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, $K_e = 50$.

$$H_2 + I_2 \leftrightarrow 2HI$$

$$K_e = \frac{[HI]^2}{[I_2][H_2]} = 50 \quad \text{vs} \quad \frac{[HI]^2}{[I_2][H_2]} = \frac{3^2}{2 \times 1.5} = \frac{9}{3} = 3$$

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

$50 > 3$

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?

Use your ICE Tables

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

	NH_4Cl	$\rightarrow$	1 $[NH_3]$	1 $[HCl]$
initial	some amount		0	0
change	$-x$		$+x$	$+x$
equilibrium	amount $- x$		x	x

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

$x = 7.7 \times 10^{-7}$

$\therefore$ for the above reaction with the given K_e value the concentrations of the products would each be 7.7×10^{-7} 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?

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

	1 $[I_2]$	$\leftrightarrow$ 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.
- Solve: $3.8 \times 10^{-5} = \frac{(2x)^2}{0.200}$

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

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

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

$$K_e = \frac{[SO_3][NO]}{[SO_2][NO_2]} = 3$$

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

$$3 = \frac{(3+x)(2+x)}{(4-x)(0.5+1.5-x)}$$

where (discard 10.7) $2x^2 - 23x + 18 = 0$

$x = 10.7$
or
0.85

$SO_{2(g)} = 4.0 - 0.85 = 3.15$ 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