
ΔS in Phase Transitions

Phase transitions such as the vaporization of a liquid at the boiling point, fusion of a solid at the melting point are all ***reversible, isothermal*** changes. These transitions take place at a certain temperature and a pressure. Since T is constant, entropy change for a phase transition may be written as;

$$\Delta S = \frac{Q_{rev}}{T}$$

Moreover, phase transitions take place at constant pressure as well. Therefore;

$$Q_{rev} = Q_p = \Delta H$$

Entropy of vaporization is;

$$\Delta S_v = \frac{\Delta H_v}{T_b}$$

where T_b is the boiling point of the liquid. Similarly, entropy of fusion of a solid can be written as;

$$\Delta S_{fus} = \frac{\Delta H_{fus}}{T_m}$$

Trouton's Rule

For most of the liquids, the entropy of vaporization at the normal boiling point has approximately the same value;

$$\Delta S_v = 21 \text{ eu/mol}$$

$$(1 \text{ eu} = 1 \text{ cal/K})$$

For liquids which obey Trouton's Rule;

$$\Delta H_v = 21T_b$$

This equation may be used to calculate the heat of vaporization from knowledge of the boiling point.

Trouton's Rule cannot be applied to liquids containing H-bonds such as water, alcohols, amines etc. It cannot be applied either to liquids with boiling points lower than 150 °K.

The Fundamental Equation of Thermodynamics

In a reversible process, $P' = P$. The first law equation may be written as;

$$dQ_{rev} = dE + PdV$$

and by using the definition of entropy the fundamental equation is obtained as;

$$dS = \frac{dQ_{rev}}{T} = \frac{1}{T}dE + \frac{P}{T}dV$$

This equation is the combined form of the first and second laws of thermodynamics. The coefficients are positive. So, the equation indicates that an increase in energy increases the entropy and an increase in volume also causes an increase in entropy. Since the energy of the system cannot be controlled, entropy changes are expressed in terms of the properties of the system.

ΔS in terms of T and V

Entropy is a function of T and V;

$$S = S(T, V)$$

The total differential of S is;

$$dS = \left(\frac{\partial S}{\partial T}\right)_v dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

dE may be written in terms of T and V;

$$dE = C_v dT + \left(\frac{\partial E}{\partial V}\right)_T dV$$

Substituting this equation in the fundamental equation yields;

$$dS = \frac{C_v}{T} dT + \frac{1}{T} \left[P + \left(\frac{\partial E}{\partial V}\right)_T \right] dV$$

At constant volume the change in entropy with temperature may be written as;

$$\Delta S = \int_{T_1}^{T_2} \frac{C_v}{T} dT$$

Comparing the two equations for dS gives;

$$\left(\frac{\partial S}{\partial T}\right)_v = \frac{C_v}{T}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \left[P + \left(\frac{\partial E}{\partial V}\right)_T \right]$$

By using the fact that cross derivatives are equal, we find that;

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

The total differential of any function can be written as;

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

According to the "**Cyclic Rule**";

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

The three properties of the systems are P, V and T. The coefficient of thermal expansion is;

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$$

and the coefficient of compressibility is;

$$\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

By using the above equations and the Cyclic Rule we find that;

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{\beta}$$

and write the change in entropy in terms of T and V as;

$$dS = \frac{C_v}{T} dT + \frac{\alpha}{\beta} dV$$

ΔS in terms of T and P

If we assume $S = S(T, P)$, the total differential of entropy can be written as;

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

In order to write the fundamental equation in terms of T and P, we use the definition of enthalpy.

$$H = E + PV$$

$$dE = dH - PdV - VdP$$

Substituting into the fundamental equation yields;

$$dS = \frac{1}{T}dH - \frac{V}{T}dP = \frac{C_P}{T}dT + \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]dP$$

Comparing this equation with the total differential equation we may write;

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]$$

By using the fact that cross derivatives are equal we may express dS in terms of T and P as;

$$dS = \frac{C_P}{T}dT - \alpha VdP$$

Entropy Changes for an Ideal Gas

The above equations have a simple form when applied to the ideal gas. For an ideal gas;

$$dE = C_v dT$$

According to the Ideal Gas Law;

$$\frac{P}{T} = \frac{R}{\bar{V}}$$

By substituting these equations in the fundamental equation, we may express the entropy change for an ideal gas in terms of T and V;

$$dS = \frac{C_v}{T} dT + \frac{R}{\bar{V}} dV$$

Since the coefficient is always positive, the entropy of the ideal gas increases with increase in volume. The rate of increase is less at large volumes. For a change in state;

$$\Delta \bar{S} = \int_{T_1}^{T_2} \frac{\bar{C}_v}{T} dT + R \int_{\bar{V}_1}^{\bar{V}_2} \frac{dV}{\bar{V}}$$

If C_v is constant;

$$\Delta \bar{S} = \bar{C}_v \ln \frac{T_2}{T_1} + R \ln \frac{\bar{V}_2}{\bar{V}_1}$$

For an ideal gas,

$$dH = C_p dT$$

According to ideal gas law;

$$\frac{\bar{V}}{T} = \frac{R}{P}$$

By substituting these equations into the fundamental equation we may write;

$$dS = \frac{C_p}{T} dT - \frac{R}{P} dP$$

This equation indicates that in an isothermal operation the entropy of the ideal gas decreases with pressure. For a change in state;

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T} dT - R \int_{P_1}^{P_2} \frac{dP}{P}$$

If C_p is constant;

$$\Delta S = C_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

Standard Entropy for an Ideal Gas

For a change in state in an isothermal transformation;

$$d\bar{S} = -\frac{R}{P} dP$$

If the initial pressure is 1 atm;

$$\bar{S} - \bar{S}^\circ = -R \ln P$$

\bar{S}° is the molar entropy at 1 atm. So, it is "standard molar entropy". The rate of decrease of the entropy with pressure is rapid at low pressures and becomes less rapid at higher pressures.