Physical Chemistry

Chapter 3 Second Law of Thermodynamic

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Chapter Description

- Aims
  - Develop the calculational path for property change and estimate enthalpy and entropy values using equation of state and generalized correlations.
  - Evaluate and prove the entropy of an isolated system must increase in an irreversible process using the second law of thermodynamics

- Expected Outcomes
  - Apply basic physical chemistry principle to solve the problem
  - Ability to communicate effectively and presenting in related topic

- Other related Information
  - **Problem Analysis** - Identify, formulate, research literature and analyse complex engineering problems reaching substantiated conclusions using first principles of mathematics, natural sciences and engineering sciences…..
  - **Communication-**Communicate effectively on complex engineering activities with the engineering community and with society at large, such as being able to comprehend and write effective reports and design documentation, make effective presentations and give and receive clear instructions

Subtopics

- 3.1 Introduction to Second Law of Thermodynamic
- 3.2 Heat engine
- 3.3 Entropy
- 3.4 Entropy Changes
- 3.5 The Gibbs energy

3.1 Introduction to Second Law of Thermodynamic

Features of Second Law

- ✓ Work can be changed to heat directly, however not the reverse.
- ✓ A process must satisfies both the 1st and the 2nd laws of thermodynamics

3.2 Heat engine

- A heat engine is a thermodynamic system operating in a thermodynamic cycle to which a net heat transfer to the system and a net work transfer from the system.

3.2 Heat engine (cont..)

Characteristics of heat engines

1. they receive heat from a high temperature source
2. they convert part of this heat to work
3. they reject the remaining wasteheat to a low temperature sink
4. they operate on a cycle

Subtopics

- **Thermal efficiency** - measure the performance of heat engines
- **Performance** = desired output/required input
- For heat engines:

$$\text{thermal efficiency} = \frac{\text{net work output}}{\text{total heat input}}$$

$$\eta_{th} = \frac{W_{net,out}}{Q_h}$$

$$\eta_{th} = 1 - \frac{Q_h}{Q_c}$$

$$\eta_{th} = 1 - \frac{Q_c}{Q_h} \quad ; W_{net,out} = Q_h - Q_c$$

$$\text{where} \quad \eta_{th} < 1.0$$

3.2 Heat engine (cont..)

- Thermal efficiency of heat engine can be maximized by supplying heat to engine at the highest possible temperature (limited by material strength) and rejecting heat from the engine at the lowest possible temperature (limited by the temperature of the cooling medium)

3.2 Heat engine (cont..)

- **Carnot Engine**
  - ✓ is reversible cycle, French engineer Sadi Carnot have proposed this engine in 1824.
  - ✓ Heat engine that funtion on the reversible
  - ✓ Thermal efficiency of heat engine

$$\eta_{th} = 1 - \frac{Q_c}{Q_h}$$

  - ✓ Thermal efficiency of Carnot heat engine as follows

$$\eta_{th,rev} = 1 - \frac{T_L}{T_H}$$

3.2 Heat engine (cont..)

- Refrigerator
  - Reversed-cycle engines
  - Heat transfer from a low temperature medium to a high temperature medium
  - operates in a cyclic devices
  - Objective – remove heat (Q_L) from the refrigerated space

3.2 Heat engine (cont..)

- Heat Pump
- Heat transfer from a low temperature medium to a high temperature medium
- Operates in a cyclic devices
- Objective – transfer heat (Q_H) to the heated space
- To ensure the heated area at high temperature (absorb heat)

3.2 (a) Heat-Work Changes

- **Spontaneous change**
  - A change that has tendency to occur without spontaneously
  - Nothing to do with speed.
  - Need not be fast
  - Example: precipitation reaction when solutions of NaCl and $AgNO_3$ are mixed.

- **Non-Spontaneous change**
  - A change that occurred only by doing work.
  - Example: reduction of gas volume

3.2 (a) Heat-Work Changes

The direction of spontaneous change:

1. The motivation of spontaneous change is tendency of the energy and mattered to become disordered.
2. A shift of a gas to spread into and fill the container it occupies (Natural direction of change corresponds to dispersal of matter)
3. Energy transfer from hot block to cold block (Natural direction of change corresponds to dispersal of energy)

3.2 (a) Heat-Work Changes

- Reversible & Irreversible Process:

1. Irreversible ~ process cannot reverse themselves spontaneously and restore the system to its initial state. (Example: Flow of energy from cold block to hot block)
2. Reversible ~ Process that can be reversed without leaving any trace on surroundings
3. All process occurring in nature are irreversible
4. Engineers interested in reversible process
   a. Deliver most works (turbine)
   b. Consume least work (pump & compressor)

3.3 Entropy,*S*

- The second law of thermodynamics leads to the definition of a new property called entropy, a measurement of the disorder for a system (how that energy is stored).
- Low *S* means little disorder; high *S* means great disorder
- It is defined as

$$dS = \left(\frac{\delta Q}{T}\right)_{\text{int rev}} \qquad \text{(kJ/K)}$$

- Entropy changes of a system during a process can be determined between initial and the final states as

$$\Delta S = S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T}\right)_{\text{int rev}} \qquad \text{(kJ/K)}$$

3.3 Entropy,*S*

The increase of entropy principles:

1. Entropy is increased by heating, which increase the motion and thus the relative disorder of the molecules or by providing more locations into which the molecules can spread.
2. $\int_1^2 \left(\frac{\delta Q}{T} \right)$ represent the entropy transfer with heat

3. Some entropy induced or created during an irreversibility process, this generation is due to the presence of irreversibility.

3.4 Entropy changes

The changes of entropy occur in the following related processes:

1. Entropy change accompanying expansion
2. Entropy change accompanying heating.
3. Entropy change when specific heats vary with temperature
4. Entropy change accompanying phase transitions
5. Entropy change in surroundings

Entropy changes (cont..)

- **Entropy change accompanying expansion:**

1. Entropy of a sample of gas increase as it expands. Why?
2. The molecules get to move in a greater volume and so have a greater degree of disorder.
3. The change in entropy when a perfect gas expands isothermally from volume V_i to a volume, V_f

$$\Delta S = \frac{q_{rev}}{T} = nR \ln \frac{V_f}{V_i}$$

Isothermal, reversible, perfect gas

Entropy changes (cont..)

- **Entropy change accompanying heating:**

1. Entropy of a sample is increase when the temperature raised from T_i to T_f. Why?
2. Thermal disorder if the system is greater and the molecules move more vigorously.

$$\Delta S = C_v \ln \frac{T_f}{T_i} = C_p \ln \frac{T_f}{T_i}$$

Constant heat capacity

Entropy changes (cont..)

- **Entropy change** when the heat capacity varies with temperature as the following formula shown:

$$\Delta S = \int_{T_i}^{T_f} \frac{CdT}{T}$$

Subtopics

- Suppose that the heat capacity depends on temperature as C = a + bT + a/T^2. Find the expression for the change of entropy accompanying heating from T_i to T_f.

$$\Delta S = a\ln\left(\frac{T_f}{T_i}\right) + b\left(T_f - T_i\right) - \frac{a}{2}\left(\frac{1}{T_f^2} - \frac{1}{T_i^2}\right)$$

Entropy changes (cont..)

- **Entropy change accompanying a phase transition:**

1. Entropy of a substance increases when it melts and boils. Why?
2. Its molecules become more disordered as it changes from solid to liquid and from liquid to vapor.

Entropy changes (cont..)

- **Entropy change accompanying a phase transition:**

3. Fusion entropy is the change of entropy per mole of substance at the melting temperature, T_f

$$\Delta S_{fus} = \frac{\Delta H_{fus}(T_f)}{T_f}$$

4. Entropy of vaporization is the change of entropy per mole of substance at the boiling temperature, T_b

$$\Delta S_{vap} = \frac{\Delta H_{vap}(T_b)}{T_b}$$

3.4 Entropy changes (cont..)

- **Determination of entropy in a phase transition instead of temperature transition -** Determine the entropy of vaporization of water at 25^oC. Given:
  C_p (H_2O, liquid) = 75.29 J/mol.K
  C_p (H_2O, vapor) = 33.58 J/mol.K
  $\Delta H_{vap} = 4.07 \times 10^4$ J/mol

  - Step 1: Entropy change for heating liquid water from 25^oC to 100^oC.
  - Step 2: Entropy of transition at 100^oC
  - Step 3: Entropy for cooling from 100^oC to 25^oC

3.4 Entropy changes (cont..)

- The entropy change of the surroundings in contact with system at temperature, T:

$$\Delta S_{surr} = \frac{q_{surr}}{T} = \frac{-q}{T}$$

- q_{surr} ~ energy supplied to the surrounding as heat

$$\Delta S_{surr} = -nR \ln \frac{V_f}{V_i}$$

Ideal gas,
Isothermal

3.5 The Gibbs Energy

- Total entropy change that accompanies a process is:

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{sur}$$

- Spontaneous change, $\Delta S_{total} > 0$.
- At constant pressure and temperature,

$$\Delta S_{total} = \Delta S_{sys} - \frac{\Delta H}{T} \qquad (1)$$

- The advantage: The total entropy of the system and surrounding is express in terms of properties of the system alone.
- Limitation: Constant temperature and pressure.

3.5 The Gibbs Energy (Free Energy)

- Gibbs energy, G is defined as

$$G = H - TS$$

- A change in Gibbs energy at constant temperature

$$\Delta G = \Delta H - T\Delta S_{sys} \qquad (2)$$

- A change in Gibbs energy at constant temperature and pressure,

$$\Delta G = -T\Delta S_{total}$$

- At constant temperature and pressure, the change in Gibbs energy is proportional to the overall change in entropy of the system + surrounding.

3.5 The Gibbs Energy (Free Energy)

Properties of Gibbs energy:

1. In a spontaneous change, $\Delta S_{total} > 0$ at constant temperature and pressure, the Gibbs energy decrease.
2. The value of ΔG for a process gives the maximum non-expansion work that can be extracted from the process at constant temperature and pressure.

$$\Delta G = w'_{\mathrm{max}}$$

Conclusion of The Chapter

- Conclusion
  1. Develop the calculation path for property change and estimate enthalpy and entropy values using equation of state and generalized correlations.

  2. Evaluate and prove the entropy of an isolated system must increase in an irreversible process using the second law of thermodynamics

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