

Unit IV  
Definitions of Acids and Bases and Chemical Equilibrium

**Definitions of Acids and Bases**

1. Arrhenius definition:

An acid is a substance that releases  $H^+$  ions in an aqueous solution.

A base is a substance that release  $OH^-$  in aqueous solution.

An acid-base reaction (neutralization reaction) is the reaction in aqueous solution of an acid and a base to form a salt and water.

a.

b.

The Arrhenius definition is limited to acid-base reactions in water solutions and to bases that produce  $OH^-$  ions.

2. Bronsted-Lowry definition

An acid is a substance that can donate a proton ( $H^+$  ion) to another substance.

A base is a substance that can accept a proton ( $H^+$  ion) from another substance.

That is, acids are proton donors and bases are proton acceptors.

An acid-base reaction involves the transfer of a proton ( $H^+$  ion) from one substance to another. That is, an acid-base reaction is a proton transfer reaction.

a.

b.

c.

d.

The stronger the acid the weaker its conjugate base. The stronger the base, the weaker its conjugate acid.

An amphoteric substance is a substance that can react as either an acid or a base depending on the other reactant.

a.

b.

A conjugate acid-base pair are related to each other by the loss or gain of a single proton.

### 3. Lewis Definition:

An *acid* is an ion or a molecule that can accept and share a pair of electrons with another ion or a molecule.

Potential Lewis acids:

A *base* is a molecule or ion that can donate and share a pair of electrons with another ion or molecule.

Potential Lewis bases:

An *acid-base* reaction involves the formation of a coordinate covalent bond.

a.

b.

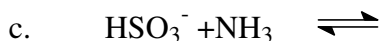
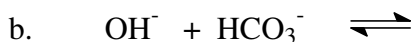
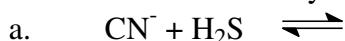
c.

### Exercise:

1. Classify each of the following as either an Arrhenius acid or Arrhenius base.

a. LiOH      b. H<sub>2</sub>S      c. HI      d. Ca(OH)<sub>2</sub>      e. HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>

2. Complete each of the following acid-base reactions and label both reactants and products that are Bronsted-Lowry acids or Bronsted-Lowry bases.



3. Which of the following species can act as both a Bronsted-Lowry acid and Bronsted-Lowry base?

a. HI      b. H<sub>2</sub>PO<sub>4</sub><sup>-</sup>      c. HNO<sub>2</sub>      d. H<sub>3</sub>O<sup>+</sup>

e. SO<sub>3</sub><sup>2-</sup>      f. HCO<sub>3</sub><sup>-</sup>

4. What Bronsted-Lowry acid can be formed from each of the following?

a. H<sub>2</sub>O      b. H<sub>2</sub>PO<sub>4</sub><sup>-</sup>      c. HS<sup>-</sup>      d. CN<sup>-</sup>      e. NH<sub>3</sub>

5. What Bronsted-Lowry base can be formed from each of the following?

a. H<sub>2</sub>CO<sub>3</sub>      b. NH<sub>3</sub>      c. H<sub>2</sub>O      d. HF      e. HS<sup>-</sup>

6. Classify each of the following as either a Lewis acid or Lewis base.

(Hint: Write Lewis electron-dot structure)

a. H<sub>2</sub>O      b. NH<sub>3</sub>      c. O<sup>2-</sup>      d. H<sub>2</sub>S      e. S<sup>2-</sup>      f. Cu<sup>2+</sup>

g. BH<sub>3</sub>



Notice that a change of 1 unit on the pH scale means a tenfold change in acidity.

$[H^+]$	pH
$1 \times 10^{-1} M = 1/10$	1.0
$1 \times 10^{-2} M = 1/100$	2.0
$1 \times 10^{-3} M = 1/1000$	3.0

The pOH concept:

$$pOH = -\log [OH^-]$$

Summary:

- 1)  $[H^+] \cdot [OH^-] = (1.0 \times 10^{-7}) (1.0 \times 10^{-7}) = 1.0 \times 10^{-14} = K_w$   
where  $K_w$  is ion-product constant for water
- 2)  $pH + pOH = 7.0 + 7.0 = 14 = pK_w$

Exercise:

- 1) What is the pH of a 0.02 M solution of HCl?
- 2) What is the pH of a 0.030 M solution of NaOH?
- 3) What is the pH of a 0.05 M solution KOH?
- 4) What is the  $[H^+]$  for a solution with pH of 12.7?

## CHEMICAL EQUILIBRIUM DYNAMIC EQUILIBRIUM

### Examples of dynamic equilibrium:

1. Liquid in a closed container:

At equilibrium the rate of evaporation = the rate of condensation

Vapor is in equilibrium with liquid.

2. A saturated solution:

At equilibrium, the rate of dissolving = the rate of crystallization.

Solid is in equilibrium with solution.

### Chemical Equilibrium:

It is achieved when reactions do not proceed to completion.



The reaction system contains a mixture of reactant and product substances.

1. It is possible to arrive at the same equilibrium condition from two different starting points.

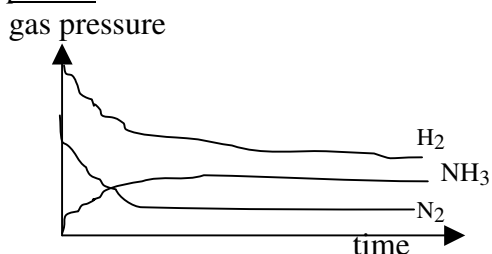


Figure-a. The equilibrium is approached beginning with H<sub>2</sub>(g) and N<sub>2</sub>(g)

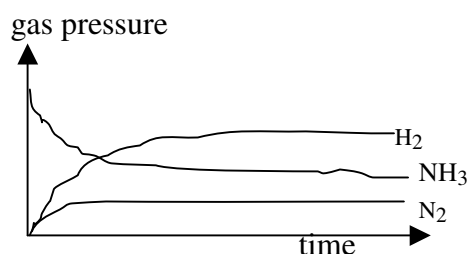
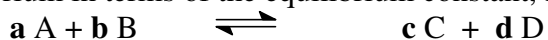


Figure- b. The equilibrium is approached beginning with NH<sub>3</sub> (g).

2. The law of mass action expresses the relative concentrations of reactants and products at equilibrium in terms of the equilibrium constant, K.



A, B, C, and D are chemical species measured at equilibrium. **a**, **b**, **c**, and **d** are the coefficients in the balanced equation.

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

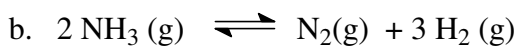
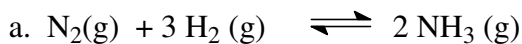
The value of the equilibrium constant, K<sub>c</sub>, does not depend on the initial concentrations of reactants and products. That is, the value of K<sub>c</sub> is constant even though the initial concentrations vary.

For solutions, the concentration is expressed in units of molarity. For gas phase reactions, we use either molarity or atmospheres of pressure.

Recall,  $P_{H_2} = X_{H_2} P_{total}$

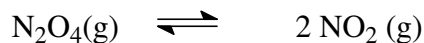
**Exercise**

Applying the law of mass action to the  $NH_3$  equations below, write the expressions for the equilibrium constants.



It is a general rule that the equilibrium constant expression for the reaction written in one direction is the reciprocal of the expression for the reverse reaction. The numerical value of K is the reciprocal, also.

3. The magnitude of K:



a. If K is very large:

b. If K is very small:

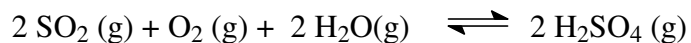
4. Predicting the spontaneity of a reaction by measuring Q and comparing it to the tabulated value of K:

a. If Q is smaller than K:

b. If Q is larger than K:

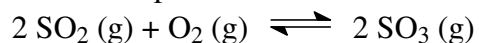
c. If Q is equal to K:

5. When two equations for two reactions are added together, the equilibrium constant for the total reaction is the product of the equilibrium constant of the individual reactions. That is, the overall equilibrium constant is equal to the product of the equilibrium constants of the steps in the mechanism.

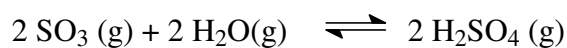


$$K_{\text{overall}} =$$

A possible two-step mechanism is:



$$K_{\text{(i)}} =$$



$$K_{\text{(ii)}} =$$

$$K_{\text{overall}} = K_{\text{(i)}} \cdot K_{\text{(ii)}} \cdot K_{\text{(iii)}} \dots\dots\dots$$

6. The numerical value of K depends on the units of concentration.  $K_p$  is not necessary equal to  $K_c$ .

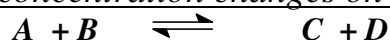
## Le Chatelier Principle

If a system at equilibrium is subjected to a change in conditions that disturbs its equilibrium, the system proceeds toward a new equilibrium state in such a direction as to partially offset the change in conditions.

Le Chatelier's principle allows us to make qualitative predictions about the response of a system at equilibrium to a perturbing change.

- Effect of concentration changes on equilibrium
- Effect of changing the pressure.
- Effect of changing the temperature
- Effect of adding a catalyst

a) Effect of concentration changes on equilibrium



i) What will happen to the position of equilibrium if we add more of reactant **A** to the equilibrium mixture?

ii) What will happen to the position of equilibrium if either **C** or **D** is added?

iii) What will happen to the position of equilibrium if either **A** or **B** is removed?

iv) How will the change in concentration effect the numerical value of the equilibrium constant, **K**?

b) Effect of changing pressure

The change in pressure will change the position of equilibrium, but will not change the value of **K**. The position of equilibrium will change if:

- the reaction involves one or more gases.
- the number of moles gaseous products and reactants are different.

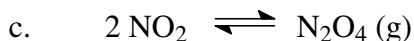
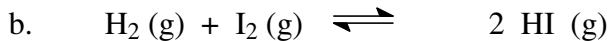
Exercise:



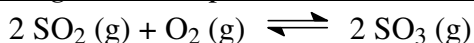
If the total pressure is increased, this will result in a reduction of the volume of the system. The position of equilibrium will shift to the \_\_\_\_\_.

**Exercise:**

Predict the effect of lowering the pressure on the equilibrium equations given below:



The change in total pressure will not change the value of K.



$K_c =$

The above shows the relationship between the number of moles of different gases and the volume change due to the variation of the total pressure.  $K_c$  remains the same if the total pressure changes.

c. Effect of changing the temperature

An increase in temperature may cause either an increase or a decrease in the value of K, depending on whether the forward or the reverse process is the one which absorbs heat.

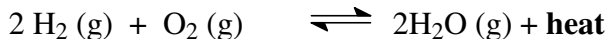
Endothermic reaction:



i) Increase in temperature will shift the position of equilibrium to the \_\_\_\_\_. K will \_\_\_\_\_.

ii) Decrease in temperature will shift the position of equilibrium to the \_\_\_\_\_. K will \_\_\_\_\_.

Exothermic reaction:

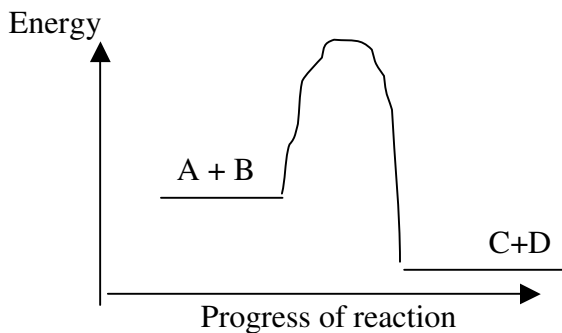
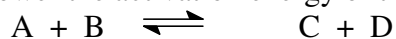


What is the effect of decreasing the temperature?

The position of equilibrium will shift to the \_\_\_\_\_ and K will \_\_\_\_\_

d. Effect of adding a catalyst to a system at equilibrium

The presence of a catalyst does not affect the position of equilibrium. The role of the catalyst is to lower the activation energy of the reaction.



The rate of both the forward and reverse reactions are increased exactly by the same amount, so that the equilibrium position remains unchanged.

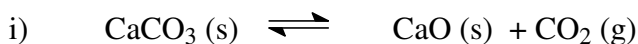
K will \_\_\_\_\_ upon the addition of the catalyst.

Homogeneous and heterogeneous equilibrium

Homogeneous equilibrium All species under equilibrium are in the same phase.

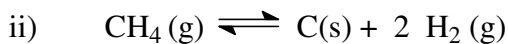


Heterogeneous equilibrium All substances at equilibrium are of different phases.



$K_c =$

$K_p =$



$K_c =$

$K_p =$

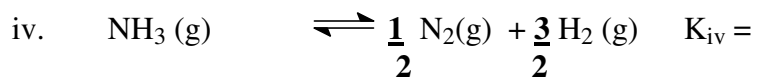
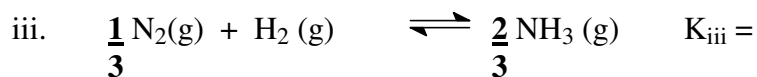
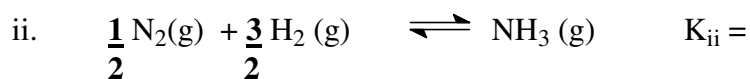
**Exercises:**

1. Predicting spontaneity of a reaction

If  $1.0 \times 10^{-2}$  mole each of  $\text{H}_2(\text{g})$  and  $\text{I}_2(\text{g})$  gases are placed in a 1.0 liter flask at  $448^\circ\text{C}$  with  $2.0 \times 10^{-3}$  mole of  $\text{HI}(\text{g})$ , will more  $\text{HI}(\text{g})$  be produced?  $K_c = 50.53$

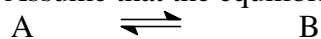


2. The reaction for the formation or the decomposition of ammonia can be written in a number of ways:



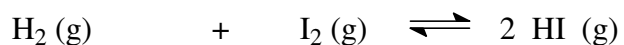
What are the equilibrium constant expressions for each formulation and how are the equilibrium constants related?

3. Suppose that **A** is present at a concentration of 0.850 mole/liter; calculate the concentration of **A** and **B** at 200 °C. Assume that the equilibrium constant for the reaction



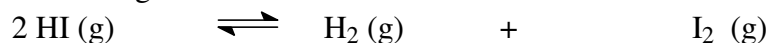
At this temperature is 24.0.

4. A mixture of 0.500 mole of  $H_2(g)$  and 0.500 mole of  $I_2(g)$  was placed in a one-liter flask at 430 °C. Calculate the concentration of  $H_2(g)$ ,  $I_2(g)$ , and  $HI(g)$  at equilibrium. The equilibrium constant for the reaction:



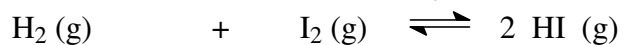
is 54.3 at the same temperature.

5. Starting with 4.20 moles of  $HI(g)$  in 9.60 liters reaction vessel, calculate the concentrations of  $H_2(g)$ ,  $I_2(g)$ , and  $HI(g)$  at equilibrium at 430 °C. The equilibrium constant for the following reaction is 0.0184:



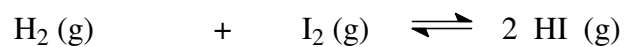
6. For the reaction:  $\text{C(s)} + \text{CO}_2(\text{g}) \rightleftharpoons 2 \text{CO}(\text{g})$   
 $K_p = 167.5$  at  $1000\text{ }^\circ\text{C}$ . What is the partial pressure of  $\text{CO}(\text{g})$  in an equilibrium system in which the partial pressure of  $\text{CO}_2(\text{g})$  is  $0.100\text{ atm}$ ?

7. A mixture of  $0.112$  mole  $\text{H}_2(\text{g})$  and  $0.0092$  mole  $\text{I}_2(\text{g})$  is sealed in a  $1$ -liter vessel and kept at  $394\text{ }^\circ\text{C}$  until equilibrium was reached. At equilibrium, the mixture was found to contain  $0.0159$  mole of  $\text{HI}$ . Calculate  $K_c$  for the reaction:



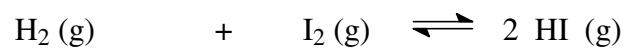
Setup:

8. The concentration equilibrium constant,  $K_c$ , for the reaction given below is 29.1 at 1000 K.

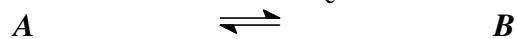


What is the concentration of  $\text{I}_2(\text{g})$  under equilibrium conditions, if the system originally contained  $[\text{HI}]$  equal to 10.0 M.

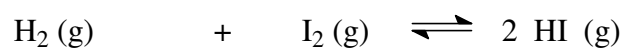
Setup:



9. What are the concentrations of **A** and **B** at equilibrium? The initial concentration of **A**=0.200 M and that of **B**= 0.100 M.  $K_c= 0.143$



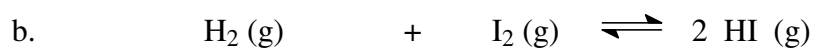
10. At the start of the reaction there are 0.0218 mole of  $\text{H}_2(\text{g})$ , 0.0145 mole of  $\text{I}_2(\text{g})$  and 0.0783 mole of  $\text{HI}$  in a 3.50 L vessel at  $430^\circ\text{C}$ ;  $K_c = 54.3$



- Predict which way the reaction will proceed.
- Calculate the concentration of the gases at equilibrium.

Setup:

a.



11. At 500 K, 1.00 mole NOCl (g) is introduced into a 1- liter container. At equilibrium, the NOCl (g) is 9.0 % dissociated. Calculate the value of K for the equilibrium at 500K.



Setup: