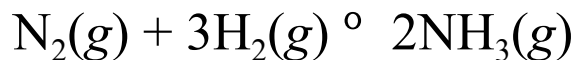


## The Equilibrium Constant $K_p$

- 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

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

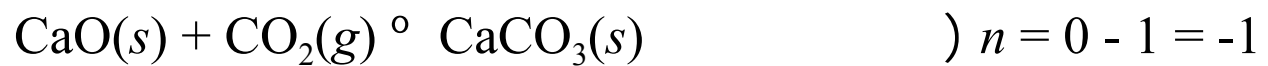
## Examples of $K_p$ and $K_c$



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



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



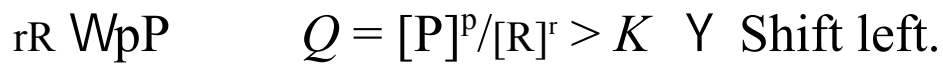
$$K_p = K_c(RT)^{-1}$$

## 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.



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



## **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:



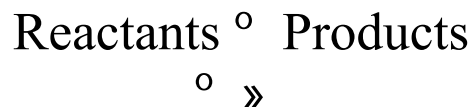
More reactants consumed, resulting in greater product concentrations and lesser reactant concentrations.

- 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 Concentration Changes

Reactants  $\circ$  Products

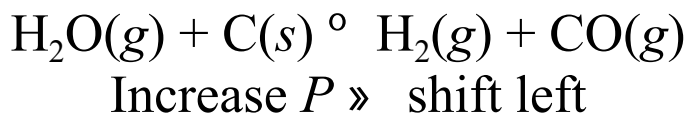
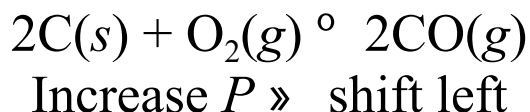
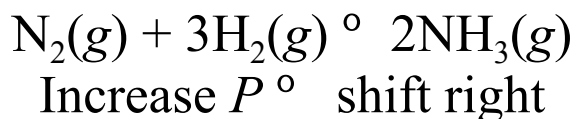
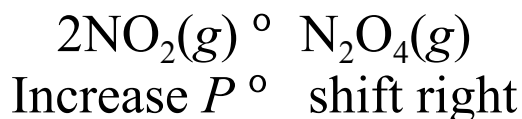
- Increase Reactant Concentrations
  - $\circ$  Shift Right (more products)
- Increase Product Concentrations
  - » Shift Left (more reactants)
- Remove Products as Formed
  - $\circ$  Shift Right (more products)

## 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.

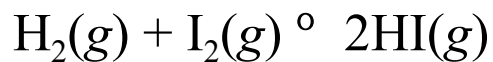
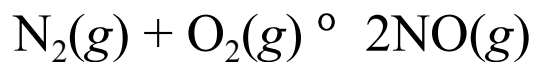
- This creates fewer gas molecules in the mixture, which reduces the total pressure ( $P_t = n_t RT/V$ ).



## Effects of Pressure Changes

$$\Delta n = 0$$

- L 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.,



## 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  $\text{NO}_2$ , decrease  $K_c$  -  
Decrease T - Y more  $\text{N}_2\text{O}_4$ , 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.