Section 13.3
Shifting Equilibria: Le Châtelier's Principle

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Learning Objectives

- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Châtelier's principle

Le Châtelier’s principle

- We’ve learned that equilibrium is a dynamic balance where the forward and reverse rates are equal.
- When subjected to a change in conditions that affects these reaction rates differently (a stress), then the equilibrium is disturbed.
- The system will undergo a net reaction in the direction of greater rate (a shift) that will re-establish the equilibrium.
- **Le Châtelier’s principle**: *If an equilibrium system is stressed, the system will experience a shift in response to the stress that re-establishes equilibrium.*

Stressers

- Reaction rates are affected primarily by concentration (reaction's rate law) and temperature (Arrhenius equation).
- An equilibrium stressed by a change in concentration will shift to re-establish equilibrium without any change in the value of the equilibrium constant, *K*.
- An equilibrium stressed by a temperature change, is re-established with a different composition and a new *K* value.

Effect of Concentration

- 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 or removing product the rate of the forward reaction exceeds the reverse.

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

- Removing reactant or adding product to an equilibrium system results in an increased rate for the reverse reaction.

$$\text{rate}_f < \text{rate}_r$$

Q Logic

- You can also rationalize the effect of concentration by considering the reaction quotient.
- When the concentration of a reactant or product in a system at equilibrium is changed the reaction quotient will no longer equal the equilibrium constant.
- The reaction will proceed in the forward or reverse direction until equilibrium is reestablished.

Effect of Volume on Gas Phase Reactions

- If the total molar amounts of reactants and products are equal a change in volume does not shift the equilibrium.
- If the molar amounts of reactants and products are different, a change in volume will shift the equilibrium in a direction that better “accommodates” the volume change.

Volume Change Example

- At equilibrium, the reaction $H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$ is described by the reaction quotient

$$Q_P = \frac{{P_{\mathrm{HI}}}^2}{P_{\mathrm{H_2}}\,P_{\mathrm{I_2}}} = K_p$$

- If the volume is decreased by a factor of 3, the partial pressures of all three species will be increased by a factor of 3:

$$Q_p{}' = \frac{(3P_{\mathrm{HI}})^2}{3P_{\mathrm{H_2}}\,3P_{\mathrm{I_2}}} = \frac{9P_{\mathrm{HI}^2}}{9P_{\mathrm{H_2}}\,P_{\mathrm{I_2}}} = \frac{P_{\mathrm{HI}^2}}{P_{\mathrm{H_2}}\,P_{\mathrm{I_2}}} = Q_P = K_P$$

$$Q_P{}' = Q_P = K_P$$

Volume Change Example

- A similar treatment to a different system, $2NO_2\,(g) \rightleftharpoons 2NO\,(g) + O_2\,(g)$ yields a different result:

$$Q_P = \frac{P_{NO}{}^2\, P_{O_2}}{P_{NO_2}{}^2}$$

$$Q_P{}' = \frac{(3P_{NO})^2\, 3P_{O_2}}{(3P_{NO_2})^2} = \frac{9P_{NO}{}^2\, 3P_{O_2}}{9P_{NO_2}{}^2} = \frac{27P_{NO}{}^2\, P_{O_2}}{9P_{NO_2}{}^2} = 3Q_P > K_P$$

$$Q_P{}' = 3Q_P > K_P$$

Effect of Temperature

- Consider the elementary reaction

$$A \rightleftharpoons B$$

- Since this is an elementary reaction, the rates laws for the forward and reverse may be derived directly from the balanced equation's stoichiometry:

$$\text{rate}_f = k_f[\text{A}]$$
$$\text{rate}_r = k_r[\text{B}]$$

Effect of Temperature

- When the system is at equilibrium,

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

- Substituting the rate laws into this equality and rearranging gives

$$k_f[\text{A}] = k_r[\text{B}]$$

$$\frac{[B]}{[A]} = \frac{k_f}{k_r} = K_c$$

- Since the rate constants vary with temperature as described by the Arrhenius equation, is stands to reason that the equilibrium constant will likewise vary with temperature

Heat as a Reagent

- 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.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = +57.20\,\mathrm{kJ}$$

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

$$\mathrm{heat} + N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Effect of a Catalyst

- The lowered transition state energy of the catalyzed reaction results in lowered activation energies for both the forward and the reverse reactions.
- Both forward and reverse reactions are accelerated, and equilibrium is achieved faster *without a change in the equilibrium constant*.