

VC210 Recitation Class 5

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2020 Nov. 2

Contents

- 1 First Law of Thermodynamics
 - Work
 - Heat
 - Enthalpy
- 2 Second Law of Thermodynamics
- 3 Third Law of Thermodynamics
- 4 Gibbs Free Energy

- 1 First Law of Thermodynamics
- 2 Second Law of Thermodynamics
- 3 Thrid Law of Thermodynamics
- 4 Gibbs Free Energy

First Law of Thermodynamics

$$\Delta U = q + w \quad (1)$$

q: heat; w: work

- Isolated system: $\Delta U = 0$, internal energy is constant.
- Constant volume: $w=0$, $\Delta U = q$.
- Energy is only transferred as heat: $\Delta U = q$.

Attention

- w: the work done to the system.
- q: the heat enters the system

Pay attention to the sign!

Type of system

	Exchange with surroundings
open system	matter & energy
closed system	energy
isolated system	nothing

Expansion Work

$$w = -P_{ex}\Delta V \quad (2)$$

P_{ex} : external pressure.

- When $\Delta V > 0$, the system expands, the work is negative.
- When the system is expands to vacuum, $P_{ex} = 0$, $w=0$.

Constant temperature: $dw = -P_{ex}dV$. This leads to:

$$w = -nRT \ln \frac{V_f}{V_i} \quad (3)$$

T: the constant temperature; V_f : final volume; V_i : initial volume.

Heat Capacity

$$c = \frac{q}{\Delta T} \quad (4)$$

Unit: $J/(kg \cdot K)$, 1 cal=4.184 J.

- Specific heat capacity: $c_s = \frac{c}{m}$.
- Molar heat capacity: $c_m = \frac{c}{n}$

Calorimeter

- Measure energy transfer
- $q = -C_{cal}\Delta T$, c_{cal} : heat capacity of calorimeter.

Heat Capacity

Heat capacity and molecular structure:

	Monoatomic	Linear	Nonlinear
$C_{v,m}$	$3/2R$	$5/2R$	$3R$
$C_{p,m}$	$5/2R$	$7/2R$	$4R$

$C_{v,m}$: constant volume & per mol;

$C_{p,m}$: constant pressure & per mol.

Enthalpy and Enthalpy change

$$H = U + PV \quad (5)$$

- Constant pressure: $\Delta H = q$.(why?)
- For chemical reaction open to atmosphere or constant pressure:
 - Exothermic: $\Delta H < 0$.
 - Endothermic: $\Delta H > 0$.

Enthalpy Change of Reactions

- Vaporization:

$$\Delta H_{vap} = H_m(vapor) - H_m(liquid) \quad (6)$$

- Fusion:

$$\Delta H_{fus} = H_m(liquid) - H_m(solid) \quad (7)$$

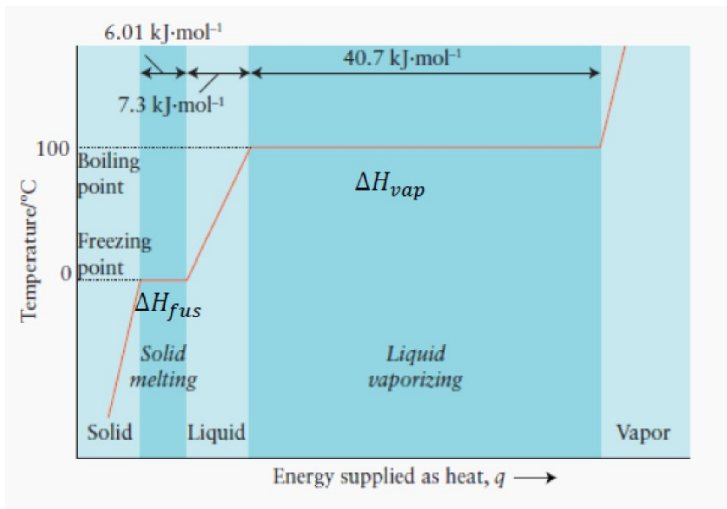
- Sublimation:

$$\Delta H_{sub} = H_m(vapor) - H_m(solid) \quad (8)$$

Reverse reaction:

$$\Delta H_{reverse} = \Delta H_{forward} \quad (9)$$

Heating Curve



Standard Reaction Enthalpy

Reaction enthalpy measured at **standard state**

Standard State in Thermodynamics

- Pressure: 1 bar
- Temperature: 298.15 K (not 273.15 K or 0°C)
- Solution concentration (if solution is involved): 1 mol/L

Denote as X°

- Standard enthalpy of formation:

$$\Delta H_f^\circ = \sum n \Delta H_f^\circ(\text{products}) - \sum n \Delta H_f^\circ(\text{reactants}) \quad (10)$$

Standard Reaction Enthalpy

- No gas is generated or consumed: $\Delta H = \Delta U$
- Gas is generated: $\Delta H = \Delta U + \Delta n_{gas}RT$

Hess's Law

$$\Delta H_{overall} = \sum \Delta H_{steps}$$



Born-Haber Cycle

Consider an ionic compound, MX_2 , composed of generic metal M and generic, gaseous halogen X.

- The enthalpy of formation of MX_2 is $\Delta H_f^\circ = -817 \text{ kJ/mol}$.
- The enthalpy of sublimation of M is $\Delta H_{\text{sub}} = 109 \text{ kJ/mol}$.
- The first and second ionization energies of M are $\text{IE}_1 = 771 \text{ kJ/mol}$ and $\text{IE}_2 = 1387 \text{ kJ/mol}$.
- The electron affinity of X is $\Delta H_{\text{EA}} = -311 \text{ kJ/mol}$. (Refer to the hint).
- The bond energy of X_2 is $\text{BE} = 231 \text{ kJ/mol}$.

Determine the lattice energy of MX_2 .

$\Delta H_{\text{lattice}} =$

kJ/mol

Heat Capacity to Enthalpy

At constant pressure,

$$\Delta H_2^\circ = \Delta H_1^\circ + (T_2 - T_1)\Delta c_p \quad (11)$$

$$\Delta c_p = \sum n c_{p,m}(\text{products}) - \sum n c_{p,m}(\text{reactants})$$

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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,

$$\Delta S = \frac{q_{rev}}{T} \quad (12)$$

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

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

For $\Delta S_{surrounding}$,

$$\Delta S_{sur} = \frac{-\Delta H}{T} \quad (13)$$

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:

$$\Delta S = nR \ln \frac{V_f}{V_i} = nR \ln \frac{P_i}{P_f} \quad (14)$$

Hence, volume \uparrow , entropy \uparrow .

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

$$\Delta S = c_V \ln \frac{T_f}{T_i} \quad (15)$$

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

$$\Delta S = \int_{T_i}^{T_f} \frac{cdT}{T} \quad (16)$$

Trouton' Rule

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

$$\Delta S = 85 J / (K \cdot mol) \quad (17)$$

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

$$\Delta S^{\circ} = \sum n\Delta S^{\circ}(\text{products}) - \sum n\Delta S^{\circ}(\text{reactants}) \quad (18)$$

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.

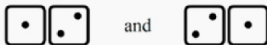
Boltzmann Formula

$$S = k \ln W \quad (19)$$

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

Example

With two dice, each numbered 1–6, there are two possible ways to roll a 3.



Thus, for the outcome of 3 (a particular macrostate), there are 2 microstates.

How many possible ways are there to roll a 4?

number of ways to roll a 4:

What is the entropy associated with an outcome of 4?

$S =$

J/K

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Gibbs Free Energy

$$\Delta G = \Delta H_{system} - T\Delta S_{system} \quad (20)$$

- $\Delta G < 0$, 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):

$$\Delta G = \sum n\Delta G(products) - \sum n\Delta G(reactants) \quad (21)$$

Maximum Non-expansion Work

$$w_{max} = -\Delta G \quad (22)$$

Non-expansion Work

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

End

Q&A