

VC210 Recitation Class for Quiz2

Wei Xiwen

UM-SJTU JI

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- 1 Second Law of Thermodynamics
- 2 Third Law of Thermodynamics
- 3 Gibbs Free Energy

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- 3 Gibbs Free Energy

Entropy

- Spontaneous change: can occur without external influences.
- Entropy (S): measure of disorder. Disorder \uparrow , entropy \uparrow .

The second law of thermodynamics: The entropy of an **isolated** system increases in the course of any **spontaneous** change.

Entropy Change

In a reversible process,

$$\Delta S = \frac{q_{rev}}{T} \quad (1)$$

If pressure is constant (e.g. vaporization, fusion, etc.), $\Delta H = q$, so

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

For $\Delta S_{surrounding}$,

$$\Delta S_{sur} = \frac{-\Delta H}{T} \quad (2)$$

Reversible Process

For a change: state 1 to state 2, if we can find some ways to get state 2 back to state 1, the change is a **reversible process**.

Ideal Gas of in a Reversible Process

- Constant temperature & reversible process & ideal gases:

$$\Delta S = nR \ln \frac{V_f}{V_i} = nR \ln \frac{P_i}{P_f} \quad (3)$$

Hence, volume \uparrow , entropy \uparrow .

- Constant volume & constant c & reverse process & ideal gases:

$$\Delta S = c_V \ln \frac{T_f}{T_i} \quad (4)$$

- Constant volume & time-varying c & reverse process & ideal gases:

$$\Delta S = \int_{T_i}^{T_f} \frac{cdT}{T} \quad (5)$$

Trouton' Rule

Approximately, for any liquid converted to vapor, the entropy change:

$$\Delta S = 85 J / (K \cdot mol) \quad (6)$$

Applying the equation $\Delta S = \frac{\Delta H}{T}$,

- $\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}$, T_b : boiling temperature.
- $\Delta S_{fus} = \frac{\Delta H_{fus}}{T_f}$, T_f : melting temperature.

Qualitatively Compare Entropy

1. Gas>Liquid>Solid
2. More **complex** the molecule, more chaotic the substance is.
3. **Heavier** atom has more energy
4. **Polar** molecules have **less** entropy

where "more complex molecule" means "have more atoms".

Standard Entropy

$$\Delta S^{\circ} = \sum n \Delta S^{\circ}(\text{products}) - \sum n \Delta S^{\circ}(\text{reactants}) \quad (7)$$

where n is the moles.

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Thrid Law of Thermodynamics

Content: The entropy of perfect crystal approaches 0 as the absolute temperature approaches 0.

Boltzmann Formula

$$S = k \ln W \quad (8)$$

- $k = \frac{R}{N_A} = 1.381 \times 10^{-23} J/K$
- W: microstates, the number of possible positions that atoms/molecules can be arranged.
- S: absolute entropy at any temperature, called "statistical entropy".

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Gibbs Free Energy

$$\Delta G = \Delta H_{system} - T\Delta S_{system} \quad (9)$$

- $\Delta G < 0$, reaction is spontaneous.
- $\Delta G = 0$, reaction is in equilibrium (no tendency to proceed in either direction).
- $\Delta G > 0$, reverse reaction is spontaneous.

Gibbs free energy of a reaction (similar to enthalpy and entropy):

$$\Delta G = \sum n\Delta G(products) - \sum n\Delta G(reactants) \quad (10)$$

Maximum Non-expansion Work

$$w_{max} = -\Delta G \quad (11)$$

Non-expansion Work

Work without change of volume. For example, electric work.

End

Welcome