CHEMICAL EQUILIBRIUM

Chapter 13

Chemical Equilibrium

Reversible Reactions:

A chemical reaction in which the products can react to re-form the reactants

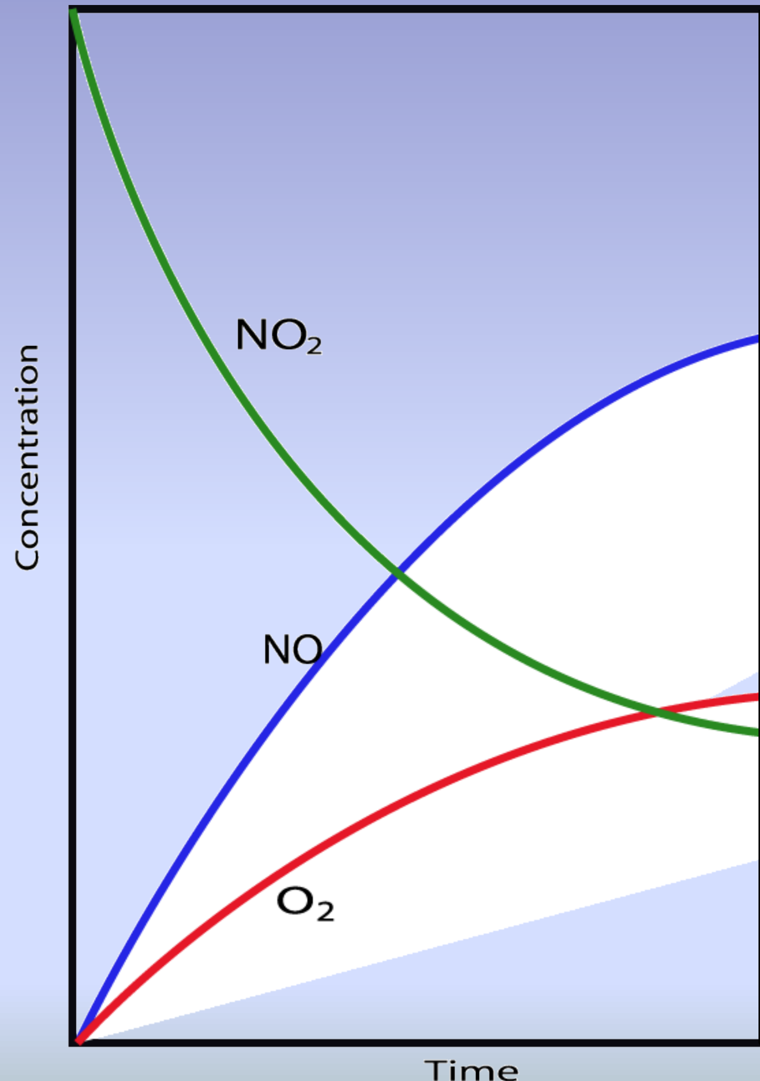
Chemical Equilibrium:

When the rate of the forward reaction equals the rate of the reverse reaction and the concentration of products and reactants remains unchanged

$$2HgO(s) \leftrightarrows 2Hg(l) + O_2(g)$$

Arrows going both directions ($\leftrightarrows$) indicates equilibrium in a chemical equation

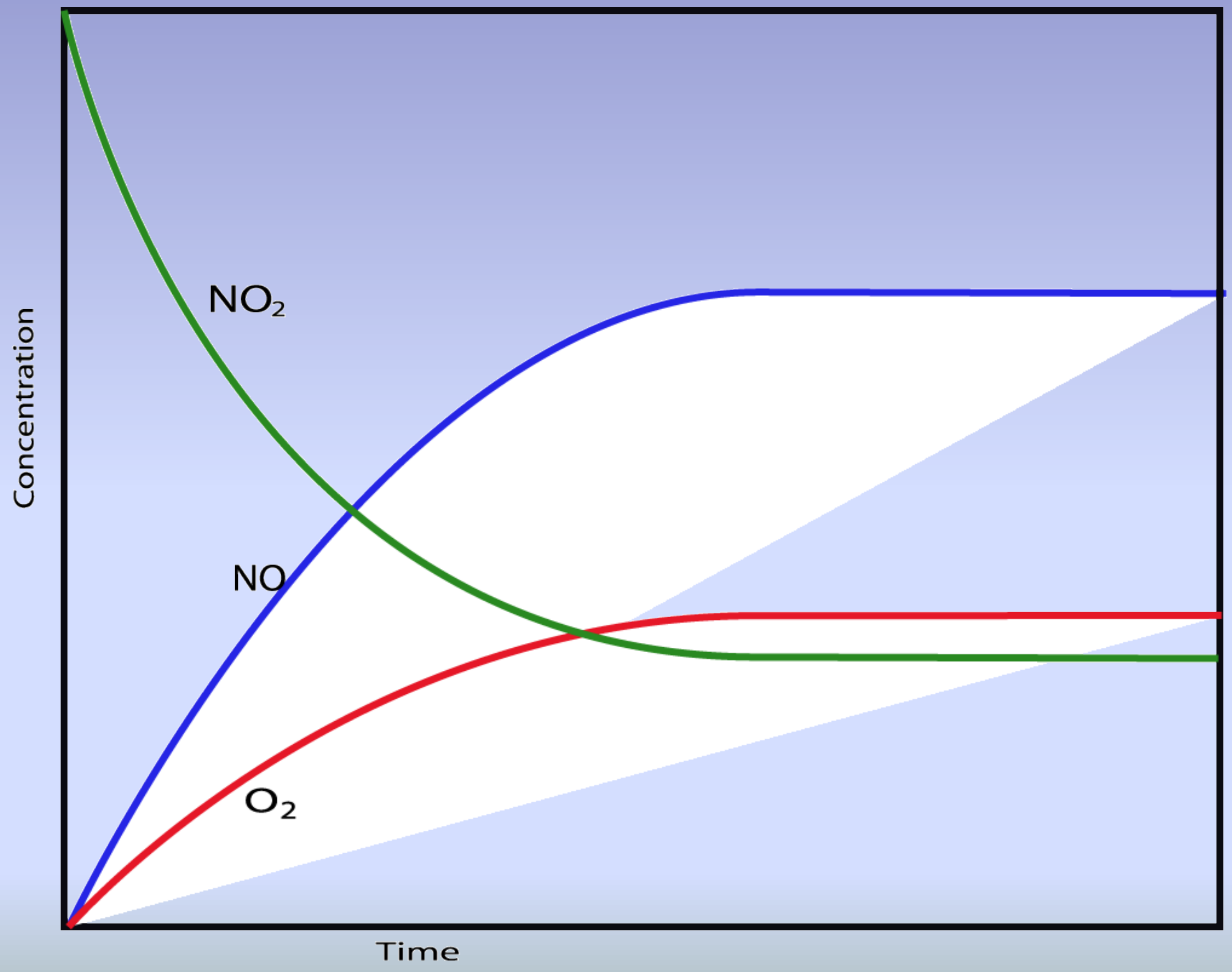
$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$



Remember this from Chapter 12?

Why was it so important to measure reaction rate at the start of the reaction (method of initial rates?)

$$2NO_2(g) \leftrightarrows 2NO(g) + O_2(g)$$



Law of Mass Action

For the reaction:

$$jA + kB \rightleftarrows lC + mD$$

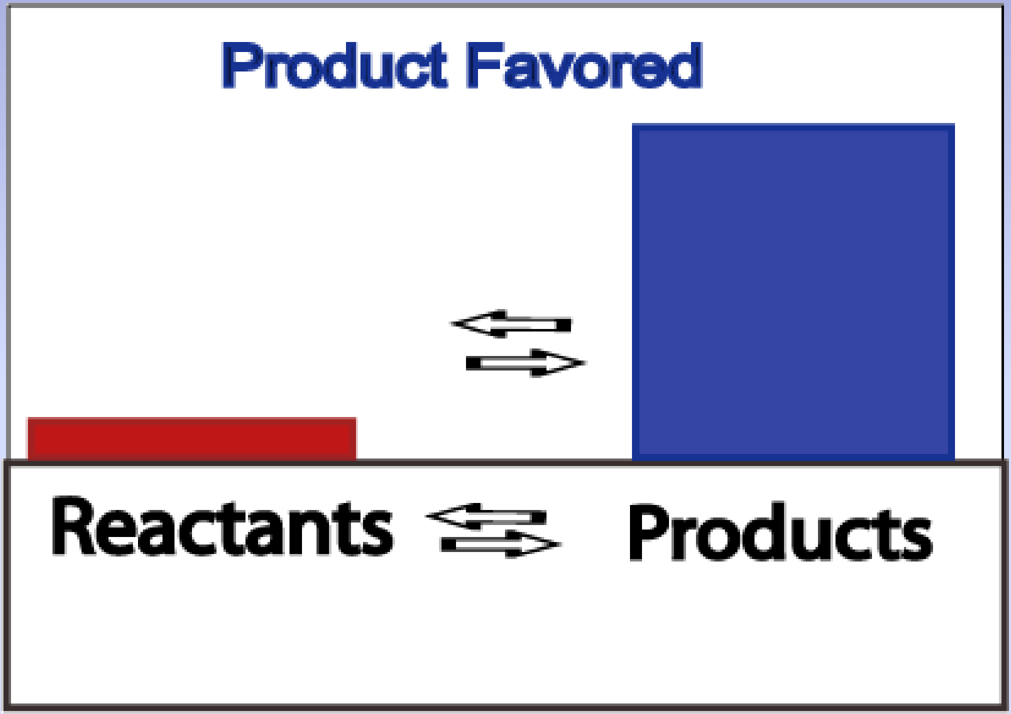
$$K = \frac{[C]^l [D]^m}{[A]^j [B]^k}$$

Where K is the equilibrium constant, and is unitless.

(Solids and pure liquids don't come)

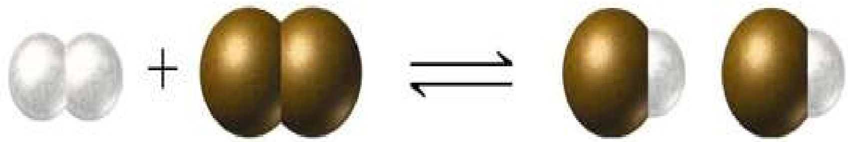
Product Favored Equilibrium

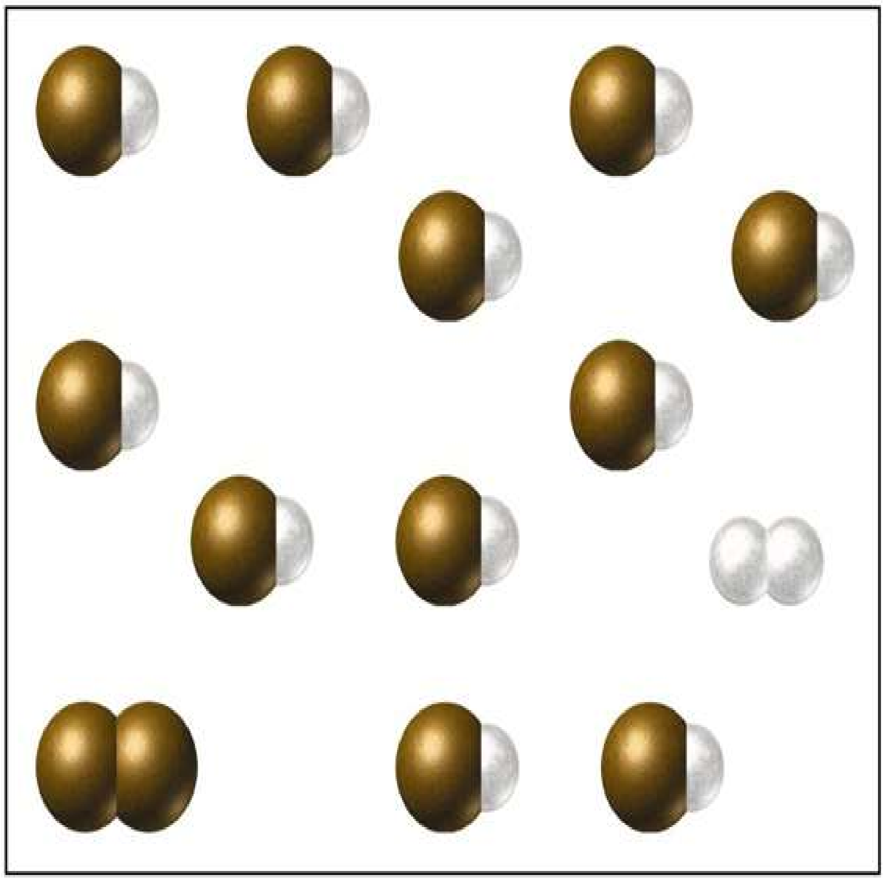
Large values for *K* signify the reaction is "product favored"



When equilibrium is achieved, <u>most reactant</u> has been <u>converted to product</u>

$$H_2(g) + Br_2(g) \rightleftharpoons 2\,HBr(g)$$

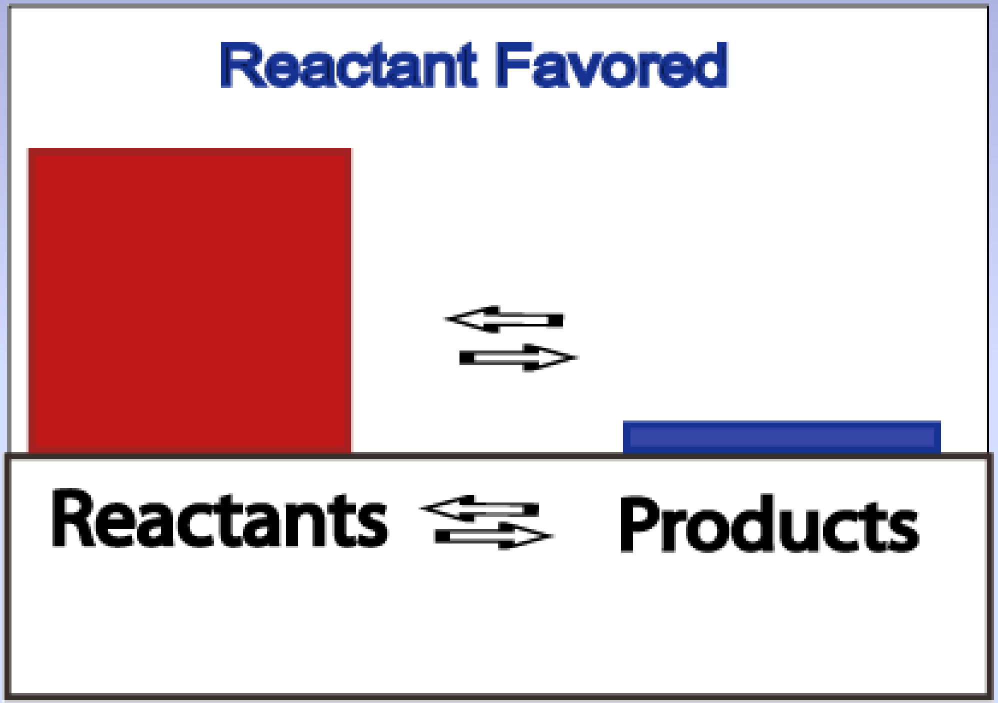




$$K = \frac{[HBr]^2}{[H_2][Br_2]} = \textbf{Large Number}$$

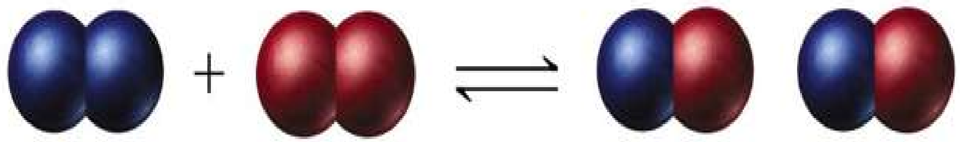
Reactant Favored Equilibrium

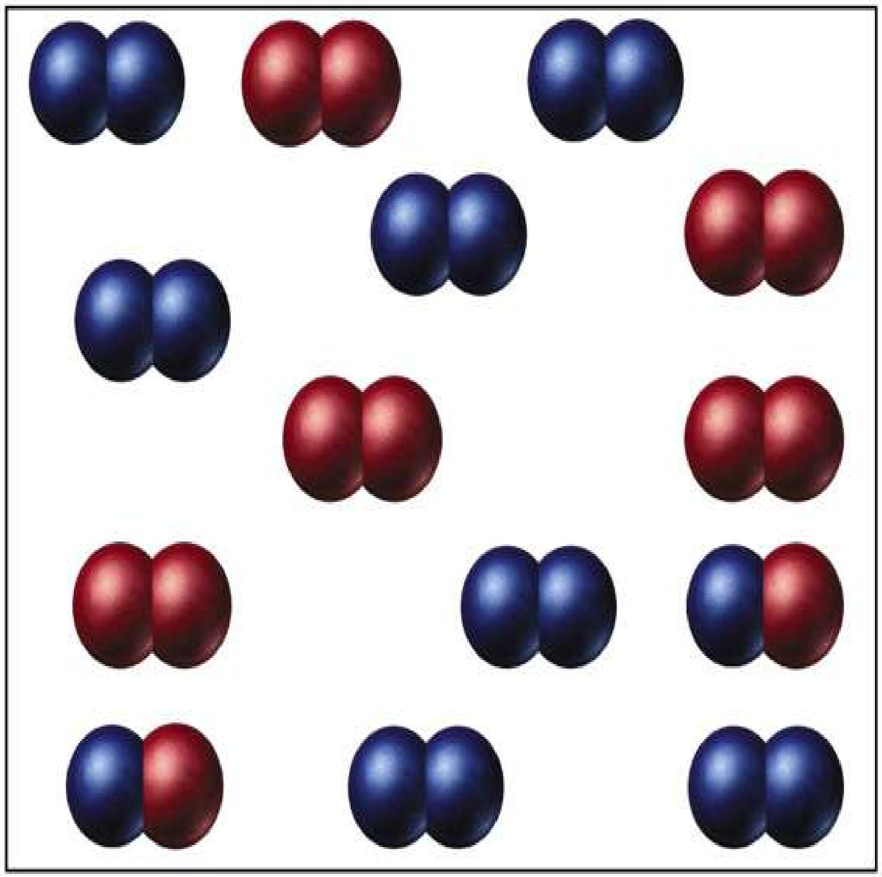
Small values for K signify the reaction is "reactant favored"



When equilibrium is achieved, very little reactant has been converted to product

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$$





$$K = \frac{[NO]^2}{[N_2][O_2]} = \textbf{Small Number}$$

Writing an Equilibrium Expression

Write the equilibrium expression for the reaction:

$$2NO_2(g) \leftrightarrows 2NO(g) + O_2(g)$$

$$K = ???$$

$$K = \frac{[NO]^2[O_2]}{[NO_2]^2}$$

Conclusions about Equilibrium Expressions

- The equilibrium expression for a reaction is the reciprocal for a reaction written in reverse

$$2NO_2(g) \leftrightarrows 2NO(g) + O_2(g)$$

$$K = \frac{[NO]^2[O_2]}{[NO_2]^2}$$

$$2NO(g) + O_2(g) \leftrightarrows 2NO_2(g)$$

$$K' = \frac{1}{K} = \frac{[NO_2]^2}{[NO]^2[O_2]}$$

Conclusions about Equilibrium Expressions

- When the balanced equation for a reaction is multiplied by a factor *n*, the equilibrium expression for the new reaction is **the original expression**, raised to the ***nth*** power.

$$2NO_2(g) \leftrightarrows 2NO(g) + O_2(g)$$

$$K = \frac{[NO]^2[O_2]}{[NO_2]^2}$$

$$NO_2(g) \leftrightarrows NO(g) + \tfrac{1}{2}O_2(g)$$

$$K^1 = K^{\frac{1}{2}} = \frac{[NO][O_2]^{\frac{1}{2}}}{[NO_2]}$$

Calculating The Equilibrium Constant

- **1. $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$**

  $[NH_3] = 0.0100M$, $[N_2] = 0.0200M$, $[H_2] = 0.0200M$

- **2. $2KClO_3(s) \leftrightarrow 2KCl(s) + 3O_2(g)$**

  $[O_2] = 0.0500M$

- **3. $H_2O(l) \leftrightarrow H^+(aq) + OH^-(aq)$**

  $[H^+] = 1x10^{-8}M$, $[OH^-] = 1x10^{-6}M$

- **4. $2CO(g) + O_2(g) \leftrightarrow 2CO_2(g)$**

  $[CO] = 2.0M$, $[O_2] = 1.5M$, $[CO_2] = 3.0M$

- **5. $Li_2CO_3(s) \leftrightarrow 2Li^+(aq) + CO_3^{2-}(aq)$**

  $[Li^+] = 0.2M$, $[CO_3^{2-}] = 0.1M$

HW:
17,19,
21, 22,

Equilibrium Expressions Involving Pressure

For the gas phase reaction:

$3H_2(g) + N_2(g) \leftrightarrows 2NH_3(g)$

$$K_P = \frac{P_{NH_3}{}^2}{(P_{N_2})(P_{H_2}{}^3)}$$

$$P_{NH_3}, P_{N_2}, P_{H_2} \ \textit{are equilibrium partial pressures}$$

$$K_p = K(RT)^{\Delta n}$$

Δn = moles of product gas – moles of reactant gas

If K_c = 9.6 at 300°C, find K_p

Heterogeneous Equilibria

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

Write the equilibrium expression for the reaction:

$PCl_5(s) \leftrightarrows PCl_3(l) + Cl_2(g)$

Pure solid

Pure liquid

$$\therefore K = [Cl_2]$$

$$\therefore K_p = P_{Cl_2}$$

HW: 25,27,29,23

The Reaction Quotient

For some time, t, when the system is not at equilibrium, the reaction quotient, Q takes the place of K, the equilibrium constant, in the law of mass action.

$$jA + kB \leftrightarrows lC + mD$$

$$Q = \frac{[C]^l [D]^m}{[A]^j [B]^k}$$

Significance of the Reaction Quotient

- If $Q = K$, the system is at equilibrium

- If $Q > K$, the system shifts to the left, consuming products and forming reactants until equilibrium is achieved

- If $Q < K$, the system shifts to the right, consuming reactants and forming products until equilibrium is achieved

Solving for Equilibrium Concentration

Consider this reaction at some temperature:

$H_2O(g) + CO(g) \leftrightarrows H_2(g) + CO_2(g)$ $K = 2.0$

Assume you start with 8 molecules of H_2O and 6 molecules of CO. How many molecules of H_2O, CO, H_2, and CO_2 are present at equilibrium?

Here, we learn about "ICE" – the most important problem solving technique in the second semester. You will use it for the next 4 chapters!

Steps to Solving Equilibrium Questions

1. Write balanced equation
2. Write equilibrium expression
3. Calculate Q and determine the direction of shift
4. I.C.E box time to find the value of “x”
5. Use “x” to find the concentrations at equilibrium
6. Check your answer

Solving for Equilibrium Concentration

Step 1: Balance Equation

$H_2O(g) + CO(g) \leftrightarrows H_2(g) + CO_2(g)$ $\quad K = 2.0$

Step 2: Equilibrium Expression

$$2.0 = \frac{[H_2][CO_2]}{[H_2O][CO]}$$

Solving for Equilibrium Concentration

Step #4: We "ICE" the problem, beginning with the Initial concentrations

$$H_2O(g) + CO(g) \leftrightarrows H_2(g) + CO_2(g)$$

	$H_2O(g)$	$CO(g)$	$H_2(g)$	$CO_2(g)$
Initial:	8	6	0	0
Change:	-x	-x	+x	+x
Equilibrium:	8-x	6-x	x	x

Solving for Equilibrium Concentration

We plug equilibrium concentrations into our equilibrium expression, and solve for x

$$H_2O(g) + CO(g) \leftrightarrows H_2(g) + CO_2(g)$$

Equilibrium:	8-x	6-x	x	x

$$2.0 = \frac{(x)(x)}{(8-x)(CO)}$$

$$\boxed{x = 4}$$

Solving for Equilibrium Concentration

Step #5: Substitute x into our equilibrium concentrations to find the actual concentrations

$$H_2O(g) + CO(g) \leftrightarrows H_2(g) + CO_2(g)$$

Equilibrium:	8-x	6-x	x	x

$$x = 4$$

Equilibrium:	8-4=4	6-4=2	4	4

Another Example

1. **Phosphorus pentachloride decomposes into phosphorous trichloride and chlorine gas. 0.500 moles of pure phosphorus pentachloride is placed in a 2.00 L bottle. What are the resulting concentrations?**

$K_c = 0.0211 \ mol \ L^{-1}$

HW: 33,37,39,41,45, more if you need it

K_{eq} and Solubility

- This is a review for things dissolved
- But remember solids aren't invited so...

- $CaF_{2(s)} \leftrightharpoons Ca^{2+}_{(aq)} + 2F^{-}_{(aq)}$

- $K_{eq} = K_{sp} = [Ca^{2+}][F^{-}]^2$

K_{eq} and Acids

- Acids go through reactions like this

- $HA_{(aq)} \leftrightharpoons H^+_{(aq)} + A^-_{(aq)}$

- $K_{eq} = K_a = [H^+][A^-]/[HA]$

K_{eq} and Bases

- Bases go through reactions like this

$$NH_{3(aq)} + H_2O_{(l)} \leftrightharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

$$K_{eq} = K_b = [NH_4^+][OH^-]/[NH_3]$$

Summary

- K_c - Constant for molar concentration
- K_p - Constant for partial pressures
- K_{sp} – Solubility product
- K_a - Acid dissociation constant for weak acids
- K_b - Base dissociation constant for weak bases
- K_w - describes the ionization of water ($K_w = 1 \times 10^{-14}$)

K_{eq} and Multistep Processes

- If a reaction happens in a series of steps, and you want to know the overall K, you can multiply the K's of the individual reactions to get the overall...
  - $A + B \leftrightharpoons C \quad K_{eq} = K_1$
  - $C \leftrightharpoons D + E \quad K_{eq} = K_2$
  - $A + B \leftrightharpoons D + E \quad K_{eq} = K_1K_2$

Easy Mode

- The solubility product constant (K_{sp}) for calcium fluoride is 5.3×10^{-9}. If 2.00 mols of calcium fluoride is placed in 0.500 L of water, what are the concentrations of the products and reactants at equilibrium?

- Hint: Product or reactant favored?

Le Chatelier's Law

When a stress is put on an equilibrium, the equilibrium will shift to relieve that stress.

$N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}$

$\Delta H = -92 kJ/mol$

- Concentration?
- Heat?
- Pressure?