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THE MULTIPLET THEORY OF CATALYSIS. STRUCTURAL FACTORS IN CATALYSIS

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Catalysis forms the basis of modern heavy chemical industry and biochemistry, and the elaboration of a theory of catalysis is of great importance. At present there exist three main theories of catalysis, which are mutually complementary: the intermediate surface compound, the multiplet, and the electronic theories. On their basis we can start to construct a unified theory of catalysis. This will solve the problem of the choice of catalysts[1], which will provide great opportunities for controlling chemical reactions[2].

1. FUNDAMENTAL PRINCIPLES OF THE MULTIPLET THEORY

The revolution in physics at the beginning of the twentieth century led to the modern theory of the structure of matter, on which the multiplet theory of organic catalysis[3,4] is based, and has evolved gradually[5-8] as the former has grown. The present state of the multiplet theory is described below. The multiplet theory generalises the experimental results on the basis of the configurations of molecules and solid lattices, as well as bond lengths and energies, and up to the present time it is the only theory in which actual catalytic reactions are considered systematically at the atomic level from this point of view.

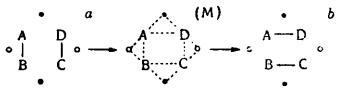
The theory of the structure of matter is based on electronic theory and quantum mechanics, and therefore these also constitute a basis of the multiplet theory; the lengths and energies of bonds represent a stable set of electronic properties of importance in catalysis[9].

The multiplet theory starts from the fact that catalysis is a chemical phenomenon. Chemical valence forces are characterised by potential curves representing the mutual potential energy of two atoms as a function of the distance between them. The bottom of the well in these curves corresponds to the bond length d and the bonding energy (allowing for the zero-point energy). The potential well is narrow and has steep sides. This implies that the atoms interact chemically when they are practically in contact, *i. e.* when they approach to the distance d. Bond lengths and energies are measured by X-ray and electron diffraction, spectroscopically, thermochemically, and by other modern physical methods. A far reaching additivity of bond lengths and also of bond energies is observed, which is of importance in their practical application.

Owing to the small range of action of chemical valence forces, catalytic reactions involve not entire molecules but individual atoms in them, which according to the above considerations should be in contact with one another (not necessarily at the same time). This principle of contact makes it easy to establish which atoms in a molecule touch

one another during each reaction step. A group of such atoms is termed an indicial group; it is the analogue of a functional group in organic chemistry. According to the principle of contact, the reactant atoms should, at some instant, be in contact also with the catalyst[5].

According to the multiplet theory, the simplest and most frequently encountered reactions are duplet reactions[10,11]:



(1.1)

Here A, B, C, and D are the atoms involved in the reaction [substituents not indicated in Eqn. (1.1) may be attached to them]. They are located (not necessarily simultaneously) on the catalyst surface. The atoms of the catalyst, the centres of which are indicated by dots and by small circles, may be of different types. Attraction to the catalyst is effected by chemical forces, under the influence of which the bonds A–B and C–D become weaker. This results in the form M, the multiplet, active complex, which is unstable and tends to pass into a more stable state, which can be either the initial state *a* or the final state *b*, depending on the thermodynamic conditions. The role of atoms denoted by dots and by circles is the same. Therefore forward and reverse reactions pass through the same complex M in opposite directions. The dots imply that, under the given conditions, thermodynamics requires that reaction shall go in the direction of rupture of the vertical bonds in *a* and formation of horizontal bonds in *b*. In this way microreversibility is observed; the distances between the dots in Eqn. (1.1) may be different from those between the centres of the circles.

Scheme (1.1) can be simplified in various ways: we can omit the circles and leave only dots associated with A, B, C, and D; sometimes we enclose the reactant atoms in a frame. The most concise way is to indicate only the atoms and the bonds of the indicial group, arranged in such a way that reaction involves the rupture of two vertical bonds with the formation of two horizontal bonds. Then the scheme (1.1) as a whole is represented by the group



(1.2)

The bonds A–B and C–D may belong either to two molecules or to the same molecule (for example in a cyclisation); therefore the group (1.2) represents not only double decompositions but also decompositions and cyclisations, as well as additions when it contains a multiple bond, for example A=B. If bonds other than those written above are present in the indicial group, they are preserved during the reaction (as are also substituents attached to A, B, C, and D).

A more complicated example is the triplet reaction having the indicial group



(1.3)

This reaction results in the rupture of three bonds A–B, C–D, and E–F with the formation of the bonds B–C, D–E, and F–A.

There is also the sextet type (see later). It is a singular fact that duplet, triplet, and sextet reactions practically exhaust the whole wealth of heterogeneous catalytic reactions known in organic chemistry. At present reactions in which the valency of the indical atoms changes are not included in the multiplet theory. However, they are few compared with the total number of reactions.

Scheme (1.2) and other schemes of the multiplet theory have a definite physical meaning. In order to elucidate it, we must consider the theory of the structure of matter, and in particular the theory of the solid state.

The faces of the crystal lattice of the catalyst contain projections corresponding to the lattice atoms (Fig. 1). Comparison of the electron and X-ray diffraction patterns shows that the surface and inner layers of a solid usually differ little in structure. Furthermore, the closest packing, for example of three identical rigid atoms, should be an equilateral triangle whether the atoms are situated within the lattice or at the surface. This permits us to apply to the surface (with some approximation) the mean additive bond lengths known for the bulk phase.

Apart from projections of atomic dimensions, the crystal faces will obviously contain indentations (*V*) between the projections (see Fig. 1). The distances between the indentations (d_1) are equal to those between the projections (*d*). Atoms entering the indentations are attracted especially strongly, for the same reason that atoms of a metal undergoing crystallisation tend to arrange themselves with the closest packing: here the potential energy is a minimum owing to the possibility of interaction with several surrounding atoms. Crystal growth takes place at sites where the atomic arrangement is especially favourable, at the so-called growth points and centres of crystallisation (see, for example, Ref. 12).

If atoms of a different substance having a similar atomic radius enter the indentations *V* or the deeper gaps *V'* (Fig. 1), crystal growth can also take place, a solid solution being formed (under certain conditions). We shall have a case of isomorphism. In crystal chemistry and in the study of alloys atomic (and ionic) radii are in everyday use (*cf.* Goldschmidt's rule). An example of a general rule applicable to alloys is that metals of atomic radius 2.2–3.0 Å show the greatest tendency to form substitutional solid solutions (Kornilov[13]). Structural conformity plays a great part also in the field of clathrate compounds[14] and molecular sieves[15].

With certain geometrical relations, the lattice of one substance can also be continued in a regular manner by that of another substance. This will be a case of epitaxy, in which crystal-chemical conformity exists at the boundaries between the solid phases (*cf.* Dankov[16] and Seifert[17]).

In oriented adsorption the parts of the molecule in contact with the adsorbent lattice can also be in crystallographic correspondence with the latter. This is none other than stereospecific adsorption.

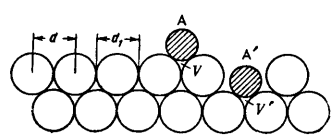


Fig. 1. Section through catalyst surface.

In the case of heterogeneous catalysis the reactant atoms A, B, C, D, etc. fall into the depression V between the surface atoms of the catalyst. We are dealing here with a kind of monolayer surface alloy. In this way several atoms of the catalyst are in contact with the reactant atoms (the indicial group), forming the multiplet.

Parts of the molecules extraneous to the catalyst need not in general bear any relation to the catalyst surface. On the other hand, those parts in contact with the catalyst, entering depressions of atomic dimensions in it, must show surface isomorphism with the catalyst. Hence follows the principle of structural conformity between reactant molecules and catalyst. From the above, it is to be expected that the active centres for catalysis will be provided by points on the surface which are active in crystallisation, *i. e.* growth centres and crystal nuclei.

In enzymic catalysis, not only the indicial atoms but also extraindicial substituents should be in contact with the catalyst. The structural conformity must be still more precise, which explains the great specificity of enzymes (see Section 8). With some variation, the same applies to antimetabolites (Section 8) and probably to antibodies[18].

We now have a continuous series of phenomena in which structural conformity plays an important part, these phenomena relating to such different branches of science as crystal chemistry, the study of alloys, epitaxy, stereospecific adsorption, heterogeneous catalysis, enzymes, antimetabolites, and immunology. In the field of epitaxy, similar views have recently been expressed by Seifert[19].

2. THE MULTIPLET THEORY AND OTHER THEORIES OF CATALYSIS

One of the main differences between the multiplet theory and Kobozev's *ensemble* theory[20], which considers that it is an amorphous phase which possesses catalytic activity, is that, according to the multiplet theory, catalysts can be either crystalline or amorphous; most often they are microcrystalline.

For structural conformity, it is important in the multiplet theory that there should be a definite mutual arrangement of atoms in the catalytically active centre, which contains a small number of atoms, and it is not usually necessary that a definite atomic arrangement should be repeated millions of times in the vicinity of this centre (although such replication may influence the properties of the active centres). Therefore active centres may be not only crystals but also certain small parts of large molecules, such as macromolecular amino-acids in enzymic catalysis, and isolated fragments of a crystal lattice, which are amorphous to X-rays and which contain six atoms in the case of sextets and still fewer with duplets and triplets. The multiplet theory discusses crystal lattices because their constants can be used to find atomic radii and the probable arrangement of atoms in the multiplet (*cf.* above).

Incidentally, although the concept of active centres appeared earlier (Constable[21], Taylor[22]), the question of the *structure* of the active centres was first raised in the multiplet theory[3].

Let us now consider what happens to the reactant atoms A, B, C, and D. At the very start the initial materials undergo molecular adsorption (and at the end of the reaction the molecularly adsorbed reaction products are desorbed). The multiplet theory assumes that in the next stage, that of catalytic adsorption, the bonds A–B and C–D [see group (1.2)] become weakened and distorted, and in the limiting case may undergo complete rupture[5,10] into chemisorbed atoms (or radicals). The new bonds A–D and B–C begin to link up in the multiplet active complex even before the original bonds are completely broken.

A completely analogous principle[23] exists in the theory of absolute reaction rates[24]: the reaction path from A–B and C–D to A–D and B–C does not pass over an elevated plateau, corresponding to complete dissociation (A + B + + C + D), but over a lower col.

On the other hand, the theory of intermediate surface compounds assumes that at first there is activated adsorption, and then the catalytic reaction. By this theory (see, for example, Rideal[25]), we imply a modernised version of Sabatier's theory, in which the bulk intermediate compounds of the latter have been replaced by the reactants which have undergone activated adsorption — adsorption accompanied by complete rupture of the bond A–B with attachment of the atoms to the surface. Thus in the formation of ethylene from alcohol on aluminium oxide, for example, it is supposed that the alcohol molecule combines chemically with the surface atoms, with the formation of an intermediate surface alkoxide, which then decomposes to yield the reaction products. Nothing is said, however, about the mechanism of the decomposition of this intermediate compound (*i. e.* the mechanism, in the terminology of the multiplet theory, of the rupture of the bond C–D and the formation of the bonds A–D and B–C).

The appearance of the multiplet theory was soon followed by Polanyi's theory of catalysis[26]. The conclusions reached by this worker, being based on quantum-mechanical considerations, are very similar to those of the multiplet theory, and can be represented in essence[10] by the indicial group (1.2). In Polanyi's theory the intermediate state is one in which the bonds A–B and C–D have been ruptured, and the atoms A, B, C, and D are combined chemically with the surface valences (Fig. 2). Polanyi points out correctly[27] that the state depicted in Fig. 2 is none other than Taylor's activated adsorption. In this respect the intermediate state is the same as in the intermediate surface compound theory, differing, however, in that here the atoms C and D also have undergone activated adsorption.

Later Eyring and Polanyi suggested the transition state theory, which was then developed in detail by the former[24]. It follows from this theory that rupture of the bonds A–B and C–D should not be complete in the intermediate state corresponding to Fig. 2, which is in agreement with the view of the multiplet theory (see above). The following comment may be made as to whether the multiplet theory regards adsorption not only at the bond A–B but also at C–D as always necessary.

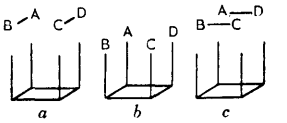


Fig. 2. Polanyi's scheme for catalysis.

Cases of purely duplet, etc. reactions have been examined above. There are, of course, other possibilities, which can also be readily explained. Bonds requiring activation must be in contact with the catalyst. If in a duplet reaction, for example, one part of the indicial group does not need to be activated, it can react without coming into contact with the catalyst. Such a "semi-duplet" scheme was suggested by the present writer[28] for esterification in solution. Hence there is a transition from heterogeneous to homogeneous catalytic reactions and, in the limit, when neither bond of the duplet group requires activation for reaction to occur, to non-catalytic reactions.

In general, however, the quite widely held view, that catalysis often takes place on impact of a molecule of the second component from the gas phase on an adsorbed molecule of the first component, should be treated with great caution. Although such cases may occur, for example with an incomplete duplet (see above), a more thorough examination usually shows that the molecules of the second component must be adsorbed too. Hinshelwood[29] holds the same opinion. It is more correct to regard impact from the gas phase as an adsorption stage which is so rapid that it does not limit the overall reaction.

A further difference between the multiplet and the intermediate surface compound theories is that, according to the former, an intermediate state is followed by a fork in the reaction path. When catalysis is then by far the more rapid, we are dealing, as Roginskii[30] puts it, with presorption catalysis; when, however, the process goes far more rapidly in the direction of activated adsorption, the impression is created that the latter precedes catalysis. The intermediate surface compound theory, on the other hand, assumes that chemisorption precedes catalysis (see above).

According to the multiplet theory, the atom A of scheme (1.1) in Fig. 1 may be located in the hollow *V* between two catalyst atoms, while atom B of the indicial group (1.1), from which A has not yet completely separated, may lie at an angle [11] to the plane of the diagram on the surface. If another atom D is present on the surface (in general at a different angle), a new bond A–D may form under favourable thermodynamic conditions. Thus in this case the position of the atom A is favourable for catalysis. However, A may roll down from *V* into a deeper recess *V'* and occupy position A', where it will have a larger number of catalyst atoms as neighbours. The potential energy at A' will be lower than that at A. The position A' will be more stable, and the energy evolved during such adsorption may be sufficient for complete rupture of the bond A–B, which corresponds to activated adsorption. When under changed conditions (for example with rise in temperature) the hollows *V* also become capable of activated adsorption, they will be poisoned for catalysis, by being filled with firmly held atoms adsorbed in this way. The hollows *V* between the catalyst atoms considered in the multiplet theory correspond to what in several theoretical papers are denoted by free valences[26] or by asterisks[31].

The adsorption responsible for catalysis must be stronger than van der Waals adsorption, since it is produced by chemical forces. Therefore a large amount of energy must be expended in order to remove the adsorbed atom A of the molecule (the atom formed by complete rupture of the bond A–B) from the hollow *V'* between the catalyst atoms. However, this does not mean that the adsorbed atoms must be fixed at a given site on the surface. It all depends on the height of the potential barrier between two neighbouring hollows. The condition necessary for relative freedom of movement is that this barrier should not be high. Migration of the atom (or radical) is then possible along Lennard-Jones valleys, *i. e.* valleys of minimum potential energy situated between projecting parts of atoms and ions forming the crystal face.

Although activated adsorption does not necessarily precede catalysis, its study, and also that of the adsorption, infra-red spectra, and magnetic properties of chemisorbed molecules, are of importance for catalysis. It is likewise important to study bulk chemical compounds similar to the supposed surface compounds, for example alkoxides in the dehydration of alcohols. From this point of view, the properties of nitrides, carbides, hydrides, and analogous compounds must also be studied. All this is necessary to enable us to assess the development of chemical forces under conditions resembling catalysis. It must not be forgotten, however, that such information is indirect, since it relates not to the actual catalytically active centres but to a larger surface, and not to the activated complex but to more stable compounds formed with the catalyst. In this respect a more direct method for the study of catalysis is the kinetic method, which has lately been enriched by the use of labelled atoms and by the stereochemical method.

Summarising the relations between the multiplet and the intermediate surface compound theories, we can say that they resemble one another in that both regard catalysis as due to chemical forces, under the influence of which several intermediate structures are obtained. The main difference is that .... [line missing in the Russian original (Ed. of Translation)] atomic radii, bond energies, etc. Other differences have been considered above. The deformation of reactant molecules and bonds is a concept from the deformation theory of catalysis due to Mendeleev, Zelinskii, and Bodenstein, developed and refined on the basis of modern data.

During recent years an electronic theory of catalysis[32-35] has been successfully developed, the achievements of which include the predictions (subsequently confirmed) that catalytic activity is linked with electrical conductivity and with the work function, of the action of illumination on catalysis, and of the effect of the valency of added ions on their effectiveness as promoters.

There must necessarily exist an intrinsic connection between the multiplet and the electronic theories of catalysis, since both theories are based on that of the structure of matter. The attraction of molecules by the lattice of a solid during adsorption and catalysis occurs as a result of coulombic and quantum-mechanical interaction between electrons and nuclei. All formulae representing these interactions contain a distance. Thus the spatial factor, which is fundamental to the structural aspect of the multiplet theory, should be important for the electronic theory. And conversely, the electronic interactions considered in the electronic theory are determined by bonding energies, a knowledge of which is necessary in order to apply the multiplet theory. It was now time to apply electronic interpretations to the theory of catalysis. Thus Vol'kenshtein writes: "The electronic mechanism of chemisorption does not at all exclude these (geometrical) factors, but emphasises their significance; it retains the geometrical schemes of the multiplet theory" [36]. Schwab[37], a spokesman for the electronic theory, recognises the value of the geometrical stereochemical factor, and says that "the main theory based on the geometrical factor has been up till now Balandin's multiplet theory". Papers have already

appeared in which the electronic and the multiplet theories are applied together (see later).

The application to heterogeneous catalysis of the theory of absolute reaction rates[24] proves to be the closest of all to the multiplet theory. This was first done by Temkin[38] on the simplifying hypothesis that the partition functions of species on a surface are unity. The theory of absolute reaction rates, based on quantum mechanics and statistics, demonstrated[24] that during adsorption, attachment of diatomic molecules (of hydrogen) to two atoms of the catalyst (carbon or nickel) is energetically more advantageous than attachment to a single atom. It showed that the actual energy of activation on solid surfaces should be small, and that for an endothermic process the activation energy should be almost equal to the heat of reaction. The theory discusses the real arrangement of atoms and the mutual energy of their valence electrons. As yet, there have been only a few applications of the theory of absolute reaction rates to actual catalytic reactions, among them being the dehydrogenation of alcohols on copper. As the present writer has shown[39], with reactions of this type, application of the theory of absolute reaction rates to the model given by the multiplet theory yields results which agree with experiment.

Thus calculation shows that the rate constant for dehydrogenation of primary alcohols k_d is, with the model illustrated in Fig. 5,

$$k_d = \frac{kT}{h} \frac{\prod_3 \left(2\pi kT \frac{I_{\neq}^{1/2}}{\theta_{\neq}^{1/2}}/h\right) \prod_3 \left(2\pi kT \frac{m_{\neq}^{1/2}}{\kappa_{\neq}^{1/2}}/h\right) f_{i_{\neq}}^{3n-7}}{\prod_3 \left(2\pi kT \frac{I_a^{1/2}}{\theta_a^{1/2}}/h\right) \prod_3 \left(2\pi kT \frac{m_a^{1/2}}{\kappa_a^{1/2}}/h\right) f_{i_a}^{3n-7}} e^{-\Delta H/kT}, \quad (2.1)$$

where I represents a moment of inertia, m a mass, θ a torsional modulus, and κ a modulus of elasticity, the subscript a denoting the adsorbed molecule, and the double cross the active state. Here the partition functions are no longer unity. The rate of dehydrogenation proves to be constant with different alcohols, in conformity with experiment.

In principle, application of the theory of absolute reaction rates should enable the velocities of catalytic reactions to be calculated from molecular models based on the multiplet theory (see preface in Ref. 24). In this way the multiplet theory is linked by stages with other theories of catalysis.

3. CONSEQUENCES OF THE MULTIPLET THEORY

Several consequences, which have been confirmed experimentally, follow from the above principles of the multiplet theory (Section 1). Some of these consequences have already been mentioned above (Section 2).

1. Catalysis takes place in a monolayer on the catalyst surface. This is consistent with the results of Langmuir's fundamental work[40].

2. The substrate molecules are oriented with their reactive groups towards the catalyst surface. This is confirmed by the very similar activation energies for different compounds in reactions having the same indicial groups, for example in the dehydrogenation of primary alcohols on copper (Constable[21] and others), the dehydration of normal primary alcohols on bauxite and on aluminium oxide[41-43], and also the present author's recent work (see Section 4).

In general it might be supposed that the catalyst combines with the molecule at a distance from the reactive atoms, and that its influence is transmitted along the hydrocarbon chain, producing increased activity at the other end of the molecule (the inductive effect). However, it is known from organic chemistry (see, for example, Ref. 44) that the inductive effect falls off very rapidly along a saturated chain. The above constancy of the activation energy disproves this hypothesis, and demonstrates that the indicial group is oriented towards the catalyst, as required by the multiplet theory.

3. Inert substituents, the extraindicial parts of the molecule, remain unchanged during catalysis, and have little influence on the course of the reaction. This is true when the substituents do not readily displace the electrons in the indicial group, which thus comprises the most important part of the reactant molecules. From this point of view, the hydrogenation of ethylene and that of an unsaturated fatty acid do not differ fundamentally from one another. However, since any substituents, even alkyl groups, somewhat displace electrons in the atoms of the indicial group, they introduce quantitative differences which, in the case of strongly electron-donor or electron-acceptor groups, may be sufficient to produce a qualitative change in the nature of the reaction. Therefore the same catalysts should correspond to the same indicial groups. This is broadly confirmed by experiment.

4. Different catalysts should correspond to different indicial groups, since different atoms in the indicial group have different affinities for the atoms of the catalyst. Therefore catalysis should be selective. This is confirmed by our entire knowledge of organic catalysis. The multiplet theory enables us to classify reactions by systematically replacing atoms in the indicial group, for example of a duplet reaction (see Section 8).

5. Ideally, all the atoms in the indicial group should be in contact with the catalyst, although not necessarily at the same time. We shall see a confirmation of this in the dehydrogenation of hydrocarbons. In fact, in the reverse reaction (hydrogenation) nickel should, according to Sabatier, give an intermediate nickel hydride; on the other hand, the olefine, too, should be adsorbed on the nickel through its carbon atoms, as is now generally accepted (see, for example, Refs. 45, 46, etc.). Obviously all these atoms should be in contact with the nickel during dehydrogenation as well. Investigation by a tracer method (deuterium exchange and hydrogenation with deuterium) shows that different hydrogen atoms and the olefine are adsorbed in a definite sequence, yielding a so-called semi-hydrogenated form and hydrogen atoms adsorbed on the surface (see Section 4).

6. Enhanced catalytic activity may be developed if some of the atoms in the indicial group are attracted to surface atoms of one kind, while other indicial atoms are attracted to atoms of a different kind on the surface. As Schwab[48] has pointed out, this enables the multiplet theory to explain the action of mixed catalysts. It can therefore be expected that catalysts consisting of different solid phases may be especially active along the interphase boundaries (lines). This has been confirmed in a series of papers from the author's laboratory (see Section 7).

7. The multiplet theory is able to explain the gradual increase in activity of a catalyst produced by the addition of

a promoter and, after a maximum has been reached, the subsequent fall in activity due to poisoning of the catalyst. Actually, if, for example, a sulphur atom is introduced into the nickel lattice, it deforms the lattice in its immediate neighbourhood, diminishing the Ni–Ni interatomic distances, and the resulting values may prove to be more favourable for catalysis. If, however, too much sulphur is present, it will screen the nickel surface, and the activity of the latter will fall.

8. Poisoning of a catalyst results from screening of its surface, the molecule of the poison preventing the reactants from coming into contact with the catalyst. Since chemical forces have a small range of action, the catalytic effect cannot develop. Maxted's remarkable investigations[49,50] serve to illustrate this principle. As Garner has pointed out[51], Maxted's results are explained by the multiplet theory.

9. The multiplet theory envisages the adsorption of molecules at two points, the deformation of bonds accompanying adsorption resulting, in the limit, in their dissociation. Taylor's discovery of activated adsorption, which has played such a large part in the theory of catalysis, has in essence confirmed this prediction. However, such far reaching adsorption does not always assist catalysis (see above).

10. Since the indicial atoms are not attached to the catalyst at the same time, free radicals formed as a result of too great a deformation of the bonds may migrate from one hollow to another if the activation barriers to migration are not too high. The migration of radicals may lead to the establishment of surface chain reactions. These will be especially probable in the case of the more stable free radicals, such as the methylene radical $:CH_2$ (see Section 5).

11. Another possible molecular movement along the catalyst surface is that of the intermediate activated complex, *i. e.* of the distorted molecule together with atoms of the catalytically active centre, either as a whole or in part. The conditions necessary for such motion were examined in Ref. 52. When the complex breaks down, the material of the catalyst proves to have been transported to another point on the surface, where new crystals with new faces (although with the same lattice) may be formed on crystallisation. It is evident from this mechanism that such transport can take place only during a catalytic reaction, but not when the catalyst is heated in an inert atmosphere to the temperature at which the catalytic reaction occurs. This phenomenon had been known previously[46,53,54] and was termed "catalytic corrosion" by Roginskii *et al.*[55], who investigated it by means of the electron microscope. Thus the multiplet theory also explains catalytic corrosion.

12. Since the surface of the catalyst is non-uniform, different portions of it should possess different catalytic and adsorptive activities. This conclusion follows from the multiplet theory (*cf.* Section 1).

Sites of maximum catalytic activity should not coincide with those of maximum adsorptive activity (for details see Ref. 56, crater-shaped curves). Therefore the particular fact that in an electron microprojector the last traces of gas can be removed from the metal only under a very high vacuum, while catalysis takes place at a higher pressure[32], does not contradict the multiplet theory. It does not at all follow from these experiments that the whole surface is covered with a gas film, but only that there are portions of the surface which are most difficult to free from adsorbed gas. However, such portions should play practically no part in catalysis, which is effected by other sites exhibiting less strong adsorption.

13. According to all that has been said above, several layers must be distinguished[11,57] in the multiplet active complex (Fig. 3). Starting from the catalyst outwards, these layers will be: (I) catalyst atoms surrounding the active centre; (II) catalyst atoms forming the multiplet; (III) atoms of the indicial group, within which the valence bonds are redistributed from the position characteristic of the starting materials to the position characteristic of the reaction products; (IV) extraindicial substituents, groups which remain unchanged during the reaction and in general are not in contact with the catalyst; (V) molecules adsorbed on the catalyst by van der Waals forces; and (VI) the adjacent layer of solvent (in the case of solutions), or in general the layer within which the starting materials and the reaction products diffuse to and from the catalyst respectively. The interface passes between layers II and III, which govern the course of the catalytic reaction. Layers I and IV exert symmetrical effects on the reaction, which are due to the influence of neighbouring atoms on the reactant atoms: in layer I the influence of the nature, number, and rearrangement of the atoms adjacent to those of the active centre of the catalyst, and in layer IV the influence of the nature and structure of the extraindicial side-chains.

14. The most important consequences following from the premises of the multiplet theory are the principles of structural and energetic conformity between reactant molecules. These principles enable us to obtain the most concrete results.

4. STERIC FACTORS. STRUCTURAL CONFORMITY

a. Duplet Reactions

Exchange of deuterium and hydrogenolysis. The simplest duplet reactions are those involving hydrogen: the high-temperature *ortho–para* conversion [group (4.1)], the reaction $H_2 + D_2 = 2HD$ [(4.2)], and exchange of deuterium with ammonia [(4.3)] and with hydrocarbons [(4.4)]:

$$\begin{matrix} H & H \\ | & | \\ H & H \end{matrix} \quad (4.1); \qquad \begin{matrix} H & D \\ | & | \\ H & D \end{matrix} \quad (4.2); \qquad \begin{matrix} N & D \\ | & | \\ H & D \end{matrix} \quad (4.3); \qquad \begin{matrix} C & D \\ | & | \\ H & D \end{matrix} \quad (4.4)$$

[*cf.* group (1.2)]. Of the three mechanisms suggested for reactions (4.1) and (4.2) (the Bonhoeffer–Farkas, Langmuir–Hinshelwood, and Eley–Rideal mechanisms) the

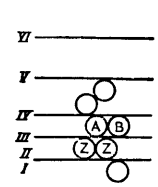


Fig. 3. Layer structure of activated complex.

second[58], which is consistent with the multiplet theory[59] (*cf.* Ref. 60), is the most probable according to the most recent kinetic data.

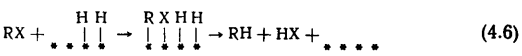
Exchange of deuterium with ammonia is effected by an indicial group analogous to (4.2) with H replaced by N. Owing to the pyramidal shape of NH_3, the remaining two hydrogen atoms should not, according to the multiplet theory, be in contact with the surface, and the molecule must be rotated for them to be exchanged for deuterium.

In the exchange of deuterium with saturated hydrocarbons, the indicial group (4.4) is closest[23] to the Farkas mechanism[61] (corrected for deformation of the molecules). The extraindicial substituents can vary. Thus we have investigated[62] the exchange of deuterium in cyclohexane on Pt and on Cr_2O_3; according to the multiplet theory, the ring is involved here at only one carbon atom. For a detailed review of deuterium exchange in hydrocarbons see Kemball[63].

A further complication of the indicial group (4.1) will be that of hydrogenolysis, in which not one but now two atoms are different from hydrogen. Thus the indicial group for hydrogenolysis of the C–C bond is

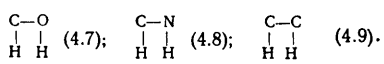
 (4.5)

Incidentally, we may note that Burwell's scheme[31] for hydrogenolysis

 (4.6)

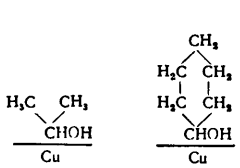
is the same as (4.5), the asterisks corresponding to the hollows V and W (*cf.* Fig. 5).

Dehydrogenation. Dehydrogenation reactions also involve two hydrogen atoms in the indicial group, as well as an additional, horizontal bond (which is converted into a double bond during the reaction); the reaction is unimolecular, and therefore more convenient for kinetic study. Such reactions have been investigated in the author's laboratory[7]. The indicial groups for the dehydrogenation of alcohols, amines, and hydrocarbons by the duplet mechanism are respectively



The role of molecular orientation and interatomic distances has been studied in these catalytic reactions.

The rate of dehydrogenation of primary alcohols on precipitated and reduced copper has been shown[64] to be almost independent of chain length, in agreement with previous investigations[21,65-67]. However, it differs for primary and for secondary alcohols. As had been found earlier[68], isopropyl alcohol and cyclohexanol, which differ only in the "superstructure" of the latter, were dehydrogenated at similar rates, indicating that they have the same orientation:



A benzene ring greatly affects the reaction velocity. All this is consistent with theory[69].

A change in the nature of the metal catalyst (having the lattices A1 and A3) greatly influences the rate of dehydrogenation and the activation energy ϵ. The latter is found to depend on the interatomic distance or atomic radius, as is to be expected from the multiplet theory. This relation proves to be linear (see Fig. 4).

In agreement with the multiplet theory, experiment shows that, on oxide catalysts as well, alcohols are oriented with their reactive group >CHOH [see indicial group (4.7)] towards the dehydrogenating catalyst. This is evident from the identity of the true activation energies of dehydrogenation ϵ, and also of the relative adsorption coefficient z of primary alcohols, and the identity of ϵ and z for secondary alcohols. This question has been dealt with most thoroughly in Refs. 70–77. Thus the values of ϵ for primary alcohols of the normal series are (in kcal mole^{-1}): C_2H_5OH 15.9, C_3H_7OH 15.6, C_4H_9OH 16.3, $C_5H_{11}OH$ 15.4, $C_6H_{13}OH$ 15.6, $C_7H_{13}OH$ 15.3, $C_8H_{15}OH$ 15.6, and $C_9H_{17}OH$ 15.3; the corresponding values for secondary alcohols are: isopropanol 12.8, butan-2-ol 11.3, 2,4-dimethylpentan-3-ol 11.5, and octan-2-ol 13.2.

The present writer has suggested[6,10] for the dehydrogenation of alcohols a duplet stereochemical model, which is suitable also for other duplet dehydrogenations, those of amines and hydrocarbons, and also the reverse reactions on Pt, Pd, Ni, etc. As an example, Fig. 5 shows a scale model for the dehydrogenation of primary n-butyl alcohol on Cu; both the reactant molecule and catalyst lattice are represented in accordance with what is known about them from the theory of the structure of matter. In conformity with the multiplet theory, the indicial atoms >CHOH [*cf.* (4.6)] are in contact with the catalyst, the extraindicial substituent C_3H_7 being oriented perpendicular to the surface. During catalysis the indicial atoms fall into hollows between the copper atoms arranged in the (111) phase of the A1 lattice. Fig. 5 shows the instant when one hydrogen atom has already split off from the carbon and passed into the adjacent hollow. The residue forms the so-called semi-hydrogenated form. The second hydrogen atom performs stretching vibrations along the C–H bond parallel to the surface, which, if their amplitude exceeds a certain limit, result in this atom being split off and subsequent combination with the first hydrogen atom. The splitting off of the second hydrogen corresponds to the energy barrier of the overall reaction of dehydrogenation;

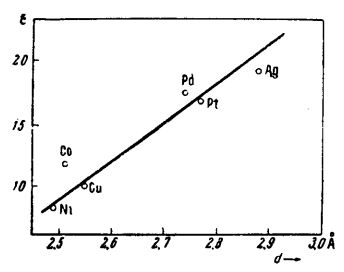


Fig. 4. Interatomic distances d and activation energies ϵ in the dehydrogenation of propan-2-ol.[69]

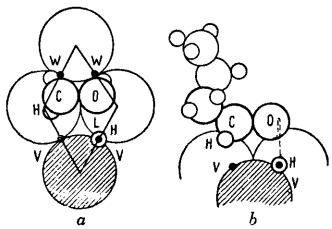


Fig. 5. Model of activated complex in the duplet dehydrogenation of n-butanol on nickel: *a*) viewed from above; *b*) side view.

in Fig. 5 it is shown as a broken line, and is represented by Eqn. (2.1). In general, one of the catalyst atoms may differ from the others. The hollows will then also differ, and may be denoted by V and W (see Fig. 5). The separate stages in the reaction are represented schematically by the equations

$$\left.\begin{array}{ll} (a) & RHCHOH + V_2W_2 = RHCHOV + HW + VW, \\ (b) & RHCHOV + VW = RHVOV + HW, \\ (c) & RHCVOV + 2HW = RHCO + H_2 + V_2W_2. \end{array}\right\} \quad (4.10)$$

Eqns. (4.10) suggest complete rupture of the bonds, but this is a limiting case. The falling of the indicial atoms into the deeper pit L (Fig. 5) corresponds to activated adsorption. The model illustrated by Fig. 5 satisfies the principle of constancy of bond angle (see p. 597), enables calculations to be made on the basis of the theory of absolute reaction rates, and gives a good indication of the various features of the theory of hydrogenation based on the multiplet theory[78-83].

The present writer and Vasyunina[84-86] investigated the kinetics of the dehydrogenation of aliphatic amines to ketimines, which they had discovered:

$$R_1R_2CHNH_2 \rightarrow R_1R_2C{=}NH + H_2. \quad (4.11)$$

The reaction takes place over Pt, Ni on Al_2O_3, and over ThO_2; ϵ also remains quite constant on a given catalyst. Thus the values of ϵ for 1-methylhexylamine, 1,3-dimethylbutylamine, 1-isopropyl-2-methylpropylamine, and *NN*-dimethyl-1-methyltetramethylenediamine are respectively (in kcal mole^{-1}): 9.72, 9.92, 9.14, and 11.4 over Pd, and 9.37, 9.55, 8.68, and 10.73 over Ni. This indicates an identical orientation of the indicial group $\rangle$CHNH towards the catalyst.

The present writer and Brusov[87] were the first to discover the ability of oxides (Cr_2O_3 and MoO_2) to effect the dehydrogenation of cyclohexane in high yield, above 70% (Lazier and Vaughen[88] had previously found that this reaction occurs to the extent of 3% on Cr_2O_3). Cyclohexene is first formed[87], and is then further dehydrogenated, yielding benzene as the final reaction product. The presence of cyclohexene, first detected from the decolorisation of bromine and permanganate[87], was then demonstrated by converting the compound into 2-methoxycyclohexylmercuric chloride[89]. A thorough investigation of the duplet dehydrogenation of cyclohexane over Cr_2O_3 was carried out by Herington and Rideal[90]. That cyclohexene is an intermediate and not a side product was first demonstrated by the fact that, with rise in temperature, its yield increases and then falls[91,92]. In this respect a rise in temperature is to some extent analogous to a decrease in the reaction time. The intermediate character of the formation of cyclohexene has been finally demonstrated quite recently by tracer experiments (using ^{14}C).[93] This work showed that at least part of the benzene formed in the dehydrogenation of cyclohexane over chromium oxide results from dehydrogenation of the intermediate cyclohexene (the rest of the benzene is formed on crystalline Cr_2O_3 by the mechanism discussed at the end of subsection *b*.). Hence in these cases cyclohexane is dehydrogenated by a duplet mechanism in conformity with the indicial group (4.8). A model of the duplet dehydrogenation of cyclohexane is illustrated in Fig. 6.

Kinetic studies[94-96] have shown that substituted cyclohexanes are dehydrogenated in a similar manner to the unsubstituted compound, with very similar activation energies. This indicates edgewise orientation of the ring with the indicial group towards the catalyst. Thus the values of ϵ for cyclohexane, methylcyclohexane, and 1,3-dimethylcyclohexane over Cr_2O_3 are respectively (in kcal mole^{-1}) 25.9, 23.7, and 22.2, the values for tetralin and 1,2,3,4-tetrahydro-6-methylnaphthalene being 29.7 and 30.4.

Five-membered rings as well as six-membered rings are capable of dehydrogenation by an edgewise duplet mechanism. The present writer and Fedorov[97] showed that, on chromium oxide, cyclopentane is dehydrogenated under the same conditions as cyclohexane. After this it was natural to study the dehydrogenation of open-chain alkanes and alkenes, as well as of alkylbenzenes over chrome catalysts, which reactions were investigated in our laboratory. Products of these reactions are important as monomers for the synthesis of rubber from petroleum gases. Similar reactions had been studied for several years before this in the USA (for a review, see Ref. 98). In contrast to this work, however, we were successful in achieving higher yields, studying the kinetics, and effecting the first catalytic preparation of several monomers (the early work is reviewed in Ref. 99). The model for the dehydrogenation of butane, for example, is analogous to that for the duplet dehydrogenation of cyclohexane (Fig. 6, but without the upper two carbon atoms). The indicial group is in all cases the same [(4.9)]. Such reactions include the preparation of butene from butane and similar reactions[100-102], of butadiene from butene[103-114], isoprene from isopentenes[115,116], isopentenes from isopentane[117], of piperylene[118], vinylcyclohexane[119], etc.

We have also studied[120-137] the preparation of styrene and its analogues: *o*-, *m*-, and *p*-divinylbenzenes, trivinylbenzene, isopropenylbenzene, *p*-diisopropenylbenzene,

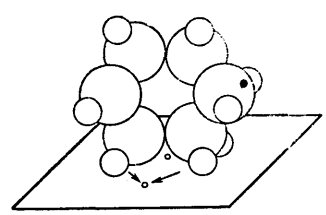


Fig. 6. Edgewise orientation of cyclohexane during dehydrogenation.

p-methylstyrene, mono- and di-butenylbenzenes, 1,1-diphenylethylene, stilbene, etc. We have recently extended these reactions to the preparation of monomers containing oxygen, sulphur, and what is especially interesting, silicon: *o*-vinylphenol, *o*-isopropenylphenol, *o*-isobutenylphenol, 2-vinylthiophen, 2-isopropenylthiophen, 1-methyldichlorosilyl-2-vinylphenylethane, etc.[138-141] It is interesting that the presence of an unsaturated bond or an aromatic ring outside the indicial group markedly changes the character of the dehydrogenation and the nature of the catalysts required. Conjugation energy is playing a part here. It must be noted that the ring takes no part in any of these reactions, and consequently is not superposed on the duplet.

The opposite reaction to hydrogenolysis is dehydrogenation accompanied by formation of a C–C (or other similar) bond between two molecules having the indicial reaction group

$$\begin{matrix} C & C \\ | & | \\ H & H \end{matrix} \qquad (4.12)$$

An example is provided by the formation of biphenyl from benzene:

$$2C_6H_6 = C_6H_5{\cdot}C_6H_5 + H_2. \qquad (4.13)$$

If both C atoms in the above indicial group form part of the same molecule, we have dehydrocyclisation, an example being the formation of fluorene from diphenylmethane over platinum[142].

A special case is the dehydrocyclisation of paraffins, which is a complicated process analogous to the preceding reaction, involving the formation of aromatic hydrocarbons by dehydrogenation of intermediate six-membered rings[143-146]. Recently, dehydrocyclisation has been extended to the formation of five-membered rings from paraffins with the production of cyclopentadiene hydrocarbons[147,148]. For the mechanism of these reactions, see Section 4*b*.

The aromatisation of branched paraffins, involving the transient formation of five-membered rings, has been considered from the point of view of a duplet mechanism[149].

Hydrogenation. A reaction which is opposite to dehydrogenation is the hydrogenation of unsaturated bonds. The indicial group for the hydrogenation of an olefinic bond is

$$\begin{matrix} C & H \\ \| & | \\ C & H \end{matrix} \qquad (4.14)$$

The multiplet reaction model is the same as in Fig. 5, but the stages take place in the reverse sequence.

A very interesting rule was found in the hydrogenation of olefines — the principle of conservation of bond angle. The principle states that, when one bond of a C=C link chemisorbed on two catalyst atoms Z is opened (see Fig. 7*a*), the bond angle should be close to the tetrahedral value $\theta = 109°$. Since the C–C and C–Z distances are known from the atomic radii, the optimum interatomic distance Z–Z of the catalyst can be calculated on this basis. This is found to correspond to metals from Pt to Fe, including not only metals crystallising in the A1 and A3 systems but also those in A2 and other systems. These metals are indeed catalytically active in the hydrogenation of the C=C bond.

Twigg and Rideal, in enunciating[150] the principle of conservation of bond angle, regarded it as applying to the final state, the paraffin hydrocarbon. The present writer and Eidus[151] showed that this principle should apply to the intermediate activated complex, and that it is completely

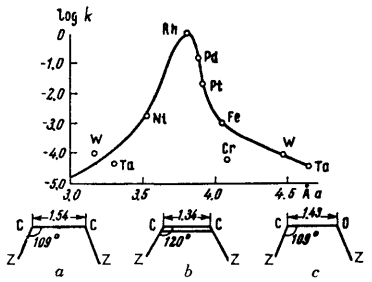


Fig. 7. Reaction velocity constant k and lattice constant a of metal catalysts in the hydrogenation of ethylene[153]. Interatomic distances in the hydrogenation of different types of bond: *a*) olefinic; *b*) acetylenic; *c*) carbonyl.

derivable from the multiplet theory, providing an important confirmation of the principle of structural conformity in the latter.

For the dehydrogenation and hydrogenation of hydrocarbons, the oxygen atom in the activated complex shown in Fig. 5 should be replaced by carbon. If on the resulting diagram the centres of the right-hand and left-hand catalyst atoms are joined with the centres of the carbon atoms in contact with the catalyst, and if the straight lines C–C and Z–Z are drawn, it is readily seen that the same trapezium is obtained as in Fig. 7*a*. Its upper angles will also be 109°, although the plane of the trapezium will be inclined to that of Fig. 5. Thus the model illustrated in Fig. 5 also satisfies the principle of conservation of the bond angle.

Beeck *et al.*[152] investigated the kinetics of the hydrogenation of ethylene on films of various metals condensed on the surface of a quartz tube, and found a relation between the lattice constant (which is proportional to the interatomic distance) and the logarithm of the rate constant for the hydrogenation. Fig. 7 shows a maximum at rhodium. As Beeck points out[153], this result supports the multiplet theory. Recently Sokol'skii[154] has discovered a similar maximum at rhodium for metallic promoters in the liquid-phase hydrogenation of cinnamic acid on Ni containing additives.

Beeck[153] considered, on the basis of electron diffraction patterns, that the (110) faces were the most active in catalysing the hydrogenation of ethylene. Later, however, Sachtler *et al.*[155], using an improved technique, showed that the (110) faces in Beeck's metallic mirrors were adjacent to the quartz, while the (111) [and to some extent the (100)] faces are turned towards the gas; this is consistent with the multiplet model in Fig. 5.

The principle of constancy of bond angle was subsequently applied by several workers, mainly English and American (see Balandin and Eidus' review[156] and also Refs. 157 and 158). Herington[158] carried out for acetylene geometrical calculations similar to those for ethylene, the bond length between the carbon atoms being smaller in the former than in the latter, while the bond angle is greater (Fig. 7*b*). The calculated activity maximum no longer occurred at rhodium but at nickel. According to Herington[158], this agrees with experiment.

From the Rh–Rh distance, which is optimum for the hydrogenation of the C=C bond, we have calculated[159] the optimum distance d_{opt} for hydrogenation of the carbonyl bond C=O, which is shorter than with C=C (Fig. 7*c*):

$$\begin{array}{l} \text{C—C } 1.54 \\ \text{C—O } 1.43 \\ \hline \Delta = 0.11\text{Å} \end{array} \quad \begin{array}{l} \text{Rh—Rh } 2.69 \\ \Delta = 0.11 \\ \hline d_{opt} = 2.58\text{Å} \end{array} \qquad (4.15)$$

Among metals which are insoluble in acids, ruthenium with d = 2.65 Å (*cf.* Table 2) approaches this optimum most closely. Thus the calculated maximum activity for hydrogenation of the C=O bond now occurs at ruthenium. This result has been confirmed experimentally, and provides a theoretical basis for the hydrolytic hydrogenation of cellulose[159,160]. The process consists in the consecutive hydrolysis and hydrogenation of cellulose to sorbitol, and of pentosans to xylitol, with a ruthenium catalyst in acid medium (yield up to 95%). We subsequently showed that lignin can also be hydrogenated over ruthenium in alkaline solution in this case, up to 35% of phenols being obtained[161]. This opens a new field in the chemical processing of wood[162,163] which is abundant in our country (*cf.* Ref. 164). From sorbitol[165] and xylitol[166], glycerol can be obtained by hydrogenolysis over nickel.

It has been shown experimentally[167] that rhodium is especially suitable for the hydrogenation of olefines and aromatic rings, and ruthenium for C=O bonds, in particular one formed by the hydrolysis of disaccharides; the higher polysaccharides were not considered. Thus this paper[167], printed a little after our first publication on ruthenium[159], supports our conclusions.

Dehydration. Let us now examine the dehydration of alcohols to olefines, for which the indicial group is

$$\begin{array}{l} \text{C—C} \\ \text{H O} \end{array} \qquad (4.16)$$

There probably exist three types of catalytic dehydration reactions. One type, the heterolytic, involves the intermediate formation of a carbonium ion[168], where the hydrogen ion acts as the catalyst. Thus phosphoric acid is the classic catalyst for the preparation of ethylene from alcohol. Incidentally, we were the first to use phosphoric acid on activated carbon[169,170], a procedure which has now become widespread.

TABLE 1. Comparison of atomic and ionic reaction mechanisms.

Reactant	Atomic exchange, %*	Ionic exchange	
		k	ϵ, kcal mole^{-1}
CH_3I	0.03	1200	15.4
$(CH_3)CH_2I$	0.05	65	19.0
$(CH_3)_2CHI$	1.4	10	20.5
		Atomic exchange	
CH_3CH_2OH		28.4*	20.2
$CH_3CH_2CH_2OH$		55.4*	18.3
$(CH_3)_2CHCH_2OH$		52.7*	16.4

* At 350°.

According to Hansford[171], the carbonium ion on the surface is not free, but is "merely a strongly polarised part of the catalytic complex". This suggests deformation and that the steric factor is important in such cases also, but the question has not yet been elucidated.

Another mechanism is the homolytic, where aluminium oxide and similar oxides act as catalysts. It is supported by the following facts. As is now known, the catalytic cracking of hydrocarbons is effected on portions of the catalyst which possess the properties of a Brønsted or Lewis acid, the catalytic activity with respect to cracking and the acidity varying together. Topchieva and Yung-p'ing[172] found that, in mixed $Al_2O_3-SiO_2$ catalysts of various compositions, the catalytic activity for the cracking of cumene and that for the dehydration of alcohol do not vary together, cracking being quite a feeble reaction on pure Al_2O_3. Hence the dehydration of alcohol is not due to the acidic properties of Al_2O_3.[172] Another argument is based on the finding of Neiman *et al.*[173], in an investigation of exchange reactions using radioactive halogens,

$$R\,Br + Br^{*-} = R\,Br^{*} + Br^{-}, \qquad (4.17)$$

$$RI^{*} + I^{-} = R^{-} + I^{*}I, \qquad (4.18)$$

that as the radical R becomes more complicated, the reaction velocity constant k falls and ϵ increases in the case of the heterolytic reactions (4.17), whereas k increases and ϵ decreases in the homolytic reactions (4.18). Comparison[52] with Bork and Tolstopyatova's results[43,174] shows (see Table 1) that dehydration on Al_2O_3 belongs to the homolytic, not the heterolytic, type of reactions, since k increases and ϵ decreases in this case.

The third mechanism, which is observed under special conditions at low pressures probably involves free radicals (see Section 5).

We shall consider only the second mechanism here. Unfortunately, the mechanism of dehydration has not yet been sufficiently elucidated for it to be possible to give a model similar to that illustrated in Fig. 5. It is probable that, just as dehydrogenation passes through a semi-hydrogenated form, so also dehydration goes through a similar unstable form. According to Topchieva[175], this is a surface alkoxide, which is converted into ether or ethylene depending on the conditions. The fact that the intermediate product in the formation of ethylene is not bulk aluminium ethoxide, as Sabatier[176] supposed, was demonstrated by the present writer and Shchekin[23]: aluminium ethoxide decomposes under different conditions, and yields different products, from those observed with alcohol on catalysis on Al_2O_3.

In the opinion of several workers, the primary product (observed at lower temperatures) of the dehydration of ethyl alcohol on Al_2O_3 is ethyl ether, which is then converted into ethylene (observed at higher temperatures). Other workers assume that formation of ethylene and ether takes place simultaneously (for review, see Ref. 177). A tracer method using ^{14}C atoms has shown[178] that ethylene can be formed from alcohol by two pathways, directly at high temperatures, and *via* ether at lower temperatures; quantitative relations have been found between the corresponding reaction velocities. In this way a long-standing controversy between different groups of investigators has been settled.

The fullest data on the effect of the structure of alcohols on their dehydration (on Al_2O_3) were obtained by Bork and

Tolstopyatova[43,174]. As with dehydrogenation, ϵ is constant for the dehydration of primary alcohols, its value being 18.0 kcal mole^{-1}. This indicates that the indicial group $\rangle$CHCO has the same orientation towards the catalyst.

Similar results have now been obtained for W_2O_5 [179] (the earlier data of Adadurov and Krainii[180] for W_2O_5 have been corrected), and also for CeO_2 [181] and ThO_2.[182]

The activation energy shows great constancy also in the dehydration of secondary alcohols over $MgSO_4$. Cyclohexanol, cyclopentanol, pentan-2-ol, and propan-2-ol were investigated, their percentage dehydration at 370° being 17.7, 17.8, 18.0, and 18.8, while the values of ϵ were 15.0, 14.4, 15.2, and 14.8 kcal mole^{-1} respectively. This also suggests an identical orientation of the molecules, with the indicial group $\rangle$CHCO towards the catalyst[183].

We have investigated[184-186] the influence of β-rays, emitted by isotopic impurities ^{35}S and ^{45}Ca in $MgSO_4-Na_2SO_4$ and $MgSO_4-CaCl_2$ solid catalysts, in the dehydration of cyclohexanol. The catalytic activity of $MgSO_4$, already an active dehydration catalyst, was almost doubled thereby. During the discussion of this work[187] at the Second International Congress on Catalysis it turned out that similar results had been obtained at the Oak Ridge National Laboratory of the U.S.A.E.C.[188] As we had found, the increase in catalytic activity caused by radioactivity becomes smaller as the latter falls (Fig. 8) not only because of change in the concentrations of ^{35}S and ^{45}Ca introduced, but also because of decay of an existing additive. Exposure to high-energy fast electrons (1.5 MeV) of high intensity has no effect. The present writer has suggested[189] the following explanation for the observed facts. Fast electrons release electrons from the catalyst atoms by impact, and the electron current increases like an avalanche. If the electrons are moving from the solid through the surface, this cascade passes into the gas phase, and the surface acquires a positive charge. This favours the formation of carbonium ions on the surface, and consequently accelerates catalytic dehydration (by a heterolytic mechanism). If the electrons are moving in the opposite direction,

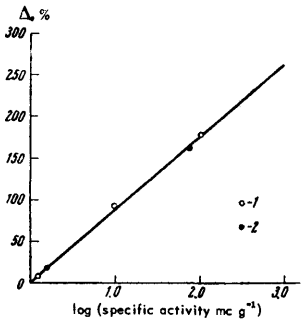


Fig. 8. Increase in degree of dehydration (Δ, %) of cyclohexanol and logarithm of the specific radioactivity of catalysts:
1) experiments with different contents of ^{35}S introduced during preparation;
2) experiments with an ^{35}S content which has decreased owing to radioactive decay (after 314 and 184 days)[185].

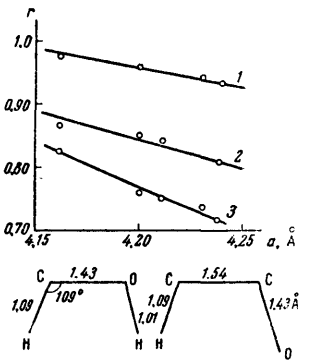


Fig. 9. Above: ratio r of percentage dehydrogenation to sum of percentage dehydrogenation and dehydration of n-butanol as a function of the lattice constant a of MgO: 1) 400°; 2) 440°; 3) 460°.[190] Below: interatomic distances in the catalytic reactions of alcohols: dehydrogenation on the left, and dehydration on the right-hand side.

almost the whole cascade remains within the solid, and the charge on the catalyst does not change. Therefore the reaction velocity is unaffected.

Rubinshtein carried out a remarkable kinetic and X-ray diffraction investigation of the catalysis of alcohols on MgO,[190] the main reactions being dehydrogenation and dehydration. The MgO (with an NaCl type of structure) had a lattice constant a which varied somewhat with the method of preparation. It was found that for greater a, *i.e.* the distance between the catalyst atoms, dehydration was more marked relative to dehydrogenation (Fig. 9, upper part). The interatomic distances in the indicial groups are greater for dehydration than for dehydrogenation (Fig. 9, lower part). There exist optimum interatomic distances for these reactions. In this way we have here an important confirmation of the principle of structural conformity in the multiplet theory.

A similar phenomenon was observed[191] for the catalysis of alcohols on the pentoxides of vanadium, niobium, and tantalum. The increase in atomic radius in the sequence vanadium (1.36 Å), niobium (1.47 Å), tantalum (1.49 Å) is accompanied by an increase in dehydration relative to dehydrogenation.

Recently Rubinshtein *et al.*[192] have observed a maximum, analogous to that observed previously[190] for the dehydration of isopropyl alcohol over Ni on Al_2O_3.

In concluding the section on duplet reactions, let us consider an example of work in which the ideas of the multiplet and the electronic theories of catalysis are applied together.

Dowden *et al.*[193] investigated deuterium–hydrogen exchange on zinc oxide. According to their results, a lattice defect possesses four F-centres, which are able to adsorb both hydrogen and deuterium, this being the condition for catalytic activity. Fig. 10 shows the chemisorption of hydrogen and deuterium on an F-centre of zinc oxide, where the missing oxygen ion has been replaced by two electrons. Due to an increase in the number of defects,

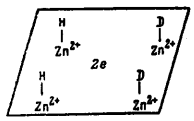


Fig. 10. Catalytically active F-centre in the exchange of deuterium and hydrogen on zinc oxide[193].

the oxide becomes increasingly n-type, which increases the electrical conductivity and promotes catalysis, in agreement with experiment.

The present writer and Sokolova[194] investigated the catalysis of alcohols by tungsten bronzes which have a defect structure. An X-ray structure analysis was also made. In spite of the presence of a defect structure, the tungsten bronzes showed little catalytic activity, in contradiction to the electronic theory of catalysis. However, the catalytic activity decreases as the bronzes are reduced and as lithium is added, in conformity with this theory; the number of defects in the structure also falls at the same time. The electron-diffraction patterns and the B.E.T. data show that the surface of the bronzes remains practically unchanged during reduction. On the other hand, the multiplet theory explains the low activity of the bronzes by the fact that structural conformity is not particularly well satisfied (the difference amounts to 16%). Fig. 11 shows how the molecule fits (the C–C of the alcohol as in ThC_2, the H of the alcohol in the Na defect, and the O of the alcohol replacing the reduced O of the bronze). Simultaneous application of the multiplet and the electronic theories of catalysis enables most of the facts observed here to be explained.

Natta[195] discovered stereospecific polymerisation, leading to the formation of isotactic chain polymers of α-olefines, in the presence of heterogeneous catalysts and activators, and explained it by oriented adsorption. But the latter is a necessary requirement of the multiplet theory, according to which the reactant atoms should be in contact with the surface, and substituents should all be located on the same side, away from the surface[9,196]. According to Natta the electronic structure — the work function and other electronic properties — also plays a large part in stereospecific polymerisation.

Electron, geometrical, and structural considerations are combined also in crystal field theory and in its recent promising application to catalysis[197].

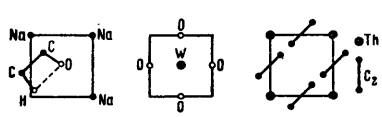
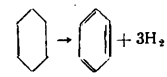


Fig. 11. Lattice of tungsten bronze and arrangement of reactant atoms on it during the dehydration of alcohol. On the right: the (100) face of the ThC_2 lattice.

Triplet reactions are known in catalysis (it is sufficient to recall the 1,4-addition of hydrogen to some dienes), but we shall not consider them here, since little work has been done on them.

b. Sextet Reactions

A sextet model was first developed in the multiplet theory for the dehydrogenation of cyclohexane and its derivatives,



(4.19)

discovered by Zelinskii[198]. The reaction takes place over metallic catalysts at about 300°. A sextet model is illustrated in Fig. 12, which shows it in perspective and in plan. Migrations of hydrogen atoms are indicated by arrows. There is a correspondence between the symmetry elements of the molecule and of the catalyst; the six-membered ring is laid flat on the face with the atoms arranged in equilateral triangles, thus satisfying principles similar to those indicated above. The reaction product, benzene, has a planar configuration, and therefore at some instant during its formation the ring must become planar; according to the sextet model this flattening occurs during the formation of the activated complex in the dehydrogenation of cyclohexane. The model for the reverse reaction, the hydrogenation of benzene at lower temperatures, has a similar form.

The model suggests that only metals (not metalloids) and then only those crystallising in the cubic (face-centred cubic, lattice A1) and in the hexagonal (lattice A3) systems, can act here as catalysts, since it is only on the octahedral faces of the former and on the basal pinacoid faces of the latter that the required arrangement of atoms, in the form of equilateral triangles, is found. Moreover, the shortest interatomic distances in the catalytic metals, which are equal to the atomic diameter d, should lie within definite limits. Otherwise, as a geometrical calculation shows[3], the hydrogen atoms in the cyclohexane will either be too distant from the catalyst atoms which are attracting them, or will not allow the ring to lie on the lattice face. Table 2, compiled[199] from recent data[200], gives a list of the elements crystallising in the A1, A2, A3, and A4 systems with an indication of their shortest interatomic distances (elements crystallising in more complicated systems, and also forms crystallising above 800° where the catalysts are known to sinter, are omitted from Table 2).

It is seen from Table 2 that elements which are known catalysts for the dehydrogenation of cyclohexane and its

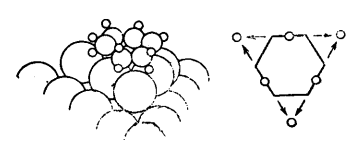


Fig. 12. Sextet model for the dehydrogenation of cyclohexane.

TABLE 2. Types of crystal lattice and minimum interatomic distances (atomic diameters) d in Å.

Face-centred cubic lattice A1	Body-centred cubic lattice A2	Hexagonal lattice A3	Diamond lattice A4
α-Ca 3.947	Cs 5.309	β-Sr 4.32; 4.324	α-Sn 2.8099
Yb 3.880	Rb 4.95	α-La 3.739; 3.770	Ge 2.4498
γ-Ca 3.877	K 4.544	Nd 3.628; 3.658	Si 2.3517
Ac 3.756	Ba 4.347	Gd 3.573; 3.636	C 1.5445
β-La 3.745	γ-Sr 4.20	Y 3.551; 3.647	
Ce 3.650	Eu 3.989	Tb 3.525; 3.601	
α-Pr 3.649	Na 3.7157	Dy 3.503; 3.590	
α-Th 3.595	β-Tl 3.362	Ho 3.486; 3.577	
δ-Pu 3.279	ε-Pu 3.150	Er 3.468; 3.559	
Sc 3.212	Li 3.0390	Tm 3.447; 3.538	
Ag 2.8894	Ta 2.86	α-Te 3.4076; 2.4566	
Au 2.8841	Nb 2.8584	Lu 3.435; 3.503	
Al 2.8635	W 2.7409	α-Po 3.345;	
Pt 2.7746	Mo 2.7251	Sc 3.256; 3.309	
Pd 2.7511	V 2.6224	Mg 3.1971; 3.2094	
Ir 2.714	Cr 2.4980	α-Zr 3.1790; 3.2313	
Rh 2.6901	γ-Fe 2.4823	α-Hf 3.1275; 3.1947	
Cu 2.5560		Cd 2.9788; 3.2933	
Co 2.5061		α-Ti 2.8956; 2.9505	
Ni 2.4916		Re 2.741; 2.760	
		Tc 2.703; 2.735	
		Os 2.6754; 2.7354	
		Zn 2.6649; 2.9129	
		Ru 2.6502; 2.7058	
		α-Be 2.2260; 2.2856	

derivatives are in fact solely metals having lattices of types A1 and A3, with d lying between 2.7746 Å (Pt) and 2.4916 Å (Ni). These elements are enclosed in frames in Table 2. Theory is seen to be fully vindicated. Table 2 shows why Ni, Co, Cu, Rh, Ir, Pd, Pt, Ru, Os, and Re are catalysts for the hydrogenation and dehydrogenation of six-membered ring hydrocarbons, while Ca, Ce, and Fe, for example, are not.

The frames in Table 2 include rhenium, the lattice structure of which was not yet known when the original table[3] was compiled. The prediction of the multiplet theory that rhenium should dehydrogenate cyclohexane, since it is within the frame, has been verified experimentally by Balandin *et al.*[201-203] who also investigated other reactions of this element. The activity of technetium, which is also located within the frame, has not yet been checked.

Whether copper, which is located within a frame in Table 2, catalyses the dehydrogenation of cyclohexane and the hydrogenation of benzene, has given rise to controversy[204,205]. A recent investigation by Erofeev and Nikiforova[206] using infra-red spectroscopy has shown that copper is actually a catalyst for both reactions. This supports the sextet model. The feeble activity of copper is explained by other factors, not structural but energetic[6].

The list of sextet dehydrogenation catalysts contains a smaller number of metals than does the list of metal catalysts whose activity is governed by the principle of constancy of bond angle. In agreement with theory, cyclohexane cannot be dehydrogenated to benzene over manganese, which possesses the more complex structure A12;[207] an olefinic bond is hydrogenated over manganese.

That a reduced iron catalyst, which is active in the hydrogenation of ethylene, is unable to effect the hydrogenation of benzene or the dehydrogenation of cyclohexane has been shown by many investigators, for example in Refs. 208–210. Actually, iron is located outside the frames in Table 2 (for iron films, see below).

According to the sextet model, benzene can be hydrogenated also on solid solutions with an increasing content of one of the metals, but only so long as the required structure (and d) are present. This has been confirmed by simultaneous kinetic and X-ray diffraction measurements on solid solutions of Ni, Co, Fe, Pd, and Ag.[208,209]

Thus the 74.9% Co + 21.7% Fe alloy with an A1 lattice is still active, while the 50% Co + 50% Fe and 24.2% Co + + 75.8% Fe alloys with the A2 lattice are not. Copper formed an apparent exception (see above). Not so long ago Rienäcker and Unger[210] made especially detailed and careful investigations of this type, with X-ray analysis and adsorption measurement of the surface; the results supported the requirements of the multiplet theory. Quite recently Rienäcker and Porubszky[211] found that, in the hydrogenation of propene (which proceeds according to the model in Fig. 5) as well, binary alloys of Ni and Fe of varying composition are active only as long as the nickel structure, *i.e.* A1, is present, which agrees with the multiplet theory.

An important confirmation of the sextet model was obtained by Rubinshtein *et al.*[212], who found that the catalytic activity for the dehydrogenation of benzene falls regularly with decrease in the intensity of the X-ray reflections from the (111) faces of platinum on carbon.

It is not yet clear why iron and tungsten films condensed from the vapours are active in the hydrogenation of benzene, as reported by Anderson and Kemball[213]. This is probably due to different reaction mechanisms on films and on reduced catalysts. Such differences have in fact been observed in other reactions (see Ref. 214 and the note by the editor of the translation in Ref. 213). A duplet mechanism is probably operative here, as in the already known case of the dehydrogenation of ethane on Pd at high temperatures[87,215].

According to the sextet model, the cyclohexane, which is adsorbed flat on the surface, is converted into benzene by all six hydrogen atoms being split off in such a way that the six-membered ring does not leave the active centre until it has been converted into a benzene ring. Therefore no cyclohexene or cyclohexadiene will be present in the gas phase.

The mono- and poly-substituted derivatives are dehydrogenated like cyclohexane itself. It is necessary that all substituents should be oriented on the same side of the plane of the ring. One or more carbon atoms of the six-membered ring may be replaced by nitrogen. Polycyclic systems should behave similarly. All these deductions are confirmed experimentally[216,217]. For the work of Linstead and his collaborators in this field, see Section 6.

Some workers have supposed[218] that cyclohexane is first dehydrogenated to cyclohexene, followed by a far more rapid disproportionation of the hydrogen in the latter, by Zelinskii's so-called irreversible catalytic reaction

$$3\,C_6H_{10} = 2\,C_6H_{12} + C_6H_6, \qquad (4.20)$$

to yield benzene. This is supposed to explain the absence of cyclohexene among the products of the catalysis. Data are now available which refute this view. It has recently been shown[202] that the irreversible catalysis over rhenium takes place more slowly than does the dehydrogenation of cyclohexane to benzene, which disproves a dehydrogenation mechanism involving irreversible catalysis for this case. The fact that cyclohexene is not an intermediate in the dehydrogenation of cyclohexane on rhenium has been shown by

direct radiochemical experiments in which labelled ^{14}C is added as cyclohexene[93]. In view of the similarity of dehydrogenation processes occurring on rhenium and on metals resembling platinum, reaction (4.20) becomes altogether unlikely.

Dehydrogenation of six-membered cycloalkanes (other than geminal forms) to aromatics is greatly favoured thermodynamically, since aromatic compounds are particularly stable owing to the presence of resonance energy (36 kcal mole^{-1} in the case of benzene[219,220]). Therefore six-membered rings can be dehydrogenated at lower temperatures (about 300°) than can other hydrocarbons.

On this basis, Taylor[221] first rejected the sextet mechanism, but later accepted it, and in his article[222] in the book "Chemical Architecture" gives a scheme involving this mechanism together with results obtained by Eyring, Beeck, Rideal, and Pauling. Trapnell[223] has devoted a review to the multiplet theory, in which he gives a detailed and generally correct account of the structural side of the theory, but does not consider its energetic aspects. However, his statement that in this theory the adsorption is supposed to be of van der Waals type is incorrect. His suggested modification of the sextet model was considered by the present writer as early as 1929 (variant III in Fig. 2 in Ref. 3 — see Fig. 13), but was rejected, since there was no longer room geometrically for the hydrogen atoms of the cyclohexane, and therefore the latter could not be superimposed on the catalyst atoms. This can be seen by constructing a three-dimensional model.

An interesting demonstration of the edgewise and planar orientation in different cases was obtained by the present writer and Isagulyants[224]. As we have seen, cyclohexane is dehydrogenated on Ni by a sextet mechanism, and on Cr_2O_3 by a duplet mechanism. This applies also to decalin. It was found that on Ni cyclohexane is dehydrogenated more rapidly than is decalin, which with the planar arrangement occupies more room on the surface (Fig. 14); this proves the planar orientation of the rings on Ni. On chromium oxide cyclohexane and decalin are dehydrogenated at the same rate: here the mechanism is no longer planar but edgewise. With cyclohexane and decalin the values of ϵ are identical both on Ni (12.5) and on Cr_2O_3 (26 kcal mole^{-1}).

Although the aromatic properties of benzene could explain why six-membered, but not other, rings can be dehydrogenated at 300°, this cannot explain why Pt and other similar metals are active in the dehydrogenation of cyclohexane, which is what the sextet model explains. In this connection the sextet mechanism can be tested in another way, by dehydrogenation of seven- and five-membered rings with the formation of non-benzenoid aromatic compounds.

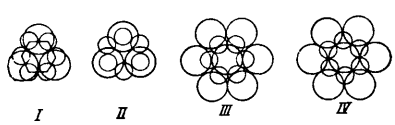


Fig. 13. Four types of planar arrangement of a six-membered ring on the (111) face of an A1 lattice[3].

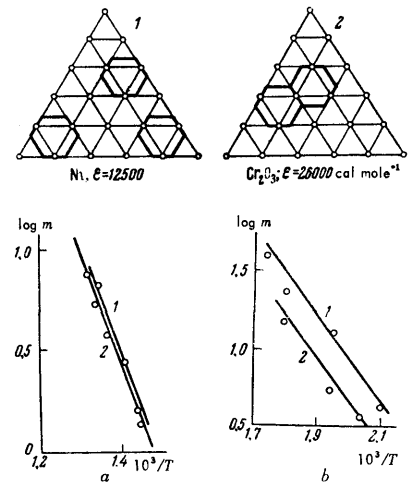
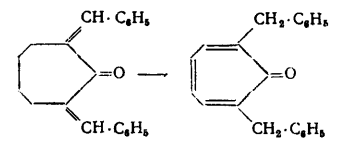


Fig. 14. Arrangement of molecules on the (111) faces of an A1 lattice. Arrhenius plots for dehydrogenation on (*a*) Ni and (*b*) Cr_2O_3 of (1) cyclohexane and (2) decalin[224].

It was found recently[225] that over Pd at 290°, 2,7-dibenzylidenecycloheptanone, is 16% converted, by isomerisation and dehydrogenation, into 2,7-dibenzyltropone, in which the seven-membered ring is aromatic in character:



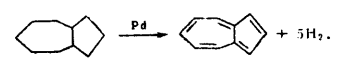
(4.21)

Derivatives substituted in the phenyl groups behave similarly. One H_2 molecule is split off, so that dehydrogenation proceeds here by a duplet mechanism. Incidentally, the isomerisation which precedes dehydrogenation is also a duplet reaction, which is known to occur on Pd; it has the indicial group



(4.22)

A remarkable confirmation of the sextet model is that bicyclo[5, 3, 0]decane is dehydrogenated over Pd to give only low yields of the aromatic hydrocarbon azulene:[226]



(4.23)

Most of the substance decomposes, and azulene is obviously formed by dehydrogenation involving a duplet mechanism. Thus aromatic character, although it does affect catalysis to a certain extent, is nevertheless unable by itself to bring about smooth dehydrogenation, such as takes place in the case of cyclohexane. In order that catalysis should occur, structural conformity is also necessary. Bicyclo[5,3,0]decane, in contrast to cyclohexane, has no symmetry elements in common with the A1 lattice of palladium, and cannot be superimposed on the latter.

The following criteria are available for deciding, in any particular case, by what mechanism, sextet or duplet, dehydrogenation will take place. Firstly, the duplet mechanism operates at higher temperatures. Secondly, formation of cyclohexene is observed with the duplet mechanism. It must not be assumed that at 300° cyclohexene cannot still be present in appreciable amount in equilibrium with cyclohexane. In several of our experiments with a specially prepared rhenium catalyst up to 1.5% of cyclohexene was detected in the dehydrogenation of cyclohexane at about 300°. Thirdly, the true activation energy is higher in duplet reactions (on oxides) than in sextet reactions, reaching 20–40 kcal mole^{-1} compared with 13–18 kcal mole^{-1}. Fourthly, the constant a in the compensation effect[7] is greater with duplet than with sextet dehydrogenation of hydrocarbons (~3.5 compared with ~2.5).

It would be incorrect to suppose that all rings must lie flat on the surface during catalysis. We have already had (Section 4*a*) many examples of edgewise orientation of rings, and of cases in which the rings are not involved, or are only partly involved, in the reaction. The number of such reactions is increased if we consider the dehydrogenation of nicotine and pyrrolidine on platinum,[227] in which a five-membered ring is dehydrogenated by a duplet mechanism; the formation of biphenyl from benzene is another example (*cf.* above).

On the other hand, a case has recently been observed[228] of a new planar orientation of cyclohexane undergoing dehydrogenation on a specimen of chromium oxide which was shown by X-ray diffraction to differ from those studied previously in being crystalline. Here the activation energy is low (13 kcal mole^{-1}), and cyclohexene is not detected, a radiochemical method showing that it is not an intermediate product, since when added at the start it does not react. The reaction model is a variant of the sextet model examined by the present writer as long ago as 1929,[3] without a central metal atom (variant IV in Fig. 13, or, what is the same, Fig. 2 in Ref. 3); in the case of metals variant I in Fig. 2 of Ref. 3, illustrated in expanded form in Fig. 12 of the present review, was preferred.

5. FREE RADICALS ON THE SURFACE

The multiplet theory envisages another orientation of cyclohexane[3] (Fig. 15*a*) in addition to those considered above. The CH_2 parts of the molecule are drawn down into the deepest hollows, situated on the (111) face of the Al lattice, which conform to the CH_2 links in the ring. According to the above, this should lead to activated adsorption, which is often accompanied by bond rupture. Bonds are ruptured here too, and free $:CH_2$ radicals are formed, which can migrate along Lennard-Jones valleys. The $:CH_2$ radical is quite stable, approaching molecules in this respect. Nitrogen-containing rings, such as piperidine and piperazine[3], undergo scission still more readily.

The $:CH_2$ radical was detected experimentally by Zelinskii and Shuikin[229], who obtained from cyclohexane, over nickel under severe conditions, methylcyclohexane, toluene, etc. Eidus and Zelinskii[230] detected methylcyclohexane and toluene in the production of Synthole from water gas in the presence of cyclohexane and benzene, thereby confirming the hypothesis put forward by Orlov, and later by Fischer and Tropsch, that Synthole is formed *via* $:CH_2$ radicals. With hydrogen, $:CH_2$ gives CH_4, and with water CO_2 (or CO) and H_2. According to the multiplet theory[231]

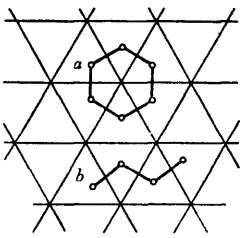


Fig. 15. Arrangement of molecules during their scission into $:CH_2$ radicals on nickel: *a*) cyclohexane; *b*) n-butane.

similar decomposition, for example of butane, with the formation of $:CH_2$ radicals, is represented by the model illustrated in Fig. 15*b*, which is analogous to that in Fig. 15*a*.

The $:CH_2$ radical is obviously also an intermediate in a peculiar type of simultaneous dehydrogenation of hydrocarbons and water discovered in the present writer's laboratory[232]. In this reaction there is a gradual shortening of the hydrocarbon chain by one unit (as in the progressive hydrogenolysis of hydrocarbons[233–235]). This shortening is checked by any structural peculiarity in its path, for example a quaternary carbon atom or a benzene ring; the final reaction products are CO_2 and H_2. Slovokhotova and the present writer[232] showed that such reactions, occurring between organic vapours and water vapour over Ni and other catalysts, are almost as general as, for example, the complete combustion of organic compounds. Reactions occurring under the influence of water vapour which have been studied are chain-shortening in isooctane, isoheptane, and isohexane, the demethylation of xylene, toluene, α-picoline, 2-methylthiophen, and *p*-cresol, the conversion of cyclopentylbenzene into benzene, the decomposition of cyclohexane and piperidine, etc.[236–244] Reactions of a similar type between hydrocarbons and CO_2 have also been studied[245].

The concept of the formation of surface free radicals has been used also to explain isomerisation. As an example, we can cite Burwell's attempt[31] to explain some exceptions to the rule of *cis*-addition (*cf.* Section 6).

Free radicals are probably formed in the dehydration of alcohols (under a pressure of a few millimetres) on $MgSO_4$, as was found from the *ortho–para* conversion of H_2 admitted to the system during the dehydration[246]. As Schwab and Agallidis showed[247] long ago, solid free radicals, such as 1,1-diphenyl-2-picrylhydrazyl[248], can effect the *ortho–para* conversion. It is probable that dehydration of the third kind given above occurs under these conditions.

The formation of radicals can also explain the exchange of a radioactive tracer (^{14}C), occurring on aluminium oxide, between methyl ether (and also methyl alcohol) and, on the other hand, isopropyl, benzyl, and octyl alcohols, ethyl ether, acetone, and ethylene, but not toluene or acetonylacetone, which can serve as a method for preparing labelled compounds[249,250].

A radical mechanism is probable in the addition of organosilicon compounds to olefines[251,252] and in the alkylation of olefines and paraffins under high pressure[253] (for the start of this work, see Refs. 254–258).

Since radicals are formed in such reactions, chain processes may be expected. The presence of surface chains in catalytic reactions is probable in syntheses from water gas[259] and in the hydrocondensation of CO with olefines[260,261].

Radical-like species are probably formed also during dehydration of the third kind, and perhaps a chain reaction takes place. Thus the present writer together with Vasserberg and Georgievskaya[262-265] have investigated the dehydration of alcohols on $MgSO_4$ in a monolayer, at degrees of surface coverage not exceeding 20%. This work has shown that the rate of dehydration of an alcohol is always diminished on addition of another alcohol, which is dehydrated less rapidly, whereas the rate of dehydration is either increased or decreased, when a less stable component is added.

Surface chain reactions in catalysis, which were still unknown not long ago, should be correctly interpreted in terms of the theory of Voevodskii *et al.*[266] which is based on electronic concepts. It is clear from all that has been said above that it needs to be supplemented by structural considerations. The latter are considered by the multiplet theory.

6. STERIC HINDRANCE AND ASYMMETRIC CATALYSIS

Hydrogenation on Pt and other metals of compounds containing a triple bond yields overwhelmingly *cis*-olefines, not the *trans*-compounds. This takes place in spite of the fact that the *trans*-olefines are thermodynamically more stable. According to the multiplet theory, the reason for such behaviour of substituted acetylenes is that, with the triple bond adsorbed at two points, both substituents are forced away from the surface.

For the same reason, the *cis*-forms of olefines are more readily hydrogenated than the *trans*-forms. This phenomenon is well known in catalytic synthesis. The *trans*-forms can fit the plane of the catalyst only on two sides, whereas the *cis*-forms fit on three sides.

The multiplet theory explains the results obtained in the extensive stereochemical work of Linstead and his collaborators[267,268] on the hydrogenation of phenanthrene derivatives over platinum. Almost exclusive formation of *cis*–*syn*–*cis*-forms takes place, atoms being added on one side of the plane of the rings (for a more detailed amount, see Ref. 196). From his work, Linstead reaches the following conclusions: (1) hydrogen is added on the side towards the catalyst (and not from the liquid or gas phase); (2) aromatic rings are arranged flat during hydrogenation on platinum; and (3) steric hindrance between catalyst and substrate plays a considerable part during hydrogenation. These results are readily seen to be in complete agreement with the multiplet theory.

Waldeland, Zartman, and Adkins (1933) attempted to hydrogenate on nickel 2,6,2′,6′-substituted derivatives of biphenyl, in which the substituents prevent free rotation of the rings, the planes of the latter being perpendicular to one another. Hydrogenation of such compounds does not take place, probably owing to steric hindrance: the molecules cannot lie flat on the catalyst surface[267].

According to the multiplet theory, the hydrogenation of disubstituted benzenes should yield *cis*-forms. Investigations with the isomeric xylenes and the eight isomers of dimethylcyclohexene have shown that this is in fact observed under mild conditions[269]. Under more severe conditions, however, the *trans*-forms appear as well. Burwell explained this phenomenon by the formation of free radicals (*cf.* Section 5).

Ehrenstein and Bunge found that derivatives of *cis*-decahydroquinoline and of *cis*-decalin are more readily dehydrogenated than the corresponding *trans*-forms; according to them, their results are consistent with the multiplet theory[270].

For steric hindrance in stereospecific polymerisation, see Section 4*a*.

At low temperatures and high pressures the adsorbed molecules are oriented in the form of a Langmuir array (see, for example, Ref. 271). Rideal and his school[272] have carried out interesting new work on chemical reactions in such oriented monolayers on a liquid surface. As an example, we can cite the lactonisation of 4-hydroxystearic acid[272]. At high surface pressures (high concentrations) only the carboxyl group is in contact with the acid solution, and lactonisation does not take place since the OH group is not in contact with the catalyst (HCl). At low pressures the hydroxyl also is in contact with the solution, and reaction takes place.

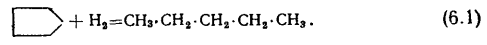
Other methods are used to determine molecular orientation in catalysis by solid surfaces, involving comparison of the chemical structure of the reactant molecules with (1) the activation energy and (2) the adsorption coefficients, which are found from the form of the decrease in reaction velocity due to displacement by foreign substances (see above[7]).

The adsorption coefficients are very high in catalytic poisoning. Maxted's extensive investigations[49,50] on the poisoning of Group VIII metal catalysts showed that during poisoning the molecules of thiols and organic sulphides are oriented with the sulphur atom towards the metal, while the aliphatic hydrocarbon chains are directed outwards. The element of area associated with one molecule of the thiol increases with the length of the hydrocarbon chain of the latter. This suggests that the molecule rotates, describing a cone with the sulphur atom at its vertex. It appears odd that this area is smaller with dithiols, which contain two sulphur atoms, but this is explained by the second atom acting as an anchor, so that rotation ceases. In this case the molecule is oriented parallel to the surface. Maxted combines structural with electronic concepts, remarking that substances containing atoms having unshared pairs of electrons, such as the sulphur atom in sulphides, are especially strong poisons.

Interesting results have been obtained from a study of adsorption at low temperatures, *i.e.* under precatalytic conditions. Vasserberg, the present writer, and Maksimova[273] have used the B.E.T. adsorption method at 25° to determine the area elements occupied by eight alcohols on aluminium oxide prepared in different ways. These areas were found to increase with increase in the number of carbon atoms in the chain of the alcohol and with its complexity. Thus at low temperatures orientation in the form of a Langmuir array, with the CHOH group towards the catalyst, is accompanied by alignment of the alcohol molecules parallel to the surface owing to the operation of van der Waals forces and hydrogen bonds. The proportion of the parallel orientation falls with rise in temperature, as is to be expected, since molecular vibrations are intensified, and the weaker bonds are ruptured. Kiselev *et al.*[274] observed similar planar adsorption of alkanes on graphitised carbon black.

Thus it follows from the experimental data that the extraindicial substituents can in some cases lie on the surface alongside the multiplet. It is reasonable to expect structural conformity in such cases. Van der Waals atomic radii, which are larger than the valence-bond radii, must usually be employed, although the interatomic distances in the molecules remain the same. Here, as also in the case of crystals having a molecular lattice, the Brigleb–Stuart molecular models should be suitable, these being inapplicable to the indicial groups, since chemical forces operate in catalysis.

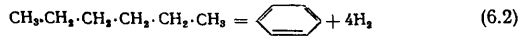
The superposition of extraindicial substituents on the surface was first considered for the opening of five-membered rings during the hydrogenation of hydrocarbons, a reaction discovered by Zelinskii *et al.*[275,276], for example:



(6.1)

Kazanskii *et al.*[277] suggested a duplet–sextet model (Fig. 16) to explain it. The five carbon atoms are arranged on the hexagon formed by platinum atoms in the (111) face, thereby producing a strain in addition to the Baeyer strain. Only two of these carbon atoms undergo reaction, a new bond being formed between them. Cyclohexane would not suffer strain under such conditions. This may explain why the cyclopentane ring is ruptured more easily than the cyclohexane ring, which does not react under such conditions, although the unadsorbed molecules with either six- or five-membered rings, show no Baeyer strain.

Similar considerations can be applied to the aromatisation of paraffins; in the simplest case



(6.2)

(see Section 4). Pitkethly and Steiner[278] suggested a duplet scheme to explain the occurrence of this reaction on chromium oxide. On platinum, however, it is possible that a duplet–sextet model, similar to that illustrated in Fig. 16, is to be preferred: a cyclohexane ring is first formed, and is then dehydrogenated as usual. The intermediate formation of cyclohexane derivatives in the aromatisation of paraffins was demonstrated experimentally by Kazanskii *et al.*[279]

It follows from the experiments of Anderson and Kemball[280] that, in the exchange of deuterium on palladium films, the cyclopentane ring is adsorbed mainly flat against the surface. As the number of D atoms introduced is increased, the percentage exchange first falls, then rises, reaching a maximum at five D atoms, and drops almost to zero at six atoms, after which it begins to increase again. The break in the curve between five and six atoms must be supposed to correspond to the ring turning over. The effect becomes weaker with rise in temperature; it is less marked with cyclohexane than with cyclopentane, and still less with cycloheptane.

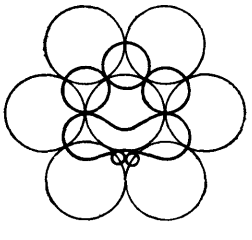
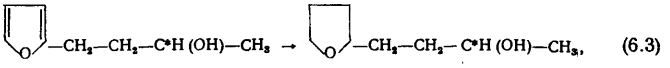


Fig. 16. Duplet–sextet model for the hydrogenolysis of cyclopentane[226].

Extremely interesting work on asymmetric catalysis was begun by Schwab, Rost, and Rudolf. Catalytic asymmetric synthesis was accomplished by Terent'ev and Klabunovskii. The reactions were carried out on metals deposited on right-handed and left-handed quartz. Optically active organic carriers give a still greater effect[281].

Cases are known in which optically active catalysts have different effects on the reaction of the (+)- and (-)-forms of optically active substrates, although the asymmetric carbon atom occurs in the extraindicial substituent, so that its bonds remain unchanged during the reaction. Thus in Ponomarev and Zelenkova's experiments[282] on the hydrogenation of 4-α-furylbutan-2-ol,



(6.3)

on nickel deposited on right-handed quartz, the resulting 4-α-tetrahydrofurylbutan-2-ol possessed an optical activity of $\alpha_D^0 = -0.04$, whereas hydrogenation over nickel on left-handed quartz yielded a different optical activity: $\alpha_D^0 = +0.03$. Since the asymmetric carbon atom is here located in the extraindicial chain, while the bonding energies within the indicial group cannot differ appreciably for the (+)- and (-)-forms, it follows that the extraindicial carbon chain lies on the catalyst surface[196]. Actually, if the chain were not in contact with the latter (as in the model illustrated in Fig. 5, for example), it would be immaterial which way the molecule branched at the asymmetric atom. If, however, the chain lies on the surface, this is no longer immaterial.

According to Klabunovskii and Patrikeev[283], the appearance of optical activity in the reaction products of asymmetric catalysis is due to asymmetric adsorption on the quartz; thus it is the adsorption, not the catalysis, which is asymmetric.

An analogous positioning of extraindicial substituents is indicated also by the fact that, in palladium catalysis obtained by Skitas's method, the presence of an optically active colloid, gum-arabic, results in asymmetric catalysis in the hydrogenation of phenyl- and α-naphthyl-glyoxylic acids[284,285].

7. THE ACTIVE SURFACE

The aim in the present section is not to report all known data on this question but only those which are especially linked with the multiplet theory.

According to this theory, active centres are undeveloped centres of crystallisation. An attempt has recently been made[286] to influence the rate of appearance of such centres, and hence the activity of the catalysts, by exposure to fast electrons (1.5 MeV). In some cases metals actually deposited from the irradiated salt solutions were 4–5 times as active as the usual catalysts (platinum) for the hydrogenation of cyclohexene; the structure of the initial platinum complexes is shown in Fig. 17.

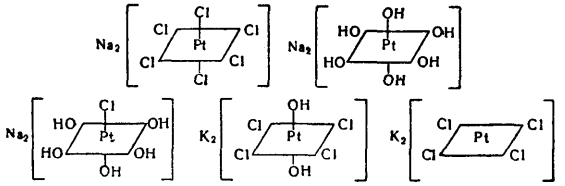


Fig.17. Structure of platinum complexes subjected to the action of fast electrons [286].

In other cases, in contrast, precipitation of the metal during exposure results in less active catalysts (palladium). It is probable that two effects are competing here, acceleration of the formation of crystal nuclei and acceleration of crystallisation, the latter leading to destruction of such nuclei.

Different crystal faces catalyse reactions at different rates. This was first discovered by Gwathmey [287,288] who worked with an optical microscope, and has been shown still more clearly by Roginskii *et al.* [55,289] using an electron microscope (*cf.* also Gomer [290]). During use the smooth, electrolytically polished surfaces of the metal single crystals, cut parallel to definite crystallographic planes, acquire regular rugosities. Thus a smooth palladium surface cut parallel to the (110) plane becomes covered with small pyramids of the octahedral faces. This is a result of catalytic corrosion (see Section 3). A similar complication obviously occurs in work with spherical points in the electron microprojector. Therefore it is impossible to say precisely to which face the maximum velocity of a given reaction corresponds. However, there is no doubt about the fact itself that different faces have different catalytic activities. It is consistent with the multiplet theory.

Ferroni *et al.* [291] established a difference in catalytic activity, for the vapour-phase hydrolysis of diethyl carbonate, between cubic and octahedral crystals of KCl.

The activity can be affected not only by the geometry of the different faces of the crystals which have been formed, but also by the different geometry of molecules trapped during formation of the catalysts and then removed. First Polyakov [292] and then Pauling [293] observed that silica gel, precipitated with acid from sodium silicate solution in the presence of various organic dyes, which were afterwards removed from it, possesses the ability to adsorb the same dyes selectively from fresh solutions thereof. In this way the adsorbent forms a matrix corresponding in shape to the dye molecule. The objection that traces of the dye remain in the silica gel, and act as crystal nuclei during its subsequent adsorption, has been refuted by recent experiments [294].

Patrikeev, Kozarenko, and the present writer [295] transferred such investigations to the field of catalysis. Silica gel which has been precipitated in a solution of dimethyldioxopiperazine and then thoroughly washed catalyses the condensation of alanine esters to the cyclic dimer to a greater extent than does silica gel which has been formed in a similar manner in a solution of alanylglycylglycine, which catalyses condensation mainly to the linear trimer [295]. This occurs probably as a result of the formation of molecular imprints.

Silica gels which adsorb (+)- and (-)-linaloöl selectively can be prepared even in the presence of the right-hand and left-hand forms of *Bacillus mycoides* [296]. Work with optically active clathrate compounds has also been undertaken in our laboratory [297].

Let us now consider the experimental determination of the size and nature of the active centres on the surface [298-302]. It is evident from the above that steric effects arise during hydrogenation. The interfering groups are then located on neighbouring carbon atoms of a C=C bond (in cases of *trans*-superposition) or are close to them. The question arises as to how rigid molecules of complicated shape, which cannot be fitted on a plane and in which the interfering groups are located quite far from the reactive centre, the indicial group, will behave on hydrogenation. With this aim the present writer and Klabunovskii [298-300] investigated the kinetics of the hydrogenation over nickel of derivatives of triptycene



(7.1)

The reaction went under mild conditions (45° and 1 atm), in spite of the possible steric hindrance. Hence it follows that the catalytically active centres must be located not on a smooth surface but on projections, in conformity with Taylor's concept of peaks [22] or Vol'kenshtein's biographic active centres [33]. What is new in our results is that such projections must have small planar faces, on which the indicial groups are arranged [in conformity with the sextet model for the hydrogenation of the benzene ring (Fig.18*a*) or the duplet model for the hydrogenation of the C=O bond (Fig.18*b*)]. At the side of the projections there must be recesses which are sufficiently deep to contain the extra-indicial substituents. The projection in Fig.18 represents the corner of a cube cut off by an octahedral face. Whereas

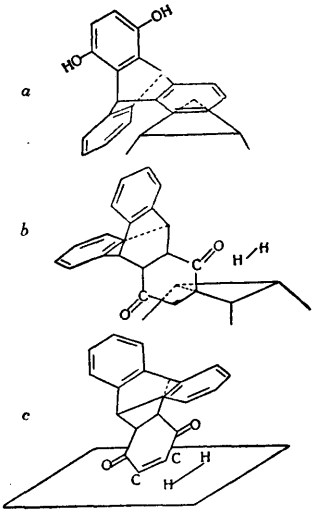
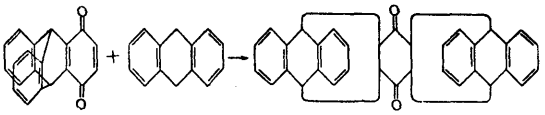


Fig.18. Orientation of molecules of triptycene derivatives on nickel: *a*) hydrogenation of benzene ring; *b*) hydrogenation of carbonyl bond; *c*) hydrogenation of olefinic bond.

reactions (*a*) and (*b*) must take place on projections, reaction (*c*), the hydrogenation of the C=C bond, can occur also on a plane, since the remaining part of the molecule can be oriented away from the catalyst. In the case of Fig.18*a* stereochemical considerations indicate that the minimum depth of the recess is 3.17 Å. Projections are necessary also in the dehydrogenation of secondary alcohols[7] and of 1,1-diphenylethane[7].

Hydrogenation of dianthrylenedihydrobenzoquinone, which was synthesised by the reaction



enabled the same workers[301] to find also the width of the active centres, which must be less than 4.8 Å. The calculations are illustrated by the stereochemical model in Fig.19. The present writer, Klabunovskii, and Antik[302] have investigated also the hydrogenation of dihydroanthrylene-naphthohydroquinone on the same basis. For the chemistry of triptycene see Theilacker *et al.*[303]

The concept of active centres as projections explains (if the random distribution of their heights is taken into account) the appearance of the dispersion parameter h in the kinetic equation for dehydrogenation, which according to work done in our laboratory holds approximately for a hundred pairs of substances on different catalysts[7].

Up to now we have been considering catalysts without additives. The multiplet theory gives two reasons for the promoting action of additives. For the first, see Section 3, paragraph 7. The second cause is entry of the added material into the active centres (for example, the shaded atom in the model illustrated in Fig.5). This cause is operative also in the case of mixed catalysts.

When instead of one phase, such as we have just been examining, two solid phases are present, we must first say something about the action of carriers. In contrast to the second component of a mixed catalyst, carriers do not usually affect the activation energy ϵ. Thus the same value of 18.04 kcal mole^{-1} was found for the dehydrogenation of decalin over platinum on carbon and over platinum on asbestos[304]. Epitaxial relations often exist between catalyst and carrier. Thus in the case of active catalysts for which the structure shown in Fig.20 is possible, the

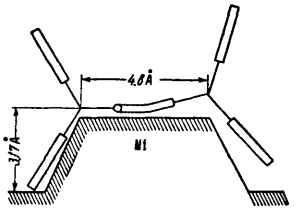


Fig.19. Orientation of the dianthrylene-benzoquinone molecule during hydrogenation on nickel, and limiting dimensions of active centre (side view)[301].

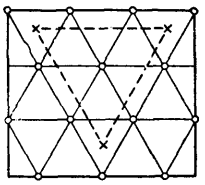


Fig.20. Epitaxial relation between Ni and Al_2O_3.

TABLE 3.

No. of catalyst	1	2	5	6	7	8	Mean
$\varepsilon_{H_2}/\varepsilon_{H_2O}$	(0.32)	0.50	0.61	0.50	0.59	0.57	0.51

ratio of the interatomic distances (M–M)/(O–O) is almost exactly a whole number[305]. For Ni on Al_2O_3, its value is 2.49/1.32 = 1.89; for Cu on Cr_2O_3, it is 2.56/1.32 = 1.94. In the case of the especially active catalyst rhenium on carbon, which we have discovered[7], this ratio is 2.74/1.45 = = 1.89. According to the multiplet theory, one of the functions of the carrier is to preserve the crystal nuclei.

For mixed catalysts consisting of two phases, it was shown in our laboratory that the catalytic activity is localised in space at the interface between the two solid phases. Thus the present writer and Rubinshtein[306,307] measured the activation energies for the dehydrogenation and the dehydration of isopentyl alcohol over catalysts consisting of Ni on Al_2O_3 prepared in different ways. The activation energies of the two processes were found to be interlinked, their ratio remaining constant at approximately 0.5 (see Table 3). But since dehydrogenation takes place on the Ni, while dehydration occurs on the Al_2O_3, the Ni and the Al_2O_3 should also be interconnected spatially: *i.e.* catalysis must occur at the interface between the Ni and the Al_2O_3. A similar result concerning the catalytic action of interfaces was obtained by a different technique for the catalytic reaction of isopropyl alcohol on Al_2O_3 + + ZnO.[308]

Steric factors play a great part also in carbonisation, which has been studied in the present writer's laboratory[309–326]. Alcohols and hydrocarbons, when decomposed on metals, form carbon dendrites. Carbonisation was found to take place by several mechanisms.

8. CLASSIFICATION OF REACTIONS[327,328]

The classification of reactions involving organic catalysis belongs to a different type of structural problem in catalytic chemistry. Reactions between molecules (not with radicals or ions) must first be distinguished according to their multiplet character, whether duplet, triplet, etc. (see above). The bond may be either covalent or semi-polar.

A further step is the systematic variation of atoms and bonds within the indicial group. Part of such a classification[5] is given in Table 4. Since different energies of bonding between the reactant molecules and the catalyst correspond to different catalysts Z, different catalysts correspond to reactions having different indicial groups.

It is also evident from Table 4 that the main classes of reactions in organic catalysis[329] are in fact represented by duplet indicial groups. The resulting classification is similar to the usual classification (after Sabatier[176]), but is distinguished by greater detail. Thus according to Sabatier the dehydrogenation of hydrocarbons and that of alcohols belong to the same class, whereas according to the multiplet classification they belong to different classes, since with alcohols the indicial group contains an oxygen atom, which is replaced by a carbon atom in the case of hydrocarbons; and in fact the catalysts in the two cases are different (see Table 4).

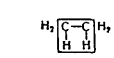
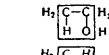
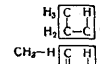
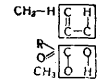
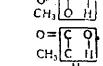
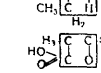
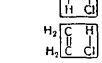
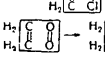
Duplet reactions are very widespread in organic catalysis. Most of the catalytic reactions studied by Zelinskii[198] are duplet reactions[216] (and almost all the remainder are sextet reactions). All the reactions in a survey of Favorskii's work[330] can be represented as duplet reactions (caustic potash is here acting as a catalyst). The paper on catalytic condensation by Adickes and Du Mont in Schwab's multivolume work[331] examines duplet indicial groups, for example condensation by the interaction of a C–H with a C=O bond, which is represented in the multiplet theory by the duplet scheme



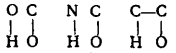
(8.1)

In several duplet reactions the same starting materials can yield the same reaction products by different paths. Such reactions were termed "olistomeric"[332], and the structural conditions for their occurrence were determined on the basis of the multiplet theory. Thus in esterification, bond rupture can theoretically take place in two ways: HO–CO·R + H–OR and H–O·CO·R + HO–R. A tracer method shows that reaction usually takes place by the first mechanism. For "semiduplet" schemes based on such experiments[333], into which duplet indicial groups for reactions in solutions are broken down, see Ref.28.

TABLE 4. Correspondence between groups of reactions and groups of catalysts.

Reaction group	Indicial group	Group of catalysts
Dehydrogenation of hydrocarbons		Cr_2O_3, MoO_2, V_2O_5
Dehydrogenation of alcohols		Cu, MnO_2, ZnO, CdO
Dehydration of alcohols		Al_2O_3, ThO_2, W_2O_5
Hydrogenation of olefines		Pt, Pd, Ni, Fe, Cu
Catalytic cracking (one of the reaction types)		$Al_2O_3 + SiO_2$
Migration of double bond		Cr_2O_3, Pd
Hydrolysis of esters		$SiO_2 \cdot nH_2O$
Decarboxylation		Ni, Cu
Ketonisation of acids		$CaCO_3$, $BaCO_3$, MnO, ThO_2
Chlorination		$BiCl_3$, $SbCl_3$, C
Addition of HCl to olefines		$AlCl_3$, $BaCl_2$
Oxidation of olefines		Os, Cu

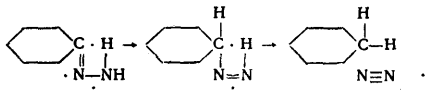
The multiplet classification is of heuristic value, assisting the discovery of types of reactions which are as yet unknown (provided that they are thermodynamically possible). Since the classification was worked out, many squares have been filled, for example, by the discovery of the formation of vinylacetylene from acetylene[335], Yur'ev's reactions[336], etc. Conscious search in the present writer's laboratory led to a series of reactions, predicted by the multiplet classification, being carried out for the first time. Examples are given in various places in the present paper. Here we may note the hydrogenolysis of *N*-bromoacetamide[23] and of t-butyl hypochlorite[23], the dehydrogenation of aliphatic amines to ketimines[84-86], and the hydrolysis of ethyl ether over mixed catalysts[337]. Al_2O_3 catalyses reactions having indicial groups (8.2) in which one atom is successively replaced:



(8.2)

i.e. the hydrolysis of ethyl ether, the preparation of *N*-monoethylaniline from alcohol and aniline, and the dehydration of alcohols to olefines. Promotion of the catalyst has different effects on these reactions, in conformity with the multiplet theory. Thus addition of oxides of Fe, Ni, and Zn accelerates the first reaction and retards the second and third[337-339]. Incidentally, the present writer and Sokolova found that Nb_2O_5 and Ta_2O_5 are good catalysts for the preparation of monoethylaniline[340], and also for the esterification of alcohols by acids[340]; Nb_2O_5 effects the condensation of acetaldehyde to crotonaldehyde[341].

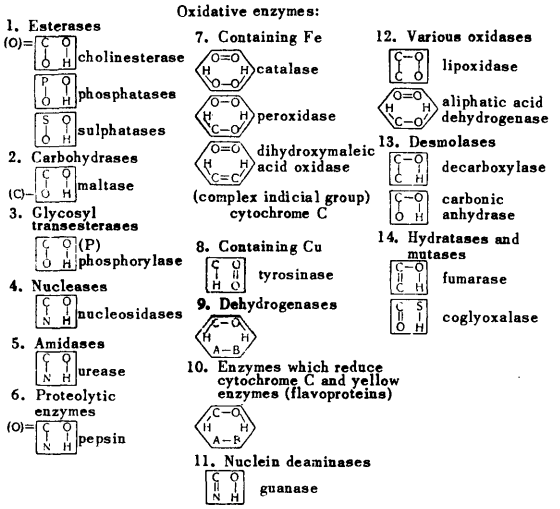
Catalytic reactions which do not fit into duplet schemes sometimes really prove to be consecutive duplet processes. An example of this type which has been studied kinetically is Kishner's reaction. The present writer and Vaskevich[6] showed that cyclohexylidenehydrazine is converted on platinum into cyclohexane (and nitrogen) *via* cyclohexyldiimine, which is short-lived (time of half-decomposition 34 sec at 150° and 1 atm):



(8.3)

Examination of the classification shows that there are still many hundreds of types of reactions awaiting discovery in organic catalysis[327].

TABLE 5. Types of enzymes and their indicial groups.



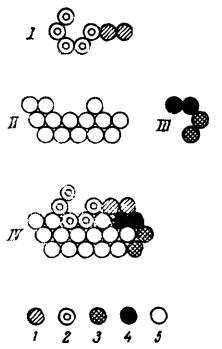


Fig. 21. Formation of intermediate complex in an enzymic reaction: I) substrate; II) protein part of enzyme; III) coenzyme; IV) intermediate complex, 1) atoms of indicial group; 2) atoms of substituents; 3) atoms of coenzyme; 4) atoms of active part of coenzyme; 5) atoms of protein part of enzyme.

This classification is valuable not only for the kinetics and equilibria of heterogeneous catalytic reactions having a duplet mechanism but also for the equilibria of homogeneous catalytic reactions, as well as non-catalytic reactions, since the equilibria do not depend on the reaction mechanism. It is interesting that the four- and six-membered cyclic activated complexes postulated by Syrkin[342] are none other than duplet and triplet indicial groups, so that the multiplet classification should be valid for them too, and is thus applicable to the kinetics of reactions other than the heterogeneous catalytic type.

Recently the multiplet theory has been applied to enzymic reactions[343-345]. Practically all of them are found to belong to the duplet or triplet type (Table 5). Their selectivity is governed by: (1) the nature of the atoms within the indicial group (Table 5); (2) the effects of extraindicial substituents on the energies of the bonds within the indicial group; and (3) the positioning of extraindicial substituents on the surface alongside the active centres (see Fig. 21), which requires a high degree of structural conformity (surface isomorphism). Antimetabolites also show surface isomorphism, but are unreactive. For further details, see Ref. 344. In the study of enzymes, conclusions similar to those of the multiplet theory have been reached by Pauling[346] and the biochemist Dreiding[347] from the Karrer school.

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