The Equilibrium Constant K_p

- If all components are gases at constant temperature and volume, it may be more convenient to express the amounts of reactants and products in partial pressures.

  T This is a variation on Gay-Lussac's Law of Combining Gas Volumes, based on the relationship $P = gn$, where $g = f(V, T)$.

  T For the Haber process at equilibrium:

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

  In terms of partial pressures, we define the equilibrium constant K_p as

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

Relationship Between K_p and K_c

- For any gas species X,

$$p_X = (n_X/V)RT = [X]RT$$

- For $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, we can write

$$K_p = \frac{([NH_3]RT)^2}{([N_2]RT)([H_2]RT)^3} = \frac{[NH_3]^2}{[N_2][H_2]^3}(RT)^{-2}$$

$$K_p = K_c(RT)^{-2}$$

  - Notice that the exponent on the RT term is the difference between the sum of coefficients on gas products minus the sum of coefficients on gas reactants:

$$\Delta n = (2) - (1 + 3) = -2$$

- In general, the relationship between K_c and K_p is expressed by the equation

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

Examples of K_p and K_c

$2NO_2(g) \rightleftharpoons N_2O_4(g)$ $\Delta n = 1 - 2 = -1$

$$K_p = K_c(RT)^{-1}$$

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $\Delta n = 2 - 2 = 0$

$$K_p = K_c$$ $\leftarrow$ Note!

$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$ $\Delta n = 0 - 1 = -1$

$$K_p = K_c(RT)^{-1}$$

The Reaction Quotient, *Q*

- We can calculate the ratio of concentrations or pressures like K_c or K_p at any time in course of a reaction.

L When the system is *not at equilibrium*, the ratio of the product concentrations raised to their stoichiometric coefficients to the reactant concentrations raised to their stoichiometric coefficients is called the *reaction quotient* and given the symbol *Q*.

L The value of *Q* relative to K_c or K_p indicates the direction in which the reaction must run to achieve equilibrium.

U If $Q < K$, the reaction must run in the forward direction, using up reactants and forming more products.

rR W pP $Q = [P]^p/[R]^r < K$ Y Shift right.

U If $Q > K$, the reaction must run in the reverse direction, using up products and reforming more reactants.

rR W pP $Q = [P]^p/[R]^r > K$ Y Shift left.

LeChatelier's Principle
Henri LeChatelier - 1884

L If a stress is applied to a system at equilibrium, the system will tend to adjust to a new equilibrium, which minimizes the stress, if possible.

- Possible stresses are changes in
  - T Concentration
  - T Pressure
  - T Temperature.

Shifts in the Position of Equilibrium

- Shift to the right:

  Reactants o Products
  o

  More reactants consumed, resulting in greater product concentrations and lesser reactant concentrations.

- Shift to the left:

  Reactants o Products
  »

  More products consumed, resulting in greater reactant concentrations and lesser product concentrations.

- Sometimes the stress cannot be alleviated by either kind of shift, in which case the original equilibrium position is maintained.

  Reactants o Products
  o »

Effects of Various Stresses

- Concentration Change:
  - T Position of equilibrium changes
  - T K_c remains the same

- Pressure Change:
  - T Position of equilibrium *may* change
  - T K_c remains the same

- Temperature Change:
  - T Equilibrium changes
  - T K_c changes

Effects of Concentration Changes

Reactants º Products

- Increase Reactant Concentrations
  - º Shift Right (more products)

- Increase Product Concentrations
  - » Shift Left (more reactants)

- Remove Products as Formed
  - º Shift Right (more products)

Effects of Pressure Changes

) *n* ... 0

L If the sums of the coefficients of gas species in the balanced reaction equation are different between reactants and products () *n* ... 0), an increase in pressure will cause a shift toward the side with the lower sum of coefficients.

- This creates fewer gas molecules in the mixture, which reduces the total pressure ($P_t = n_t R\mathrm{T}/V$).

$2NO_2(g)$ o $N_2O_4(g)$
Increase *P* o shift right

$N_2(g) + 3H_2(g)$ o $2NH_3(g)$
Increase *P* o shift right

$2C(s) + O_2(g)$ o $2CO(g)$
Increase *P* » shift left

$H_2O(g) + C(s)$ o $H_2(g) + CO(g)$
Increase *P* » shift left

Effects of Pressure Changes

$\Delta n = 0$

- If the sums of gas species coefficients are the same on both sides of the equation ($\Delta n = 0$), pressure will have no effect on the position of the equilibrium; e.g.,

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

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

$$C(s) + O_2(g) \rightleftharpoons CO_2(g)$$

Effects of Temperature Changes

L Changing temperature changes the value of K_c.

- If we know whether the reaction is exothermic or endothermic we can predict the *qualitative* effect of a temperature change.

T Raising the temperature will cause a shift that uses some of the added heat; i.e., added heat drives the endothermic process.

$$2NO_2(g) \ ^{o}\ N_2O_4(g) + \text{heat}$$

Increase T • Y more NO_2, decrease K_c –
Decrease T – Y more N_2O_4, increase K_c •

$$\text{heat} + CO_2(g) + H_2(g) \ ^{o}\ CO(g) + H_2O(g)$$

Increase T • Y more products, increase K_c •
Decrease T – Y more reactants, decrease K_c –

Effect of a Catalyst

- A catalyst has no effect on equilibrium.

- The catalyst offers an alternative path to products, but it does not affect the ratio of products to reactants at equilibrium.

- The catalyst merely influences the rate at which equilibrium will be established.