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CALCULATION OF THE ACTIVATION ENERGY OF CHEMICAL REACTIONS ON THE BASIS OF THE ADDITIVITY PRINCIPLE

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1. INTRODUCTION

A great mass of experimental data has now accumulated in the literature on chemical kinetics and urgently requires generalisation and classification. However, to appraise this mass of disconnected and often contradictory facts is quite a complex task, made difficult by the fact that the theoretical premises and the methods of calculation of the kinetic parameters for most chemical reactions are still in an "embryonic" state.

The now generally accepted theoretical treatment of the nature of the elementary act of a chemical reaction is based on the "activated complex" method developed by Eyring[1] and by Evans and Polanyi[2]. It is based on the concept that the configuration of the atoms of a system, whilst changing continuously during the course of a reaction, passes through some critical intermediate configuration, which has received the name of "activated complex" or "transition state". A quite important concept introduced in this method is the potential-energy surface with a saddle point corresponding to the "transition state". The height of this point in comparison with the initial system gives the activation energy of the chemical reaction.

In its quantitative aspect the activated complex method frequently allows the pre-exponential factors in the Arrhenius equation to be calculated satisfactorily[3]. The accuracy of the results thus obtained is approximately one order of magnitude.

As regards calculations of activation energy, the results obtained so far have been much more modest. The most developed theory is that for the simplest system of three hydrogen atoms, which corresponds to reaction (1):

$$H\cdot + H_2 \rightarrow H_2 + H\cdot \qquad (1)$$

Many studies[4-12] have been devoted to quantum-mechanical calculations of system (1), but it is only very recently that the use of computer techniques has allowed agreement

with the experimental results to be reached[12]: the calculated value is $E = 6.2$ kcal†, and the experimental activation energy is ~7 kcal.[13]

The difficulty of direct quantum-mechanical calculations of activation energy stimulated the creation of the so-called "semiempirical" method, proposed by Eyring and Polanyi[13] and somewhat modified by Sato[14]. In this method the well-known London formula for the energy of a three-electron system[15] is used in conjunction with empirical curves of the Morse type for the potential energy of diatomic molecules[16]. However, here agreement with experiment is reached by the introduction into the formulae of an arbitrary parameter, the value of which is selected to "fit" the calculated activation energy to the experimental value. Hence "the semiempirical method introduces considerable uncertainty into activation energy calculations, in which it is material that the inaccuracy in the determination of E is theoretically completely uncontrollable"[17].

Matters are even worse for multi-electron atoms and molecules, especially when p-electrons participate in the elementary act. Here the picture of the interaction is complicated by the specific arrangement of the electron clouds and the transfer to this system of the conclusions and analyses made on the basis of the semiempirical method for 1s-electrons is quite inadmissable.

Hence the problem of the direct theoretical calculation of the activation energy of chemical reactions remains unsolved. Because of this, various empirical relations between activation energies and various factors characterising the reacting molecules or radicals have become important. These relations connect indirectly the rate of a chemical reaction with the structure of the molecule and the thermodynamics of the reaction. The clearest connection between the activation energy E and the exothermicity ΔH is for radical substitutions of type (2):

$$R\cdot + R'X \rightarrow RX + R'\cdot \qquad (2)$$

It was found empirically[17-21] that on changing either R or R′ the value of E is a linear function of ΔH (Polanyi's rule). This makes it possible to express the dependence of E on ΔH in the following generalised form:

$$E = a + b\Delta H \qquad (3)$$

where a and b are constants for a given homologous series.

By generalising much experimental material, Semenov[17] concluded that Eqn. (3) can be written in the form (4) with sufficient approximation:

$$E = 11.5 - 0.25\,\Delta H \qquad (4)$$

for exothermic reactions, and as (4′) for endothermic:

$$E = 11.5 + 0.75\,\Delta H. \qquad (4')$$

Relations (4) and (4′) allow the activation energy of radical reactions to be evaluated with an accuracy of 2–3 kcal. These relations are satisfactory for various atoms and radicals, but not for halogen atoms and reactions of type (1) involving H and D atoms. However, since the reactions which satisfy this relation are all radical reactions there is great interest in seeking more general relationships which are applicable to a wider class of reactions, both radical and molecular.

The principles described below allow the activation energy of the most varied reactions, both radical and molecular, to be determined with good accuracy.

2. STRUCTURE OF ACTIVATED COMPLEXES OF CHEMICAL REACTIONS

The principal feature of every chemical reaction is that during it some chemical bonds are broken and others are formed. In homolytic reactions the breaking of the bonds takes place in such a way that the atoms which form the bond do not acquire electrical charges. This signifies that the electron pair of the chemical bond is divided and each electron remains at its "own" atom. Consequently, in the rupture of every chemical bond two free valencies arise, which can either be used in the same elementary act for the formation of other bonds, or remain unutilised.

The breaking of some and the formation of new bonds proceeds gradually during the continuous change of the coordinates of the atoms in the system. The energy maximum of the system corresponds to the transition state, in which there are weakened breaking bonds and also even weakened new bonds. Hence in the activated complex instead of the bonds which are being broken and formed we have other weaker bonds, which we will conventionally term "activated" subsequently.

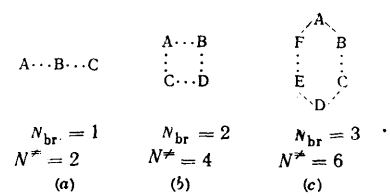
To understand the nature of the elementary chemical act it is necessary to find the structure of the activated complex. For radical reactions (2) the activated complex has the form A...B...C, where the dots denote activated bonds. For molecular reactions of a different type four-membered and six-membered cyclic complexes have been proposed[22]. Hence the number of activated bonds can be different. When the valency of the atoms of a system is constant, it can be shown that the number of activated bonds satisfies the following simple relationship:

$$N^{\neq} = 2N_{br} - \frac{\Delta n}{2} \qquad (5)$$

where N_{br} is the number of bonds broken during the course of the reaction, and Δn the change in the number of free valencies.

From this relation clearly Δn is always even, that is, only pairs of free valencies can appear or disappear during the course of the reaction. When there is a single free valency in the initial system then it cannot disappear (the "indestructibility of the free valency").

Let us consider what happens with $\Delta n = 0$. Here $N^{\neq}$ equals 2, 4, and 6 for $N_{br} = 1$, 2, and 3 respectively. The structure of the activated complexes for these instances is shown in scheme (A):



(A)

Activated complex (*a*) corresponds to radical reactions, (*b*) and (*c*) to molecular ones.

† For brevity, here and subsequently we write kcal instead of kcal mole^{-1}.

For $\Delta n \neq 0$ two variants are most frequently encountered: $N_{br} = 1$, $\Delta n = \pm 2$ [scheme (B)]:

$$\begin{array}{cc} A\cdots B & \begin{matrix} A\cdots B \\ \diagdown\!C\!\diagup \end{matrix} \\ \Delta n = 2 & \Delta n = -2 \\ N^{\neq} = 1 & N^{\neq} = 3 \\ (d) & (e) \end{array} \quad (B)$$

Activated complex (*d*) corresponds to dissociation of the molecule into two radicals, (*e*) to the reaction of the molecule with a biradical.

In the schemes shown for the activated complexes the species A, B, etc. can be either atoms or radicals consisting of a few atoms.

The schemes described include only activated bonds. In reality, in addition to these bonds the activated complex also has ordinary chemical bonds which enter into the composition of the reacting components A, B, etc. However, only the activated bonds determine whether chemical reactions occur since the other bonds are unchanged during the course of the reaction.

Hence the structure of the activated complex can be represented in the usual way employed for molecules. The main differences are that activated bonds denoted by dots are much weaker than chemical bonds and their number does not obey the usual valence rules. These differences arise because the activated bond is not the usual two-electron bond. It is easily seen that the total number of electrons participating in all the activated bonds is:

$$m = 2N_{br} + n_0$$

where n_0 is the number of unpaired electrons of the initial system which participate in the reaction, and therefore the number of electrons taking part in one activated bond does not equal zero in the general case. However, despite the major difference in the nature of the activated and ordinary chemical bonds, the above method of representing the structure of the activated complex gives good results and (as will be shown later) allows the activation energies of the most diverse chemical reactions to be calculated with reasonable accuracy.

3. ADDITIVITY OF THE ENERGY OF AN ACTIVATED COMPLEX

The principle of the additivity of the bond energies of the atoms in molecules is well-known; according to it the atomisation energy of a molecule equals the sum of the mean energies of the bonds between the various atoms:

$$V = \sum Q. \quad (6)$$

This principle allows the heats of various types of chemical reaction and certain thermodynamic properties of substances to be calculated.

From the theoretical standpoint the validity of the additivity principle signifies that the interaction of the atoms which are not directly connected to one another can be neglected. This possibility is not obvious.

On considering a molecule as a multi-electron system and rigorously solving the corresponding Schrödinger equation, we also have to include in the Hamiltonian operator terms which describe the interaction of electrons belonging to different valence bonds. It is known[23] that allowance for this interaction leads to an increase in the energy of the system, in other words, electrons which are not paired with one another are repulsed. Under certain assumptions the energy of the molecule can be represented[24] by the approximate additive formula:

$$E = \sum Q_{ij} + \sum A_{ii} - \frac{1}{2}\sum_{i \neq j} A_{ij} \quad (7)$$

where Q_{ij} is the coulombic energy of all the electron pairs, A_{ii} the exchange energy of the paired electrons which form the bond, A_{ij} the exchange energy of pairs of electrons which do not form a bond.

In Eqn. (7) there are terms which describe the interaction of electrons of different valence bonds. Hence quantum mechanics leads with known approximation to the idea of the additivity of the energy of the molecule, but with allowance for the repulsion of non-bonded atoms. The fact that the usual additive scheme for the calculation of energy gives good results is evidence that these additional terms can be neglected.

Note that there is a class of molecules where the atoms which are not directly connected have a quite significant effect—these are the molecules with conjugated multiple bonds. Conjugation lowers the energy of the molecule and in Eqn. (6) it is then necessary to introduce a corresponding correction allowing for the presence of conjugation[25]:

$$V = \sum Q + \Delta Q_{conj}.$$

Another factor which greatly affects the energy of certain molecules is the deformation of the valence angles in cyclic structures. This increases the energy of the molecule and in Eqn. (6) it is necessary to introduce the deformation energy (strain energy)[26]:

$$V = \sum Q - \Delta Q_{def}.$$

An analysis of many experimental results on the chemical kinetics led us to conclude that the additivity principle can be extended to the bond energies of the atoms in the activated complex[27,28]. This makes it possible to calculate the activation energy of a variety of chemical reactions.

For the change from the initial system to the activated complex energy equal to ΣQ_{br} must be expended in breaking some of the chemical bonds. During this, activated bonds are formed and energy is released, equal to $\Sigma Q^{\neq}$. Therefore the activation energy of the chemical reaction, which is equal to the energy expended in going from the initial system to the activated complex, can be represented by the following equation:

$$E = \sum Q_{br} - \sum Q^{\neq}; \quad (8)$$

in other words, the activation energy equals the sum of the energies of bonds which are broken minus the sum of the energies of the activated bonds.

Eqn. (8) is applicable both for the forward and for the reverse reaction. Since the activated complex for the elementary acts of the forward and reverse reactions is the same, the corresponding difference in activation energies will equal the difference between the energies of the bonds broken in the forward and reverse reactions, that is, the exothermicity:

$$E - E' = \sum Q_{br} - \sum Q'_{br} = \Delta H.$$

Eqn. (8) allows the activation energy of a chemical reaction to be calculated when the energies of the activated bonds are known.

The most rigorous path for the determination of the value of $Q^{\neq}$ consists in the direct quantum-mechanical calculation of the activated complex. However, as noted above, quantum chemistry has not yet achieved the necessary accuracy in calculating the activated complex in even the simplest instances.

Another way consists in using reliable experimental data on the kinetics of certain reactions to calculate the energies of the activated bonds by Eqn. (8). The energies of the activated bonds thus found allow the activation energies of many other chemical reactions to be calculated.

We show below the applicability of the additivity principle in the calculation of activation energies for radical reactions, and then also for molecular reactions. The necessity for considering radical and molecular reactions separately stems from the different requirements as regards the accuracy of the activation energy calculations. For molecular reactions, which usually have an activation energy E of between 20 and 65 kcal, an accuracy of 3–4 kcal in the calculation seems quite satisfactory. However, with radical reactions, for which a value of E of ~10 kcal or less is characteristic, it is desirable to carry out the calculations with an accuracy of ~1 kcal. This is also responsible for some differences in the corresponding calculation procedures.

Strictly speaking, Eqn. (8) gives us an expression for the "microscopic" activation energy, determinable as the difference in the zero energy levels of the activated complex and the initial system. In practice, however, we will be dealing with experimental activation energies determinable from the slope of the curve giving the temperature dependence of the reaction rate constant in Arrhenius coordinates.

As Temkin has shown[29], the experimental activation energy corresponds to the statistical determination of this quantity as the difference between the mean energies of the reacting molecules and the initial ones. At moderately high temperatures the "microscopic" and "statistical" activation energies are almost the same. The difference between them—a quantity of the order of RT—usually lies within the limits of experimental error. Therefore subsequently we will assume that the experimental activation energy is equal to the energy barrier of the reaction.

4. RADICAL SUBSTITUTIONS

For the radical substitution (9):

$$R\cdot + R'X \rightarrow RX + R'\cdot \qquad (9)$$

the activated complex, which is of the form R...X...R', belongs to type (*a*) (see p. 512). In this reaction one chemical bond is broken, R'–X, and in the activated complex there are two activated bonds, R...X and R'...X.

Before turning to the calculation of activation energy, we will give the following definition: the energy for the breaking of an activated bond $Q_{R...X}$ is that part of the heat change $D_{R...X...R'}$ of the dissociation of the activated complex with formation of the free radicals R' and R'' and the atom X at 0°K in the gas phase which is associated with one activated bond:

$$R...X...R' \rightarrow R\cdot + X + R'\cdot \qquad (10)$$

Since in this reaction there is the simultaneous breaking of two activated bonds, the above definition is actually within the framework of our postulated principle for the additivity of the activation energy of the complex. The essense of this principle comprises the following two assumptions:

1. The energy for the dissociation of the activated complex equals the sum of the energies for the breaking of the activated bonds:

$$D_{R...X,..R'} = Q_{R...X} + Q_{R'...X}. \qquad (11)$$

2. The energy for the breaking of an activated bond $Q_{R...X}$ is independent of the radical R'' and is therefore constant and characteristic of the RX molecule.

These assumptions are generally true only to a certain approximation. The nature of a substituent can influence to a certain extent the bond energies of the atoms in the molecule. Hence the nature of the radical R'' can change the energy of the activated bond $Q_{R...X}$ within certain limits. However, we assume that this influence is small and can be allowed for in the appropriate way.

To calculate the activation energy of reaction (9) it is necessary to know the energy consumed in going from the initial system to the activated complex. For this purpose we will divide this change into two stages. First let the chemical bond R'–X be broken with the formation of atom X and radical R''. Then let a reaction take place, the reverse of reaction (10). In this, the energy released is equal to $D_{R...X...R'}$. Hence the activation energy of reaction (9) is

$$E = Q_{R'-X} - (Q_{R...X} + Q_{R'...X}) \qquad (12)$$

which agrees with general Eqn. (8). However, it must be remembered that the quantities in Eqn. (12) are energies for the breaking of bonds.

For the reverse reaction the activation energy is expressed by a similar relation:

$$E' = Q_{R-X} - (Q_{R...X} + Q_{R'...X})$$

so that the difference in these quantities:

$$E - E' = Q_{R'-X} - Q_{R-X} = \Delta H$$

equals the heat of reaction.

To calculate the activation energy by Eqn. (12) the energies of the activated bonds $Q_{R...X}$ and $Q_{R'...X}$ must be known. These quantities can be determined with the aid of the same equation from experimental data on the activation energies of certain reactions[27]. Table 1 gives the energies thus calculated for some activated bonds, together with the corresponding experimental data used for the calculations.

Note that to calculate each of the quantities $Q_{R...X}$ the experimental value of the activation energy of the corresponding reaction is used. Consequently the accuracy of the calculation of $Q_{R...X}$ depends on the reliability of the experimental results used. Therefore the quantities used in Table 1 are not, strictly speaking, definitive and could be refined subsequently.

The values given in Table 1 for the energies of the breaking of the bonds in molecules are recommended for use in calculating activation energy, since these particular values are used for calculating the energies for the breaking of activated bonds.

An illustration of the applicability of Eqn. (12) for calculating the activation energy of radical reactions is given by Table 2, in which calculated activation energies are compared with corresponding published values. Clearly,

TABLE 1. Energies for the breaking of bonds in molecules and activated complexes at 0°K.

Bond	Q_{R-X}, kcal	Ref.	$Q_{R\ldots X}$, kcal	Calculated for the reaction	E_{expt}, kcal	Ref.
H...CH_3	101 5	32	43.6	$CH_3+CH_4 \rightarrow CH_4+CH_3$	14.3	38
H...C_2H_5	97 0	30	43.0	$CH_3+C_2H_6 \rightarrow CH_4+C_2H_5$	10.4	39
H...C_{prim}	94.9*		41.3	$CH_3+(CH_3)_4C \rightarrow CH_4+(CH_3)_3CCH_2$	10.0	39
H...C_{sec}	92.0*		40.3	$CH_3+n\text{-}C_5H_{12} \rightarrow CH_4+C_5H_{11}$	8.1	39
H...C_{tert}	87.2*		36.0	$CH_3+iso\text{-}C_4H_{10} \rightarrow CH_4+C_4H_9$	7.6	39
H...H	103.3	32	44.3	$H+C_2H_6 \rightarrow H_2+C_2H_5$	9.7	62
H...OH	118.0	32	48.5	$OH+C_2H_6 \rightarrow H_2O+C_2H_5$	5.5	45
H...O	101.4	32	47.5	$O+n\text{-}C_4H_{10} \rightarrow OH+C_4H_9$	4.2	42
H...NH_2	104.0	32	50.6	$CH_3+NH_3 \rightarrow CH_4+NH_2$	9.8	51
H...CH_3CO	79 0	30	27.9	$CH_3+CH_3CHO \rightarrow CH_4+CH_3CO$	7.5	52
H...CF_3	101.0	32	46.5	$CF_3+C_2H_6 \rightarrow CF_3H+C_2H_5$	7.5	49
H...$C_6H_5CH_2$	83.0	30	31.1	$CH_3+C_6H_5CH_3 \rightarrow CH_4+C_6H_5CH_2$	8.3	39
H...CH_2–$CH=CH_2$	77.0	30	25.7	$CH_3+C_3H_6 \rightarrow CH_4+C_3H_5$	7.7	39

* Calculated by Voevodskii's formula[31] for propane and isobutane.

TABLE 2. Activated energies of radical reactions.

Reaction	E_{calc}, kcal	E_{expt}, kcal	Ref.
$H+CH_4 \rightarrow H_2+CH_3$	13.6	13.0	59
$H+C_3H_8 \rightarrow H_2+C_3H_7$	7.4	8.2	33
$H+n\text{-}C_4H_{10} \rightarrow H_2+s\text{-}C_4H_9$	7.4	7.1	34
$H+iso\text{-}C_4H_{10} \rightarrow H_2+(CH_3)_3C$	6.9	6.8	35
$H+(CH_3)_4C \rightarrow H_2+(CH_3)_3CCH_2$	9.3	9.3	36
$H+CH_3CHO \rightarrow H_2+CH_3CO$	6.8	6.0	37
$CH_3+C_2H_6 \rightarrow CH_4+C_2H_5$	8.1	8.0	39
$CH_3+n\text{-}C_4H_{10} \rightarrow CH_4+s\text{-}C_4H_9$	8.1	8.1	39
$CH_3+n\text{-}C_6H_{14} \rightarrow CH_4+s\text{-}C_6H_{13}$	8.1	8.1	39
$CH_3+(CH_3)_3CC(CH_3)_3 \rightarrow CH_4+(CH_3)_3CC(CH_3)_2CH_2$	10.0	9.5	39
$CH_3+(CH_3)_2CHCH(CH_3)_2 \rightarrow CH_4+(CH_3)_2CHC(CH_3)_2$	7.6	7.8	39
$CH_3+(CH_3)_2CHCH(CH_3)CH(CH_3)_2 \rightarrow CH_4+(CH_3)_2CCH(CH_3)CH(CH_3)_2$	7.6	7.9	39
$CH_3+\Delta\text{-}C_6H_{12} \rightarrow CH_4+\Delta\text{-}C_6H_{11}$	8.1	8.3	39
$O+H_2 \rightarrow OH+H$	11.5	11.7	53
$O+CH_4 \rightarrow OH+CH_3$	10.4	8.7	40
$O+C_2H_6 \rightarrow OH+C_2H_5$	6.5	7 5	41
$O+\Delta\text{-}C_6H_{12} \rightarrow OH+\Delta\text{-}C_6H_{11}$	4.2	4.5	55
$O+CH_3CHO \rightarrow OH+CH_3CO$	3.6	3.0	43
$O+NH_3 \rightarrow OH+NH_2$	5.9	4.9	54
$OH+H_2 \rightarrow H_2O+H$	10.5	10.0	56
$OH+CH_4 \rightarrow H_2O+CH_3$	9.4	9.0	44
$OH+CH_3CHO \rightarrow H_2O+CH_3CO$	2.6	4.0	46
$CF_3+CH_4 \rightarrow CF_3H+CH_3$	11.4	11.0	47
$CF_3+C_3H_8 \rightarrow CF_3H+iso\text{-}C_3H_7$	5.2	6.2	48
$CF_3+n\text{-}C_4H_{10} \rightarrow CF_3H+s\text{-}C_4H_9$	5.2	5.3	48
$CF_3+(CH_3)_4C \rightarrow CF_3H+(CH_3)_3CCH_2$	7.1	7.6	48
$CF_3+iso\text{-}C_4H_{10} \rightarrow CF_3H+(CH_3)_3C$	4.7	4.7	49
$CF_3+C_6H_5CH_3 \rightarrow CF_3H+C_6H_5CH_2$	5.4	5.4	50
$CF_3+\Delta\text{-}C_6H_{10} \rightarrow CF_3H+\Delta\text{-}C_6H_9$	5.1	4.7	48

the difference between the calculated and experimental values usually does not exceed 0.5–0.7 kcal.

If it is assumed that the accuracy of the experimental determination of activation energies of radical reactions is comparatively moderate (1–2 kcal), the approximation obtained must be considered good.

The additivity rule is obeyed by the reactions of various radicals with the most varied molecules. Exceptions are the reaction of free halogen atoms and reactions of type (1) with the participation of H and D atoms. It is remarkable that these particular reactions do not obey the Semenov relation. Possibly, here the direct interaction of radicals R and R′, not allowed for in Eqn. (12), is significant.

It is interesting to note that there is a clear linear correlation between the energies of breaking of the activated and the ordinary chemical bond (Fig. 1). The dependence of $Q_{R\ldots H}$ on Q_{R-H}, where R is a hydrocarbon radical, can be expressed by the simple relation:

$$Q_{R\ldots H} = 0.83\,(Q_{R-H} - 45)\ \text{kcal}\ . \qquad (13)$$

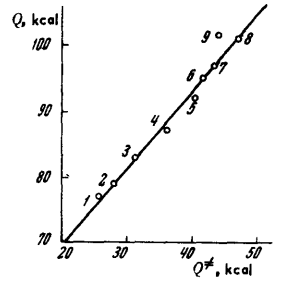


Fig. 1. Relation between the energies for breaking bonds between the atoms in the molecule and in the activated complex of radical reactions:
1) H–C_3H_5; 2) H–CH_3CO; 3) H–$C_6H_5CH_2$; 4) H–t-C_nH_{2n+1}; 5) H–s-C_nH_{2n+1}; 6) H–n-C_nH_{2n+1} ($n \geq 3$); 7) H–C_2H_5; 8) H–CF_3; 9) H–CH_3 (from the data of Table 1).

This relation allows the energy of an activated bond to be evaluated approximately in those instances when the experimental data needed for more accurate calculation are not available.

Note, however, that the accuracy of the results obtainable in this calculation (2–3 kcal) is somewhat worse than when using tabulated data.

Relation (13) agrees with the Polanyi rule and with the Semenov relation. In this connection we will examine several reactions in which radical R is changed but the R′X molecule remains the same. On substituting Eqn. (13) for $Q_{R\ldots X}$ and $Q_{R'\ldots X}$ in Eqn. (12) we obtain:

$$E = A - 0.17\Delta H, \qquad (14)$$

where $A = 74.7 - 0.66Q_{R-X}$.

We have arrived at a relation close to that of Semenov, Eqn. (4). Since $Q_{R\ldots X}$ for alkanes has a value of ~90 to 100 kcal, here A = 9–15 kcal.

An interesting feature of Eqn. (14), equally true of the Semenov relation (4), is that since the coefficient of ΔH is small, change in energy of the bond being broken (or the heat of reaction) has comparatively little effect on the value of the activation energy.

However, for the same reason the use of these relations for the reverse calculation of thermal effects (or bond energies) with the aid of data on activation energies leads to considerable errors. For example, an inaccuracy in Eqn. (14) of 3 kcal gives an error of ~18 kcal in the determination of ΔH. Therefore in using relations (4) and (14) extreme care must be taken and it can only be used for direct calculations of activation energy.

5. ACTIVITY OF RADICALS AND MOLECULES

From the above, three quantities must be known to calculate the activation energy of radical reactions: $Q_{R'-X}$, $Q_{R\ldots X}$, and $Q_{R'\ldots X}$.

However, often all these quantities are unknown. Therefore there is interest in those modifications of the additivity principle which would allow less information to be used. The following two corollaries of Eqn. (12) are useful for this purpose.

First corollary (relative activities of radicals). Let us consider two reactions for different radicals R_1 and R_2 with the same substance RX. The activation energies of these reactions, according to Eqn. (12), are:

$$E_1 = Q_{R-X} - (Q_{R_1\ldots X} + Q_{R\ldots X})$$
$$E_2 = Q_{R-X} - (Q_{R_2\ldots X} + Q_{R\ldots X}).$$

On subtracting one equation from the other we obtain:

$$E_1 - E_2 = Q_{R_2\ldots X} - Q_{R_1\ldots X}. \qquad (15)$$

In other words, *the difference in the activation energies for the reactions of two given radicals* R_1 *and* R_2 *with the same substance* RX *is independent of the nature of this substance and is a constant quantity*. This difference is determined by the energies of the activated bonds $Q_{R_1\ldots X}$ and $Q_{R_2\ldots X}$, and the greater the energy of the activated bond the less the activation energy.

Hence the energy of an activated bond can serve as a quantitative characteristic of the activity of a given radical. If we conventionally take the activity of any one radical (for example, CH_3) as zero, then the difference $Q_{R_i\ldots X} - Q_{CH_3\ldots X}$, or the equal difference between the corresponding activation energies, will characterise the *relative* activity (α) of the radicals in comparison with the radical CH_3. By the relative activity of a radical (in relation to CH_3) we understand the difference between the activation energies of the reactions of CH_3 and this radical with the same substance.

Table 3 gives a series of radicals in order of increasing activity. The relative activities in this table were calculated from the data in Table 1.

It must be pointed out that this determination of the relative activity of radicals differs from Semenov's proposal[17]. By relative activity this author[17] means the difference in the heats of the corresponding reactions, and not the difference in activation energies.

Naturally, between these two determinations‡ it is easy to find an unambiguous relation according to Polanyi's rule since the series of radical activities given in Table 3 can in principle be obtained from the corresponding Semenov series.

An illustration of the accuracy which is achieved with the first corollary of the additivity principle is provided in Table 4, which gives published data on the reactions of the hydrogen atom and the CF_3 radical with various substances. Obviously the difference $E_1 - E_2$ is constant with an accuracy of 0.2–0.3 kcal and agrees with that calculated in Table 3.

TABLE 3. Relative activity of radicals in reactions of the type $R_i + RH \rightarrow R_iH + R$.

Radical R_i	$CH_2{=}CH{-}CH_2$	$C_6H_5CH_2$	C_6H_5	CH_3	H	CF_3	O	OH
Relative activity, α	—17.9	—12.5	—0.6	0	0.7	2.9	3.9	4.9

‡ Semenov also mentioned[17] the possibility of compiling series of activities of free radicals from activation energies (as has been done by the author of this review) (Russian editorial note).

TABLE 4. Activation energies for the reactions of H· and CF_3 with various substances.

Substance	$H+RH \rightarrow H_2+R$		$CF_3+RH \rightarrow CF_3H+R$		E_1-E_2
	E_1	Reference	E_2	Reference	
C_2H_6	9.7	62	7.5	49	2.2
C_3H_8	8.2	33	6.2	48	2.0
$n\text{-}C_4H_{10}$	7.1	34	5.3	48	1.8
$iso\text{-}C_4H_{10}$	6.8	35	4.7	49	2.1
$(CH_3)_4C$	9.3	36	7.6	48	1.7
CH_3COCH_3	9.0	57	6.9	58	2.1

By using the relative activities of the radicals, the activation energies of reactions of a given radical with any substance can be calculated if the activation energy of the reaction of another radical with the same substance is known:

$$E_1 = E_2 + \alpha_2 - \alpha_1.$$

For calculation by this equation only one quantity E_2 need be known.

The series of relative activities of the radicals can be quite useful for classifying the available experimental data on the kinetics of radical reactions. It allows the reliability of the available data to be evaluated and clearly unreliable values to be rejected. An important point is that in this method it is necessary to have the minimal information, namely: the value of only one activation energy of any radical of this series with the substance of interest. From this standpoint the second corollary is quite useful.

Second corollary (relative reactivities of substances). Let us consider two reactions of a single radical R with two different molecules R_1X and R_2X. The activation energies of these reactions, according to the additivity principle, are:

$$E_1 = Q_{R_1-X} - (Q_{R\ldots X} + Q_{R_1\ldots X})$$
$$E_2 = Q_{R_2-X} - (Q_{R\ldots X} + Q_{R_2\ldots X}).$$

Subtracting one equation from the other, we obtain

$$E_1 - E_2 = Q_{R_1\ldots X} - Q_{R_1\ldots X} - (Q_{R_2-X} - Q_{R_2\ldots X}) \qquad (15a)$$

that is, *the difference in the activation energies of reactions of the same radical with two given substances is independent of the nature of this radical and is a constant*, which can be determined solely by the quantities characteristic for the molecules taken: $Q_{R-X} - Q_{R_1\ldots X}$.

The values of $Q_{R_i-X} - Q_{R_i\ldots X}$ can therefore serve as a quantitative characteristic of the reactivity of a given substance. If it is conventionally assumed that the reactivity of one particular substance (for example, H_2) equals zero, then the difference of corresponding activation energies gives the *relative* reactivity of the different substances in comparison with hydrogen. Hence by the relative reactivity of a given substance (relative to H_2) we mean the difference between the activation energies for the reaction of H_2 and of this substance with the same radical.

As for the activity of the radicals, our determination of the relative reactivity differs from Semenov's proposal[17]; however, Polanyi's rule here allows us to establish a single-valued relation between them.

Table 5 gives a series of relative reactivities β for certain substances which we have obtained from an analysis of many experimental results, including those given in Table 2.

TABLE 5. Relative reactivity of R_iH molecules in reactions of the $R + R_iH \rightarrow RH + R_i$ type (kcal).

Substance R_iH	H_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_6H_6	CH_3CHO
Relative reactivity, β	0	1.0	4.6	5.6	6.7	7.3	7.8

TABLE 6. Activation energy for various radicals with CH_4 and C_2H_6.

Radical, R	$R+CH_4 \rightarrow RH+CH_3$		$R+C_2H_6 \rightarrow RH+C_2H_5$		$E_1 - E_2$, kcal
	E_1, kcal	Reference	E_2, kcal	Reference	
H	13.0	59	9.7	32	3.3
OH	9.0	45	5.5	45	3.5
CH_3	14.3	38	10.4	39	3.9
CN	—	—	—		3.7 [60]
CF_3	11.0	47	7 5	49	3.5

Table 6 gives published data which illustrate the second corollary of the additivity principle. They suggest that the difference in activation energies of the reactions of CH_4 and C_2H_6 molecules with various radicals is constant, irrespective of the nature of the radical, and agrees within 0.2–0.3 kcal with the value $E_1 - E_2 = 3.6$ kcal calculated from the data of Table 5.

By using a series of relative reactivities β_i of substances the activation energy for the reaction of a given radical with any substance can be calculated when the activation energy of a reaction of this radical with even a single substance of this series is known:

$$E_1 = E_2 + \beta_2 - \beta_1.$$

It is necessary to know only one value E_2 for calculation by this relation. A series of relative reactivities can be useful for a comparative evaluation of experimental data from the reactions of one radical with different molecules.

6. MOLECULAR REACTIONS

The additivity principle postulated for radical reactions can be extended to the reactions of saturated molecules. This makes it easy to calculate the activation energies of corresponding reactions. Such calculations are especially important since in distinction from radical reactions molecular reactions have as yet no relations for evaluating the activation energy. The existing theories of the rate of molecular reactions [61] in essence do not even mention the problem of the calculation of activation energy and only discuss the possibility of determining the pre-exponential factors.

The activated complex of most molecular reactions belongs to one of two types (*b*) and (*c*) (see scheme A), that is, in these reactions two or three chemical bonds are broken and four or six activated bonds respectively are formed.

The activated bond energies needed for calculating the values of E by Eqn. (8) can be determined with the aid of reliable experimental data on the kinetics of certain reactions.

Since in molecular, as opposed to radical, reactions several chemical bonds are broken simultaneously it is desirable to use the mean energies of the bonds between atoms of different elements. This somewhat reduces the accuracy of the calculation but considerably broadens the region of its use.

Table 7 gives the mean bond energies of the atoms in the molecules at 0°K and the corresponding mean energies of the activated bonds. The values of Q are taken from Moelwyn-Hughes [63], but we have rounded them off to whole numbers to simplify the calculations. Naturally, these quantities are not sufficiently precise and their value can be judged solely from how well they allow the activation energies of chemical reactions to be calculated.

Just as for molecules, the mean energy of an activated bond is that part of the heat of atomisation of an activated complex associated with one activated bond. When there are ordinary chemical bonds as well as the activated bonds in the activated complex then in the calculation of the heat of atomisation they are given the mean energies of bonds in molecules.

Hence we will use Eqn. (8) to calculate the activation energies of molecular reactions, taking Q_{br} and $Q^{\neq}$ in this equation to be *mean* bond energies, with one exception, which will be mentioned below. As stated above, the deformation of valence angles in rings leads to a departure from additivity by the strain energy of the ring:

$$V = \sum Q - \Delta Q_{def.} \qquad (16)$$

Because of this the energy for the rupture of a C–C bond in rings is considerably less than the mean energy of a C–C bond in alkanes; it is 50, 60, and 72 kcal for cyclopropane, cyclobutane, and cyclopentane, respectively [26]. This shows that the equality

$$Q_r \simeq Q - \Delta Q_{def.}$$

where Q_r is the energy of rupture of the C–C bond in cyclanes, is obeyed with sufficient accuracy for our purposes.

TABLE 7. Mean bond energies in molecules and activated complexes at 0°K.

Bond	Q, kcal	$Q^{\neq}$, kcal
H—H	103	45
C—H	99	45
σ– C—C in alkanes	79	28
π– C⋯C in alkenes	61	17
π– C≡C in acetylene	56	9
σ– C—O	80	18
π–C⋯O	88	27
O—H	105	55
C_{prim}—Cl	76	18
C_{sec}—Cl		25
C_{tert}—Cl		32
C_{prim}—Br	63	16
C_{sec}—Br		21
C_{tert}—Br		26
C_{prim}—I	47	8
C_{sec}—I		16
C_{tert}—I		24
H—Cl	102	40
H—Br	87	33
H—I	70	23
Correction for conjugation $\Delta Q^{\neq}_{conj.}$	—	12

Then Eqn. (16) can be written in the form

$$V = \sum_{n-1} Q + Q_r \qquad (17)$$

which is formally similar to the general equation (6), but in which one value of the mean energy is replaced by the bond rupture energy.

Hence if during the course of a reaction bonds forming part of a ring are broken then in Eqn. (8) for the calculation of E one energy of rupture of a C–C bond in a ring is substituted for the corresponding activated bond energy.

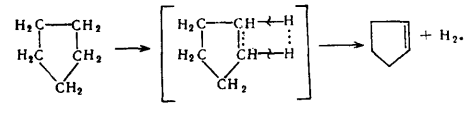
When there is a system of conjugated double bonds in an *activated complex* then the energy of *each* conjugated activated bond must be increased by the quantity $\Delta Q^{\neq}_{conj}$, equal to 12 kcal. Here it does not matter, to the first approximation, which double bonds are conjugated: C=C or C=O.

The author found the value of this correction, like the activated bond energies, by selection from many experimental results on kinetics. We do not make a correction for conjugation in the initial system since it is usually comparatively small and does not affect the calculated activation energy within the limits of error of the calculation.

As Fig. 2 shows, there is a linear relation between the energies of the C–H bonds in the molecules and in the activated complexes, in agreement with Eqn. (13). The existence of this relation allows the energy of the activated bonds to be determined when the energy of the bonds in the molecule differs considerably from the mean value shown in Table 7. For example, for activated bonds in cyclopropane, cyclobutane, and cyclopentane we obtain 4, 12, and 22 kcal respectively. In calculating activation energies it is recommended that the mean energies of the bonds of atoms in molecules given in Table 7 be used, since the activated bond energies found agree with these values.

We will illustrate the calculation of activation energies by examples.

1. The dehydrogenation of cyclopentane:

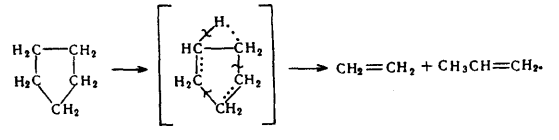


In this reaction two C–H bonds are broken and four activated bonds are formed: two C–H, one H–H, and one π-C–C. According to Eqn. (8) the activation energy is:

$$E = 2 \times 99 - (2 \times 45 + 45 + 17) = 46 \text{ kcal.}$$

The experimental value of E is 44 kcal.[64]

2. The decomposition of cyclopentane:



In this reaction three bonds are broken: two σ-C–C bonds in the five-membered ring and one C–H bond. In the activated complex there are six activated bonds: two C–H, two σ-C–C, and two π-C–C. Here the activated double bonds are conjugated.

$$E = 72 + 79 + 99 - (22 + 28 + 2 \times 45 + 2 \times 17 + 2 \times 12) = 52 \text{ kcal.}$$

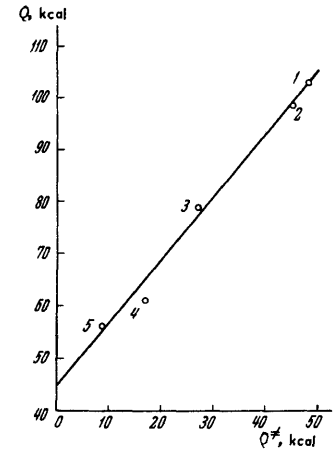
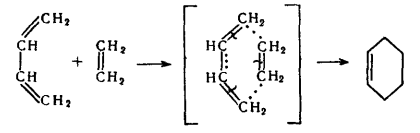


Fig. 2. Relation between the mean C–H bond energies in the molecule and activated complex for molecular reactions.

The experimental activation energy is 49.6 kcal.[64]

3. The Diels–Alder condensation:



During this reaction three π-C–C bonds are broken and a system of six activated bonds is formed: four π-C–C and two σ-C–C bonds. The three activated double bonds are conjugated:

$$E = 3 \times 61 - (4 \times 17 + 2 \times 28 + 3 \times 12) = 23 \text{ kcal.}$$

The experimental value of E is 26.7 kcal.[87]

In exactly the same way we calculated the activation energies of a large number of reactions of very different types. Table 8 gives the corresponding data.

These results show that calculated values of the activation energy agree well with the experimental values of E throughout the whole range of activation energies (25 to 70 kcal). The mean deviation does not exceed 2–3 kcal.

The additivity principle seems valid for reactions of the most varied types with molecules of different structure.

The additive scheme of calculating activation energy can be used for revealing the mechanism of a reaction and for obtaining a more accurate structure for the activated complex. A marked difference between the calculated and experimental activation energy suggests that the reaction does not proceed in the manner assumed. For example, in the decomposition of acetone under certain conditions the main products are keten and methane[99] and a molecular mechanism can be proposed for this reaction:

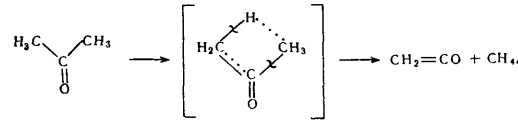
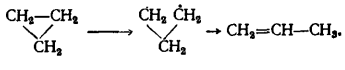


TABLE 8. Activation energies of molecular reactions.

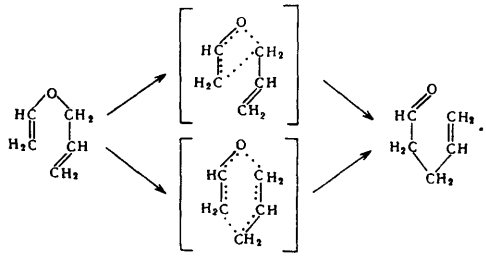
Reaction	E_{calc}, kcal	E_{expt}, kcal	Ref.
Cyclopentane → H_2 + cyclopentene	46	44.0	64
Cyclopentane → C_2H_4 + C_3H_6	52	49.6	64
d-Pinene → dipentene	43	43.7	65
Vinylcyclopropane → cyclopentene	51	50	66
Ethyl acetate → C_2H_4 + CH_3COOH	44	47.8	67
Isopropyl acetate → C_3H_6 + CH_3COOH	44	45	70
Ethyl formate → C_2H_4 + HCOOH	44	44.1	70
Isopropyl formate → C_3H_7 + HCOOH	44	44	70
Ethyl propionate → C_2H_4 + C_2H_5COOH	44	48.5	69
Cyclobutene → buta-1,3-diene	34	32.5	68
1-Methylcyclobutene → 2-methylbuta-1,3-diene	34	35.1	71
1,2-Dimethylcyclobutene → 2,3-dimethylbuta-1,3-diene	34	36	72
Cyclobutane → $2C_2H_4$	65	62.5	73
Methylcyclobutane → C_2H_4 + C_3H_6	65	62	74
Isopropylcyclobutane → C_2H_4 + alkene	65	62.6	75
Isopropenylcyclobutane → C_2H_4 + diene	53	51	76
Isopropenylcyclobutane → 1-methylcyclohexene	47	51	76
1-Chloroethane → HCl + C_2H_4	55	56.6	77
1-Chloropropane → HCl + C_3H_6	55	55	78
2-Chloropropane → HCl + C_3H_6	48	50.5	79
2-Chlorobutane → HCl + C_4H_8	48	49.6	80
2-Chloro-2-methylpropane → HCl + isobutene	41	41.4	81
Allyl vinyl ether → pent-4-enal	30	30.6	82
Allyl isopropenyl ether → allylacetone	30	29.3	83
CH_2=CH–O–C_2H_5 → C_2H_4 + CH_3CHO	47	43.8	84
CH_2=CH–O–$CH(CH_3)_2$ → C_3H_6 + CH_3CHO	47	43.6	85
3,7-Dimethylocta-1,6-diene → 3-isopropyl-1,2-dimethylcyclopentane	34	35.2	86
1,3-Butadiene + C_2H_4 → cyclohexene	23	26.7	87
2(Buta-1,3-diene) → vinylcyclohexene	23	23.1	88
2(Penta-1,3-diene) → dimer	23	25.4	89
Hepta-1,5-diene → 3-methyl-1,5-hexadiene	29	32.5	90
1-Bromoethane → HBr + C_2H_4	51	52.3	91
1-Bromopropane → HBr + C_3H_6	51	50.7	92
2-Bromopropane → HBr + C_3H_6	46	47.8	93
2-Bromo-2-methylpropane → HBr + isobutylene	41	41.0	94
1-Iodoethyl → HI + C_2H_4	53	53.7	95
2-Iodopropane → HI + C_3H_6	45	45.3	96
2-Iodobutane → HI + C_4H_8	45	47.9	97
2-Iodo-2-methylpropane → HI + isobutylene	37	36.4	98

However, the activation energy calculated by this mechanism (43 kcal) differs considerably from the experimental value (68 kcal), which compels us to reject the molecular mechanism in favour of a chain mechanism with loss of CH_3 as the first stage.

An analogous picture is observed for the isomerisation of cyclopropane into propene. The activation energy calculated by an additive scheme for a molecular mechanism is 38 kcal. The experimental value of $E = 65.0$ kcal [100] differs considerably from the calculated value. Obviously here the reaction proceeds through the formation of an intermediate biradical:



In several instances the additivity principle allows one of several proposed activated complexes for a single reaction to be chosen. For example, for the isomerisation of allyl vinyl ether into pent-4-enal two activated complexes, four-membered and six-membered, can be written:



Calculation gives $E = 51$ kcal for the four-membered complex, and $E = 30$ kcal for the six-membered. The experimental value [82], $E = 30.6$ kcal, shows that the reaction proceeds by the second path.

7. NATURE OF THE ACTIVATED BOND

A characteristic feature of the above approach to the calculation of activation energy is the hypothesis that an activated complex can be considered as a molecule the atoms of which are linked to one another by activated bonds. It is essential that the activated bonds introduced in this way have constant energies and the energy of the transition state is obtained by simple summation of the energies of all the activated bonds. The theoretical interpretation of the additivity principle involves explaining the nature of the activated bond and developing methods of calculating it.

Within the framework of the Heitler–London approximate quantum theory the energy of a two-electron bond is given by the expression:

$$Q = A + \alpha \qquad (18)$$

where A and α are the coulombic and exchange integrals.

Since the activated bond, as we have seen, is not the ordinary two-electron bond it is interesting to find, from the standpoint of the Heitler–London theory, a corresponding expression for the energy of an activated bond.

For the radical reactions of substitution (9) the activated complex can be considered as a three-electron system with an energy expressed by the London formula:

$$V = A + B + C - \left\{\frac{1}{2}[(\alpha-\beta)^2 + (\beta-\gamma)^2 + (\gamma-\alpha)^2]\right\}^{1/2}. \qquad (19)$$

On the other hand, according to Eqn. (11), Eqn. (20) is valid:

$$V = Q_{R\ldots X} + Q_{R'\ldots X}. \qquad (20)$$

The applicability of the additivity rule signifies that direct interaction of radicals R and R′ within the activated complex can be neglected (this is equivalent to the condition $C = 0$, $\gamma = 0$). Moreover, since the activated bonds are independent, for simplicity the radicals R and R′ can be put identical. Then $A = B$, $\alpha = \beta$, $V = 2Q_{R\ldots X}$, and from Eqn. (19) we obtain Eqn. (21):

$$Q_{R\ldots X} = A + 0.5\,\alpha. \qquad (21)$$

Here, as already shown [101], the curve giving the dependence of $A + 0.5\alpha$ on the interatomic distance shows a minimum at the point corresponding to the dimensions of the activated complex, which makes it possible in principle to calculate the length of the activated bond and consequently also the pre-exponential factor in the Arrhenius equation.

However, it is easy to show [102] that Eqn. (21) has a more general character and is applicable not only to a radical but also to molecular reactions, the activated complex of which can be considered as a multi-electron system, the energy of which is obtained by solution of the corresponding secular equation. In particular, for a four-membered complex of type (*b*), considered as a four-electron system, the same London equation can be written, in which $A = A_1 + A_2$; $B = B_1 + B_2$; $\alpha = \alpha_1 + \alpha_2$; $\beta = \beta_1 + \beta_2$.

The applicability of the additivity principle in this instance shows that the interaction of non-neighbouring

atoms can be neglected, that is, here also we have $C = 0$ and $\gamma = 0$. Assuming, as before, that all four activated bonds are identical, we obtain $A = 4A_1$, $V = 4Q^{\neq}$ and Eqn. (19) is changed into the following equation:

$$Q^{\neq} = A_1 + 0.5\,\alpha_1 .$$

which is identical with Eqn. (21).

For a six-membered complex the position is somewhat complicated by the absence of a clear analytical expression for the energy of a six-electron system. However, here it is possible to use the result of a calculation of the energy of a benzene molecule, where all six π-bonds are also identical. If the interaction of non-adjacent atoms is neglected, then for the energy of the system we have[103] Eqn. (22):

$$V = \sum A + 2.61\,\alpha . \qquad (22)$$

Since here the activated complex consists of six identical bonds, Eqn. (23) which is similar to that obtained earlier, is valid for $Q^{\neq}$:

$$Q^{\neq} = A + 0.435\,\alpha . \qquad (23)$$

Hence from the standpoint of the approximate quantum theory, which represents the energy of a chemical bond as the sum of coulombic and exchange integrals, the energy of an activated bond can be represented approximately by Eqn. (19). Since the exchange integral constitutes the main part of the energy of a covalent bond, an activated bond is considerably weaker than an ordinary one. It must also be borne in mind that the quantities A and α which enter into the expression of the energy of an activated bond have another (lesser) value than in the molecule. This is because the distance between the atoms in the activated complex is greater than in the molecule.

Note that although the energies of various activated bonds can be calculated by quantum-mechanical methods using Eqn. (19), such calculations can hardly give results which agree numerically with experiment. The approximations which form the basis of the London formula used in deriving relation (19) are too rough for such agreement.

Therefore the problem of a more correct quantum-mechanical treatment of the additivity principle and a development of methods for calculating the energy of activated bonds are extremely pressing§.

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The above-mentioned principle of the additivity of the energy of the activated complex directly connects the reactivity of different molecules and radicals with their structure. It allows a simple and graphical interpretation of the activation energy of most varied reactions to be given—including extremely complex reactions which are at present inaccessible to other theories. The additive scheme of calculation makes it possible to determine the activation energy of various chemical reactions very easily and with an accuracy sufficient for practical purposes.

This work shows that to a certain extent a formal approach to the nature of an activated complex which considers it by methods used for ordinary molecules is sufficiently well-founded, both qualitatively and quantitatively.

The purely empirical concept of an activated bond which exhibits a definite energy evidently has a very real significance.

The most important task standing now in this direction is that of defining more accurately the physical essence of the nature of the activated bond and of providing a theoretical basis for and understanding the additivity principle. This is an extremely complex quantum-mechanical problem the solution of which will facilitate to a great extent an understanding of the essence of the elementary chemical act.

§ After the manuscript of the present article had been submitted to the Editors, Szabo's paper[104] appeared, in which an attempt was made to calculate the activation energy by the equation $E = \Sigma Q_{br} - \alpha \Sigma Q_{form}$, outwardly similar to our Eqn. (8), where α is a coefficient empirically selected for each type of reaction. Unlike Eqn. (8) here the second term depends *solely* on the bonds formed. The additivity of the energy of the activated complex is not discussed in Szabo's paper.

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