

Louisiana Tech University, Chemistry 102 POGIL Exercise on Chapter 14. Chemical Equilibrium 1

Why?

When opposing forces or issues are balanced, a system is said to be at equilibrium. Equilibrium in chemical reactions are dynamic because the forward and reverse reactions rates are equal. Le Chaterlier's Principle provides a simple qualitative rule for analyzing the effects of perturbations on equilibrium. You can use it in evaluating the direction and extent of change that will take place. Equilibrium expression and constant allows quantitative prediction of direction and change of concentrations.

Learning Objectives

Understand Chemical equilibrium

Characteristics of Chemical Equilibrium

Equilibrium at the Nanoscale

The Equilibrium Expression and Constant

The Meaning of Equilibrium Constant

Shifting a Chemical Equilibrium: Le Chatelier's Principle

Success Criteria

1. Recognize a system at equilibrium and describe the properties of equilibrium systems (Section 14.1).
2. Describe the dynamic nature of equilibrium and the changes in concentrations reactants and products that occur as a system approaches equilibrium sections 14.1 and 14.2).
3. Show by using Le Chatelier's principle how changes in concentrations, pressure or volume, and temperature shift chemical equilibria (Section 14.6). Write equilibrium constant expressions, given balanced chemical equations (Section 14.2).
4. Obtain equilibrium constant expressions for related reactions from the Expression for one or more known reactions (Section 14.2).

Resources

Chemistry: The Molecular Science 1st Edition, John W. Moore, Conrad L. Stanitski and Peter C. Jurs.

Prerequisites

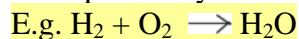
Chemical equations, stoichiometric coefficients, Concentration (molarity= mole/ L; mol dm^{-3} ; [reactant] or [products])

Reactant - a substance that is consumed by a chemical reaction

Product - a substance that is produced by a chemical reaction.

New Concepts

Irreversible or complete reactions: Chemical reactions can be considered to have forward and backward reactions. In most chemical reactions, the rate of backward reaction is so small all reactants are completely converted to products. This condition is usually represented in a chemical equation by an arrow pointing to **right** \rightarrow



Equilibrium Chemical Reactions: On the other hand, there are many chemical reactions that stop far short of completion represented by double pointing arrows \rightleftharpoons . An example is the dissociation of dinitrogen tetraoxide:



Dynamic Equilibrium: The reactants and products will interchange constantly, however maintaining same concentrations of reactants and products. This change maintains a constant concentration of reactants and products.

Homogenous equilibrium: where reactants and products are in same phase.

E.g. $3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

Heterogeneous equilibrium: where at least one phase of a reactant or product is different from the rest. E.g. $\text{MgCO}_3(\text{s}) \rightleftharpoons \text{MgO}(\text{s}) + \text{CO}_2(\text{g})$

Law of Mass Action: Law of mass action describes an equilibrium process by quantifying the equilibrium concentration of reactants and products. It uses the ratio of backward and forward reactions and express it terms of an equilibrium constant (K). For example consider a hypothetical equation:

$$j \text{ A} + k \text{ B} \rightleftharpoons l \text{ C} + m \text{ D}$$

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

[A]... are equilibrium concentration of A, B, C, D
 [A] of pure (l) and (s) equals 1.
 j, k, l, m are stoichiometric coefficients
 K = equilibrium constant

K = ∞ (infinity) - Irreversible reactions; **product favored**

K = 0 - No reaction- **reactant favored**

K = between 0 and 1 - Equilibrium reactions- **reactant favored**

K (Kc): Equilibrium expression when mol/L concentrations are used.

Kp: Equilibrium expression when partial pressures are used for gaseous chemicals.

E.g. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

$$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = 6.02 \times 10^{-2} \text{ L}^2/\text{mol}^2 \text{ at } 127^\circ\text{C} \text{ (experimentally determined)}$$

$\text{MgCO}_3(\text{s}) \rightleftharpoons \text{MgO}(\text{s}) + \text{CO}_2(\text{g})$; $K = [\text{CO}_2]$; $K_p = P_{\text{CO}_2}$; P_{CO_2} = Partial pressure of CO_2
Equilibrium constant of reverse reaction: 1/K

Multiplying equation: (K)_n; n = multiplicand

Adding two equilibria:

$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}); K_{c1}$

$2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g}); K_{c2}$

$\text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g}); K$

$$K_{c1} = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}; K_{c2} = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]}$$

$$K = K_{c1} \times K_{c2} = \frac{[\text{NO}_2]^2}{[\text{N}_2][\text{O}_2]^2}$$

Subtracting two equilibria: K = K_{c1} / K_{c2}

Shifting a Chemical Equilibrium: Le Chatelier's Principle

Le Chatelier's principle is used to predict the shift of an equilibrium. It simply states that: If a change is imposed on a system at Equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change.

Listed below are how various "changes" that affect equilibria:

- 1) Adding products cause the equilibrium to shift (left) to produce more reactants.
- 2) Adding reactants cause the equilibrium to shift (right) to produce more products.
- 3) Removing reactants cause the equilibrium to shift (left) to produce more reactants.
- 4) Removing products cause the equilibrium to shift (right) to produce more products.

5) Increasing temperature of exothermic ($\Delta H_{\text{rxn}} = \text{negative}$, shift (left)) or endothermic ($\Delta H_{\text{rxn}} = \text{positive}$, shift (right)) and vice versa.

6) Increasing pressure affect a reaction if there is change stoichiometric coefficients (Δn) of gaseous reactants and products: (Δn) = 0, no change; (Δn) = +, shift (left)); (Δn) = -, shift (right)) and vice versa. $\Delta n = \sum n$ (products) - $\sum n$ (reactants).

E.g. $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g}); \text{H} = 40 \text{ kJ}$

1) shift left, 2)) shift right, 3) to shift (left), 4) shift (right), 5) $T \downarrow$, shift (left); $T \uparrow$, shift (right); 6) (Δn) = 0, no change E.g.

Increasing T of the equilibrium should shift equilibrium to left and vice versa.

Increasing P will shift equilibrium to right and vice versa.

Note: **volume changes** can be considered as pressure changes. Increased volume have the same effect as a decrease in pressure.

Key Questions (relatively simple to answer using the Focus Information)

- 1) Chemical equilibrium is reached in a reaction when
 - a) All reactions stop.
 - b) The forward reaction stop.
 - c) The concentration of products and reactants become equal.
 - d) Rate of forward and reverse reaction become equal.
 - e) The temperature become constant.
- 2) For the equilibrium : $\text{A}(\text{g}) + \text{B}(\text{g}) \rightleftharpoons \text{C}(\text{g}) + \text{D}(\text{g})$. Are the concentrations of A,B,C, and D changing if 100 molecules per second of A and B are being converted into C and D by the forward reaction and 100 molecules per second of C and D are being converted in to A and B by the reverse reaction? Explain.
- 3) What is an example of dynamic equilibrium you have seen?
- 4) What are the homogenous and heterogeneous equilibria among the following?
 - a) $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$
 - b) $\text{NH}_4\text{Cl}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$
 - c) $\text{NaCl}(\text{s}) \rightleftharpoons \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
- 5) What items goes into the numerator and denominator in equilibrium constant expression?
- 6) What determines the exponent of each concentration in the equilibrium constant expression?
- 7) What is the difference between initial $[\text{A}]_i$ and equilibrium $[\text{A}]_{\text{eq}}$ concentrations?

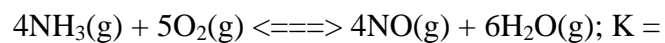
- 8) Which will be present in the largest amounts, reactants or products, when
- The equilibrium constant is large?
 - The equilibrium constant is small?
- 9) Write the equilibrium expression for following reactions:
- $\text{CO(g)} + \text{Cl}_2\text{(g)} \rightleftharpoons \text{COCl}_2\text{(g)} : K =$
 - $\text{N}_2\text{O}_4\text{(g)} \rightleftharpoons 2\text{NO}_2\text{(g)} : K =$
 - $\text{MgCO}_3\text{(s)} \rightleftharpoons \text{MgO(s)} + \text{CO}_2\text{(g)} : K =$
 - $\text{NaCl(s)} \rightleftharpoons \text{Na}^+\text{(aq)} + \text{Cl}^-\text{(aq)} : K =$
- 10) What is the difference between K and K_p ?
Write K and K_p for the reaction: $\text{CO(g)} + \text{Cl}_2\text{(g)} \rightleftharpoons \text{COCl}_2\text{(g)}$
 $K =$ $K_p =$
- 11) Given the equilibrium constant, concentration of reactants and products of reaction, How could you determine if the reaction is at equilibrium or not?
- 12) Given the concentrations of reactants and products and the equilibrium constant, how could you determine whether the reaction will proceed in the forward or the reverse direction to reach equilibrium?

Exercise

- 13) For the reaction, $5\text{CO(g)} + \text{I}_2\text{O}_5\text{(s)} \rightleftharpoons \text{I}_2\text{(g)} + 5\text{CO}_2\text{(g)}$
- the expression for K_c is:
 - the expression for K_p is:
- 14) Consider the equilibrium $3\text{H}_2\text{(g)} + \text{N}_2\text{(g)} \rightleftharpoons 2\text{NH}_3\text{(g)}$ at a certain temperature. An equilibrium mixture in a 4.00-L vessel contains 1.60 mol $\text{NH}_3\text{(g)}$, 0.800 mol $\text{N}_2\text{(g)}$, and 1.20 mol $\text{H}_2\text{(g)}$. What is the value of K_c ?
- 15) According to La Chatelier's Principle, for the following reaction at equilibrium:
 $2\text{NO(g)} + \text{Cl}_2\text{(g)} \rightleftharpoons 2\text{ClNO(g)}; \Delta H = -$ (exothermic)

- a) If the pressure of the reaction container is decreased, what can you say about pressure or the concentration of Cl_2 ?
- b) If the temperature is increased, which way the equilibrium would shift?

16) Consider the reaction:



- a) The equilibrium constant expression of the reaction is: K
- b) The equilibrium constant expression for reverse of this reaction in terms of K is:
- c) The equilibrium constant expression for of this reaction multiplied by a factor of two and in terms of K is: