How I taught Chemistry 636: Inorganic Reaction Rates and Pathways

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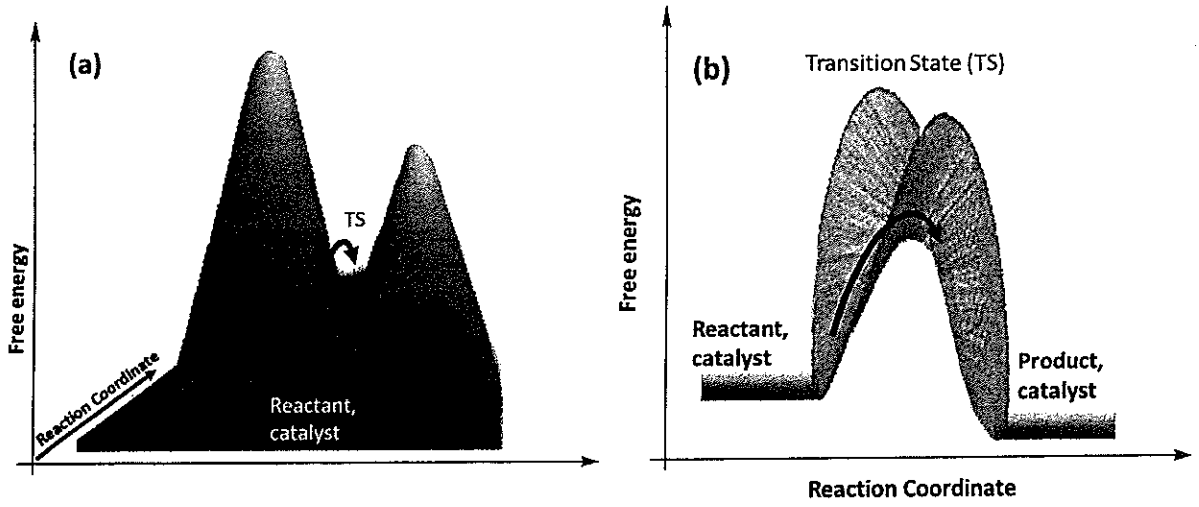
Understanding the temperature dependence of rate constants.

- First let make sure we understand transition-state and what activation energy means, i.e., it is not two-dimensional as typically defined. NOT A HILL but A VALLEY—



(a) Multidimensional space representation of free energy *vs* reaction coordinate. (b) Traditional two-dimensional representation of free energy *vs* reaction coordinate.

The general form for the temperature dependence of the rate constant for an elementary reaction is

$$k = CT^{n}\exp\left(-\frac{U}{RT}\right)$$, where U has the dimensions of energy.

k: rate constant

C and U are adjustable parameters.

Calories – $R = 1.987$ cal/mol-K or $4.184\ J = 1$ calorie

SI units Joules – $R = 8.314$ J/mol-K

The exponent n is usually assigned a value of 0, ½, or 1 dependent on the theoretical model chosen.

Hence, a plot of the data as $\ln k T^{-n}$ vs T^{-1} should be linear with a slope of $-\frac{U}{R}$ as seen by the relationship.

$$\ln \frac{k}{T^n} = \ln C - \left(\frac{U}{R}\right) T^{-1}$$

By such methods one obtains the values of the two adjustable parameters C and U.

The three most common forms of the equation are:

(i) Arrhenius

$$k = A \exp\left(-E_a/RT\right)$$

The two parameters are the preexponential factor A (or frequency factor, only in the case of a unimolecular reaction does A have frequency dimensions, i.e., sec^{-1}) and E_a (Arrhenius activation energy). A is taken as being independent of temperature, i.e., $n = 0$.

(ii) The collision theory – the relationship for bimolecular reactions in the gas phase is given by

$$k = p Z \exp\left(-\frac{E^*}{RT}\right)$$

(E^* ← critical collision energy; p ← steric factor; Z ← collision frequency)

(iii) The Eyring or activated complex/absolute rate theory relationship employs as well two adjustable parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$.

$\Delta H^{\neq}$: activation enthalpy

$\Delta S^{\neq}$: activation entropy

The preexponential shows a first-power temperature dependence, i.e., $n = 1$.

$$k = \kappa \frac{RT}{Nh} \exp\left(\frac{\Delta S^{\neq}}{R}\right) \exp\left(-\frac{\Delta H^{\neq}}{RT}\right)$$

κ: the transmission coefficient — usually taken as unity. It represents the fraction of molecules that, having reached the T.S., proceeds to product.

- From Arrhenius relation, $E_a = -R \dfrac{d \ln k}{d(1/T)}$, recall $\ln k = \ln A - E_a/RT$

- From Eyring relation, $\Delta H^{\neq} = -R \dfrac{d \ln(k/T)}{d(1/T)} = -R \dfrac{d \ln k}{d(1/T)} - R \dfrac{d \ln(1/T)}{d(1/T)}$

* $\ln(k/T) = \ln k + \ln(1/T)$

* recall $d(\ln u) = u^{-1} du$

if $u = 1/T$ $\quad \dfrac{d \ln(1/T)}{d(1/T)} = T$ Therefore,

$$\boxed{\Delta H^{\neq} = E_a - RT}$$

Hence, near ambient temperature, E_a is roughly 2.5 kJ-mol^{-1} larger than $\Delta H^{\neq}$.

It is also possible to derive a relationship between $\Delta S^{\ddagger}$ (Eyring) and A (Arrhenius).

$$\text{i.e.,} \quad k = Ae^{-E_a/RT} = \frac{RT}{Nh} e^{\Delta S^{\ddagger}/R} \cdot e^{-\Delta H^{\ddagger}/RT}$$

Substituting $\Delta H^{\ddagger} = E_a - RT$

$$Ae^{-E_a/RT} = \frac{RT}{Nh} e^{\Delta S^{\ddagger}/R} \cdot e^{-(E_a - RT)/RT} \quad \text{and} \quad e^{RT/RT} = e$$

$$= \frac{eRT}{Nh} e^{\Delta S^{\ddagger}/R} \cdot e^{-E_a/RT}$$

Therefore, $$A = \boxed{\frac{eRT}{Nh}} e^{\Delta S^{\ddagger}/R}$$

$$\frac{2.718 \times 8.314 \text{ J/mol-K} \times 298 \text{ K}}{6.02 \times 10^{23} \text{ mol}^{-1} \times 6.626 \times 10^{-34} \text{ J-sec}}$$

$$= 1.69 \times 10^{13} \text{ sec}^{-1}$$

NOTE: When $\Delta S^{\ddagger}$ is minus, A must be less than 1.69×10^{13} sec^{-1}, and when $\Delta S^{\ddagger}$ is positive, A will be larger than $1.69 \times 10^{+13}$ sec^{-1}.

The exponential energy term is usually so dominant that the differences is using $n = 0$, $1/2$, or 1 are negligible.

e.g., in a typical reaction whose rate at 300K roughly doubles over a 10deg. temperature increase. U $\approx$ 50 kJ/mol or 12 kcal/mol

$$\frac{k_{310}}{k_{300}} = \left(\frac{310}{300}\right)^n \exp\left[\frac{U}{R}\left(\frac{1}{300} - \frac{1}{310}\right)\right], \quad \text{for } n=0 \text{ ratio} = 1.91$$

$$n = 1/2 \quad = 1.94$$

$$n = 1 \quad = 1.97$$

Clearly, the exponential term is dominant.

Let's now consider the temperature dependence of composite rate constants.

It is common to encounter rate expressions in which the experimental rate constant is a composite of the rate constants and/or equilibrium constants for several reactions.

Consider two mechanisms for the net reaction $A \rightarrow C$.

(a) $A \rightleftharpoons B$, $K_1 \ll 1$ $\qquad K_1 = \frac{[B]}{[A]}$ or $[B] = K_1[A]$

$B \xrightarrow{k_2} C$ the rate-limiting step

$-\frac{d[A]}{dt} = k_2 K_1 [A]$, see the form of the temperature dependence below:

$$k_{apparent} = k_2 K_1 = \left(\frac{RT}{Nh}\right) \exp\left(\frac{\Delta S_2^{\neq}}{R}\right) \exp\left(-\frac{\Delta H_2^{\neq}}{RT}\right) \exp\left(\Delta S_1^{\circ}/R\right) \exp\left(-\Delta H_1^{\circ}/RT\right)$$

*recall, $K_{eq} = K_1 = e^{-\Delta G^{\circ}/RT}$ and $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$

Combining terms $\Rightarrow$

$$k_{apparent}/T = \frac{k_2 K_1}{T} = \frac{R}{Nh} \exp\left(\frac{\Delta S_1^{\circ} + \Delta S_2^{\neq}}{R}\right) \exp\left(\frac{-(\Delta H_1^{\circ} + \Delta H_2^{\neq})}{RT}\right)$$

a plot of $\ln k_{app}/T$ vs $\frac{1}{T}$ will be linear

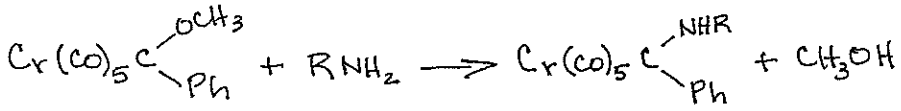
The apparent enthalpy of activation ($-R \cdot$ slope) is the sum of ΔH_1° and $\Delta H_2^{\neq}$. If ΔH_1° for the equilibrium step is negative, the observed enthalpy of activation will be lower than the value of $\Delta H_2^{\neq}$ for the rate limiting step. *Remember $\Delta H^{\neq}$ is always positive.

* However, occasionally a negative value of $\Delta H^{\neq}_{obsd}$ may result, and the reaction rate actually decreases with increasing temperature.

Indeed, we observed this behavior in a dramatic way while doing some chemistry in the early 70s on metal carbonyl carbene derivatives where the reaction did not take place at ambient temperature, but occurred rapidly at dry ice temperature.

i.e., aminolysis of a Fischer carbene complex (E.O. Fischer, JOMC, 28, 367 (1971)).

1973 Nobel Prize in Chemistry



a fourth-order rate law was observed $= k_{app}[\text{Cr complex}][RNH_2][HX][Y]$

RNH_2 represents a proton donor; Y represents a proton acceptor

Reaction carried out in decane: $HX = Y = RNH_2$

in CH_3OH, $HX = CH_3OH$ or $RNH_2 = Y$

in dioxane, $HX = RNH_2$, $Y = RNH_2$ or $C_4H_8O_2$

* The results of the kinetic study are consistent with a consecutive step mechanism which starts with the formation of a 1:1 adduct of the carbene complex and the proton donor HX and includes the activation of the attacking amine by the proton acceptor Y.

$$\text{rate} = k K_1 K_2 [\text{Cr complex}][RNH_2][HX][Y]$$

$$[\text{Cr complex}] + HX \overset{K_1}{\rightleftharpoons} A$$

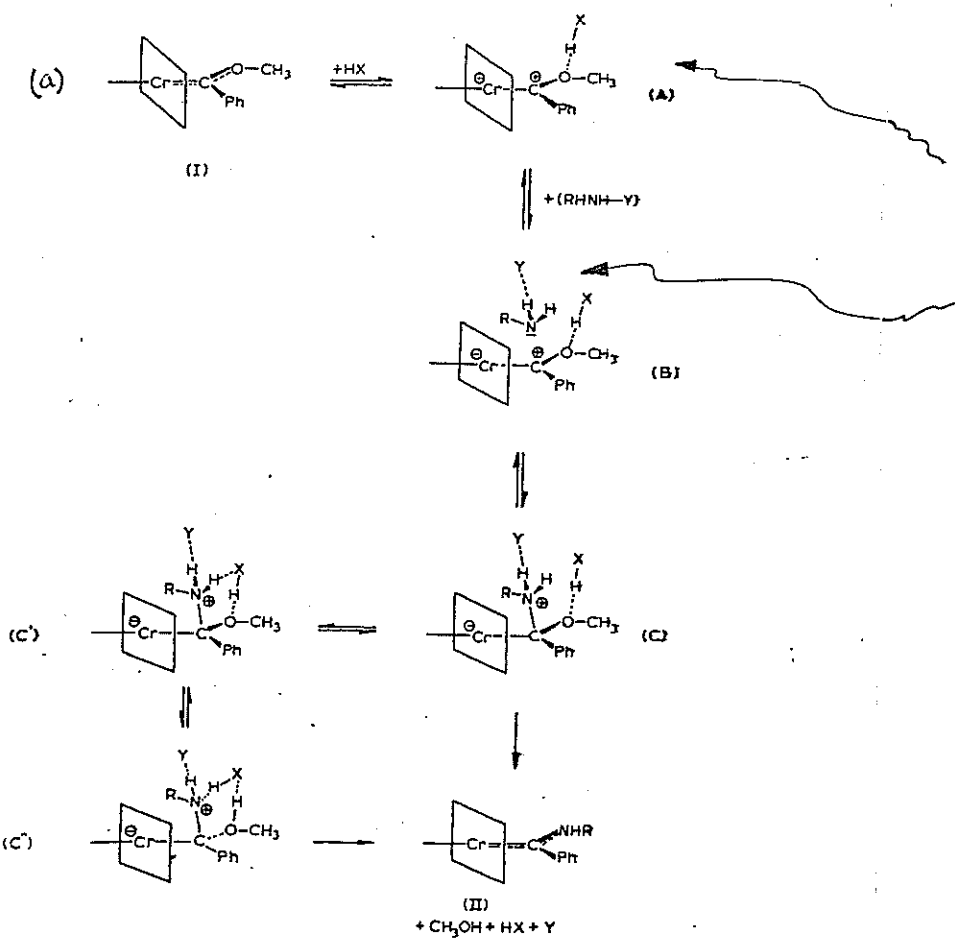
$$RH_2 + Y \overset{K_2}{\rightleftharpoons} (RNH_2 \cdots Y)$$

in decane

$\Delta H^{\neq}_{app} = -7.9$ kcal/mol

$\Delta S^{\neq}_{app} = -82.3$ e.u.

* Reaction is fast at T = 195 K and no reaction at ambient temperature.



The existence of these hydrogen bonds were shown by NMR studies

Y could be dioxane or methanol also

(b) A mechanism which consists of parallel pathways for the reaction of A

$$A \xrightarrow{k_3} C \quad \text{and} \quad A \xrightarrow{k_4} B$$

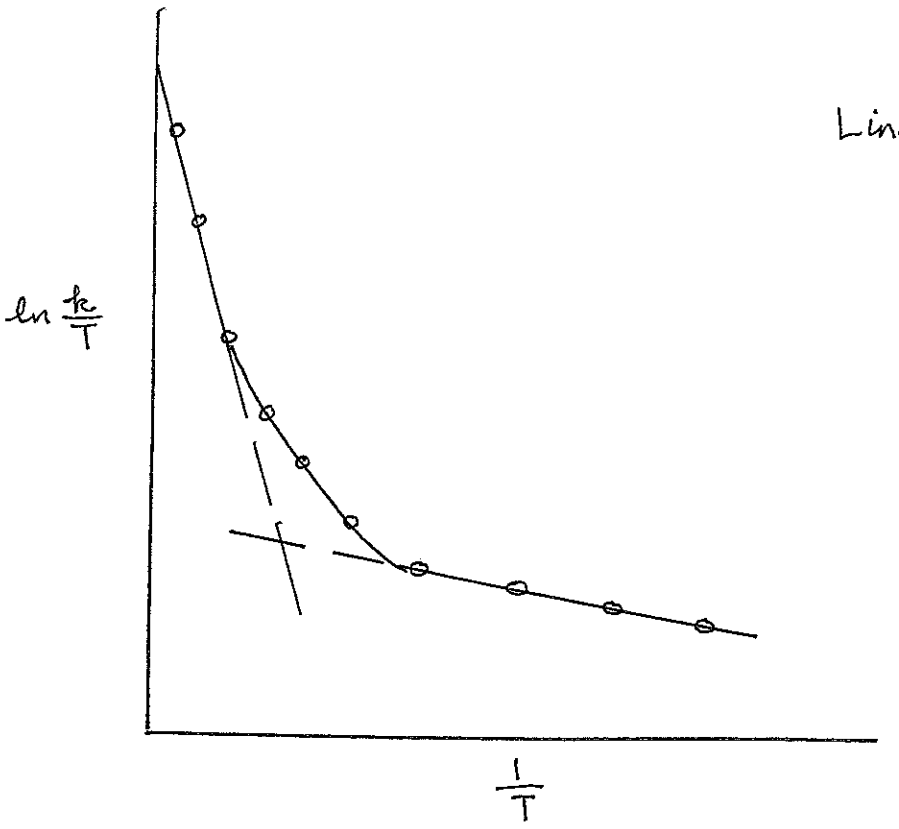
$$B \longrightarrow C \text{ (fast)}$$

$$-\frac{d[A]}{dt} = (k_3 + k_4)[A]$$

If we substitute for k_3 and k_4 a composite rate constant k_{34}

$$\frac{k_{34}}{T} = C_1 \exp\left(-\frac{\Delta H_3^{\ddagger}}{RT}\right) + C_2 \exp\left(-\frac{\Delta H_4^{\ddagger}}{RT}\right)$$, the Eyring equation

The rate constant having the larger value of $\Delta H^{\ddagger}$ will rise more steeply with increasing temperature, until at some value of T, it will effectively dominate; by analogy, the rate constant having the lower value of $\Delta H^{\ddagger}$ will dominate at lower temperature.



Linear over short ranges of temperature.

Summary =

- $\Delta H^{\ddagger}$ reflects bond strength differences within or between reactants. In general, the larger the value of $\Delta H^{\ddagger}$, the slower the reaction.

* An increase of 5.7 kJ/mol (or 1.36 kcal/mol) in $\Delta H^{\ddagger}$ corresponds to a factor of 10 in rate constant at ambient temperature.

If the reaction occurs with a value of $\Delta H^{\ddagger}$ much less than the dissociation energy of a particular group in the molecule, you can generally conclude that the bond to this group has not been broken during the activation process.

If $\Delta H^{\neq}$ and k are reliable parameters at a given T, $\Delta S^{\neq}$ can be obtained by simply rearranging the equation (1).

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

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

Hence, a plot of $T \times \ln \frac{k}{T}$ vs T $\Rightarrow$ $\Delta S^{\neq}$ from slope and $\Delta H^{\neq}$ from intercept

extrapolation to T = 0 K (unreliable?)

$$\nabla(\Delta S^{\neq}) = \frac{1}{T_{ave}} \nabla(\Delta H^{\neq})$$
$$= \nabla(\Delta H^{\neq}) \times 0.003\ K^{-1}$$

Diffusion Controlled Reactions

Some bimolecular reactions are successful at every encounter, e.g., radical combinations. Their rates are dependent mainly on the viscosity of the solvent.

* Assumes two spherical species colliding

$$k = \frac{8RT}{3000\eta}$$

η ← viscosity (poise = g/sec-cm)

k ← second-order rate constant (liter/mol-sec)

J = 10^7 ergs

R = 8.31×10^7 ergs/mol-K

erg = Newton – m
= kg·m/sec² × m

k at 300°K
$$= \frac{8 \times 8.31 \times 10^7 \left(\text{kg} \cdot \text{m}/\text{sec}^2 \times \text{m}\right)(300\text{K})}{3000\,(10\ \text{g/sec-cm})}$$
$$= 6.65 \times 10^9\ \text{liter/mol-sec}$$

liter = $1000\ \text{cm}^3$
kg = 1000 g

- $\Delta S^{\neq}$ includes contributions from requirements imposed by the orientation and steric bulk of the reactants and by their solvation.

(a) A unimolecular reaction may have $\Delta S^{\neq}$ near zero owing to the lack of orientational factor (loss of internal degrees of freedom in the transition state).

(b) If the activation process involves dissociation, e.g., bond breaking within a single species, a large and positive value of $\Delta S^{\neq}$ is likely.

(c) The contribution of $\Delta S^{\neq}$ includes the negative value resulting from bringing two separate reactants each with 1 mol/dm^3 conc. ~ -11 J-mol^{-1}/K.

(d) The more negative the value of $\Delta S^{\neq}$, the lower the reaction rate, decreasing by a factor of 10 for a decrease of -19 J-mol^{-1}/K in $\Delta S^{\neq}$.

$\times$ 300 K = 5.7 kJ.

A common misconception about the Eyring equation

See, *New J. Chem.* **2005**, *29*, 759-760, also ESI.

"The value of the entropy of activation is unreliable because it is calculated by extrapolation to infinite temperature."

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

k_B = Boltzmann's constant $= \frac{R}{N}$ $= 1.38 \times 10^{-23}$ J/K

$$\ln \frac{k}{T} = -\frac{\Delta H^{\neq}}{RT} + \frac{\Delta S^{\neq}}{R} + \ln \frac{k_B}{h}$$

Plot of $\ln \frac{k}{T}$ vs $\frac{1}{T}$ $\Rightarrow$ $\Delta H^{\neq}$ from slope and $\Delta S^{\neq}$ from intercept.

Temperature range studied is usually narrow (20-30°).

For typical reactions in organic solvents at 25°C, $k \sim 10^9 - 10^{10}$, and for typical diffusion controlled reactions, apparent activation energies are 2 to 3 kcal/mol (8-12 kJ/mol). * For reactions with activation energies > 10 kcal/mol or 41 KJ/mol, viscosity usually will have no effect until a glassy state is reached.

$\eta \approx 10.3$ (17°C) for organics

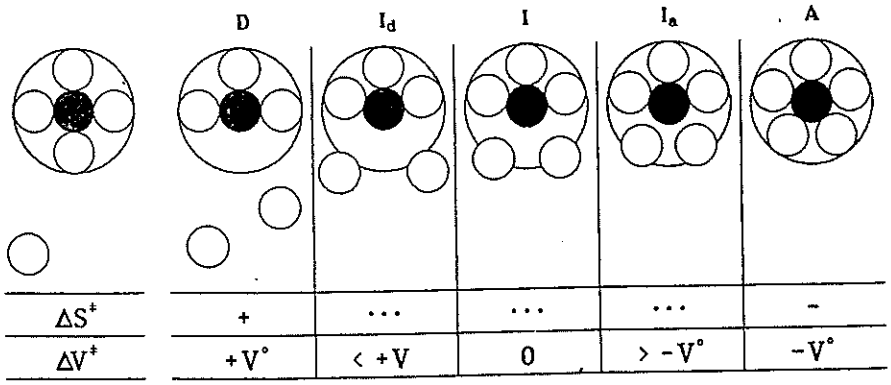
≈ 10.1 (20°C) for H_2O

Typical rate constants are:

	$10^{-10} k$ (20°C)
$n\text{-}C_6H_{14}$	2.1
C_6H_6	1.0
CCl_4	0.67
C_2H_5OH	0.55

Volume of Activation

$\Delta V^{\neq}$ partial molar volume of TS − partial molar volume of the reactants.



large circles are boundries of coordination sphere.

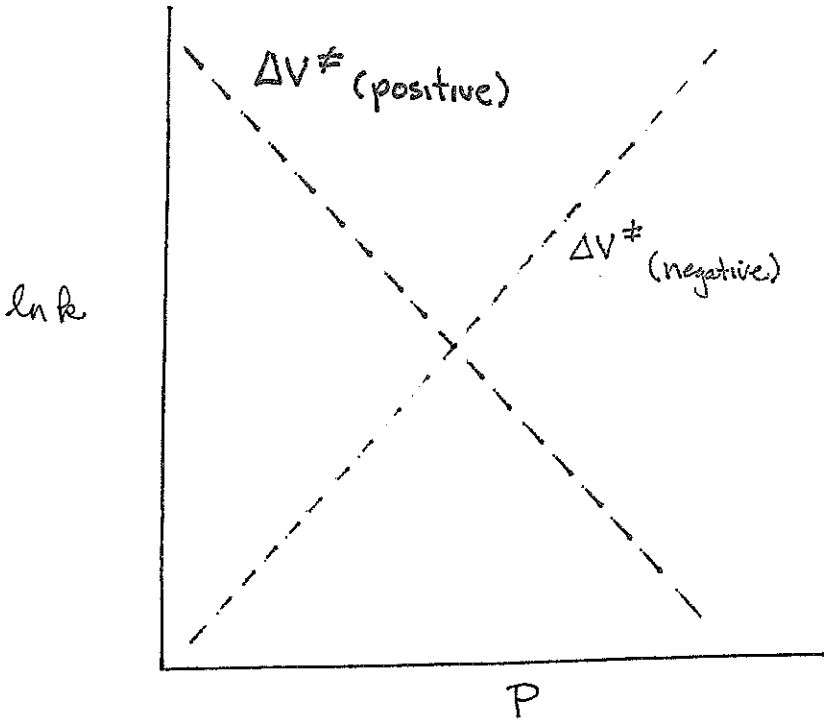
Figure 6.3. Schematic representation of solvent exchange reactions proceeding by different mechanisms. The small black circle in the middle of the idealized "flat" complex represents the central atom. The small open circles represent the bound and free ligands (solvent molecules). The large circles enclosing the small ones represent the boundaries of the first coordination sphere. For a *D* mechanism, the entropy and volume of activation are positive; for an *A* mechanism they are negative. V° is the solvent molar volume.

$$\left(\frac{d \ln k}{dP}\right)_T = \frac{-\Delta V^{\neq}}{RT} \qquad P=0 \rightarrow P$$

Need very large changes in pressure to compress a liquid, e.g., 0.1 MPa → 170 MPa

1 atm.

On the other hand for temperature changes, 20–40 deg.



OPINION

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A common misconception about the Eyring equation†

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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.

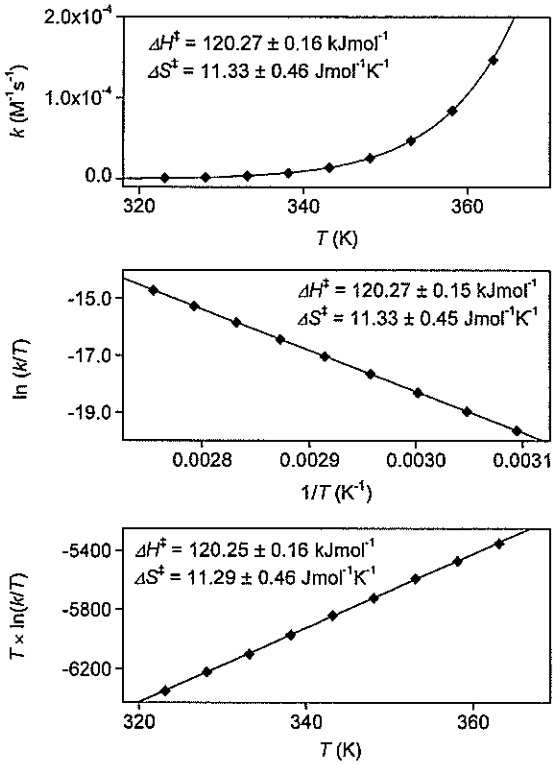

Fig. 1 Eyring plots according to eqn (1)–(3).

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

† 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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References

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2 J. H. Espenson, in *Chemical Kinetics and Reaction Mechanisms*, McGraw-Hill, New York, 1995, 2nd edn., p. 158.
3 A. J. Poë, in *Mechanisms of Inorganic and Organometallic Reactions*, ed. M. V. Twigg, Plenum Press, New York, 1994, vol. 8, ch. 10, p. 220.
4 G. Lente and I. Fábián, *Inorg. Chem.*, 2004, **43**, 4019.

Supplementary Material (ESI) for New Journal of Chemistry

Supplementary Information
for

A common misconcept about the Eyring Equation

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Original data for the example used in the main text

Chemical reaction: $H^+ + S_2O_6^{2-} = H_2O\ SO_2 + HSO_4^-$

Values of rate constants:

T (°C)	T (K)	k ($M^{-1}s^{-1}$)
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	$\Delta H^\ddagger$ (kJ mol^{-1})	$\Delta S^\ddagger$ (J mol^{-1} 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.

Mathemathical derivation of equation (4)

Rate constants k_1, k_2, k_3, ... are measured at temperatures T_1, T_2, T_3, ... 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:

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

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

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

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, $s_x << n \times x^2$, 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

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

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Summary

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  If the reaction occurs with a value of $\Delta H^{\ddagger}$ much less than the dissociation energy of a particular group in the molecule, you can generally conclude that the bond to this group has not been broken during the activation process.

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  (a) A unimolecular reaction may have $\Delta S^{\ddagger}$ near zero owing to the lack of orientational factor (loss of internal degrees of freedom in the transition state).
  (b) If the activation process involves dissociation, e.g., bond breaking within a single species, a large and positive value of $\Delta S^{\ddagger}$ is likely.
  (c) The contribution of $\Delta S^{\ddagger}$ includes the negative value resulting from bringing two separate reactants each with 1 mol/dm^3 conc. ~ -11 J-mol^{-1}/k.
  (d) The more negative the value of $\Delta S^{\ddagger}$, the lower the reaction rate, decreasing by a factor of 10 for a decrease of -19 J-mol^{-1}/k (19 x 300 K = 5.7 kJ) in $\Delta S^{\ddagger}$.