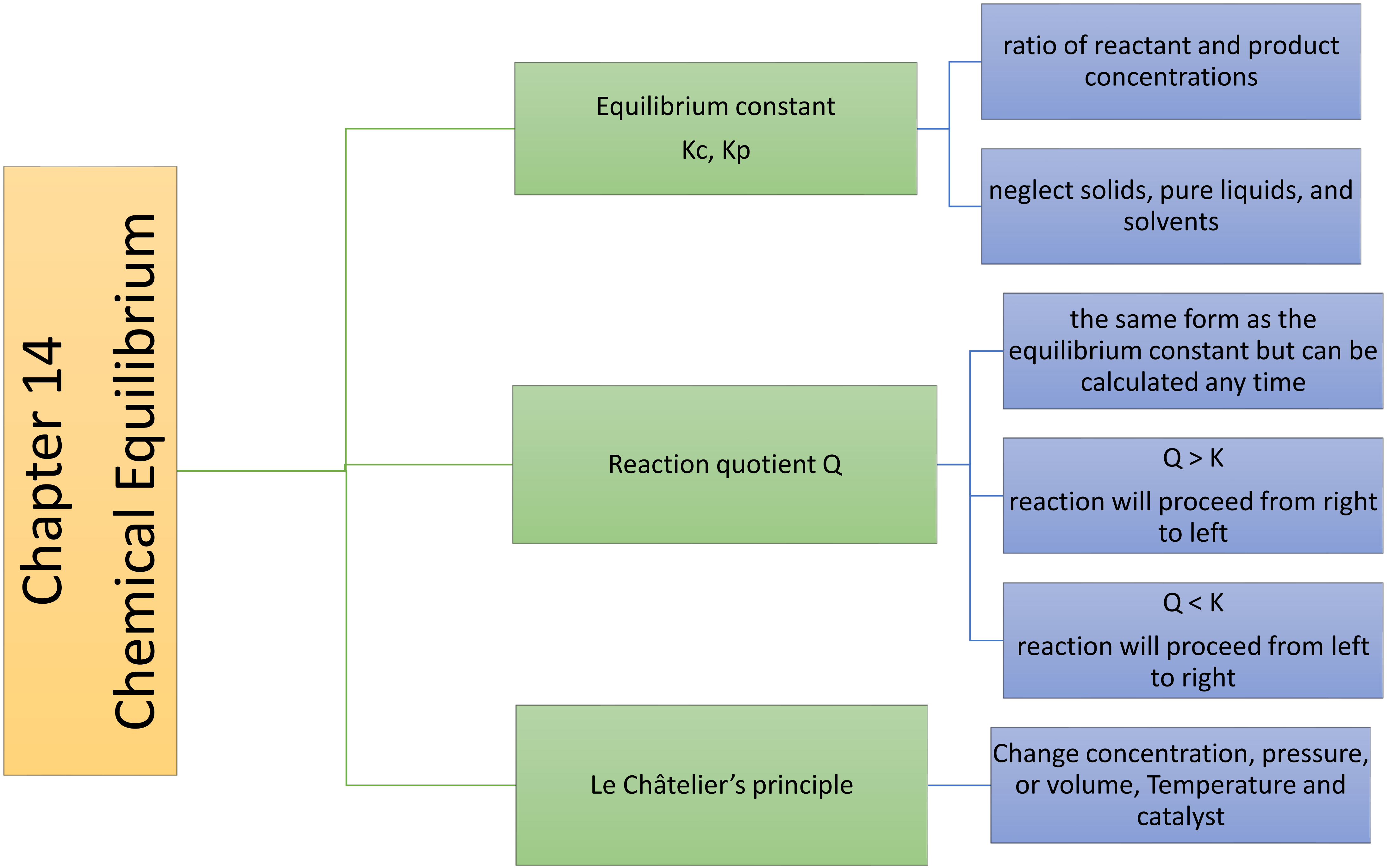
Chapter 14

Chemical Equilibrium

Dr. Dalal Alezi
dalezi@kau.edu.sa

02/12/2018


Chapter 14
Chemical Equilibrium
Equilibrium constant
Kc, Kp
ratio of reactant and product concentrations
neglect solids, pure liquids, and solvents
Reaction quotient Q
the same form as the equilibrium constant but can be calculated any time
Q > K
reaction will proceed from right to left
Q < K
reaction will proceed from left to right
Le Châtelier’s principle
Change concentration, pressure, or volume, Temperature and catalyst

Write the type of reaction for the following reactions, homogenous OR heterogeneous reaction

A) $C_2H_5OH_{(aq)} + CH_3COOH_{(aq)} \rightleftharpoons CH_3COOC_2H_{5\,(aq)}\ H_2O_{(l)}$ Homogenous reaction (l and aq all are the same phase)

B) $Zn_{(s)} + Cu^{+2}_{(aq)} \rightleftharpoons Cu_{(s)} + Zn^{+2}_{(aq)}$ Heterogeneous reaction (s and aq phase, different phases)

C) $SnO_{2\,(s)} + 2CO_{(g)} \rightleftharpoons Sn_{(s)} + 2CO_{2\,(g)}$ Heterogeneous reaction (s and g phase, different phases)

D) $CaCO_{3\,(s)} \rightleftharpoons CaO_{(s)} + CO_{2\,(g)}$ Heterogeneous reaction (s and g phase, different phases)

Which one of the following is the correct equilibrium constant expression (K_c) for this equation.

$$CO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)}$$

A) $K_c = \frac{[H_2CO_3]}{[CO_2][H_2O]}$

B) $K_c = \frac{[CO_2][H_2O]}{[H_2CO_3]}$

C) $K_c = \frac{[H_2CO_3]}{[CO_2]}$

D) $K_c = \frac{[CO_2]}{[H_2CO_3]}$

$H_2O_{(l)}$ is not included in the equilibrium constant expression.

Q2: Which is the correct equilibrium constant expression (K_p) for the following reaction?

$$Fe_2O_{3(s)} + 3H_{2(g)} \rightleftharpoons 2Fe_{(s)} + 3H_2O_{(g)}$$

A) $K_p = \frac{P_{Fe_2O_3} \times P_{H_2}^3}{P_{Fe}^2 \times P_{H_2O}^3}$

B) $K_p = \frac{P_{Fe}^2 \times P_{H_2O}^3}{P_{Fe_2O_3} \times P_{H_2}^3}$

C) $K_p = \frac{P_{H_2}}{P_{H_2O}}$

D) $K_p = \frac{P_{H_2O}^3}{P_{H_2}^3}$

$Fe_2O_{3(s)}$ and $Fe_{(s)}$ are not included in the equilibrium constant expression.

Write an expression for the equilibrium constant for the formation of two moles of ammonia gas (NH_3) from nitrogen and hydrogen in their standard states

$$N_2(g) + 3\,H_2(g) \rightleftarrows 2\,NH_3(g)$$

$$K_c = \frac{[\mathrm{NH_3}]^2}{[N_2]\,[H_2]^3}$$

Write the correct K_c and K_p expressions for the following reaction?

$$C_3H_{8\,(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(g)}$$

$$K_c = \frac{[CO_2]^3[H_2O]^4}{[C_3H_8]\,[O_2]^5}$$

$$K_p = \frac{P^3{}_{CO2}\;P^4{}_{H2O}}{P_{C3H8}\,P^5{}_{O2}}$$

Write an expression for the equilibrium constant for this reaction.

$$Ca(OH)_{2(s)} + 2H^+{}_{(aq)} \leftrightarrow 2H_2O_{(l)} + Ca^{2+}{}_{(aq)}$$

$$K_c = \frac{[Ca^{2+}]}{[H^+]^2}$$

For the reaction $2A + B \rightarrow 2C$ the appropriate form for the equilibrium constant expression is:

a. $[A][B]^2/[C]$

b. $[A]^2[B]/[C]^2$

c. $[C]^2/[A]^2[B]$

d. $[A][B]^2[C]$

e. none of the above

Write the equilibrium expression for the reaction

$$Zn^{2+}(aq) + 2\ NH_3(aq) \leftrightarrow Zn(NH_3)^{2+}(aq)$$

a. $K = [Zn^{2+}] + 2[NH_3] + [Zn(NH_3)^{2+}]$

b. $K = \dfrac{[Zn^{2+}] + 2[NH_3]}{[Zn(NH_3)^{2+}]}$

c. $K = \dfrac{[Zn^{2+}][NH_3]^2}{[Zn(NH_3)^{2+}]}$

d. $K = \dfrac{[Zn(NH_3)^{2+}]}{[Zn^{2+}][NH_3]^2}$

e. $K = [Zn(NH_3)^{2+}] - [Zn^{2+}] - 2[NH_3]$

At 2000°C, carbon dioxide decomposes as shown.

$$2CO_2(g) \Leftrightarrow 2CO(g) + O_2(g)$$

If K_c is 6.4×10^{-7} and the concentrations of $CO(g)$ and $O_2(g)$ are 2.0×10^{-3} mol/L and 1.0×10^{-3} mol/L at equilibrium, respectively, calculate the concentration of carbon dioxide.

$$K = \frac{[CO]^2[O_2]}{[CO_2]^2}, [CO_2]^2 = \frac{[CO]^2[O_2]}{K}$$

$$[CO_2] = \sqrt{\frac{\left(2.0\times10^{-3}\right)^2\left(1.0\times10^{-3}\right)}{\left(6.4\times10^{-7}\right)}} = 7.9\times10^{-2}\ \text{mol/L}$$

Q. If the reaction quotient Q has a smaller value than the related equilibrium constant, K, ___________

A. the reaction is at equilibrium.

B. the reaction is not at equilibrium, and will make more products at the expense of reactants.

C. the reaction is not at equilibrium, and will make more reactants at the expense of products.

D. the value of K will decrease until it is equal to

Q. If the reaction quotient Q has a larger value than the related equilibrium constant, K, ___________

A. the reaction is at equilibrium.

B. the reaction is not at equilibrium, and will make more products at the expense of reactants.

C. the reaction is not at equilibrium, and will make more reactants at the expense of products.

D. the value of K will increase until it is equal to Q

For the reaction represented above, the value of the equilibrium constant, K_p, is 3.1×10^{-4} at 700. K.

$$N_2(g) + 3\,H_2(g) \leftrightarrow 2\,NH_3(g)$$

(a) Write the expression for the equilibrium constant, K_p, for the reaction

$$K_p = \frac{p^2_{NH_3}}{p_{N_2} \times p^3_{H_2}}$$

(b) Predict the direction in which the reaction will proceed at 700. K if you Assume that the initial partial pressures of the gases are as follows: p_{N2} = 0.411 atm, p_{H2}= 0.903 atm, and p_{NH3}= 0.224 atm

$$Q = \frac{p^2_{NH_3}}{p_{N_2} \times p^3_{H_2}} = \frac{(0.224)^2}{(0.411)(0.903)^3}$$

$$Q = 0.166$$

Since $Q > K_p$

so the reaction must proceed from right to left to establish equilibrium

(c) Calculate the value of the equilibrium constant, K_c for this reaction

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

$$K_p = K_c(RT)^{\Delta n}$$

$$\Delta n = 2 - 4 = -2$$

$$K_p = K_c(RT)^{-2}$$

$$3.1 \times 10^{-4} = K_c\left(0.0821\ \frac{\text{L atm}}{\text{mol K}} \times 700\ \text{K}\right)^{-2}$$

$$3.1 \times 10^{-4} = K_c(57.5)^{-2}$$

$$3.1 \times 10^{-4} = K_c(3.0 \times 10^{-4})$$

$$1.0 = K_c$$

If 0.01 M of H2 was added to 0.01 M of CO2 in 1 L vessel, and the following reaction occurred:

$$H_2\,(g) + CO_2\,(g) \Leftrightarrow H_2O\,(g) + CO\,(g)$$

Calculate the concentration of all species at equilibrium at 750 K, Kc = 0.771

Step 1:

	H_2	CO_2	H_2O	CO
Initial	0.01	0.01	0	0
Change	-x	-x	+x	+x
Equilibrium	(o.o1 –x)	(o.o1 –x)	x	x

Step 2:

$$K_c = \frac{[H_2O][CO]}{[H_2][CO_2]} \qquad 0.711 = \frac{(x)(x)}{(0.01-x)(0.01-x)}$$

$$0.711 = \frac{(x)^2}{(0.01-x)^2} \qquad \sqrt{0.711} = \sqrt{\frac{(x)^2}{(0.01-x)^2}} \qquad x = 4.68\times10^{-3}$$

Step 3:

So $[H_2O] = [CO] = 0.00468M$

and $[H_2] = [CO_2] = 0.0100 - 0.00468 = 0.00532M$

In a certain experiment, 0.243 M of NOCl, 0.146 M of NO and 1.98 M of Cl_2 are placed in a container at 400°C. Will there be a net reaction to form more NO and Cl_2 or more NOCl (K_c=2.1 ×10^{-2})?

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

1. Calculate Q_c

$$Q_c = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

$$Q_c = \frac{[0.146]^2[1.98]}{[0.243]^2}$$

$$Q_c = 0.71$$

2. Compare between Q_c and K_c

$$Q_c > K_c$$

To reach equilibrium, products (NO and Cl_2) must be converted to the reactant (NOCl).

Q. Consider the following reaction at equilibrium:

$$2NH_3\,(g) \leftrightarrow N_2\,(g) + 3H_2\,(g) \qquad \Delta H° = +92.4\ kJ$$

Le Châtelier's principle predicts that adding N_2 (g) to the system at equilibrium will result in ___________.

A. a decrease in the concentration of H_2 (g)

B. a decrease in the concentration of NH_3 (g)

C. removal of all of the H_2 (g)

D. an increase in the value of the equilibrium constant

Q. Consider the following reaction at equilibrium:

$$2NH_3\,(g) \leftrightarrow N_2\,(g) + 3H_2\,(g)$$

Le Châtelier's principle predicts that the moles of H_2 in the reaction container will increase with...........

A. an increase in total pressure by the addition of helium gas (V and T constant)

B. addition of some N_2 to the reaction vessel (V and T constant)

C. a decrease in the total volume of the reaction vessel (T constant)

D. a decrease in the total pressure (T constant)

The reaction below is exothermic:

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

Le Châtelier's Principle predicts that ___________ will result in an increase in the number of moles of SO_3 (g) in the reaction container.

A. increasing the pressure

B. increasing the volume of the container

C. decreasing the pressure

D. increasing the temperature

For the endothermic reaction

$$CaCO_3\ (s) \leftrightarrow CaO\ (s) + CO_2\ (g)$$

Le Châtelier's principle predicts that ___________ will result in an increase in the number of moles of CO_2.

A. decreasing the temperature

B. removing some of the $CaCO_3$ (s)

C. increasing the pressure

D. increasing the temperature

In which of the following reactions would increasing pressure at constant temperature not change the concentrations of reactants and products, based on Le Châtelier's principle?

A. $2N_2 (g) + O_2 (g) \leftrightarrow 2N_2O (g)$

B. $N_2 (g) + 3H_2 (g) \leftrightarrow 2NH_3 (g)$

C. $N_2 (g) + O_2 (g) \leftrightarrow 2NO (g)$

D. $N_2O_4 (g) \leftrightarrow 2NO_2 (g)$

Consider the following reaction at equilibrium:

$$2CO_2\ (g) \leftrightarrow 2CO\ (g) + O_2\ (g) \qquad \Delta H° = -514\ kJ$$

Le Châtelier's principle predicts that an increase in temperature will ___________.

A. increase the partial pressure of CO

B. decrease the value of the equilibrium constant

C. increase the value of the equilibrium constant

D. increase the partial pressure of O_2 (g)

For the following reaction, write how the each of the changes will affect the indicated quantity, assuming a container of fixed size. Write “increase”, “decrease”, or “no change”.

$$H_2(g) + Br_2(g) \leftrightarrow 2HBr(g) \qquad \Delta H^\circ = -103.7\ kJ$$

Change	$[H_2]$	$[Br_2]$	[HBr]	K value
Some H_2 added	decrease	decrease	increase	No change
Some HBr added	increase	increase	decrease	No change
Some H_2 removed	increase	increase	decrease	No change
Some HBr removed	decrease	decrease	increase	No change
The temperature is increased	increase	increase	decrease	decrease
The temperature is decreased	decrease	decrease	increase	inceasee
Pressure is increased and the container volume decreased	No change	No change	No change	No change

Given the following reaction:

$$2A_{(g)} \leftrightarrow B_{(g)} + C_{(g)} \qquad \Delta H° = +27 \text{ kJ} \qquad K = 3.2 \times 10^{-4}$$

Which of the following would be true if the temperature were increased from 25°C to 100°C?

1. The value of K would be smaller.
2. The concentration of $A_{(g)}$ would be increased.
3. The concentration of $B_{(g)}$ would increase.

A. 1 only

B. 2 only

C. 3 only

D. 1 and 2 only

How would you regulate the temperature in this reaction (all substances are gases)

$$PCl_5 \leftrightarrow PCl_3 + Cl_2 + heat$$

In order to do the following:

- A-increase the concentration of PCl_5

∴ we need to raise the temperature to increase the reactant concentration because reverse reaction will be favoured

- - decrease the concentration of PCl_3

∴ we need to raise the temperature to decrease the product concentration because reverse reaction will be favoured

- C-increase the amount of Cl_2

we need to decrease the temperature to increase the product concentration because forward reaction will be favoured

- Decrease the K_{eq}

In exothermic reaction, increasing temperature will decrease the K_{eq} by decreasing the product

Temperature increase favour the **endothermic reaction,**

Temperature decrease favours an **exothermic reaction**

This is an exothermic reaction
So, increasing the temperature will favour the reverse reaction while decreasing temperature will favour the forward reaction

How would decreasing the volume of the vessel reaction affect these equilibria (consider all the substances are gases):

$CO + H_2 \Leftrightarrow H_2CO$

$\Delta n=1-2=-1$

So the reaction shift to the product (right)

(forward reaction will be the favoured)

Decreasing the volume (increasing the pressure) will favour the reaction that **<u>decrease</u> the number of moles of gases.**

$NH_4HS \Leftrightarrow NH_3 + H_2S$

$\Delta n=2-1=1$

So the reaction shift to the reactant (left)

(reverse reaction will be the favoured)

$2NbCl_4 \Leftrightarrow NbCl_3 + NbCl_5$

$\Delta n=2-2=0$

So the reaction will not change (remain unchanged)