I would like particularly to thank Miss M. R. Buchanan, M.Sc., for giving me great assistance with the wave-length calculations involved in the preceding work. My hearty thanks are due also to my friend, Mr. Cunningham, for placing liquid air facilities at my disposal at a difficult time, and also to my colleague, Mr. Wylie, for his generous assistance with the design and construction of the large grating mounting with which part of this work was done.

DESCRIPTION OF PLATE 19.

SPECTRUM 1.—Helium at 30 mm. pressure. Carbon electrodes. Mild condensed discharge. Shows the new line spectrum of Carbon, Helium lines and bands. The strongest lines are marked.

SPECTRUM 2.—Same conditions as above. Shows the negative band-spectrum of Carbon strongly developed. The strongest heads and also the new lines in this region are marked.

SPECTRUM 3.—Helium at 30 mm. pressure. Carbon electrodes. Uncondensed discharge. Shows Comet-Tail bands and the new associated bands. All the bands are somewhat abbreviated by the process of reproduction.

The Mechanism of Catalytic Decomposition.

By F. H. CONSTABLE, Strathcona Research Student of St. John's College, Cambridge.

In recent years a large amount of evidence has accumulated showing that the range of molecular attraction is very small[*] ; hence the specific catalytic action of each substance must decrease very fast as the distance of the reacting molecules from the surface increases. The catalytic action must therefore be confined to the surface layer of adsorbed molecules alone. When alcoholic substances react at copper surfaces below 280° C., only the $-CH_2OH$ group is changed.[†] The only molecules which react, therefore, are those which have the $-CH_2OH$ group in contact with the copper.

[*] Langmuir, ' J. Amer. Chem. Soc.,' vol. 38, p. 2221 (1916).

[†] *See* series of papers on " Catalytic Action of Copper on Alcohols," ' Roy. Soc. Proc.,' A, vol. 98, p. 13 ; vol. 99, p. 412 ; vol. 101, p. 178 ; vol. 106, p. 251 ; vol. 107, pp. 255, 270, 279.

The behaviour of cetyl alcohol on water,* and on glass and steel,† shows that the hydroxyl group is the active agent in orientating the film structure. It is known also that alcohol will displace hydrocarbons from copper foil.‡ The polar hydroxyl group is attracted to the copper surface more strongly than is the hydrocarbon chain. The evidence, therefore, shows that not only are the molecules that react adsorbed with the hydroxyl group in contact with the surface, but that the whole layer in contact with the catalyst is orientated in this manner. It may be that the molecules in the successive layers are also arranged similarly, but the evidence is scanty. In the case of the fatty acids, X-ray analysis gives confirmation of this arrangement.§

The Mechanism of the Dehydrogenation.

The catalyst surface is the same for all the alcohols, and the hydrocarbon chains have nearly all the same cross-section; hence the packing of the $-CH_2OH$ groups will be the same for all the primary alcohols. At the same temperature the energy relations at the alcohol-copper interface will be the same for all primary alcohols. It would be therefore expected that the primary alcohols would all react with the same velocity at the same temperature.‖ This prediction has been verified for ethyl, propyl, butyl, iso-butyl, and iso-amyl alcohols. On account of this close agreement with experiment it is interesting to attempt a quantitative treatment of the subject from the point of view of statistical mechanics, taking into account the energy changes at the catalyst surface.

The general chemical change that occurs is described by the equation

$$R \cdot CH_2OH \longrightarrow R \cdot C\overset{\displaystyle O}{\underset{\displaystyle H}{\Big\langle}} + H_2.$$
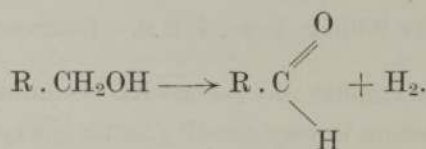
Thus two hydrogen atoms leave the alcohol molecule for the copper surface. In order that this decomposition should occur, it is necessary that an alcohol

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* Langmuir, see also Adam, *ibid.*, vol. 99, p. 336 ; vol. 101, pp. 452 and 516 (1922), *et seq.*

† Hardy, *ibid.*, vol. 100, p. 550 ; vol. 101, p. 487.

‡ Pockels, ' Wied. Ann.,' vol. 67, p. 660 (1899).

§ Piper and Grindly, ' J. Chem. Soc.,' vol. 123, p. 2043 (1923). Muller and Shearer, *ibid.*, p. 3156. " These long-chain compounds form real crystals which are all built up after the same fashion, the length of the molecule lying perpendicular to the cleavage flakes. These latter lie perpendicular to the surface on which they crystallise out."

‖ Palmer and Constable, ' Roy. Soc. Proc.,' A, vol. 107, p. 255.

molecule should possess energy above the average quantity characteristic of the temperature of the film. Only the $-CH_2OH$ group is changed. It is therefore probable that this excess of energy, called the energy of " activation," must be present in this group, and it must become the energy of oscillation of atoms, since a study of the specific heats of solids has shown that the energy content of the electrons is negligible at the temperature of reaction.* Thus the hydrogen atoms are lost because their energy is sufficient to enable them to oscillate from the alcohol molecule on to the copper surface.

From the extent of the thermal dissociation at various temperatures Langmuir deduced that the reaction $H_2 = 2H$ (neutral atoms) occurs with the absorption of 85,000 cals. Horton and Miss Davies from the ionisation potentials of hydrogen obtained the value 81,300 cals., a value in fair agreement with Langmuir ; but in the production of two completely ionised atoms—the most violent change which the molecule can undergo—731,000 cals. are absorbed.

The " heat of activation " in the dehydrogenation is about 22,000 cals. ; since it is highly probable that two neutral hydrogen atoms are lost from the alcohol molecule, the energy of activation being insufficient to separate the proton from the oxygen-electron system without an accompanying electron.

The catalyst reduces the energy content of the hydrogen atoms necessary to cause them to oscillate from the alcohol molecule on to the copper surface. Direct proof can be given of this. In the absence of catalysts, decomposition only occurs above 500° C., two reactions taking place :—

$$C_2H_5OH-\begin{cases} C_2H_4 + H_2O\dagger \\ CH_3CHO + H_2. \end{cases}$$
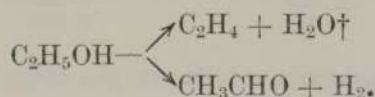
The temperature must rise to 500° C. before a sufficient number of hydrogen atoms have sufficient energy to fly off the molecule.

In the $-CH_2OH$ group the hydrogen atom of the hydroxyl group is more reactive chemically than the others, meaning that less energy is necessary to displace it by other atoms. Proof that the work done to remove this hydrogen atom from combination is less than is the case for the hydrogen atoms attached to carbon atoms, is obtained by the comparison of processes in which the hydrogen atom is lost directly from the carbon atom with dehydrogenation processes.

* Einstein, ' Ann. der Physik,' vol. 22, p. 180 (1907) ; Koenigsberger, ' Zeitsch. Electrochem.,' vol. 17, p. 289 (1911) ; Debye, ' Ann. Physik,' p. 789 (1912).

† " But owing to the high temperature the resultants react among themselves to give a complex system." Berthelot ' Traité de Chimie Organique,' p. 164.

The reaction $C_2H_6 \longrightarrow C_2H_4 + H_2$ occurs with the absorption of 30,000 cals. The values of the equilibrium constant

$$K_1 = \frac{C_2H_4 \times H_2}{C_2H_6}$$

observed by Rittman* are tabulated below—

Temperature. °C.	K.
500	0·027
750	0·074
900	1·28

He concludes that "the formation of a double bond is an endothermic reaction, the first stage of the cracking process requiring the continuous supply of a considerable amount of energy in a paraffinoid hydrocarbon, amounting to approximately 30,000 cals. per gram-mol."

The heat of dissociation of ethyl alcohol is only about 10,000 cals. per gramm-mol. The values observed by Rideal† for the quantity

$$K = \frac{CH_3CHO \times H_2}{C_2H_5OH}$$

are also tabulated for comparison—

Temperature. °C.	K.
200	0·012
225	0·045
250	0·232
275	0·910

The effect of the introduction of the oxygen atom is very marked, causing complete decomposition at much lower temperatures. Since the linking of one hydrogen atom only has changed, it is very probable that the energy of activation is all contained in the hydrogen atom of the hydroxyl group, which atom oscillates on to the copper surface.

When the first hydrogen atom has been lost, the oxygen atom is attached by two electrons only to the carbon atom, being only univalent. The readjustment of the electrons in the carbon atom to make it quadrivalent necessitates the expulsion of the other hydrogen atom from the molecule. The release of the second valency thus probably occurs from within the carbon atom, no large amount of "energy of activation" being necessary, the hydrogen atom escaping with the average energy characteristic of the temperature.

* 'J. Ind. Eng. Chem.,' vol. 6, p. 1029 (1915); vol. 7, p. 945, vol. 8, p. 20 (1916).
† 'Roy. Soc. Proc.,' A, vol. 99, p. 153.

Additional support for this view is obtained from the study of iso-propyl alcohol containing the secondary alcohol group $= CHOH.$* If energy of activation were required for the removal of the hydrogen atom attached to the carbon atom, the probability that one of the two H atoms in the $- CH_2OH$ group would have the requisite energy is greater than in the $= CH(OH)$ group. Thus the primary alcohols would react faster than the secondary, which is untrue. Hence the initial assumption is incorrect, and this evidence also supports the suggestion that the " heat of activation " or the critical increment is located in the hydrogen atom of the hydroxyl group.

The heat of activation thus becomes related to the energy of oscillation of one hydrogen atom. The function of the catalyst is to reduce the energy of activation necessary to remove this H atom from the alcohol molecule on to the copper surface, and part of this energy is supplied by the catalyst itself, as work done at the instant of adsorption into the unimolecular layer on the surface. This work consists in increasing the distance between the H and O atoms in the hydroxyl group, rendering less the energy of oscillation required in order that the H atom may become free.

Thus the heat of activation would be expected to vary from catalyst to catalyst,† and, moreover, to vary with the arrangement of atoms in each individual catalyst. A simple explanation is thus given of the results in the papers, "The Catalytic Action of Copper," Parts 2 and 4 (*loc. cit.*), various crystal planes being exposed on the surface of the grains at various temperatures of reduction.‡

The Source of the Energy of Activation.

The evidence is much in favour of activation taking place by collision in the case of thermal reactions.§ Sir J. J. Thomson‖ states that " monomolecular reactions are regarded as due to the accumulation of thermal energy in particular molecules until these have sufficient energy to dissociate or evaporate, as the case may be. Maxwell's law of the distribution of energy among the molecules of a gas expresses the fact that, owing to collisions, the energy

* Sabatier and Senderens, 'Compt. Rend.,' vol. 136, pp. 738, 921, and 983; also 'Roy. Soc. Proc.,' A, vol. 107, p. 255.

† Hinshelwood and Tingey, 'J. Chem. Soc.,' vol. 121, p. 1668 (1922); Hinshelwood and Topley, 'J. Chem. Soc.,' vol. 124, p. 1014 (1923).

‡ See 'Roy. Soc. Proc.,' A, vol. 107, p. 270.

§ See discussion 'Trans. Faraday Soc.,' vol. 17, Part I. (1922); Lewis, 'J. Chem. Soc.,' vol. 113, p. 471 (1918); Taylor, 'Nature,' vol. 108, p. 210 (1921); Christiansen and Kramers, 'Z. Physikal. Chem.,' vol. 104 (1923).

‖ 'Phil. Mag.,' No. 287 (ii), p. 337 (1924).

accumulates in some molecules until it reaches a value far above the normal, though naturally the number of molecules which have energy much in excess of the normal diminishes rapidly as the excess increases. In gases the accumulation of energy is due to collision among the molecules of the gas.

In solids, where the molecules form connected space lattices, the transference and accumulation of energy is due to pulses of displacement of molecules travelling in great number through the solid, and producing superposition effects whose magnitudes are governed by the same principles as those which determine the resultant amplitude of a large number of vibrations of an arbitrary phase."

The adsorption films are in a class intermediate between gases and solids. They are bombarded from the vapour phase. They receive wave impulses from the solid. The energy of activation may come from both sources.

Attempted Quantitative Treatment.

The previous considerations, taken together with the experimental evidence, show that the alcohol is first adsorbed from the vapour phase, forming a film of orientated molecules on the copper surface. The $- CH_2OH$ groups are in contact with the surface, while the hydrocarbon chains are in contact perpendicular to the surface. Energy pulses from the atoms of copper, and collision from the vapour, combine to produce an excess of energy in various degrees of freedom of the adsorbed molecule. When this excess exceeds the quantity ε and is present in the H atom of the hydroxyl group, reaction occurs, the second H atom being automatically released. Now the fraction of the alcohol molecules which have energy in the H atom of the hydroxyl group equal to or greater than ε is given by $e^{-\varepsilon/RT}$.[*]

If S = the area of the copper surface,

　　n = the number of alcohol molecules adsorbed per unit area of the surface,

　　ε = minimum energy necessary, for the hydrogen atom to oscillate from the alcohol molecule on to the copper surface,

　　σ = the mean life of a molecule in the layer next to the catalyst surface.[†]

then $\ln/\sigma$ new molecules will be present in the surface layer every second. Of these the fraction $e^{-\varepsilon/RT}$ have the energy necessary to react, where T

[*] Lewis, 'System of Physical Chem.,' vol. 3, p. 171, shows that for one internal degree of freedom the expression assumes the form stated.

[†] Not the average life in the whole film, since the film may be more than one molecule thick.

represents the mean temperature of the reacting film. Therefore, on the whole surface,

$$\frac{S \cdot n}{\sigma} \cdot e^{-\epsilon/RT}$$

molecules react per second. But N molecules occupy 22·3 litres at S.T.P., where N is Avogadro's number. Hence the reaction velocity in litres of hydrogen per second

$$v = \frac{22 \cdot 3\, n \cdot S}{N \cdot \sigma} e^{-\epsilon/RT}. \qquad (a)$$

This is the type of relation between v and T found by experiment, but the constant $\frac{22 \cdot 3nS}{N\sigma}$, though agreeing with previous work in having the dimensions T^{-1}, does not agree with the results of experiment.

The series of experiments on dehydrogenation by supported copper films produced by reduction from copper oxide at the temperatures tabulated below (*see* 'Roy. Soc. Proc.,' A., vol. 106, p. 262) show that the quantity A (= observed value of $22 \cdot 3nS/N\sigma$) varies very considerably with ϵ. The data obtained are tabulated below.

Table I. (Series I.)

Temperature of Reduction.	A ÷ 10^{10}.	ϵ.	v_{250°.
° C.		cals.	c.cs. per min.
225	13·0	25,610	2·18
235	7·5	25,030	2·58
257	2·1	23,890	2·06
266	0·38	22,070	2·20
275	0·38	21,610	2·96
280	0·51	22,250	2·36
319	2·8	25,190	0·764
368	0·44	22,320	1·95
386	0·70	22,950	1·73
406	0·87	22,750	0·259
420	0·38	20,490	0·978
350	0·19	21,590	1·608

(Series II.)

Temperature of Reduction.	$A \div 10^9$.	ϵ.	v_{250°
°C.		cals.	c.cs. per min.
225	5·1	22,020	2·96
240	1·9	20,720	3·70
275	4·0	21,700	3·11
300	3·0	21,130	4·00
320	3·7	21,750	2·88
346	1·3	20,840	2·44
378	2·3	21,370	2·52
385	1·0	20,720	1·78
400	4·5	22,610	1·48

Reaction Centres.

It was assumed in the argument leading to equation (a) that all the alcohol molecules on the surface were capable of reacting provided a critical increment ε was supplied to them. Some other condition is necessary, and there is no alternative but that it exists in the surface itself. All the adsorbed molecules are orientated in the same manner. The atoms in the surface beneath must, therefore, be arranged in some special way in order to cause the necessary increase in distance between the H atom and the O atom of the hydroxyl group. This favoured arrangement can only occur at isolated points on the surface, and consequently reaction only occurs at a few points on the catalyst. All adsorbed alcohol molecules, with heat of activation ε, have not the same chance of reaction. Some are more favoured than others. It is proposed to call the arrangement of an adsorbed alcohol molecule over a favoured arrangement of copper atoms* a " reaction centre." With the aid of this conception it is possible to give a simple explanation of many puzzling observations in catalysis described in recent years.

Experimental Evidence that a Catalyst Surface is not Uniformly Active.†

(A) From the fact that the amount of " poison " necessary to reduce the catalytic activity to zero is sufficient to cover only a very small fraction of the surface, Armstrong and Hilditch‡ suggest " . . . an active catalyst is merely

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* Lindemann, ' Phil. Mag.,' vol. 29, p. 127 (1915), suggests that a metal consists of two interleaved space lattices, one consisting of metallic atoms, the other of electrons. *See also* Haber, ' Sitzungsber. Preuss. Akad. Wiss. Berlin,' pp. 506, 990, A., ii., 424 (1919).

† *See* " Third Report of the Committee on Contact Catalysis," H. S. Taylor ' J. Phys. Chem.,' vol. 28, p. 911 (1924).

‡ ' Faraday Soc. Discussion,' vol. 17, p. 670 (1922).

an average term, expressing a surface on which a number of patches of maximum activity occur . . . selective adsorption at few points causing the disappearance of practically all the catalytic effect."

(B) From a study of the adsorption and catalytic activity of copper, the poisoning of the catalyst by mercury, and de-activation by heat treatment, Pease* suggests " it is probable that active adsorbing centres of all degrees of activity are scattered over the surface. It would seem that the de-activation of the active centres could proceed in steps, so that while a given active centre is completely prevented from adsorbing hydrogen, it can still adsorb ethylene strongly." To define further the active centres Pease states :—

" One would look for atoms of this character in surfaces of high degree of curvature†—in peaks in the surface—rather than in the valleys or capillaries."

" The activity is . . . due not to isolated active atoms scattered over the surface, but to groups of these atoms."

(C) Gauger and Taylor,‡ from a study of adsorption on nickel, state that the results " would point to different adsorptive activities of individual atoms in the surface."

The idea that some group of atoms can be more active than another has thus already been propounded. In the present work the characteristic arrangement of copper atoms necessary to cause reaction has been called a " centre of activity," and the arrangement of an adsorbed alcohol molecule over this arrangement of copper atoms has been named a " reaction centre."

The Seat of the Activity in Reduced Copper.

It has been shown by many experiments from the whole field of catalysis, that chemical reaction probably occurs at isolated points on the catalyst surface, and that the action at these points (really very small areas) is caused by the electrostatic and electromagnetic fields consequent on the orientation of the adsorbed molecule on a characteristic group of atoms on the catalyst, lowering the critical increment to such an extent that reaction occurs in measurable quantity. It would be expected that the lowering of the critical increment would be different on various parts of the surface, since the atoms are not all arranged in exactly the same way.

In the case of copper (the argument is, however, quite general), any type of

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* ' J. Amer. Chem. Soc.,' vol. 45, pp. 1196, 2235, 2297 (1923).

† This cannot be true in general, as liquid surfaces also act as catalysts, *e.g.* Hg on H_2O_3, and molten Sn and Cd on alcohol.

‡ ' J. Amer. Chem. Soc.,' vol. 45, p. 920 (1923).

change that alters the density of copper atoms in the surface affects the reaction centre density on the surface. Thus there are three factors which may influence the catalytic activity :—

(1) The existence of amorphous metal in the granules.
(2) Allotropic modifications.
(3) Alterations in the orientation of the grains.

The effect of these three factors has already been discussed.*

To explain the periodic variation of the activity† and the reproducibility of the catalyst, hypothesis (3) was used. It thus appeared probable that a few of the crystal planes were active, and the rest inactive. The seat of the catalytic activity, therefore, lies probably on particular faces of the crystal, but even then the whole face is not active. The size of the hydrocarbon chain also controls the packing of the reacting molecules on the surface, since at a "reaction centre" both the adsorbed molecule and the surface atoms must have a definite orientation.

A Quantitative Expression for the Velocity of Decomposition based on the Idea of Reaction Centres.

Whether the cause of the activity of copper lies in the existence of allotropes, or of amorphous metal, or whether it merely exists in definite crystal planes, it is possible to get a general expression for the reaction velocity showing the variation of the A factor. Equation (*a*) (p. 361) neglected the nature of the surface. It has been shown that reaction takes place on definite centres on the surface. Moreover, since the "heat of activation" ε varies for the same catalyst, the value of ε on individual centres also varies.

Let ε_1 and ε_2 be the lower and upper limits of ε on the surface. Let the number of reaction centres on 1 sq. cm. of surface having a value of ε lying between ε and $\varepsilon + \delta\varepsilon$ be classified according to the value of ε shown on them. Let $F(\varepsilon)$ be a function defined so that the number of reaction centres having a "heat of activation" lying between ε and $\varepsilon + \delta\varepsilon$ is given by

$$\delta n = F(\varepsilon)\,\delta\varepsilon. \qquad (1)$$

Hence the total number of reaction centres on 1 sq. cm.

$$= \int_{\varepsilon_1}^{\varepsilon_2} F(\varepsilon)\,\delta\varepsilon,$$

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* " The Catalytic Action of Copper, Part VI " (*loc. cit.*).
† " The Catalytic Action of Copper, Part IV " (*loc. cit.*).

and the mean value of ε for the reaction centres on the surface

$$= \frac{\int_{\epsilon_1}^{\epsilon_2} \varepsilon F(\varepsilon)\, \delta\varepsilon}{\int_{\epsilon_1}^{\epsilon_2} F(\varepsilon)\, \delta\varepsilon}. \tag{2}$$

The value of ε required is, however, the mean value for one *reacting* gram-molecule. Consider the centres lying between ε and $\varepsilon + \delta\varepsilon$. There are $F(\varepsilon)\,\delta\varepsilon$ of these. Let σ_ϵ be the mean life of a molecule on these centres. Then $F(\varepsilon)\,\delta\varepsilon/\sigma_\epsilon$ fresh molecules arrive on these centres every second. Of these a fraction $e^{-\epsilon/RT}$ have sufficient energy to react. Therefore

$$\frac{F(\varepsilon)\, e^{-\epsilon/RT}\, \delta\varepsilon}{\sigma_\epsilon} \quad \text{molecules react per second.} \tag{3}$$

Therefore the mean value of ε for the reacting molecules is given by

$$\frac{\int_{\epsilon_1}^{\epsilon_2} \dfrac{\varepsilon F(\varepsilon)\, e^{-\epsilon/RT}\, \delta\varepsilon}{\sigma_\epsilon}}{\int_{\epsilon_1}^{\epsilon_2} \dfrac{F(\varepsilon)\, e^{-\epsilon/RT}\, \delta\varepsilon}{\sigma_\epsilon}} = \bar{\varepsilon}. \tag{4}$$

The Equation for the Reaction Velocity.

Let $S =$ the area of the catalyst surface. Then from (3) $\dfrac{S \cdot F(\varepsilon)\, e^{-\epsilon/RT}\, \delta\varepsilon}{\sigma_\epsilon}$ molecules react per second on centres having values of ε between ε and $\varepsilon + \delta\varepsilon$. Hence the reaction velocity

$$v = \int_{\epsilon_1}^{\epsilon_2} \frac{S \cdot F(\varepsilon)\, e^{-\epsilon/RT}\, \delta\varepsilon}{\sigma_\epsilon}. \tag{5}$$

This equation gives the reaction velocity in terms of ε_1 and ε_2 and also the function $F(\varepsilon)$. It is to be observed that the equation combines two independent factors. The portion $S \cdot F(\varepsilon)$ which represents the distribution of the characteristic groupings of copper atoms over the surface, and which is thus independent of the temperature for a stable catalyst; and the portion $\dfrac{1}{\sigma_\epsilon} e^{-\epsilon/RT}$ which represents the rate of reaction on one of these centres. The equation is the limit of progress in general terms. The next step must be an attempt to evaluate the form of the unknown function.

The Distribution of Centres of Activity.

Amorphous Substances.—In liquids the molecules are capable of independent motion, and by virtue of their kinetic energy, they are distributed in random

fashion at distances approximating to their mean distance. The deviations from the mean distance are occasioned by so many independent causes, which "must necessarily be general and alike in all cases, since the causes of error are alike but unknown." The normal law of errors thus applies to the deviations of individual pairs of atoms from the mean distance.*

If $z =$ the proportional frequency of observations measuring x,

$a =$ the arithmetic mean of the group,

$C =$ a constant called the modulus,

then

$$z = \frac{1}{\sqrt{\pi}C} e^{-\frac{(x-a)^2}{C^2}}.$$

This is the normal law of errors.

Let $d_1, d_2, \ldots d_n$ be the distances of the atoms from each other in a centre of activity, n being necessary and sufficient to define the arrangement. Then the probability that a pair of atoms shall be separated by d_1 is

$$\frac{1}{\sqrt{\pi}C} e^{-\left(\frac{d_1-\beta_1}{C}\right)^2},$$

where $\beta_1, \beta_2, \ldots \beta_n$ are the distances of the atoms from one another in the equilibrium arrangement. The probability that a third atom shall be near the first at a distance d_2 is the product

$$\left(\frac{1}{\sqrt{\pi}C}\right)^2 e^{-\left(\frac{d_1-\beta_1}{C}\right)^2} e^{-\left(\frac{d_2-\beta_2}{C}\right)^2}.$$

Thus the proportional frequency of centres of activity defined by d_1, $d_2, \ldots d_n$ is

$$\left(\frac{1}{\sqrt{\pi}C}\right)^n \cdot \prod_{1 \to n} \cdot e^{-\left(\frac{d-\beta}{C}\right)^2}$$

or

$$\int = \left(\frac{1}{\sqrt{\pi}C}\right)^n e^{-\frac{1}{C^2}\Sigma(d-\beta)^2}. \tag{b}$$

This relation represents the distribution due to purely random causes.

Amorphous solids are supercooled liquids the atoms of which are incapable of independent motion; in fact, the chaotic arrangement of the liquid state has been fixed. Thus equation (b) also applies to an amorphous solid. Each centre of activity is in a state of strain. The arrangement $\beta_1, \beta_2, \ldots \beta_n$ is in equilibrium,

* The following reasoning is more particularly concerned with simple structures in which there is no association or combination of atoms to form molecules. A similar type of reasoning would be applicable to a structure of complex molecules.

and therefore is unstrained; thus the strain varies with $(d - \beta)$, etc. It is easy to find the relation between the two by the method of dimensions.

Let y be the strain energy present between two atoms.

Then

$$y = \mu (d - \beta)^n,$$

where μ is a constant, and n is to be evaluated. e represents energy. Thus $(d - \beta)$ has dimensions ML^2T^{-3}, and therefore $n = 2$. Hence

$$y = \mu (d - \beta)^2. \qquad (c)$$

The strain energy in the whole structure is the sum of the energies in the separate parts. Hence the total strain in a centre of activity

$$E = \mu \sum_{1 \to n} (d - \beta)^2, \quad \text{and hence} \quad E/\mu = \sum_{1 \to n} (d - \beta)^2.$$

Therefore, from (b)

$$\int = \left(\frac{1}{\sqrt{\pi} C}\right)^n e^{-\frac{E}{\mu C^2}}. \qquad (6)$$

This equation is general for amorphous substances, μ and C, and the limits of E being variables for each. The strain E also measures the magnitude of the external field, which in turn causes the lowering of the critical increment from the maximum value α to the value on the reaction centre.*

Thus $(\alpha - \varepsilon)$ is also a measure of E. Let

$$(\alpha - \varepsilon) = \gamma E, \text{ where } \gamma \text{ is a constant.}†$$

Then from (6)

$$\int = \left(\frac{1}{\sqrt{\pi} C}\right)^n e^{-\frac{(\alpha - \varepsilon)}{\mu \gamma C^2}}.$$

Hence $\int = A . e^{k\varepsilon}$ where A and k are positive constants, depending only on the nature of the substance and not at all on the temperature, and the relation is restricted between the limits ε_1 and ε_2.

Let n be the total number of reaction centres present, then $\int = \dfrac{dn}{d\varepsilon}$; thus $\int$ is proportional to the number of centres present with heat of activation ε. Hence

$$\delta n = A . e^{k\varepsilon} \delta\varepsilon. \qquad (7)$$

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* *See* Norrish, 'J. Chem. Soc.,' vol. 123, p. 3007 (1923).

† The constant γ more particularly than any other is characteristic of an individual catalyst. It is a measure of the efficiency of the field E in weakening the intramolecular forces in a molecule.

There is thus an exponential distribution of reaction centres on an amorphous surface, stretching from the value of the heat of activation ε_1 to ε_2, both of which are variables for various substances, as are the constants A and k. All these quantities are independent of the temperature of the surface, provided sintering does not occur.

The Grain Surface in a Crystalline Solid.

It is known that the fields of force at the surface of a thin film may be modified by the nature of the underlying material.* The effect is, in fact, due to the transmission of the underlying fields of force through the surface film. This will occur with an amorphous film supported on a crystalline substance. Thus the energy of each reaction centre will be changed to $(E \pm \delta_1)$, and ε will be changed to $(\varepsilon \mp \delta_2)$. This change is virtually a shift of the limits of ε on the surface. It is, therefore, probably impossible to predict the activity in the crystalline state from that of the amorphous solid.

The methods of producing catalytically active copper, by reduction from oxide, or by heating copper formate,† are directed towards suddenly producing these meta-stable arrangements of atoms, under such conditions of temperature that the arrangement cannot subsequently be changed by the mere thermal agitation of the atoms of the structure. Study of the growth of crystals supports the view that the " new condensed molecules are at first in a mobile state on the surface of the crystal...."‡

Let $r =$ the short time during which the atoms on the copper surface are mobile at the instant they are produced by reduction from oxide. During the time r the centres of activity can sinter.§ We have seen that $(\alpha - \varepsilon)$ measures the strain in the centres with heat of activation ε. The quantity $\int$, as before, gives the density of the centres with heat of activation ε. The rate of decay of $\int$ is proportional to the number of centres present, since each decays

* See Bredig and Weinmayr, ' Boltzmann Festschrift,' p. 839 (1904), " On the Catalytic Activity of Mercury Films "; Pring, ' Zeit. Elektrochemie,' vol. 19, p, 255 (1913), " Overvoltage at Films "; Oberbeck, ' Wied. Ann.,' vol. 31, p. 337 (1887), " E.M.F. at Films "; Wiener, *ibid.*, vol. 31, p. 629 (1887), " Reflection at Films "; Wald, ' Zeit. Phys. Chem.,' vol. 7, p. 514 (1891), ' Vapour Pressure of Films "; Hardy, ' Roy. Soc. Proc.,' A, vol. 100, p. 550; vol. 101, p. 487, " Lubrication."

† Copper formate gives metallic copper on heating at 200° C. Electrolytic copper is inactive (Part I.).

‡ See ' Zeit. Phys. Chem.,' vol. 102, pp. 267–75, " On the Growth of Crystals of Tin and Cadmium."

§ See Part 6. The structure is fixed at the instant of reduction.

independently of the others, and it is also greater the greater the strain in the centre.

Hence $\qquad -\dfrac{d\int}{dt} \propto (\alpha - \varepsilon)\int \qquad$ or $\qquad \dfrac{d\int}{dt} = -\lambda\,(\alpha - \varepsilon)\int,$

where λ is a constant depending on the conditions at the instant of reduction. Therefore

$$d\int/\int = -\lambda\,(\alpha - \varepsilon)\,dt$$

or

$$\log\int = -\lambda\,(\alpha - \varepsilon)\,t + \text{const.}$$

But when $t = 0$, $\int_0$ represents the frequency of centres of activity in the liquid state. Hence

$$\int_0 = A e^{k\varepsilon}.$$

When $t = r$, sintering is at an end; thus $\int_r$ defines the distribution in the reduced copper, and we have

$$\log\int = \log\,(A e^{k\varepsilon}) - \lambda\,(\alpha - \varepsilon)\,r,$$

i.e.

$$\int = A e^{k\varepsilon} e^{-\lambda r\,(\alpha - \varepsilon)} = A e^{-\alpha\lambda r}\, e^{(k + \lambda r)\cdot\varepsilon},$$

or

$$\delta n = C_T \cdot e^{h\varepsilon}\,\delta\varepsilon, \qquad\qquad (8)$$

where $C_T = A \cdot e^{-\alpha\lambda r}$ and is constant at constant temperature of reduction, and $h = k + \lambda r$.

The equation is again restricted between the limits ε_1 and ε_2.

The Constancy of the Distribution Constant h.

Any change in the distribution constant h due to the increasing temperature of reduction, will be caused by an increase in the product λr, since k is constant. Investigation shows that the consequent change in C_T is of such magnitude as to make any but a slight change in h impossible in an active catalyst. For

$$\frac{\delta C}{C} = -\alpha \cdot \delta\,(\lambda r) \quad\text{and}\quad \frac{\delta h}{h} = \frac{\delta\,(\lambda r)}{h},$$

therefore

$$\frac{\delta C/C}{\delta h/h} = -\alpha h = 30 \text{ approx.}^*$$

---

* *I.e.*, a 1 per cent. increase in λr causes a 30 per cent. fall in the catalytic activity without any change in the temperature coefficient. Thus sintering at the instant of reduction does not alter the temperature coefficient.

The values of α and h deduced at the end of the paper are used to get this numerical result.

It is now evident that the periodic relation* obtained between the catalytic activity and the temperature at which the copper is produced by reduction from oxide is caused by the superposition of two factors. There is a general falling off of activity above 300° C., due to a very slight increase in the product λr; and superposed on this relation is a periodic relation due to a predomination of various active crystal planes in the surface. This periodic change is accompanied by change in the observed temperature coefficient of the reaction, caused by the alteration of the limits of ε on the surface in accord with the nature of the transmitted field of force. This change can be used to evaluate h for the surfaces used in the experiments.

Having also found the first approximation to the reaction centre distribution equation, we are now in a position to solve the general equations for the rate of reaction at the surface.

The Evaluation of the General Equations.

The function $F(\varepsilon)$ must be replaced by $C \cdot e^{h\varepsilon}$ restricted between the limits ε_1 and ε_2. The mean value of ε for the centres on the surface, equation (2) becomes

$$\frac{\int_{\varepsilon_1}^{\varepsilon_2} \varepsilon\, e^{h\varepsilon}\, \delta\varepsilon}{\int_{\varepsilon_1}^{\varepsilon_2} e^{h\varepsilon}\, \delta\varepsilon} = \frac{\left[e^{h\varepsilon}/h\left(\varepsilon - \frac{1}{h}\right)\right]_{\varepsilon_1}^{\varepsilon_2}}{\left[e^{h\varepsilon}/h\right]_{\varepsilon_1}^{\varepsilon_2}}$$

$$= \frac{e^{h\varepsilon_2}\left(\varepsilon_2 - \frac{1}{h}\right) - e^{h\varepsilon_1}\left(\varepsilon_1 - \frac{1}{h}\right)}{e^{h\varepsilon_2} - e^{h\varepsilon_1}}$$

$$= \frac{\left(\varepsilon_2 - \frac{1}{h}\right) - e^{-h\,(\varepsilon_2 - \varepsilon_1)} \cdot \left(\varepsilon_1 - \frac{1}{h}\right)}{1 - e^{-h\,(\varepsilon_2 - \varepsilon_1)}}. \qquad (9)$$

But since $e^{h\varepsilon_2}$ is much greater than $e^{h\varepsilon_1}$, the result lies very near $\left(\varepsilon_2 - \frac{1}{h}\right)$ which is determined chiefly by the upper limit of ε on the surface. The mean value of ε for the reacting molecules (4) becomes

$$\bar{\bar{\varepsilon}} = \frac{\int_{\varepsilon_1}^{\varepsilon_2} \varepsilon e^{h\varepsilon} e^{-\varepsilon/RT}\, \delta\varepsilon}{\int_{\varepsilon_1}^{\varepsilon_2} e^{h\varepsilon} e^{-\varepsilon/RT}\, \delta\varepsilon} = \frac{\int_{\varepsilon_1}^{\varepsilon_2} \varepsilon e^{(h\varepsilon - \varepsilon/RT)}\, \delta\varepsilon}{\int_{\varepsilon_1}^{\varepsilon_2} e^{(h\varepsilon - \varepsilon/RT)}\, \delta\varepsilon}.$$

* "The Catalytic Action of Copper, Part IV."

Experiment shows that $h - \dfrac{1}{RT}$ is negative, $= -\lambda$ say.

Then

$$\bar{\varepsilon} = \frac{\displaystyle\int_{\varepsilon_1}^{\varepsilon_2} \varepsilon e^{-\lambda \varepsilon}\, \delta\varepsilon}{\displaystyle\int_{\varepsilon_1}^{\varepsilon_2} e^{-\lambda \varepsilon}\, \delta\varepsilon} = \frac{e^{-\lambda \varepsilon_1}\left(\varepsilon_1 + \dfrac{1}{\lambda}\right) - e^{-\lambda \varepsilon_2}\left(\varepsilon_2 + \dfrac{1}{\lambda}\right)}{e^{-\lambda \varepsilon_1} - e^{-\lambda \varepsilon_2}}, \tag{10}$$

which function, since $-\lambda$ is negative, lies very close to ε_1, the lower limit of ε on the surface. Thus most of the decomposition, as would be expected on general grounds, takes place on those reaction centres with the lowest ε. This is therefore the criterion of an active catalyst.—It must possess a great surface density of reaction centres having a low value of ε. Expectations are held that this is the cause of promoter action; the promoter may increase the number or decrease ε on the reaction centres. So far insufficient experimental data are available to test the theory in this case. But it may be remarked that Hurst and Rideal* have suggested that the promoter action of palladium on copper is due to the effects at the interface.

The Equation for the Reaction Velocity.

Equation (5) becomes

$$v = \int_{\varepsilon_1}^{\varepsilon_2} \frac{C_T S \cdot e^{h\varepsilon} e^{-\varepsilon/RT}}{\sigma_\varepsilon}\, \delta\varepsilon = \int_{\varepsilon_1}^{\varepsilon_2} \frac{C_T S \cdot e^{\varepsilon\left(h - \frac{1}{RT}\right)}}{\sigma_\varepsilon}\, \delta\varepsilon.$$

Assuming σ_ε varies only slowly with ε, we obtain

$$v = \frac{C_T S}{\left(h - \dfrac{1}{RT}\right)\sigma}\left(e^{h\varepsilon_1} \cdot e^{-\varepsilon_1/RT} - e^{h\varepsilon_2} \cdot e^{-\varepsilon_2/RT}\right)$$

and substitution of numerical results shows that the second term is negligible. The final expression for the reaction velocity in molecules decomposed per unit time is

$$v = \frac{C_T S \cdot e^{h\varepsilon_1} \cdot e^{-\frac{\varepsilon_1}{RT}}}{\left(h - \dfrac{1}{RT}\right)\sigma} \tag{11}$$

and in cubic centimetres H_2 per sec. becomes

$$v = \frac{22 \cdot 3 \times 10^3\, C_T S \cdot e^{h\varepsilon_1} e^{-\varepsilon_1/RT}}{\left(h - \dfrac{1}{RT}\right)\sigma N}.$$

* Hurst and Rideal, ' J. Chem. Soc.,' vol. 125, p. 685 (1924).

In this equation the factor A varies slowly with T, and Richardson* has shown that in these cases the experimental evidence is quite insufficient to distinguish such a relation from the simple exponential law. This equation is completely in accord with experience, in so far as it can be tested. The A factor shows the required variation with ε, and the relation between v and T is also satisfied. Further experiment shows that the velocity changes only slightly with the pressure, as would be expected, since σ only varies slowly with pressure (Part 7).

$$A = \frac{C_T \cdot S e^{h\varepsilon}}{\left(h - \dfrac{1}{RT}\right)\delta} \; .$$

To evaluate h we must first correct the observed values of A for the sintering of the centres of activity occurring at the higher temperatures of reduction, since sintering occurs without change in the temperature coefficient of the reaction. The discussion in Part 6† attributed the periodic variation of the activity to change in orientation in the surface planes exposed, but no single cause could be found for the change. The position of the maxima of activity also changes, as also do the values of these maxima ; hence it is probable that the variation is random. Hence, if a smooth curve be drawn symmetrically through the periods, this curve will give the falling-off of the activity due to the increased temperature at which copper is produced by reduction from oxide.

The values of the reaction velocity at 250° C. obtained by this means are tabulated against the corresponding reduction temperatures in Table II. Let C_0 be the constant value of C over the range of reduction temperatures 200 to 300° C., and C_t the value at T° C. Then the ratio

$$v_0/v_t = C_0/C_t = 10^x$$

from the formula (11), since it has been shown that ε is unaltered by sintering at the instant of formation. The values of $\log_{10} C_0/C_t = x$ so calculated are also shown in Table II.

* ‘ The Emission of Electricity from Hot Bodies.’
† *Loc. cit.*

Table II.

Temp. at which CuO was reduced.	Series I.		Series II.	
	$v_{250°}$	x.	$v_{250°}$	x.
° C.	c.c. per min.		c.c. per min.	
220	2·5	0·00	3·5	0·00
300	2·3	0·04	3·4	0·02
320	2·1	0·08	3·2	0·04
340	1·9	0·12	3·0	0·07
360	1·7	0·17	2·8	0·10
380	1·4	0·25	2·2	0·20
400	1·0	0·41	1·8	0·28
420	0·7	0·56	1·2	0·47

but

$$A = \frac{C_T \cdot S \cdot e^{h\epsilon}}{\left(h - \dfrac{1}{RT}\right)} \qquad \text{from (11),}$$

therefore,

$$\log_{10} A = \log_{10} \frac{C_T \cdot S}{\left(h - \dfrac{1}{RT}\right)\sigma} + \cdot 434\, h\epsilon,$$

therefore,

$$\log_{10} A + x = \log_{10} \frac{C_0 \cdot S \cdot}{\left(h - \dfrac{1}{RT}\right)\sigma} + \cdot 434\, h\epsilon.$$

Thus the corrected values of $\log_{10} A$ and ϵ give a straight-line curve, whose slope is $0\cdot4343\,h$. The data of Part 4, tabulated on pp. 361–362 above, show that this is the case (*see* figs. 1 and 2). The error to be expected is considerable* ; thus the agreement is satisfactory.

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* S may vary to some extent, and there is considerable error in the deduction of A from ϵ by the equation

$$\log v = \log A - \epsilon/RT.$$

For

$$\frac{\delta A}{A} = \frac{\delta \epsilon}{RT} \quad \text{but} \quad \epsilon/RT = 20 \text{ approx.}$$

i.e.

$$\frac{\delta A}{A} = \frac{20\delta\epsilon}{\epsilon}, \text{ or a 1 per cent. error in } \epsilon \text{ makes 20 per cent. error in A.}$$
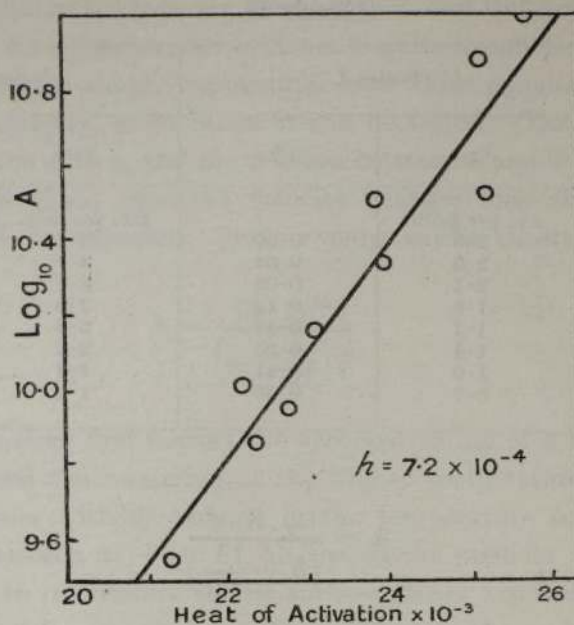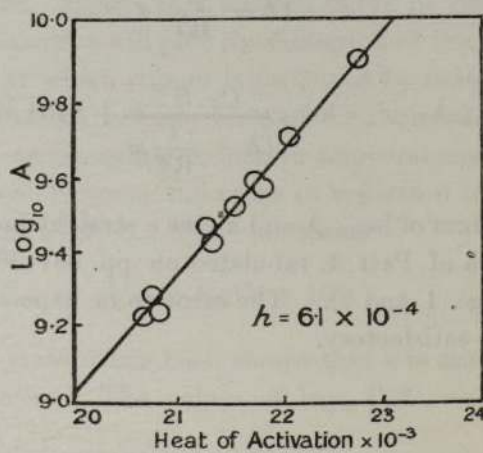
FIG. 1.—Series I.

FIG. 2.—Series II.

The deduced values of h are :—

Series I.	Series II.	Mean.
$h = 7\cdot2\times10^{-4}$	$6\cdot1\times10^{-4}$	$6\cdot6\times10^{-4}$

$1/RT = 9\cdot66\times10^{-4}$ at $250°$ C., hence $h-1/RT = 3\cdot1\times10^{-4}$

and is negative throughout the range of temperature employed in the experiments, as is required by the theory. A is therefore defined by the relation

$$A = \frac{C_T S \cdot e^{0 \cdot 00066 \epsilon}}{(h - 1/RT)\,\sigma},$$

and the distribution of centres of activity by the equation

$$\delta n = C_T e^{0 \cdot 00066 \epsilon}\, \delta \epsilon,$$

where C_T denotes the value of the constant for the temperature of reduction used in the production of the copper. It has been shown that C_T is independent of the temperature of the catalyst surface at the temperatures at which the dehydrogenation occurred.

The frequency of reaction on centres with heat of activation ϵ is given by the relation

$$\delta v = \frac{C_T S \cdot e^{-0 \cdot 00031 \epsilon}}{\sigma}, \quad \text{at } 250^\circ \text{ C.}$$

Thus while the number of reaction centres increases rapidly as the critical increment increases, the number of molecules that react on the increasing number of centres diminishes rapidly.

Deductions concerning the Nature of the Surface from these Measurements.

It is not possible to estimate ϵ_2; but it is easy to assign a minor limit to this quantity in order that the second term of the equation

$$\mu = \frac{C \cdot S \cdot}{\left(h - \dfrac{1}{RT}\right)\sigma}\left(e^{h\epsilon_1}\, e^{-\epsilon_1/RT} - e^{h\epsilon_2}\, e^{-\epsilon_2/RT}\right)$$

should be negligible compared with the first. The ratio of the second term to the first is

$$e^{-\lambda \epsilon_2}/e^{-\lambda \epsilon_1} = e^{-\lambda(\epsilon_2 - \epsilon_1)} \qquad \text{where} \qquad \lambda = -\left(h - \frac{1}{RT}\right).$$

Let ϵ_1 be taken as 20,000 calories per gram-molecule.

Value of ϵ_2.	30,000.	40,000.	50,000.	Calories.
Ratio of second to first term at 250° C. $\lambda = 3 \cdot 1 \times 10^{-4}$	per cent. 2·9	per cent. 0·1	per cent. 0·0	

The minimum range of ε is from 20,000 to 40,000 calories. This result was used to calculate the mean values of ε on the surface; the results obtained must be considered an approximation only in so far as they depend on ε_2. The values of ε_1 and λ can be found directly from the observations. Assuming $\varepsilon_1 = 20,000$ cals. and $\varepsilon_2 = 40,000$ cals., THE MEAN VALUE OF ε ON THE SURFACE (9) = 38,400 calories.

THE MEAN VALUE OF ε FOR THE REACTING MOLECULES (10) = 23,300 cals., and this value is independent of the value of ε_2.* THE VALUE OF ε FROM THE TEMP. COEFFICIENT = 20,000 calories. The mean value of ε on the surface can only be regarded as the lower limit of the true value; whereas the other values rest entirely on measured quantities. This remarkable difference between ε measured from the temperature coefficient and ε for the reacting molecules may explain why, in some cases of true photochemical change, the maximum acceleration of the velocity of reaction occurs with a wave-length different from that calculated from the temperature coefficient of the thermal reaction. It shows clearly that considerable change may take place in the value of ε on the centres on the surface, and yet from temperature coefficient measurements only the distribution could not be detected.

The variation in the measured temperature coefficient thus takes a new aspect. The value of ε ranges upwards on the reaction centres from varying values of ε_1; the distribution constant remains fixed. It has also been shown that the value of ε_2 is unimportant in deciding the velocity of the dehydrogenation.

Calculation can also be made showing what fraction of the surface is active. Half of the reaction occurs in the range ε_1 to $\varepsilon_1 + 1/\lambda$ calories,† the rest in the range $\varepsilon_1 + 1/\lambda$ to ε_2 cals. Therefore the fraction of the surface causing half decomposition

$$= \frac{\int_{\varepsilon_1}^{\varepsilon_1 + 1/\lambda} e^{\lambda \varepsilon} \, \delta\varepsilon}{\int_{\varepsilon_1}^{\varepsilon_2} e^{\lambda \varepsilon} \, \delta\varepsilon} = \frac{e^{\lambda(\varepsilon_1 + 1/\lambda)} - e^{\lambda \varepsilon_1}}{e^{\lambda \varepsilon_2} - e^{\lambda \varepsilon_1}}$$

$$= e^{-\lambda(\varepsilon_2 - \varepsilon_1 - 1/\lambda)} \text{ approximately.}$$

To obtain a lower limit to the value of this quantity we may assume $\varepsilon_2 = 30,000$ cals. It is certainly not possible to reduce the heat of activation further, as curves for the reaction velocity which were not exponential in character

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* However much greater than 40,000 cals. it may become.

† Since $\varepsilon_1 + \dfrac{1}{\lambda}$ is a close approximation to the mean value of ε for the reacting molecules (Equation 10).

would be obtained as the temperature was raised.* The lower limit to the fraction of the surface causing half decomposition is thus 1·7 per cent. With $\varepsilon_2 = 40,000$ the fraction becomes of the order 10^{-5}. Thus the values obtained for the active fraction of the surface are of the same order of magnitude as those found by Rideal for nickel (10^{-3}). They emphasise again that only a very small portion of the surface is active.

It has thus been shown, from considerations of probability, that the distribution of centres of activity over a catalyst surface is, to the first approximation, exponential. Such surfaces cause decomposition as if they contained centres of activity with heat of activation equal to the lowest value in the exponential distribution. The constants for the distribution have been worked out for the case of copper. The results are in agreement with experiment.

Summary.

Chemical reaction takes place in a unimolecular layer, in which the alcohol molecules are orientated with the $-CH_2OH$ group in contact with the copper surface. It is predicted that the velocity of dehydrogenation of all primary alcohols should be equal. This has been verified experimentally.

The mechanism of the change is the loss of neutral hydrogen atoms, the energy of activation becoming the energy of oscillation of the hydrogen atom of the hydroxyl group. The second hydrogen atom is automatically released with the mean kinetic energy characteristic of the temperature.

Activation of the alcohol molecule by the catalyst consists in increasing the distance between the hydrogen atom and the oxygen atom in the hydroxyl group. Quantitative treatment on this basis leads to an equation which is not in agreement with experiment.

The source of this discrepancy lies in assuming that the whole of the surface is active. The conception of activation increasing the distance between the H and the O atom in the hydroxyl group leads to the idea of a " reaction centre." At these areas the adsorbed alcohol molecule is situated over some characteristic group of copper atoms.

The work of Taylor, Pease, and Armstrong and Hilditch, is summarised.

Application of the theory of probability to the problem of the centre of activity shows that the proportional frequency of centres with heat of activation ε is connected with ε by an exponential relation.

The periodic relation between the catalytic activity of copper and the tem-

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* *See* ' Roy. Soc. Proc.,' A, vol. 106, p. 261, fig. 6 (1924).

perature at which the copper was produced by reduction from oxide, has been
split up into a general falling-off of activity, due to sintering of the centres at the
instant of reduction, and a random periodic variation accompanied by change
in the temperature coefficient of the reaction.

Study of this latter change enables the constants in the distribution formula
to be evaluated. The reaction-velocity expression finally deduced takes the
form

$$= \frac{C_T . S . e^{h\epsilon_1}}{\left(h - \frac{1}{RT}\right)\sigma} e^{-\epsilon_1/RT}.$$

This equation is in accord with experience in so far as it can be tested.

My thanks are due to Mr. W. G. Palmer for his interest in this work.

Thermal Separation in Gaseous Mixtures.

By G. A. Elliott, B.Sc., University College, London, and Irvine
Masson, D.Sc., University of Durham.

It was pointed out by Chapman ('Phil. Trans.,' A, vol. 216, p. 279 (1915);
'Roy. Soc. Proc.,' A, vol. 93, p. 1 (1917)) that, according to his development
of the kinetic theory of gases, the composition of a gaseous mixture should vary
when the temperature is made to vary from point to point within it, the
extent of separability depending upon the character of the intermolecular
force-fields and upon the relative molecular weights, sizes and numerical
concentrations. The prediction was verified, qualitatively, with mixtures of
hydrogen with carbon dioxide (Chapman and Dootson, 'Phil. Mag.' (vi), vol.
33, p. 248 (1917)), in which a difference in composition of about 3 per cent.
was found when an equimolecular mixture was kept in two communicating
vessels at 10° and 230° respectively.

The present experiments were at first subordinate to certain other work in
which thermal diffusion would have affected the results, but they have yielded
data which are of more general interest. Meanwhile, Ibbs ('Roy. Soc. Proc.,'
A, vol. 99, p. 385 (1921)) had further confirmed Chapman's theory when he