Chapter Notes

Subject: Chemistry

Class: XI

Chapter: Thermodynamics

Top concepts

1. The branch of science which deals with study of different forms of energy and their interconversion is called thermodynamics.
2. A system in thermodynamics refers to that part of universe in which observations are made.
3. The remaining portion of universe which is not part of system constitutes the surroundings. The surroundings include everything other than the system.
4. The wall (real or imaginary) that separates the system from the surroundings is called boundary.
5. Types of the System

Types of the System	Exchange of energy	Exchange of matter
Open	Yes	Yes
Closed	Yes	No
Isolated	No	No

6. The state of a thermodynamic system is described by its measurable or macroscopic (bulk) properties. The state of the surroundings can never be completely specified.
7. State variables are the measurable properties of system required to describe the state of the system. Examples are temperature, pressure, volume etc.
8. Various types of processes

Type of process	Definition
Isothermal	Process in which temperature of system remains constant
Adiabatic	Process in which there is no transfer of heat between the system and surroundings
Isobaric	Process in which pressure of system

	remains constant
Isochoric	Process in which volume of system remains constant

9. Every substance possesses definite amount of energy which depends on factors such as chemical nature, temperature and pressure etc. Internal energy, U of the system represents the total energy of the system

10. Work done in a adiabatic process and sign convention

Work done (w_{ad})	Sign of w
By the system	-
On the system	+

11. Heat changes and sign convention

Heat(q)transferred	Sign of q
From surroundings to the system	+
From system to the surroundings	-

12. First Law of Thermodynamics: $\Delta U = q + w$

13. First law of thermodynamics is also called as law of conservation of energy i.e. energy can neither be created nor destroyed. It also states that the energy of an isolated system is constant.

14. Absolute value of the internal energy can never be determined only change in internal energy can be determined.

15. A process or 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.

16. For an isothermal reversible process

$$q = -w_{rev} = -2.3.30nRT\log\frac{V_f}{V_i}$$

17. For isothermal irreversible change $\quad q = -w = p_{ex}\left(V_f - V_i\right)$

18. Expansion of a gas in vacuum ($p_{ex} = 0$) is called free expansion. No work is done during free expansion of an ideal gas whether the process is reversible or irreversible

19. For adiabatic change, $q = 0$ and $\Delta U = w_{ad}$

20. The enthalpy of a system may be defined as the sum of the internal energy and the product of its pressure and volume. It is denoted by the symbol H and is given by H = U + PV

21. Change in enthalpy $\Delta H = \Delta U + p\Delta V$

22. Enthalpy change and sign convention

Type of reaction	Definition	ΔH
Exothermic reactions	Reactions in which heat is evolved during the reaction	-
Endothermic reactions	Reactions in which heat is absorbed during the reaction	+

23. An extensive property is a property whose value depends on the quantity or size of matter present in the system. Examples are mass, volume, internal energy, enthalpy, heat capacity, etc

24. An intensive property is a property whose value does not depend on the quantity or size of matter present in the system. Examples are temperature, density, pressure etc.

25. Specific heat, also called specific heat capacity is the quantity of heat required to raise the temperature of one unit mass of a substance by one degree Celsius (or one Kelvin).

26. Relation between amount of heat, *q*, required to raise the temperatures of a sample, specific heat of the substance, c and change in temperatures is given as $q = mc\,\Delta T = C\Delta T$

27. At constant pressure as $q_p = C_p\Delta T = \Delta H$

28. At constant volume as $q_V = C_V\Delta T = \Delta U$

29. For a mole of an ideal gas, $C_p - C_V = R$

30. Calorimetry is an experimental technique that helps determining energy changes associated with chemical or physical processes

31. The enthalpy change accompanying a reaction is called the reaction enthalpy **($\Delta_r H$)**

$\Delta_r H$= (sum of enthalpies of products)- (sum of enthalpies of reactants)

32. The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states. The standard state of a substance at a specified temperature is its pure form at pressure of 1 bar.

33.Different types of enthalpy

No.	Type of enthalpy	Definition	Symbol
1	Standard Enthalpy of fusion **or** Molar enthalpy of fusion	The enthalpy change that accompanies melting of one mole of a solid substance in standard state	$\Delta_{fus}H^{\theta}$
2	Standard Enthalpy of vaporization **or** Molar enthalpy of vaporization	The enthalpy change that accompanies vaporizing of one mole of a liquid at constant temperature and under standard pressure (1bar)	$\Delta_{vap}H^{\theta}$
3	Standard Enthalpy of sublimation	The enthalpy change when one mole of a solid substance sublimes at a constant temperature and under standard pressure (1bar)	$\Delta_{sub}H^{\theta}$
4	Enthalpy of formation **or** Standard molar enthalpy of formation	The enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation	$\Delta_{f}H^{\theta}$
5	Enthalpy of combustion	Enthalpy change when 1 mole of substance is completely burnt in excess of oxygen or air	$\Delta_{comb}H^{\theta}$ or $\Delta_{c}H^{\theta}$
7	Enthalpy of atomisation	Enthalpy change in breaking one mole of bonds of a substance completely into atoms in gaseous state	$\Delta_{a}H^{\theta}$
8	Bond dissociation enthalpy	Amount of energy required to break one mole of bond of a particular type between atoms in gaseous state	$\Delta_{bond}H^{\theta}$
9	Enthalpy of	Enthalpy of solution of a substance is	$\Delta_{sol}H^{\theta}$

	solution	the enthalpy change when one mole of substance dissolves in a specified amount of solvent	

34. A balanced chemical equation together with the value of its $\Delta_r H^\theta$ is called a thermochemical equation

35. Hess's Law of Constant Heat Summation: If a reaction takes place in several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction may be divided at the same temperature

36. Born-Haber Cycle is used to determine lattice enthalpy of ionic compounds since they cannot be determined by experiment directly.

37. The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state

38. $\Delta_{sol} H^\theta = \Delta_{lattice} H^\theta + \Delta_{hyd} H^\theta$

39. A process that has natural tendency of occurrence in a particular direction and is reversible only by application of some external agency is known as spontaneous process.

40. The processes which are forbidden and are made to take place only by supplying energy continuously from outside the system are called non-spontaneous process.

41. Entropy (S) is the measure of randomness of a system. It is a state function.

42. Entropy increases from solid to gas. Entropy is maximum for gases as they have maximum disorder.

43. According to Second law of thermodynamics entropy of the universe always increases during a spontaneous change

44. For reversible process entropy change is given by

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

q_{rev} is heat absorbed or released during the reaction
T is the temperature of the reaction

45. At constant pressure $q_{rev} = \Delta H$

$$\therefore \Delta S = \frac{\Delta H}{T}$$

46. For spontaneous process $\Delta S(total) = \Delta S(sys) + \Delta S(surr) > 0$

47. Decrease in enthalpy and increase in entropy of system independently cannot serve the criteria for spontaneity

48. Gibbs function or Gibbs energy is denoted by G.

   G=H−TS

49. The criteria for spontaneous reaction in relation to Δ G at constant pressure and constant temperature.

   If Δ G < 0, process is spontaneous

   If Δ G = 0, process is in equilibrium

   If Δ G > 0, process is non-spontaneous

50. Relation between Gibbs energy change ($\Delta_r G^0$) and equilibrium constant (K) $\Delta_r G^0 = -RTlnK$

51. In case of endothermic reactions enthalpy of reaction ($\Delta_r H^\theta$) is large and positive. In such a case, value of equilibrium constant(K) will be much smaller than 1 and the reaction is unlikely to form much product

52. In case of exothermic reactions enthalpy of reaction ($\Delta_r H^\theta$) is negative and $\Delta_r G^0$ is also large and negative. In such cases equilibrium constant (K) is larger than 1 and reactions go to completion

53. Effect of temperature on Spontaneity of Reactions

$\Delta_r H^\ominus$	$\Delta_r S^\ominus$	$\Delta_r G^\ominus$	Description*
−	+	−	Reaction spontaneous at all temperature
−	−	− (at low T)	Reaction spontaneous at low temperature
−	−	+ (at high T)	Reaction nonspontaneous at high temperature
+	+	+ (at low T)	Reaction nonspontaneous at low temperature
+	+	− (at high T)	Reaction spontaneous at high temperature
+	−	+ (at all T)	Reaction nonspontaneous at all temperatures