“A” students work 
(without solutions manual)
~ 10 problems/night.

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Module #15:
Introduction to Equilibrium

1. Define Equilibrium, 
And equilibrium constant

Gaseous Chemical Equilibrium

1. Can balance equations
2. Can predict direction of reaction 
(ΔH)
3. Can compute rates
   \[ \text{rate} = -\frac{d[A]}{dt} = k[A]^n \]
4. Can we predict what happens at end?

Our Friend for this Chapter

Dinitrogen tetroxide

A. Intermediate in:
   • nitric acid & sulfuric acid production
   • nitration of organic compound & explosives
   • manufacture of oxidized cellulose compound (hemostatic cotton)
B. Used to bleach flour
C. Proposed as oxidizing agent in rocket propulsion nitrogen dioxide.

We studied its decomposition kinetics in
The preceding chapter

\[ N_2O_4(g) \rightarrow 2NO_2(g) \]

Consider the reaction at 100 °C, where the initial 
Pressure of dinitrogen tetroxide is 1 atm:

\[ N_2O_4(g) \rightarrow 2NO_2(g) \]

The decomposition of dinitrogen tetroxide vs time
Is shown in the table below

<table>
<thead>
<tr>
<th>s</th>
<th>N2O4, atm</th>
<th>NO2, atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>0.6</td>
<td>0.8</td>
</tr>
<tr>
<td>40</td>
<td>0.35</td>
<td>1.3</td>
</tr>
<tr>
<td>60</td>
<td>0.22</td>
<td>1.56</td>
</tr>
<tr>
<td>80</td>
<td>0.22</td>
<td>1.56</td>
</tr>
<tr>
<td>100</td>
<td>0.22</td>
<td>1.56</td>
</tr>
</tbody>
</table>

The reaction order and 
Rate constant can be determined by various time/conc. plots
\[ \text{review} \]

\[ \text{rate} = k[A]^t \]

\[ [A] = [A_0] - kt \]

\[ \ln [A] = \ln [A_0] - kt \]

\[ \frac{1}{[A]} \frac{1}{[A_0]} = k t \]

\[ N_2O_4(g) \rightarrow 2NO_2(g) \]

\[ \text{What do you observe?} \]

\[ \text{1. Conc. Are "stable"} \]

\[ \text{2. Rate forward = rate backward} \]

\[ \text{Using the rate Constants the Rate at each time Can be calculated} \]

\[ \text{"Equilibrium" = "steady state concentrations"} \]

\[ \text{1. occurs when rate forward = rate backward} \]

\[ \text{Rate forward = Rate backward} \]

\[ k_f \frac{P_{N_2O_4}}{P_{N_2O_4}^{eq}} = k_b \left( \frac{P_{NO_2}}{P_{N_2O_4}^{eq}} \right)^t \]

\[ \text{2. concentrations are also constant (steady state)} \]

\[ \text{rate} = k_f \frac{P_{N_2O_4}}{P_{N_2O_4}^{eq}} \]

\[ \text{rate} = k_b \left( \frac{P_{NO_2}}{P_{N_2O_4}^{eq}} \right)^t \]

\[ \text{3. BOTH reactions are occurring competitively} \]

\[ N_2O_4(g) \rightarrow 2NO_2(g) \]
4. An equilibrium constant describes the steady state concs at 100 °C for any starting set of concentrations

\[ K_{\text{equilibrium}} = \frac{[P_\text{NO}_2]}{[P_\text{N}_2\text{O}_4]} \]

<table>
<thead>
<tr>
<th>Experiment</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>time</td>
<td>N2O4</td>
<td>NO2</td>
<td>N2O4</td>
</tr>
<tr>
<td>t=0</td>
<td>1.00</td>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>t=equilibrium</td>
<td>0.22</td>
<td>1.56</td>
<td>0.86</td>
</tr>
</tbody>
</table>

\[ K_{\text{equilibrium}} = \frac{[\text{NO}_2]}{[\text{N}_2\text{O}_4]} \]

Hamilton’s Bar: Legal occupancy: 10

The stupid analogy

Hamilton’s appears to have an unchanged population, but constant exchange of drinkers is occurring. The equilibrium is 10/3.

FITCH Rules

G1: Suzuki is Success
G2. Slow me down
G3. Scientific Knowledge is Referential
G4. Watch out for Red Herrings
G5. Chemists are Lazy

C1. It’s all about charge
C2. Everybody wants to “be like Mike”
C3. Size Matters
C4. Still Waters Run Deep
C5. Alpha Dogs eat first

The “Generic” Rule

Stoichiometry shows up as power

\[ aA + bB \rightleftharpoons cC + dD \]

Pressure

\[ K_{\text{Pressure}} = \frac{\left(P_C\right)^c \left(P_D\right)^d}{\left(P_A\right)^a \left(P_B\right)^b} \]

An equilibrium constant can be written in terms of Molarity also
\[ PV = nRT \]
\[ \frac{P}{RT} = \frac{n}{V} = [\text{molarity}] \]
\[ P = RT [\text{molarity}] \]
\[ K_{\text{Pressure}} = \left( \frac{P_C}{P_A} \right)^c \left( \frac{P_A}{P_B} \right)^d \]
\[ K_{\text{Pressure}} = \left( \frac{RT(C)}{(RT(D))^d} \right)^c \left( \frac{RT(A)}{(RT(B))^b} \right)^d \]
\[ K_{\text{Pressure}} = \left( \frac{RT)^c (RT)^d}{(RT)^a (RT)^b} \right) K_{\text{Concentration}} \]
\[ K_{\text{Pressure}} = \left( \frac{RT)^c (RT)^d}{(RT)^a (RT)^b} \right) K_{\text{Concentration}} \]

When doing problems watch out that they are not switching units on you!!!!!!

**Module #15: Introduction to Equilibrium**

Sample calculation of K

Consider the Haber Reaction which “fixes” nitrogen and is immensely important for the large scale production of ammonia used in explosives fertilizers.

If we mix nitrogen and hydrogen gases will we get ammonia?

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

Haber found a Catalyst to make reaction go

When doing problems watch out that they are not switching units on you!!!!!!

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“Sample calculation of K”

- **Calculate the Kc for the reaction at 25°C:**

\[ 2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g) \]

if the equilibrium pressures are \( P_{\text{NOCl}} = 1.2 \text{ atm} \); \( P_{\text{NO}} = 5.0 \times 10^{-2} \text{ atm} \); and \( P_{\text{Cl}_2} = 3.0 \times 10^{-1} \text{ atm} \).

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Example What is $K_C$ for the Haber Process at 127°C if the equilibrium concentrations of gases are $[NH_3] = 3.1 \times 10^{-2}$ mol/L; $[N_2] = 8.5 \times 10^{-1}$ mol/L; and $[H_2] = 3.1 \times 10^{-3}$ mol/L?

\[
K = \frac{[NH_3]^2}{[N_2][H_2]^3}
\]

\[
K = \frac{3.1 \times 10^{-2} \text{ mol/L}^2}{8.5 \times 10^{-1} \text{ mol/L} \cdot 3.1 \times 10^{-3} \text{ mol/L}^3}
\]

\[
K = 3.8 \times 10^4 \frac{1}{M^2}
\]

Let's reverse the reaction

\[
N_2 + 3H_2 \rightleftharpoons 2NH_3
\]

\[
K' = \frac{1}{K}
\]

\[
K' = 2.6 \times 10^{-6} M^2
\]
An example of adding chemical reactions

\[ \begin{align*}
\text{SO}_2(g) + \frac{1}{2} O_2(g) &\rightleftharpoons \text{SO}_3(g) & K_{\text{SO}_2} = 2.3 \\
\text{NO}_2(g) + \text{NO}(g) &\rightleftharpoons \frac{1}{2} O_2(g) & K_{\text{NO}_2} = 4.0 \\
\text{SO}_2(g) + \text{NO}_2(g) &\rightleftharpoons \text{NO}(g) + \text{SO}_3(g) & K_{\text{rx}} = K_{\text{SO}_2} K_{\text{NO}_2}
\end{align*} \]

\[ K_{\text{SO}_2} = \frac{[\text{SO}_3] [\text{O}_2]}{[\text{SO}_2] [\text{O}_2]} = \frac{[\text{NO}_2] [\text{O}]}{[\text{NO}] [\text{O}_2]}^{\frac{1}{2}} \]

\[ K_{\text{rx}}(K_{\text{SO}_2}) = \left( \frac{[\text{SO}_3] [\text{O}_2]}{[\text{SO}_2] [\text{O}_2]} \right) \left( \frac{[\text{NO}_2] [\text{O}]}{[\text{NO}] [\text{O}_2]}^{\frac{1}{2}} \right) = \left( \frac{[\text{SO}_3] [\text{O}_2]}{[\text{SO}_2] [\text{O}_2]} \right) \left( \frac{[\text{NO}_2] [\text{O}]}{[\text{NO}] [\text{O}_2]} \right)^\frac{1}{2} = K_{\text{rx}} \]

\[ K_{\text{rx}} = K_{\text{SO}_2} K_{\text{NO}_2} = 2.3 \times 4.0 = 9.2 \]

Reversing Reactions

\[ aA + bB \rightleftharpoons cC + dD \quad K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \]

Same patterns

For \( K_p \)

Summing reactions

\[ aA + bB \rightleftharpoons cC + dD \quad K_{ab} \]
\[ cC + dD \rightleftharpoons eE + fF \quad K_{ef} \]
\[ aA + bB \rightleftharpoons eE + fF \quad (K_{ab} K_{ef}) \]

Multiplying reactions

\[ n(aA + bB \rightleftharpoons cC + dD) \quad K_n = K^* \]

Heterogeneous Equilibria

Are equilibria that involve more than one phase

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

\[ K_p = P_{\text{CO}_2} \]

The position of a heterogeneous equilibrium does not depend on the amounts of the pure solids or liquids present

Example Problem: Bone is called apatite and can dissolve:

\[ \text{Ca}_{10}^2 \left( \text{PO}_4 \right)_{6} \left( \text{OH} \right)_{2,s} \rightleftharpoons 10 \text{Ca}_{aq}^{2+} + 6 \text{PO}_{aq}^{3-} + 2 \text{OH}_{aq}^- \]

What is the proper grammar for \( K_p \)?

\[ K = \frac{[\text{Ca}_{aq}^{2+}]^{10} [\text{PO}_{aq}^{3-}]^{6} [\text{OH}_{aq}^-]^{2}}{[\text{Ca}_{10} \left( \text{PO}_4 \right)_{6} \left( \text{OH} \right)_{2,s}]} \]

\[ K = \frac{[\text{Ca}_{aq}^{2+}]^{10} [\text{PO}_{aq}^{3-}]^{6} [\text{OH}_{aq}^-]^{2}}{\left[ \text{Ca}_{10} \left( \text{PO}_4 \right)_{6} \left( \text{OH} \right)_{2,s} \right]} \]
3. **Use $K_{\text{conc}}$ to determine if a Rx will go:**
   a. **Compute Q, the “reaction quotient”**
   b. If $Q < K_{\text{conc}}$, rx goes to right
      - If $Q = K_{\text{conc}}$, rx is at equilibrium
      - If $Q > K_{\text{conc}}$, rx goes to left

What is Q?

$Q = \frac{[C_i]^c[D_i]^d}{[A_i]^a[B_i]^b}$

$i=\text{initial}$

$K_C = \frac{[C_{eq}]^c[D_{eq}]^d}{[A_{eq}]^a[B_{eq}]^b}$

**Example 1:** Use old friend $N_2O_4$

What happens when 0.2 mole of $N_2O_4$ and 0.2 mole of $NO_2$ are added together in a 4 L vol? Recall $K_{\text{conc}} = 0.36M$

<table>
<thead>
<tr>
<th>KNOW</th>
<th>Don’t KNOW</th>
</tr>
</thead>
<tbody>
<tr>
<td>mole = 0.2 mol</td>
<td>initial conc.</td>
</tr>
<tr>
<td>vol = 4 L</td>
<td>rx?</td>
</tr>
<tr>
<td>K = 0.36M</td>
<td></td>
</tr>
</tbody>
</table>

$N_2O_4 \rightleftharpoons 2NO_2(g)$

$\frac{[N_2O_4]_{\text{eq}}}{[N_2O_4]_{\text{init}}} = \frac{0.2 \text{ mol}}{4L} = 0.05 M$

$K = 0.36M = \frac{[NO_2]^2}{[N_2O_4]}$

$\frac{[NO_2]_{\text{eq}}}{[NO_2]_{\text{init}}} = \frac{0.2 \text{ mol}}{4L} = 0.05 M$

$Q = \frac{[NO_2]^2}{[N_2O_4]}_{\text{init}} = \frac{(0.05 M)^2}{0.05 M} = 0.05 M$

$Q < K \Rightarrow rx \rightleftharpoons$
Rules for Equilibrium Calculations

1. Write balanced reaction
2. Write the equilibrium expression
3. Calculate the initial conc., $C_i$
4. Calculate $Q$ and determine if rx goes to left or to right.
5. Express “equil. C” ($C_{eq}$) in terms of init C and change, $x$, ($C_{eq} = C_i + x$)
6. Write $K$ and put in $C_{eq}$, solve for $x$
7. Calculate equilibrium molarities
8**** Check your answer!!!!!

EXAMPLE 2: A BIT SIMPLE

For the system (all are gases) $K_c$ is 0.64 at 900 K:

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

Suppose we start with $CO_2$ and $H_2$, both at a concentration of 0.100 mol/L.

When the system reaches equilibrium, what are the concentrations of products and reactants at 900K?

Red herrings?

1. Balance Equation
   already done

2. Write $K_c$

$$K_c = \frac{[CO][H_2O]}{[CO_2][H_2]}$$

$K_c$ is 0.64 at 900 K. Suppose we start with $CO_2$ and $H_2$, both at a concentration of 0.100 mol/L.

3. Calculate Original or Initial Concentrations

$$[CO_2]_{init} = 0.100 \text{ mol/L}$$
$$[H_2]_{init} = 0.100 \text{ mol/L}$$

4. Calculate $Q$ and determine if rx goes l or r.

$$Q = \frac{[CO][H_2O]}{[CO_2][H_2]} = \frac{0.100 \times 0.100}{0.100 \times 0.100} = 1$$

$Q = 0 < K_c = 0.64$; rx $\rightarrow \text{right}$
5. Express “equil. C” in terms of init C+ or - x

\[ \text{CO}_2 + H_2 \rightleftharpoons CO + H_2O \]

\[ Q = 0 < K_c = 0.64; \text{eq} \rightarrow \text{rxn} \]

Mass balance Limiting reaction

\[
\begin{align*}
[\text{CO}_2]_{eq} &= [\text{CO}]_{eq} - x \\
[\text{CO}]_{eq} &= [\text{CO}]_{initial} + x \\
[H_2]_{eq} &= [H_2O]_{eq} - x \\
[H_2O]_{eq} &= [H_2O]_{initial} + x
\end{align*}
\]

OR: Construct an ICE chart

<table>
<thead>
<tr>
<th>Reaction</th>
<th>CO(_2) + H(_2) ⇌ CO + H(_2)O</th>
<th>Initial Conc</th>
<th>Change (to right)</th>
<th>Equil. Conc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.100  0.100</td>
<td>0 0</td>
<td>-x -x +x +x</td>
<td>0.100-x 0.100-x 0+x 0+x</td>
</tr>
</tbody>
</table>

6. Write K and put in equil Conc:

\[
K = \frac{[\text{CO}]_{eq}[\text{H}_2\text{O}]_{eq}}{[\text{CO}_2]_{eq}[\text{H}_2]_{eq}} = \frac{(x)(x)}{(0.100 - x)(0.100 - x)} = \left( \frac{x}{0.100 - x} \right)^2
\]

7. Calculate equilibrium molarities

\[
\begin{align*}
\text{CO}_2 & \quad \text{H}_2 & \quad \text{CO} & \quad \text{H}_2\text{O} \\
\text{stoichiometry} & = 1 & = 1 & = 1 & = 1 \\
\text{initial conc} & = 0.100 & = 0.100 & = 0 & = 0 \\
\text{change (to right)} & -x & -x & +x & +x \\
\text{equil. conc} & = 0.100-x & = 0.100-x & = 0+x & = 0+x \\
\end{align*}
\]

\[
[\text{CO}_2]_{eq} = [\text{H}_2]_{eq} = 0.100-x = 0.05556 \text{ M}
\]

\[
[\text{CO}]_{eq} = [\text{H}_2\text{O}]_{eq} = 0.0444 \text{ M}
\]

8. Check your answer!!!!!!

Suggestions for ways?

\[
K = \frac{[\text{CO}]_{eq}[\text{H}_2\text{O}]_{eq}}{[\text{CO}_2]_{eq}[\text{H}_2]_{eq}} = \frac{(0.0444 M)(0.0444 M)}{(0.05556 M)(0.05556 M)} = 0.638
\]

OJO: When I round first and then check I get:

\[ K_c = 0.60. \]
EXAMPLE PROBLEM 3: More difficult

If we add 0.1 mol of N₂O₄ in 1 L, what are the equilibrium concentrations? Recall that K_c = 0.36 M.

1. Balance Equation

\[ N₂O₄ \rightarrow 2NO₂ \]

2. Write K

\[ K_c = \frac{[NO₂]^2}{[N₂O₄]} \]

= 0.36 M

3. Calculate Original or Initial Concentrations

0.1 mol of N₂O₄ in 1 L

\[ [N₂O₄] = \frac{0.1 \text{ mol}}{1 \text{ L}} = 0.1 \text{ M} \]

\[ [NO₂] = \frac{0.0 \text{ mol}}{1 \text{ L}} = 0.0 \text{ M} \]

4. Calculate Q and determine if rx goes l or r

\[ Q = \frac{[NO₂]^2}{[N₂O₄]} = \frac{(0.0 \text{ M})^2}{0.1 \text{ M}} = 0.0 \text{ M} < K_c \rightarrow \text{rx right} \]

5. Express “equil. C” in terms of orig C+ or - x

\[ N₂O₄ \rightarrow 2NO₂ \]

\[ 1 \]

\[ \text{Initial conc} \]

\[ \text{Change (to right)} \]

\[ \text{Equil. conc} \]

\[ \text{stoichiometry} \]

\[ \text{OJO!!} \]

6. Write K and put in equil Conc.

\[ K = 0.36 M \]

\[ K = \frac{[NO₂]^2}{[N₂O₄]} \]

\[ = \frac{([NO₂]_{eq})^2}{([N₂O₄]_{eq} - x)} \]

and solve for x
If we add 0.1 mol of N₂O₄ in 1 L, what are the equilibrium concentrations? Recall that \( K_c = 0.36 \text{ M} \).

\[
\begin{align*}
\text{Initial conc} & \quad \text{N}_2\text{O}_4 \quad \text{NO}_2 \\
0.1 & \quad 0 \\
\text{Change (to right)} & \quad -x \quad +2x \\
\text{Equil. conc} & \quad 0.1-x \quad 0+2x \\
\end{align*}
\]

\[
x = \frac{-0.36 \pm \sqrt{0.36^2 - 4(4)(-0.036)}}{2(4)} = \frac{-0.36 \pm \sqrt{0.7056}}{8}
\]

\[
x = \frac{-0.36 \pm 0.84}{8} = 0.06 \text{ and } -0.15
\]

Which is plausible?

No, not plausible. We would be forced to conclude:
\[ x = -0.15 \]
\[ 2x = [\text{NO}_2] = -0.3 \text{ M} \]

7. Calculate equilibrium molarities

\[
x = 0.060
\]

<table>
<thead>
<tr>
<th>Initial conc</th>
<th>\text{N}_2\text{O}_4</th>
<th>\text{NO}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Change (to right)</td>
<td>-x</td>
<td>+2x</td>
</tr>
<tr>
<td>Equil. conc</td>
<td>0.1-x</td>
<td>0+2x</td>
</tr>
</tbody>
</table>

Equilibrium [\text{N}_2\text{O}_4] = 0.04 \text{ M}

Equilibrium [\text{NO}_2] = 0.12 \text{ M}

8**** Check your answer!!!!!
For the reaction of hydrogen gas with iodine gas at room temperature the $K_p$ is $1 \times 10^{-2}$. Suppose that you mix HI at 0.5, H$_2$ at 0.01 and I$_2$ at 0.005 atm in 5 liter volume. Calculate the equilibrium pressures.

3. Calculate Original or Initial Conc or Pressure
A bit of red herring = already know them.

$$P_{HI} = 0.5 \text{ atm}_{init}$$
$$P_{H2} = 0.01 \text{ atm}_{init}$$
$$P_{I2} = 0.005 \text{ atm}_{init}$$

4. Calculate $Q$ and determine if rx goes l or r

$$Q = \frac{(P_{eq,H2})^2}{(P_{eq,HI})(P_{eq,I2})} = \frac{(0.5 \text{ atm})^2}{(0.01 \text{ atm})(0.005 \text{ atm})} = 0.00015$$

5. Express “equil. C” in terms of orig C+ or - x

6. Write K and put in equil Pressures

$$K_p = \frac{(0.5 - 2x)^2}{(0.01 + x)(0.005 + x)}$$

$$K_p(0.01 + x)(0.005 + x) = (0.5 - 2x)^2$$

$$K_p(5 \times 10^{-5} + 0.015x + x^2) = 0.25 - 2x + 4x^2$$

$$5 \times 10^{-5} K_p + 0.015xK_p + x^2 K_p = 0.25 - 2x + 4x^2$$

$$0.25 - 2x + 4x^2 - \left(5 \times 10^{-5} K_p + 0.015xK_p + x^2 K_p\right) = 0$$

$$\left(4x^2 - 2x + 0.25\right) - 5 \times 10^{-5} K_p - 0.015xK_p - x^2 K_p = 0$$

$$\left(4x^2 - x^2 K_p\right) + \left(-2x - 0.015xK_p\right) + \left(0.25 - 5 \times 10^{-5} K_p\right) = 0$$

$$\left(4 - K_p\right)x^2 - x\left(2 + 0.015K_p\right) + \left(0.25 - 5 \times 10^{-5} K_p\right) = 0$$

$$\left(4 - 0.01\right)x^2 - x\left(2 + 0.00015\right) + \left(0.25 - 5 \times 10^{-7}\right) = 0$$

$$\left(3.99\right)x^2 - x(2.00015) + (0.2499995) = 0$$
Which do we use + or -?

\[ x = 0.237739 \]
\[ x = 0.263552 \]

<table>
<thead>
<tr>
<th>stoichiometry</th>
<th>( H_2 )</th>
<th>( I_2 )</th>
<th>HI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial conc</td>
<td>.01</td>
<td>.005</td>
<td>2</td>
</tr>
<tr>
<td>Change (to left)</td>
<td>+x</td>
<td>+x</td>
<td>-2x</td>
</tr>
<tr>
<td>Equil. conc</td>
<td>.01+x</td>
<td>.005+x</td>
<td>0.5-2x</td>
</tr>
</tbody>
</table>

If we use the second answer then we will get

\[ P_{H,eq} = 0.5 - 2x = 0.5 - 2(0.263552) = -0.0271 \]

Not plausible

\[ x = 0.237739 \]

\[ K = \frac{(P_{H,eq})^2}{(P_{I,eq})(P_{I,eq})} = \frac{(0.024523)^2}{(0.242739)(0.242739)} = 0.01 \]

Checks!!!
FITCH Rules

G1: Suzuki is Success
G2. Slow me down
G3. Scientific Knowledge is Referential
G4. Watch out for Red Herrings
G5. Chemists are Lazy
C1. It’s all about charge
C2. Everybody wants to “be like Mike”
C3. Size Matters
C4. Still Waters Run Deep
C5. Alpha Dogs eat first

For systems with multiple reactions
Need to simply = ASSUMPTIONS

Example on Using Simplifications

If 1.0 mol NOCl is placed in a 2.0 L flask what are the equilibrium concentrations of NO and Cl₂ given that at 35 °C the equilibrium constant, Kₑ, is 1.6x10⁻⁵ mol/L?

Red herrings: 35 °C is a red herring
Clues?
K is “small” compared to others (<< 1) we have worked with !!!!!

Example 2: CO₂(g) + H₂(g) → CO(g) + H₂O(g) Kₑ = 0.64.
Example 3: N₂O₄(g) → 2NO₂(g) Kₑ = 0.36M
Example 4: H₂(g) + I₂(g) → 2HI(g) Kₑ is 1x10⁻².

We will define Small in the Next chapter!

If 1.0 mol NOCl is placed in a 2.0 L flask what are the equilibrium concentrations of NO and Cl₂ given that at 35 °C the equilibrium constant, Kₑ, is 1.6x10⁻⁵ mol/L?

Red herrings: 35 °C is a red herring
Clues?
K is “small” compared to others (<< 1) we have worked with !!!!!

We are starting with reactants

1. Balance Equation
2. Write K
3. Calculate or Initial Concentrations
4. Calculate Q and determine if rx goes l or r

2NOCl(g) → 2NO(g) + Cl₂(g)

\[ K = \frac{[NO]^2[Cl_2]}{[NOCl]^2} \]
5. Express “equil. C” in terms of orig C+ or - x

\[
\begin{align*}
2\text{NOCl} \rightleftharpoons 2\text{NO} + \text{Cl}_2 \\
\text{stoichiometry} & : \text{NOCl} : \text{NO} : \text{Cl}_2 \\
\text{Initial conc} & : 0.5 : 0 : 0 \\
\text{Change (to right)} & : -2x : +2x : x \\
\text{Equil. conc} & : 0.5 - 2x : 0 + 2x : 0 + x \\
\text{Assumptions} & : \sim 0.5, 2x, x
\end{align*}
\]

Assumptions are based on
a) K is small so x is small
b) If x is small then sig fig rules eliminate x

6. Write K and put in equil Conc

\[
K = \frac{(2x)^2 \cdot x}{(0.5)^2} = 0.25 = 16x^3
\]

\[
x = 10^{-2}
\]

\[
\begin{align*}
\text{stoichiometry} & : \text{NOCl} : \text{NO} : \text{Cl}_2 \\
\text{Initial conc} & : 0.5 : 0 : 0 \\
\text{Change (to right)} & : -2x : +2x : x \\
\text{Equil. conc} & : 0.5 - 2x : 0 + 2x : 0 + x \\
\text{Assumptions} & : \sim 0.5, 2x, x
\end{align*}
\]

\[
\begin{align*}
\left[\text{NOCl}_{eq}\right] & = 0.5 - 2x \\
\left[\text{NO}_{eq}\right] & = 0.5 - 2 \times 10^{-2} \\
\left[\text{Cl}_2_{eq}\right] & = x = 10^{-2}
\end{align*}
\]

ARE WE DONE?

\[
\begin{align*}
K = 16x^3 \\
1.6 \times 10^{-5} = 16x^3 \\
1.6 \times 10^{-5} = x^3 \\
10^{-6} = x^3 \\
\sqrt[3]{10^{-6}} = x \\
x = 10^{-2}
\end{align*}
\]

7. Calculate equilibrium molarities

\[
\begin{align*}
\text{CHECK ASSUMPTIONS} \\
\text{error} = \frac{\text{real} - \text{estimated}}{\text{real}} \times 100 \\
\text{error} = \frac{0.48 - 5}{0.48} \times 100 = 4\%
\end{align*}
\]

Are we done yet?
S**** Check your answer!!!!!
\[
\begin{align*}
[\text{NOCl}_{\text{eq}}] &= 0.5 \\
[\text{NO}_{\text{eq}}] &= 2x = 2 \times 10^{-2} \\
[\text{Cl}_{\text{eq}}] &= x = 10^{-2} \\
K_e &= \frac{[\text{NO}]^2 [\text{Cl}]}{[\text{NOCl}]^2} = 1.6 \times 10^{-5} M \\
K_e &= \frac{[2 \times 10^{-2}]^2 [10^{-2}]}{[0.5]^2} = 1.6 \times 10^{-5} M \\
K_e &= 1.6 \times 10^{-5} = 1.6 \times 10^{-5} M
\end{align*}
\]

POINT of ASSUMPTIONS

1. Avoid using polynomial equations
2. Can do it with small K values
3. Assume little change (get rid of an x)
4. Must check the assumptions

Multiple Equilibria are not solvable
With simple cubic, quadratic equations

Chemists are Lazy!

I WANT YOU TO PRACTICE EVERY DAY!

“A” students work (without solutions manual)
~ 10 problems/night.

Chemists are ___

If we don’t have to calculate can we make qualitative descriptions of equilibrium?

Le Châtelier’s Principle
if a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change
Effects of Changes on the System

1. Addition of inert gas does not affect the equilibrium position.
2. Concentration: The system will shift away from the added component.
3. Decreasing the volume shifts the equilibrium toward the side with fewer moles.
4. Temperature: $K$ will change depending upon the temperature (treat the energy change as a reactant).

LeChatelier Examples

Example: (Inert gas) Suppose we have the reaction initially at equilibrium

$$2SO_{2,g} + O_{2,g} \rightarrow 2SO_{3,g} \quad K_{e,1000K} = 2.8\times10^3$$

What happens when we add some $N_2,g$ , does Q change?

$$K_e = \frac{[SO_{2,eq}]}{[O_{2,eq}][SO_{3,eq}]}$$

Addition of inert gas does not affect the equilibrium position. Similarly……

Example: (Effect of Solid)

What is the effect on equilibrium in the calcination (decomposition)

$$CaCO_{3,s} \rightarrow CaO_{s} + CO_{2,g}$$

of limestone produced by adding a small quantity of CaCO$_3$(s)?

$$K_e = \frac{[CaO]_{eq}}{[CaCO_3]} \quad \text{Change in quantity of solids do not affect direction of equilibria. So addition of more}$$

limestone is irrelevant.

Example What is the effect on equilibrium in the (decomposition)

$$CaCO_{3,s} \rightarrow CaO_{s} + CO_{2,g}$$

of removing some $CO_{2,g}$, does Q change?

$$[CO_{2,eq}] < [CO_{2,eq}] = \frac{[CO_{2,eq}]}{x} \quad Q = \frac{[CO_{2,eq}]}{x} = K_e = [CO_{2,eq}]^{\text{new,eq}}$$

Example Suppose we have the reaction initially at equilibrium:

$$2SO_{2,g} + O_{2,g} \rightarrow 2SO_{3,g} \quad K_{e,1000K} = 2.8\times10^3$$

What happens when we add some $SO_{3,g}$, does Q change?

$$[SO_{3,eq}] > [SO_{3,eq}] = \frac{[SO_{3,eq}]}{x} \quad Q = \frac{[SO_{3,eq}]}{x} = K_e = [SO_{3,eq}]^{\text{new,eq}}$$

Concentration: The system will shift away from the added component.
Example What happens if we decrease the volume of the container?

\[ 2\text{SO}_2 + O_2 \rightarrow 2\text{SO}_3 \]

\[
K_e = \left[ \text{SO}_3 \right] \left[ O_2 \right] \left[ \text{SO}_2 \right]^{-2}
\]

\[
K_c = \left[ \frac{\text{SO}_3}{\left[ O_2 \right] \left[ \text{SO}_2 \right]^{-2}} \right]^{V_{eq}}
\]

\[
V_{eq} = \frac{x}{K_c} = \left[ \frac{\left[ \text{SO}_3 \right]^{-1}}{\left[ O_2 \right] \left[ \text{SO}_2 \right]^{-2}} \right]^{V_{eq}}
\]

Q changes when we change volume because of differences in stoichiometry.

Decreasing the volume (increasing P) shifts the equilibrium toward the side with fewer moles.

\[ 2\text{SO}_2 + O_2 \rightarrow 2\text{SO}_3 \quad K_c = 280_{1000K} \]

Decrease volume, what happens?

Number of moles of reactants?
Number of moles of products?

If we form reactants we get 3 moles
If we form products we get 2 moles.

reaction moves to decrease moles
moves to the right.

Effect of Temperature????

Consider effect of raising temperature on two reactions:

\[ 2\text{SO}_2 + O_2 \rightarrow 2\text{SO}_3 \quad \Delta H^o = -180kJ \]

\[ N_2 + 2\text{H}_2 \rightarrow 2\text{NH}_3 \quad \Delta H^o = +181kJ \]

What will happen?

Another way to see this is to write the rxs by considering heat.
As a product or reactant. Reaction shifts away from heat:

\[ 2\text{SO}_2 + O_2 \rightarrow 2\text{SO}_3 + \text{heat} \quad \rightarrow \left[ \text{eq} \right] \]

\[ N_2 + 2\text{H}_2 \rightarrow 2\text{NH}_3 \quad \rightarrow \left[ \text{eq} \right] \]

Temperature: \( K \) will change depending upon the temperature (treat the energy change as a reactant).
Jabir ibn Hayyan, 170
Marie the Jewess, 300
Isaac Newton, 1627-1691
Anders Celsius, 1737-1798
Gilbert N Lewis, 1875-1946
Niels Bohr, 1885-1962
Linus Pauling, 1901-1994

<table>
<thead>
<tr>
<th>Chemical Reaction</th>
<th>Expression for $K$</th>
<th>Expression for $Q$</th>
<th>Distinguish between initial and final or equilibrium concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$</td>
<td>$\Delta H^\circ = -92.2,kJ$</td>
<td>$K = 6 \times 10^5 \left</td>
<td>_{25^\circ C} \right.$ Predict first using LeChatelier’s principle: will it get larger or smaller? You try it!, we will compare to calc.</td>
</tr>
</tbody>
</table>

$$\ln \left[ \frac{K_1}{K_2} \right] = -\frac{\Delta H_{\text{forward}}^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$  
Van’t Hoff equation (1852-1911)

$$\ln \left[ \frac{k_1}{k_2} \right] = \left[ -\frac{E_a}{R} \right] \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$  
Arrhenius Equation

$$\ln \left[ \frac{P_1}{P_2} \right] = \left[ -\frac{\Delta H_{\text{vap}}}{R} \right] \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$  
Clausius-Clapeyron equation

$\Delta H^\circ = -92.2\,kJ$  
What is $K$ at 100 °C?

$K = 6 \times 10^5 \left|_{25^\circ C} \right.$ Predict first using LeChatelier’s principle: will it get larger or smaller? You try it!, we will compare to calc.

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) + \text{heat}$

$$\ln \left[ \frac{K_1}{K_2} \right] = -\frac{\Delta H_{\text{forward}}^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$  
$$= \frac{6 \times 10^5}{K_2} = e^{7.48628} = 1783.405$$

$$\ln \left[ \frac{P_1}{P_2} \right] = \left[ -\frac{\Delta H_{\text{vap}}}{R} \right] \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \left[ \frac{6 \times 10^8}{K_2} \right] = \frac{11095.07}{\text{Kelvin}} \left[ \frac{0.00675}{\text{Kelvin}} \right] = 7.48628$$  
$$= \frac{6 \times 10^8}{1783.405} = K_2 = 336.435$$

What have we learned?

1. Expression for $K$
2. Expression for $Q$
3. Distinguish between initial and final or equilibrium concentrations.
4. How to predict direction of a reaction
5. How to calculate the equilibrium conc.
6. How to make assumptions to ease the calculations.
7. How to check the calculations
8. How to use Le Chat.... principle to effect of conc., pressure, volume, and temp. on a reaction.
“A” students work (without solutions manual) ~7 problems/night.