Chemistry 132 NT

Pretty much all the honest truth-telling there is in the world is done by children.

Oliver Wendell Holmes

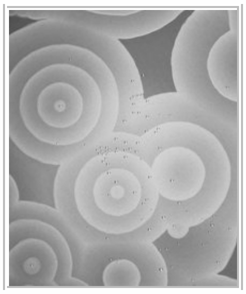
Chem 132 NT

Chemical Equilibrium

Module 3

Le Chatelier's Principle

- **Removing Products or Adding Reactants**
- **Changing the Pressure and Temperature**
- **Effect of a Catalyst**



Oscillating patterns formed by a reaction far from equilibrium

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Review

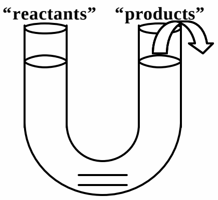
- Qualitatively interpreting the equilibrium constant.
- Predicting the direction of reaction using $\mathbf{Q_c}$.
- Calculating equilibrium concentrations (also using the quadratic equation).

Le Chatelier's Principle

- Obtaining the **maximum** amount of product from a reaction depends on the proper set of reaction conditions.
  - **Le Chatelier's principle** states that when a system in a chemical equilibrium is disturbed by a **change of temperature, pressure, or a concentration**, the **equilibrium will shift** in a way that tends to counteract this change.

Removing Products or Adding Reactants

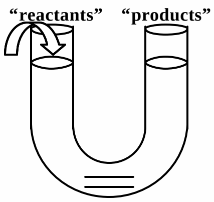
- Let's refer back to the illustration of the U-tube in the first section of this chapter.



It's a simple concept to see that if we were to **remove products** (analogous to dipping water out of the right side of the tube) the **reaction would shift to the right** until equilibrium was reestablished.

Removing Products or Adding Reactants

- Let’s refer back to the illustration of the U-tube in the first section of this chapter.



Likewise, if **more reactant is added** (analogous to pouring more water in the left side of the tube) the **reaction would again shift to the right** until equilibrium is reestablished.

A Problem To Consider

- Predict the direction of reaction when H_2 is removed from a mixture (lowering its concentration) in which the following equilibrium has been established.

$$H_2(g) + I_2(g) \underset{\longleftarrow}{\rightleftharpoons} 2HI(g)$$

  - When H_2 is removed from the reaction mixture, lowering its concentration, **the reaction goes in the reverse direction** to partially restore the H_2 that was removed.

Effects of Pressure Change

- A pressure change caused by changing the volume of the reaction vessel can affect the yield of products in a gaseous reaction **only if the reaction involves a change in the total moles of gas present**.
  - The methanation reaction below is an example of a change in the moles of gas.

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

Effects of Pressure Change

- A pressure change caused by changing the volume of the reaction vessel can affect the yield of products in a gaseous reaction **only if the reaction involves a <u>change in the total moles of gas present</u>.**
  - When the reaction goes in the forward direstion, **four** moles of reactant gas (CO + 3 H_2) become **two** moles of product gas (CH_4 + H_2O).

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

Effects of Pressure Change

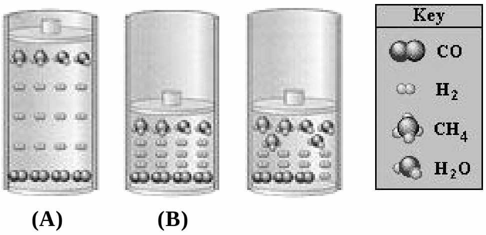
- If the products in a gaseous reaction contain **fewer moles of gas** than the reactants, it is logical that they would require less space.
  - So, reducing the volume of the reaction vessel would favor the products in this case.

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

(A)

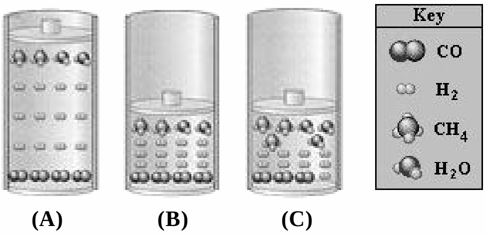
(A) The original equilibrium mixture of CO, H_2, CH_4, and H_2O.

$$\mathrm{CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)}$$



(B) The gases are compressed to one-half the original volume, increasing their partial pressures…no longer at equilibrium.

$$\mathrm{CO(g) + 3H_2(g) \overset{\longrightarrow}{\rightleftharpoons} CH_4(g) + H_2O(g)}$$



(C) Equilibrium is reestablished when the reaction goes in the forward direction.

Effects of Pressure Change

- So literally “squeezing” the reaction will cause a **shift in the equilibrium toward the fewer moles of gas**.
  - It’s a simple step to see that reducing the pressure in the reaction vessel by increasing its volume would have the opposite effect.

Effects of Pressure Change

- So literally “squeezing” the reaction will cause a **shift in the equilibrium toward the fewer moles of gas**.
  - In the event that the **number of moles of gaseous product equals the moles of gaseous reactant, vessel volume will have no effect on the position of the equilibrium.**

For example, $$\underbrace{H_2(g) + I_2(g)}_{\textbf{2 moles of gas}} \rightleftharpoons \underbrace{2HI(g)}_{\textbf{2 moles of gas}}$$

A Problem To Consider

- Look at the following equations and decide whether an increase in pressure (by decreasing the volume) will **increase**, **decrease**, or have **no effect** on the amount of products.

$$\mathbf{CO(g) + Cl_2(g) \leftrightarrows COCl_2(g)}$$

  - This reaction decreases the molecules of gas (from two to one).
  - According to LeChatelier’s principle, an increase in pressure should **increase** the amount of product.

A Problem To Consider

- Look at the following equations and decide whether an increase in pressure (by decreasing the volume) will **increase**, **decrease**, or have **no effect** on the amount of products.

$$\mathbf{2H_2S(g) \leftrightarrows 2\ H_2(g) + S_2(g)}$$

  - This reaction **increases** the molecules of gas (from one to two).
  - According to LeChatelier’s principle, an increase in pressure should **decrease** the amount of product.

A Problem To Consider

- Look at the following equations and decide whether an increase in pressure (by decreasing the volume) will **increase**, **decrease**, or have **no effect** on the amount of products.

$$C(s) + S_2(g) \leftrightarrows CS_2(g)$$

  - This reaction does not change the number of molecules of gas. (note that we ignore solid carbon)
  - According to LeChatelier's principle, an increase in pressure has **no effect.**

Effect of Temperature Change

- **Temperature** has a significant effect on most reactions.
  - Reaction rates generally increase with an increase in temperature, consequently, equilibrium is established sooner.
  - In addition, **the numerical value of the equilibrium constant K_c varies with temperature.**

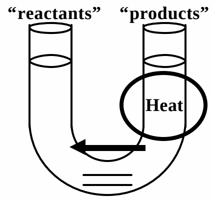
Effect of Temperature Change

- Let's look at "heat" as if it were a **product in exothermic reactions** and a **reactant in endothermic reactions.**
  - This ultimately has the same effect as if heat were a physical entity.
  - We see that **increasing the temperature** is analogous to adding **more product (in the case of exothermic reactions)** or adding **more reactant (in the case of endothermic reactions).**

Effect of Temperature Change

- For example, consider the following generic exothermic reaction.

reactants $\rightleftharpoons$ products + "heat" (DH is negative

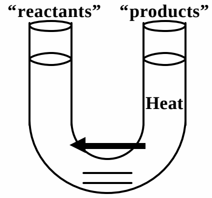


- Increasing temperature would be analogous to adding more product **causing the equilibrium to shift left.**

Effect of Temperature Change

- For example, consider the following generic exothermic reaction.

reactants $\rightleftharpoons$ products + "heat" (DH is negative

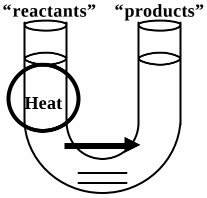


- Since "heat" does not appear in the equilibrium-constant expression, this would result in a **smaller numerical value for K_c.**

Effect of Temperature Change

- For an endothermic reaction, the opposite is true.

"heat" + reactants $\rightleftharpoons$ products (DH is positive

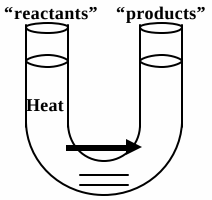


- Increasing temperature would be analogous to adding more reactant **causing the equilibrium to shift right.**

Effect of Temperature Change

- For an endothermic reaction, the opposite is true.

"heat"+reactants ⇌ products (DH is positive



- This results in more product at equilibrium resulting in a **larger numerical value for K_c**.

Effect of Temperature Change

- So, in summary:
  - For an **endothermic reaction** (ΔH positive) the amounts of products are increased at equilibrium by an increase in temperature **(K_c is larger at higher temperatures).**
  - For an **exothermic reaction** (ΔH is negative) the amounts of reactants are increased at equilibrium by an increase in temperature **(K_c is smaller at higher temperatures).**

A Problem To Consider

- Carbon monoxide is formed when carbon dioxide reacts with solid carbon (graphite).

CO_2(g) + C(graphite) ⇆ 2 CO (g) ; DHº = 172.5 kJ

Is a **high** or **low** temperature more favorable to the formation of carbon monoxide?

- The reaction absorbs heat in the forward direction. That is:

HEAT + CO_2(g) + C(graphite) ⇆ 2 CO (g)

A Problem To Consider

- Carbon monoxide is formed when carbon dioxide reacts with solid carbon (graphite).

CO_2(g) + C(graphite) $\leftrightarrows$ 2 CO (g) ; DH^o = 172.5 kJ

Is a **high** or **low** temperature more favorable to the formation of carbon monoxide?

  - As the temperature is raised, reaction occurs in the forward direction.

$$\textbf{HEAT} + CO_2(g) + C(graphite) \overset{\longrightarrow}{\leftrightarrows} 2\,CO\,(g)$$

A Problem To Consider

- Carbon monoxide is formed when carbon dioxide reacts with solid carbon (graphite).

CO_2(g) + C(graphite) $\leftrightarrows$ 2 CO (g) ; DH^o = 172.5 kJ

Is a **high** or **low** temperature more favorable to the formation of carbon monoxide?

  - Thus, **high temperature** is more favorable to the formation of carbon monoxide.

$$\textbf{HEAT} + CO_2(g) + C(graphite) \overset{\longrightarrow}{\leftrightarrows} 2\,CO\,(g)$$

Effect of a catalyst

- A **catalyst** is a substance that increases the rate of a reaction but is not consumed by it.
  - It is important to understand that **a catalyst has no effect on the equilibrium composition** of a reaction mixture.
  - A catalyst merely speeds up the attainment of equilibrium.

Key Equations

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad Q_c = \frac{[C]_i^c[D]_i^d}{[A]_i^a[B]_i^b}$$

Operational Skills

- Solving equilibrium problems
- Applying Le Chatelier’s principle

Time for a few review questions.