

CHAPTER SEVEN

EQUILIBRIUM CONCEPTS

AND

ACID-BASE

EQUILIBRIUM

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Objectives of the Chapter:

- ◆ Explain the dynamic nature of a chemical equilibrium
- ◆ Predict the response of a stressed equilibrium using Le Châtelier's principle
- ◆ Identify acids, bases based on the three acid-base concepts
- ◆ Calculate the pH and pOH of a given solution
- ◆ Describe the composition and function of acid-base buffer
- ◆ Calculate the pH of the buffer before and after the addition of added acid or base

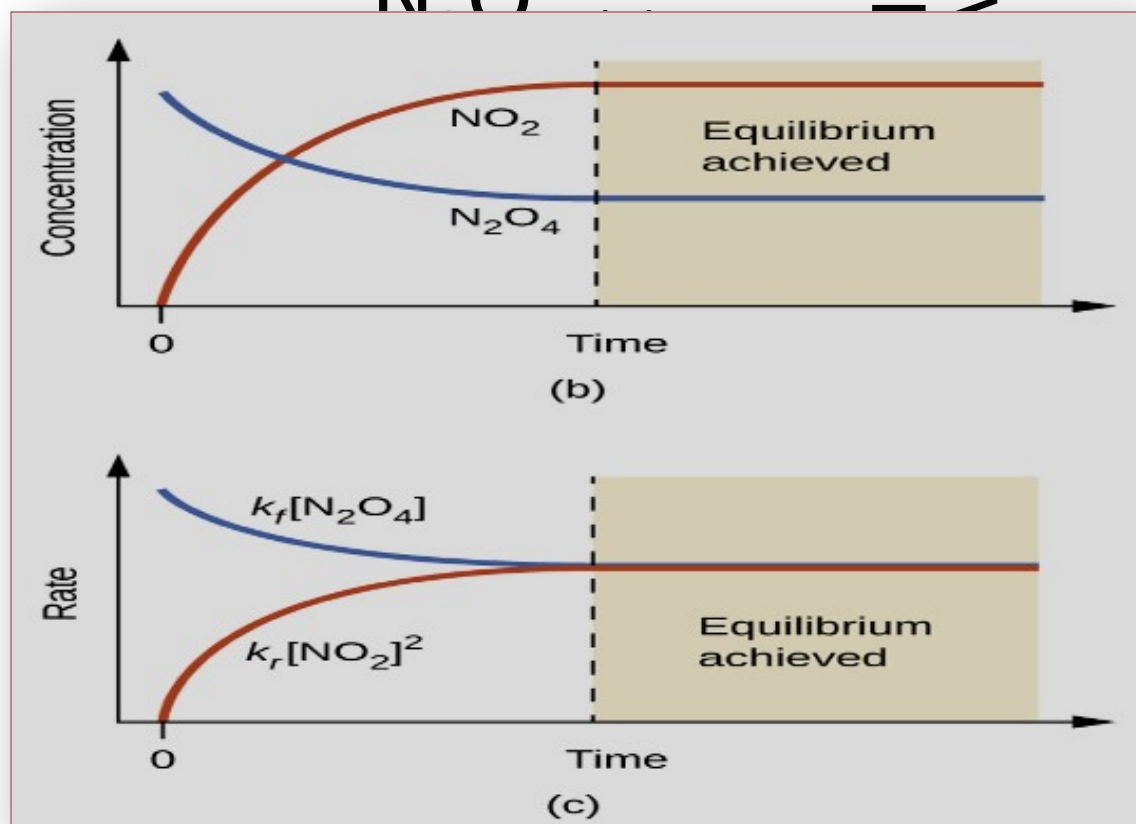
7.1. Introduction

- ✚ The convention for writing chemical equations involves placing reactant formulas on the left side of a reaction arrow and product formulas on the right side.
- ✚ By this convention, and the definitions of “**reactant**” and “**product**,” a chemical equation represents the reaction in question as proceeding from **left to right**.
- ✚ **Reversible reactions**, however, may proceed in both forward (left to right) and reverse (right to left) directions.

✚ When the rates of the forward and reverse reactions are **equal**, the concentrations of the reactant and product species remain constant over time and the system is at **equilibrium**.

✚ The relative concentrations of reactants and products in **equilibrium** systems vary greatly; some systems contain mostly products at equilibrium, some contain mostly reactants, and some contain appreciable amounts of both.

Figure 7.1: Illustrates fundamental equilibrium concepts using the **reversible** decomposition of colorless dinitrogen tetroxide to yield brown nitrogen dioxide, an elementary reaction described by the equation:



(b) Changes in concentration over time as the decomposition reaction achieves equilibrium.

(c) At

✚ It's important to emphasize that chemical equilibria are dynamic; a reaction at equilibrium has not “**stopped**,” but is proceeding in the **forward** and **reverse** directions at the same rate.

✚ Physical changes, such as **phase transitions**, are also reversible and may establish equilibria. As one example, consider the vaporization of bromine:



7.2. Chemical Equilibrium

- The status of a reversible reaction is conveniently assessed by evaluating its **reaction quotient (Q)**. For a reversible reaction described by:



- The reaction quotient is derived directly from the stoichiometry of the balanced equation as:

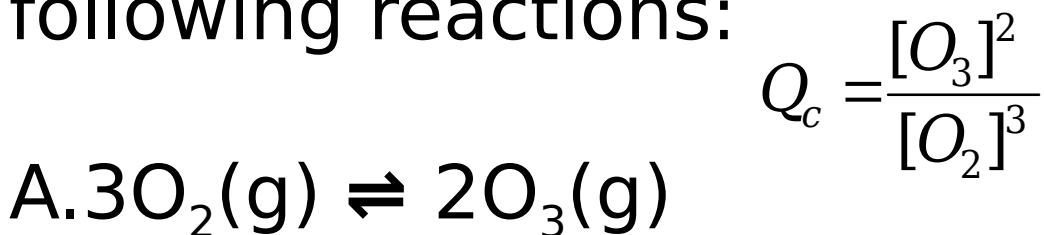
$$Q_c = \frac{[\text{C}]^x [\text{D}]^y}{[\text{A}]^m [\text{B}]^n}$$

- **Where:** The subscript **C** denotes the use of molar concentrations in the expression.

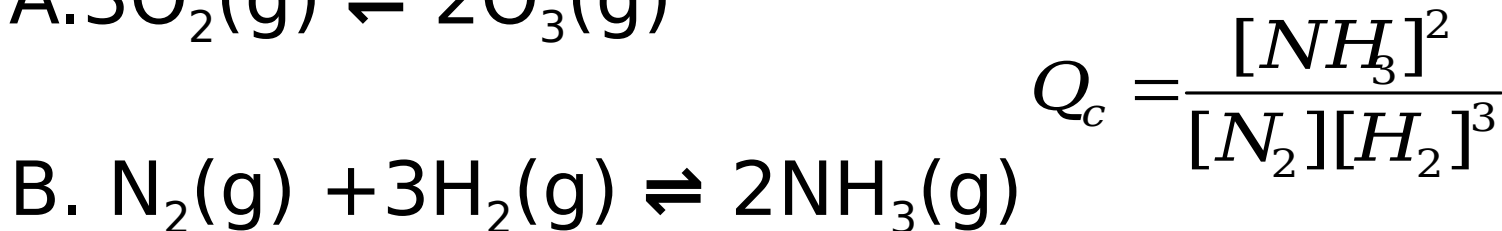
✚ If the reactants and products are gaseous, a reaction quotient may be similarly derived using

$$Q_p = \frac{P_C^x P_D^y}{P_A^m P_B^n}$$

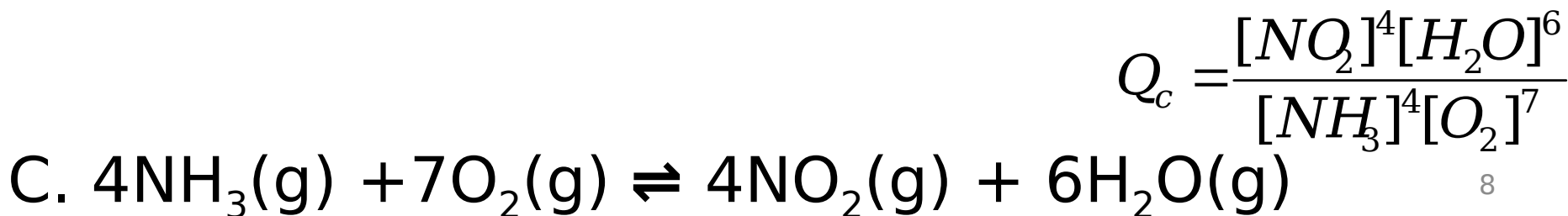
Example 7.1: Write the concentration-based reaction quotient expression for each of the following reactions:



$$Q_c = \frac{[\text{O}_3]^2}{[\text{O}_2]^3}$$



$$Q_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$



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

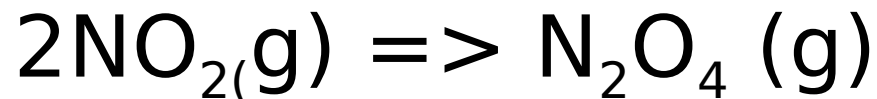
✚ The **numerical** value of **Q** varies as a reaction proceeds towards equilibrium; therefore, it can serve as a useful indicator of the reaction's status.

✚ The constant value of **Q** exhibited by a system at equilibrium is called the **equilibrium constant, K**:

$$K_c = Q_c = \frac{[C]^x [D]^y}{[A]^m [B]^n} \text{ at equilibrium}$$

Example 7.2: Evaluating a Reaction Quotient

- Gaseous nitrogen dioxide forms dinitrogen tetroxide according to this equation:



- When 0.10 mol NO_2 is added to a 1.0-L flask at 25°C, the concentration changes so that at equilibrium, $[\text{NO}_2] = 0.016 \text{ M}$ and $[\text{N}_2\text{O}_4] = 0.042 \text{ M}$.

- a. What is the value of the reaction quotient before any reaction occurs?

Solution

a. Before any reaction started or before any product is formed the concentrations of:

$$[NO_2] = \frac{0.1 \text{ mol}}{1.0 \text{ L}} = 0.1 \text{ M}$$

$$[N_2O_4] = 0$$

Thus, $K_c = Q_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0}{(0.1 \text{ M})^2} = 0$

b. At equilibrium: The Equilibrium Constant is 1.6×10^2

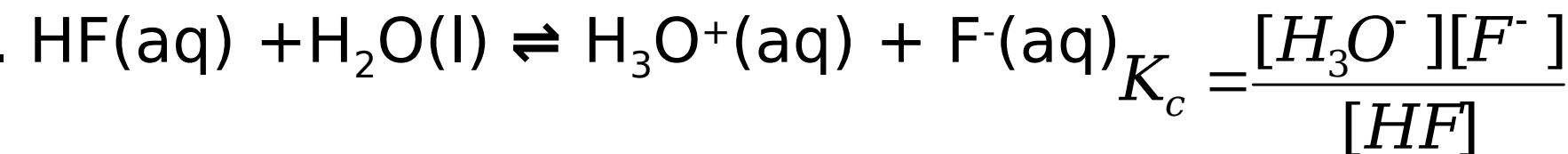
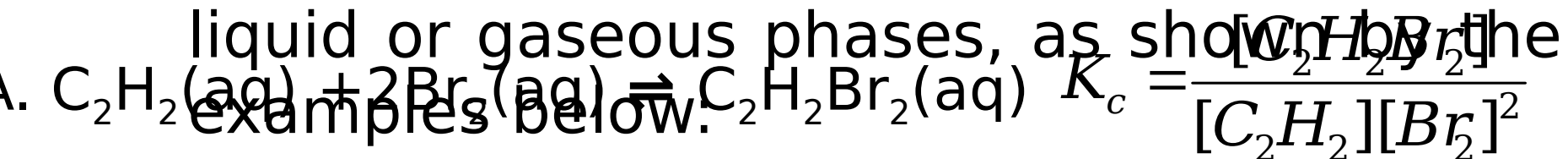
$$K_c = Q_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{(0.042 \text{ M})}{(0.016 \text{ M})^2} = 1.6 \times 10^2$$

7.2.1. Homogeneous Equilibria

✖ A homogeneous equilibrium is one in which all reactants and products are present in the **same phase**.

✖ By this definition, homogeneous equilibria take place in **solutions**.

✖ These solutions are most commonly either liquid or gaseous phases, as shown by the



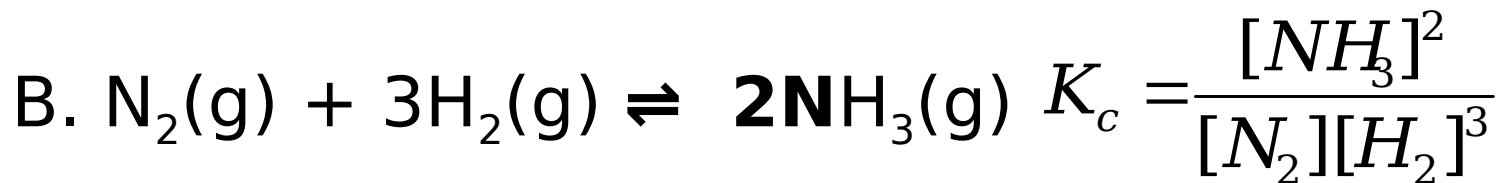
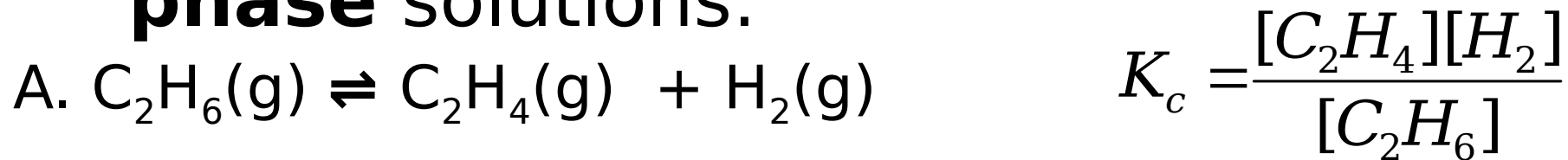
✚ These examples all involve aqueous solutions, those in which water functions as the solvent.

✚ In the examples, water also functions as a reactant, but its concentration is *not* included in the reaction quotient.

✚ **The reason for this omission is related to the more rigorous form of the Q (or K) expression in which *relative concentrations for liquids and solids are equal to 1 and needn't be included.***

✚ Consequently, reaction quotients include concentration or pressure terms only for

 The equilibria below all involve **gas-phase** solutions:

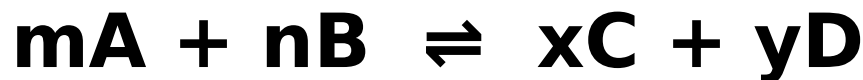


► For gas-phase solutions, the equilibrium constant may be expressed in terms of either the molar concentrations (**K_c**) or partial pressures (**K_p**) of the reactants and products.

► A relation between these **two K** values may be simply derived from the ideal gas equation and the definition of molarity:

$$PV = nRT \quad P = \left(\frac{n}{V} \right) RT = MRT$$

🌱 For the gas-phase reaction:



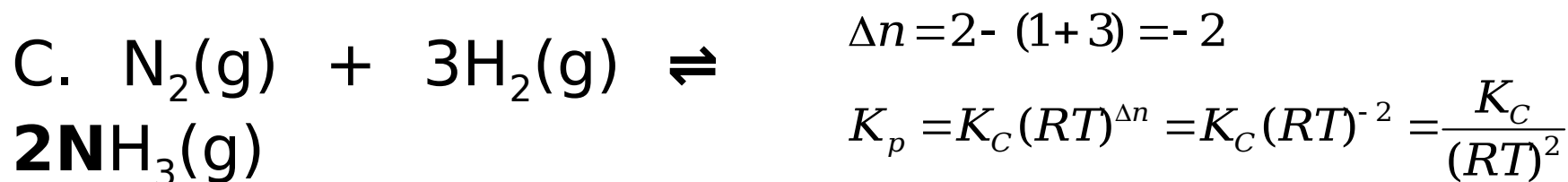
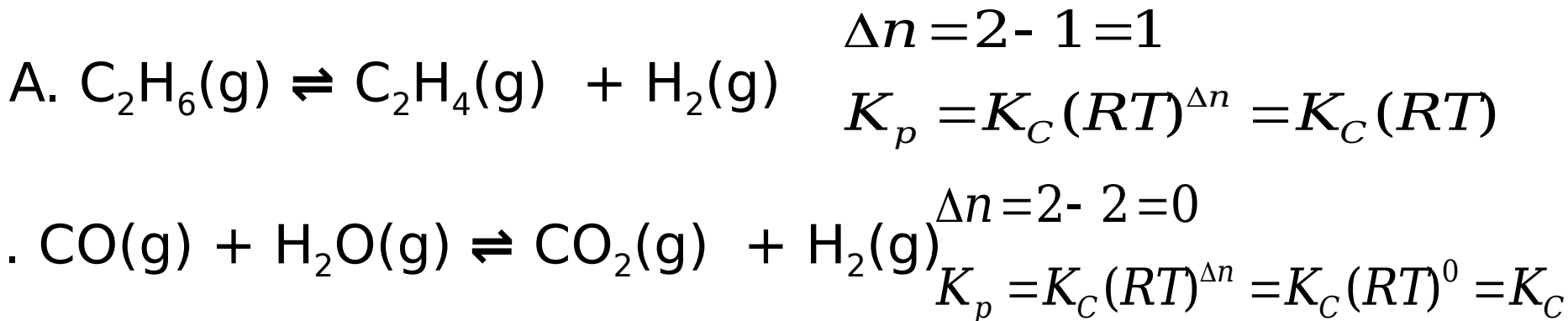
$$K_p = \frac{(P_C)^x (P_D)^y}{(P_A)^m (P_B)^n}$$

$$K_p = \frac{([C] \times RT)^x ([D] \times RT)^y}{([A] \times RT)^m ([B] \times RT)^n}$$

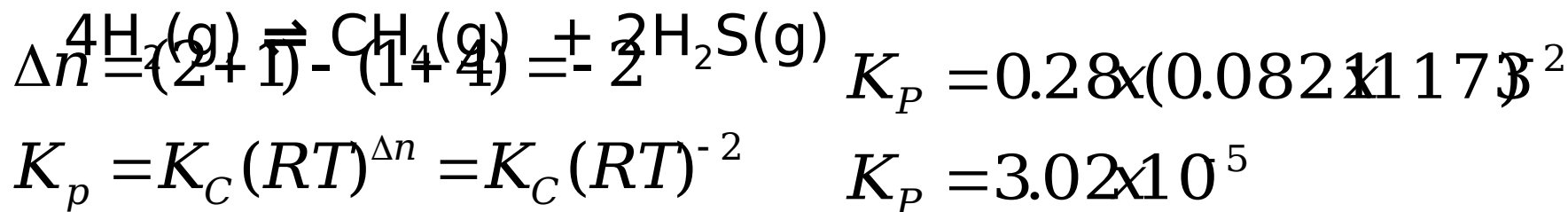
$$K_p = \frac{[C]^x [D]^y}{[A]^m [B]^n} \times \frac{(RT)^{x+y}}{(RT)^{m+n}} = K_C (RT)^{(x+y) - (m+n)}$$

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

Example 7.3: Write the equations relating **K_c** to **K_p** for each of the following reactions:

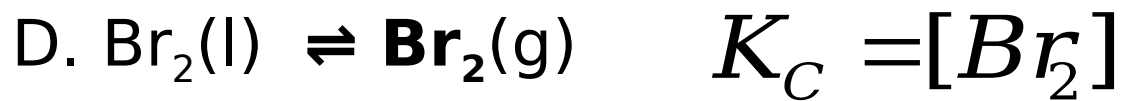
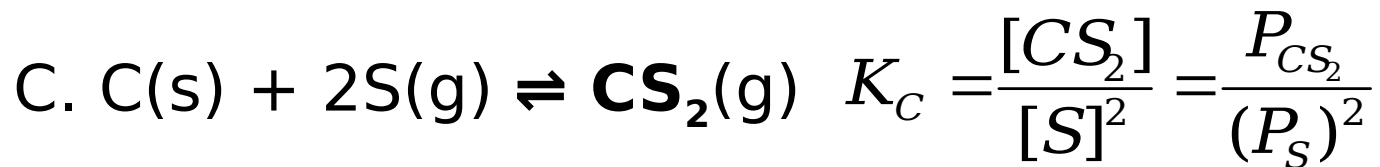
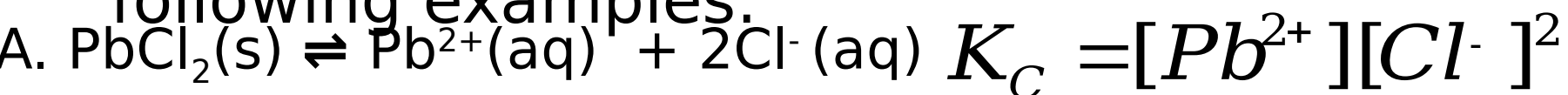


D. **K_c** is equal to 0.28 for the following reaction at 900 °C: What is **K_p** at this temperature?



7.2.2. Heterogeneous Equilibria

A heterogeneous equilibrium involves reactants and products in **two or more different phases**, as illustrated by the following examples:



7.3. Le Chatelier's Principle

- ✖ A system at equilibrium is in a state of dynamic balance, with forward and reverse reactions taking place at equal rates.
- ✖ If an equilibrium system is subjected to a change in conditions that affects these reaction rates differently (a stress), then the rates are no longer equal and the system is not at equilibrium.
- ✖ The system will subsequently experience a net reaction in the direction of greater rate (a shift) that will re-establish the equilibrium.

✖ This phenomenon is summarized by **LeChâtelier's** principle: if an equilibrium system is stressed, the system will experience a shift in response to the stress that re-establishes equilibrium.

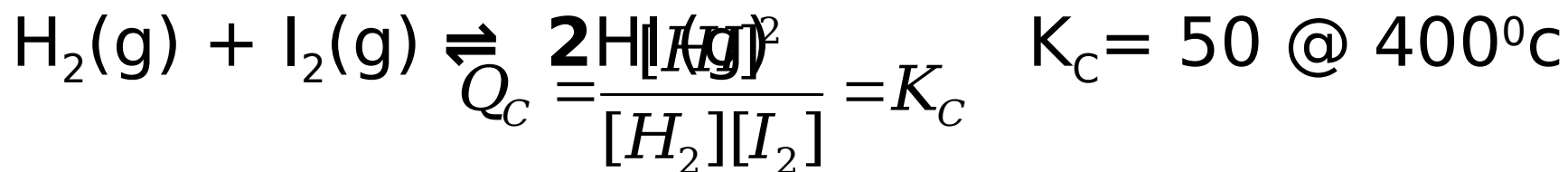
✖ Reaction rates are affected primarily by **concentrations**, as described by the reaction's rate law, and **temperature**, as described by the Arrhenius equation.

✖ Consequently, changes in concentration and temperature are the two stresses that can shift an equilibrium.

7.3.1. Effect of a Change in Concentration

✚ If an equilibrium system is subjected to a change in the concentration of a reactant or product species, the rate of either the forward or the reverse reaction will change.

✚ As an example, consider the equilibrium reaction:



- When this system is at equilibrium, the forward and reverse reaction rates are equal.

$$\text{Rate}_f = \text{Rate}_r$$

- If the system is stressed by adding reactant, either H₂ or I₂, the resulting increase in concentration causes the rate of the forward reaction to increase, exceeding that of the reverse reaction:

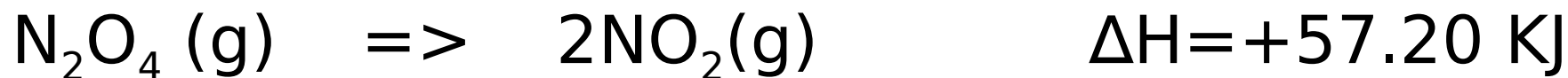
$$\text{Rate}_f > \text{Rate}_r$$

- This same shift will result if some product HI is removed from the system, which decreases the rate of the reverse reaction, again resulting in the same imbalance in rates.

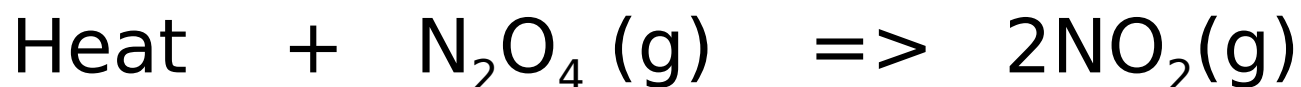
7.3.2. Effect of a Change in Temperature

- ✚ When an equilibrium shifts in response to a temperature change, it is re-established with a different relative composition that exhibits a different value for the equilibrium constant.
- ✚ Predicting the shift an equilibrium will experience in response to a change in temperature is most conveniently accomplished by considering the enthalpy change of the reaction.

- For example, the decomposition of dinitrogen tetroxide is an endothermic (heat consuming) process:



- For purposes of applying Le Chatelier's principle, heat (q) may be viewed as a reactant:



- Raising the temperature of the system is causing to increasing the amount of a product, and so the equilibrium will shift to the right.

- Lowering the system's temperature will

7.3.3.Effect of Change in Pressure

- ◆ According to Le Chatelier's principle, if the pressure at equilibrium is increased then the reaction will proceed in that direction where the pressure is reduced.
- ◆ Since the pressure depends upon the number of moles, on increasing the pressure the reaction will proceed in that direction where the number of moles are reduced.
- ◆ If the pressure at equilibrium is decreased then the reaction will proceed in that

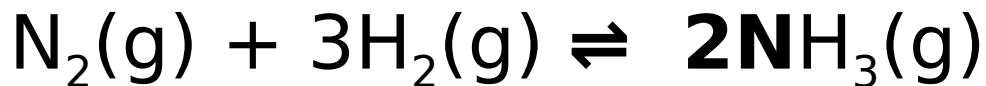
■ For a general reaction, $m\text{A} + n\text{B} \rightleftharpoons x\text{C} + y\text{D}$

■ The effect of pressure is decided by Δn . $\Delta n = (x+y)-(m+n)$

■ If $\Delta n > 0$, that means the total moles of products is greater than the total moles of reactants. Lowering of pressure will favour the reaction in forward direction. That is, more products will be formed at equilibrium if the pressure is lowered.

■ If $\Delta n < 0$, that means the total moles of products is less than the total moles of reactants. Increasing the pressure will favour the reaction in forward direction.

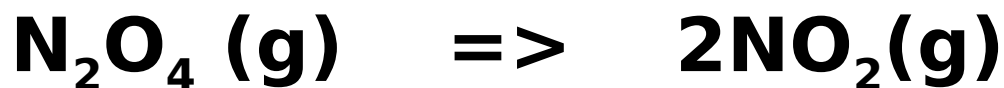
For Example: In the formation of Ammonia



$$\Delta n = \mathbf{2-(1+3) = -2}$$

✚ Therefore, an increase in pressure at equilibrium will favour the forward reaction.

For the dissociation of dinitrogen tetroxide,



$$\Delta n = \mathbf{2-(1) = 1}$$

✚ The decrease in pressure at equilibrium, favours the forward reaction.

7.4. Equilibrium Calculations

A. Calculation of an Equilibrium Constant

Example 7.4: Iodine molecules react reversibly with iodine ions to produce triiodide ions.

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

$K_c = \frac{[I_3^-]}{[I_2][I^-]}$

If a solution with the concentrations of I_2 and I^- both equal to $1 \times 10^{-3} M$ before reaction gives an equilibrium concentration of $6.61 \times 10^{-4} M$, what is the equilibrium constant for the reaction?

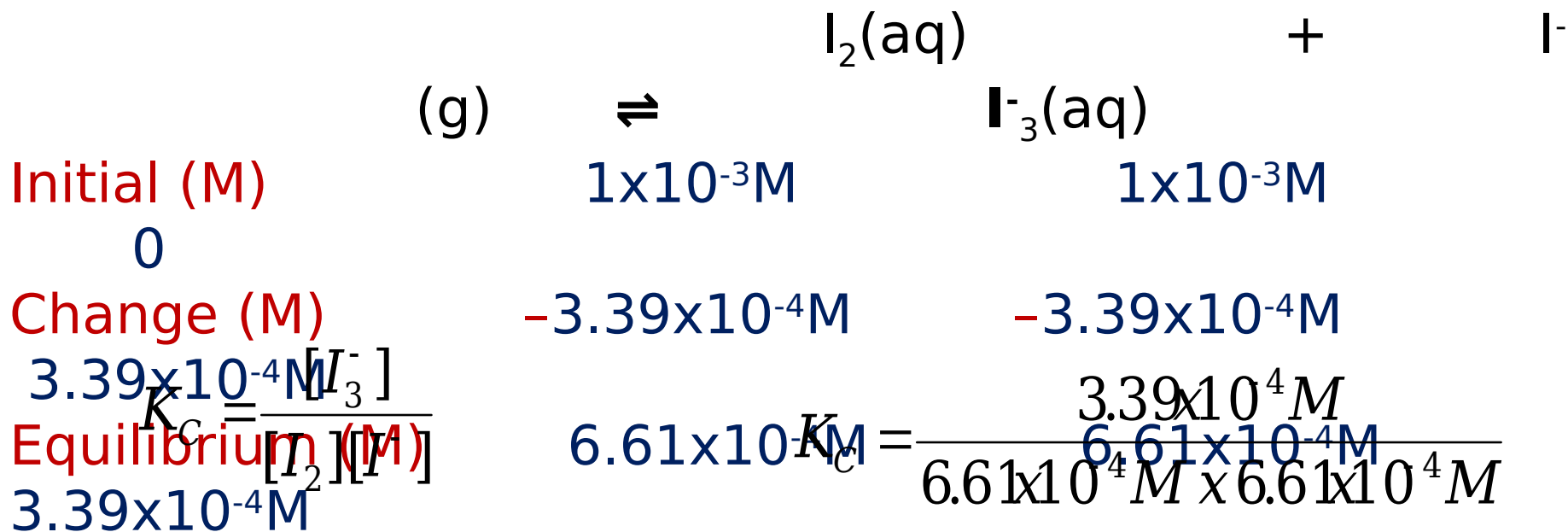
Solution:



At equilibrium the concentration of I_2 is

$$6.61 \times 10^{-4} M \text{ so that } 6.61 \times 10^{-4} M$$

$$x = 3.39 \times 10^{-4} M$$



$$K_C = 776$$

B. Calculation of a Missing Equilibrium Concentration

Example: At **2000 °C**, the value of the **K_c** for the reaction, **N₂(g) + O₂(g) ⇌ 2NO(g)**, is **4.1x10⁻⁴**. Calculate the equilibrium concentration of NO(g) in air at **1 atm** pressure. The equilibrium concentrations of N₂ and O₂ at this pressure and temperature are **0.036 M** and **0.0089 M** respectively.

Solution:

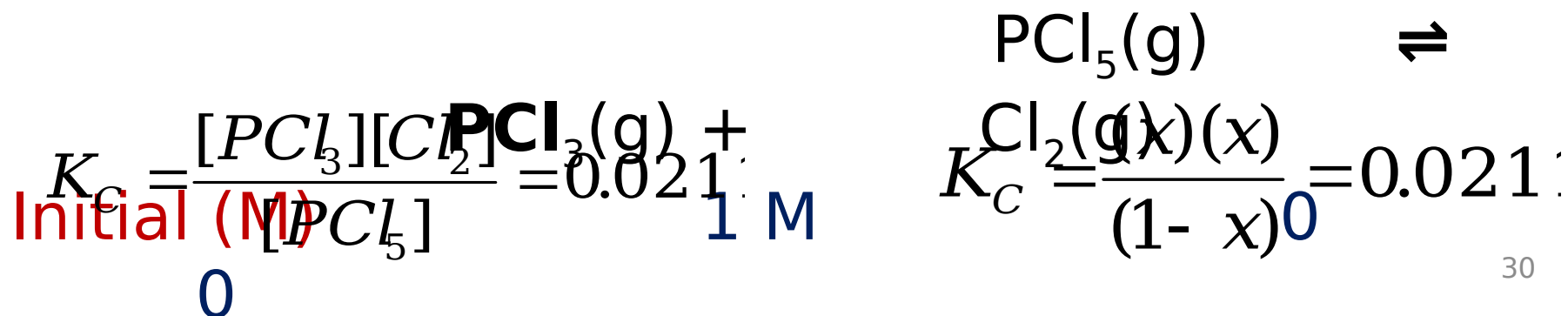
$$[NO] = \sqrt{(4.1 \times 10^{-4})(0.036)(0.0089)}$$

$$[NO] = 3.6 \times 10^{-4} M$$

C. Calculation of Equilibrium Concentrations from Initial Concentrations

Example 7.6: Under certain conditions, the equilibrium constant **K_c** for the decomposition of **PCl₅(g)** into **PCl₃(g)** and **Cl₂(g)** is **0.0211**. What are the equilibrium concentrations of **PCl₅**, **PCl₃** and **Cl₂** in a mixture that initially contained only **PCl₅** at a concentration of **1 M**?

Solution:



$$0.0211 = \frac{x^2}{(1-x)}$$

$$0.0211(1-x) = x^2$$

$$x^2 + 0.0211x - 0.0211 = 0$$

- The quadratic equation **$ax^2+bx+c=0$** form can be rearranged to solve for **x** :

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

$$x = \frac{-0.0211 \pm \sqrt{(0.0211)^2 - 4(1)(-0.0211)}}{2(1)}$$

$$x = 0.135M$$

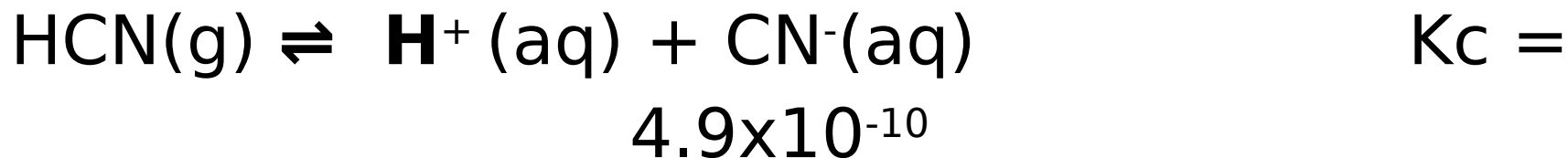
 The equilibrium concentrations are:

✖ $[PCl_5] = 1.0 - 0.135 = 0.87 \text{ M}$

✖ **$[PCl_3] = 0.135 \text{ M}$**

✖ $[Cl_2] = 0.135 \text{ M}$

Example 7.7: What are the concentrations at equilibrium of a 0.15 M solution of HCN?



Solution

$$K_c = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]}$$

$$K_c = \frac{x^2}{0.15 - x} = 4.9 \times 10^{-10}$$

$x \ll 0.15$ then $(0.15 - x) \cong 0.15$

$$4.9 \times 10^{-10} = \frac{x^2}{0.15}$$

$$x^2 = 7.4 \times 10^{-11}$$

$$x = 8.6 \times 10^{-6} \text{ M}$$

7.5. Concepts of Acid-Base

7.5.1. Arrhenius Concept

✚ An Arrhenius acid dissociates in water to form hydrogen ions (H^+), while an Arrhenius base dissociates in water to form hydroxide ions (OH^-).

✚ **Limitation:**

✖ The Arrhenius definitions of acidity and alkalinity are restricted to aqueous solutions.

✖ Thus, the Arrhenius definition can only describe acids and bases in an aqueous

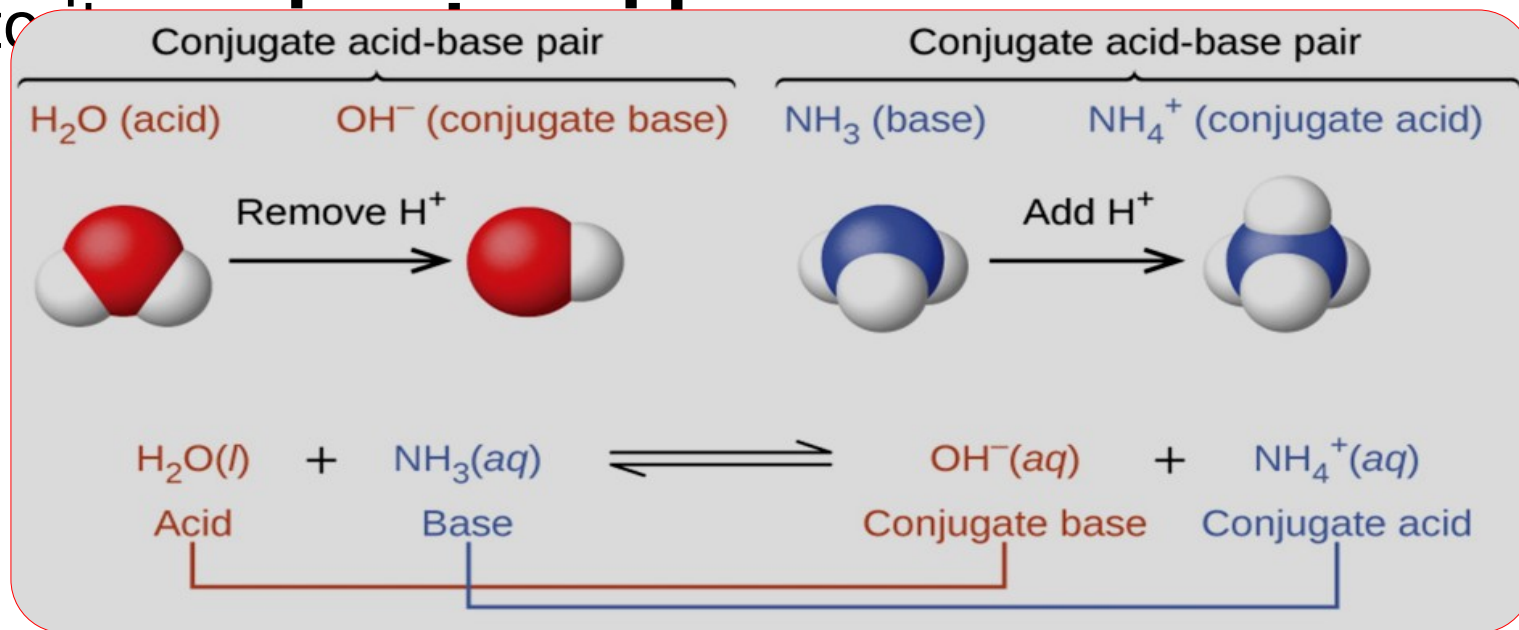
7.5.2. Brønsted-Lowry Concept

- ✚ An acid is a **proton donor**, any species that donates an H^+ ion.
 - ✚ An acid must contain H in its formula; HNO_3 and H_2PO_4^- are two examples, all Arrhenius acids are Brønsted-Lowry acids.
- ✚ A base is a **proton acceptor**, any species that accepts an H^+ ion.
 - ✚ A base must contain a lone pair of electrons to bind the H^+ ion; a few examples are NH_3 , CO_3^{2-} , F^- , as well as OH^- .
 - ✚ Brønsted-Lowry bases are not Arrhenius bases, but all Arrhenius bases contain the Brønsted-Lowry base OH^- .

✚ The concept of **conjugate pairs** is useful in describing Brønsted-Lowry acid base reactions (and other reversible reactions, as well).

✚ When an acid donates H^+ , the species that remains is called the **conjugate base** of the acid because it reacts as a proton acceptor in the reverse reaction.

✚ Likewise, when a base accepts H^+ , it is converted to its conjugate acid.



7.5.3. Lewis concept

■ A Lewis acid is defined as an **electron pair acceptor**, and a Lewis base as an **electron pair donor**.

■ **Examples of Lewis Acids:** H^+ , K^+ , Mg^{2+} , Fe^{3+} , BF_3 , AlCl_3 , Br_2 .

■ **Examples of Lewis Bases:** OH^- , F^- , H_2O ,



◆ **Lewis Acid**: a species that **accepts** an electron pair (i.e., an **electrophile**) and will have vacant orbitals, or the ability to form a vacant orbital.

◆ **Lewis Base**: a species that **donates** an electron pair (i.e., a **nucleophile**) and will have lonepair electrons.

◆ In a Lewis Acid-Base reaction a **bond** is formed where both electrons come from the Lewis base, and this is called a **Coordinate Covalent bond**

◆ **Lewis Acids** are the three general types of Lewis Acids, that is, chemical species that can accept electrons.

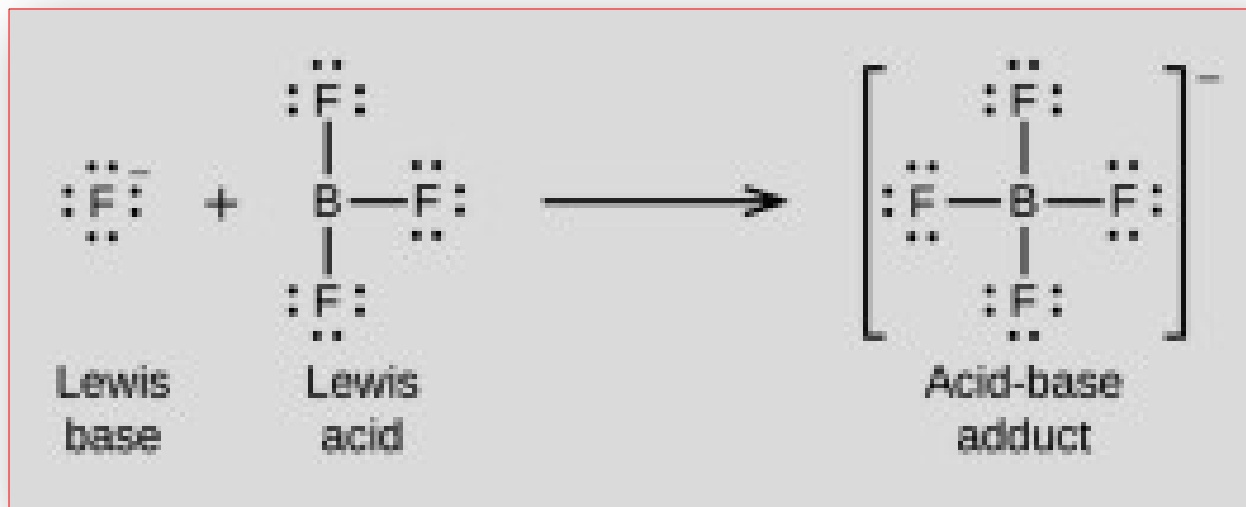
A. Molecules with an incomplete octet

B. Molecules with double bonds

C. Metal ions with vacant d-orbitals.

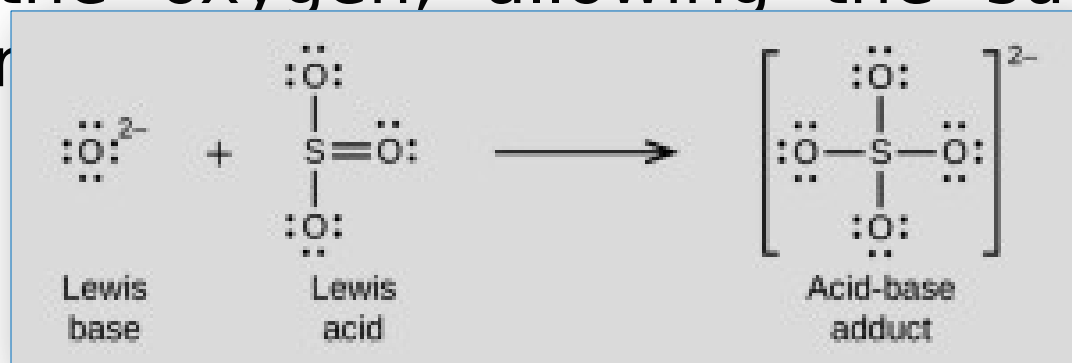
A. Incomplete Octets

- ✚ **Boron Trifluoride** is an exception to the octet rule and has an incomplete octet, and can thus accept electrons to form a bond.
- ✚ In the process it goes from **sp²** hybrid to **sp³** hybrid.



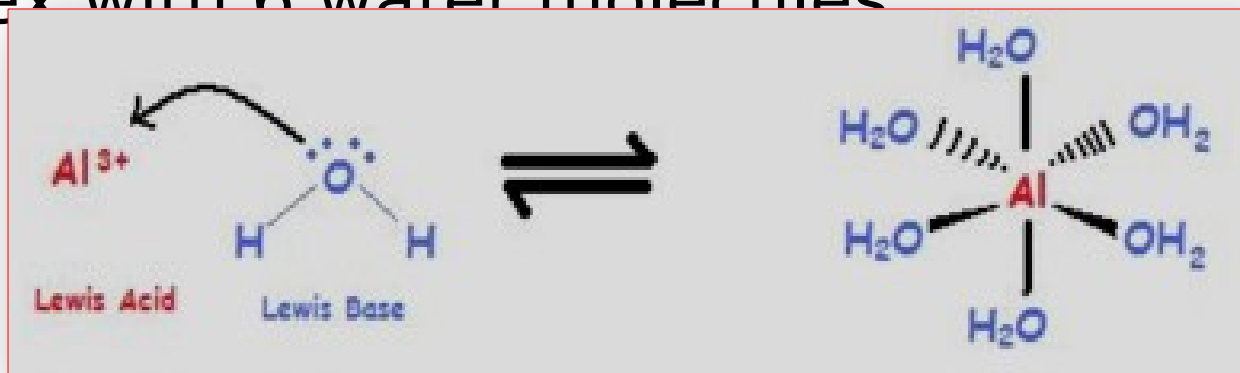
B. Double Bonds

- ◆ A double bond has **4 electrons** shared between **2 atoms** in a **PI** and **sigma** orbital.
- ◆ If you break the pi bond and move the two electrons to a non-bonding orbital on one atom, the other atom develops an incomplete octet and can function as a Lewis acid.
- ◆ This is shown next figure where the pi electrons move onto the oxygen, allowing the sulfur to receive electrons



C. Metal Cations

- ◆ Many metals have vacant **d-orbitals** that can accept electrons and thus behave as Lewis Acids.
- ◆ In fact, most metals react with water when they dissolve in water to form what is called a complex ion.
- ◆ For example, aluminum(III) is not a free ion, but a complex with 6 water molecules



7.6. pH and pOH

 **pH/pOH** is a measure of **acidity** or **basicity** of a solution.

 **pH** is defined as the negative logarithm of the **hydronium ion** $[\text{H}_3\text{O}^+]$ molar concentration in **mol/L**.

$$\text{pH} = -\log[\text{H}^+] = -\log [\text{H}_3\text{O}^+]$$

■ The hydronium ion molarity yields the equivalent expression:

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$



pOH of a solution is defined as the negative logarithm of the **hydroxide ion** molar concentration in **mol/L**.

$$\mathbf{pOH = -\log[OH^-]}$$

■ The hydroxide ion molarity yields the equivalent expression:

$$\mathbf{[OH^-] = 10^{-pOH}}$$



From the definitions of pH and pOH and the ion-product of water,

$$\mathbf{pH + pOH = 14}$$



The pH and pOH of a solution is dimensionless

7.6.1. Dissociation of Water

✚ **Ion-product** of water:



✚ The dissociation constant for the above reaction is:

$$- \log K_w = - \log ([\text{H}_3\text{O}^+][\text{OH}^-])$$

$$- \log K_w = (- \log [\text{H}_3\text{O}^+]) + (- \log [\text{OH}^-])$$

$$pK_w = pH + pOH$$

✚ Where K_w is ion product of water, which is temperature dependent at 25°C, K_w is 1×10^{-14} .

✚ In **pure water**, or in a **neutral** solution of salts in water, the concentration of the **H₃O⁺** and **OH⁻** ions is **equal**.

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{K_w} = 1 \times 10^{-7} \text{ M, at } 25^\circ\text{C}$$

✚ In **acidic** solutions, the concentration of the hydronium ions is greater than that of the hydroxyl ions, or:

$$\text{✚ } [\text{H}_3\text{O}^+] > 1.0 \times 10^{-7} \text{ M and}$$

$$\text{✚ } [\text{OH}^-] < 1.0 \times 10^{-7} \text{ M.}$$

✚ In **basic** or alkaline solutions:

$$\text{✚ } [\text{OH}^-] > [\text{H}_3\text{O}^+], \text{ or}$$

$$\text{✚ } [\text{OH}^-] > 1.0 \times 10^{-7} \text{ M}$$

Example 7.8: What is the **pH** of stomach acid, a solution of HCl with a hydronium ion concentration of $1.2 \times 10^{-3} \text{ M}$?

$$pH = -\log[H_3O^+] \quad pH = -\log(1.2 \times 10^{-3} \text{ M})$$

Solution:

$$pH = 3 - \log 1.2 \quad pH = 2.92$$

Example 7.9: Calculate the **hydronium ion** concentration of blood, the pH of which is **7.3**.

$$pH = 7.3 \quad 7.3 = -\log[H_3O^+]$$

Solution:

$$[H_3O^+] = 10^{-pH} \quad [H_3O^+] = 10^{-7.3} = \text{antilog of } -7.3$$

$$[H_3O^+] = 5 \times 10^{-8} \text{ M}$$

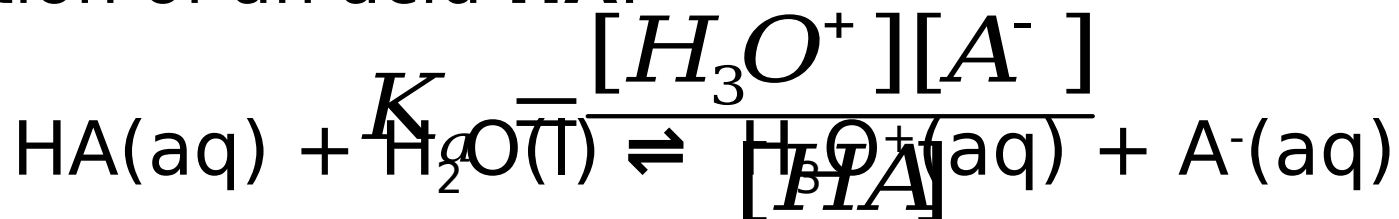
7.7. Relative Strength of Acids and Bases

► The relative strength of an acid or base is the extent to which it ionizes when dissolved in water.

► If the **ionization** reaction is essentially **complete**, the acid or base is termed **strong**; if

Strong Acids	Strong Bases
Perchloric Acid, HClO_4	Lithium Hydroxide, LiOH
Hydrochloric Acid, HCl	Sodium Hydroxide, NaOH
Hydrobromic Acid, HBr	Potassium Hydroxide, KOH
Hydroiodic	Calcium

- The relative strengths of acids or bases may be quantified by measuring their **equilibrium** constants in aqueous solutions.
- In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions than do weaker acids.
- The equilibrium constant for an **weak acid** is called the **acid-ionization constant, K_a** . For the reaction of an acid **HA**:



■ The equilibrium constant for an **weak Base** is called the **Base-ionization constant, K_b** . For the reaction of an acid **B**:



$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

■ Another measure of the strength of an acid or base is its percent ionization.

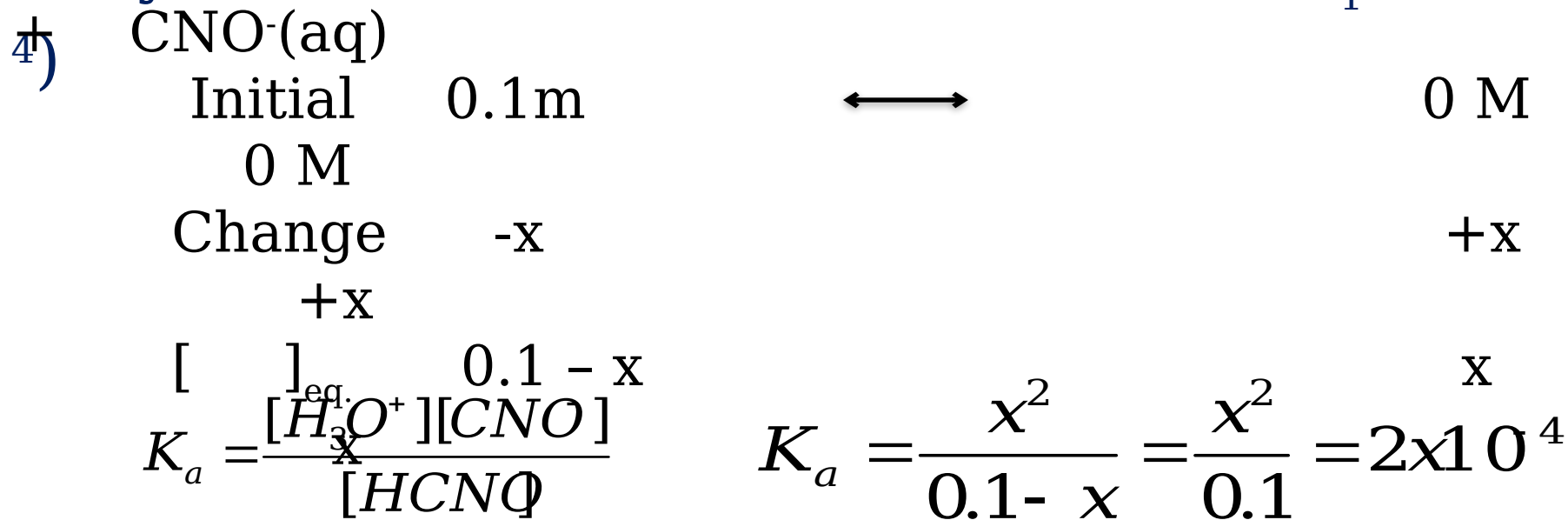
■ The **percent or degree of ionization** of a **acid or base** is defined in terms of the composition of an equilibrium mixture:

$$\%ionization_{\alpha} = \frac{[H_3O^+]}{[HA]} \times 100$$

$$\%ionization_{\alpha} = \frac{[OH^-]}{[B]} \times 100$$

Example 7.10: Calculate the $[H^+]$ in a 0.1 M HCNO solution. What is the degree of ionization of cyanic acid in this same solution? ($K_1 = 2 \times 10^{-4}$)

Solution: - $HCNO(aq) + H_2O(aq) \rightleftharpoons H_3O^+(aq) + CNO^-(aq)$

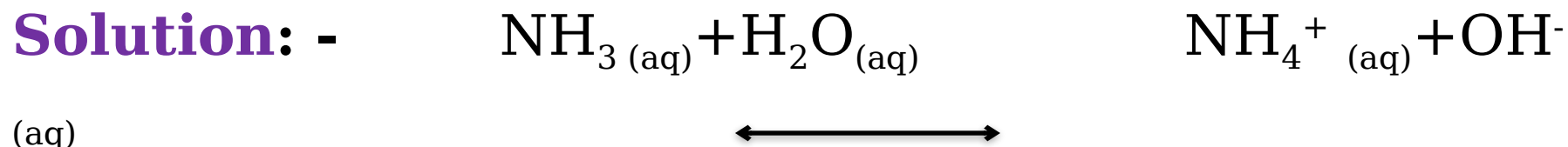


$$x = [H^+] = [CNO] = 0.0045 M$$

$$\alpha = \frac{[H_3O^+]}{[HCNO]} \times 100 = \frac{0.0045 M}{0.1 M} \times 100 = 4.5\%$$

ionization of NH_3 solution in this same solution? ($K_b = 1.8 \times 10^{-5}$)

Solution: -



Initial 0.4 M 0 M

0 M

Change -x +x

+x

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{0.4 - x} = \frac{x^2}{0.4} = 1.8 \times 10^{-5}$$

$$x = [\text{OH}^-] = 2.7 \times 10^{-3} \text{ M}$$

$$\alpha = \frac{[\text{OH}^-]}{[\text{NH}_3]} \times 100 \quad \alpha = \frac{2.7 \times 10^{-3} \text{ M}}{0.4 \text{ M}} \times 100 = 0.675\%$$

7.7.1. *p-Functions*

- ✚ The p- value is the negative base (-10) logarithm of the molar concentration of a certain species:

$$\mathbf{pX = -\log [X] = \log 1/[X]}$$

- ✚ We can also express equilibrium constants for the strength of acids and bases in a log form:

$$\mathbf{pK_a = - \log(K_a)}$$

$$\mathbf{pK_b = - \log (K_b)}$$

$$\mathbf{K_w = K_a * K_b}$$

7.7.2. Strength of Acids and Bases

		ACID	BASE		
100 percent ionized in H_2O	Strong	HCl	Cl	Negligible	
		H_2SO_4	HSO_4^-		
		HNO_3	NO_3^-		
	Weak	$H^+ (aq)$	H_2O	Weak	
		HSO_4^-	SO_4^{2-}		
		H_3PO_4	$H_2PO_4^-$		
		HF	F^-		
		$HC_2H_3O_2$	$C_2H_3O_2^-$		
		H_2CO_3	HCO_3^-		
		H_2S	HS^-		
		$H_2PO_4^-$	HPO_4^{2-}		
		NH_4^+	NH_3		
		HCO_3^-	CO_3^{2-}		
		HPO_4^{2-}	PO_4^{3-}		
	Negligible	H_2O	OH^-	Strong	
		HS	S^{2-}		
		OH^-	O_2^{2-}		
		H^-	H^-		
Acid strength increases		Base strength increases			
		100 percent protonated in H_2O			

Strength of Acids and Bases

TABLE 17.3 Ionization Constants of Some Weak Acids and Weak Bases in Water at 25 °C

Ionization Equilibrium		Ionization Constant K	p K
Acid		$K_a =$	p $K_a =$
Iodic acid	$\text{HIO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{IO}_3^-$	1.6×10^{-1}	0.80
Chlorous acid	$\text{HClO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{ClO}_2^-$	1.1×10^{-2}	1.96
Chloroacetic acid	$\text{HC}_2\text{H}_2\text{ClO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{C}_2\text{H}_2\text{ClO}_2^-$	1.4×10^{-3}	2.85
Nitrous acid	$\text{HNO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_2^-$	7.2×10^{-4}	3.14
Hydrofluoric acid	$\text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^-$	6.6×10^{-4}	3.18
Formic acid	$\text{HCHO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CHO}_2^-$	1.8×10^{-4}	3.74
Benzoic acid	$\text{HC}_7\text{H}_5\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{C}_7\text{H}_5\text{O}_2^-$	6.3×10^{-5}	4.20
Hydrazoic acid	$\text{HN}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{N}_3^-$	1.9×10^{-5}	4.72
Acetic acid	$\text{HC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{C}_2\text{H}_3\text{O}_2^-$	1.8×10^{-5}	4.74
Hypochlorous acid	$\text{HOCl} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OCl}^-$	2.9×10^{-8}	7.54
Hydrocyanic acid	$\text{HCN} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CN}^-$	6.2×10^{-10}	9.21
Phenol	$\text{HOC}_6\text{H}_5 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{C}_6\text{H}_5\text{O}^-$	1.0×10^{-10}	10.00
Hydrogen peroxide	$\text{H}_2\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HO}_2^-$	1.8×10^{-12}	11.74
Base		$K_b =$	p $K_b =$
Diethylamine	$(\text{C}_2\text{H}_5)_2\text{NH} + \text{H}_2\text{O} \rightleftharpoons (\text{C}_2\text{H}_5)_2\text{NH}_2^+ + \text{OH}^-$	6.9×10^{-4}	3.16
Ethylamine	$\text{C}_2\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_2\text{H}_5\text{NH}_3^+ + \text{OH}^-$	4.3×10^{-4}	3.37
Ammonia	$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$	1.8×10^{-5}	4.74
Hydroxylamine	$\text{HONH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HONH}_3^+ + \text{OH}^-$	9.1×10^{-9}	8.04
Pyridine	$\text{C}_5\text{H}_5\text{N} + \text{H}_2\text{O} \rightleftharpoons \text{C}_5\text{H}_5\text{NH}^+ + \text{OH}^-$	1.5×10^{-9}	8.82
Aniline	$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	7.4×10^{-10}	9.13

Acid strength

Base strength

7.7.3. The Common Ion Effect

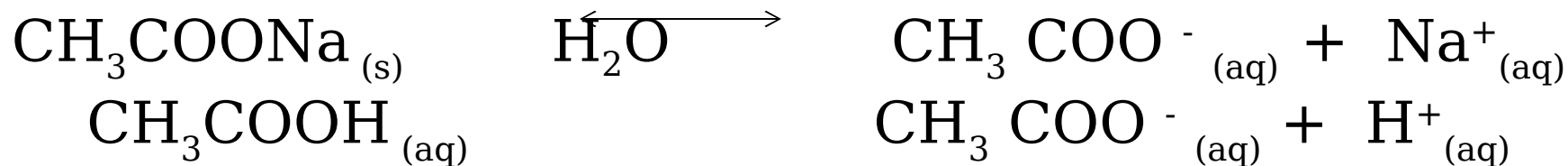


In acid-base ionization of a single electrolyte there is formation of one anion and one cation of the solute material.



What happens when a solution contains two different dissolved compounds?

Example 7.12: - Both CH_3COONa and CH_3COOH are in solution and they dissociate and ionize to produce CH_3COO^- ions:



CH_3COONa is a strong electrolyte, so it dissociates completely in solution, but CH_3COOH , a weak acid, ionizes partially.

■ According to ***Le Chatelier's principle***, the addition of CH_3COO^- ions from CH_3COONa to a solution of CH_3COOH will **suppress** the ionization of CH_3COOH , that is, shifts the equilibrium to the **left** there by **decreasing** the H^+ ion concentration.

■ Thus, a solution containing both CH_3COOH and CH_3COONa will be **less acidic** than a solution containing only CH_3COOH at the same concentration.

■ The shift in equilibrium of the CH_3COOH ionization is caused by the additional acetate, CH_3COO^- , ions which comes from the salt.

■ The shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substances is called the ***Common ion effect***. It is a special case of Le Chatelier's principle.

7.8. Buffer solutions

✚ It is a solution that has the ability to resist change in pH up on the addition of small amounts of either acid or base.



Buffer solution is a solution of a weak acid/weak base and its salt.

✚ A buffer solution must contain an acid to react with OH^- ions that may be added to it and a base to react with any added H^+ ions.

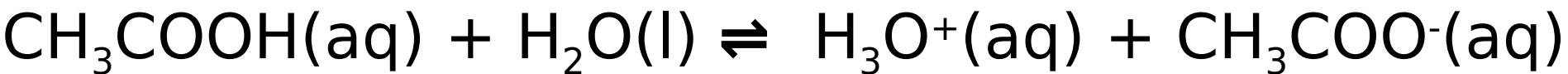
✚ Furthermore, the acid and the base components of the buffer must not consume each other in a neutralization reaction.

Buffer solution

Types of buffer solution

- a. **Acidic buffer** CH_3COOH and $\text{CH}_3\text{COONH}_4$
- b. **Basic buffer:** NH_4OH and NH_4Cl
- c. **Salt or neutral buffer** $\text{CH}_3\text{COONH}_4$

Now, to find the pH, Let us consider



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

$$-\log[\text{H}_3\text{O}^+] = -\log K_a - \log \frac{[\text{Acid}]}{[\text{Salt}]}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

✗ Since CH_3COOH is partially ionized, so most of CH_3COO^- will come from the salt.

✗ Hence $[\text{CH}_3\text{COO}^-] = [\text{Salt}]$

✗ Taking log of both sides

✗ **Similarly, for Basic Buffer**

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

Example 7.13: Calculate the pH of a buffer solution containing 0.1 M each of acetic acid and sodium acetate. ($K_a = 1.8 \times 10^{-5}$)

- What will be the change in pH on adding
 - (a) 0.01 moles of HCl to 1.0 L of solution?
 - (b) 0.01 moles of NaOH to 1.0 L of solution?
- Assume that no change in volume occurs on the addition of HCl or NaOH.

Solution:

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

$$pH = -\log(1.8 \times 10^{-5}) + \log \frac{0.1}{0.1} \quad pH = 4.745 + 0$$

$$pH = 4.745$$

a) 0.01 moles of HCl give 0.01 moles of H^+ which reacts with 0.01 moles of CH_3COO^- to form CH_3COOH . Therefore,

$$[CH_3COO] = 0.1 - 0.01 = 0.09M$$

$$[CH_3COOH] = 0.1 + 0.01 = 0.11M$$

$$pH = 4.745 + \log \frac{0.09}{0.11} \qquad pH = 4.745 - 0.087$$

$$pH = 4.658$$

► **Change in pH = 4.745 - 4.658 = 0.087 units.**

► **Hence, pH will decrease!**

(b) On adding 0.01 moles of NaOH to a litre of solution, 0.01 moles of OH⁻ will react with 0.01 moles of CH₃COOH. Therefore,

$$[CH_3COO^-] = 0.1 + 0.01 = 0.11 M$$

$$[CH_3COOH] = 0.1 - 0.01 = 0.09 M$$

$$pH = 4.745 + \log \frac{0.11}{0.09} \qquad pH = 4.745 + 0.086$$

$$pH = 4.831$$

► **Change in pH = 4.831 - 4.745 = 0.086 units.**

► **Hence, pH will increase!**