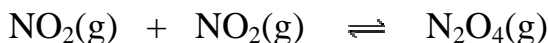


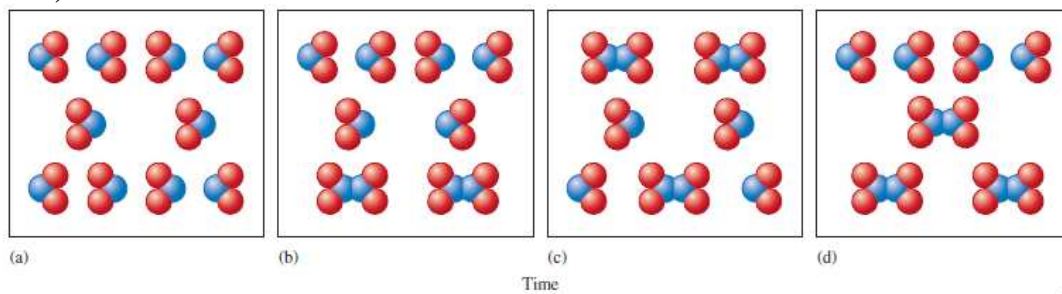
# CHEMISTRY 1102 NOTES

## ZUMDAHL CHAPTER 13 - CHEMICAL EQUILIBRIUM

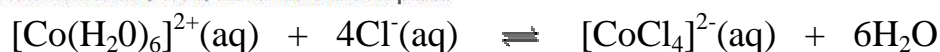
Examples are:



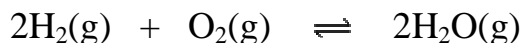
(Figure 13.1)



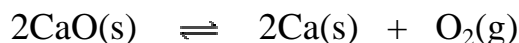
**FIGURE 13.1**  
A molecular representation of the reaction  $2\text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$  over time in a closed vessel. Note that the numbers of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  in the container become constant (c and d) after sufficient time has passed.



An example of a reaction which goes essentially to completion is:



An example of a reaction which does not go at all is:



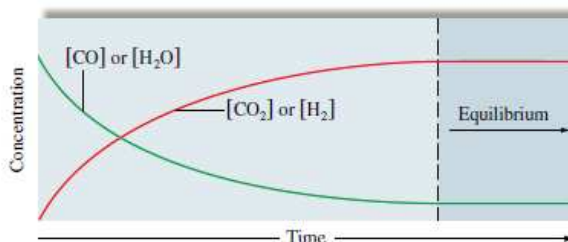
### 1. The Equilibrium Condition

Example system ("water gas shift reaction"):



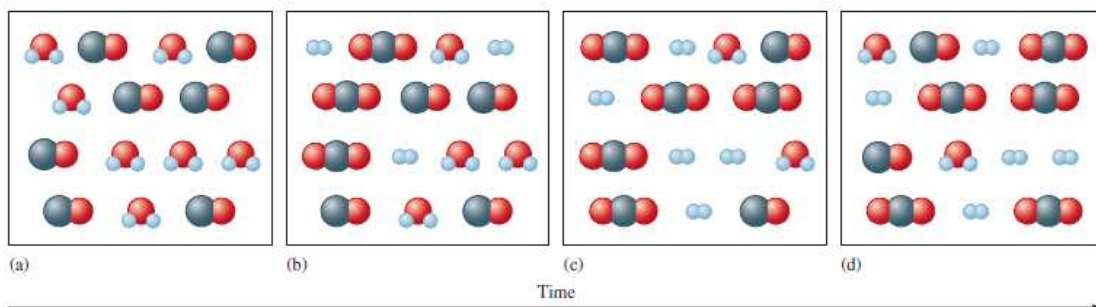
The reactants are consumed until the forward and reverse reactions occur at the same rate. (Figure 13.2) Note that the concentration of the reactants never goes to zero.

**FIGURE 13.2**  
The changes in concentrations with time for the reaction  $\text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{CO}_2(\text{g})$  when equimolar quantities of  $\text{H}_2\text{O}(\text{g})$  and  $\text{CO}(\text{g})$  are mixed.



We need a way to answer questions about what happens if, for example, we add more H<sub>2</sub>O. Obviously, doing so will speed up the forward reaction because there will be more collisions of reactants, but this will also increase the number of product molecules eventually so that the reverse reaction will also speed up. What is the net result?

Figure 13.3 illustrates the molecular process taking place.



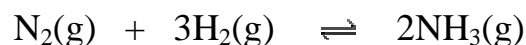
**FIGURE 13.3**  
 (a) H<sub>2</sub>O and CO are mixed in equal numbers and begin to react (b) to form CO<sub>2</sub> and H<sub>2</sub>. After time has passed, equilibrium is reached (c) and the numbers of reactant and product molecules then remain constant over time (d).

Factors affecting the equilibrium position include:

- The initial concentrations.
- The heat of reaction.
- The relative order among reactants and products (entropy change).
- The temperature at which the reaction is occurring.

## 2. The Characteristics of Chemical Equilibrium

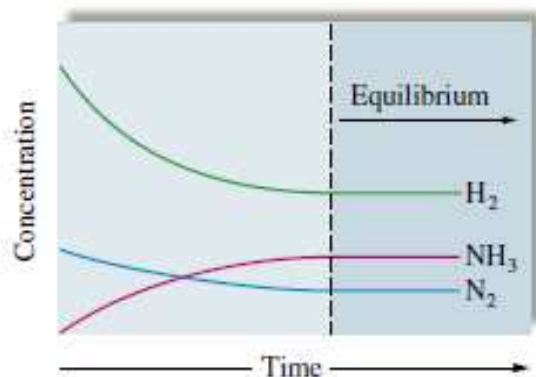
Example (Haber process) :



There are always two possible reasons why a reaction is "stopped":

- The system is at equilibrium.
- The reaction is too slow to detect concentration changes.

It is the second reason which applies to the ammonia/hydrogen reaction at normal pressures and at room temperature. Figure 13.5 shows the reaction progress at higher temperature and pressure. Note how the stoichiometry is illustrated by the curves.



**FIGURE 13.5**

A concentration profile for the reaction  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$  when only  $\text{N}_2(\text{g})$  and  $\text{H}_2(\text{g})$  are mixed initially.

### 3. The Equilibrium Constant (Law of Mass Action)

For a reaction:



The *equilibrium expression* is:

$$K = \frac{[\text{C}]^l[\text{D}]^m}{[\text{A}]^j[\text{B}]^k}$$

where  $K$  is the *equilibrium constant*.

For example, for the reaction



$$K = \frac{[\text{NO}_2]^4[\text{H}_2\text{O}]^6}{[\text{NH}_3]^4[\text{O}_2]^7}$$

#### **Exercise (13.2):**

The following equilibrium concentrations were observed for the Haber process at 127 °C:

$$[\text{NH}_3] = 3.1 \times 10^{-2} \text{ mol/L}$$

$$[\text{N}_2] = 8.5 \times 10^{-1} \text{ mol/L}$$

$$[\text{H}_2] = 3.1 \times 10^{-3} \text{ mol/L}$$

- Calculate the value of  $K$  at 127 °C.
- Calculate the value of  $K$  for the reverse reaction.
- Calculate the value of  $K$  for the reaction rewritten to produce one mole of  $\text{NH}_3$
- $K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(3.1 \times 10^{-2} \text{ mol/L})^2}{(8.5 \times 10^{-1} \text{ mol/L})(3.1 \times 10^{-3} \text{ mol/L})^3}$

$$= 3.8 \times 10^4 \text{ L}^2 \text{ mol}^{-2}$$

$$\text{e. } K' = [\text{N}_2][\text{H}_2]^3/[\text{NH}_3]^2 = 1/k = 1/(3.8 \times 10^4 \text{ L}^2 \text{ mol}^{-2}) = 2.6 \times 10^{-5} \text{ mol}^2 \text{ L}^{-2}$$

$$\text{f. } K' = [\text{NH}_3]/[\text{N}_2]^{1/2}[\text{H}_2]^{3/2} = K^{1/2} = (3.8 \times 10^4 \text{ L}^2 \text{ mol}^{-2})^{1/2} = 1.9 \times 10^2 \text{ L mol}^{-1}$$

Note that:

- The equilibrium constant for the reverse reaction is always the reciprocal.
- The equilibrium constant for the reaction multiplied by n is always  $K_{\text{new}} = (K_{\text{orig}})^n$

The law of mass action works for mixtures of gases (except sometimes at very high pressures) and for solutions (except sometimes at high concentrations).

TABLE 13.1 Results of Three Experiments for the Reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$			
Experiment	Initial Concentrations	Equilibrium Concentrations	$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$
I	$[\text{N}_2]_0 = 1.000 \text{ M}$ $[\text{H}_2]_0 = 1.000 \text{ M}$ $[\text{NH}_3]_0 = 0$	$[\text{N}_2] = 0.921 \text{ M}$ $[\text{H}_2] = 0.763 \text{ M}$ $[\text{NH}_3] = 0.157 \text{ M}$	$K = 6.02 \times 10^{-2}$
II	$[\text{N}_2]_0 = 0$ $[\text{H}_2]_0 = 0$ $[\text{NH}_3]_0 = 1.000 \text{ M}$	$[\text{N}_2] = 0.399 \text{ M}$ $[\text{H}_2] = 1.197 \text{ M}$ $[\text{NH}_3] = 0.203 \text{ M}$	$K = 6.02 \times 10^{-2}$
III	$[\text{N}_2]_0 = 2.00 \text{ M}$ $[\text{H}_2]_0 = 1.00 \text{ M}$ $[\text{NH}_3]_0 = 3.00 \text{ M}$	$[\text{N}_2] = 2.59 \text{ M}$ $[\text{H}_2] = 2.77 \text{ M}$ $[\text{NH}_3] = 1.82 \text{ M}$	$K = 6.02 \times 10^{-2}$

Always distinguish between equilibrium position - there are an infinite number of possibilities, and equilibrium constant - which is unique for a given temperature.

#### 4. Equilibrium Expressions Involving Pressures and Concentrations

For gases, we can write equilibrium expressions in terms of pressures. Remember that:

$$PV = nRT \quad \text{or} \quad P = (n/V)RT = CRT$$

Since  $C = n/V$  ie moles over volume it is the molar concentration:

$$K_c = [\text{NH}_3]^2/[\text{N}_2][\text{H}_2]^3 = C_{\text{NH}_3}^2/C_{\text{N}_2} \cdot C_{\text{H}_2}^3$$

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

Generally though:

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

where  $\Delta n$  = the sum of the coefficients of the gaseous products - the sum of the coefficients of the gaseous reactants in the chemical equation. For the generic equilibrium given at the beginning:



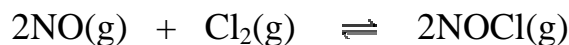
where:

$$K = [C]^l[D]^m / [A]^j[B]^k$$

$$\Delta n = (l+m) - (j+k)$$

### Exercise: (13.5)

For the reaction (at 25°C:



The value of  $K_p = 1.9 \times 10^3 \text{ atm}^{-1}$ . Calculate the value of  $K$ .

$$\Delta n = 2 - (2+1) = -1$$

so:

$$K_p = K(RT)^{-1} = K/(RT)$$

$$K = K_p(RT) = (1.9 \times 10^3 \text{ atm})(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})(298 \text{ K}) = 4.6 \times 10^4 \text{ L mol}^{-1}$$

A final note on units: if the sum of the powers on the top and the bottom of the equilibrium expression are the same,  $K$  and  $K_p$  will be unitless and equal. Otherwise,  $K$  and  $K_p$  are unequal. Nevertheless, it is common practice (though sloppy) to list  $K$  values without their units.

## 5. Heterogeneous Equilibria

Reactions described so far have all reagents and products in the same phase: solution or gas. These are called *homogenous equilibria*. When more than one phase is involved we refer to *heterogeneous equilibria*. Consider the reaction:



$$K' = [CO_2][CaO]/[CaCO_3]$$

But it turns out experimentally that  $[\text{CaCO}_3]$  and  $[\text{CaO}]$  seem to be constant so:

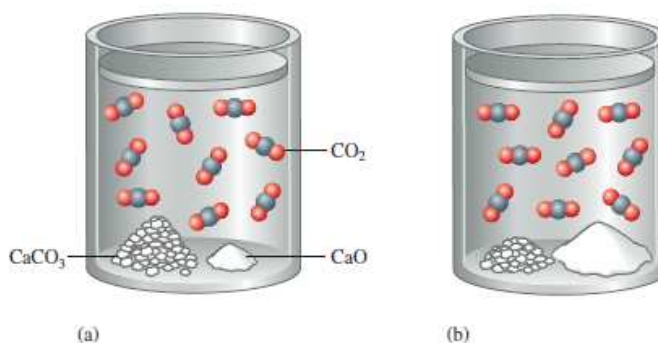
$$K' = [\text{CO}_2]C_1/C_2 \quad \text{or} \quad K = [\text{CO}_2]$$

where:

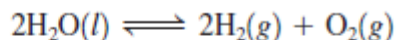
$$K = K'C_2/C_1$$

**FIGURE 13.6**

The position of the equilibrium  $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$  does not depend on the amounts of  $\text{CaCO}_3(s)$  and  $\text{CaO}(s)$  present.



The same situation occurs if a pure liquid is involved. The decomposition of liquid water to  $\text{H}_2(g)$  and  $\text{O}_2(g)$  would be an example if it happened.

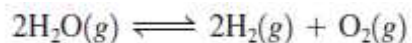


where

$$K = [\text{H}_2]^2[\text{O}_2] \quad \text{and} \quad K_p = (P_{\text{H}_2})^2(P_{\text{O}_2})$$

$$K = [\text{H}_2]^2[\text{O}_2]$$

However, if the reaction were carried out under conditions where the water is a gas rather than a liquid, that is,



then

$$K = \frac{[\text{H}_2]^2[\text{O}_2]}{[\text{H}_2\text{O}]^2} \quad \text{and} \quad K_p = \frac{(P_{\text{H}_2})^2(P_{\text{O}_2})}{P_{\text{H}_2\text{O}}^2}$$

because the concentration or pressure of water vapor can change.

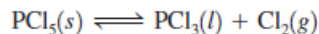
### Sample Exercise 13.6

Write the expressions for  $K$  and  $K_p$  for the following processes:

- Solid phosphorus pentachloride decomposes to liquid phosphorus trichloride and chlorine gas.
- Deep blue solid copper(II) sulfate pentahydrate is heated to drive off water vapor to form white solid copper(II) sulfate.

#### Solution

- a. The reaction is

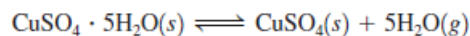


The equilibrium expressions are

$$K = [\text{Cl}_2] \quad \text{and} \quad K_p = P_{\text{Cl}_2}$$

In this case neither the pure solid  $\text{PCl}_5$  nor the pure liquid  $\text{PCl}_3$  is included in the equilibrium expressions.

- b. The reaction is



The equilibrium expressions are

$$K = [\text{H}_2\text{O}]^5 \quad \text{and} \quad K_p = (P_{\text{H}_2\text{O}})^5$$

The solids are not included.

## 6. Applications of the Equilibrium Constant

Consider the reaction:



Suppose the equilibrium constant is 16. Then:

$$(\text{N}_C)(\text{N}_D)/(\text{N}_A)(\text{N}_B) = 16$$

Suppose we start with 9 of A and 12 of B. Then 5 A's and B's disappear and 5 C's and D's appear. Then the *reaction quotient* is:

$$(5)(5)/(4)(7) = 0.9 \quad \text{not equal to 16!}$$

Suppose  $x$  of A and B disappear and  $x$  of C and D appear. Now we would write the reaction quotient as:

$$(x)(x)/(9-x)(12-x)$$

and the question is what must  $x$  be so that the quotient = 16. It cannot be 9 or greater or the quotient would become infinity. By trial and error we can see  $x$  must equal 8.

Nobody does things this way!

### The Extent of a Reaction

Qualitatively we can see that if  $K$  is much greater than 1, a reaction will favour the products, and if it is much less than 1 the reactants will be predominant. It is important to remember though that the *time taken to reach equilibrium* is not related to  $K$ .

### Reaction Quotient

0. If the reaction quotient =  $K$ , the reaction is at equilibrium.
1. If the reaction quotient <  $K$ , the reaction must produce more products.
2. If the reaction quotient >  $K$ , the reaction has gone too far and reactants must be regenerated.

### Exercise (13.7):

The equilibrium constant for the Haber process at 500°C is  $6.0 \times 10^{-2} \text{ L}^2 \text{ mol}^{-2}$ . For a mixture containing  $1 \times 10^{-3} \text{ M NH}_3$ ,  $1 \times 10^{-5} \text{ M N}_2$  and  $2 \times 10^{-3} \text{ M H}_2$ , which way, if at all, must the equilibrium shift?

$$Q = \frac{[\text{NH}_3]_0^2}{[\text{N}_2]_0[\text{H}_2]_0^3} = 1.3 \times 10^7 \text{ L}^2 \text{ mol}^{-2}$$

$Q$  is very much greater than  $K$  so ammonia must be converted back to  $\text{H}_2$  and  $\text{N}_2$ .

### Calculating Equilibrium Pressures and Concentrations

The most common calculation actually involves finding equilibrium concentrations from the constant and a set of starting concentrations. This can potentially cause mathematical problems, but certain types of calculation are standard situations:

**Exercise (13.8)** Just apply the formula type:

Consider the reaction:



At a certain temperature  $K_p = 0.133 \text{ atm}$ . At equilibrium the pressure of  $\text{N}_2\text{O}_4$  is found to be 2.71 atm. What is the pressure of  $\text{NO}_2$ ?

$$P_{\text{NO}_2}^2 / P_{\text{N}_2\text{O}_4} = 0.133$$

Therefore:



$$P_{\text{NO}_2}^2 = K_p \cdot P_{\text{N}_2\text{O}_4} = (0.133)(2.71) = 0.360 \text{ atm}^2$$

$$P_{\text{NO}_2} = (0.360 \text{ atm}^2)^{1/2} = 0.600 \text{ atm}$$

**Exercise (13.9)** Some missing concentrations at equilibrium:

In a 1.00 L flask are placed 0.298 mol  $\text{PCl}_3(\text{g})$  and  $8.70 \times 10^{-3}$  mol  $\text{PCl}_5(\text{g})$ . Equilibrium is established at a particular temperature and  $2.00 \times 10^{-3}$  mol  $\text{Cl}_2$  are found. Calculate the equilibrium concentrations of all the species and K. The reaction is:



The equilibrium quantities will be:

$$[\text{Cl}_2] = 2.00 \times 10^{-3} \text{ mol} / 1 \text{ L} = 2.00 \times 10^{-3} \text{ M}$$

$$[\text{PCl}_3] = (0.298 \text{ mol} + 2.00 \times 10^{-3} \text{ mol}) / 1 \text{ L} = 0.300 \text{ M}$$

$$[\text{PCl}_5] = (8.70 \times 10^{-3} \text{ mol} - 2.00 \times 10^{-3} \text{ mol}) / 1 \text{ L} = 6.70 \times 10^{-3} \text{ M}$$

and:

$$K = [\text{Cl}_2][\text{PCl}_3]/[\text{PCl}_5] = (2.00 \times 10^{-3} \text{ M})(0.300 \text{ M})/6.70 \times 10^{-3} \text{ M} \\ = 8.96 \times 10^{-2} \text{ M}$$

**Exercise (13.10)** No equilibrium concentrations - case I - the perfect square:

The equilibrium constant for the water gas shift reaction at 700 K is 5.10. Calculate the equilibrium concentrations if 1.000 mol of each component is mixed in a 1 L flask. The reaction is:



First we check to see if the system is at equilibrium:

$$Q = [\text{CO}_2]_o[\text{H}_2]_o/[\text{CO}]_o[\text{H}_2\text{O}]_o = (1.000)(1.000)/(1.000)(1.000) = 1.000$$

Therefore the reaction must go to the right - x mol of CO and  $\text{H}_2\text{O}$  are consumed,  $\text{CO}_2$  and  $\text{H}_2$  are produced:

$$K = [\text{CO}_2][\text{H}_2]/[\text{CO}][\text{H}_2\text{O}] = (1.000 + x)(1.000 + x)/(1.000 - x)(1.000 - x) \\ = (1.000 + x)^2/(1.000 - x)^2 = 5.10$$

$$(5.1)^{1/2} = 2.26 = (1.000 + x)/(1.000 - x)$$

$$x = 0.387 \text{ M}$$

$$[\text{CO}] = [\text{H}_2\text{O}] = 1.000 - 0.387 = 0.613 \text{ M}$$

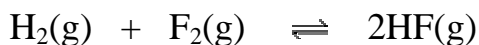
$$[\text{CO}_2] = [\text{H}_2] = 1.000 + 0.387 = 1.387 \text{ M}$$

Check:  $K = [\text{CO}_2][\text{H}_2]/[\text{CO}][\text{H}_2\text{O}] = (1.387)^2/(0.613)^2 = 5.12$

**Example: No equilibrium concentrations - case II - the "monster":**

Suppose 6.000 mol of  $\text{F}_2$  and 3.000 mol of  $\text{H}_2$  are mixed in a 3.000 L container to make HF and that the equilibrium constant at the appropriate temperature is  $1.15 \times 10^2$ , calculate the equilibrium concentrations.

The reaction is:



$$K = [\text{HF}]^2/[\text{H}_2][\text{F}_2] = 1.15 \times 10^2$$

Starting concentrations are:

$$[\text{HF}] = 0$$

$$[\text{H}_2] = 3.000/3.000 = 1.000 \text{ M}$$

$$[\text{F}_2] = 6.000/3.000 = 2.000 \text{ M}$$

We really need not calculate Q since clearly the reaction must go right. Assume A M of  $\text{H}_2$  and  $\text{F}_2$  are consumed and 2A M of HF is produced. Then the equilibrium concentrations are:

$$[\text{HF}] = 2A \text{ M}$$

$$[\text{H}_2] = 1.000 - A \text{ M}$$

$$[\text{F}_2] = 2.000 - A \text{ M}$$

$$1.15 \times 10^2 = (2A)^2/(1.000 - A)(2.000 - A)$$

$$(1.000 - A)(2.000 - A)(1.15 \times 10^2) = 4A^2$$

$$(1.15 \times 10^2)A^2 - 3.000(1.15 \times 10^2)A + 2.000(1.15 \times 10^2) = 4A^2$$

$$(1.11 \times 10^2)A^2 - (3.45 \times 10^2)A + 2.30 \times 10^2 = 0$$

This has the quadratic form  $ax^2 + bx + c = 0$  with solutions:

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

$$A = 2.14 \text{ or } 0.968 \text{ mol/L}$$

The first answer is impossible since a negative concentration for  $H_2$  makes no sense.

The equilibrium concentrations are therefore:

$$[HF] = 2A = 1.936 \text{ M}$$

$$[H_2] = 1.000 - A = 1.000 - 0.968 = 3.2 \times 10^{-2} \text{ M}$$

$$[F_2] = 2.000 - A = 2.000 - 0.968 = 1.032 \text{ M}$$

Check:

$$[HF]^2/[H_2][F_2] = (1.936)^2/(3.2 \times 10^{-2})(1.032) = 1.13 \times 10^2$$

### Treating Systems that have Small Equilibrium Constants

We have already seen the simplification that occurs with cases that work out to a perfect square. Another simplification occurs if the value of the equilibrium constant is particularly small (or large):

#### **Example:**

Consider the decomposition (at 35 °C):



$$K = [\text{NO}]^2[\text{Cl}_2]/[\text{NOCl}]^2 = 1.6 \times 10^{-5} \text{ mol/L}$$

One mole of NOCl is placed in a 2 L flask. What are the equilibrium concentrations?

At equilibrium, let the concentrations be:

$$[\text{NOCl}] = 0.5 - 2A$$

$$[\text{NO}] = 2A$$

$$[\text{Cl}_2] = A$$

Then:

$$1.6 \times 10^{-5} = (2A)^2(A)/(0.5 - 2A)^2$$

This would simplify(!) to:

$$4A^3 - 1.6 \times 10^{-5}A^2 + 3.2 \times 10^{-5}A - 0.4 \times 10^{-5} = 0$$

which can be solved but not very easily. It is not necessary to struggle with such an equation if it is recognized that  $2A$  will be very small compared to  $0.5$ , therefore:

$$0.5 - 2A \sim 0.5$$

and:

$$1.6 \times 10^{-5} = (2A)^2(A)/(0.5)^2$$

so:

$$0.4 \times 10^{-5} = 4A^3 \quad \text{or} \quad A^3 = 1.0 \times 10^{-6} \quad \text{or} \quad A = 1.0 \times 10^{-2} \text{ mol/L}$$

In this case:

$$(0.5 - 2A) = 0.48$$

in other words we make an error of about 4% as a result of the approximation.

## 7. Solving Equilibrium Problems

General Procedure:

1. Write the balanced equation for the reaction.
2. Write the equilibrium expression.
3. List initial Concentrations.
4. Calculate  $Q$  and determine the necessary shift.
5. Write down the equilibrium concentrations in terms of one unknown ( $x$ ).
6. Substitute into the equilibrium expression and solve for  $x$ .
7. **Check you answer!**

### Le Châtelier's Principle

The principle states that:

*If a change is imposed on a system at equilibrium, the position of the equilibrium will shift in such a way as to minimize the change.*

## The Effect of a Change in Pressure (by changing the volume)

**TABLE 13.2 The Percent by Mass of NH<sub>3</sub> at Equilibrium in a Mixture of N<sub>2</sub>, H<sub>2</sub>, and NH<sub>3</sub> as a Function of Temperature and Total Pressure\***

Temperature (°C)	Total Pressure		
	300 atm	400 atm	500 atm
400	48% NH <sub>3</sub>	55% NH <sub>3</sub>	61% NH <sub>3</sub>
500	26% NH <sub>3</sub>	32% NH <sub>3</sub>	38% NH <sub>3</sub>
600	13% NH <sub>3</sub>	17% NH <sub>3</sub>	21% NH <sub>3</sub>

\*Each experiment was begun with a 3:1 mixture of H<sub>2</sub> and N<sub>2</sub>.

Note that 3 volumes or moles of H<sub>2</sub> and 1 volume or mole of N<sub>2</sub> react together to make 2 volumes or moles of NH<sub>3</sub>, thus the reaction is accompanied by a decrease in pressure. Imposing an increase in pressure will drive the equilibrium towards the ammonia side of the reaction in order to reduce the pressure.

The effect is strikingly illustrated by the reaction:



The mixture is contained in a syringe. The colour actually lightens from brown to pale beige as the volume is reduced (pressure increases). See the photos in the text.

Remember that pressure, volume and concentration are connected through the ideal gas law:

$$PV = nRT$$

## The Effect of a Change in Pressure (by adding an inert gas)

The equilibrium constant is a function of *concentrations* or partial pressures so adding an inert gas will have no effect on the equilibrium position.

## The Effect of a Change in Concentration

Consider again the Haber process, at equilibrium:

$$[\text{N}_2] = 0.399 \text{ M}$$

$$[\text{H}_2] = 1.197 \text{ M}$$

$$[\text{NH}_3] = 0.202 \text{ M}$$

$$K = \frac{[\text{NH}_3]_o^2}{[\text{N}_2]_o[\text{H}_2]_o^3} = \frac{(0.202)^2}{(0.399)(1.197)^3} = 5.96 \times 10^{-2}$$

and now dump in another 1.000 mol/L of N<sub>2</sub>

$$[\text{N}_2] = 1.399 \text{ M}$$

$$[\text{H}_2] = 1.197 \text{ M}$$

$$[\text{NH}_3] = 0.202 \text{ M}$$

$$Q = \frac{[\text{NH}_3]_o^2}{[\text{N}_2]_o[\text{H}_2]_o^3} = \frac{(0.202)^2}{(1.399)(1.197)^3} = 1.70 \times 10^{-2}$$

Q is less than K so the equilibrium must shift to the right. The new position is:

$$[\text{N}_2] = 1.348 \text{ M}$$

$$[\text{H}_2] = 1.044 \text{ M}$$

$$[\text{NH}_3] = 0.304 \text{ M}$$

Notice that, in accord with Le Ch,telier's Principle, the concentration of  $\text{N}_2$  has decreased relative to the amount after the addition. The changes can be explained by considering the effect on the number of collisions between reactant molecules and product molecules.

### **The Effect of a Change in Temperature**

Remember the forward and reverse reaction rates both increase with temperature, but the reaction originating at the downhill side with respect to the energy (~enthalpy) will speed up more relative to the other. The equilibrium shifts in opposition to the heat producing direction. The simplest way to remember this is to pretend that the heat is part of the balanced equation written it so that the enthalpy is a positive quantity:



Imagine adding heat as a "reagent". Then the effect is the same as adding any other reagent - the system will establish a new equilibrium so as to remove some of the heat