7.5 Quantitative Changes in Equilibrium Systems

What is Q?

- Q is the reaction quotient.
- It is a mathematical application of Le Châtelier's Principle
- Use the equilibrium constant expression. But, use initial or given concentrations instead of equilibrium concentrations.
- Solve using equilibrium equation
- Compare Q value to actual equilibrium value K_e
    - If $Q < K_e$, products will be formed (reaction goes to the right)
    - If $Q > K_e$, reactants will be formed (reaction goes to the left)
    - If $Q = K_e$, there will not be a change in concentration

- E.g. When 3.0 mol of HI, 2.0 mol of H_2 and 1.5 mol of I_2 are placed in a 1.0 L container at 448ºC, ~~will a reaction occur~~? ~~If so~~, which reaction takes place? At 448ºC, $K_e = 50$.

$$H_2 + I_2 \leftrightarrow 2HI$$

$$K_e = \frac{[HI]^2}{[H_2][I_2]} = 50 \quad \text{vs} \quad Q = \frac{[HI]^2}{[H_2][I_2]} = \frac{[3.0]^2}{[2.0][1.5]} = \frac{9.0}{3.0} = 3.0$$

$K_e > Q$, 守 the reaction goes to the right and HI is formed

How to solve an equilibrium problem.

a. Write the equilibrium reaction equation.
b. Write the equilibrium constant expression.
c. Identify the problem type.
  Type 1: equilibrium [reactant(s)] and [product(s)] are given, find the value of K_e.
  Type 2: K_e given; find the values of [reactant(s)] and [product(s)] at equilibrium.
d. Solve.

Solving a Type 1 Problem

- Input concentrations of solutes or gases (or partial pressure of gases) into K_e expression and calculate K_e.
- Units of all equilibrium species must be the same (usually mol/L)

Solving a Type 2 Problem

- Range from simple to difficult.
- If only one concentration missing, substitute and solve.
- If presented with unknown concentrations use ICE method. (Initial, Change, Equilibrium).
  a. Input the algebraic representations for [reactant(s)] and [product(s)] into K_e expression and solve to given value of K_e.
  b. Isolate for “x” in simple cases and re-substitute “x” into algebraic expressions for [reactant(s)] and [product(s)] to determine exact values.

E.g. For the reaction: $NH_4Cl_{(s)} \leftrightarrow NH_{3(g)} + HCl_{(g)}$

K_e is found to be 6.0×10^{-9}. What is the concentration of the products at equilibrium?

守 $K_e = [NH_3][HCl] = 6.0 \times 10^{-9}$

Use your ICE Tables

	NH_4Cl	$\leftrightarrow$	$[NH_3]$	$[HCl]$
initial	some amount		0	0
change			+x	+x
equilibrium			x	x

$K_e = [NH_3][HCl]$

$$6.0 \times 10^{-9} = (x)\,(x)$$

$$x = 7.7 \times 10^{-5}$$

守 for the above reaction with the given K_e value the concentrations of the products would each be 7.7×10^{-5} mol/L

- If both the numerator and denominator in the K_e expression are squares, solve by taking the root of both sides and isolate for "x". See example on p. 467.
- If only the numerator or the denominator in the K_e expression is a square (the other is not) solve by approximation or the quadratic equation. See example on p. 469 and p. 476.

E.g. $I_{2(g)} \leftrightarrow 2I_{(g)}$ where $K_e = 3.8 \times 10^{-5}$

What are the concentrations at equilibrium if you initially start with 0.200 mol/L of I_2?

$$K_e = \frac{[I]^2}{[I_2]} = 3.8 \times 10^{-5}$$

	$[I_2]$ $\longleftrightarrow$	2 $[I]$
initial	0.200	0
change	$-x$	$+2x$
equilibrium	$0.200 - x$	$2x$

substitute: $$3.8 \times 10^{-5} = \frac{(2x)^2}{(0.200 - x)}$$

Option 1: approximation

- Use approximation rule to see if it can be solved by approximation.
- If the concentration from which "x" is being subtracted from, or to which "x" is added, must be at least 100 times larger than the value of the given K_e.

check: $\frac{0.200}{3.8 \times 10^{-5}} = 5260$ *, since it is greater than 100 you can use the approximation* $0.200 \approx (0.200 - x)$

- What does this mean? The concentration of the product is very small compared to the reactant. Very little I produced.

$$3.8 \times 10^{-5} = \frac{(2x)^2}{(0.200)}$$

Solve: $x = 1.38 \times 10^{-3}$

$[I_2] = 0.200 - x = 0.200 - 1.38 \times 10^{-3} = 0.198$ mol/L

$[I] = 2x = 2(1.38 \times 10^{-3}) = 0.003$ mol/L

Option 2: quadratic equation

$$3.8 \times 10^{-5} = \frac{(2x)^2}{(0.200 - x)}$$

$4x^2 + 3.8 \times 10^{-5}x - 7.6 \times 10^{-6} = 0$

substitute into: $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$x = 1.38 \times 10^{-3}$

$[I_2] = 0.200 - x = 0.200 - 1.38 \times 10^{-3} = 0.198$ mol/L

$[I] = 2x = 2(1.38 \times 10^{-3}) = 0.003$ mol/L

Quantitative Aspects of Le Châtelier's Principle

- When a system in equilibrium is disturbed, the equilibrium position will shift.

E.g. Analysis of an equilibrium mixture is shown to be:
$[SO_2] = 4.0$ mol/L; $[SO_3] = 3.0$ mol/L;
$[NO_2] = 0.50$ mol/L; and $[NO] = 2.0$ mol/L.

Using the reaction equation below, what is the new equilibrium concentrations when 1.5 mol of NO_2 is added to a litre of the mixture.

$SO_{2(g)} + NO_{2(g)} \leftrightarrow SO_{3(g)} + NO_{(g)}$

$$K_e = \frac{[SO_3][NO]}{[SO_2][NO_2]} = \frac{(3.0)(2.0)}{(4.0)(0.50)} = 3.0$$

		$SO_{2(g)}$	+ $NO_{2(g)}$	$\leftrightarrow$	$SO_{3(g)}$	+ $NO_{(g)}$
(I)	1st equilibrium	4.0	0.50		3.0	2.0
(C)	change	–x	1.5–x		+x	+x
(E)	2nd equilibrium	(4.0 –x)	(0.50+1.5–x)		(3.0+x)	(2.0+x)

$$K_e = \frac{[SO_3][NO]}{[SO_2][NO_2]} = \frac{(3.0 + x)(2.0 + x)}{(4.0 - x)(0.50 + 1.5 - x)} = 3.0$$

$$2.0x^2 - 23x + 18 = 0$$

where $x = 0.85$ (discard 10.7)

$SO_{2(g)}$ = 4.0 – 0.85 = 3.15 mol/L
$NO_{2(g)}$= 2.0 – 0.85 = 1.15 mol/L
$SO_{3(g)}$ = 3.0 + 0.85 = 3.85 mol/L
$NO_{(g)}$ = 2.0 + 0.85 = 2.85 mol/L

Homework

- Practice 1,2,3,4,5,6,7,8,9,10 and Questions 1,2,3,4,5,6,7,8