CHEMICAL EQUILIBRIUM_____
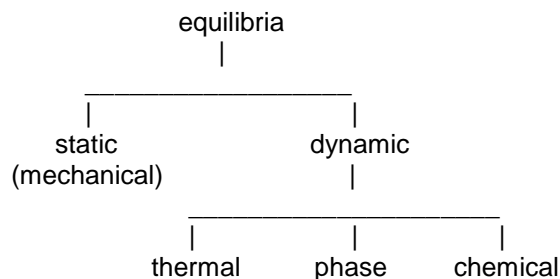
"When a system is in chemical equilibrium, a change in one of the parameters of the equilibrium produces a shift in such a direction that, were no other actors involved in this shift, it would lead to a change of opposite sign in the parameter involved."   **Henri Louis Le Châtelier, 1888**

6.1 The Equilibrium Condition

```
                    equilibria
                        |
        _____
        |                              |
     static                        dynamic
   (mechanical)                        |
                            _____
                            |           |           |
                         thermal      phase      chemical
```
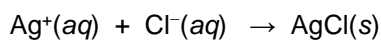
attributes of equilibrium

isolated from outside interference
macroscopic properties constant
spontaneously reach equilibrium state
forward rate = reverse rate
   (dynamically balanced)
reached from products or reactants

phase equilibria - phase boundaries in a phase diagram; colligative properties examine phase equilibria in mixtures, primarily in liquids
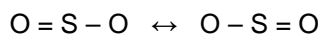
steady state - system with macroscopic concentrations not changing with time but it is not at equilibrium; rather than a dynamic balance between forward and reverse processes a steady state is achieved by competition between a process that supplies components and another process that removes components; common for chemical reactions in biological systems
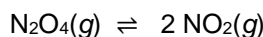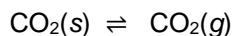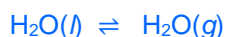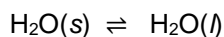
Arrows of Chemistry

   reaction

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

   resonance

$$O = S - O \leftrightarrow O - S = O$$

   equilibrium

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$

Phase Equilibria

$$H_2O(s) \rightleftharpoons H_2O(l)$$

$$H_2O(l) \rightleftharpoons H_2O(g)$$

$$CO_2(s) \rightleftharpoons CO_2(g)$$

equilibrium constant, K
K - concentration (K_c)
K_P - pressure
K_a - ionization of weak acid
K_b - ionization of weak base
K_{sp} - dissolution of slightly soluble salt

Vapor pressure of water as a function of temperature
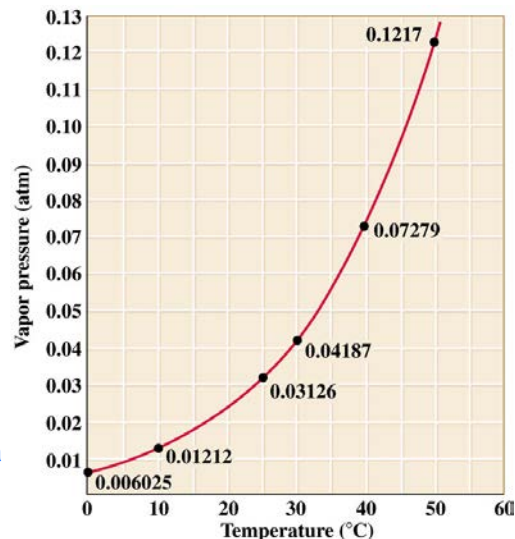
6.2, 6.4, 6.9 (H 8-2) The Equilibrium Constant, K

Law of Mass Action

For   aA + bB   <=>   cC + dD the equilibrium constant K is

$$K = \frac{\mathcal{A}^c_C \; \mathcal{A}^d_D}{\mathcal{A}^a_A \; \mathcal{A}^b_B}$$

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

Products / Reactants

where $\mathcal{A}^a_A$ is the activity (Zumdahl p. 178, 194; Harris p. 164) of species A raised to its stoichiometric coefficient a. The expression for the activity depends upon the manner in which composition is expressed. For concentration in molarity (K), $\mathcal{A}_A = \gamma_A[A] / [\text{ref}]$; for pressure ($K_P$), $\mathcal{A}_A = \gamma_A P_A / P_{ref}$; for molality, $\mathcal{A}_A = \gamma_A m_A / m_{ref}$; for mole fraction $\mathcal{A}_A = \gamma_A \chi_A / \chi_{ref}$, etc. The reference composition is usually chosen to be 1 and insures that the equilibrium constant is unitless, i.e., $P_{ref} = 1$ atm (or bar) for pressure. γ is the activity coefficient and is where all deviations from an ideal gas or an ideal solution is expressed. In the ideal case $\gamma = 1$ and the mass action expression reduces to just the composition variables. The activity of all pure solids and pure liquids is 1 and leads to their "omission" in the equilibrium constant expression. It is understood that all compositions are measured at equilibrium. In this chapter we will assume that all gases and solutions are ideal and recognize that reference compositions of unity are understood to be used though we need not explicitly write them. Note that the numerical value of K will generally be different if expressed in different units of composition.

EX 1. At 1000 K the equilibrium gas mixture contains 0.562 atm SO_2, 0.101 atm O_2, and 0.332 atm SO_3. What is K?

$$2\ SO_2(g)\ +\ O_2(g)\quad \rightleftharpoons\quad 2\ SO_3(g)$$
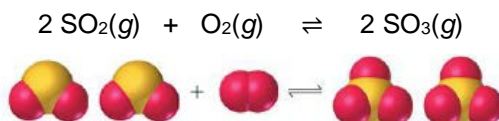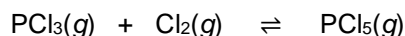

6.3 Equilibrium Expressions Involving Pressures, K_P

The Relation between K and K_P

$$P = (n/V)RT$$
$$= (\text{concentration in mol/L}) \times RT$$

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

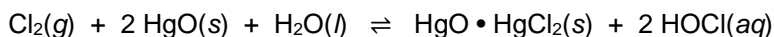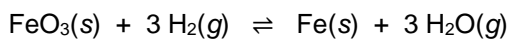**EX 2**. At 250°C the equilibrium concentrations are $[PCl_3] = [Cl_2] = 0.280$ M and $[PCl_5] = 1.885$ M for

$$PCl_3(g)\ +\ Cl_2(g)\quad \rightleftharpoons\quad PCl_5(g)$$
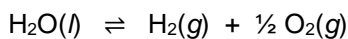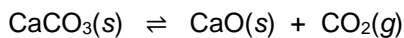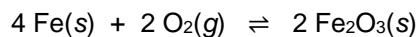
a) What is K?

b) What is K_P?

6.5 Heterogeneous Equilibria

EX 3. Write the equilibrium constant expression for each of the following reactions:
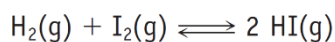
$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$H_2O(l) \rightleftharpoons H_2(g) + \frac{1}{2} O_2(g)$

$FeO_3(s) + 3 H_2(g) \rightleftharpoons Fe(s) + 3 H_2O(g)$

$Cl_2(g) + 2 HgO(s) + H_2O(l) \rightleftharpoons HgO \cdot HgCl_2(s) + 2 HOCl(aq)$

EX 4. What is the value of K if an equilibrium mixture contains 1.0 mol Fe, 1.0×10^{-3} mol O_2, and 2.0 mol $Fe_2O_3(s)$ in a 2.0-L container'?

$$4 Fe(s) + 2 O_2(g) \rightleftharpoons 2 Fe_2O_3(s)$$
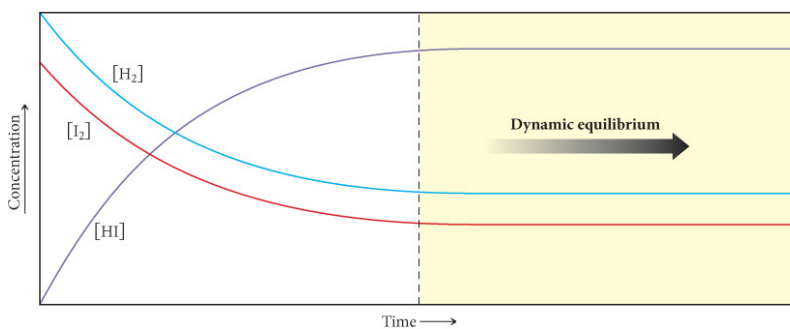
EQ

6.2 Relationship of K's of Related Equilibria

K_P = 55.6 at a temperature where $P_{H2} = 2.12$, $P_{I2} = 0.12$, $P_{HI} = 3.76$ for

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

$$K_p = \frac{P_{HI}^2}{P_{H_2} P_{I_2}}$$

[H₂]

[I₂]

Dynamic equilibrium

[HI]

Concentration →

Time →

As concentration of product increases, and concentrations of reactants decrease, rate of forward reaction slows down, and rate of reverse reaction speeds up.

Dynamic equilibrium: Rate of forward reaction = rate of reverse reaction. Concentrations of reactant(s) and product(s) no longer change.

EX 5. For the above reaction what is K_P for:

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

b) $2 H_2(g) + 2 I_2(g) \rightleftharpoons 4 HI(g)$

c) $\frac{1}{2} H_2(g) + \frac{1}{2} I_2(g) \rightleftharpoons HI(g)$
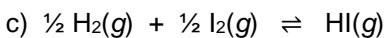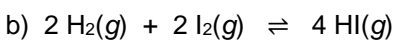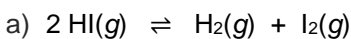
Relationship of K's of Simultaneous Equilibria

EX 6. Find the equilibrium constant for

$$SO_2(g) + CO_2(g) \rightleftharpoons SO_3(g) + CO(g)$$

if you know the equilibrium constants for the following reactions:

1) $SO_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons SO_3(g)$ $\qquad\qquad\qquad$ $K_1 = P_{SO_3} / P_{SO_2} P^{1/2}_{O_2}$

2) $CO_2(g) \rightleftharpoons CO(g) + \frac{1}{2} O_2(g)$ $\qquad\qquad\qquad$ $K_2 = P_{CO} P^{1/2}_{O_2} / P_{CO_2}$

EX 7. Find the equilibrium constant for

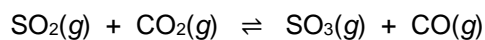$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

if you know the equilibrium constants for the following reactions:

1) $PCl_5(s) \rightleftharpoons PCl_3(g) + Cl_2(g)$ $\qquad\qquad\qquad$ K_1

2) $PCl_5(s) \rightleftharpoons PCl_5(g)$ $\qquad\qquad\qquad\qquad$ K_2
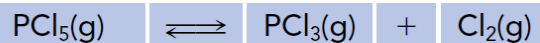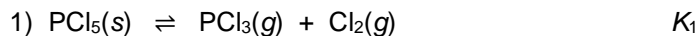
Summary

adding reactions: a + b => multiply K's => $K = K_a K_b$

subtracting reactions: a - b => divide K's => $K = K_a / K_b$

$\qquad\qquad$ [taking the inverse – multiplying by -1]

6.6 Applications of the Equilibrium Constant

We wish to know how far a reaction has gone (reactions seldom go to completion). We also want to know if a given set of initial concentrations represent an equilibrium situation. If not, which way does the system shift to obtain equilibrium?

- reactions eventually reach a state of equilibrium
- want a number which defines this equilibrium situation
- no net change => some fixed relationship between reactants and products
- equilibrium constant gives the relationship; some examples at 25 ^{0}C:

$$H_2(g) \ + \ \tfrac{1}{2} O_2(g) \ \rightleftharpoons \ H_2O(g) \qquad\qquad K \ = \ \frac{[H_2O]}{[H_2][O_2]^{1/2}} \ = \ 5.6 \times 10^{40}$$

$$Cl_2O(g) \ + \ H_2O(g) \ \rightleftharpoons \ 2\ HOCl(g) \qquad\qquad K \ = \ \frac{[HOCl]^2}{[Cl_2O][H_2O]} \ = \ 0.0900$$

$$N_2(g) \ + \ O_2(g) \ \rightleftharpoons \ 2\ NO_2(g) \qquad\qquad K \ = \ \frac{[NO_2]^2}{[N_2][O_2]} \ = \ 4.7 \times 10^{-31}$$

1) $K > 1$ => product-favored; $K \gg 1$ => reaction essentially complete
2) $K < 1$ => reactant-favored; $K \ll 1$ => essentially no reaction

- reaction quotient, Q, tells how reaction approaches equilibrium: For the general reaction

$$aA + bB \ \ <=> \ \ cC + dD$$
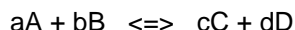
$$\text{Reaction quotient} = Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad \text{or} \qquad Q = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

$Q \ < \ K$ => reaction proceeds left to right
$Q \ = \ K$ => reaction is at equilibrium
$Q \ > \ K$ => reaction proceeds right to left

concentrations or pressures used in Q are the initial ones

green line should start at 0.1000 M

Experiment 1   Experiment 2   Experiment 3

t_e = time for equilibrium to be reached
— mol Cu^{2+}
— mol Sn^{2+}
— mol Cu^+
— mol Sn^{4+}
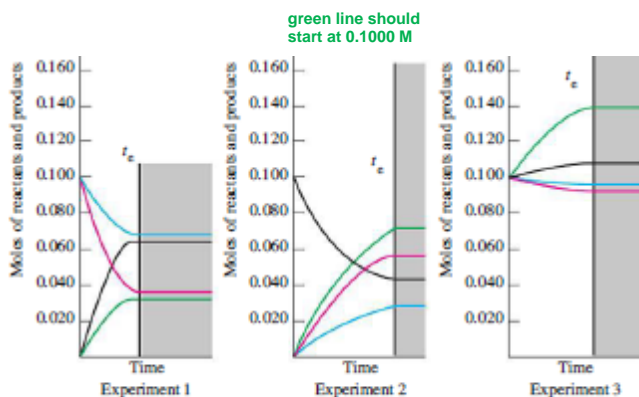
Three Approaches to Equilibrium in the Reaction
$$2\ Cu^{2+}(aq) + Sn^{2+}(aq) \rightleftharpoons 2\ Cu^+(aq) + Sn^{4+}(aq)$$

	Cu^{2+}(aq)	Sn^{2+}(aq)	Cu^+(aq)	Sn^{4+}(aq)
Experiment 1				
Initial amounts, mol/L	0.100	0.100	0.000	0.000
Equilibrium amounts, mol/L	0.0360	0.0680	0.0640	0.0320
Experiment 2				
Initial amounts, mol/L	0.000	0.000	0.100	0.100
Equilibrium amounts, mol/L	0.0567	0.0283	0.0433	0.0717
Experiment 3				
Initial amounts, mol/L	0.100	0.100	0.100	0.100
Equilibrium amounts, mol/L	0.0922	0.0961	0.1078	0.1039

In the first experiment only Cu^{2+} and Sn^{2+} are present initially; in a second experiment only Cu^+ and Sn^{4+}; and in the third experiment, all four ions are present. From the plots on the left one sees that in no case is any reacting species completely consumed. Furthermore, if one were to calculate K, the value would be the same for all three experiments.

## 6.7 Solving Equilibrium Problems (using the **ICE** tables introduced on p. 183)

EX 8. 4.00 atm of $H_2(g)$ and 2.00 atm of $I_2(g)$ are mixed and allowed to react. When equilibrium is reached 3.76 atm of HI(g) is formed. What is K_p for the reaction?

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

Initial   4.00 atm   2.00 atm
Change
Equilibrium   3.76 atm
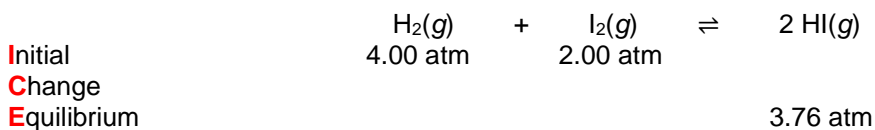
### 1. Using K to Determine Equilibrium Amounts of Reactants and Products

Given K and all equilibrium partial pressures but one, find the missing pressure

EX 9. At 425°C K_p = 55.6 for the following reaction. If P_{H2} = 2.12 atm and P_{I2} = 0.12 atm at 425°C what is the equilibrium partial pressure of HI?

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

EQ
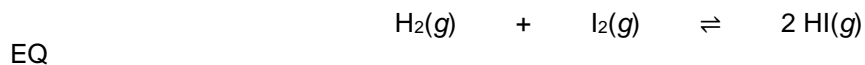
Given K find equilibrium partial pressures of gaseous products from decomposition of a solid.

EX 10. If K_P = 2.9 × 10^{-3} at 25°C what are the equilibrium partial pressures of NH_3 and CO_2?

$$NH_4OCONH_2(s) \quad \rightleftharpoons \quad 2\ NH_3(g) \quad + \quad CO_2(g)$$

EQ
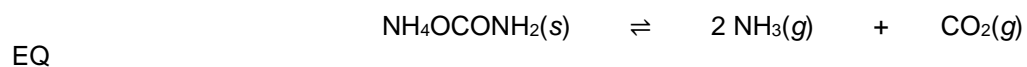
Given K find the equilibrium concentration of the ions from a sparingly soluble salt. (Chapter 8 - Solubility Equilibria and the Solubility Product)

EX 11. What are the equilibrium concentration of the ions at 25°C if Ksp = 3.2 × 10^{-25}

$$AuCl_3(s) \quad \rightleftharpoons \quad Au^{3+}(aq) \quad + \quad 3\ Cl^-(aq)$$

EQ

---

2. Using Initial and Equilibrium Amounts (as in EX 8)

EX 12. The equilibrium concentration of gaseous chlorine is 0.030 M when 0.075 and 0.033 M hydrogen chloride and oxygen gas, respectively, are initially placed in a reaction vessel. How much hydrogen chloride and oxygen gas are left unreacted at equilibrium?

$$4\ HCl(g) \quad + \quad O_2(g) \quad \rightleftharpoons \quad 2\ Cl_2(g) \quad + \quad 2\ H_2O(g)$$

I
C
E

---
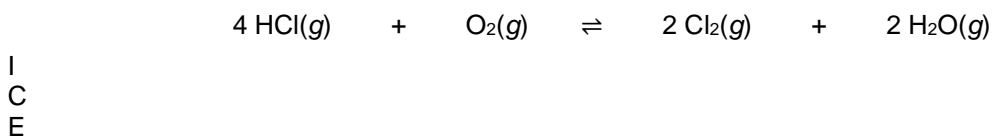
3. Using K and Initial Amounts

EX 13. If 2.00 mol of HBr were introduced into a 1.00 L vessel at 1495 K what would be the equilibrium concentration of all species if K = 2.86 × 10^{-5}?

$$2\ HBr(g) \quad \rightleftharpoons \quad H_2(g) \quad + \quad Br_2(g)$$

I
C
E
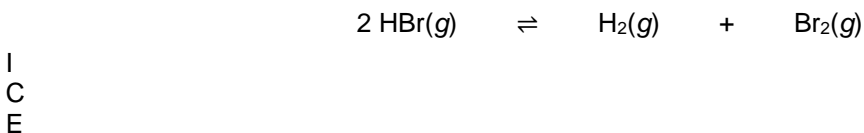
### 4. Equilibrium Calculations Involving the Quadratic Equation

for $ax^2 + bx + c = 0$ the solution is $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

EX 14. At a particular temperature $K = 9.1 \times 10^{-4}$. Determine the concentration of all ions in a solution that is initially 2.0 M $FeSCN^{2+}$.

$$FeSCN^{2+}(aq) \quad \rightleftharpoons \quad Fe^{3+}(aq) \quad + \quad SCN^-(aq)$$
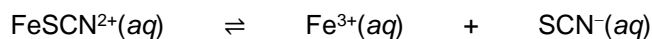
I
C
E

EX 15. If 1.00×10^{-3} M H_2 and 2.00×10^{-3} M I_2 are mixed and allowed to react at 425°C what are the equilibrium concentrations if $K = 55.6$?

$$H_2(g) \quad + \quad I_2(g) \quad \rightleftharpoons \quad 2\,HI(g)$$
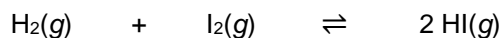
I
C
E

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5. Treating Systems That Have Small Equilibrium Constants (systematic approach next week)

EX 16. What is the concentration of $[H_3O^+]$ in a 1.00 M solution of acetic acid at 25°C if $Ka = 1.8 \times 10^{-5}$ (Chapter 7 - Acid-Base Equilibria)

$$CH_3COOH(aq) \quad + \quad H_2O(g) \quad \rightleftharpoons \quad H_3O^+(aq) \quad + \quad CH_3COO^-(aq)$$
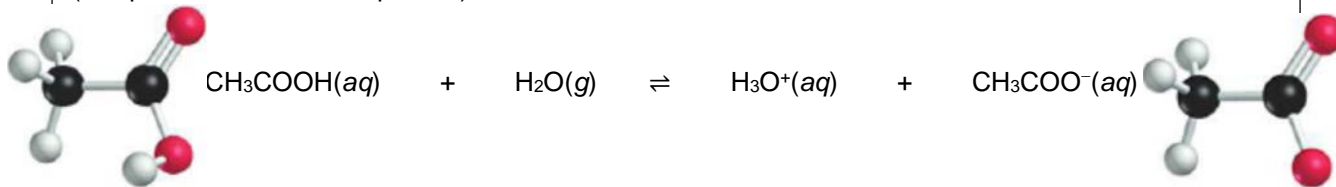
I
C
E

6.8 Le Châtelier's Principle

"When a system is in chemical equilibrium, a change in one of the parameters of the equilibrium produces a shift in such a direction that, were no other actors involved in this shift, it would lead to a change of opposite sign in the parameter involved."

Henri Louis Le Châtelier, 1888

If a change in conditions (a "stress') is imposed on a system at equilibrium, the equilibrium position will shift in a direction that tends to reduce that change in conditions.

    I. change of **temperature** at constant pressure
    II. change of **total pressure** at constant temperature

        a) add or remove gaseous reactant or product at constant volume
        b) change volume of container
        c) add inert gas (one not involved in the reaction) at constant volume

    III. change of **concentration/partial pressure**

Le Châtelier's Principle predicts

    effect on K
    direction of equilibrium shift
    effect on concentrations/partial pressures

I. temperature - only stress that can change value of K

    l) phase equilibria

$$H_2O(l) \;\rightleftharpoons\; H_2O(g) \qquad K = P_{H2O(g)} \text{ where } P_{H2O(g)}(T)$$

2) An exothermic reaction gives off heat while an endothermic reaction requires heat for the reaction to proceed. One can make an analogy with the stress imposed by adding or removing a gaseous reactant if one were to consider heat as a "reactant" in the case of an endothermic reaction and as a "product" for an exothermic reaction.
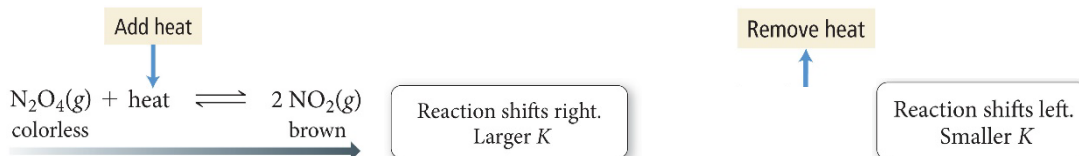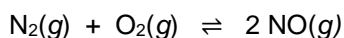

EX 17. For each of the following reactions determine whether the value of K would be larger or smaller at a higher temperature.

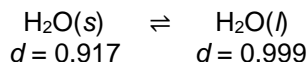a) At 500 K, $K = 90$ for the following exothermic reaction

$$N_2(g) \;+\; 3\,H_2(g) \;\rightleftharpoons\; 2\,NH_3(g)$$
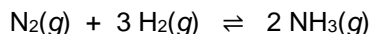
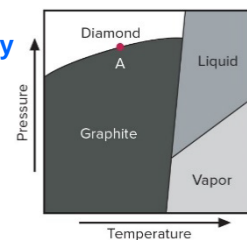b) At 25°C, $K = 10^{-31}$ for the following endothermic reaction.

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

II. total pressure change

1) pressure induced phase transition **shifts reaction to side with greater density**

$$H_2O(s) \quad \rightleftharpoons \quad H_2O(l)$$
$$d = 0.917 \qquad d = 0.999$$

phase diagram for water has a negative slope for the solid/liquid coexistence line unlike the more usual phase diagrams such as carbon shown on the right
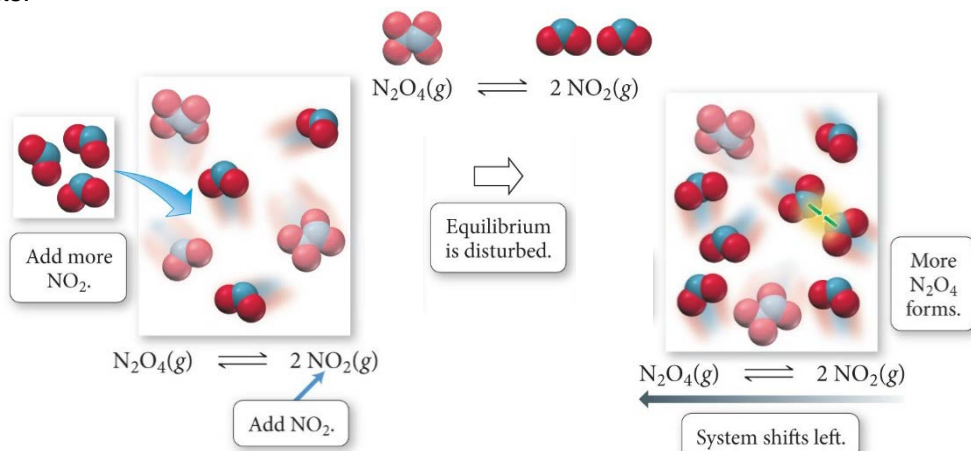
density = m/V => liquid water has a larger volume in which to accommodate a given mass of molecules than ice does => ice melts under pressure.

2) increase P_{TOT} by adding an inert gas at constant T, V. **no effect**

Since $P_i = n_i RT/V$, the partial pressures of all gases participating in the equilibrium reaction are unaffected by the presence of the inert gas. Hence the equilibrium constant is also unaffected.

3) increase P_{TOT} by adding a gaseous reactant or product at constant T, V (same as change in concentration). **shifts reaction to opposite side**
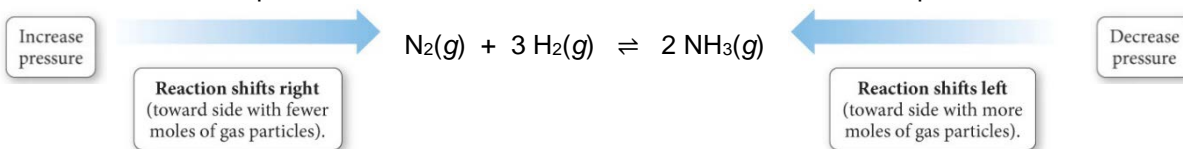
Again $P_i = n_i RT/V$ so that only the partial pressure of the added gas is changed, the others remain constant at the moment of addition. However the equilibrium constant is a constant so long as the temperature is not changed. Therefore if the added gas were a reactant, K would decrease unless the equilibrium shifts to products. Similarly, were the added gas a product, the equilibrium would shift toward reactants.

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$

Equilibrium is disturbed.

Add more NO$_2$.

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$

Add NO$_2$.

More N$_2$O$_4$ forms.

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$

System shifts left.

4) increase P_{TOT} at constant T **shifts reaction to side with smaller volume, less moles**

Consider a certain increase in total pressure. Since $P_i = x_i P_{TOT}$, each P_i in K (actually Q until the new equilibrium is established) would also be increased by the same amount. If the total number of moles of reactant gases in the balanced chemical equation for the equilibrium is the same as the total number of moles of product gases then there would be no effect. This is due to the fact that the powers that the P_i are raised to in the numerator of K are the same as in the denominator. Otherwise, a pressure increase shifts the equilibrium to the side with fewer moles in the balanced equation.

Increase pressure

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

Decrease pressure

Reaction shifts right (toward side with fewer moles of gas particles).

Reaction shifts left (toward side with more moles of gas particles).

EX 18. For the above chemical reaction what would be the effect on the equilibrium if the volume were changed so that the total pressure was increased 10-fold?

III. concentration change – same as adding or removing a gaseous reactant