

On Relations between Activation Energies and Frequency Exponents in Chemical Kinetics

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It is well known from the literature¹⁻³ that a relation exists between the two parameters of the Arrhenius equation⁴. The relation is often approximately linear. As shown by Polanyi and Evans³ similar relations also occur in the case of equilibrium constants, *e. g.* in case of solubilities.

An explanation of such relations has been given in a special case by Schwab². Schwab considers the case of catalysts of different catalytic activities, and he has shown by rather conclusive experiments that there is a correlation between the preparation temperature of the catalyst and the activation energy and the frequency exponent (the logarithm of the frequency factor) of the same reaction catalysed by catalysts of different activities.

Of course, such assumptions are excluded in the case of reactions in homogeneous systems. For such systems rather satisfactory explanations have been given by Moelwyn-Hughes⁵ and by la Mer and co-workers⁶.

It seems, however, that in principle the matter may be treated in a simpler and perhaps more general way. The idea is that in the expression for the logarithm of the velocity constant, the factor over T or RT must represent the free energy of activation (comp. Christiansen⁷), but what we measure is on account of the restricted temperature range always the energy of activation that is, what we know is only the tangent of the $(\ln k, T^{-1})$ curve, not the curve itself.

We may remark in passing that strictly speaking we should in the above replace the word energy by enthalpy as in the case of solutions we always measure velocities at constant pressure.

Let

$$\ln k = -\frac{G}{T} + B \quad (1)$$

where B is independent of temperature.

From this we get

$$H = T^2 \frac{\partial}{\partial T} \ln k = G - T \frac{\partial G}{\partial T} \quad (2)$$

If we have no theory for the evaluation of G as a function of T , we cannot do better than empirically to determine a value H_0 around a certain temperature T_0 . In other words, we replace the true curve by its tangent, the position and direction of which may be derived from experiments with a fair accuracy. Let the empirical equation of the tangent be

$$\ln k = -\frac{H_0}{T} + I_0 \quad (3)$$

Now (1) and (3) are not identical, but at $T = T_0$ the values of $\ln k$ according to the two equations must coincide. We therefore get

$$G_0 - H_0 = T_0(B - I_0) \quad (4)$$

or, when applying (2):

$$\left(\frac{\partial G}{\partial T}\right)_0 = B - I_0 \quad (5)$$

Now there are cases where some theory shows that G depends significantly on T . The meaning of this somewhat loose expression may be illustrated by means of two examples.

1. A linear dependence on T cannot be significant as any member in G of the form aT after division by T must disappear in the constant B of equation (1).

2. A member in G of the form $bT \ln T$ cannot be significant if the pure number b is not excessively great, as in the expression for k we get in that case a factor of the form T^b before the exponential term against which the form of the exponential curve is very insensitive. The same thing appears from the fact that in expressions of the form

$$-\frac{Q}{RT} + b \ln T$$

$b \ln T$ can with fair approximation be considered a constant even if T at ordinary or higher temperature is varied between rather wide limits.

There are, however, cases where some theory shows that G is at least approximately of the form $A + KD^{-1}$, where A and K are constants while D is strongly

dependent on T . For instance in the case of ionic reactions in solutions D may represent the dielectric constant of the solvent^{8,9}. It is known⁵ that D is strongly variable with temperature as it may be represented approximately by $D = Ce^{-\alpha T}$.

Consequently we get

$$\frac{\partial G}{\partial T} = KD^{-1}\alpha \quad (6)$$

or from (5)

$$B - I_0 = KD_0^{-1}\alpha \quad (7)$$

where D_0 is the value of D at T_0 .

Furthermore from (2)

$$H = A + KD^{-1}(1 - \alpha T) \quad (8)$$

or

$$H_0 = A + KD_0^{-1}(1 - \alpha T_0) \quad (9)$$

By insertion of (7) we get

$$H_0 = A + (B - I_0) \left(\frac{1}{\alpha} - T_0 \right) \quad (10)$$

that is if we compare different reactions with equal values of A and B and in the same solvent (same α), a linear relation between the different values of H_0 and I_0 will exist if the same T_0 is chosen. If the solvents are different (different α 's), the relation may not be linear, but an interdependency will still exist, and if the different T_0 's are chosen so as to make $\frac{1}{\alpha} - T_0$ constant the relation becomes linear.

By a completely analogous reasoning it can be proved that a similar relation prevails in the case of equilibrium constants.

It should be added that Waring and Becher have recently shown¹⁰ that for the fluidity of liquids similar relations exist, and furthermore that the thermodynamic properties of the fluidity function seem to reappear in the functions expressing the velocity constants for reactions in the same liquids. This seems to mean that the fluidity (or the diffusion coefficient) enters into the expression for the free enthalpy of activation, G .

SUMMARY

A derivation from well known assumptions of the relationship between activation-energy and frequency-exponent is given.

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