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OPINION

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A common misconception about the Eyring equation†

Gábor Lente,*[a] István Fábián[a] and Anthony J. Poë[b]

[a] *Department of Inorganic and Analytical Chemistry, University of Debrecen, P.O.B. 21, Hungary, H-4010. E-mail: lenteg@delfin.unideb.hu; Fax: +36 52 489-667; Tel: +36 52 512-900/2373*
[b] *Lash Miller Chemical Laboratories, University of Toronto, Toronto, Canada M5S 3H6*

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Linearization and direct fitting to the Eyring equation both give the entropy of activation with the same reliability as that of the enthalpy of activation.

The Eyring equation[1] is generally used in mechanistic research to interpret the temperature dependence of second-order rate constants. The most common form of the equation is:

$$k = \frac{k_B T}{h} \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right) = \frac{k_B T}{h} \exp\left(-\frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R}\right) \quad (1)$$

where k is the second-order rate constant, k_B is Boltzmann's constant, h is Planck's constant, R is the gas constant, T is the absolute temperature, ΔG is the free energy of activation, $\Delta H^{\ddagger}$ is the enthalpy of activation, and $\Delta S^{\ddagger}$ is the entropy of activation. There is a widespread view in the community of chemical kineticists concerning the Eyring equation: "*The value of the entropy of activation is unreliable because it is calculated by extrapolation to infinite temperature.*"

This statement is usually based on a linearized form of eqn (1):

$$\ln\frac{k}{T} = -\frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R} + \ln\frac{k_B}{h} \quad (2)$$

Thus ln(k/T) is plotted *vs.* $1/T$, $\Delta H^{\ddagger}$ is obtained from the slope and $\Delta S^{\ddagger}$ from the intercept. The intercept is where $1/T = 0$ or $T = \infty$, hence $\Delta S^{\ddagger}$ involves an extrapolation to infinite temperature and is consequently unreliable—so the anecdotal argument goes.

The problem with this line of reasoning is that once ΔH and k are known at a particular temperature, $\Delta S^{\ddagger}$ can be obtained by simple rearrangement of eqn (1). How is it possible to compute an inherently unreliable result from reliably known parameters?

In fact, a different linearized form of eqn (1) is:

$$T \times \ln\frac{k}{T} = T \times \left(\ln\frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R}\right) - \frac{\Delta H^{\ddagger}}{R} \quad (3)$$

One thus plots $T \times \ln(k/T)$ *vs.* T, and can obtain $\Delta S^{\ddagger}$ from the slope and $\Delta H^{\ddagger}$ from the intercept. It could even be argued that $\Delta H^{\ddagger}$ is an extrapolation to $T = 0$ K and is unreliable! This example emphasizes that using slopes and intercepts is a visually attractive interpretation of the two parameters, but may lead to biased conclusions regarding reliability.

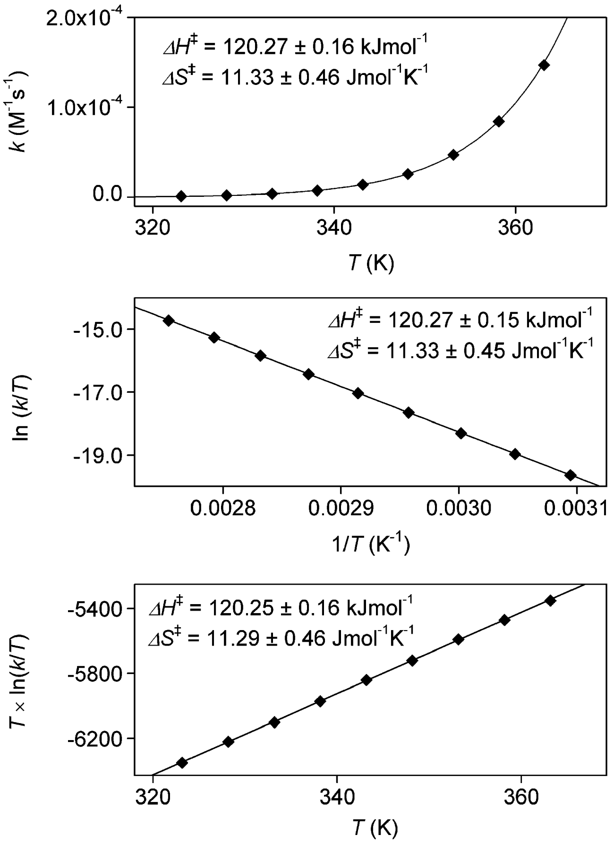

Fig. 1 Eyring plots according to eqn (1)–(3).

Statistical analysis of the Eyring equation (see ESI†) clearly confirms that the standard errors of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ correlate (T_{av} is the centre of the temperature range used):

$$\sigma(\Delta S^{\ddagger}) = \frac{1}{T_{av}}\sigma(\Delta H^{\ddagger}) \quad (4)$$

It follows that in most solution phase studies $\sigma(\Delta S^{\ddagger}) \approx \sigma(\Delta H^{\ddagger}) \times 0.003\ \mathrm{K}^{-1}$. This correlation has been mentioned elsewhere.[2,3]

It is generally advisable to use the original form of any non-linear equation in least-squares analysis with appropriate weighting.[2] However, the Eyring equation is more forgiving. It is usually possible to calculate the same activation parameters and standard errors using all three methods. This is demonstrated here (see ESI†) by the rate constants of the acid-catalyzed disproportionation of dithionate ion[4] (these data were used to create the graphs in Fig. 1 for illustration). The underlying reason for this agreement between the three methods

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† Electronic supplementary information (ESI) available: List of rate constants and activation parameters. See http://www.rsc.org/suppdata/nj/b5/b501687h/.

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and for the correlation between the standard errors of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is that the temperature range of rate constants is usually only a small fraction (10–20%) of the actual absolute temperature.

In conclusion, ambiguity in the mechanistic interpretation of $\Delta S^{\ddagger}$ can only arise from its limited diagnostic value, but not from the lack of numerical precision.

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