CHEMICAL EQUILIBRIUM

Concrete Production and Weathering

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

- Accelerators or retardants: affect the speed of the hardening process.

Mathematical Relationships

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

$$\mathrm{R} \rightleftarrows \mathrm{P}$$

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

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

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

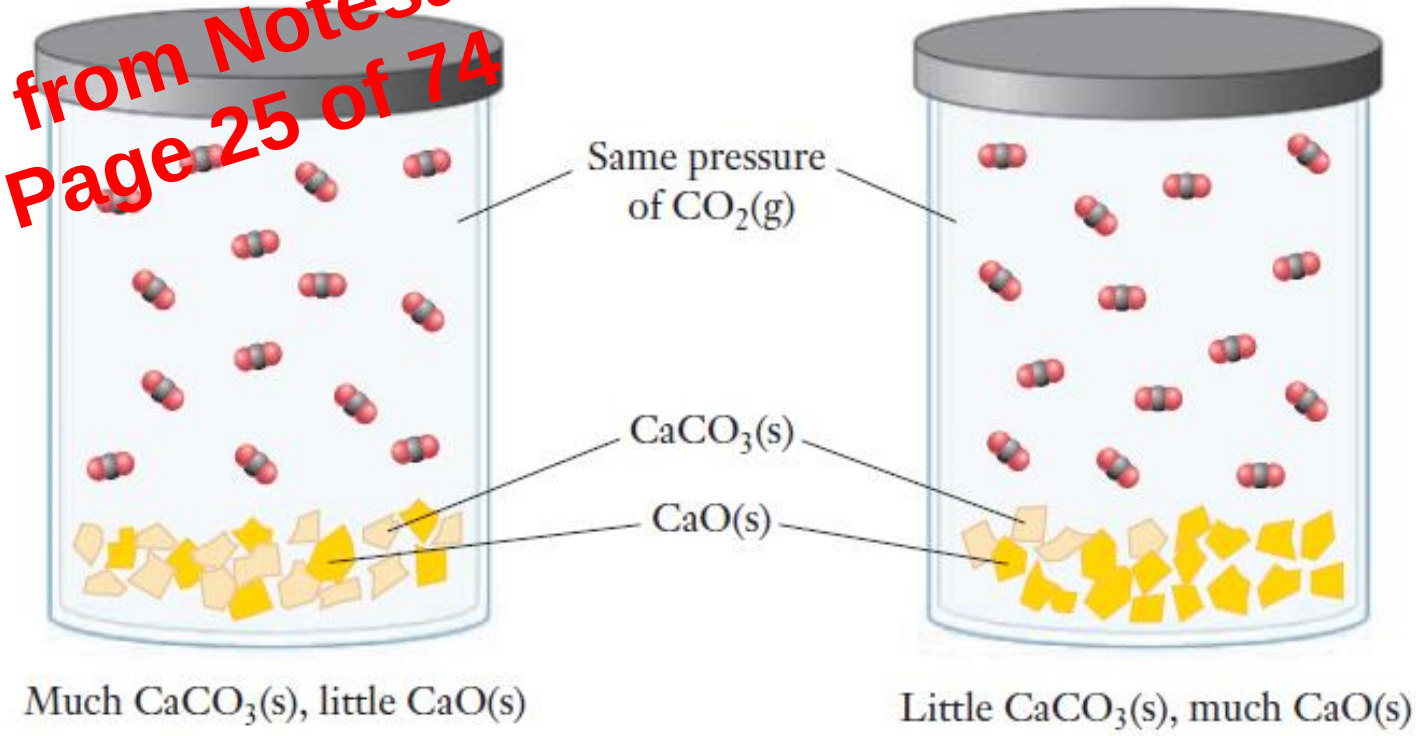
Example Problem 1:

PROBLEM: Concrete used in smokestacks has to be designed to withstand sometimes caustic conditions. Sulfur oxides in particular are produced in some cases, and they would establish equilibrium if they did not disperse:

$$2\ SO_2(g) + O_2(g) \rightleftarrows 2\ SO_3(g)$$

Write the equilibrium expression for this reaction.

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.

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.

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

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

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

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.

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.

Example Problem 6:

SOLUTION:

	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 2*x* for the products.
- Substitute the algebraic final concentration terms into the equilibrium concentration and solve for *x*.

Example Problem 6:

SOLUTION:

$$K = \frac{[HI]^2}{[H_2][I_2]}$$

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

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

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

$$0.385 - 7.7x = 2x$$

$$2x + 7.7x = 0.385$$

$$9.7x = 0.385$$

$$x = \frac{0.385}{9.7}$$

$$x = 0.040$$

$[H_2] = [I_2] = 0.050 - x$

$[H_2] = [I_2] = 0.050 - 0.040$

$[H_2] = [I_2] = 0.010M$

$[HI] = 2x$

$[HI] = 2(0.040)$

$[HI] = 0.080M$

Effect of a Change in Temperature on Equilibrium

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

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

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.