CHEMISTRY

Chapter 13 FUNDAMENTAL EQUILIBRIUM CONCEPTS

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HW problems: 9, 17, 19, 31, 37, 43, 49, 53, 61, 63, 67, 79

CH. 13 OUTLINE

- 13.1 Chemical Equilibria
- 13.2 Equilibrium Constants
- 13.3 Shifting Equilibria: Le Châtelier’s Principle
- 13.4 Equilibrium Calculations

REVERSIBLE REACTIONS

- All reactions are technically reversible
- For all intents and purposes, many reactions proceed from reactants to products until the limiting reagent is exhausted and the products persist
  - $A + B \rightarrow C + D$
- Other reactions have measurable amounts of both reactants and products present
  - $A + B \rightleftarrows C + D$
- Conditions can be altered to affect the amounts of “reactants” and “products”

EQUILIBRIUM

- Equilibrium is a state in which there are no **observable** changes as time goes on.
  - Dynamic, not static
- Equilibrium is achieved when:
  - the rates (skipped kinetics in chapter 12…) of the forward and reverse reactions are equal, and
  - the concentrations of the reactants and products remain constant (but NOT necessarily equal!!!!!)

Chemical equilibrium

$N_2O_4(g) \rightleftarrows 2NO_2(g)$

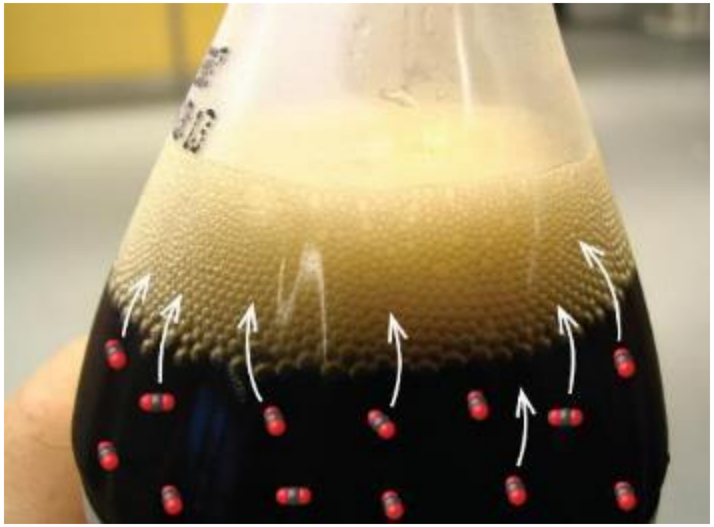
Physical equilibrium

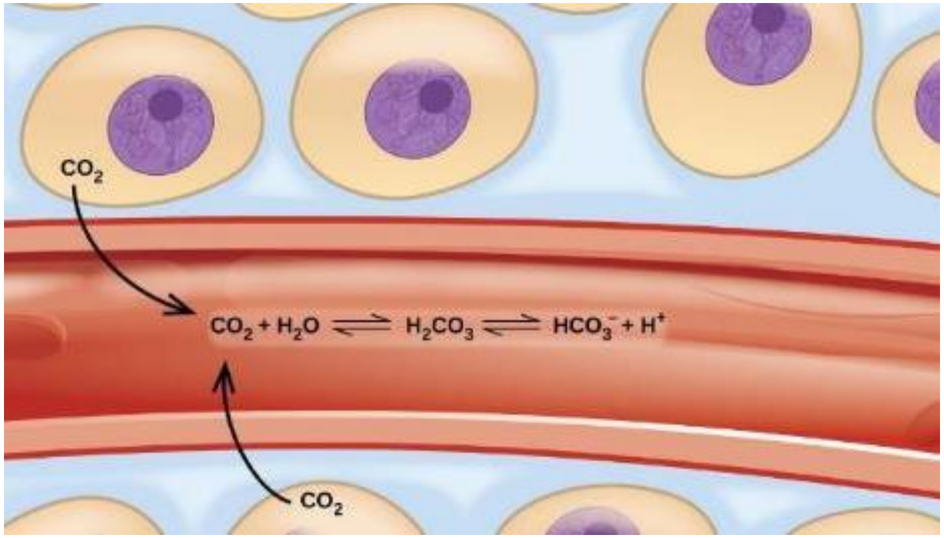
$H_2O(l) \rightleftarrows H_2O(g)$

FIGURE 13.3

- These jugglers provide an illustration of dynamic equilibrium. Each throws clubs to the other at the same rate at which he receives clubs from that person. Because clubs are thrown continuously in both directions, the number of clubs moving in each direction is constant, and the number of clubs each juggler has at a given time remains (roughly) constant.

SODA, BLOOD, AND STATUES



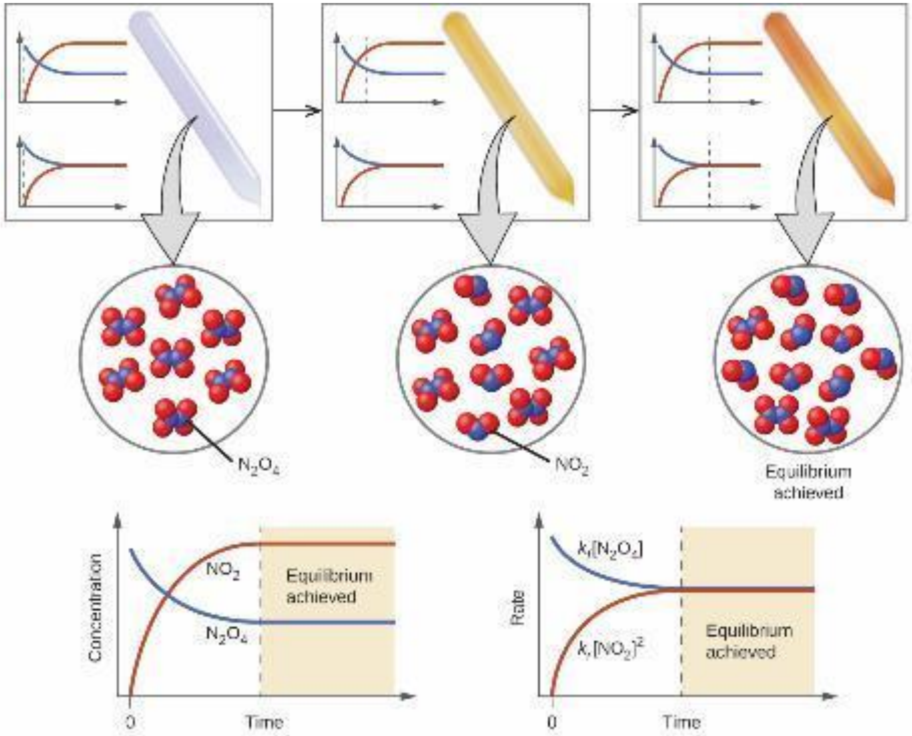


- When a soft drink is opened, several equilibrium shifts occur. (credit: modification of work by “D Coetzee”/Flickr)
- $CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$
- This multi-part equilibrium is critical to blood pH as well as the environmental problems of acid rain and destruction of limestone statues

FIGURE 13.5

- $Br_2\,(l) \rightleftarrows Br_2(g)$
- An equilibrium is pictured between liquid bromine, $Br_2\,(l)$, the dark liquid, and bromine vapor, $Br_2(g)$, the reddish-brown gas. Because the container is sealed, bromine vapor cannot escape and equilibrium is maintained. (credit: http://images-of-elements.com/bromine.php)

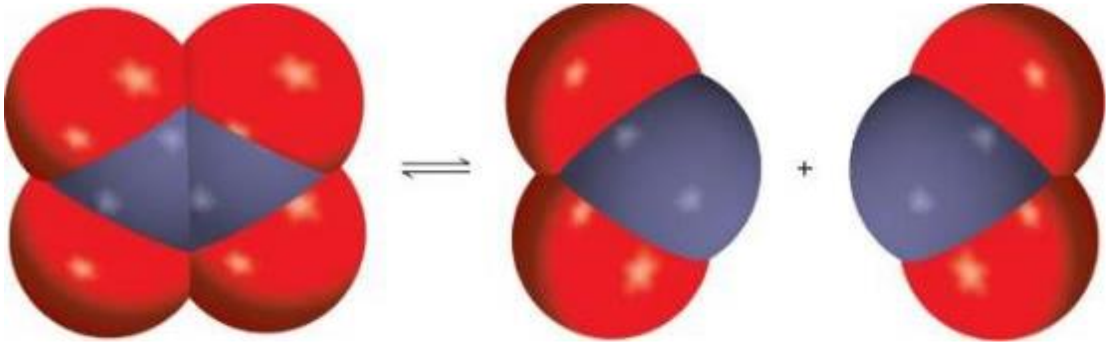
FIGURE 13.2



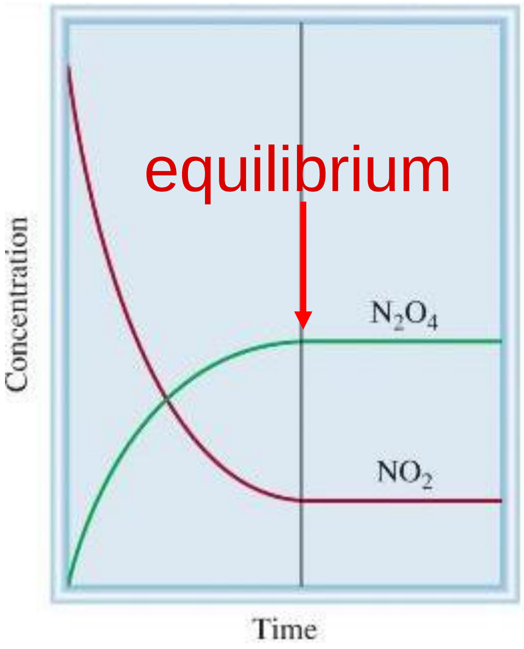
- Colorless N_2O_4 reacts to form brown NO_2. As the reaction proceeds toward equilibrium, the color of the mixture darkens due to the increasing concentration of NO_2.
- (Skipped kinetics in chapter 12…)

EQUILIBRIUM OF N_2O_4

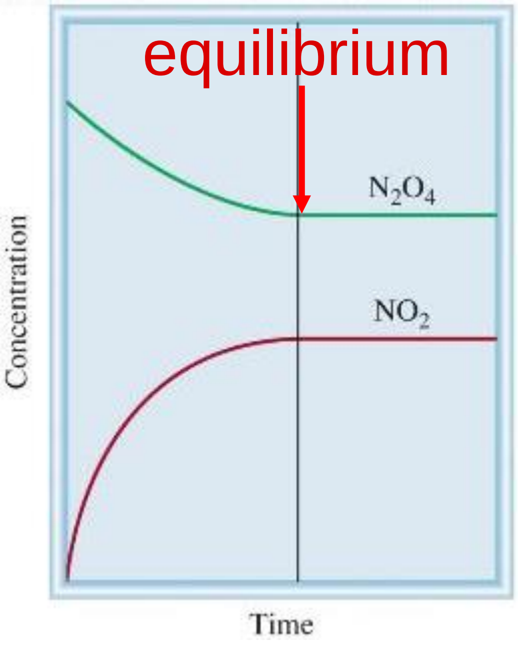
$$N_2O_4(g) \rightleftarrows 2NO_2(g)$$



Start with NO_2

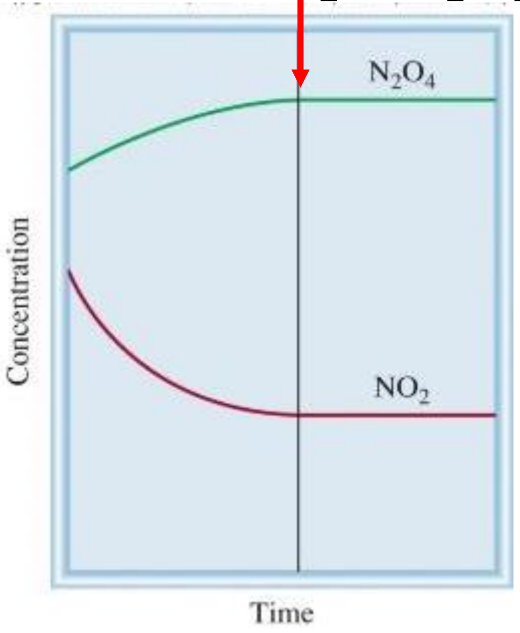

equilibrium

Start with N_2O_4

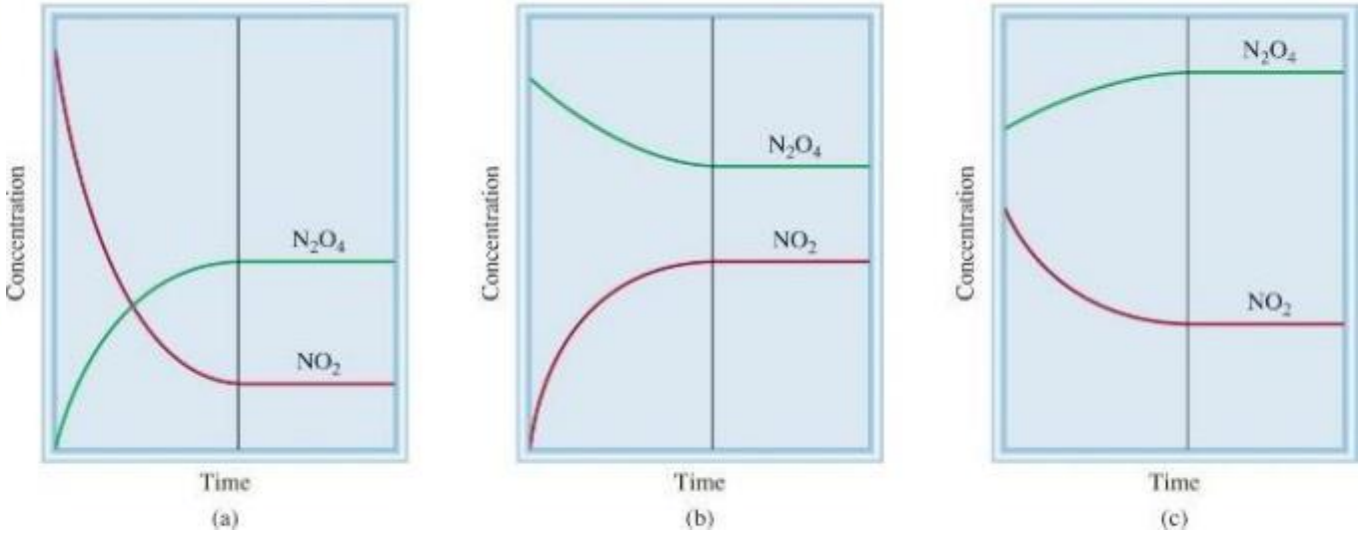

equilibrium

equilibrium

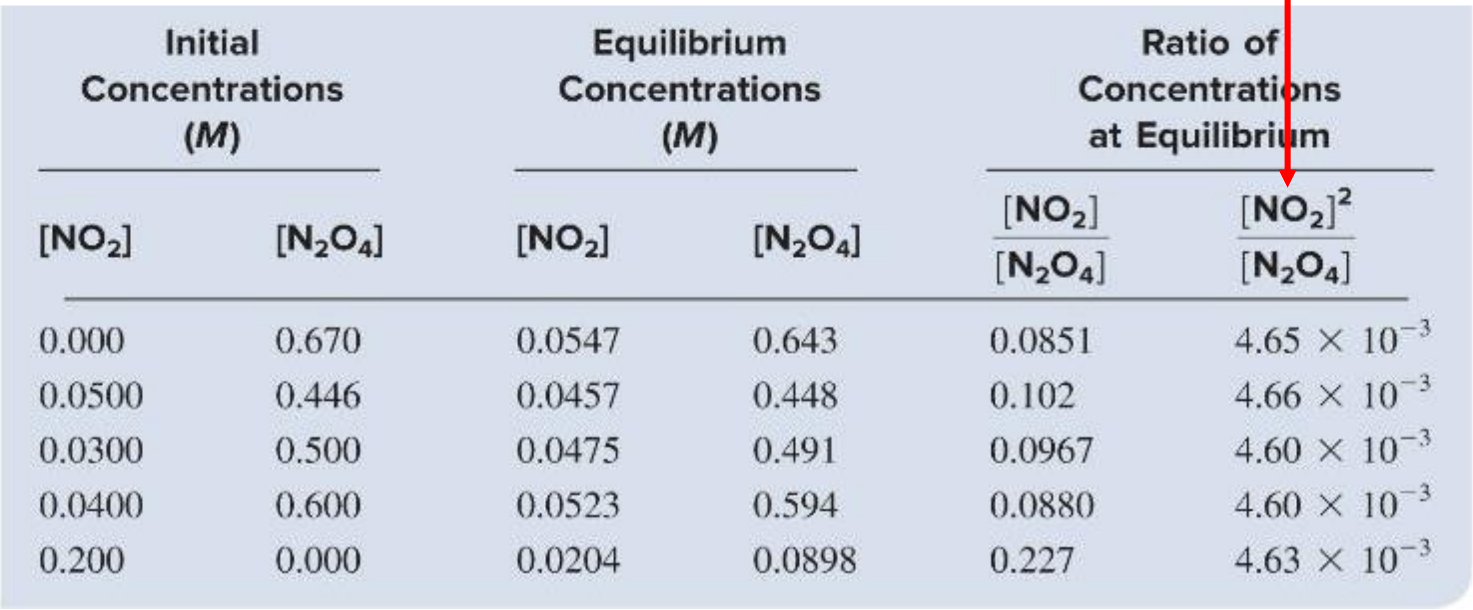
Start with NO_2 & N_2O_4



EQUILIBRIUM OF N_2O_4 (CONT'D)



constant



Initial Concentrations (*M*)		Equilibrium Concentrations (*M*)		Ratio of Concentrations at Equilibrium	
$[NO_2]$	$[N_2O_4]$	$[NO_2]$	$[N_2O_4]$	$\frac{[NO_2]}{[N_2O_4]}$	$\frac{[NO_2]^2}{[N_2O_4]}$
0.000	0.670	0.0547	0.643	0.0851	4.65×10^{-3}
0.0500	0.446	0.0457	0.448	0.102	4.66×10^{-3}
0.0300	0.500	0.0475	0.491	0.0967	4.60×10^{-3}
0.0400	0.600	0.0523	0.594	0.0880	4.60×10^{-3}
0.200	0.000	0.0204	0.0898	0.227	4.63×10^{-3}

CH. 13 OUTLINE

- 13.1 Chemical Equilibria
- **13.2 Equilibrium Constants**
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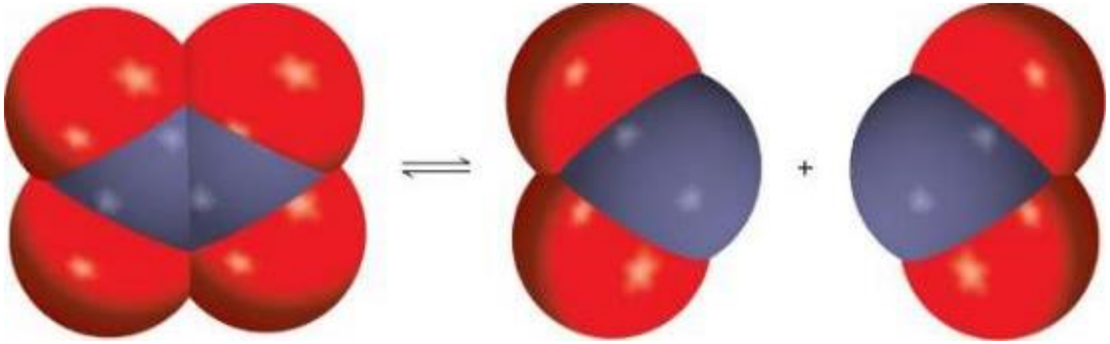
EQUILIBRIUM OF N_2O_4 (CONT'D)

$$N_2O_4(g) \rightleftarrows 2NO_2(g)$$



$$K = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3}$$

- Concentrations vary, but ratio is constant (at given T).

$$aA + bB \rightleftarrows cC + dD$$

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Law of Mass Action

- K is unitless
- Can use concentrations (K_c) or pressures (K_p)
- No solids, no liquids (activities are beyond the scope of this class/textbook

SIGNIFICANCE OF THE VALUE OF K

$$a\text{A} + b\text{B} \rightleftarrows c\text{C} + d\text{D} \qquad K = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}$$

$K \ll 1$

$K \gg 1$

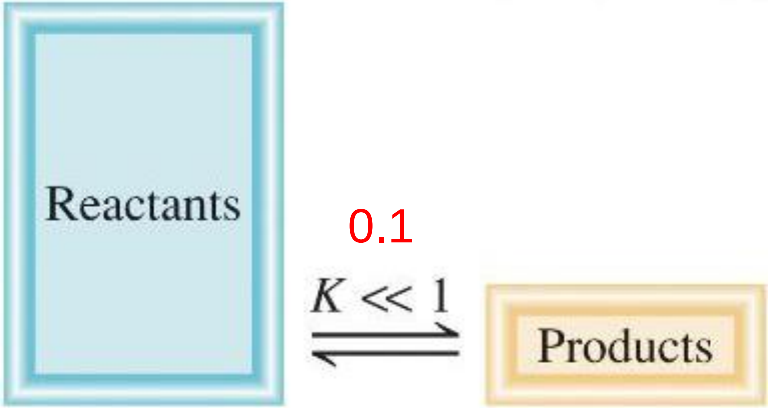
the equilibrium will…

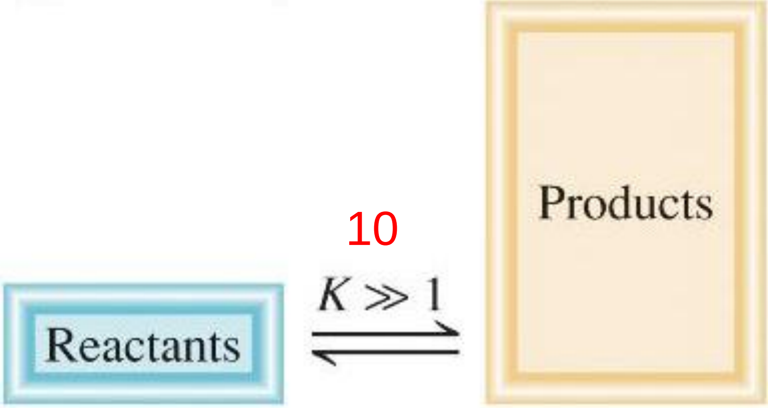
“Lie to the left”

“Lie to the right”

Favor “reactants”

Favor “products”





REACTION QUOTIENT

- The ***reaction quotient*** $(\boldsymbol{Q_c})$ is calculated by substituting the initial concentrations of the reactants and products into the equilibrium constant (K_c) expression.
- Think of it as “K right now.”

IF:

- $Q_c < K_c$system proceeds from left to right to reach equilibrium
  - “too little product” or “too much reactant”
- $Q_c = K_c$ the system is at equilibrium
- $Q_c > K_c$ system proceeds from right to left to reach equilibrium
  - “too little reactant” or “too much product”

EXAMPLE

At the start of a reaction, there are 0.249 mol N_2, 3.21×10^{-2} mol H_2, and 6.42×10^{-4} mol NH_3 in a $3.50 - L$ reaction vessel at $375°C$. If the equilibrium constant (K_c) for the reaction

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

is 1.2 at this temperature, decide whether the system is at equilibrium. If it is not, predict which way the net reaction will proceed.

SOLUTION (1)

- Strategy

We are given the initial amounts of the gases (in moles) in a vessel of known volume (in liters), so we can calculate their molar concentrations and hence the reaction quotient $(\mathrm{Q_c})$. How does a comparison of Q_c with K_c enable us to determine if the system is at equilibrium or, if not, in which direction will the net reaction proceed to reach equilibrium?

SOLUTION (2)

- The initial concentrations of the reacting species are

$$[\mathrm{N_2}]_0 = \frac{0.249\mathrm{mol}}{3.50\mathrm{L}} = 0.0711\ M$$

$$[\mathrm{H_2}]_0 = \frac{3.21 \times 10^{-2}\mathrm{mol}}{3.50\mathrm{L}} = 9.17 \times 10^{-3}\ M$$

$$[\mathrm{NH_3}]_0 = \frac{6.42 \times 10^{-4}\mathrm{mol}}{3.50\mathrm{L}} = 1.83 \times 10^{-4}\ M$$

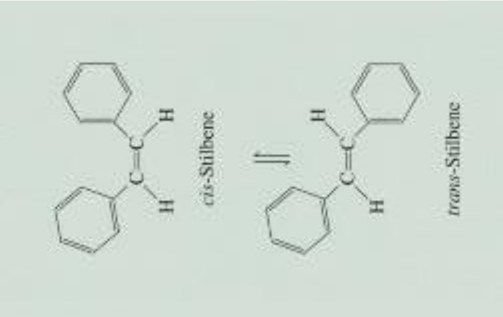
SOLUTION (3)

- Next we write

- $Q_c = \frac{[NH_3]_0^2}{[N_2]_0[H_2]_0^3} = \frac{\left(1.83\times10^{-4}\right)^2}{(0.0711)(9.17\times10^{-3})^3} = 0.611$

- Because Q_c is smaller than K_c (1.2), the system is not at equilibrium. The net result will be an increase in the concentration of NH_3 and a decrease in the concentrations of N_2 and H_2. That is, the net reaction will proceed from left to right until equilibrium is reached.

CALCULATING EQUILIBRIUM CONCENTRATIONS



K_c = 24.0 at 200°C. If the [cis isomer] = 0.850M initially, what are the eq. concentrations?

$$24.0 = \frac{x}{0.850 - x} \qquad x = 0.816M, cis = 0.034M$$

1. Express the equilibrium concentrations of all species in terms of the initial concentrations and a single unknown *x*, which represents the change in concentration. (ICE table)

2. Write the equilibrium constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant, solve for *x*.

3. Having solved for *x*, calculate the equilibrium concentrations of all species.

EXAMPLE

- A mixture of 0.500 mol $\mathrm{H_2}$ and 0.500 mol $\mathrm{l_2}$ was placed in a $1.00-\mathrm{L}$ stainless-steel flask at $430°$ C. The equilibrium constant K_c for the reaction $\mathrm{H_2}(g)+\mathrm{l_2}(g)\rightleftharpoons \mathrm{2Hl}(g)$ is 54.3 at this temperature. Calculate the concentrations of $\mathrm{H_2}$, $\mathrm{l_2}$, and HI at equilibrium

SOLUTION (1)

Strategy

- We are given the initial amounts of the gases (in moles) in a vessel of known volume (in liters), so we can calculate their molar concentrations. Because initially no HI was present, the system could not be at equilibrium. Therefore, some H_2 would react with the same amount of I_2 (why?) to form HI until equilibrium was established.

SOLUTION (2)

- We follow the preceding procedure to calculate the equilibrium concentrations.

- *Step 1:* The stoichiometry of the reaction is 1 mol H_2 reacting with 1 mol I_2 to yield 2 mol HI. Let *x* be the depletion in concentration (mol/L) of H_2 and I_2 at equilibrium. It follows that the equilibrium concentration of HI must be $2x$. We summarize the changes in concentrations as follows:

	$H_2 +$	I_2	$\rightleftharpoons$	$2HI$
Initial (M):	0.500	0.500		0.000
Change (M):	$-x$	$-x$		$+2x$
Equilibrium (M):	$(0.500 - x)$	$(0.500 - x)$		$2x$

SOLUTION (3)

Step 2: The equilibrium constant is given by

$$K_c = \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}][\mathrm{I_2}]}$$

Substituting, we get

$$54.3 = \frac{(2x)^2}{(0.500 - x)(0.500 - x)}$$

Taking the square root of both sides, we get

$$7.37 = \frac{2x}{0.500 - x}$$

$$x = 0.393\ M$$

SOLUTION (4)

Step 3: At equilibrium, the concentrations are

- $[\mathrm{H_2}] = (0.500 - 0.393)M = \mathbf{0.107}\boldsymbol{M}$
- $[\mathrm{I_2}] = (0.500 - 0.393)M = \mathbf{0.107}\boldsymbol{M}$
- $[\mathrm{HI}] = 2 \times 0.393M = \mathbf{0.786}\boldsymbol{M}$

- ***Check*** You can check your answers by calculating K_c using the equilibrium concentrations. Remember that K_c is a constant for a particular reaction at a given temperature.

EXAMPLE

- For the same reaction and temperature as in the previous Example, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, suppose that the initial concentrations of H_2, I_2, and HI are $0.00623\ M$, $0.00414\ M$, and $0.0224\ M$, respectively.
- Calculate the concentrations of these species at equilibrium.

SOUTION (1)

Strategy

- From the initial concentrations we can calculate the reaction quotient (Q_c) to see if the system is at equilibrium or, if not, in which direction the net reaction will proceed to reach equilibrium. A comparison of Q_c with K_c also enables us to determine if there will be a depletion in H_2 and I_2 or HI as equilibrium is established.

SOLUTION (2)

First we calculate Q_c as follows:

$$Q_c = \frac{[\mathrm{HI}]_0^2}{[\mathrm{H_2}]_0[\mathrm{I_2}]_0} = \frac{(0.0224)^2}{(0.00623)(0.00414)} = 19.5$$

Because Q_c (19.5) is smaller than K_c (54.3), we conclude that the net reaction will proceed from left to right until equilibrium is reached (see Figure 14.4); that is, there will be a depletion of $\mathrm{H_2}$ and $\mathrm{l_2}$ and a gain in HI.

SOLUTION (3)

Step 1: Let x be the depletion in concentration $(\mathrm{mol/L})$ of $\mathrm{H_2}$ and $\mathrm{I_2}$ at equilibrium. From the stoichiometry of the reaction it follows that the increase in concentration for HI must be $2x$. Next we write

	$\mathrm{H_2} +$	$\mathrm{I_2}$	$\rightleftharpoons$	$\mathrm{2HI}$
Initial (*M*):	0.00623	0.00414		0.0224
Change (*M*):	$-x$	$-x$		$+2x$
Equilibrium (*M*):	$(0.00623 - x)$	$(0.00414 - x)$		$(0.0224 + 2x)$

SOLUTION (4)

Step 2: The equilibrium constant is

$$K_c = \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}][\mathrm{I_2}]}$$

Substituting, we get

$$54.3 = \frac{(0.0224 + 2\mathrm{x})^2}{(0.00623 - x)(0.00414 - x)}$$

It is not possible to solve this equation by the square root shortcut, as the starting concentrations $[\mathrm{H_2}]$ and $[\mathrm{I_2}]$ are unequal. Instead, we must first carry out the multiplications

$$54.3(2.58 \times 10^{-5} - 0.0104x + x^2) = 5.02 \times 10^{-4} + 0.0896x + 4x^2$$

SOLUTION (5)

Collecting terms, we get

$$50.3x^2 - 0.654x + 8.98 \times 10^{-4} = 0$$

This is a quadratic equation of the form $ax^2 + bx + c = 0$. The solution for a quadratic equation is

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Here we have a $= 50.3$, $b = -0.654$, and $c = 8.98 \times 10^{-4}$, so that

$$x = \frac{0.654 \pm \sqrt{(-0.654)^2 - 4(50.3)(8.98 \times 10^{-4})}}{2 \times 50.3}$$

$x = 0.0114\ M$ *or* $x = 0.00156\ M$

SOLUTION (6)

- The first solution is impossible because the amounts of H_2 and I_2 reacted would be more than those originally present. The second solution gives the correct answer. Note that in solving quadratic equations of this type, one answer is always impossible, so choosing a value for x is easy.
- Thus, at equilibrium, the concentrations are

$$[H_2] = (0.00623 - 0.00156)\ M = \mathbf{0.00467}\ \boldsymbol{M}$$

$$[I_2] = (0.00414 - 0.00156)\ M - \mathbf{0.00258}\ \boldsymbol{M}$$

$$[HI] = (0.0224 + 2 \times 0.00156)\ M = \mathbf{0.0255}\ \boldsymbol{M}$$

- You can check the answers by calculating K_c using the equilibrium concentrations. Remember that K_c is a constant for a particular reaction at a given temperature.

HOMOGENEOUS EQUILIBRIUM

- Homogeneous equilibrium applies to reactions in which all reacting species are in the same phase.

$$N_2O_4(g) \rightleftarrows 2NO_2(g)$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} \qquad K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}}$$

- In most cases

$$K_c \neq K_p$$

$$aA(g) + bB(g) \rightleftarrows cC(g) + dD(g)$$

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

Δn = moles of gaseous products – moles of gaseous reactants

= $(c + d) - (a + b)$ No Δn?... $K_p = K_c$

HOMOGENEOUS EQUILIBRIUM (CONT'D)

$$\mathrm{CH_3COOH}(\mathrm{a}q) + \mathrm{H_2O}(l) \rightleftarrows \mathrm{CH_3COO^-}(\mathrm{a}q) + \mathrm{H_3O^+}(\mathrm{a}q)$$

$$K_c' = \frac{[\mathrm{CH_3COO^-}][\mathrm{H_3O^+}]}{[\mathrm{CH_3COOH}][\mathrm{H_2O}]}$$

$$[\mathrm{H_2O}] = \mathrm{constant}$$

$$K_c = \frac{[\mathrm{CH_3COO^-}][\mathrm{H_3O^+}]}{[\mathrm{CH_3COOH}]} = K_c'[\mathrm{H_2O}]$$

General practice <u>not</u> to include units for the equilibrium constant.

Preview: No (s) and no (l) (as above) in K… they're constant, too.

EXAMPLE

- Write expressions for K_c, and K_p if applicable, for the following reversible reactions at equilibrium:

$$\mathrm{HF}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{F^-}(aq)$$

$$2\mathrm{NO}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\mathrm{NO_2}(g)$$

$$\mathrm{CH_3COOH(a}q) + \mathrm{C_2H_5OH(a}q) \rightleftharpoons \mathrm{CH_3COOC_2H_5(a}q) + \mathrm{H_2O}(l)$$

SOLUTION (1)

Strategy

- Keep in mind the following facts: (1) the K_p expression applies only to gaseous reactions and (2) the concentration of solvent (usually water) does not appear in the equilibrium constant expression.

SOLUTION (2)

$$\mathrm{HF}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{F^-}(aq)$$

Because there are no gases present, K_p does not apply and we have only K_c.

$$K_\mathrm{c}' = \frac{[\mathrm{H_3O^+}][\mathrm{F^-}]}{[\mathrm{HF}][\mathrm{H_2O}]}$$

HF is a weak acid, so that the amount of water consumed in acid ionizations is negligible compared with the total amount of water present as solvent. Thus, we can rewrite the equilibrium constant as

$$\boldsymbol{K_\mathrm{c} = \frac{[\mathrm{H_3O^+}][\mathrm{F^-}]}{[\mathrm{HF}]}}$$

SOLUTION (3)

$$2\mathrm{NO}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\mathrm{NO_2}(g)$$

$$\boldsymbol{K}_{\mathrm{c}} = \frac{[\mathbf{NO_2}]^2}{[\mathbf{NO}]^2[\mathbf{O_2}]} \qquad \boldsymbol{K}_{p} = \frac{\boldsymbol{P}^2_{\mathrm{No_2}}}{\boldsymbol{P}^2_{\mathrm{NO}}\boldsymbol{P}_{\mathrm{o_2}}}$$

$$\mathrm{CH_3COOH}(\mathrm{a}q) + \mathrm{C_2H_5OH}(\mathrm{a}q) \rightleftharpoons \mathrm{CH_3COOC_2H_5}(\mathrm{a}q) + \mathrm{H_2O}(l)$$

The equilibrium constant K_{c}' is given by

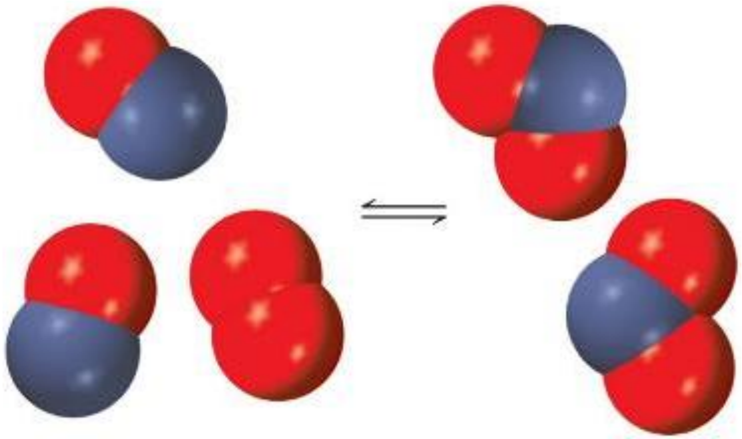
$$K_{\mathrm{c}}' = \frac{[\mathrm{CH_3COOC_2H_5}][\mathrm{H_2O}]}{[\mathrm{CH_3COOH}][\mathrm{C_2H_5OH}]}$$

Because the water produced in the reaction is negligible compared with the water solvent, the concentration of water does not change. Thus, we can write the new equilibrium constant as

$$\boldsymbol{K}_{\mathrm{c}} = \frac{[\mathbf{CH_3COOC_2H_5}]}{[\mathbf{CH_3COOH}][\mathbf{C_2H_5OH}]}$$

EXAMPLE

The following equilibrium process has been studied at 230°C: $2\mathrm{NO}(g) + \mathrm{O}_2(g) \rightleftharpoons 2\mathrm{NO}_2(g)$



In one experiment, the concentrations of the reacting species at equilibrium are found to be
$[\mathrm{NO}] = 0.0542M$, $[\mathrm{O}_2] = 0.127M$, and $[\mathrm{NO}_2] = 15.5M$.

Calculate the equilibrium constant (K_c) of the reaction at this temperature.

SOLUTION (1)

- Strategy: The concentrations given are equilibrium concentrations. They have units of $\mathrm{mol/L}$, so we can calculate the equilibrium constant (K_c) using the law of mass action [Equation (14.2)].
- The equilibrium constant is given by

$$K_\mathrm{c} = \frac{[\mathrm{NO_2}]^2}{[\mathrm{NO}]^2[\mathrm{O_2}]}$$

Substituting the concentrations, we find that

$$K_\mathrm{c} = \frac{(15.5)^2}{(0.0542)^2(0.127)} = \mathbf{6.44 \times 10^5}$$

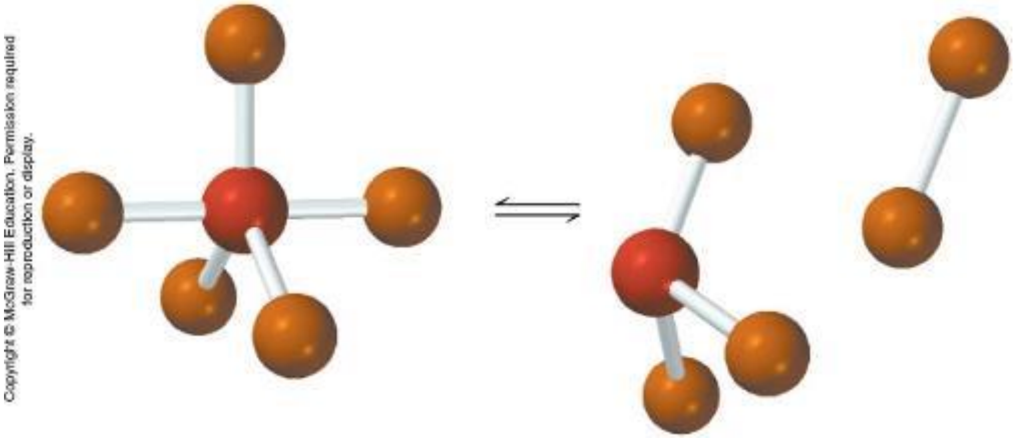
SOLUTION (2)

- Check: Note that K_c is given without units. Also, the large magnitude of K_c is consistent with the high product (NO_2) concentration relative to the concentrations of the reactants $(NO$ and $O_2)$.

EXAMPLE

- The equilibrium constant K_P for the decomposition of phosphorus pentachloride to phosphorus trichloride and molecular chlorine is found to be 1.05 at 250° C.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$



- If the equilibrium partial pressures of PCl_5 and PCl_3 are 0.875 atm and 0.463 atm, respectively, what is the equilibrium partial pressure of Cl_2 at 250°C?

SOLUTION (1)

- Strategy: The concentrations of the reacting gases are given in atm, so we can express the equilibrium constant in K_P. From the known K_P value and the equilibrium pressures of $\mathrm{PCl_3}$ and $\mathrm{PCl_5}$, we can solve for $P_{\mathrm{Cl_2}}$.

SOUTION (2)

- First, we write K_P in terms of the partial pressures of the reacting species

$$K_p = \frac{P_{\mathrm{PCl_3}} P_{\mathrm{Cl_2}}}{P_{\mathrm{PCl_5}}}$$

- Knowing the partial pressures, we write

$$1.05 = \frac{(0.463)\left(P_{\mathrm{Cl_2}}\right)}{(0.875)}$$

- or

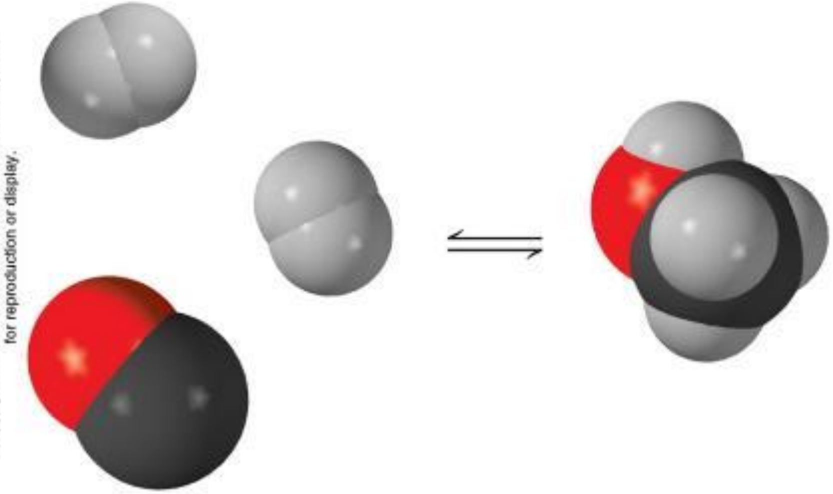
$$P_{\mathrm{Cl_2}} = \frac{(1.05)(0.875)}{(0.463)} = \mathbf{1.98\ atm}$$

- Note that we have added atm as the unit for $P_{\mathrm{Cl_2}}$.

EXAMPLE

- Methanol (CH_3OH) is manufactured industrially by the reaction

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$



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- The equilibrium constant (K_c) for the reaction is 10.5 at 220°C.

- What is the value of K_P at this temperature?

SOLUTION (1)

- Strategy: The relationship between K_c and K_P is given by Equation (14.5). What is the change in the number of moles of gases from reactants to product?
- Recall that $\Delta n =$ moles of gaseous products $-$ moles of gaseous reactants
- What unit of temperature should we use?

SOLUTION (2)

- The relationship between K_C and K_P is

$$K_P = K_c(0.0821T)^{\Delta n}$$

- Because $T = 273 + 220 = 493$ K and $\Delta n = 1 - 3 = -2$, we have

$$K_p = (10.5)(0.0821 \times 493)^{-2}$$
$$= \mathbf{6.41 \times 10^{-3}}$$

- Note that K_P, like K_c, is a dimensionless quantity. This example shows that we can get a quite different value for the equilibrium constant for the same reaction, depending on whether we express the concentrations in moles per liter or in atmospheres.

HETEROGENEOUS EQUILIBRIUM

- Heterogenous equilibrium applies to reactions in which reactants and products are in different phases.

$$CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g)$$

$$K_c' = \frac{[CaO][CO_2]}{[CaCO_3]}$$

$[CaCO_3]$ =constant

$[CaO]$ =constant

(proof on next slide)

$$K_c' \frac{[CaCO_3]}{[CaO]} = K_c = [CO_2]$$

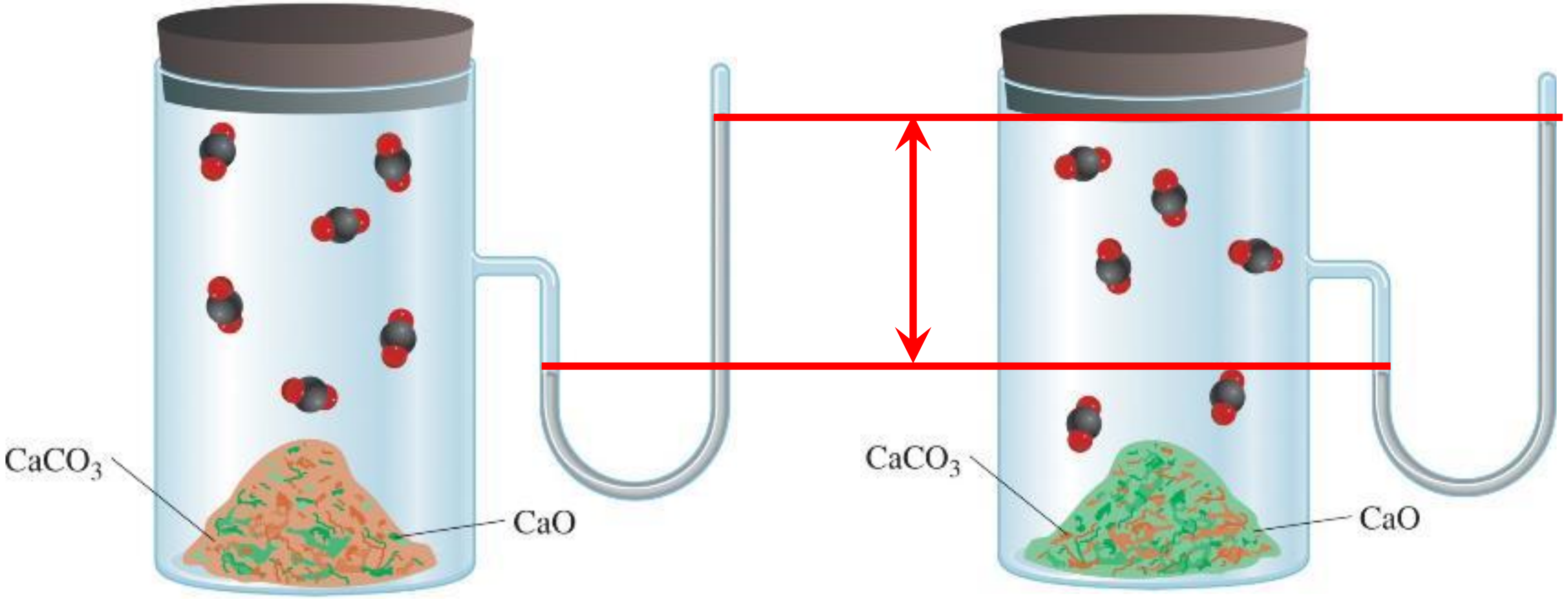
$$K_p = P_{co_2}$$

The concentration of <u>solids</u> and <u>pure liquids</u> are <u>not</u> included in the equilibrium constant expression.

We are ignoring the concept of “activities” (at least for now).

HETEROGENEOUS EQUILIBRIUM (CONT'D)

$$\mathrm{CaCO_3}(s) \rightleftarrows \mathrm{CaO}(s) + \mathrm{CO_2}(g)$$



- $P_{\mathrm{CO_2}} = K_p$

$P_{\mathrm{CO_2}}$ does not depend on the amount of $\mathrm{CaCO_3}$ or CaO

EXAMPLE

Write the equilibrium constant expression K_c, and K_P if applicable, for each of the following heterogeneous systems:

a) $(NH_4)_2Se(s) \rightleftharpoons 2NH_3(g) + H_2Se(g)$

b) (b) $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

c) (c) $P_4(s) + 6Cl_2(g) \rightleftharpoons 4PCl_3(l)$

SOLUTION (1)

- Strategy: We omit any pure solids or pure liquids in the equilibrium constant expression because their concentrations are constants (activities are unity).

(a) Because $(NH_4)_2$Se is a solid, the equilibrium constant K_c is given by

$$K_c = [NH_3]^2[H_2Se]$$

- Alternatively, we can express the equilibrium constant K_P in terms of the partial pressures of NH_3 and H_2Se:
  - $K_p = P_{NH_3}^2 P_{H_2Se}$

SOLUTION (2)

(b) Here AgCl is a solid so the equilibrium constant is given by

$$\boldsymbol{K_c = [\mathrm{Ag^+}][\mathrm{Cl^-}]}$$

- Because no gases are present, there is no K_P expression.

(c) We note that $\mathrm{P_4}$ is a solid and $\mathrm{PCl_3}$ is a liquid, so they do not appear in the equilibrium constant expression. Thus, K_c is given by

$$\boldsymbol{K_c = \frac{1}{[\mathrm{Cl_2}]^6}}$$

Alternatively, we can express the equilibrium constant in terms of the pressure of $\mathrm{Cl_2}$:

$$\boldsymbol{K_p = \frac{1}{P_{\mathrm{Cl_2}}^6}}$$

EXAMPLE

- Consider the following heterogeneous equilibrium:

$$\mathrm{CaCO_3}(s) \rightleftharpoons \mathrm{CaO}(s) + \mathrm{CO_2}(g)$$

- At $800°$ C, the pressure of $\mathrm{CO_2}$ is 0.236 atm.

- Calculate (a) K_p and (b) K_c for the reaction at this temperature.

SOLUTION (1)

- Strategy: Remember that pure solids do not appear in the equilibrium constant expression, and remember the relationship between K_p and K_c.
- Solution:

$$K_P = P_{CO_2}$$
$$= \mathbf{0.236}$$

- We know

$$K_P = K_c(0.0821T)^{\Delta n}$$

- In this case, $T = 800 + 273 = 1073$ K and $\Delta n = 1$, so we substitute these values in the equation and obtain

$$0.236 = K_c(0.0821 \times 1073)$$
$$K_c = \mathbf{2.68 \times 10^{-3}}$$

MULTIPLE EQUILIBRIA

$$
\begin{array}{lll}
\mathrm{A} + \mathrm{B} \rightleftarrows \cancel{\mathrm{C}} + \cancel{\mathrm{D}} & K_c' & K_c' = \dfrac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]} \\
\cancel{\mathrm{C}} + \cancel{\mathrm{D}} \rightleftarrows \mathrm{E} + \mathrm{F} & K_c'' & K_c'' = \dfrac{[\mathrm{E}][\mathrm{F}]}{[\mathrm{C}][\mathrm{D}]} \\
\hline
\mathrm{A} + \mathrm{B} \rightleftarrows \mathrm{E} + \mathrm{F} & K_c & K_c = \dfrac{[\mathrm{E}][\mathrm{F}]}{[\mathrm{A}][\mathrm{B}]}
\end{array}
$$

$$K_c = K_c' \times K_c''$$

If a reaction can be expressed as the sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.

EQUILIBRIUM CONSTANT OF REVERSE REACTION

$$N_2O_4(g) \rightleftarrows 2NO_2(g)$$

$$2NO_2(g) \rightleftarrows N_2O_4(g)$$

$$K = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3}$$

$$K' = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{K} = 216$$

When the equation for a reversible reaction is written in the opposite direction, the equilibrium constant becomes the reciprocal of the original equilibrium constant.

EXAMPLE

The reaction for the production of ammonia can be written in a number of ways:

a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

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

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

- Write the equilibrium constant expression for each formulation. (Express the concentrations of the reacting species in $\mathrm{mol/L}$.)

- How are the equilibrium constants related to one another?

SOLUTION (1)

- Strategy: We are given three different expressions for the same reacting system. Remember that the equilibrium constant expression depends on how the equation is balanced, that is, on the stoichiometric coefficients used in the equation.

SOLUTION (2)

- $K_a = \frac{[NH_3]^2}{[N_2][H_2]^3}$
- $K_b = \frac{[NH_3]}{[N_2]^{\frac{1}{2}}[H_2]^{\frac{3}{2}}}$
- $K_c = \frac{[NH_3]^{\frac{2}{3}}}{[N_2]^{\frac{1}{3}}[H_2]}$

$K_a = K_b^2$

$K_a = K_c^3$

$K_b^2 = K_c^3$ or $K_b = K_c^{\frac{3}{2}}$

WRITING EQUILIBRIUM CONSTANT EXPRESSIONS

- The concentrations of the reacting species in the condensed phase are expressed in M. In the gaseous phase, the concentrations can be expressed in M or in atm.
- The concentrations of pure solids, pure liquids and solvents do not appear in the equilibrium constant expressions.
- The equilibrium constant is a dimensionless quantity.
- In quoting a value for the equilibrium constant, you must specify the balanced equation and the temperature.
- If a reaction can be expressed as a sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.

CH. 13 OUTLINE

- 13.1 Chemical Equilibria
- 13.2 Equilibrium Constants
- **13.3 Shifting Equilibria: Le Châtelier’s Principle**
- 13.4 Equilibrium Calculations

LE CHÂTELIER'S PRINCIPLE

- If an external stress is applied to a system at equilibrium, the system adjusts in such a way that the stress is (partially) offset as the system reaches a new equilibrium position.

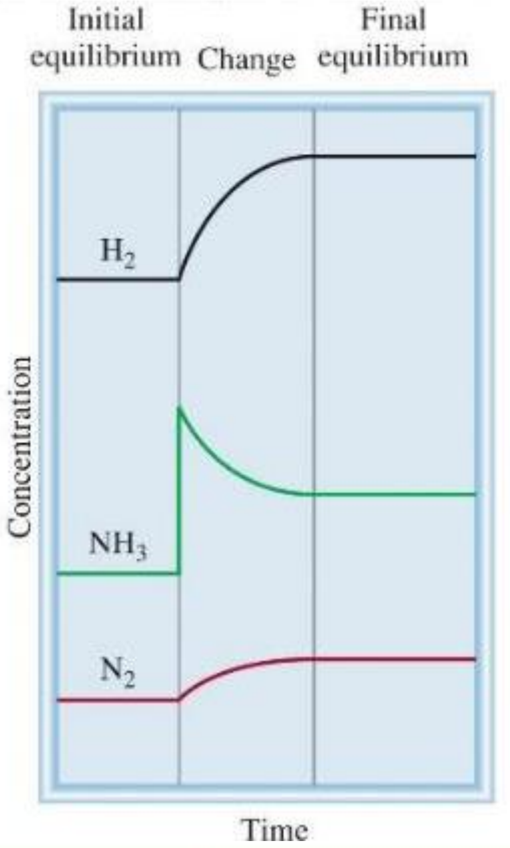
- Changes in concentration

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

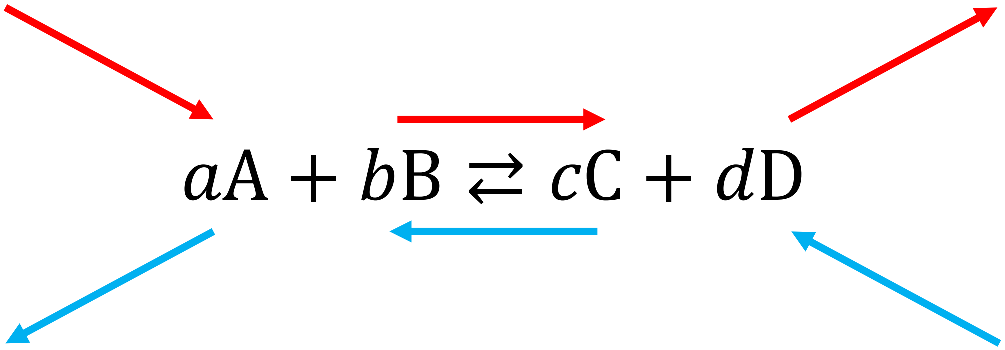
Equilibrium shifts left to offset stress

Add NH_3

Q>K



LE CHÂTELIER: CHANGES IN CONC. (CONT’D)



$$a\mathrm{A} + b\mathrm{B} \rightleftarrows c\mathrm{C} + d\mathrm{D}$$

Change	**Shifts the equilibrium**
Increase concentration of product(s)	left
Decrease concentration of product(s)	right
Increase concentration of reactant(s)	right
Decrease concentration of reactant(s)	left

EXAMPLE

At $720°$ C, the equilibrium constant K_c for the reaction shown is 2.37×10^{-3}. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

In a certain experiment, the equilibrium concentrations are $[N_2] = 0.683\ M$, $[H_2] = 8.80\ M$, and $[NH_3] = 1.05\ M$.

Suppose some NH_3 is added to the mixture so that its concentration is increased to 3.65 M.

(a) Use Le Châtelier’s principle to predict the shift in direction of the net reaction to reach a new equilibrium. (b) Confirm your prediction by calculating the reaction quotient Q_c and comparing its value with K_c.

SOLUTION (1)

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

- Strategy: What is the stress applied to the system? How does the system adjust to offset the stress?
- At the instant when some NH_3 is added, the system is no longer at equilibrium. How do we calculate the Q_c for the reaction at this point? How does a comparison of Q_c with K_c tell us the direction of the net reaction to reach equilibrium.

SOLUTION (2)

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

(a) The stress applied to the system is the addition of NH_3. To offset this stress, some NH_3 reacts to produce N_2 and H_2 until a new equilibrium is established. The net reaction therefore shifts from right to left:

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

SOLUTION (3)

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

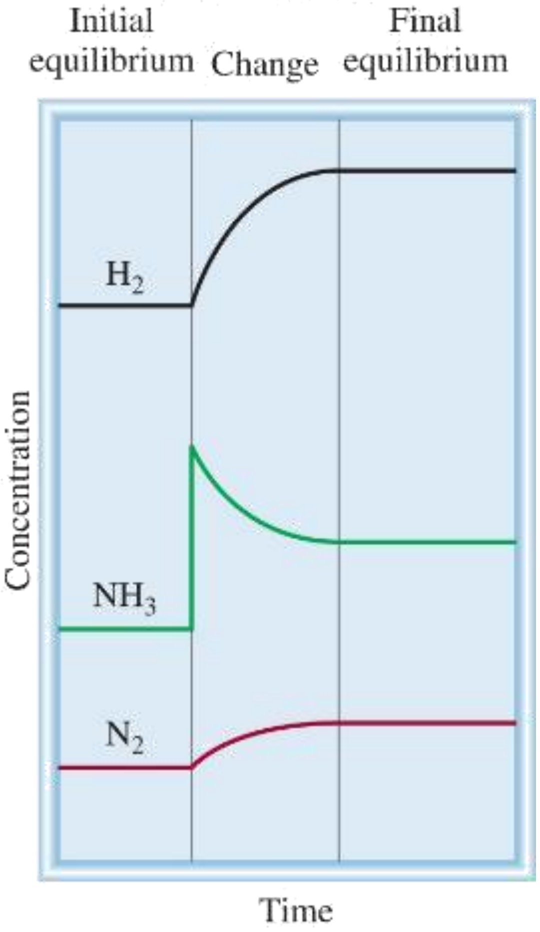
(b) At the instant when some of the NH_3 is added, the system is no longer at equilibrium. The reaction quotient is given by

$$Q_c = \frac{[NH_3]_0^2}{[N_2]_0[H_2]_0^3}$$

$$= \frac{(3.65)^2}{(0.683)(8.80)^3}$$

$$= 2.86 \times 10^{-2}$$

Because this value is greater than 2.37×10^{-3}, the net reaction shifts from right to left until Q_c equals K_c.



LE CHÂTELIER: CHANGES IN V AND/OR P

$$\mathrm{A}(g) + \mathrm{B}(g) \rightleftarrows \mathrm{C}(g)$$

Change	**Shifts the equilibrium to the:**
Increase pressure	Side with fewest # moles of gas
Decrease pressure	Side with most # moles of gas
Increase volume	Side with most # moles of gas
Decrease volume	Side with fewest # moles of gas

No change in the number of moles of gas? NO SHIFT!

EXAMPLE

Consider the following equilibrium systems:

(a) $2\text{PbS}(s) + 3\text{O}_2(g) \rightleftharpoons 2\text{PbO}(s) + 2\text{SO}_2(g)$

(b) $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$

(c) $\text{H}_2(g) + \text{CO}_2(g) \rightleftharpoons \text{H}_2\text{O}(g) + \text{CO}(g)$

Predict the direction of the net reaction in each case as a result of increasing the pressure (decreasing the volume) on the system at constant temperature.

SOLUTION (1)

- Strategy: A change in pressure can affect only the volume of a gas, but not that of a solid because solids (and liquids) are much less compressible. The stress applied is an increase in pressure. According to Le Châtelier’s principle, the system will adjust to partially offset this stress. In other words, the system will adjust to decrease the pressure. This can be achieved by shifting to the side of the equation that has fewer moles of gas. Recall that pressure is directly proportional to moles of gas: $PV = nRT$ so $P \propto n$.

SOLUTION (2)

- $2\text{PbS}(s) + 3\text{O}_2(g) \rightleftharpoons 2\text{PbO}(s) + 2\text{SO}_2(g)$

Consider only the gaseous molecules. In the balanced equation, there are 3 moles of gaseous reactants and 2 moles of gaseous products. Therefore, the net reaction will shift toward the products (to the right) when the pressure is increased.

- $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$

The number of moles of products is 2 and that of reactants is 1; therefore, the net reaction will shift to the left, toward the reactant.

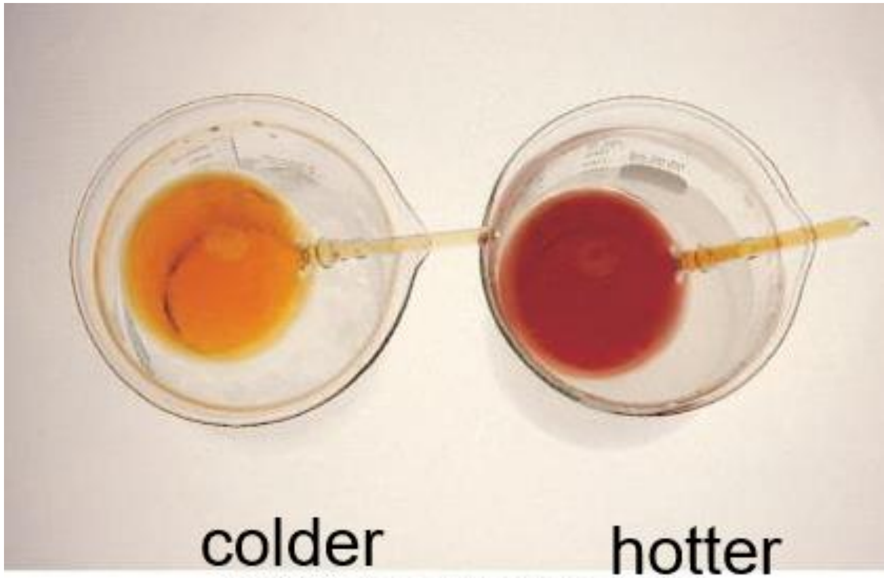
- $\text{H}_2(g) + \text{CO}_2(g) \rightleftharpoons \text{H}_2\text{O}(g) + \text{CO}(g)$

The number of moles of products is equal to the number of moles of reactants, so a change in pressure has no effect on the equilibrium.

LE CHÂTELIER: CHANGES IN TEMPERATURE

Change	**Exothermic Rx** heat is a product	**Endothermic Rx** heat is a reactant
Increase temperature (“add heat”)	*K* decreases (shift L)	*K* increases (shift R)
Decrease temperature (“remove heat”)	*K* increases (shift R)	*K* decreases (shift L)

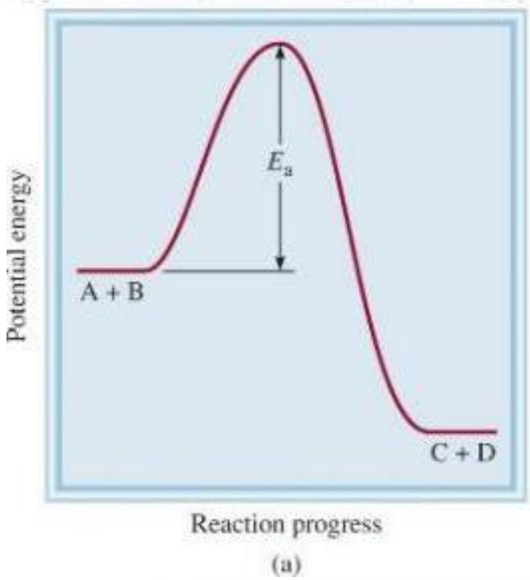
$N_2O_4(g) + heat \rightleftarrows 2NO_2(g)$ $\Delta H^\circ = 58.0\ \text{kJ/mol}$



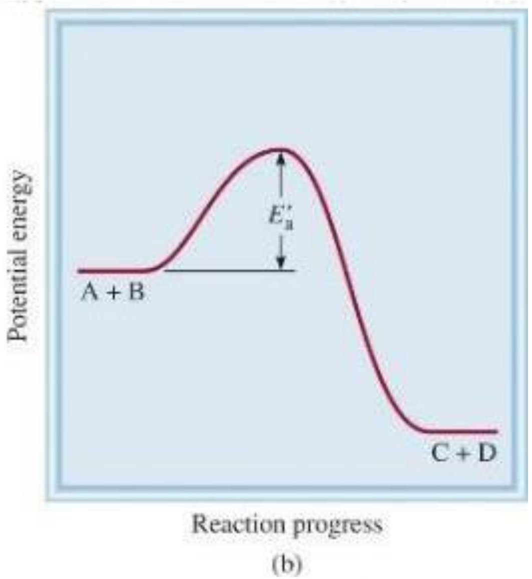
LE CHÂTELIER: ADDITION OF A CATALYST

- Does not change K
- Does not shift the position of an equilibrium system
- Catalyst lowers E_a for both forward and reverse rx
- System will reach equilibrium sooner

uncatalyzed



catalyzed



LE CHÂTELIER’S PRINCIPLE - SUMMARY

Change	**Shift equilibrium?**	**Change K?**
Concentration	yes	no
Pressure	yes*	no
Volume	yes*	no
Temperature	yes	yes
Catalyst	no	no

*Depends on relative # of moles of gaseous react and prod

EXAMPLE

Consider the following equilibrium process between dinitrogen tetrafluoride and nitrogen difluoride:

$$\mathrm{N_2F_4}(g) \rightleftharpoons 2\mathrm{NF_2}(g) \qquad \Delta H^\circ = 38.5\ \mathrm{kJ/mol}$$

Predict the changes in the equilibrium if

(a) the reacting mixture is heated at constant volume;

(b) some $\mathrm{N_2F_4}$ gas is removed from the reacting mixture at constant temperature and volume;

(c) the pressure on the reacting mixture is decreased at constant temperature; and

(d) a catalyst is added to the reacting mixture.

SOLUTION (1)

Strategies:

a) What does the sign of ΔH° indicate about the heat change (endothermic or exothermic) for the forward reaction?

b) Would the removal of some $\mathrm{N_2F_4}$ increase or decrease the Q_c of the reaction?

c) How would the decrease in pressure change the volume of the system?

d) What is the function of a catalyst? How does it affect a reacting system not at equilibrium? at equilibrium?

SOLUTION (2)

(a) The stress applied is the heat added to the system. Note that the $N_2F_4 \rightarrow 2NF_2$ reaction is an endothermic process $\left(\Delta H^{\circ} > 0\right)$, which absorbs heat from the surroundings. Therefore, we can think of heat as a reactant:

$$\text{heat} + N_2F_4(g) \rightleftharpoons 2NF_2(g)$$

The system will adjust to remove some of the added heat by undergoing a decomposition reaction (from left to right).

SOLUTION (3)

The equilibrium constant $K_c = \frac{[NF_2]^2}{[N_2F_4]}$

will therefore increase with increasing temperature because the concentration of NF_2 has increased and that of N_2F_4 has decreased. Recall that the equilibrium constant is a constant only at a particular temperature. If the temperature is changed, then the equilibrium constant will also change.

(b) The stress here is the removal of N_2F_4 gas. The system will shift to replace some of the N_2F_4 removed. Therefore, the system shifts from right to left until equilibrium is reestablished.

As a result, some NF_2 combines to form N_2F_4.

SOLUTION (4)

Comment:

The equilibrium constant remains unchanged in this case because temperature is held constant. It might seem that K_c should change because $\mathrm{NF_2}$ combines to produce $\mathrm{N_2F_4}$. Remember, however, that initially some $\mathrm{N_2F_4}$ was removed. The system adjusts to replace only some of the $\mathrm{N_2F_4}$ that was removed, so that overall the amount of $\mathrm{N_2F_4}$ has decreased. In fact, by the time the equilibrium is reestablished, the amounts of both $\mathrm{NF_2}$ and $\mathrm{N_2F_4}$ have decreased. Looking at the equilibrium constant expression, we see that dividing a smaller numerator by a smaller denominator gives the same value of K_c.

SOLUTION (5)

(c) The stress applied is a decrease in pressure (which is accompanied by an increase in gas volume). The system will adjust to remove the stress by increasing the pressure.

Recall that pressure is directly proportional to the number of moles of a gas. In the balanced equation we see that the formation of NF_2 from N_2F_4 will increase the total number of moles of gases and hence the pressure. Therefore, the system will shift from left to right to reestablish equilibrium. The equilibrium constant will remain unchanged because temperature is held constant.

SOLUTION (6)

(d) The function of a catalyst is to increase the rate of a reaction. If a catalyst is added to a reacting system not at equilibrium, the system will reach equilibrium faster than if left undisturbed. If a system is already at equilibrium, as in this case, the addition of a catalyst will not affect either the concentrations of NF_2 and N_2F_4 or the equilibrium constant.

CHEMISTRY IN ACTION

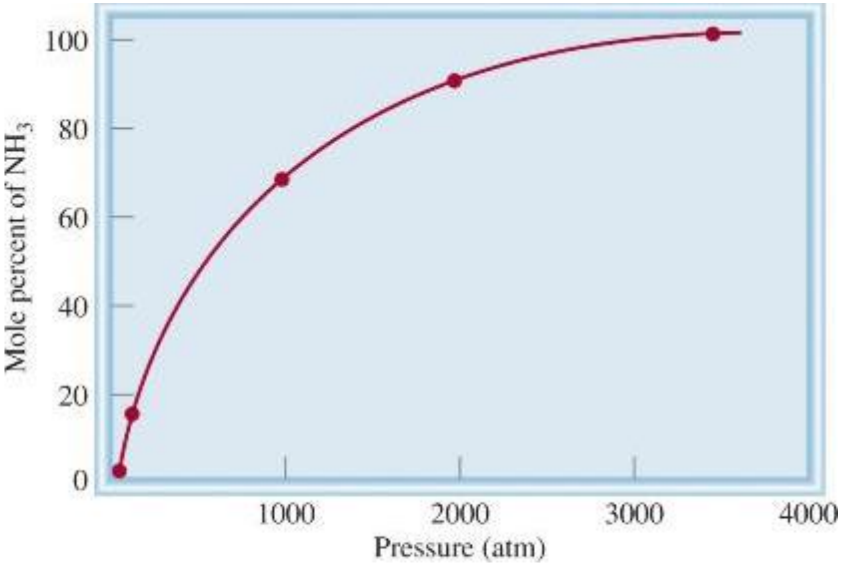
Life at High Altitudes and Hemoglobin Production

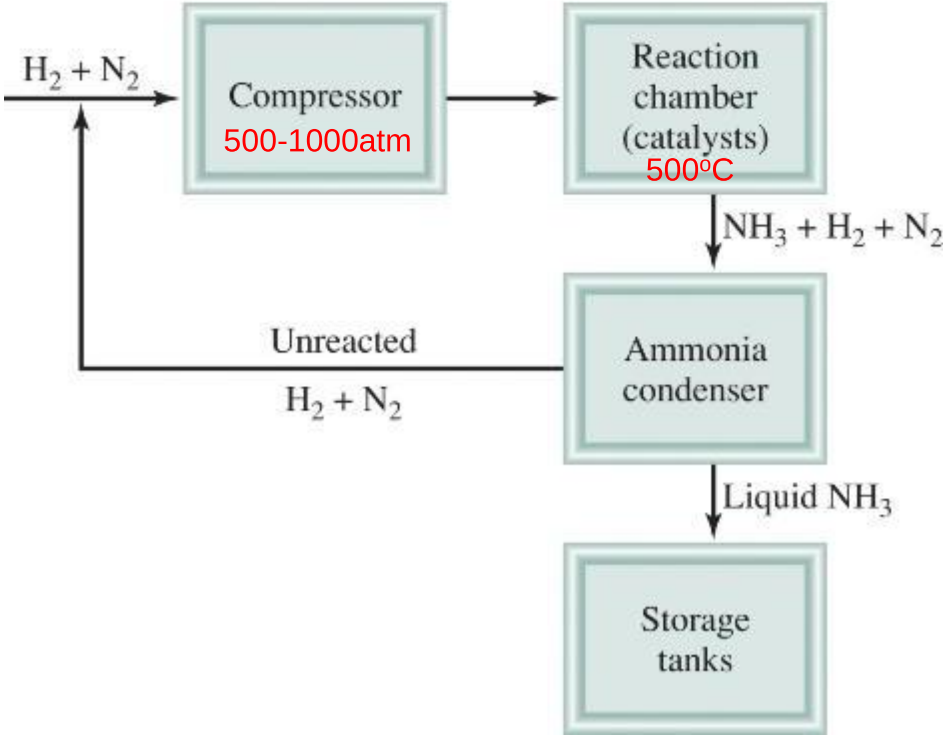
$$\mathrm{Hb}(aq) + \mathrm{O_2}(aq) \rightleftarrows \mathrm{HbO_2}(aq)$$

$$K_c = \frac{[\mathrm{HbO_2}]}{[\mathrm{Hb}][\mathrm{O_2}]}$$

CHEMISTRY IN ACTION: THE HABER PROCESS

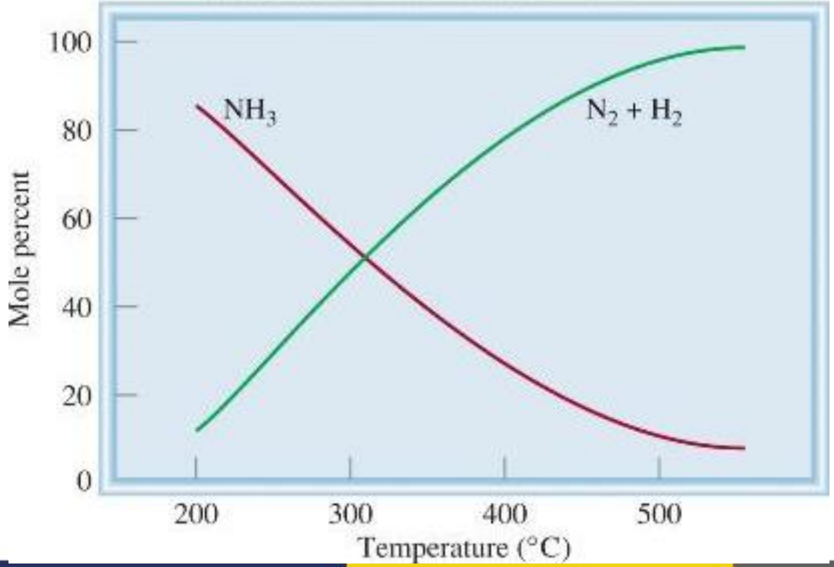
$$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)\ \Delta H^{\circ} = -92.6\ \text{kJ/mol}$$





500-1000atm

$500^{o}C$



CH. 13 OUTLINE

- 13.1 Chemical Equilibria
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- **13.4 Equilibrium Calculations**

EXAMPLE CALCULATIONS

- Check out pages 736-747 (Ex 13.5-13.10)

Chapter 13 Fundamental Equilibrium Concepts

HW problems: 9, 17, 19, 31, 37, 43, 49, 53, 61, 63, 67, 79