Biophysical chemistry

Part A
Chapter: 2
Chemical Equilibrium
Lecture - 2

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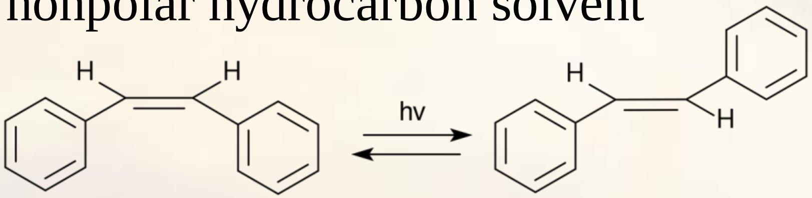
Calculating Equilibrium Concentrations

Let us consider the following system involving two organic compounds, cis-stilbene and trans-stilbene, in a nonpolar hydrocarbon solvent

cis-stilbene ↔ trans-stilbene



cis-stilbene trans-stilbene

The equilibrium constant (Kc) for this system is 24.0 at 200°C. Suppose that initially only cis-stilbene is present at a concentration of 0.850 mol/L. How do we calculate the concentrations of cis- and trans-stilbene at equilibrium?

	cis-stilbene $\rightleftharpoons$	*trans*-stilbene
Initial (M):	0.850	0
Change (M):	$-x$	$+x$
Equilibrium (M):	$(0.850 - x)$	x

$$K_c = \frac{[trans\text{-stilbene}]}{[cis\text{-stilbene}]}$$

$$24.0 = \frac{x}{0.850 - x}$$

$$x = 0.816\ M$$

Calculating Equilibrium Concentrations

$$[cis\text{-stilbene}] = (0.850 - 0.816)\ M = 0.034\ M$$
$$[trans\text{-stilbene}] = 0.816\ M$$

A mixture of 0.500 mol H_2 and 0.500 mol I_2 was placed in a 1.00-L stainless-steel flask at 430°C. The equilibrium constant K_c for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 54.3 at this temperature. Calculate the concentrations of H_2, I_2, and HI at equilibrium.

Step 1: The stoichiometry of the reaction is 1 mol H_2 reacting with 1 mol I_2 to yield 2 mol HI. Let x be the depletion in concentration (mol/L) of H_2 and I_2 at equilibrium. It follows that the equilibrium concentration of HI must be $2x$. We summarize the changes in concentrations as follows:

	H_2	+	I_2	$\rightleftharpoons$	$2HI$
Initial (M):	0.500		0.500		0.000
Change (M):	$-x$		$-x$		$+2x$
Equilibrium (M):	$(0.500 - x)$		$(0.500 - x)$		$2x$

Calculating Equilibrium Concentrations

Step 2: The equilibrium constant is given by

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

Substituting, we get

$$54.3 = \frac{(2x)^2}{(0.500 - x)(0.500 - x)}$$

Taking the square root of both sides, we get

$$7.37 = \frac{2x}{0.500 - x}$$

$$x = 0.393\ M$$

Step 3: At equilibrium, the concentrations are

$$[H_2] = (0.500 - 0.393)\ M = 0.107\ M$$

$$[I_2] = (0.500 - 0.393)\ M = 0.107\ M$$

$$[HI] = 2 \times 0.393\ M = 0.786\ M$$

Calculating Equilibrium Concentrations

For the same reaction and temperature as in Example 14.9, suppose that the initial concentrations of H_2, I_2, and HI are 0.00623 *M*, 0.00414 *M*, and 0.0224 *M*, respectively. Calculate the concentrations of these species at equilibrium.

Strategy From the initial concentrations we can calculate the reaction quotient (Q_c) to see if the system is at equilibrium or, if not, in which direction the net reaction will proceed to reach equilibrium. A comparison of Q_c with K_c also enables us to determine if there will be a depletion in H_2 and I_2 or HI as equilibrium is established.

Solution First we calculate Q_c as follows:

$$Q_c = \frac{[\mathrm{HI}]_0^2}{[\mathrm{H_2}]_0[\mathrm{I_2}]_0} = \frac{(0.0224)^2}{(0.00623)(0.00414)} = 19.5$$

Because Qc (19.5) is smaller than Kc (54.3), we conclude that the net reaction will proceed from left to right until equilibrium is reached (see Figure 14.4); that is, there will be a depletion of H2 and I2 and a gain in HI.

Calculating Equilibrium Concentrations

Step 1: Let x be the depletion in concentration (mol/L) of H_2 and I_2 at equilibrium. From the stoichiometry of the reaction it follows that the increase in concentration for HI must be $2x$. Next we write

	H_2	+	I_2	$\rightleftharpoons$	$2HI$
Initial (M):	0.00623		0.00414		0.0224
Change (M):	$-x$		$-x$		$+2x$
Equilibrium (M):	$(0.00623 - x)$		$(0.00414 - x)$		$(0.0224 + 2x)$

Step 2: The equilibrium constant is

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

Substituting, we get

$$54.3 = \frac{(0.0224 + 2x)^2}{(0.00623 - x)(0.00414 - x)}$$

Calculating Equilibrium Concentrations

$$54.3(2.58 \times 10^{-5} - 0.0104x + x^2) = 5.02 \times 10^{-4} + 0.0896x + 4x^2$$

Collecting terms, we get

$$50.3x^2 - 0.654x + 8.98 \times 10^{-4} = 0$$

This is a quadratic equation of the form $ax^2 + bx + c = 0$. The solution for a quadratic equation (see Appendix 4) is

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Here we have $a = 50.3$, $b = -0.654$, and $c = 8.98 \times 10^{-4}$, so that

$$x = \frac{0.654 \pm \sqrt{(-0.654)^2 - 4(50.3)(8.98 \times 10^{-4})}}{2 \times 50.3}$$

$$x = 0.0114\ M \qquad \text{or} \qquad x = 0.00156\ M$$

Step 3: At equilibrium, the concentrations are

$$[H_2] = (0.00623 - 0.00156)\ M = 0.00467\ M$$

$$[I_2] = (0.00414 - 0.00156)\ M = 0.00258\ M$$

$$[HI] = (0.0224 + 2 \times 0.00156)\ M = 0.0255\ M$$

Factors That Affect Chemical Equilibrium

Chemical equilibrium represents a balance between forward and reverse reactions.

In most cases, this balance is quite delicate. Changes in experimental conditions may disturb the balance and shift the equilibrium position so that more or less of the desired product is formed.

Variables that can be controlled experimentally are concentration, pressure, volume, and temperature.

Le Châtelier’s Principle

states that if an external stress is applied to a system at equilibrium, the system adjusts in such a way that the stress is partially offset as the system reaches a new equilibrium position.

The word “stress” here means a change in concentration, pressure, volume, or temperature that removes the system from the equilibrium state.

Factors That Affect Chemical Equilibrium

Changes in Concentration

Iron(III) thiocyanate [$Fe(SCN)_3$] dissolves readily in water to give a red solution. The red color is due to the presence of hydrated $FeSCN^{2+}$ ion.

$$\underset{\text{red}}{FeSCN^{2+}(aq)} \rightleftharpoons \underset{\text{pale yellow}}{Fe^{3+}(aq)} + \underset{\text{colorless}}{SCN^{-}(aq)}$$

if we add some sodium thiocyanate (NaSCN) → an increase in the concentration of SCN2

The equilibrium shifts from right to left : Consequently, the red color of the solution deepens

$$FeSCN^{2+}(aq) \longleftarrow Fe^{3+}(aq) + SCN^{-}(aq)$$

if we added iron(III) nitrate [Fe(NO3)3] to the original solution →

the red color would also deepen because the additional $Fe3^{+}$ ions from [Fe(NO3)3] would shift the equilibrium from right to left

Changes in Concentration

suppose we add some oxalic acid (H2C2O4) to the original solution. Oxalic acid ionizes in water to form the oxalate ion, C2O4 22, which binds strongly to the Fe^{3+} ions.

The formation of the stable yellow ion Fe(C2O4)3 32 rem
solution. Consequently, more FeSCN21 units dissociate a
from left to right:

$$FeSCN^{2+}(aq) \longrightarrow Fe^{3+}(aq$$

The red solution will turn yellow due to the formatio

(a) (b) (c) (d)

Figure 14.7 *Effect of concentration change on the position of equilibrium. (a) An aqueous $Fe(SCN)_3$ solution. The color of the solution is due to both the red $FeSCN^{2+}$ and the yellow Fe^{3+} ions. (b) After the addition of some NaSCN to the solution in (a), the equilibrium shifts to the left. (c) After the addition of some $Fe(NO_3)_3$ to the solution in (a), the equilibrium shifts to the left. (d) After the addition of some $H_2C_2O_4$ to the solution in (a), the equilibrium shifts to the right. The yellow color is due to the $Fe(C_2O_4)_3^{3-}$ ions.*

Factors That Affect Chemical Equilibrium

Changes in Concentration

At 720°C, the equilibrium constant K_c for the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

is 2.37×10^{-3}. In a certain experiment, the equilibrium concentrations are $[N_2] = 0.683\ M$, $[H_2] = 8.80\ M$, and $[NH_3] = 1.05\ M$. Suppose some NH_3 is added to the mixture so that its concentration is increased to 3.65 *M*. (a) Use Le Châtelier's principle to predict the shift in direction of the net reaction to reach a new equilibrium. (b) Confirm your prediction by calculating the reaction quotient Q_c and comparing its value with K_c.

Solution (a) The stress applied to the system is the addition of NH_3. To offset this stress, some NH_3 reacts to produce N_2 and H_2 until a new equilibrium is established. The net reaction therefore shifts from right to left; that is,

$$N_2(g) + 3H_2(g) \longleftarrow 2NH_3(g)$$

Factors That Affect Chemical Equilibrium

Changes in Concentration

(b) At the instant when some of the NH_3 is added, the system is no longer at equilibrium. The reaction quotient is given by

$$Q_c = \frac{[NH_3]_0^2}{[N_2]_0[H_2]_0^3}$$
$$= \frac{(3.65)^2}{(0.683)(8.80)^3}$$
$$= 2.86 \times 10^{-2}$$

Because this value is greater than 2.37×10^{-3}, the net reaction shifts from right to left until Q_c equals K_c.

Factors That Affect Chemical Equilibrium

Changes in Volume and Pressure

Changes in pressure ordinarily do not affect the concentrations of reacting species in condensed phases (say, in an aqueous solution) because liquids and solids are virtually incompressible.

On the other hand, concentrations of gases are greatly affected by changes in pressure.

$$PV = nRT$$

$$P = \left(\frac{n}{V}\right)RT$$

The greater the pressure, the smaller the volume, and vice versa. Note, too, that the term (n/V) is the concentration of the gas in mol/L, and it varies directly with pressure

Factors That Affect Chemical Equilibrium

Changes in Volume and Pressure

Suppose that the equilibrium system is in a cylinder fitted with a movable piston.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

What happens if we increase the pressure on the gases by pushing down on the piston at constant temperature?

the volume decreases, the concentration (n/V) of both NO2 and N2O4 increases.

$$Q_c = \frac{[NO_2]_0^2}{[N_2O_4]_0}$$

increase in pressure increases the numerator more than the denominator.

Thus, Qc >Kc and the net reaction will shift to the left until Qc = Kc

Conversely, a decrease in pressure (increase in volume) would result in Qc <Kc, and the net reaction would shift to the right until Qc = Kc.

Factors That Affect Chemical Equilibrium

Changes in Volume and Pressure

In general, an increase in pressure (decrease in volume) favors the net reaction that decreases the total number of moles of gases (the reverse reaction, in this case)

a decrease in pressure (increase in volume) favors the net reaction that increases the total number of moles of gases (here, the forward reaction).

For reactions in which there is no change in the number of moles of gases, a pressure (or volume) change has no effect on the position of equilibrium.

Factors That Affect Chemical Equilibrium

Changes in Volume and Pressure

Consider the following equilibrium systems:

(a) $2PbS(s) + 3O_2(g) \rightleftharpoons 2PbO(s) + 2SO_2(g)$

(b) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(c) $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$

Predict the direction of the net reaction in each case as a result of increasing the pressure (decreasing the volume) on the system at constant temperature.

(a) Consider only the gaseous molecules. In the balanced equation, there are 3 moles of gaseous reactants and 2 moles of gaseous products. Therefore, the net reaction will shift toward the products (to the right) when the pressure is increased.

(b) The number of moles of products is 2 and that of reactants is 1; therefore, the net reaction will shift to the left, toward the reactant.

(C)The number of moles of products is equal to the number of moles of reactants, so a change in pressure has no effect on the equilibrium.

Factors That Affect Chemical Equilibrium

Effect of Change of Temperature

Chemical reactions consist of two opposing reactions. If the forward reaction proceeds by the evolution of heat (exothermic), the reverse reaction occurs by the absorption of heat (endothermic). Both these reactions take place at the same time and equilibrium exists between the two.

If temperature of a reaction is raised, heat is added to the system. The equilibrium shifts in a direction in which heat is absorbed in an attempt to lower the temperature

A drop in temperature “removes” heat from the system and equilibrium shifts in a direction in which heat is released in an attempt to increase the temperature.

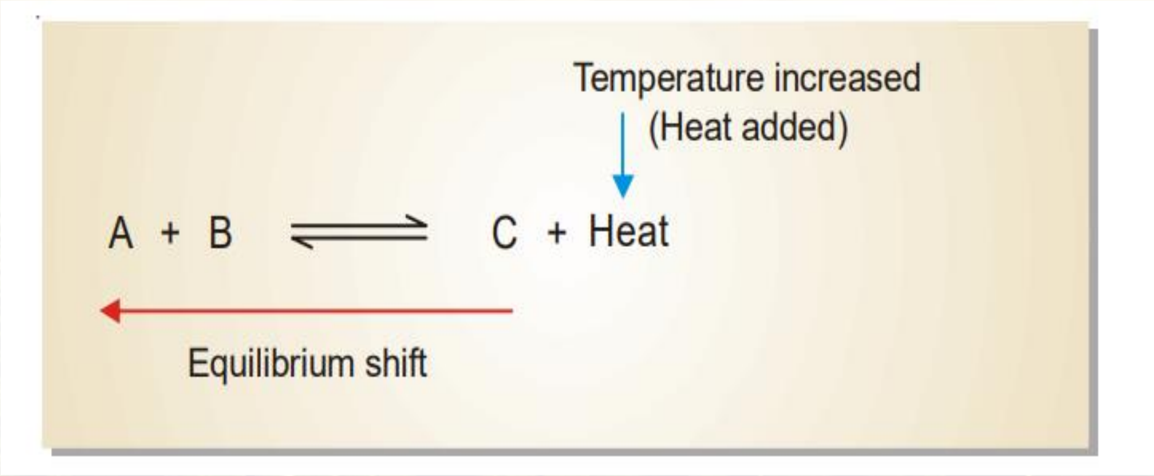
Factors That Affect Chemical Equilibrium

Effect of Change of Temperature

Let us consider an exothermic reaction

$$A + B \leftrightarrow C + heat$$

When the temperature of the system is increased, heat is supplied to it from outside. According to Le Chatelier's principle, the equilibrium will shift to the left which involves the absorption of heat. This would result in the increase of the concentration of the reactants A and B



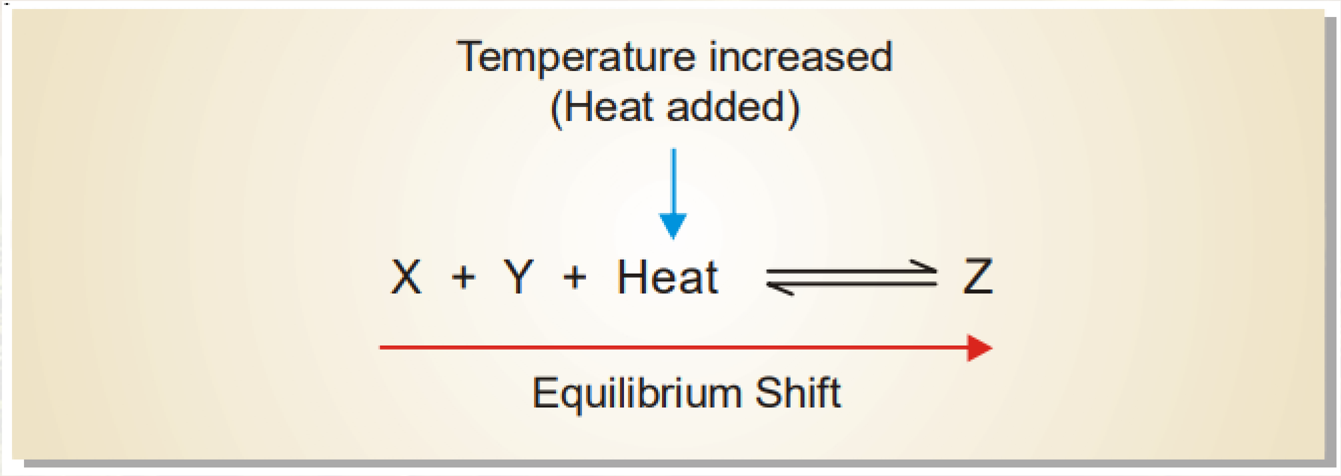
Factors That Affect Chemical Equilibrium

Effect of Change of Temperature

In an endothermic reaction

$$X + Y + heat \leftrightarrow Z$$

the increase of temperature will shift the equilibrium to the right as it involves the absorption of heat. This increases the concentration of the product Z.



Factors That Affect Chemical Equilibrium

Effect of Change of Temperature

Consider the equilibrium between the following ions

$$\underset{\text{blue}}{CoCl_4^{2-}} + 6H_2O \rightleftharpoons \underset{\text{pink}}{Co(H_2O)_6^{2+}} + 4Cl^-$$

The formation of $CoCl_4^{2-}$ is endothermic. On heating, the equilibrium shifts to the left and the solution turns blue. Cooling favors the exothermic reaction [the formation of $Co(H2O)_6^{2-}$] and the solution turns pink (Figure 14.11).

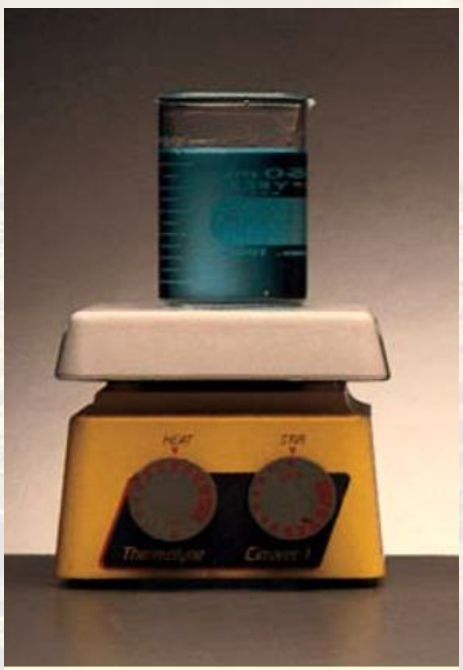


Figure 14.11 *(Left) Heating favors the formation of the blue $CoCl_4^{2-}$ ion. (Right) Cooling favors the formation of the pink $Co(H_2O)_6^{2+}$ ion.*

In summary, a temperature increase favors an endothermic reaction, and a temperature decrease favors an exothermic reaction