

Equilibrium in Chemical Reactions. (15% of Chemistry 30)

What is happening in a system at equilibrium?

How do scientists predict shifts in the equilibrium of a system?

Key Concepts

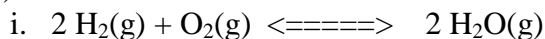
- chemical equilibrium systems
- reversibility of reactions
- Le Chatelier's principle
- equilibrium law expression
- equilibrium constants K_c

1. Terms about equilibrium

- a. at equilibrium, the **macroscopic** properties of a system remain **constant**.
- b. macroscopic properties include observable properties – **concentration, temperature, color and pH**
- c. when a chemical reaction has reached equilibrium, the concentrations of the **reactants** and **products** do not change. The forward and reverse reactions continue to occur, but at the **same** rate.
- d. when an equilibrium system is changing at the molecular level, it is called **adynamic** equilibrium
- e. when reactants and products of a reaction are all in the same phase and the system reaches equilibrium, it is called a **homogeneous** equilibrium
- f. when the reactants and products of a reaction are not in the same phase and the system reaches equilibrium, it is called a **heterogeneous** equilibrium
- g. an equilibrium can only be achieved in a **closed** system at a constant **temperature** or in an **isolated** system.

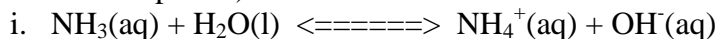
2. define K_c to predict the extent of the reaction and write equilibrium-law expressions for given chemical equations, using lowest whole-number coefficients

- a. according to the Law of **Equilibrium**, when a chemical system reaches equilibrium, there is a constant ratio of products and reactants in a chemical reaction
- b. write the equilibrium law expression for any homogeneous (see general form p. 641)



$$K_c = \frac{[\text{H}_2\text{O}(\text{g})]^2}{[\text{H}_2(\text{g})]^2 [\text{O}_2(\text{g})]}$$

- c. be able to write the equilibrium law expression for any heterogeneous reaction (see discussion p. 644)



$$K_c = \frac{[\text{NH}_4^+(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{NH}_3(\text{aq})]}$$

- ii. in heterogeneous reactions, there is often a pure liquid or solid. Since the concentration of these pure substances does not change, their concentrations are **not included** in the equilibrium law expression
 - d. Certain conditions **generally** exist and can be described qualitatively
 - i. when $K > 1$, **products** are favoured
 - ii. when $K \approx 1$, there are approximately equal concentrations of products and reactants at equilibrium
 - iii. when $K < 1$, **reactants** are favoured
 - iv. these statements are generalizations and depend on the form of the equilibrium expression
- 3. predict, qualitatively, using Le Chatelier's principle, shifts in equilibrium caused by changes in temperature, pressure, volume, concentration or the addition of a catalyst and describe how these changes affect the equilibrium constant
 - a. Le Chatelier's principle states that a dynamic equilibrium tends to respond so as to relieve the effect of any change in the conditions that affect the equilibrium
 - b. a change in temperature is the only condition that can cause a change in the equilibrium constant
 - c. Generally the following conditions will have the following results (p. 650)
 - i. increasing a reactant shift toward the (**products** / reactants)
 - ii. decreasing a product shift toward the (**products** / reactants)
 - iii. decreasing a reactant shift toward the (products / **reactants**)
 - iv. increasing a product shift toward the (products / **reactants**)
 - v. using a catalyst no effect – equilibrium reached **faster**
 - vi. increasing temp in exo reaction shift toward the (products / **reactants**)
 - vii. increasing temp in endo reaction shift toward the (**products** / reactants)
 - viii. decreasing temp in endo reaction shift toward the (products / **reactants**)
 - ix. decreasing temp in exo reaction shift toward the (**products** / reactants)

for vi. – ix. the K_c value will also change because the temperature changes

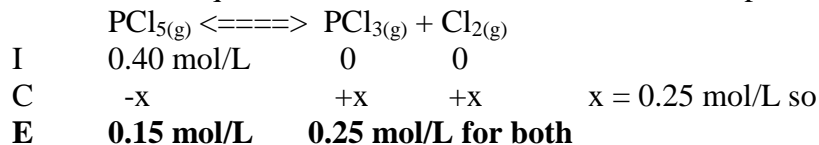
- x. decreasing volume – increasing pressure shift toward side with **least** coeff.
- xi. increasing volume – decreasing pressure shift toward side with **most** coeff.

x and xi hold unless sums of coefficients are equal on both sides

- xii. adding a non reacting gas **no effect**
- 4. The reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$ is endothermic with a $H = +56.9 \text{ kJ/mol}$. How will the amount of NO_2 at equilibrium be affected by
 - a. adding N_2O_4 (**increased**, decreased, not affected)
 - b. lowering the pressure (**increased**, decreased, not affected)
 - c. increasing the volume of the container (**increased**, decreased, not affected)
 - d. raising the temperature (**increased**, decreased, not affected)
 - e. adding a catalyst to the system (increased, decreased, **not affected**)
 - f. Which of these will alter the value of K_{eq} **d**

5. When 4.0 moles of PCl_5 is heated in a 10.0 L container, an equilibrium is established in which 2.5 moles of Cl_2 is present. $\text{PCl}_{5(g)} \rightleftharpoons \text{PCl}_{3(g)} + \text{Cl}_{2(g)}$

- a. What are the equilibrium concentrations of all three components?



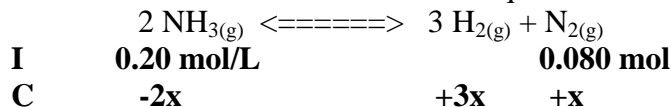
- b. What is the K_c value for the reaction?

$$K_c = \frac{[\text{PCl}_{3(g)}][\text{Cl}_{2(g)}]}{[\text{PCl}_{5(g)}]}$$

$$K_c = (0.25 \text{ mol/L})(0.25 \text{ mol/L}) / 0.15 \text{ mol/L} = \mathbf{0.42} \quad (\text{units unnecessary})$$

6. When 1.00 mole of NH_3 gas and 0.40 moles of N_2 gas are placed in a 5.0 L container and allowed to reach an equilibrium at a certain temperature, it is found that 0.75 moles of NH_3 is present. The reaction is:

- a. What are the concentrations of H_2 and N_2 at equilibrium?



final concentration of $\text{NH}_3 = 0.75 \text{ mol} / 5 \text{ L} = 0.15 \text{ mol/L}$

final moles of $\text{NH}_3 = 0.75$ so $0.20 - 0.15 = 0.05$ change

$$0.05 = 2x \text{ so } x = 0.025$$



- b. What is the K_c for this reaction at this temperature?

$$K_c = \frac{[\text{H}_{2(g)}]^3 [\text{N}_{2(g)}]}{[\text{NH}_{3(g)}]^2}$$

$$= (0.075 \text{ mol/L})^3 (0.105 \text{ mol/L}) / (0.15 \text{ mol/L})^2$$

$$= \mathbf{0.015}$$

7. A mixture of H_2 and I_2 is allowed to react at 448°C . When equilibrium is established, the concentrations of the participants are found to be $[\text{H}_2] = 0.46 \text{ mol/L}$, $[\text{I}_2] = 0.39 \text{ mol/L}$, and $[\text{HI}] = 3.0 \text{ mol/L}$.

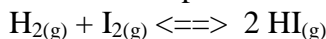
- a. Calculate the value of the K_{eq} at 448°C . $\text{H}_{2(g)} + \text{I}_{2(g)} \rightleftharpoons 2 \text{HI}_{(g)}$

$$K_c = \frac{[\text{HI}_{(g)}]^2}{[\text{H}_{2(g)}][\text{I}_{2(g)}]}$$

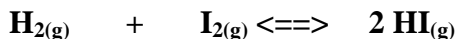
$$= (3.0 \text{ mol/L})^2 / (0.46 \text{ mol/L})(0.39 \text{ mol/L})$$

$$= \mathbf{50}$$

8. The equilibrium constant, for the reaction represented below, is 50 at 448°C



- What are the equilibrium concentrations of each species, when 0.50 moles of H_2 is mixed with 0.50 moles of I_2 in a 0.50 L container and allowed to react at 448°C ?



I	1.0	1.0	0
C	- x	-x	+2x
E	1.0 - x	1.0 - x	2x

$$K_c = \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]} \quad 50 = \frac{(2x)^2}{(1.0-x)(1.0-x)}$$

$$50 = \frac{(2x)^2}{(1.0-x)^2} \quad \text{square root both sides}$$

$$7.07 = \frac{x}{1.0-x}$$

$$7.07 - 7.07x = 2x$$

$$7.07 = 9.07x$$

$$x = 0.78 \text{ mol/L}$$

number

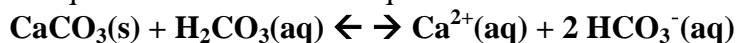
$$\text{H}_2(\text{g}) = 1.0 - x = 1.0 - 0.78 = 0.22 \text{ mol/L}$$

$$\text{I}_2(\text{g}) = 1.0 - x = 1.0 - 0.78 = 0.22 \text{ mol/L}$$

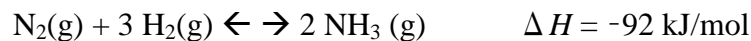
$$\text{HI}(\text{g}) = 2x = 2(0.78) = 1.56 \text{ mol/L}$$

9. if the equilibrium constant for a reaction is very small, (less than 1000x the concentration of the reactants), x can be eliminated from the bottom of the equation.
10. color intensity can be used to quantitatively measure the amount of a product or reactant at equilibrium
11. Apply equilibrium knowledge in various life examples including
 - a. SCUBA diving
 - i. large pressure on a SCUBA diver in deep water changes the equilibrium between gaseous nitrogen and dissolved nitrogen in the lining of the **lungs** and thus in the blood stream.
 - ii. high concentrations of nitrogen in the blood can cause **nitrogen narcosis** with results similar to alcohol impairment
 - iii. high concentrations of nitrogen in the blood can form bubbles in the blood if a diver rises too quickly after being submerged for an extended time at depth. This is referred to as the **bends**.

- b. carbon monoxide poisoning in houses
- carbon monoxide bonding is favoured when compared to oxygen bonding to the **hemoglobin** molecule in red blood cells. Carbon monoxide poisoning results in oxygen deprivation.
- c. formation of stalagmites, stalactites and corals
- the equilibrium between solid calcium carbonate and dissolved carbonic acid is responsible for the formation of the above calcium deposits. Write an equation that shows this equilibrium.



- d. Haber-Bosch process for manufacturing ammonia
- an understanding of the effects of pressure and temperature on the position of equilibrium between nitrogen and hydrogen gases and ammonia allowed Haber and Bosch to develop an efficient method of synthesizing ammonia. Write an equation that shows this equilibrium



- Predict 3 ways to improve the production of ammonia in the process using LeChatelier's ideas.
 - increase the reactants**
 - remove the products**
 - take away heat – but keep it at a high enough temperature to react**
 - increase the pressure**

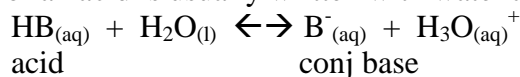
Equilibrium Applied to Acids and Bases (15% of Chemistry 30)

Key Concepts:

- acid-rain and its effects
 - Brønsted–Lowry acids and bases
 - acid-base equilibrium
 - conjugate pairs of acids and bases
 - amphiprotic substances
 - titration curves
 - equilibrium law expression
 - equilibrium constants
 - K_w , K_a , K_b
 - buffers
 - indicators
- describe the processes involved in acid rain formation and acid deposition
 - carbon dioxide** in air reacts with rain water to form carbonic acid which makes natural rain water slightly acidic
 - motor vehicles with combustion engines release **nitrogen** oxides into the atmosphere
 - power and heating plants that burn fossil fuels and smelting plants release **sulfur** oxides into the atmosphere

- d. when **nitrogen** oxides or **sulfur** oxides react with water in the atmosphere they form nitrous acid, nitric acid, sulphurous acid and sulphuric acid which fall to Earth as acid deposition
- e. acid deposition harms plant and animal life on land and in lakes and streams by (increasing / **reducing**) pH
- f. Alberta's predominantly **limestone** geological formations buffer ponds and lake water
- g. acidic lakes and ponds can be treated with limestone to reduce the damage caused by acidic **shock** in spring when acidic snow melts and flows into bodies of water
2. describe Brønsted–Lowry acids and bases
 - a. Brønsted and Lowry developed a theory of acids and bases that was more general than that of Arrhenius
 - b. A Brønsted–Lowry acid is a proton **donor**
 - c. A Brønsted–Lowry base is a proton **acceptor**
3. identify acid base conjugate pairs
 - a. According to the Brønsted–Lowry theory, an acid must react with a **base** and vice versa
 - b. When a Brønsted–Lowry acid donates a proton it becomes the conjugate **base** of the acid
 - c. When a Brønsted–Lowry base accepts a proton it becomes the conjugate **acid** of the base
4. a compound that can either donate or accept a proton is called an **amphiprotic** substance
 - i. water is an amphiprotic substance
 - ii. anions formed from **polyprotic** acids losing one hydrogen ion are amphiprotic.
5. write Brønsted–Lowry equations, including indicators, and predict whether reactants or products are favoured for acid-base equilibrium reactions for monoprotic and polyprotic acids and bases
 - a. the position of the acid base equilibrium can be predicted using an acid base table
 - i. If the acid on the reactants side is stronger than the acid on the products side, the **products** will be favoured at equilibrium
 - ii. If the acid on the products side is stronger than the acid on the reactants side, the **reactants** will be favoured at equilibrium
6. Label the acid and base and the conjugate base and conjugate base
 - a. $\text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \leftrightarrow \text{CH}_3\text{NH}_3^+ + \text{OH}^-$
base acid c. acid c. base
 - b. $\text{C}_6\text{H}_5\text{COOH} + \text{H}_2\text{O} \leftrightarrow \text{C}_6\text{H}_5\text{COO}^- + \text{H}_3\text{O}^+$
acid base c. base c. base
7. recall the concepts of pH and hydronium ion concentration and pOH and hydroxide ion concentration, in relation to acids and bases
8. a strong acid ionizes **100%**
9. the equilibrium for the ionization of a weak acid or base can be treated in a similar way as the equilibrium for any reaction.

- a. The equation for an acid is usually written with water as a reactant.

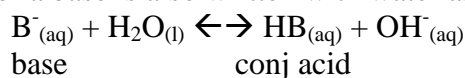


- b. the equilibrium constant for the ionization of a weak acid is called the acid ionization constant and is given the symbol, **K_a**
 c. the equilibrium expression for the ionization of an acid can be written (see p. 691)
 The ion product for water is symbolized K_w

i. $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$

ii. at 25°C, $K_w = 1.0 \times 10^{-14}$

- d. the equilibrium constant for a ionization of a weak base is called the base ionization constant and is given the symbol, **K_b**
 e. the equilibrium expression for the ionization of a base can be written (see p. 696)
 f. the equation for a base is also written with water as a reactant

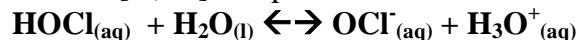


g. at 25°C, $\text{pH} + \text{pOH} = 14$

- h. K_b can be calculated by using K_w/K_a for the conjugate acid

10. and use these to determine pH, pOH, $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ of acidic and basic solutions

- a. find the $[\text{H}_3\text{O}^+]$ and pH of 0.0100 mol/L of hypochlorous acid



I	0.0100 M	0	0
C	-x	+x	+x
E	0.01-x	x	x

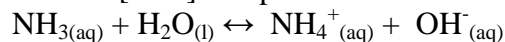
$$K_a = \frac{[\text{OCl}^-_{(\text{aq})}][\text{H}_3\text{O}^+_{(\text{aq})}]}{[\text{HOCl}_{(\text{aq})}]} \quad 4.0 \times 10^{-8} = \frac{x^2}{0.01 - x} \quad \text{x can be eliminated}$$

$$4.0 \times 10^{-10} = x^2$$

$$x = 2 \times 10^{-5} \text{ mol/L} = [\text{H}_3\text{O}^+_{(\text{aq})}]$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+_{(\text{aq})}] = -\log(6.3 \times 10^{-5}) = 4.70$$

- b. find the $[\text{OH}^-]$ and pH of 0.0100 mol/L $\text{NH}_3_{(\text{aq})}$



I	0.0100 M	0	0
C	-x	+x	+x
E	0.010-x	x	x

$$K_b = \frac{[\text{NH}_4^+_{(\text{aq})}][\text{OH}^-_{(\text{aq})}]}{[\text{NH}_3_{(\text{aq})}]} \quad K_b = 1.0 \times 10^{-14} / K_a$$

$$K_b = 1.0 \times 10^{-14} / 5.6 \times 10^{-10}$$

$$K_b = 1.8 \times 10^{-5}$$

$$1.8 \times 10^{-5} = \frac{x^2}{0.01 - x} \quad \text{x can be eliminated}$$

$$1.8 \times 10^{-7} = x^2$$

$$x = 4.3 \times 10^{-4} = [\text{OH}^-_{(\text{aq})}]$$

$$[\text{H}_3\text{O}^+(\text{aq})] = 1.0 \times 10^{-14} / [\text{OH}^-(\text{aq})]$$

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

$$[\text{H}_3\text{O}^+(\text{aq})] = 1.0 \times 10^{-14} / 4.3 \times 10^{-4}$$

$$[\text{H}_3\text{O}^+(\text{aq})] = 2.4 \times 10^{-11} \text{ mol/L}$$

$$\text{pH} = -\log(2.4 \times 10^{-11} \text{ mol/L})$$

$$\text{pH} = 10.63$$

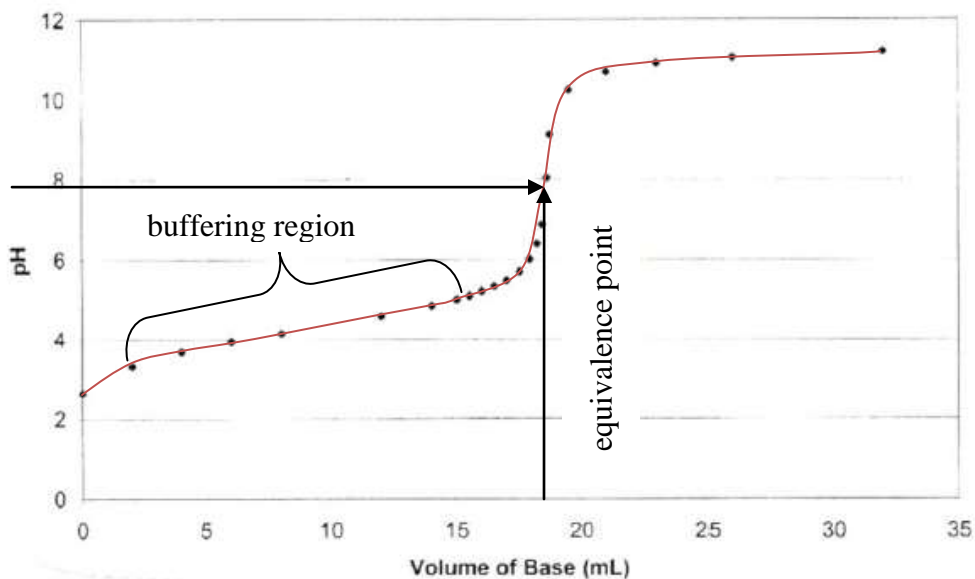
Note: Examples that require the application of the quadratic equation are excluded

- you can use the same strategy when solving problems involving K_a that you used when solving problems for K_c
- the rule of 1000 allows you to determine whether you can use the approximation that the equilibrium concentration of a weak acid or base is approximately equal to the initial concentration

11. Acid base indicators

- indicators change **color** over a small pH range, they can be used to show the endpoint of a titration
- indicators are weak **acids** and their conjugate **bases** that have different colors depending on the **pH** of the solution they are found in
- to observe the pH throughout a titration of an acid or a base, you need to use a **pH meter**. If the results are graphed a pH or titration curve is the result
- a buffering region is a region shown in a titration curve in which the pH changes **slowly**, they proceed a quick change in the pH which can be used to calculate the concentration of the acid or base

Graph of pH vs Volume of Base



12. Using the curve above

- Draw in a smooth curve
- locate the equivalence point on the graph. **~ 18.0 mL**
- What is the pH value at this point? **~7.8**
- locate the buffering region (**between 2mL and 15 mL**)
- this is a titration of a (**weak / strong**) (**acid / base**) with a strong (acid / **base**)

- f. the concentration of the base is 0.500 mol/L. What is the concentration of the acid if 10.00 mL of the acid was used in the titration?
 $n = cv = 0.500 \text{ mol/L} \times 0.0180 \text{ L} = 0.00900 \text{ mol}$
 $0.00900 \text{ mol} \times 1/1 = 0.00900 \text{ mol}$
 $c = n / v = 0.00900 \text{ mol} / 0.0100 \text{ L} = 0.900 \text{ mol/L}$
- g. describe how the titration curve would have looked if HCl were used instead of this acid. (**would have started lower closer to 1 pH**)
- h. describe how the titration curve would have looked if H₂SO₄(aq) were used instead of this acid (**would have had two steep sections, instead of 1**)
- i. describe how the titration curve would have looked if NaOH(aq) were titrated with a strong acid (**opposite of f, pH starts near 13, buffers, drops and finishes near 1**)
13. define a buffer as relatively large amounts of a **weak** acid or base and its conjugate in equilibrium that maintain a relatively **constant** pH when small amounts of acid or base are added.
- a buffer solution resists a change in **pH** on addition of a little strong base or strong acid
 - a solution that contains a weak acid-conjugate base mixture, or a weak base-conjugate acid mixture is called a **buffer**.
 - you can control the **pH** range of the buffer by choosing an acid-base pair carefully
 - the most important buffer system in the blood stream is the equilibrium among carbon dioxide, water, carbonic acid, hydrogen carbonate ion
 - the ability of hemoglobin in red blood cells to carry oxygen is sensitive to pH. If the pH falls below 7.34, **acidosis** result. If the pH rises above 7.44, **alkalosis** results.