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THE MULTIPLET THEORY OF CATALYSIS — ENERGY FACTORS IN CATALYSIS

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An earlier review[1] has surveyed work on the principle of structural correspondence in the multiplet theory of catalysis. However, this principle alone is insufficient according to the theory. Thus ThO_2 and CaF_2 have the same structure, but different catalytic effects on alcohols[2]. A second principle which follows from the multiplet theory — that of energetic correspondence — will be examined below.

1. FUNDAMENTAL EQUATIONS OF THE MULTIPLET THEORY

Spatial (structural) and energetic factors in catalysis are linked by potential-energy curves. Fig. 1 shows such a curve for the chemisorption of an atom A on the surface of a catalyst K. The x axis is taken to pass through the centre of the sorbed atom A and be normal to the plane of the catalyst surface KK. On the atomic scale the profile of the surface is represented by the wavy line ZZ. The adsorbed atom A will be in a more stable position in the trough K' between the surface atoms[1]. In Fig. 1, therefore,

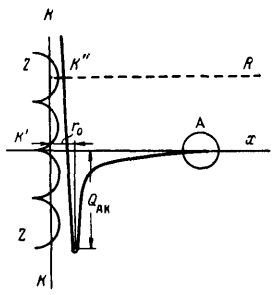


Fig. 1. Diagrammatic potential-energy curve for the chemisorption interaction of an atom A with the surface of a catalyst. This curve is to be imagined as lying in a plane perpendicular to the plane of the paper.

the horizontal axis must be drawn through the point K'. If this axis is displaced to the parallel position $K''R$, the form of the corresponding potential-energy curves will, of course, be different. However, it is the configuration in Fig. 1 which will have the decisive role, and to this approximation we shall regard Q_{AK} as the energy of bonding with the surface, and r_0 as the bond length (see Fig. 1).

Infrared spectra show[3] that hydrogen chemisorbed on platinum includes both weakly and strongly adsorbed atoms (H_w and H_s respectively). Pliskin and Eischens represent this by the scheme

$$\begin{matrix} H_w & & H_w \\ | & & | \\ Pt\cdot & H_s & \cdot Pt \end{matrix} \qquad (1.1)$$

which is consistent with Fig. 1, H_w being adsorbed at the sites K'', and H_s at K'.

Let us compare the energy of the bond A–B in the AB *molecule* when the latter is present in the gas and when it is chemically adsorbed on a catalyst surface as the atoms A and B. Let us denote by Q_{AB} the energy of the A–B bond in the gas, and by Q_{AK} (see above) the energy of the A–K bond between the A atom and the catalyst. (Henceforward Q_{XY} will always denote the energy of the X–Y bond.)

According to the multiplet theory, the energy $E_{AB,K}$ required to cleave the bond A–B into atoms adsorbed on the catalyst will differ from Q_{AB}. By definition we have the thermochemical equation

$$A{-}B + 2K = A[K] + B[K] - Q_{AB,K} \qquad (1.2)$$

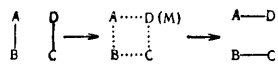
where A[K] and B[K] represent A and B atoms adsorbed on the catalyst K. We also have the self-evident thermochemical equations A–B = A + B – Q_{AB}; A + K = A[K] + Q_{AK}; B + K = B[K] + Q_{BK}, summation of which gives

$$A{-}B + 2K = A[K] + B[K] - Q_{AB} + Q_{AK} + Q_{BK}. \qquad (1.3)$$

From Eqns. (1.2) and (1.3) we find that

$$E_{AB,K} = -Q_{AB} + Q_{AK} + Q_{BK}. \qquad (1.4)$$

Thus the A–B bond will be weakened on the catalyst compared with the gas. The quantity $E_{AB,K}$ is the heat of chemisorption of the molecule A–B on the catalyst. If $Q_{AB} > Q_{AK} + Q_{BK}$, this will be a case of a negative heat of adsorption, recently considered by de Boer[5]. Two bonds are involved in the duplet reaction[1]



(1.5)

Surface atoms of the catalyst and substituents attached to A, B, etc. are omitted from this scheme, the physical meaning of which is discussed in Ref. 1.

As above, the heat of formation of the multiplet complex M will be

$$E' = -Q_{AB} - Q_{CD} + (Q_{AK} + Q_{BK} + Q_{CK} + Q_{DK}), \qquad (1.6)$$

and the heat of decomposition of M into the reaction products[6,7]

$$E'' = Q_{AD} + Q_{BC} - (Q_{AK} + Q_{BK} + Q_{CK} + Q_{DK}). \qquad (1.7)$$

The quantity $-E'$ is the height of the energy barrier to the reaction, and the same applies to $-E''$. If $-E'$ is lower than $-E''$, the multiplet complex will break down more often into the starting materials than into the reaction products, and the reaction will go with difficulty or not at all. If, however, the barrier $-E''$ is lower than $-E'$, the multiplet complex will break down into the reaction products, which will evaporate from the surface. The catalyst atoms are thereby disengaged, and again become ready to exert their catalytic effect. The cause of catalysis here is the lowering of the energy barrier resulting from the weakening of bonds on the catalyst compared with the gas phase — see Eqns. (1.6) and (1.7).

The overall reaction velocity is limited by the height of the energy barrier $-E$, where E represents E' or E'', whichever is the more negative:

$$E = \min(E, E'', L). \qquad (1.8)$$

In general $L = 0$, but as a result of complicating factors L may have a constant (small) value differing from zero — *cf.* Eqn. (1.9). The greater is E, the lower is the energy barrier, and the higher the reaction velocity (below the Schwab inversion point).

Soon after the appearance of a paper on the multiplet theory[7], Polanyi published[8] a very similar theory of catalysis, which provided a quantum-mechanical basis for views analogous to those underlying Eqns. (1.6) and (1.7) of the multiplet theory. Polanyi agrees with London[9] that a gaseous reaction AB + CD = AD + BC is hindered by the existence of the repulsion inherent in the nature of chemical valency forces: thus the atom A combined with B repels any other atom, for example D. For reaction to occur, the molecules AB and CD must come together with A beside D, and B beside C. In such a position, however, calculation shows the repulsive forces to be a maximum. On the other hand, the activation energy of a reaction involving a molecule and a free atom is small. According to Polanyi, free valencies project from the catalyst surface, and act as free atoms, which greatly facilitates double decomposition between AB and CD. This part of Polanyi's paper[8] can be regarded as a quantum-mechanical demonstration of the fundamental assumptions of the multiplet theory. Furthermore, Polanyi's arguments show why in endothermic reactions the energy barrier is little higher than the negative heat of reaction: this follows from the similarity to free-radical reactions.

In contrast to Ref. 7, however, Polanyi's paper[8] gave no formulae and no applications to actual reactions. He

did this only in 1935,[10] when he examined one reaction, the para–ortho conversion of the hydrogen molecule. The formulae given for this case were the same as Eqns. (1.6) and (1.7). Temkin[11] developed Polanyi's theory, and in 1957 obtained[11] the same equations (1.6) and (1.7) as the Reviewer, obviously because of the similarity of the main premises.

However, in addition to the closeness of the views expressed in Refs. 8, 10, and 11 with those of the multiplet theory, there are also important differences, these papers assuming complete cleavage of the A–B and C–D bonds into radicals. In contrast to this, the multiplet theory assumed right from the start — as a development of the views of Mendeleev, Zelinskii, and Bodenstein on molecular deformation as a cause of catalysis[1] — that formation of the intermediate complex does not necessarily involve complete rupture of chemical bonds[6,7]. It was specially stressed[12] that the complete "dissociation" assumed in Eqns. (1.6) and (1.7) "measures the deformation of the molecules".

The quantitative relation between the heat of formation (or decomposition) E of the multiplet intermediate complex and the activation energy ϵ is given by the formula

$$\varepsilon = A - \gamma E. \qquad (1.9)$$

In 1946 the Reviewer[13] suggested Eqn. (1.9) with values of $\gamma = \frac{3}{4}$ and $A = 0$, and applied it to endothermic reactions of dehydrogenation and dehydration. In 1955 Semenov[14] examined a large quantity of experimental data on the reaction AB + C = AC + B, involving free atoms and radicals, and found Eqn. (1.9) to be applicable. It is interesting that Semenov finds the same value of $\gamma = \frac{3}{4}$ for endothermic reactions as does the Reviewer; for exothermic reactions $\gamma = \frac{1}{4}$. The constant A is small (11.5 kcal). With different materials and a different notation, Eqn. (1.9) is known as the Brønsted equation.

Eqn. (1.9) can be interpreted qualitatively on the basis of the theory of rate processes[15]. The electron pairs in the molecules AB and CD are delocalised in the resulting activated complex M, and are then localised afresh in the reaction products. When the reaction velocity is controlled by the adsorption stage, the activation energy ϵ is lower than E, the energy of complete rupture of the bonds A–B and C–D, because of the energy gained from the incipient formation of the bonds A–D and B–C; the stronger are these new bonds, the lower will ϵ be. The chemical reaction takes place at this point, when equilibrium is disturbed. If, on the other hand, the reaction velocity is controlled by the desorption stage, an increase in the energy of the bonds A–D and B–C results in an increase in ϵ.

What has been stated previously[1] about the similarity between the multiplet theory and the theory of rate processes[15] as applied to catalysis can be supplemented by the following common features of the two theories. (1) In a reaction the new bonds begin to be formed before the old bonds on the surface have been complete broken: *i.e.* molecules do not usually break down into radicals. In this respect the theory of rate processes diverges from the standpoint of Polanyi's previous theory[8,9]; such a view was adopted in the multiplet theory from the start (see above). (2) Potential-energy curves are considered, in detail in the theory of rate processes (potential-energy surfaces), and in the multiplet theory points on these curves corresponding to the bond lengths and energies are taken. (3) The theory of rate processes demonstrates that chemisorption, for example of a hydrogen molecule on carbon[16] or on nickel[17], occurs at the two atoms, as is assumed in the multiplet theory. (4) In several cases the structures of active and multiplet complexes are identical, for example in the dehydrogenation of alcohols[18], and then the theory of rate processes enables the reaction velocity to be calculated from the model given by the multiplet theory (see preface to Ref. 15). Both theories are based on theories of the structure of matter, but the theory of rate processes, which has the wider scope, proceeds by deduction from quantum mechanics, whereas the multiplet theory is obtained inductively by generalising experimental results on catalysis, taking into account the theory of the structure of matter.

Eqns. (1.6)–(1.9) form the main energy equations of the multiplet theory. They enable the comparative ease of occurrence of a reaction to be assessed if the bond energies Q are known. The latter depend on the nature of the bonds and the catalysts. In fact, ϵ can be calculated from Q by means of Eqns. (1.6)–(1.9). After substitution for ϵ in the Arrhenius equation, bearing in mind the compensation effect, we obtain

$$k = \kappa e^{\varepsilon\left(h - \frac{1}{RT}\right)} \qquad (1.10)$$

whence we find the rate constant k since the parameters κ and h remain fairly constant for reactions and catalysts of the same type[19]. The approximate character of such calculations must be realised, but nevertheless they are broadly correct.

If we now regard Q_{AK}, Q_{BK}, ... as variables, we can transform Eqns. (1.6)–(1.9) into a form convenient for the consideration of problems of catalyst selection, the central problem of catalysis. Let us examine the duplet reaction (1.5) and write its heat of reaction as $u = -Q_{AB} - Q_{CD} + Q_{AD} + Q_{BC}$, the total energy of the bonds broken and formed as $s = Q_{AB} + Q_{CD} + Q_{AD} + Q_{BC}$, and the adsorption potential energy as $q = Q_{AK} + Q_{BK} + Q_{CK} + Q_{DK}$. Then Eqns. (1.6) and (1.7) become

$$E' = q - \frac{s}{2} + \frac{u}{2} \qquad (1.11)$$

for adsorption, and

$$E'' = -q + \frac{s}{2} + \frac{u}{2} \qquad (1.12)$$

for desorption. Eqns. (1.11) and (1.12) are illustrated graphically in Fig. 2 for endothermic (I) and exothermic (II) reactions. The coordinates of the maximum are

$$E_0 = u/2, \quad q_0 = s/2. \qquad (1.13)$$

The straight lines have a slope of 45°, since the coefficients of q are unity. On the basis of Eqn. (1.8) the lower portions of these straight lines are chosen (the thick lines). They form what have been termed "volcano-shaped curves", and can be expressed also in analytic form[13] by the use of Dirichlet's discontinuity factor. In Fig. 2 FH is the height

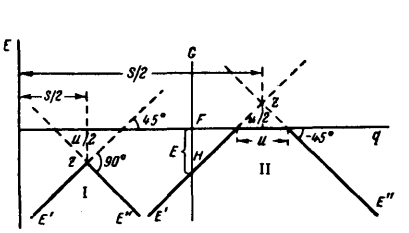


Fig. 2. Volcano-shaped curves (for key see text).

of the energy barrier $-E$, which is lowest at the maximum, *i.e.* when $E' = E''$.

The condition for selection of the optimum catalyst (in case I) is evidently that the adsorption potential energy q should be the mean $s/2$ of the values for the broken and new bonds. The optimum height of the energy barrier is then half the heat of reaction $u/2$ for the catalytic reaction. Thus it follows from the multiplet theory that energetic as well as structural correspondence must exist in catalysis. The principle of energetic correspondence is expressed mathematically by the equation

$$q = s/2. \qquad (1.14)$$

which has been subsequently obtained also by Temkin[11].

This method enables us to reach the practically significant conclusion whether a given catalyst is the most active possible for a given reaction, or whether it can be further improved. For this purpose the activation energy ϵ must be determined experimentally, and from it E found. If E differs greatly in magnitude from $u/2$, the catalyst can still be improved on. However, the condition $E = u/2$ does not signify the limit of activity, since it is still possible to change the reaction mechanism.

The catalyst should be not only the most active but also the most selective. Let us therefore examine the condition for the preferential occurrence of one reaction in the model case of the two reactions (I) and (II). Instead of the one volcano-shaped curve of Fig. 2, we shall now have two such curves and two intersecting lines (Fig. 3). In order to make the discussion more concrete, let reaction (I) be dehydrogenation and (II) dehydration of an alcohol on nickel. Here all quantities are known (including E from Table 4, below), and Fig. 3 can be drawn to scale. Since the point of intersection H lies considerably above H', dehydrogenation is decisively predominant, in agreement with experiment. The limit of sensitivity of the analytical method employed is provided by the lower boundary AB of the reaction zone $ABqO$.

The activity (and sensitivity) of a catalyst having a given $q = q_1$ can be raised by varying the components Q_{AK}, Q_{BK}, Q_{CK}, and Q_{DK} (the intercepts on the horizontal axis in Fig. 2) in such a way that q_1 approaches closer to the optimum condition $q = s/2$. If, therefore, $q_1 < s/2$, the reaction velocity will increase when

$$0 < \Delta q_1 < s - 2q_1. \qquad (1.15)$$

The first method for achieving this is to replace one of the atoms in the multiplet by another. The employment of mixed catalysts is relevant here, reaction often taking place at the interface between two phases. Condition (1.15) is a quantitative formulation of the enhanced activity of boundaries. Another method for increasing the activity and selectivity of catalysts is to change the nature, number, and arrangement of atoms in the catalyst adjacent to the active centre (see Section 6).

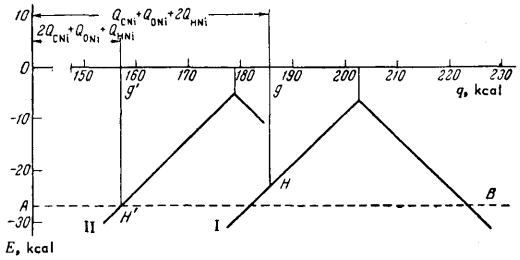


Fig. 3. Volcano-shaped curves for alcohols (drawn to scale): I) dehydrogenation; II) dehydration.

2. BOND ENERGIES

In order to apply the equations of the multiplet theory, it is necessary to know energies of bonding with the catalyst Q_{AK}. These can be found experimentally by thermochemical, comparative, and kinetic methods. Adsorption methods[20,21] and calculation[22] have also been proposed, but are as yet little developed, and have not found practical application.

Thermochemical Method

In this method Q_{AK} is found from the bulk heats of formation U of compounds. We shall regard such replacement of surface by bulk properties as legitimate if the sublimation term is taken into account (see Section 6). The term "thermochemical" is to be understood in a broader sense: U can be obtained not only calorimetrically but also, for example, by a spectroscopic method. However, the calculations involve an additive procedure based on Hess's thermochemical law.

Comparative Method

In this method[4,6,7,23] comparison is made of the relative rates of reactions of the same type involving different bonds in the same molecule on a given catalyst. Application of Eqns. (1.6) and (1.7) of the multiplet theory to a set of such molecules and bonds enables a series of inequalities to be set up, from which the relative magnitudes of Q_{AK} can be established to within 1 kcal. The zero on the scale is obtained by comparing one of the bond energies thus obtained for this system, for example Q_{HNi}, with the value found by the thermochemical method.

System of Q Values Adopted

Combination of the above two methods yields a set of bond energies (Table 1) which are important for organic catalysis. In Table 1 values of Q obtained earlier[6,4,23] have been recalculated on the basis of the new energies of atomisation of carbon and nitrogen. Cottrell's data[24] (1958)

TABLE 1. Energies of atomisation A (at 25°) and bond energies Q_{AB} and Q_{AK}, kcal.

A	C	N	O	H	Cl	Br	
	170.9	112.9	59.5	52.1	28.9	26.7	
Q	C	N	O	H	Cl	Br	C = π bond
C	82.6						63.2
N	72.8	75.3*					74.2
O	85.5	53	35				92.0
H	98.7	93.4	110.6	104.2			
Cl	81	46	52	103.1	57.9		
Br	68	—	48	87.4	—	46.1	
Ni	14	27	48.5	55	67	54	=C—Ni 27

* From Ref. 25.

are taken as more recent and more detailed for energies of atomisation A, *i.e.* the heats of formation of the gaseous atoms from the elements in their standard state (see upper part of Table 1), and for the thermochemical bond energies in the molecules Q_{AB}. They are almost identical (except for a few) with Kondrat'ev's data[25] (1957) and with the calculated values in Ref. 26.

The last column of Table 1 contains the energies of breaking the first reactive bond C=C, C=N, and C=O. The new information supplied by the Reviewer[6,23] relates to the energy of bonding the reactant atoms to the most thoroughly studied catalyst, nickel (Q_{ANi} — see bottom line in Table 1 — for the solid state, starting from solid nickel). The Q_{ANi} values for the bonds formed by nickel with chlorine and bromine were calculated from recent thermochemical data on the heats of formation of $NiCl_2$ and $NiBr_2$ and from the energies of atomisation in Table 1. The energy of the Ni–H bond was determined also from NiH_2 and NiH[27] and found to be 55 kcal. The energies Q_{ANi} for the bonds of Ni with C, N, and O were obtained by the above comparative method. With fixed values of Q_{HNi}, Q_{ClNi}, and Q_{BrNi} such comparison fixes the values of Q_{CNi}, Q_{NNi}, and Q_{ONi} to within 1 kcal. The value thus obtained for Q_{ONi} = 48.5 is below the thermochemical value of 59 kcal (from NiO), probably because of the sublimation term (see Section 6). No thermochemical data are yet available for Q_{CNi} and Q_{NNi}, but the values obtained (Table 1) arrange themselves in the sequence C < N < O, in agreement with the data of inorganic chemistry.

As in any additive scheme (in the case of molecular refraction, for example) constitutional corrections must be made. The value of Q_{CNi} = 14 kcal is applicable to reactions in which no double bond is either formed or broken, for example in the hydrogenolysis of ethane. The value of Q_{CNi} = 27 kcal applies to a carbon atom linked by a double bond with a neighbouring C, N, or O atom in the molecule either inside or outside the indicial group: this is the value to be used in the hydrogenation of a double bond, as well as for dehydrogenation, since the reverse reaction passes through the same intermediate state as does the forward reaction. With further refinement it may perhaps be necessary to introduce similar corrections for a double bond with the atoms N, O, and S.

The bond energies Q are fairly strongly affected by substituents. Thus the values of Q for the C=O double bond in HCHO, RCHO, and R_2CO are 166, 176, and 179 kcal respectively. The data in Refs. 23 and 24 show that a strong substituent effect is the rule, not an exception. However, this fact is of no great importance in catalysis, since substituents have similar effects on Q_{AB} and Q_{AK}, and these quantities occur in both Eqn. (1.6) and Eqn. (1.7), with opposite signs. In catalysis, therefore, the effects of substituents often cancel out (*cf.* Section 4).

From time to time, with improvements in experimental accuracy, the values of A, the dissociation energies D of the elements (for example N_2), and the sublimation energies (of solid carbon) have been revised, and therefore the system adopted for Q has changed (see Refs. 6, 4, and 23 as well as the present review). Nevertheless, this should not affect E. In fact

$$Q_{AB} = D_{A_2}/m + U_{AB} + D_{B_2}/n, \quad (2.1)$$

$$Q_{AK} = D_{A_2}/m + U_{AK}, \quad (2.2)$$

$$Q_{BK} = D_{B_2}/n + U_{BK}, \quad (2.3)$$

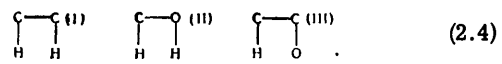
where the U (also additive) are the energies of bond formation, not from the atoms (like the Q) but from the molecules or the solids, while m and n are valencies. When Eqns. (2.1)–(2.3) are substituted in Eqn. (1.4), the D cancel out, as does also the sublimation energy. The thermochemical quantities U, however, remain unchanged. The data given below correspond to the Q values in Table 1.

The heats of reaction should be based on the absolute zero, since elementary processes are being considered. However, the fact that they have actually been found for 298°K does not entail substantial corrections, since multiplet complexes on a surface form a condensed system.

Kinetic Method

First variant. The method consists[13] in determining on a given catalyst the activation energies ϵ of as many reactions as there are different kinds of atoms in the given duplet indicial groups. This gives as many equations (1.6) as there are unknown Q_{AK}.

The first variant is more suitable for oxide catalysts. Here we have a square matrix of the coefficients in a set of linear equations. The dehydrogenation of hydrocarbons (I), dehydrogenation of alcohols (II), and dehydration of alcohols (III) provide a convenient group of reactions. On oxides the reactions (II) and (III) usually occur simultaneously. Here the indicial groups are



(2.4)

Fig. 4 (from Ref. 41) illustrates volcano-shaped curves (to scale) for these reactions. The vertical distances between such a curve and the horizontal axis represent the E values. Such vertical lines are drawn on the left, not on the right, of the maxima, as in the case of nickel (Fig. 3), where theoretical calculation has shown that $E = E'$, not E'', for $E' > E''$ (Table 4). From the set of equations of the type of Eqn. (1.6) for the reactions (I)–(III) together with the equation

$$\varepsilon = -0.75\,E' \quad (2.5)$$

based on Eqn. (1.9), we find that

$$Q_{HK} = \tfrac{1}{3}(-\varepsilon_1 - 2\varepsilon_2 + 2\varepsilon_3) + \tfrac{1}{2}(Q_{CH} - Q_{CO} + Q_{OH}), \quad (2.6)$$

$$Q_{CK} = \tfrac{1}{3}(-\varepsilon_1 + 2\varepsilon_2 - 2\varepsilon_3) + \tfrac{1}{2}(Q_{CH} + Q_{CO} - Q_{OH}), \quad (2.7)$$

$$Q_{OK} = \tfrac{1}{3}(3\varepsilon_1 - 2\varepsilon_2 - 2\varepsilon_3) + \tfrac{1}{2}(Q_{CH} - Q_{CO} - Q_{OH}). \quad (2.8)$$

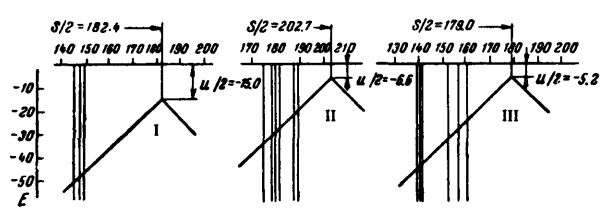


Fig. 4. Vertical intercepts from horizontal axis to volcano-shaped curves representing heights of energy barriers – E found experimentally (drawn to scale) for:
I) dehydrogenation of hydrocarbons; II) dehydrogenation of alcohols; III) dehydration of alcohols.

Substituting known values of Q_{CH}, Q_{CO}, and Q_{OH} from Table 1 (identical with those in Ref. 24), we obtain values of 62.0, 36.8, and 48.6 respectively for the second groups of terms (containing the Q) on the right-hand sides of Eqns. (2.6)–(2.8). By means of these equations we can find from the activation energies the energies of bonds between hydrogen, carbon, or oxygen atoms and the catalyst.

Examples of the results[28-56] are given in Table 2 in the form of the values of Q_{AK} found for catalysts prepared by the same method (precipitation by ammonia from nitrate solution) when tetralin and isopropanol (usually) are passed over them†. The method used for the kinetic determinations has been described previously[47]. Experiments have shown that the activation energy ϵ is practically the same for identical indicial groups with different substituents on the same catalyst. This confirms that the molecules are oriented in the reactions with these particular indicial groups towards the catalyst, in conformity with the multiplet theory. The values obtained for the energy of bonding with the catalyst are of reasonable magnitude. No incongruities, in the shape of negative, too large, or, on the other hand, nearly zero values, are found.

It is very significant that, on the average, energies of bonding with different oxides (Table 2) are comparable with the corresponding values for nickel obtained by the combined–comparative and thermochemical methods (*cf.* Table 2 with the bottom row in Table 1).

The values obtained for Q_{OK} show that in oxides the active centre consists (at least predominantly) of metal atoms, not oxygen. Indeed, firstly we would otherwise have a peroxy--bond, which is, however, weaker (Q_{O-O} = 35 kcal); and secondly Q_{AK} has similar values for MoO_{3-x} and MoS_2 (Q_{HK} = 61.0 and 60.3; Q_{CK} = 27.7 and 26.8; Q_{OK} = 42.9 and 52.5 kcal respectively).

Similar methods are used to find the energy of bonding of nitrogen with the catalyst ThO_2 (Q_{NThO_2} = 31.8 kcal). Thus $Q_{CK} < Q_{NK} < Q_{OK}$, in agreement with other chemical results.

Adsorption potentials q can also be determined. For cyclohexane and Cr_2O_3 we thus have q = 167.2 kcal, which is still quite far from the maximum on the volcano-shaped curve, for which q_0 = 182.4 kcal from Eqn. (1.13). Hence theory indicates that the catalyst can still be improved. Table 2 will be discussed in greater detail in Section 5.

TABLE 2. Bond energies Q_{AK} with oxide catalysts, kcal.

Atomic No.	Oxide	Q_{HK}	Q_{CK}	Q_{OK}	Ref.	Atomic No.	Oxide	Q_{HK}	Q_{CK}	Q_{OK}	Ref.
4	BeO	49.8	19.6	66.8	32	42	MoO_{3-x}	61.3	27.7	42.9	42
22	TiO_2	60.5	28.6	46.3	38	57	La_2O_3	47.5	17.2	64.9	36
23	V_2O_3	56.4	26.7	42.5	46	58	CeO_2	57.6	19.8	49.9	36
24	Cr_2O_3	60.9	22.7	51.8	33	59	Pr_2O_3	52.9	11.4	72.0	36
25	MnO	50.7	26.7	38.8	34	60	Nd_2O_3	52.8	16.0	64.7	36
30	ZnO*	48.6	23.1	61.7	45	64	Gd_2O_3	54.8	15.0	65.2	36
31	Ga_2O_3	62.8	24.9	50.6	44	74	WO_{3-x}	52.6	27.6	43.5	35
39	Y_2O_3	53.6	22.1	58.8	39	90	ThO_2	52.3	21.6	61.3	40
40	ZrO_2	61.3	11.8	29.8	29	92	U_3O_8	48.9	25.6	40.3	41

* Obtained by the second variant of the kinetic method.

† Where previous values of Q_{AK} were based on Q_{AB} values from Ref. 23, conversion to the new Q_{AB} system (Table 1) is effected by adding 8.3 kcal to Q_{CK}. No changes are required in Q_{HK} and Q_{OK}.

If the law of mass action is regarded as the first stage of generalisation in catalytic kinetics, the adsorption isotherm as the second stage, application of the Arrhenius and Frenkel' equations to the temperature dependence of the rate constants and adsorption coefficients respectively as the third stage, and consideration of surface heterogeneity and in particular the compensation effect as the fourth stage, the resolution of the activation energy into its component bonding energies in accordance with Eqns. (1.6) and (1.9) can rightly be regarded as a higher, fifth stage of generalisation in the kinetics of reactions subject to heterogeneous catalysis.

Second variant. The second variant of the kinetic method which has been developed[48-52] is also based on the application of Eqns. (1.6) and (2.5) of the multiplet theory, and is most applicable to metallic catalysts. Here the matrix of the coefficients is no longer square but triangular. The first step is to determine Q_{HK} for the para–ortho conversion of H_2, whose indicial group contains atoms of only one kind

$$\begin{matrix} H & H \\ | & | \\ H & H \end{matrix}. \qquad (2.9)$$

Therefore one reaction is sufficient to determine the energy of bonding of hydrogen with a catalyst if the activation energies ϵ have been found experimentally. The latter can be taken from published data. In Eqn. (1.6) let us substitute H for A, B, C, and D, and Ni for K. Then from the known ϵ_1 = 5.9 and Q_{H-H} = 104.2 kcal, together with Eqn. (2.5), we find that

$$Q_{H-Ni} = \frac{1}{2} Q_{H-H} - \frac{1}{3}\varepsilon_1 \simeq 50.1 \text{ kcal}. \qquad (2.10)$$

(Similarly, from the ortho–para conversion of deuterium, where Q_{D-D} = 106.0 kcal, we obtain Q_{D-Ni} = 50.1 kcal.)

The next step is calculation for a reaction whose duplet indicial group contains hydrogen together with another type of atom, and for which Q_{HNi} has already been found. Such a reaction may be the hydrogenation of ethylene, having the index

$$\begin{matrix} C & H \\ \| & | \\ C & H \end{matrix}. \qquad (2.11)$$

Proceeding as before, we find that

$$Q_{=CNi} = \frac{1}{2}(Q_{C=C} + Q_{H-H}) - Q_{H-Ni} - \frac{2}{3}\varepsilon_3, \qquad (2.12)$$

where ϵ_3 = 8.2 and $Q_{C=C}$ = 63.2 kcal (energy of rupture of the π bond). On substituting the known values of Q_{HK} and Q_{HNi}, we obtain Q_{CNi} = 28.1 kcal; from other data we obtain a value of 26.8 kcal. The isotopic exchange of ethylene with deuterium yields the not greatly differing value of 31.5 kcal.

By continuing in this way with reactions in whose indicial group new atoms are continually appearing, it is possible to find the energies of bonding of nickel with the various elements in organic compounds. Apart from the above reactions, such calculations have been made for the hydrogenation of propene, acetylene, and propyne, the hydrogenolysis of ethane and methylcyclopropane, and deuterium exchange with methane, water, isopropanol, ammonia, etc. The results[52] are listed in Table 3.

TABLE 3. Bond energies Q_{AK} with metallic catalysts, kcal.[52]

	H	D	−C	=C	≡C	ΔC	O	N
Ni	50.1	50.1	16.0	28.1	42.7	31.8	57.7	29.3
Fe	49.4	50.2	15.0	27.5	—	30.1	58.9	32.1
Pt	54.2	55.2	13.5	22.3	36.6	28.8	34.3	27.4
Pd	53.3	54.3	13.8	23.5	38.0	31.3	44.1	25.1

The bond energies found by this form of the kinetic method are remarkably close to those obtained by a quite different method (Table 1) long before the activation energies had been determined. Thus the values obtained by the two methods for the bonding energy (in kcal) of nickel are respectively — 50.1 and 55 with H, 16.0 and 14 with C, 28.1 and 27 with C, 57.5 and 48.5 with O, and 29.3 and 27 with N (*cf.* Tables 3 and 1). The fact that two independent methods yield the same results provides convincing evidence of the correctness of the theory.

In almost all cases with nickel the adsorption potential energies q calculated from the activation energies are close to the maximum values of $s/2$. Hence the activity of nickel catalysts is close to the maximum.

Values of Q_{AK} for platinum, palladium, and iron calculated in a similar manner are included in Table 3.

3. EFFECT OF EXTRAINDICIAL ATOMS

Hydrogenolysis on Nickel

The Q_{AK} values in Table 1 can be used to give a quantitative prediction of the reaction products. Let us first consider hydrogenolysis[6,4,22,53], which is specified by the index



(3.1)

Here variation occurs only in the left-hand portion, the atoms A and B. We shall regard a reaction as taking place more readily than another if it occurs at a lower temperature. Table 4 gives (above) the indices (3.1) of reactions over nickel arranged in the observed sequence of increasing ease of occurrence. The sequence based on Q_{AB} (see first row of numerals in Table 4) is evidently quite different, the numbers fluctuating without any regularity.

In contrast, the required sequence in ease of reaction on nickel is strictly observed by the values of E calculated from Eqn. (1.6). In Table 4 all the E values for hydrogenolysis do in fact increase from left to right, in agreement with experiment.

TABLE 4. E_{calc} for reactions on nickel catalyst, kcal.

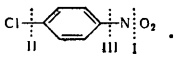
C H | C H	C H | N H	C H | O H	N H | N H	C H | Cl H	C H | Br H	O H | O H	N H | O H
$Q_{AB}=82.6$	72.8	85.5	75.3	81	68	35	53
$E'=-48.8$	−26.0	−17.2	−15.5	5.8	5.8	$E''=14$	$E''=18.5$
C—C | H H	N C | H N	C—N | H H	C—C | H O	C C | H C	C—C | H C	C—O | H H	C H || N H
$E'=-33.4$	−30.2	−28.1	−26.4	−25.9	−25.9	−23.8	−14.4

Calculation of E from Eqn. (1.6) shows also that multiple bonds A=B and A≡B should first be hydrogenated to a single bond A–B, after which the hydrogenolyses listed in Table 4 can begin. Therefore Table 4 is suitable also for compounds containing multiple bonds.

Let us now consider the hydrogenolysis of a multifunctional molecule, *i.e.* one containing different C–N, C–O, C–Cl, etc. bonds. Such a molecule can react in different ways. The question can be posed as to which type of bond will be the first to be broken, which the second, etc. The less stable a bond, the lower the temperature at which it is ruptured. Hydrogen adds on to the valencies which are set free on rupture. What substances can be formed on cleavage? And on what properties of the given molecules and catalyst does this sequence depend?

Experiment shows that Table 4, in particular the top row, gives unambiguously the sequence of ease of hydrogenolysis. This is important evidence in support of the multiplet theory. Since the molecule is oriented with the ruptured bonds towards the catalyst, Table 4 conveys also the orientation of the molecules at different temperatures.

As an example we can consider more fully the hydrogenolysis of *p*-chloronitrobenzene over nickel[54]



According to theory, the N–O bond (E = 18.5 kcal mole^{-1}) should be the first to be broken, then the C–Cl bond because it has a lower E (5.8), after this the C–N bond (-26.0), and only then the C–C bond (-48.8). Analysis of the reaction products at increasing temperatures showed that the predictions of theory are completely confirmed by experiment: *p*-chloroaniline and water are first obtained, then aniline and HCl, then benzene and NH_3, and finally CH_4.

The multiplet theory bases the sequence of hydrogenolysis in Table 4 on a vast number of experimental data, as is evident from Table 5, which gives results of calculations

TABLE 5. Sequence of hydrogenolysis reactions on nickel.

Class of compounds	Compound	Products: A) expected; B) observed
Amides	$CH_3\cdot CO\cdot NH_2$	A. 1) $CH_3CH_2NH_2$; H_2O; 2) CH_3CH_3; NH_3; 3) CH_4 B. 1) $CH_3CH_2NH_2$; H_2O; 2) CH_3CH_3; NH_3; 3) CH_4
Nitroalkanes	$CH_3\cdot CH_2\cdot NO_2$	A. 1) $CH_3CH_2NH_2$; H_2O; 2) CH_3CH_3; NH_3; 3) CH_4 B. 1) $CH_3CH_2NH_2$; H_2O; 2) CH_3CH_3; NH_3; 3) CH_4
Nitrites	$CH_3\cdot O\cdot NO$	A. 1,2) CH_3OH; NH_3; H_2O; 3) CH_4; H_2O B. 1,2) CH_3OH; NH_3; H_2O; 3) CH_4; H_2O
Ketoximes	$(CH_3)_2C{=}N\cdot OH$	A. 1) $(CH_3)_2C{=}NH\rightarrow(CH_3)_2CHNH_2$; H_2O; 2) $(CH_3)_2CH_2$; NH_3 B. 1) $(CH_3)_2C{=}NH\rightarrow(CH_3)_2CHNH_2$; H_2O; 2) $(CH_3)_2CH_2$; NH_3
Amines	$C_6H_5\cdot CH_2\cdot NH_2$	A. 1) $C_6H_5CH_3$; NH_3 B. 1) $C_6H_5CH_3$; NH_3
Aromatic alcohols	$C_6H_5\cdot CH_2\cdot OH$	A. 1) $C_6H_5CH_3$; H_2O B. 1) $C_6H_5CH_3$; H_2O
Aryl chlorides	$C_6H_5\cdot Cl$	A. 1) C_6H_6; HCl; 2) CH_4 B. 1) C_6H_6; HCl; 2) CH_4
Esters of chlorinated acids	$CH_2\cdot Cl\cdot COOR$	A. 1) CH_3COOR; HCl B. 1) CH_3COOR; HCl
Brominated arylamines	$BrC_6H_5\cdot NH_2$	A. 1) $C_6H_5NH_2$; HBr; 2) $C_6H_5\cdot NH_2$; 3) CH_4 B. 1) $C_6H_5NH_2$; HBr; 2) $C_6H_5\cdot NH_2$; 3) CH_4

analogous to the above example with chloronitrobenzene. Table 5 lists classes of compounds subjected to hydrogenolysis (taken from Sabatier's book[55]) and as examples one compound from each class, (A) indicating the products expected theoretically, and (B) the observed reaction products. The agreement with theory is seen to be excellent. The rule is obeyed by all the substances investigated with extremely rare exceptions. The following compounds‡ have been taken as starting materials — nitromethane, nitroethane, nitrobenzene, *o*- and *m*-nitrotoluenes, 1-nitronaphthalene, *m*-dinitrobenzene, 1,5-dinitrotoluene, nitrophenols, methyl nitrite, ethyl nitrite, propyl nitrite, isobutyl nitrite, isopentyl nitrite, acetaldehyde oxime, acetone oxime, ethyl methyl ketone oxime, methyl propyl ketone oxime, diisopropyl ketone oxime, diethyl ketone oxime, acetophenone oxime, ethyl phenyl ketone oxime, benzophenone oxime, phenyl propyl ketone oxime, cyclohexanone oxime, ethylcyclohexanone oxime, 3-methylcycloheptanone oxime, menthanone oxime, camphor oxime, acetamide, propionamide, ethyl isocyanate, ethylurea, phenyl isocyanate, aniline, toluidines, *N*-methylaniline, *N*-methyltoluidine, *NN*-dimethyltoluidine, *N*-ethylaniline, diphenylamine, benzylamine, ethylamine, pentylamine, hydrocyanic acid, acetonitrile, propionitrile, γ-methylvaleronitrile, methylmalononitrile, benzonitrile, *p*-tolunitrile, phenylhydrazine, azobenzene, benzyl alcohol, phenethyl alcohol, diphenylmethanol, phenyl-*p*-tolylmethanol, triphenylmethanol, 2-*p*-tolylpropan-2-ol, furfuryl alcohol, 2-methylfuran, benzaldehyde, methylcyclopentanone, dihydrocamphorone, succinic anhydride, phthalic anhydride, camphoric anhydride, phenol, cresols, xylenols, quinol, resorcinol, catechol, quinones, acetophenone, methyl *p*-tolyl ketone, *p*-butylphenyl methyl ketone, benzylacetone, benzophenone, benzyl phenyl ketone, dibenzyl ketone, 1,1-diphenylacetone, methyl 1(and 2)-naphthyl ketones, 1-naphthyl propyl ketone, hexahydroanthrone, benzil, benzoin, 1-phenylbutane-1,3--dione, anisole, methyl tolyl ethers, methyl 1-naphthyl ether, phenyl oxide, diethyl ether, cyclohexene oxide, cyclohexanone, methylcyclohexanone, cyclopentanone, acetone, chlorobenzene, dichlorobenzene, perchlorobenzene, chlorotoluene, trichlorophenol, chloroaniline, chloronitrobenzene, mono-, di-, and tri-acetic esters, bromobenzene, *p*-bromotoluene, bromoaniline, bromonitrobenzene, 2,4,6-tribromophenol, and monobromoacetic esters.

We see what a variety of substances obey the energetic requirements of the multiplet theory. In fact this list must be increased to several hundreds of reactions, since the hydrogenolysis products of the starting materials undergo in turn further hydrogenolysis, which also conforms to the observed rule[6].

The requirements of the multiplet theory are met not only by hydrogenolysis but also by many other reactions investigated. The energy barriers to the types of reactions whose indices are indicated in the lower half of Table 4 have been calculated for nickel from Table 1. The calculated sequence of reactions agrees with experiment. The lower row in Table 4 gives in order of increasing E the reactions — dehydrogenation of hydrocarbons, formation of secondary from primary amines (for example of diphenylamine and ammonia from aniline, where the C–Ni bond is close to =C–Ni), dehydrogenation of amines, dehydration of alcohols, dimerisation of ethylene to butene, migration of the C=C bond in the chain, dehydrogenation of alcohols, and hydrogenation of the C=N bond. The reactions occur in the same sequence with increasing ease on nickel. In conformity with thermodynamics, calculation shows that the difference between E for hydrogenation of an alkene and E for dehydrogenation of the alkane is equal to the heat of hydrogenation ΔH = -30 kcal mole^{-1}.

It must be specially stressed that the values of E for all fourteen indices not containing halogen in Table 4 have been calculated, in agreement with experiment, from only five Q_{AK} values, namely Q_{-CNi}, $Q_{=CNi}$, Q_{NNi}, Q_{HNi}, and Q_{ONi}. This is an indication of far reaching additivity, and confirms Eqns. (1.6) and (1.7).

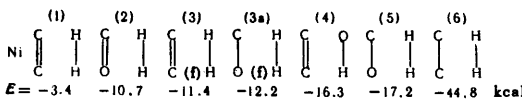
Some of the reactions in Table 4 were predicted in advance, and later carried out experimentally in our laboratory, among them being hydrogenolysis of the N–Br, O–Cl, and O–O bonds (accomplished in the formation of acetamide from *N*-bromoacetamide, of t-butanol from t-butyl chlorite, and of alcohols from peroxides and hydroperoxides), dehydrogenation of amines to aliphatic ketimines, etc.[1]

Hydrogenolysis on Carbon

It was of interest to apply the same method to another catalyst, for which the Q_{AK} values were known. We therefore investigated reactions on carbon between hydrogen and several chlorinated and brominated hydrocarbons[56] and, in greater detail, cyclohexanol[57]. Calculation and experiment showed that, in contrast to nickel, the reaction velocity is controlled by the desorption stage. Calculated and observed reaction sequences showed in general good agreement. The coefficient γ in Eqn. (1.9) should have a lower value with carbon than with nickel. Another difference is that, when a duplet complex is formed on carbon, E must be corrected for the formation of a three-membered carbon ring, in conformity with the fact that the valencies of carbon, but not those of metals, are directional (*cf.* Pauling[58]).

Furan Derivatives[59,60]

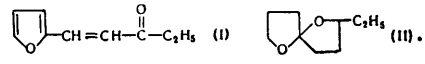
The sequence of reactions involving hydrogenation, cyclisation, and hydrogenolysis of furan derivatives on nickel, predicted from calculations of E based on Table 1, is



(3.2)

where the indices relate to hydrogenation of (1) a C=C bond, (2) a side-chain C=O bond, (3) a C=C bond in the furan ring, and (3a) an ether link in the furan ring, formation of (4) a spiran, and hydrogenolysis of (5) a C–O bond, and (6) a C–C bond. In the hydrogenation of the furan ring it is assumed that the multiplet complex contains half the conjugation energy of furan ($\sigma/2$ = 8 kcal). The volcano-shaped curves are shown in Fig. 5.

As an example, let us consider the reactions of 1-fur--2′-ylpent-1-en-3-one (I)



According to calculation, hydrogenation of (I) over nickel should yield successively — (1) 1-fur-2′-ylpentan-3-one,

‡ Several uncertain names have been translated literally (Ed. of Translation).

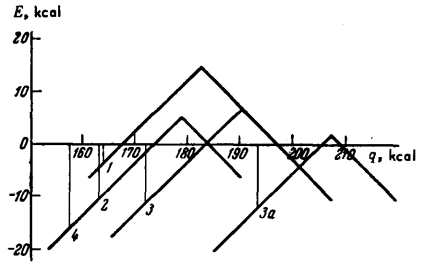
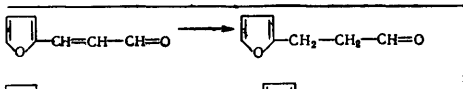
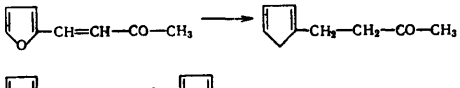
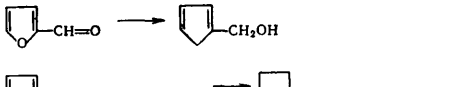
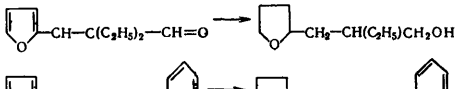
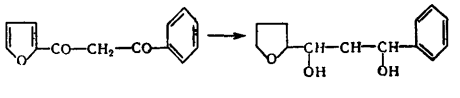
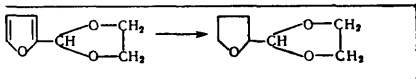
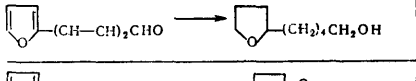
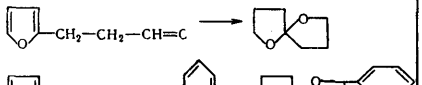
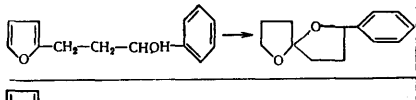
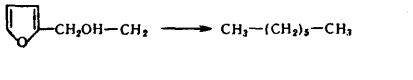


Fig.5. Volcano-shaped curves and heights of energy barriers in the hydrogenation of furan derivatives. Numbering of reactions (1)–(3a) as in Eqn.(3.2).

(2) 1-fur-2′-ylpentan-3-ol, (3) 1-tetrahydrofur-2′-ylpentan-3-ol, and (4) 5-ethyl-2,2′-spirobitetrahydrofuran (II): then, after a series of similar stages involving fission of the ether links, (5) n-nonane, and finally (6) methane.

Some further examples are listed in Table 6. The position of the comma in the column headed *A* in Table 6 indicates between which two successive conversions in Eqn. (3.2) the given reaction halted under the given conditions. This position was found experimentally. An increasing numerical sequence under *A* implies agreement between theory and experiment, as is the case. The higher the temperature the farther to the right is the comma located, which is also consistent with theory.

TABLE 6.

	A	*t*°
	1.236	25
	1.236	
	2.356	90
	23.456	135
	123.456	
	13.56	130
	123.56	
	134.56	140
	134.56	
	12345.6	>300

The theory has been tested on the following§ compounds — β-furylacrolein, furfurylideneacetone, 1-furyl-8-methyl-oct-1-en-3-one, furfurylideneacetofuran, difurfurylideneacetone, vinylfuran, furfuraldehyde, 6-furylhexa-3,5-dien-2-one, 1-furyl-5-methylhex-1-en-3-one, furfurylidenecamphor, 3-furylpropan-1-ol, 3-(5-methylfur-2-yl)propan-1-ol, 4-furylbutan-2-ol, 4-(5-methylfur-2-yl)butan-2-ol, 1-furylpentan-3-ol, 1-furylhexan-3-ol, 1-furylheptan-3-ol, 1-furyloctan-3-ol, 1-furyl-7-methyloctan-3-ol, 3-furyl-1-phenylpropan-1-ol, 1-furyl-5-phenylpentan-3-ol, 3-furyl-2-methyl-1-phenylpropan-1-ol, 3-furylpropionaldehyde, 1,5-difuryl-3-phenylpropane-1,3-dione [*sic*], 1-furylbutane-1,3-dione, furfurylidenebutyraldehyde, difurfurylidenecyclohexanone, 1-furylhex-1-en-3-one, furan, 2-methylfuran, 2-ethylfuran, 2-n-propylfuran, 2-n-pentylfuran, 1-furylbut-1-ene, 2-benzylfuran, 2,5-dimethylfuran, furfuryl alcohol, 1-furylethanol, 1-furylpropanol, 1-furylbutanol, α-furylbenzyl alcohol, 6-furylhexan-2-ol, furfural diethylacetal, 2-furyldioxolan, 2,2′-furoin, 5-hydroxymethylfurfural, 5-furylpenta-2,4-dienal, 6-furylhexa-3,5-dien-2-one, 7-furylhepta-4,6-dien-3-one, 1,9-difurylnona-1,3,6,8-tetraen-5-one, β-furylpropionaldehyde, β-(5-methylfur-2-yl)propionaldehyde, 1,5-difurylpentan-3-ol, tetrahydrofuran, furfurylideneacetophenone, tetrahydro-2-methylfuran, and spirobitetrahydrofuran. Experiment confirmed theory. When both furan and benzene rings are present in a molecule, the former is hydrogenated more readily, in conformity with the requirements of theory, since the resonance energy to be overcome in it is lower (see Section 4). This list has recently been further supplemented by the work of Ponomarev and of Til' [61]. Furan derivatives can be obtained from agricultural waste products, and the above results are of value for exploitation of the latter.

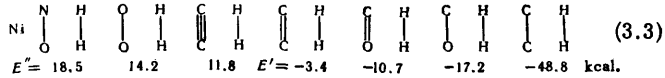
Hydrogenation of Triptycene Derivatives

The Reviewer and Klabunovskii [1,62] investigated the kinetics of the hydrogenation of triptycene derivatives on nickel at 45° and 1 atm. The experimental results were consistent with the calculations of *E*.

Hydrogenation of Peroxides and Hydroperoxides

Interesting results have been obtained [63-67] in a study of the kinetics of the hydrogenation of organic peroxides and hydroperoxides over nickel, palladium, and platinum. Until then almost nothing was known about this class of reactions, and still less about their kinetics.

On the basis of Table 1, the multiplet theory makes the following predictions: (1) peroxide compounds should be readily hydrogenated on nickel, since calculation indicates that the height of the energy barrier is $-E = -14.3$ kcal; (2) the activation energy of such reactions should be close to 7 kcal, from Eqn. (1.9); (3) the rate of hydrogenation should be affected by the structure of the molecules; (4) on hydrogenation over nickel, multifunctional peroxides should undergo, according to Table 1, consecutive reactions in the sequence



(3.3)

§ In view of the uncertainties and inconsistencies of the Russian nomenclature, several names in this list have been left in a semi-trivial form (Ed. of Translation).

(The value 11.8 has been calculated from the data in Table 3); and (5) this sequence may be somewhat different with other catalysts, as follows from Eqns. (1.6) and (1.7).

These expectations have been confirmed by experiment. The reactions already occur at 5–30°, and are of zero or the first order. Some of the results obtained with nickel are indicated in Table 7. The sequence observed with palladium did in fact prove to be different from that with platinum.

The reduction of 2-isopropylanthraquinone with hydrogen over nickel has also been investigated[68], together with the production of hydrogen peroxide when the reaction products oxidise in the air. In agreement with calculation, the C=O bond is reduced sooner than the aromatic ring.

Effect of Substitution within the Indicial Group — General Case[69]

Let one of the atoms, *e.g.* A, in the indicial group (1.5) be replaced by another atom. In order to learn how this affects the energy barrier to the reaction $-E'$, we must examine the variation of E' with respect to A in Eqn. (1.6). Since the remaining quantities are practically independent of A, such variation gives

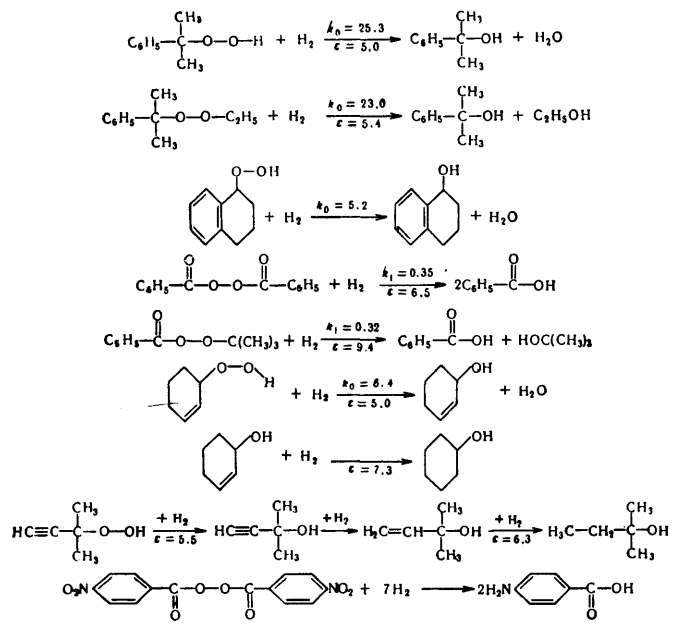
$$\delta E' = -\delta Q_{AB} + \delta Q_{AK} \qquad (3.4)$$

whence

$$\delta E' < 0, \text{ when } \delta Q_{AB} > \delta Q_{AK}. \qquad (3.5)$$

This important relation can be expressed in words as follows: when an atom A in a duplet indicial group is replaced, *i.e.* when $A^1 \rightarrow A^2$, the first of two comparable reactions goes more rapidly than the second ($E_1 > E_2$) if the energy of bonding of atom A with atom B increases more (or decreases less) than the energy of bonding of A with the catalyst K ($Q_{A^2-B} - Q_{A^1-B} > Q_{A^2-K} - Q_{A^1-K}$). Thus on nickel, hydrogenolysis of the Cl–C bond, in which A^1 = Cl, is more rapid than that of the N–C bond, where A^2 = N; and in fact $\delta Q_{AB} = Q_{N-C} - Q_{Cl-C} = 72.8 - 81.0 = -8.2$ is greater (a less negative quantity) than $\delta Q_{AK} = Q_{NNi} - Q_{Cl-N} = 27 - 67 = -40$ kcal (*cf.* Table 4).

TABLE 7.



4. EFFECT OF INTRAINDICIAL SUBSTITUENTS

That part of the multiplet theory which deals with the influence of substituents which are not in contact with the catalyst recalls the theory of colour in organic compounds[70]. The indicial group corresponds to the chromophoric group. The position of the maximum on the volcano-shaped curve along the q axis corresponds to that of the centre of an absorption band in the spectrum, while the influence of extraindicial substituents on E is equivalent to the displacement of an absorption band under the influence of auxochromic groups. Similar views have been expressed by Langenbeck[71].

As a result of the change in electron density, a substituent attached to A, for example, influences the bond energies Q_{AB} and Q_{AK}, and hence also E'. For a quantitative assessment of this effect we again vary Eqn. (1.6) with respect to A. Now, however, A^1 and A^2 denote, not different atoms as above, but the same atom A with different extraindicial substituents. The result of the variation is obviously again conveyed by the formulae (3.4) and (3.5) and by the above verbal formulation, but according to the new definition it is "a substituent attached to an atom A", not the atom itself, which is replaced. The extent to which a substituent influences Q_{AB} has been discussed in Section 2.

Eqn. (3.4) contains the fundamentally important result that in catalytic reactions, unlike non-catalytic reactions, the influence of substituents on reaction velocity and on E must be allowed for twice — on Q_{AB} and Q_{AK} — the two effects being opposed. This explains in particular the apparently contradictory result that in a homologous series the rate in some cases decreases (this occurs when $\delta Q_{AB} > \delta Q_{AK}$), in other cases increases (when $\delta Q_{AB} < \delta Q_{AK}$), and in still other cases remains unchanged (when $\delta Q_{AB} = \delta Q_{AK}$). This last type of behaviour is found in the dehydrogenation of primary alcohols — in the work of Palmer and Constable, Bork and the Reviewer, Lüttich and Briecht¶ (on copper), and especially of Bogdanova, the Reviewer, and Shcheglova (the papers are listed in Ref. 1) — where ϵ remained constant for normal primary alcohols from C_2 to C_9 (on an oxide catalyst). Such cancelling out of the effects of δQ_{AB} and δQ_{AK} is not found in the dehydration of alcohols, and 1-, 2-, and 3-substitution each contributes its own increment to ϵ (according to the work of Dohse and Kölberer¶ on bauxite, of Bork and Tolstopyatova on Al_2O_3, and of the Reviewer, Tolstopyatova, and Stshizhevskii on W_2O_5).[1]

The rate of hydrogenation of alkenes on platinum falls with increasing substitution by alkyl groups of hydrogen atoms adjacent to the double bond (Lebedev's rule[72]). It also falls with increase in the number of phenyl radicals replacing alkyl radicals adjacent to the double bond (Kazanskii and Tatevosyan[73]).

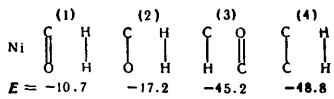
The rate of hydrogenation under pressure decreases on passing from benzene to hexamethylbenzene over Ni on Al_2O_3, but it increases in this sequence over WS_2 (Lozovoi[74,75]).

¶ The spellings of some of the non-Russian names are conjectural (Ed. of Translation).

Chain branching retards the hydrogenation of ketones over platinum (Vavon[76]). A decrease in reaction velocity on substitution implies that $\delta Q_{AB} > \delta Q_{AK}$.

Hydrogenation of Monosaccharides

The multiplet theory has proved useful also in investigating the hydrogenation of monosaccharides[77]. Calculation of E from Table 1 leads us to expect the following reaction sequence



(4.1)

where the indices represent — (1) hydrogenation of the monosaccharide to a polyhydric alcohol, (2) reduction of a hydroxy-group, (3) the Cannizzaro–Tishchenko reaction with formation of gluconic acids, and (4) hydrogenolysis of a C–C bond, for example the formation of glycerol from sorbitol. This sequence is actually observed[77] as the temperature is raised (from 120° to 230° at 150–300 atm). We have made a special investigation of reaction (4).[78,79]

It is especially interesting that it has proved possible[77] also to indicate the effect of extraindicial substituents. As above, let such a substituent be attached to atom A in formula (1.5). By varying the expressions for E' [Eqn. (1.6)] and for u (see Section 1) with respect to A, and using the well-known equation $\Delta F = -u - T\Delta S$, where F is the free energy and S the entropy, we obtain

$$\left.\begin{aligned} \delta E' &= \delta Q_{AK} - \delta Q_{AB} \\ \delta u &= \delta Q_{AD} - \delta Q_{AB} \\ \delta \Delta F &= -\delta u - T\delta\Delta S \end{aligned}\right\}. \qquad (4.2)$$

From the set of equations (4.2) it follows that

$$\delta E' = -\delta\Delta F - (T\delta\Delta S - \delta Q_{AD} + \delta Q_{AK}). \qquad (4.3)$$

For condensed (*i.e.* solid and liquid) systems $\delta\Delta S$ is small, and the difference $\delta Q_{AD} - \delta Q_{AK}$ is also small compared with $\delta\Delta F$. Hence in this case we find from the multiplet theory that

$$\varepsilon E' \simeq -\delta\Delta F, \qquad (4.4)$$

i.e. that when there is no evolution of gas (for example methane), the change $-\delta E'$ in the energy barrier due to substitution should be approximately equal to ΔF. The values of ΔF can be estimated, and Tables 8 and 9 have been compiled on this basis. The δE values in these tables must be added to E in Eqn. (4.1). The values of E themselves do not vary in parallel with ΔF. In agreement with experiment, Tables 8 and 9 show in particular that — (1) C–C and C–O bonds behave differently depending on their position in the molecule; (2) a C–C bond occurring in the middle of a polyhydric alcohol molecule undergoes cleavage most readily; and (3) a C–O bond is more readily broken when attached to primary than to secondary carbon atoms. Some of these generalisations were known earlier[77], but the multiplet theory has provided an explanation of them.

TABLE 8. Hydrogenolysis of polyhydric alcohols at the C–O bond.

Reaction (H_2O formed in each case)	$\delta E = -\delta\Delta F$, kcal
Hexitol → methylpentitol	2.6
Pentitol → methylerythritol	2.6
Erythritol → methylglycerol	2.7
Erythritol → butene-1,2,4-triol	−0.3
Glycerol → propylene glycol	2.1
Glycerol → trimethylene glycol	−1.3
Propylene glycol → n-propanol	−1.6
Propylene glycol → isopropanol	2.5
Ethylene glycol → ethanol	−2.7

TABLE 9. Hydrogenolysis of polyhydric alcohols at a C–C bond.

Reaction	$\delta E = -\delta\Delta F$, kcal
Hexitol → 2 (glycerol)	1.2
Hexitol → erythritol + ethylene glycol	0.4
Hexitol → methanol + pentitol	0.16
Methylpentitol → glycerol + propylene glycol	0.7
Methylpentitol → methylglycerol + ethylene glycol	0.5
Methylpentitol → methylerythritol + methanol	−1.06
Pentitol → ethylene glycol + glycerol	1.10
Pentitol → erythritol + methanol	−0.04
Methylerythritol → ethylene glycol + propylene glycol	0.6
Methylerythritol → ethanol + glycerol	−0.6
Methylerythritol → methanol + methylglycerol	−0.04
Erythritol → 2 (ethylene glycol)	1.2
Erythritol → glycerol + methanol	0.2
Methylglycerol → ethanol + ethylene glycol	−1.2
Methylglycerol → methanol + propylene glycol	0.2
Glycerol → ethylene glycol + methanol	−0.04

Strain in Rings

According to thermochemical calculations[26] Q_{C-C} has values of 73.8, 76.4, 81.7, and 82.9 kcal in the series of cycloalkanes from cyclopropane to cyclohexane. Also $Q_{C_{Ar}-C_{Ar}} = 112.0$ and $Q_{C_{Ar}-C_{Alk}} = 95.2$ kcal. Levi and the Reviewer[80] calculated the comparative ease of closing and opening carbon rings on platinum and on palladium, and obtained results which all agreed with the experimental data of Kazanskii and his coworkers.

Recently Lukina[81] has found a very interesting parallel between the ease of hydrogenation of cyclopropane hydrocarbons and their electronic structure. From the point of view of the multiplet theory this means that the electronic structure influences the Q_{AB} of different bonds in these hydrocarbons, and Q_{AB} is more strongly affected than Q_{AK} in equations of the type (1.6). The cyclopropane ring forms with a double bond a conjugated system, and we thus come up against the problem of the effect of conjugation energy on the rates of catalytic reactions.

Effect of Conjugation Energy

The influence of conjugation energy σ on rate of catalytic hydrogenation has been examined from the standpoint of the multiplet theory[82–85]. When σ is taken into account, Eqn. (1.6) for the hydrogenation of an olefinic bond will be

$$E' = -Q_{C_1=C} - Q_{H-H} + Q_{C_1-K} + Q_{C-K} + 2Q_{H-K} - r\sigma. \qquad (4.5)$$

The appearance of conjugation energy is due to electron delocalisation resulting from interaction of two π-electron systems, and $r \simeq \frac{1}{2}$ is the proportion of σ remaining in the active complex, C_1 being the carbon atom at which the substituent is changed. By varying Eqn. (4.5) we find the effect on E of the nature of the substituent:

$$\delta E = -\delta Q_{C_1=C} + \delta Q_{C-K} - r\delta\sigma, \qquad (4.6)$$

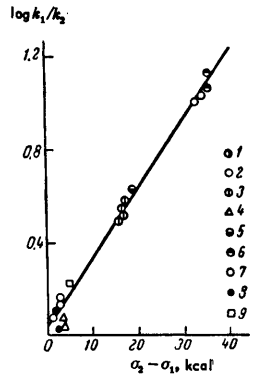


Fig.6. Relation between conjugation energy and rate constant for hydrogenation:
1) cyclopentadiene and benzene;
2) eugenol and *cis*-isoeugenol;
3) dihydrofuran and furan;
4) cyclopentane and cyclopentadiene;
5) furan and benzene;
6) cyclohexa-1,4-diene and benzene;
7) cyclohexa-1,3-diene and benzene;
8) cyclohexa-1,4- and -1,3-dienes;
9) diphenylmethane and biphenyl.

where $\delta Q_{C_1=C}$ and δQ_{C-K} are the changes in the induction and hyperconjugation effects, and $\delta\sigma$ is the change in conjugation energy on substitution. The relation (4.6) is fairly complex in form: in order to find the effect of σ, it is obviously necessary to compare compounds whose structures are such that $\delta Q_{C_1=C}$ and δQ_{C-K} remain as constant as possible. It follows that, under otherwise identical conditions, the disappearance of conjugation energy during a reaction makes hydrogenation more difficult, and similarly its appearance on dehydrogenation should accelerate the latter.

Experiments on the hydrogenation of different compounds under comparable conditions — in solution at 5–60° and 1 atm — over rhodium (0.1–2.5% Rh on Al_2O_3) showed[82] that: (1) an increase in the conjugation energy of the reactant lowers the hydrogenation rate constant k; (2) with small differences in conjugation energy the induction (and hyperconjugation) effects are more strongly developed; and (3) the nature of the solvent has no decisive importance.

A new relation (resembling the Hammett equation) has been discovered[82]

$$\log(k_2/k_1) = a(\sigma_1 - \sigma_2) + b, \qquad (4.7)$$

the subscripts 1 and 2 indicating two different compounds with different conjugation energies, and a and b being constants. The results are illustrated in Fig. 6. The 1,1-diphenyl-2--picrylhydrazyl free radical is difficult[85] to hydrogenate under these conditions; this can be explained by the necessity for overcoming the stabilising effect of the conjugation energy. We have investigated the kinetics of the dehydrogenation of several alkyl-aromatic hydrocarbons (for summary see Ref. 86), and found that, under conditions such that ethylbenzene is readily converted into styrene, ethylcyclohexane remains almost unchanged[87]. This is consistent with what has been said above. The appearance of conjugation energy makes it clear why the dehydrogenation of butane and that of ethylbenzene require different catalysts[88].

The electronic concepts of modern organic chemistry, examples of the application of which have been discussed above, must be expected to prove very useful in developing the multiplet theory: they will be able to explain how bond energies vary, and the latter can be utilised by the multiplet theory.

5. EFFECT OF NATURE OF CATALYST

We have examined above the influence on catalysis of changes in the nature and structure of molecules; in this and the next section we shall consider the analogous effect of changes in the nature of the active centre on the catalyst and in its environment, in accordance with the layer structure proposed for the multiplet complex (see Fig. 3 in Ref. 1).

The Reviewer has suggested[89] that the catalytic properties of elements depend on their position in the Periodic System. Knowledge of the dependence of bond energies between elements and organic radicals Q_{AK} on the position of the former may be expected to be a great help in solving the problem of choice of catalyst. It may be hoped that rules will be discovered which will facilitate the task of selection and eliminate the complications due to method of preparation of catalyst, etc. Then, when a few Q_{AK} values are known, E can be calculated for a larger number of reactions by the method of volcano-shaped curves. The rules which we have already found in this field are given below.

1. Interesting results have been obtained for the rare earths[8], for which Q_{AK} proves to be a periodic function linked with the magnetic moment μ of the ions of the oxides. The values of Q_{HK} and Q_{CK} vary in parallel with μ, while Q_{OK} varies in the opposite sense (Fig. 7). Values of the

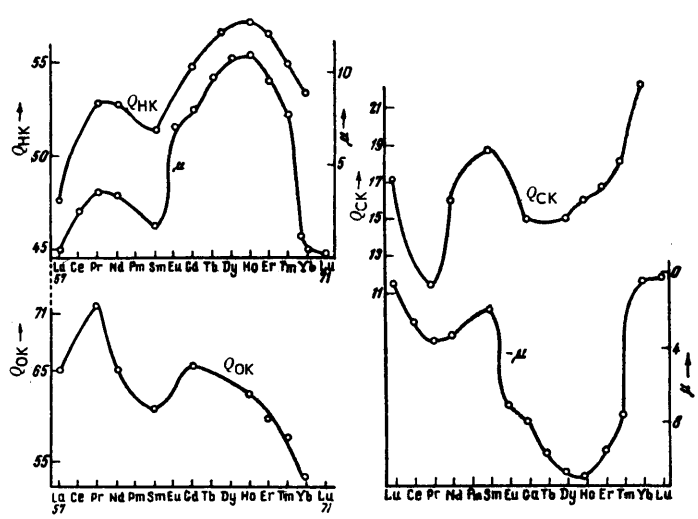


Fig.7. Dependence of bond energies Q_{HK}, Q_{OK}, and Q_{CK} in kcal and of magnetic moment μ in Bohr magnetons on atomic number of rare-earth elements.

activation energy of dehydrogenation of tetralin and alcohols, employed in the calculation of Q_{AK} from Eqns. (2.6)–(2.8), do not vary periodically but monotonically, though irregularly. Hence the Q_{AK} are primary quantities, and the ϵ secondary, in which periodic effects cancel out. This result is important also for electronic theory, since it shows that the inner 4*f* electrons play a part in catalysis (just as they influence other chemical properties).

2. The energy of bonding of oxygen in the reactant molecule with the oxide Q_{OK}^{ki} determined kinetically as a function of the atomic number *n* varies in parallel with Q_{OM}^{th}, the energy of bonding of the metal with oxygen in the oxide determined by a thermochemical method[42] (see Fig. 8). The Q_{OK}^{ki} are located below and somewhat differently from Q_{OM}^{th} because of the presence of the sublimation term λ (*cf.* Section 6). In Fig. 8 the atomic number *n* of the element is plotted as abscissa and the corresponding Q_{OK}^{ki} from Table 2 as ordinate. The parallelism between Q_{OK}^{ki} and Q_{OM}^{th} indicates firstly that the former is a periodic function of atomic number, since the latter is such a function; secondly it confirms that in catalysis on oxides the molecules are adsorbed predominantly on the metal atoms, not the oxygen atoms (*cf.* Section 1).

Activation energies have been determined[44] for several reactions on zinc oxide, to whose catalytic properties a combined approach from the viewpoints of the multiplet and the electronic theories was shown to be possible by Dowden *et al.*[90] Values have been found[44] for Q_{HK}, Q_{CK}, and Q_{OK} (see Table 2), and Q_{NK} = 30.8 kcal. Calculation based on these data shows that, in contrast to the situation with nickel, a C=O bond should be hydrogenated on zinc before a C=C bond, and in fact Freidlin and Gorshkov[91] have confirmed this experimentally in several cases.

By means of Eqns. (2.6)–(2.8) it has been possible[92] to use previously known activation energies for the dehydrogenation of alcohols ϵ_2 and their dehydration ϵ_3 to calculate beforehand the sequence of ϵ_1 for the dehydrogenation of hydrocarbons on oxides of metals in Group II of the Periodic System. It follows from these equations that

$$\varepsilon = \frac{2}{3}(\varepsilon_3 + \varepsilon_3) + Q_{OK} - 48.6. \qquad (5.1)$$

Substitution of thermochemical values of Q_{OK} showed that the duplet dehydrogenation of hydrocarbons is impossible on BeO and MgO, can take place with difficulty on ZnO, and is entirely possible on CdO. This theoretical prediction has been confirmed by experiments with cyclohexane, cyclohexene, butene, and ethylbenzene[92,93].

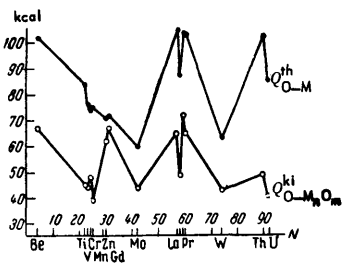


Fig. 8. Parallelism between energy of bonding of oxygen with the surface of an oxide catalyst $Q_{O-M_nO_m}^{ki}$ in kcal determined by a kinetic method and the energy of the metal–oxygen bond in the solid oxide Q_{O-M}^{th} in kcal determined thermochemically from the heat of formation of this oxide from the elements, as functions of atomic number.

Reactions have been studied on the oxides of vanadium, niobium, and tantalum[94–97] and on the oxides and sulphides of molybdenum and tungsten[37,98] in order to determine Q_{AK}.

Eqn. (3.4), which follows from the multiplet theory, explains the reversal of order in catalytic efficiency when one catalyst K_1 is replaced by another K_2: if the term δQ_{AK} predominated with K_1, δQ_{AB} may predominate with K_2, so that $\delta E'$ in Eqn. (3.4) changes sign. This question was discussed in Ref. 69, where a theoretical analysis was given of the change in reactivity when one of the atoms forming the active centre is replaced by another. An attempt has been made to determine Q_{AK} values for Cr_2O_3–Fe_2O_3 mixed catalysts[99].

The work of Jouy and Balaceanu[100] is close in conception to the multiplet theory. These workers used mixed catalysts whose components activated both the O–O and H–H bonds (oxidation) and the C–H and H–H bonds (dehydrogenation), and were able to facilitate the dehydrogenation of cyclohexane and the aromatisation of hept-2-ene and heptane by adding O_2 to them.

6. EFFECT OF ENVIRONMENT OF ACTIVE CENTRE

The activity and the selectivity of a catalyst are affected by the nature, number, and arrangement of its atoms around the active centre. This appears in the influence of the mode of preparation, aging, carriers, etc., and also, in certain cases, of additives.

Let us examine this effect[13,101]. The energy of bonding Q_{A-K} of an atom A with an atom K_1 of the active centre comprises two parts — the energy of bonding with the catalyst lattice Q_{A-K}^0 and the sublimation term λ_A — the latter representing the aggregate effect of atoms adjacent to the active centre:

$$Q_{A-K} = Q_{A-K}^0 + \lambda_A. \qquad (6.1)$$

The quantity λ_A is itself composite. It is demonstrated in the multiplet theory that

$$\lambda_A = \alpha\lambda_K - \lambda_{A-K_1} + \lambda_{A-K_1,K}, \qquad (6.2)$$

where λ_K is the heat of sublimation, *i.e.* the energy of removal of an atom K (see Fig. 9) from inside the catalyst into the gas phase, $\alpha\lambda_K$ is the heat of sublimation of an atom K_1 from the surface (for a smooth surface $\alpha = \frac{1}{2}$ according to Laplace's theorem), λ_{A-K_1} the energy of bonding of the atom A to a surface atom K_1, and $\lambda_{A-K_1,K}$ the energy of bonding of the active complex $A-K_1$ to the surface atom K.

Let us give this proof in brief[101]. When we use a thermochemical method to calculate the bond energy Q_{A-K}^0 from the standard heat of formation of the compound A–K, this relates to the process

$$K(latt.) + A(gas) = A-K(latt.) + Q_{A-K}^0 + \epsilon_0, \qquad (6.3)$$

where ϵ_0 is the energy of electronic excitation. In order to calculate the energy of attraction of an atom A by an active centre of the catalyst K_1, which we denote as the bond energy Q_{A-K_1}, we must examine the process represented by the thermochemical equation

$$K_1(act.\ centre) + A(gas) = A-K_1, K(surf) + Q_{A-K_1} + \epsilon_0. \qquad (6.4)$$

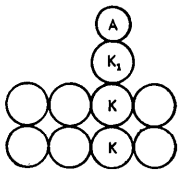


Fig.9. Diagram illustrating physical significance of individual terms in Eqn.(6.2). A fuller explanation will be found in the text.

Let us consider how to pass from Eqn. (6.3) to (6.4). Subtracting the latter from the former, we obtain

$$K(latt.)-K_1(act.\ centre)=A-K(latt.)-A-K_1,\ K(surf)+Q^0_{A-K}-Q_{A-K}. \quad (6.5)$$

Further, we have by definition the following thermochemical equations

$$K(latt.)=K_1(act.\ centre)-\alpha\lambda_K, \quad (6.6)$$

$$A-K(gas)=A-K(latt.)+\lambda_{A-K_1}, \quad (6.7)$$

$$A-K(gas)=A-K_1\ K(surf)+\lambda_{A-K_1,K}. \quad (6.8)$$

It is readily seen from Eqn. (6.6) that the left-hand side of Eqn. (6.5) is equal to $-\alpha\lambda_K$. Subtracting (6.8) from (6.7), we find that

$$A-K(latt.)-A-K_1,\ K(surf.)=-\lambda_{A-K,}+\lambda_{A-K_1,\ K}.$$

Substituting this result in the right-hand side of Eqn. (6.5), we obtain

$$Q_{A-K}=Q^0_{A-K}+\alpha\lambda_K-\lambda_{A-K,}+\lambda_{A-K_1,K}. \quad (6.9)$$

Comparison of Eqns. (6.1) and (6.9) yields (6.2).

Eqn. (6.2) shows that λ_K can be either positive (when $\alpha\lambda_K+\lambda_{A-K_1,K}>\lambda_{A-K_1}$) or negative (when $\alpha\lambda_K+\lambda_{A-K_1,K}<\lambda_{A-K_1}$). In Langmuir's work the adsorbed oxygen film is evaporated from W in the form of WO_3 before the evaporation of O and especially of W, whence $\lambda_W>\lambda_{O-W}>\lambda_{O-W,W}$. This gives an idea of the sequence of λ values.

When $\lambda_{A-K_1,K}$ is small, the multiplet complex may move along the surface[1].

Analogous equations to (6.2) occur also for the bonds B-K, C-K, and D-K. Therefore

$$\begin{aligned} Q_{AK}&=Q^0_{AK}+\lambda_A\\ Q_{BK}&=Q^0_{BK}+\lambda_B\\ &\cdots\cdots\cdots\\ q&=q^0+\lambda \end{aligned} \quad (6.10)$$

i.e. the adsorption potential energy q (which according to the principle of energetic correspondence should be close to $s/2$ for a good catalyst — *cf.* Fig. 2) consists of two parts, q^0 and λ. The controversy between Roginskii[102], who regards supersaturation as the main factor determining the activity of a catalyst, and Boreskov[103], who considers that with the same surface only its chemical nature is significant, comes down to a different relative assessment of q^0 and λ: according to Boreskov q^0 predominates, and according to Roginskii λ. In particular cases the specific catalytic activity may not be affected by microscopic roughness (with sintered catalysts, for example), and λ is then approximately constant, but this cannot be true in general, since the mode of preparation is known to influence the selectivity of catalysis.

If in a given reaction λ for a catalyst prepared in one way is lower than for a catalyst prepared in a different manner, the adsorption potential energy of the first catalyst will be lower than that of the second: $q_1<q_2$.

It follows from condition (1.15) that, if $q_1<s/2$ and if $\Delta\lambda$ is the change in λ on passing from the second to the first catalyst, the reaction velocity will increase when

$$\Delta\lambda<s-2q_1, \quad (6.11)$$

being a maximum when $\Delta\lambda=s/2-q_1$.

When the surface contains a set of active centres having different values of $\Delta\lambda$, but such that the highest adsorption potential energy does not exceed $s/2$, *i.e.* such that $q_1+\Delta\lambda\leqslant s/2$, an increase in adsorption potential energy produces an increase in E and hence in the reaction velocity. This is in agreement with Taylor's views[104]. However, further increase in adsorption, and hence in the adsorption potential energy, now diminishes E' and retards catalysis, in contradiction to his views. Thus catalysis occurs at active centres having some intermediate adsorption potential energy. The maxima on promotion curves may in some cases be due to such an influence of $\Delta\lambda$.

As Sachtler[105] points out, the work function, the Volta potential, the photoelectric emission, emission microscopy, the electrical conductivity of films, the magnetic properties of small particles, and infrared spectra indicate that a chemisorption bond between metal and adsorbate is very similar to the normal bond, their strengths differing by at most 10%. A metal atom involved in chemisorption to some extent loses its metallic properties, with consequent changes in conductivity and intensity of magnetisation. The metal–metal bond is partly ruptured, and a bond is formed with the absorbate, whence follows the ready mobility of the metal atom. All these results are similar to the conclusions of the multiplet theory.

Fig. 3 was first realised in work[106] on Cr_2O_3 catalysts prepared in seven different ways. Differential heating curves and X-ray powder diagrams were recorded for them, and activation energies determined for the dehydrogenation and the dehydration of isopropanol. Volcano-shaped curves were obtained, and values of q determined from ϵ by means of Eqns. (2.5) and (1.11). In agreement

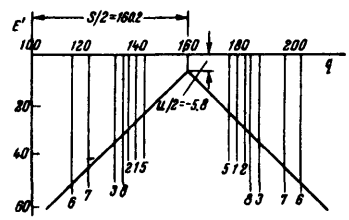


Fig.10. Volcano-shaped curve for dehydration of ethanol on aluminium oxide prepared in different ways[107]. Adsorption potential energies q in kcal and heights of energy barriers $-E$ in kcal; catalyst numbers indicated on vertical lines.

with theory, the observed maximum changes in q (Δq = = 30 kcal mole^{-1}) are less than $\frac{1}{2}\lambda_K$ = 70 kcal mole^{-1} for Cr_2O_3.

Hsi Hsiao-fang and Wu Yüeh[107] applied the method of volcano-shaped curves to the dehydration of ethanol over Al_2O_3 prepared by eight methods. The reaction velocity constants ϵ, E, and q were determined (see Fig. 10, where the Q_{AB} are taken from the scheme in Ref. 23, and the numerals adjacent to the energy barriers denote the catalyst numbers). It is evident that the adsorption potential energy is greatly influenced by the origin of the catalyst, and can fluctuate over the range 25 kcal < $\frac{1}{2}\lambda_K$ [< 55 kcal (Ed. of Translation)] for Al_2O_3.

In agreement with theory, Q_{HK}, Q_{CK}, and Q_{OK} depend appreciably on the method of preparation. This is shown for Cr_2O_3 in Table 10 (abridged from Ref. 30). The bond energies, too, are influenced by different gas pretreatments of the chromium oxide[108,109,33].

Dutch workers have recently published volcano-shaped curves. Fahrenfort *et al.*[110] have made a combined kinetic, infrared, calorimetric, and mass-spectrometric investigation of the decomposition of formic acid on various metals. They conclude that the reaction involves the intermediate formation of an adsorption complex of surface nickel formate type. Comparison of the heat of formation $-\Delta H_f$ of the formate of the corresponding metal with the temperature T_r at which a fixed degree of conversion r is reached ($\log r$ = -0.8) yielded a broken line "resembling Balandin's volcano-shaped curves" (Fig. 11). A catalyst half covered with the adsorption complex is the most active. The reaction investigated by these workers differs from those which we have examined, but it is significant that oxides show the same selectivity towards the decomposition of alcohols and that of formic acid (Mars, Fig. 1 in Ref. 111).

TABLE 10. Effect on Q_{AK} (in kcal) of method of preparation.

Cr_2O_3 catalyst prepared from	Q_{HK}	Q_{CK}	Q_{OK}
$(NH_4)_2CrO_4$	60.8	17.1	45.2
$(NH_4)_2CrO_4$ on asbestos	57.7	23.1	35.1
$Cr(NO_3)_3$, by precipitation with Na_2CO_3	54.7	19.3	71.8
$Cr(NO_3)_3$, by precipitation with Na_2CO_3 on asbestos	60.7	20.2	44.9
$Cr(NO_3)_3$, by precipitation with ammonia	60.9	22.7	51.8

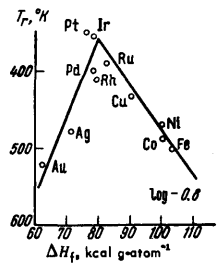


Fig. 11. Volcano-shaped curve[110] for decomposition of formic acid on various metals: $-\Delta H_f$ = heat of formation of metal formate; T_r = = temperature at which 15% conversion is reached.

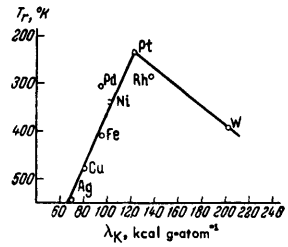


Fig. 12. Volcano-shaped curve[113] for exchange of ammonia with deuterium: λ_K = heat of sublimation of metal in kcal g-atom^{-1}; T_r = temperature at which specified degree of conversion is reached.

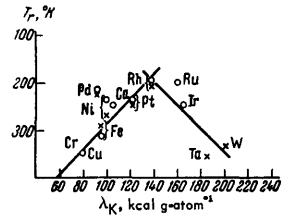


Fig. 13. Volcano-shaped curve[113,115] for hydrogenation of ethylene: λ_K = heat of sublimation of metal in kcal g-atom^{-1}; T_r = temperature at which specified degree of conversion is reached.

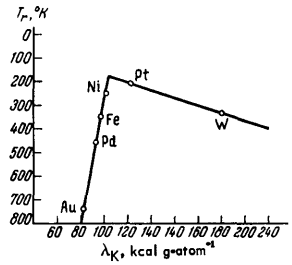


Fig. 14. Volcano-shaped curve[113,117] for hydrogenation of acetone: λ_K = heat of sublimation of metal in kcal g-atom^{-1}; T_r = = temperature at which specified degree of conversion is reached.

In a paper at the Paris Congress on Catalysis, Sachtler and Fahrenfort[112] give additional information on volcano-shaped curves and mention that a similar relation between catalytic activity and the stability of the intermediate complex has been "qualitatively predicted by Balandin".

Schuit *et al.*[113] have computed volcano-shaped curves for still other reactions from results obtained by several workers — deuterium exchange with NH_3 (Fig. 12[114]), hydrogenation of ethylene (Fig. 13[115,116]), and hydrogenation of acetone (Fig. 14[117]). Values of T_r are plotted as ordinates,

and heats of sublimation of the metals λ_K as abscissae. The latter vary in parallel with $q = Q_{AK} + Q_{BK} + \ldots$, which contain λ_K as a component in accordance with Eqns. (6.1) and (6.2). Zelinskii and the Reviewer[118] pointed out long ago the parallelism between the melting points of metals (or λ_K in accordance with Trouton's rule) and the activation energies for the dehydrogenation of cyclic hydrocarbons on them. The T_γ values are inversely proportional to ϵ or E corrected for complicating factors, as a result of which the volcano-shaped curves in Figs. 12–14 are unsymmetrical.

However, changes in λ_K alone are insufficient to explain the position: q contains also the terms Q^0_{AK}, Q^0_{BK}, ..., and graphs having similar volcano shapes are actually obtained[113] if T_γ for the same reactions is plotted against the heat of formation of the corresponding metal oxide Q^I_{OM} or $Q_f(MO)$ in the notation of Ref. 113. Fig. 8 suggests a parallelism between Q^{th}_{OM} and Q^{ki}_{OK}, and Fig. 7 the possibility of a parallelism between Q_{OK} and Q_{HK} (complicated by the mode of production of the catalyst) for the transition metals, too. But Q_{HK} is the predominant term in q for the indices of all three reactions indicated above. This may explain the observed relationships.

It is remarkable that the existence of volcano-shaped curves has received[110,112,113] fresh experimental confirmation of a quantitative character†.

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† Two more recent papers must be mentioned, which cannot be covered in the present review and which are of interest from the point of view of the ideas developed here[119,120].

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THE PRINCIPLES OF BIOCATALYST MODELLING

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I. INTRODUCTION

One hundred and thirty years ago a compound was discovered in malt extract that catalysed the conversion of starch to sugar. Payen and Persoz, the discoverers of this natural catalyst, called it "diastase" ("separating"), because it separates dextrin from the starch grain envelope[1]. These workers could never have surmised that it had fallen to them to reach the boundary of a field in which the activity of amazing chemical "machines" is related to life by elusive threads. The increasing attractive force of the problems of enzymology directed the attention of chemists and physicists to this subject, and none of them found in this new and mysterious world anything that could be regarded as trivial from the point of view of their own sciences.

Biocatalysts are products of a long evolution that appears to have extended over several thousand million years. During this time the compounds generally used in technology as catalysts (oxides, salts, sulphides, etc.) were to a large extent deactivated; it is well known that freshly prepared compounds are more active than the naturally occurring forms. Thus, catalytically active systems in the biological field developed in a manner fundamentally different from the evolution typical of inorganic products.

Biocatalysis is one of the facets of life. When it was shown that nearly all chemical processes occurring in cells are catalytic, biocatalysts became particularly important in speculations on the fundamental laws of biochemistry. The development and perfection of forms of life, as well as its origin, have thus been found to be due to the combined action of catalysts. The biological activity of various organisms was a most important channel for the reduction of chemical potentials even in geologically remote times. Therefore, the appearance and development of biocatalysts may be considered as the expression of a general law, according to which potential-equalisation processes in some way set up the mechanisms they require in nature.

In practice circumstances are such that nearly any energy-rich compound formed on the earth as a result of radiation or heating may become the substrate for the nutrition of some organism, heterotrophic or autotrophic. The catalytic systems are found to be unusually versatile. Enzymes, or more accurately aggregates of enzymes, can produce effects that are difficult, and sometimes impossible, to achieve with ordinary catalysts.

Enzymes are virtually the same in both the simplest and most complex organisms, which underlines their versatility as chemical tools. Moreover, the evolution of forms of living organisms has had hardly any effect on the chemical nature of the catalysts required for biological activity.

One of the most striking conclusions that evolutionary biochemistry has led to is that the formation of biochemical systems responsible for metabolic processes was largely completed in remote times[2]. Thus, whatever stimuli acted up to that time ceased, for unknown reasons, to play the part of chemical rearranging factors, as if the function they performed at some stage of development was no longer necessary.

It would be interesting to discover why a certain factor ceased its "creative" activity, and why under certain conditions chemical evolution of the most important catalytic systems was greatly retarded and virtually ceased. Obviously, in our present state of knowledge an answer to this question can be given only in the most general form. If we consider any part whatever of a complex chemical system and examine how the effect of a given chemical factor is reflected in the structure of the chosen part of the system, we observe a number of successive changes in composition and also in macrostructure. The operating factor may be, for example, oxidation by means of hydrogen peroxide, or phosphorylation leading to the formation of pyrophosphate bonds. These factors may cease to operate for two reasons. First, molecules, or groups of molecules, that are unaffected by the given factor, may appear. In this case the resistance may not be constant, since chemical evolution may be resumed as a result of the accumulation of matter. Second, some catalyst may appear in the part of the system under consideration: for example, the oxidative effect and corresponding chemical rearrangement of the system under the influence of hydrogen peroxide became impossible as soon as evolution led to the emergence of catalase. The appearance of enzymes that transfer phosphoric-acid residues, of course, introduce a controlling element into the processes by which phosphoric esters are formed, and so on.

One may imagine a rough sequence in which external chemical attacks lost their random deforming character and, thanks to the development of catalytic systems, became trigger systems for coordinated processes, maintained by the same catalysts.

Processes associated with the transfer of energy-rich groups, and also hydrogen-transfer processes, are probably among the oldest, that is, the earliest to be subjected to control. Much later, processes in which molecular oxygen took part were subjected to control and ceased their deformative activity. This also appears to apply to photosynthetic processes. Kamen[3] points out that anaerobes