Lecture 31  Chapt 26.7-8

Announce:
• Seminar today

Outline:
temperature dependence of rates
transition state theory
elementary reactions
detailed balance
sequential (series) reactions

Review
can use isolation or initial rates to solve for rate law exponents.
initial rates:

\[ v_1 = -\frac{1}{V_A} \left( \frac{\Delta A}{\Delta t} \right)_1 = k[A]^m[B]^n \]

\[ v_2 = -\frac{1}{V_A} \left( \frac{\Delta A}{\Delta t} \right)_2 = k[A]^m[B]^n \]

Dividing these two equations gives:

\[ \frac{v_1}{v_2} = \left( \frac{[B_1]}{[B_2]} \right)^{m_B} \quad \text{or} \quad m_B = \ln \left( \frac{v_1}{v_2} \right) \ln \left( \frac{[B_1]}{[B_2]} \right) \]

Derivation of rate law and half-life for any reaction order
\[ d[A] = k[A]^m \, dt \]
rearrange so you can integrate (limits \([A_0]\) to \([A]\) and 0 to \(t\))
to get half-life, set \([A] = \frac{1}{2}[A_0]\)

Reversible reactions:

\[ -\frac{d[A]}{dt} = (k_1 + k_{-1})[A] - k_{-1}[A]_0 \]
can find sum of rates

\[ \frac{k_1}{k_{-1}} = \frac{[Z]_{eq}}{[A]_{eq}} = K_{eq} \]
can find ratio
**Temperature dependence of rates**

Empirically, we find that most reaction rates depend very strongly on temperature. Much more than you would expect just from the collision rates of molecules. From empirical studies,

\[
\frac{d \ln k}{dT} = \frac{const}{RT^2}
\]

This constant behaves like energy, and we call it activation energy.

\[
\frac{d \ln k}{dT} = \frac{E_a}{RT^2}
\]

or

\[
\frac{d \ln k}{d\left(\frac{1}{T}\right)} = -\frac{E_a}{R}
\]

This integrates to

\[
\int d(\ln k) = \frac{E_a}{R} \int T^{-2}dT
\]

\[
\ln k = -\frac{E_a}{RT} + \text{Const}(\ln A)
\]

\[
k = Ae^{-\frac{E_a}{RT}}
\]

(Arrhenius 1889)

The constant \(A\) is called the pre-exponential factor. \(E_a\) is the (internal \(U\)) energy difference between reactants and the transition state along a coordinate called the reaction coordinate. For something like \(I_2\) dissociating it is the I-I bond length. For other reactions it is a complex collection of coordinates.
Transition state theory

There are a number of theories for reaction kinetics. One of the more successful simple theories is transition state theory. In it, we assume that the transition state lives long enough to be in equilibrium with the reactants.

Define the equilibrium between ‡ and reactants (A and B)

\[
K^\ddagger = \frac{[‡]}{[A][B]} = \frac{[‡]c^0}{[A][B]c^0} \quad \text{or} \quad [‡] = \frac{K^\ddagger[A][B]}{c^0}
\]

Also define a frequency with which transition states cross over barrier to products (this is just a first order rxn of transition state to products. \(f\) is rate constant)

\[
v(t) = \frac{d\text{products}}{dt} = f[‡] = \frac{fK^\ddagger[A][B]}{c^0}
\]

assuming we have a simple rate law, \(v = k[A][B]\) and then \(k = \frac{fK^\ddagger}{c^0}\)

From lots of statistical mechanics, partition functions… \(f = \frac{k_BT}{\hbar}\)

The frequency factor (yes \(h\) is Planck’s constant). This is not a trivial result. Your text derives this for you, though they don’t point it out. It depends on three important assumptions:

1) Molecules in transition state obey Maxwell-Boltzmann statistics with the reactants (and among themselves).
2) Molecules that have crossed barrier cannot turn around and recross.
3) Motion along the reaction coordinate may be separated from other motions and treated classically as translation.

Finally, the free energy difference can be related to the equilibrium constant just like we did a few chapters ago…

\[
\Delta G^\ddagger = -RT \ln K^\ddagger
\]

so \(K^\ddagger = e^{-\Delta G^\ddagger/RT}\)
Plugging back in
\[ k = \frac{k_B T}{\hbar c^0} e^{-\Delta G^\ddagger / RT} = \frac{k_B T}{\hbar c^0} e^{\frac{\Delta S^\ddagger}{R}} e^{-\Delta H^\ddagger / RT} \]

This is the Eyring equation (also simultaneously Evans and Polanyi)

Another detail from statistical mechanics relates the activation energy to enthalpy:

\[ E_a = \Delta^t H + 2RT \]

or

\[ \Delta^t H = E_a - 2RT \]

The factor of 2 is related to the change in # moles. Depending on the exact derivation, this number sometimes is 1, or even 0 ($E_a \gg 2RT$ is often valid). ($\Delta n$ through $\Delta H = \Delta U + \Delta(PV) = \Delta U + \Delta nRT.$) If we keep the 2RT term:

\[ k = \frac{e^2 k_B T}{\hbar c^0} e^{\frac{\Delta S^\ddagger}{R}} e^{-\frac{E_a}{RT}} \]

or with assumption that 2RT is negligible compared to $E_a$ and that $c^0 = 1$:

\[ k = \frac{k_B T}{\hbar} e^{\frac{\Delta S^\ddagger}{R}} e^{-\frac{E_a}{RT}} \]

comparing to our empirical relation of Arrhenius gives:

\[ A = \frac{k_B T}{\hbar} e^{\frac{\Delta S^\ddagger}{R}} \text{ or } A = \frac{e^2 k_B T}{\hbar c^0} e^{\frac{\Delta S^\ddagger}{R}} \]

So, Arrhenius factor depends on entropy difference between reactants and transition state. Note that there is a temperature dependence in the Arrhenius prefactor, not just in the activation energy term (but linear factor is mild compared to exponential factor)