. With propionaldehyde and methyl ether the accommodation coefficients may be assumed to be low. (This assumption will be discussed later). Hence comparatively few of the molecules are adsorbed and reach thermal equilibrium with the filament. The majority of the molecules are reflected more or less specularly and very little energy is transferred to them. There is therefore a very abrupt drop in temperature at the surface of the wire, followed by the usual more gradual skin effect. If this assumption is correct, the mean temperature of the layer in which reaction occurs will be considerably below the temperature of the filament itself.

The high temperature coefficient of the reaction may therefore be explained in two ways:

(a) We may interpret the high temperature coefficient as being due solely to the cause mentioned above. The temperature scale used in calculating the heat of activation of the reaction should therefore be shifted to somewhat lower temperatures. The heat of activation is inversely proportional to $(1/T_1 - 1/T_2)$. If we lower both temperatures by a constant amount, the calculated value of the heat of activation will therefore decrease.

We may calculate, for propionaldehyde, the lowering of the temperature required to bring the heat of activation from 96,500 calories to 55,000 calories. The value obtained is in the neighbourhood of 275°. If we repeat the previous calculations for propionaldehyde on the assumption that the temperature of the gas is not

1166°K. but 1166 - 275 = 891°K., we find that the fraction of the molecules activated is now 1.35×10^{-10}, assuming that $s = 100 \times 10^{-8}$ cms., which is certainly the maximum allowable effective diameter of the molecule. This gives a radius for the effective zone in which reaction occurs of 0.04 mm. This is rather large, especially since the maximum possible value of s has been used. It also seems unlikely that as great a drop as 275° should occur suddenly at the surface of the filament.

(b) It has been observed that accommodation coefficients increase with increasing temperature. We may therefore explain the high temperature coefficient of the reaction in a much more reasonable way by assuming that the accommodation coefficients are low, but not excessively low, and vary with temperature. The temperature coefficient of the reaction is therefore a composite one, and includes the temperature coefficient of the accommodation coefficient. It is thus unnecessary to assume such a pronounced drop in temperature at the surface of the filament.

The specific action of the surface remains to be explained. If the foregoing assumptions are valid, the accommodation coefficients for ethyl ether and acetone are near unity while those for propionaldehyde and methyl ether are quite low. Accommodation coefficients usually rise in the presence of a layer of adsorbed gas. It is therefore by no means improbable that the specific action depends on the relative adsorption of the various products formed in the decompositions. It has been noticed that a small amount of carbon is deposited in the decomposition of propionaldehyde and of methyl ether, but not in the other cases.

This deposit is sufficient to change the appearence of the filament but it is not thick enough to alter very greatly the electrical resistance of the filament. Even a unimolecular deposit of carbon, however, would be expected to have a pronounced effect on the accommodation coefficients.

SUMMARY.

The kinetics of the thermal decomposition of dimethyl ether in the gaseous state, in contact with heated platinum filaments has been investigated, The decomposition is unimolecular and occurs in a hot gas layer surrounding the filament. The heat of activation is found to be 67,000 calories as compared with 58,500 for the homogeneous reaction.

A number of other homogeneous unimolecular decomposition reactions have been investigated on heated platinum filaments. The methyl ether investigation is an addition to this series. The reactions invariably take place in the gas layer surrounding the filament, and are not catalysed. In the case of ethyl ether and of acetone the gas layer is in thermal equilibrium with the filament, and the apparent heat of activation calculated from the temperature coefficient of the reaction agrees with that of the homogeneous reaction.

With propionaldehyde and with methyl ether the apparent heat of activation is much higher than that of the homogeneous reaction. An examination of the molecular statistics of these reactions shows that they also take place in the layer of gas surrounding the filament. The high temperature coefficients of

these reactions can be explained on the assumption that the accommodation coefficients for these gases are low, and hence thermal equilibrium with the filament is not attained by colliding gas molecules.

Montreal, April 22nd., 1933.

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