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QUANTITATIVE ASPECTS OF GAS-PHASE CHEMICAL KINETICS

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Chemical kinetics has long been, by its very nature, a quantitative science, concerned mainly with measuring the rates of chemical reactions. However, measurements of the reaction rates under a given set of conditions (temperature and pressure, initial composition, presence or absence of an inert diluent) give no indication at all of the rate of the same reaction under arbitrarily prescribed conditions. Yet the main value of kinetic investigations lies, both from the theoretical and especially from the practical point of view, in the ability to predict the rate of a given chemical reaction over a wide range of different conditions. A knowledge of the reaction mechanism and of the rate constants of (at least) all the main elementary processes involved is an invariable prerequisite.

At present, the mechanism of the oxidation (combustion) of hydrogen, and of reaction in hydrogen–halogen systems, among those of complex gas-phase reactions, have been studied in some detail, as has the mechanism of the oxidation (combustion) of carbon monoxide (but far from exhaustively); the mechanism of chemical changes in the nitrogen–oxygen system has been examined in broad outline; and individual steps in the oxidation of hydrocarbons and in various other complex reactions have been elucidated. Studies of the mechanism of a variety of chemical reactions, vigorously pursued over a wide front by physical chemists of many countries, are steadily adding to the number of reactions whose mechanism is understood. However, we are still at a relatively early stage, and a large number of reaction mechanisms (including those of technically important reactions) still remain to be investigated and made more precise.

In spite of the many studies devoted to measurements of the rate constants of elementary processes, and in spite of the very large number of kinetic constants which have now been measured, our existing fund of constants is far from adequate for a prediction of the rates of chemical reactions under prescribed conditions. Even in the rare instances where the reaction mechanism is known, and the rate constants of all the main elementary processes have been measured, the precision of the constants is often found to be inadequate. This is particularly true when it becomes necessary to extrapolate to high temperatures the values of these constants measured at relatively low temperatures (a problem which present-day practice often puts to chemical kineticists).

Before discussing the present state of the problem of the rate constants of elementary chemical processes, we shall review briefly some modern experimental methods of measurement.

The experimental methods used to measure rate constants of elementary chemical processes can be divided into two groups: in the first, the constants are measured in the course of the reaction itself, whilst in the second group a single process (often the primary process for the particular experimental conditions) is artificially isolated from the many concomitant elementary processes. The second group of methods is often used to measure the rate constants of processes in which atoms and free radicals interact with molecules or with each other, the atoms and radicals being generated thermally, photochemically, or electrically. Generation can be effected either in the reaction zone or elsewhere. Thus, the photochemical generation of active reaction centres is most frequently carried out in the reaction vessel, whereas when the active centres are generated electrically they appear in a region of electrical discharge, and they are led to the reactor, through a jet, by the flowing gas.

The method of crossed molecular beams is ideal for studying a single, isolated elementary process, but its application has so far been severely limited by the difficulty of measuring the reaction rates.

Among the first group of methods should be listed the shock tube method and the related method of adiabatic compression. The problem of measuring the dissociation constants of diatomic molecules, when the progress of the reaction is usually monitored from the change in concentration of the experimental gas (e.g. by absorption spectroscopy), is solved most easily by the shock tube method. The main difficulty, arising from insufficient accuracy in the measurements, is encountered in the analytical presentation of the measured rate constant. In using the expression from classical collision theory for the dissociation rate constant[1]

$$k_d = c\sqrt{T}\left(\frac{D}{RT}\right)^n e^{-D/RT} \quad (1)$$

(where c is a constant factor, D the dissociation energy, and n the number of internal degrees of freedom involved in activation of the dissociating molecule), a value of n is usually chosen such that the experimentally observed temperature variation of the constant k_d is described as accurately as possible by formula (1). The extent to which such choice can vary (as a direct consequence of the low precision of the measurements) can be assessed from Table 1.

One important result from the shock tube method for measuring k_d has been to verify the correctness of the expression

$$K = \frac{k_d}{k_r}, \quad (2)$$

where K is the equilibrium constant and k_r the rate constant for recombination of the atoms (the reverse of the molecular dissociation process).

Measurements of the dissociation rate constants of polyatomic molecules are usually complicated by the great variety of secondary processes which follow the primary process. Thus, all stages of cracking, as far as carbon, have been demonstrated in the thermal decomposition of methane:

$$CH_4 \rightarrow C_2H_6 \rightarrow C_2H_4 \rightarrow C_2H_2 \rightarrow C.$$

However, the initial stage of the reaction can be isolated by restricting the reaction time. In this way, formulae for the dissociation rate constant in which the dissociation energy and the preexponential factor have closely similar values have been reported in three independent studies[8-10] of the decomposition of methane.

To interpret the experimental results from this type of work correctly, it is essential to ascertain correctly whether the primary process involves dissociation of the methane molecules by the mechanism $CH_4 \rightarrow CH_3 + H$ or by the mechanism $CH_4 \rightarrow CH_2 + H_2$, and whether this process follows first-order or second-order kinetics.

The first of these two questions can now be said to have been resolved in favour of the process $CH_4 \rightarrow CH_3 + H$. A strong argument in its favour was the identity of the activation energy measured for the primary process with the dissociation energy of the H_3C-H bond, and also the fact that CH_3 radicals have been detected, by the Paneth mirror technique [by the formation of $(CH_3)_2Te_2$] in the gas stream issuing from the region of methane cracking, whilst no CH_2 radicals were detected (absence of CH_2Te).[11]

The problem of the order of reaction has been analysed in a previous paper[10], which showed that the process $CH_4 \rightarrow CH_3 + H$ is a first-order reaction (at least, under the experimental conditions of the adiabatic compression method[12]). Thus, the statistical theory of unimolecular decomposition[13] gives for the rate constant of the second-order process $CH_4 + Ar = CH_3 + H + Ar$ the formula

$$k_{d,2} = 10^{21} e^{-E/RT} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1},$$

correct to an order of magnitude at temperatures below 1860°K. Furthermore, the same theory shows that decomposition will occur by a first-order law if

$$k_{d,2}[Ar] > k_{d,1}, \quad (3)$$

where $k_{d,1}$ is the first-order dissociation constant, and [Ar] the concentration of argon. (The reactions occur in methane diluted with 20–100 times its volume of argon.) Substituting in this inequality the formula obtained[10] for $k_{d,1}$

$$k_{d,1} = 10^{15} e^{-E/RT} \text{ s}^{-1},$$

and [Ar] = 10^{-3} mole cm^{-3} (degree of adiabatic compression = 20) we obtain $10^{21} \times 10^{-3} = 10^{18} \gg 10^{15}$, showing that the condition for unimolecular decomposition by the first-order law is satisfied.

Studies of the thermal decomposition of polyatomic molecules in shock tubes sometimes lead to an Arrhenius formula for the decomposition rate constant in which the activation energy E is considerably lower than the dissociation energy. Thus, the following formulae have been obtained[14-17] for the rate constant of the thermal dissociation of CO_2:

$$k_d = 3 \times 10^{11} \sqrt{T}\, e^{-86\,000/RT} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}, \quad M = Ar, \quad T = 2500\text{–}3000^\circ K,^{14}$$

$$k_d = 1.5 \times 10^{14} e^{-87\,000/RT} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}, \quad M = CO_2, \quad T = 3000\text{–}5500^\circ K,^{15,16}$$

$$k_d = 2.9 \times 10^{11} \sqrt{T}\, e^{-74\,700/RT} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}, \quad M = Ar, \quad T = 3500\text{–}6000^\circ K,^{17}$$

$$k_d = 2.5 \times 10^{11} \sqrt{T}\, e^{-74\,500/RT} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}, \quad M = N_2, \quad T = 3500\text{–}6000^\circ K,^{17}$$

whereas the dissociation energy of CO_2 into CO and O is D = 125.75 kcal mole^{-1}. The k_d constants measured in this work can also be represented by formulae of the type of Eqn. (1):

$$k_d = 1.2 \times 10^2 \sqrt{T} \left(\frac{D}{RT}\right)^{7.11} e^{-D/RT} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1},^{14}$$

$$k_d = 3 \times 10^7 \sqrt{T} \left(\frac{D}{RT}\right)^{6} e^{-D/RT} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1},^{15,16}$$

$$k_d = 5.8 \times 10^{10} \sqrt{T} \left(\frac{D}{RT}\right)^{4.36} e^{-D/RT} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1},^{17}$$

$$k_d = 2.0 \times 10^{10} \sqrt{T} \left(\frac{D}{RT}\right)^{4.72} e^{-D/RT} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}.^{17}$$

TABLE 1. Temperature dependence of the preexponential factor in the expression for the rate constant of the dissociation of the O_2 molecule ($O_2 + O_2 = 2O + O_2$), as reported by various workers (D = 118 000 cal mole^{-1}).

$k_d e^{D/RT}$, cm^3 mole^{-1} s^{-1}	T, °K	Ref.
$7.4 \cdot 10^{11} \sqrt{T} (D/RT)^{1.5 \pm 0.2}$	6000—7000	2
$2.25 \cdot 10^{12} \sqrt{T} (D/RT)^{1.5}$	3000—8000	3
$5.5 \cdot 10^{11} \sqrt{T} (D/RT)^{2}$	2800—3900	2, 4
$5.4 \cdot 10^{10} \sqrt{T} (D/RT)^{3}$	3000—5000	5
$5.1 \cdot 10^{10} \sqrt{T} (D/RT)^{3}$	4000—7000	6
$4.6 \cdot 10^{9} \sqrt{T} (D/RT)^{4}$	2600—7000	7

Since the exponent of the term D/RT cannot exceed 5 when M = Ar, and therefore the number 7.11 has no physical significance, Brabbs et al.[14] assumed that the thermal dissociation of carbon dioxide occurs in the two steps

$$CO_2(^1\Sigma) + Ar = CO_2^*(^3\Pi) + Ar,$$
$$CO_2^*(^3\Pi) \rightarrow CO + O,$$

of which the first is rate-determining†. These authors[14] interpret the glow (characteristic of the CO flame) which is observed during the thermal dissociation as evidence for the participation of electronically excited CO_2^* molecules. They base one of their two methods for measuring the rate constant of the dissociation of CO_2 on measurements of the intensity of this glow.

According to Davies[17], however, the glow is a secondary process, associated with the recombination of CO + O leading to the formation of electronically excited CO_2^* ($^3\Pi$) molecules; while the dissociation of CO_2 occurs in a single step, $CO_2 + M = CO + O + M$ (in Davies' formulae $n < 5$).

To establish the true mechanism of the thermal dissociation of CO_2 it is very important to determine the difference in energy between the $^3\Pi$ and $^1\Sigma$ levels, which is not known at present. It is interesting to note that in the thermal dissociation of carbon disulphide, for which the activation energy E is also smaller than the energy required to break the SC–S bond, but for which the excitation energy of the $^3\Pi$ level is known from spectroscopic data, the value of E agrees[18] with the energy difference between the $^3\Pi$ and $^1\Sigma$ levels. This is convincing evidence in favour of the two-stage mechanism for the reaction.

Two-stage thermal decomposition has been established also in the case of SO_2, for which the activation energy calculated from the formula

$$k_d = 10^9 \sqrt{T} \left(\frac{E}{RT}\right)^3 e^{-E/RT} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1},$$

coincides with the excitation energy of the triplet state[19] of the SO_2 molecule. The dissociation process in this case occurs according to the scheme

$$SO_2 + M = SO_2^* + M - 73.6 \text{ kcal mole}^{-1},$$
$$SO_2^* + SO_2 = SO_3 + SO + 25.6 \text{ kcal mole}^{-1},$$

where M denotes any species.

The thermal ionisation of the inert gases has also been shown to be a two-stage process. Thus, the ionisation of xenon in a shock tube proceeds according to the scheme[20,21]

$$Xe + M = Xe^* + M,$$
$$Xe^* + M = Xe^+ + e^- + M.$$

Whereas measurements of the rate of decomposition of saturated molecules, needed in order to determine rate constants, present no special difficulties, measurements of the rates of reactions involving atoms and free radicals, formed in the reaction itself or generated externally, present a much more difficult problem. To determine the rate constants in these cases, the concentration of active centres taking part in the reaction must be measured, or else the rate constant of another reaction involving the same active species must be known.

† The second stage can be written

either $CO_2^*(^3\Pi) + Ar = CO + O + Ar$ or $CO_2^*(^3\Pi) + CO_2 = 2CO + O_2$.

Without attempting to list existing methods of measuring concentrations of atoms and free radicals, we shall only state that the electron spin resonance (e.s.r.) method, recently included among these methods on account of its potentialities, now appears to be the most effective and the most promising. Kinetic investigations of reactions involving H and O atoms, halogen atoms, and OH radicals have already been successfully carried out with the help of the e.s.r. method.

An example of this is the recent work of Panfilov[22], who has measured the rate constants of twelve reactions of the type $H + RH = H_2 + R$, as well as of the reaction $H + O_2 = OH + O$ in low-pressure oxyhydrogen flames (500–600°C, 3–6 mmHg) containing small quantities of the compound RH, the concentrations of H atoms being measured by e.s.r. spectroscopy.

The measurement of the rate constant of one reaction from the known rate constant of another reaction usually relies on the change in the combustion limits[23-30]. The basis of this method can be understood by considering the hydrogen–oxygen flame. With fairly rich hydrogen–oxygen mixtures (the lower combustion limit is set by the removal of H atoms at the walls), if a small amount of a substance M with which H atoms can react is present in the gas mixture, the displacement (in pressure) of the lower limit Δp_1 can be expressed by the formula

$$\frac{\Delta p_1}{p_1^0} = \frac{k[M]}{k_0}, \quad (4)$$

where p_1^0 is the pressure at the lower limit in the absence of the additive, k the rate constant of the reaction between H atoms and the substance M (for example, the rate constant of the reaction $H + RH = H_2 + R$, if M = RH), and k_0 the rate constant for the heterogeneous removal of H atoms.

Nalbandyan and his coworkers[31] have tried, by appropriate treatment of the walls of the reaction vessel, to induce the reaction to occur in the diffusion region, where the constant k_0 can be calculated very accurately in terms of the diffusion coefficient. Thus, from a knowledge of k_0 combined with measurements of the relative displacement of the lower combustion limit $\Delta p_1/p_1^0$ at various values of [M], they calculated the constant k as the slope of the linear plot of Eqn. (4). A common drawback of the method of limit displacement is the fact that the temperature range over which reliable results are obtained is relatively narrow.

The method of "competing reactions", extensively used by Steacie, and also by Trotman-Dickenson, Noyes, and others to study the reactivity of methyl radicals, also relies on measuring the rate constant of one reaction in terms of the rate constant of another reaction.

In the simplest case, when only one substance (e.g. acetone) is present in the system initially, thermal or photochemical decomposition generates CH_3 radicals, which proceed to recombine or to react with acetone molecules, splitting off an H atom. The kinetic equations for this system lead to the relationship

$$\frac{R_{CH_4}}{\sqrt{R_{C_2H_6}}} = \frac{k[CH_3COCH_3]}{\sqrt{k_r}}, \quad (5)$$

where R_{CH_4} and $R_{C_2H_6}$ are the rates of formation of methane and ethane respectively, k is the rate constant of the reaction $CH_3 + CH_3COCH_3 = CH_4 + CH_2COCH_3$, and k_r is the recombination constant of methyl radicals. Thus, formula (5) allows the rate constant k to be calculated from measurements of R_{CH_4} and $R_{C_2H_6}$ if the constant k_r is known.

At this stage, we must make the following observation. The constant k_r is often assumed to be independent both of temperature and of pressure. Thus, for example, Trotman-Dickenson and Steacie adopt a value of 7×10^{13} cm^3 mole^{-1} s^{-1} for the constant k_r in their paper[32] on the reactions of the methyl radical with acetone and with hydrocarbons; Brinton[33] takes k_r to be 4.5×10^{13} cm^3 mole^{-1} s^{-1} in his work on the reactions of the CH_3 radical with various imines; Gray and Thynne[34] studied reactions of the type CH_3 + + CH_3NH_2 = CH_4 + CH_3NH or CH_4 + CH_2NH_2, and adopted the value $k_r = 2.2 \times 10^{13}$ cm^3 mole^{-1} s^{-1}; and so on. All these workers calculate the value of k_r from data obtained in Kistiakowsky's laboratory[35,36], or from the same data, corrected by refinements of the theory of the sector method[37]. Yet it was shown[38] in Kistiakowsky's own laboratory that at low pressures of acetone vapour the constant k_r varies with pressure (in the temperature range 180–240°C) approximately as

$$k_r = \frac{k_{r,2}}{1 + \frac{3.6}{p}}, \qquad (6)$$

where p is the pressure of acetone vapour in mmHg. Lossing and his coworkers have demonstrated[39,40] a dependence of k_r upon helium pressure. By comparing the results of these workers with those already mentioned we conclude that helium is approximately one-fifteenth as effective as acetone in the role of the species M in the reaction

$$CH_3 + CH_3 + M = C_2H_6 + M.$$

Lossing and his coworkers also reported a temperature dependence of the third-order recombination constant (in the range 434–1087°K). When interpreted by means of an Arrhenius expression, these results lead to an activation energy of $E = -1.5 \pm 0.5$ kcal mole^{-1}; when substituted in a power law ($\propto T^{-n}$) they give $n = 1.0$–1.5. On analysing all available data on the recombination constant of methyl radicals, we conclude that the second-order (high-pressure) recombination constant should be expressed by the formula

$$k_{r,2} = 1.1 \times 10^{12} \sqrt{T} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1},$$

and the third-order (low-pressure) recombination constant should be expressed by the formula

$$k_{r,3} = 4.3 \times 10^{19} e^{(1500 \pm 500)/RT} \text{ cm}^6 \text{ mole}^{-2} \text{ s}^{-1}$$

for M = CH_3COCH_3, and by

$$k_{r,3} = 2.9 \times 10^{18} e^{(1500 \pm 500)/RT} \text{ cm}^6 \text{ mole}^{-2} \text{ s}^{-1}$$

for M = He. The identical temperature dependence of the constant $k_{r,3}$ when M = CH_3COCH_3 and when M = He is based on the assumption[39,40] that it is mainly due to the increase in probability of dissociation of the complex $[CH_3 \cdot CH_3]^*$ with increase in temperature.

Thus, it is evident that rate constants calculated in terms of the recombination rate constant of methyl radicals on the assumption that the latter is independent of both temperature and pressure stand in need of revision.

We shall discuss next the method of measuring rate constants in which active species are produced in an electrical discharge and are led by the gas stream into the reaction vessel, where they interact with various substances. This method was used in Steacie's early work, and also by Avramenko, Kaufman, Schiff, and others. Its most extensive application is found in the work of Avramenko[41].

In the simplest case, when the discharge produces active particles of a single kind (atoms of A), which react with the added molecules of M by a single path to give the reaction product P, the kinetic equations can be written

$$-\frac{d[A]}{dt} = (k_0 + k[M])\ [A],$$

$$\frac{d[P]}{dt} = k[M]\ [A],$$

where k is the rate constant of the reaction A + M → P and k_0 the rate constant for the disappearance of A atoms. If the atoms are removed by a first-order process (e.g. by adsorption on the walls), k_0 is independent of the concentration of A atoms. In this case, assuming negligible consumption of the substance M and replacing [M] by the initial concentration $[M]_0$, and making the further assumption that the gas stream emerging from the reaction vessel contains practically no A atoms, the above kinetic equations can be solved to give

$$\frac{1}{[P]} = \frac{1}{[A]_0} + \frac{k_0}{k[M]_0[A]_0}. \qquad (7)$$

If the reciprocal of the measured concentration of reaction product is plotted (vertically) against the reciprocal of the initial concentration of M for various values of $[M]_0$ (with $[M]_0 - [M] \ll [M]_0$, and $[A]_0$ constant), Eqn. (7) leads to a linear plot whose parameters yield the ratio of the constants k/k_0.

Avramenko obtained the constant k_0 from measurements of the relative concentrations of A at different points in the reaction vessel. This, in conjunction with the ratio of k/k_0 obtained from the linear plot of Eqn. (7), allows the constant k to be calculated.

However, this simple method demands great care to ensure that the underlying assumptions are satisfied. Thus, when the rate constant of a homogeneous process is being measured, it must be quite certain that A and M do not interact on the walls of the reaction vessel. Nevertheless, the relatively low pressures normally used in the experiments by the electrical discharge method greatly increase the probability of heterogeneous reaction. Furthermore, we must know that the constant k_0 is unaffected by the presence or absence of the substance M. Since at low pressures and low concentrations the active particles are usually lost at the walls, on which they become adsorbed, there is likely to be an effect of impurities on the adsorption properties of the walls. It is also necessary to check that the value of $[A]_0$ remains constant at different values of $[M]_0$. Further complications are introduced by the possibility of reactions between A and M by two or more paths, when formula (7) is replaced by

$$\frac{1}{\Sigma[P_i]} = \frac{1}{[A]_0} + \frac{k_0}{\Sigma k_i [M]_0 [A]_0}, \qquad (7')$$

or, if the yield of only one of the products (P_1) is monitored, by the formula

$$\frac{1}{[P_1]} = \frac{\Sigma k_i}{k_1} \frac{1}{[A]_0} + \frac{k_0}{k_1 [M]_0 [A]_0}. \qquad (7'')$$

It is easy to see that formula (7′) allows only the sum of the rate constants Σk_i for the interaction of A and M to be determined. From formula (7″), on the other hand, we can obtain the rate constant of a single process k_1 if the initial concentration of A particles is measured independently.

We have assumed that the reaction products whose concentration is measured during the experiment are obtained by direct interaction between A and M. However, the primary products of an interaction of this type are often certain intermediates, which undergo further transformation to give the products whose yield is taken as a measure of the rate of interaction of A and M by a particular path. Thus, for example, when we measure the rate constant of the reaction $O + H_2 = OH + H$ from the yield of water, we must be absolutely certain that the rate of this reaction and the rate of formation of water are either identical or interrelated in a specific (and known) way.

It follows from what has been said that the rate constants of elementary chemical reactions measured by the electrical discharge method can be considered reliable only if all possible factors affecting the course of the reaction have been carefully weighed and evaluated.

We will now turn to the photochemical method of producing atoms and free radicals, whose rates of interaction with various substances it is desired to measure. This method has been used extensively by Steacie, Noyes, Cvetanović, Nalbandyan, and others. One of its advantages over the electrical discharge method is the fact that chemical reactions can be studied at relatively high pressures, when heterogeneous processes may be ignored.

However, the photochemical method also presents one very important disadvantage, which compels us to regard with the greatest caution the rate constants measured by this method. This drawback arises from the possibility of producing "hot particles", whose reactivity is higher than that of similar particles having an equilibrium (or close to equilibrium) energy distribution.

The possibility of obtaining hot particles in photochemical reactions, and their role in the reaction, were pointed out[42] as early as 1934 (although the concept of "hot particles" came later). In that investigation, the proportion of hydrogen iodide which was oxidised was measured by irradiating a mixture of $HI + O_2$ in Uviol ($\lambda > 2800$ Å) and quartz ($\lambda > 2000$ Å) vessels near room temperature. Since in the first case the maximum energy of the H atoms produced by the primary process $HI + h\nu = H + I^*$ did not exceed 10 kcal mole^{-1}, whilst in the second case it reached 20 kcal mole^{-1} ($\lambda = 2537$ Å) or more, the approximate doubling of the amount of HI oxidised, observed when the Uviol vessel was replaced by a quartz vessel, was ascribed to the high reactivity of the intermediate HO_2 radical, formed by the reaction between a fast ("hot") H atom and an O_2 molecule. An alternative explanation was also put forward: in the presence of fast H atoms, a different intermediate process becomes possible, namely $H + O_2 = OH + O - 16.7$ kcal mole^{-1}, and this can lead to an increase in the fraction of HI which is oxidised.

The formation of hot H atoms in the photolysis of HI has recently been confirmed by Dzantiev et al.[43], who studied the photochemical reaction in mixtures of HI and ethylene at temperatures between 0° and 250°C. They showed that the main product of this reaction is ethane, and that its yield is independent of temperature over the experimental temperature range (curve *a*, Fig. 1), is practically unaffected by dilution with argon (curve *a*, Fig. 2), and decreases sharply when the mixture is diluted with helium (curve *b*, Fig. 2). The mixture diluted with helium showed a variation in yield of ethane of the Arrhenius type (curve *b*, Fig. 1), corresponding to an effective activation energy of 3.5 kcal mole^{-1}.

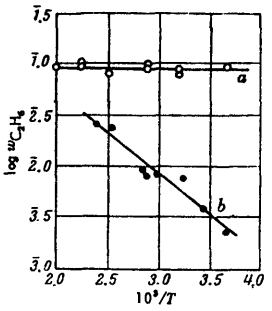


Fig. 1. Variation of the rate of formation of ethane (cm^3 min^{-1}) with temperature: *a*) HI : C_2H_4 = 9 : 1; *b*) HI : C_2H_4 : He = 9 : 1 : 40.

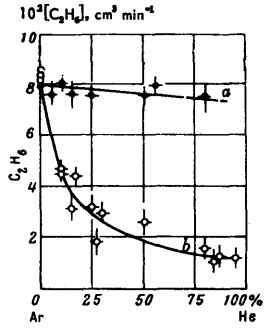


Fig. 2. Variation of the yield of ethane on dilution with: *a*) argon; *b*) helium.

These results were interpreted by postulating that the hot H atoms, which are mainly consumed by the reaction $H + HI = H_2 + I$, can react also with ethylene to some extent, forming "hot" $C_2H_5^*$ radicals which then react with HI according to the scheme $C_2H_5^* + HI = C_2H_6 + I$. Dilution with helium brings about thermal equilibration of the hot H atoms, as evidenced by the lower yield of C_2H_6 and by the appearance of a temperature dependence of the reaction rate.

Whereas in this work the hot C_2H_5 radicals are formed through the agency of the primary hot H atoms, many instances are known of the formation of hot radicals in the primary photochemical act. We shall mention only one example[44], which showed that the photolysis of azomethane CH_3NNCH_3 produces a certain proportion of hot CH_3^* radicals. Until they have reach thermal equilibrium, these radicals can easily abstract H atoms from hydrocarbon molecules at room temperature. As in the work on the oxidation of hydrogen iodide, the activity of the CH_3 radicals was found to decrease with increase in wavelength (since the relative yield of methane decreases).

The problem of hot particles, and in particular of the particles formed during photolysis, cannot as yet be considered fully solved. However, in view of the above and other similar observations, it is evident that great caution must be exercised in the quantitative interpretation of kinetic results obtained under conditions admitting the formation of hot particles and their participation in the reaction.

The conclusion to be drawn from this discussion of the methods for measuring the rate constants of chemical processes is that each method has some unsatisfactory features, and that a critical approach is imperative in dealing with quantitative data based on these methods. The lack of a duly critical attitude, particularly on the part of the authors themselves (who do not always attach due weight to the errors in their measurements), is often responsible for the large discrepancies found between the quantitative results obtained by different authors using different or even the same methods.

The results given above (Table 1) for the rate constant of the dissociation of oxygen serve to illustrate the large errors involved in measurements of this type. Further simple examples are given below.

Table 2 lists the rate constants for the reaction $H + O_2 + H_2 = HO_2 + H_2$ reported by various workers. It can be seen that the extreme values differ by a factor of 10^4.

The values of the constant k_r obtained by different workers from measurements of the second combustion limit of hydrogen in the neighbourhood of 800°K do not differ by more than a factor of 2, averaging[48,53] about 10^{16} cm^6 mole^{-2} s^{-1}. Since the temperature dependence of the recombination constant is usually expressed by a formula of the type

$$k_r = aT^{-n}, \qquad (8)$$

where $1 \leqslant n \leqslant 2$, extrapolation to 300°K gives $k_r = 2.6 \times 10^{16}$ for $n = 1$ and $k_r = 7.0 \times 10^{16}$ for $n = 2$. Comparing these values with those set out in Table 2 we conclude that the only admissible value is[48] 4×10^{16}. Of all the data given in Table 2, this can be considered the most reliable.

Table 3 gives data for the reaction $H + CH_4 = H_2 + CH_3$. With one exception, the activation energy and the preexponential term increase with temperature. We may conclude that the large scatter of the rate formulae obtained by different authors is due essentially to a large error in the measurement of the temperature variation of the constant k. The correctness of this conclusion is confirmed by the almost identical values given by three of the five formulae at a constant temperature (800°K). We may therefore adopt as the most reliable formula for the constant

$$k = 10^{13.17} \exp(-11\,200/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1},$$

obtained as the geometric mean of the three formulae.

TABLE 2. Rate constant of the reaction $H + O_2 + H_2 = HO_2 + H_2$ at room temperature.

k_r, cm^6 mole^{-2} s^{-1}	Method	Ref.
6.9×10^{15}	electrical discharge; concn. of H determined from ortho–para conversion	45
3.3×10^{14}	photochemical oxidation of HI	46
4.3×10^{14}	electrical discharge; rate of formation of HO_2 determined from yield of H_2O_2	47
4.0×10^{16}	electrical discharge; concn. of H determined from HNO glow	48
1.8×10^{17}	Hg photosensitisation of $H_2 + O_2$ reaction	49
2.9×10^{17}	electrical discharge; products estimated mass-spectroscopically	50, 51
6.1×10^{17}	Hg photosensitisation of $H_2 + O_2$ reaction	52

TABLE 3. Rate constant of the reaction $H + CH_4 = H_2 + CH_3$.

k, cm^3 mole^{-1} s^{-1}	T, °K	k(800°K)	Ref.
$10^{10.0} \exp(-4500/RT)$	372–436	$10^{8.77}$	54
$10^{12.5} \exp(-9000/RT)$	403–503	$10^{10.03}$	55
$10^{13.925} \exp(-14\,100/RT)$	773–873	$10^{10.06}$	22
$10^{13.08 \pm 0.25} \exp(-10\,600 \pm 1000/RT)$	843–933	$10^{10.18}$	56,57
$10^{14.3} \exp(-11\,500 \pm 1500/RT)$	1100–1900	$10^{11.15}$	58

The formulae obtained by different authors for the reaction $OH + HCHO = H_2O + HCO$ show even greater scatter, as can be seen in Table 4. Measurements obtained in Refs. 59–61 are described accurate to a factor of 3 by the formula

$$k = 10^{13} \exp(-6300/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$$

(see Fig. 3).

The formulae obtained by different authors for the reaction $OH + H_2 = H_2O + H$ are presented in Table 5. We see that there is close agreement between the first three formulae, obtained by different methods, whereas in the last three formulae the activation energy differs considerably. This is due to the difference between the measured value[65] of the rate constant at 310°K — $(4.3 \pm 1.0) \times 10^9$ cm^3 × × mole^{-1} s^{-1} — and the values extrapolated to that temperature by means of the first three formulae of Table 5, amounting to 2–3 orders of magnitude.

It is interesting to note that a value of 5 kcal mole^{-1} has been obtained[68] for the difference $E_{OH+H_2} - E_{OH+CO}$. Hence, with $E_{OH+H_2} = 10$ kcal mole^{-1} we find that E_{OH+CO} = = 5 kcal mole^{-1}, a value consistent with measurements by various authors (ranging from 3.4 to 10.3 kcal mole^{-1}), whereas if $E_{OH+H_2} = 5.9$ kcal mole^{-1} we obtain ~1 kcal × × mole^{-1} for the activation energy of the process $OH + CO = CO_2 + H$. Further experimental work is needed to solve the problem of the true activation energies of the reactions $OH + H_2 = H_2O + H$ and $OH + CO = CO_2 + H$.

TABLE 4. Rate constant of the reaction $OH + CH_2O = H_2O + HCO$.

k, cm^3 mole^{-1} s^{-1}	T, °K	Ref.
$1.2 \cdot 10^{13} \exp(-900/RT)$	346–489	59
$5.1 \cdot 10^{14} \exp(-3650/RT)$	798–923	60
$5 \cdot 10^{13} \exp(-13\,000/RT)$	1250–1400	61

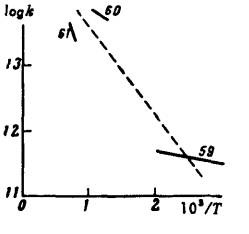


Fig. 3. Rate constant of the reaction $OH + CH_2O = H_2O + HCO$ according to different workers.

TABLE 5. Rate constant of the reaction OH + + H_2 = H_2O + H.

k, cm³ mole⁻¹ s⁻¹	T, °K	Ref.
$2.3 \cdot 10^{14} \exp(-1100/RT)$	900—1400	62
$1.4 \cdot 10^{14} \exp(-10\,400/RT)$	380—490	63
$2.5 \cdot 10^{14} \exp(-10\,000/RT)$	1660—1850	64
$10^{13.8 \pm 0.7} \exp(-5900 \pm 1000/RT)$	310 and 1500	65
$10^{13.48} \exp(-5500 \pm 600/RT)$	310 and 915	66
$10^{13.6} \exp(-5700/RT)$	1500—2600	67

From these examples, to which many more could be added, it is evident that the present situation regarding the problem of the rate constants of elementary chemical reactions is unsatisfactory. This introduces great difficulties in the practical application of kinetic data.

In view of the difficulties in every experimental method of measuring the rate constants of chemical reactions, various theoretical or semi-theoretical indirect methods are often used with success. The statistical method for calculating second-order rate constants for the thermal dissociation of molecules must be mentioned first (see Ref. 13, p. 25). The method relies on the formula

$$k_d = Z g_s(E_0) \exp(-E_0/RT)/F(s-1), \quad (9)$$

where Z is the collision factor of the kinetic theory of gases ($Z \simeq 10^{14}$ cm³ mole⁻¹ s⁻¹),

$$g_s(E_0) = \left(\frac{E_0 + E_z}{h\bar{\omega}}\right)^{s-1} \frac{1}{(s-1)!},$$

E_0 is the dissociation energy, $E_z = \frac{1}{2}\Sigma h\omega_i$ is the zero-point vibrational energy, $\bar{\omega}$ is the mean vibration frequency, defined as

$$\bar{\omega} = \left(\prod_i \omega_i\right)^{1/s},$$

s is the total number of vibrational degrees of freedom, and $F(s-1)$ is the vibrational partition function. The k_d constants calculated from formula (9) agree with experiment to within an order of magnitude [69].

We have shown above (p. 894), using the thermal decomposition of methane as an example, that the order of a reaction can be ascertained from approximate calculations of the rate constant. The recombination constant of H + O_2 provides another example of this. Direct measurements of this constant at room temperature gave widely divergent values (see Table 2): we can calculate it through the dissociation constant and the equilibrium constant K from the formula

$$k_r = \frac{k_d}{K}. \quad (2')$$

If we calculate the constant k_d for 800°K and 300°K from formula (9) and adopt tabulated values [70] for the H + $O_2 \rightleftharpoons HO_2$ equilibrium constant at these temperatures, we obtain $k_r = 9 \times 10^{15}$ and 1.5×10^{16} cm⁶ mole⁻² s⁻¹ for the respective temperatures. Since it is assumed, in evaluating the number of vibrational degrees of freedom s, that the particle M is an atom, we can obtain values of the constant k_r for M = H_2 by multiplying the above values by 5, it having been shown [71] that the relative efficiencies of H_2 and Ar in the reaction H + O_2 + M = HO_2 + M at 800°K are in the ratio 5 : 1. This gives $k_r = 4.5 \times 10^{16}$ (800°K) and $k_r = 7.5 \times 10^{16}$ (300°K). These values are only slightly higher than the experimental value of k_r reported above (p. 898) for 800°K and the value measured [48] at 300°K. We should note that the two experimental values of k_r differ by a factor of 4. Since the ratio of the temperatures (800° and 300°K) is 2.7, we may tentatively conclude that $k_r \propto 1/T^{3/2}$.

We shall discuss one more example. Szwarc [72] measured the rate constant for the unimolecular decomposition of hydrazine, and interpreted it as a first-order constant:

$$k_d = 4 \times 10^{12} \exp(-60\,000/RT) \text{ s}^{-1}.$$

However, Gilbert [73] has since shown that the decomposition of N_2H_4 under Szwarc's experimental conditions should obey a second-order law, and he has reinterpreted Szwarc's data to give the following formula for the second-order dissociation constant

$$k_d \simeq 10^{19} \exp(-60\,000/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}.$$

Since this formula agrees exactly with that calculated by Nikitin and Sokolov [69], Gilbert's views appear to be correct.

It is important to note that the theoretical formula (9) for the constant k_d implies that the temperature dependence of the preexponential factor in k_d is different at low and at high temperatures respectively. In the low-temperature region ($T < h\omega/k$, where ω is the lowest vibrational frequency of the dissociating molecule) the vibrational partition function $F(s)$ is practically unity, and the temperature dependence of the preexponential factor A becomes indistinguishable from that of the collision factor Z of the kinetic theory of gases: i.e. $A \propto \sqrt{T}$. In the limit at fairly high temperatures, however, when $F(s)$ is expressed as $\prod_i (kT/h\omega_i)$, the temperature dependence of the preexponential factor takes the form

$$A \sim T^{1.5s-s}. \quad (10)$$

It follows that it is impossible, in principle, to express the dissociation rate constant k_d by a formula of the type

$$k_d = A \exp(-E_0/RT), \quad (11)$$

in which the preexponential factor A is either constant or of the form $A = A_0 T^{-n}$ (n remaining constant over a wide range of temperatures). Another important test of the correctness of the interpretation of experimental kinetic results could be to calculate the preexponential factor in the expression for the bimolecular rate constant from the activated complex theory. Unfortunately, however, this method still lacks adequate theoretical development, and has been used in relatively few instances (see, for example, Refs. 53 and 74–78).

Application of the Polanyi–Semenov rule can also be of some value when testing the results of direct measurements. With a few exceptions, the linear relation

$$E = a - bQ \quad (12)$$

between the activation energy E and the heat of reaction Q is approximately obeyed in series of chemical reactions of similar type. Fig. 4 shows the variation of E with Q for the reactions H + RH = H_2 + R (curve a) and O + RH = OH + + R (curve b), where R = CH_3, NH_2, OH, and F. It is evident that the Polanyi–Semenov rule can be applied satisfactorily to both types of reaction within the limits of experimental error‡.

‡ In this plot the average of all measured values of E has been taken, and the mean deviation calculated accordingly. The error in the values of Q is determined by the inaccuracy of the corresponding thermochemical data.

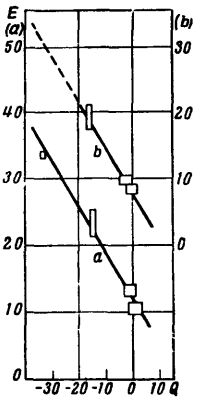


Fig. 4. Test of the Polanyi-Semenov rule for the reactions:
a) H + RH = H_2 + R;
b) O + RH = OH + R (R = CH_3, NH_2, OH, F).

The unsatisfactory state of our understanding of kinetic constants, which has been stressed in this review, exists also, to a greater or lesser degree, in other fields of science. In view of the vast and annually growing store of experimentally determined constants, presented with an almost complete lack of critical assessment, we are faced with an urgent need to rationalise the whole problem.

At the moment, the necessary measures are being taken (or planned) in many countries. Committees and organisations responsible for the compilation of tested and critically assessed quantitative data are being set up. In the Soviet Union, this is the responsibility of the State Committee for Standards, Measures, and Measuring Apparatus, which has begun to plan and develop efforts to produce and keep up to date exhaustive compilations of the best, most reliable, critically selected data in various fields.

As far as is known, in the USA the selection of reliable data has been undertaken by the National Bureau of Standards. The programme known as the National Standard Reference Data System [NSRDS], described in a paper by E. L. Brady of the Bureau of Standards, may be mentioned in this context.

It is obvious, however, that the critical evaluation and selection of the most reliable data should be organised on an international basis. To this end, the International Council of Scientific Unions (ICSU), acting on a report by the foreign secretary of the National Academy of Sciences of the USA, Dr. Harrison Brown, established in June 1965 a special group including representatives from many countries, charged with studying the problem of international cooperation in the preparation of international critical tables. This group will report its findings to the next session of the Executive Committee of the ICSU.

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METAL SELENOCYANATES AND THEIR PROPERTIES

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I. INTRODUCTION

Selenocyanates find practical use as sensitisers in photographic emulsions and for the preparation of organic derivatives of selenium. The use of selenocyanates is very promising for the production of metal selenides, which are of great value in electronics. It may also be assumed that the selenocyanates will find use in analytical chemistry, especially in various titrations in non-aqueous solutions and also in the separation of selenium and tellurium with the object of obtaining these elements in a high state of purity.

Investigation of the selenocyanates is also of great theoretical significance in connection with the more profound elucidation of the chemical individuality of selenium. Nevertheless, there are no reviews on the selenocyanates. Only the dissociation constants of silver, mercury, and cadmium selenocyanates are given in a handbook[1]. Even the book by Williams[2] on cyanogen and its compounds with various elements gives only general information about a few metal selenocyanates.

The present paper is the first attempt to systematise published information on the selenocyanates.