Thermodynamics

6

Chapter

① THERMODYNAMIC TERMS

- (i) **System** - Part of universe under observation.
  (ii) **Surroundings** - Include everything other than system.
- There are three **types of system.**
  (i) **Open system** - Exchange of energy and matter between system and surroundings.
  (ii) **Closed system** - No exchange of matter but exchange of energy is possible.
  (iii) **Isolated system** - There is no exchange of energy or matter between the system and surroundings.
- The state of a thermodynamic **system** is described by its measurable properties. P, V, T, n etc are called **state variables** or **state functions** because their values depend only on the state of the system and not on how it is reached.

② FIRST LAW OF THERMODYNAMICS

- Commonly known as the law of conservation of energy i.e. energy can neither be created nor be destroyed.
- $\Delta U = q + w$ is mathematical statement of the first law of thermodynamics

Internal Energy (U)

- Sum of chemical, electrical, mechanical or any other type of energy of the system.

Work (W)

- Work is done on an ideal gas when it is compressed and work is done by an ideal gas when it is expanded

$$W = -\int_{V_i}^{V_f} P_{ex} dV$$

- A process or a change is said to be **reversible**, if a change is brought out in such a way that the process could, at any moment, be reversed by an infinitesimal change. Process other than **reversible** are known as **irreversible processes**.
- For isothermal irreversible change $q = -W = P_{ex}(V_f - V_i)$
- For isothermal reversible change $q = -W = nRT \ln \frac{V_f}{V_i}$
- For adiabatic change, $q = 0 \quad \Delta U = W_{ad}$
- $W = 0$ in free expansion

③ ENTHALPY (H)

- Thermodynamic function is equal to $U + pV$
- It is a state function.
- $\Delta H = q_P$, heat absorbed by system at constant pressure.
- $\Delta U = q_V$ at constant volume
- $\Delta H > 0$ for endothermic and $\Delta H < 0$ for exothermic reaction.
- $\Delta H = \Delta U + \Delta n_g RT$ where Δn_g is change in gaseous moles.

④ EXTENSIVE AND INTENSIVE PROPERTIES

- An extensive property is a property whose value depends on the quantity or size of matter present in the system e.g. mass, volume, enthalpy etc.
- Properties which do not depend on the quantity or size of matter present are known as **intensive properties** e.g. temperature, density, molar heat capacity etc.

Heat Capacity

- Molar heat capacity is the quantity of heat required to raise the temperature of one unit mole of a substance by 1°C or 1 K, $q = nc\Delta T$
- Molar heat capacity at constant pressure is C_P and molar heat capacity at constant volume is C_V and $C_P - C_V = R$.
- Bomb calorimeter is used to find ΔU.

⑤ REACTION ENTHALPY ($\Delta_R H$)

- The standard **enthalpy of reaction** is the enthalpy change for a reaction when all the participating substances are in their standard states.

Enthalpy Change During Phase Transformation

- The enthalpy change that accompanies melting of one mole of solid substance in standard state is called **standard enthalpy of fusion** ($\Delta_{fus}H^\circ$).
- Amount of heat required to vaporise one mole of liquid at constant temperature and under standard pressure (1 bar) is called **standard enthalpy of vaporisation** $\Delta_{vap}H^\circ$.

- **Standard enthalpy of sublimation**, ($\Delta_{sub}H^\circ$) is the change in enthalpy when one mole of a solid substance sublimes at constant temperature and under standard pressure (1 bar).

  Standard Enthalpy of Formation ($\Delta_f H^\circ$) is the standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation.

Standard Molar Enthalpies of Formation ($\Delta_f H^\circ$) at 298 K of a few Selected Substances

Substance	$\Delta_f H^\circ$ / (kJ mol^{-1})	Substance	$\Delta_f H^\circ$ / (kJ mol^{-1})
$Br_2(l)$	0	$H_2O(l)$	–285.83
$Br_2(g)$	+30.91	NO(g)	+90.25
C(diamond)	+1.89	$NO_2(g)$	+33.18
C(graphite)	0	$SiO_2(s)$ (quartz)	–910.94
$Cl_2(g)$	0	C(g)	+716.68
$H_2(g)$	0	H(g)	+217.97
$H_2O(g)$	–241.82	Cl(g)	+121.68

Hess's Law of Constant Heat Summation

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

  Standard Enthalpy of Combustion ($\Delta_C H^\circ$) is defined as the enthalpy change per mole of a substance, when it undergoes combustion and all the reactants and products being in their standard states at the specified temperature.

  Bond Enthalpy ($\Delta_{bond}H^\circ$) is energy required to break a bond or energy released when a bond is formed.

  Enthalpy of Atomization ($\Delta_a H^\circ$) is the enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase.
- In case of diatomic molecules, the enthalpy of atomization is also the bond **dissociation** enthalpy.
- $\Delta_r H^\circ = \sum \text{bond enthalpies}_{reactants} - \sum \text{bond enthalpies}_{products}$

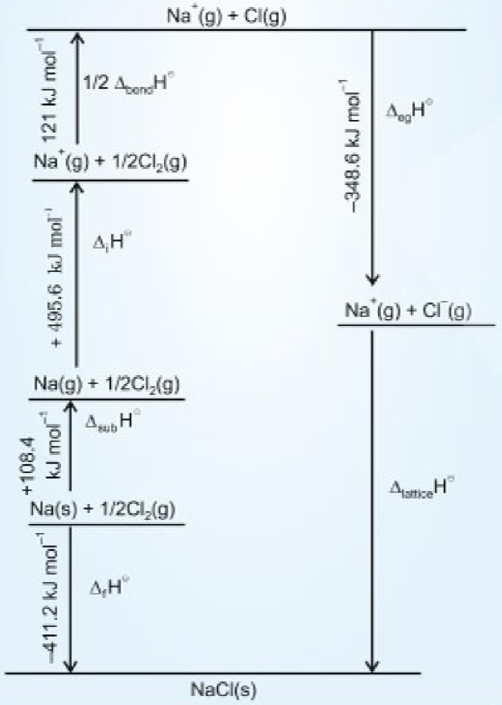
Some Mean Multiple Bond Enthalpies in kJ mol^{-1} at 298 K

N = N	418	C = C	611	O = O	498
N ≡ N	946	C ≡ C	837		
C = N	615	C = O	741		
C ≡ N	891	C ≡ O	1070		

Lattice Enthalpy of an ionic compound is the enthalpy change which occurs when one mole of a ionic compound dissociates into its ions in gaseous state.

- It is impossible to determine lattice enthalpies directly by experiment therefore we use indirect method **Born-Haber cycle.**

Enthalpy diagram for lattice enthalpy of NaCl



Ionization Energy and Electron Affinity

Ionization energy and electron affinity are defined at absolute zero. At any other temperature, heat capacities for the reactants and the products have to be taken into account. Enthalpies of reactions for

$M(g) \rightarrow M^+(g) + e^-$ (for ionization)

$M(g) + e^- \rightarrow M^-(g)$ (for electron gain)

at temperature, T is

$$\Delta_rH^\circ(T) = \Delta_rH^\circ(0) + \int_0^T \Delta_rC_p^\circ dT$$

The value of C_p for each species in the above reaction is 5/2 R (C_V = 3/2R)

So, $\Delta_rC_p^\circ = +5/2\,R$ (for ionization)

$\Delta_rC_p^\circ = -5/2\,R$ (for electron gain)

Therefore,

Δ_rH° (ionization enthalpy)

$= E_0$ (ionization energy) + 5/2 RT

Δ_rH° (electron gain enthalpy)

= –A (electron affinity) – 5/2 RT

Enthalpy of Solution ($\Delta_{sol}H^\circ$) is the enthalpy change when one mole of it dissolves in a specified amount of solvent.

$$\begin{tikzcd} AB(S) \arrow[rr, "\Delta_{sol}H^\circ"] \arrow[dr, "\Delta_{lattice}H^\circ"'] & & A^+(aq) + B^-(aq) \\ & A^+(g) + B^-(g) \arrow[ur, "\Delta_{hyd}H^\circ"'] & \end{tikzcd}$$

- $\Delta_{sol}H^\circ = \Delta_{lattice}H^\circ + \Delta_{hyd}H^\circ$

⑥ SECOND LAW OF THERMODYNAMICS

- It explain the criterion of spontaneity.

Spontaneity

- A spontaneous process is an irreversible process and may only be reversed by some external agency.

  Entropy S is measure of the degree of randomness or disorder in the system.

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

- $\Delta S_{total} = \Delta S_{system} + \Delta S_{surr} > 0$ of a spontaneous process.
- $\Delta S = 0$ and S in maximum at equilibrium.

Gibbs Energy (G) and spontaneity

- $G = H - TS$ or $\Delta G = \Delta H - T\Delta S$.
- Gibbs function, G is an extensive property and a state function.
- If $\Delta G < 0$, process is spontaneous.
- If $\Delta G > 0$, process is non spontaneous.
- $\Delta G^\circ = -RT \ln K = -2.303\,RT \log K$.
- $\Delta_rG^\circ = \Delta_rH^\circ - T\Delta_rS^\circ = -RT \ln K$.

Δ_rH°	Δ_rS°	Δ_rG°	Description
–	+	–	Reaction spontaneous at all temperatures
–	–	– (at low T)	Reaction spontaneous at low temperature
–	–	+ (at high T)	Reaction non-spontaneous at high temperature
+	+	+ (at low T)	Reaction non-spontaneous at low temperature
+	+	– (at high T)	Reaction spontaneous at high temperature
+	–	+ (at all T)	Reaction non-spontaneous a all temperatures

⑦ ABSOLUTE ENTROPY AND THIRD LAW OF THERMODYNAMICS

- The entropy of any pure crystalline substance approaches zero as the temperature approaches absolute zero. This is called third law of thermodynamics

Sharpen Your Understanding

NCERT Based MCQs

1. Select the incorrect statement among the following. [NCERT Pg. 162]
   (1) System and the surroundings together constitute the universe
   (2) System is separated from the surroundings by some sort of wall which may be real or imaginary
   (3) In closed system exchange of heat is possible but no exchange of work is possible with surroundings
   (4) In an isolated system, there is no exchange of energy or matter between the system and the surroundings

2. Path function is [NCERT Pg. 162]
   (1) H (2) W
   (3) U (4) S

3. A system absorbed 400 J of heat and done 300 J of work. The change in internal energy of the system is [NCERT Pg. 164]
   (1) 100 J (2) –100 J
   (3) 700 J (4) –700 J

4. If heat of atomization of $CH_4(g)$ is x J then average bond enthalpy of C – H bond is [NCERT Pg. 178]
   (1) x (2) $\frac{x}{4}$
   (3) $\frac{4}{x}$ (4) 4x

5. Enthalpy change on freezing of 1.0 mol of water at 40°C to ice at 0°C is ($\Delta_{fus}H$ = 6 kJ mol^{-1} at 0°C, $C_P[H_2O(l)]$ = 75 J mol K^{-1}]) [NCERT Pg. 172]
   (1) –1.5 kJ (2) –4.5 kJ
   (3) –6.5 kJ (4) –9 kJ

6. If enthalpy of combustion of carbon to CO_2 is –400 kJ mol^{-1} then how much heat will be released upon formation of 8.8 g CO_2 from carbon and dioxygen gas? [NCERT Pg. 176]
   (1) 40 kJ (2) 80 kJ
   (3) 400 kJ (4) 800 kJ

7. A reaction is non spontaneous at all temperatures when [NCERT Pg. 186]
   (1) $\Delta_rH > 0$ and $\Delta_rS > 0$
   (2) $\Delta_rH < 0$ and $\Delta_rS > 0$
   (3) $\Delta_rH < 0$ and $\Delta_rS < 0$
   (4) $\Delta_rH > 0$ and $\Delta_rS < 0$

8. If equilibrium constant is 2 atm at 300 K then the standard free energy change at 300 K and 1 atm pressure is [NCERT Pg. 187]
   (1) 1728.9 J mol^{-1} (2) –1728.9 J mol^{-1}
   (3) 309 J mol^{-1} (4) –309 J mol^{-1}

9. In which of the following entropy decreases? [NCERT Pg. 183]
   (1) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
   (2) $2H(g) \rightarrow H_2(g)$
   (3) A solid melts into liquid
   (4) $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$

10. $\Delta_rH°$ of the reaction is equal to

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$$

[NCERT Pg. 176]
   (1) $\Delta_fH°$ of CO_2 (2) $\Delta_fH°$ of H_2O
   (3) $\Delta_fH°$ of C_4H_{10} (4) $\Delta_cH°$ of C_4H_{10}

11. In isothermal free expansion of an ideal gas [NCERT Pg. 166]
   (1) $\Delta H = 0$ (2) $\Delta U = 0$
   (3) $\Delta W = 0$ (4) All of these

12. Intensive property among the following is [NCERT Pg. 168]
   (1) Molar heat capacity
   (2) Entropy
   (3) Internal energy
   (4) Enthalpy

13. 10 mol of ideal gas expanded reversibly isothermally from 1 L to 10 L at 100 K. The work done during the process is [NCERT Pg. 166]
   (1) –1.91 kJ (2) –0.95 kJ
   (3) –19.1 kJ (4) –38.2 kJ

14. If Δ_rH of $A \rightarrow B$; $B \rightarrow C$ and $A \rightarrow D$ are x, y and z kJ mol^{-1} respectively then Δ_rH of $C \rightarrow D$ is [NCERT Pg. 176]
   (1) z – x – y (2) x + y – z
   (3) x – y – z (4) x + y + z

15. Bomb calorimeter is used to measure [NCERT Pg. 169]

(1) ΔU (2) W

(3) ΔG (4) ΔS

16. If $\Delta_f H^\circ$ of $CaCO_3(s)$, CaO(s) and $CO_2(g)$ are –1200, –630 and –400 kJ mol^{-1} respectively then $\Delta_r H^\circ$ of the reaction $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ is [NCERT Pg. 171]

(1) –170 kJ mol^{-1} (2) 170 kJ mol^{-1}

(3) –2230 kJ mol^{-1} (4) 2230 kJ mol^{-1}

17. For which of the following $\Delta H = \Delta U$? [NCERT Pg. 167]

(1) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

(2) $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$

(3) $C(s) + O_2(g) \rightarrow CO_2(g)$

(4) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$

18. Select the correct relation. [NCERT Pg. 186]

(1) $\Delta_r G^\circ = -RT \ln K$

(2) $\Delta_r G^\circ = -2.303\ RT \ln K$

(3) $\Delta_r G^\circ = RT \ln K$

(4) $\Delta_r G^\circ = 2.303\ RT \ln K$

19. Reference state of oxygen at 25°C and 1 bar pressure is [NCERT Pg. 173]

(1) $O_2(g)$ (2) $O_3(g)$

(3) O(g) (4) $O_2(l)$

20. Process occurring at constant volume is known as [NCERT Pg. 166]

(1) Isobaric (2) Isochoric

(3) Adiabatic (4) Isothermal

Thinking in Context

1. At equilibrium, $\Delta_{sys}G$ is equal to ________. [NCERT Pg. 188]
2. The ________ of any pure crystalline substance approaches zero as the temperature approaches absolute zero. [NCERT Pg. 185]
3. ________ is sum of $\Delta_{lattice}H^\circ$ and $\Delta_{hyd}H^\circ$. [NCERT Pg. 180]
4. Sum of heat and work is a ________ function. [NCERT Pg. 164]
5. Maximum mean single bond enthalpy is of ________. [NCERT Pg. 178]
6. For a spontaneous process, ΔS_{total} is ________ than zero. [NCERT Pg. 183]
7. According to 1st law of thermodynamics, q + w is equal to _______. [NCERT Pg. 188]
8. Heat of reaction at constant pressure is equal to ________. [NCERT Pg. 188]
9. For 1 mol of ideal gas, the difference between molar heat capacity at constant pressure and molar heat capacity at constant volume is ________. [NCERT Pg. 169]
10. For adiabatic process q is equal to ________. [NCERT Pg. 163]
11. ________ is used to determine lattice enthalpies. [NCERT Pg. 180]
12. All the fast reactions are ________. [NCERT Pg. 185]
13. A reversible process takes ________ time for completion. [NCERT Pg. 166]
14. During an adiabatic process, if system absorbs 10 J heat from surrounding then the value of ΔU is ________. [NCERT Pg. 167]
15. Diffusion of gases have ΔH ________ to zero and ΔS ________ than zero. [NCERT Pg. 182]
16. More negative the $\Delta_f H^\circ$, ________ is the thermodynamic stability. [NCERT Pg. 191]
17. Unit of entropy is ________. [NCERT Pg. 183]
18. $\Delta U = W$, for ________ process. [NCERT Pg. 190]
19. Sum of all kind of energies is known as ________. [NCERT Pg. 163]
20. According to 1st law of thermodynamics, the energy of an isolated system is ________. [NCERT Pg. 164]

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