
Lecture #9**THE THIRD LAW OF THERMODYNAMICS**

Entropy is a measure of disorder. The most ordered aggregate state is the solid state. So, it has the lowest entropy. Consider heating of a solid from absolute zero to some T below its melting point at constant pressure;

Solid (0°K , P) → Solid (T, P)

The entropy change is;

$$\Delta S = S_T - S_0 = \int_0^T \frac{C_p}{T} dT$$

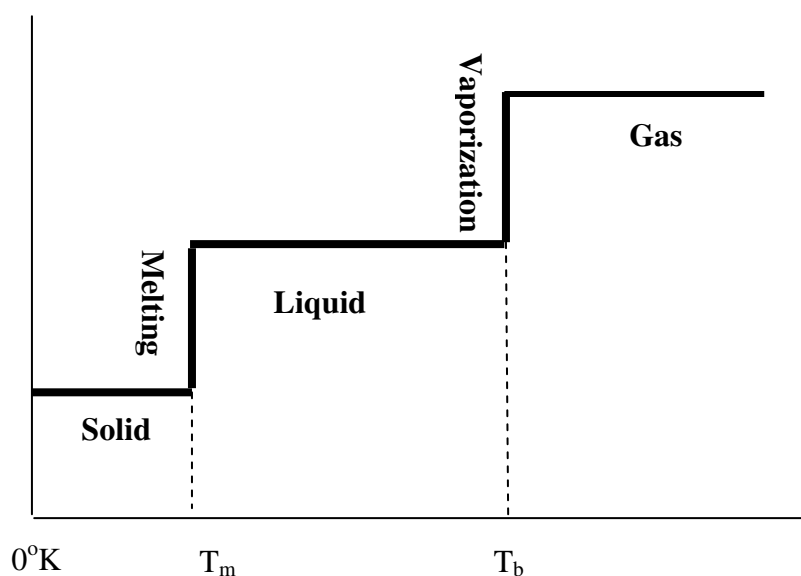
$$S_T = S_0 + \int_0^T \frac{C_p}{T} dT$$

Moreover, entropy increases with temperature. The lowest entropy that can be attained is 0°K . Based on these facts, the third law of thermodynamics has been developed by Planck. The smallest absolute entropy belongs to a solid at 0°K . The third law of thermodynamics states that the entropy of a pure, perfectly crystalline substance is zero at the absolute zero of temperature.

Therefore, **absolute entropy of a solid at T°K** may be written as;

$$S_T(s) = \int_0^T \frac{C_p}{T} dT$$

If the pressure is 1 atm, then the entropy is designated as S° and called "standard entropy".



Substances are solids in the temperature range 0°K and the melting point of the substance T_m . At the melting point, a phase transition occurs. The solid substance melts and forms a liquid. Up to the boiling point T_b it stays as a liquid. Finally, at the boiling point a second phase change occurs. The liquid vaporizes and forms a gas.

A change in the state of aggregation such as melting, vaporization increases the entropy. Phase changes should be taken into account in the calculation of the entropies for liquids and gases.

Absolute entropy of a liquid at T:

$$S_T^\circ(l) = \int_0^{T_m} \frac{C_p^\circ(s)}{T} dT + \frac{\Delta H_{fus}^\circ}{T_m} + \int_{T_m}^T \frac{C_p^\circ(l)}{T} dT$$

Absolute entropy of a gas at T:

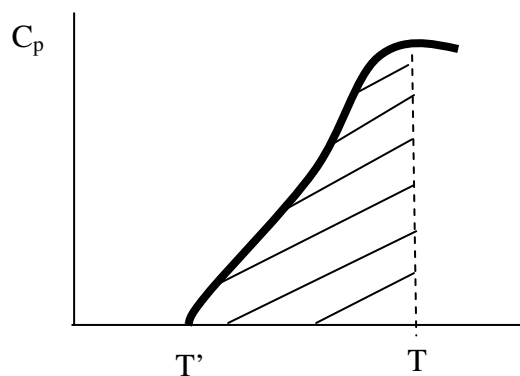
$$S_T^o(g) = \int_0^{T_m} \frac{C_p^o(s)}{T} dT + \frac{\Delta H_{fus}^o}{T_m} + \int_{T_m}^{T_b} \frac{C_p^o(l)}{T} dT + \frac{\Delta H_v^o}{T_b} + \int_{T_b}^T \frac{C_p^o(g)}{T} dT$$

However, there is a problem. Measurements of heat capacity can only be made down to $T' = 10\text{k}$ or 15k . At such low temperatures, the heat capacity obeys "**Debye T-cubed Law**";

$$C_v = aT^3$$

Where a is a constant for each substance. At these temperatures, C_v and C_p are indistinguishable. So, Debye T-cubed Law is used to calculate C_p below T' . The value obtained for T' gives the constant a . For temperatures higher than T' , the integral;

$$\int_{T'}^T \frac{C_p}{T} dT = \int_{T'}^T C_p d(\ln T)$$



is evaluated graphically to obtain the entropy of the solid at T . The area under the curve gives the entropy.

The standard molar entropies of all substances have been calculated by using the above principals and listed in entropy tables. An examination of such a table reveals the following results;

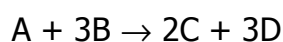
- Entropies of gases are larger than those of liquids which are larger than those of solids.

$$\bar{S}_g > \bar{S}_l > \bar{S}_s$$

- The entropies of gases increases logarithmically with the mass.
- For gases having the same mass, rotational motion affects the entropy. Cp depends upon the number of modes of rotational motion.
- For gases with the same mass and same heat capacity, entropy differences arise from the shapes of the molecules. The symmetrical molecule has the lower entropy than the one for an asymmetrical molecule.
- A tightly bound solid has lower entropy and lower heat capacity but high vibrational frequency.
- If the particles composing a solid are held together by van der Waal's forces, then the entropy is high.
- If there are complex units in the solid, the entropy is greater than the one consisting simple units.

Entropy Changes in Chemical Reactions

ΔS for chemical reactions is calculated by using the absolute molar entropies of the substances. For a general reaction; ΔS can be calculated as follows;



$$\Delta S^\circ = S_P^\circ - S_R^\circ$$

$$S_P^\circ = 2\bar{S}_C^\circ + 3\bar{S}_D^\circ$$

$$\bar{S}_R^{\circ} = S_A^{\circ} + 3\bar{S}_B^{\circ}$$

ΔS at 298 K is;

$$\Delta S^{\circ} = 2\bar{S}_C^{\circ} + 3\bar{S}_D^{\circ} - \bar{S}_A^{\circ} - 3\bar{S}_B^{\circ}$$

Temperature Dependence of ΔS

The simplest equation giving ΔS is;

$$\Delta S = S_P^{\circ} - S_R^{\circ}$$

Taking the derivatives with respect to T gives;

$$\left(\frac{\partial \Delta S}{\partial T}\right)_P = \left(\frac{\partial S_P}{\partial T}\right)_P - \left(\frac{\partial S_R}{\partial T}\right)_P$$

$$= \frac{(C_p)_P}{T} - \frac{(C_p)_R}{T} = \frac{\Delta C_p}{T}$$

we obtain;

$$\int_{T_o}^T d(\Delta S) = \int_{T_o}^T \frac{\Delta C_p}{T} dT$$

$$\Delta S_T = \Delta S_{T_o} + \int_{T_o}^T \frac{\Delta C_p}{T} dT$$