13

Chemical Thermodynamics

QUICK LOOK

Thermochemistry is a branch of physical chemistry which is concerned with energy changes accompanying chemical transformation. It is also termed as chemical energetics. It is based on the first law of thermodynamics.

First Law of Thermodynamics

First law of thermodynamics is equivalent to law of conservation of energy, when heat energy is supplied to a gas, two things may occur: the internal energy of the gas may change and the gas may do external work by expanding. According to this law if heat ΔQ is added to a system then it will show up either as a change in internal energy dU of the system and/or as work ΔW per formed by the system *i.e.,* $\Delta Q = dU + \Delta W$ (all are in same unit)

Sign conventions

ΔQ	Positive	When heat is supplied to a system
	Negative	When heat is drawn from the system
ΔW	Positive	When work done by the gas (expansion)
	Negative	When work done on the gas (compression)
ΔU	Positive	When temperature increases, internal energy increases
	Negative	When temperature decreases, internal energy decreases

Table 13.1: First Law of Thermodynamics Applied to Different Processes

S. No.	Process	ΔQ	$-dU$	$+dW$
1	Cyclic	ΔW	0	Area of the closed curve
2.	Isochoric	ΔU	$\mu C_v \Delta T$	0
3.	Isothermal	ΔW	0	$\mu RT \log_e\left(\frac{V_f}{V_i}\right)$
4.	Adiabatic	0	$-\Delta W$	$\frac{\mu R(T_f - T_i)}{(1-\gamma)}$
5.	Isobaric	$\mu C_p \Delta T$	$\mu C_v \Delta T$	$p(V_f - V_i) = \mu R(T_f - T_i)$

Enthalpy and Enthalpy Change: Heat content of a system at constant pressure is called enthalpy denoted by 'H'.

From first law of thermodynamics, $q = E + PV$ . . .(*i*)

Heat change at constant pressure can be given as

$$\Delta q = \Delta E + P\Delta V \quad \text{. . .}(ii)$$

At constant pressure heat can be replaced at enthalpy.

$$\Delta H = \Delta E + P\Delta V \quad \text{. . .}(iii)$$

$\therefore$ $\Delta H =$ Heat change or heat of reaction (in chemical process) at constant pressure

$\Delta E =$ Heat change or heat of reaction at constant volume. (E or U Internal Energy)

In case of solids and liquids participating in a reaction,

$$\Delta H = \Delta E (P\Delta V \approx 0)$$

Difference between ΔH and ΔE is significant when gases are involved in chemical reaction.

$$\Delta H = \Delta E + P\Delta V$$

$$\Rightarrow \quad \Delta H = \Delta E + \Delta nRT$$

$$P\Delta V = \Delta nRT\ ;$$

Here, $\Delta n = n_P - n_R$

Specific Heat (or specific heat capacity) of a substance is the quantity of heat (in calories, joules, kcal, or kilo joules) required to raise the temperature of 1g of that substance through 1°C. It can be measured at constant pressure (c_p) and at constant volume (c_v).

Molar Heat Capacity of a substance is the quantity of heat required to raise the temperature of 1 mole of the substance by 1°C.

$\therefore$ Molar heat capacity = Specific heat capacity × Molecular weight, *i.e.,* $C_v = c_v \times M$ and $C_p = c_p \times M$.

Since gases on heating show considerable tendency towards expansion if heated under constant pressure conditions, an additional energy has to be supplied for raising its temperature by 1°C relative to that required under constant volume conditions, *i.e.,* $C_p > C_v$ or $C_p = C_v +$ Work done in expansion, $P\Delta V (= R)$

where, C_p = molar heat capacity at constant pressure

C_v = molar heat capacity at constant volume.

Some Useful Relations of C_p and C_v

- $C_p - C_v = R = 2$ calories $= 8.314$J
- $Cv = \frac{3}{2}R$ (for mono-atomic gas) and $Cv = \frac{3}{2} + x$ (for di and polyatomic gas), where x varies from gas to gas.
- $\frac{C_p}{C_v} = \gamma$ (Ratio of molar capacities)

- For mono-atomic gas, C_V=3 calories whereas, $C_p = C_v + R = 5$ calories.
- For mono-atomic gas, $(\gamma) = \frac{C_p}{C_v} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = 1.66$
- For diatomic gas $(\gamma) = \frac{C_p}{C_v} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = 1.40$
- For triatomic gas $(\gamma) = \frac{C_p}{C_v} = \frac{8R}{6R} = 1.33$

Spontaneous Process and Enthalpy Change: A spontaneous process is accompanied by decrease in internal energy or enthalpy, *i.e.,* work can be obtained by the spontaneous process. It indicates that only exothermic reactions are spontaneous. But the melting of ice and evaporation of water are endothermic processes which also proceeds spontaneously. It means, there is some other factor in addition to enthalpy change (ΔH) which explains the spontaneous nature of the system. This factor is entropy.

Entropy and Entropy Change: Entropy is a thermodynamic state quantity which is a measure of randomness or disorder of the molecules of the system.
Entropy is represented by the symbol "S". It is difficult to define the actual entropy of a system. It is more convenient to define the change of entropy during a change of state.

The entropy change of a system may be defined as the integral of all the terms involving heat exchanged (q) divided by the absolute temperature (T) during each infinitesimally small change of the process carried out reversibly at constant temperature.

$$\Delta S = S_{final} - S_{initial} = \frac{q_{rev}}{T}$$

If heat is absorbed, then $\Delta S = +ve$ and if heat is evolved, then $\Delta S = -ve$.
Entropy, S is related to thermodynamic probability (W) by the relation, $S = k \log_e W$ and $S = 2.303\ k \log_{10} W$ where, k is Boltzmann's constant

Units of Entropy: Since entropy change is expressed by a heat term divided by temperature, it is expressed in terms of calorie per degree, *i.e.,* cal $\deg^{-1}$. In SI units, the entropy is expressed in terms of joule per degree Kelvin, *i.e.,* JK^{-1}..

Entropy Change during Phase Transition
The change of matter from one state (solid, liquid or gas) to another is called phase transition. Such changes occur at definite temperature such as melting point (solid to liquid). Boiling point (liquid to vapours) *etc,* and are accompanied by absorption or evolution of heat.

When a solid changes into a liquid at its fusion temperature, there is absorption of heat (latent heat). Let ΔH_f be the molar heat of fusion. The entropy change will be $\Delta S_f = \frac{\Delta H_f}{T_f}$

Similarly, if the latent heat of vaporisation and sublimation are denoted by ΔH_{vap} and ΔH_{sub}, respectively, the entropy of vaporisation and sublimation are given by

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}$$

and $\Delta S_{sub} = \frac{\Delta H_{sub}}{T_s}$

Since, $\Delta H_f, \Delta H_{vap}$ and ΔH_{Sub} are all positive, these processes are accompanied by increase of entropy and the reverse processes are accompanied by decrease in entropy.

Entropy Change for an Ideal Gas
In going from initial to final state, the entropy change, ΔS for an ideal gas is given by the following relations,

- When T and V are two variables, $\Delta S = nC_V \ln\frac{T_2}{T_1} + nR \ln\frac{V_2}{V_1}$. Assuming C_v is constant.
- When T and p are two variables, $\Delta S = nC_P \ln\frac{T_2}{T_1} - nR \ln\frac{p_2}{p_1}$

  Assuming C_p, is constant
  (a) Thus, for an isothermal process (T constant), $\Delta S = nR \ln\frac{V_2}{V_1}$ or $= -nR \ln\frac{p_2}{p_1}$

  (b) For isobaric process (p constant), $\Delta S = nC_p \ln\frac{T_2}{T_1}$

  (c) For isochoric process (V constant), $\Delta S = nC_v \ln\frac{T_2}{T_1}$

  (d) Entropy change during adiabatic expansion: In such process q = 0 at all stages.
  Hence, $\Delta S = 0$. Thus, reversible adiabatic processes are called isoentropic process.

Table 13.2: Criteria for Spontaneity of Reaction

ΔH	**ΔS**	**ΔG**	**Reaction characteristics**	**Example**
–	+	Always negative	Reaction is spontaneous at all temperatures	$2O_3(g) \longrightarrow 3O_2(g)$
+	–	Always positive	Reaction is non spontaneous at all temperatures	$3O_2(g) \longrightarrow 2O_3(g)$
–	–	Negative at low temperature but positive at high temperature	Reaction is spontaneous at low temperature but becomes non spontaneous at high temperature	$CaO(s) + CO_2(g) \longrightarrow CaCO_3(s)$
+	+	Positive at low temperature but negative at high temperature	Reaction is non spontaneous at low temperature but becomes spontaneous at high temperature	$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

Exothermic Reactions: The chemical reactions which proceed with the evolution of heat energy are called exothermic reactions. The heat energy produced during the reactions is indicated by writing +q or more precisely by giving the actual numerical value on the products side. In general exothermic reactions may be represented as,

$$A + B \longrightarrow C + D + q(\text{heat energy})$$

In the exothermic reactions the enthalpy of the products will be less than the enthalpy of the reactants, so that the enthalpy change is negative as shown below:

$$\Delta H = H_p - H_r;\ H_p < H_r; \Delta H = -ve$$

Endothermic Reactions: The chemical reactions which proceed with the absorption of heat energy are called endothermic reactions. Since the heat is added to the reactants in these reactions, the heat absorbed is indicated by either putting (–) or by writing the actual numerical value of heat on the reactant side $A + B \longrightarrow C + D - q\,(\text{heat energy})$

The heat absorbed at constant temperature and constant pressure measures enthalpy change. Because of the absorption of heat, the enthalpy of products will be more than the enthalpy of the reactants. Consequently, ΔH will be positive (+ve) for the endothermic reactions.

$$\Delta H = H_p - H_r;\ H_p > H_r;\ \Delta H = +ve$$

Heat of Reaction or Enthalpy of Reaction: Heat of reaction is defined as the amount of heat evolved or absorbed when quantities of the substances indicated by the chemical equation have completely reacted. The heat of reaction (or enthalpy of reaction) is actually the difference between the enthalpies of the products and the reactants when the quantities of the reactants indicated by the chemical equation have completely reacted. Mathematically, Enthalpy of reaction (heat of reaction)

$$= \Delta H = \Sigma H_P - \Sigma H_R$$

Factors Which Influence the Heat of Reaction: There are a number of factors which affect the magnitude of heat of reaction.

- **Physical state of reactants and products:** Heat energy is involved for changing the physical state of a chemical substance. For example in the conversion of water into steam, heat is absorbed and heat is evolved when steam is condensed. Considering the following two reactions

  $$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(g); \qquad \Delta H = -57.8\,\text{kcal}$$

  $$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(l); \qquad \Delta H = -68.32\,\text{kcal}$$

  It is observed that there is difference in the value of ΔH if water is obtained in gaseous or liquid state. ΔH value in second case is higher because heat is evolved when steam condenses. Hence, physical sate always affects the heat of reaction.
- **Allotropic forms of the element:** Heat energy is also involved when one allotropic form of an element is converted into another. Thus, the value of ΔH depends on the allotropic form used in the reaction. For example, the value of ΔH is different when carbon in the form of diamond or in amorphous form is used.

  $$\text{C (diamond)} + O_2(g) \longrightarrow CO_2(g);\ \ \Delta H = -94.3\,\text{kcal}$$

  $$\text{C (amorphous)} + O_2(g) \longrightarrow CO_2(g);\ \ \Delta H = -97.6\,\text{kcal}$$

  The difference between the two values is equal to the heat absorbed when 12g of diamond is converted into 12g of amorphous carbon. This is termed as heat of transition.
- **Temperature:** Heat of reaction has been found to depend upon the temperature at which reaction is occurring. The variation of the heat of reaction with temperature can be ascertained by using Kirchhoff's equation.

  $$\frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \Delta C_P$$

  Kirchhoff's equation at constant volume may be given as,

  $$\frac{\Delta E_{T_2} - \Delta E_{T_1}}{T_2 - T_1} = \Delta C_v$$
- **Reaction carried out at constant pressure or constant volume:** When a chemical reaction occurs at constant volume, the heat change is called the internal energy of reaction at constant volume. However, most of the reactions are carried out at constant pressure; the enthalpy change is then termed as the enthalpy of reaction at constant pressure. The difference in the values is negligible when solids and

liquids are involved in a chemical change. But, in reactions which involve gases, the difference in two values is considerable.

$\Delta E + \Delta nRT = \Delta H$ or $q_v + \Delta nRT = q_p$

$\Delta E = q_v =$ heat change at constant volume;

$\Delta H = q_p =$ heat change at constant pressure,

Δn = total number of moles of gaseous product–total number of moles of gaseous reactants.

Heat of Reaction: The heat evolved or absorbed in a chemical reaction is measured by carrying out the reaction in an apparatus called calorimeter. The principle of measurement is that heat given out is equal to heat taken, *i.e.,* $Q = (W + m) \times s \times (T_2 - T_1)$,

Where Q is the heat of the reaction (given out), W is the water equivalent of the calorimeter and m is the mass of liquid in the calorimeter and s its specific heat, T_2 is the final temperature and T_1 the initial temperature of the system. Different types of calorimeters are used but two of the common types are,
(*i*) Water calorimeter and (*ii*) Bomb calorimeter.

Bomb Calorimeter: This is commonly used to find the heat of combustion of organic substances.
Since the reaction in a bomb calorimeter proceeds at constant volume, the heat of combustion measured is ΔE

$$\Delta E = \frac{(W + m)(t_2 - t_1) \times s}{w_1} \times M\,\text{kcal}$$

Where M is the molecular mass of the substance, w_1 is the weight of substance taken, W is the water equivalent of calorimeter, m is the mass of liquid in the calorimeter and s is the specific heat of liquid.
ΔH can be calculated from the relation, $\Delta H = \Delta E = \Delta nRT$

Laws of Thermo Chemistry

- **Levoisier and Laplace law:** According to this law enthalpy of decomposition of a compound is numerically equal to the enthalpy of formation of that compound with opposite sign, For example,

  $C(s) + O_2 \longrightarrow CO_2(g);\ \Delta H = -94.3\,\text{kcal}$

  $CO_2(g) \longrightarrow C(s) + O_2(g);\ \Delta H = +94.3\,\text{kcal}$

- **Hess's law (the law of constant heat summation):** This law was presented by Hess in 1840. According to this law "If a chemical reaction can be made to take place in a number of ways in one or in several steps, the total enthalpy change (total heat change) is always the same, i.e. the total enthalpy change is independent of intermediate steps involved in the change." The enthalpy change of a chemical reaction depends on the initial and final stages only. Let a substance A be changed in three steps to D with enthalpy change from A to B, ΔH_1 calorie, from B to C, ΔH_2 calorie and from C to D, ΔH_3 calorie. Total enthalpy change from A to D will be equal to the sum of enthalpies involved in various steps,
  Total enthalpy change $\Delta H_{\text{steps}} = \Delta H_1 + \Delta H_2 + \Delta H_3$

Now if D is directly converted into A, let the enthalpy change be ΔH_{direct}. According to Hess's law $\Delta H_{\text{steps}} + \Delta H_{\text{direct}} = 0$, i.e. ΔH_{steps} must be equal to ΔH_{direct} numerically but with opposite sign. In case it is not so, say ΔH_{steps} (which is negative) is more that ΔH_{direct} (which is positive), then in one cycle, some energy will be created which is not possible on the basis of first law of thermodynamics. Thus, ΔH_{steps} must be equal to ΔH_{direct} numerically.

Applications of Hess's Law

- For the determination of enthalpies of formation of those compounds which cannot be prepared directly from the elements easily using enthalpies of combustion of compounds.
- For the determination of enthalpies of extremely slow reactions.
- For the determination of enthalpies of transformation of one allotropic form into another.
- For the determination of bond energies. $\Delta H_{\text{reaction}} = \Sigma$ Bond energies of reactants – Σ Bond energies of products.
- For the determination of resonance energy.
- For the determination of lattice energy.

Bond Energy or Bond Enthalpies

When a bond is formed between atoms, energy is released. Obviously same amount of energy will be required to break the bond. The energy required to break the bond is termed bond dissociation energy. The more precise definition is, "The amount of energy required to break one mole of bond of a particular type between the atoms in the gaseous state, *i.e.,* to separate the atoms in the gaseous state under 1 atmospheric pressure and the specified temperature is called bond dissociation energy."

$H-H(g) \longrightarrow 2H(g);\quad \Delta H = +433\,\text{kJ mol}^{-1}$

$Cl-Cl(g) \longrightarrow 2Cl(g);\quad \Delta H = +242.5\,\text{kJ mol}^{-1}$

$H-Cl(g) \longrightarrow H(g) + Cl(g);\quad \Delta H = +431\,\text{kJ mol}^{-1}$

The bond dissociation energy of a diatomic molecule is also called bond energy. However, the bond dissociation energy depends upon the nature of bond and also the molecule in which the bond is present.

MULTIPLE CHOICE QUESTIONS

Thermometry

1. The freezing point on a thermometer is marked as 20° and the boiling point at as 150°. A temperature of 60°C on this thermometer will be read as:

a. 40°
b. 65°
c. 98°
d. 110°

2. A thermometer is graduated in mm. It registers –3 mm when the bulb of thermometer is in pure melting ice and 22 mm when the thermometer is in steam at a pressure of one atm. The temperature in °C when the thermometer registers 13mm is:

a. $\frac{13}{25}\times 100$
b. $\frac{16}{25}\times 100$
c. $\frac{13}{22}\times 100$
d. $\frac{16}{22}\times 100$

Thermal Expansion

3. A iron rod of length 50 cm is joined at an end to an aluminium rod of length 100 cm. All measurements refer to 20°C. The coefficients of linear expansion of iron and aluminium are $12\times 10^{-6}/°\text{C}$ and $24\times 10^{-6}/°\text{C}$ respectively. The average coefficient of composite system is:

a. $36\times 10^{-6}/°\text{C}$
b. $12\times 10^{-6}/°\text{C}$
c. $20\times 10^{-6}/°\text{C}$
d. $48\times 10^{-6}/°\text{C}$

4. The coefficient of apparent expansion of a liquid in a copper vessel is C and in a silver vessel S. The coefficient of volume expansion of copper is γ_C. What is the coefficient of linear expansion of silver?

a. $(C+\gamma_C+S)/3$
b. $(C-\gamma_C+S)/3$
c. $(C+\gamma_C-S)/3$
d. $(C-\gamma_C-S)/3$

First Law of Thermodynamics and Hess Law

5. A thermodynamic system is taken through the cycle PQRSP process. The net work done by the system is:

a. 20 J
b. – 20 J
c. 400 J
d. – 374 J

6. The relation between the internal energy U and adiabatic constant γ is:

a. $U=\frac{PV}{\gamma-1}$
b. $U=\frac{PV^{\gamma}}{\gamma-1}$
c. $U=\frac{PV}{\gamma}$
d. $U=\frac{\gamma}{PV}$

7. 110 J of heat is added to a gaseous system, whose internal energy change is 40 J, and then the amount of external work done is:

a. 150 J
b. 70 J
c. 110 J
d. 40 J

8. A gas is compressed at a constant pressure of 50N/m^2 from a volume of 10m^3 to a volume of 4m^3. Energy of 100 J is then added to the gas by heating. Its internal energy is:

a. Increased by 400 J
b. Increased by 200 J
c. Increased by 100 J
d. Decreased by 200 J

9. 5 Moles of an ideal gas undergoes an isothermal process at 500K in which its volume is doubled. The work done by the gas system is:

a. 3500 J
b. 14400 J
c. 17800 J
d. 5200 J

10. During an adiabatic process, the pressure of a gas is found to be proportional to the cube of its absolute temperature. The ratio C_p/C_v for the gas is:

a. $\frac{3}{2}$
b. $\frac{4}{3}$
c. 2
d. $\frac{5}{3}$

11. A monoatomic ideal gas, initially at temperature T_1, is enclosed in a cylinder fitted with a frictionless piston. The gas is allowed to expand adiabatically to a temperature T_2 by releasing the piston suddenly. If L_1 and L_2 are the lengths of the gas column before and after expansion respectively, then T_1/T_2 is given by:

a. $\left(\frac{L_1}{L_2}\right)^{2/3}$
b. $\frac{L_1}{L_2}$
c. $\frac{L_2}{L_1}$
d. $\left(\frac{L_2}{L_1}\right)^{2/3}$

12. A thermally insulated container is divided into two parts by a screen. In one part the pressure and temperature are P and T for an ideal gas filled. In the second part it is vacuum. If now a small hole is created in the screen, then the temperature of the gas will:

a. Decrease
b. Increase
c. Remain same
d. None of these

13. A gas expands 0.25m^3 at constant pressure 10^3N/m^2, the work done is:

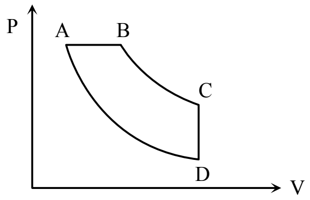
a. 2.5 ergs
b. 250 J
c. 250 W
d. 250 N

14. At 100°C the volume of 1kg of water is 10^{-3} m^3 and volume of 1 kg of steam at normal pressure is 1.671 m^3. The latent heat of steam is $2.3\times10^6\,J/kg$ and the normal pressure is105 N/m^2. If 5kg of water at 100°C is converted into steam, the increase in the internal energy of water in this process will be:

a. 8.35×10^5 J **b.** 10.66×10^6 J

c. 11.5×10^6 J **d.** Zero

15. In pressure-volume diagram given below, the isochoric, isothermal, and isobaric parts respectively, are:



a. BA, AD, DC **b.** DC, CB, BA

c. AB, BC, CD **d.** CD, DA, AB

16. The first law of thermodynamics is only:

a. The law of conservation of energy

b. The law of conservation of mass

c. The law of conservation of momentum

d. Both a. and b.

17. A mixture of two moles of carbon monoxide and one mole of oxygen, in a closed vessel is ignited to convert the carbon monoxide to carbon dioxide. If ΔH is the enthalpy change and ΔE is the change in internal energy, then:

a. $\Delta H > \Delta E$

b. $\Delta H < \Delta E$

c. $\Delta E = \Delta E$

d. The relationship depends on the capacity of the vessel

18. For the reaction of one mole of zinc dust with one mole of sulphuric acid in a bomb calorimeter, ΔU and *w* correspond to:

a. $\Delta U < 0, w = 0$ **b.** $\Delta U = 0, w < 0$

c. $\Delta U > 0, w = 0$ **d.** $\Delta U < 0, w > 0$

19. For the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3;\ \Delta H =$

a. $\Delta E - RT$ **b.** $\Delta E - 2RT$

c. $\Delta E + RT$ **d.** $\Delta E + 2RT$

20. The work done in ergs for the reversible expansion of one mole of an ideal gas from a volume of 10 litres to 20 litres at 25°C is:

a. $2.303\times298\times0.082\log2$

b. $298\times10^7\times8.31\times2.303\log2$

c. $2.303\times298\times0.082\log0.5$

d. $8.31\times10^7\times298-2.303\log0.5$

21. The enthalpies of the elements in their standard states are assumed to be:

a. Zero at 298 K **b.** Unit at 298 K

c. Zero at all temperatures **d.** Zero at 273 K

22. An ideal gas at constant temperature and pressure expands, then its:

a. Internal energy remains same

b. Internal energy decreases

c. Internal energy increases

d. Entropy first increases and then decreases

23. Work done during isothermal expansion of one mole of an ideal gas from 10 atm to 1 atm at 300 K is: (Gas constant = 2)

a. 938.8 cal. **b.** 1138.8 cal.

c. 1381.8 cal. **d.** 1581.8 cal.

24. At 27°C, one mole of an ideal gas is compressed isothermally and reversibly from a pressure of 2 atm to 10 atm. The values of ΔE and q are: (R = 2)

a. 0, – 965.84 cal

b. – 965.84 cal, + 965.84 cal

c. + 865.58 cal, – 865.58 cal

d. – 865.58 cal, – 865.58 cal

25. Work done during isothermal expansion of one mole of an ideal gas from 10 atom to 1 atm at 300K is:

a. 4938.8 *J* **b.** 4138.8 *J*

c. 5744.1 *J* **d.** 6257.2 *J*

26. If gas, at constant temperature and pressure expands then its:

a. Entropy increases and then decreases

b. Internal energy increases

c. Internal energy remains the same

d. Internal energy decreases

27. One mole of an ideal gas is allowed to expand reversibly and adibatically from a temperature of 27°C. If the work done during the process is 3 kJ, then final temperature of the gas is: $(C_V = 20\,J/K)$

a. 100 K **b.** 150 K

c. 195 K **d.** 255 K

28. ` $2C + O_2 \longrightarrow 2CO;\ \Delta H = -220\,kJ$

Which of the following statement is correct for this reaction?

a. Heat of combustion of carbon is 110 kJ

b. Reaction is exothermic
c. Reaction needs no initiation
d. All of these are correct

29. Internal energy is:
a. Partly potential and partly kinetic
b. Totally kinetic
c. Totally potential
d. None of these

30. During an isothermal expansion of an ideal gas its:
a. Internal energy increases
b. Enthalpy decreases
c. Enthalpy remains unaffected
d. Enthalpy reduces to zero

Entropy

31. When enthalpy and entropy change for a chemical reaction are -2.5×10^3 cal and 7.4 cal deg^{-1} respectively. Predict the reaction at 298 K is:
a. Spontaneous
b. Reversible
c. Irreversible
d. Non-spontaneous

32. For chemical reactions, the calculation of change in entropy is normally done
a. At constant pressure
b. At constant temperature
c. At constant temperature and pressure both
d. At constant volume

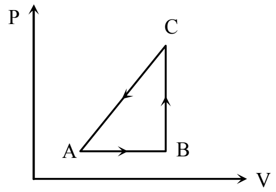
33. The enthalpy change for the transition of liquid water to steam, $\Delta H_{vap} = 37.3\,\text{kJ mol}^{-1}$ at 373K. The entropy change for the process is:
a. $111.9\,\text{J mol}^{-1}\text{K}^{-1}$
b. $37.3\,\text{J mol}^{-1}\text{K}^{-1}$
c. $100\,\text{J mol}^{-1}\text{K}^{-1}$
d. $74.6\,\text{J mol}^{-1}\text{K}^{-1}$

34. In a spontaneous process, the entropy of the system and its surroundings:
a. Equals zero
b. Decreases
c. Increases
d. Remains constant

35. If 900 J/g of heat is exchanged at boiling point of water, then what is increase in entropy?
a. 43.4 J/mole
b. 87.2 J/mole
c. 900 J/mole
d. Zero

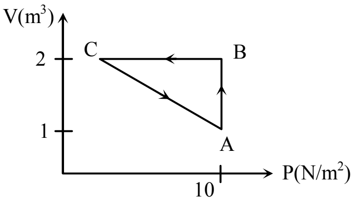
Cyclic and Non-cyclic Process

36. The P–V diagram of a system undergoing thermodynamic transformation is shown in figure. The work done on the system in going from A → B → C is 50 J and 20 cal heat is given to the system. The change in internal energy between A and C is:



a. 34 J
b. 70 J
c. 84 J
d. 134 J

37. An ideal gas is taken through the cycle A → B → C → A, as shown in the figure. If the net heat supplied to the gas in the cycle is 5J, the work done by the gas in the process C → A is:



a. – 5 J
b. – 20 J
c. – 15 J
d. – 10 J

Specific Heat and Latent Heat

38. Two spheres made of same substance have diameters in the ratio 1: 2. Their thermal capacities are in the ratio of:
a. 1 : 2
b. 1 : 8
c. 1 : 4
d. 2 : 1

39. When 300 J of heat is added to 25 gm of sample of a material its temperature raises from 25°C to 45°C. The thermal capacity of the sample and specific heat of the material are respectively given by?
a. 15 J/°C, 600 J/kg °C
b. 600 J/°C, 15 J°/kg °C
c. 150 J/°C, 60 J/kg °C
d. None of these

40. Latent heat of ice is 80 calorie/gm. A man melts 60 g of ice by chewing in 1 minute. His power is:
a. 4800 W
b. 336 W
c. 1.33 W
d. 0.75 W

41. The heat evolved in the combustion of benzene is given by

$$C_6H_6 + 7\frac{1}{2}O_2 \longrightarrow 6CO_2(g) + 3H_2O(l); \Delta H = -3264.6\,\text{kJ}$$

Which of the following quantities of heat energy will be evolved when $39\,\text{g}\,C_6H_6$ are burnt?
a. 816.15 kJ
b. 1632.3 kJ
c. 6528.2 kJ
d. 2448.45 kJ

42. Evaporation of water is:

a. An endothermic change
b. An exothermic change
c. A process where no heat change occurs
d. A process accompanied by chemical reaction

43. The absolute enthalphy of neutralisation of the reaction $MgO(s)+2HCl(aq) \longrightarrow MgCl_2(aq)+H_2O(l)$ will be:

a. Less than -57.33 kJ mol^{-1}
b. -57.33 kJ mol^{-1}
c. Greater than -57.33 kJ mol^{-1}
d. 57.33 kJ mol^{-1}

44. If ΔH_f° for H_2O_2 and H_2O are –188kJ/mole and –286kJ/mole. What will be the enthalpy change of the reaction?

$2H_2O_2(l) \longrightarrow 2H_2O(l)+O_2(g)$

a. -196 kJ / mole **b.** 146 kJ / mole
c. -494 kJ / mole **d.** -98 kJ / mole

45. Heat of combustion ΔH of CH_4, C_2H_6, C_2H_4 and C_2H_2 gases are –212.8, –373.0, –337.0 and –310.5 kcal respectively at the same temperature. The best fuel among these gases is

a. CH_4 **b.** C_2H_6
c. C_2H_4 **d.** C_2H_2

46. Which of the following values of heat of formation indicates that the product is least stable?

a. -94 kcal **b.** -231.6 kcal
c. $+21.4$ kcal **d.** $+64.8$ kcal

47. Standard molar enthalpy of formation of CO_2 is equal to:

a. Zero
b. The standard molar enthalpy of combustion of gaseous carbon
c. The sum of standard molar enthalpies of formation of CO and O_2
d. The standard molar enthalpy of combustion of carbon (graphite)

48. When 50 cm^3 of a strong acid is added to cm^3 of an alkali, the temperature rises by 5°C. If 250 cm^3 of each liquid are mixed, the temperature rise would be?

a. 5°C **b.** 10°C
c. 25°C **d.** 20°C

Bond Energy or Bond Enthalpies

49. The work done during the expansion of a gas from a volume of 4 dm^3 to 6 dm^3 against a constant external pressure of 3atm is: $(1 L\,atm = 101.32 J)$

a. + 304 J **b.** –304 J
c. – 6 J **d.** –608 J

50. The entropy changed involved in the conversion of 1 mole of liquid water at 373 K to vapour at the same temperature will be: $CO_2(g), H_2O(l)$

a. 0.119 kJ **b.** 0.109 kJ
c. 0.129 kJ **d.** 0.120 kJ

51. Which one of the following has ΔS° greater than zero:

a. $2CO_2(g)+3H_2O(l), \rightleftharpoons \Delta_C H,$
b. $NaCl(aq) \rightleftharpoons NaCl(s)$
c. $NaNO_3(s) \rightleftharpoons Na^+(aq)+NO_3^-(aq)$
d. $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$

52. Energy required to dissociate 4 gm of gaseous hydrogen into free gaseous atoms is 208 kcal at 25°C. The bond energy of H–H bond will be:

a. 104 kcal **b.** 10.4 kcal
c. 1040 kcal **d.** 104 cal

53. The bond dissociation energies of gaseous H_2, Cl_2 and HCl are 104, 58 and 103 kcal respectively. The enthalpy of formation of HCl gas would be:

a. – 44 kcal **b.** 44 kcal
c. – 22 kcal **d.** 22 kcal

54. The H–H bond energy is 430 kJ mol and Cl–Cl bond energy is 240 kJ mol^{-1}. ΔH for HCl is –90 kJ. The H–Cl bond energy is about:

a. 180 kJ mol^{-1}
b. 360 kJ mol^{-1}
c. 213 kJ mol^{-1}
d. 425 kJ mol^{-1}

55. If the bond energies of H–H, BR–Br and HBr are 433, 192 and 364 kJ mol^{-1} respectively, the ΔH° for the reaction, $H_2(g)+Br_2(g) \longrightarrow 2HBr(g)$ is:

a. + 261 kJ
b. – 103 kJ
c. – 261 kJ
d. + 103 kJ

NCERT EXEMPLAR PROBLEMS

More than One Answer

56. Which of the following relation(s) represent(s) adiabatic process?

a. $\log\frac{T_1}{T_2}=(1-\gamma)\frac{V_2}{V_1}$

b. $\log\frac{T_1}{T_2}=(1-\gamma)\log\frac{V_2}{V_1}$

c. $\log\frac{T_1}{T_2}=(1-\gamma)\log\left(\frac{V_2}{V_1}\right)$

d. $\log\frac{T_2}{T_1}=(1-\gamma)\log\frac{V_2}{V_1}$

57. Two moles of a monatomic ideal gas ($C_V = 1.5$ R) initially at 400 K in an isolated, 1.0 L, piston is allowed to expand against a constant of a 1.0 atm till the final volume reaches to 10 L which of the following conclusion regarding the above change (s) is (are) true?

a. The final temperature of the gas is 363.45 K

b. If the same process were carried out to the same final volume but under reversible final temperature would have been less than 363.45 K

c. In the above, process, the initial and final temperatures and volumes related $\left[\frac{T_1}{T_2}\right]=\left[\frac{V_2}{V_1}\right]^{\gamma-1}$

d. Entropy change of a system (ΔS_{Syst}) is zero

58. Which of the following thermodynamic relation (s) is/are correct?

a. In a cyclic process, $\oint ds=0$

b. $\Delta G=-T\Delta S_{univ}$

c. $\left[\frac{dG}{dP}\right]_P=-S$

d. $\Delta G=\Delta G^{\ominus}+RT\ln Q,\ Q=\text{Reaction quotient}$

59. In which of the following process, entropy of the system is increasing?

a. $NH_3(g)+HCl(g)\longrightarrow NH_4Cl(s)$

b. $N_2(g)+3H_2(g)\longrightarrow 2NH_3(g)$

c. $COCl_2(g)\longrightarrow CO(g)+Cl_2(g)$

d. $H_2O(g)+C(g)\longrightarrow H_2(g)+CO(g)$

60. For which of the following processes $\Delta E=0$?

a. A cyclic process

b. An isothermal process

c. An isochoric process

d. Adiabatic process

61. Identify the correct statement (s):

a. Relation of ΔG and ΔG° in a reaction system is $\Delta G=\Delta G^\circ-RT\ \ln Q$ where, Q is the reaction quotient

b. For an ideal gas $\Delta G=nRT\ \ln\left[\frac{P_2}{P_1}\right]$ for n moles at constant temperature

c. $\left[\frac{d\Delta G}{dp}\right]_T=V$

d. The entropy change during isothermal reversible expansion of an ideal gas is $R\ \ln\left[\frac{V_2}{V_1}\right]^{\frac{1}{n}}$ where, n is the no. moles of the gas

62. Which is an irreversible process?

a. Mixing of two gases

b. Evaporation of water at 373 K and 1 atm in a closed system

c. Dissolution of NaCl in water

d. H_2O (s) at –4ºC

63. Which of the following are thermodynamically stable?

a. C (diamond)

b. C (graphite)

c. P_4 (white)

d. P_4 (black)

64. $C(s)+1/2O_2\longrightarrow CO(g);\Delta H^\circ=-26\text{ Kcal mol}^{-1}$

$CO(g)+1/2O_2\longrightarrow CO_2(g);\Delta H^\circ=-68\text{ Kcal mol}^{-1}$

a. Heat of formation of CO_2 is -68 Kcal mol^{-1}

b. Heat of formation of C(s) is -26 Kcal mol^{-1}

c. Heat of formation of $CO_2(g)$ is -94 Kcal mol^{-1}

d. Heat of formation of CO (g) is -26 Kcal mol^{-1}

65. Heat of neutralization of weak acid with strong base is -50 KJ and weak acid, weak base is -41.4 KJ then:

a. Heat of ionization of weak acid is 7.4 KJ/mole

b. Heat of strong acid and strong base neutralization is -57.4 KJ

c. Heat of ionization of weak base is 16 KJ/mole

d. Heat of ionization of weak base is 8.6 KJ/mole

66. Correct reactions among the following are:

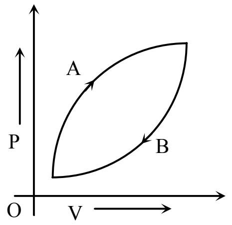
a. $\Delta H^\circ_{formation}$ of $CO_2(g)=\Delta H^\circ_{combustion}$ or graphite

b. $\Delta H^\circ_{sublimation}$ of carbon(s) $=\Delta H^\circ_{atomization}$ of carbon (graphite)

c. $\Delta H^\circ_{formation}$ of $B_2O_3(s)=2\times\Delta H^\circ_{formation}$ of boron(s)

d. $\Delta H^\circ_{combustion}$ of $CO(g)$ $=\Delta H^\circ_{formation}$ of $CO_2(g)$

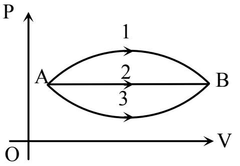
67. In the cyclic process shown in figure, ΔU_1 and ΔU_2 represent the change in internal energy in the process A and B respectively. If ΔQ be the net heat given to the system in the process and ΔW be the net work done by the system in the process, then:



a. $\Delta U_1 + \Delta U_2 = 0$ **b.** $\Delta U_1 - \Delta U_2 = 0$

c. $\Delta Q - \Delta W = 0$ **d.** $\Delta Q + \Delta W = 0$

68. A gas undergoes change in its state form position A to position B, via three different paths as shown in the figure. Select the correct alternatives:



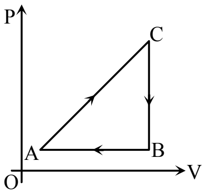
a. Change in internal energy in all the three paths is equal

b. In all the three paths heat is absorbed by the gas

c. Heat absorbed/released by the gas is maximum in path (1)

d. Temperature of the gas first increases and then decreases continuously in path (1)

69. An ideal gas undergoes a thermodynamic cycle as shown in the figure. Which of the following statements are correct?



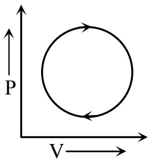
a. Straight line AB cannot pass through O

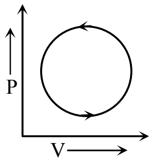
b. During process AB, temperature decreases while during process BC it increases

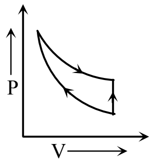
c. During process BC, work is done by the gas against external process and temperature of the gas increases

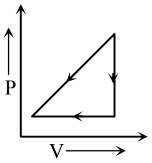
d. During process CA, work is done by the gas against external pressure and heat supplied to the gas is exactly equal to this work.

70. The following are one P-V diagrams for the cyclic processes for a gas. In which of these processes is heat absorbed by the gas:

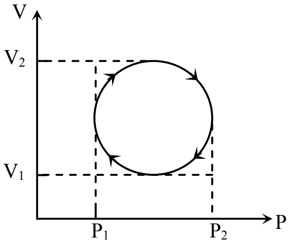
a.


b.


c.


d.


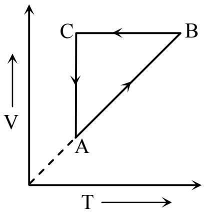
71. In the cyclic process shown on the V-P diagram, the magnitude of the work done cannot be equal to:

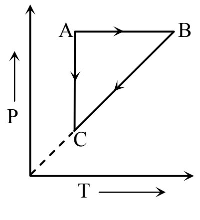


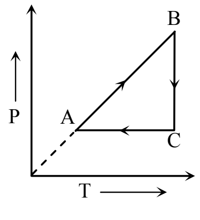
a. $\pi\left(\frac{P_1 - P_2}{2}\right)^2$ **b.** $\pi\left(\frac{V_1 - V_2}{2}\right)^2$

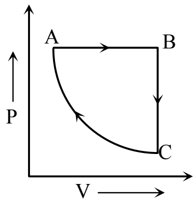
c. $\frac{\pi}{4}(P_1 - P_2)(V_2 - V_1)$ **d.** $\pi(P_2V_2 - V_1P_1)$

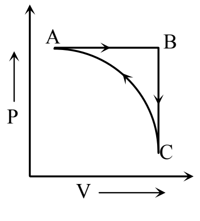
72. An ideal gas undergoes a thermodynamic cycle as shown in figure. Which of the following graphs represent the same cycle?



a.


b.


c.


d.


73. An ideal gas is taken from the state A (pressure p, volume V to the state B (pressure p/2, volume 2V) along a straight line path in the p-V diagram. Select the correct statements from the following:

a. The work done by the gas in the process A to B exceeds the work that would be done by it if the system were taken from A to B along an isotherm

b. In the T-V diagram, the path AB becomes a part of a parabola

c. In the p-T diagram, the path AB becomes a part of a hyperbola

d. In going from A to B, the temperature T of the gas first increases to a maximum value and then decrease

74. The figure shows the p-V plot an ideal gas taken through a cycle ABCDA. The part ABC is a semi-circle and CDA is half of an ellipse. Then,

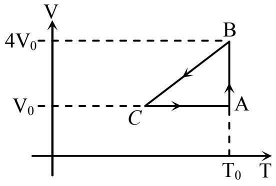
a. the process during the path $A \rightarrow B$ is isothermal

b. heat flows out of the gas during the path $B \rightarrow C \rightarrow D$

c. work done during the path $A \rightarrow B \rightarrow C$ is zero

d. positive work is done by the gas in the cycle ABCDA

75. One mole of an ideal gas in initial state A undergoes a cyclic process ABCA, as shown in figure. Its pressure at A is p_0. Choose the correct option(s) from the following:



a. Internal energies at A and B are the same

b. Work done by the gas in process AB is $p_0V_0 \ln 4$

c. Pressure at C is $\frac{p_0}{4}$

d. Temperature at C is $\frac{T_0}{4}$

Assertion and Reason

Note: Read the Assertion (A) and Reason (R) carefully to mark the correct option out of the options given below:

a. If both assertion and reason are true and the reason is the correct explanation of the assertion.

b. If both assertion and reason are true but reason is not the correct explanation of the assertion.

c. If assertion is true but reason is false.

d. If the assertion and reason both are false.

e. If assertion is false but reason is true.

76. **Assertion:** Entropy of ice is less than water.
Reason: Ice have cage like structure.

77. **Assertion:** The heat absored during the isothermal expansion of an ideal gas against vacuum is zero.
Reason: The volume occupied by the molecules of an ideal gas is zero.

78. **Assertion:** Absolute values of internal energy of substance cannot be determined.
Reason: It is impossible to determine exact values of constituent energies of the substances.

79. **Assertion:** Mass and volume are extensive properties.
Reason: Mass / volume is also an extensive parameter.

80. **Assertion:** Molar entropy of vaporization of water is different from ethanol.
Reason: Water is more polar than ethanol.

81. **Assertion:** The increase in internal energy (ΔE) for the vaporiation of one mole of water at 1 atm and 373K is zero.
Reason: For all isothermal processes $\Delta E = 0$.

82. **Assertion:** ΔH and ΔE are almost the same for the reaction.
$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$.
Reason: All reactants and products are gases.

83. **Assertion:** The enthalpies of neutralisation of strong acids and strong bases are always same.
Reason: Neutralisation is heat of formation of water.

84. **Assertion:** If a refrigerator's door is kept open room gets cooled.
Reason: Material kept inside the refrigerator reamins cool.

85. **Assertion:** Enthalpy and entropy of any elementary substance in the standard state are taken as zero.
Reason: At zero degree absolute, the constituent particles become completely motionless.

Comprehension Based

Paragraph –I

Mixture of gases is very common. On mixing, some gases may react with each other to form a new chemical compound gas. Some of them do not react chemically. They have different physical properties. If two such gases are mixed then answer the following questions for the mixture.

86. If m_1 and m_2 are their molar masses, n_1 and n_2 are the number of moles mixed, C_{V_1} and C_{V_2} are their molar specific heats at constant volume then the specific heat at constant volume for the mixture is:

a. $\frac{C_{V_1} + C_{V_2}}{2}$

b. $\frac{n_1C_{V_1} + n_2C_{V_2}}{n_1 + n_2}$

c. $\frac{n_1n_2(C_{V_1} + C_{V_2})}{n_1 + n_2}$

d. None of these

87. Specific heat of mixture at common pressure is:

a. $\frac{n_1 C_{P_1} + n_2 C_{P_2}}{n_1 + n_2}$

b. $\frac{n_1 n_2}{n_1 + n_2}(C_{P_1} + C_{P_2})$

c. $\frac{C_{P_1} + C_{P_2}}{2}$

d. None of these

88. Ratio $\gamma = \frac{C_P}{C_V}$ for two gases is γ_1 and γ_2, then for the mixture γ_m is:

a. $\gamma_m = \frac{n_1\gamma_1 + n_2\gamma_2}{n_1 + n_2}$

b. $\frac{n_1 + n_2}{\gamma_m} = \frac{n_1}{\gamma} + \frac{n_2}{\gamma_2}$

c. $\frac{n_1 + n_2}{\gamma_m + 1} = \frac{n_1}{\gamma + 1} + \frac{n_2}{\gamma + 1}$

d. $\frac{n_1 + n_2}{(\gamma_m - 1)} = \frac{n_1}{\gamma_1 - 1} + \frac{n_2}{\gamma_1 - 1}$

Paragraph –II

A diatomic gas is enclosed in a cylinder at pressure $10^5\ N/m^2$ at temperature 27°C. It is subjected to a cyclic process. In the first process its pressure is doubled keeping volume constant. Then it is made to expand adiabatically to original pressure. Then it is made of suffer isobaric compression bringing it back to initial volume 2 litre.

89. Temperature of gas after its pressure is doubled at constant volume is:

a. 327°C

b. 127°C

c. 177°C

d. 148°C

90. After adiabatic expansion the new volume will be:

a. 4.12 litre

b. 3.27 litre

c. 2.58 litre

d. 1.88 litre

91. Which of the following is correct statement?

a. Entropy increases in first process, during second process entropy remains constant and during last process, it decreases

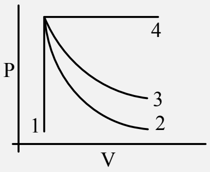
b. Entropy remains constant in first step, increases in second step and decreases in 3rd step

c. Entropy decreases in first step, increases in 2nd step and remains constant in 3rd step

d. Entropy goes on increasing in all steps

Match the Column

92. Thermodynamic changes in gases can be expressed graphically between changes in pressure and corresponding changes in volume. Column I give the thermodynamic change while column II shows the P-V graphs marked in serial no. 1 to 4. Match the changes given in column I with the graph given in figure in column II:

Column I	Column II
(A) Isothermal change	
(B) Adiabatic change	
(C) Isobaric change	
(D) Isochoric change	

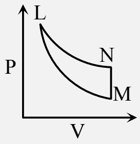
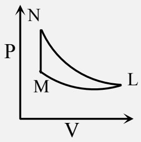
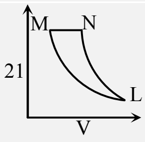
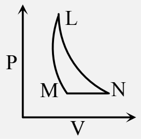
a. A→1; B→2; C→3; D→4

b. A→4; B→3; C→2; D→1

c. A→3; B→2; C→4; D→1

d. A→1; B→4; C→2; D→3

93. Thermodynamic changes are of more significance to describe the working of heat engine etc. The graphs showing variation of P-V curves are given in column I showing all the isothermal isochoric, isobaric and adiabatic changes. Column II gives choices of curves in corresponding figures. Match the figures in column I with proper choices in column II:

Column I	Column II
(A) 	**1.** LN isotherm LM adiabatic MN isochoric
(B) 	**2.** LM isotherm LN adiabatic MN isochoric
(C) 	**3.** LM adiabatic LN isotherm MN isochoric
(D) 	**4.** LN adiabatic LM isotherm MN isochoric

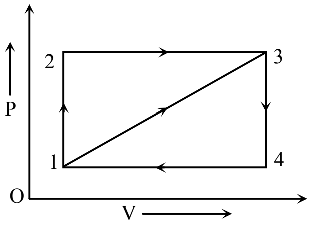
a. A→4; B→3; C→2; D→1

b. A→1; B→2; C→4; D→3

c. A→3; B→4; C→2; D→1

d. A→2; B→4; C→1; D-3

94. The figure shown an indicator diagram. During the path 1-2-3, 100 cal of heat is given to system and external work done is equal to 40 cal. During the path 1-4-3, the work done is 10 cal. The match statements in column I with the numerical value of equivalent heat in column II:



Column I	Column II
(A) Heat given to system during path	**1.** 65 cal
(B) Work done to bring system from 3 to 1 along straight line path	**2.** 70 cal
(C) Heat ejected by the system in path 3-1 is	**3.** 85 cal
(D) Internal energy in state 3 exceeds that in state I by	**4.** 25 cal

a. A→1; B→2; C→3; D→4

b. A→4; B→3; C→2; D→1

b. A→3; B→2; C→1; D→4

d. A→2; B→4; C→3; D→1

95. Match the statement of Column I with those in Column II:

Column I	Column II
(A) Joule–Thomson coefficient	**1.** $\left(\frac{\partial U}{\partial V}\right)_T = 0$
(B) Kirchhoff's equation	**2.** $\left(\frac{2a}{RT} - b\right) = 0$
(C) Ideal gas	**3.** $\left(\frac{\partial \Delta H}{\partial T}\right)_P = \Delta C_P$
(D) Inversion temperature	**4.** $\left(\frac{\partial T}{\partial P}\right)_H = \frac{-(\partial H/\partial P)_T}{C_P}$

a. A→4; B→3; C→1; D→2

b. A→2; B→4; C→3; D→1

c. A→1; B→3; C→2; D→4

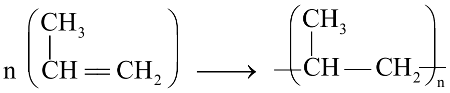
d. A→4; B→1; C→3; D→2

Integer

96. Bond dissociation energy of XY, X_2, and Y_2 (all diatomic molecules) are in the ratio of 1: 1 : 05 and ΔH_f of XY is $-100\,\text{kJ mol}^{-1}$.

The bond dissociation energy of X_2 is 100 *x*. Find the value of x:

97. The polymerisation of propene to linear polypene is represented by the reaction



$$n\left(\overset{\displaystyle CH_3}{\overset{|}{C}H}=CH_2\right) \longrightarrow \left(\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_2\right)_n$$

Where n has large integral value, the average enthalpies of bond dissociation for (C == C) and (C—C) at 298K are + 590 and +331 kJ mol^{-1}, respectively. The enthalpy of polymerization is $-360\,\text{kJ mol}^{-1}$.

Find the value of n?

98. $\Delta_f H^-$ of hypothetical MgCl is –125 kJ mol^{-1} and for $MgCl_2$ is $-642\,\text{kJ mol}^{-1}$. The enthalpy of disproportionaton of MgCl is -49*x*.

Find the value of *x*:

99. The lattice energy of solid KCl is 181 k cal mol^{-1} and the enthalpy of solution of KCl in H_2O is 1.0 kcal mol^{-1}. If the hydration enthalpies of K^+ and Cl^- ions are in the ratio of 2: 1 then the enthalpy of hydration of K^+ is –20*x* K cal mol^{-1}.

Find the value of *x*:

100. In the process: $H_2O(s, -10°C, 1atm) \longrightarrow H_2O(l, 10°C, 1atm)$;

C_P for ice = 9 cal $\text{deg}^{-1}\,\text{mol}^{-1}$, C_P for $H_2O = 18\,\text{cal deg}^{-1}$ mol^{-1}. Latent heat of fusion of ice = 1440 cal mol^{-1} at 0°C. The entropy change for the above process is 6.258 cal. $\text{deg}^{-1}\,\text{mol}^{-1}$.

Give the total number of steps in which the third law of thermodynamics is used:

ANSWER

1.	**2.**	**3.**	**4.**	**5.**	**6.**	**7.**	**8.**	**9.**	**10.**
c	b	c	c	b	a	b	a	b	a
11.	**12.**	**13.**	**14.**	**15.**	**16.**	**17.**	**18.**	**19.**	**20.**
d	c	b	b	d	d	b	a	b	b
21.	**22.**	**23.**	**24.**	**25.**	**26.**	**27.**	**28.**	**29.**	**30.**
a	a	c	a	c	c	b	b	a	c
31.	**32.**	**33.**	**34.**	**35.**	**36.**	**37.**	**38.**	**39.**	**40.**
a	c	c	c	a	d	a	b	a	b
41.	**42.**	**43.**	**44.**	**45.**	**46.**	**47.**	**48.**	**49.**	**50.**
b	a	a	a	a	d	d	a	d	b
51.	**52.**	**53.**	**54.**	**55.**	**56.**	**57.**	**58.**	**59.**	**60.**
c	a	c	d	b	a,b,d	a,b	a,b,d	c,d	b,c
61.	**62.**	**63.**	**64.**	**65.**	**66.**	**67.**	**68.**	**69.**	**70.**
b,c	a,c,d	b,c	c,d	a,b,d	a,b,c	a,c	a,b,c	b,d	a,b,c
71.	**72.**	**73.**	**74.**	**75.**	**76.**	**77.**	**78.**	**79.**	**80.**
a,b,d	a,c	a,b,d	b,d	a,b	b	c	a	b	b
81.	**82.**	**83.**	**84.**	**85.**	**86.**	**87.**	**88.**	**89.**	**90.**
a	b	a	e	c	b	a	d	a	b
91.	**92.**	**93.**	**94.**	**95.**	**96.**	**97.**	**98.**	**99.**	**100.**
a	c	b	d	a	4	5	8	6	2

SOLUTION

Multiple Choice Questions

1. **(c)** Temperature on any scale can be converted into other scale by $\frac{X-LFP}{UFP-LFP}$ = Constant for all scales

$$\therefore \quad \frac{X-20°}{150°-20°}=\frac{C-0°}{100°-0°}$$

$$\Rightarrow \quad X=\frac{C\times 130°}{100°}+20°=\frac{60°\times 130°}{100°}+20°=98°$$

2. **(b)** For a constant volume gas thermometer temperature in °centigrade is given as $T_c=\frac{P-P_0}{P_{100}-P_0}\times 100°C$

$$\Rightarrow \quad T_c=\frac{13-(-3)}{22-(-3)}\times 100°C=\frac{16}{25}\times 100$$

3. **(c)** initially (at 20^oC) length of composite system

L = 50 + 100 = 150 cm

Length of iron rod at 100°C

$=50[1+12\times 10^{-6}\times(100-20)]=50.048\,\text{cm}$

Length of aluminum rod at 100°C

$=100[1+24\times 10^{-6}\times(100-20)]=100.192\,\text{cm}$

Finally (at 100^oC) length of composite system L'

$=50.048+100.192=150.24\,\text{cm}$

Change in length of the composite system $\Delta L = L' - L$

= 150.24 – 150 = 0.24 cm

$\therefore$ Average coefficient of expansion at 100^oC

$$\alpha=\frac{\Delta L}{L\times\Delta T}=\frac{0.24}{150\times(100-20)}=20\times 10^{-6}/°C$$

4. **(c)** Apparent coefficient of volume expansion for liquid $\gamma_{app}=\gamma_L-\gamma_s$

$\therefore \quad \gamma_L=\gamma_{app}+\gamma_s$

Where γ_s is coefficient of volume expansion for solid vessel.

When liquid is placed in copper vessel then

$\gamma_L = C + \gamma_{copper}$ . . . (*i*)

[As $\gamma_{app.}$ for liquid in copper vessel = C]

When liquid is placed in silver vessel then

$\gamma_L = S + \gamma_{silver}$ . . . (*ii*)

[As $\gamma_{app.}$ for liquid in silver vessel = S]

From equation (*i*) and (*ii*) we get $C + \gamma_{copper} = S + \gamma_{silver}$

$\therefore \quad \gamma_{silver}=C+\gamma_{copper}-S$

Coefficient of volume expansion = 3 × Coefficient of linear expansion

$$\Rightarrow \quad \alpha_{silver}=\frac{\gamma_{silver}}{3}=\frac{C+\gamma_{copper}-S}{3}$$

5. **(b)** Work done by the system = Area of shaded portion on P-V diagram = $(300-100)10^{-6}\times(200-10)\times 10^3=20$J and direction of process is anticlockwise so work done will be negative *i.e.* $\Delta W = -20$ J.

6. **(a)** Change in internal energy = $\Delta U=\mu c_v\Delta T$

$\Rightarrow \quad U_2-U_1=\mu c_v(T_2-T_1)$

Let initially $T_1=0$ so $U_1=0$ and finally

$T_2=T$ and $U_2=U$ $U=\mu\, c_vT=\mu T\times c_v$

$=\frac{PV}{R}\times\frac{R}{\gamma-1}=\frac{PV}{\gamma-1}$ [As $PV=\mu RT$

$\therefore \quad \mu T=\frac{PV}{R}$ and $c_v=\frac{R}{\gamma-1}$]

7. **(b)** $\Delta Q=\Delta U+\Delta W$

$\Rightarrow \quad 110=40+\Delta W$

$\Rightarrow \quad \Delta W=70\,J$

8. **(a)** $\Delta Q=\Delta U+\Delta W$

$\Rightarrow \quad \Delta Q=\Delta U+\Delta dV$

$\Rightarrow \quad 100=\Delta U+50(4-10)$

$\Rightarrow \quad 100=\Delta U-300$

$\therefore \quad \Delta U=400\,J$

9. **(b)** $\Delta W = \mu RT \log_e \left(\frac{V_f}{V_i} \right) = 5 \times 8.3 \times 500 \times \log_e \left(\frac{2V}{V} \right)$

$= 5 \times 8.3 \times 500 \times 0.69 \approx 14400 J.$

10. **(a)** Given $P \propto T^3$. But for adiabatic process $P \propto T^{\frac{\gamma}{\gamma-1}}$.

So, $\frac{\gamma}{\gamma-1} = 3 \Rightarrow \gamma = \frac{3}{2}\ \frac{C_p}{C_v} = \frac{3}{2}$

11. **(d)** For an adiabatic process $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$

$\Rightarrow \frac{T_1}{T_2} = \left[\frac{V_2}{V_1} \right]^{\gamma-1} = \left[\frac{L_2 A}{L_1 A} \right]^{5/3-1} = \left[\frac{L_2}{L_1} \right]^{2/3}$.

12. **(c)** In second part there is a vacuum *i.e.* P = 0.

So, work done in expansion = $P\Delta V = 0$

13. **(b)** As we know, work done

$= P\Delta V = 103 \times 0.25 = 250$ J

14. **(b)** Heat required to convert 5 kg of water into steam

$\Delta Q = mL = 5 \times 2.3 \times 10^6 = 11.5 \times 10^6$ J

Work done in expanding volume,

$\Delta W = P\Delta V = 5 \times 10^5 [1.671 - 10^{-3}] = 0.835 \times 10^6$ J

Now by first law of thermodynamics $\Delta U = \Delta Q - \Delta W$

$\Rightarrow \Delta U = 11.5 \times 10^6 - 0.835 \times 10^6 = 10.66 \times 10^6$ J

15. **(d)** Process CD is isochoric as volume is constant, Process DA is isothermal as temperature constant and Process AB is isobaric as pressure is constant.

16. **(d)** First law of thermodynamics is also known as Law of conservation of mass and energy.

17. **(b)** Formation of CO_2 from CO is an exothermic reaction; heat is evolved from the system, *i.e.*, energy is lowered. Thus, exothermic reactions occur spontaneously on account of decrease in enthapy of system. Thus, $\Delta E > \Delta H$.

18. **(a)** Bomb calorimeter is commonly used to find the heat of combustion of organic substances which consists of a sealed combustion chamber, called a bomb. If a process is run in a sealed container then no expansion or compression is allowed, so w = 0 and $\Delta U = q$. $\Delta U < 0$, $w = 0$

19. **(b)** $\Delta H = \Delta E + \Delta nRT$; Since $\Delta n = -2$

Than $\Delta H = \Delta E - 2RT$.

20. **(b)** $W = 2.303\ nRT \log \frac{V_2}{V_1}$

$= 2.303 \times 1 \times 8.314 \times 10^7 \times 298 \log \frac{20}{10}$

$= 298 \times 10^7 \times 8.314 \times 2.303 \log 2.$

21. **(a)** The enthalpies of all elements in their standard state at 25°C or 298K are zero.

22. **(a)** At constant T and P internal energy of ideal gas remains unaffected.

23. **(c)** $-W = +2.303 nRT \log \frac{p_1}{p_2}$

$-W = 2.303 \times 1 \times 2 \times 300 \log \frac{10}{1} = 1381.8$ cal.

24. **(a)** $W = 2.303 nRT \log \frac{P_2}{P_1}$

$= 2.303 \times 1 \times 2 \times 300 \log \frac{10}{2} = 965.84$

at constant temperature, $\Delta E = 0$.

$\Delta E = q + w$; $q = -w = -965.84$ cal.

25. **(c)** Given that $P_1 = 10$ atm, $P_2 = 1$ atm, $T = 300K$, n=1

$R = 8.314 J/K/mol$ Now, by using

$W = 2.303 nRT \log_{10} \frac{P_2}{P_1} = 2.303 \times 1 \times 8.314 \times 300 \log_{10} \frac{1}{10}$

$W = 5744.1$ Joule

26. **(c)** We knows that internal energy of a gas depends upon its pressure and temperature. Thus if a gas expands at constant temperature and pressure, then its internal energy remains same.

27. **(b)** Given number of moles =1

Initial temperature $= 27^\circ C = 300K$

Work done by the system $= 3KJ = 3000K$

It will be (–) because work is done by the system.

Heat capacity at constant volume $(Cv) = 20 J/k$

We know that work done $W = -nC_V (T_2 - T_1)$;

$3000 = -1 \times 20 (T_2 - 300)$; $3000 = -20T_2 + 6000$

$20T_2 = 3000$; $T_2 = \frac{3000}{20} = 150K$

28. **(b)** $2C + O_2 \longrightarrow 2CO$; $\Delta H = -220 KJ$

This reaction does not represent complete combustion of carbon; hence heat of combustion of carbon will not be equal to 110 kJ. The negative sign of ΔH indicates that this reaction is exothermic. Also, despite being spontaneous reaction, it requires initiation.

29. **(a)** The exact value of internal energy is not known as it includes all type of energies of molecules constituting the given mass of matter such as translational, vibrational, rotational. The kinetic & potential energy of the nuclei and electron with in the individual molecules and the manner in which the molecule are linked together etc.

$E = E_{translational} + E_{rotational} + E_{vibrational}$

Thus, we can say that internal energy is partly potential and partly kinetic.

30. **(c)** During isothermal expansion of ideal gas, $\Delta T = 0$

$\Delta H = \Delta E + P\Delta V = \Delta E + nR\Delta T = 0 + 0 = 0.$

31. **(a)** When ΔH =–*ve*, ΔS = +*ve* and ΔG = –*ve* than reaction is spontaneous .

32. **(c)** Calculation of change in entropy is done at constant temperature and pressure both.

33. **(c)** $\Delta S_{vap} = \frac{\Delta H_{vap}}{T} = \frac{37.3\,KJ\,mol^{-1}}{373\ K}$

$= 0.1\,kJ\,mol^{-1}\,K^{-1} = 100\ J\,mol^{-1}\,K^{-1}.$

34. **(c)** $\Delta S = +ve$ than process is spontaneous.

35. **(a)** $\Delta S_{vap} = \frac{(900\times18)}{373} = 43.4\ JK^{-1}\ mol^{-1}$.

36. **(d)** Heat given $\Delta Q = 20\,cal = 20\times4.2 = 84\,J$.

Work done ΔW = – 50 J [As process is anticlockwise]

By first law of thermodynamics

⇒ $\Delta U = \Delta Q - \Delta W = 84 - (-50) = 134J$

37. **(a)** For a cyclic process. Total work done

$= W_{AB} + W_{BC} + W_{CA}$

⇒ $\frac{1}{2}\times1.0\times10 = 10\times(2-1) + 0 + W_{CA}$

[W_{BC} = 0 since there is no change in volume along BC]

⇒ $5J = 10J + W_{CA} \Rightarrow W_{CA} = -5J$

38. **(b)** Thermal capacity = Mass × Specific heat

Due to same material both spheres will have same specific heat

∴ Ratio of thermal capacity $= \frac{m_1}{m_2} = \frac{V_1\rho}{V_2\rho}$

$= \frac{\frac{4}{3}\pi r_1^3}{\frac{4}{3}\pi r_2^3} = \left(\frac{r_1}{r_2}\right)^3 = \left(\frac{1}{2}\right)^3 = 1:8$

39. **(a)** Thermal capacity = mc

$= \frac{Q}{\Delta T} = \frac{300}{45-25} = \frac{300}{20} = 15J/°C$

Specific heat = $\frac{\text{Thermal capacity}}{\text{Mass}}$

$= \frac{15}{25\times10^{-3}} = 600J/kg°C$

40. **(b)** Work done by man = Heat absorbed by ice = mL

= 60 × 80 = 4800 calorie = 20160 J

∴ Power = $\frac{W}{t} = \frac{20160}{60} = 336W$

41. **(b)** 78*g* of benzene on combustion produces

Heat = – 3264.6 kJ

∴ 39g will produce $= \frac{-3264.6}{2} = -1632.3\,kJ.$

42. **(a)** Change of liquid to vapour takes energy in the form of heat so it is endothermic reaction.

43. **(a)** Heat of neutralisation will be less than –57.33 kJ/mol because some amount of this energy will be required for the dissociation of weak base (MgO)

44. **(a)** $H_2 + O_2 \longrightarrow H_2O_2 \quad \Delta H_f^o = -188\,kJ/mole$ ....(*i*)

$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O \quad \Delta H_f^o = -286\,kJ/mole$ ....(*ii*)

eq. (*i*) – eq. (*ii*) × 2 gives the required result.

45. **(a)** CH_4 is the best fuel because its calorific value $= \frac{-212.8}{16} = -13.3\,kcal/g$ is higher among the other gases.

46. **(d)** In the formation of a compound, more the heat absorbed, less stable is the compound.

47. **(d)** Standard molar heat enthalpy (H°) of a compound is equal to its standard heat of formation from most stable states of initial components.

48. **(a)** No doubt heat evolved during neutralisation of 250 cm^3 of each acid and base is five time the heat evolved during neutralisation of $50cm^3$ of each acid and base but the quantity if solution taking heat is also five time thus same temperature rise is noticed.

49. **(d)** $W = -p\Delta V$; $W = -3\times(6-4)$

$W = -6\times101.32$ ($\therefore 1\,L\,atm = 101.32\,J$) $W = -608\,J$

50. **(b)** $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$, $\Delta S = \frac{\Delta H_{vap}}{T}$,

$\Delta H_{vap.} = 2.257\,KJ/g$

Or $\Delta H_{vap} = 2.257\times18\,kJ/mol. = 40.7\,KJ/mol$

Hence, $\Delta S = \frac{40.7}{373} = 0.109$ kJ/mol/K.

51. **(c)** $NaNO_3$ is a solid, which is converted to liquid ions.

52. **(a)** 4g H_2 = 2 moles. Bond energy for 1 mole of H_2 = 208/2 = 104 k cal.

53. **(c)** Aim: $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \longrightarrow HCl$

$$\Delta H = \Sigma B.E._{(Products)} - \Sigma B.E._{(Reactants)}$$

$$= B.E.(HCl) - \left[\frac{1}{2}B.E.(H_2) + \frac{1}{2}B.E.(Cl_2)\right]$$

$$= -103 - \left[\frac{1}{2}(-104) + \frac{1}{2}(-58)\right]$$

$$= -103 - (-52 - 29) = -22 \text{ kcal.}$$

54. **(d)** $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \longrightarrow HCl,\ \Delta H = -90\,KJ$

$\therefore \quad \Delta H = \frac{1}{2}E_{H-H} + \frac{1}{2}E_{Cl-Cl}$

or $\quad -90 = \frac{1}{2} \times 430 + \frac{1}{2} \times 240 - E_{HCl}$

$\therefore \quad E_{H-Cl} = 425\,kJ\,mol^{-1}$

55. **(b)** $H-H + Br-Br \longrightarrow 2H-Br$

$433 + 192 \qquad 2 \times 364$

$625 \qquad 728$

Energy absorbed = Energy released

Net energy released $= 728 - 625 = 103\,kJ$

i.e., $= \Delta H = -103\,KJ$

NCERT Exemplar Problems

More than One Answer

56. **(a, b, d)** $\log\frac{T_1}{T_2} = (1-\gamma)\frac{V_2}{V_1}$,

$\log\frac{T_1}{T_2} = (1-\gamma)\log\frac{V_2}{V_1}$; $\log\frac{T_2}{T_1} = (1-\gamma)\log\frac{V_2}{V_1}$

57. **(a, b)** The final temperature of the gas is 363.45 K, If the same process were carried out to the same final volume but under reversible final temperature would have been less than 363.45 K.

58. **(a, b, d)** In a cyclic process, $\oint ds = 0$, $\Delta G = -T\Delta S_{univ}$,

$\Delta G = \Delta G^{\ominus} + RT \ln Q,\ Q = \text{Reaction quotient}$

59. **(c, d)** $COCl_2(g) \longrightarrow CO(g) + Cl_2(g)$;

$H_2O(g) + C(g) \longrightarrow H_2(g) + CO(g)$

60. **(b, c)** An isothermal process, An isochoric process.

61. **(b, c)** For an ideal gas $\Delta G = nRT \ln\left[\frac{P_2}{P_1}\right]$ for n moles at constant temperature, $\left[\frac{d\Delta G}{dp}\right]_T = V$

62. **(a, c, d)** (a) Mixing of two gases, Dissolution of NaCl in water, H_2O (s) at –4ºC

63. **(b, c)** C (graphite), P_4 (white).

64. **(c, d)** Heat of formation of $CO_2(g)$ is $-94\,Kcal\,mol^{-1}$, Heat of formation of CO(g) is $-26\,Kcal\,mol^{-1}$.

65. **(a, b, d)** Heat of ionization of weak acid is 7.4 KJ/mole, Heat of strong acid and strong base neutralization is –57.4KJ, Heat of ionization of weak base is 8.6 KJ/mole.

66. **(a, b, c)** $\Delta H^\circ_{formation}$ of $CO_2(g) = \Delta H^\circ_{combustion}$ or graphite, $\Delta H^\circ_{sublimation}$ of carbon (s) $= \Delta H^\circ_{atomization}$ of carbon (graphite).

67. **(a, c)** For a cyclic process, ΔU = 0

$\Delta U = \Delta U_1 + \Delta U_2 = 0$

From relation ΔQ = ΔU + ΔW As ΔU = 0

Hence ΔQ =ΔW or ΔQ–ΔW = 0

68. **(a, b, c)** Internal energy (U) depends only on the initial and final states. Hence, ΔU will be same in all the three paths. In all the three paths, work done by the gas is positive and the product PV or temperature T is increasing. Therefore, internal energy is also increasing. So, from the first law of thermodynamics, heat will be absorbed by the gas. Further, area under P–V graph is maximum in path 1 while ΔU is same for all the three paths. Therefore heat absorbed by the gas is maximum in path 1. For temperature of the gas we can see that product PV first increases in path 1 but whether it is decreasing or increasing later on we cannot say anything about it unless the exact values are known to us.

69. **(b, d)** For an isothermal process, PΔ = constant

or $\quad P = \frac{\text{constant}}{V}$ or $P \propto \frac{1}{V}$

It means, for an isothermal process the graph between P and 1/V will be a straight line passing through origin. Hence, the straight line AB will pass through origin. Hence, option (a) is wrong.

During process AB, the pressure P remains constant but 1/V increases. It means volume V decrease. Hence, AB is isobaric compression. Since, volume of the gas decreases at constant process, therefore, its temperature decreases. But temperature at C is equal to that of A. Hence, during the process BC, the temperature of the gas increases. In fact, process BC is an isochoric heating. Therefore, option (b) is correct. Since, during the process BC, volume remains constant, therefore, no work is done by the gas against external pressure. Therefore Option (c) is wrong.

During process CA, 1/V decreases, it means volume V increases. Since, the volume increases, therefore, work is done by the gas against external pressure.

Since, process CA in a isothermal process, therefore, no change in internal energy of the gas takes place. Hence, according to first law of thermodynamics Q =W+ΔU; heat supplied during this process is equal to work done by the gas against external pressure. Hence, option (d) is correct.

70. **(a, b, c)** In a cyclic process, heat is absorbed by a gas when the work done by it is positive, *i.e.,* when work is done by the gas if the closed curve in a P–V diagram is clockwise with P on the y-axis and V on the x-axis. If the axes for P and V are interchanged work done is again positive for an anticlockwise curve.

71. **(a, b, d)** For a cyclic plotted on the P–V diagram, the work done = area inside the closed curve. Treat the circle as an ellipse of semi-major axis $\frac{1}{2}(P_2 - P_1)$

72. **(a, c)** Process AB in the given figure is an isobaric process. During this process $V \propto T$. But $PV = nRT$ or $PV \propto T$.

Therefore, during this process, pressure P remains constant. Process BC is an isochoric cooling. During this process, volume of the gas remains constant but the temperature decreases.

Process CA is an isothermal process. During this process, volume decreases and temperature remains constant. Hence, pressure increases during this process. Hence, on P–V diagram, process AB will be a straight line parallel to V-axis and process BC will be a straight line parallel to P-axis and CA will be a rectangular hyperbola. Hence, option (c) and (d) is wrong.

On P–T diagram, process AB will be straight line parallel to T-axis, during which temperature increase. Process BC will be a straight line passing through origin, during which temperature and pressure both decreases and process CA will be a straight line parallel to P-axis during which pressure increase. Hence, option (a) is correct while (b) is wrong.

73. **(a, b, d)** (a) Work done = Area under p –V graph $A_1 > A_2$

$\therefore \quad W_{\text{given process}} > W_{\text{isothermal process}}$

(b) In the given process p –V equation will be of a straight line with negative slope and positive intercept *i.e.,* $p = -\alpha V + \beta$ (Here α and β are positive constants)

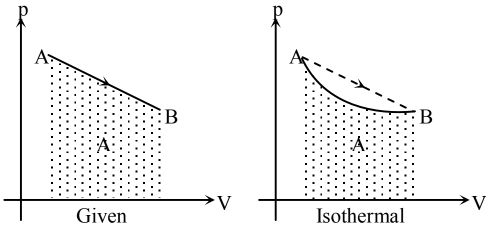
$$\Rightarrow \quad pV = -\alpha V^2 + \beta V$$

$$\Rightarrow \quad nRT = -\alpha V^2 + \beta V$$

$$\Rightarrow \quad T = \frac{1}{nR}(-\alpha V^2 + \beta V) \qquad \ldots(i)$$

This is an equation of parabola in T and V.

(d) $\frac{dT}{dV} = 0 = \beta - 2\alpha V \Rightarrow V = \frac{B}{2\alpha}$



Given Isothermal

Now, $\frac{d^2T}{dV^2} = -2\alpha = -ve$; *ie,*T has some maximum value.

Now, $T \propto pV$ and $(pA)_A = (pV)_B \Rightarrow T_A = T_B$

We conclude the temperatures are same at A and B and in between temperature has a maximum value. Therefore, in going from A to B, T will first increase to a maximum value and then decrease.

74. **(b, d)** (a) p–V graph is not rectangle hyperbola. Therefore, process A – B is not isothermal.

(b) In process BCD, product of pV (therefore temperature and internal energy) is decreasing. Further, volume is decreasing. Hence, work done is also negative.

Hence, Q will be negative or heat will flow out of the gas.

(c) W_{ABC} = positive

(d) For clockwise cycle on p–V diagram with P on y-axis, net work done is positive.

75. **(a, b)** $T_A = T_B \quad \therefore U_A = U_B$

$$W_{AB} = (1)(R)T_0 \ln\left(\frac{V_f}{V_i}\right) = RT_0 \ln\left(\frac{4V_0}{V_0}\right) = p_0V_0 \ln(4)$$

Information regarding p and T at C cannot be obtained from the given graph. Unless it is mentioned that line BC passes through origin or not.

Assertion and Reason

76. **(b)** Entropy of ice is less than water because water molecules in solid state lose kinetic energy and hence their tendency of movement minimise. Hence entropy decreases in solid state. The reason that ice have cage like structure is also correct but reason is not or correct explanation for assertion.

77. **(c)** During isothermal expansion of an ideal gas against vacuum is zero because expansion is isothermal. The reason, that volume occupied by the molecules of an ideal gas is zero, is false.

78. **(a)** It is fact that absolute values of internal energy of substances cannot be determined. It is also true that to determine exact values of constituent energies of the substance is impossible.

79. **(b)** Mass and volume are extensive properties. Mass/volume is also an extensive parameter. Here, both assertion and reason are true.

80. **(b)** The molar entropy of vaporization of water it differ from ethanol due to hydrogen bonding according to VSEPR theory water molecule having two lone pair of electron by which it angular and show some polarity which is higher than that of ethanol so both assertion and reason are correct but reason is not explanation assertion.

81. **(a)** The assertion that the increase in internal energy for the vaporisation of one mole of water at 1 atm and 373 K is zero is true and this is because that for all isothermal process internal energy is zero.

82. **(b)** $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

We know that $\Delta H = \Delta E + \Delta nRT$; $\Delta n = 2 - 2 = 0$

Hence, $\Delta nRT = 0$.

Therefore, $\Delta H = \Delta E$

83. **(a)** The enthalpies of neutralisation of strong acids and strong bases are same they are 13.7 Kcal. The reason is that it is heat of formation of water from H^+ and OH^- ions. $H^+OH^- \longrightarrow H_2O, \Delta H = 13.7\,\text{K cal}$. Thus, both assertion and reason are true.

84. **(e)** If a refrigerator's door is kept open room gets heated as heat energy is released to the surroundings.

85. **(c)** Enthalpy is zero but entropy is not zero. Vibrational motion exists even at absolute zero.

Comprehension Based

86. **(b)** $(C_V)_{\text{mixture}} = \dfrac{n_1C_1 + n_2C_2}{n_1 + n_2}$

If heat required is equal to their internal energy per mole per degree °C

87. **(a)** $C_{P_1} = C_{V_1} + R$ or $n_1C_{P_1} = n_1C_{V_1} + n_1R$

$C_{P_2} = C_{V_2} + R$ or $n_2C_{P_2} = n_2C_{V_2} + n_2R$

$$\frac{n_1C_{P_1} + n_2C_{P_2}}{n_1 + n_2} = \frac{n_1C_{V_1} + n_2C_{V_2}}{n_1 + n_2} + R = C_V + R$$

Hence, $C_P = \dfrac{n_1C_{P_1} + n_2C_{P_2}}{n_1 + n_2}$ $(\because C_P = C_V + R)$

88. **(d)** $\gamma_m = \dfrac{C_P}{C_V}$, $\therefore\ \gamma_m - 1 = \dfrac{C_P}{C_V} - 1 = \dfrac{C_P - C_V}{C_V} = \dfrac{R}{C_V}$

$\therefore$ $C_V = \dfrac{R}{\gamma_m - 1}$ Also $n_1C_{V_1} = \dfrac{n_1R}{\gamma_1 - 1}, n_2C_{V_2} = \dfrac{n_2R}{\gamma_2 - 1}$

or $n_1C_{V_1} + n_2C_{V_2} = \dfrac{n_1R}{\gamma_1 - 1} + \dfrac{n_2R}{\gamma_2 - 1} = (n_1 + n_2)C_V$

Where C_V is specific heat of mixture.

Hence, $(n_1 + n_2)C_V = \dfrac{(n_1 + n_2)R}{\gamma_m - 1} = \dfrac{n_1R}{\gamma_1 - 1} + \dfrac{n_2R}{\gamma_2 - 1}$

or, $\dfrac{n_1 + n_2}{\gamma_m - 1} = \dfrac{n_1}{\gamma_1 - 1} + \dfrac{n_2}{\gamma_2 - 1}$

89. **(a)** At constant volume for given mass of gas $\dfrac{P_1}{P_2} = \dfrac{T_1}{T_2}$

$\therefore$ $\dfrac{P}{2P} = \dfrac{300}{T}$; $T = 600K = 327°C$

90. **(b)** $P_1V_1^\gamma = P_2V_2^\gamma$ [$\gamma = 7/5$ for diatomic gas]

$P \times 2^{7/5} = PV_2^{7/5}$

$\Rightarrow$ $P_1 = 2P, P_2 = P$; $V_2 = 2 \times 2^5 \simeq 2.27$ litre

91. **(a)** Entropy increases with increase in temperature in Ist step. In II^nd step as no heat is allowed to enter or leave, the system entropy remains constant. In 1st step temperature falls so entropy decreases.

Match the Column

92. **(c)** Isothermal changes are changes in pressure and volume where temperature remains constant

$\therefore$ $P \propto \dfrac{1}{V}$

The graph is hyperbolic graph but slope of adiabatic is steeper than slope of isotherm.

Adiabatic changes are expressed by the equation PV= constant

The graph is hyperbolic but its slope is larger than slope of isothermal curve.

Isochoric changes are those changes in which pressure remains constant.

Isochoric changes are those changes in which volume remains constant.

93. **(b)** A→1; B→2; C→4; D-3

In fig (A), slope of LM > slope of LM

$\therefore$ LN isotherm, LM adiabatic. Also V constant for MN. So MN is isochoric. In fig (B) slope of LN > Slope of LM

$\therefore$ LM isotherm, LM adiabatic, V is constant for MN So MN is isochoric. In Fig (C), slope of LN > Slope of LM

$\therefore$ LN adiabatic, LM isotherm, P constant for MN so MN is isobaric. In fig (D), slope of LM > Slope of LN, LM adiabatic, LN isotherm, P, is constant of MN.

$\therefore$ MN is isobaric.

94. **(d)** A→2; B→4; C→3; D→1

Work done in path 1-3 is mean of work done in path 1-2-3 and 1-4-3. Thus by considering areas

$100-40 = x-10$

$x = 70$ cal

Mean work done in path 3 to 1

$= \frac{40+10}{2} = 25\,\text{cal}$

The potential energy is ΔU then form 1st law of thermodynamic

$\Delta Q = \Delta U + \Delta W$

$\therefore \quad \Delta U = \Delta Q - \Delta W$

As heat is evolved must be at the expense of potential energy

$\therefore \quad \Delta U = 40-100 = -60\,\text{cal}$

Mean work done $\Delta W = -25\,\text{cal}$

$\because$ Work is done on the gas

$\therefore \quad \Delta Q = \Delta U + \Delta W = -60-25 = -85\,\text{cal}$

Internal energy of gas in state 3 increases as compared to that in state 1 by 65 cal

95. **(a)** A→4; B→3; C→1; D→2

Kirchoff's equation relates the variation of enthalpy with temperature.

For ideal gas, $\left(\frac{\partial U}{\partial V}\right)_T = 0$

Inversion temperature, $T_i = \frac{2a}{Rb}$

Integer

96. **(4)** $\frac{1}{2}X_2 + \frac{1}{2}Y_2 \longrightarrow XY;\ \Delta H = -100\,\text{kJ}$

Let the bond dissociation energy of X_2,Y_2 and XY be $a : \frac{a}{2} : a$ (the given ratio) kJ mol^{-1}, respectively.

$\therefore \quad \frac{a}{2} + \frac{a}{4} - a = -100 \quad \therefore a = 400$

$100x = 400 \quad \Rightarrow x = 4$

97. **(5)** Energy released = Energy due to formation of two single bonds $= 2\times 331 = 662\,\text{kJ mol}^{-1}$ of propane

ΔH polymerization/mol $= 590-662 = -72\,\text{kJ mol}^{-1}$

ΔH polymerization $= -72\times n = -360 \ \Rightarrow n = 5$

98. **(8)** $2\text{MgCl} \longrightarrow \text{Mg} + \text{MgCl}_2 \quad \Delta H = ?$

$\text{Mg(s)} + 1/2\text{Cl}_2\text{(g)} \longrightarrow \text{MgCl}$

$\Delta H_1 = -125\text{kJ mol}^{-1}$

$\text{Mg(s)} + \text{Cl}_2\text{(g)} \longrightarrow \text{MgCl}_2$

$\Delta H_2 = -642\text{kJ mol}^{-1}$

$\Delta H = \Delta H_2 - 2\Delta H_1 \ = -642 - (2\times -125) = -392\text{kJmol}^{-1}$

$\therefore \quad -4x = -392 \ \Rightarrow x = 8$

99. **(6)** $\text{KCl(s)} \longrightarrow \text{K}^+\text{(g)} + \text{Cl}^-\text{(g)},$

$\Delta H_1 = 181\,\text{kcl mol}^{-1}$

$\text{KCl(s)} + \text{aq} \longrightarrow \text{K}^+\text{(aq)} + \text{Cl}^-\text{(aq)},$

$\Delta H_2 = 1.0\text{kcl mol}^{-1}$

Let the enthalpy of hydration of K^+ is 2Clkcal mol^{-1}

$\text{K}^+\text{(g)} + \text{aq} \longrightarrow \text{K}^+\text{(aq)}, \qquad \Delta H_3 = 2a$

$\text{Cl}^-\text{(g)} + \text{aq} \longrightarrow \text{Cl}^-\text{(aq)}, \qquad \Delta H_4 = a$

$\therefore \quad \Delta H_3 = -\Delta H_1 + \Delta H_2 - \Delta H_4$

$2a = -181 + 1 - a$

$3a = -180, a = -60$

$\therefore \quad \Delta_{\text{hyd}}H^-$ of $\text{K}^+ = 2a = -60\times 2 = -120$

$\therefore \quad -20x = -120 \ \Rightarrow x = 6$

100. **(2) Step (i):** (using the third law of thermodynamics): For changing

$\text{H}_2\text{O(s)}(-10°\text{C}, 1\,\text{atm}) \longrightarrow \text{H}_2\text{O(s}, 0°\text{C}\,1\,\text{atm)}$

$\Delta S_1 \int_{-10}^{0} n\frac{C_P}{T}dT \ = 1\times 9\times 2.3\times \log\frac{273}{263}$

$= 0.336$ cal deg^{-1} mol^{-1}

Step (ii): (using the second law of thermodynamics)

$\text{H}_2\text{O(s)}(0°\text{C}, 1\,\text{atm}) \longrightarrow \text{H}_2\text{O}(l)(0°\text{C}, 1\,\text{atm})$

$\Delta S_2 = \frac{q_{\text{rew}}}{T} = \frac{1440}{273} = 5.258\,\text{cal deg}^{-1}\ \text{mol}^{-1}$

Step (iii): (using the third law of thermodynamics):

$\text{H}_2\text{O}(l)(0°\text{C}, 1\,\text{atm}) \longrightarrow \text{H}_2\text{O}(l)\,(0°\text{C}, 1\,\text{atm})$

$\Delta S_3 = \int_{0}^{10} n\frac{C_P}{T}dT \ = 1\times 18\times 2.3\times \log\frac{283}{273}$

$= 0.647\text{cal deg}^{-1}\ \text{mol}^{-1}$

$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 \ = 0.336 + 5.258 + 0.647$

$= 6.258\,\text{cal deg}^{-1}\ \text{mol}^{-1}$

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