Week 4

Reaction Mechanisms

4.1 TST and Overview of Mechanisms

• More TST theory.

- We can intuitively rationalize concentration as q/V by thinking of the partition function in some way giving some information about the number of particles. When we divide this by V, we thus get *some* information about concentration.

- δ is the finite window in which the activated complex is loosely defined to exist.

- ν_c is the frequency of crossing the δ region in the energy diagram.

- We substitute $[\text{AB}^\ddagger] = [\text{A}][\text{B}]K_c^\ddagger/c^\circ$ from the equilibrium constant expression.

- The translational partition function plays a role. Note that $m^\ddagger$ is the mass of the activated complex.

$$q_{\text{trans}} = \frac{\sqrt{2\pi m^\ddagger k_\text{B} T}}{h}\delta$$

■ Dimensional analysis (as an analysis of units to help appreciate the term): $k_\text{B} T$ is energy ($E \propto mv^2/2$) and $m^\ddagger$ is mass, so their product is momentum squared ($p^2 \propto mv^2$).

■ Thus, the top of the expression gives momentum, and h/δ also gives momentum.

■ Remember that the momentum is rather like that of the particle in a box.

- We have that

$$q^\ddagger = q_{\text{trans}}^\ddagger \cdot q_{\text{int}}^\ddagger$$

where $q^\ddagger$ is the partition function for the whole species, which we can split.

- This permits

$$\begin{aligned}
K_c^\ddagger &= \frac{(q^\ddagger/V)c^\circ}{(q_\text{A}/V)(q_\text{B}/V)} \\
&= \frac{\sqrt{2\pi m^\ddagger k_\text{B} T}}{h}\delta\frac{(q_{\text{int}}^\ddagger/V)c^\circ}{(q_\text{A}/V)(q_\text{B}/V)}
\end{aligned}$$

and the following

$$k = \nu_c\frac{\sqrt{2\pi m^\ddagger k_\text{B} T}}{hc^\circ}\delta\frac{(q_{\text{int}}^\ddagger/V)c^\circ}{(q_\text{A}/V)(q_\text{B}/V)}$$

- We now define the speed of the activated complex crossing the barrier top (gas collision). This is $\langle u_{\text{ac}}\rangle$, where $\langle u_{\text{ac}}\rangle = \nu_c\delta$ (the frequency x distance).

- We have that

$$\langle u_{\mathrm{ac}} \rangle = \int_0^\infty u f(u) \, \mathrm{d}u = \sqrt{\frac{m^\ddagger}{2\pi k_{\mathrm{B}} T}} \int_0^\infty u \mathrm{e}^{-m^\ddagger u^2/2 k_{\mathrm{B}} T} \, \mathrm{d}u = \sqrt{\frac{k_{\mathrm{B}} T}{2\pi m^\ddagger}}$$

and the following

$$k = \frac{k_{\mathrm{B}} T}{hc^\circ} \frac{(q_{\mathrm{int}}^\ddagger/V)c^\circ}{(q_{\mathrm{A}}/V)(q_{\mathrm{B}}/V)} = \frac{k_{\mathrm{B}} T}{hc^\circ} K^\ddagger$$

  - We start at zero instead of $-\infty$ because we're only considering the forward direction of the reaction. If we did $-\infty$, we'd be accounting for the reverse reaction as well.
- Introducing $\Delta^\ddagger G^\circ = -RT \ln K^\ddagger = \Delta^\ddagger H^\circ - T\Delta^\ddagger S^\circ$ yields the **Eyring equation**

$$k(T) = \frac{k_{\mathrm{B}} T}{hc^\circ} \mathrm{e}^{-\Delta^\ddagger G^\circ/RT} = \frac{k_{\mathrm{B}} T}{hc^\circ} \mathrm{e}^{\Delta^\ddagger S^\circ/R} \mathrm{e}^{-\Delta^\ddagger H^\circ/RT}$$

- We can relate the Eyring equation to the Arrhenius equation by differentiating the logarithm.

$$\frac{\mathrm{d}\ln k}{\mathrm{d}T} = \frac{1}{T} + \frac{\mathrm{d}\ln K^\ddagger}{\mathrm{d}T} \qquad\qquad \frac{\mathrm{d}\ln K_c}{\mathrm{d}T} = \frac{\Delta U^\circ}{RT^2}$$

gives

$$\frac{\mathrm{d}\ln k}{\mathrm{d}T} = \frac{1}{T} + \frac{\Delta^\ddagger U^\circ}{RT^2}$$

- This all serves to relate thermodynamics and kinetics.
- Additionally, since $\Delta^\ddagger H^\circ = \Delta^\ddagger U^\circ + \Delta^\ddagger PV = \Delta^\ddagger U^\circ + \Delta^\ddagger nRT$, we have that

$$\frac{\mathrm{d}\ln k}{\mathrm{d}T} = \frac{\Delta^\ddagger H^\circ + 2RT}{RT^2}$$

  - Note that $\Delta n = -1$ for bimolecular gas phase reactions.
  - $\Delta(PV)^\ddagger$ is the difference in the number of moles of gaseous products and reactants.
  - $\Delta n^\ddagger = 0$: Unimolecular.
  - $\Delta n^\ddagger = -1$: Bimolecular.
  - $\Delta n^\ddagger = -2$: Trimolecular.
- Comparing with the Arrhenius $\mathrm{d}\ln k/\mathrm{d}T = E_a/RT^2$ gives

$$E_a = \Delta^\ddagger H^\circ + 2RT$$

- Substituting into the Eyring equation yields

$$k(T) = \frac{\mathrm{e}^2 k_{\mathrm{B}} T}{hc^\circ} \mathrm{e}^{\Delta^\ddagger S^\circ/R} \mathrm{e}^{-E_a/RT}$$

- Gas, uni: $E_a = \Delta H^\ddagger + RT$, $A = \mathrm{e} k_{\mathrm{B}} T/h \cdot \mathrm{e}^{\Delta S^\ddagger/R}$.
- Gas, bi: $E_a = \Delta H^\ddagger + 2RT$, $A = \mathrm{e}^2 k_{\mathrm{B}} T/hc^\circ \cdot \mathrm{e}^{\Delta S^\ddagger/R}$.
- Gas, tri: $E_a = \Delta H^\ddagger + 3RT$, $A = \mathrm{e}^3 k_{\mathrm{B}} T/h(c^\circ)^2 \cdot \mathrm{e}^{\Delta S^\ddagger/R}$.

- Important things to memorize from TST.

  - The Eyring equation.
  - Don't worry about the partition function mathematics, but understand the dimensional analysis.
    - Know that we collapse two $k_{\mathrm{B}} T$ terms together; one from q_{trans} and one from $\langle u_{\mathrm{ac}} \rangle$.

- Consider cyclohexane conformations.

- We have that

$$\Delta^{\ddagger}H^{\circ} = 31.38 \, \text{kJ} \, \text{mol}^{-1} \qquad \Delta^{\ddagger}S^{\circ} = 16.74 \, \text{J} \, \text{mol}^{-1} \, \text{K}^{-1} \qquad T = 325 \, \text{K}$$

- We want to know $\Delta^{\ddagger}G^{\circ}$.
- But by the definition of the Gibbs energy,

$$\Delta^{\ddagger}G^{\circ} = \Delta^{\ddagger}H^{\circ} - T\Delta^{\ddagger}S^{\circ} = 25.94 \, \text{kJ} \, \text{mol}^{-1}$$

- It follows that

$$k = \frac{k_{\text{B}}T}{h} e^{-\Delta^{\ddagger}G^{\circ}/RT} = 4.59 \times 10^8 \, \text{s}^{-1}$$

- Overview of key mechanism concepts.

  - Reaction mechanisms can involve more than one elementary step.
  - Reactions can be sequential (single- or multi-step).
  - To establish a mechanism, we use several techniques, approaches, assumptions, and approximations.
  - Establish rate determining steps: The rate law and rate constants associated with these steps tend to dominate the kinetics of the overall reaction.
  - Invoke the steady-state approximation to help solve the complicated mathematics of reaction kinetics.
  - Enzyme kinetics, Michaelis-Menten mechanism involves an SS approximation.

- Oftentimes, reactions are of the form

$$\text{E} + \text{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{ES} \xrightarrow{k_r} \text{P} + \text{E}$$
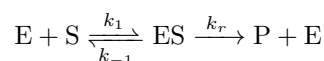
 - Note that this form is very much analogous to the form analyzed in TST.

- **Elementary reaction**: A reaction that does not involve the formation of a reaction intermediate; the products must be formed directly from the reactants.

  - Denoted by the double arrow.
  - An elementary reaction can still be reversible.

- **Molecularity** (of an elementary reaction): The number of reactant molecules involved in the chemical reaction.

- **Unimolecular** (reaction): An elementary reaction with molecularity one. *General form*

$$\text{A} \Longrightarrow \text{products}$$
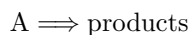
Rate law

$$v = k[\text{A}]$$

- **Bimolecular** (reaction): An elementary reaction with molecularity two. *General form*

$$\text{A} + \text{B} \Longrightarrow \text{products}$$
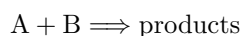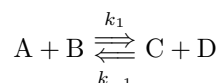
Rate law

$$v = k[\text{A}][\text{B}]$$

- **Termolecular** (reaction): An elementary reaction with molecularity three. *General form*

$$A + B + C \Longrightarrow \text{products}$$

  Rate law

$$v = k[A][B][C]$$

- No elementary reaction with molecularity greater than three is known, and the overwhelming majority of elementary reactions are bimolecular.

- When a complex reaction is at equilibrium, the rate of the forward process is equal to the rate of the reverse process for each and every step of the reaction mechanism.

  - We denote a reversible elementary reaction as follows.

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D$$

  - A reversible elementary reaction signifies that the reaction occurs in both the forward and reverse directions to a significant extent and that the reaction in each direction is an elementary reaction.
  - The rate laws are

$$v_1 = k_1[A][B] \qquad\qquad v_{-1} = k_{-1}[C][D]$$

  - At equilibrium,

$$k_1[A]_{eq}[B]_{eq} = k_{-1}[C]_{eq}[D]_{eq}$$
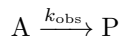
$$\frac{k_1}{k_{-1}} = \frac{[C]_{eq}[D]_{eq}}{[A]_{eq}[B]_{eq}} = K_c$$

- **Principle of detailed balance**: The following relationship, which holds for all reversible elementary reactions. *Given by*

$$K_c = \frac{k_1}{k_{-1}}$$

4.2   The Two-Step Consecutive Reaction Mechanism

4/20:
- Consider the general complex reaction

$$A \xrightarrow{k_{obs}} P$$

  - Suppose that the reaction occurs by the two step mechanism

$$A \xrightarrow{k_1} I \qquad\qquad\qquad I \xrightarrow{k_2} P$$

  - Because each step of this mechanism is an elementary reaction, the rate laws for each species are

$$\frac{d[A]}{dt} = -k_1[A] \qquad\qquad \frac{d[I]}{dt} = k_1[A] - k_2[I] \qquad\qquad \frac{d[P]}{dt} = k_2[I]$$

  - Thus, assuming that the initial concentrations at time $t = 0$ are $[A] = [A]_0$ and $[I]_0 = [P]_0 = 0$, we have that

$$[A] = [A]_0 e^{-k_1 t}$$

$$[I] = \frac{k_1[A]_0}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t})$$

$$[P] = [A]_0 - [A] - [I] = [A]_0\left\{1 + \frac{1}{k_1 - k_2}(k_2 e^{-k_1 t} - k_1 e^{-k_2 t})\right\}$$

- Distinguishing the two-step consecutive reaction mechanism unambiguously from the one-step reaction.

  - For a single step reaction,
  $$[P] = [A]_0(1 - e^{-k_1 t})$$

  - The two-step consecutive reaction mechanism has the following alternate form.

  $$[P] = [A]_0 \left\{ 1 + \frac{1}{k_1 - k_2}(k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right\}$$

  - However, if $k_2 \gg k_1$, then

  $$[P] = [A]_0 \left\{ 1 + \frac{1}{k_1 - k_2}(k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right\}$$
  $$\approx [A]_0 \left\{ 1 + \frac{1}{-k_2} k_2 e^{-k_1 t} \right\}$$
  $$= [A]_0(1 - e^{-k_1 t})$$

  - If $k_1 \gg k_2$, the reaction reduces to
  $$[P] \approx [A]_0(1 - e^{-k_2 t})$$

  - Thus, the only ambiguous situation is $k_2 \gg k_1$.

- The steady-state approximation simplifies rate expressions.

  - We assume that $d[I]/dt = 0$, where I is a reaction intermediate.
  - Given the above differential equation for $d[I]/dt$, making the above assumption yields
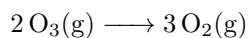 $$[I]_{SS} = \frac{k_1[A]}{k_2}$$

  - It follows that
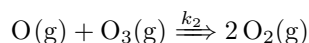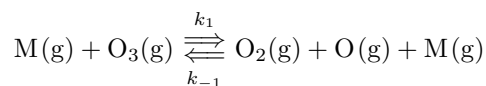 $$[I]_{SS} = \frac{k_1}{k_2}[A]_0 e^{-k_1 t}$$

  - Thus,
  $$\frac{d[I]_{SS}}{dt} = \frac{-k_1^2}{k_2}[A]_0 e^{-k_1 t}$$

  - We get $k_2 \gg k_1^2[A]_0$ and $[P] = [A]_0(1 - e^{-k_1 t})$.

- Example: Decomposition of ozone.
  $$2\,O_3(g) \longrightarrow 3\,O_2(g)$$

  - The reaction mechanism is

  $$M(g) + O_3(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2(g) + O(g) + M(g)$$

  $$O(g) + O_3(g) \overset{k_2}{\Longrightarrow} 2\,O_2(g)$$

  where M is a molecule that can exchange energy with the reacting ozone molecule through a collision, but M itself does not react.

  - The rate equations for $O_3(g)$ and $O(g)$ are
  $$\frac{d[O_3]}{dt} = -k_1[O_3][M] + k_{-1}[O_2][O][M] - k_2[O][O_3]$$
  $$\frac{d[O]}{dt} = k_1[O_3][M] - k_{-1}[O_2][O][M] - k_2[O][O_3]$$

– Invoking the steady-state approximation for the intermediate O yields

$$[O] = \frac{k_1[O_3][M]}{k_{-1}[O_2][M] + k_2[O_3]}$$

– Substituting this result into the rate equation for O_3 gives

$$\frac{d[O_3]}{dt} = -\frac{2k_1k_2[O_3]^2[M]}{k_{-1}[O_2][M] + k_2[O_3]}$$

4.3   Complex Reactions

4/22:
- Expect the midterm to be 2 hours in length, available all next week, and to incorporate largely HW-like questions but also some open-ended, design-an-experiment questions. Completely open note.

- The rate law for a complex reaction does not imply a unique mechanism.
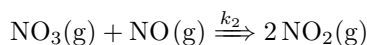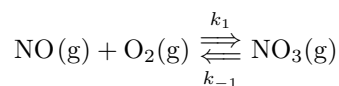
  – Consider the reaction
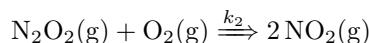 $$2\,NO\,(g) + O_2(g) \xrightarrow{k_{obs}} 2\,NO_2(g)$$
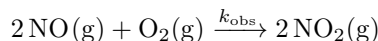
  – The rate law is
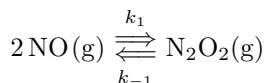 $$\frac{1}{2}\frac{d[NO_2]}{dt} = k_{obs}[NO]^2[O_2]$$

  – Experimental studies confirm that the reaction is not an elementary reaction, but we can propose multiple mechanisms that would both yield the same rate law. Here are two examples.
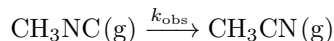
    ■ Mechanism 1.

    $$NO\,(g) + O_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_3(g)$$

    $$NO_3(g) + NO\,(g) \xrightarrow{k_2} 2\,NO_2(g)$$

    ■ Mechanism 2.

    $$2\,NO\,(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2(g)$$

    $$N_2O_2(g) + O_2(g) \xrightarrow{k_2} 2\,NO_2(g)$$

  – One experiment to design is to capture or otherwise detect the intermediate species.
  – Through such an experiment, we can verify Mechanism 2.

- The Lindemann Mechanism explains how unimolecular reactions occur.

  – Consider the reaction
  $$CH_3NC\,(g) \xrightarrow{k_{obs}} CH_3CN\,(g)$$

  – The following rate law is only correct at high $[CH_3NC]$.

  $$\frac{d[CH_3NC]}{dt} = -k_{obs}[CH_3NC]$$

  – At low $[CH_3NC]$, we have
  $$\frac{d[CH_3NC]}{dt} = -k_{obs}[CH_3NC]^2$$

  which is not the rate law for a unimolecular reaction.

- The Lindemann mechanism for unimolecular reactions of the form $A(g) \longrightarrow B(g)$ is

$$A(g) + M(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A(g)^* + M(g)$$

$$A(g)^* \overset{k_2}{\Longrightarrow} B(g)$$
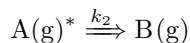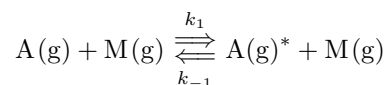
- The symbol $A(g)^*$ represents an energized reactant molecule. $M(g)$ is the collision partner.
- By the steady-state approximation, we have that

$$\frac{d[A^*]}{dt} = 0 = k_1[A][M] - k_{-1}[A^*][M] - k_2[A^*]$$

$$[A^*] = \frac{k_1[M][A]}{k_2 + k_{-1}[M]}$$

so that

$$\frac{d[B]}{dt} = k_2[A^*]$$

$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} = \underbrace{\frac{k_2 k_1[M]}{k_2 + k_{-1}[M]}}_{k_{\text{obs}}}[A]$$

- At high $[M]$, we have that $k_{-1}[M][A^*] \gg k_2[A^*]$, or $k_{-1}[M] \gg k_2$. Thus,

$$k_{\text{obs}} = \frac{k_1 k_2}{k_{-1}}$$

- At low $[M]$, we have that $k_2 \gg k_{-1}[M]$ so that

$$\frac{d[B]}{dt} = k_1[M][A]$$

$$= k_1[A]^2$$

- This mechanism was proposed by the British chemists J. A. Christiansen in 1921 and F. A. Lindemann in 1922. Their work underlies the current theory of unimolecular reaction rates.

- Some reaction mechanisms involve chain reactions.

  - Chain reactions involve amplification.
  - For example, $H_2(g) + Br_2(g) \rightleftharpoons 2\,HBr(g)$ follows the ensuing mechanism.
    - Initiation.
    $$Br_2 + M(g) \overset{k_1}{\Longrightarrow} 2\,Br(g) + M(g)$$

    - Propagation.

    $$Br(g) + H_2(g) \overset{k_2}{\Longrightarrow} HBr(g) + H(g)$$

    $$H(g) + Br_2(g) \overset{k_3}{\Longrightarrow} HBr(g) + Br(g)$$

    - Inhibition.

    $$HBr(g) + H(g) \overset{k_{-2}}{\Longrightarrow} Br(g) + H_2(g)$$

    $$HBr(g) + Br(g) \overset{k_{-3}}{\Longrightarrow} H(g) + Br_2(g)$$

■ Termination.

$$2\,\mathrm{Br} + \mathrm{M}\,(\mathrm{g}) \xrightarrow{k_{-1}} \mathrm{Br}_2(\mathrm{g}) + \mathrm{M}\,(\mathrm{g})$$
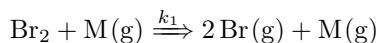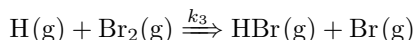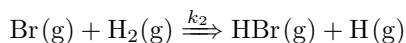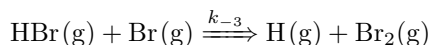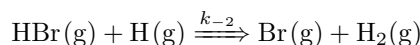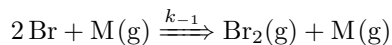
– The fifth step can be ignored.

– Notice that the inhibition and termination reactions are the reverse reactions of the propagation and initiation reaction(s), respectively.

■ Termination does not need to be the reverse of initiation, though. Termination just kills any reactive species.

■ Inhibition is the reverse of propagation, though.

– When you want to design a chain reaction species, make sure you have a reactive species (like bromine) for the initiation step. Notice, for instance, that hydrogen does not initiate.

– This leads to the experimentally determined rate law

$$\frac{1}{2}\frac{\mathrm{d}[\mathrm{HBr}]}{\mathrm{d}t} = \frac{k[\mathrm{H}_2][\mathrm{Br}_2]^{1/2}}{1 + k'[\mathrm{HBr}][\mathrm{Br}_2]^{-1}}$$

– Deriving said rate law.

■ We have that

$$\frac{\mathrm{d}[\mathrm{HBr}]}{\mathrm{d}t} = k_2[\mathrm{Br}][\mathrm{H}_2] - k_{-2}[\mathrm{HBr}][\mathrm{H}] + k_3[\mathrm{H}][\mathrm{Br}_2]$$

$$\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}t} = k_2[\mathrm{Br}][\mathrm{H}_2] - k_{-2}[\mathrm{HBr}][\mathrm{H}] - k_3[\mathrm{H}][\mathrm{Br}_2]$$

$$\frac{\mathrm{d}[\mathrm{Br}]}{\mathrm{d}t} = 2k_1[\mathrm{Br}_2][\mathrm{M}] - k_{-1}[\mathrm{Br}]^2[\mathrm{M}] - k_2[\mathrm{Br}][\mathrm{H}_2] + k_{-2}[\mathrm{HBr}][\mathrm{H}] + k_3[\mathrm{H}][\mathrm{Br}_2]$$

■ We can apply the SS approximation to the second and third equations above, which both describe intermediate species.

$$0 = k_2[\mathrm{Br}][\mathrm{H}_2] - k_{-2}[\mathrm{HBr}][\mathrm{H}] - k_3[\mathrm{H}][\mathrm{Br}_2]$$

$$0 = 2k_1[\mathrm{Br}_2][\mathrm{M}] - k_{-1}[\mathrm{Br}]^2[\mathrm{M}] - k_2[\mathrm{Br}][\mathrm{H}_2] + k_{-2}[\mathrm{HBr}][\mathrm{H}] + k_3[\mathrm{H}][\mathrm{Br}_2]$$

■ Solving the two equations above for [H] and [Br], respectively, is made substantially easier by noting that the negative of the first expression appears in its entirety in the second expression. Thus, we may simply substitute the former into the latter and solve to find an expression for [Br].

$$0 = 2k_1[\mathrm{Br}_2][\mathrm{M}] - k_{-1}[\mathrm{Br}]^2[\mathrm{M}] - 0$$

$$[\mathrm{Br}] = \left(\frac{k_1}{k_{-1}}\right)^{1/2}[\mathrm{Br}_2]^{1/2}$$

$$[\mathrm{Br}] = (K_{c,1})^{1/2}[\mathrm{Br}_2]^{1/2}$$

■ Resubstituting yields an expression for [H].

$$0 = k_2[\mathrm{Br}][\mathrm{H}_2] - k_{-2}[\mathrm{HBr}][\mathrm{H}] - k_3[\mathrm{H}][\mathrm{Br}_2]$$

$$0 = k_2(K_{c,1})^{1/2}[\mathrm{Br}_2]^{1/2}[\mathrm{H}_2] - (k_{-2}[\mathrm{HBr}] + k_3[\mathrm{Br}_2])[\mathrm{H}]$$

$$[\mathrm{H}] = \frac{k_2(K_{c,1})^{1/2}[\mathrm{Br}_2]^{1/2}[\mathrm{H}_2]}{k_{-2}[\mathrm{HBr}] + k_3[\mathrm{Br}_2]}$$

■ Substituting these two expressions back into the original differential equation for [HBr] yields

$$\frac{\mathrm{d}[\mathrm{HBr}]}{\mathrm{d}t} = k_2[\mathrm{Br}][\mathrm{H}_2] - k_{-2}[\mathrm{HBr}][\mathrm{H}] + k_3[\mathrm{H}][\mathrm{Br}_2]$$

$$= k_2(K_{c,1})^{1/2}[\mathrm{Br}_2]^{1/2}[\mathrm{H}_2] - k_{-2}[\mathrm{HBr}] \cdot \frac{k_2(K_{c,1})^{1/2}[\mathrm{Br}_2]^{1/2}[\mathrm{H}_2]}{k_{-2}[\mathrm{HBr}] + k_3[\mathrm{Br}_2]}$$

$$+ k_3 \cdot \frac{k_2(K_{c,1})^{1/2}[\mathrm{Br}_2]^{1/2}[\mathrm{H}_2]}{k_{-2}[\mathrm{HBr}] + k_3[\mathrm{Br}_2]} \cdot [\mathrm{Br}_2]$$

$$= k_2(K_{c,1})^{1/2}[\mathrm{Br}_2]^{1/2}[\mathrm{H}_2] - \frac{k_2 k_{-2}(K_{c,1})^{1/2}[\mathrm{HBr}][\mathrm{Br}_2]^{1/2}[\mathrm{H}_2]}{k_{-2}[\mathrm{HBr}] + k_3[\mathrm{Br}_2]}$$

$$+ \frac{k_2 k_3(K_{c,1})^{1/2}[\mathrm{Br}_2]^{3/2}[\mathrm{H}_2]}{k_{-2}[\mathrm{HBr}] + k_3[\mathrm{Br}_2]}$$

$$= k_2(K_{c,1})^{1/2}[\mathrm{Br}_2]^{1/2}[\mathrm{H}_2]\left(1 - \frac{k_{-2}[\mathrm{HBr}]}{k_{-2}[\mathrm{HBr}] + k_3[\mathrm{Br}_2]} + \frac{k_3[\mathrm{Br}_2]}{k_{-2}[\mathrm{HBr}] + k_3[\mathrm{Br}_2]}\right)$$

$$= k_2(K_{c,1})^{1/2}[\mathrm{Br}_2]^{1/2}[\mathrm{H}_2]\left(\frac{k_{-2}[\mathrm{HBr}] + k_3[\mathrm{Br}_2]}{k_{-2}[\mathrm{HBr}] + k_3[\mathrm{Br}_2]} - \frac{k_{-2}[\mathrm{HBr}] - k_3[\mathrm{Br}_2]}{k_{-2}[\mathrm{HBr}] + k_3[\mathrm{Br}_2]}\right)$$

$$= k_2(K_{c,1})^{1/2}[\mathrm{Br}_2]^{1/2}[\mathrm{H}_2] \cdot \frac{2k_3[\mathrm{Br}_2]}{k_{-2}[\mathrm{HBr}] + k_3[\mathrm{Br}_2]}$$

$$\frac{1}{2}\frac{\mathrm{d}[\mathrm{HBr}]}{\mathrm{d}t} = k_2(K_{c,1})^{1/2}[\mathrm{Br}_2]^{1/2}[\mathrm{H}_2] \cdot \frac{1}{(k_{-2}/k_3)[\mathrm{HBr}][\mathrm{Br}_2]^{-1} + 1}$$

$$= \frac{k_2(K_{c,1})^{1/2}[\mathrm{H}_2][\mathrm{Br}_2]^{1/2}}{1 + (k_{-2}/k_3)[\mathrm{HBr}][\mathrm{Br}_2]^{-1}}$$

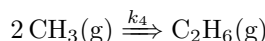$$= \frac{k[\mathrm{H}_2][\mathrm{Br}_2]^{1/2}}{1 + k'[\mathrm{HBr}][\mathrm{Br}_2]^{-1}}$$

where we have substituted $k = k_2(K_{c,1})^{1/2}$ and $k' = k_{-2}/k_3$ in the last expression.

• Problem 29-24.

– The reaction

$$\mathrm{CH_3CHO\,(g)} \xrightarrow{k_{\mathrm{obs}}} \mathrm{CH_4\,(g)} + \mathrm{CO\,(g)}$$

proceeds by the mechanism

$$\mathrm{CH_3CHO\,(g)} \xrightarrow{k_1} \mathrm{CH_3\,(g)} + \mathrm{CHO\,(g)}$$

$$\mathrm{CH_3\,(g)} + \mathrm{CH_3CHO\,(g)} \xrightarrow{k_2} \mathrm{CH_4\,(g)} + \mathrm{CH_3CO\,(g)}$$

$$\mathrm{CH_3CO\,(g)} \xrightarrow{k_3} \mathrm{CH_3\,(g)} + \mathrm{CO\,(g)}$$

$$2\,\mathrm{CH_3\,(g)} \xrightarrow{k_4} \mathrm{C_2H_6\,(g)}$$
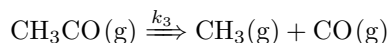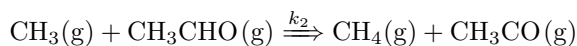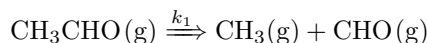
– The initiation step is the first equation, the propagation steps are the second and third equations, and the termination step is the fourth equation.

– We can write the rate laws

$$\frac{\mathrm{d}[\mathrm{CH_4}]}{\mathrm{d}t} = k_2[\mathrm{CH_3}][\mathrm{CH_3CHO}]$$

$$\frac{\mathrm{d}[\mathrm{CH_3}]}{\mathrm{d}t} = k_1[\mathrm{CH_3CHO}] - k_2[\mathrm{CH_3}][\mathrm{CH_3CHO}] + k_3[\mathrm{CH_3CO}] - 2k_4[\mathrm{CH_3}]$$

$$\frac{\mathrm{d}[\mathrm{CH_3CO}]}{\mathrm{d}t} = k_2[\mathrm{CH_3}][\mathrm{CH_3CHO}] - k_3[\mathrm{CH_3CO}]$$

– Applying the SS approximation to the last second and third equations yields (respectively)

$$[CH_3] = \frac{k_1[CH_3CHO] + k_3[CH_3CO]}{k_2[CH_3CHO] + 2k_4} \qquad [CH_3CO] = \frac{k_2}{k_3}[CH_3][CH_3CHO]$$

– Substituting the right equation above into the left equation above and solving for $[CH_3]$ yields an expression for $[CH_3]$ purely in terms of $[CH_3CHO]$.

$$[CH_3] = \frac{k_1[CH_3CHO] + k_2[CH_3][CH_3CHO]}{k_2[CH_3CHO] + 2k_4}$$
$$k_2[CH_3][CH_3CHO] + 2k_4[CH_3] = k_1[CH_3CHO] + k_2[CH_3][CH_3CHO]$$
$$2k_4[CH_3] = k_1[CH_3CHO]$$
$$[CH_3] = \frac{k_1}{2k_4}[CH_3CHO]$$

– The final result is

$$\frac{d[CH_4]}{dt} = k_2\left(\frac{k_1}{2k_4}[CH_3CHO]\right)[CH_3CHO]$$
$$= k_2\left(\frac{k_1}{2k_4}\right)^{1/2}[CH_3CHO]^{3/2}$$

■ What's the issue here?

4.4 Chapter 26: Chemical Equilibrium

From McQuarrie and Simon (1997).

4/28:
- "Thermodynamics enables us to predict with confidence the equilibrium pressures or concentrations of reaction mixtures" (McQuarrie & Simon, 1997, p. 963).

- Goal of this chapter: Derive a relationship between the standard Gibbs energy change and the equilibrium constant.

- We begin by considering the following general gas-phase reaction.

$$\nu_A\,A\,(g) + \nu_B\,B\,(g) \rightleftharpoons \nu_Y\,Y\,(g) + \nu_Z\,Z\,(g)$$

- **Extent of reaction**: A measure of how far along its reaction coordinate a chemical reaction is. *Denoted by* $\boldsymbol{\xi}$. *Units* **mol**. *Given by*

$$n_A = n_{A0} - \nu_A\xi \qquad\qquad n_Y = n_{Y0} + \nu_Y\xi$$
$$n_B = n_{B0} - \nu_B\xi \qquad\qquad n_Z = n_{Z0} + \nu_Z\xi$$

where n_j is the number of moles for each species at the time during the reaction corresponding to extent of reaction ξ and n_{j0} is the initial number of moles for each species.

  – As the reaction proceeds, ξ varies from zero to some maximum value.
  – An example of the units of ξ: If n_{A0} equals ν_A moles and n_{B0} equals ν_B moles, then ξ varies from zero moles to one mole over the course of the reaction.

- Relating the change in Gibbs energy to the change in extent of reaction.

- The Gibbs energy for this multicomponent system depends on T, P, and n_j for the two reactants and the two products. Thus,

$$
\begin{aligned}
\mathrm{d}G =& \left(\frac{\partial G}{\partial T}\right)_{P,n_j} \mathrm{d}T + \left(\frac{\partial G}{\partial P}\right)_{T,n_j} \mathrm{d}P + \left(\frac{\partial G}{\partial n_A}\right)_{T,P,n_{j\neq A}} \mathrm{d}n_A \\
&+ \left(\frac{\partial G}{\partial n_B}\right)_{T,P,n_{j\neq B}} \mathrm{d}n_B + \left(\frac{\partial G}{\partial n_Y}\right)_{T,P,n_{j\neq Y}} \mathrm{d}n_Y + \left(\frac{\partial G}{\partial n_Z}\right)_{T,P,n_{j\neq Z}} \mathrm{d}n_Z \\
=& -S\,\mathrm{d}T + V\,\mathrm{d}P + \mu_A\,\mathrm{d}n_A + \mu_B\,\mathrm{d}n_B + \mu_Y\,\mathrm{d}n_Y + \mu_Z\,\mathrm{d}n_Z
\end{aligned}
$$

- Taking T, P to be constant simplifies the above to

$$
\mathrm{d}G = \mu_A\,\mathrm{d}n_A + \mu_B\,\mathrm{d}n_B + \mu_Y\,\mathrm{d}n_Y + \mu_Z\,\mathrm{d}n_Z
$$

- Differentiating the equations used to define the extent of reaction yields

$$
\begin{aligned}
\mathrm{d}n_A &= -\nu_A\,\mathrm{d}\xi & \mathrm{d}n_Y &= \nu_Y\,\mathrm{d}\xi \\
\mathrm{d}n_B &= -\nu_B\,\mathrm{d}\xi & \mathrm{d}n_Z &= \nu_Z\,\mathrm{d}\xi
\end{aligned}
$$

so that

$$
\begin{aligned}
\mathrm{d}G &= -\nu_A\mu_A\,\mathrm{d}\xi - \nu_B\mu_B\,\mathrm{d}\xi + \nu_Y\mu_Y\,\mathrm{d}\xi + \nu_Z\mu_Z\,\mathrm{d}\xi \\
&= (\nu_Y\mu_Y + \nu_Z\mu_Z - \nu_A\mu_A - \nu_B\mu_B)\,\mathrm{d}\xi \\
\left(\frac{\partial G}{\partial \xi}\right)_{T,P} &= \nu_Y\mu_Y + \nu_Z\mu_Z - \nu_A\mu_A - \nu_B\mu_B
\end{aligned}
$$

- $\boldsymbol{\Delta_r G}$: The change in Gibbs energy when the extent of reaction changes by one mole. *Units* $\mathbf{J\,mol^{-1}}$. *Given by*

$$
\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \nu_Y\mu_Y + \nu_Z\mu_Z - \nu_A\mu_A - \nu_B\mu_B
$$

- Relating standard and nonstandard states.

  - Let all partial pressures be sufficiently low to assume ideality.
  - Then substituting the equation $\mu_j(T,P) = \mu_j^\circ(T) + RT\ln(P_j/P^\circ)$ yields

$$
\Delta_r G = \nu_Y\mu_Y^\circ(T) + \nu_Z\mu_Z^\circ(T) - \nu_A\mu_A^\circ(T) - \nu_B\mu_B^\circ(T) + RT\left(\nu_Y\ln\frac{P_Y}{P^\circ} + \nu_Z\ln\frac{P_Z}{P^\circ} - \nu_A\ln\frac{P_A}{P^\circ} - \nu_B\ln\frac{P_B}{P^\circ}\right)
$$

$$
= \underbrace{\nu_Y\mu_Y^\circ(T) + \nu_Z\mu_Z^\circ(T) - \nu_A\mu_A^\circ(T) - \nu_B\mu_B^\circ(T)}_{\Delta_r G^\circ} + RT\ln\underbrace{\frac{(P_Y/P^\circ)^{\nu_Y}(P_Z/P^\circ)^{\nu_Z}}{(P_A/P^\circ)^{\nu_A}(P_B/P^\circ)^{\nu_B}}}_{Q}
$$

- $\boldsymbol{\Delta_r G^\circ(T)}$: The change in standard Gibbs energy for the reaction between unmixed reactants in their standard states at temperature T and a pressure of one bar to form unmixed products in their standard states at the same temperature T and pressure of one par.

  - Note that since P° is taken to be $1\,\mathrm{bar}$, the P°'s are usually dropped in the definition of Q. However, they must be remembered in the sense that they make Q unitless whether shown or not.

- **Equilibrium**: The position of the reaction system at which the Gibbs energy is a minimum with respect to any displacement.

  - Mathematically, we have that at equilibrium, $\Delta_r G = 0$.

– It follows that at equilibrium,

$$0 = \Delta_r G^\circ(T) + RT \ln \left(\frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}} \right)_{\text{eq}}$$

$$\Delta_r G^\circ(T) = -RT \ln \left(\frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}} \right)_{\text{eq}}$$

- **Equilibrium constant**: A constant describing the relative pressures of reactants to products that will result in the reaction system achieving equilibrium. *Denoted by* $\boldsymbol{K_P(T)}$. *Given by*

$$K_P(T) = \left(\frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}} \right)_{\text{eq}}$$

  – The value of the equilibrium constant depends on how we write the chemical equation for the reaction at hand. For instance, the equilibrium constant expression for $3\,H_2 + N_2 \rightleftharpoons 2\,NH_3$ is the square of the equilibrium constant expression for $\frac{3}{2}H_2 + \frac{1}{2}N_2 \rightleftharpoons NH_3$.

- An equilibrium constant is a function of temperature only.

  – This is because in deriving the equilibrium constant expression, we set $\Delta_r G(T, P) = 0$, and pressure appears nowhere else in the equation $\Delta_r G^\circ(T) + RT \ln Q$.

  – In particular, the ratio that defines Q must remain constant at different initial pressures of reactants and products.

- Thinking through some equilibrium concepts in an example.

  – Consider the reaction

  $$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

  – The equilibrium constant expression is

  $$K_P(T) = \frac{P_{PCl_3} P_{Cl_2}}{P_{PCl_5}}$$

  – If we initially have one mole of PCl_5 and no PCl_3 or Cl_2, then when the reaction occurs to an extent ξ, there will be $1 - \xi$ moles PCl_5 and ξ moles PCl_3 and Cl_2. This leads to an overall $1 + \xi$ moles of gas.

  – It follows that if ξ_{eq} is the extent of reaction at equilibrium, then the partial pressures of each gas at equilibrium are given by

  $$P_{PCl_3} = P_{Cl_2} = \frac{\xi_{\text{eq}}}{1 + \xi_{\text{eq}}} P \qquad\qquad P_{PCl_5} = \frac{1 - \xi_{\text{eq}}}{1 + \xi_{\text{eq}}} P$$

  where P is the total pressure.

  – Thus, the equilibrium constant expression is

  $$K_P(T) = \frac{\xi_{\text{eq}}^2}{1 - \xi_{\text{eq}}^2} P$$

  – While the above expression sure makes it seem like $K_P(T)$ depends on P, we know by the above that it can't. Thus, it must be the position of the equilibrium along the extent of reaction that changes as P changes.

  – In particular, as per **Le Châtelier's principle**, we can note that for $K_P > 1$, increasing pressure favors lesser extents of reaction (i.e., favors the reactants). This should make intuitive sense harkening back to AP Chemistry since it stands to reason that pressure increases would favor shifting the equilibrium to have fewer moles of gas. Now, however, we have a quantitative rule for how changes in pressure will affect the equilibrium.

- **Le Châtelier's principle**: If a chemical reaction at equilibrium is subjected to a change in conditions that displaces it from equilibrium, then the reaction adjusts toward a new equilibrium state.

- Note that we can also express the equilibrium constant in terms of concentration via the relationship $P = cRT$ where $c = n/V$ is the concentration.

$$K_P = \frac{c_Y^{\nu_Y} c_Z^{\nu_Z}}{c_A^{\nu_A} c_B^{\nu_B}} \left(\frac{RT}{P^\circ}\right)^{\nu_Y + \nu_Z - \nu_A - \nu_B}$$

- **c°**: The standard concentration. *Given by*

$$c^\circ = 1 \tfrac{\text{mol}}{\text{L}}$$

- The standard concentration enables the following definitions.

$$K_P = \underbrace{\frac{(c_Y/c^\circ)^{\nu_Y}(c_Z/c^\circ)^{\nu_Z}}{(c_A/c^\circ)^{\nu_A}(c_B/c^\circ)^{\nu_B}}}_{K_c} \left(\frac{c^\circ RT}{P^\circ}\right)^{\nu_Y + \nu_Z - \nu_A - \nu_B}$$

  - Note that both K_c and the term by which it is multiplied above are unitless.
  - As such, we have to be careful what units we use for R. In the standard situation of $P^\circ = 1\,\text{bar}$ and $c^\circ = 1\,\text{mol}\,\text{L}^{-1}$, we must use $R = 0.083\,145\,\text{L}\,\text{bar}\,\text{mol}^{-1}\,\text{K}^{-1}$.

- By combining the two equations below (both given in derivations above), we can obtain a relation between the equilibrium constant K_p and the standard molar Gibbs energies (i.e., chemical potentials) of the relevant substances.

$$\Delta_r G^\circ(T) = -RT \ln K_P$$
$$\Delta_r G^\circ(T) = \nu_Y \mu_Y^\circ(T) + \nu_Z \mu_Z^\circ(T) - \nu_A \mu_A^\circ(T) - \nu_B \mu_B^\circ(T)$$

  - Note that $\mu_j^\circ(T) = \Delta_f G^\circ[j]$ if we choose appropriate standard states.
  - Thus, we can use tables of standard molar Gibbs energies of formation to calculate equilibrium constants.

- Example: Deriving a function for the Gibbs energy of a reaction in terms of the extent of reaction.

  - Consider the following reaction, which occurs at $298.15\,\text{K}$.

$$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\,\text{NO}_2(\text{g})$$
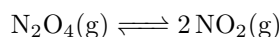
  - Let the initial conditions be one mole of N_2O_4 and no NO_2. Then

$$\begin{aligned}
G(\xi) &= n_{\text{N}_2\text{O}_4}\overline{G}_{\text{N}_2\text{O}_4} + n_{\text{NO}_2}\overline{G}_{\text{NO}_2} \\
&= (1-\xi)\overline{G}_{\text{N}_2\text{O}_4} + 2\xi\overline{G}_{\text{NO}_2} \\
&= (1-\xi)G_{\text{N}_2\text{O}_4}^\circ + 2\xi G_{\text{NO}_2}^\circ + (1-\xi)RT \ln P_{\text{N}_2\text{O}_4} + 2\xi RT \ln P_{\text{NO}_2}
\end{aligned}$$

  - Let the reaction be carried out at a constant total pressure of one bar. This assumption combined with the fact that the total number of moles in the reaction mixture is $(1-\xi)+2\xi = 1+\xi$ reveals that

$$P_{\text{N}_2\text{O}_4} = x_{\text{N}_2\text{O}_4}P_{\text{total}} = \frac{1-\xi}{1+\xi}\cdot 1 = \frac{1-\xi}{1+\xi} \qquad P_{\text{NO}_2} = x_{\text{NO}_2}P_{\text{total}} = \frac{2\xi}{1+\xi}\cdot 1 = \frac{2\xi}{1+\xi}$$

  so that

$$G(\xi) = (1-\xi)G_{\text{N}_2\text{O}_4}^\circ + 2\xi G_{\text{NO}_2}^\circ + (1-\xi)RT \ln \frac{1-\xi}{1+\xi} + 2\xi RT \ln \frac{2\xi}{1+\xi}$$

– Choosing appropriate standard states, we can obtain the final form

$$G(\xi) = (1 - \xi)\Delta_f G^\circ_{N_2O_4} + 2\xi\Delta_f G^\circ_{NO_2} + (1 - \xi)RT \ln \frac{1 - \xi}{1 + \xi} + 2\xi RT \ln \frac{2\xi}{1 + \xi}$$

– Plugging in

$$\Delta_f G^\circ_{N_2O_4} = 97.787\,\text{kJ mol}^{-1} \qquad\qquad \Delta_f G^\circ_{NO_2} = 51.258\,\text{kJ mol}^{-1}$$

we can determine that the minimum of the curve occurs at $\xi_{\text{eq}} = 0.1892\,\text{mol}$.

– Thus,

$$K_P = \frac{P^2_{NO_2}}{P_{N_2O_4}} = \frac{[2\xi_{\text{eq}}/(1 + \xi_{\text{eq}})]^2}{(1 - \xi_{\text{eq}})/(1 + \xi_{\text{eq}})} = \frac{4\xi^2_{\text{eq}}}{1 - \xi^2_{\text{eq}}} = 0.148$$

∎ Note that this value compares exactly with the one obtained via the $-RT \ln K_P = \sum \nu_j \mu^\circ_j(T)$ method.

– Note that differentiating our final form for $G(\xi)$ wrt. ξ yields $\Delta_r G = \Delta_r G^\circ + RT \ln K_P$, as expected.

• **Reaction quotient**: A quantity describing the relative amounts of reactants and products present in the reaction system at a given instant in time. *Denoted by $\boldsymbol{Q_P}$. Given by*

$$Q_P = \frac{P^{\nu_Y}_Y P^{\nu_Z}_Z}{P^{\nu_A}_A P^{\nu_B}_B}$$

• We have that

$$\begin{aligned}
\Delta_r G &= \Delta_r G^\circ + RT \ln Q_P \\
&= -RT \ln K_P + RT \ln Q_P \\
&= RT \ln \frac{Q_P}{K_P}
\end{aligned}$$

– Thus, the ratio of the reaction quotient to the equilibrium constant determines the direction in which a reaction will proceed.

• The sign of $\Delta_r G$ and not that of $\Delta_r G^\circ$ determines the direction of reaction spontaneity.

– Indeed, the sign of $\Delta_r G^\circ$ determines the direction of reaction spontaneity only when all substances are mixed at one bar partial pressures (i.e., when $\Delta_r G = \Delta_r G^\circ$).

• "The fact that a process will occur spontaneously does not imply that it will necessarily occur at a detectable rate" (McQuarrie & Simon, 1997, p. 977).

– For example, the negative $\Delta_r G^\circ$ of water at one bar and $25\,°\text{C}$ tells us that the reaction $2\,H_2 + O_2 \rightleftharpoons 2\,H_2O$ will occur spontaneously. However, experimental evidence reveals that a spark or catalyst is needed to convert hydrogen and oxygen to water; once said activation energy is introduced, the reaction proceeds explosively.

– Indeed, "the 'no' of thermodynamics is emphatic. If thermodynamics says that a certain process will not occur spontaneously, it will not occur. The 'yes' of thermodynamics, on the other hand, is actually a 'maybe'" (McQuarrie & Simon, 1997, p. 977).

4/29:
• Deriving a relationship between K_P and T.

– Recall the Gibbs-Helmholtz equation

$$\left(\frac{\partial \Delta G^\circ / T}{\partial T} \right)_P = -\frac{\Delta H^\circ}{T^2}$$

- Substituting $\Delta G^\circ(T) = -RT \ln K_P(T)$ yields the **Van't Hoff equation**.

$$\left(\frac{\partial \ln K_P(T)}{\partial T}\right)_P = \frac{d \ln K_P}{dT} = \frac{\Delta_r H^\circ}{RT^2}$$

- Qualitatively, the above equation tells us that if $\Delta_r H^\circ > 0$ (i.e., if the reaction is endothermic), then $K_P(T)$ increases with temperature, as expected since more available energy should drive an endothermic reaction, and vice versa if $\Delta_r H^\circ < 0$.

  ■ This is another example of Le Châtelier's principle.

- Quantitatively, the above equation can be integrated to give

$$\ln \frac{K_P(T_2)}{K_P(T_1)} = \int_{T_1}^{T_2} \frac{\Delta_r H^\circ(T)}{RT^2} \, dT$$

- If the temperature range or the magnitude change of $\Delta_r H^\circ(T)$ is sufficiently small, we may take $\Delta_r H^\circ$ to be constant and write

$$\ln \frac{K_P(T_2)}{K_P(T_1)} = -\frac{\Delta_r H^\circ(T)}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

  ■ One implication of this equation is that over a sufficiently small temperature range, a plot of $\ln K$ vs. $1/T$ is linear with slope $-\Delta_r H^\circ/R$.

- If the temperature range is not sufficiently small, we still have options.

- For example, recall that

$$\Delta_r H^\circ(T_2) = \Delta_r H^\circ(T_1) + \int_{T_1}^{T_2} \Delta C_P^\circ(T) \, dT$$

  where ΔC_P° is the difference between the heat capacities of the products and reactants.

- Alternatively, we may present experimental heat capacity data as a polynomial in temperature of the form

$$\Delta_r H^\circ(T) = \alpha + \beta T + \gamma T^2 + \delta T^3 + \cdots$$

  so that

$$\ln K_P(T) = -\frac{\alpha}{RT} + \frac{\beta}{R} \ln T + \frac{\gamma}{R} T + \frac{\delta}{2R} T^2 + A$$

  where A is a constant of integration.

  ■ It follows from this equation that in reality, a plot of $\ln K_P$ vs. $1/T$ is not linear but has a slight curvature.

- More generally, we may always take

$$\ln K_P(T) = \ln K_P(T_1) + \int_{T_1}^{T} \frac{\Delta_r H^\circ(T')}{RT'^2} \, dT$$

  regardless of how $\Delta_r H^\circ$ varies with temperature.

- **Van't Hoff equation**: An ordinary differential equation describing the temperature dependence of the equilibrium constant. *Given by*

$$\frac{d \ln K_P}{dT} = \frac{\Delta_r H^\circ}{RT^2}$$

- A note on the similarity in form between the integrated Van't Hoff equation at constant $\Delta_r H^\circ$ and the Clausius-Clapeyron equation: "These equations are essentially the same because the vaporization of a liquid can be represented by the 'chemical equation' $X(l) \rightleftharpoons X(g)$" (McQuarrie & Simon, 1997, p. 980).

4/30: • Calculating equilibrium constants in terms of partition functions.

– Consider the general homogeneous gas-phase reaction

$$\nu_A \, A\,(g) + \nu_B \, B\,(g) \rightleftharpoons \nu_Y \, Y\,(g) + \nu_Z \, Z\,(g)$$
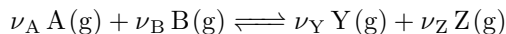
in a reaction vessel at fixed volume and temperature.

– It follows that

$$dA = \mu_A \, dn_A + \mu_B \, dn_B + \mu_Y \, dn_Y + \mu_Z \, dn_Z$$

– As before, this equation gives the condition for chemical equilibrium as

$$\nu_Y \mu_Y + \nu_Z \mu_Z - \nu_A \mu_A - \nu_B \mu_B = 0$$

– We now express the chemical potentials above in terms of partition functions.

– Since the species are independent in an ideal gas, we have that

$$Q(N_A, N_B, N_Y, N_Z, V, T) = Q(N_A, V, T)Q(N_B, V, T)Q(N_Y, V, T)Q(N_Z, V, T)$$
$$= \frac{q_A(V,T)^{N_A}}{N_A!} \frac{q_B(V,T)^{N_B}}{N_B!} \frac{q_Y(V,T)^{N_Y}}{N_Y!} \frac{q_Z(V,T)^{N_Z}}{N_Z!}$$

– Thus, for example,

$$\mu_A = -RT \left(\frac{\partial \ln Q(N_A, N_B, N_Y, N_Z, V, T)}{\partial N_A} \right)_{N_j, V, T} = -RT \ln \frac{q_A(V,T)}{N_A}$$

where we have used Stirling's approximation for $N_A!$.

– Substituting the above equation and its variations for B, Y, and Z into the equilibrium conditions yields

$$0 = \nu_Y \left(-RT \ln \frac{q_Y}{N_Y} \right) + \nu_Z \left(-RT \ln \frac{q_Z}{N_Z} \right) - \nu_A \left(-RT \ln \frac{q_A}{N_A} \right) - \nu_B \left(-RT \ln \frac{q_B}{N_B} \right)$$
$$= \ln \frac{q_Y^{\nu_Y}}{N_Y^{\nu_Y}} + \ln \frac{q_Z^{\nu_Z}}{N_Z^{\nu_Z}} - \ln \frac{q_A^{\nu_A}}{N_A^{\nu_A}} - \ln \frac{q_B^{\nu_B}}{N_B^{\nu_B}}$$
$$e^0 = \frac{\frac{q_Y^{\nu_Y} q_Z^{\nu_Z}}{q_A^{\nu_A} q_B^{\nu_B}}}{\frac{N_Y^{\nu_Y} N_Z^{\nu_Z}}{N_A^{\nu_A} N_B^{\nu_B}}}$$
$$\frac{N_Y^{\nu_Y} N_Z^{\nu_Z}}{N_A^{\nu_A} N_B^{\nu_B}} = \frac{q_Y^{\nu_Y} q_Z^{\nu_Z}}{q_A^{\nu_A} q_B^{\nu_B}}$$

– Now $N_j/V = \rho_j$ is concentration, so dividing every term in the left expression above by V^{ν_j} gives K_c.

$$K_c(T) = \frac{\rho_Y^{\nu_Y} \rho_Z^{\nu_Z}}{\rho_A^{\nu_A} \rho_B^{\nu_B}} = \frac{(q_Y/V)^{\nu_Y} (q_Z/V)^{\nu_Z}}{(q_A/V)^{\nu_A} (q_B/V)^{\nu_B}}$$

■ Recall that q_j/V is a function of temperature only. Thus, the above of definition does give $K_c(T)$ in terms of the partition functions and as a function of temperature only, as it should.

– Lastly, recall that we can use the definition of K_P in terms of K_c to calculate K_P in terms of partition functions.

• McQuarrie and Simon (1997) goes through two examples of using the above result to calculate the equilibrium constant from molecular parameters.

– Using the rigid-rotator harmonic oscillator approximation (which we may recall is the basis of all partition functions we've derived thus far) gives results in good (but not great) agreement with experiment.

5/1:
- We can achieve better agreement with experimental data using more laborious calculations.

- Alternatively, we can turn to tabulated data, such as the **JANAF tables**.

- **JANAF tables**: The joint, army, navy, air force tables (Chase, 1985), which are one of the most extensive tabulations of the thermochemical properties of substances.

  - The JANAF tables use as a reference point for relative data the standard molar enthalpies at 298.15 K.

- McQuarrie and Simon (1997) works through several examples of how to use the JANAF tables and manipulate the thermodynamic equations we've derived thus far to best suit them.

- McQuarrie and Simon (1997) discusses equilibrium constants for real gases and solutions.

Problems

26-14. Show that
$$\frac{d \ln K_c}{dT} = \frac{\Delta_r U^\circ}{RT^2}$$

for reactions involving ideal gases.

*Answer.* Starting from the Van't Hoff equation, we have that

$$\frac{d \ln K_P}{dT} = \frac{\Delta_r H^\circ}{RT^2}$$

$$\frac{d}{dT} \ln \left(K_c \left(\frac{c^\circ RT}{P^\circ} \right)^{\nu_Y + \nu_Z - \nu_A - \nu_B} \right) = \frac{\Delta_r U^\circ + \Delta_r(PV)}{RT^2}$$

$$\frac{d \ln K_c}{dT} + \frac{d}{dT} \{[(\nu_Y + \nu_Z) - (\nu_A + \nu_B)] \ln T\} + \frac{d}{dT} \left(\frac{c^\circ R}{P^\circ} \right) = \frac{\Delta_r U^\circ + \Delta_r(nRT)}{RT^2}$$

$$\frac{d \ln K_c}{dT} + \frac{n_f - n_i}{T} + 0 = \frac{\Delta_r U^\circ}{RT^2} + \frac{\Delta_r n}{T}$$

$$\frac{d \ln K_c}{dT} = \frac{\Delta_r U^\circ}{RT^2}$$

as desired. $\square$

4.5 Chapter 28: Chemical Kinetics I — Rate Laws

From McQuarrie and Simon (1997).

- **Transition state**: The transient species in the vicinity of the top of the activation barrier to reaction. *Also known as* **activated complex**. *Denoted by* $AB^\ddagger$.

- **Transition-state theory**: A theory focusing on the transition states that can be used to estimate reaction rate constants. *Also known as* **activated-complex theory**.

  - Developed in the 1930s by Henry Eyring.

- We will now develop the fundamental postulates of transition state theory and use them to express the rate constant, activation energy, and Arrhenius pre-exponential factor of the reaction

$$A + B \longrightarrow P$$
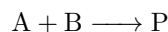
where P represents one or more products in terms of thermodynamic quantities including partition functions as well as more fundamental variables and constants.
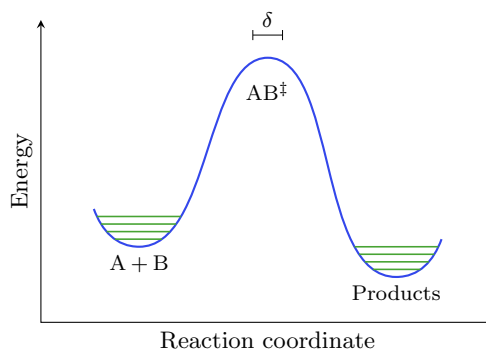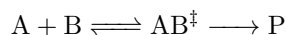
Figure 4.1: Transition state theory energy diagram.

- The first assumption of transition state theory is that the activated complex is in equilibrium with the reactants as per

$$A + B \rightleftharpoons AB^{\ddagger} \longrightarrow P$$

- It follows from the definition of the concentration equilibrium constant that the transition-state equilibrium is defined by

$$K_c^{\ddagger} = \frac{[AB^{\ddagger}]/c^{\circ}}{[A]/c^{\circ}[B]/c^{\circ}} = \frac{[AB^{\ddagger}]c^{\circ}}{[A][B]}$$

- We can substitute partition functions into the above expression as follows

$$K_c^{\ddagger} = \frac{(q^{\ddagger}/V)c^{\circ}}{(q_A/V)(q_B/V)}$$

where q_A, q_B, and $q^{\ddagger}$ are the partition functions of A, B, and $AB^{\ddagger}$, respectively.

- The second assumption of transition state theory is that the activated complex is stable throughout a small region of width δ centered at the top of the energy barrier (see Figure 4.1).

- It follows from this assumption that we can define the rate of product formation in terms of the concentration of the preceding intermediate (the activated complex), as we have been throughout this chapter. This may be done as follows.

$$\frac{d[P]}{dt} = \nu_c[AB^{\ddagger}]$$

- ■ ν_c functions as a type of rate constant.
- ■ The form of this expression implies that "the motion of the reacting system over the barrier top is a one-dimensional translational motion" (McQuarrie & Simon, 1997, p. 1166).

- We also have from the original chemical equation that

$$\frac{d[P]}{dt} = k[A][B]$$

- Thus, solving the expression defining $K_c^{\ddagger}$ for $[AB^{\ddagger}]$ and substituting into the above, we have that

$$\frac{d[P]}{dt} = \nu_c[AB^{\ddagger}] = \nu_c\frac{[A][B]K_c^{\ddagger}}{c^{\circ}} = \underbrace{\frac{\nu_c K_c^{\ddagger}}{c^{\circ}}}_{k}[A][B]$$

- ■ This expression gives k in units of $M^{-1}\,s^{-1}$.

- Since the rate law in terms of $[AB^\ddagger]$ implies 1D translational motion and the 1D translational partition function is

$$q_{\text{trans}} = \frac{\sqrt{2\pi m^\ddagger k_B T}}{h}\delta$$

we have that $q^\ddagger = q_{\text{trans}}q_{\text{int}}^\ddagger$.

- Thus,

$$k = \frac{\nu_c}{c^\circ}K_c^\ddagger$$

$$= \frac{\nu_c}{c^\circ}\frac{(q^\ddagger/V)c^\circ}{(q_A/V)(q_B/V)}$$

$$= \nu_c \frac{\sqrt{2\pi m^\ddagger k_B T}}{hc^\circ}\delta\frac{(q_{\text{int}}^\ddagger/V)c^\circ}{(q_A/V)(q_B/V)}$$

- This equation is looking pretty good, but it still contains ν_c and δ, both tricky quantities to define and determine. Their product $\langle u_{ac}\rangle$, however, has a much nicer interpretation.

- Consequently, we have that

$$k = \sqrt{\frac{k_B T}{2\pi m^\ddagger}}\frac{\sqrt{2\pi m^\ddagger k_B T}}{hc^\circ}\frac{(q_{\text{int}}^\ddagger/V)c^\circ}{(q_A/V)(q_B/V)}$$

$$= \frac{k_B T}{hc^\circ}K^\ddagger$$

- Since we can relate $K^\ddagger$ and the **standard Gibbs energy of activation** by

$$\Delta^\ddagger G^\circ = -RT\ln K^\ddagger$$

we have that

$$k(T) = \frac{k_B T}{hc^\circ}e^{-\Delta^\ddagger G^\circ/RT}$$

- Since we can express the standard Gibbs energy of activation in terms of the **standard enthalpy of activation** and the **standard entropy of activation** via

$$\Delta^\ddagger G^\circ = \Delta^\ddagger H^\circ - T\Delta^\ddagger S^\circ$$

we have that

$$k(T) = \frac{k_B T}{hc^\circ}e^{\Delta^\ddagger S^\circ/R}e^{-\Delta^\ddagger H^\circ/RT}$$

- We now look to use the above equation as a launch point to relate the activation energy and Arrhenius pre-exponential factor to molecular quantities.

- Recall that the differential Arrhenius equation is

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

- It follows using a previous form of $k(T)$ that

$$\frac{d\ln k}{dT} = \frac{d}{dT}\ln\left(\frac{k_B}{hc^\circ}\right) + \frac{d\ln T}{dT} + \frac{d\ln K^\ddagger}{dT} = \frac{1}{T} + \frac{d\ln K^\ddagger}{dT}$$

- Invoking the result of Problem 26-14 yields

$$\frac{d\ln k}{dT} = \frac{1}{T} + \frac{\Delta^\ddagger U^\circ}{RT^2}$$

- Additionally, since

$$\Delta^{\ddagger}H^{\circ} = \Delta^{\ddagger}U^{\circ} + \Delta^{\ddagger}PV = \Delta^{\ddagger}U^{\circ} + RT\Delta^{\ddagger}n = \Delta^{\ddagger}U^{\circ} - RT$$

$$\Delta^{\ddagger}H^{\circ} + RT = \Delta^{\ddagger}U^{\circ}$$

we have that

$$\frac{\mathrm{d}\ln k}{\mathrm{d}T} = \frac{RT}{RT^2} + \frac{\Delta^{\ddagger}H^{\circ} + RT}{RT^2}$$

$$= \frac{\Delta^{\ddagger}H^{\circ} + 2RT}{RT^2}$$

- Therefore, we have by direct comparison with the Arrhenius equation that

$$E_a = \Delta^{\ddagger}H^{\circ} + 2RT$$

- Substituting this result into the form of $k(T)$ containing $\Delta^{\ddagger}H^{\circ}$ yields

$$k(T) = \frac{k_{\mathrm{B}}T}{hc^{\circ}}\mathrm{e}^{\Delta^{\ddagger}S^{\circ}/R}\mathrm{e}^{-\Delta^{\ddagger}H^{\circ}/RT}$$

$$= \frac{k_{\mathrm{B}}T}{hc^{\circ}}\mathrm{e}^{\Delta^{\ddagger}S^{\circ}/R}\mathrm{e}^{-E_a/RT}\mathrm{e}^{2RT/RT}$$

$$= \frac{\mathrm{e}^2 k_{\mathrm{B}}T}{hc^{\circ}}\mathrm{e}^{\Delta^{\ddagger}S^{\circ}/R}\mathrm{e}^{-E_a/RT}$$

- Once again, we have by direct comparison with the Arrhenius equation that

$$A = \frac{\mathrm{e}^2 k_{\mathrm{B}}T}{hc^{\circ}}\mathrm{e}^{\Delta^{\ddagger}S^{\circ}/R}$$

- $\boldsymbol{\nu_c}$: The frequency with which the activated complex crosses over the barrier top.

- $\boldsymbol{m^{\ddagger}}$: The mass of the activated complex.

- $\boldsymbol{q_{\mathrm{int}}^{\ddagger}}$: The partition function accounting for all the remaining degrees of freedom of the activated complex.

- $\boldsymbol{\langle u_{\mathrm{ac}} \rangle}$: The average speed with which the activated complex crosses the barrier. *Given by*

$$\langle u_{\mathrm{ac}} \rangle = \nu_c \delta = \sqrt{\frac{k_{\mathrm{B}}T}{2\pi m^{\ddagger}}}$$

  - The latter expression is derived using the one-dimensional Maxwell-Boltzmann distribution (a 1D molecular velocity component Gaussian distribution), which applies since "we have assumed that the reactants and activated complex are in equilibrium" (McQuarrie & Simon, 1997, p. 1167).

$$\langle u_{\mathrm{ac}} \rangle = \int_0^{\infty} u f(u) \, \mathrm{d}u$$

$$= \sqrt{\frac{m^{\ddagger}}{2\pi k_{\mathrm{B}}T}} \int_0^{\infty} u \mathrm{e}^{-m^{\ddagger}u^2/2k_{\mathrm{B}}T} \, \mathrm{d}u$$

$$= \sqrt{\frac{k_{\mathrm{B}}T}{2\pi m^{\ddagger}}}$$

  ■ We integrate over only the positive values because we are only interested in the particles traveling over the activation barrier in the forward direction.

- **$K^{\ddagger}$**: The "equilibrium constant" for the formation of the transition state from the reactants, but the motion along the reaction coordinate excluded in $q_{\mathrm{int}}^{\ddagger}$. *Given by*

$$K^{\ddagger} = \frac{(q_{\mathrm{int}}^{\ddagger}/V)c^{\circ}}{(q_{\mathrm{A}}/V)(q_{\mathrm{B}}/V)}$$

- **Standard Gibbs energy of activation**: The change in Gibbs energy in going from the reactants at a concentration c° to the transition state at a concentration c°. *Denoted by* $\boldsymbol{\Delta^{\ddagger}G^{\circ}}$.

- **Standard enthalpy of activation**: The change in enthalpy in going from the reactants at a concentration c° to the transition state at a concentration c°. *Denoted by* $\boldsymbol{\Delta^{\ddagger}H^{\circ}}$.

- **Standard entropy of activation**: The change in entropy in going from the reactants at a concentration c° to the transition state at a concentration c°. *Denoted by* $\boldsymbol{\Delta^{\ddagger}S^{\circ}}$.

  - Values of $\Delta^{\ddagger}S^{\circ}$ give information about the relative structures of the activated complex and the reactants.
  - For example, if the activated complex is less ordered than the reactants, then $\Delta^{\ddagger}S^{\circ} = +$, and vice versa if the activated complex is more ordered than the reactants.

- **$\boldsymbol{\Delta^{\ddagger}n}$**: The change in the number of molecules from the reactants to the transition state.

  - $\Delta^{\ddagger}n = 0$ for a unimolecular reaction (here both the reactants and transition state consist of one molecule).
  - $\Delta^{\ddagger}n = -1$ for a bimolecular reaction (here the reactants consist of two molecules while the transition state consists of one molecule).
  - $\Delta^{\ddagger}n = -2$ for a termolecular reaction (here the reactants consist of three molecules while the transition state consists of one molecule).

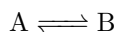## 4.6   Chapter 29: Chemical Kinetics II — Reaction Mechanisms

From McQuarrie and Simon (1997).

- Goals for this chapter.

  - Consider how reactants are converted to products.
  - Discuss commonly encountered **mechanisms**.
  - Derive the rate law for a **complex reaction** using a mechanism and several approximations.
  - Cover the mechanisms of **unimolecular** reactions and **chain reactions**.
  - Explore chemical and biochemical/enzymatic catalysis.

- **Elementary reaction**: A chemical reaction that occurs in a single step and does not involve any intermediates.

  - The rate law of an elementary reaction can be determined from the reaction stoichiometry.

- **Complex reaction**: A reaction that does not occur in a single step.

- **Mechanism**: The sequence of elementary reactions by which a complex reaction occurs.

- Notation.

  - "The arrows $\Rightarrow$ and $\Leftarrow$ will be used to indicate reactions currently thought to be elementary" (McQuarrie & Simon, 1997, p. 1182).
  - "The arrows $\rightarrow$ and $\leftarrow$ will be used to indicate complex reactions" (McQuarrie & Simon, 1997, p. 1182).

- Note that we commonly convey doubt with respect to whether or not a certain reaction is elementary because only a few have been studied in sufficient depth to confirm that they are elementary.

- McQuarrie and Simon (1997) defines **molecularity** as well as **unimolecular**, **bimolecular**, and **termolecular** elementary reactions.

- Although we previously learned that rate laws can only be determined experimentally, the rate law of an *elementary* reaction can be deduced from the balanced chemical equation itself.

  - Indeed, because an elementary reaction does not involve the formation of intermediates, the products must be formed directly from the reactants.

  - Thus, the rate law for a unimolecular reaction, for instance, is first order in the reactant.

  - For bimolecular reactions, we may recall that the collision frequency between reactants in an ideal gas Z_{AB} is proportional to their number densities (or concentrations). This combined with the fact that "to have a collision and also not form any reaction intermediates, an elementary reaction must be one in which all the reactants collide simultaneously, with the reaction occurring immediately upon this collision" tells us that a bimolecular reaction is first order in each reactant and second order overall (McQuarrie & Simon, 1997, p. 1182).

  - Termolecular reactions are similar to bimolecular reactions, with $v = k[A][B][C]$.

- If we are asked to deduce the rate law for a reaction denoted by a single arrow, answer that this is not an elementary reaction and thus we need experimental data.

- **Reversible elementary reaction**: A reaction that occurs in both the forward and reverse directions to a significant extent and that is elementary in each direction. *Denoted by*

$$\text{Reactants} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Products}$$
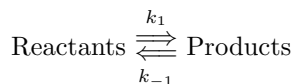
  - Does the principle of microscopic reversibility imply that all reactions that are elementary in one direction are elementary in the others?

- McQuarrie and Simon (1997) derives and defines the **principle of detailed balance**.

- An example of using the principle of detailed balance in the analysis of a complex reaction.

  - Suppose the reaction
$$A \rightleftharpoons B$$
proceeds via the following mechanism, which consists of two competing steps.

$$A + C \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B + C \qquad\qquad A \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} B$$

    - Note that although the right step above is of an identical form to the overall complex reaction, the overall reaction is not elementary because there are two pathways (the two above) by which the reaction can occur. In general, an overall reaction may not be elementary even though an elementary reaction equivalent to it can be one of the pathways.

  - According to the principle of detailed balance, when the overall reaction is at equilibrium, each step must be, too. Thus, at equilibrium,

$$v_1 = v_{-1} \qquad\qquad v_2 = v_{-2}$$

– Consequently, since

$$v_1 = k_1[\text{A}]_\text{eq}[\text{C}]_\text{eq} \qquad\qquad v_2 = k_2[\text{A}]_\text{eq}$$
$$v_{-1} = k_{-1}[\text{B}]_\text{eq}[\text{C}]_\text{eq} \qquad\qquad v_{-2} = k_{-2}[\text{B}]_\text{eq}$$

and

$$K_c = \frac{([\text{B}]_\text{eq}/c^\circ)}{([\text{A}]_\text{eq}/c^\circ)} = \frac{[\text{B}]_\text{eq}}{[\text{A}]_\text{eq}}$$

we have that

$$k_1[\text{A}]_\text{eq}[\text{C}]_\text{eq} = k_{-1}[\text{B}]_\text{eq}[\text{C}]_\text{eq} \qquad\qquad k_2[\text{A}]_\text{eq} = k_{-2}[\text{B}]_\text{eq}$$
$$\frac{k_1}{k_{-1}} = \frac{[\text{B}]_\text{eq}[\text{C}]_\text{eq}}{[\text{A}]_\text{eq}[\text{C}]_\text{eq}} \qquad\qquad \frac{k_2}{k_{-2}} = \frac{[\text{B}]_\text{eq}}{[\text{A}]_\text{eq}}$$
$$= \frac{[\text{B}]_\text{eq}}{[\text{A}]_\text{eq}} \qquad\qquad = K_c$$
$$= K_c$$

– It follows by transitivity that

$$\frac{k_1}{k_{-1}} = \frac{k_2}{k_{-2}}$$

i.e., that the four rate constants are not independent of one another.

– Note that we can also derive $K_c = k_1/k_{-1}$ via the above relation between the rate constants and the alternate equilibrium condition $v_1 + v_2 = v_{-1} + v_{-2}$.

• When a general reaction is the *sum* of two reversible elementary reactions, its equilibrium constant is the *product* of the equilibrium constants of the elementary reactions.

– In particular, for a reaction of the form

$$\text{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{I} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{B}$$
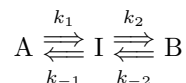
where K_c describes the overall equilibrium (i.e., that between A and B), $K_{c,1}$ describes the equilibrium between A and I, and $K_{c,2}$ describes the equilibrium between I and B, we have that

$$K_c = K_{c,1}K_{c,2}$$

• The rate laws for the mechanism $\text{A} \overset{k_1}{\Longrightarrow} \text{I} \overset{k_2}{\Longrightarrow} \text{P}$ constitute a system of **coupled differential equations** that can be solved analytically, as in class and in Problem 29-5 of PSet 3.

• McQuarrie and Simon (1997) discusses distinguishing the two-step consecutive reaction mechanism unambiguously from the one-step reaction.

– Take-away: "The observation of identical rate constants for the decay of the reactant and the growth of the product does not necessarily mean that no chemical intermediates arise along the reaction path," as this could simply be a case of $k_2 \gg k_1$ (McQuarrie & Simon, 1997, p. 1189).

• **Rate-determining step**: The one step in a reaction mechanism, if it exists, that is much slower than any of the other steps. *Also known as* **RDS**.

– Acting as a bottleneck, the RDS effectively controls the overall reaction rate.

• Consider the reaction mechanism
$$\text{A} \overset{k_1}{\Longrightarrow} \text{I} \overset{k_2}{\Longrightarrow} \text{P}$$
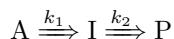
- **Steady-state approximation**: The approximation that $d[I]/dt = 0$ in the above mechanism. *Also known as* **SS approximation**.

  - The steady-state approximation becomes better as k_2 becomes larger relative to k_1.
  - This is because when $k_1 \gg k_2$, I builds up really quickly and then decomposes. When $k_2 \gg k_1$, however, I decomposes as fast as it can be produced, keeping I at a relatively steady, low concentration.

- Qualitatively, the SS approximation corresponds to the case that I is so reactive that $[I] \approx 0$.

- A more rigorous bound on when the steady-state approximation is good to use.

  - As in class, we can determine that

  $$\frac{d[I]_{ss}}{dt} = -\frac{k_1^2}{k_2}[A]_0 e^{-k_1 t}$$

  - But the SS approximation postulates that $d[I]/dt = 0$, not that $d[I]/dt$ is a time-dependent function. Thus, in order to use the steady-state approximation, we must ensure that the above expression is sufficiently close to zero.
  - In particular, we want $-k_1^2[A]_0/k_2 \to 0$, i.e., we want

  $$k_2 \gg k_1^2[A]_0$$

- McQuarrie and Simon (1997) goes through the decomposition of ozone example from class.

- McQuarrie and Simon (1997) goes through the $2\,NO + O_2 \longrightarrow 2\,NO_2$ example from class.

  - McQuarrie and Simon (1997) also shows that both mechanisms lead to the experimental rate law.
  - Two ways to capture or detect the intermediate species are by direct observation (somehow show that it exists in the reaction flask) or by introducing reagents to the reaction mixture that would selectively react with NO_3 (for instance) to form a stable product that can be isolated and characterized.
  - Note also that here once again, we have a rate law that would fit if the reaction were elementary overall, but we know that the reaction is *not* elementary overall.

- McQuarrie and Simon (1997) discusses the $CH_3NC \longrightarrow CH_3CN$ example as an intro to the **Lindemann mechanism**.

  - Note that another troubling observation is that the activation energies of "unimolecular" reactions can be quite large compared with $k_B T$. Thus, we need to identify the external energy source.

- **Lindemann mechanism**: A "unimolecular" reaction mechanism that predicts first-order kinetics at high concentration and second-order kinetics at low concentration. *Given by*

  $$A\,(g) + M\,(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A\,(g)^* + M\,(g)$$

  $$A\,(g)^* \overset{k_2}{\Longrightarrow} B\,(g)$$
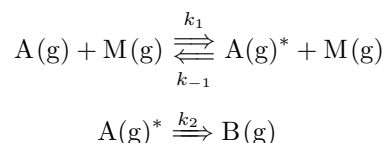
  - The key proposition inherent in this mechanism is that the external energy source is another molecule/collision partner.
  - Another postulate is that there must be a time lag between the collision (or energizing step) and the ensuing reaction; during this lag, the energized molecule could undergo a deactivating bimolecular collision.

- **A(g)***: An energized reactant molecule.

- **M(g)**: The collision partner.

  - The collision partner can be a second reactant molecule, a product molecule, or a nonreactive buffer gas such as N_2 or Ar.

- McQuarrie and Simon (1997) does the Lindemann mechanism analysis.

  - Note that the reason we initially compare $k_1[M][A^*]$ and $k_2[A^*]$ is because at high concentrations, we expect $v_{-1} \gg v_2$.

- Relating the observed activation energy and Arrhenius pre-exponential factor to those for the individual elementary steps involved in the Lindemann mechanism.

  - We have from our Lindemann mechanism analysis that

  $$k_{\mathrm{obs}} = \frac{k_1 k_2}{k_{-1}}$$

  - We also have that

  $$k_{\mathrm{obs}} = A_{\mathrm{obs}} \mathrm{e}^{-E_{a,\mathrm{obs}}/RT} \quad k_1 = A_1 \mathrm{e}^{-E_{a,1}/RT} \quad k_{-1} = A_{-1} \mathrm{e}^{-E_{a,-1}/RT} \quad k_2 = A_2 \mathrm{e}^{-E_{a,2}/RT}$$

  - It follows by combining substituting the four equations above into the first equation that

  $$E_{a,\mathrm{obs}} = E_{a,1} + E_{a,2} - E_{a,-1} \qquad\qquad A_{\mathrm{obs}} = \frac{A_1 A_2}{A_{-1}}$$

  - Thus, the measured values of E_a and A do not correspond to a single step, but rather are influenced by every step.

- McQuarrie and Simon (1997) does the $H_2 + Br_2 \rightleftharpoons 2\,HBr$ chain reaction analysis.

  - Note that by the experimentally determined rate law, the accumulation of HBr slows the mechanism down.

  - We can ignore the fifth step because it is massively endothermic.