BSK1133 PHYSICAL CHEMISTRY

CHAPTER 5
THERMODYNAMICS
(PART B)

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Description

Aims

- To understand the entropy of a reaction.
- To determine the entropy change of the universe, surroundings and system.
- To predict spontaneity and determine the equilibrium of a system based on the change in Gibbs free energy.

Description

Expected Outcomes

- ❖ Able to describe the change of the entropy for a system that attributed to the change of the dispersal energy
- ❖ Able to calculate the value of entropy change of system, surrounding and universe
- ❖ Able to predict spontaneity and describe the equilibrium of a system based on the change in Gibbs free energy

References

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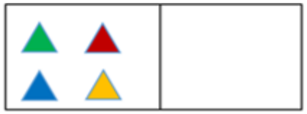
5.5 Entropy

ENTROPY

I. Introduction

- Measurement of the energy dispersion of a system in different ways.

i. Microstates and Entropy

a)


b)


c)


a) Only 1 way in the arrangement

b) 4 ways: three in the left and one in the right

c) 6 ways: every compartment consists of two

- ✓ Distribution (c) is the most probable cause there are 6 microstates.
- ✓ Distribution (a), only 1 microstate (least probable).
- ✓ Therefore, the probability of distribution (state) depends on microstates.

ii.Changes in Entropy

$$\Delta S = S_{\text{final state}}(\text{product}) - S_{\text{initial state}}\ (\text{reaction})$$

- the increase in the dispersal of energy results in the increase in entropy of a system

Processes:

a) Melting Process

- In solid, atoms or molecules are rigid to its position. Thus, low microstates.
- When melting, these atoms and molecules can occupy any positions freely.
- Consequently, the increase in the microstates cause an increase in entropy.

b) Vaporization Process

- **Greater entropy** is observed **compare to melting process** cause much **greater space** that can be occupy by molecules in gas phase.

c) Solution Process

- When a substance in solid form dissolves in water, **broke down** of the **structure** for the solid and water happen.
- Hence, the solution **exhibits higher microstates** than its element or compound.

iii. Standard Entropy

- ✓ **Standard entropy**: absolute entropy of a substance at standard state (**1 atm and 25 °C**). (**Unit: J/K or J/(K mol)** because the values of entropy are small).
- ✓ Standard state, refers to 1 atm. However, addition condition of 25 °C is due to most experiments are carried out at room temperature.
- ✓ **Entropies for all elements and compounds are greater than 0** (**$S° > 0$**).
- ✓ Meanwhile, standard enthalpy of formation (ΔH_f°) for

  a. elements in stable state: $H_f^{\circ} = 0$ b. compounds: may $H_f^{\circ} > 0$ or $H_f^{\circ} < 0$

- ○ Different states of Br_2: $S^{\circ}_{vapor} > S^{\circ}_{liquid}$
- ○ Different substances with the same phase: complexity of the molecular altering the entropy of a system

  Example: Ethane (more complex structure): $S^{\circ}_{ethane} > S^{\circ}_{methane}$

- ○ Monoatomic gases of Helium and Neon, which cannot execute rotational or vibrational motions. Heavier atoms demonstrates more closely spaced energy levels. Neon has a greater molar mass than He. $S^{\circ}_{Neon} > S^{\circ}_{Helium}$

II. The Second Law of Thermodynamics

Second Law of Thermodynamics: the entropy of the universe demonstrates an increment in a spontaneous process and constant in an equilibrium process.

Mathematically, For a spontaneous process: $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0$

For an equilibrium process: $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} = 0$

i. Entropy Changes in the System

Standard entropy of reaction, ΔS°_{rxn} is given by difference of standard entropies between products and reactants.

$$\Delta S^{\circ}_{rxn} = \Sigma nS^{\circ}(\text{products}) - \Sigma mS^{\circ}(\text{reactants})$$

which $\Delta S^{\circ}_{rxn} = \Delta S_{system}$, m and n for the stoichiometric coefficients

Example: $aA + bB \longrightarrow cC + dD$

$$\Delta S^{\circ}_{rxn} = [cS^{\circ}(C) + dS^{\circ}(D)] - [aS^{\circ}(A) + bS^{\circ}(B)]$$

Rules:

a. $\Delta S^{\circ} > 0$: a reaction forms more molecules

$CaCO_3\,(s) \longrightarrow CaO\,(s) + CO_2\,(g)$ **ΔS° = 160.5 J/K mol**

b. $\Delta S^{\circ} < 0$: total number of gas molecules diminishes

$N_2\,(g) + 3H_2\,(g) \longrightarrow 2NH_3\,(g)$ **ΔS° = - 199 J/K mol**

c. $\Delta S^{\circ} > 0$, $\Delta S^{\circ} < 0$ number of gas molecules remain constant

$H_2\,(g) + Cl_2\,(g) \longrightarrow 2HCl\,(g)$ **ΔS° = 20 J/K mol (small increase)**

ii. Entropy Changes in the Surroundings (Determine $\Delta S_{surroudings}$)

Condition I:

- Exothermic process in system: heat transferred to surroundings.
  - increase of microstates
  - increase of entropy in the surroundings
- Endothermic process in system: system gains heat from surroundings
  - decrease of microstate
  - decrease of entropy in the surroundings

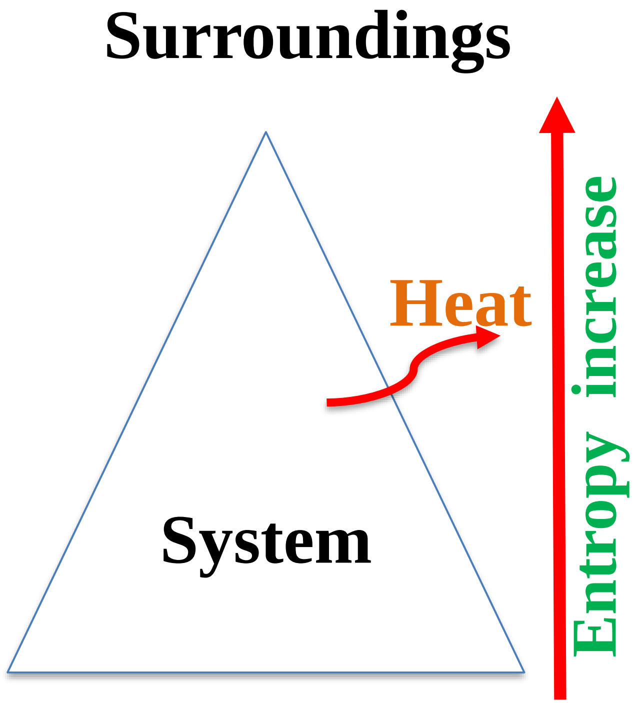
- For constant-pressure processes, the heat change is equal to ΔH_{system}. Therefore

$$\Delta S_{surr} \quad \alpha \quad -\Delta H_{sys}$$

(positive means increase in entropy) (exothermic)

$$-\Delta S_{surr} \quad \alpha \quad \Delta H_{sys}$$

(negative means decrease in entropy) (endothermic)



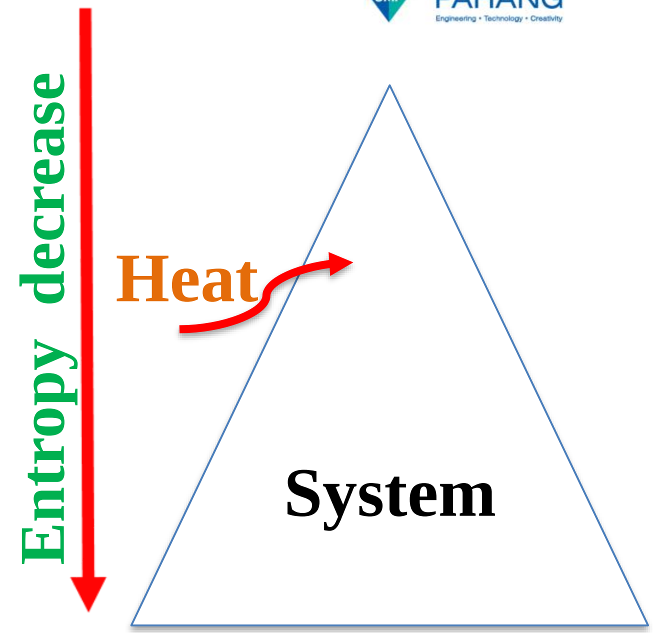
Surroundings

Heat

System

Entropy increase

An exothermic process, which heat is lost to the surroundings and lead to an increment of the entropy in the surroundings.



Surroundings

Entropy decrease

Heat

System

An endothermic process, which heat is gained and lead to a decrement of the entropy in the surroundings.

Condition II:

- Molecules consists of high kinetic energy when high temperature in the surroundings is high.
- Hence, the heat energy that can gain from an exothermic process does not give any significant impact on molecular motion and the resulting increase in entropy of the surroundings will be insignificant.
- In contrast, high impact for the case of low temperature in the surroundings where a more great increase in molecular motion and a huge increase in entropy.
- Therefore, inverse relationship between ΔS_{surr} and temperature:

$$\Delta S_{\mathrm{surr}} = \frac{-\Delta H_{sys}}{T}$$

Example: Predict whether the following reaction is spontaneous at 35 °C. (Given: ΔS_{sys} = -199 J/K mol)

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

$$\Delta S_{\mathrm{surr}} = \frac{-[(-92.6\ x\ 1000)]J/mol}{298.15\ K} = 300.5\ \mathrm{J/K\ mol}$$

5.6 Gibbs Free Energy

GIBBS FREE ENERGY

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

$\Delta G < 0$: spontaneous (forward direction).

$\Delta G > 0$: nonspontaneous (forward direction).

$\Delta G = 0$: The system is at equilibrium. There is no net change.

Standard free-energy of reaction (ΔG°_{rxn})

✓ In standard-state conditions, free-energy change when reactants are converted to products.

$$\Delta G^{\circ}_{rxn} = \Sigma n \Delta G^{\circ}_{f}(\text{products}) - \Sigma m \Delta G^{\circ}_{f}(\text{reactants})$$

Example: $aA + bB \longrightarrow cC + dD$

$$\Delta G^{\circ}_{rxn} = [c\Delta G^{\circ}_{f}(C) + d\Delta G^{\circ}_{f}(D)] - [a\Delta G^{\circ}_{f}(A) + b\Delta G^{\circ}_{f}(B)]$$

Standard free-energy of formation (ΔG_f°)

- ➢ free-energy change when 1 mole of substance is fabricated from its element in the standard state conditions.

Applications of Equation

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

- ✓ If ΔS andΔH are > 0, then ΔG < 0 when TΔS term is greater in magnitude than ΔH (when T is large)
- ✓ If ΔS andΔH are < 0, then ΔG < 0 when TΔS term is smaller in magnitude than ΔH (when T is small)
- ✓ If ΔS < 0 and ΔH > 0, then ΔG > 0 regardless T.
- ✓ If ΔS > 0 and ΔH < 0, then ΔG < 0 regardless T.

Phase Transition

It is occurred at the particular temperature (melting or boiling point) and the system is said at equilibrium ($\Delta G = 0$).

$$\Delta G = \Delta H - T\Delta S$$

$$0 = \Delta H - T\Delta S$$

$$\Delta S = \frac{\Delta H}{T}$$

Examples:

i. Ice-water equilibrium

For the ice → water transition, ΔH is the molar heat of fusion and T is the melting point. Given: ΔH_{fus}= 6.01 kJ/mol.

$$\Delta S_{fus} = \frac{6010\ \text{J/mol}}{273.15\ K} = 22\ \text{J/(K mol)} \longrightarrow$$

INCREASE ENTROPY

1 mole of ice is melted at 0 °C, gives an increase in entropy, ΔS = 22 J/(K mol).

ii. Water-ice equilibrium

Water → ice transition

$$\Delta S_{vap} = \frac{6010\ \text{J/mol}}{273.15\ K} = -\ 22\ \text{J/(K mol)} \longrightarrow$$

DECREASE ENTROPY

5.7 Free Energy and Chemical Equilibrium

FREE ENERGY AND CHEMICAL EQUILIBRIUM

$$\Delta G = \Delta G^\circ + RT \ln Q$$

R = gas constant (8.314 J/(K mol)

Q = reaction quotient

T = absolute temperature of the reaction,

At equilibrium, where $\Delta G = 0$ and $Q = K$ (where K is equilibrium constant)

$$\boxed{\Delta G = \Delta G^\circ + RT \ln K}$$

→ ΔG varies when the reaction progresses and become zero at equilibrium.
ΔG° is constant for a particular reaction at a given temperature.

$$\Delta G^\circ = - RT \ln K$$

K_p is for gases.

K_c is for solution in the reaction.

$\Delta G^\circ = 0$, products and reactants are equally.

$\Delta G^\circ < 0$, more products.

$\Delta G^\circ > 0$, more reactants.

Conclusion

- The value of entropy change of a system, surrounding or universe can be calculated.

- $\Delta G < 0$ is a spontaneous process, $\Delta G > 0$ is a nonspontaneous process and $\Delta G = 0$ is an equilibrium pross at constant temperature and pressure.

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