Chem 107: More Kinetics
Arrhenius Theory

Energy profile for a reaction

Energy

“Reaction Coordinate”

Reactants

Products

\( E_a \)

\( \Delta E_{rxn} \)

“activated complex”

Rate-determining Quantity

Thermodynamic Quantity
Eₐ, The Activation Energy

- Energy of activation for forward reaction:
  \[ E_a = E_{\text{transition state}} - E_{\text{reactants}} \]

- A reaction can’t proceed unless reactants possess enough energy to give \( E_a \).

- \( \Delta E \), the thermodynamic quantity, tells us about the net reaction. The activation energy, \( E_a \), must be available in the surroundings for the reaction to proceed at a measurable rate.
Temperature, qualitative effect

Increases in temperature increase the fraction of molecules that have the activation energy ($E_a$).

$T = 300 \text{ K}$

$T = 900 \text{ K}$

Maxwell-Boltzmann Distribution

$$\frac{N(u)}{N_{total}} = 4\pi \left[ \frac{M}{2\pi RT} \right]^{3/2} u^2 e^{-\frac{Mu^2}{2RT}}$$

"kills it off" at high $u$
Arrhenius Equation

- Arrhenius noted that reaction rates could be understood to depend on $E_a$ and $T$ with the exponential form:

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

- Or, in logarithmic form:

$$\ln k = \ln A - (E_a/RT)$$

using base 10 logs: $[\log k = \log A - (E_a/2.303RT)]$
Arrhenius Eqn., Alternative Form

Taking two measured values of the rate (at two different temperatures) one can write:

\[
\ln k_1 = \ln A - \left(\frac{E_a}{RT_1}\right) \\
\ln k_2 = \ln A - \left(\frac{E_a}{RT_2}\right) \\
\ln k_2 - \ln k_1 = - \left(\frac{E_a}{R}\right)[(1/T_2)-(1/T_1)] \\
\ln \left(\frac{k_2}{k_1}\right) = - \left(\frac{E_a}{R}\right)[(1/T_2)-(1/T_1)]
\]

Arrhenius Eqn., Graphical Form

A “best fit” to many data is better!

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

slope = \(-E_a/R\)
If a reaction has an activation energy of 50 kJ/mol, then how much should the rate of the reaction accelerate if the temperature is raised from 300 K to 310 K?

\[
\ln\left(\frac{k_{310}}{k_{300}}\right) = -\frac{E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]
\]

\[-\frac{50,000 \text{ J/mol}}{8.314 \text{ J/mol K}} \cdot \left[\frac{1}{310\text{K}} - \frac{1}{300\text{K}}\right] = 0.647\]

\[
k_{310} = e^{0.647}k_{300}
\]

roughly, rate doubles for every 10 °C.
Catalysts - lowering $E_a$. Mechanism may change.

Catalytic Converters, $2\text{NO} \xrightarrow{\text{Pt}} \text{O}_2 + \text{N}_2$

$2\text{NO}(g) \rightarrow \text{O}_2(g) + \text{N}_2(g)$
Reversible Reactions, Equilibrium

\[ 2\text{H}_2\text{O}_2 \xrightarrow{\text{MnO}_2} 2\text{H}_2\text{O} + \text{O}_2 \]
Reversible Elementary Reaction

\[ 2 \text{NO} \rightleftharpoons \text{N}_2\text{O}_2 \]

- At equilibrium, forward and backward rates equal:
  \[ \text{forward rate} = \text{reverse rate} \]
  \[ \dot{k}_f [\text{NO}]^2 = \dot{k}_r [\text{N}_2\text{O}_2] \]

- From this:
  \[ \frac{\dot{k}_f}{\dot{k}_r} = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2} = \text{constant} = K_{eq} \]

Equilibrium Constants

- In general, for ANY reversible chemical reaction:
  \[ \alpha \text{A} + \beta \text{B} \rightleftharpoons \gamma \text{C} + \delta \text{D} \]

- We define an equilibrium constant:
  \[ K_{eq} = \frac{[\text{C}]^{\gamma} [\text{D}]^{\delta}}{[\text{A}]^{\alpha} [\text{B}]^{\beta}} = \frac{"products"}{"reactants"} \]

- Value of \( K_{eq} \) depends on specific reaction and temperature.
**K_{eq} - important features**

- Although we have introduced the concept of an equilibrium constant in discussing reaction rates, the value of the equilibrium constant depends only on thermodynamics! The quantitative relationship is $\Delta G^\circ = -RT \ln K_{eq}$ (more on this later).

- If a catalyst decreases $E_a$, it will increase both $k_f$ and $k_r$ and does not affect $K_{eq}$.

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Equilibrium: Connection to Thermodynamics
Magnitude of $K_{eq}$

- What does it mean if $K_{eq}$ is very large?
  
  \[ \text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]

- At 25°C, $K_{eq}$ is about $10^{140}$, so we don’t usually write the “$\rightleftharpoons$” symbol.

- Recall form of $K_{eq}$:
  “products/reactants”

- With huge $K_{eq}$, lots of products, no reactants. Reaction goes to completion. ($\Delta G^\circ \ll 0$)

Magnitude of $K_{eq}$

- What does it mean if $K_{eq}$ is very small?
  
  \[ \text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO} \]

- At 25°C, $K_{eq}$ is $4.6 \times 10^{-31}$

- Recall form of $K_{eq}$:
  products/reactants

- With tiny $K_{eq}$, lots of reactants, no products. No detectable reaction. ($\Delta G^\circ \gg 0$)
Equilibrium Calculations

- If $K_{eq}$ is neither huge nor tiny, both products and reactants will be present at equilibrium. ($\Delta G$ is neither very positive nor very negative.)
- We can use value of $K_{eq}$ to find equilibrium amounts from initial amounts.
- Use stoichiometry to relate changes in concentration of various substances.

Equilibrium Calculation

- Consider the reaction
  \[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \]
  — called the “water-gas shift reaction”
- Place 1.00 mol each of CO, H$_2$O in a 50.0 L vessel at 1000 °C.
- If $K_{eq} = 0.58$, what will the equilibrium concentrations of all 4 substances be?
- Some hints on next slide.
Equilibrium Calculation: Strategy

- Start by writing expression for $K_{eq}$
- Think about what will happen. Which concentrations will increase? Decrease?
- Use stoichiometry to write changes in concentrations in terms of one variable.
- Set up equilibrium constant expression and solve for the variable introduced above, then calculate final concentrations.

\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \]

- Write equilibrium constant expression in terms of equilibrium concentrations:

\[ K_{eq} = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} \]

Think about the chemistry. Starting with only CO & H$_2$O, reaction must go to the right to form some CO$_2$ & H$_2$. 
Use stoichiometry to write equilibrium concentrations in terms of one variable.

\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2
\]

initial: \(0.02 \text{ M} \) \(0.02 \text{ M} \) \(0\) \(0\)

change: \(-x\) \(-x\) \(+x\) \(+x\)

final: \(0.02 - x\) \(0.02 - x\) \(x\) \(x\)

Find \(x\) by plugging into expression for \(K_{eq}\) and solving for \(x\).

\[
K_{eq} = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{(x)(x)}{(0.02 - x)(0.02 - x)}
\]

\[
0.58 = \frac{x^2}{(0.02 - x)^2}
\]

Solve and find \(x = 0.0086\)

Finally, use \(x\) to find concentrations.
Direction of Reaction

- In that example, we knew which way reaction had to go because only reactants were present at start.

- Suppose both reactants & products are present. How can we tell which way reaction would go to reach equilibrium?

Reaction Quotient \((Q)\)

- Define a “reaction quotient,” \(Q\). Looks just like \(K_{eq}\), except that concentrations need not be equilibrium ones.

\[
\alpha A + \beta B \rightleftharpoons \gamma C + \delta D
\]

\[
K_{eq} = \frac{[C]_\text{eq}^\gamma [D]_\text{eq}^\delta}{[A]_\text{eq}^\alpha [B]_\text{eq}^\beta}
\]

\[
Q = \frac{[C]_\gamma [D]_\delta}{[A]^\alpha [B]^\beta}
\]
Reaction Quotient

■ Compare Q and K to see which way reaction should go.
■ Q < K : need more products, so reaction goes from left to right
■ Q > K : need more reactants, so reaction goes from right to left
■ Q = K : reaction is already at equilibrium

Example Problem (Haber Process)

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \]

■ 1.00 mol N\textsubscript{2}, 3.00 mol H\textsubscript{2}, and 0.500 mol NH\textsubscript{3} are placed in a 50.0 L vessel at 400 °C. At this T, \( K_{eq} = 0.500 \).
■ Will more \text{NH}_3 form, or will \text{NH}_3 dissociate to form more \text{N}_2 and \text{H}_2?
■ Set up an equation to find the equilibrium concentrations.
Haber Process - answer, 1st part

- Compare the value of Q with $K_{eq}$

\[
Q = \frac{[NH_3]^2}{[N_2][H_2]^2} = \frac{(0.01)^2}{(0.02)(0.06)^3} = 23.15
\]

This larger than 0.5 ($= K_{eq}$). Rxn. shifts left.

- $[NH_3]$ will decrease from its initial value, $[H_2]$ and $[N_2]$ will increase.

Haber Process - answer, 2nd part

\[N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)\]

define $x$ as the amount that $[NH_3]$ decreases:

initial: 0.02M 0.06M 0.01M
change: +(1/2)x +(3/2)x $-x$

\[
K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^2} = \frac{(0.01-x)^2}{(0.02 + x/2)(0.06 + 3x/2)^3}
\]

\[
0.500 = \frac{(0.01-x)^2}{(0.02 + x/2)(0.06 + 3x/2)^3} \Rightarrow x \approx .0079
\]

(Solution found graphically)
Le Châtelier's Principle

■ “When a change is imposed on a system at equilibrium, the system will react in the direction that reduces the amount of change.”

■ “Changes” include adding or removing material, or changes in pressure or temperature.

Using Le Châtelier's Principle

\[
\text{CO(g)} + 3\text{H}_2(g) \rightleftharpoons \text{CH}_4(g) + \text{H}_2\text{O}(g)
\]

■ An equilibrium mixture at 1200 K contains 0.613 mol CO, 1.839 mol H\textsubscript{2}, 0.387 mol CH\textsubscript{4} and 0.387 mol H\textsubscript{2}O, all in a 10.0 L vessel. (What is \(K_{eq}\)?)

■ All of the H\textsubscript{2}O is somehow removed, and equilibrium is re-established.

■ What will happen to the amount of CH\textsubscript{4}?

■ Set up eqn. for final amount of CH\textsubscript{4}.
Using Le Châtelier's Principle - Set up

\[ K_{eq} = \frac{[CH_4][H_2O]}{[CO][H_2]^3} \]

\[ CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g) \]

init. \( .0613 \quad .1839 \quad .0387 \quad .0387 \) M

chg. \( .0613 \quad .1839 \quad .0387 \quad 0.0 \) M

Equilibrium is re-established by production of more \( H_2O \) (let the final \( [H_2O] = x \)):

fin. \( .0613-x \quad .1839-3x \quad .0387+x \quad x \) M

Using Le Châtelier's Principle - Set up

\[ K_{eq} = 3.93 = \frac{(0.0387 + x)x}{(0.1839 - 3x)^3(0.0613 - x)} \]
Changes in Temperature

- The equilibrium “constant” is not constant with temperature.

Le Châtelier’s Principle would suggest:

- Qualitatively, if a reaction is endothermic then the equilibrium “constant” increases with temperature
- If a reaction is exothermic then the equilibrium “constant” decreases with temperature

Changes in Pressure

Consider the equilibrium (significant at 700 °C):

\[ \text{CaO(s) + CO}_2\text{(g) } \rightleftharpoons \text{CaCO}_3\text{(s)} \]

Le Châtelier’s Principle would suggest:

If the pressure is suddenly increased, say by suddenly compressing the container, more CO\(_2\) would react with CaO to produce more CaCO\(_3\).