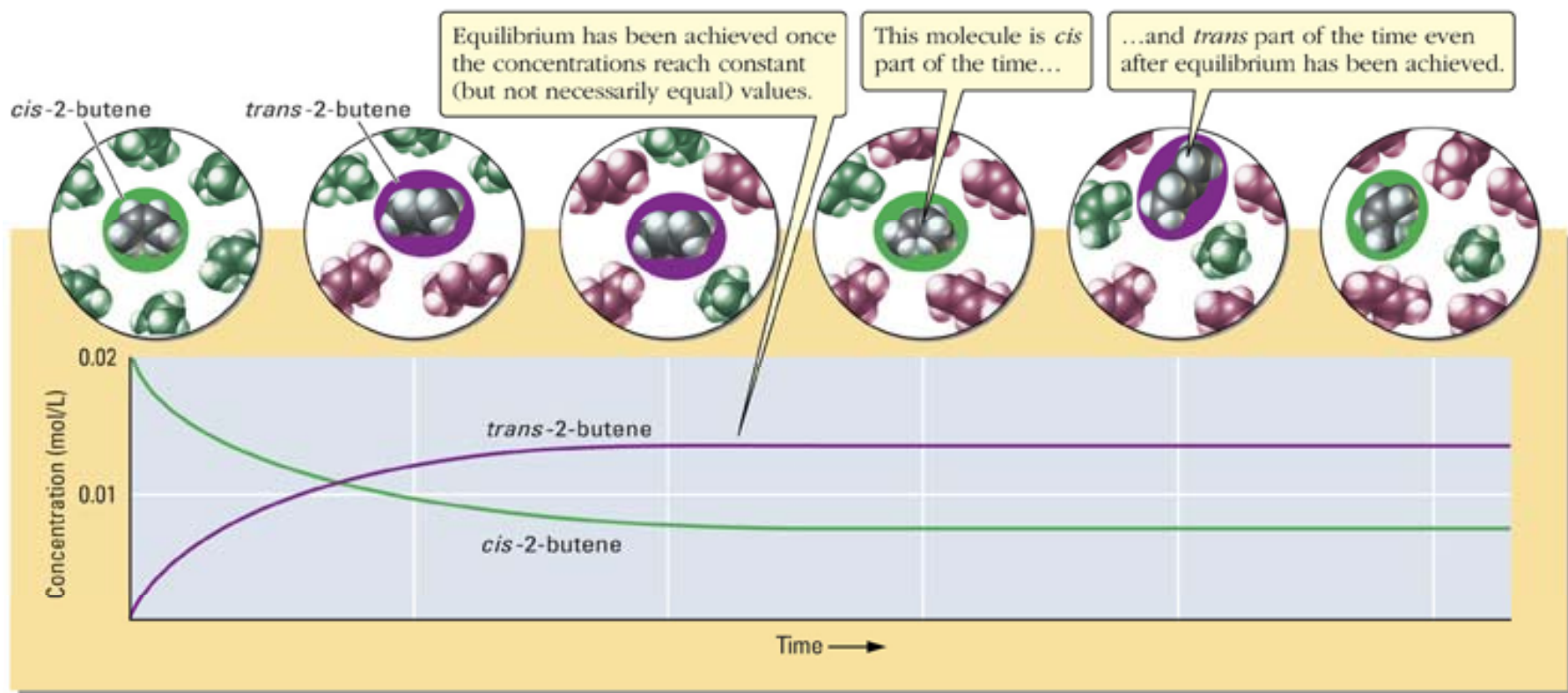


# Chapter 14

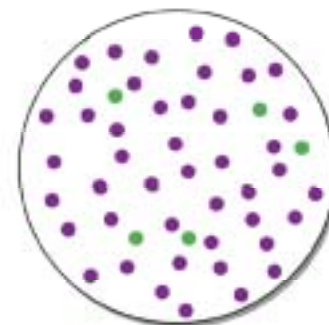
## Chemical Equilibrium

# Approach to Equilibrium

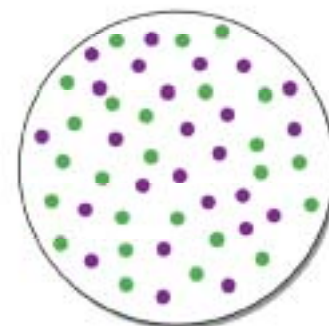


# Concentrations of Reactants and Products

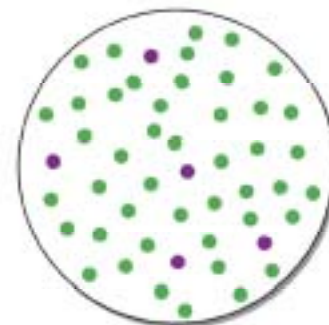
At different temperatures



(a)  $K_c = 9$



(b)  $K_c = 1$

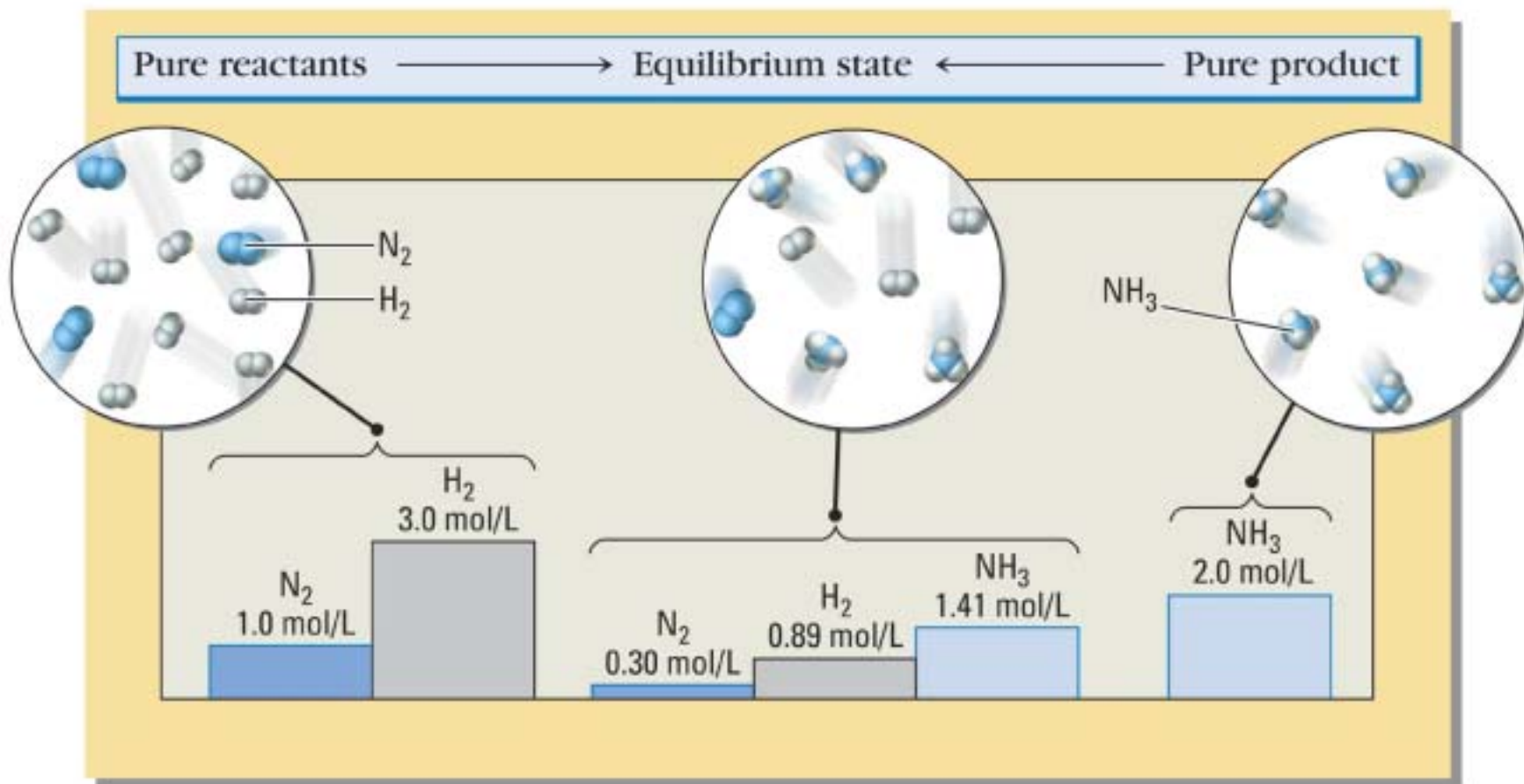


(c)  $K_c = 1/9$

# Chemical Equilibrium

- condition of a reversible reaction where the rate of the forward reaction is equal to the rate of the reverse reaction
- a dynamic condition, meaning that the reaction continues with no net change in the amounts of reactants and products
- independent of direction of approach
- catalyst only changes how fast equilibrium is reached

# Reactants, Products, and Equilibrium



# Law of Mass Action



## Equilibrium Constant

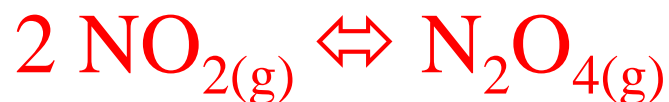
$$K_c = \frac{[P]^p [Q]^q [R]^r \cdots}{[A]^a [B]^b [C]^c \cdots}$$

# Meaning of Equilibrium Constant

- $K \gg 1$ : reaction is product-favored; equilibrium concentrations of products are greater than equilibrium concentrations of reactants.
- $K \ll 1$ : reaction is reactant-favored; equilibrium concentrations of reactants are greater than equilibrium concentrations of products.

## Values of $K_c$

- value of equilibrium constant of a reaction, and that for its reverse reaction, are reciprocals of each other



$$K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$$



# Heterogeneous Equilibrium



$$K_c = \frac{[\text{CaO}_{(s)}][\text{CO}_{2(g)}]}{[\text{CaCO}_{3(s)}]}$$

- concentrations of pure solids and liquids are constant are dropped from expression

$$K_c = [\text{CO}_{2(g)}]$$

# Acid Dissociation Constant



$$K = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{H}_2\text{O}][\text{HC}_2\text{H}_3\text{O}_2]}$$

$$K_a = K \times [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

# Base Dissociation Constant



$$K = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{H}_2\text{O}][\text{NH}_3]}$$

$$K_b = K \times [\text{H}_2\text{O}] = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

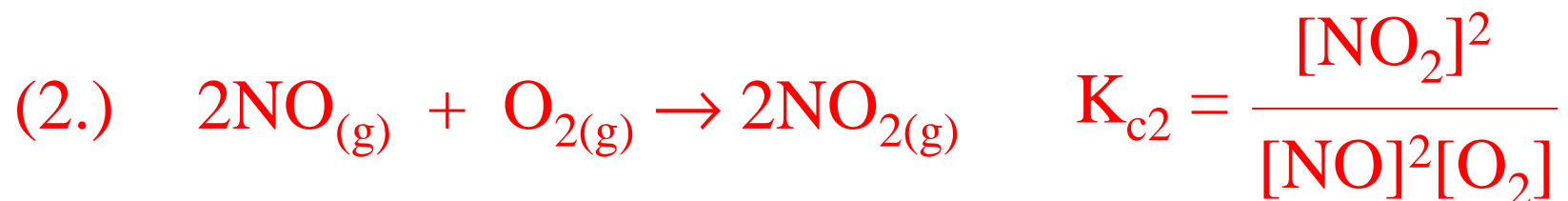
# Autoionization of Water



$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

$$K_w = K [\text{H}_2\text{O}]^2 = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

# Stepwise Equilibrium



Combine (1.) & (2.)



$$K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} \times \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]} = K_{c1} \times K_{c2}$$

# Ideal Gas Law

$$PV = nRT$$

$$P = (n/V)RT$$

$$P_A = [C]RT$$

$$[C] = P_A/RT$$

# Pressure Equilibrium Constants



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

$$\begin{aligned} K_c &= \frac{P_{\text{NH}_3}^2 (1/RT)^2}{(P_{\text{N}_2}(1/RT))(P_{\text{H}_2}^3(1/RT)^3)} \\ &= \frac{P_{\text{NH}_3}^2 (1/RT)^2}{P_{\text{N}_2} P_{\text{H}_2}^3 (1/RT)(1/RT)^3} = K_p \frac{(1/RT)^2}{(1/RT)(1/RT)^3} \end{aligned}$$

## $K_c$ vs. $K_p$



$$K_c = K_p \frac{(1/RT)^2}{(1/RT)(1/RT)^3} = K_p (1/RT)^{-2}$$

In General

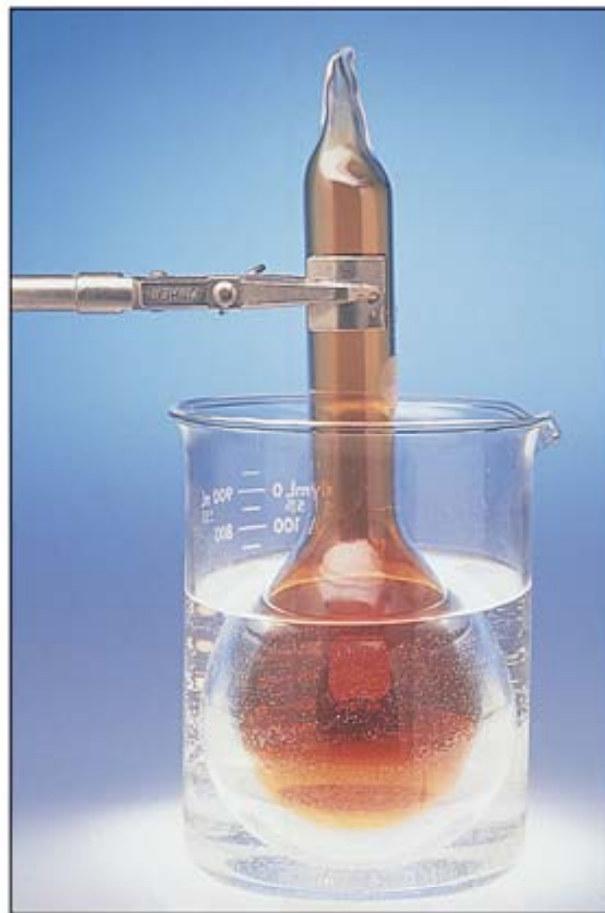
$$K_c = K_p (1/RT)^{\Delta n}$$

where  $\Delta n = \text{\#moles gaseous products}$   
-  $\text{\# moles gaseous reactants}$



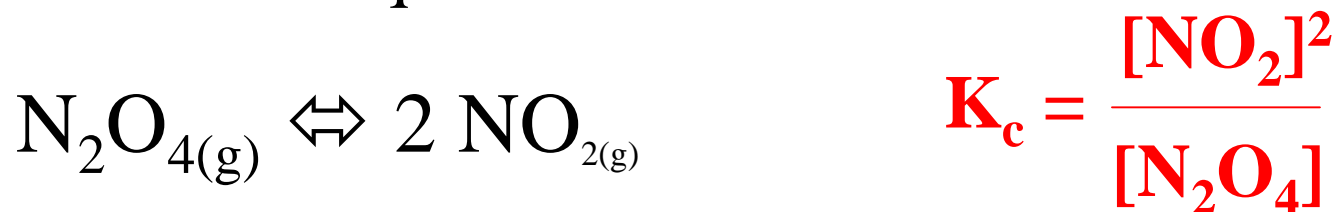


(a)



(b)

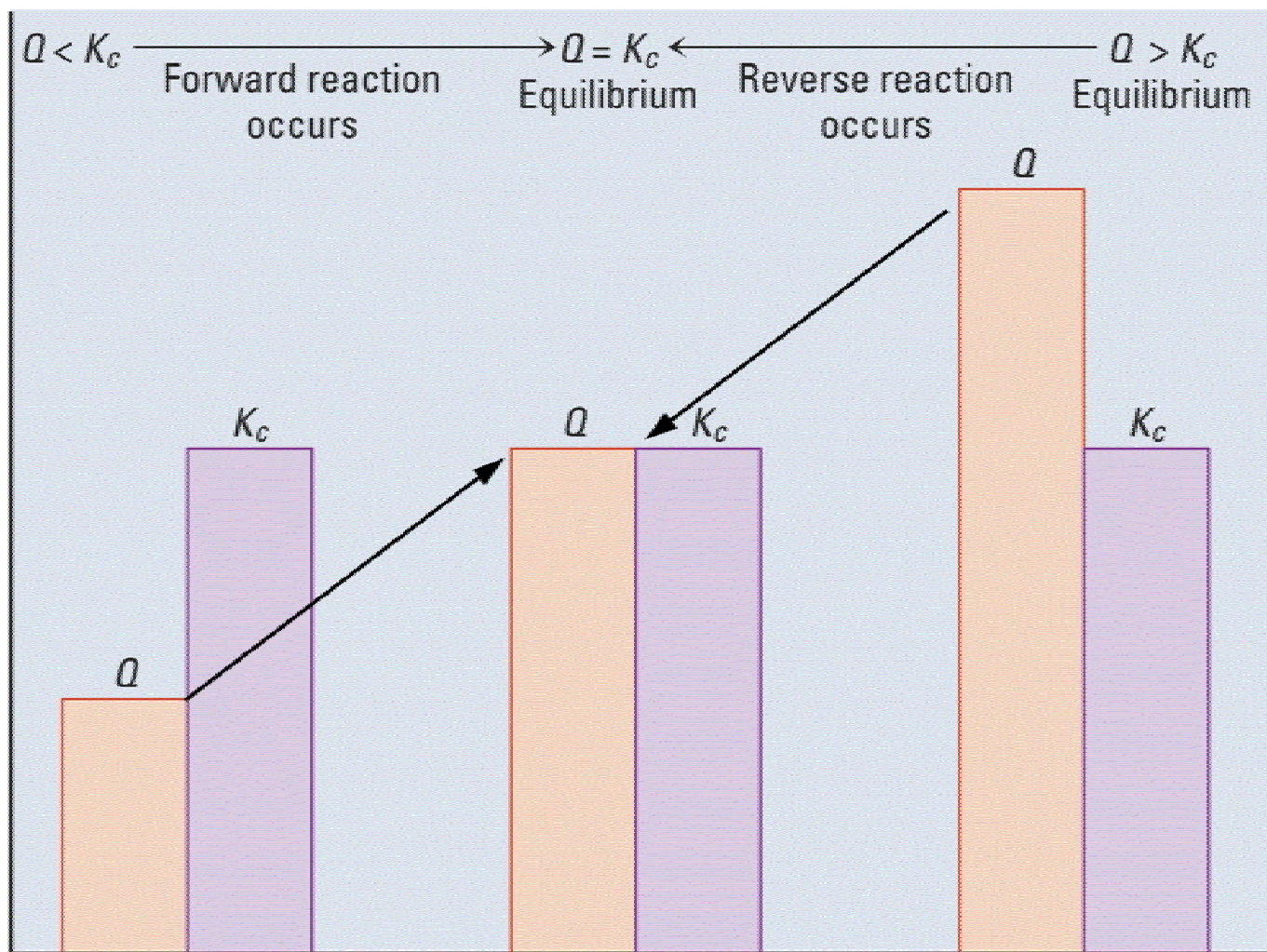
**Example:** An equilibrium is established by placing 2.00 moles of  $\text{N}_2\text{O}_{4(g)}$  in a 5.00 L and heating the flask to 407 K. It was determined that at equilibrium the concentration of the  $\text{NO}_{2(g)}$  is 0.525 mol/L. What is the value of the equilibrium constant?



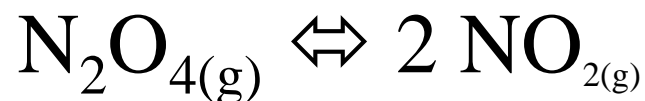
	$\text{N}_2\text{O}_{4(\text{g})} \rightleftharpoons 2 \text{NO}_{2(\text{g})}$	
[Initial] {mol/L)	0.40	0
[change]	-1/2x	x
[Equilibrium]	0.40 - 1/2x= 0.138	0.525 = 0 + x

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(0.525)^2}{0.138} = 2.00$$

# Predicting the Direction of a Reaction



**Example:** An equilibrium is established by placing 2.00 moles of  $\text{N}_2\text{O}_{4(g)}$  in a 5.00 L at 298 K. What are the equilibrium concentrations of  $\text{N}_2\text{O}_{4(g)}$  and  $\text{NO}_{2(g)}$ ?  
 $K_c = 1.70 \times 10^2$  at 298 K.



$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 170$$

---

	$\text{N}_2\text{O}_{4(g)} \rightleftharpoons 2 \text{NO}_{2(g)}$	
[Initial] {mol/L}	0.400	0
[change]	-x	2x
[Equilibrium]	0.400 - x	2x

---

- continued

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 170 = \frac{(2x)^2}{(0.40 - x)}$$

$$68 - 170x = 4x^2 \quad x = 0.396 \text{ mol/L}$$

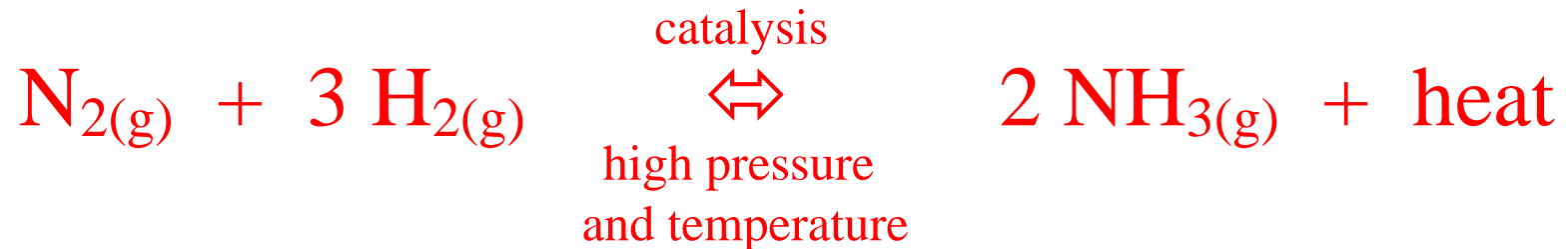
$$[\text{NO}_2] = 2(0.396 \text{ mol/L}) = 0.792 \text{ mol/L}$$

$$[\text{N}_2\text{O}_4] = 0.400 - 0.396 = 0.004 \text{ mol/L}$$

# Le Chatelier's Principle

If a stress, such as a change in concentration, pressure, temperature, etc., is applied to a system at equilibrium, the equilibrium will shift in such a way as to lessen the effect of the stress.

# Production of Ammonia



# Increase in Concentration or Partial Pressure



an increase in  $\text{N}_2$  and/or  $\text{H}_2$  concentration (or partial pressure), will cause the equilibrium to shift towards the production of  $\text{NH}_3$



# Decrease in Concentration or Partial Pressure



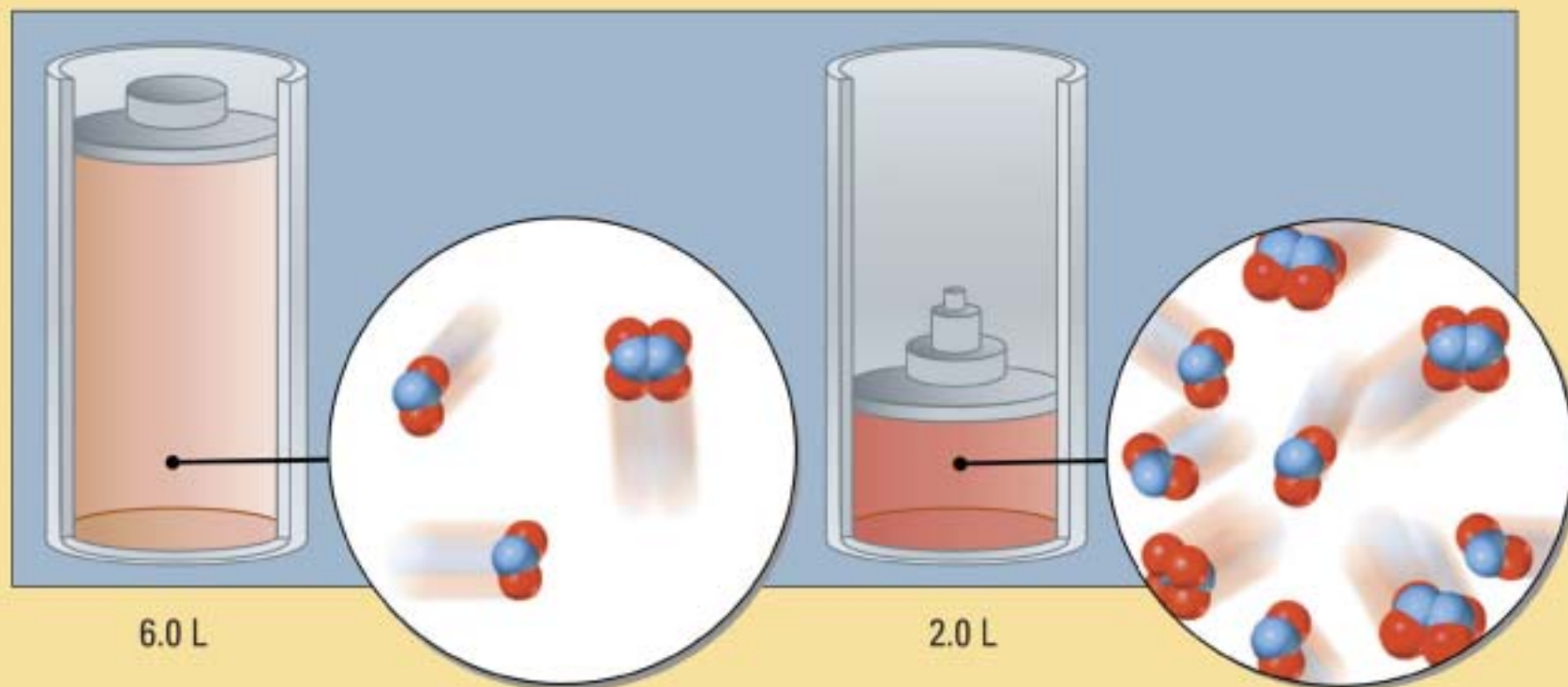
likewise, a decrease in  $\text{NH}_3$  concentration (or partial pressure) will cause more  $\text{NH}_3$  to be produced

# Changes in Temperature

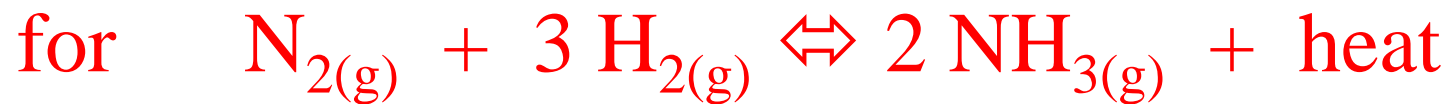
for  $\text{N}_{2(g)} + 3 \text{H}_{2(g)} \rightleftharpoons 2 \text{NH}_{3(g)} + \text{heat}$

- for an exothermic reaction, an increase in temperature will cause the reaction to shift back towards reactants

# Shifting of Equilibrium



# Decrease in Volume



- a decrease in volume, causes the equilibrium to shift to the right where there are fewer gaseous molecules

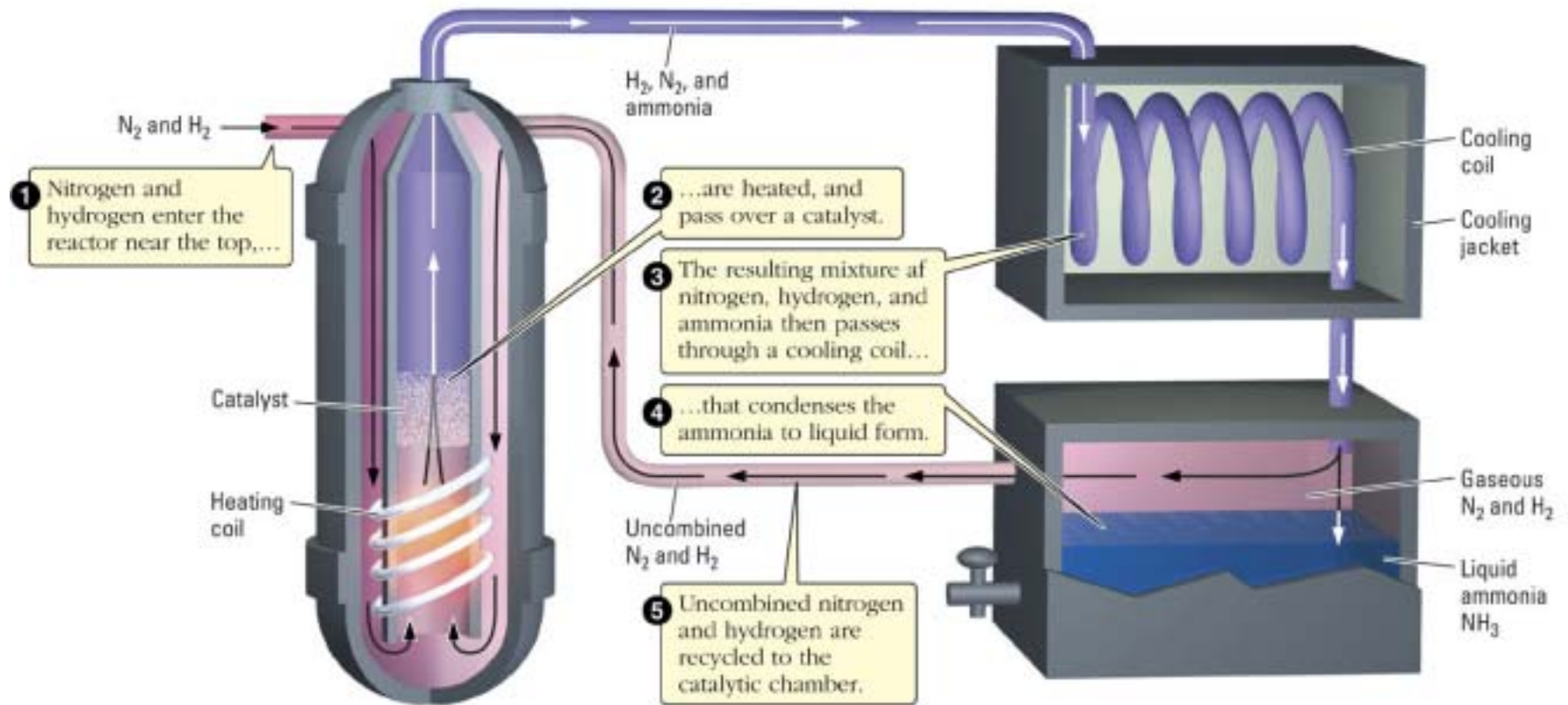
# Reaction Rates

- reactions occur faster in gaseous phase than solids and liquids
- reactions rates increase as temperature increases
- reactions rates increase as concentration increases
- reactions rates increase with a catalyst

# Ammonia Synthesis

- reaction is slow at room temperature, raising temperature, increases rate but lowers yield
- increasing pressure shifts equilibrium to products
- liquefying ammonia shifts equilibrium to products
- use of catalyst increases rate

# Haber-Bosch Process



# Entropy

- measure of the disorder in the system
- more disorder for gaseous systems than liquid systems, more than solid systems



# Equilibrium Systems

- product-favored if  $K > 1$
- exothermic reactions favor products
- increasing entropy in system favors products
- at low temperature, product-favored reactions are usually exothermic
- at high temperatures, product-favored reactions usually have increase in entropy