The Development of the Arrhenius Equation

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Today the influence of temperature on the rates of chemical reactions is almost always interpreted in terms of what is now known as the Arrhenius equation. According to this, a rate constant k is the product of a pre- exponential ("frequency") factor A and an exponential term

$$k = Ae^{-E/RT} \tag{1}$$

where R is the gas constant and E is the activation energy. The apparent activation energy E_{app} is now *defined* (1) in terms of this equation as

$$E_{app} \equiv R\left(\frac{\partial \ln k}{\partial(1/T)}\right)_P \tag{2}$$

Often A and E can be treated as temperature independent. For the analysis of more precise rate-temperature data, particularly those covering a wide temperature range, it is usual to allow A to be proportional to T raised to a power m, so that the equation becomes

$$k = A'T^m e^{-E/RT} \tag{3}$$

where now A' is temperature independent. Recently Gardiner (2) has shown that eqn. (3) applies satisfactorily, and better than eqn. (1), to a number of reactions; he has also discussed reasons for the failure of eqn. (1). In modern compilations (3) the procedure often employed is to use eqn. (1) for data of lower precision or where the temperature range is limited, and to analyze more precise data in terms of eqn. (3).

Although the temperature dependence of rates is now almost universally interpreted in terms of these equations, for a period of over 60 years (ca. 1850 to ca. 1910), in spite of considerable experimental effort, there was much uncertainty and controversy. Mellor's famous textbook of kinetics (4) published in 1904 quotes Ostwald as saying that temperature dependence "is one of the darkest chapters in chemical mechanics." In van't Hoff's pioneering textbook of physical chemistry (5) published in 1898 the evidence was reviewed with respect to a number of empirical relationships between k and T, and the author concluded his survey by saying that "It is so far impossible to choose between the above equations."

Some of these early struggles with the problem have recently been reviewed by King (6, 7), who in a very interesting way has covered both scientific and historical aspects. Besides being of considerable historical interest, a study of the early work on temperature dependence provides us with considerable insight as to how scientific progress is made not merely from an analysis of data but from theoretical considerations of broad applicability.

The Empirical Approach: A Brief Historical Survey

Wilhelmy (8) appears to have been the first to propose, in 1850, an equation relating the rate constant of a reaction to the temperature. He used the Celsius temperature θ, and his equation can be written as[1]

$$k = AF^\theta (1 + G\theta) \tag{4}$$

In terms of the absolute temperature T, the equation can be written as

$$k = A'F^T(1 + G'T) \tag{5}$$

In 1862 Berthelot (9) presented the equation

$$\ln k = A' + DT \qquad \text{or} \qquad k = Ae^{DT} \tag{6}$$

A considerable number of workers supported this equation, which was taken seriously at least until 1908 (10).

In 1881 Warder (11, 12) proposed the relationship

$$(a + k)(b - T) = c \tag{7}$$

where a, b, and c are constants, and later Mellor (4) pointed out that if one multiplies out this formula, expands the factor in T and accepts only the first term, the result is

$$k = a' + b'T^2 \tag{8}$$

Equation (7) received some support from results obtained by Urech (13–15) and by Reicher (16, 17), but it did not prove at all popular.

In 1883 Schwab (18), working in van't Hoff's laboratories in Amsterdam, proposed the relationship

$$\ln k = A' - \frac{B}{T} + DT \qquad \text{or} \qquad k = Ae^{-(B-DT^2)/T} \tag{9}$$

and demonstrated that it applied to the conversion of dibromosuccinic acid into bromomaleic acid and to the reaction between hydroxide ions and monochloroacetate ions. In the following year van't Hoff's famous textbook on chemical dynamics (19) appeared, and it contained a discussion of the temperature dependence of equilibrium constants in terms of an equation that we can now express in the form

$$\left(\frac{\partial \ln K_c}{\partial T}\right)_P = \frac{\Delta U^\circ}{RT^2} \tag{10}$$

where K_c is the concentration equilibrium constant and ΔU° the standard internal energy change. Van't Hoff pointed out that since K_c is the ratio of rate constants k_1 and k_{-1} for reaction in forward and reverse directions, these rate constants are also expected to obey an equation of the same form

$$\left(\frac{\partial \ln k}{\partial T}\right)_P = \frac{E}{RT^2} \tag{11}$$

where E is an energy change that relates to the particular reaction.

Van't Hoff acknowledged having received inspiration for these ideas from a paper by Pfaundler (20), who as early as

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[1] To avoid confusion, the early equations have all been converted to a consistent notation, and natural logarithms have been used throughout. Constants such as A, A', B, C, D, F, G, a, b, a', and b' are temperature independent.

1867 had given a qualitative discussion of equilibrium and rates in terms of molecular motions and Maxwell's law of distribution of molecular speeds. Pfaundler saw clearly that when chemical equilibrium is established, forward and reverse reactions are occurring at equal rates. Maxwell's law had led to the conclusion that the fraction of molecules having energy greater than a critical value E is equal to $\exp(-E/RT)$ and can increase markedly with temperature. Pfaundler suggested that only those molecules possessing more than a critical energy E could undergo chemical change. Pfaundler's work is now largely forgotten, but he was responsible for important concepts that are usually attributed to van't Hoff and Arrhenius.

Van't Hoff did not assume $\Delta U°$ and E to be temperature independent; he also considered the possibility that $\Delta U°$ and E might involve a temperature independent term and in addition a negative term proportional to T^2. He thus considered two possible forms for the temperature dependence of k, eqn. (9) and also the simpler relationship

$$\ln k = A' - \frac{B}{T} \quad \text{or} \quad k = Ae^{-B/T} \quad (12)$$

We have seen that eqn. (9) was supported by the work of Schwab (18); it was also supported by work of Spohr (21), van't Hoff and Reicher (22), Buchböch (23), and Wegscheider (24).

In the meantime Hood was making careful kinetic studies of a number of reactions in solution, and in a paper published in 1885 (25) he interpreted his results in terms of Berthelot's formula, eqn. (6). This equation remained popular for another 20 or more years; a number of papers supported it, including those of Tammann (26), Remsen and Reid (27), and Perman and Greaves (10).

A very important contribution to the problem was made in 1889 by Arrhenius (28), whose approach was rather different from that of the other workers. Starting with van't Hoff's equation (eqn. (11)) Arrhenius pointed out that the magnitudes of the temperature effects on rates are usually much too large to be explicable on the basis of how temperature affects the molecular translational energies, or of the temperature dependence of the viscosity of the medium. He concluded that the explanation must be that an equilibrium is established between normal and active reactant molecules, and that this equilibrium shifts in the manner predicted by van't Hoff's equation (eqn. (10)). He did not concern himself with a possible temperature dependence of this energy difference; in fact he tacitly assumed no temperature dependence and therefore favored the simple eqn. (1).

An equation in which the pre-exponential factor also has a temperature dependence was first proposed in 1893 by Kooij (29), whose equation may be expressed as

$$\ln k = A' - \frac{B}{T} + C \ln T \quad \text{or} \quad k = AT^C e^{-B/T} \quad (13)$$

This equation was supported by Trautz (30) in 1909. As previously noted, this equation (equivalent to eqn. (3)) is perhaps the most satisfactory of the equations; data that do not fit the simple eqn. (1) usually fit eqn. (13) very precisely.

In 1865–67 Harcourt and Esson (31–33) made pioneering contributions to chemical kinetics, being the first to relate reactant and product concentrations to the time by means of equations that they obtained by integrating the differential equations for rates of reaction. Some 30 years later they collaborated again on a very long paper (34) presented as a Bakerian Lecture to the Royal Society. In this publication they gave very precise results for the reaction between hydrogen peroxide and hydrogen iodide, obtained from 0°C to 50°C at intervals of about 5°. They presented a very detailed analysis of the temperature dependence and concluded that it was best represented by equations of the form

$$\ln k = A' + C \ln T \quad \text{or} \quad k = AT^C \quad (14)$$

This type of relationship did not receive much encouragement from others, but it was supported by some work of Veley (35) on the affinity constants of bases. One particularly interesting feature of Harcourt and Esson's work is that they

Table 1. Summary of Temperature-Dependence Equations

Differential Form	Integrated Form	Expression for k	Eqn. Number in Text	Supported by	Reference
$\dfrac{d\ln k}{dT} = \dfrac{B + CT + DT^2}{T^2}$	$\ln k = A' - \dfrac{B}{T} + C\ln T + DT$	$k = AT^C e^{-(B-DT^2)/T}$	15	van't Hoff, 1898	5
				Bodenstein, 1899	42
$\dfrac{d\ln k}{dT} = \dfrac{B + CT}{T^2}$	$\ln k = A' - \dfrac{B}{T} + C\ln T$	$k = AT^C e^{-B/T}$	13	Kooij, 1893	29
				Trautz, 1909	30
$\dfrac{d\ln k}{dT} = \dfrac{B + DT^2}{T^2}$	$\ln k = A' - \dfrac{B}{T} + DT$	$k = Ae^{-(B-DT^2)T}$	9	Schwab, 1883	18.
				van't Hoff, 1884	19
				Spohr, 1888	21
				van't Hoff and Reicher, 1889	22
				Buchböck, 1897	23
				Wegscheider, 1899	24
$\dfrac{d\ln k}{dT} = \dfrac{CT + DT^2}{T^2}$	$\ln k = A' + C\ln T + DT$	$k = AT^C e^{DT}$	16	. . .	. . .
$\dfrac{d\ln k}{dT} = \dfrac{B}{T^2}$	$\ln k = A' - \dfrac{B}{T}$	$k = Ae^{-B/T}$	12	van't Hoff, 1884	19
				Arrhenius, 1889	28
				Kooij, 1893	29
$\dfrac{d\ln k}{dT} = \dfrac{C}{T}$	$\ln k = A' + C\ln T$	$k = AT^C$	14	Harcourt and Esson, 1895	34
				Veley, 1908	35
				Harcourt and Esson, 1912	36
$\dfrac{d\ln k}{dt} = D$	$\ln k = A' + DT$	$k = Ae^{DT}$	6	Berthelot, 1862	9
				Hood, 1885	25
				Spring, 1887	37
				Veley, 1889	38
				Hecht and Conrad, 1889	39
				Pendelbury and Seward, 1889	40
				Tammann, 1897	26
				Remsen and Reid, 1899	27
				Bugarszky, 1904	41
				Perman and Greaves, 1908	10

made no assumption as to the absolute zero; they represented the absolute temperature as $x + \theta$, where θ is the centigrade (Celsius) temperature, and found x to be 272.6°, in very good agreement with the modern value of 273.15°. They had thus established, quite independently of thermodynamics, a kinetic absolute zero of temperature, at which chemical reaction would cease.

Most other workers, however, favored different temperature-dependence equations, and in 1912 Harcourt and Esson returned to the fray with another lengthy paper (36), in which they analyzed many of the results obtained by others. They claimed that eqn. (14) interprets the temperature dependence better than the rival equations, and for some reactions this claim is reasonable. For several reactions, however, agreement can be obtained only if C is allowed to be significantly temperature dependent—it sometimes decreases with increasing T, but more often increases. To explain deviations from their equation, they suggested that "the conditions for a stable communication of heat energy to chemical energy are not secured." Harcourt and Esson's two papers make no reference at all to Arrhenius' ideas, and make only a disparaging reference to the arguments of van't Hoff.

In his 1898 book, van't Hoff (5) pointed out that most of the previously presented equations were special cases of the equations

$$\ln k = A' - \frac{B}{T} + C \ln T + DT \qquad \text{or} \qquad k = AT^C e^{-(B - DT^2)/T}$$

$$(15)$$

They can be arrived at by dropping one or two of the constants B, C, or D. This is illustrated, and the equations and references summarized, in Table 1. We will refer to the general equation (eqn. 15) as a three-parameter equation, since three parameters B, C, and D are concerned with the temperature dependence and remain when the equation is put into its differential form. Dropping one of the three constants leads to three two-parameter equations, eqns. (13) and (9) and a third equation

$$\ln k = A' + C \ln T + DT \qquad \text{or} \qquad k = AT^C e^{DT} \quad (16)$$

which seems to have received no consideration or support. Dropping two of the constants leads to the three one-parameter equations, eqns. (12), (14), and (6).

In the following year (1899) Bodenstein (42) published the results of very careful measurements, over a wide temperature range (283°–508°C), on the gas phase reaction between hydrogen and iodine, on the reverse decomposition of hydrogen iodide, and on the equilibrium $H_2 + I_2 \rightleftharpoons 2HI$. He analyzed his results in terms of the three-parameter eqn. (15) and obtained very good agreement. However, from the modern point of view his analysis would hardly be considered satisfactory. For example, for the combination of hydrogen and iodine he fitted his temperature data to the formula

$$\ln k = -\frac{21{,}832}{T} - 12.872 \ln T + 0.01751\, T + 101.487 \quad (17)$$

(note the extravagant use of significant figures). This means that the preexponential factor varies with temperature according to $T^{-12.9}$, which now seems to be an unreasonably strong dependence. Since his pre-exponential factor decreases strongly with increasing temperature, Bodenstein's parameter BR corresponds to an activation energy (181.7 kJ mol^{-1}) that is significantly higher than the presently accepted E_{app} value (3b, c) of 171.4 kJ mol^{-1}.

In 1908–1909 Trautz and Volkmann (43, 44) also analyzed data of others on the basis of various formulae, including the three-parameter eqn. (15). Their analysis also leads to abnormally large negative temperature dependencies of the pre-exponential factors, and therefore to apparent activation energies that are too high according to modern interpretations.

It is a curious historical fact that in spite of the controversy that had been raging for some 60 years, by the second decade of the present century all formulae except eqns. (1) and (3) had been quietly dropped. For example, the important papers of Trautz (45) and Lewis (46) on the significance of the pre-exponential factor use only the simple Arrhenius equation (eqn. (1)). As far as the Harcourt-Esson equation is concerned, I am not aware of any papers that quote it except as an historical anomaly (see, for example, ref. (47)).

The most important reason for the acceptance of the Arrhenius equations is that all of the other relationships are theoretically sterile. The parameter B in eqn. (12) is related to an energy E which can be related to the height of an energy barrier for the reaction. The parameters C and D that appear in the Harcourt-Esson and Berthelot formulations, on the other hand, cannot easily be related to any meaningful physical quantity. The undoubted fact that, for certain reactions, the Harcourt-Esson equation fits the data better than other equations is not a compelling argument in view of the fact that it does not lead to any understanding of the way in which a chemical reaction occurs.

Comparison of the Empirical Equations

At first sight it appears surprising that equations as widely different as some of those listed in Table 1 can all give a reasonably good fit to the same experimental data. We may first focus attention on the three one-parameter eqns. (12), (14), and (6). A fit to these separate equations is confirmed if the following plots are linear:

eqn. (12):	$\ln k$ against $1/T$
eqn. (14):	$\ln k$ against $\ln T$
eqn. (6):	$\ln k$ against T

The reason that all of these plots can give reasonably good linear fits with the same data is that over the narrow temperature ranges usually employed in kinetic studies, $1/T$, $\ln T$, and T are more or less linearly related to each other. For practical reasons the temperature range of a kinetic study is often only about 40°–50°, and it is sometimes even less. Moreover, the temperature range is often somewhere around room temperature and is frequently much higher. For example, if a study is carried out from 0°C to 50°C, the range is 273 K to 323 K, and the variation in absolute temperature is therefore only about 20%.

Figure 1 shows $\ln T$ and T plotted against $1/T$, for the temperature range from 0°C to 100°C. The plot of $\ln T$ against $1/T$ shows little curvature, and if the range were only 40° or so, as in many experiments, the curvature would be hardly detectable. If we expand $\ln T$ about the mid point of the range (323 K) and accept only the first term, the result is

$$\ln (T/\text{K}) = 4.78 + 3.10 \times 10^{-3}(T/\text{K}) \quad (18)$$

Over the 0–100°C range this equation represents the relationship with an error of less than 0.2%.

The plot of T against $1/T$ shows a little more curvature. In reality such a plot is a hyperbola (see inset in Fig. 1), but in the 0–100°C range one is at the far reaches of the hyperbola where there is little curvature. An expansion of $1/T$ about the mid point of the range leads to

$$\frac{1}{T/\text{K}} = 6.19 \times 10^{-3} - 9.59 \times 10^{-6}\,(T/\text{K}) \quad (19)$$

Over the 0–100°C range this equation is valid to within 3%.

It follows that if $\ln k$ is plotted against any one of the three functions $1/T$, $\ln T$, and T and a straight line is obtained, the plot will be almost linear if either of the other two functions is employed. This is illustrated in Figure 2 for the very reliable data of Harcourt and Esson (34) on the reaction between hydrogen peroxide and hydrogen iodide, the temperature range being 0°C to 50°C. The open circles are for a plot of ln
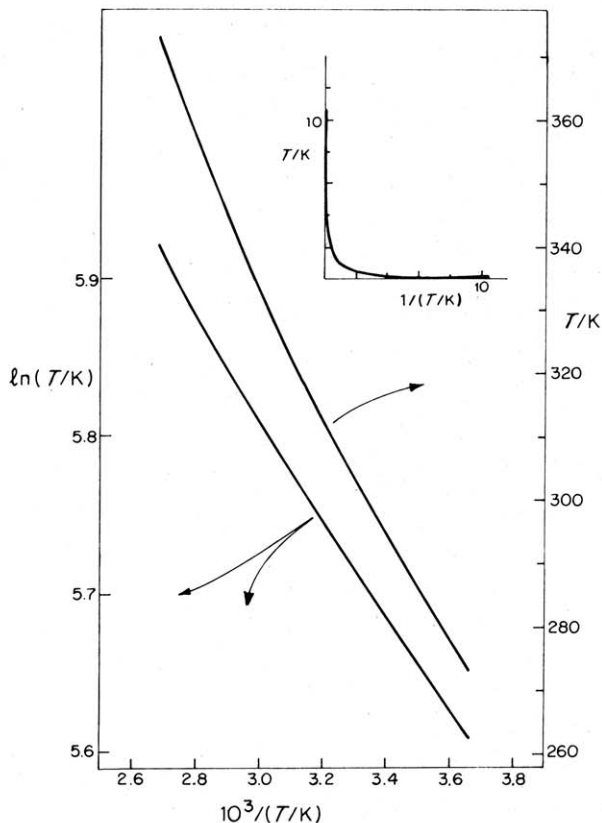
Figure 1. Plots of $\ln(T/K)$ and T/K against $1/(T/K)$, for the temperature range $0°–100°C$. The inset shows a plot of T/K against $1/(T/K)$ for the range 0 K to 10 K.

Table 2. Relationship between the Arrhenius Activation Energy $E(\equiv RT^2 d \ln k/dT)$ and the Temperature Parameters

Equation	Activation energy E
15	$R(B + CT + DT^2)$
13	$R(B + CT)$
9	$R(B + DT^2)$
16	$R(CT + DT^2)$
12	RB
14	RCT
6	$RDTv4^2$

k against $\ln T$, corresponding to the formula favored by Harcourt and Esson (eqn. (14)), while the filled circles are for an Arrhenius plot of $\ln k$ against $1/T$. It is certainly true, as Harcourt and Esson concluded, that the $\ln k$ against $\ln T$ plot is more linear than the other, so that their preference for eqn. (14) is justified *on purely empirical grounds.*

The slope of the plot of $\ln k$ against $\ln T$ leads to a value of 20.4 for Harcourt and Esson's parameter C; i.e., their temperature dependence is expressed by

$$k = A(T/K)^{20.4} \qquad (20)$$

The Arrhenius parameter B in eqn. (12) has an average value of 6.05×10^3 K, corresponding to an activation energy of 50.3 kJ mol^{-1}. Table 2 shows the relationships between the Arrhenius activation energy defined by eqn. (2), and the parameters in the various equations. In terms of the Harcourt and Esson parameter C, the activation energy is RCT and will therefore range from 46.3 kJ mol^{-1} at 0°C to 54.8 kJ mol^{-1} at 50°C. This, however, as shown by the plot in Figure 2, does not correspond to a very large curvature, and might easily have been overlooked if the data had been less precise.

Most kinetic data can be interpreted almost equally well by any of the three one-parameter equations. This being so, the introduction of an additional parameter into any of these equations will probably give a completely reliable fit; thus, the
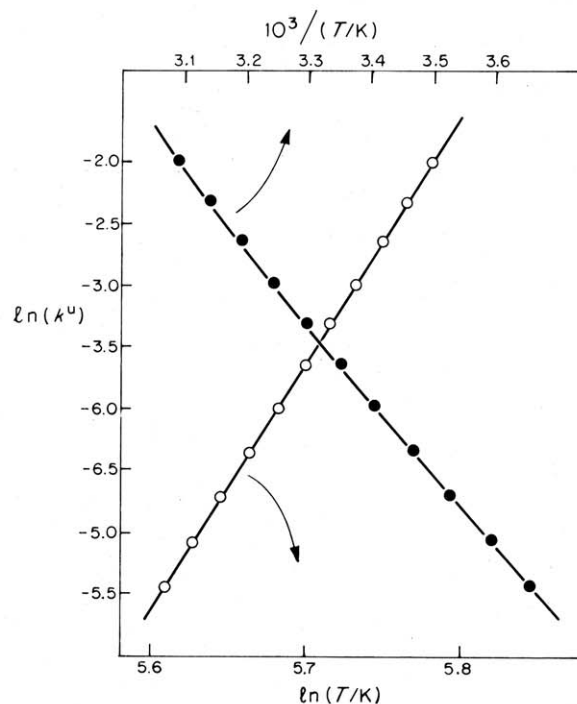

Figure 2. Plots for the data of Harcourt and Esson (*34*) for the reaction between hydrogen peroxide and hydrogen iodide. The units of the rate constant are not stated but are probably dm^3 mol^{-1} min^{-1}. The natural logarithm of the *value k^u* of the rate constant is plotted against $\ln(T/K)$ (open circles) and against $1/(T/K)$ (filled circles).

three two-parameter equations, eqns. (13), (9), and (16), will be equally reliable. The three-parameter eqn. (15) will hardly ever be significantly better than any of the two-parameter equations; indeed, as we have noted with reference to Bodenstein's analysis, the three-parameter equation may be disadvantageous in that there may be a variety of assignments of parameters that will lead to equally good agreement with experiment.

It is to be emphasized that finding out which equation gives the best fit to experimental data is not necessarily the most satisfactory way of making scientific progress. A significant point is that certain plots are inherently more likely to be linear than certain other plots. The more often one takes logarithms, the more linear do plots become. This is well illustrated by an equation of the form $xy = $ constant. A simple plot of y against x gives a hyperbola, whereas a plot of $\ln y$ against $\ln x$ gives a straight line; plots of $\ln y$ against x, or of y against $\ln x$, give lines of much less curvature than the hyperbola.

Harcourt and Esson's plots of $\ln k$ against $\ln T$ are inherently more likely to be linear than plots of $\ln k$ against T or $1/T$, because the variation in $\ln T$ over any range is considerably less than that of T or of $1/T$. Thus in the 0 to 50°C range, T and $1/T$ vary by 17%, whereas $\ln T$ only varies by 3%.

Harcourt and Esson's work is nevertheless of considerable interest and significance. Perhaps their most important contribution was to demonstrate the kinetic absolute zero. Although their equation was not the most fruitful one, it did represent the temperature dependence very well for certain reactions, including the one they studied in detail. The Arrhenius equations (eqns. (1) and (3)) give zero rate at the absolute zero because as $T \rightarrow 0$, $-E/RT \rightarrow -\infty$ and therefore $\exp(-E/RT)$ approaches zero. In the same way $\ln T \rightarrow -\infty$ as $T \rightarrow 0$; therefore according to the Harcourt-Esson formula, as $T \rightarrow \infty$, $\ln K \rightarrow -\infty$ and therefore k approaches zero. Thus, although their formula was not a fruitful one, in that it did not lead to a useful theoretical concept of a chemical reaction, it did lead to their important discovery of the kinetic absolute zero.

Further Progress

After it had been recognized, in the second decade of the present century, that eqns. (1) and (3) were the most satisfactory, progress in kinetics was much more rapid. During the last century chemists had been largely content with factual information about the products and speeds of a chemical reaction; the question of the mechanisms of reactions was hardly considered. Until the end of the nineteenth century physical chemistry was still in its infancy, having made its most important advances in the treatment of solutions of electrolytes. Ostwald and Arrhenius were the pioneers in this field, and Harcourt played a similar pioneering role in kinetics; in his lectures he was constantly emphasizing the importance of finding out how and why chemical change occurs (48, 49). It is unfortunate that, because he supported a sterile treatment of temperature dependence, he was himself unable to bring this laudable aim to a successful conclusion.

From the beginning of the second decade of this century one can discern three distinct lines of development in the theory of kinetics, all based on the Arrhenius equation and all coming together in 1935 with the formulation of transition-state theory (50, 51).

1) In 1911 Kohnstamm and Scheffer (52), in a paper that now seems years ahead of its time, attempted a thermodynamic formulation of reaction rates. This work was further developed by Brandsma and Scheffer (53–55).
2) In 1914 Marcelin (56, 57) treated a chemical reaction in terms of motion over what we would now call a "potential-energy surface." The dynamics of such motion was further treated by Eyring and Polanyi (58) and by Pelzer and Wigner (59).
3) In 1916 Trautz (60), and in 1918 Lewis (61) developed a treatment of the pre-exponential factor A in terms of the kinetic theory of gases. This treatment was supported and developed by many workers, particularly by Hinshelwood (62) and Moelwyn-Hughes (63).

A number of papers attempted to bridge the gap between these rather different approaches. La Mer (64), for example, combined the kinetic theories of collisions with the thermodynamic formulations, and represented the preexponential factor as the product of a collision frequency and a term $\exp(\Delta S^{\ddagger}/R)$, where $\Delta S^{\ddagger}$ is the entropy of activation.

It was in 1935 that the most general and comprehensive treatment of reaction rates was formulated, independently by Eyring (50) and by Evans and Polanyi (51). This theory, now generally called *transition-state theory*, has been extensively applied to a wide variety of physical and chemical processes (65, 66). Pacey (67) has recently discussed the relationships, which are sometimes not entirely straightforward between the Arrhenius activation energy and the height of an energy barrier.

Subsequent treatments of rates, such as those concerned with the dynamics of motion over a potential-energy surface, have been of great value, but they are much more complicated than transition-state theory and are less general in their application. The results of calculations on the basis of these treatments are to a good approximation consistent with transition-state theory and with the Arrhenius equation.

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