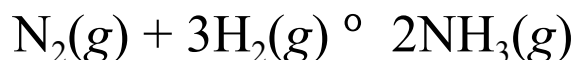


The Equilibrium Constant K_p

- 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:



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

$$K_p = \frac{(p_{\text{NH}_3})^2}{(p_{\text{N}_2})(p_{\text{H}_2})^3}$$

Relationship Between K_p and K_c

- For any gas species X,

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

- For $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$, we can write

$$K_p = \frac{([\text{NH}_3]RT)^2}{([\text{N}_2]RT)([\text{H}_2]RT)^3} = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}(RT)^{-2}$$

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

T 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:

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

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

$$K_p = K_c(RT)^n$$

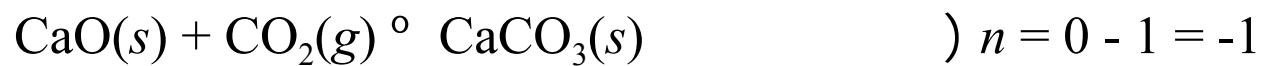
Examples of K_p and K_c



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



$$K_p = K_c \quad \text{7 Note!}$$



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

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.

$$rR \rightleftharpoons WpP \quad Q = \frac{[P]^p}{[R]^r} < K \quad \text{Y Shift right.}$$

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

$$rR \rightleftharpoons WpP \quad Q = \frac{[P]^p}{[R]^r} > K \quad \text{Y Shift left.}$$

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:



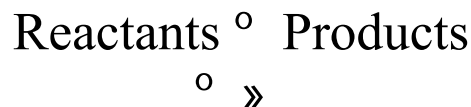
More reactants consumed, resulting in greater product concentrations and lesser reactant concentrations.

- Shift to the left:



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.



Effects of Various Stresses

- Concentration Change:
 - † Position of equilibrium changes
 - † K_c remains the same
- Pressure Change:
 - † Position of equilibrium *may* change
 - † K_c remains the same
- Temperature Change:
 - † Equilibrium changes
 - † K_c changes

Effects of Concentration Changes

Reactants \circ Products

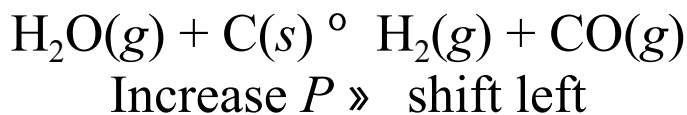
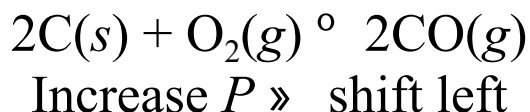
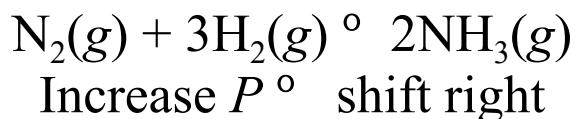
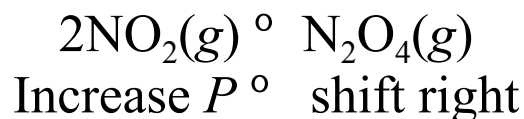
- Increase Reactant Concentrations
 - \circ Shift Right (more products)
- Increase Product Concentrations
 - » Shift Left (more reactants)
- Remove Products as Formed
 - \circ Shift Right (more products)

Effects of Pressure Changes

) $n \dots 0$

L If the sums of the coefficients of gas species in the balanced reaction equation are different between reactants and products ($\sum n_{\text{reactants}} \neq \sum n_{\text{products}}$), an increase in pressure will cause a shift toward the side with the lower sum of coefficients.

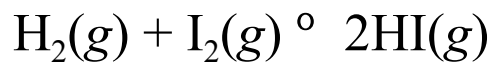
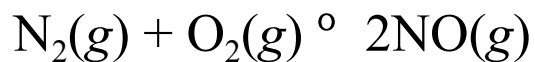
- This creates fewer gas molecules in the mixture, which reduces the total pressure ($P_t = n_t RT/V$).



Effects of Pressure Changes

) $n = 0$

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



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



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

Effect of a Catalyst

- L A catalyst has no effect on equilibrium.
- L The catalyst offers an alternative path to products, but it does not affect the ratio of products to reactants at equilibrium.
- L The catalyst merely influences the rate at which equilibrium will be established.