General Equilibrium

AP Chemistry 30 – Ms. Hayduk

Reversible Reactions

- Up to now, only seen irreversible reactions
- Reactants → products
- Rate of decomposition of reactants will start off quickly and decrease until no reactants remain
- Examples of irreversible reactions: combustion, oxidation, cooking

Reversible Reactions

- Reversible reactions: two reactions occurring at the same time: forward and reverse reaction
- General form:

$$A + B \rightleftharpoons AB$$

- Reactions "undo" each other
- For example:

$$3\ H_2 + N_2 \rightarrow 2\ NH_3 \text{ (forward)}$$
$$3\ H_2 + N_2 \leftarrow 2\ NH_3 \text{ (reverse)}$$

Combine to be written with a double arrow:

$$3\ H_2 + N_2 \rightleftharpoons 2\ NH_3$$

Bailing Beakers Demo

What happens to the volume of the two buckets when:

- Both people have the same size cups?
- One person has two cups?

To apply this, imagine that:

- One bucket represents "reactants" and the other is "products".
- The volume of water in each bucket represents the concentration of that species.
- The amount being transferred between buckets is the rate of reaction.

Reversible Reactions

- Reactants will not run out; reaction can continue indefinitely
- Eventually, concentrations of products and reactants will become constant
- Forward and reverse reactions happening at same rate, a point called equilibrium
- Equilibrium is dynamic – reaction is still occurring

Equilibrium

Equilibrium IS:

- Forward/reverse reactions occurring at same rate
- Constant concentrations/volumes of products and reactants
- Permanent, unless a change is made to the system
- Only able to be reached in a closed system

Equilibrium is NOT:

- The end of the reaction (it's still happening)
- Equal concentrations/volumes of reactants and products

Equilibrium Constant

- Relationship between concentrations of products and reactants in a system
- Defined by a number, the eqm constant, K
- No units
- Temperature dependent

Equilibrium Constant

- For the general reversible reaction:

$$aA + bB \rightleftharpoons cC + dD$$

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

- [ ] means concentration in mol/L
- [ ] will always equal 1 for solids and liquids, because concentration doesn't change – just amounts (e.g. water does not have a "concentration")

Equilibrium Constant

- K can also be written for partial pressures (derived from IGL)

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

Equilibrium Constant

- Constant for a reaction at a certain temperature
- Lets you find eq'm concentrations of all species based on original amounts
- K < 1 means the reaction favours the reactants
- K > 1 means the reaction favours the products

Example: K Expression

Write the equilibrium expression for the reactions:

$CH_4\,(g) + H_2O\,(g) \rightleftharpoons CO\,(g) + 3H_2\,(g)$

$SO_2\,(g) + 2H_2S\,(g) \rightleftharpoons 3S\,(s) + H_2O\,(g)$

$P_4\,(s) + 6Cl_2\,(g) \rightleftharpoons 4PCl_3\,(l)$

Example: K_P Expression

Write the expression for K_p for the reactions:

$P_4\,(s) + 6Cl_2\,(g) \rightleftharpoons 4PCl_3\,(l)$

Deep blue solid copper(II) sulfate pentahydrate is heated to drive off water vapour to form white solid copper(II) sulfate

K_c Calculation Example

Find the value of K_{eq} for the reaction.

$FeO\ (s) + CO\ (g) \leftrightharpoons Fe\ (s) + CO_2\ (g)$

At equilibrium,

FeO = 5.00 g
[CO] = 0.713 M
[CO_2] = 0.478 M
Fe =2.88 g

K_p Calculation Example

Find the value of K_p for the reaction at 25°C.

$2\ NO\ (g) + Cl_2\ (g) \rightleftharpoons 2\ NOCl\ (g)$

At equilibrium,

P_{NOCl} = 1.2 atm
$P_{NO} = 5.0 \times 10^{-2}$ atm
$P_{Cl2} = 3.0 \times 10^{-1}$ atm

Stoichiometry of Eqm Expressions

- Changing coefficients:
  - When coefficients are multiplied by some factor, K is raised to the power of that factor
  - e.g. 2x is K^2
- Reversing equations:
  - Reciprocal of K (1/K)
- Adding equations
  - Multiply respective K values

Example: Calculating K Values

For the Haber process at 127°C:

[NH_3] = 3.1×10^{-2} M (product)

[N_2] = 8.5×10^{-1} M

[H_2] = 3.1×10^{-3} M

a. Calculate K for this reaction.
b. Calculate K for the decomposition of NH_3
c. Calculate K for this reaction if coefficients are divided by 2

K_p and K_c

- Not interchangeable
- Related by:

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

Where R is 0.0821 L·atm/mol·K
T is temperature in Kelvin

- **When are they equal?**

Reaction Quotient

- Use when system is not at equilibrium

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

- If $Q_c > K$ (too big), system is not at equilibrium = shifts towards reactants
- If $Q_c < K$ (too small), system is not at equilibrium = shifts towards products
- If $Q_c = K$, the system is at equilibrium

Reaction Quotient Example

$2NH_3\,(g) \rightleftharpoons N_2\,(g) + 3H_2\,(g)$, $K_C = 0.0076$

The initial concentrations are $[N_2] = 0.400M$, $[NH_3] = 0.600M$ and $[H_2] = 1.00M$. Which way will the equilibrium shift?

ICE Tables

- ICE tables are used to identify the relationship between the **initial** concentrations, the **change** in concentrations and the **equilibrium** concentrations.
- Find the equilibrium concentrations based on the initial concentrations of the system – given K

ICE Tables

<u>Steps</u>

1. Write the expression for the equilibrium constant.
2. Set up your ICE table. Make sure you use **concentration** (not moles!).
3. Substitute the equilibrium concentrations (with *x*) into the expression for K.
4. Solve for *x*.
5. Substitute *x* back into the "E" values in your ICE table.

ICE Tables

1. If it does not say an initial concentration for a species, assume it is zero!
2. When in doubt, write the equilibrium constant expression (K =…) and try an ICE table.

ICE Table Example 1

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

$K_c = 25.0$

2.00 mol of hydrogen and 3.00 mol of iodine are placed in a 2.00 L reaction vessel.

a. Write the equilibrium constant expression.
b. Create an ice table that models this system.

ICE Table Example 2

Consider an experiment in which gaseous N_2O_4 was placed in a flask and allowed to reach equilibrium at a temperature where $K_p = 0.133$. At equilibrium, the pressure of N_2O_4 was found to be 2.71 atm. Calculate the equilibrium pressure of NO_2 (g).

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

ICE Table Example 3

In the reaction

$$2\ HI\ (g) \rightleftharpoons H_2\ (g) + I_2\ (g)$$

The initial concentration of HI is 0.025 M, and K_c is 2.2×10^{-3}. What are the equilibrium concentrations of all of the species?

ICE Table Example 4

Initially, a mixture of 0.100 M NO, 0.050 M H_2 and 0.100 M H_2O was allowed to reach equilibrium. At equilibrium, the concentration of NO was found to be 0.062 M. Calculate K_c.

$$2\ NO\ (g) + 2\ H_2\ (g) \rightleftharpoons N_2\ (g) + 2\ H_2O\ (g)$$

ICE Table Example 5

Assume that gaseous hydrogen iodide is synthesized from hydrogen gas and iodine vapour at a temperature where the equilibrium constant is 100.0. Suppose HI at 0.5000 atm, H_2 at 0.01000 atm and I_2 at 5.000×10^{-3} atm are mixed in a 5.000 L flask. Calculate the equilibrium pressures of all species.

Le Chatelier's Principle

If conditions in a system at equilibrium are changed, the system will "shift" to reach a new equilibrium.

The shift changes the constant volume/concentration of the reactants and products in favour of one side.

Le Chatelier's Principle

Shift <u>right</u>: <u>forward</u> reaction occurs more rapidly until a new equilibrium is reached

Shift <u>left:</u> <u>reverse</u> reaction occurs more rapidly until the new equilibrium is reached

In general, anything that increases reaction rate can shift equilibrium

Le Chatelier's Principle

$$A + 2B \rightleftharpoons C + D$$

Shift by adding or removing reactants, adding or removing products or changing pressure/volume (for gases) or temperature

Le Chatelier's Principle

Concentration

$A + 2B \rightleftharpoons C + D$

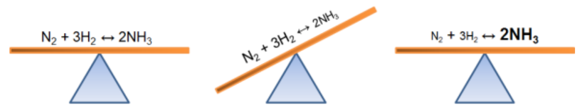
Adding reactants or removing products

- "excess" reactant needs to be converted into products
- Forward rate increases temporarily
- SHIFTS RIGHT (towards products)

Adding products or removing reactants

- "excess" product needs to be converted into reactants
- Reverse rate increases temporarily
- SHIFTS LEFT (towards reactants)

Le Chatelier's Principle



Le Chatelier's Principle

Temperature

$A + 2B \rightleftharpoons C + D + \text{heat}$

Think of heat as a reactant (endothermic) or product (exothermic)

Increase temperature:

Heat needs to be used up (eqm shifts away from the side that creates heat)

Decrease temperature:

Reaction that uses heat slows down (eqm shifts towards the side that creates heat)

Le Chatelier's Principle

Pressure and Volume

$A + 2B \rightleftharpoons C + D$

Will ONLY affect gases

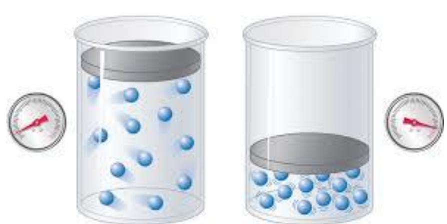
Increase in pressure (e.g. decrease in volume) shifts towards the side with fewer molecules.

- In the example, this is towards the RIGHT.

Decrease in pressure shifts towards the side with more molecules.

- In the example, this is towards the LEFT.

Le Chatelier's Principle



(a) Low pressure (b) High pressure

Le Chatelier's Principle

Inert Species and Catalysts

Inert species do not change equilibrium (do not participate in the reaction)

Catalysts have no effect because they affect both forward and reverse reactions equally.

Any compound or chemical added that does not participate in the reaction will not change the equilibrium

- EXCEPT if it changes the pressure in gaseous system
- If it is added but the system volume changes to accommodate the added pressure, the system does not shift

Example 1: Le Chatelier's Principle

Given the reaction:

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

Which way will the reaction shift if:

a. Hydrogen is removed
b. Ammonia is added

Example 2: Le Chatelier's Principle

Given the reaction:

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

Which way will the reaction shift if:

a. Oxygen is removed
b. Pressure is increased

Example 3: Le Chatelier's Principle

Given the reaction:

$$C_2H_2\ (g) + H_2O\ (g) \leftrightharpoons CH_3CHO\ (g)\ \Delta H = -151 kJ$$

Which way will the reaction shift if:

a. Temperature is increased
b. Pressure is increased
c. Nitrogen gas is added in a
    a. Fixed-volume container
    b. Variable-volume container

Example 4: Le Chatelier's Principle

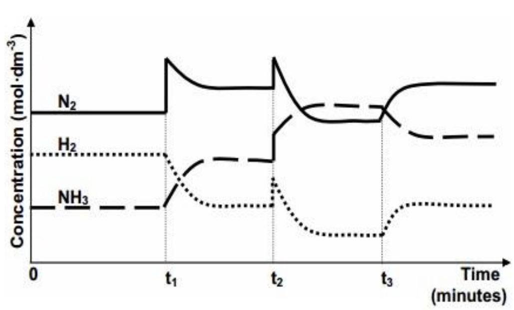
Given the reaction:

$$CO\ (g) + Fe_3O_4\ (s) \leftrightharpoons CO_2\ (g) + 3\ FeO\ (s)$$

Which way will the reaction shift if:

a. A catalyst is added
b. Pressure is increased
c. Carbon dioxide is added

Example 5: Le Chatelier's Principle



Example 6: Le Chatelier's Principle

A system contains 4.00 mol/L of A and 6.50 mol/L of B, at equilibrium.

$$A\ (g) \leftrightharpoons B\ (g)$$

a. Determine K_{eq} for this system.
b. If the concentration of A is increased by 1.50 mol/L, determine the new equilibrium concentration of each species.