THERMODYNAMICS

ENTHALPIES FOR DIFFERENT TYPES OF REACTIONS

Entropy Change in Isolated System (Isolated System = sys + surer)

Consider a system taken from state A to state B by an irreversible path and returned to state A by a reversible path. Since one of the steps is irreversible, according to Clausius inequality, sum of q/T over the cycle must be less than zero. Hence



$$\sum_{A \to B} \frac{q_{irr}}{T} + \sum_{B \to A} \frac{q_{rev}}{T} \le 0 \qquad \qquad \Longrightarrow \xrightarrow{A \to B} \frac{q_{irr}}{T} = -\sum_{B \to A} \frac{q_{rev}}{T}$$

But $-\sum_{B \to A} \frac{q_{rev}}{T} = \sum_{A \to B} \frac{q_{rev}}{T}$ since the process is reversible for infinitesimally small change

$$\left(\frac{dq}{T}\right)_{A \to B} = ds_{system A \to B}$$

$$\Rightarrow dS_{system} \left(\frac{dq}{T}\right)_{A \to B} > 0$$

$$\Rightarrow dS_{system A \to B} + dS_{sur A \to B} > 0$$

$$\Rightarrow \Delta S_{Total isolated sys} > 0$$

Entropy Calculation in Process Involving Ideal Gases.

From First law

$$dq = dU + PdV$$
$$\frac{dq_{rev}}{T} = \frac{dU}{T} + \frac{PdV}{T}$$

 \Rightarrow

But for ideal gas

$$\frac{dU}{T} = \frac{nC_{v}dT}{T} \qquad \{\Theta \ dU = nC_{V}dT\}$$

 \Rightarrow

Integration gives

 $dS_{sys} =$

$$\Delta S = nC_V \ln \frac{\frac{T_2}{T_1} + nR \ln \left(\frac{V_2}{V_1}\right)}{2}$$

 $\frac{nC_{_V}dT}{T} + \frac{nR}{V}\,dV$

For isothermal process

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

For adiabatic process

$$v_1 = v_2$$

$$\Delta \mathbf{S} = \mathbf{n} \mathbf{C}_{\mathrm{V}} \ln \frac{\mathrm{T}_2}{\mathrm{T}_1}$$

For isochoric process

$$\Delta S = nC_V \ln \frac{T_2}{T_1}$$

For isobaric process

$$\Delta S = nC_p \ln \frac{T_2}{T_1}$$

Class- XI

Chemistry

Entropy Change in Chemical Reaction

From application of third law absolute entropy of every compound or element can be deduced for a general chemical reaction taking place at given condition

$$aA + bB ---> cC + dD$$

 $\Delta S = \Delta S_{system} = entropy change of reaction$
 $= (aS_C + dS_D - aS_A - bS_B)$

where S_C , S_D , S_A and S_B are molar entropy of substance A, B, C and D under given circumstance.

Entropy Change in Phase Transition

Fusion: When solid ice is heated below 273 K at external pressure of 1 atm it's temperature slowly rises. At 273 K however. its start melting into liquid without increase in temperature. The process is reversible phase transition from solid to liquid represented as:

$$H_{20}(s)$$
 $H_{20}(\lambda)$

Since process is reversible (you can safely assume that phase transition at constant temperature and pressure are reversible phase transitions).

$$\Delta S_{\text{fustion}} = \text{entropy of fusion at Melting point.}$$

Vapourisation: From you day to day experience you know that under atmospheric pressure temperature of H_2O (λ) cannot exceed 373 K. Since at 373 K liquid H_2O undergo phase transition.

$$\Delta \mathbf{S}_{\mathrm{vap}} = \frac{\Delta \mathbf{H}_{\mathrm{vap}}}{\mathbf{T}_{\mathrm{b}}}$$

Class- XI

Chemistry

Sublimation: It is the process in which solid directly changes into gaseous state

$$X(s) \stackrel{\Box}{=} \stackrel{\Box}{=} \frac{\Delta H_{sub}}{T_{sub}}$$

Phase Transition: $Allotrope_1 \Box \Box \Box$ Allotrope₂

$$\Delta S_{\text{transition}} = \frac{\Delta H_{\text{transition}}}{T_{\text{transition}}}$$

Boiling point at 1 atm pressure is called normal boiling point. There can be infinite boiling points of liquid depending upon external pressure we applying on boiling vessel.