Equilibrium Law

Section 7.2

Homework

Equilibrium Law (7.2)
Pg. 431 Practice #1-3
Pg. 434 Practice #1
Pg. 436 #1-6 (skip 4)

Reaction Quotient (7.5)
Pg. 451 Practice #1-3
Worksheet

Equilibrium Law quantitatively describes the equilibrium position of a system.

For the reaction a**A** + b**B** $\rightleftharpoons$ c**C** + d**D**,

$$K = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

Product concentrations

Reactant concentrations

Equilibrium constant
(NO UNITS)

- All concentrations AT EQUILIBRIUM (mol/L)
- Exponents from balanced chemical equation

Practice 1: Write equilibrium law equations for the reactions:

a) $H_{2\,(g)} + I_{2\,(g)} \rightleftharpoons 2\ HI_{(g)}$

b) $N_{2\,(g)} + 3\ H_{2\,(g)} \rightleftharpoons 2\ NH_{3\,(g)}$

For a given reaction carried out **at the same temperature**, the value of K is CONSTANT.
- regardless of initial concentrations

Table 13.1 ▸ Results of Three Experiments for the Reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Experiment	Initial Concentrations	Equilibrium Concentrations	$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$
I	$[N_2]_0 = 1.000\ M$ $[H_2]_0 = 1.000\ M$ $[NH_3]_0 = 0$	$[N_2] = 0.921\ M$ $[H_2] = 0.763\ M$ $[NH_3] = 0.157\ M$	$K = 6.02 \times 10^{-2}$
II	$[N_2]_0 = 0$ $[H_2]_0 = 0$ $[NH_3]_0 = 1.000\ M$	$[N_2] = 0.399\ M$ $[H_2] = 1.197\ M$ $[NH_3] = 0.203\ M$	$K = 6.02 \times 10^{-2}$
III	$[N_2]_0 = 2.00\ M$ $[H_2]_0 = 1.00\ M$ $[NH_3]_0 = 3.00\ M$	$[N_2] = 2.59\ M$ $[H_2] = 2.77\ M$ $[NH_3] = 1.82\ M$	$K = 6.02 \times 10^{-2}$

Example 1.

Sulfur dioxide and oxygen combine to form sulfur trioxide:

$$2\,SO_{2\,(g)} + O_{2\,(g)} \rightleftharpoons 2\,SO_{3\,(g)}$$

At 600°C, the following results are collected:

Initial	Equilibrium
$[SO_2]_0 = 2.00\ M$	$[SO_2] = 1.50\ M$
$[O_2]_0 = 1.50\ M$	$[O_2] = 1.25\ M$
$[SO_3]_0 = 3.00\ M$	$[SO_3] = 3.50\ M$

a) Write the equilibrium law equation
- K = [products]/[reactants]
- use coefficients to find exponents

$$K = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

b) Calculate the value of K
- plug in concentrations at equilibrium
- K is unitless

$$K = \frac{[3.50]^2}{[1.50]^2\,[1.25]} = 4.36$$

The value of K for the **reverse process**:

$$\mathbf{2\,SO_{2\,(g)} + O_{2\,(g)} \rightleftharpoons 2\,SO_{3\,(g)}}$$

Forward:

$$2\,SO_{2\,(g)} + O_{2\,(g)} \rightarrow 2\,SO_{3\,(g)}$$

$$K_f = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

Reverse:

$$2\,SO_{3\,(g)} \rightarrow 2\,SO_{2\,(g)} + O_{2\,(g)}$$

$$K_r = \frac{[SO_2]^2\,[O_2]}{[SO_3]^2}$$

$$\boxed{K_r = \frac{1}{K_f}}$$

At 600°C,

$K_f = 4.36$ (Example 1)

$\therefore K_r = \frac{1}{4.36} = 0.229$

What does K tell you?

- The value of K indicates how far the forward reaction proceeds to completion.
- It does NOT tell you how QUICKLY the reaction proceeds
  - we addressed this with rate laws in Ch. 6
  - unfortunately – two constants, same letter – don't get them confused!
- However, equilibrium constant K can be derived from the rate constants, k, for the forward and reverse reactions
  - see pg. 432 of your text

The magnitude of K indicates the extent to which the forward reaction proceeds to completion.

$$K = \frac{[products]}{[reactants]}$$

K << 1
At equilibrium, concentrations of reactants exceeds products.

Equilibrium lies far to left (very few products)

K = 1
At equilibrium, concentrations of reactants and products are equal

K >> 1
At equilibrium, concentrations of products exceeds reactants.

Equilibrium lies far to right (reaction proceeds towards completion)

Learning Checkpoint

- The Equilibrium Law states that for a reaction at a given temperature, the RATIO of [product] to [reactant] will always be the same.
  - Measured quantitatively using the equilibrium constant, K.
- For the reaction aA + bB $\rightleftharpoons$ cC, the equilibrium law equation is

$$\mathbf{K} = \frac{[\boldsymbol{C}]^{c}}{[\boldsymbol{A}]^{a}\,[\boldsymbol{B}]^{b}}$$

- The magnitude of K indicates how far the reaction proceeds to completion.
  - K >> 1 … Reaction proceeds towards completion. Products are favoured.
- For the reverse process, the value of K is the reciprocal of K for the forward process: $\mathbf{K_r} = \mathbf{K_f}^{-1}$

K equations depend on the type of equilibrium system.

- **Homogeneous equilibria** – Equilibrium systems involving reactants and products that are all in the same state
  - $2\ SO_{2\,(g)} + O_{2\,(g)} \rightleftharpoons 2\ SO_{3\,(g)}$

$$K = \frac{[SO_{3\,(g)}]^2}{[SO_{2\,(g)}]^2\,[O_{2\,(g)}]}$$

- **Heterogeneous equilibria** – Involve reactants and products in at least two different states
  - $CaCO_{3\,(s)} \rightleftharpoons CaO_{(s)} + CO_{2\,(g)}$

$$K = [CO_{2\,(g)}]$$

- Pure solids and liquids have **constant concentrations:** their concentrations can't change
- As such, concentrations of solid and liquid entities are NOT INCLUDED in an equilibrium law equation.
- See pg. 432 for mathematical logic

Practice

Write the equilibrium law expression for the reaction

$$PCl_{5\,(s)} \rightleftharpoons PCl_{3\,(l)} + Cl_{2\,(g)}$$

Learning Checkpoint

- When writing a rate law equation for a heterogeneous equilibrium system, concentrations of pure solids and liquids are always omitted.

<u>Homework</u>

- Pg. 431 Practice #1-3
- Pg. 434 Practice #1
- Pg. 436 #1-6 (skip 4)

Calculating the **Reaction Quotient (Q)** will tell you whether a system is at equilibrium.

- Calculated in the same way as K
  - BUT uses **instantaneous concentrations** instead of equilibrium concentrations

$$Q = \frac{[\text{products at instant } t]}{[\text{reactants at instant } t]} \qquad K = \frac{[\text{products at equilibrium}]}{[\text{reactants at equilibrium}]}$$

If Q = K, then the system is at equilibrium.

Example 2. $N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$

For the synthesis of ammonia, the expression for the reaction quotient, Q is:

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

For this reaction at 500°C, it is known the equilibrium constant, $\mathbf{K = 6.0 \times 10^{-2}}$.

In a system at 500°C, these concentrations are measured:

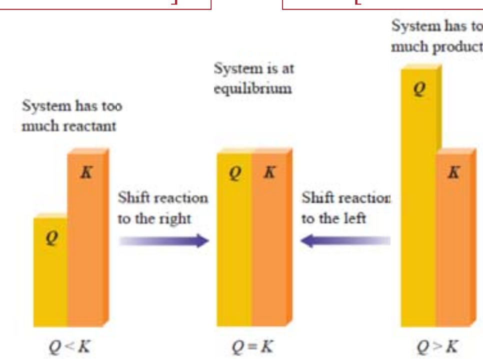
$[NH_3] = 1.0 \times 10^{-3}$ M $[N_2] = 1.0 \times 10^{-5}$ M $[H_2] = 2.0 \times 10^{-3}$ M

$$Q = \frac{(1.0 \times 10^{-3})^2}{(1.0 \times 10^{-5})(2.0 \times 10^{-3})^3} = 1.3 \times 10^7$$

Since Q ≠ K, the system is NOT at equilibrium.

If not at equilibrium, the system will "shift" until it reaches equilibrium concentrations.

$$\boxed{Q = \frac{[\text{products at instant } t]}{[\text{reactants at instant } t]}} \qquad \boxed{K = \frac{[\text{products at equilibrium}]}{[\text{reactants at equilibrium}]}}$$



(from Example 2…)

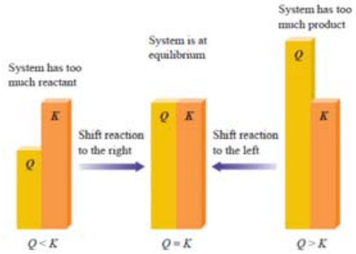
$$Q = \frac{[\text{products at instant } t]}{[\text{reactants at instant } t]}$$

Given: Equilibrium Constant, K = 6.0×10^{-2}

Found: Reaction quotient, Q = 1.3×10^{7}

a) Which entities – reactants or products – are in excess?

b) The system will continue to move towards equilibrium.
In which direction – left or right – will the system shift?



Summary

- The value of the equilibrium constant, K, is the always same for a chemical reaction at a given temperature.
  - Indicates extent to which forward reaction is favoured
- The value of the reaction quotient, Q, is compared to K.
  - When Q = K, the system is at equilibrium
  - If Q ≠ K, the system will continue to proceed towards equilibrium. The direction will be dictated by the value of K.

Homework

Equilibrium Law (7.2)

- Pg. 431 Practice #1-3
- Pg. 434 Practice #1
- Pg. 436 #1-6 (skip 4)

Reaction Quotient

- Pg. 451 Practice #1-3
- Worksheet