KINETICS OF CHEMICAL CHANGE
IN
GASEOUS SYSTEMS

THESIS.

THE KINETICS OF CHEMICAL CHANGE IN GASEOUS SYSTEMS.

The Decomposition of Propionic Aldehyde in Contact with Platinum.

Richard Morton, B.Sc.

Submitted to the Faculty of
Graduate Studies and Research of
McGill University, in partial
fulfilment of the requirements
for the degree of Master of Science.

CONTENTS.

INTRODUCTION.

The kinetics of a chemical reaction can be best studied by observations of the rates of reaction, and the influence of temperature and pressure on these rates. Of the three states of aggregation - solid, liquid, and gaseous, the latter is the easiest to study because the kinetic theory applies to it best.

The ordinary chemical equations by which reactions are usually represented show the initial and final conditions only. They do not give an indication of the actual mechanism and therefore of the number of molcules participating in the reaction. The number of molecules entering into a reaction, i.e., its order, is determined by measuring the velocity of the reaction and seeing whether it obeys certain equations.

The equation representing a monomolecular reaction is $dx/dt=k_m\ (a-x)$ which on integration becomes

$$k_m.t=\ln a/a-x$$

where a= initial concentration, and x= amount decomposed at time "t". For a bimolecular reaction $dx/dt=k_b(a-x)^2$ which on integration becomes

$$k_b t=x/a(a-x)$$

In a gas the concentration is proportional to the partial pressure if the volume is constant, so that the velocity constant may be obtained by noting the increase in pressure at certain times, and substituting in the equation. If the reaction follows the unimolecular law "k_m" should be constant throughout the experiment. A much more satisfactory criterion for determining the order of a reaction is the time taken for a fraction of the reactant to change. Calling the time for 50% of the reactant to change T_{50}, we get for a unimolecular reaction

$$T_{50} = 1/k_m . \ln 2$$

i.e., T_{50} is independent of the initial pressure. While for a bimolecular reaction

$$T_{50} = 1/k_b p_o . \qquad \text{where } p_o = \text{initial pressure.}$$

In general in a reaction of the "n"th order

$$T_x = k1/p_o^{n-1}$$

Temperature has a great effect on the velocity of a reaction.

The van't Hoff equation gives the relation between the equilibrium constant "K" and the heat of the reaction "Q" as

$$d.\ln K/dT = Q/RT^2$$

Arrhenius (1) found empirically that the relation between the velocity constant "k" and temperature can be expressed by

$$\frac{d.\ln k}{dT} = \frac{E}{RT^2}$$

Where "E" is called the heat of activation.

The same relation was derived by Marcelin (2) and Rice(3) from considerations of statistical mechanics, and also by W.C.McC. Lewis (4) in his discussion of the radiation theory of activation. "E" is considered to be the critical energy which a molecule must possess in order to be able to react. Although the total energy possessed by a system of molecules at a certain temperature is constant, the distribution of this energy among the molecules will not be equal. The probable number of molecules which will possess an energy greater than "E" will be approximately $e^{-E/RT}$, and these can be called "active" molecules. The variation of this active number of molecules with temperature is the same as the variation of reaction velocity. So that for a bimolecular reaction where the reaction velocity is dependent on the initial concentration, and therefore on the number of collisions between molecules of the reactants,

number of molecules reacting = number colliding . $e^{-E/RT}$.

"E" can be obtained independently from the temperature coefficient, and substituting in the above equation the absolute rate of reaction calculated. In six out of the seven examples of bimolecular reactions studied this calculated reaction velocity agrees with that actually measured, within the experimental error. In the case of unimolecular reactions, however, the velocity is apparently independent of the initial concentration, and therefore of the number of collisions. It is, therefore, problematical how a single molecule can become activated if not by collision with others. There have been several theories proposed to explain the mechanism of activation. The radiation theory has been propounded by M.Trautz (5), J. Perrin (6) and W.C.McC.Lewis(7), but has been practically abandoned. Christiansen and Kramers (8) have suggested the chain theory, while Lindemann (9), in discrediting the radiation theory, believes that it is possible for a reaction to proceed according to the unimolecular law and the molecules to be activated by impacts from others. He assumes the following condition to exist:

$$\text{Normal molecules} \overset{\text{fast}}{\rightleftarrows} \text{Activated molecules} \xrightarrow{\text{slow}} \text{Reaction.}$$

That is, molecules become activated and deactivated by collision, and time elapses between activation and reaction. The fraction of activated molecules, i.e., possessing the energy "E", will be constant and nearly proportional to $e^{-E/RT}$. Of these, most will become deactivated before they have a chance to react, and only a small fraction "K" will be transformed. Thus the number reacting in unit time will be $Ke^{-E/RT}$, that is, independent of the concentration or pressure.

According to Lindemann's concept the unimolecular velocity constant should fall off at very low pressures, because the time between collisions will become comparable with that elapsing between activation and reaction, so that the molecules removed by reaction will greatly diminish the concentration of activated molecules.

Lindemann's theory, however, fails to account for very fast rates of reaction, and has accordingly been modified by Hinshelwood & Fowler (10). They take into account all the internal degrees of freedom of the molecule, and also all kinds of energy in every possible distribution in a large number of degrees of freedom. Now the chance that a molecule, having "n" degrees of freedom, contains an amount of energy greater than "E" is approximately

$$\frac{e^{-E/RT}.\ (E/RT)^{\frac{1}{2}n-1}}{\underline{\left|\,{}^{1}/_{2}\ n-1\right.}}$$

For large values of "n" this is much larger than $e^{-E/RT}$. It is significant to note that unimolecular reactions are characteristic of more complex molecules possessing a large number of internal degrees of freedom.

In order to further amplify our knowledge of unimolecular reactions, their mechanism, and mode of activation, it is necessary to have further experimental data concerning them. Moreover, it has been found that when homogeneous bimolecular reactions are allowed to proceed in contact with a catalyst, they become apparently unimolecular and the heat of activation is very much lowered. It is, therefore, of interest to determine whether a catalyst has any effect on a homogeneous unimolecular reaction. That is, whether the course of the reaction is altered, or its heat of activation affected.

C.N. Hinshelwood (11) in his treatment of unimolecular reactions gives a summary of the results of the homogeneous unimolecular decomposition of the following substances:

N_2O_5

$CH_3.CO.CH_3$

$C_2H_5.CHO$

$C_2H_5.O.C_2H_5$

$CH_3.O.CH_3$

$CH_3.N{:}N.CH_3$

$C_3H_7.N{:}N.C_3H_7$

$C_3H_7.O.C_3H_7$

In addition there is the racemization of $C_{10}H_{16}$, and the decomposition of SO_2Cl_2 which is not homogeneous when carried out in ordinary glass vessels. Of the above substances the corresponding heterogeneous decomposition of only two has been studied. These are:-

1) Acetone (12)

2) Diethyl Ether (13)

In this work the decomposition of propionic aldehyde (C_2H_5CHO) on a hot platinum wire was studied in order to compare it with the homogeneous decomposition which was investigated by Hinshelwood(14).

APPARATUS:

The apparatus used (fig.1) is similar to that described by C.N. Hinshelwood(15) for the decomposition of nitrous oxide and is the same as that used by Steacie and Campbell (13) for the decomposition of diethyl ether. It consists of a reaction bulb "H", about 15cms. long and having a capacity of about 125ml., through which a platinum wire (o.15 mm.dia.) is sealed through longitudinally. This bulb is connected by means of capillary tubing in one direction to a manometer "M", and in the opposite direction to a three way stopcock "C". The connecting

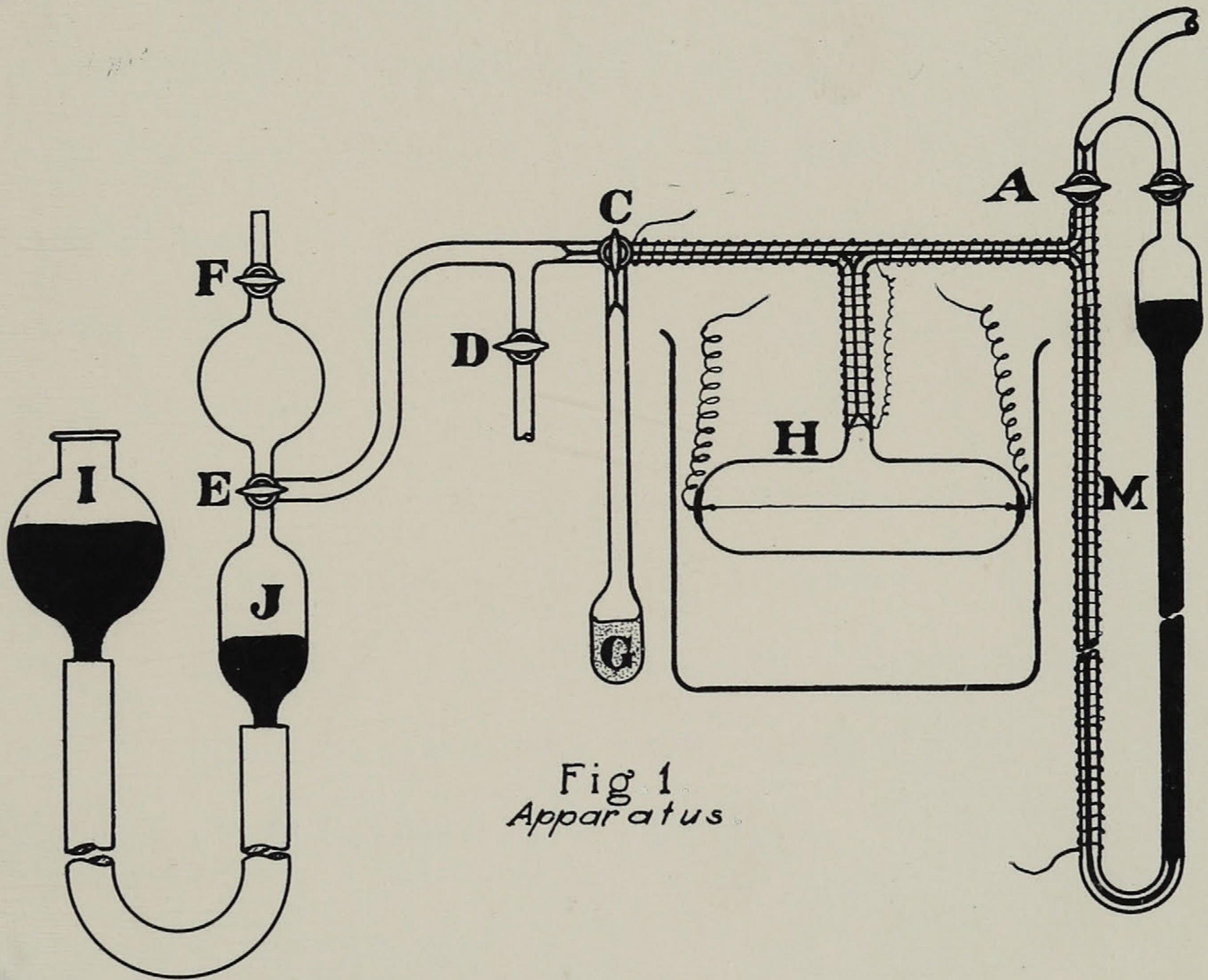


Fig 1
Apparatus

capillary tubing is wound with nichrome wire through which a small current is sent in order to prevent condensation in the tubing. The tap "C" connects to a bulb "G" in which is kept the propionic aldehyde, and also to a pumping system " I " and " J " which permits gas to be removed for analysis. The whole apparatus is connected to a Langmuir (mercury condensation) pump, backed by a "Hyvac' oil pump, which arrangement results in a vacuum of less than 0.001mm. The bulb " H " is immersed in an oil bath fitted with an electric heater " K " (fig.2) and a stirrer. In series with this heater is a rheostat which is so regulated as to keep the bath at about 45°C. In series with the filament of the bulb is a lamp-bank " L", a rheostat "R_s", and an ammeter " I", across which is a shunt " S ". A voltmeter "E_1", is placed across the filament so as to obtain its voltage. The propionic aldehyde used was made by Kahlbaum, redistilled, and boiled over between 48°- 50°C.

EXPERIMENTAL PROCEDURE.

Calibration of the filament for temperature.

The temperature of the filament was obtained by the measurement of its resistance, by the ammeter-voltmeter method. A curve of resistance against current was plotted and upon extrapolation to zero current the resistance at the temperature of the bath was obtained. From this value and the temperature coefficient of resistance of platinum as given by Mueller(16), the resistance at any temperature could be calculated. A curve of these resistances against

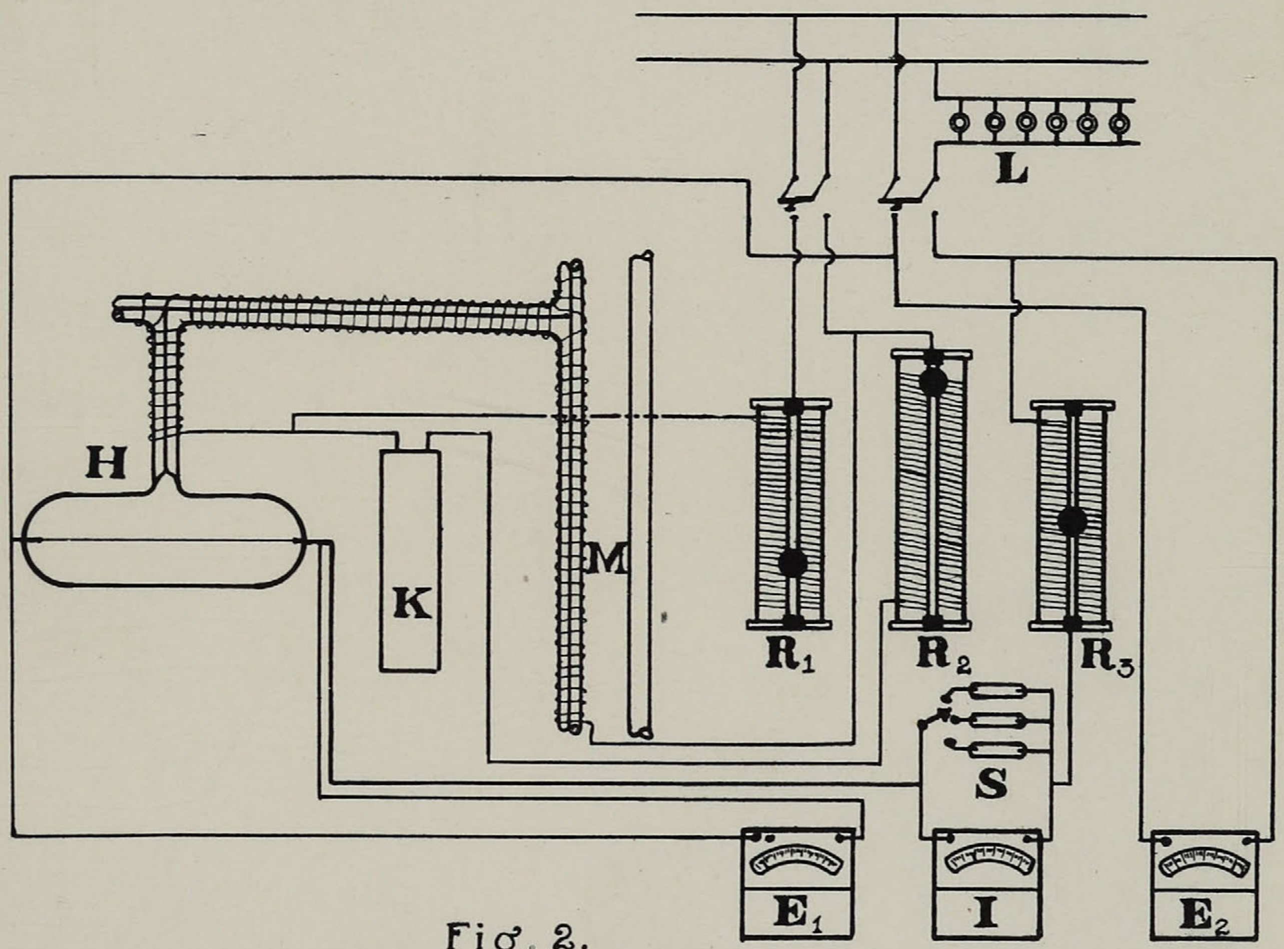


Fig. 2.
Electrical Diagram.

absolute temperature was plotted, and upon extrapolation to zero resistance was found to be within sufficient proximity of the absolute zero. At high temperatures a check was made with an optical pyrometer. Even if the temperatures as hereafter used are not exactly correct, they will still be relatively correct, and therefore give concordant results, and not affect the temperature coefficient.

Making a run.

Before making a run the temperature of the bath was brought up to about 45°C. and kept within two degrees of that temperature throughout the run. At 300°Abs. a variation of 3° in the temperature causes an error of 1%. As the best accuracy of measurement to be hoped for in an experiment of this nature is about 2%, allowing a variation of 6°, the above variation of 2° is well within that limit.

The whole apparatus was evacuated. Taps "A" and "B" were then closed and "C" opened, thus admitting propionaldehyde vapour to the initial pressure at which it was desired to make the run. A current was then sent through the filament, and its magnitude adjusted by means of the rheostat "R_3" to give such a value of filament resistance as to correspond to the desired temperature. The current was switched off and the system again evacuated. This adjustment of resistance had to be done before every run of a different initial pressure in order to obtain the correct temperature upon switching on the filament. After evacuation "A" and "B" were again closed and "C" opened to admit propionaldehyde vapour. The initial cold pressure was recorded corresponding to zero time; the filament was switched on and a stop-watch set going at the same instant. At suitable intervals of time the pressure(hot) was noted. As the reaction proceeded the conductivity of the resulting gases changed, usually causing a drop in voltage. In order to maintain the proper resistance of the filament and thus to keep its temperature constant it was necessary, throughout a run, to constantly adjust the rheostat "R_3". The variation of temperature thus caused was not more than 3%. Upon completion of a run the hot pressure was noted and the filament immediately switched off. The gas was allowed to cool to the temperature of the bath, and the cold pressure noted. The ratio of final hot to final cold pressure was obtained and on multiplying by the initial cold pressure the initial hot pressure (P_0) was found.

After a run was completed the resulting gas was removed for analysis as follows. The three way stopcock "E"(fig.1) is opened so as to connect both bulbs, and tap "F" is opened. The mercury reservoir "I" is raised so as to fill both bulbs. "F" is then closed, and the mercury lowered thus evacuating the bulbs. "E" is now opened to connect "J" to the system and on opening "C" the gas from "H" fills the whole system. "C" is now closed, "E" opened, and the mercury raised to the level of "E" forcing the gas into the upper bulb. "E" is now closed, the mercury lowered and some more gas admitted through "C" , which is in turn forced into the upper bulb. This was repeated until most of the gas from "H" was transferred to the collecting bulb, whence it was removed for analysis. With an initial cold pressure of about 200mm.(the maximum attainable with the propionic aldehyde at room temperature) three runs at the same temperature were necessary in order to collect slightly over 100cc. of the gas(atmospheric pressure) for analysis.

EXPERIMENTAL RESULTS.

The course of the reaction.

The simplest possible decomposition of propionic aldehyde would be

$$C_2H_5CHO = C_2H_6 + CO$$

As a result of the homogeneous decomposition Hinshelwood(14) found the following products.

	604°C.	506°C
CO	44%	51%
CH_4	33	18.5
C_2H_6	18	26.5

Initial pressure was 300mm. in each case.

In addition there was about 2% CO_2 and ethylene.

In the present investigation the following products were obtained using initial pressures of 260 - 275 mm.

T = 867°C.

CO_2	2.2%
Unsaturated	20.7
O_2	0.9
CO	37.0
H_2	20.7
Hydrocarbons	18.5

T = 893°C.

	No.1	No.2
CO_2	3.1%	2.3%
Unsaturated	23.3	23.3
O_2	1.9	1.2
CO	37.0	37.8
H_2	21.0	22.0
CH_4	7.8	6.6
C_2H_6	5.8	6.9

T = 935°C.

CO_2	1.3%	1.8%
Unsaturated	26.6	26.6
O_2	1.3	0.8
CO	35.8	36.2
H_2	24.5	22.9
CH_4	5.9	7.4
C_2H_6	4.5	3.8

It is thus seen that the main products of the reaction are different from those formed during the homogeneous reaction except that CO is largely formed in both cases. It is possible however, that the course of the reaction is the same as the homogeneous one, with the addition of the C_2H_6 splitting up into some unsaturated hydrocarbons, and hydrogen, at the higher temperatures used in this investigation.

As regards the total pressure increase resulting from the reaction, a peculiar abnormality was found in the homogeneous reaction. When the initial pressure was greater than 200mm. the total increase was very nearly 100%. For initial pressures of 100 - 150mm. the increase is greater, but for pressures of about 40mm. the relative increase is again about 100%.

In the heterogeneous reaction the following pressure increase at different temperatures and initial pressures was observed.

TOTAL PRESSURE INCREASE.

T = 867°C		T = 893°C	
P_o	Increase	P_o	Increase
266mm.	120%	274mm.	134%
197	119	200	132
127	113	129	131
66	125	68	135

T = 915°C.		T = 935°C	
P_o	Increase	P_o	Increase
251mm.	145%	265mm.	146%
197	146	212	144
125	149	152	146
77	142	82	142

As can be seen from Fig.3 the pressure continues to increase slowly toward the end of the reaction. That is why at lower temperatures the percentage increase is somewhat small. Otherwise the increase is about the same at different temperatures and initial pressures.

On referring this pressure increase to the products of reaction it seems likely that the predominant reaction is

$$C_2H_5CHO = C_2H_6 + CO$$

This and the subsequent breaking up of the C_2H_6, partly into C_2H_4 and H_2, resulting in a pressure increase above 100%.

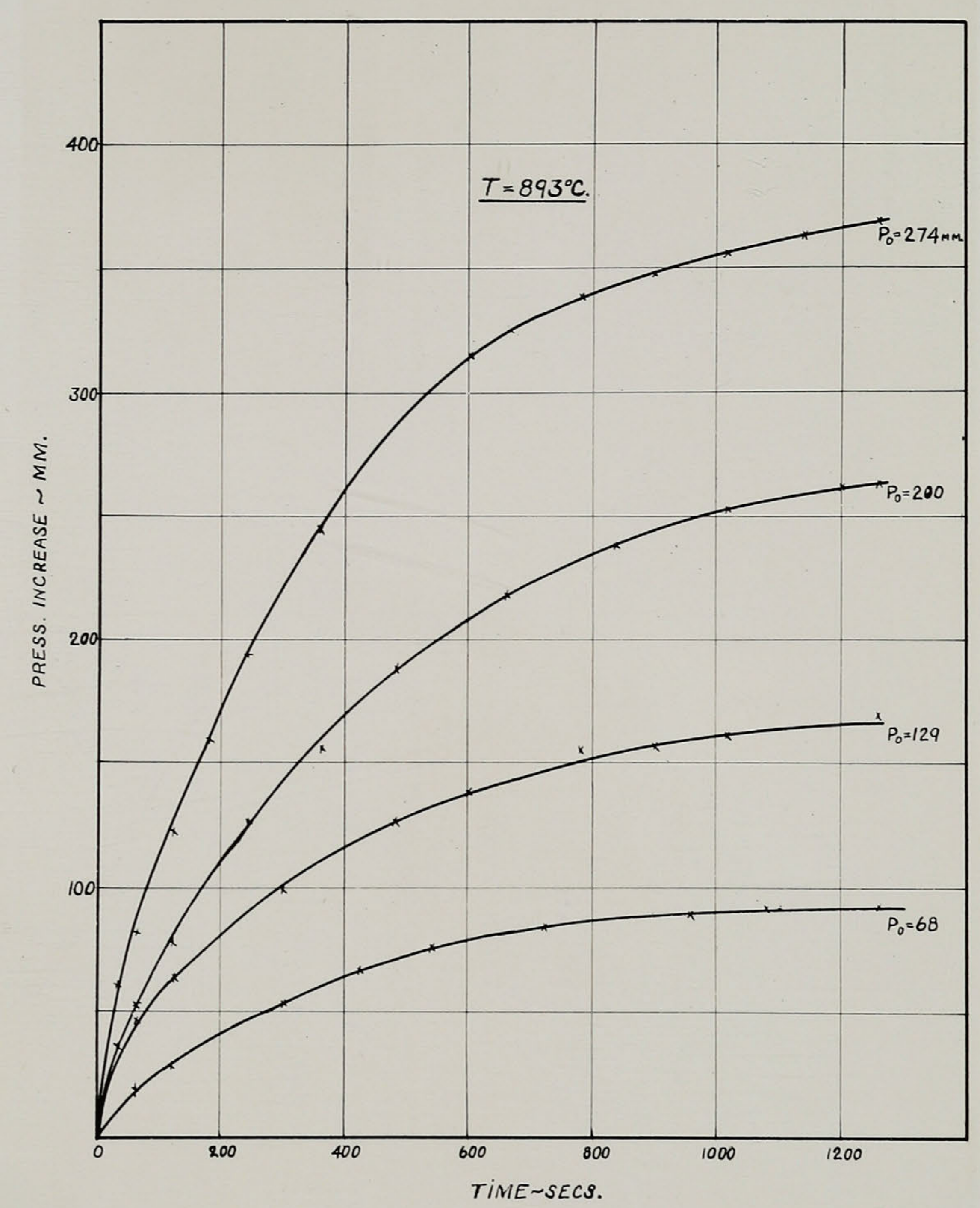
ORDER OF THE REACTION.

Below are tabulated the monomolecular and bimolecular velocity constants "k_m" and "k_b" as obtained from the equations

$$k_m = 1/t.\ln a/(a-x)$$

$$k_b = 1/t.\frac{x}{a(a-x)}$$

FIG.3.



PRESSURE INCREASE CURVES.

P_o=274mm. T=893°C. a =368mm.

Time secs.	Press. Incr.mm. X	a /a-x	ln a/a-x	$K_m.10^3$	x/a(a-x)	$K_b.10^3$
0	0	--	--	--	---	--
30	61	1.20	0.1823	6.08	0.00054	0.018
60	83	1.292	0.2562	4.27	0.000734	0.0122
120	123	1.501	0.4061	3.38	0.001361	0.0132
180	160	1.770	0.57098	3.17	0.00209	0.0116
240	194	2.119	0.75088	3.12	0.00303	0.0126
360	245	2.992	1.0959	3.04	0.00541	0.0150
600	315	6.94	1.9373	3.22	0.0161	0)0268
780	339	12.7	2.5416	3.26	0.0318	0.0408
900	348	18.4	2.9123	3.23	0.0473	0.0525
1020	357	33.5	3.5115	3.44	0.0882	0.0865
1140	363	73.6	4.2986	3.76	0.197	0.173
1260	368	--	---	--	--	--

P_o=68mm. T=893°C. a=92mm.

0	0	--	---	--	---	--
60	20	1.28	0.2468	4.12	0.00302	0.0504
120	29	1.46	0.3784	3.16	0.0050	0.0416
300	53	2.36	0.8586	2.96	0.01478	0.0492
420	67	3.68	1.3029	3.10	0.0291	0.0693
540	77	6.14	1.8148	3.36	0.0558	0.1030
720	84	11.50	2.4423	3.39	0.114	0.1582
960	89	30.7	3.4242	3.56	0.320	0.333

P_o=265mm. T=935°C. a =388mm.

Time secs.	Press. Incr.mm. x	a /a-x	ln a/a-x	$K_m.10^3$	x/a(a -x)	$K_b.10^3$
0	0	---	---	--	--- --	-
7	52	1.155	0.1441	20.6	0.000399	0.0076
14	102	1.358	0.3060	21.8	0.00092	0.0657
28.5	152	1.644	0.4971	17.4	0.00166	0.0583
51	202	2.085	0.7348	14.4	0.00280	0.055
69	252	2.850	1.0473	15.2	0.00477	0.069
86	302	4.51	1.5063	17.5	0.00905	0.105
128	352	10.2	2.3224	18.2	0.0252	0.197
300	388	--	---	--	---	-

P_o=82mm. T=935°C. a =116mm.

0	0	--	---	--	---	-
18	36	1.45	0.3715	20.6	0.00388	0.215
49	66	2.32	0.8415	17.2	0.0114	0.233
87	91	4.64	1.5347	17.2	0.0313	0.360
120	105	10.55	2.3561	19.6	0.0823	0.685
180	116	---	---	---	---	---

It can be readily seen that the values of "k_m" are fairly constant, and do not fall off at low pressures, while those of "k_b" vary widely. Hence the conclusion may be drawn that the reaction is apparently a unimolecular one. To further substantiate this, the times taken for the original pressure to increase by 25% and 50% were calculated and some of these are tabulated below.

Time to 25% and 50% Increase in Pressure.

T = 820°C.

P_0	T_{25}	T_{50}	P_0	T_{25}	T_{50}
258mm.	920secs.	2271secs.	79mm.	1320secs.	2740secs.
258	916	2250	74	1146	2752
255	955	2460			
		T = 847°C.			
255	413	1090	140	360	813
253	353	814	169	366	788
202	366	807	101	340	855
197	271	741	89	353	780
		T = 867°C			
266	128	367	169	158	357
264	126	368	149	167	381
259	156	340	143	131	363
254	133	324	108	135	---
202	153	351	84	120	350
198	159	380	84	132	301

T = 893°C.

P_o	T_{25}	T_{50}	P_o	T_{25}	T_{50}
294mm.	47secs.	137secs.	211mm.	37secs.	120secs.
274	40	142	205	51	137
266	63	141	145	56	130
265	66	152	142	60	143
265	64	139	129	26	126
265	61	145	83	56	155
263	68	152	83	71	158
263	55	144	83	63	133
260	64	152	68	51	157
260	56	137	62	40	108
260	60	156			

T = 915°C.

272	32	65	146	47	69
258	31	75	145	30	74
251	29	53	144	25	63
214	28	57	144	33	68
201	24	47	91	35	70
197	28	58	77	22	44
158	35	72	61	26	52

T = 935°C.

272	14	28	206	13	29
269	9	24	206	11	29
268	10	25	150	10	19
267	10	25	82	8	19
266	13	34	82	10	22
265	9	23	79	10	20

At each temperature the average T_{25} and T_{50} was taken of all the runs made at that temperature. These average values are used below to obtain the heat of activation.

Temperature Coefficient and Heat of Activation.

As previously mentioned, the variation of reaction velocity with temperature is satisfactorily expressed by the Arrhenius equation

$$\frac{d \ln k}{dT^{\circ}} = -\frac{E}{RT^{2}}$$

Now T_x — the time for any fraction of the reactant to decompose — is proportional to $1/k$, so that we can write

$$\frac{d \ln T_x}{dT^{\circ}} = -\frac{E}{RT^{2}}$$

which on integration becomes

$$\ln T_x = -\frac{E}{RT^{\circ}} + I$$

Hence if $\log T_{50}$ or $\log T_{25}$ is plotted against the reciprocal of the absolute temperature $(1/T^{\circ})$ a straight line should be obtained whose slope is $1/(2.3) . E/R$. In this way the heat of activation(E) can be obtained.

The values obtained in the following table are plotted in fig. 4.

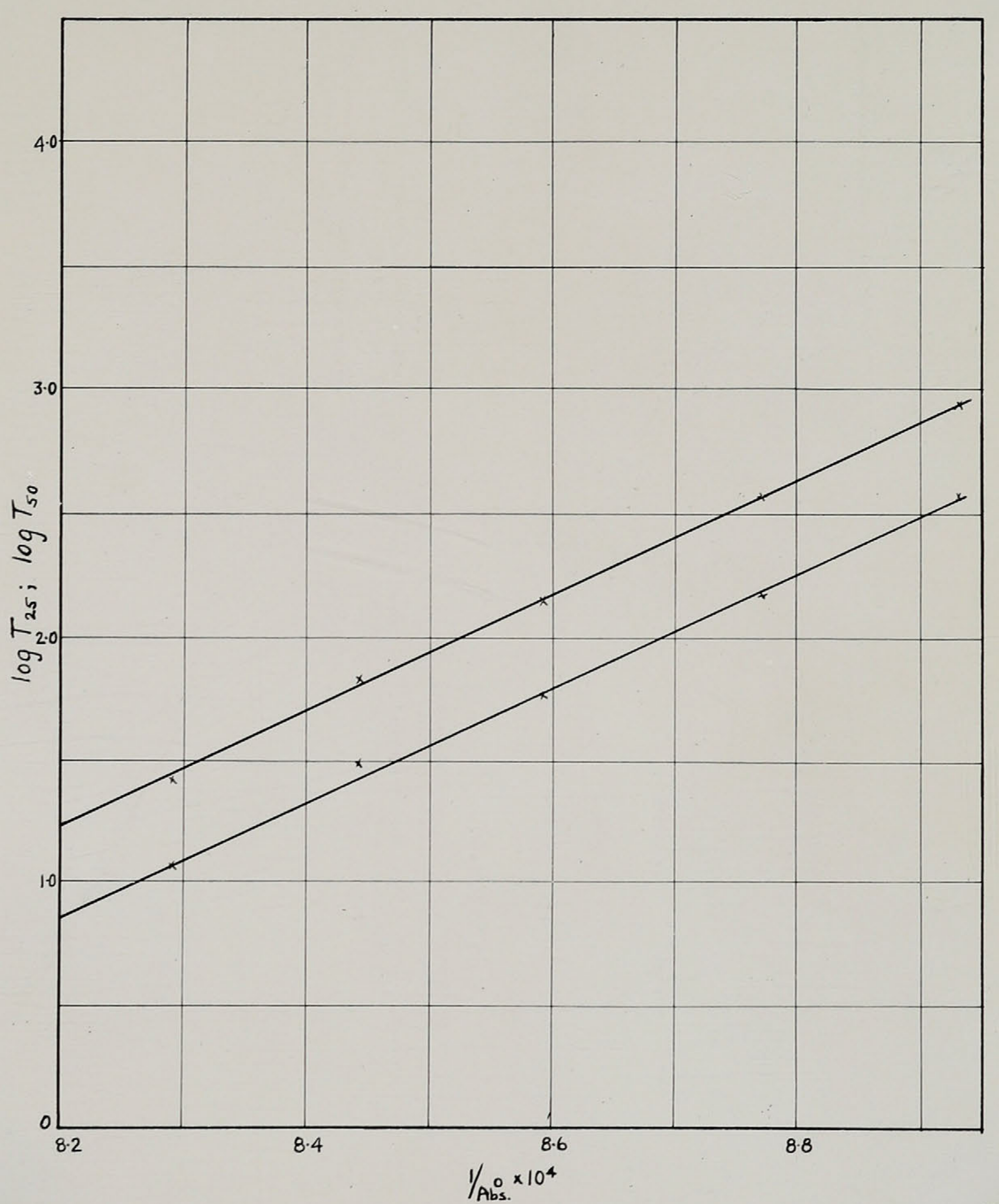
T°C.	1/T° x 10^4	T_{25} secs.	log T_{25}	T_{50} secs.	log T_{50}
820°C.	9.15	1051	3.0216	2494	3.3969
847	8.93	368	2.5658	870	2.9395
867	8.77	147.1	2.1676	360	2.5563
893	8.59	56.4	1.7513	140.5	2.1476
915	8.44	31.4	1.4969	66.9	1.8254
935	8.29	11.7	1.0682	26.5	1.4232

The slope of the line representing values of log T_{25} corresponds to a heat of activation of 107,900 calories, and the slope of the line representing values of log T_{50} — to 105,200 calories. That is, the lines are practically parallel, and the mean value of the heat of activation is 106,500 calories.

DISCUSSION.

The average value obtained by Hinshelwood(14) for the heat of activation of the homogeneous reaction is 55,000 calories. It was also found that the unimolecular velocity constant falls off at lower pressures. In the present investigation no such falling off has been noticed, the reaction proceeding unimolecularly throughout the range of pressures and temperatures used. The heat of activation obtained in the present investigation is about double that obtained for the homogeneous reaction. This is rather peculiar and not in harmony with results obtained in similar investigations.

FIG. 4.



Taylor (12) found that the decomposition of acetone proceeded unimolecularly and with the same heat of activation, whether carried out homogeneously or in contact with platinum. This would indicate that in the latter case the reaction proceeds homogeneously in the layer of hot gas immediately surrounding the platinum filament. A similar conclusion was drawn by Steacie and Campbell (13) from the study of the decomposition of diethyl ether in contact with platinum. In both these cases it is presumed that the energy of activation is derived by collision with the hot filament, or by radiation from it. With acetone and nickel the reaction was definitely catalytic, but the course of the reaction was entirely different from that of the homogeneous decomposition, and hence the results were not comparable.

In the case of the propionaldehyde decomposition, the products of the reaction in contact with platinum are somewhat different from those of the homogeneous decomposition. It is possible, however, that the main reaction may be the same in both cases, viz.

$$C_2H_5CHO \longrightarrow C_2H_6 + CO.$$

In order to obtain measurable rates, the catalytic reaction has to be investigated at temperatures about 200° - 300° higher than the homogeneous reaction. At these higher temperatures the ethane formed in the primary decomposition might itself decompose subsequently to give ethylene and hydrogen. This would give at least a qualitative explanation of the difference between the products of the two reactions.

The supposition might be made that the decomposition of the aldehyde is fast, while that of the ethane is slow, and hence that the real reaction under investigation is merely the slow secondary decomposition of ethane. This, however, is quite untenable since it would necessitate an immediate increase in pressure of 100 percent followed by a slow further increase as the ethane decomposed; whereas in reality the pressure changes slowly and regularly at all stages of the reaction. There is therefore no doubt that it is really the decomposition of propionaldehyde which is being investigated.

The fact that the heat of activation is quite different from that of the homogeneous decomposition seems to definitely establish the fact that the reaction proceeds heterogeneously on the surface of the platinum. In the case of a heterogeneous reaction the concept of the activation energy is somewhat complicated. The apparent heat of activation, as measured, is in error on account of the change in adsorption as the temperature changes. According to the Hinshelwood - Polanyi equation, in the case of a reaction which is not retarded by the products, the true activation energy will be greater than the apparent activation energy. This is obviously of no help in this case, since it will merely cause an increase in the discrepancy between the activation energies of the homogeneous and heterogeneous reactions. If the reaction were strongly retarded by the products, however, the true heat of activation might be smaller than the apparent one. This cannot be the case, however, since there is no evidence of any retarding action in the experimental results. It may therefore be concluded that the difference between the heats of activation is a real one, that of the heterogeneous reaction being definitely much higher than that corresponding to the homogeneous decomposition.

This behaviour is difficult to explain. The difference in the heats of activation indicates that the homogeneous reaction occurs more readily than the heterogeneous reaction, i.e. a molecule needs a lower energy content in the former case. It would therefore be expected that the homogeneous reaction in the hot gas layer surrounding the filament would predominate over the surface reaction. Actually, however, the heterogeneous reaction predominates. The explanation that every molecule hitting the wire reacts cannot be valid, since this would give a low temperature coefficient depending merely on the number of molecules hitting the wire, while actually the temperature coefficient of the reaction is extremely high.

It becomes necessary to explain how a molecule can get through the hot gas layer, collide with the filament, and be reflected without reaction; while those molecules which become adsorbed are enabled to react. The most plausible assumption would seem to be that molecules which are reflected (i.e. strike but are not adsorbed) never reach thermal equilibrium with the filament. If this is the case the hot gas layer immediately surrounding the filament is at an appreciably lower temperature and conditions for the homogeneous reaction are therefore much less favourable. Those molecules which become adsorbed, however, reach thermal equilibrium and the distribution of molecular energies will be the Maxwellian distribution corresponding to the temperature of the filament.

There is a further possibility which is very unlikely, but is perhaps worth mentioning. It has been mentioned that the velocity constants of the homogeneous reaction fall off at low pressures, the reaction tending to become bimolecular. According to the theory of Rice and Ramsperger (17) the falling-off pressure should become higher as the temperature increases. If the real variation of the falling-off pressure were much greater than that predicted by Rice and Ramsperger, it would be possible that at the higher temperatures used in this investigation the homogeneous reaction has become bimolecular. If this were the case the heat of activation would by analogy be expected to be about doubled, i.e. 110,000 calories. This is higher than that of the heterogeneous reaction, and the latter might therefore predominate.

SUMMARY.

The rate of decomposition of gaseous propionic aldehyde, in contact with a heated platinum filament, has been studied, in order to compare it with the homogeneous reaction.

It is found that the reaction is catalysed by the platinum. It proceeds apparently unimolecularly, and does not fall off at low pressures. The products of reaction are different from the homogeneous decomposition products, and the heat of activation is 106,500 calories.

Montreal, Canada.
May, 1931.

LITERATURE REFERENCES.

(1) S.A.Arrhenius Z.physik. Chem. 4, 226 (1889)

(2) R. Marcelin Ann. de Phys. [IX] 3, 120 (1915)

(3) F.O.Rice Brit.Assoc. REP. p.397 (1915)

(4) W.C.McC.Lewis J. Chem. Soc. 113, 471 (1918)

(5) M. Trautz Z. anorg. Chem. 102, 81 (1918)

(6) J.Perrin Ann. de Phys. [IX] 11 , 1 (1919)

(7) W.C.McC.Lewis J. Chem. Soc. 109,796 (1916)
111,389,457(1917)

(8) Christiansen & Kramers
Z. physik. Chem. 104, 451 (1923)

(9) F.A.Lindemann Trans. Far. Soc. 17, 598 (1922)

(10)Hinshelwood Proc. Roy. Soc. A 113, 230 (1926)
Fowler & Rideal Proc. Roy. Soc. A 113, 570 (1927)

(11) C.N.Hinshelwood "The Kinetics of Chemical Change in Gaseous Systems",Oxford Univ. Press(1929) p.126

(12) H.A.Taylor J. Physical Chem. 33, 1793 (1929)

(13) E.W.R.Steacie & H.N.Campbell
Proc. Roy. Soc. A 128, 451 (1930)

(14) Hinshelwood & Thompson
Proc. Roy. Soc. A 113, 221 (1926)

(15) Hinshelwood & Prichard
J. Chem. Soc. 127, 327 (1925)

(16) Mueller Int.Crit.Tables Vol.6, p. 136

(17) O.K.Rice & H.C.Ramsperger
J.A.C.S. 49, 1617, (1927)