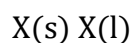


THERMODYNAMICS

ENTHALPY CHANGE, ΔR_x OF A REACTION – REACTION ENTHALPY

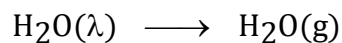
Change in Internal Energy and Enthalpy in Phase Transition: At certain temperature under one atmospheric pressure, one phase changes into other phase by taking certain amount of Heat. The temperature at which this happens is called transition temperature and heat absorbed during the process is called Enthalpy of phase transition. Heat absorbed during transition is exchanged at constant pressure and temperature and it is significant to know that the process is reversible.

Fusion: Solid ice at 273K and 1 atm pressure reversibly changes into liquid water. Reversibly, isothermally and isobarically, absorbing heat known as latent heat of fusion. Or enthalpy of fusion.



Vaporisation: Water at 373K and 1 atm pressure changes into its vapors absorbing heat known as latent heat of vaporisation. The latent heat of vaporisation is heat exchanged isothermally, isobarically and reversibly to convert water into its vapour at boiling point.

Internal energy change of phase transitions involving gas phase has no practical significance because it is not possible to carry out ΔU of phase transition directly through an experiment. However, ΔU of phase transition can be determined theoretically from experimentally obtained value of ΔH of phase transition.



$$\Delta H_{\text{vaporisation}} = \Delta U_{\text{vaporisation}} + P(V_f - V_i)$$

$$\Delta H_{\text{vaporisation}} = \Delta U_{\text{vaporisation}} + \{RT/V\}\{V_g\}$$

ignoring volume of liquid as compared to molar volume of gas

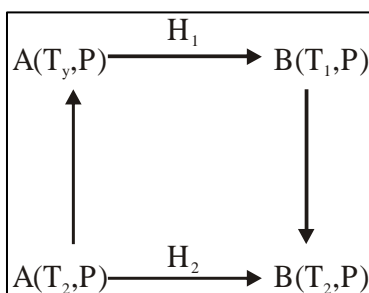
$$\Rightarrow \Delta H_{\text{vap.}} = \Delta U_{\text{vap.}} + RT$$

where R is gas constant and T absolute temperature for condensed phase transitions like solid liquid transitions

$$\Delta H_{\text{vap.}} \simeq \Delta U_{\text{vap.}}$$

Variation of Enthalpy with Temperature (KIRCHHOFF'S EQUATION): The enthalpy of chemical reactions and phase transition do vary with temperature. Although the variation in ΔH with temperature is usually small compared to the value of ΔH itself,

consider a reaction $A \longrightarrow B$ at temperature T_1 and pressure P



$$\Rightarrow \Delta H_2 - \Delta H_1 = \Delta_r C_p (T_2 - T_1)$$

If $\Delta_r C_p$ is independent of 'temperature'

$$\text{where } \Delta_r C_p = \sum n_p x(C_p)_{\text{products}} - \sum n_r x(C_p)_{\text{reactants}}$$

$n_p \rightarrow$ stoichiometric coefficients of products

$n_r \rightarrow$ stoichiometric coefficients of reactants