Arrhenius Temperature Dependence

The Arrhenius "law" is an empirical description of the T dependence of the rate constant:

$$k = A \, e^{-E_a / RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$\ln k$

$1/T$

The pre-exponential factor is often interpreted as a collision rate.

Collision theory predicts $T^{\frac{1}{2}}$ dependence for A.

Transition-state theory predicts linear T dependence for A.

The exponential factor describes the fraction of collisions with sufficient energy for reaction, as predicted by the Boltzmann distribution

$n(E)$

E_a

E

Curvature in the Arrhenius plot is often attributed to tunneling, but there are many other potential reasons.

$\ln k$

$1/T$
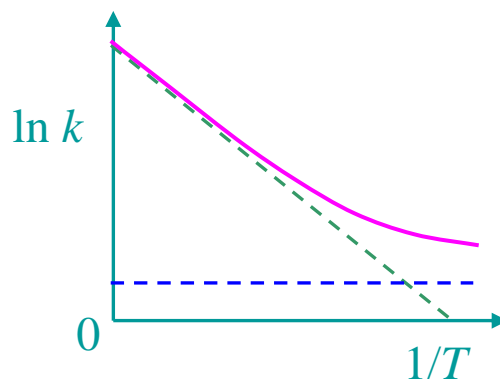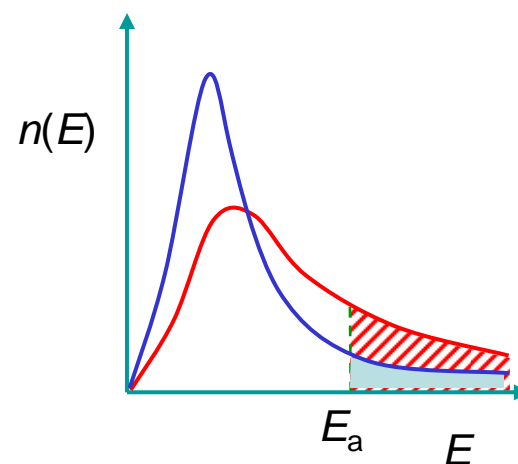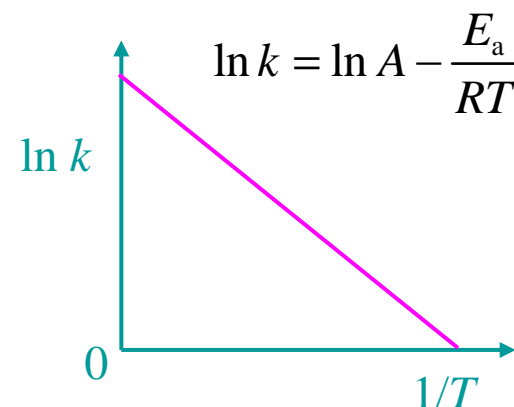
Empirical Temperature Dependence

Activation energy is defined by $E_a = RT^2 \dfrac{d \ln k}{dT}$

If theory predicts $k = A_{th} T^m \, e^{-E_{th}/RT}$ $\ln k = \ln A_{th} + m \ln T - \dfrac{E_{th}}{RT}$

the empirical parameters are $E_a = E_{th} + mRT$ $A = A_{th} T^m \exp\{(E_a - E_{th})/RT\}$

Simple Collision Theory $k = p Z(T) e^{-E_{min}/RT} = p(\pi\sigma^2) \sqrt{\dfrac{8RT}{\pi\mu}} \, e^{-E_{min}/RT}$

Transition State Theory $k = \dfrac{RT}{Lh} K_c^{\ddagger} = \dfrac{RT}{Lh} \dfrac{1}{c_0} e^{\Delta S^{\ddagger}/R} \, e^{-\Delta H^{\ddagger}/RT}$
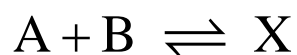
$E_a = \Delta U^{\ddagger} + RT = \Delta H^{\ddagger} - \Delta\nu RT + RT$ for gases

Unimolecular gas reaction: $E_a = \Delta H^{\ddagger} + RT$ $A = \dfrac{e \, RT}{hL} e^{\Delta S^{\ddagger}/R}$

Bimolecular gas reaction: $E_a = \Delta H^{\ddagger} + 2RT$ $A = \dfrac{e^2 \, RT}{hLc_0} e^{\Delta S^{\ddagger}/R}$

Liquid phase reaction: $E_a = \Delta H^{\ddagger} + RT$ $A = \dfrac{e \, RT}{hLc_0} e^{\Delta S^{\ddagger}/R}$

Thermodynamic Formulation of TST

$$A + B \rightleftharpoons X$$

For gases, $\quad \Delta G° = -RT \ln K°$ $\quad$ where $\quad$ $K° = \dfrac{(p_X / p°)}{(p_A / p°)(p_B / p°)}$

Substitute into the Eyring Equation:

$$= K_c \left(\frac{p°}{RT} \right) \qquad \frac{p}{p°} = \frac{nRT}{Vp°} = c \left(\frac{RT}{p°} \right)$$
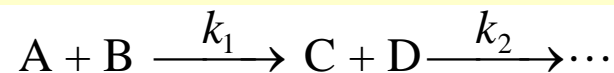
$$k_2 = \kappa \left(\frac{RT}{hL} \right) K_c^{\ddagger} = \kappa \left(\frac{RT}{hL} \right) \left(\frac{RT}{p°} \right) K^{\ddagger}$$

$$= \kappa \left(\frac{RT}{hL} \right) \left(\frac{RT}{p°} \right) e^{-\Delta G^{\ddagger}/RT} = \left(\frac{RT}{hL} \right) \left(\frac{RT}{p°} \right) e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT}$$

Since $\quad E_{act} = \Delta U^{\ddagger} + RT = \Delta H^{\ddagger} + 2RT \quad$ (for gases only)

$$k_2 = \left\{ e^2 \left(\frac{RT}{hL} \right) \left(\frac{RT}{p°} \right) e^{\Delta S^{\ddagger}/R} \right\} e^{-E_{act}/RT}$$

Temperature Dependence of Complex Reactions

Assume some complex reaction for which the overall reaction rate constant can be expressed in terms of the elementary steps:

$$A + B \xrightarrow{\ k_1\ } C + D \xrightarrow{\ k_2\ } \cdots$$

$$k_{\text{overall}} = \frac{k_1^{n_1} k_2^{n_2} \cdots}{k_3^{n_3} \cdots}$$

If each rate constant obeys the Arrhenius expression,

$$k_i = A_i \, e^{-E_i/RT}$$

$$k_{\text{overall}} = \left(\frac{A_1^{n_1} A_2^{n_2} \cdots}{A_3^{n_3} \cdots} \right) \exp\left\{ -(n_1 E_1 + n_2 E_2 - n_3 E_3 - \ldots)/RT \right\}$$

i.e. The Arrhenius parameters are

$$A_{\text{overall}} = \prod_i A_i^{n_i} \qquad E = \sum_i n_i E_i$$

The overall "activation energy" may be negative, if one or more n_i is negative and the corresponding E_i is large enough.

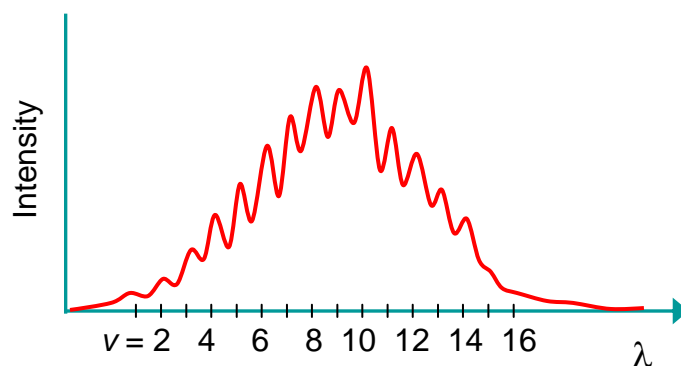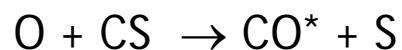Also, for a pre-equilibrium reaction where

$$k_{\text{overall}} = K_1 k_2$$

$$E_a = RT^2 \frac{d \ln k_{\text{overall}}}{dT} = RT^2 \frac{d \ln K_1}{dT} + E_2 = \Delta H_1 + E_2$$

E_2 is positive but ΔH can be negative.

Chemiluminescence

e.g. IR emission
from the reaction

$O + CS \rightarrow CO^* + S$

CO* is
vibrationally
excited

Useful for measurement of microscopic (state-to-state) rate constants

Typical results: relative $k(v)$ for product HX

	$v =$	1	2	3	4
$H + Cl_2 \rightarrow HCl + Cl$		0.28	1.00	0.92	0.08
$H + Br_2 \rightarrow HBr + Br$		0.10	0.19	1.00	0.88
$F + H_2 \rightarrow HF + H$		0.31	1.00	0.48	
$Cl + HI \rightarrow HCl + I$		0.18	0.32	1.00	0.74

Basis for chemical lasers (John Polanyi, Nobel Prize 1986)

State-to-State Reactions

Rotational as well as vibrational excitation is possible.
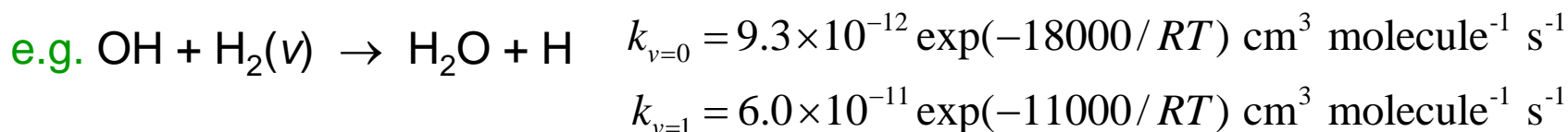
e.g. for $F + H_2 \rightarrow HF + H$
the excess energy is partitioned

67% vibrational
7% rotational
26% translational

Reaction from selective states is also possible, but even if the reactant states are in thermal equilibrium, non-Arrhenius behaviour is expected.

e.g. $OH + H_2(v) \rightarrow H_2O + H$

$$k_{v=0} = 9.3 \times 10^{-12} \exp(-18000/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{v=1} = 6.0 \times 10^{-11} \exp(-11000/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
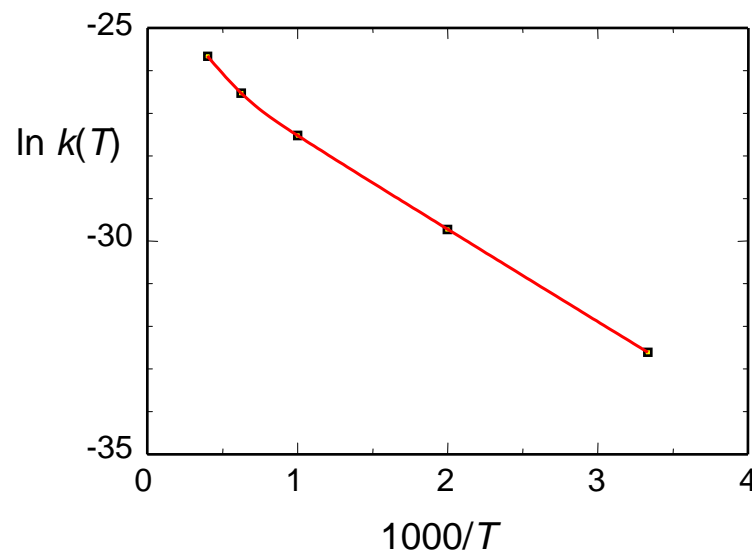
The populations of the H_2 states are

$$f_{v=0} = \frac{1}{1 - e^{-\Delta E/RT}} \quad \text{and} \quad f_{v=1} = \frac{e^{-\Delta E/RT}}{1 - e^{-\Delta E/RT}}$$
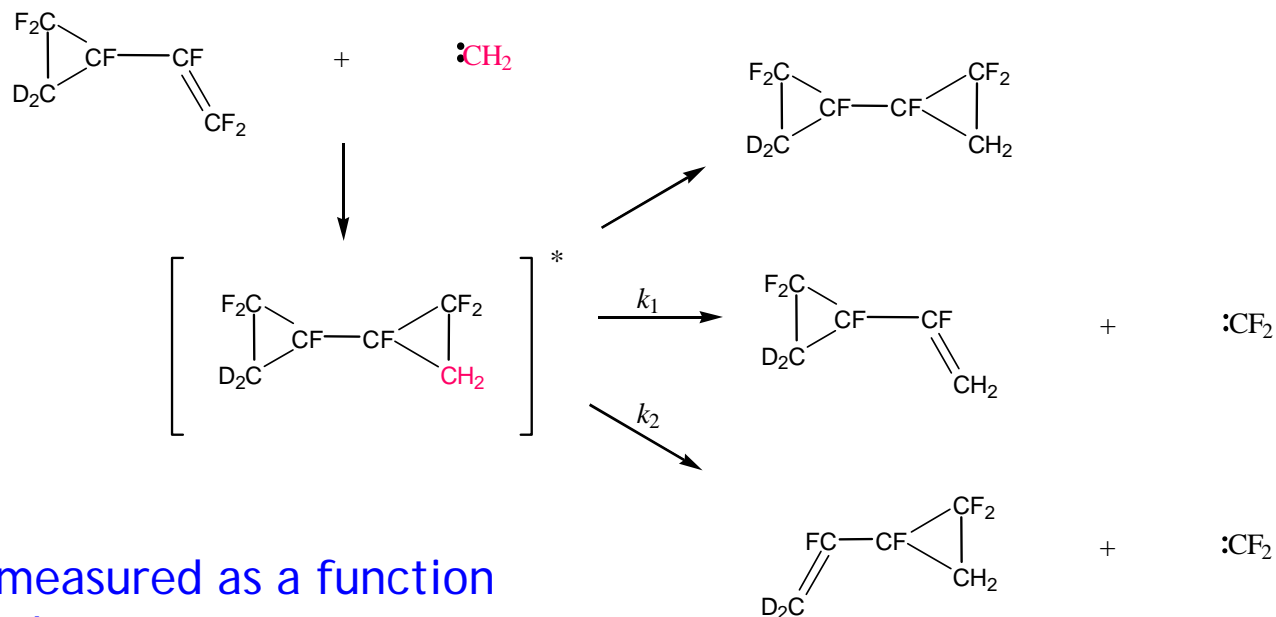
$$\Delta E = 49.6 \text{ kJ mol}^{-1}$$

and the effective thermal rate constant is

$$k(T) = f_{v=0} \, k_{v=0} + f_{v=1} \, k_{v=1}$$

Time-scale for Energy Flow in a Molecule

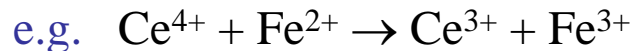k_1/k_2 was measured as a function of pressure by mass spectrometry.

At low pressure $\dfrac{k_1}{k_2} = 1$

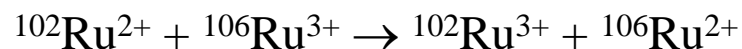At high pressure $\dfrac{k_1}{k_2} > 1$

Not enough time for energy to flow from right to left before reaction or deactivation.

Conclusion: $\tau \sim 10^{-12}$ s
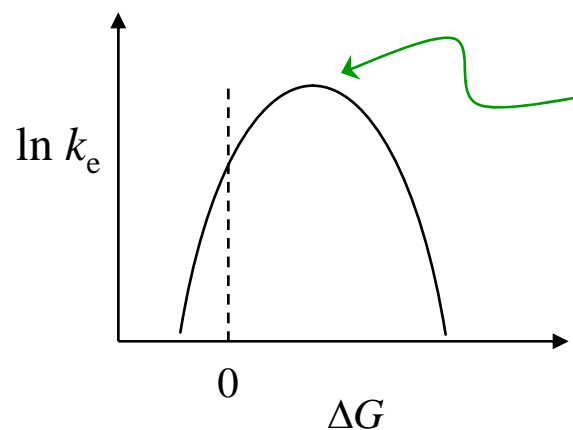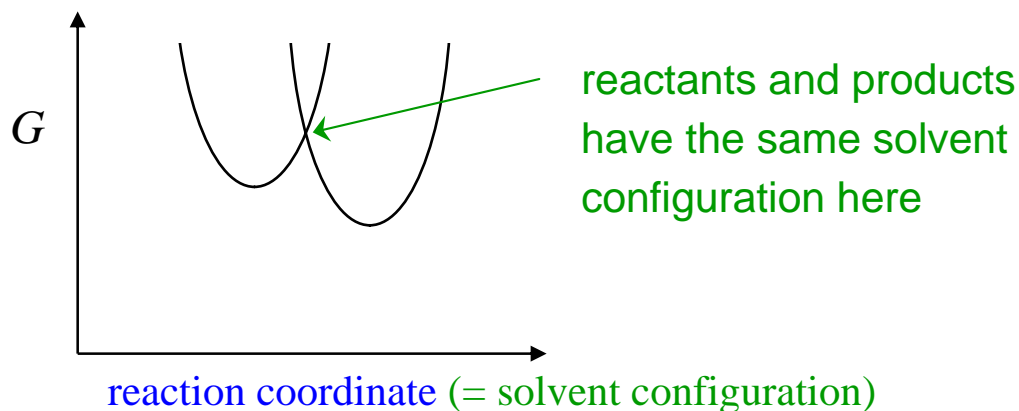
Electron Transfer Reactions in Solution

e.g. $Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$

$\Delta G^{\mathrm{o}} \neq 0$

$^{102}Ru^{2+} + {}^{106}Ru^{3+} \rightarrow {}^{102}Ru^{3+} + {}^{106}Ru^{2+}$

$\Delta G^{\mathrm{o}} = 0$

Reaction is slow if solvent reorganization is required in the TS.

Marcus Theory

Nobel Prize 1992

$$k_{\mathrm{e}} = A\exp\left\{ \frac{-\lambda}{4RT}\left(1 + \frac{\Delta G^{\mathrm{o}}}{\lambda}\right)^2 \right\}$$

reactants and products have the same solvent configuration here

G

reaction coordinate (= solvent configuration)

$\ln k_{\mathrm{e}}$

0

ΔG

k_{e} is a maximum when $\Delta G^{\mathrm{o}} = -\lambda$, the solvent reorganization term.

$\Delta G^{\ddagger} = 0$

G

λ

reaction coordinate