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ON ESTABLISHING THE VALIDITY OF ENTHALPY-ENTROPY RELATIONSHIPS

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Abstract—All the methods so far proposed for deriving enthalpy-entropy relations fail to take into consideration the physical reasons for implied functional dependence between the activation parameters. In order to avoid spurious results it is essential to establish first the physical basis upon which the variation in the specific reaction rate itself depends, and then to carry that information through to the enthalpy-entropy plane.

The proposals made here are of general application for establishing valid functional enthalpy-entropy relations, whatever their form, and in this context linear correlations are merely a subset.

INTRODUCTION

The effects of temperature on chemical reaction rates can be described either in terms of classical collision theory by the Arrhenius equation,[1]

$$k = A\,e^{-E/RT}, \tag{1}$$

or according to the activation complex theory, by the Eyring equation,[2]

$$k = \frac{RT}{Nh}\,e^{-\Delta H^{*}/RT}\,e^{\Delta S^{*}/R}. \tag{2}$$

In these equations k is the specific reaction rate, R the universal gas constant and T the absolute temperature; N is the Avogadro number and h Planck's constant. E is the Arrhenius activation energy and A the Arrhenius constant, while ΔH^{*} is the enthalpy of activation and ΔS^{*} the entropy of activation of the Eyring equation. In practice the numerical values of the activation parameters are derived from the common logarithmic forms of the equations,

$$\log k = \log A - \frac{E}{2{\cdot}303RT}, \tag{3}$$

$$\log k = \log\frac{RT}{Nh} - \frac{\Delta H^{*}}{2{\cdot}303RT} + \frac{\Delta S^{*}}{2{\cdot}303R}. \tag{4}$$

In this form these equations predict a linear regression between the common logarithm of the specific reaction rate and the reciprocal of the absolute temperature, relating E and ΔH^{*} to the regression coefficient and $\log A$ and ΔS^{*} to the regression constant.

With the accumulation of data in this field it emerged that for sets of closely related reactions differing, say, with respect to the chemical structure of a participating component, or in solvent medium composition, the activation parameters varied together and in the same sense, so that E and $\log A$, or ΔH^{*} and ΔS^{*} were linearly correlated. These observations were of considerable theoretical interest, because they appeared to provide a basis for inference about process mechanisms at molecular level, and led to the generalization known as the isokinetic relationship, or compensation law.[3-5]

The potentially artefactual nature of such correlations has long been recognized,[5-8] but it was Exner[7] who brought out their inherent deficiency, which is that E and $\log A$, or ΔH^{*} and ΔS^{*} are *a priori* mutually dependent, because both parameters in each pair are derived from essentially the same quantity, $\log k_1/k_2$ where k_1 and k_2 are the specific reaction rates at the absolute temperatures T_1 and T_2 respectively. In Exner's view, therefore, linear enthalpy-entropy relationships are not valid unless corresponding correlations exist between the mutually independent variables $\log k_1$ and $\log k_2$. However, this is not in itself a sufficient criterion of validity because it still does not include the physical basis of any implied enthalpy-entropy relationship. In order to do that it is necessary to go back one step further and first establish the physical basis on which the variation in the specific reaction rate itself depends.

METHODS

As Exner[7] has stated, the derivation of E and $\log A$ or ΔH^{+} and ΔS^{+}, from reaction rates k_1 and k_2 measured at temperatures T_1 and T_2 ($T_1 > T_2$) is equivalent to a linear transformation of coordinates from the plane $\log k_1$ vs $\log k_2$ to the plane E vs $\log A$ viz.

$$E = \frac{2\cdot 303RT_1T_2}{T_1 - T_2}(\log k_1 - \log k_2), \qquad (5)$$

$$\log A = \frac{T_1}{T_1 - T_2}\left(\log k_1 - \frac{T_2}{T_1}\log k_2\right). \qquad (6)$$

A linear relationship in the one set of co-ordinates must, therefore, correspond with a linear relationship in the other. However Exner,[7] Banks *et al*,[8] together with the authors they criticise, all confuse the fitting of straight line regressions in a purely statistical way with the establishing of linear functional relationships. Each member of a reacting series has exactly one value of $\log k_1$ and one value of $\log k_2$ associated with it, and, in fitting a straight line in the $\log k_1$ vs $\log k_2$ plane, it is important to distinguish between two possible situations:

(i) If a straight line is fitted in the $\log k_1$ vs $\log k_2$ plane simply to show a trend of one variable with the other, that is, a purely statistical relationship is assumed, then two possible regression lines, $\log k_1$ on $\log k_2$ and $\log k_2$ on $\log k_1$, can be established and, as Exner[7] has shown, the images of these lines in the E vs $\log A$ plane are not coincident with the regression line which can be established directly in that plane.

It must be emphasised that for lines fitted in a purely statistical way, with no physical basis for assuming a true linear functional relationship in either plane, there is no question of a regression line in the one plane being more "correct" than in the other. Interpretation of the regressions must be undertaken with great care, for the possible *a priori* correlations between the variables can lead to inevitable linear regressions.

(ii) If there is a functional relationship between $\log k_1$ and $\log k_2$ there must be definite physical reasons for assuming that this relationship is linear, and establishing a good straight line fit in a purely statistical way is not sufficient. If a true linear relationship does exist then only one line can be fitted in each plane, as compared with the two of the first case, and it is not correct to use the methods employed in (i) for establishing regression lines. A full discussion of this topic can be found in Kendall and Stuart.[9] However, as we shall show later, the fitting of such lines in the $\log k_1$ vs $\log k_2$ plane or in the E vs $\log A$ plane is neither necessary nor desirable.

In trying to establish the relationship between $\log k_1$ and $\log k_2$ and between E and $\log A$, attention must be paid to the order in which the points representing the members of the reacting series occur. If T_2/T_1 is near to unity, then, for example, the points in $\log k_1$ vs $\log k_2$ could lie on a parabola of small latus rectum, and yet a good straight line fit could be established in a purely statistical way.

We suggest that the correct approach to establishing a relationship in the E vs $\log A$ plane is as follows.

Assuming that E and $\log A$ do not vary with temperature then, for any member of the reacting series, E and $\log A$ remain constant for the values of $\log k_1$ and $\log k_2$ obtained at temperatures T_1 and T_2. By ranking the members of the reacting series according to some physical characteristic, an attempt can be made to fit smooth curves in the $\log k_1$ vs $\log k_2$ and E vs $\log A$ planes, through the points in the order in which they are ranked. Hence the following steps should be carried out.

(i) Rank the members of the series according to ascending values of a physical characteristic, x.

(ii) Plot points in the $\log k_1$ vs x and $\log k_2$ vs x planes.

(iii) Fit smooth curves through the points in each of the two planes. Preferably mathematically but if the points are few then graphically.

(iv) Plot both the actual and fitted points in the $\log k_1$ vs $\log k_2$ and in the E vs $\log A$ planes, and hence the fitted curves.

The fitted curves thus obtained should be looked at as a set. Although this may not lead to an exact mathematical description of the curve in the E vs $\log A$ plane, it will certainly give a much better guide to its general shape than anything that has so far been achieved.

We turn now, in the light of these considerations to a few examples which illustrate the application of this approach. These examples were chosen from the literature and they are controversial, for their enthalpy-entropy relationships have variously been reported as linear, non-linear or non-existent. Although brief comment is offered where appropriate, it is not our intention to discuss reaction mechanisms in any detail; our object is merely to draw attention to what seems to be a more general and useful approach to the derivation of enthalpy-entropy relationships.

EXAMPLES AND DISCUSSION

1. *Solvolysis of t-butyl chloride in ethanol-water mixtures.*

The specific reaction rates for this example were measured by acidimetric analysis of a series of reacting mixtures in the concentration range 0–50% ethanol at 0° and 25°.[10,11] Although serial rates are reported up to 100% ethanol,[10] the corresponding measured values at 0°[11] are not available for the 50–100% range; moreover, above 50% ethanol, halide analysis was employed. We have therefore confined our study to the 0–50% ethanol concentration range, and we have converted percentage concentration to mole fraction water.

In this example the choice of physical characteristic (x) that defines the sequence of the points is unequivocally the concentration variable, and Fig. 1 shows the plotted points and the mathematically fitted curve for $\log k$ vs mole fraction water at 0° and 25°. The curve fitting was carried out by least squares approximation to the sets of data points according to Forsythe's[12] method, using orthogonal polynomials. The measure of best fit is as described by Forsythe,[12] and for both temperatures the lowest order best-fitting polynomial, below order 10, was

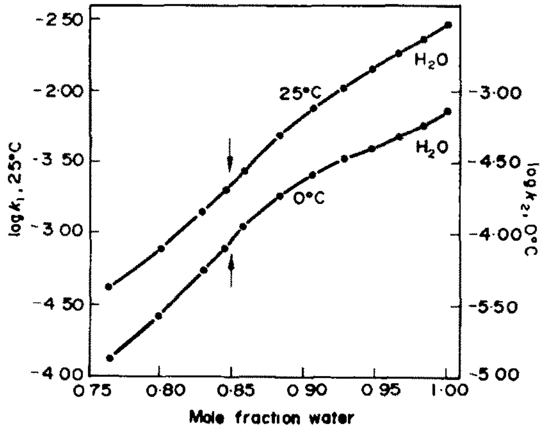

Fig 1. Mathematically fitted plots of log k *vs* mole fraction water for the solvolysis of t-butyl chloride in ethanol-water mixtures at 0° and 25°C. The diameters of the points are approximately proportional to the estimated error.

found to be of order four. It was worth while to fit the data mathematically in this example because of the large number of points available, and to show that even complicated curves can be fitted well.

The curve for log k_1 vs log k_2 (Fig. 2) exhibits the same excellent fit, and the transformation of these points and their fitted curve to E vs log A is shown in Fig. 3. We conclude, therefore, in agreement with Winstein & Fainberg[11] that the valid enthalpy-entropy relationship of this system is a smooth, complex curve.

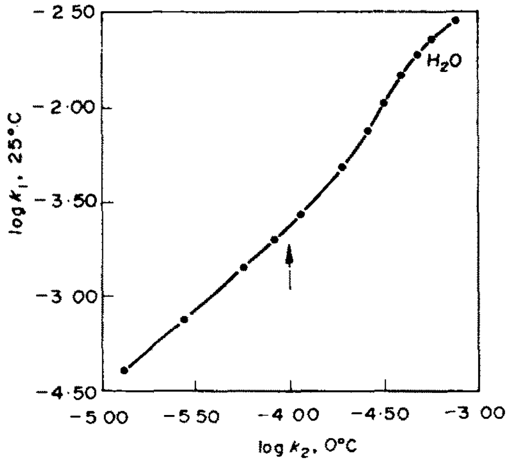

Fig 2. Mathematically fitted plot of log k_1 *vs* log k_2 for the solvolysis of t-butyl chloride in ethanol-water. The diameters of the points represent the approximate estimated error.

Exner's evaluation of this example is rather different, and he considered the whole concentration range of 0–100% ethanol. In Exner's view, because of the differences between the results obtained by the two analytical methods, experimental error is higher than that reported by the original authors. On that basis, therefore, he fitted three straight lines to the overall data of log k_1 vs log k_2 and then showed that the transformations of these are good approximate fits in E vs log A. With respect to the data presented here, Exner's approach calls for two fitted straight lines intersecting about 0·85 mole fraction water, denoted by the arrows in Figs 1–3. It is of course feasible that two straight lines, meeting at 0·85 could be fitted in the log k_1 vs x plane and would result in pairs of straight lines in the other planes, but there is no justification for so doing unless strong physical reasons indicate that this should be so. The concentration range discussed here refers only to acidimetrically measured rates and the error is small. In our view only approximate linear fits can be established, and these at the expense of neglecting pronounced systematic variation about the lines, especially in the 0·85–1·00 concentration range. The success of Exner's evaluation of the data is more apparent than real. It arises because the physical characteristic which defines the sequence of the points in the series is wholly unequivocal. An approximate linear fit in the one plane is, therefore, the inevitable consequence of an approximate linear fit in the other.

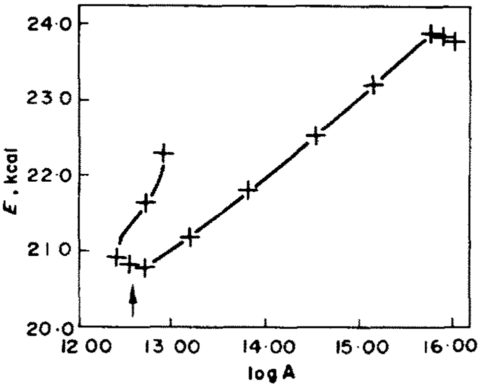

Fig 3. Mathematically fitted plot of E *vs* log A for the solvolysis of t-butyl chloride in ethanol-water. The dimensions of the crosses represent the estimated error.

2. *Saponification of halogen-substituted ethyl phenoxyacetates*

The rates for this example were obtained from the study by Brown & Newsom[13] on the hydrolysis of halogen-substituted ethyl phenoxyacetates by NaOH in 98·5 weight per cent aqueous ethanol at 0° and 30°. In that work the authors themselves drew attention to the difficulties they encountered in trying to evaluate their results. It is probably for the same underlying reasons that we have found it impossible to choose a single physical characteristic that defines the sequence of members in all three series. Nevertheless, by using a simple physical characteristic, the atomic number of the halogen substituent, we are able to illustrate our approach with the 2-substituted series. Fig 4 shows how log k varies with the halogen atomic number at 0° and 30°. Smooth curves can be drawn through the points and the resulting curve—graphically fitted because of lack of data—in the log k_1 vs log k_2

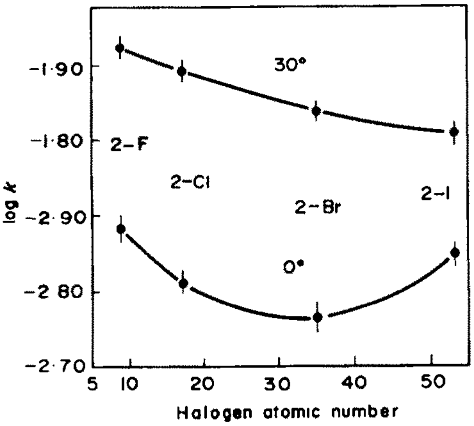

Fig 4. Graphic plots of log k *vs* halogen atomic number for the saponification of 2-halogen-substituted ethyl phenoxyacetates in alcoholic caustic soda at 0° and 30°C. The vertical lines represent the estimated errors.

plane, which is shown in Fig 5, resembles a parabola. The transformation to E vs $\log A$, which is given in Fig 6, resembles a straight line of semi-infinite* extent with some points having a 2–1 correspondence. We conclude, therefore, that although the distribution of points in E vs $\log A$ proposed by Brown and Newsom[13] is correct, it is incorrect to relate these points by a best-fitting straight line. The difficulty in defining an appropriate overall physical characteristic for these substances does not mean that physical characterization is impossible; it is, rather, a confession of ignorance about the detailed physical characteristics of these substances. The ionization potentials of the halogen-substituted free acids could be more appropriate in this context, but we have been unable to locate these in the literature.

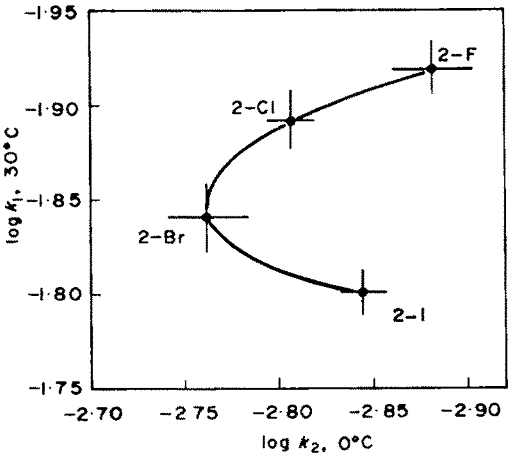

Fig 5. Graphic plot of log k_1 *vs* log k_2 for the saponification of the 2-substituted halogen ethyl phenoxyacetates. The crosses denote the estimated errors.

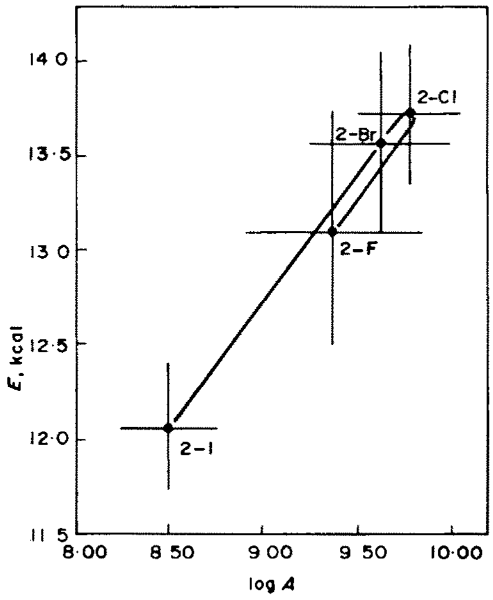

Fig 6. Graphic plot of E *vs* log A for the saponification of the 2-substituted halogen ethyl phenoxyacetates. The crosses are proportional to the estimated error.

This example shows that the variation of $\log k$ with the physical characteristic (x) approximates well to a parabola and since this type of quadratic dependence seems to occur quite frequently in practice (for example, Good & Stone[14]), we now present a general statement of the problem, together with its mathematical solution.

Expressing the variation of $\log k$ with the physical characteristic (x) we take

$$\log k_1 = a_1 + b_1 x + c_1 x^2 + \epsilon f(x), \tag{7}$$

and

$$\log k_2 = a_2 + b_2 x + c_2 x^2 + \epsilon g(x), \tag{8}$$

where the a, b and c's are all distinct constants, ϵ is a small quantity and $f(x)$ and $g(x)$ two functions of x of order unity in magnitude. This gives

$$E = p_1[(a_1 - a_2) + (b_1 - b_2)x + (c_1 - c_2)x^2 + \epsilon(f(x) - g(x))], \tag{9}$$

and

$$A = p_2\left[\left(a_1 - \frac{T_2}{T_1}a_2\right) + \left(b_1 - \frac{T_2}{T_1}b_2\right)x + \left(c_1 - \frac{T_2}{T_1}c_2\right)x^2 + \epsilon\left(f(x) - \frac{T_2}{T_1}g(x)\right)\right], \tag{10}$$

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*This is a technical description of the "doubling back" type of curve depicted in Fig 6.

where

$$p_1 = \frac{2{\cdot}303RT_1T_2}{T_1 - T_2}, \quad p_2 = \frac{T_1}{T_1 - T_2}.$$

If the relationship between E and $\log A$ is linear then this requires that there exists two constants, α and β say, such that

$$\left(a_1 - \frac{T_2}{T_1}a_2\right) + \left(b_1 - \frac{T_2}{T_1}b_2\right)x + \left(c_1 - \frac{T_2}{T_1}c_2\right)x^2 + \epsilon\left(f(x) - \frac{T_2}{T_1}g(x)\right)$$

$$= \alpha[(a_1 - a_2) + (b_1 - b_2)x + (c_1 - c_2)x^2 + \epsilon(f(x) - g(x))] + \beta. \qquad (11)$$

We now choose α and β such that the coefficients of x^0 and x^1 balance and we conclude that if the remaining terms are small then a linear relationship is almost valid. The terms in ϵ are small thus we require the coefficient in x^2 small, that is

$$\frac{1}{(b_1 - b_2)}[(b_2c_1 - b_1c_2)(1 - T_2/T_1)]. \qquad (12)$$

This expression is small for $(1 - T_2/T_1)$ small if

(i) $\left(1 - \frac{b_1}{b_2}\right)$ is not small

or

(ii) $\left(1 - \frac{b_1}{b_2}\right)$ small and $\left(1 - \frac{c_1}{c_2}\right)$ small.

In the example considered here $(1 - b_1/b_2)$ is not small and we can conclude that in such cases the E vs $\log A$ variation is almost linear. This is verified by Fig 6.

When considering the variation of $\log k_1$ vs $\log k_2$ it is sufficient to approximate expressions (7) and (8) by

$$\log k_1 = a_1 + b_1x + c_1x^2, \qquad (13)$$

$$\log k_2 = a_2 + b_2x + c_2x^2, \qquad (14)$$

since ϵ is small and we are not subtracting two almost equal quantities.

Eliminating x from equations (13) and (14) results in the relationship

$$\begin{vmatrix} c_1 & b_1 & a_1 - \log k_1 \\ c_2 & b_2 & a_2 - \log k_2 \\ (b_1c_2 - b_2c_1)^2 & 2(b_1c_2 - b_2c_1)(a_1c_2 - a_2c_1) & (a_1c_2 - a_2c_1)^2 \\ & & -(c_2\log k_1 - c_1\log k_2)^2 \end{vmatrix} = 0. \qquad (15)$$

between $\log k_1$ and $\log k_2$. It is observed that this is a parabola which in the limiting case when $c_1 = c_2$ and $b_1 = b_2$ becomes a straight line. The parabolic variation is confirmed by Fig 5.

3. *The fluidity of aqueous electrolytes containing at least one positively hydrated ion species*

This example is taken from an evaluation by Good and Ingham[15] of enthalpy-entropy relations in the fluid kinetics of positively hydrated aqueous electrolytes. Here, the specific reaction rates k_1 and k_2 refer to the fluidity in poise^{-1} (rhes) of the solutions at 25° and 18° respectively, and the ranking physical characteristic (x) is increasing molal concentration.

The variation in $\log k_1$ and $\log k_2$ with molality is shown in Fig 7. Although these curves exhibit strong linear correlations, the best fit to the data, using the method described by Forsythe,[12] is a third order polynomial. The mathematically fitted curve and the experimental points in the plane $\log k_1$ vs $\log k_2$ are given in Fig 8. It is perhaps slightly more obvious that this relationship is non-linear, but nevertheless the data approximate closely to a statistically significant linear correlation. However, when this fitted curve is transformed to the E vs $\log A$ plane (Fig 9), the result is a highly non-linear relationship. Since the electrolytes in this group all appear to behave in this

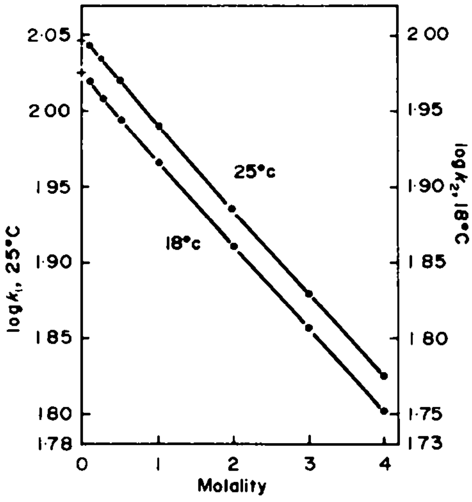

Fig 7. Mathematically fitted plots of log k vs molality for the fluidity of aqueous lithium chloride at 18° and 25°C. The diameters of the points are approximately proportional to the estimated error.

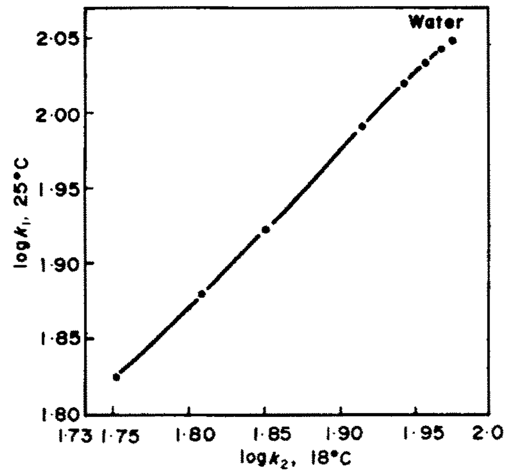

Fig 8. Mathematically fitted plot of log k_1 *vs* log k_2 for the fluidity of aqueous lithium chloride. The points are approximately proportional to the estimated error.

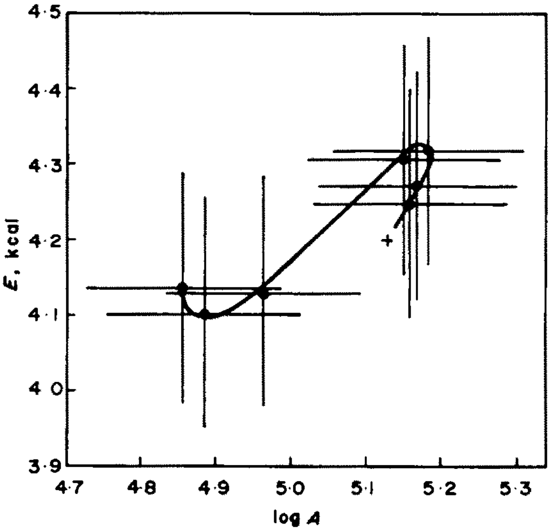

Fig 9. Mathematically fitted plot of E *vs* log A for the fluidity of aqueous lithium chloride. The crosses denote the estimated errors.

way, a general statement and mathematical solution is presented below.

In general, for systems which display an approximate linear relationship in the log k vs x plane, we approximate log k_1 and log k_2 by

$$\log k_1 = a_1 + b_1x + \epsilon r(x), \tag{16}$$

and

$$\log k_2 = a_2 + b_2x + \epsilon s(x), \tag{17}$$

where again ϵ is a small quantity, the a and b's constants but this time b_1 is close to b_2 and $r(x)$ and $s(x)$ are functions of x of order unity in magnitude.

Eliminating the term in x from equations (16) and (17) gives

$$b_2\log k_1 - b_1\log k_2 = a_1b_2 - a_2b_1 + \epsilon[b_2r(x) - b_1s(x)]. \tag{18}$$

Since ϵ is small this leads to an almost linear relationship between log k_1 and log k_2. It now remains to determine the relationship between E and log A, the values of which are given by

$$E = p_1[(a_1 - a_2) + (b_1 - b_2)x + \epsilon(r(x) - s(x))], \tag{19}$$

and

$$\log A = p_2\left[\left(a_1 - \frac{T_2}{T_1}a_2\right) + \left(b_1 - \frac{T_2}{T_1}b_2\right)x + \epsilon\left(r(x) - \frac{T_2}{T_1}s(x)\right)\right]. \tag{20}$$

Since T_2/T_1 and b_2/b_1 are close to unity then the coefficients in the x terms are small and in fact the ϵ term could be as large, if not larger, than these terms. Hence no simple relationship can, in general, be obtained between E and log A, as confirmed by Figs 7, 8 and 9.

In general the log k vs x relationship will be neither linear nor quadratic, but will be of the form

$$\log k_1 = a_1 + b_1x + c_1x^2 + d_1x^3 + \cdots \tag{21}$$

and

$$\log k_2 = a_2 + b_2x + c_2x^2 + d_2x^3 + \cdots \tag{22}$$

In order for *both* relationships log k_1 vs log k_2 and E vs log A to be linear then there must exist four constants, say u, v, w and z, such that

$$\log k_1 = u\log k_2 + v, \tag{23}$$

and

$$\log A = wE + z. \tag{24}$$

This leads to the following relationships between the coefficients in expressions (21) and (22).

$$\begin{array}{ll} a_1 = ua_2 + v, & a_1 - T_2/T_1\,a_2 = w(a_1 - a_2) + z, \\ b_1 = ub_2, & b_1 - T_2/T_1\,b_2 = w(b_1 - b_2), \\ c_1 = uc_2, & c_1 - T_2/T_1\,c_2 = w(c_1 - c_2), \\ d_1 = ud_2, & d_1 - T_2/T_1\,d_2 = w(d_1 - d_2), \\ & \text{etc.} \end{array} \tag{25}$$

It is seen that given $a_1, b_1, c_1, \ldots$ and two of the quantities with suffix 2, say a_2 and b_2, then all other constants with suffix 2 are determinable. This, in physical terms, means that given a detailed variation of log k_1 with x and the value of log k_2 and d/dx (log k_2) at $x = 0$ then the variation of log k_2 for all values of x is determined. If such were the case, a physical and not a mathematical reason should be sought for the phenomenon.

Thus we conclude that in general we would expect the relationships log k_1 vs log k_2 and E vs log A to be non linear but if they are both linear then there should be a more thorough investigation of the physical reason for this.

4. *The decomposition of 2,2'-azobis-(2-methylpropionitrile) in various solvents.*

This example refers to the thermal decomposition, measured precisely by nitrogen evolution, of 2,2'-azobis-(2-methylpropionitrile) in N-methylpropionamide(1), propylene carbonate(2), diphenylmethane(3) and N,N-dimethylaniline(4) at 66° and 72°, see Petersen, Markgraf and Ross.[16] In this instance we were unable to discover any physical characteristic to relate these solvents, but nevertheless the criterion of mutual compatibility can be used to cast some light on the problem. The original authors noted that the activation parameters for this reaction in these solvents were virtually collinear (Fig 10), but ascribed this result to errors in ΔH^* and ΔS^*, which they discussed in some detail. However, the plot of log k_1 vs log k_2 given in Fig 11 suggests something rather different. The error in log k is small and it is highly likely that the sequential joining of the points in the same order as in E vs log A is justified. According to our criteria, therefore, there is probably a non-linear functional relationship between E and log A. The parabolic-type curve of small latus rectum in log k_1 vs log k_2 becomes transformed to one of small curvature in E vs log A. If we understand correctly the comments made by Exner[7] about this example, he believes that this is a valid isokinetic relationship, with linearity between enthalpy and entropy, and cites the differing linear order of the points in support of that contention. By our criteria the incompatible linear order is precisely the reason why the linear fit should be rejected.

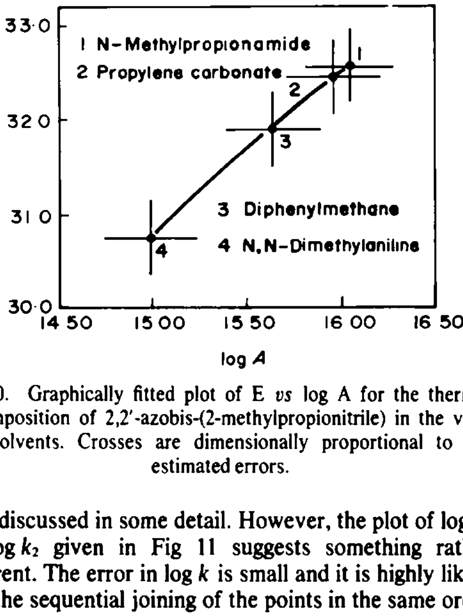

Fig 10. Graphically fitted plot of E *vs* log A for the thermal decomposition of 2,2'-azobis-(2-methylpropionitrile) in the various solvents. Crosses are dimensionally proportional to the estimated errors.

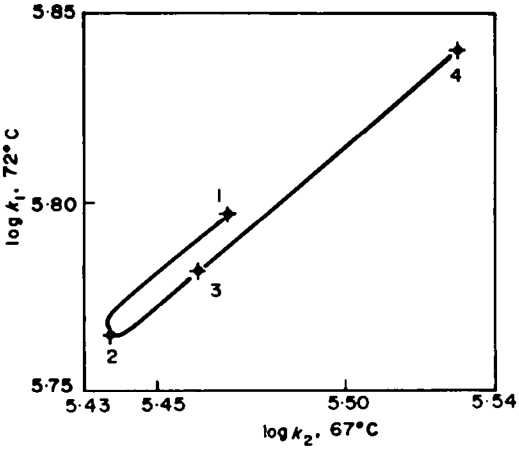

Fig 11. Graphically fitted plot of the log k_1 *vs* log k_2 for the thermal decomposition of the substance. Crosses are dimensionally proportional to the estimated errors.

CONCLUSIONS

We have shown here that in order to avoid spurious results the physical basis for enthalpy-entropy relationships must be established at the earliest possible stage in the evaluation of the data. Thus, if the physical characteristic (x) can be identified and the data are sufficient, the mathematically fitted plot of log k vs x will show the variations that will occur in the log k_1 vs log k_2 and E vs log A planes. However, even if data are scant, a simple graphical plot of log k vs x will often indicate what variation should be expected in the E vs log A plane.

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