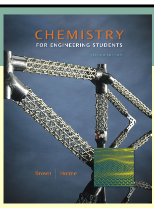

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Chapter 12
Chemical Equilibrium

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Chapter Objectives

- List chemical reactions important in the production and weathering of concrete.
- Explain that equilibrium is dynamic and that at equilibrium, the forward and backward reaction rates are equal. State these ideas in your own words.
- Write the equilibrium constant expression for any reversible reaction.
- Calculate equilibrium constants from experimental data.

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Chapter Objectives

- Calculate equilibrium composition from initial data and the numerical value of the equilibrium constant.
- Calculate molar solubility from K_{sp}, or vice versa.
- Write equilibrium constants for the dissociation of weak acids and weak bases and use them to calculate pH or the degree of ionization.
- Use Le Châtelier's principle to explain the response of an equilibrium system to an applied stress.

3

Chapter Objectives

- Calculate the new equilibrium composition of a system after an applied stress.
- Explain the importance of both kinetic and equilibrium considerations in the design of an industrial chemical process.

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Concrete Production and Weathering

- Traditionally, concrete has been composed of cement, water, and aggregate.
- Modern concrete includes admixtures, which are additives that manipulate concrete into having desired properties.
- Most concrete uses Portland cement, which begins with the production of CaO from limestone.

$$\mathrm{CaCO_3 \rightarrow CaO + CO_2}$$

  - This process accounts for an estimated 5% of CO_2 released into the atmosphere annually.

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Concrete Production and Weathering

- Cement also includes oxides of silicon and aluminum.
- The combination is hydrated (water is added) when concrete is mixed. Three representative hydration reactions:

$$\mathrm{3CaO \bullet Al_2O_3 + 6H_2O \rightarrow Ca_3Al_2(OH)_{12}}$$

$$\mathrm{2CaO \bullet SiO_2} + x\,\mathrm{H_2O \rightarrow Ca_2SiO_4} \bullet x\,\mathrm{H_2O}$$

$$\mathrm{3CaO + SiO_2} + (x+1)\mathrm{H_2O \rightarrow Ca_2SiO_4} \bullet x\mathrm{H_2O + Ca(OH)_2}$$

- These reactions release heat from net formation of bonds.

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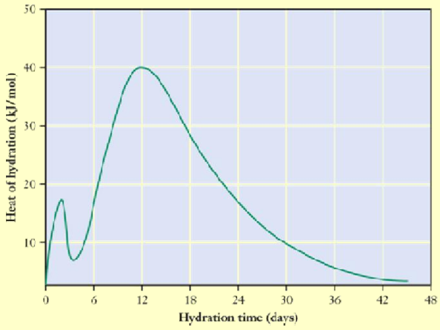
Concrete Production and Weathering



Energy liberated from concrete hydration as a function of time.

7

Concrete Production and Weathering

- The use of fly ash to partially replace Portland cement has become common recently.
  - Fly ash is generated when coal is burned in power plants. Minerals present in the coal react with oxygen at high temperatures to produce fly ash.
  - The average composition of fly ash is similar to Portland cement with the main components being SiO_2, Al_2O_3, Fe_2O_3, and CaO.
  - Fly ash typically consists of small spherical particles and can improve the strength of concrete.

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Concrete Production and Weathering

- Uses of admixtures
  - Water reducers: lower the amount of water in the concrete without affecting the ability to work with it.
  - Air entraining admixtures: improve concrete durability by stabilizing small air bubbles within the cement portion of concrete, particularly when exposed to freeze-thaw cycles.
  - Waterproofers: combat effects of moisture.
  - Accelerators or retardants: affect the speed of the hardening process.

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Concrete Production and Weathering

Table 12.1

Chemical composition of selected admixtures

Function	Compound	Origin
Water reduction	Lignosulfonate	Wood/pulp byproduct
Water reduction	Hydroxycarboxylic acids	Chemical production
Air entrainment	Abietic and pimeric acids	Wood resins
Air entrainment	Alkyl-aryl sulphonates	Industrial detergents
Waterproofing	Fatty acids	Vegetable and animal fats
Acceleration	Calcium chloride	Chemical production
Acceleration	Calcium formate	Chemical production byproduct
Acceleration	Triethanolamine	Chemical production
Retardation	Borates	Borax mining
Retardation	Magnesium salts	Chemical production

- Uses for admixtures and common chemicals that provide desired characteristics in concrete.

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Concrete Production and Weathering

- Weathering of concrete
  - Freeze-thaw cycles
  - Aging of concrete through carbonation, where CO_2 from the air diffuses into the concrete.

$$Ca(OH)_2(s) \longrightarrow Ca^{2+}(aq) + 2OH^-(aq)$$
$$Ca^{2+}(aq) + 2OH^-(aq) + CO_2(g) \longrightarrow CaCO_3(s) + H_2O(l)$$

    - Interior of concrete appears pink with phenolphthalein indicator, which is pink under basic conditions.
    - The exterior of concrete will not turn pink because carbon dioxide from air reacts with hydroxide to neutralize it.

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Chemical Equilibrium

- For complex chemical reactions, there are several variables that must be considered.
- The nature of the reactants, including the equilibrium that ultimately dictates the efficiency of the reaction, is the first issue that must be considered.
- Water in an open system, such as a glass, will slowly evaporate, decreasing the amount of liquid water over time.
- Water in a closed system, such as a covered glass, will establish a dynamic equilibrium, where the amount of liquid water present does not decrease over time.

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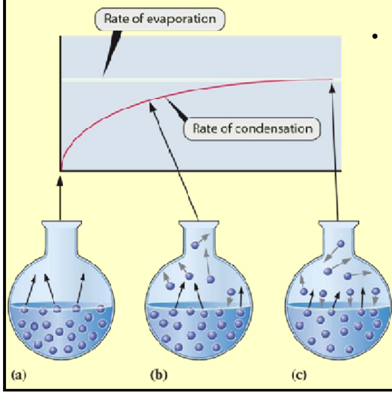
Forward and Reverse Reactions

- This photo sequence shows the water level in two glasses over the course of 17 days. The glass on the left is covered.

Forward and Reverse Reactions

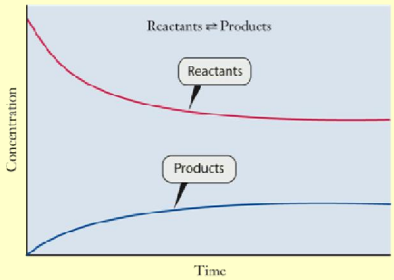


- The equilibrium between liquid and vapor in a closed container is governed by the kinetics of evaporation and condensation.
  - In (c), the two rates are equal.

Forward and Reverse Reactions

- At the start of a chemical reaction, the reactant concentrations decrease over time, with a corresponding decrease in rate of the forward reaction.
- As the reactants are being consumed, the product concentration increases, with a corresponding increase in the rate of the reverse reaction.
- When the rate of the forward reaction equals the rate of the reverse reaction, the reaction has reached equilibrium.
  - Reactants form products at the same rate the products reform the reactants.
  - The concentrations of reactants and products do not change over time at equilibrium.

Forward and Reverse Reactions



- A chemical system reaches equilibrium when the rate of the forward reaction equals the rate of the reverse reaction.
- The concentration of products and reactants does not change at equilibrium.

Mathematical Relationships

- For any reaction involving reactants, R, and products, P, the chemical reaction is written at equilibrium with a double arrow.

R Ä P

- Rate laws for the forward and reverse reaction can be written.

$$\text{Rate}_{\text{for}} = k_{\text{for}}[\text{R}]$$

$$\text{Rate}_{\text{rev}} = k_{\text{rev}}[\text{P}]$$

Mathematical Relationships

- At equilibrium $\text{Rate}_{\text{for}} = \text{Rate}_{\text{rev}}$.
  - Therefore

$$k_{\text{for}}[\text{R}]_{\text{eq}} = k_{\text{rev}}[\text{P}]_{\text{eq}}$$

  - or

$$\frac{k_{\text{for}}}{k_{\text{rev}}} = \frac{[\text{P}]_{\text{eq}}}{[\text{R}]_{\text{eq}}}$$

Mathematical Relationships

$$\frac{k_{\text{for}}}{k_{\text{rev}}} = \frac{[\text{P}]_{\text{eq}}}{[\text{R}]_{\text{eq}}}$$

- Since both k_{for} and k_{rev} are constants, and as long as temperature does not change, the left hand side of the equation is a constant.
- This means at a given temperature, the ratio $[P]_{eq}/[R]_{eq}$ is also a constant.

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Equilibrium Constants

- The amounts of reactants and products are determined using a mathematical model to describe equilibrium.
  - A relationship exists between reactant and product concentrations at equilibrium (the ratio of products to reactants is constant at a given temperature).
- This relationship is often called the law of mass action.

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The Equilibrium (Mass Action) Expression

- For the general chemical equation

$$a\,\text{A} + b\,\text{B} \rightleftharpoons c\,\text{C} + d\,\text{D}$$

- A ratio of concentrations, whether or not at equilibrium, can be defined, where Q is the reaction quotient.

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

- At equilibrium, Q = *K*, the equilibrium constant, and this ratio becomes the equilibrium expression.

$$K = \frac{[\text{C}]^c_{\text{eq}}[\text{D}]^d_{\text{eq}}}{[\text{A}]^a_{\text{eq}}[\text{B}]^b_{\text{eq}}}$$

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Example Problem 12.1

- Write the equilibrium expression for this reaction.

$$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$$

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Gas Phase Equilibria: K_P vs. K_C

- Equilibrium expressions can be written for gas phase reactions using partial pressures.
  - K_p is the equilibrium constant in terms of partial pressures.

$$a\ \text{A(g)} + b\ \text{B(g)} \rightleftharpoons c\ \text{C(g)} + d\ \text{D(g)}$$

$$K_{\text{P}} = \frac{(\text{P}_\text{C})^c_{\text{eq}}(\text{P}_\text{D})^d_{\text{eq}}}{(\text{P}_\text{A})^a_{\text{eq}}(\text{P}_\text{B})^b_{\text{eq}}}$$

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Gas Phase Equilibria: K_P vs. K_C

- The values of K_c and K_p are not necessarily equal. The relationship between K_c and K_p is:

$$K_{\text{P}} = K_{\text{C}} \times RT^{(\Delta n_{\text{gas}})}$$

  - Δn_{gas} is moles of product gas minus the moles of reactant gas.
  - Only when $\Delta n_{gas} = 0$ does $K_P = K_C$.
  - All equilibrium constants in this text are based on molar concentrations. The subscript "c" will not be used.

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Homogeneous and Heterogeneous Equilibria

- Homogeneous equilibria - the reactants and products are in the same phase, either gaseous or aqueous.
- Heterogeneous equilibria - the reactants and products are in different phases.
  - Heterogeneous equilibrium expressions *do not contain terms for solids and liquids*.
    - The concentration of a solid or liquid does not change because these substances are pure.

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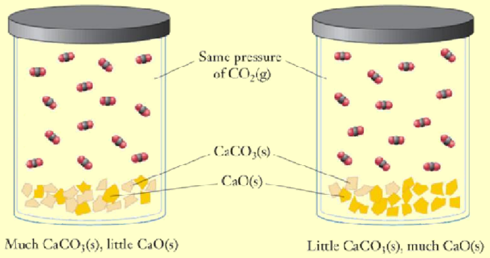
Homogeneous and Heterogeneous Equilibria



- For the decomposition reaction of $CaCO_3$(s) forming CaO(s) and CO_2(g), the equilibrium constant only depends on the CO_2 concentration because $CaCO_3$ and CaO are solids.

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Example Problem 12.2

- Calcium hydroxide will precipitate from solution by the following equilibrium:

$$\mathrm{Ca^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Ca(OH)_2(s)}$$

- Write the equilibrium expression for this reaction.

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Numerical Importance of the Equilibrium Expression

- The size of the equilibrium constant indicates the direction a chemical reaction will likely proceed.

$$K = \frac{[\text{products}]}{[\text{reactants}]}$$

  - For large values of *K*, *K* >> 1, products are favored.
  - For small values of *K*, *K* << 1, reactants are favored.

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Example Problem 12.3

- In Example Problem 12.2, we saw that hydroxide ions precipitate with calcium. Magnesium ions show similar behavior. The two pertinent equilibria are:

$$\mathrm{Ca^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Ca(OH)_2(s)} \qquad K = 1.3 \times 10^5$$
$$\mathrm{Mg^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Mg(OH)_2(s)} \qquad K = 6.7 \times 10^{11}$$

- Which ion is more likely to precipitate hydroxide from a solution, assuming roughly equal concentrations of calcium and magnesium ions?

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Mathematical Manipulation of Equilibrium Constants

- When reversing a chemical reaction by switching the reactants and products, the value of the equilibrium constant for the new reaction is the inverse of the value of the original equilibrium constant.

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D} \qquad K = \frac{[\mathrm{C}]_{eq}^c [\mathrm{D}]_{eq}^d}{[\mathrm{A}]_{eq}^a [\mathrm{B}]_{eq}^b}$$

$$c\mathrm{C} + d\mathrm{D} \rightleftharpoons a\mathrm{A} + b\mathrm{B} \qquad K' = \frac{[\mathrm{A}]_{eq}^a [\mathrm{B}]_{eq}^b}{[\mathrm{C}]_{eq}^c [\mathrm{D}]_{eq}^d}$$

$$K' = \frac{1}{K}$$

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Adjusting the Stoichiometry of the Chemical Reaction

- If changes are made to the stoichiometry (represented by factor *n*), the changes affect the equilibrium expression.
  - Multiply the stoichiometric coefficients in a chemical reaction by a factor *n*, the *K* for the new chemical equation, *K*′, equals K^{n}.

$$aA + bB \ \text{Ä} \ \ cC + dD \qquad K = \frac{[C]_{eq}^{c}[D]_{eq}^{d}}{[A]_{eq}^{a}[B]_{eq}^{b}}$$

$$\frac{a}{2}A + \frac{b}{2}B \ \text{Ä} \ \ \frac{c}{2}C + \frac{d}{2}D \qquad K' = \frac{[C]_{eq}^{\frac{c}{2}}[D]_{eq}^{\frac{d}{2}}}{[A]_{eq}^{\frac{a}{2}}[B]_{eq}^{\frac{b}{2}}}$$

  - Equation 1 was multiplied by *n* = 1/2.
  - $K' = K^{n}$ or $K' = K^{1/2}$

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Example Problem 12.4

- Write equilibrium expressions for:

$$N_2(g) + 3H_2(g) \,\text{Ä}\ \ 2NH_3(g)$$

  - the reaction written
  - the reverse reaction
  - the reaction as written with all coefficients in the equation halved

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Equilibrium Constants for a Series of Reactions

- When two chemical reactions are added (summed), the equilibrium constant for the new chemical reaction is the product of the equilibrium constants for the two original chemical reactions.
  - Where K_1 and K_2 are equilibrium constants for the two chemical reactions being combined and K_3 is the equilibrium constant for the new combined chemical reaction.

$$K_3 = K_1 \times K_2$$

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Example Problem 12.5

- Given the following equilibria:

$$CO_2(g) \ \text{Ä} \ \ CO(g) + \frac{1}{2}O_2(g)$$

$$H_2(g) + \frac{1}{2}O_2(g) \,\text{Ä}\ \ H_2O(g)$$

Determine the equilibrium expression for the sum of the two reactions.

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Units and the Equilibrium Constant

- The equilibrium constant *K* is dimensionless.
  - The concentrations used to calculate the equilibrium constant are divided by the standard concentration of 1 M, which has no numerical consequence.
  - A dimensionless *K* is required when *K* is used as the argument in a natural log function.

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Equilibrium Concentrations

- The equilibrium concentrations of reactants and products for a chemical reaction can be predicted using the balanced chemical equation and known equilibrium constants.
  - There are three basic features for the strategy used in any equilibrium calculation.
    - Write a balanced chemical equation for the relevant equilibrium or equilibria.
    - Write the corresponding equilibrium expression or expressions.
    - Create a table of concentrations for all reacting species.

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Equilibrium Concentrations

- Equilibrium concentrations can be determined from initial concentrations by realizing:
  - The first row contains the initial concentrations.
  - The second row contains the changes in the initial concentrations as the system come to equilibrium.
  - The third row contains the final equilibrium concentrations.
- Equilibrium concentrations can be determined from initial concentrations by realizing which direction the reaction will shift to achieve equilibrium, express the concentration change in terms of a single variable, and solve for the equilibrium concentrations using the equilibrium expression.

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Example Problem 12.6

- Calculate the equilibrium concentrations of H_2, I_2 and HI, if the initial concentrations are 0.050 M each for H_2 and I_2 and K = 59.3 at 400ºC.

$$\mathrm{H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)}$$

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Equilibrium Concentrations from Initial Concentrations

- The concentration of HI = 0 initially, so the reaction will shift to the right to achieve equilibrium.

	H_2	I_2	HI
Initial Concentration	0.050 M	0.050 M	0 M
Change in Concentration			
Final Concentration			

- For every x moles of H_2 and I_2 consumed, $2x$ moles of HI are produced.

	H_2	I_2	HI
Initial Concentration	0.050 M	0.050 M	0 M
Change in Concentration	$-x$	$-x$	$+2x$
Final Concentration			

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Equilibrium Concentrations from Initial Concentrations

	H_2	I_2	HI
Initial Concentration	0.050 M	0.050 M	0 M
Change in Concentration	$-x$	$-x$	$+2x$
Final Concentration	$0.050 - x$	$0.050 - x$	$2x$

- The final concentrations are expressed in terms of the initial concentration minus x for the reactants and initial concentration plus $2x$ for the products.
- Substitute the algebraic final concentration terms into the equilibrium concentration and solve for x.

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Equilibrium Concentrations from Initial Concentrations

$$K=\frac{[\mathrm{HI}]^2}{[\mathrm{H_2}][\mathrm{I_2}]}=\frac{(2x)^2}{(0.050-x)(0.050-x)}=59.3$$

$$\sqrt{\frac{(2x)^2}{(0.050-x)(0.050-x)}}=\sqrt{59.3}$$

$$\frac{2x}{0.050-x}=7.70$$

$$0.39=9.70x$$

$$x=0.040$$

$$[\mathrm{H_2}]=[\mathrm{I_2}]=0.050-x$$

$$[\mathrm{H_2}]=[\mathrm{I_2}]=0.050-0.040=0.010\ \mathrm{M}$$

$$[\mathrm{HI}]=2x=0.080\ \mathrm{M}$$

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Example Problem 12.7

- The equilibrium constant for the reaction of chlorine gas with phosphorous trichloride to form phosphorus pentachloride is 33 at 250° C. If an experiment is initiated with concentrations of 0.050 M PCl_3 and 0.015 M Cl_2, what are the equilibrium concentrations of all three gases?

$$\mathrm{Cl_2(g) + PCl_3(g) \rightleftharpoons PCl_5(g)}$$

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Mathematical Techniques for Equilibrium Calculations

- For complex equilibria that cannot be solved using the quadratic equation, software packages such as Maple®, and Mathematica® must be used.
- Equilibrium expressions help process engineers determine ways to manipulate equilibria to improve efficiency.

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Le Châtelier's Principle

- Le Châtelier's principle - When a system at equilibrium is stressed, it responds by reestablishing equilibrium to reduce the stress.
- There are three common means to introduce a stress to an equilibrium.
  - Changes in concentration
  - Changes in pressure
  - Changes in temperature

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Effect of a Change in Concentration

- For a reaction at equilibrium, a change in concentration for one or more of the reactants and/or products will disturb the equilibrium.
  - The system will react to re-establish equilibrium.
- For a reaction at equilibrium, increasing the concentration of one of the reactants will shift the equilibrium toward the products.
  - The reactant concentration will decrease as reactant is converted to product, and the product concentration will increase until equilibrium is re-established.

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Effect of a Change in Concentration

- The increase in product concentration for a reactant concentration increase can be rationalized by examining the reaction quotient.
  - The reactant quotient, *Q*, is defined as the ratio of the product to the reactants.
  - For a reaction at equilibrium, *K* = *Q*.

$$Q = \frac{[\text{products}]}{[\text{reactants}]}$$

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Effect of a Change in Concentration

- For a reactant concentration increase, the value of *Q* becomes small compared to *K*.
- To re-establish equilibrium, *Q* must equal *K*.
  - The value of *Q* will approach *K* as the reactant concentration decreases and as the product concentration increases.

$$Q = \frac{[\text{products}]}{[\text{reactants}]}$$

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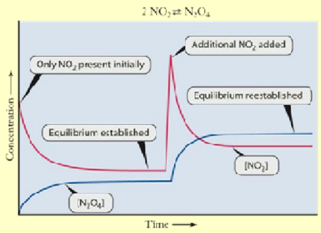
Effect of a Change in Concentration



- Placed in an empty flask, NO_2 achieves equilibrium by reacting to form N_2O_4.
- Once at equilibrium, additional NO_2 is added. The system responds to this stress by shifting the equilibrium toward N_2O_4.

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Effect of a Change in Concentration

Table 12.2

The effects of concentration changes on equilibrium can be rationalized by considering the reaction quotient, Q, and comparing it to the equilibrium constant, K.

Type of Concentration Change	Resulting Change in Q	Response of System
[Products] increased	$Q > K$	More reactants formed
[Products] decreased	$Q < K$	More products formed
[Reactants] increased	$Q < K$	More products formed
[Reactants] decreased	$Q > K$	More reactants formed

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Example Problem 12.8

- Predict the change in the reaction quotient, Q, when:

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

  - sodium acetate is added
  - additional acetic acid is added
  - sodium hydroxide is added
- Then, explain how the equilibrium shifts in response to each stress.

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Effect of a Change in Pressure

- For reactions involving gases, if the number of moles of gas differs between reactants and products, a shift in pressure (due to a volume change) will result in a change in equilibrium position.
  - For an increase in pressure, the equilibrium will shift toward the side of the equation with fewer moles of gas.
  - For a decrease in pressure, the equilibrium will shift toward the side of the equation with more moles of gas.

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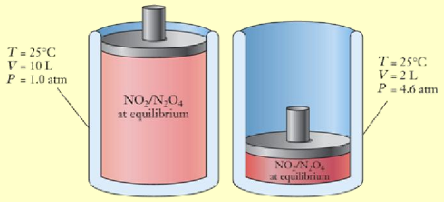
Effect of a Change in Pressure



- For the equilibrium between NO_2 and N_2O_4, the increase in pressure is offset by reducing the moles of gas present by forming N_2O_4.
- Decreasing the volume to 2 L initially increases the pressure to 5.0 atm.
  - Equilibrium is re-established when the pressure is reduced to 4.6 atm by reacting 2 NO_2 to form N_2O_4.

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Example Problem 12.9

- Predict the direction in which the reaction will go to respond to the indicated stress.

$NH_3(g) + CH_4(g) \rightleftharpoons HCN(g) + 3H_2(g)$; pressure is increased

$2NH_3(g) + 2CH_4(g) + 3O_2(g) \rightleftharpoons 2HCN(g) + 6H_2O(g)$; pressure is decreased

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Effect of a Change in Temperature on Equilibrium

- During a temperature change, heat flows in or out of the reacting system.
  - Heat is treated as a product for an exothermic reaction.

$$\text{reactants} \rightleftharpoons \text{products} + \text{heat}$$

  - Heat is treated as a reactant for an endothermic reaction.

$$\text{reactants} + \text{heat} \rightleftharpoons \text{products}$$

- Increase the temperature, equilibrium shifts away from the side with the heat.
- Decrease the temperature, equilibrium shifts toward the side with the heat.

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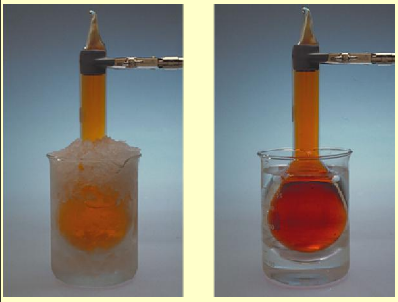
Effect of a Change in Temperature on Equilibrium



- Temperature effect on the equilibrium between NO_2 and N_2O_4, an exothermic reaction.
  - As temperature increases, the amount of NO_2 increases, as indicated by the deepening color of the NO_2 gas in the 50ºC water bath (right) compared to the ice bath (left).

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Effect of a Change in Temperature on Equilibrium

Table 12.3

The effects of temperature changes on a chemical system at equilibrium depend on whether the reaction is exothermic or endothermic. Unlike concentration or pressure changes, temperature changes also alter the *value* of the equilibrium constant.

Type of Reaction	Type of Temperature Change	Response of System
Exothermic	*T* increase	More reactants formed
Exothermic	*T* decrease	More products formed
Endothermic	*T* increase	More products formed
Endothermic	*T* decrease	More reactants formed

- Summary of the effects a temperature change will have on exothermic and endothermic reactions at equilibrium.

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Effect of a Catalyst on Equilibrium

- When a catalyst is added to a system at equilibrium, there is no impact on the equilibrium position.
  - Catalysts speed up the rate of the forward and reverse reactions **to the same extent**.
  - The equilibrium concentrations of products and reactants do not change.

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Free Energy and Chemical Equilibrium

- Equilibrium is a state of minimum free energy.
  - ΔG = 0 at equilibrium.
- A chemical system tends to move spontaneously toward equilibrium.
  - When equilibrium is reached, the change in free energy is zero.

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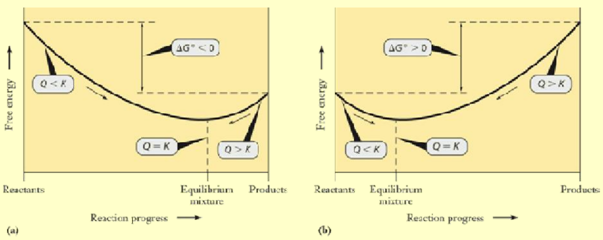
Graphical Perspective



- Chemical reactions always proceed toward a minimum in free energy.

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Free Energy and Nonstandard Conditions

- For reactions with negative free energy changes, the equilibrium is product-favored, or the value of *K* is greater than 1.
- For reactions with positive free energy changes, the equilibrium is reactant-favored, or the value of *K* is less than 1.
- The value of the equilibrium constant can be calculated from the Gibbs free energy change, or vice versa.

$$\Delta G^o = -RT \ln K$$

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Example Problem 12.15

- Using tabulated thermodynamic data, calculate the equilibrium constant for the following reaction at 25˚C:

$$CH_4(g) + \frac{1}{2}O_2(g) \rightleftharpoons CH_3OH(l)$$

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Borates and Boric Acid

- Borax is used as a cross-linker during polymer synthesis.
- Boric acid, $B(OH)_3$, is produced from the reaction between borax, $Na_2B_4O_7{\bullet}10H_2O$, and sulfuric acid.
- Borates are used in a number of industrial applications.
  - They are used to manufacture fiberglass, which is used in both insulation and textiles.
    - Borates are used to control the temperature at which glass melts, allowing melted glass to be pulled into fibers.

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Borates and Boric Acid

- Borosilicate glasses are important in the lab and kitchen because of their resistance to heat-induced deformation.
  - The heat resistance of borosilicate glass is applied to the production of halogen headlights and the cathode ray tubes found in traditional television sets and computer monitors.
- As polymer additives, borates impart fire resistance.
  - Zinc borates have the important property of retaining their waters of hydration at high temperatures, which retards fires.
  - Fires involving plastics containing zinc borate spread more slowly and produce less smoke.

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