

Thermodynamic Terms

System: Part of universe under investigation.

Surroundings: Rest part of universe except system.

Boundary: Divide system and surroundings.

System

Open	Closed	Isolated
Energy and matter can exchange	Only energy can exchange	Neither energy nor matter can exchange

State function	Path function
Properties for which change depends only on initial and final state of the system and not on the process or path. e.g. U, H, S, G, etc.	Change depends on path or process. e.g. work, heat

Thermodynamic Properties

Extensive	Intensive
Properties which are dependent on amount of matter (size and mass) present in system	Properties which are independent of amount of matter (size and mass) present in system.
Volume Number of moles Mass Free Energy (G) Entropy (S) Enthalpy (H) Internal energy (E and U) Heat capacity	Molar volume Density Refractive index Surface tension Viscosity Free energy per mole Specific heat Pressure Temperature Boiling point, freezing point etc.

Processes

Isothermal	Isochoric	Isobaric	Adiabatic	Cyclic
$T = \text{const.}$	$V = \text{const.}$	$P = \text{const.}$	No heat exchange $dq = 0$	Initial and final state of system are same

Reversible process	Irreversible process
<ul style="list-style-type: none"> ❖ Slow process ❖ At any time, system and surrounding are in equilibrium. ❖ $P_{\text{sys}} = P_{\text{surr}} \pm dP$ 	<ul style="list-style-type: none"> ❖ Fast process ❖ Equilibrium between system and surrounding only at initial and final stages. ❖ $P_{\text{sys}} = P_{\text{surr}} \pm \Delta P$

Heat (q)

Energy exchange due to temperature difference:

$$q = C\Delta T,$$

$$q = nC_m\Delta T,$$

$$q = ms\Delta T$$

C = Heat capacity

C_m = Molar heat capacity

s = Specific heat capacity

m = Mass of substance

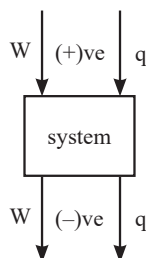
General values of C_V and C_P for an ideal gas can be taken as follows.

Atomicity		n_{tr}	n_{Rot}	n_{Vib}	C_V		C_P		γ	
					Excl. Vib	Incl. Vib	Excl. Vib	Incl. Vib	Excl. Vib	Incl. Vib
Mono		3	0	0	$\frac{3}{2}R$	$\frac{3}{2}R$	$\frac{5}{2}R$	$\frac{5}{2}R$	$\frac{5}{3}$	$\frac{5}{3}$
Di		3	2	1	$\frac{5}{2}R$	$\frac{7}{2}R$	$\frac{7}{2}R$	$\frac{9}{2}R$	$\frac{7}{5}$	$\frac{9}{7}$
Tri	Linear	3	2	4	$\frac{5}{2}R$	$\frac{13}{2}R$	$\frac{7}{2}R$	$\frac{15}{2}R$	$\frac{7}{5}$	$\frac{15}{13}$
	Non Linear	3	3	3	$3R$	$6R$	$4R$	$7R$	$\frac{4}{3}$	$\frac{7}{6}$

Work (w)

Reversible	Irreversible
$w_{rev} = - \int_{V_1}^{V_2} P_{ext} dV$	$w_{irr} = -P_{ext} (V_2 - V_1)$

Sign Convention



Work done on system = Positive

Work done by the system = Negative

Heat given to system = Positive

Heat given by the system = Negative

Internal Energy (E & U)

Every system having some quantity of matter is associated with a definite amount of energy called internal energy.

$$U = U_{Kinetics} + U_{Potential} + U_{Electronic} + U_{nuclear} + \dots$$

First Law of Thermodynamics

Law of conservation of energy

$$\Delta U = q + w$$

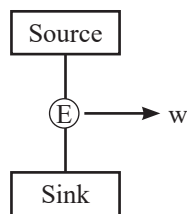
Enthalpy

$$H = U + PV, \Delta H = \Delta U + (\Delta n_g) RT$$

Process	Expression for w	Expression for q	Work on PV-graph
Reversible isothermal	$w = -nRT \ln \frac{V_2}{V_1}$ $= -nRT \ln \frac{P_1}{P_2}$	$q = nRT \ln \left(\frac{V_2}{V_1} \right)$ $q = nRT \ln \left(\frac{P_1}{P_2} \right)$	
Reversible adiabatic process	$w = nC_V(T_2 - T_1)$ $= \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$	$q = 0$ $PV^\gamma = \text{constant}$ $TV^{\gamma-1} = \text{constant}$ $TP^{1-\gamma/\gamma} = \text{constant}$	

Statements of Second Law of Thermodynamics

- (i) No cyclic engine is possible which take heat from one single source and in a cycle completely convert it into work without producing any change in surroundings.



- (ii) In an irreversible process entropy of universe increases but it remains constant in a reversible process.

$$\Delta S_{\text{syt}} + \Delta S_{\text{sur}} = 0 \quad \text{for rev. process}$$

$$\Delta S_{\text{syt}} + \Delta S_{\text{sur}} > 0 \quad \text{for irrev. process}$$

$$\Delta S_{\text{syt}} + \Delta S_{\text{surr}} \geq 0 \quad (\text{In general})$$

Calculation of Entropy Change for an Ideal Gas

General Expression

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = nC_P \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

Reversible & irreversible isothermal expansion or contraction

$$\text{of an ideal gas } \Delta S = nR \ln \frac{V_2}{V_1}$$

Third Law of Thermodynamics

“At absolute zero, the entropy of a perfectly crystalline substance is zero”. which means that at absolute zero every crystalline solid is in a state of perfect order and its entropy should be zero.

Variation of ΔS_r with Temperature & Pressure

$$(\Delta S_r)_{T_2} - (\Delta S_r)_{T_1} = (\Delta C_P)_r \ln \frac{T_2}{T_1}$$

$$(\Delta S_r)_{P_2} - (\Delta S_r)_{P_1} = \Delta n_g R \ln \frac{P_1}{P_2}$$

Similarly

$$(\Delta H_r)_{T_2} - (\Delta H_r)_{T_1} = (\Delta C_P)_r (T_2 - T_1) \quad \{\text{Krichoff's equation}\}$$

$$(\Delta U_r)_{T_2} - (\Delta U_r)_{T_1} = (\Delta C_V)_r (T_2 - T_1)$$

Gibbs Free Energy (G) and Spontaneity

A new thermodynamic state function G, the Gibbs free energy is defined as:

$$G = H - TS$$

At constant temperature and pressure

$$\Delta G = \Delta H - T \Delta S$$

If $(\Delta G)_{T,P} < 0$ Process is irreversible (spontaneous)

$(\Delta G)_{T,P} = 0$ Process is reversible

$(\Delta G)_{T,P} > 0$ Process is impossible (non spontaneous)

Some Facts to be Remembered

(a) Standard condition

❖ For gases/solid/liquid

$$P = 1 \text{ bar}$$

❖ For ion/substance in solution

$$\text{Concentration} = 1 \text{ M}$$

$$(b) \Delta G_r = (\Delta G_f)_{\text{product}} - (\Delta G_f)_{\text{reactant}}$$

$$\Delta H_r = (\Delta H_f)_{\text{product}} - (\Delta H_f)_{\text{reactant}}$$

$$\Delta S_r = (\Delta S_f)_{\text{product}} - (\Delta S_f)_{\text{reactant}}$$

(All above equation will be derived in thermochemistry)

Thermochemistry

Bond Enthalpy

Average amount of enthalpy required to dissociate one mole gaseous bond into separate gaseous atoms.

$\Delta_r H = (\text{Sum of bond enthalpy of gaseous reactant}) - (\text{Sum of bond enthalpy of gaseous product})$

Resonance Energy

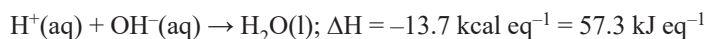
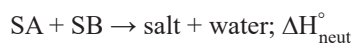
$$\Delta H_{\text{resonance}}^\circ = \Delta_f H^\circ (\text{experimental}) - \Delta_f H^\circ (\text{calculated})$$

$$= \Delta_c H^\circ (\text{calculated}) - \Delta_c H^\circ (\text{experimental})$$

Enthalpy of Neutralization (ΔH_{neut})

(Always exothermic)

Change in enthalpy when one gram equivalent of an acid is completely neutralized by one g-equivalent of a base in dilute solution.



In case of weak acid/ base or both $|\Delta H_{\text{N}}^\circ| < 13.7 \text{ kcal/eq}^{-1}$ and the difference is enthalpy of ionisation of weak species except in case of HF when $|\Delta H_{\text{N}}^\circ| > 13.7 \text{ kcal/eq}^{-1}$ due to hydration of F^- .

NOTES: In a reaction if heat of reactant & products are given then, heat of that reaction can be measured as follows:

(a) For heat of combustion & for bond enthalpy

$$\Delta_r H = \sum (\Delta H_C)_{\text{reactant}} - \sum (\Delta H_C)_{\text{product}}$$

(b) For heat of formation

$$\Delta_r H = \sum (\Delta H_f)_{\text{product}} - \sum (\Delta H_f)_{\text{reactant}}$$