Chapter 19
Chemical Thermodynamics

Review

- **Spontaneous process:** one that proceeds on its own without any outside assistance, <mark>processes that are spontaneous in one direction are nonspontaneous in the opposite direction.</mark>
- **Reversible process:** can restore the system to its original condition with no net change to either the system or its surroundings.
- **Irreversible process:** one that cannot simply be reversed to restore the system and its surroundings to their original states.
    1) In the isothermal reversible process, the system do the greatest work to the surrounding;
    2) The reversible process is an ideal process, all real processes are irreversible;
    3) Any spontaneous process is irreversible;
    4) Reversible process is not the reversible reaction;

- **Enthalpy (H=E+pV):** the thermodynamic quantity equivalent to the total heat content of a system. It is equal to the internal energy of the system plus the product of pressure and volume.
- **Enthalpy change:**
    1) When there is only the volume work, the enthalpy change equals the sum of the change of internal energy and the volume work under constant pressure ($\Delta H = \Delta E + p\Delta V$).
    2) The enthalpy change is the heat absorbed by a system during a constant pressure process ($\Delta H = q_p$).

- **Entropy (S):** a measure of the randomness or disorder in a system.
- **Entropy change (ΔS):**
    1) Depend only on the initial and final states of the system and not on the path taken from one state to the other.

$$\Delta S = S_{final} - S_{initial} = \frac{q_{rev}}{T} \text{ (constant T)}$$

    2) The entropy change in a chemical reaction equals the sum of the entropies of the products minus the sum of the entropies of the reactants:

$$\Delta S^o = \Sigma n S^o(products) - \Sigma m S^o(reactants)$$

- <mark>**The first law of thermodynamics:** energy cannot be created or destroyed, but can be converted from one to another.</mark>

$$\mathbf{\Delta E = q + w}$$

- <mark>**The second law of thermodynamics:** any irreversible process results in an increase in the entropy of the universe, whereas any reversible process results in no change in the entropy of the universe.</mark>

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0 \text{ (reversible process)}$$
$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0 \text{ (irreversible process)}$$

- **Boltzmann equation:** entropy is a measure of how many microstates are associated with a particular macroscopic state.

$$S = k \ln W$$

$$\Delta S = k \ln W_{final} - k \ln W_{initial} = k \ln \frac{W_{final}}{W_{initial}}$$

k: Boltzmann constant=1.38×10^{-23} J/K;

W: number of microstates of a system;

ΔS: entropy increases with the number of microstates of the system;

- **Microstate:**
  1) a single possible arrangement of the positions and kinetic energies of the molecules when the molecules are in a specific thermodynamic state;
  2) a particular microscopic arrangement of the atoms or molecules of the system that corresponds to the given state of the system;
- **The number of microstates (the entropy) tend to increase with increases in:**
  1) Temperature;
  2) Volume;
  3) The number of independently moving molecules;
- **Molecular motion:**
  1) Translational motion: movement of the entire molecule from one place to another;
  2) Vibrational motion: the atoms in the molecule move periodically toward and away from one another;
 3) Rotational motion: the molecule spins about an axis.

  Note: More atoms means more microstates (more possible molecular motions).

bending

symmetric stretching

asymmetric stretching

vibrational motion   **rotational motion**   **translational motion**
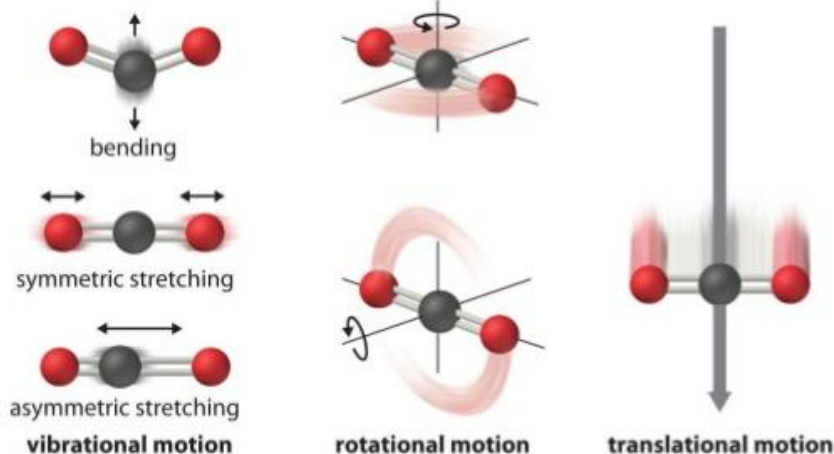
- **The third law of thermodynamics:** the entropy of a pure, perfect crystalline substance at absolute zero is zero: S (0 K) = 0

- **Standard molar entropy (S_m^o) :** molar entropies for substances in their standard states (J•mol^{-1}•K^{-1}).

  1) Standard molar entropy of gas is greater than that of liquid and solid;
  2) It increases with the increasing molar mass for similar substances;
  3) It increases with an increasing number of atoms in the formula of substances;
  4) It increases with the structural complexity of substances which have the same molar mass;
  5) It increases with the higher temperature for the same substances;
  6) The influence of pressure on solid and liquid is less, while for gas is great.
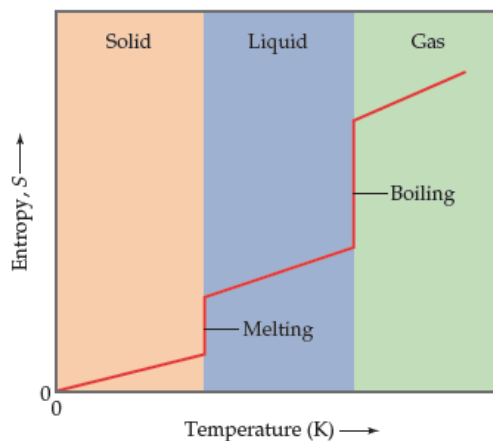
- **Gibbs free energy (G): G = H – TS (state function)**
- **Gibbs-Helmholtz Equation: for an isothermal process**

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

$$-\frac{\Delta G}{T} = -\frac{\Delta H}{T} + \Delta S$$

$$-\frac{\Delta G}{T} = \Delta S_{surr} + \Delta S_{sys} = \Delta S_{univ}$$

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

$$(at\ constant\ P,\ T: \Delta S_{surr} = \frac{q_{surr\cdot}}{T} = -\frac{q_{sys}}{T} = -\frac{\Delta H_{sys}}{T})$$

1) If $\Delta S_{univ} > 0$ ($\Delta G_{T,p} < 0$), the reaction is spontaneous in the forward direction;
2) If $\Delta S_{univ} = 0$ ($\Delta G_{T,p} = 0$), the reaction is at equilibrium;
3) If $\Delta S_{univ} < 0$ ($\Delta G_{T,p} > 0$), the reaction is spontaneous in the reverse direction;

- **Standard Gibbs free energy of formation (ΔG_f^o):** the change of Gibbs free energy that accompanies the formation of 1 mole of a substance in its standard state from its constituent elements in their standard states.

State of Matter	Standard State
Solid	Pure solid
Liquid	Pure liquid
Gas	1 atm pressure
Solution	1 M concentration
Element	$\Delta G_f^o = 0$ for element in standard state

- **Standard free-energy change for chemical processes:**

$$\Delta G^o = \Sigma n\Delta G_f^o(\text{products}) - \Sigma m\Delta G_f^o(\text{reactants})$$

- **Free-energy change under nonstandard condition:**

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

R: ideal-gas constant;
T: absolute temperature;
Q: the reaction quotient for the reaction mixture of interest;

- **Relationship between ΔG° and K: at equilibrium, $\Delta G=0$, $Q=K$**

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

$0 = \Delta G^\circ + RT \ln K$

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

$\ln K = \dfrac{\Delta G^o}{-RT}$

$K = e^{-\Delta G^o/RT}$