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The Interpretation of Apparent Activation Energies Derived by the Least-Squares Treatment of Kinetic Data

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The majority of reported values of activation energy and pre-exponential factor have been obtained by fitting experimental results to the logarithmic form of the Arrhenius equation, $\ln k = \ln A - E_a/RT$ where E_a and A are the apparent activation energy and pre-exponential factor and both are, to a first approximation, considered to be independent of temperature. The statistical technique of line-fitting by least-squares is frequently used to obtain E_a and $\ln A$.

Theoretical treatments of rate constant give equations in which the activation energy and pre-exponential factor may vary with temperature so that the graph of $\ln k$ vs. $1/T$ is actually a curve and not a straight line. The apparent and theoretical activation energies will, therefore, differ.

In this paper the differences between E_a derived by the least-squares method and the theoretical activation energy have been calculated for a wide range of experimental conditions and for two types of theoretical equation. In addition, conditions for detection of curvature in the graph of $\ln k$ vs. $1/T$ have been determined.

Because in practice the curvature is slight and not usually detected, the most interesting conclusion drawn from these calculations is that differences between apparent and theoretical values as great as 5 kcal/mole can exist while the experimental results still appear to fit the Arrhenius equation. Further, if apparent activation energies from two different reactions are compared, as a rough approximation, only differences greater than 3–4 kcal/mole are likely to be significant.

INTRODUCTION

The study of the rates of processes and their dependence upon temperature is one of the most common in the physical sciences and, in most cases, the results are treated by fitting them to an exponential equation. In the case of chemical reactions, the specific rate constant and the absolute temperature are fitted to the well-known Arrhenius equation (given in logarithmic form):

$$\ln k = \ln A - E_a/RT \qquad (1)$$

where E_a is the apparent activation energy and A the pre-exponential factor and both are, to a first approximation, taken to be independent of temperature.

The measurements of rate constants are subject to experimental error; the parameters E_a and $\ln A$ are, therefore, frequently estimated by fitting the experimental data to the Arrhenius equation by the statistical technique of least-squares and measuring the slope and intercept of the least-squares line.

Theoretical equations for the rate constant, in contrast to the Arrhenius equation, contain parameters which are dependent upon temperature. Two important examples of these equations are given below; the first is based upon the absolute rate theory (*1*),

$$\ln k = \ln(\mathrm{k}/h) + \ln T + \Delta S^*/R - \Delta H^*/RT \qquad (2)$$

where ΔH^* and ΔS^* are the enthalpy and entropy of activation, respectively, and both may vary with temperature; k is the Boltzmann constant and h is Plank's constant. The second equation is based upon the collision theory (*2*),

$$\ln k = \ln(PZ) - E_0/RT$$

where Z is the collision frequency, P the steric factor, and E_0 the activation energy. Both P and Z are temperature-dependent and the equation can be conveniently rewritten

$$\ln k = \ln A_0 + p \ln T - E_0/RT \qquad (3)$$

with E_0 and A_0 independent of temperature over the range of measurement; p is a constant, commonly equal to $n/2$ with n a small integer (*6*).

Other theoretical equations have been proposed but they may also be reduced to the form of Eqs. (2) or (3).

In this paper the validity of the theoretical equations will not be considered but only the consequences for the interpretation of the apparent activation energy and pre-exponential factor derived by the least-squares treatment. If either Eqs. (2) or (3) is correct, then the graph of $\ln k$ vs. $1/T$ is a curve and apparent values estimated from the Arrhenius equation will not be equal to the true values. Over the temperature ranges typically employed, say 100°K, the predicted curvature of the theoretical equations is small compared to the experimental error in measuring the rates. The curvature is not, therefore, detectable in a statistically significant way and so many results appear to fit the Arrhenius equation quite well.

Because apparent activation energies and pre-exponential factors are so frequently estimated from the Arrhenius equation and quoted without further interpretation, it is desirable to calculate the possible differences between the apparent values estimated by least-squares method and true values. Without a knowledge of these differences it is not possible to make reliable comparisons between different activation energies derived from different sets of data.

In this paper equations have been derived which enable the difference between apparent and true values to be calculated for any set of experimental conditions. These equations assume an exact knowledge of the temperature dependence of the parameters in Eqs. (2) or (3). In most cases, this knowledge is not available but it is still possible to make good approximations for the differences in those cases where the experimental results appear to fit the Arrhenius equation.

DERIVATION

Two important assumptions are made in this derivation, firstly, that the reaction rate is governed by a single activation energy; secondly, that errors in the measurement of temperature can be neglected compared with those in the reaction rate.

In the first part of the derivation Eq. (2) is assumed to be correct. The variation with temperature of the enthalpy and entropy of activation is treated conventionally, in the same way as the enthalpy and entropy of reaction. In the Absolute rate theory ΔC_p^* is defined as the specific heat difference between the activated complex and the reactants. The temperature dependence of ΔC_p^* is not generally known but, by analogy with measurable specific heats, is assumed to be approximated by the following expression:

$$\Delta C_p^* = \alpha + \beta T + \gamma T^2 \qquad (4)$$

where α, β, and γ are constants. By insertion of ΔC_p^* into the following equations the variation of ΔH^* and ΔS^* with temperature is found:

$$\Delta H_i^* = \Delta H_1^\circ + \int_{T_1}^{T_i} \Delta C_p^* \, dT$$

$$\Delta S_i^* = \Delta S_1^\circ + \int_{T_1}^{T_i} (\Delta C_p^*/T) \, dT \qquad (5)$$

ΔH_i^* and ΔS_i^* are the values at T_i: ΔH_1° and ΔS_1° are the values at the lowest temperature of measurement T_1, reactants and products in their appropriate standard states.

The apparent activation energy and pre-exponential factor are derived from measurements made over a finite temperature range. For this reason, the apparent values are best compared to the mean enthalpy and entropy of activation for the same temperature range and not the values at one temperature. The mean values for the range, highest temperature T_2 to lowest temperature T_1, are defined by

$$\overline{\Delta H}_{12}^\circ = \int_{T_1}^{T_2} \Delta H_i^* \, dT \bigg/ \int_{T_1}^{T_2} dT;$$

$$\overline{\Delta S}_{12}^\circ = \int_{T_1}^{T_2} \Delta S_i^* \, dT \bigg/ \int_{T_1}^{T_2} dT$$

Substitution from (4) and (5) then integration gives

$$\overline{\Delta H}_{12}{}^\circ = \Delta H_1{}^\circ + \left(\frac{\alpha}{2}\right)(T_2 - T_1) + \left(\frac{\beta}{6}\right) \times (T_2{}^2 + T_1T_2 - 2T_1{}^2) + \left(\frac{\gamma}{12}\right) \times (T_2{}^3 + T_2{}^2T_1 + T_2T_1{}^2 - 3T_1{}^3) \quad (6a)$$

$$\overline{\Delta S}_{12}{}^\circ = \Delta S_1{}^\circ + \frac{\alpha[T_2(\ln T_2 - 1) - T_1(\ln T_1 - 1)]}{(T_2 - T_1)} + \left(\frac{\beta}{2}\right)(T_2 - T_1) + \left(\frac{\gamma}{6}\right) \times (T_2{}^2 + T_2T_1 - 2T_1{}^2) \quad (6b)$$

In the following derivation these symbols are used: $Y_{ij} = \ln k_{ij}$, where k_{ij} is the jth replicate determination of the rate constant at T_i; $x_i = 1/T_i$; $M = E_a/R$; $m = \overline{\Delta H}_{12}{}^\circ/R$; r_i is the number of replicate determinations at T_i, i.e., $j = 1, 2, 3, \ldots r_i$;

$$Y_{ij} = \left(\ln \frac{\mathrm{k}}{h} + \frac{\overline{\Delta S}_{12}{}^\circ}{R}\right) - f - (m - d)x_i - a \ln x_i + \frac{b}{x_i} + \frac{c}{x_i{}^2} + e_{ij} \quad (7)$$

where $a = (1 + \alpha/R)$; $b = \beta/2R$; $c = \gamma/6R$;

$$d = \left(\frac{\alpha}{2R}\right)(T_2 + T_1) + \left(\frac{\beta}{6R}\right) \times (T_2{}^2 + T_2T_1 + T_1{}^2) + \left(\frac{\gamma}{12R}\right) \times (T_2{}^3 + T_2{}^2T_1 + T_2T_1{}^2 + T_1{}^3)$$

$$f = \frac{\alpha(T_2 \ln T_2 - T_1 \ln T_1)}{R(T_2 - T_1)} + \left(\frac{\beta}{2R}\right)(T_2 + T_1) + \left(\frac{\gamma}{6R}\right)(T_2{}^2 + T_2T_1 + T_1{}^2)$$

and e_{ij} is the experimental error in the measurement of $\ln k_{ij}$.

Now the least-squares line is chosen so that the sum of the squares of the deviations (SSD) of the experimental points from that line is a minimum. In most applications of the least-squares technique to fit linear equations the assumption is made that the SSD minimized are due solely to experimental error. This assumption is not true in the case under discussion because the SSD minimized are composed of random experimental error and systematic deviation due to the curvature of the theoretical equation. Implicit in the derivation that follows is that the two types of deviation are not correlated, i.e., the experimental error is independent of the curvature. The importance of this assumption is that it allows the difference between the apparent and true values to be expressed as the sum of two independent terms. The first term depends solely upon the systematic deviation due to curvature and the second term depends solely upon the random experimental error.

Let the equation of the line fitted to the experimental points by the least-squares method be

$$y_i = \ln A - Mx_i$$

where

$$M = \frac{\Sigma x_i(Y_{ij} - \bar{Y})}{sxx} \quad \text{and} \quad \ln A = \bar{Y} + M\bar{x}$$

with

$$sxx = \Sigma r_i(x_i - \bar{x})^2; \qquad \bar{Y} = \Sigma Y_{ij}/\Sigma r_i$$
$$\bar{x} = \Sigma r_i x_i/\Sigma r_i; \qquad \bar{e}_i = \Sigma(e_{ij}/r_i)$$

Substituting for Y_{ij} into the expressions for M and $\ln A$ gives

$$M = m - d + \frac{a[\Sigma r_i \ln x_i(x_i - \bar{x})] - b[\Sigma(r_i/x_i)(x_i - \bar{x})] - c[\Sigma(r_i/x_1{}^2)(x_i - \bar{x})]}{sxx} + \frac{\Sigma r_i\bar{e}_i(x_i - \bar{x})}{sxx}$$

$$\ln A = (\ln \mathrm{k}/h + \overline{\Delta S}_{12}{}^\circ/R) - f - (m - d - M)\bar{x} - a\frac{\Sigma x_i \ln x_i}{\Sigma r_i} + b\Sigma\frac{(r_i/x_i)}{\Sigma r_i} + \frac{c\Sigma(r_i/x_i{}^2)}{\Sigma r_i} + \frac{\Sigma r_i\bar{e}_i}{\Sigma r_i}$$

The random error terms e_{ij} are treated by assuming that they are normally distributed about a mean of zero with a variance of $\sigma^2_{\ln k}$. This experimental error variance is taken to be constant over the whole temperature range. With this assumption confidence limits can be set for the error terms; using standard statistical treatment (*3*) these confidence limits are substituted in the equations above and lead to the final equations for the difference between apparent and true values.

$$\Delta E = E_{\mathrm{a}} - \overline{\Delta H}_{12}{}^{\circ} = \Delta E_{\mathrm{C}} \pm \Delta E_{\mathrm{E}}$$

$$\Delta E_{\mathrm{C}} = \frac{R}{sxx}\Bigg[a\Sigma r_i \ln x_i(x_i - \bar{x}) - b\Sigma\left(\frac{r_i}{x_i}\right)(x_i - \bar{x}) - c\Sigma\left(\frac{r_i}{x_1{}^2}\right)(x_i - \bar{x}) - dsxx\Bigg] \quad (8a)$$

$$\Delta E_{\mathrm{E}} = \frac{Rt\sigma_{\ln k}}{(sxx)^{1/2}} \quad (8b)$$

$$\Delta \ln A = \ln A - \left(\frac{\ln \mathrm{k}}{h} + \frac{\overline{\Delta S}_{12}{}^{\circ}}{R}\right) = \Delta \ln A_{\mathrm{C}} \pm \Delta \ln A_{\mathrm{E}}$$

$$\Delta \ln A_{\mathrm{C}} = \frac{(\Delta E_{\mathrm{C}}}{R} + d)\bar{x} - f - \frac{[a\Sigma r_i \ln x_i - b\Sigma(r_i/x_i) - c\Sigma(r_i/x_i{}^2)]}{\Sigma r_i} \quad (9a)$$

$$\Delta \ln A_{\mathrm{E}} = t\sigma_{\ln k}\left[\frac{\Sigma r_i x_i{}^2}{sxx\Sigma r_i}\right]^{1/2} \quad (9b)$$

The value of t in these equations depends upon the confidence limits chosen; for the frequently chosen 95% confidence limits $t = 1.96$; other limits can be obtained from published tables (*3*, p. 100).

As explained above the differences ΔE and $\Delta \ln A$ are composed of two terms, ΔE_{C} and $\Delta \ln A_{\mathrm{C}}$ due solely to curvature and ΔE_{E} and $\Delta \ln A_{\mathrm{E}}$ due solely to random experimental error. The random terms do not depend upon the nature of the theoretical rate equation so that the values of ΔE_{E} and $\Delta \ln A_{\mathrm{E}}$ given by Eqs. (8b) and (9b) can also be used in calculations when Eq. (3) is the correct theoretical equation.

The values of ΔE and $\Delta \ln A$ will depend upon the number of measurements and will approach some limiting value as the number of measurements increases. The best possible straight-line approximation to the true curve would arise from an infinite number of measurements made by increasing the temperature in infinitesimal increments from the lowest to the highest temperature. The best straight-line approximation values will be the minimum possible. By comparing the values from a finite number of measurements with these minimum values the efficiency of a given number of measurements in approximating the curve may be assessed.

To obtain the best straight-line approximation, summations in Eqs. (8a) and (9a) are replaced with integrals, with integration limits T_1 and T_2, the lowest and highest temperatures of the range. Because there are an infinite number of measurements the expressions for ΔE_{min} and $\Delta \ln A_{\mathrm{min}}$ do not contain error terms. The equations for ΔE_{min} and $\Delta \ln A_{\mathrm{min}}$ are as follows:

$$\Delta E_{\mathrm{min}} = \frac{R}{(x_2 - x_1)^3} \times \Bigg\{3a\left[x_1{}^2 - x_2{}^2 + 2x_1x_2 \ln\left(\frac{x_2}{x_1}\right)\right] + 6b\left[2(x_2 - x_1) - \ln\left(\frac{x_2}{x_1}\right)\right] + 6c\left[\left(\frac{x_1{}^2 - x_2{}^2}{x_2x_1}\right) + 2\ln\left(\frac{x_2}{x_1}\right)\right] - d(x_2 - x_1)^3\Bigg\} \quad (10)$$

$$\Delta \ln A_{\mathrm{min}} = \left(\frac{\Delta E_{\mathrm{min}}}{R} + d\right)\frac{(x_2 + x_1)}{2} + a[x_1(\ln x_1 - 1) - x_2(\ln x_2 - 1)] + \frac{b\ln(x_2/x_1)}{(x_2 - x_1)} - \frac{c}{x_2x_1} - f \quad (11)$$

The calculations presented so far assume an exact knowledge of the temperature dependence in Eqs. (2) and (3) and, in most cases, this knowledge is not available. Even without this knowledge, however, useful limits for the difference between apparent and true values can still be calculated for cases where the results appear to fit the Arrhenius equation. The approach adopted is to calculate the maximum curvature that can be present without detection at a given experimental accuracy. The differences between apparent and true values corresponding to the maximum curvature, therefore, are the maximum differences that can exist while the experimental results still appear to fit the Arrhenius equation. In the introduction it was emphasized that in the majority of reported results the Arrhenius equation appears to be obeyed quite well so that the calculations to be presented should have widespread application.

In order to decide whether curvature can be detected under a given set of circumstances the total sum of the squares of the deviations is required; if the deviation at T_i is d_{ij} then the SSD is given by,

$$S_T^2 = \Sigma d_{ij}^2 = \Sigma(Y_{ij} - y_i)^2 \tag{12}$$

Let the number of temperatures at which measurements are made be s,

$$i = 1, 2, 3 \ldots s$$

To avoid a very cumbersome expression only the case of an equal number, r, of replicate measurements at each temperature will be considered. The grand total of measurements is thus $N = rs$. The following functions are defined:

$$F_0 = -a \sum \ln x_i(x_i - \bar{x}) + b \sum \left(\frac{1}{x_i}\right)(x_i - \bar{x}) + c \sum \left(\frac{1}{x_i^2}\right)(x_i - \bar{x})$$

$$F(x_i) = -a\left[\frac{(\Sigma \ln x_i)}{s} - \ln x_i\right] + b\left[\frac{(\Sigma 1/x_i)}{s} - \frac{1}{x_i}\right] + c\left[\frac{(\Sigma 1/x_i^2)}{s} - \frac{1}{x_i^2}\right]$$

Substituting into Eq. (12) for Y_{ij} leads to

$$S_T^2 = \sum \left\{ r \frac{[F_0 + r\bar{e}_i(x_i - \bar{x})]}{\Sigma r(x_i - \bar{x})^2}(x_i - \bar{x}) + rF(x_i) + r(\bar{e}_i - \bar{e}) \right\}^2 \tag{13}$$

After expansion Eq. (13) is found to contain two types of terms: those which are due solely to curvature and those due solely to random error. After treating the random terms by standard statistical means (*3*, p. 100) the following expression is derived for the expected value of S_T^2:

$$S_T^2 = r\left\{\sum [F(x_i)]^2 - \frac{F_0^2}{\Sigma(x_i - \bar{x})^2}\right\} + (s - 2)\sigma^2_{\ln k}$$

$$M_T^2 = \frac{r}{(s-2)}\left\{\sum [F(x_i)]^2 - \frac{F_0^2}{\Sigma(x_i - \bar{x})^2}\right\} + \sigma^2_{\ln k} = M_C^2 + M_E^2 \tag{14}$$

where M_C^2 is the mean sum of squares attributable to curvature and M_E^2 is the mean sum of squares attributable to experimental error. The expected value of M_E^2 is $\sigma^2_{\ln k}$ but actual values will fall within limits on either side of this expected value.

When the curvature is detectable M_T^2 is significantly greater than M_E^2. The appropriate significance test which determines that M_T^2 is greater than M_E^2 is the variance ratio F test (*4*) given, in this instance by $F = M_T^2/\sigma^2_{\ln k}$. F must exceed a critical value governed by the degrees of freedom of M_T^2 which are s-2 and the chosen level of significance, commonly 0.05, in order that curvature should be detectable. Values of F can be found in extensive compilations (*5*).

In a given situation the experimental error variance $D^2_{\ln k}$, which is sufficiently small to just detect curvature, can be readily calculated

$$D^2_{\ln k} = M_C^2/(F - 1) \tag{15}$$

From Eqs. (14) and (15), $D^2_{\ln k}$ may be calculated for different values of α, β, and γ. The set of values which make $D^2_{\ln k}$ equal to the actual experimental error variance can then be substituted in Eqs. (8a) and (9a) to calculate ΔE_C and $\Delta \ln A_C$, which are then the maximum differences possible while curvature is only just detectable. This procedure is to some extent arbitary because different combinations of α, β, and γ could be found which would give the same value of $D^2_{\ln k}$, but different values of ΔE_C and $\Delta \ln A_C$. It will be shown in the discussion that this problem is not serious in practice.

Having calculated the maximum values of ΔE_C and $\Delta \ln A_C$, the maximum values of ΔE and $\Delta \ln A$ are simply obtained by adding ΔE_E and $\Delta \ln A_E$ to these terms.

The equations for differences and curvature derived for the case when Eq. (2) is assumed to be correct, can easily be modified to cover the case when Eq. (3) is assumed correct. There are no complications about mean theoretical values because the activation energy E_0 and the pre-exponential factor A_0 are not dependent upon temperature. The same initial equation (7) can be used with the following substitutions: $a = p$; $b, c, d, f = 0$; $(\ln k/h + \overline{\Delta S_{12}}°/R) = \ln A_0$; $m = E_0/R$. After making these substitutions the following expressions are derived for ΔE_C and $\Delta \ln A_C$:

$$\Delta E_C = pR \frac{[\Sigma r_i \ln x_i(x_i - \bar{x})]}{sxx} \qquad (16a)$$

$$\Delta \ln A_C = \frac{px[\Sigma r_i \ln x_i(x_i - \bar{x})]}{sxx} - \frac{p\Sigma r_i \ln x_i}{\Sigma r_i} \qquad (16b)$$

The values of ΔE_E and $\Delta \ln A_E$ are those given by Eqs. (8b) and (9b), and as before the total differences are given by

$$\Delta E = E_a - E_0 = \Delta E_C \pm \Delta E_E;$$
$$\Delta \ln A = \ln A - \ln A_0 = \Delta \ln A_C \pm \Delta \ln A_E$$

The best possible straight-line approximation values are

$$\Delta E_{\min} = 3pR \frac{[x_1^2 - x_2^2 + 2x_2x_1 \ln(x_2/x_1)]}{(x_2 - x_1)^3}$$

$$\Delta \ln A_{\min} = \frac{\Delta E_{\min}}{R} \frac{(x_2 + x_1)}{2} + \frac{p[x_1(\ln x_1 - 1) - x_2(\ln x - 1)]}{(x_2 - x_1)}$$

The expression for the mean sum of squares due to curvature is given in full as it is much simpler than in the case when Eq. (2) is assumed correct

$$M_C{}^2 = \frac{rp^2}{(s - 2)} \left\{ \sum \left[\frac{(\Sigma \ln x_i)}{s} - \ln x_i \right]^2 - \left[\frac{\Sigma \ln x_i(x_i - \bar{x})}{\Sigma (x_i - \bar{x})^2} \right]^2 \right\} \qquad (17)$$

The maximum values of ΔE and $\Delta \ln A$ that can exist without curvature being detected are found by using Eq. (15) to find the value of p which makes $D^2_{\ln k}$ equal to the actual experimental error variance. This value of p is then substituted into Eqs. (16a) and (16b) to calculate the maximum values of ΔE_C and $\Delta \ln A_C$. There is no ambiguity in this case because only one constant p is involved.

RESULTS

To illustrate the magnitude of the differences that might occur under some specific experimental conditions, Tables 1–3 have been prepared. Temperatures from 323 to 1023°K have been covered in the ranges of 100°; to show the effect of using a very wide temperature range one set of calculations has been made for the range 323–823°K. The number of measurements considered in each range are 4, 6, 11, and ∞, the best possible straight-line approximation values. In the ranges of 100° the measurements are spaced as in the following example: $N = 4$, 323°, 363°, 403°, 423°; $N = 6$, 323°, 343°, 363°, 383°, 403°, 423°0; N = 11, 323°, 333°, 343°, 353°, 363°, 373°, 383°, 393°, 403°, 413°, 423°; $N = \infty$, integration limits 323° and 423°; for the range 323°–823°: $N = 6$, 323°, 423°, 523°, 623°, 723°, 823°.

To conform to common usage, in all the calculations logarithms to base 10 have been used rather than natural logarithms (ln). In all the Tables, $r_i = 1$ for all values of i. In Table 1 the calculated values of ΔE_C and $\Delta \log A_C$ are shown for several sets of values of α, β, and γ. In addition, the confidence limits (95% conf. limits) of an individual measurement of rate constant required in order that curvature may just be detected are shown. The smaller the degree of curvature, the narrower these limits become. These limits are calculated by taking $D_{\log k}$ from Eq. (15) and substituting in the following expression:

$$\text{C.L.} = \pm 1.96 D_{\log k} \times 100\%$$

In Table 2 ΔE_C, $\Delta \log A_C$, and C.L. are shown for different values of p in the case when Eq. (3) is assumed to be correct. If values at some other value of p are required, e.g., p_1, then the values given for $p = 1$ should be multiplied by p_1.

In Table 3 ΔE_E and $\Delta \log A_E$ are shown calculated for three different values of standard deviation $\sigma_{\log k}$. The confidence limits (95%) on an individual rate measurement corresponding to these three values are

TABLE 1

ΔE_C (kcal/mole), $\Delta \log A_C$ and the 95% Confidence Limits (C.L.) on an Individual Measurement of Rate Constant Required to Detect Curvature with Different Values of α, β, γ in Eq. (2)

Temp. range (K°)	No. of measurements	$\alpha = 10, \beta = 10^{-3}, \gamma = 10^{-6}$			$\alpha = 10, \beta = 10^{-4}, \gamma = 10^{-7}$			$\alpha = 10, \beta = 0.0, \gamma = 0.0$			$\alpha = 5, \beta = 10^{-4}, \gamma = 10^{-7}$			$\alpha = 5, \beta = 0.0, \gamma = 0.0$		
		ΔE_C	$\Delta \log A$	C.L. (± %)	ΔE_C	$\Delta \log A_C$	C.L. (± %)	ΔE_C	$\Delta \log A_C$	C.L. (± %)	ΔE_C	$\Delta \log A_C$	C.L. (± %)	ΔE_C	$\Delta \log A_C$	C.L. (± %)
323–423°	4	0.674	2.989	15.5	0.677	2.989	5.1	0.677	2.989	2.0	0.703	2.996	3.8	0.704	2.996	1.2
	6	0.681	2.989	14.3	0.684	2.990	4.8	0.684	2.990	2.0	0.708	2.996	3.5	0.708	2.996	1.2
	11	0.688	2.991	15.1	0.690	2.992	5.0	0.690	2.992	2.1	0.711	2.997	3.7	0.711	2.997	1.2
	∞	0.674	2.971	—	0.676	2.981	—	0.676	2.982	—	0.703	2.991	—	0.704	2.992	—
523–623°	4	1.092	3.184	14.7	1.095	3.185	4.1	1.095	3.185	0.9	1.113	3.188	3.2	1.123	3.187	0.5
	6	1.098	3.185	14.0	1.101	3.186	3.8	1.101	3.186	0.8	1.117	3.188	2.9	1.117	3.188	0.5
	11	1.102	3.186	15.0	1.105	3.186	4.1	1.105	3.186	1.2	1.119	3.187	3.1	1.119	3.187	0.7
	∞	1.093	3.158	—	1.097	3.180	—	1.097	3.183	—	1.114	3.184	—	1.114	3.186	—
723–823°	4	1.499	3.317	16.5	1.502	3.318	3.8	1.503	3.318	0.5	1.516	3.320	3.0	1.517	3.320	0.3
	6	1.505	3.318	16.1	1.508	3.319	3.6	1.508	3.319	0.8	1.519	3.320	2.8	1.520	3.320	0.5
	11	1.508	3.319	17.6	1.510	3.319	3.8	1.511	3.319	1.0	1.521	3.320	3.0	1.521	3.320	0.6
	∞	1.502	3.273	—	1.506	3.313	—	1.506	3.317	—	1.518	3.315	—	1.519	3.319	—
923–1023°	4	1.901	3.419	19.9	1.905	3.419	3.8	1.906	3.419	0.5	1.917	3.420	3.1	1.917	3.420	0.3
	6	1.907	3.419	19.9	1.911	3.420	3.6	1.911	3.420	0.8	1.920	3.421	2.9	1.920	3.421	0.4
	11	1.908	3.419	22.0	1.911	3.420	3.9	1.912	3.420	1.0	1.920	3.421	3.2	1.921	3.421	0.4
	∞	1.905	3.350	—	1.909	3.412	—	1.910	3.419	—	1.919	3.413	—	1.920	3.420	—
323–823°	6	0.092	2.992	63.4	0.159	3.004	29.5	0.166	3.006	22.9	0.564	3.076	19.5	0.572	3.077	13.4
	∞	0.020	2.890	—	0.062	2.910	—	0.467	3.001	—	0.511	3.022	—	0.727	3.073	—

TABLE 1 (*Continued*)

Temp. range (K°)	No. of measurements	$\alpha = 2.5, \beta = 10^{-4}, \gamma = 10^{-7}$			$\alpha = 1, \beta = 10^{-4}, \gamma = 10^{-7}$			$\alpha = 1, \beta = 10^{-5}, \gamma = 10^{-8}$			$\alpha = 1, \beta = 0.0, \gamma = 0.0$		
		ΔEc	$\Delta \log Ac$	C.L. (± %)	ΔEc	$\Delta \log Ac$	C.L. (± %)	ΔEc	$\Delta \log Ac$	C.L. (± %)	ΔEc	$\Delta \log Ac$	C.L. (± %)
323–423°	4	0.717	2.999	3.0	0.725	3.001	2.4	0.725	3.001	0.9	0.725	3.001	0.5
	6	0.720	2.999	2.8	0.727	3.001	2.2	0.727	3.001	0.8	0.727	3.001	0.5
	11	0.722	3.000	2.9	0.728	3.001	2.3	0.728	3.002	0.9	0.729	3.002	0.5
	∞	0.717	2.995	—	0.725	2.998	—	0.725	2.999	—	0.725	2.999	—
523–623°	4	1.122	3.189	2.6	1.128	3.190	2.1	1.128	3.190	0.7	1.128	3.190	0.2
	6	1.124	3.190	2.4	1.129	3.190	2.0	1.129	3.190	0.6	1.129	3.190	0.2
	11	1.126	3.190	2.5	1.130	3.190	2.1	1.130	3.191	0.7	1.130	3.191	0.3
	∞	1.123	3.186	—	1.128	3.188	—	1.128	3.189	—	1.128	3.190	—
723–823°	4	1.523	3.321	2.5	1.527	3.321	2.2	1.528	3.321	0.6	1.528	3.321	0.1
	6	1.525	3.321	2.4	1.529	3.321	2.1	1.529	3.321	0.6	1.529	3.321	0.2
	11	1.526	3.321	2.5	1.529	3.321	2.2	1.530	3.321	0.6	1.530	3.321	0.2
	∞	1.524	3.320	—	1.528	3.317	—	1.529	3.321	—	1.529	3.321	—
923–1023°	4	1.922	3.421	2.7	1.926	3.421	2.4	1.927	3.421	0.6	1.927	3.421	0.1
	6	1.925	3.421	2.6	1.928	3.422	2.3	1.928	3.422	0.6	1.928	3.422	0.2
	11	1.925	3.421	2.8	1.928	3.421	2.5	1.928	3.422	0.6	1.928	3.422	0.2
	∞	1.924	3.414	—	1.927	3.415	—	1.928	3.421	—	1.928	3.421	—
323–823°	6	0.767	3.112	14.2	0.889	3.133	10.9	0.896	3.135	6.4	0.896	3.135	5.7
	∞	0.727	3.074	—	0.861	3.107	—	0.870	3.111	—	0.870	3.111	—

TABLE 2

ΔE_C (KCAL/MOLE), $\Delta \log A_C$, AND THE 95% CONFIDENCE LIMITS (C.L.) ON AN INDIVIDUAL MEASUREMENT OF RATE CONSTANT REQUIRED TO DETECT CURVATURE WITH DIFFERENT VALUES OF p IN EQ. (3)

Temp. range (K°)	No. of measurements	$p = 1.0$			$p = 2.0$			$p = 3.0$		
		ΔE_C	$\Delta \log A_C$	C.L. (± %)	ΔE_C	$\Delta \log A_C$	C.L. (± %)	ΔE_C	$\Delta \log A_C$	C.L. (± %)
323–423°	4	0.731	3.002	0.47	1.461	6.004	0.94	2.193	9.005	1.41
	6	0.732	3.002	0.66	1.463	6.004	1.32	2.196	9.006	1.98
	11	0.733	3.003	1.05	1.466	6.005	2.10	2.199	9.009	3.15
	∞	0.731	3.001	—	1.462	6.002	—	2.193	9.003	—
523–623°	4	1.132	3.191	0.22	2.263	6.381	0.44	3.396	9.573	0.66
	6	1.133	3.191	0.28	2.265	6.382	0.56	3.399	9.573	0.84
	11	1.133	3.191	0.61	2.266	6.382	1.21	3.399	9.573	1.83
	∞	1.132	3.190	—	2.264	6.380	—	3.396	9.570	—
723–823°	4	1.531	3.322	0.12	3.061	6.643	0.24	4.593	9.966	0.36
	6	1.532	3.322	0.28	3.063	6.643	0.56	4.596	9.966	0.84
	11	1.532	3.322	0.50	3.064	6.643	0.99	4.596	9.966	1.50
	∞	1.531	3.321	—	3.062	6.642	—	4.593	9.963	—
923–1023°	4	1.929	3.422	0.12	3.858	6.843	0.24	5.787	10.266	0.36
	6	1.930	3.422	0.28	3.860	6.844	0.56	5.790	10.266	0.84
	11	1.930	3.422	0.50	3.860	6.843	0.99	5.790	10.266	1.50
	∞	1.930	3.422	—	3.860	6.844	—	5.790	10.266	—
323–823°	6	0.977	3.149	7.6	1.955	6.299	15.20	2.931	9.467	22.8
	∞	0.960	3.133	—	1.920	6.266	—	2.880	9.399	—

±10%, ±5%, and ±1%, representing low, medium, and high experimental accuracy.

To illustrate the use of these tables, suppose that ΔE and $\Delta \log A$ were required for the situation where six measurements had been made over a temperature range of 523–623°K. The experimental error standard deviation was 0.050 and the theoretical constants were known to be $\alpha = 1.0$,

TABLE 3

ΔE_E (KCAL/MOLE), $\Delta \log A_E$ FOR DIFFERENT VALUES OF STANDARD DEVIATION, $\sigma_{\log k}$ AND USING 95% CONFIDENCE LIMITS

Temp. range (K°)	No. of measurements	$\sigma_{\log k} = 0.005$		$\sigma_{\log k} = 0.025$		$\sigma_{\log k} = 0.050$	
		ΔE_E	$\Delta \log A_E$	ΔE_E	$\Delta \log A_E$	ΔE_E	$\Delta \log A_E$
323–423°	4	0.080	0.024	0.398	0.117	0.796	0.234
	6	0.073	0.018	0.366	0.089	0.733	0.177
	11	0.059	0.061	0.293	0.052	0.586	0.104
523–623°	4	0.190	0.036	0.950	0.181	1.900	0.362
	6	0.175	0.027	0.873	0.145	1.747	0.272
	11	0.140	0.016	0.697	0.080	1.395	0.160
723–823°	4	0.347	0.049	1.735	0.245	3.471	0.489
	6	0.319	0.037	1.595	0.184	3.190	0.370
	11	0.255	0.022	1.273	0.108	2.546	0.217
923–1023°	4	0.551	0.062	2.754	0.256	5.509	0.617
	6	0.506	0.047	2.531	0.231	5.062	0.505
	11	0.404	0.027	2.020	0.126	4.039	0.273

$\beta = 10^{-4}$, and $\gamma = 10^{-7}$. Then, from Tables 1 and 3

$$\Delta E = 1.13 \pm 1.74 \text{ kcal/mole}; \quad \Delta \log A = 3.19 \pm 0.67$$

The limits of the difference between the apparent and true activation energy are 3.87 and −0.61 kcal/mole and between the apparent and true pre-exponential factor 3.86 and 2.52.

DISCUSSION

Before discussing the results presented in this paper, brief mention will be made of other methods of relating apparent and theoretical activation energies. It has been realized for some time that the two values will differ and several expressions have been derived previously to relate the two values (*2*, p. 278). These earlier expressions are all based upon the following equation for the apparent activation energy:

$$RT^2(\partial \ln k/\partial T) = E_a^* \qquad (18)$$

The apparent activation energy given by Eq. (18) does not, however, correspond exactly to the apparent activation energy commonly derived by fitting experimental results to the Arrhenius equation. The operation corresponding to Eq. (18) is to draw a tangent to the graph of $\ln k$ vs. $1/T$ at temperature T, and then substitute the measured slope into Eq. (18). The practical application of Eq. (18) is also limited by the fact that it does not explicitly take into account experimental error. The approach adopted in this paper, therefore, represents an advance over the previous method because only quantities determined by experimental techniques and their associated errors are treated.

The next part of the discussion refers only to those calculations for a temperature range of 100°; the wider range of 500° will be discussed later. The calculated values in Tables 1 and 2 show that ΔE_C and $\Delta \log A_C$ are almost independent of the number of experimental measurements; the values derived from four measurements are almost equal to the values from the best straight-line approximation. The total difference between apparent and true values does not, therefore, approach zero as the number of measurements increases, but the best straight-line approximation value. The error terms ΔE_E and $\Delta \log A_E$ do approach zero as the number of measurements increases but these terms are only part of the total difference. There is thus little to be gained by increasing the number of measurements made, once the error terms have been reduced to a small fraction of the curvature terms, e.g., beyond $\Delta E_E = 0.1\ \Delta E_C$.

The results in Table 1 show that ΔE_C and $\Delta \log A_C$ are almost independent of α, β, and γ. Values of α, β, and γ greater than those shown in Table 1 have not been considered because greater values would introduce severe curvature beyond that commonly observed. A very simple approximation for ΔE_C can be derived from Eq. (8a) provided that $T_2 - T_1$ does not exceed 100°

$$\Delta E_C \simeq R(T_2 + T_1)/2 = RT_{av}$$

This approximation is within 9% of the exact value in the lowest temperature range and within 1% in the highest range and is completely independent of α, β, and γ.

The very weak dependence of ΔE_C and $\Delta \log A_C$ upon α, β, and γ leads to considerable simplification in treating the problem of the maximum differences which can occur without curvature being detected. Curvature does depend upon the values of α, β, and γ; in Table 1 at one extreme curvature is so marked that it would be detected at the low experimental accuracy of ±15%; at the other extreme the curvature is so slight that the very high accuracy of ±0.1% would be needed. Over this entire range of curvature, however, ΔE_C and $\Delta \log A_C$ are almost constant and so are also, to a good approximation, the maximum values that can exist while the results still appear to obey the Arrhenius equation. The complications mentioned in the derivation concerning combinations of α, β, and γ are thus not relevant unless exact values are required. In most cases, calculations by substitution in Eqs. (10) and (11) with an arbitrary set of values of α, β, and γ or to a lesser approximation for ΔE_C by RT_{av} will give satisfactory estimates.

ΔE_E and $\Delta \log A_E$ are completely independent of α, β, and γ so that the total difference expected, e.g., $\Delta E_C \pm \Delta E_E$, is to a good approximation independent of these same constants. To indicate the likely magnitude expected in practice, consider six measurements each made with an experimental accuracy of $\pm 5\%$; then the limits for ΔE and $\Delta \log A$ will be

323–423°K: ΔE lies between 1.07 and 0.33 kcal/mole, $\Delta \log A$ lies between 3.22 and 2.78;

923–1023°K: ΔE lies between 4.45 and -0.61 kcal/mole, $\Delta \log A$ lies between 4.00 and 2.80.

Looking at the case when Eq. (3) is assumed correct, from Table 2 it is clear that ΔE_C, $\Delta \log A_C$ and the curvature all depend upon the constant p. The pre-exponential factor can be shown theoretically to contain translational, vibrational, and rotational partition functions and the temperature variation of these terms governs the value of p. For gas-phase reactions it seems that p is unlikely to exceed 3 (*6*). Even at this upper limit for p the results in Table 2 show that curvature would not usually be detected. It is possible to have larger values for ΔE and $\Delta \log A$ in this case without apparent deviation from the Arrhenius equation than when Eq. (2) holds.

The values of ΔE_C and $\Delta \log A_C$ can be calculated to a good approximation by the best possible straight-line equation or to a lesser approximation for ΔE_C by pRT_{av}. To compare with the values calculated for Eq. (2) in the examples above, the same experimental conditions are used with a typical value $p = 2$.

323–423°K: ΔE lies between 1.84 and 1.10 kcal/mole, $\Delta \log A$ lies between 6.22 and 5.78;

923–1023°K: ΔE lies between 6.39 and 1.33 kcal/mole, $\Delta \log A$ lies between 7.41 and 6.27.

If the maximum value of p allowable while curvature is not detectable is calculated from Eq. (17) it is often found that an unrealistically large value of p may be found. It seems more reasonable for gas-phase reactions to use the theoretical upper limit to calculate maximum differences rather than use the purely statistical criterion. Using $p = 3$, the large values $\Delta E_{max} = 8.2$ kcal/mole and $\Delta \log A_{max} = 10.8$ are possible at the highest temperatures $932-1023$°K (same experimental conditions as in previous paragraphs).

The calculations in this paper show that if either Eqs. (2) or (3) is correct then significant differences exist between the apparent activation energy and pre-exponential factor and the corresponding true values and yet the experimental results appear to fit the Arrhenius equation. Apparent activation energies for two different reactions measured over different temperature ranges might differ by several kcal/mole without any corresponding difference in true activation energies. Reactions whose rates are governed by Eq. (3) would yield different apparent activation energies if the true activation energy was the same in both reactions but p differed. In the absence of information about the temperature dependence of the parameters in the theoretical equation, conclusions based upon differences in apparent activation energies should be drawn with caution; as a rough approximation only differences greater than 3–4 kcal/mole should be regarded as significant.

When apparent values are derived by the least-squares method, confidence limits for E_a and $\log A$ are often calculated using an error variance given by $S_T^2/(s\text{-}2)$. This procedure is correct when a truly linear equation is being approximated but when curvature is present $S_T^2/(s\text{-}2)$ overestimates the error term by an amount equal to the mean sum of squares due to curvature [see Eq. (14)]. It is not correct to use this estimate in calculating ΔE_E and $\Delta \log A_E$. The correct method is to make several replicate measurements at each temperature and to use the within-replicate variation to estimate $\sigma_{\log k}$.

If there is sufficient knowledge about the rate equation, E_a can be interpreted as an approximation to either $\overline{\Delta H_{12}}°$ or to E_0. In the absence of such theoretical information it is still possible to make a preferred interpretation. In a system of reacting molecules the equilibrium constant K can be expressed as the ratio of the rate constants of the forward k_f and backward reactions k_b for the case where a single activation energy governs the reaction.

$$K = k_f/k_b = \exp(\Delta S/R)\exp(-\Delta H/RT)$$

where ΔH and ΔS are the enthalpy and entropy changes. This equation implies that the individual rate equations can be written in the form

$$k_f = \nu \exp(S^*/R)\exp(-H^*/RT) \quad (19)$$

where H^* and S^* are the enthalpy and entropy of activation and ν has the dimensions of frequency. Now K is known in a large number of cases to be temperature-dependent and so H^* and S^* must also depend upon temperature. On thermodynamic grounds, therefore, E_a is best regarded as an approximation to $\overline{\Delta H}_{12}^{\circ}$ .This choice leads to simplicity in computation because the difference between E_a and $\overline{\Delta H}_{12}^{\circ}$ is, to a good approximation, dependent only on the extreme temperatures of the range and does not require information about the actual variation of H^* with temperature for its calculation.

Unfortunately, no such simple interpretation of log A is possible because from Eq. (19)

$$A = \nu \exp(S^*/R)$$

and the value of ν depends upon the particular theoretical model chosen.

Finally, the results for the wide temperature range 323–823°K are examined briefly. In the case when Eq. (2) is correct Table 1 shows that ΔE_C depends markedly upon α, β, and γ and also upon the number of measurements. Table 2 shows only slight dependence upon the number of measurements but still a marked dependence upon p. In both tables the expected effect of increased sensitivity in detecting curvature is shown clearly. Such increased sensitivity is desirable but the experimental difficulties in utilizing such a wide temperature range are, of course, very great.

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