

Supplementary Information for

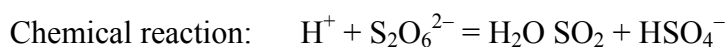
A common misconception about the Eyring Equation

Gábor Lente^{*1}, István Fábrián¹ and Anthony Poë²

¹ Department of Inorganic and Analytical Chemistry, University of Debrecen, P.O.B. 21, H-4010, Hungary. Fax: + 36 52 489-667; Tel: + 36 52 512-900/2373; E-mail: lenteg@delfin.unideb.hu

² Department of Chemistry, University of Toronto, Canada

Original data for the example used in the main text



Values of rate constants:

T (°C)	T (K)	k ($\text{M}^{-1}\text{s}^{-1}$)
50.0	323.2	9.54×10^{-7}
55.0	328.2	1.91×10^{-6}
60.0	333.2	3.76×10^{-6}
65.0	338.2	7.33×10^{-6}
70.0	343.2	1.38×10^{-5}
75.0	348.2	2.56×10^{-5}
80.0	353.2	4.71×10^{-5}
85.0	358.2	8.43×10^{-5}
90.0	363.2	1.47×10^{-4}

Parameters calculated by least squares fitting:

Equation	ΔH^\ddagger (kJ mol^{-1})	ΔS^\ddagger ($\text{J mol}^{-1} \text{K}^{-1}$)
Eq. (1), no weighing	118.80 ± 0.41	7.2 ± 1.1
Eq. (1), proportional weighing	120.27 ± 0.16	11.33 ± 0.46
Eq. (2)	120.27 ± 0.15	11.33 ± 0.45
Eq. (3)	120.25 ± 0.16	11.29 ± 0.46

Proportional weighing: the weight used for the experimental value of k at each temperature is $1/k^2$. Proportional weighing for the untransformed equation is necessary because the values of the second-order rate constant k span more than 2 orders of magnitude. this type of weighing assumes that the relative errors of the rate constants determined are independent of temperature.

When equation 2 or 3 is used, proportional weighing does not make a difference because the transformed values, $\ln(k/T)$ and $T \times \ln(k/T)$ span a narrow range of values on the y axis.

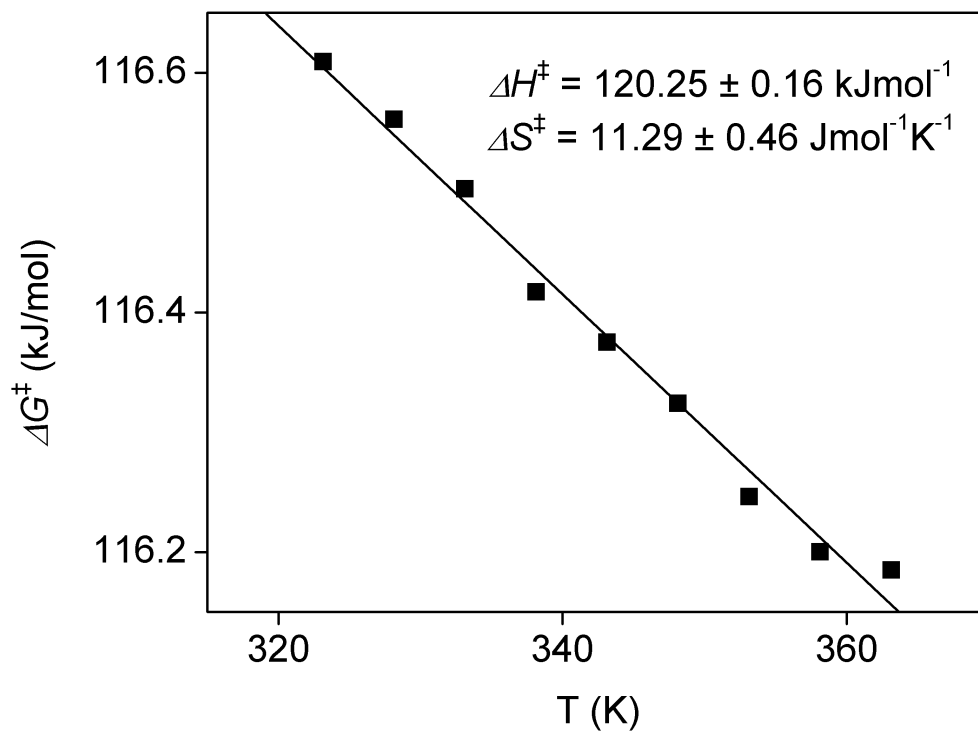


Figure S1 Calculated values of ΔG^\ddagger plotted as a function of T for the data set used in this paper and the activation parameters derived.

This plot is statistically equivalent to equation (3) in the main text as also shown by the identical activation parameters obtained.

Mathematical derivation of equation (4)

Rate constants k_1, k_2, k_3, \dots are measured at temperatures T_1, T_2, T_3, \dots for Eyring analysis. The least squares method (see e.g. the web site <http://mathworld.wolfram.com/LeastSquaresFitting.html>) gives the following values for the values and standard errors of enthalpy and entropy of activation, respectively:

$$\Delta H^\ddagger = R \times \frac{s_{xy}}{s_x} \qquad \sigma(\Delta H^\ddagger) = R \times \frac{s}{\sqrt{s_x}}$$

$$\Delta S^\ddagger = R \times y - \Delta H^\ddagger \times x - R \times \ln \frac{k_B}{h} \qquad \sigma(\Delta S^\ddagger) = R \times s \times \sqrt{\frac{1}{n} + \frac{x^2}{s_x}}$$

where the following quantities are used:

$$x = \frac{1}{n} \sum_{i=1}^n \frac{1}{T_i} \qquad y = \frac{1}{n} \sum_{i=1}^n \ln \frac{k_i}{T_i}$$

$$s_x = \frac{1}{n} \sum_{i=1}^n \left(\frac{1}{T_i} - x \right)^2 \qquad s_{xy} = \frac{1}{n} \sum_{i=1}^n \left(\frac{1}{T_i} - x \right) \left(\ln \frac{k_i}{T_i} - y \right)$$

$$s = \sqrt{\sum_{i=1}^n \left(\ln \frac{k_i}{T_i} - \ln \frac{k_{i,fit}}{T_i} \right)^2}$$

Dividing the standard errors of the activation entropy and activation enthalpy:

$$\frac{\sigma(\Delta S^\ddagger)}{\sigma(\Delta H^\ddagger)} = \sqrt{\frac{s_x}{n} + x^2}$$

In this formula, $s_x \ll n \times x^2$, therefore the following simplification can be used:

$$\frac{\sigma(\Delta S^\ddagger)}{\sigma(\Delta H^\ddagger)} = \sqrt{\frac{s_x}{n} + x^2} \cong x = \frac{1}{n} \sum_{i=1}^n \frac{1}{T_i} \cong \frac{1}{T_{av}} \qquad T_{av} = \frac{1}{n} \sum_{i=1}^n T_i$$

Upon rearrangement, Eq. (4) is obtained

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