Chapter 5

Chemical Thermodynamics

EXTENSIVE AND INTENSIVE VARIABLES

(a) Extensive property of a system are those whose magnitude depends on the amount of matter present in the system. These are additive in nature. For example, volume, internal energy, enthalpy, entropy, mass etc. Sum, subtraction and multiplication of two extensive property is extensive.

(b) The property whose magnitude does not depend upon quantity of matter present in a system is known as intensive property of the system. It is not an additive property. Examples are : temperature, pressure, density etc. Sum, subtraction, multiplication division of two intensive properties is intensive.

INTERNAL ENERGY (U)

It is the energy associated with a system by virtue of its molecular constitution and motion of its molecule. Such motion may be translational, rotational, vibrational etc.

Internal energy is a state function and an extensive property.

Heat supplied to system is denoted by q.

(1) When $q > 0$, heat has been supplied to system.

(2) When $q < 0$, system has rejected heat.

(3) When $q = 0$, no heat exchange ; process is adiabatic.

Work done on system (W)

(1) When $W > 0$ work is done on system.

(2) When $W < 0$ work is done by system.

Processes :

When a change is observed in the properties of system, a process is said to be taking place. This may be a chemical reaction or a physical process, like crystallization. Processes are of two types.

(1) Reversible : No change in entropy of universe.

(2) Irreversible : Entropy of universe increases.

q and W for some simple processes

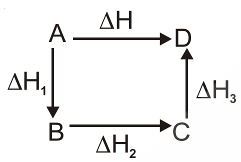
Table for ideal gases (only)

Reversible Process	q	W
Isothermal expansion	$nRT\ln\frac{V_f}{V_i}$ V_i = Initial volume V_f = Final volume	$-nRT\ln\frac{V_f}{V_i}$
Isobaric expansion	$nC_P\Delta T$	$-P\Delta V$
Adiabatic expansion	0	$\frac{nR}{\gamma-1}[T_2-T_1]$
Isochoric heating	$nC_V\Delta T$	0

HESS'S LAW OF CONSTANT HEAT SUMMATION

The enthalpy change for a reaction is the same whether it occurs in one step or in a series of steps.

If a reaction is the sum of two or more constituent reactions, then ΔH for the overall process must be sum of the ΔH of the constituent reactions.



For A → D, $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$.

ENTROPY AND ENTROPY CHANGE

Entropy is a measure of randomness. Higher the disorder, higher is the entropy.

Entropy for solid < liquid < gas

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

where q_{rev} = Heat absorbed when the process is carried out reversibly and isothermally.

Entropy change is given in unit of J/K or JK^{-1}.

Example : For reversible isothermal expansion of an ideal gas $\Delta S = nR\ln\frac{V_f}{V_i}$.

GIBB'S ENERGY AND SPONTANEITY OF REACTION

Gibbs defined a function by the relation.

$G = H - TS$

Use :

(i) At a given pressure and temperature if for an anticipated change dG for system is negative, process is spontaneous and if positive, process is spontaneous in reverse direction. Also if dG = 0, system is in equilibrium with respect to the given reaction or process.

(ii) –dG = maximum work done by system on non-expansion surrounding *e.g.*, cell doing electrical work on circuit.

Spontaneity of the reaction

ΔH	ΔS	$\Delta G = \Delta H - T\Delta S$	Reaction Spontaneity
–	+	–	Spontaneous at all temperature
–	–	– or +	Spontaneous at low temperatures where ΔH outweighs $T\Delta S$ ($T\Delta S < \Delta H$) Non-spontaneous at high temperatures where, $T\Delta S$ outweighs ΔH
+	–	+	Non-spontaneous at all temperatures
+	+	– or +	Spontaneous at high temperatures where $T\Delta S$ outweighs ΔH ($T\Delta S > \Delta H$) Non-spontaneous at low temperatures where ΔH outweighs $T\Delta S$

IMPORTANT POINTS

(1) Relation between ΔG and $\Delta G°$

$\Delta G = \Delta G° + 2.303RT \log Q$ (Q = reaction quotient)

(2) **$\Delta G°$ and equilibrium constant :**

At equilibrium, $\Delta G = 0$ and $Q = K$

$\therefore \Delta G^o = -RT \log_e K$

$= -2.303 \; RT \log_{10} K$

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