Chemistry

Chapter 13
Chemical Equilibrium

Section 1

Chapters:

13.1 The equilibrium condition
13.2 The equilibrium constant
13.3 Equilibrium – pressure
13.4 Heterogeneous equilibria

Review – Chemical Equations

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

1. The number of atoms on the left must equal the right
2. The coefficients on each species represents the number of moles of each species.

The Equilibrium Condition

- The equilibrium state is the point at which the concentration of the products and reactants remains constant with time.

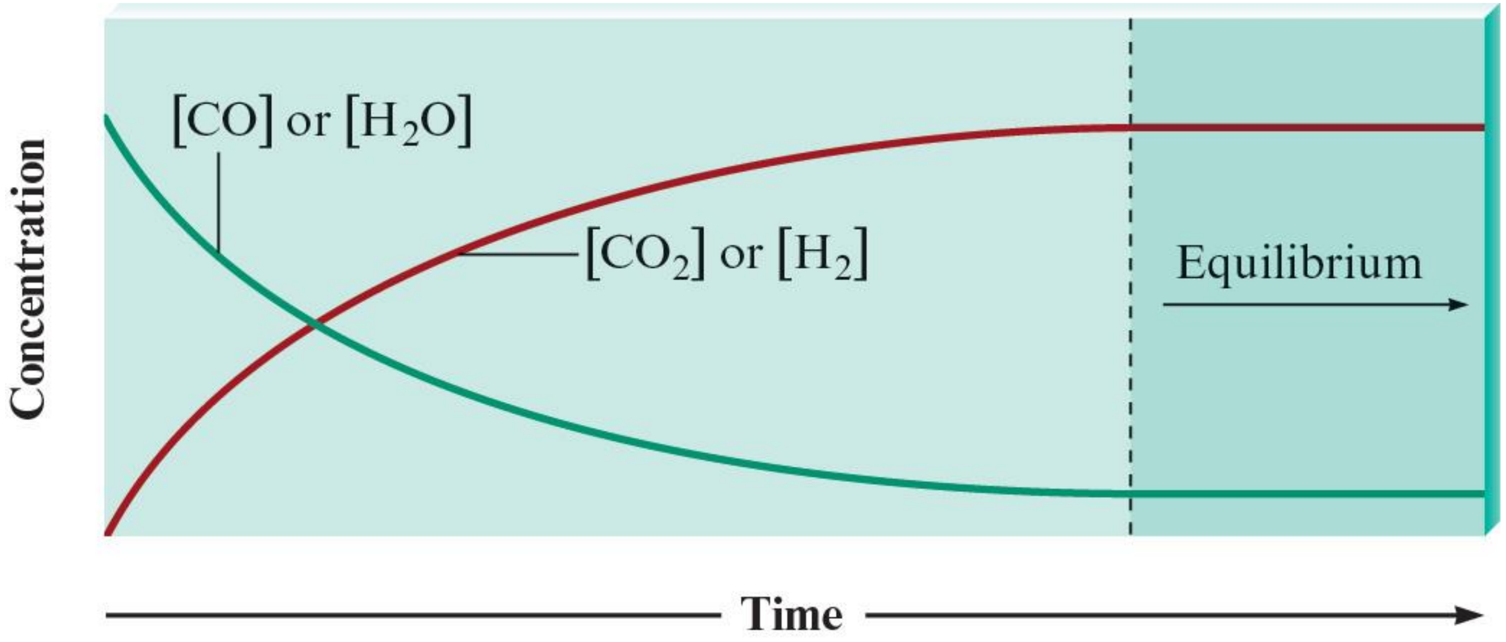
- This means that the rate of the forward reaction equals the rate of the reverse reaction.

The Equilibrium Condition

- If the reactants are favoured then the equilibrium position of the reaction lies far to the left and vice versa.

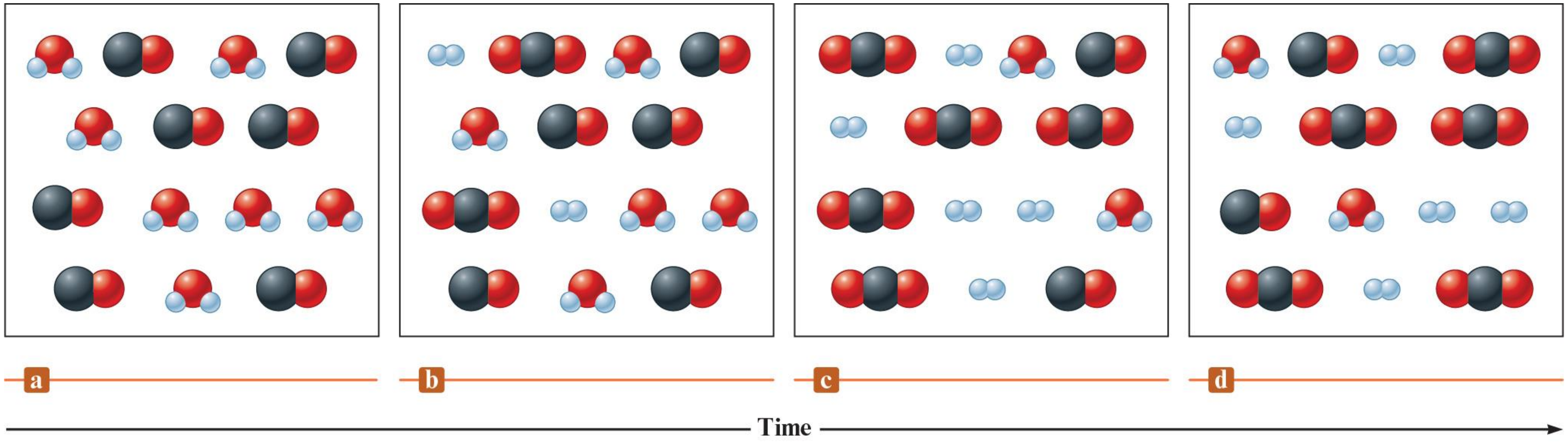
The Equilibrium Condition

$$CO + H_2O \rightarrow CO_2 + H_2$$



The Equilibrium Condition

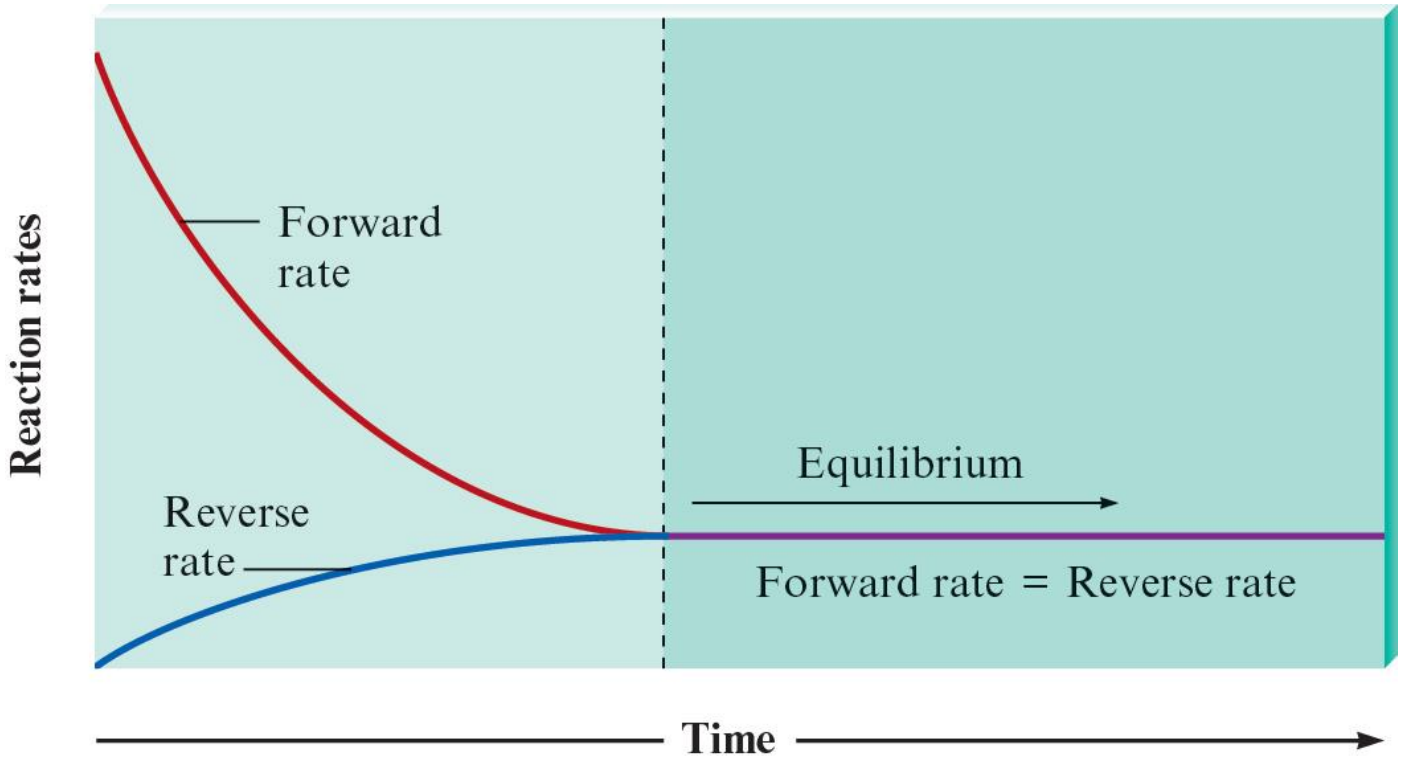
$$CO + H_2O \rightarrow CO_2 + H_2$$



The Equilibrium Condition

$$Forward\ Reaction:\ CO + H_2O \rightarrow CO_2 + H_2$$

$$Reverse\ Reaction: CO_2 + H_2 \rightarrow CO + H_2O$$



The Equilibrium Condition

- There are a few factors that determine the equilibrium position of a reaction.

1. The initial concentrations
2. The relative energies of the reactants and products (I.E. Temperature, Pressure, etc.)
3. The relative degree of organization of reactants and products.

The Equilibrium Condition

- When in chemical equilibrium the concentrations of the products and reactants do not change.
- This is because the rate at which the products are being made equal the rate at which the reactants are being made.
- Once this happens we say the system has reached chemical equilibrium.

The Equilibrium Condition

Consider the following reaction…

$$CO + H_2O \rightarrow CO_2 + H_2$$

Which of these statements must be true when the reaction reaches equilibrium?

The Equilibrium Condition

$$CO + H_2O \rightarrow CO_2 + H_2$$

1. $[CO_2] = [H_2]$ because it’s a one to one molar ratio

2. The total concentration of the reactants equals the total concentration of the products.

3. The total concentration of the reactants is greater than the concentration of the products.

4. The rate of the forward reaction equals the rate of the reverse reaction.

The Equilibrium Constant

- This is a number that tells us information about the equilibrium state of the reaction.
- Very large numbers = a product favored equilibrium
- Very small numbers = a reactant favored equilibrium
- The constant is unit-less

The Equilibrium Constant

- For a general chemical expression

$$jA + kB \ \rightarrow lC + mD$$

- Where A,B,C, and D are chemical species and j,k,l, and m are the coefficents.

- The equilibrium constant K is

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

The Equilibrium Constant

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

- The equilibrium constant is always found by taking the products divided by the reactants.
- [A] = the concentration of the species in mols/liter
- The superscripts represent the coefficients in the original chemical equation.
- Remember K is the equilibrium constant!

The Equilibrium Constant

Write the chemical equilibrium expression for the following reaction.

$$4NH_3(g) + 7O_2(g) \rightarrow 4NO_2(g) + 6H_2O(g)$$

Coefficient of NO_2

Coefficient of H_2O

$$K = \frac{[NO_2]^4 [H_2O]^6}{[NH_3]^4 [O_2]^7}$$

Coefficient of O_2

Coefficient of NH_3

The Equilibrium Constant

Let’s do it again but this time we will have initial concentrations to actually calculate K.

The Equilibrium Constant

Given the chemical equation below and the initial concentrations, calculate the chemical equilibrium constant.

$$\frac{1}{2}N_2\,(g) + \frac{3}{2}H_2(g) \;\rightarrow NH_3$$

$$[\mathrm{NH_3}] = 3.1 \times 10^{-2}\ \mathrm{mol/L}$$

$$[\mathrm{N_2}] = 8.5 \times 10^{-1}\ \mathrm{mol/L}$$

$$[\mathrm{H_2}] = 3.1 \times 10^{-3}\ \mathrm{mol/L}$$

Hint: Balance the reaction first! Make sure all the coefficients are whole numbers.

The Equilibrium Constant

$$2 * \left(\frac{1}{2} N_2\ (g) + \frac{3}{2} H_2(g)\ \rightarrow NH_3\right)$$

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

$$K = \frac{[NH_3]^2}{[N_2]^1[H_2]^3}$$

$$K = \frac{[3.1\ * 10^{-2}]^2}{[8.5\ * 10^{-1}]^1[3.1\ * 10^{-3}]^3} = 3.8\ * 10^4$$

We always write K without units.

The Equilibrium Constant

- You can also find the equilibrium constant for the reverse reaction.
- We call this K' or K prime
- All you have to do is divide 1 by K

$$K' = \frac{1}{K} = \frac{1}{3.8 \ * 10^4} = 2.6 \ * 10^{-5}$$

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

The Equilibrium Constant

- There is also a way to calculate the equilibrium constant using the law of mass action. This only works if we have the equilibrium constant determined for an ideally balanced equation.

The Equilibrium Constant

Let's go back to our last example.

$$\frac{1}{2}N_2\,(g) + \frac{3}{2}H_2(g) \;\rightarrow NH_3$$

If the problem wants us to use the law of mass action to calculate the equilibrium constant then we leave the equation balanced with fraction coefficients.

The Equilibrium Constant

$$\frac{1}{2}N_2\ (g) + \frac{3}{2}H_2(g)\ \rightarrow NH_3$$

$$K = \frac{[NH_3]^2}{[N_2]^1[H_2]^3}$$

$$K^{\frac{1}{2}} = \left(\frac{[NH_3]^2}{[N_2]^1[H_2]^3}\right)^{\frac{1}{2}} = K''$$

$$K^{\frac{1}{2}} = (3.8\ * 10^4)^{\frac{1}{2}} = 1.9\ * 10^2 = K''$$

The Equilibrium Constant

Simply put for a general chemical equation

$$njA + nkB \rightarrow nlC + nmD$$

Where n is some constant being multiplied to each species in our equation.

$$K'' = \frac{[C]^{nl}[D]^{nm}}{[A]^{nj}[B]^{nk}} = K^{n}$$

The Equilibrium Constant

The chemical equilibrium constant we calculate only holds true for a specific temperature and pressure in the system. At a certain temperature and pressure though, K will always be the same for a reaction. No matter what.

The Equilibrium Constant

Experiment	Initial Concentrations	Equilibrium Concentrations	$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$
I	$[N_2]_0 = 1.000\ M$ $[H_2]_0 = 1.000\ M$ $[NH_3]_0 = 0$	$[N_2] = 0.921\ M$ $[H_2] = 0.763\ M$ $[NH_3] = 0.157\ M$	$K = 6.02 \times 10^{-2}$
II	$[N_2]_0 = 0$ $[H_2]_0 = 0$ $[NH_3]_0 = 1.000\ M$	$[N_2] = 0.399\ M$ $[H_2] = 1.197\ M$ $[NH_3] = 0.203\ M$	$K = 6.02 \times 10^{-2}$
III	$[N_2]_0 = 2.00\ M$ $[H_2]_0 = 1.00\ M$ $[NH_3]_0 = 3.00\ M$	$[N_2] = 2.59\ M$ $[H_2] = 2.77\ M$ $[NH_3] = 1.82\ M$	$K = 6.02 \times 10^{-2}$

The Equilibrium Constant

Equilibrium position	Equilibrium constant
• Refers to each set of equilibrium concentrations • There can be infinite number of positions for a reaction • Depends on initial concentrations	• One constant for a particular system at a particular temperature • Remains unchanged • Depends on the ratio of concentrations

The Equilibrium Constant

- The following results were collected for two experiments involving the reaction at 600° C between gaseous SO_2 and O_2 to form gaseous sulfur trioxide:

Experiment 1		Experiment 2	
Initial	**Equilibrium**	**Initial**	**Equilibrium**
$[SO_2]_0 = 2.00\ M$	$[SO_2] = 1.50\ M$	$[SO_2]_0 = 0.500\ M$	$[SO_2] = 0.590\ M$
$[O_2]_0 = 1.50\ M$	$[O_2] = 1.25\ M$	$[O_2]_0 = 0$	$[O_2] = 0.0450\ M$
$[SO_3]_0 = 3.00\ M$	$[SO_3] = 3.50\ M$	$[SO_3]_0 = 0.350\ M$	$[SO_3] = 0.260\ M$

  - Show that the equilibrium constant is the same in both cases

The Equilibrium Constant

First we need to determine the balanced reaction.

We have SO_2 reacting with O_2 to form SO_3

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

The Equilibrium Constant

Now we are going to build our general equilibrium expression

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]^1}$$

The Equilibrium Constant

Now we are going to plug in our concentrations at equilibrium

Experiment 1		Experiment 2	
Initial	Equilibrium	Initial	Equilibrium
$[SO_2]_0 = 2.00\ M$	$[SO_2] = 1.50\ M$	$[SO_2]_0 = 0.500\ M$	$[SO_2] = 0.590\ M$
$[O_2]_0 = 1.50\ M$	$[O_2] = 1.25\ M$	$[O_2]_0 = 0$	$[O_2] = 0.0450\ M$
$[SO_3]_0 = 3.00\ M$	$[SO_3] = 3.50\ M$	$[SO_3]_0 = 0.350\ M$	$[SO_3] = 0.260\ M$

$$K_1 = \frac{(3.50)^2}{(1.50)^2(1.25)} = 4.36 \qquad K_2 = \frac{(0.260)^2}{(0.590)^2(0.0450)} = 4.32$$

The Equilibrium Constant

- Which of the following statements is false regarding chemical equilibrium?
  a. A system that is disturbed from an equilibrium condition responds in a manner to restore equilibrium
  b. The value of the equilibrium constant for a given reaction mixture at constant temperature is the same regardless of the direction from which equilibrium is attained
  c. When two opposing processes are proceeding at identical rates, the system is at equilibrium
  d. A system moves spontaneously toward a state of equilibrium
  e. All of these statements are true

The Equilibrium Constant

The equilibrium constant for $A + 2B \rightarrow 3C$ is 2.1 x 10^{-6} using the law of mass action determine the equilibrium constant for $2A + 4B \rightarrow 6C$.

$$K'' = K^n = (2.1\, x\, 10^{-6})^2 = 4.4\, x\, 10^{-12}$$

The Equilibrium Constant

The equilibrium constant for $A + 2B \rightarrow 3C$ is 2.1 x 10^{-6} using the law of mass action determine the equilibrium constant for $2A + 4B \rightarrow 6C$.

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The Equilibrium Expression Involving Pressures

- Consider the ideal gas equation

$$PV = nRT \quad \text{(or)} \quad P = \left(\frac{n}{V}\right)RT = CRT$$

  - *C* represents the molar concentration of a gas
    - $C = n/V$ or *C* equals the number of moles *n* of gas per unit volume *V*

The Equilibrium Expression Involving Pressures

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The Equilibrium Expression Involving Pressures

- In terms of concentration:

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{C_{NH_3}{}^2}{(C_{N_2})(C_{H_2}{}^3)} = K_C$$

- In terms of equilibrium partial pressures of gases:

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

The Equilibrium Expression Involving Pressures

- In these equations:
  - K and K_C are the commonly used symbols for an equilibrium constant in terms of concentrations
  - K_p is the equilibrium constant in terms of partial pressures

The Equilibrium Expression Involving Pressures

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  - K and K_C are the commonly used symbols for an equilibrium constant in terms of concentrations
  - K_p is the equilibrium constant in terms of partial pressures

The Equilibrium Expression Involving Pressures

Consider the reaction for the formation of nitrosyl chloride at 25 ℃. Calculate K_p for this reaction.

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$

The pressures at equilibrium were found to be

$$P_{\mathrm{NOCl}} = 1.2 \text{ atm}$$

$$P_{\mathrm{NO}} = 5.0 \times 10^{-2} \text{atm}$$

$$P_{\mathrm{Cl_2}} = 3.0 \times 10^{-1} \text{ atm}$$

The Equilibrium Expression Involving Pressures

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$

$$K_p = \frac{(P_{NOCl}{}^2)}{(P_{NO_2})^2(P_{Cl_2})} = \frac{(1.2)^2}{(5.0 \times 10^{-2})^2(3.0 \times 10^{-1})}$$

$$K_p = 1.9 \times 10^3$$

The Equilibrium Expression Involving Pressures

The relationships between K and K_p can be described below.

$$K_{\mathrm{p}} = K(RT)^{\Delta n}$$

Δn represents the sum of the coefficients of the gaseous products minus the sum of the coefficients of the gaseous reactants.

The Equilibrium Expression Involving Pressures

- For a general reaction,

$$K_p = \frac{(P_C^{\,l})(P_D^{\,m})}{(P_A^{\,j})(P_B^{\,k})} = \frac{(C_C \times RT)^l (C_D \times \mathrm{RT})^m}{(C_A \times \mathrm{RT})^j (C_B \times RT)^k}$$

$$= \frac{(C_C^{\,l})(C_D^{\,m})}{(C_A^{\,j})(C_B^{\,k})} \times \frac{(RT)^{l+m}}{(RT)^{j+k}} = K(RT)^{(l+m)-(j+k)}$$

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

  - $\Delta n = (l + m) - (j + k)$
    - Difference in the sums of the coefficients for the gaseous products and reactants

The Equilibrium Expression Involving Pressures

For the following reaction at 25℃ the value of K_p was determined to be $1.9\ x\ 10^3$. Calculate K for the following reaction.

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$

The Equilibrium Expression Involving Pressures

- The value of K_p can be used to calculate K using the formula $K_p = K(RT)^{\Delta n}$
  - $T = 25 + 273 = 298$ K
  - $\Delta n = 2 - (2+1) = -1$

Sum of product coefficients

Sum of reactant coefficients

- Thus,

Δn

$$K_p = K(RT)^{-1} = \frac{K}{RT}$$

The Equilibrium Expression Involving Pressures

- Therefore,

$$
\begin{aligned}
K &= K_{\mathrm{p}}(RT) \\
&= (1.9 \times 10^{3})(0.08206)(298) \\
&= 4.6 \times 10^{4}
\end{aligned}
$$

Heterogeneous + Homogenous Equilibria

- Homogenous equilibria is what we've been seeing this whole time. It occurs when all species in our chemical equation are in the same state.

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$

- Heterogeneous occurs when some species in our chemical equation are not in the same state.

$$CaCO_2(s) \rightarrow CaO(s) + CO_2(g)$$

Heterogeneous + Homogenous Equilibria

- Simply put, we do not count solids or liquids in our chemical equilibrium expression. We only count gases and aqueous solutions.

$$CaCO_2(s) \rightarrow CaO(s) + CO_2(g)$$

$$K = [CO_2]$$

Heterogeneous + Homogenous Equilibria

Write the general equilibrium expression for the following reaction.

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

$$K = [Cl_2] \text{ and } K_p = P_{Cl_2}$$

Chemistry

Chapter 13
Chemical Equilibrium

Section 1

HW (Not Collected, for reals): Pg 546 – 547b

Problems: 12 – 18, 25, 27, 29 – 45, 48, 49, 50