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Thermodynamics

It involves a study of interrelation of various kinds of energy accompanying physical or chemical changes. Initially it meant for studies accompanying heat changes (*thermos* = heat, *dynamics* = flow) and interrelate heat energy with work. Now the term in broader sense involves all kinds of energy changes accompanying the process.

Terminology of Thermodynamics :

System: A specified part of universe selected for the study of effect of certain properties such as P, T, etc.

Surroundings: The adjacent part of universe outside the real or imaginary boundaries of system.

Types of Systems:

1. Homogeneous system : A system is supposed to homogeneous if it is uniform throughout, *i.e.*, all the substances present in it have only one phase.

2. Heterogeneous system : Not uniform throughout, *i.e.*, it has more than one phase.

Classification of system may also be made as;

1. Open system : A system which can exchange matter as well as energy with surroundings, *e.g.*, liquid kept in a beaker.

2. Closed system : A system which can exchange only energy with surroundings, *e.g.*, liquid in a sealed tube.

3. Isolated system : Neither exchange of matter nor exchange of energy is possible with surroundings.

State functions: The measurable properties of a system which depend only upon the state of system are known as state variables, *e.g.*, P, V, T, composition, energy, etc.

The cyclic rule: For 1 mole of an ideal gas

$$\left(\frac{\partial P}{\partial V}\right)_T \times \left(\frac{\partial V}{\partial T}\right)_P \times \left(\frac{\partial T}{\partial P}\right)_V = -1 \quad \text{or}$$

$$\left(\frac{\partial P}{\partial T}\right)_V \times \left(\frac{\partial T}{\partial V}\right)_P \times \left(\frac{\partial V}{\partial P}\right) = -1$$

State of system : The state of the system at a time signify for the fact that the variable factors, *e.g.*, P, V, T, etc. (which completely define the state of system) are known.

Properties of system : The thermodynamic properties of a system are divided as:

1. Intensive properties : Mass independent properties, *e.g.*, temperature, pressure, viscosity, density, refractive index, surface tension, chemical potential, etc.

2. Extensive properties : Mass dependent properties, *e.g.*, mass, volume, energy, heat enthalpy, entropy.

Note : An extensive property becomes intensive by specifying a unit amount of matter, *e.g.*, mass and volume are extensive but density = M/V is intensive property.

Thermodynamic process : The operations by which the changes from one state to other are made, are known as thermodynamic process. All thermodynamic properties satisfy

$$\Delta U = q + w$$

$$H = U + PV$$

$$S = \frac{q_{\text{rev}}}{T} \qquad \ldots(1)$$

1. Reversible process : A reversible or quasistatic process is one in which all changes occurring at any part of the process are exactly reversed, when it is carried out in opposite direction. A reversible process involves :

(a) A slow change during investigations.

(b) Driving force is infinitesimally greater than the opposing force and *vice-versa*.

(c) The process may take place in either direction.

(d) Maximum work is obtained.

2. Irreversible process : A process whose direction cannot be reversed by small changes in variables is irreversible process. It involves :

(a) A fast change during investigation.

(b) Driving force is much different than opposing force.

(c) The unidirectional process.

(d) Net work somewhat lesser than maximum work, is obtained.

Heat and Temperature :

1. Heat is a measure of quantity of energy transferred from one body to other as a result of temperature difference between them.

2. Temperature is a measure of intensity of energy, *i.e.*, how much energetic each individual particle is.

Work : Work is expressed as the product of two factors, *i.e.*,

$$W = \text{intensity factor} \times \text{capacity factor}$$

Intensity factor is measure of force against which work is done. Capacity factor is the extent for which work is done.

i.e., Mechanical work = force × displacement = $F \times d$

Gravitational work = gravitational force × height = $mg \times h$

Electrical work =

pot. difference × quantity of current = $E \times Q$

Work of expansion =

pressure × change in volume = $P \times \Delta V$

A –ve sign is given for work done by the system.

A +ve sign is given for work done on the system.

The general expression for all types of PV work can be written as

$$W = -P\Delta V$$

For expansion :

$\Delta V = V_2 - V_1 = +\text{ve}$ $(\because V_2 > V_1)$ $\therefore$ $W = -\text{ve}$

For compression :

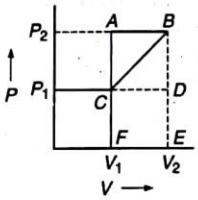
$\Delta V = V_2 - V_1 = -\text{ve}$ $(\because V_2 < V_1)$ $\therefore$ $W = +\text{ve}$

Units of work : W = dyne cm or erg in C.G.S.
= newton m or joule in M.K.S.
= calorie

$$1 \text{ cal} = 4.184 \times 10^7 \text{ erg} = 4.184 \text{ J}$$

It is thus, evident that work, heat and energy have same units.

In P-V diagram as



$w_{AC} = 0$, since no area is covered by straight line.

w_{AB} = Area covered by square $ABEF$.

w_{BC} = Area covered by $BCEF$

$$= \text{Area of square } CDEF + \text{Area of triangle } BCD$$

$$= P_1 \times (V_2 - V_1) + \frac{1}{2} \times \text{Area of square } ABCD$$

$$= P_1 \times (V_2 - V_1) + \frac{1}{2} \times (P_2 - P_1) \times (V_2 - V_1)$$

Also in a cyclic process $w = -\text{ve}$ if clockwise and $w = +\text{ve}$ if anticlockwise.

Internal energy : Each substance is associated with a definite amount of energy involving the energy depending upon the chemical nature of substance and the conditions of P, V, T. It includes many types of energies such as translational, vibrational, rotational, coulombic, potential energy, etc. Therefore, exact magnitude of internal energy cannot be determined. Furthermore, it is a state function and denoted by U and is independent of path. In thermodynamics we deal with the change in internal energy of two states,

$$\Delta U = U_2 - U_1$$

Heat enthalpy or heat content : Enthalpy 'H' is also a state function and independent of path. It is expressed as

$$H = U + PV$$

Like U, in thermodynamics we deal with change in heat enthalpy ΔH;

$$\Delta H = H_2 - H_1$$

Relation in between ΔH and ΔU : The two are related by

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

at constant volume $\Delta H = \Delta U$ $(\because \Delta V = 0)$

First law of thermodynamics : According to this law, mass and energy of an isolated system remains constant. The law is expressed mathematically as

$dq = dU + (-dW)$ ...(1) (For an infinitesimal change)

where, dU = Change in internal energy
dq = Heat supplied to system
$-dW$ = Work done by the system

Also, $q = \Delta U + (-W)$ ...(2)

or $\Delta U = q + W$ (For finite change)

Some useful formulae based upon I law :

1. **Isothermal process :** A process in which temperature of the system remains constant throughout the studies.

$\because$ $\Delta T = 0$ $\therefore$ $\Delta U = 0$

$\therefore$ By Eq. (2) $q = -W$

i.e., heat given to a system is used in work done by the system.

2. **Adiabatic process :** A process during which no exchange of heat takes place in between system and surroundings.

$\because$ $q = 0$

$\therefore$ By Eq. (2) $+\Delta U = W$

or $-\Delta U = -W$

i.e., work is done by the system on the cost of its internal energy.

3. **Cyclic process :** A process in which initial state of system is regained after a series of operations.

$\because$ $\Delta U = 0$

$\therefore$ By Eq. (2) $q = -W$

4. **Isochoric process :** A process in which volume of the system remains constant throughout the investigations.

$\because$ $\Delta V = 0$

$\therefore$ By Eq. (2) $q_v = \Delta U$

i.e., heat given to a system under constant volume is used up in increasing internal energy.

5. **Isobaric process :** A process in which pressure of the system remains constant throughout the investigations.

$\because$ $\Delta P = 0$

Consider a system showing increase in volume from V_1 to V_2 at a constant pressure P, during absorption of heat q. The expansion work or work done by the system is $W = -P\Delta V$

Thus by Eq. (2)

$$\begin{aligned} q_p &= \Delta U - (-P\Delta V) \\ &= U_2 - U_1 - [-P(V_2 - V_1)] \\ &= (U_2 + PV_2) - (U_1 + PV_1) \\ &= H_2 - H_1 \qquad (\because H = U + PV) \\ q_p &= \Delta H \end{aligned}$$

i.e., heat given to a system under constant P is used up in increasing heat enthalpy of system. Work done in isobaric process $= dU - dq$

$$\begin{aligned} &= nC_v \cdot dT - nC_p \cdot dT = -nRdT \\ &= -nR\,(T_{\text{final}} - T_{\text{initial}}) \end{aligned}$$

6. Work done in irreversible isothermal process : Suppose an ideal gas expands against external pressure P and its volume changes by an amount dV then work done W can be given by

$$W = -PdV$$

(a) **Free expansion :** $W = 0$, Since, $P = 0$

(b) **Expansion or compression against external pressure *P***

For a finite change V_1 or V_2,

Total work done on the system W is derived by

$$W = -P(V_2 - V_1)$$

or $\quad W_{\text{irr}} = -P(V_2 - V_1)$ ...(3)

Also, $\quad \Delta U = \Delta H = 0$ ...(4)

If $V_2 > V_1$ then W_{irr} is –ve, *i.e.*, expansion work or work done by the system.

If $V_2 < V_1$ then W_{irr} is +ve, *i.e.*, compression work or work done on the system.

7. Work done in isothermal reversible process : Consider a system under isothermal condition, showing reversible expansion of an ideal gas by a volume dV, then

$$\because \ \Delta U = 0 \ \therefore \ dq = -dW = +PdV \quad (\because dW = -PdV)$$

The total work done during expansion of gas from V_1 to V_2

$$\int dW = \int_{V_1}^{V_2} -P\,dV = \int_{V_1}^{V_2} -\frac{nRT}{V} \cdot dV$$

$$W_{\text{rev}} = -nRT \log_e \frac{V_2}{V_1} = -2.303\, nRT \log_{10} \frac{V_2}{V_1} \quad \text{...(5)}$$

$$(\because P \propto 1/V)$$

$$\text{Also, } W_{\text{rev}} = -2.303\, nRT \log_{10} \frac{P_1}{P_2} \quad \text{...(6)}$$

8. Work done in adiabatic reversible process : Consider a system under adiabatic conditions, showing reversible expansion of an ideal gas by a volume dV, then from I law of thermodynamics,

$(\because dq = 0)$

$$+dU = dW$$

$$\because \quad dU = nC_v\, dT \text{ or } +C_v \cdot n \times dT = dW$$

This equation reveals on further treatment within temperature limits of T_1 and T_2, reveals

$$\begin{aligned} dW &= +C_v \times n \times dT \\ C_p - C_v &= R \\ \frac{C_p}{C_v} - \frac{C_v}{C_v} &= \frac{R}{C_v} \\ \gamma - 1 &= \frac{R}{C_v} \\ C_v &= \frac{R}{(\gamma - 1)} \end{aligned}$$

Therefore, $\quad dW = +\dfrac{R}{(\gamma - 1)} \times n \times dT$

$$dW = \frac{nR}{(\gamma - 1)} \cdot dT$$

on integration $\quad \displaystyle\int dW = \frac{nR}{\gamma - 1} \int_{T_1}^{T_2} dT$

$$W_{\text{rev}} = \frac{nR}{\gamma - 1}[T_2 - T_1] \quad \text{...(7)}$$

If $T_2 > T_1$ then W_{rev} = +ve, *i.e.*, work done on the system

If $T_2 < T_1$ then W_{rev} = –ve, *i.e.*, work done by the system

where γ is Poisson's ratio $= \dfrac{C_p}{C_v}$ ...(8)

Also, $\quad \Delta H = nC_p\,(T_2 - T_1)$ ...(9)

If final temperature is not known :

$$w = -nC_v T_1 \left[1 - \left(\frac{P_2}{P_1}\right)^{R/C_p}\right] \quad \text{...(10)}$$

Some important results of adiabatic expansions

1. PV^{γ} = constant ...(11)
2. $T^{r} P^{1-\gamma}$ = constant ...(12)
3. $V^{\gamma-1} T$ = constant ...(13)

9. Work done in adiabatic irreversible expansion or compression :

(a) Expansion against vacuum or free expansion : $w = 0$

(b) Expansion or compression against external pressure :

$$w = -n \times P_{\text{ext}} \times R\left[\frac{P_1 T_2 - P_2 T_1}{P_1 P_2}\right] \quad \text{...(14)}$$

Efficiency η of Carnot cycle

(a) $\quad \eta = \dfrac{W}{Q_2} = \dfrac{T_2 - T_1}{T_2} = \dfrac{Q_2 - Q_1}{Q_2}$ ...(15)

where, Q_2 is the heat absorbed from the source at T_2 and $-Q_1$ is the heat lost to the sink at T_1. From Eq. (15).

$$\eta = 1 - \frac{T_1}{T_2} = 1 - \frac{Q_1}{Q_2}$$

Thus **"it is impossible to convert heat into equivalent amount of work without compensation."**

(b) $\eta = 1$ (100% efficiency) only when $T_1 = 0\,\text{K}$, (*i.e.*, $-273°\text{C}$) which is not practically possible.

(c) Greater the difference between T_2 and T_1 greater is the value of η. Hence, *superheated steam* (under high pressure) is used in an engine with a boiler.

Joule-Thomson Effect : *The phenomenon of change of temperature produced when a gas is made to expand adiabatically from a region of high pressure to a region of extremely low pressure through a small jet is called Joule-Thomson effect.*

(a) The temperature below which a gas becomes cooler on expansion is known as the inversion temperature T_i. Above this temperature gas shows heating effect.

$$T_i = \frac{2a}{Rb} \qquad \text{...(16)}$$

where, a and b called van der Waal's constant.

(b) Joule-Thomson effect is zero for an ideal gas in which van der Waal's forces of attraction are negligible and there is no expenditure of energy in overcoming these forces of attraction.

Joule-Thomson coefficient μ_{JT} is given by

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = -\left(\frac{\partial H}{\partial P}\right)_T / C_p \qquad \text{...(17)}$$

$\mu_{JT} = 0$ for an ideal gas, $\mu_{JT} = -\text{ve}$ for heating effect;
$\mu_{JT} = +\text{ve}$ for cooling effect.

Entropy : Entropy (S) is a state function and is a measure of degree of disorder or randomness of system. More is the disorder in system, higher is its entropy. It is normally expressed in terms of change in entropy.

1. For a reaction entropy change (ΔS) is given by

$$\Delta S = \Sigma S_{\text{Products}} - \Sigma S_{\text{Reactants}} \qquad \text{...(18)}$$

2. $$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{W_{\text{rev}}}{T} = \frac{nRT \log_e \frac{V_2}{V_1}}{T} = nR \log_e \frac{V_2}{V_1}$$

$$= 2.303\, nR \log_{10} \frac{V_2}{V_1} \qquad \text{...(19)}$$

$$= 2.303\, nR \log_{10} \frac{P_1}{P_2} \qquad \text{...(20)}$$

where, q_{rev} is the heat supplied to a system at temperature T (K) under reversible conditions.

3. At constant P, $q_{\text{rev}} = \Delta H_{\text{rev}}$

$$\Delta S = \frac{\Delta H_{\text{rev}}}{T} \qquad \text{...(21)}$$

i.e., entropy change of fusion :

$$\Delta S_f = \frac{\Delta H_f}{T} \qquad \text{...(22)}$$

where T is freezing point

and entropy change of vaporization :

$$\Delta S_v = \frac{\Delta H_v}{T} \qquad \text{...(23)}$$

where T is boiling point

4. Entropy of one mole of a substance in pure state at one atmosphere and 25°C is termed as standard entropy, S°.

For a reaction in standard state, $A \longrightarrow B$

$$\Delta S^\circ = S_B^\circ - S_A^\circ \qquad \text{...(24)}$$

5. Entropy, S, is related to thermodynamic probability, W by the relation :

$$S = k \log_e W \quad \text{or} \quad S = 2.303\, k \log_{10} W \qquad \text{...(25)}$$

where, k is Boltzmann's constant.

6. At absolute zero temperature, a solid is supposed to have highly ordered state, *i.e.*, $W = 1$ and hence $S = 0$, *i.e.*, $\lim_{T \to 0} S = 0$. This is zeroth law of thermodynamics.

Gibbs energy F or G : Free energy (F or G) is also a state function and is a measure of maximum work done. It is expressed as

$$G = H - TS \qquad \text{...(26)}$$

or $$\Delta G = \Delta H - T\Delta S \quad \text{at constant } T \qquad \text{...(27)}$$

Standard Gibbs energy change (ΔG°) :

1. $\Delta G^\circ = -2.303\, RT \log_{10} K$ ...(28)
2. At equilibrium $\Delta G = 0$.
3. The decrease in free energy ($-\Delta G$) is given as :

$$-\Delta G = W_{\text{net}} = 2.303\, nRT \log_{10} \frac{V_2}{V_1} \qquad \text{...(29)}$$

4. ΔG_f° for free elemental state $= 0$.
5. $\Delta G_f^\circ = G^\circ_{\text{Products}} - G^\circ_{\text{Reactants}}$ ...(30)

Conditions for spontaneity of reaction : For a spontaneous change $\Delta G = -\text{ve}$. Thus, following results can also be evaluated for spontaneous process.

ΔH	ΔS		$\Delta H - T\Delta S$	Nature
−ve	+ve	∴	$\Delta G = -\text{ve}$	Spontaneous
+ve	−ve	∴	$\Delta G = +\text{ve}$	Non-spontaneous
+ve	+ve	if	$\Delta H < T\Delta S; \Delta G = -\text{ve}$	Spontaneous
−ve	−ve		$\Delta G = -\text{ve}$	Spontaneous
		if	$\Delta H > T\Delta S$	
			i.e., T is low	
			$\Delta G = +\text{ve}$	Non-Spontaneous
		if	$\Delta H < T\Delta S$	
			i.e., T is high	

Gibbs-Helmholtz equations : It interrelates ΔG and ΔH at constant pressure :

$$\Delta G = \Delta H + T\left[\frac{\delta(\Delta G)}{\delta T}\right]_p \qquad \text{...(31)}$$

or $$\frac{\Delta G - \Delta H}{T} = \left[\frac{\delta(\Delta G)}{\Delta T}\right]_p \qquad \text{...(32)}$$

or $$-\Delta S = \left[\frac{\delta(\Delta G)}{dT}\right]_p \qquad \text{...(33)}$$

$$\Delta S = nF\left[\frac{\delta E_{\text{cell}}}{\delta T}\right]_p \quad (\because \Delta G = -nEF) \qquad \text{...(34)}$$

Thus, temperature coefficient of the emf of a cell is

$$\left[\frac{\delta E_{\text{cell}}}{dT}\right]_p = \frac{\Delta S}{nF} \quad \text{...(35)}$$

Temperature dependence of vapour state or The Clapeyron – Clausius equation.

Variation of the vapour pressure for the liquid $\rightleftharpoons$ gas equilibrium is given by Clapeyron – Clausius equation.

$$\log P = -\frac{\Delta H_v}{2.303\,R}\left(\frac{1}{T}\right) + K \quad \text{...(36)}$$

Eq. (36) represents the equation of a straight line. Hence, the plot of $\log P$ vs $\frac{1}{T}$ yields a straight line with slope $= -\frac{\Delta H_v}{2.303\,R}$ and intercept $= K$. This enables the evaluation of ΔH_v, **the latent heat of vaporization.**

If vapour pressure P_1 and P_2 at temperatures T_1 and T_2 are known then by Eq. (36).

$$\log\frac{P_2}{P_1} = \frac{\Delta H_v}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \quad \text{...(37)}$$

ΔH_v is latent heat of vaporisation in cal mol^{-1} or J mol^{-1}

• NUMERICAL PROBLEMS •

1. A system is provided 50 J of heat and work done on the system is 10 joule. What is the change in internal energy?
2. The work done by a system is 8 joule, when 40 joule heat is supplied to it. Calculate the increase in internal energy of system.
3. A gas occupies 2 litre at STP. It is provided 300 joule heat so that its volume becomes 2.5 litre at 1 atm. Calculate change in its internal energy.
4. A certain electric motor produced 15 kJ of energy each second as mechanical work and lost 2 kJ as heat to the surroundings. What is the change in the internal energy of the motor and its power supply each second?
5. An insulated container is divided into two equal portions. One portion contains an ideal gas at pressure P and temperature T. The other portion is a perfect vacuum. If a hole is opened between two portions, calculate :
   (a) the change in internal energy
   (b) the change in temperature of gas.
6. Two litre of N_2 at 0°C and 5 atm pressure are expanded isothermally against a constant external pressure of 1 atm until the pressure of gas reaches 1 atm. Assuming gas to be ideal, calculate work of expansion.
7. 2.8 g of N_2 gas at 300 K and 20 atm was allowed to expand isothermally against a constant external pressure of 1 atm. Calculate $\Delta U, q$ and W for the gas.
8. Calculate the work done in open vessel at 300 K, when 92 g Na reacts with water. Assume ideal gas nature.
9. The internal energy change in the conversion of 1.0 mole of the calcite form of $CaCO_3$ to the aragonite form is + 0.21 kJ. Calculate the enthalpy change when the pressure is 1.0 bar; given that the densities of the solids are 2.71 g cm^{-3} and 2.93 g cm^{-3} respectively.
10. Calculate the work done when a system raises a column of water of radius 5.0 mm through 10 cm.
11. Calculate the work done when 50 g of iron reacts with hydrochloric acid in (i) a closed vessel of fixed volume (ii) an open beaker at 25°C.
12. A gas present in a cylinder fitted with a frictionless piston expands against a constant pressure of 1 atm from a volume of 2 litre to a volume of 6 litre. In doing so, it absorbs 800 J heat from surroundings. Determine increase in internal energy of process.
13. Work done in expansion of an ideal gas from 4 litre to 6 litre against a constant external pressure of 2.5 atm was used to heat up 1 mole of water at 293 K. If specific heat of water is $4.184 \text{ J g}^{-1} \text{ K}^{-1}$, what is the final temperature of water?
14. A gas expands from 3 dm^3 to 5 dm^3 against a constant pressure of 3 atm. The work done during expansion is used to heat 10 mole of water of temperature 290 K. Calculate final temperature of water. Specific heat of water $= 4.184 \text{ J g}^{-1} \text{ K}^{-1}$. **(Roorkee 1993)**
15. Calculate the maximum work done in expanding 16 g of oxygen at 300 K and occupying a volume of 5 dm^3 isothermally until the volume becomes 25 dm^3.
16. Calculate q, W, ΔU and ΔH for the isothermal reversible expansion of one mole of an ideal gas from an initial pressure of 1.0 bar to a final pressure of 0.1 bar at a constant temperature of 273 K. **(Roorkee 2000)**
17. What work is to be done on 2 mole of a perfect gas at 27°C if it is compressed reversibly and isothermally from a pressure of $1.01 \times 10^5 \text{ Nm}^{-2}$ to $5.05 \times 10^6 \text{ Nm}^{-2}$? Also calculate the Gibbs energy change.
18. 1 mole of an ideal gas undergoes reversible isothermal expansion from an initial volume V_1 to a final volume $10V_1$ and does 10 kJ of work. The initial pressure was 1×10^7 Pa.
   (a) Calculate V_1.
   (b) If there were 2 mole of gas, what must its temperature have been? **(Roorkee 2001)**
19. 10 g of argon gas is compressed isothermally and reversibly at a temperature of 27°C from 10 L to 5L. Calculate $q, W, \Delta U$ and ΔH for this process. $R = 2.0 \text{ cal K}^{-1} \text{ mol}^{-1}$, $\log_{10} 2 = 0.30$. Atomic mass of $Ar = 40$. **(Roorkee 1997)**
20. At 27°C, one mole of an ideal gas is compressed isothermally and reversibly from a pressure of 2 atm to 10 atm. Calculate ΔU and q.
21. One mole of an ideal gas is heated at constant pressure from 0°C to 100°C.
   (a) Calculate work done.
   (b) If the gas was expanded isothermally and reversibly at 0°C from 1 atm to some other pressure P_t, what must be the final pressure if the maximum work is equal to the work involved in (a)?
22. Water is boiled under a pressure of 1.0 atm. When an electric current of 0.50 A from a 12V supply is passed for 300 s through a resistance in thermal contact with it, it is found that 0.789 g of water is vaporized. Calculate the molar internal energy and enthalpy changes at boiling point (373.15 K).
23. In an insulated container 1 mole of a liquid, molar volume 100 mL at 1 bar. Liquid is steeply taken to 100 bar, when volume of liquid decreases by 1 mL. find ΔH and ΔU for the process. **(IIT 2004)**
24. Calculate the standard internal energy change for the reaction;

$$OF_2(g) + H_2O(g) \longrightarrow O_2(g) + 2HF(g)$$

at 298 K. The standard enthalpies of formation of $OF_2(g)$, $H_2O(g)$, $HF(g)$ are $+20, +250$ and $-270\ \text{kJ mol}^{-1}$.

25. Two mole of a perfect gas undergo the following processes :

(a) a reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L).

(b) a reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L).

(c) a reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L).

(i) Sketch with labels each of the processes on the same *P-V* diagram.

(ii) Calculate the total work (w) and the total heat change (q) involved in the above processes.

(iii) What will be the values of ΔU, ΔH and ΔS for the overall process? **(IIT 2002)**

26. 14 g oxygen at 0°C and 10 atm are subjected to reversible adiabatic expansion to a pressure of 1 atm. Calculate the work done in :

(a) Litre atm.

(b) Calorie (Given, $C_p / C_v = 1.4$).

27. A flask of 1 litre having $NH_3(g)$ at 2.0 atm and 200 K is connected with another flask of volume 800 mL having $HCl(g)$ at 8 atm and 200 K through a narrow tube of negligible volume. The two gases reacts to form $NH_4Cl(s)$ with evolution of 43 kJ mol^{-1} heat. If heat capacity of $HCl(g)$ at constant volume is 20 $\text{JK}^{-1}\ \text{mol}^{-1}$ and neglecting heat capacity of flask, NH_4Cl and volume of solid NH_4Cl formed, calculate the heat produced, final temperature and final pressure in flasks. (Assume $R = 0.08$ litre-atm $\text{K}^{-1}\ \text{mol}^{-1}$).

28. A sample of argon gas at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm^3 to 2.50 dm^3. Calculate the enthalpy change in this process. $C_{v.m}$ for argon is 12.48 $\text{JK}^{-1}\ \text{mol}^{-1}$. **(IIT 2000)**

29. Calculate the equilibrium constant for the reaction given below at 400K, if $\Delta H^\circ = 77.2\ \text{kJ mol}^{-1}$ and $\Delta S^\circ = 122\ \text{JK}^{-1}\ \text{mol}^{-1}$.

$$PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$$

30. A sample of ideal gas ($\gamma = 1.4$) is heated at constant pressure. If an amount of 140 J of heat is supplied to gas, find ΔU and W.

31. One mole of an ideal gas which $C_v = \frac{3}{2}R$ is heated at a constant pressure of 1 atm from 25°C to 100°C. Calculate ΔU, ΔH and the entropy change during the process.

32. Consider a class room of dimensions $5 \times 10 \times 3\ \text{m}^3$ at temperature 20°C and pressure 1 atm. There are 50 peoples in the room, each losing energy at the average of 150 watt. Assuming that the walls, ceiling, floor and furniture perfectly insulated and none of them absorbing heat, how much time will be needed for rising the temperature of air in the room to body temperature, *i.e.*, 37°C? For air $C_p = \frac{7}{2}R$. Loss of air to the outside as the temperature rises may be neglected.

33. 50 students sitting in the room of $5 \times 10 \times 3\ \text{m}^3$ dimensions. The air inside the room is at 27°C and 1 atm pressure. If each student loses 100 watt heat per second assuming the walls, ceiling, floor and all the material present inside the room is perfectly insulated as well as neglecting loss of air to the outside as the temperature is raised, how much rise in temperature will be noticed in 10 minutes? Given $C_p = \frac{7}{2}R$ for air.

34. An athlete in a gymnasium room lifts a 50 kg mass through a vertical distance of 2.0 m; $g = 9.8\ \text{m s}^{-2}$. The mass is allowed to fall through 2.0 m distance while coupled to an electrical generator. The electrical generator produces an equal amount of electrical work. This electrical work is used to produce aluminium by Hall's process involving the change.

$$Al_2O_3\,(\text{molten}) + 3C(s) \longrightarrow 2\,Al(l) + 3CO(g)$$

The reaction require standard free energy change equal to 593 kJ. How many times must the athlete lift the 50 kg mass and to drop and couple with generator to produce sufficient Gibbs free energy to produce 27 g Al?

35. An aeroplane weighing 63,000 kg flies up from sea level to a height of 8000 metre. Its engine run with pure normal octane (C_8H_{18}) has a 30% efficiency. Calculate the fuel cost of the flight, if octane sells at Rs. 3 per litre. Given density of octane $= 0.705\ \text{g mL}^{-1}$, heat of combustion of octane $= 1300\ \text{kcal mol}^{-1}$. ($g = 981\ \text{cm / sec}^2$)

36. A lead bullet weighing 18.0 g and travelling at 500 m/s is embedded in a wooden block of 1.00 kg. If both the bullet and the block were initially at 25.0°C, what is the final temperature of block containing bullet? Assume no temperature loss to the surroundings. (Heat capacity of wood $= 0.5$ kcal/kg-K; heat capacity of lead $= 0.030$ kcal / kg - K)

37. A mixture contains 8 g He and 14 g N_2 in a vessel at 300K. How much heat is required to increase the rms speed of these molecules to double their value? Also, calculate the final temperatures.

38. Calculate the Gibbs energy change when 1 mole of NaCl is dissolved in water at 298 K. Given,

(a) Lattice energy of NaCl = 778 kJ mol^{-1}.

(b) Hydration energy of NaCl = 774.3 kJ mol^{-1}.

(c) Entropy change at 298 K = 43 J mol^{-1}.

39. How much heat is requied to change 10 g ice at 0°C to steam at 100°C? Heat of fusion and heat of vaporization for H_2O are 80 cal/g and 540 cal/g respectively. Specific heat of water is 1 cal/g.

40. A steam boiler made up of steel weighs 900 kg. The boiler contains 400 kg of water. Assuming 70% of the heat is delivered to boiler and water, how much heat is required to raise the temperature of the whole from 10°C to 100°C? Heat capacity of steel is 0.11 kcal/kg-K and heat capacity of water is 1 kcal/kg-K.

41. Determine whether or not, it is possible for sodium to reduce aluminium oxide to aluminium at 298 K. Also calculate equilibrium constant. Given that G_f° of Al_2O_3 at 298 K $= -1582$ kJ mol^{-1}; G_f° of $Na_2O(s)$ at 298 K $= -377$ kJ mol^{-1}.

42. The vapour pressure of benzene is 1.53×10^4 Nm^{-2} at 303 K and 5.2×10^4 Nm^{-2} at 333 K. Calculate the mean latent heat of evaporation of benzene over this temperature range.

43. Calculate the change in entropy for the fusion of 1 mole of ice. The melting point of ice is 273 K and molar enthalpy of fusion for ice $= 6.0$ kJ mol^{-1}.

44. Molar heat capacity of CD_2O (deuterated form of formaldehyde) at constant pressure is 14 cal mol^{-1} K^{-1} at 1000 K. Calculate the entropy change associated with cooling of 3.2 g of CD_2O vapour from 1000 to 900 K.

45. Calculate entropy change for vaporization of 1 mole of liquid water to steam at 100°C, if $\Delta H_v = 40.8$ kJ mol^{-1}.

46. For a reaction at 25°C enthalpy change (ΔH) and entropy change (ΔS) are -11.7×10^3 J mol^{-1} and -105 J mol^{-1} K^{-1} respectively. Find out whether this reaction is spontaneous or not?

47. Determine the entropy change for the reaction given below;

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

at 300 K. If standard entropies of $H_2(g), O_2(g)$ and $H_2O(l)$ are 126.6, 201.20 and 68.0 J K^{-1} mol^{-1} respectively.

48. 1 mole of an ideal gas at 25°C is subjected to expand reversibly ten times of its initial volume. Calculate the change in entropy of expansions.

49. A sample of 100 g H_2O is slowly heated from 27°C to 87°C. Calculate the change in entropy during heating (Specific heat of water = 4200 J/kg-K).

50. Calculate the entropy change when 1 kg of water is heated from 27°C to 200°C forming super heated steam under constant pressure. Given specific heat of water $= 4180$ J / kg - K and specific heat of steam $= 1670 + 0.49T$ J/kg-K and latent heat of vaporization $= 23 \times 10^5$ J/kg.

51. Titanium metal is extensively used in aerospace industry because the metal imparts strength to structures but does not unduly add to their masses. The metal is produced by the reduction of $TiCl_4(l)$ which in turn is produced from mineral rutile $TiO_2(s)$. Can the following reaction for production of $TiCl_4(l)$ be carried out at 25°C?

$$TiO_2(s) + 2Cl_2(g) \longrightarrow TiCl_4(l) + O_2(g)$$

Given that, H_f° for $TiO_2(s), TiCl_4(l), Cl_2(g)$ and $O_2(g)$ are -944.7, -804.2, 0.0, 0.0 kJ mol^{-1}. Also S° for $TiO_2(g)$, $TiCl_4(l), Cl_2(g)$ and $O_2(g)$ are 50.3, 252.3, 233.0, 205.1 J mol^{-1} K^{-1} respectively.

52. For a reaction $M_2O(s) \rightarrow 2M(s) + \frac{1}{2}O_2(g)$; $\Delta H = 30$ kJ mol^{-1} and $\Delta S = 0.07$ kJ K^{-1} mol^{-1} at 1 atm. Calculate up to which temperature the reaction would not be spontaneous?

53. Calculate the temperature at which the reaction give below is at equilibrium, $Ag_2O(s) \rightarrow 2Ag(s) + \frac{1}{2}O_2(g)$. Given, $\Delta H = 30.5$ kJ mol^{-1} and $\Delta S = 0.066$ kJ $K^{-1} mol^{-1}$.

54. The standard enthalpy and entropy changes for the reaction in equilibrium for the forward direction are given below :

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

$\Delta H^\circ_{300\,K} = -41.16$ kJ mol^{-1};

$\Delta S^\circ_{300\,K} = -4.24 \times 10^{-2}$ kJ mol^{-1}

$\Delta H^\circ_{1200\,K} = -32.93$ kJ mol^{-1};

$\Delta S^\circ_{1200\,K} = -2.96 \times 10^{-2}$ kJ mol^{-1}

Calculate K_p at each temperature and predict the direction of reaction at 300 K and 1200 K, when $P_{CO} = P_{CO_2} = P_{H_2} = P_{H_2O} = 1$ atm at initial state.

55. One mole of CH_3COOH undergoes dimerization in vapour phase at 127°C as :

$$2CH_3COOH(g) \rightleftharpoons (CH_3COOH)_2(g)$$

Calculate the change in standard entropy during dimerization if dimer formation is due to two H-bonds involved in dimer, each of 33 kJ strength and the degree of dimerisation of acetic acid 98.2%.

56. Derive a relation showing reversible work of expansion from volume V_1 to V_2 by '*n*' moles of a real gas obeying van der Waals' equation at temperature T where volume occupied by molecules may be taken as negligible in comparison to total volume of gas.

SOLUTIONS (Numerical Problems)

1. $q = 50\,\text{J}$

$W = +10\,\text{J}$ (work done on the system)

∴ $\Delta U = q + W = 50 + 10$

∴ $\Delta U =$ **60 J**

2. $W = -8\,\text{J}$; $q = 40\,\text{J}$

From I law $\Delta U = q + W = 40 - 8$

∴ $=$ **32 joule**

3. Work done $= -P \times dV = 1 \times (2.5 - 2.0)$

$= -0.5$ litre−atm

∵ Work is carried out at constant P and thus irreversible.

$$= -\frac{0.5 \times 1.987 \times 4.184}{0.0821}\ \text{joule} = -50.63\,\text{J}$$

From I law of thermodynamics

∵ $q = \Delta U - W$

$300 = \Delta U + 50.63$ ∴ $\Delta U =$ **249.37 joule**

4. Energy is lost from the system as work thus W is negative.

$W = -15\,\text{kJ}$

Energy is lost as heat, so $q = -2\,\text{kJ}$

Therefore, by first law of thermodynamics :

$\Delta U = q + W = -2 - 15 =$ **−17 kJ**

5. The system being thermally insulated and thus $q = 0$. The gas expands through hole in other portion to show free expansion, *i.e.*,

$w = -\int P\Delta V = 0$ (Since, $P = 0$)

Also from I law of thermodynamics

$q = \Delta U + w$

Since, $q = 0$; $w = 0$ ∴ $\Delta U =$ **0**

Also internal energy $U = \frac{3}{2}RT$. Since, internal energy remains same (∵ $\Delta U = 0$) and thus temperature will also remains **constant.**

6. Since, the external pressure is greatly different from the pressure of N_2 and thus, process is irreversible.

∴ $W = -P_{\text{ext}}(V_2 - V_1)$

$W = -1 \times (V_2 - V_1)$

Given, $V_1 = 2$ litre $V_2 = ?$ $T = 273\,\text{K}$

$P_1 = 5\,\text{atm}$ $P_2 = 1\,\text{atm}$

∴ $P_1V_1 = P_2V_2$

∴ $V_2 = \frac{2 \times 5}{1} = 10$ litre

∴ $W = -1 \times (10 - 2) = -8$ litre-atm

$$= -\frac{8 \times 1.987}{0.0821}\ \text{calorie} = -\frac{8 \times 1.987 \times 4.184}{0.0821}\ \text{J}$$

$=$ **810.10 joule**

7. Initially for N_2

$20 \times V_1 = \frac{2.8}{28} \times 0.0821 \times 300$ ∴ $V_1 = 0.123$ litre

Finally for N_2

$1 \times V_2 = \frac{2.8}{28} \times 0.0821 \times 300$ ∴ $V_2 = 2.463$ litre

∴ $W = -P \times \Delta V$ [∵ work is done against constant P ∴ irreversible]

$= -1 \times (2.463 - 0.123)$

$= -2.340$ litre-atm

$$= -\frac{2.340 \times 1.987}{0.0821}\ \text{calorie}$$

$$= -\frac{2.340 \times 1.987 \times 4.184}{0.0821}\ \text{J}$$

$W =$ **−236.95 J**

Now $q = \Delta U - W$

$q = 0 + 236.95$ (∵ $\Delta U = 0$ for isothermal process)

$q =$ **236.95 joule**

8. $2Na + 2H_2O \longrightarrow 2NaOH + H_2$

Mole of Na $= \frac{92}{23} = 4$

Mole of H_2 formed $= \frac{1}{2} \times$ Mole of Na used $= \frac{1}{2} \times 4 = 2$

Work is done in giving out 2 mole H_2. Thus,

$W = -P \times V_{H_2} = n_{H_2}\ RT = -2 \times 8.314 \times 300 =$ **− 4988.4 J**

The H_2 liberated pushes the atmospheric gas back and thus, does work in driving back the atmosphere. Note that in case of closed vessel $\Delta V = 0$, ∴ $W = 0$.

9. $\Delta H = \Delta U + P\Delta V$

Given, $\Delta U = +0.21\,\text{kJ mol}^{-1} = 0.21 \times 10^3\ \text{J mol}^{-1}$,

$P = 1\,\text{bar} = 1.0 \times 10^5\ \text{Pa}$

$\Delta V = V_{(\text{aragonite})} - V_{(\text{calcite})}$

$$= \left(\frac{100}{2.93} - \frac{100}{2.71}\right)\text{cm}^3\ \text{mol}^{-1}\ \text{of}\ CaCO_3 = -2.77\,\text{cm}^3$$

$= -2.77 \times 10^{-6}\ \text{m}^3$

∴ $\Delta H = 0.21 \times 10^3 - 1 \times 10^5 \times 2.77 \times 10^{-6}$

$=$ **209.72 J = 0.20972 kJ mol^{-1}**

10. Work is given : $W = -mgh$

where, $m = \text{volume} \times \text{density} = \pi r^2 l \times d$

$= \frac{22}{7} \times (0.5)^2 \times 10 \times 1$

$g = 980\,\text{cm s}^{-2}$

$h = \frac{10}{2} = 5\,\text{cm}$

(The centre of mass of column lies half way along its length l therefore the centre of mass is raised to a height $h = \frac{1}{2}l$)

∴ $W = -\frac{22}{7} \times (0.5)^2 \times 10 \times 1 \times 980 \times 5 = -38.5 \times 10^3\ \text{erg}$

$=$ **-3.85×10^{-3} J**

The negative sign shows that system shows a decrease in internal energy.

11. (i) Vessel is of fixed volume, hence $\Delta V = 0$. No work is done.

$W = 0$

(ii) The gas drives back the atmosphere hence,

$W = -P_{\text{ext}} \cdot \Delta V$

Also, $\Delta V = V_{\text{final}} - V_{\text{initial}} \simeq V_{\text{final}}$ $(\because V_{\text{initial}} = 0)$

$\therefore$ $\Delta V = \dfrac{nRT}{P_{\text{ext}}}$ or $W = -P_{\text{ext}} \cdot \dfrac{nRT}{P_{\text{ext}}} = -nRT$

where, n is the number of mole of H_2 gas obtained from n mole of Fe(s).

$$\underset{1\text{ mole}}{Fe(s)} + 2HCl(aq.) \longrightarrow FeCl_2(aq.) + \underset{1\text{ mole}}{H_2(g)}$$

$\therefore$ $n = \dfrac{50}{56} = 0.8929$ mole

$\therefore$ $W = -0.8929 \times 8.314 \times 298 = \mathbf{-2212.22\ J}$

The reaction mixture in the given system does 2.212 kJ of work driving back to atmosphere.

12. Since, work is done against constant pressure and thus, irreversible.

Given, $\Delta V = (6-2) = 4$ litre; $P = 1$ atm

$\therefore$ $W = -1 \times 4$ litre-atm $= -\dfrac{1 \times 4 \times 1.987}{0.0821}$ cal

(since 0.0821 litre-atm = 1.987 cal)

$= -96.81$ cal $= -96.81 \times 4.184$ J $(\because 1\text{ cal} = 4.184\text{ J})$

$= -405.05$ J

Now from I law of thermodynamics

$q = \Delta U - W$

$800 = \Delta U + 405.05$ $\therefore$ $\Delta U = \mathbf{394.95\ joule}$

13. Since, work is done against constant pressure and thus irreversible.

Given, $\Delta V = (6-4) = 2$ litre; $P = 2.5$ atm

$\therefore$ $W = -P_{\text{ext}} \times \Delta V = -2.5 \times 2 = -5$ litre-atm

$= -\dfrac{5 \times 1.987}{0.0821}$ cal $= -\dfrac{5 \times 1.987 \times 4.184}{0.0821}$ J

$= -506.31$ J

Now this work is used in heating 1 mole water

$W = n \times C \times \Delta T$

$506.31 = 1 \times 4.184 \times 18 \times \Delta T$ $\left[\begin{array}{l} \because C = 4.184\ \text{J g}^{-1}\ \text{K}^{-1} \\ \therefore \quad = 4.184 \times 18\ \text{J mol}^{-1} \end{array}\right]$

$\therefore$ $\Delta T = 6.723$

$\therefore$ Final temperature $T_1 + \Delta T = 293 + 6.723 = \mathbf{299.723\ K}$

14. Since, work is done against constant P and thus, irreversible

$\Delta V = 5 - 3 = 2\ \text{dm}^3 = 2$ litre; $P = 3$ atm

$\therefore$ $W = -P.\Delta V = -3 \times 2$ litre-atm

$= -\dfrac{6 \times 4.184 \times 1.987}{0.0821}$ joule $= -607.57$ joule

Now this work is used up in heating water

$\therefore$ $W = n \times C \times \Delta T$

$607.57 = 10 \times 4.184 \times 18 \times \Delta T$ $\therefore$ $\Delta T = 0.81$

$\therefore$ Final temperature $T_1 + \Delta T = 290 + 0.81 = \mathbf{290.81\ K}$

15. Since, maximum work and thus, process is reversible

$n_{O_2} = \dfrac{w}{M} = \dfrac{16}{32}$, $R = 8.314$ J, $T = 300$ K,

$V_1 = 5\ \text{dm}^3$, $V_2 = 25\ \text{dm}^3$

$W = -2.303\, nRT \log_{10} \dfrac{V_2}{V_1}$

$= -2.303 \times \dfrac{16}{32} \times 8.314 \times 300 \log_{10} \dfrac{25}{5}$

$= \mathbf{-2.01 \times 10^3\ joule}$

16. For isothermal reversible expansion :

$W = -2.303\, nRT \log \dfrac{P_1}{P_2} = -2.303 \times 1 \times 8.314 \times 273 \log \dfrac{1.0}{0.1}$

$W = \mathbf{-5227.2\ J}$

At constant temperature, for expansion $\Delta T = 0$; Therefore, $\Delta U = \mathbf{0}$

Also, $\Delta U = 1 \times C_v \times \Delta T = 0$ (For 1 mole)

and $\Delta U = q + W$ $\therefore$ $q = -W = \mathbf{5227.2\ J}$

Also when temperature is constant $P_1V_1 = P_2V_2$ or PV is constant.

Thus, $\Delta H = \Delta U + \Delta(PV)$ $\therefore$ $\Delta H = \mathbf{0}$

17. For reversible process :

$W_{\text{rev}} = -2.303\, nRT \log \dfrac{P_1}{P_2}$

$= -2.303 \times 2 \times 8.314 \times 300 \log_{10} \dfrac{1.01 \times 10^5}{5.05 \times 10^6}$

$= \mathbf{+1.9518 \times 10^4\ joule}$

Since, W_{rev} is a measure of free energy change

$\therefore$ $-\Delta G = -W_{\text{rev}} = -W_{\max}$

or $\Delta G = \mathbf{1.9518 \times 10^4\ joule\ mol^{-1}}$

18. (a) $W = -2.303\, nRT \log \dfrac{V_2}{V_1}$

Where, W is work done by the system under isothermal reversible conditions, note that work done by the system is negative

$-10 \times 10^3 = -2.303 \times 1 \times 8.314 \times T \log \dfrac{P_1}{P_2}$ ...(i)

Also, $P_1V_1 = P_2V_2$ at constant temperature

$1 \times 10^7 \times V_1 = P_2 \times 10V_1$ $\therefore$ $P_2 = \dfrac{1 \times 10^7}{10} = 10^6$ Pa

$\therefore$ By Eq. (i), $-10 \times 10^3 = -2.303 \times 1 \times 8.314 \times T \log \dfrac{10^7}{10^6}$

$\because$ $T = 522.27$ K

Now, using $PV = nRT$ for 1 mole of gas;

$P = 1 \times 10^7\ \text{Pa} = 10^7\ \text{Nm}^{-2}$

$1 \times 10^7 \times V_1 = 1 \times 8.314 \times 522.27$

$V = \mathbf{4.34 \times 10^{-4}\ m^3}$

(b) If 2 mole of gas have been used, the temperature would have been

$\dfrac{522.27}{2} = \mathbf{261.13\ K}$

19. $W = -2.303\, nRT \log_{10} \dfrac{V_2}{V_1} = -2.303 \times \dfrac{10}{40} \times 2 \times 300 \log_{10} \dfrac{5}{10}$

$W = 103.991$ cal

$\Delta U = 0$

$\because$ $q = \Delta U - W$ $\therefore$ $q = -W = -103.991$ cal

Also when temperature is constant $P_1V_1 = P_2V_2$ or PV = constant

$\therefore$ $\Delta H = \Delta U + \Delta(PV) = 0 + 0 = \mathbf{0}$

20. $$W = -2.303\, nRT \log_{10} \frac{P_1}{P_2}$$

$$W = -2.303 \times 1 \times 2 \times 300 \log_{10} \frac{2}{10} = +965.84 \text{ cal}$$

For isothermal change $\Delta U = 0$

Also $q = \Delta U - W = 0 - 965.84$ cal

$\therefore$ $q = \mathbf{-965.84\ cal}$

21. (a) Work involved in heating of gas

$$\begin{aligned} W_a &= -P \cdot \Delta V = -P(V_2 - V_1) \\ &= -P\left(\frac{nRT_2}{P} - \frac{nRT_1}{P}\right) \\ &= -nR\,(T_2 - T_1) = -1 \times 1.987(373 - 273) \\ &= \mathbf{-198.7\ cal} \end{aligned}$$

(b) Now the work equivalent to 198.7 cal is used up in causing reversible isothermal expansion of gas at 0°C, then

$$W_R = -2.303\, nRT \log_{10} \frac{P_1}{P_2}$$

$\therefore$ $$-198.7 = -2.303 \times 1 \times 1.987 \times 273 \log_{10} \frac{1}{P_t}$$

$\therefore$ $P_t = \mathbf{0.694\ atm}$

22. The vaporization occurs at constant pressure therefore the enthalpy change is equal to the work done by the heater :

$$\Delta H' = 0.50 \times 12 \times 300 \qquad (\Delta H = i \times V \times t)$$
$$= 1800 \text{ J} = +1.8 \text{ kJ}$$

$\therefore$ Molar enthalpy of vaporization

$$\Delta H = \frac{\Delta H'}{\text{mole of } H_2O} = \frac{\Delta H}{n_{H_2O}}$$

$$= \frac{1.8}{\left(\frac{0.798}{18}\right)} = \mathbf{40.6\ kJ\ mol^{-1}}$$

Also, $\Delta H = \Delta U + P\Delta V = \Delta U + \Delta n_g\, RT = \Delta U + RT$

$(\because H_2O(l) \rightleftharpoons H_2O(g), \Delta n_g = 1)$

$\therefore$ ΔU = molar internal energy change

$$= \Delta H - RT = 40.6 - 8.314 \times 10^{-3} \times 373.15$$

$$= \mathbf{37.5\ kJ\ mol^{-1}}$$

23. Volume of 1 mole liquid = 100 mL at pressure 1 bar

Volume of 1 mole liquid = 99 mL at pressure 100 bar

The process is irreversible as it is steeply changed from 1 bar to 100 bar. Therefore,

$$W = -P(V_2 - V_1) = -100(99 - 100)$$
$$= 100 \text{ bar mL}$$

Also, $\Delta U = q + W$

$q = 0$ since container is insulated

$\therefore$ $\Delta U = 100$ bar mL

Also, $\Delta H = \Delta U + P\Delta V = \Delta U + P_2V_2 - P_1V_1$

$$= 100 + (100 \times 99 - 1 \times 100) = \mathbf{9900\ bar\ mL}$$

24. $\Delta H^\circ_{\text{Reaction}} = \Sigma H^\circ_{\text{Products}} - \Sigma H^\circ_{\text{Reactants}}$

$= [2 \times H^\circ_{HF}(g) + H^\circ_{O_2}(g)] - [H^\circ_{OF_2}(g) + H^\circ_{H_2O}(g)]$

$\because$ H° of free elements $= 0$ $\quad \therefore H^\circ_{O_2} = 0$

$\because$ $\Delta H^\circ_f = H^\circ$, *i.e.*, standard heat of formation

= standard heat enthalpy of a compound

Also, ΔH°_f for F_2O is +ve; ΔH°_f for H_2O is −ve, because heats of combination are exothermic.

$$\Delta H^\circ_R = [2 \times (-270)] + 0 - [20 + (-250)] = -310 \text{ kJ}$$

Now $\Delta H^\circ = \Delta U^\circ + \Delta nRT$

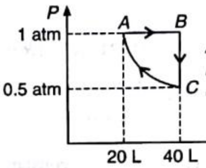
$\because$ $\Delta H^\circ_R = -310 \times 10^3$ J; $\Delta n = 3 - 2 = 1$

$R = 8.314$ J; $T = 298$ K

$\therefore$ $-310 \times 10^3 = \Delta U^\circ + 1 \times 8.314 \times 298$

$\therefore$ $\Delta U^\circ = -312477.5$ joule $\therefore \Delta U^\circ = \mathbf{-312.4775\ kJ}$

25. The overall process is cyclic one, *i.e.*, initial state is regained, thus, $\Delta U = 0$; $\Delta H = 0$ and $\Delta S = 0$.



AB — isobaric expansion ($W = -$ ve)

BC — isochoric change ($W = 0$)

CA — isothermal compression ($W = +$ ve)

Now, total work $W = W_{A \to B} + W_{B \to C} + W_{C \to A}$

$$\therefore\ W = \underbrace{-P\,(V_B - V_A)}_{\text{(work of expansion)}} + 0 + \underbrace{2.303\ nRT \log \frac{V_C}{V_A}}_{\text{(work of compression)}}$$

$$= -1 \times (40 - 20) + 0 + 2.303 \times P_AV_A \log \frac{V_C}{V_A}$$

$$(\because P_AV_A = nRT)$$

$$= -20 + 2.303 \times 1 \times 20 \times \log \frac{40}{20}$$

$$= -20 + 13.87 = -6.13 \text{ litre-atm}$$

$$= -\frac{6.13 \times 8.314}{0.0821} \text{ J} = -620.77 \text{ J}$$

Also, $q = -w = \mathbf{+620.77\ J}$ (For cyclic process)

26. $P_1 = 10$ atm at $T = 273$ K for $\frac{14}{32}$ mole O_2

$P_2 = 1$ atm at $T = T_2$ for $\frac{14}{32}$ mole O_2

For adiabatic expansion we have $T^\gamma \cdot P^{1-\gamma}$ = constant

$\therefore$ $\left(\frac{T_1}{T_2}\right)^\gamma = \left(\frac{P_2}{P_1}\right)^{1-\gamma}$ or $\gamma \log \frac{T_1}{T_2} = (1 - \gamma) \log \frac{P_2}{P_1}$

or $1.4 \log \frac{273}{T_2} = (1 - 1.4) \log \frac{1}{10}$ $\therefore T_2 = 141.4$ K

Work done in adiabatic expansion $= \frac{nR}{(\gamma - 1)}(T_2 - T_1)$

$$\textbf{In litre-atm} = \frac{14}{32} \times \frac{0.0821(141.4 - 273)}{(1.4 - 1)}$$

$$W_{\text{rev}} = \mathbf{-11.82\ liter\text{-}atm}$$

$$\textbf{In calorie} = \frac{14}{32} \times \frac{2 \times (141.4 - 273)}{(1.4 - 1)}$$

$$W_{\text{rev}} = \mathbf{-287.88\ cal}$$

27. $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s); \Delta H = -43.0\ \text{kJ}$

Initial mole $\frac{1\times 2}{0.08\times 200}$ $\frac{8\times 0.8}{0.08\times 200}$

$= 0.125$ $= 0.4$ 0

Final mole 0 0.275 0.125

$\therefore$ Heat produced $= 0.125\times 43 = \mathbf{5.375\ kJ}$

The heat produced is used to increase the temperature of HCl left in flask since heat capacity of flask and $NH_4Cl = 0$

$$\therefore \quad Q = n\times C_v\times \Delta T$$

$$5.375\times 10^3 = 0.275\times 20\times \Delta T \ \therefore\ \Delta T = \mathbf{977.27}$$

$\therefore$ Final temperature $= 200 + 977.27 = \mathbf{1177.27\ K}$

Also final pressure $= \frac{nRT}{V} = \frac{0.275\times 0.08\times 1177.27}{1.8}$

$$= \mathbf{14.39\ atm}$$

28. $$\Delta H = n\times C_p\times \Delta T$$

and $C_p = C_v + R = 12.48 + 8.314 = 20.794\ \text{JK}^{-1}$ (R in J)

For a given sample of argon gas, mole (n)

$$n = \frac{PV}{RT} = \frac{1\times 1.25}{0.0821\times 300} = 0.05$$

Also for reversible adiabatic change $(TV)^{\gamma-1} =$ constant

or $T_2V_2^{\gamma-1} = T_1V_1^{\gamma-1}$ or $T_2 = T_1\times\left(\frac{V_1}{V_2}\right)^{\gamma-1}$

($\gamma = 1.66$ for argon)

$$= 300\times\left(\frac{1.25}{2.50}\right)^{1.66-1} = 300\times\left(\frac{1}{2}\right)^{0.66}$$

$$\therefore \quad T_2 = 189.85\ \text{K}$$

$$\therefore \quad \Delta T = T_2 - T_1 = 189.85 - 300 = -110.15$$

Thus, $\Delta H = 0.05\times 20.794\times(-110.15) = \mathbf{-114.52\ J}$

29. $$\Delta H^\circ = 77.2\ \text{mol}^{-1}$$

$$\Delta S^\circ = 122\ \text{JK}^{-1}\ \text{mol}^{-1}$$

$$T = 400\ \text{K}$$

$$\therefore \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = 77200 - 400\times 122 = 28400\ \text{J}$$

Also, we have $-\Delta G^\circ = 2.303\,RT\log_{10}K_C$

where, K_C is equilibrium constant

$$\therefore \quad -28400 = 2.303\times 8.314\times 400\log_{10}K_C$$

$$\therefore \quad K_C = \mathbf{1.958\times 10^{-4}}$$

30. Gas is diatomic as $\gamma = 1.4$, thus, $C_v = \frac{5}{2}R$ and $C_p = \frac{7}{2}R$

Given, $\Delta H = 140\ \text{J}$ at constant pressure

$$\therefore \quad \Delta H = q_p = n\times C_p\times \Delta T$$

Also, $\Delta T = \frac{140}{nC_p} = \frac{140\times 2}{7n\times R} = \frac{40}{n}$

Now, $W = -nR\Delta T = -n\times 2\times\frac{40}{n} = \mathbf{-80\ J}$

Also, $q_p = \Delta H = \Delta U + (-W)$

$$\Delta U = \Delta H + W$$

$$\therefore \quad = 140 - 80$$

$$\Delta U = \mathbf{60\ J}$$

31. $\because \quad C_v = \frac{3}{2}R \ \therefore\ C_p = C_v + R = \frac{3}{2}R + R = \frac{5}{2}R$

$\therefore$ Heat given at constant pressure $= m\cdot C_p\cdot\Delta T$

or ΔH or $q_p = 1\times\frac{5}{2}\times R\times(373-298)$

or $\Delta H = 1\times\frac{5}{2}\times 1.987\times 75 = 372.56\ \text{cal}$

Now work done in the process $= -P\Delta V$

$$W = -P(V_2 - V_1) = -P\left(\frac{nRT_2}{P} - \frac{nRT_1}{P}\right)$$

$(\because PV = nRT)$

$$= -nR(T_2 - T_1) = -1\times 1.987\times(373-298)$$

$$= \mathbf{-149.025\ cal}$$

$\therefore$ From I law of thermodynamics

$\Delta U = q + W = 372.56 - 149.05 \ \therefore\ \Delta U = \mathbf{223.51\ cal}$

Also, $dq_{\text{rev}} = nC_p\cdot dT$

$$dS = \frac{dq_{\text{rev}}}{T} \ \therefore\ dS = \frac{nC_p\cdot dT}{T}$$

or $$\Delta S = \int_{T_1}^{T_2}\frac{nC_p\cdot dT}{T} = nC_p\log e\frac{T_2}{T_1}$$

$$\therefore \quad \Delta S = 2.303\,nC_p\log_{10}\frac{T_2}{T_1}$$

$$= 2.303\times 1\times\frac{5}{2}\times R\times\log_{10}\frac{373}{298}$$

$$= \mathbf{1.122\ cal\ K^{-1}\ mol^{-1}}$$

32. Volume of air in the room

$$= 5\times 10\times 3 = 150\ \text{m}^3 = 150\times 10^6\ \text{cm}^3$$

$\therefore$ Mole of air $= n = \frac{PV}{RT} = \frac{1\times 150\times 10^6}{10^3\times 0.0821\times 293} = 6.236\times 10^3$

Also, $\left(\frac{\delta H}{\delta T}\right)_p = C_p = \frac{\Delta H}{\Delta T}$ (for 1 mole)

$\therefore \quad \Delta H = n\cdot C_p\cdot\Delta T$ (for n mole)

$$= 6.236\times 10^3\times\frac{7}{2}\times 8.314\times(310-293)$$

$$= 3.085\times 10^6\ \text{J}$$

Thus, heat needed to heat the room to 37°C $= 3.085\times 10^6$ J

Also, heat released by 50 peoples

$$= 150\times 50\ \text{J/sec} = 7500\ \text{J/sec}$$

7500 J heat is provided in 1 sec

$\therefore$ 3.085×10^6 J heat will be provided in $\frac{1\times 3.085\times 10^6}{7500}$

$$= \mathbf{411.3}\ \textbf{second}$$

33. Volume of the room $5\times 10\times 3 = 150\ \text{m}^3 = 1.5\times 10^4\ l$

Mole of air in the room at 27°C and 1 atm P,

$$n = \frac{PV}{RT} = \frac{1\times 15\times 10^4}{0.0821\times 300}$$

$$= 6.1\times 10^3$$

Heat produced per sec by 50 students

$$= 100\times 50 = 5000\ \text{watt/sec}$$

Heat produced in 10 minutes

$$= 5000\times 10\times 60\ \text{watt} = 3\times 10^6\ \text{watt or Js}^{-1}$$

$\therefore$ Change in enthalpy of air, $\Delta H = n \times C_p \times \Delta T$

$$3 \times 10^6 = 6.1 \times 10^3 \times \frac{7}{2} \times 8.314 \times \Delta T \quad \therefore \quad \Delta T = \mathbf{16.90}$$

Thus, a rise in 16.90°C will be noticed in air temperature.

34. ΔG° needed for 54 g Al = 593 kJ

$\therefore$ ΔG° needed for 27 g Al $= \frac{593}{2}$ kJ

Heat produced when 50 kg mass falls from 2 m is Q.

Then, $Q = mgh = 50 \times 9.8 \times 2 = 980$ J

Thus, number of lifting and fall $n = \frac{\Delta G^\circ}{Q} = \frac{593 \times 10^3}{2 \times 980}$

$$= \mathbf{302.6}$$

Thus, athlete should go for 303 lifting.

35. Mass of the plane $= 6.3 \times 10^7$ g

Height of the plane $= 8 \times 10^5$ cm

$\therefore$ Work required to lift it to this height $= mgh$

$$= 6.3 \times 10^7 \times 981 \times 8 \times 10^5 \text{ erg} = 4.9442 \times 10^{16} \text{ erg}$$

$$= \frac{4.9442 \times 10^{16}}{4.18 \times 10^7} \text{ cal} = 1.1828 \times 10^9 \text{ cal}$$

$\because$ Efficiency of fuel is 30%

$\therefore$ Work obtained by 1 mole fuel $= \frac{1300 \times 30}{100}$ kcal

$\because$ $\frac{1300 \times 30}{100}$ kcal work is obtained by 1 mole fuel

$\therefore$ 1.1828×10^6 kcal work is obtained by 1 mole fuel

$$= \frac{1.1828 \times 10^6 \times 100}{30 \times 1300} = 3.033 \times 10^3 \text{ mol}$$

$$= 3.033 \times 10^3 \times 114 \text{ g} = 3.46 \times 10^5 \text{ g}$$

$\therefore$ Volume of fuel $= \frac{3.46 \times 10^5}{d} = \frac{3.46 \times 10^5}{0.705}$ mL

$$= 4.908 \times 10^5 \text{ mL} = 4.908 \times 10^2 \text{ litre}$$

$\therefore$ Cost of fuel $= 490.8 \times 3 =$ **1472.4 Rs.**

36. Kinetic energy of bullet is converted into heat.

$$\text{KE} = \frac{1}{2} mu^2 = \frac{1}{2} \times 18 \times 10^{-3} \times (500)^2 = 2.25 \times 10^3 \text{ J}$$

$$= \frac{2.25 \times 10^3}{4.184 \times 10^3} \text{ kcal} = 0.538 \text{ kcal}$$

Also, $q = \text{KE} = mS\Delta T \quad \therefore \quad \Delta T = \frac{\text{KE}}{mS}$

$$mS = mS \text{ for bullet} + mS \text{ for wooden block}$$

$$= (18 \times 10^{-3} \times 0.030 + 1 \times 0.50)$$

$$\Delta T = \frac{0.538}{(18 \times 10^{-3} \times 0.030 + 1 \times 0.500)}$$

$$= 1.08 \text{ K} = 1.08°\text{C}$$

$\therefore$ Final temperature $= (25.0 + 1.08) =$ **26.08°C**

37. Mole of He $= \frac{8}{4} = 2$

Mole of $N_2 = \frac{14}{28} = 0.5$

KE of He at 300 K $= \frac{3}{2} \times 2 \times 8.314 \times 300 = 7.4833 \times 10^3$ J

KE of N_2 at 300 K $= \frac{3}{2} \times 0.5 \times 8.314 \times 300 = 1.871 \times 10^3$ J

Now, since $\text{KE} = \frac{1}{2} M (U_{\text{rms}})^2$

On doubling U_{rms}, kinetic energy will becomes four times of initial value

$\therefore$ New KE of He $= 4 \times 7.483 \times 10^3 \text{ J} = 2.99 \times 10^4$ J

New KE of $N_2 = 4 \times 1.871 \times 10^3 \text{ J} = 7.484 \times 10^3$ J

Thus, for He $4 \times 7.483 \times 10^3 = \frac{3}{2} RT \times n$

(T is new temperature)

$$= \frac{3}{2} \times 2 \times 8.314 \times T$$

$\therefore$ $T = \mathbf{1200\ K}$

Now, heat given at constant volume to gases to heat them from 300 K to 1200 K is

$$\Delta H_{\text{He}} = n \times C_v \times \Delta T = n \times \frac{3}{2} R \times \Delta T$$

$$= 2 \times \frac{3}{2} \times 8.314 \times (1200 - 300) \left[C_v \text{ for He} = \frac{3}{2} R\right]$$

$$= 22447.8 \text{ J.}$$

$$\Delta H_{N_2} = 0.5 \times \frac{5}{2} \times 8.314 \times (1200 - 300) = 9353.25 \text{ J}$$

$$\left[C_v \text{ for } N_2 = \frac{5}{2} R\right]$$

$\therefore$ Heat provided $= 22447.8 + 9353.25 = 31801.05$ J

$$= 3.18 \times 10^4 \text{ J}$$

38. $\Delta H_{\text{dissolution}} = \Delta H_{\text{(ionisation)}} + \Delta H_{\text{(hydration)}} = 778 - 774.3$

$$= 3.7 \text{ kJ mol}^{-1} = 3700 \text{ J mol}^{-1}$$

$$\Delta S_{\text{dissolution}} = 43 \text{ J mol}^{-1}$$

$\therefore$ $\Delta G_{\text{dissolution}} = \Delta H - T\Delta S = 3700 - 298 \times 43 = -9114$ J

$$\Delta G = \mathbf{-9.114\ kJ}$$

39. $\Delta H_{\text{total}} = \Delta H_{\text{fusion}} + \Delta H_{\text{heating}} + \Delta H_{\text{vaporization}}$

$$= 10 \times 80 + 10 \times 1 \times 100 + 10 \times 540 = \mathbf{7200\ cal}$$

40. ΔH required for heating $= \underset{\text{(boiler)}}{mS\Delta T} + \underset{\text{(water)}}{mS\Delta T}$

$$= 0.11 \times 900 \times 90 + 1 \times 400 \times 90 = 44910 \text{ kcal}$$

Since, only 70% of heat given is used up to do so.

Thus, actual heat required $= \frac{44910 \times 100}{70} =$ **64157 kcal**

41. The given reaction is :

$$Al_2O_3(s) + 6Na(s) \longrightarrow 3Na_2O(s) + 2Al(s)$$

Hence, $\Delta G^\circ = 3 \times G_f^\circ(Na_2O) - G_f^\circ(Al_2O_3)$

(G° for Na and Al = 0)

$$= 3 \times (-377) - (-1582) = +451 \text{ kJ mol}^{-1}$$

The reaction cannot occur since ΔG°(298 K) is positive.

Also, $\Delta G^\circ = -2.303 RT \log_{10} K$

$$451 = -2.303 \times 8.314 \times 10^{-3} \times 298 \log_{10} K$$

$\therefore$ $\text{Log } K = -79.04$

$$K = \mathbf{9.1 \times 10^{-80}}$$

42. Using Clausius-Clapeyron equation :

$$2.303 \log_{10} \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \frac{[T_2 - T_1]}{T_1 T_2}$$

$$\Delta H_v = \frac{2.303 R T_1 T_2}{(T_2 - T_1)} \log_{10} \frac{P_2}{P_1}$$

We have $\Delta H_v = \frac{2.303 \times 8.314 \times 303 \times 333}{(333 - 300)} \log_{10} \frac{5.2 \times 10^4}{1.53 \times 10^4}$

$$= 31.1 \times 10^3 \text{ J} = \mathbf{31.1\ kJ}$$

43. For entropy change of fusion, $\Delta S_f = \frac{\Delta H_f}{T}$

Given, $\Delta H_f = 6 \times 10^3$ J; $T = 273$ K

$\therefore \quad \Delta S_f = \frac{6 \times 10^3}{273} = \mathbf{21.97\ JK^{-1}\ mol^{-1}}$

44. ΔH for cooling $CD_2O = mS\Delta T = \frac{3.2}{32} \times 14 \times 100 = 140$ cal

$\because$ Cooling is exothermic $\Delta H = -140$ cal.

Now, $\quad \Delta S = \frac{\Delta H}{T} = -\frac{140}{900} = \mathbf{-0.1555\ cal\ deg^{-1}}$

45. For entropy change of vaporization, $\Delta S_v = \frac{\Delta H_v}{T}$

Given, $\quad \Delta H_v = 40.8 \times 10^3$ J; $\quad T = 373$ K

$\therefore \quad \Delta S_v = \frac{40.8 \times 10^3}{373} = \mathbf{109.38\ JK^{-1}\ mol^{-1}}$

46. Given, $\quad \Delta H = -11.7 \times 10^3 \text{ J mol}^{-1}$

$\Delta S = -105 \text{ J mol}^{-1} \text{ K}^{-1}$

$T = 298$ K

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

$= -11700 - 298 \times (-105) = 19590$ J

$= \mathbf{+19.59\ kJ}$

Since, $\quad \Delta G = +$ ve $\quad \therefore$ reaction is not spontaneous.

47. $\quad \Delta S_{\text{Reaction}} = \Sigma S_{\text{Product}} - \Sigma S_{\text{Reactants}}$

$= 2 \times S_{H_2O} - [2 \times S_{H_2} + S_{O_2}]$

$= 2 \times 68 - [2 \times 126.6 + 201.20]$

$\Delta S = \mathbf{-318.4\ JK^{-1}}$

48. We have, $\quad \Delta S = \frac{q_1}{T} = \frac{2.303\, nRT \log_{10} \frac{V_2}{V_1}}{T}$

Given, $\quad n = 1$, $R = 8.314$ J, $T = 298$ K, $V_1 = V$, $V_2 = 10V$

$\therefore \Delta S = 2.303 \times 1 \times 8.314 \log_{10} \frac{10V}{V} = \mathbf{19.15\ JK^{-1} mol^{-1}}$

49. $\quad \Delta S = 2.303 \times m \times C_p \times \log \frac{T_2}{T_1}$

$= 2.303 \times \frac{100}{1000} \times 4200 \log \frac{360}{300} = \mathbf{76.59\ J}$

50. $\quad \Delta S = 2.303 m \times C_p \times \log \frac{T_2}{T_1}$

[where m in kg and C_p in J/kg]

Entropy change for heating water from 27° to 100°C.

$$\Delta S = 2.303 \times 4180 \log \frac{373}{300} = 910.55 \text{ J}$$

Entropy change for heating 1 kg H_2O to 1 kg steam at 100°C.

$$\Delta S = \frac{\Delta H_v}{T} = \frac{23 \times 10^5}{373} = 6166.21 \text{ J}$$

Entropy change for heating 1 kg steam from 373 to 473 K, m in kg.

$$\Delta S = \int_{373}^{473} \frac{nC_p \cdot dT}{T} = m\int_{373}^{473} \frac{(1670 + 0.49T)dT}{T}$$

$$= m\int_{373}^{473} \frac{1670 dT}{T} + m\int_{373}^{473} 0.49\, dT$$

$$= m \times 1670 \times 2.303 [\log T]_{373}^{473} + m \times 0.49 [T]_{373}^{473}$$

$$= 1 \times 1670 \times 2.303 \log \frac{473}{373} + 1 \times 0.49 \times 100$$

$$= 396.73 + 49 = 445.73 \text{ J}$$

$\therefore$ Total entropy change $= 910.55 + 6166.21 + 445.73$

$= \mathbf{7522.50\ J}$

51. ΔH° for reaction

$$= \left[H^\circ_{TiCl_4}(l) + H^\circ_{O_2}(g) - H^\circ_{TiO_2} - H^\circ_{Cl_2} \times 2\right]$$

$$= [-804.2 + 0.0 - (-944.7) - 0.0] = 140.5 \text{ kJ}$$

Also, ΔS° for reaction

$$= \left[S^\circ_{TiCl_4}(l) + S^\circ_{O_2}(g) - S^\circ_{TiO_2}(s) - S^\circ_{Cl_2}(g) \times 2\right]$$

$$= [252.3 + 205.1 - 50.3 - 2 \times 233.0]$$

$$= -58.9 \text{ J} = -0.0589 \text{ kJ}$$

Now, $\Delta G^\circ = \Delta H^\circ - T\Delta S$

$= 140.5 - 298.15 \times (-0.0589) = \mathbf{158.06\ kJ}$

Positive value of ΔG° suggests that reaction is not possible.

52. Given, for the change

$\Delta H = 30 \times 10^3 \text{ J mol}^{-1}$

$\Delta S = 70 \text{ JK}^{-1} \text{ mol}^{-1}$

For a non-spontaneous reaction $\Delta G = +$ ve

Since, $\quad \Delta G = \Delta H - T\Delta S \quad \therefore \quad \Delta H - T\Delta S$ should be +ve

or $\quad \Delta H > T\Delta S$ or $T < \frac{\Delta H}{\Delta S}$

$< \frac{30 \times 10^3}{70}$

$\mathbf{T < 428.57\ K}$

53. $\because \quad \Delta G = \Delta H - T\Delta S$

Also, ΔG at equilibrium $= 0 \therefore \Delta H = T\Delta S$

$30.5 = T \times 0.066 \therefore T = \frac{30.5}{0.066} = \mathbf{462.12\ K}$

54. At equilibrium : $\quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\therefore \quad \Delta G^\circ_{300\text{ K}} = -41.16 - 300 \times (-4.24 \times 10^{-2}) = \mathbf{-28.44\ kJ}$

and

$\Delta G^\circ_{1200\text{ K}} = -32.93 - 1200 \times (-2.96 \times 10^{-2}) = \mathbf{+2.59\ kJ}$

Thus, at 300 K, reaction will proceed in forward direction and at 1200 K in backward direction.

Also, $\quad \Delta G^\circ = -2.303 RT \log K_p$

At, 300 K, $-28.44 = -2.303 \times 8.314 \times 10^{-3} \times 300 \log K_p$

$\therefore \qquad K_p = 8.94 \times 10^4$

Similarly, at 1200 K, $K_p = \mathbf{0.77}$

55.
$$\begin{array}{ccc} 2CH_3COOH(g) & \rightleftharpoons & (CH_3COOH)_2(g) \\ 1 & & 0 \\ 1-0.982 & & \frac{0.982}{2} \end{array}$$

$$K^\circ = \frac{(CH_3COOH)_2}{(CH_3COOH)^2} = \frac{0.982}{2 \times (0.018)^2} = 1515.4$$

Now, ΔH° for dimerization $= -2 \times 33\ \text{kJ} = -66\ \text{kJ}$

Thus, $\qquad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$-2.303RT \log K^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$-2.303 \times 8.314 \times 400 \times \log(1515.4) = -66 \times 10^3 - 400 \times \Delta S^\circ$$

$$-24359.2 = -66000 - 400\,\Delta S^\circ$$

$$\therefore \qquad \Delta S^\circ = -\frac{41640.8}{400} = \mathbf{-104.102\ J/mol}$$

56. For a real gas, $\left[P + \frac{n^2a}{V^2}\right][V - nb] = nRT$

If $nb << V$, (as given), then

$$\left[P + \frac{n^2a}{V^2}\right]V = nRT \text{ or } P = \frac{nRT}{V} - \frac{n^2a}{V^2}$$

Now work done in reversible expansion is

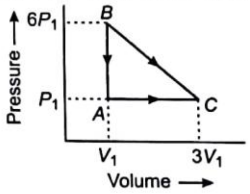
$$w = -\int P\,dV = -\int_{V_1}^{V_2} \frac{nRT\,dV}{V} + \int_{V_1}^{V_2} \frac{n^2a}{V^2} \cdot dV$$

$$= -nRT \log \frac{V_2}{V_1} - \left[\frac{n^2a}{V_2} - \frac{n^2a}{V_1}\right]$$

$$= -nRT \log \frac{V_2}{V_1} - n^2a\left[\frac{1}{V_2} - \frac{1}{V_1}\right]$$

• SINGLE INTEGER ANSWER PROBLEMS •

1. 6 kJ heat is provided to a system as well as work equivalent to 2 kJ is done on the system. The total change in internal energy during these operations in kJ is ......
2. Specific heat at constant volume of a monoatomic gas is 0.075 cal/g. 1 mole of this gas requires 3 cal of heat to raise the temperature of 1 mole gas. The heat required to raise the temperature through 1°C of 1 mole gas at constant pressure is ...... cal.
3. Exactly 3.0 g of carbon was burned to CO_2 in copper calorimeter. The mass of calorimeter is 1.5 kg and the mass of water in calorimeter is 2 kg. The initial temperature was 20°C and final temperature was 31.5°C. If specific heat of copper is 0.0826 cal/g-K, the heat value to closest integer of carbon in kcal/g is ......
4. A new element E forms a compound with chlorine which contains 1.455 g Cl per g E. The specific heat of E was found 0.05 cal/g. If eq. mass of element is 24, what is x in $E\text{Cl}_x$?
5. The enthalpy of transition of crystalline boron to amorphous boron at 1500°C is 0.4 kcal mol^{-1}. Assuming atomic mass of boron 10, the change in enthalpy of transition 50 g boron from crystalline to amorphous form is ......
6. If ΔG and ΔS for the reaction : $A_{(g)} + B_{(g)} \longrightarrow P_{(g)}$ at 300 K are − 600 cal and −10 cal/K. The ΔU for the reaction in kcal is ......
7. At 0°C, if enthalpy of fusion of ice is 1365 kcal/mol. The molar entropy change for melting of ice at 0°C is ...... kcal.
8. A certain number of mole of gas is allowed to heat from 300 K to 500 K at constant P. By doing so gas is expanded to do work on boundries equivalent to 9.9768 kJ. How many mole of gas were used ?
9. 'a' mole of Na reacts with sufficient water in an open vessel at 300 K. The work done by the liberated gas H_2 is equivalent to 4988.4 J. What is a ?
10. A reversible reaction is carried out at 500 K, where its equilibrium constant is unity. If ΔH° at 500 K is 4.0 kJ, the value of ΔS° is equal to ......
11. A reaction becomes spontaneous only at 500 K. If ΔH at 500 K is 3.0 kJ, the change in entropy at 500 K.
12. A certain amount of gas ($P = 5$ atm, $V = 2$L, $T = 500$ K) in state A is compressed to state B ($P = 2$ atm, $T = 100$ K, $V = ?$). The final volume of state B in litre is :
13. One mole of monoatomic ideal gas at $P = 2$ bar and $T = 273$ K is compressed to 4 bar pressure following a reversible path obeying P/V = constant. Assume $C_v = 12.5\ \text{J mol}^{-1}\ \text{K}^{-1}$. The value of $\frac{\Delta U}{W}$ for this process is minus.
14. How much of the following are intensive properties? Vapour pressure, Molarity, Refractive index, Dielectric constant, Osmotic pressure, Molarity, Specific gravity, Molar volume
15. Out of the following properties how many are path functions?
Heat enthalpy, Internal energy, Temperature, Work, Heat, Specific heat
16. Out of the following properties how many are state functions?
Heat enthalpy, Internal energy,Temperature, E_{cell}, Work, Heat, Specific heat, Resistance
17. Out of the following properties how many are extensive properties?
Resistance, Electromotive force, Ionic mobility, Dipole moment, Heat capacity, Specific heat, Density, Specific volume
18. How many of the following are intensive properties? Vapour pressure, Molarity, Refractive index, Dielectric constant, Osmotic pressure, Molality, Specific gravity, Molar volume
19. An ideal gas shows the cyclic process $ABCA$ as represented by figure. The net work done during the cycle is $a\,PV$. The value of a is ......

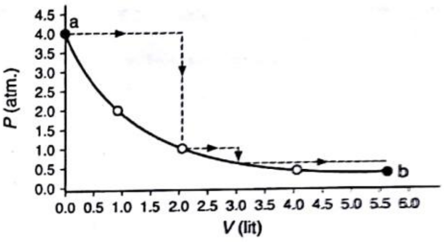


20. The work done in kJ on decomposition of 6.8 g H_2O_2 in open vessel at 27°C is approximately -2.50×10^a J. The value of a is ......
21. The average molar heat capacity (in cal) at constant volume of a gaseous mixture containing 2 mole of gas $A\left(C_v = \frac{3}{2}R\right)$ and 2 mole of gas $B\left(C_v = \frac{5}{2}R\right)$ is ......
22. If a gas expands adiabatically at constant pressure such that $T \propto V^{-1/2}$. The value of $C_p : C_v$ for it is a :2. The value of a is......
23. Two mole of an ideal monoatomic gas undergoes a reversible process for which PV^2 = constant . The gas expands from 1 litre to 3 litre starting from initial temperature of 300 K and the value of ΔH for the expansion in kcal is ......

24. The degree of freedom for a triatomic gas is ......
25. An ideal engine operates in a carnot cycle between 327°C and 127°C. It absorbs 9 kcal of heat at high temperature. The amount of heat in kcal rejected to sink is ......
26. Following gases are placed at same temperature and pressure and expanded adiabatically to double their original volume.

    $O_2, N_2, Ar, Ne, SO_2, O_3, H_2O_2, Cl_2$

    How much of these gases will require the greatest quantity of heat isochorically to restore their original temperature.
27. One mole of an ideal gas is taken from a to b along two paths denoted by the solid and dashed line as shown in graph below. If the work done along the solid line is w_s and that along the dotted line path is w_d, then the integer closest to the ratio w_d / w_s is ...... **(IIT 2010)**



ANSWERS

1. Eight **2.** Five **3.** Eight **4.** Five **5.** Two **6.** Three **7.** Five **8.** Six **9.** Four **10.** Eight **11.** Six **12.** One
13. Three **14.** Seven **15.** Three **16.** Three **17.** Three **18.** Seven **19.** Nine **20.** Two **21.** Four **22.** Three **23.** Two **24.** Six
25. Six **26.** Two (Ar, Ne) **27.** Two

OBJECTIVE PROBLEMS (One Answer Correct)

1. An equilibrium $\text{Hexane}_{(l)} \rightleftharpoons \text{Hexane}_{(V)}$ exists at 300 K. If 29 kJ energy is absorbed for conversion of 1 mole $\text{hexane}_{(l)}$ to hexane vapours at 300 K, the change in entropy during the conversion of 1 g $\text{hexane}_{(l)}$ to 1 g hexane vapours is :
(a) $96.67\ \text{JK}^{-1}$ (b) $1.124\ \text{JK}^{-1}$
(c) $0.097\ \text{JK}^{-1}$ (d) $1.124 \times 10^{-3}\ \text{JK}^{-1}$

2. If for the reaction at 300 K : $2\text{Mg}_{(s)} + \text{O}_{2(g)} \longrightarrow 2\text{MgO}_{(s)};\ \Delta_r H = -1202\ \text{kJ mol}^{-1}$ and $\Delta_r S = -217.0\ \text{JK}^{-1}\ \text{mol}^{-1}$. The total entropy change $(\Delta S)_T$ and Gibbs energy change during the course of reaction $(\Delta_r G)$ are respectively :
(a) 3.79×10^3 J, -1136.9 kJ
(b) 3.79×10^3 J, $+1000$ J
(c) $+1000$ J, 3.79×10^3 J
(d) -1136.9 kJ, 3.79×10^3 J

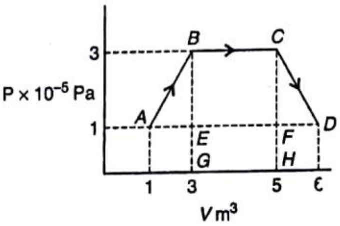
3. Given,

$$2\text{Fe}_2\text{O}_{3(s)} \longrightarrow 4\text{Fe}_{(s)} + 3\text{O}_{2(g)};\quad \Delta_r G_1^\circ = +1487\ \text{kJ mol}^{-1}$$

$$6\text{CO}_{(g)} + 3\text{O}_{2(g)} \longrightarrow 6\text{CO}_{2(g)};\quad \Delta_r G_2^\circ = -1543.2\ \text{kJ mol}^{-1}$$

Select the correct statement :
(a) $\Delta_r G^\circ$ for reduction of iron oxide by CO is + 56.2 kJ mol^{-1}
(b) Fe_2O_3 can be reduced by CO spontaneously
(c) Fe_2O_3 cannot be reduced by CO spontaneously
(d) The reduction of Fe_2O_3 takes part in higher part of blast furnace.

4. The net work done through a series of changes reported in figure for an ideal gas is :



(a) -6×10^5 J (b) -7×10^5 J
(c) -12×10^5 J (d) $+12 \times 10^5$ J

5. For adiabatic expansion of a perfect gas $\frac{dP}{P}$ is :
(a) $\frac{dV}{V}$ (b) $\gamma . \frac{dV}{V}$
(c) $-\gamma \frac{dV}{V}$ (d) $-\gamma^2 \frac{dV}{V}$

6. Specific heat at constant pressure of a diatomic gas having molar mass M is approximately equal to :
(a) $\frac{\gamma R}{M(\gamma - 1)}$ (b) $\frac{\gamma}{RM}$
(c) $\frac{M}{R(\gamma - 1)}$ (d) $\frac{\gamma RM}{\gamma + 1}$

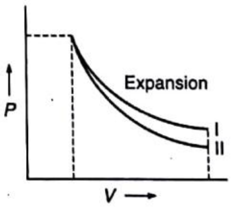
7. Which of the following is incorrect for the change shown below ?

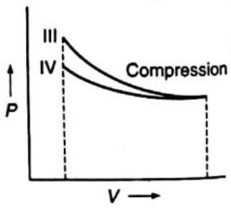
$$\begin{array}{ccc} \underset{(298\ \text{K})}{aA + bB} & \xrightarrow{\Delta_r S_1^\circ} & \underset{(298\ \text{K})}{cC + dD} \\ \Delta_r S_2^\circ \downarrow & & \uparrow \Delta_r S_4^\circ \\ \underset{(0\ \text{K})}{aA + bB} & \xrightarrow{\Delta_r S_3^\circ} & \underset{(0\ \text{K})}{cC + dD} \end{array}$$

(a) $\Delta_r S_1^\circ = cS_C^\circ + dS_D^\circ - (aS_A^\circ + bS_B^\circ)$
(b) $\Delta_r S_2^\circ = -[aS_A^\circ + bS_B^\circ]$
(c) $\Delta_r S_3^\circ = 0$
(d) $\Delta_r S_4^\circ = -[cS_C^\circ + dS_D^\circ]$

8. In a thermodynamic process helium gas obeys the law $\frac{T}{P^{2/5}}$ = constant. The heat given to n mole of He in order to raise the temperature from T to $2T$ is :
(a) 8 RT (b) 4 RT
(c) 16 RT (d) zero.

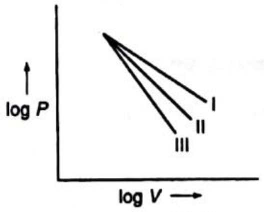
9. Which of the following figures given below shows adiabatic process ?





(a) II, III (b) I, III
(c) II, IV (d) I, IV

10. The following curves represents adiabatic expansions of gases He, O_2 and O_3 not necessarily in order. Which curve represents for O_3 :



(a) I (b) II
(c) III (d) any one of these

11. During an adiabatic expansion a gas obeys $VT^3 = \text{constant}$. The gas must be :

(a) monoatomic (b) diatomic

(c) polyatomic (d) either of these

12. He, N_2 and O_3 are expanded adiabatically and their expansion curves between log P and log V are plotted under similar conditions. About the ratio of the slopes, which one is not correct ?

(a) The ratio of slopes of log P *vs* log V curves for He and O_3 is 1.25

(b) The ratio of slopes of log P *vs* log V curves for He and N_2 is 1.20

(c) The ratio of slopes of log P *vs* log V curves for N_2 and O_3 is 1.05

(d) The slope of He is least steeper and for O_3 is most steeper

13. Which expansion will produce more change in entropy during reversible and isothermal process ?

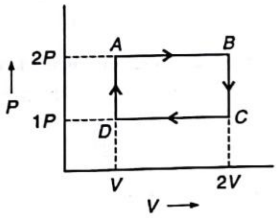
(a) 1 mole H_2 at 300 K from 2 litre to 20 litre

(b) 1 mole N_2 at 400 K from 1 litre to 10 litre

(c) 1 mole O_3 at 500 K from 3 litre to 30 litre

(d) All have same ΔS

14. An ideal monoatomic gas follows the path *ABCD*. The work done during the complete cycle is :



(a) $-PV$ (b) $-2PV$

(c) $-\frac{1}{2}PV$ (d) zero

15. Molar heat capacity of a gas at constant temperature and pressure is :

(a) $\frac{3}{2}R$ (b) $\frac{5}{2}R$

(c) depends on gas (d) infinity

16. The maximum change in entropy is observed during mixing of :

(a) 8.6 g hexane + 10.0 g heptane

(b) 8.6 g hexane + 5.0 g heptane

(c) 4.3 g hexane + 10.0 g heptane

(d) 1 g hexane + 10.0 g heptane

17. Heat of neutralisation of strong acid and strong base under 1 atm and 25°C is −13.7 kcal. If standard Gibbs energy change for dissociation of water to H^+ and OH^- is −19.14 kcal, the change in standard entropy for dissociation of water in cal K^{-1} mol^{-1} is :

(a) 18.25 (b) 110.2

(c) −18.25 (d) None of these

18. C_p and C_v for a gas are 0.125 cal/g and 0.075 cal/g respectively. Which one of the gas has these values?

(a) He (b) O_2

(c) Ar (d) Ne

19. An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If T_i is the initial temperature and T_f is the final temperature, which of the following statement is correct?

(a) $(T_f)_{\text{irrev.}} > (T_f)_{\text{rev.}}$

(b) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process

(c) $(T_f)_{\text{rev.}} = (T_f)_{\text{irrev.}}$

(d) $T_f = T_i$ for both reversible and irreversible process

20. The W/Q of a carnot engine is 1/6. When temperature of sink is reduced by 62°C, this ratio becomes twice, therefore the initial temperature of the sink and source are:

(a) 33°C, 67°C (b) 37°C, 99°C

(c) 67°C, 33°C (d) 97 K, 97 K

21. A scientist says that the efficiency of his heat engine which works at source temperature 127°C and sink temperature (27°C) is 26%, then :

(a) it is impossible

(b) it is possible

(c) it is possible but less probable

(d) data is incomplete

22. In a closed insulated container, a liquid is stirred with a paddle to increase the temperature, then which of the following is true:

(a) $\Delta U = w \neq 0, q = 0$ (b) $w = 0, \Delta U = q \neq 0$

(c) $\Delta U = 0, w = q \neq 0$ (d) $\Delta U = w = q \neq 0$

23. An ideal gas heat engine operates in a carnot cycle between 227°C and 127°C. It absorbs 6 kcal at the higher temperature. The amount of heat converted into work in kcal is equal to:

(a) 4.8 (b) 3.5

(c) 1.6 (d) 1.2

24. On the basis of reaction : $\frac{4}{3}Al + O_2 \rightarrow \frac{2}{3}Al_2O_3$; $\Delta G = -827\,\text{kJ mol}^{-1}$ of O_2, the minimum emf required to carry out electrolysis of Al_2O_3 is:

(a) 6.42 V (b) 8.56 V

(c) 2.14 V (d) 4.28 V

25. The densities of graphite and diamond are 2 and 3 g/mL at 298 K respectively. If the $\Delta H - \Delta U$ for the change $C_G \rightarrow C_D$ is equal to 100 J mol^{-1}, the pressure at which graphite will be transformed into diamond is:

(a) 5×10^7 Pa (b) 9.92×10^5 Pa

(c) 9.92×10^{10} Pa (d) 9.92×10^8 Pa

26. One mole of an ideal gas at an initial temperature T K, does $6R$ J of work adiabatically. If the ratio of specific heats of this gas at constant P and V respectively is 5/3, the final temperature of gas will be:

(a) $(T+2.4)$ K (b) $(T-2.4)$ K

(c) $(T+4)$ K (d) $(T-4)$ K

27. Considering entropy(s) as the thermodynamic parameter, the criterion for the spontaneity of any process is:

(a) $\Delta S_{sys}+\Delta S_{surr}>0$ (b) $\Delta S_{sys}-\Delta S_{surr}>0$

(c) Only $\Delta S_{sys}>0$ (d) Only $\Delta S_{surr}>0$

28. The molar specific heat at constant pressure for an ideal gas is $\frac{7}{2}R$. Which of the following is correct:

(a) $\gamma=1.44$, and atomicity = 3

(b) $\gamma=1.33$, and atomicity = 3

(c) $\gamma=1.66$, and atomicity = 1

(d) $\gamma=1.44$, and atomicity = 2

29. The enthalpy and entropy change for the reaction:

$$Br_{2(l)}+Cl_{2(g)}\rightarrow 2BrCl_{(g)}$$

are 30 kJ mol^{-1} and 105 JK^{-1} mol^{-1} respectively. The temperature at which the reaction will be in equilibrium is:

(a) 450 K (b) 300 K

(c) 285.7 K (d) 273 K

30. If Q, U and W denotes respectively the heat added, change in internal energy and work done in a closed cycle process, then:

(a) $\Delta U=0$ (b) $Q=0$

(c) $W=0$ (d) $Q=W=0$

31. For the reaction : $PCl_{5(g)}\rightarrow PCl_{3(g)}+Cl_{2(g)}$, which one is true ?

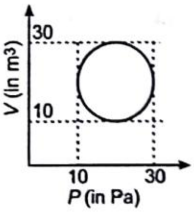
(a) $\Delta H=-ve$; $\Delta S=+ve$

(b) $\Delta H=+ve$; $\Delta S=+ve$

(c) $\Delta H=+ve$; $\Delta S=0$

(d) $\Delta H=+ve$; $\Delta S=-ve$

32. A system works under cyclic process as shown in figure. Heat absorbed during the process is:



(a) $\frac{22}{7}\times10^2$ J

(b) $\frac{22}{7}\times10^3$ J

(c) $\frac{22}{7}\times10^4$ J

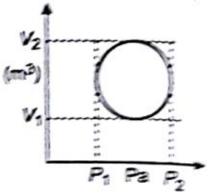
(d) $\frac{22}{7}\times10^5$ J

33. For two mole of an ideal gas:

(a) $C_p-C_v=2R$ (b) $C_p-C_v=R$

(c) $C_p-C_v=\frac{R}{2}$ (d) none of these

34. The PV diagram shown in figure is in circle for a cyclic process. The work done during the process can not be given by:



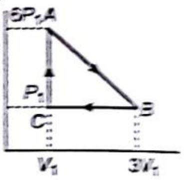
(a) $\frac{\pi}{4}\times(P_2-P_1)^2$

(b) $\frac{\pi}{4}\times(V_2-V_1)^2$

(c) $\pi(P_2-P_1)\times(V_2-V_1)$

(d) $\frac{\pi}{4}(P_2-P_1)(V_2-V_1)$

35. An ideal gas shows $P-V$ work done in cyclic process as shown in figure. The net work done by the gas during the cycle is:



(a) $12P_1V_1$

(b) $6P_1V_1$

(c) $9P_1V_1$

(d) $5P_1V_1$

36. The work done by 3.4 g $H_2O_{2(l)}$ on decomposition to $H_2O_{(l)}$ and $O_{2(g)}$ against a pressure of 1 atm at 25°C:

(a) -3.2×10^2 J (b) $+3.2\times10^2$ J

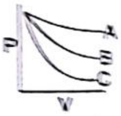
(c) 1.24×10^2 J (d) -1.24×10^2 J

37. During an adiabatic process pressure of the gas $=T^5$. The Poison's ratio for gas is:

(a) $\frac{3}{2}$ (b) $\frac{5}{3}$

(c) $\frac{7}{2}$ (d) $\frac{4}{3}$

38. Plots of P vs V are made during adiabatic process of three gases as shown in figure. Which of the statement is correct:



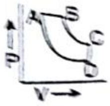
(a) C is for monoatomic gas

(b) B is for diatomic gas

(c) A is for polyatomic gas

(d) All of these

39. In the pressure-volume diagram given below, the isochoric, isothermal, isobaric and isoentropic process are respectively:



(a) BA, AD, DC, CB

(b) DC, CB, BA, AD

(c) AB, BC, CD, DA

(d) CD, DA, AB, BC

40. A sample of an ideal gas is expanded from $1m^3$ to $3m^3$ in a reversible process for which $P=KV^2$ having $K=6$ bar m^{-6}. Work done by the gas in (bar m^3) is:

(a) 5.2 (b) 15.6

(c) 52 (d) 55

41. 100 mole of an ideal gas at 8.21 atm is heated to show a linear graph between $\log V$ and $\log T$. The slope of the line is:

(a) 1/2 (b) 1

(c) 1/3 (d) 1/4

42. An ideal gas at 27°C is compressed adiabatically to $\frac{8}{27}$ of its original volume if $\gamma=\frac{5}{3}$, then rise in temperature is:

(a) 405 K (b) 225 K
(c) 375 K (d) 305 K

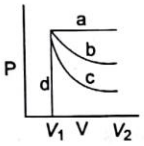
43. The pressure(P) and density(ρ) of a diatomic gas $\left(\gamma = \frac{7}{5}\right)$ changes from $P_1\rho_1$ to $P_2\rho_2$. If $\frac{\rho_1}{\rho_2} = 32$, the value of $\frac{P_1}{P_2}$ is :

(a) 32 (b) $\frac{1}{32}$
(c) 128 (d) 164

44. An ideal gas expands isothermally from a volume V_1 to V_2 and `then compressed to original volume V_1 adiabatically. Initial pressure was P_1 and final pressure was P_3. The total work done is w, then:

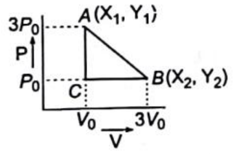
(a) $P_3 > P_1, w = +\text{ve}$ (b) $P_3 < P_1, w = -\text{ve}$
(c) $P_3 > P_1, w = -\text{ve}$ (d) $P_3 = P_1, w = 0$

45. In which of the following graphs work done is maximum?



(a) a
(b) b
(c) c
(d) d

46. n mole of an ideal gas undergo a process ABC as shown in figure. Maximum temperature of the gas during the process AB is:



(a) $\frac{4P_0V_0}{nR}$
(b) $\frac{P_0V_0}{nR}$
(c) $\frac{2P_0V_0}{nR}$
(d) $\frac{3P_0V_0}{nR}$

47. Molar heat capacity of water in equilibrium with ice at constant pressure is:

(a) zero (b) infinite
(c) 40.45 kJ K^{-1} mol^{-1} (d) 75.48 kJ K^{-1} mol^{-1}

48. Assuming complete dissociation of 1 mole each of H_2, N_2, O_2 and Cl_2 into respective atoms *i.e.*, in monoatomic gaseous atoms under identical conditions of P, V and T, which will show greater entropy ?

(a) Cl (b) O
(c) N (d) H

49. One mole of an ideal gas is compressed isothermally to half of its initial volume and then heated to twice of its temperature under isochoric condition, the change in entropy is :

(a) $C_v \ln 2$ (b) $C_p \ln 2$
(c) $R \ln 2$ (d) $(C_v - R) \ln 2$

50. A gas expands adiabatically such that its temperature $T \propto \frac{1}{\sqrt{V}}$. The value of poisson's ratio (γ) for gas is :

(a) 1.30 (b) 1.50
(c) 1.70 (d) 2

51. A sample of an ideal gas at pressure P and volume V proceed for an isothermal process showing an entropy change of ΔS. The work done by the gas is :

(a) $-\frac{PV\Delta S}{nR}$ (b) $-nR\Delta S$
(c) $-PV$ (d) $-\frac{P\Delta S}{nRV}$

52. Given :

$$Fe_2O_3(s) + \underset{1\text{ mole}}{3CO} \rightleftharpoons 2Fe(s) + \underset{1\text{ mole}}{3CO_2}\,;\ \Delta G_{25°C} = -10\text{ kJ}$$

What is the value of $\Delta G_{25°C}$ for

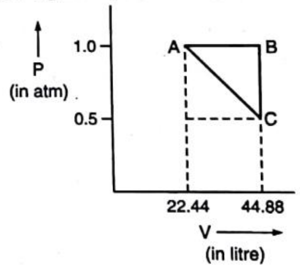
$$2Fe(s) + \underset{2\text{ mole}}{3CO_2} \rightleftharpoons Fe_2O_3(s) + \underset{2\text{ mole}}{3CO}$$

(a) + 10 kJ (b) + 11.717 kJ
(c) 8.28 kJ (d) 9.45 kJ

53. How many times a diatomic gas should be expanded adiabatically to reduce its root mean square speed to half?

(a) 16 (b) 40
(c) 32 (d) 8

54. One mole sample of a monoatomic ideal gas is allowed to proceed for a given cycle as shown in the figure :



The temperatures at A, B and C (in K) are respectively :

(a) 273, 546, 273 (b) 546, 273, 273
(c) 273, 273, 273 (d) 546, 546, 273

55. n mole of an ideal gas undergo a process ABC as shown in figure. Maximum temperature of the gas during the process AB is :

(a) $\frac{4P_0V_0}{nR}$ (b) $\frac{P_0V_0}{nR}$

(c) $\frac{2P_0V_0}{nR}$ (d) $\frac{3P_0V_0}{nR}$

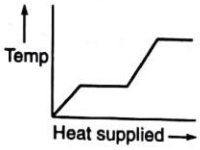
56. Molar heat capacity of water in equilibrium with ice at constant pressure is :

(a) zero (b) infinite

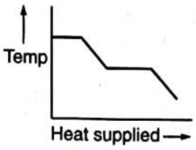
(c) 40.45 kJ $K^{-1}mol^{-1}$ (d) 75.48 kJ $K^{-1}mol^{-1}$

57. A block of ice at –10°C is slowly heated and converted to steam at 100°C. Which of the following curves represents the phenomenon correctly.

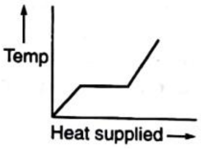
(a)



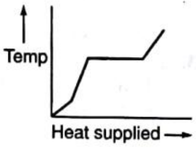
(b)



(c)



(d)



58. Select the incorrect statement :

(a) during adiabatic change specific heat is zero

(b) during isothermal change specific heat is infinite

(c) the ratio of the slopes of adiabatic and isothermal change is equal to γ

(d) a room can be cooled by opening the door of a running refrigerator in a closed room

59. Select the incorrect statement :

(a) work can be completely converted into heat

(b) heat can be completely converted into work

(c) chemical energy a part of internal energy can be converted into kinetic energy

(d) during condensation, kinetic energy remains constant

60. A mixture contains n_1 moles of monoatomic gas and n_2 moles of diatomic gas. If $\gamma = 1.50$ for mixture, the ratio of $n_1 : n_2$ is :

(a) 1 : 1 (b) 1 : 2

(c) 2 : 1 (d) 2 : 3

61. For the reaction, $2Cl(g) \longrightarrow Cl_2(g)$, the signs of ΔH and ΔS respectively are :

(a) +, – (b) +, +

(c) –, – (d) –, +

62. What is ΔG for the reaction $X_2O_4(l) \longrightarrow 2XO_2(g)$; at 27°C Given ΔU and ΔS are 2.1 k cal mol^{-1} and 20 cal $K^{-1}mol^{-1}$:

(a) 2.7 k cal (b) 1.5 k cal

(c) 3.3 k cal (d) 4.4 k cal

63. Which process is isothermal and adiabatic both ?

(a) Free expansion of ideal gas

(b) Work done by gas at constant temperature

(c) Work done on gas at constant temperature

(d) Cyclic process

64. For water $\Delta H_{vap} = 540 \text{cal g}^{-1}$. ΔS for water at its boiling point 100°C in cal $K^{-1}mol^{-1}$ is :

(a) 540 (b) 1.45

(c) 26.06 (d) 35.60

65. The efficiency of an engine operating between 110°C and an unknown temperature *T* is 23.3%. What is *T*?

(a) 394 K (b) 294 K

(c) 194 K (d) 494 K

66. Enthalpy of vaporisation of a certain liquid is 24.914 kJ mol^{-1} and the entropy of vaporisation is 94.684 $JK^{-1}mol^{-1}$. The temperature at which both the phases coexist is :

(a) 263.12 K (b) 363.12 K

(c) 10 K (d) 110 K

67. The enthalpy of a system increases by 50 kJ when its internal energy is increased by 113 kJ. What is the pressure in k Nm^{-2} of the system if the volume of gas is reduced by 10 m^3 at constant pressure ?

(a) 16.13 (b) 6.3

(c) 5 (d) 30.2

68. The reaction between H_2 and O_2 to produce water vapour is given by the equation : $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$

The work done at STP is :

(a) –2.27 J (b) +2.27 J

(c) –2.27 kJ (d) +2.27 kJ

69. The molar heat capacity of a diatomic gas at constant pressure is :

(a) 8.314 $JK^{-1}mol^{-1}$ (b) 20.8 $JK^{-1}mol^{-1}$

(c) 29.1 $JK^{-1}mol^{-1}$ (d) 28.0 $JK^{-1}mol^{-1}$

70. Select the correct statement about

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$

(a) work is done on surroundings

(b) work done is negative

(c) work done is positive

(d) no work is done

71. The change in internal energy (in J mol^{-1}) of 1 mole of a diatomic gas when its temperature increases by 15°C.

(a) 75 (b) 311.75

(c) 41.59 (d) 83.14

72. Select the correct statement :

(i) standard Gibb's energy has no effect on equilibrium constant

(ii) standard Gibb's energy is proportional to logarithm of equilibrium constant

(iii) equilibrium constant can be obtained from standard Gibb's energy

(iv) only K_p can be obtained from standard Gibb's energy

(a) (i) and (iv) (b) (ii) and (iii)

(c) (i) and (ii) (d) (iii) and (iv)

73. For a given reaction $\Delta H = 35.5$ kJ mol^{-1} and $\Delta S = 83.6$ JK^{-1}mol^{-1}. The reaction is spontaneous at :

(Assume that ΔH and ΔS do not vary with temperature)

(a) T < 425 K
(b) T > 425 K
(c) all temperatures
(d) T > 298 K

74. A gas is allowed to expand in a well insulated container against a constant external pressure of 2.5 atm from an initial volume of 2.50 L to a final volume of 4.50 L. The change in internal energy ΔU of the gas in joule will be :

(a) 1136.25 J
(b) −500 J
(c) −505 J
(d) +505 J

SOLUTIONS (One Answer Correct)

1. (b) $\Delta S_v = \dfrac{\Delta H_v}{T} = \dfrac{29\times10^{+3}}{300} = 96.67\ \text{JK}^{-1}\ \text{mol}^{-1}$

$= \dfrac{96.67}{86} = 1.124\ \text{JK}^{-1}\ \text{g}^{-1}$

2. (a) $\Delta G = \Delta H - T\Delta S$

$= -1202 - (-217\times10^{-3}\times300) = -1136.9$ kJ

Heat released will be absorbed by the surroundings to increase the entropy of surroundings.

$$\Delta S_{\text{surr.}} = +\frac{1202\times10^3}{300} = +4.01\times10^3\ \text{J mol}^{-1}$$

$\therefore\ \Delta S_{\text{total}} = -217 + 4.01\times10^3 = +3793\ \text{J mol}^{-1}$

3. (b) $\Delta_r G^\circ$ for $2Fe_2O_3 + 6CO \longrightarrow 4Fe + 6CO_2$

$= \Delta_r G_1^\circ + \Delta_r G_2^\circ$

$= +1487 - 1543.2 = -56.2\ \text{kJ mol}^{-1}$

The reduction occurs spontaneously in lower part of blast furnace.

4. (b) Net work done = Area covered by PV curve

= Area of ΔABE + Area of square $BCEF$ + Area of ΔCDF

$$= -\left[\frac{1}{2}(3\times10^{+5} - 1\times10^5)\times2\right.$$
$$\left. + 3\times10^5\times2 + \frac{1}{2}[(1\times10^5 - 3\times10^5)\times1]\right]$$

$= -[2\times10^5 + 6\times10^5 - 1\times10^5] = -7\times10^5$ J

5. (c) For adiabatic expansion PV^γ = constant

On differentiating $P\cdot\gamma\cdot V^{\gamma-1}dV + V^\gamma dP = 0$

$$-P.\gamma.V^{\gamma-1}dV = V^\gamma dP \text{ or } \frac{dP}{P} = -\gamma\cdot\frac{V^{\gamma-1}}{V^\gamma}dV = -\gamma\cdot\frac{dV}{V}$$

6. (a) $C_p - C_v = R$

$$c_p - c_v = \frac{R}{M}$$

$$\frac{c_p}{c_v} = \gamma$$

$\therefore\ c_p - \dfrac{c_p}{\gamma} = \dfrac{R}{M}$

$\therefore\ c_p\dfrac{(\gamma-1)}{\gamma} = \dfrac{R}{M}$

$\therefore\ c_p = \dfrac{R\gamma}{(\gamma-1).M}$

7. (d) $\Delta_r S_4^\circ = \Sigma S_P - \Sigma S_R = cS_C^\circ + dS_D^\circ - 0 - 0$

8. (d) $T = K\times P^{2/5}$

$\because PV = RT = R.K.P^{2/5}$ or $P^{3/5}\times V = K'$ or $PV^{5/3} = K'$

or $PV^\gamma = K'$ (γ for He = 5/3)

$\therefore$ Process is adiabatic and $\Delta H = 0$.

9. (a) Adiabatic slope are more steeper than isothermal

Slope of adiabatic process = $\gamma\times$ slope of isothermal process

10. (a) PV^γ = constant or $\log P = -\gamma\log v$

γ is slope for $P - V$ plots for He, O_2 and O_3, *i.e.*, $\frac{5}{3}, \frac{7}{5}$ and $\frac{4}{3}$ respectively.

11. (c) VT^3 = constant,

Also, $V^{\gamma-1}.T$ = constant for adiabatic expansion

$\therefore\ V.T^{\frac{1}{\gamma-1}}$ = constant or $\dfrac{1}{\gamma-1} = 3$

$\gamma = \dfrac{4}{3}$, *i.e.*, polyatomic gas.

12. (d) Ratio of slope $= \dfrac{\gamma \text{ for gas I}}{\gamma \text{ for gas II}}$; slope for He, N_2 and O_3 are 5/3, 7/5 and 4/3 respectively.

13. (d) $\Delta S = 2.303\, nR \log\dfrac{V_2}{V_1} = 2.303\times1\times8.314\log10$

$$= 19.15\ \text{J K}^{-1}\ \text{mol}^{-1}.\left(\frac{V_2}{V_1} = 10 \text{ for all}\right)$$

14. (a) Net work done during the complete cycle is equal to area under the cycle (−ve if cycle is clockwise, *i.e.*, work done by the gas and +ve when cycle is anticlockwise, *i.e.*, work done on the gas)

$$w = -P\times V = -(2P - P)\times(2V - V) = -PV$$

15. (d) $\left(\dfrac{\delta H}{\delta T}\right)_P = \infty$ $\therefore C_P = \infty$

(δT is zero at constant P and T)

16. (a) Mole of hexane $= \dfrac{8.6}{86} = 0.1$,

Mole of heptane $= \dfrac{10}{100} = 0.1$

Also, $\Delta S = R\,\Sigma X\cdot\ln X$, when X is mole fraction.

17. (b) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ ΔH° for $H_2O \rightleftharpoons H^+ + OH^-$ is + 13.7 kcal

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{+13.7 + 19.14}{298}$$

$= 0.1102\ \text{kcal K}^{-1}\text{mol}^{-1} = 110.2\ \text{cal K}^{-1}\ \text{mol}^{-1}$

18. (c) $C_p - C_v = \frac{R}{M} \quad \therefore \quad M = 40$, *i.e.*, gas is Argon.

19. (a) Work done in (–ve) reversible process is maximum. Thus, in reversible process $T_{f\ \text{rev.}} << T_{f\ \text{irrev.}}$

20. (b) $\eta_1 = \frac{T_2 - T_1}{T_2} = \frac{1}{6}$

$$\eta_2 = \frac{T_2 - (T_1 - 62)}{T_2} = 2 \times \frac{1}{6} = \frac{1}{3}$$

$$\therefore T_1 = 372\,\text{K} = 99^\circ\,\text{C}$$

$$T_2 = 310\,\text{K} = 37^\circ\,\text{C}$$

21. (a) Efficiency $= 1 - \frac{T_{\text{sink}}}{T_{\text{source}}}$

$$= 1 - \frac{300}{400} = 25\%$$

22. (a) $q = 0$ for insulated container.

23. (d) $\eta = \frac{W}{Q} = 1 - \frac{T_2}{T_1}$

(T_1, T_2 are temperature of source and sink respectively)

$$\therefore \quad \frac{W}{6 \times 10^3} = 1 - \frac{400}{500}$$

$$\therefore \quad W = 1.2 \times 10^3\ \text{cal} = 1.2\ \text{kcal}$$

24. (c) $\Delta G = -nEF \qquad 4e + (\text{O}^0)_2 \rightarrow 2\text{O}^{-2}$

$$-827 \times 10^3 = -4 \times E \times 96500$$

$$\therefore \quad E = \frac{827 \times 10^3}{4 \times 96500} = 2.14\ \text{V}$$

25. (a) $\text{C}_{(G)} \rightarrow \text{C}_D \qquad \left[\begin{array}{l} V_D = \frac{12}{3}\ \text{mL} \\ V_G = \frac{12}{2}\ \text{mL} \end{array}\right]$

$$\Delta H = \Delta U + P_2V_2 - P_1V_1$$

$$\Delta H - \Delta U = P \times (V_D - V_G)$$

$$-10^2\ \text{J} = P \times \left[\frac{12}{3} - \frac{12}{2}\right] \times 10^{-6}$$

$$P = \frac{10^{+2}}{10^{-6} \times 2} = 5 \times 10^7\ \text{Nm}^{-2}$$

26. (d) Work done by gas adiabatic process

$$= \frac{nR}{\gamma - 1}[T_i - T_f] = \frac{R \times (T_i - T_f)}{\frac{5}{3} - 1} = 6R$$

$$\therefore \quad T_f - T_i = -4$$

$$T_f = [T_i - 4]\ \text{K}$$

27. (a) For irreversible process which are spontaneous $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$.

28. (d) $C_p = \frac{7}{2}R \qquad \therefore C_v = \frac{7}{2}R - R = \frac{5}{2}R$

$$\therefore \quad \gamma = \frac{C_p}{C_v} = \frac{7}{5} = 1.44, \textit{ i.e.}, \text{ diatomic gas.}$$

29. (c) At eq. $\Delta G = 0$

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

$$T = \frac{\Delta H}{\Delta S} = \frac{30 \times 10^3}{105} = 285.7\ \text{K}$$

30. (a) For a cyclic process change in internal energy ΔU is zero.

31. (b) Decomposition of PCl_5 is endothermic process. Also formation of two gas results increase in disorder.

32. (a) For cyclic process $dU = 0$, on absorbing heat work is done by the system

$$\therefore \quad q = dU + (-w)$$

$\therefore \quad q = -w =$ area occupied by circle

$$= \pi r^2 = \frac{22}{7} \times 10^2 = \frac{22}{7} \times 10^2\ \text{J}$$

33. (b) $C_p - C_v = R$ as the value of C_p and C_v are expressed for 1 mole.

No doubt the difference in molar heat capacity, *i.e.*, $2C_p - 2C_v = 2(C_p - C_v) = 2R$

34. (c) For cyclic process ; $q = -w =$ area occupied by circle

$$= \pi \times \left(\frac{P_2 - P_1}{2}\right)\left(\frac{V_2 - V_1}{2}\right)$$

$$= \frac{\pi}{4}(P_2 - P_1) \times (V_2 - V_1)$$

$$= \frac{\pi}{4}(P_2 - P_1)^2 = \frac{\pi}{4}(V_2 - V_1)^2$$

$\because \quad P_2 - P_1 = V_2 - V_1$ for circle

35. (d) Net work done $= w_{AB} + w_{BC} + w_{CA}$ (All are clockwise)

(w_{AB} is expansion work, w_{BC} is compression work and $w_{CA} = 0$

$$= \left[-\frac{1}{2}(P_2 + P_1)(V_2 - V_1)\right] + P_2(V_2 - V_1) + 0$$

$$= \left[-\frac{1}{2}(6P_1 + P_1)(3V_1 - V_1)\right] + P_1(3V_1 - V_1)$$

$$= -7P_1V_1 + 2P_1V_1 = -5P_1V_1$$

36. (d) $2\text{H}_2\text{O}_{2(l)} \rightarrow 2\text{H}_2\text{O}_{(l)} + \text{O}_{2(g)}$

Mole of $\text{H}_2\text{O}_2 = \frac{3.4}{34} = 0.1$

$\therefore$ Mole of O_2 formed $= 0.05$

$\therefore$ Work done by the gas $\text{O}_2 = -P \times \Delta V$

$$= \Delta nRT = -0.05 \times 298 \times 8.314$$

$$= -123.86\ \text{J}$$

37. (a) For adiabatic process $T^{\frac{\gamma}{1-\gamma}} \cdot P = \text{constant}$

$$P \propto T^3 \quad \therefore \quad PT^{-3} = \text{constant}$$

or $\qquad \frac{\gamma}{1 - \gamma} = -3 \quad \therefore \quad \gamma = \frac{3}{2}$

38. (d) For adiabatic expansion

$$PV^\gamma = \text{constant}$$

$$\gamma PV^{\gamma - 1}dV + V^\gamma dP = 0$$

$$\gamma PdV + VdP = 0$$

Slope $= \frac{dP}{dV} = -\frac{\gamma P}{V}$

For mono atomic slope $= -\frac{1.67P}{V}$

For diatomic slope $= -\frac{1.4P}{V}$

For polyatomic slope $= -\frac{1.33\,P}{V}$

39. (d) CD is isochoric as V remains constant.

40. (c) $\int dw = -\int P dv$

$$= -\int 6V^2 dv = -6\int \frac{V_2^3}{3} - \frac{V_1^3}{2}\Bigg]$$

$$= -6\left[\frac{3^3}{3} - \frac{1^3}{3}\right] = -6\times\frac{26}{3} = 52\,\text{bar m}^3$$

41. (b) $V = \frac{nRT}{P} = \frac{100\times 0.0821\times T}{8.21} = T$

$\therefore\ \log V = \log T$

or slope of line is 1.

42. (c) $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$ $\qquad (\because\ T\gamma^{1-\gamma} = \text{constant})$

$$\frac{T_2}{T_1} = \left(\frac{27}{8}\right)^{\frac{5}{3}-1} = \frac{9}{4}$$

$\therefore\ T_2 = \frac{9}{4}\times 300 = 675\,\text{K}$

$\therefore$ rise in temperature $= 675 - 300 = 375$ K

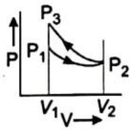
43. (c) $P_1V_1^{\gamma} = P_2V_2^{\gamma}$

$$\frac{P_1}{P_2} = \left(\frac{V_2}{V_1}\right)^{\gamma} = \left(\frac{\rho_1}{\rho_2}\right)^{\gamma} = (32)^{7/5} \qquad \left[\because V \propto \frac{1}{\rho}\right]$$

$$= (2^5)^{7/5} = 2^7 = 128$$

44. (c) Slope of isothermal curve is lesser than adiabatic and thus PV work done in compression is lesser than PV work done in expansion, *i.e.*, net work is done by gas or $w = -$ve.

45. (a) Work done = Area under P-V curve between volume V_1 and V_2.



46. (a) Equation of line AB is

$$Y - Y_1 = \frac{Y_1 - Y_2}{X_1 - X_2}(X - X_1)$$

$$P - 3P_0 = \frac{3P_0 - P_0}{V_0 - 3V_0}(V - V_0) \qquad \text{...(i)}$$

$$\frac{nRT}{V} - 3P_0 = -\frac{P_0}{V_0}(V - V_0)$$

or $\quad nRT = 3P_0V - \frac{P_0}{V_0}\cdot V^2 + P_0V \qquad$ ...(ii)

Differentiating w.r.t. V

$$\frac{nRdT}{dV} = 3P_0 - \frac{2P_0}{V_0}\cdot V + P_0 = 4P_0 - \frac{2P_0}{V_0}\cdot V$$

For max. value of T, $\frac{dT}{dV} = 0$

$\therefore\ P^0\left[4 - \frac{2V}{V_0}\right] = 0$ or $V = 2V_0$

Now from (ii)

$$nRT_{\max} = 6P_0\cdot V_0 - \frac{P_0}{V_0}\cdot 4V_0^2 + P_0\cdot 2V_0 = 4P_0V_0$$

$\therefore\ T_{\max} = \frac{4P_0V_0}{nR}$

47. (b) $\Delta C_p = \frac{\Delta H}{\Delta T}$ At equilibrium $\Delta T = 0$

48. (d) Due to low molar mass, H-atom will move more fastly and thus show more disorder.

49. (d) During compression for isothermal process

$$\Delta S = nR\ln\frac{V_2}{V_1} = -R\ln 2 \qquad \left(V_2 = \frac{V_1}{2}\right)$$

During heating for isochoric process

$$\Delta S = nC_v\ln\frac{T_2}{T_1} = C_v\ln 2 \qquad (T_2 = 2T_1)$$

Thus, total change in entropy $= C_v\ln 2 - R\ln 2$
$= (C_v - R)\ln 2$

50. (b) For adiabatic process $TV^{\gamma-1} =$ constant

Given $T(V)^{1/2} =$ constant

$\therefore \qquad \gamma - 1 = \frac{1}{2}$

or $\qquad \gamma = \frac{3}{2} = 1.5$

51. (a) $-\Delta S = \frac{dq}{T} = \frac{\text{Work done by the gas } (W)}{T}$

$$W = -\Delta S\times T = \frac{-\Delta S\times PV}{nR}$$

52. (a) Initial equilibrium

$$\Delta G = \Delta G^\circ + RT\ln Q$$

$$-10 = \Delta G^\circ + RT\ln\frac{(1)^3}{(1)^3}$$

$\therefore \qquad \Delta G^\circ = -10$ kJ

Thus, ΔG° for the reverse reaction $= +\,10000$ J

$2Fe(s) + \underset{2\text{ mole}}{3CO_2} \rightleftharpoons Fe_2O_3(s) + \underset{2\text{ mole}}{3CO}$;

$\Delta G^\circ = 10000$ J

Also, $\Delta G = \Delta G^\circ + 2.303RT\log_{10}\frac{(2)^3}{(2)^3}$

$= 10000 + 0$

$= 10000$ J

53. (c) $\frac{u_{rmsT_1}}{u_{rmsT_2}} = \sqrt{\frac{T_1}{T_2}}$

$$\frac{2\times u}{u} = \sqrt{\frac{T_1}{T_2}} \qquad \left(u_{rmsT_2} = \frac{u_{rmsT_1}}{2}\right)$$

or $\qquad \frac{T_1}{T_2} = 4$

i.e., $\qquad T_2 = \frac{T_1}{4}$

From $TV^{\gamma-1} =$ constant for adiabatic expansion

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

or $\qquad \left[\frac{V_1}{V_2}\right]^{\gamma-1} = \frac{T_2}{T_1} = \frac{1}{4}$

$\therefore \quad \left(\frac{V_1}{V_2}\right)^{1.4-1} = \frac{1}{4}$

or $\quad \frac{V_2}{V_1} = 32$

54. (a) At A : $T_1 = \frac{PV}{nR} = \frac{1 \times 22.44}{1 \times 0.0821} = 273\text{ K}$

At B : $T_2 = \frac{PV}{nR} = \frac{1 \times 44.88}{1 \times 0.0821} = 546\text{ K}$

At C : $T_3 = \frac{PV}{nR} = \frac{0.5 \times 44.88}{1 \times 0.0821} = 273\text{ K}$

55. (a) Equation of line AB is $Y - Y_1 = \frac{Y_1 - Y_2}{X_1 - X_2}(X - X_1)$

$$P - 3P_0 = \frac{3P_0 - P_0}{V_0 - 3V_0}(V - V_0) \qquad \ldots \text{(i)}$$

$$\frac{nRT}{V} - 3P_0 = -\frac{P_0}{V_0}(V - V_0)$$

or
$$nRT = 3P_0V - \frac{P_0}{V_0}V^2 + P_0V \qquad \ldots \text{(ii)}$$

Differentiating w.r.t. V

$$\frac{nRdT}{dV} = 3P_0 - \frac{2P_0}{V_0}V + P_0 = 4P_0 - \frac{2P_0}{V_0}V$$

For max. value of T, $\frac{dT}{dV} = 0$

$$\therefore \quad P^0\left[4 - \frac{2V}{V_0}\right] = 0 \text{ or } V = 2V_0$$

Now from (ii)

$$nRT_{\text{max}} = 6P_0V_0 - \frac{P_0}{V_0}4V_0^2 + P_0 2V_0 = 4P_0V_0$$

$$\therefore \quad T_{\text{max}} = \frac{4P_0V_0}{nR}$$

56. (b) $\Delta C_p = \frac{\Delta H}{\Delta T}$ At equilibrium $\Delta T = 0$

57. (a) At f.pt. and b.pt., curves become parallel to x-axis during phase transition.

58. (d) Rest all are correct.

59. (b) It is against the 2nd law of thermodynamics.

60. (a)
$$C_{v_m} = \frac{n_1 \times \frac{3R}{2} + n_2 \times \frac{5R}{2}}{n_1 + n_2} = \frac{3Rn_1 + 5Rn_2}{2(n_1 + n_2)}$$

$$C_{p_m} = \frac{n_1 \times \frac{5}{2} + n_2 \times \frac{7R}{2}}{n_1 + n_2} = \frac{5Rn_1 + 7Rn_2}{2(n_1 + n_2)}$$

$$\therefore \quad \frac{C_{p_m}}{C_{v_m}} = 1.50 = \frac{5R \times n_1 + 7R \times n_2}{3R \times n_1 + 5R \times n_2}$$

or
$$4.50Rn_1 + 7.5Rn_2 = 5Rn_1 + 7Rn_2$$
$$0.5Rn_2 = 0.5Rn_1$$

$$\therefore \quad \frac{n_1}{n_2} = 1$$

61. (c) Formation of bond releases energy *i.e.*, $\Delta H = -$ ve. Also entropy decreases during association *i.e.*, $\Delta S = -$ve.

62. (a)
$$\Delta H = \Delta U + \Delta nRT$$
$$= 2100 + 2 \times 2 \times 300$$
$$= 3300 \text{ cal/mol}$$
$$\Delta G = \Delta H - T\Delta S$$
$$= 3300 - 300 \times 20$$
$$= 2700 \text{ cal}$$

63. (a) For free expansion $P_{ext} = 0; dw = 0; dq = 0;$

$\therefore \quad du = 0$ and so $dT = 0$

64. (c)
$$\Delta S = \frac{\Delta H}{T} = \frac{540 \times 18}{373}\text{ cal mol}^{-1}$$
$$= 26.06 \text{ cal K}^{-1}\text{ mol}^{-1}$$

65. (b)
$$\eta = \frac{T_2 - T_1}{T_2}$$
$$\frac{23.3}{100} = \frac{383 - T}{383}$$
$$\therefore \quad T = 294\text{ K}$$

66. (a) For: Liquid $\rightleftharpoons$ Vapour $\qquad \Delta G = 0$

$\therefore \quad \Delta H = T\Delta S$

$$T = \frac{\Delta H}{\Delta S} = \frac{24.914 \times 10^3}{94.684} = 263.12\text{ K}$$

67. (b)
$$\Delta H = \Delta U + P\Delta V$$
$$\therefore \quad P = \frac{\Delta H - \Delta U}{\Delta V} = \frac{50 - 113}{-10} = 6.3\text{ k Nm}^{-2}$$

68. (c)
$$w = P(V_2 - V_1)$$

At STP, $\text{P} = 101325\text{ Nm}^{-2}$

Initial volume $= 3 \times 22.4\text{ dm}^3$

$= 67.2\text{ dm}^3 = 67.2 \times 10^{-3}\text{ m}^{-3}$

Final volume $= 2 \times 22.4\text{ dm}^3$

$= 44.8\text{ dm}^3 = 44.8 \times 10^{-3}\text{ m}^{-3}$

$$\therefore \quad w = 101325 \times [44.8 \times 10^{-3} - 67.2 \times 10^{-3}]$$
$$= -101325 \times 22.4 \times 10^{-3}$$
$$= -2.27\text{ kJ}$$

69. (c)
$$C_p = \frac{5}{2}R + R = \frac{7}{2}R = \frac{7 \times 8.314}{2}$$
$$= 29.1\text{ JK}^{-1}\text{mol}^{-1}$$

70. (d) $\Delta n = 0$

71. (b) $\Delta U = n \times C_v \times \Delta T = 1 \times \frac{5}{2} \times 8.314 \times 15 = 311.75$

72. (b) $\Delta G^\circ = 2.303RT\log K_p$

73. (b) For a spontaneous reaction, $\Delta G = -$ve, Thus from

$$\Delta H < T\Delta S$$
$$T > \frac{\Delta H}{\Delta S} = \frac{35.5 \times 1000}{83.6} = 425\text{ K}$$

74. (c) $q = 0$ (For insulated systems)

From I law $q = \Delta U + (-W)$ Work done by the system

$$\Delta U = +W$$
$$\therefore \quad \Delta U = W = -P_{ext} \times \Delta V$$
$$= -2.5 \times (4.5 - 2.5)$$
$$= -5 \text{ L-atm}$$
$$= -5 \times 101 = -505\text{ J}$$

• PREVIOUS YEARS PROBLEMS •

1. A monoatomic ideal gas undergoes a process in which the ratio of P to V at any instant is constant and equals to 1 atm litre^{-1}. What is the molar heat capacity of gas? **(IIT 2006)**

(a) $\frac{4R}{2}$ (b) $\frac{3R}{2}$

(c) $\frac{5R}{2}$ (d) 0

2. Which one of the following statement is false? **(IIT 2001)**

(a) Work is a state function
(b) Temperature is state function
(c) Change in the state is completely defined when initial and final states are specified
(d) Work appears at the boundary of the system

3. In thermodynamics, a process is called reversible when: **(IIT 2001)**

(a) surroundings and system changes into each other
(b) there is no boundary between system and surroundings
(c) the surroundings are always in equilibrium with system
(d) the system changes into the surroundings spontaneously

4. One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95 K) $\rightarrow$ (4.0 atm, 5.0 L, 245 K) when a change in internal energy $\Delta U = 30.0$ L - atm. The change in enthalpy (ΔH) of the process is L-atm is: **(IIT 2002)**

(a) 40.0
(b) 42.3
(c) 44.0
(d) not defined because pressure is not constant

5. Two mole of an ideal gas expanded isothermally and reversibly from 1 litre to 10 litre at 300 K. The enthalpy change (in kJ) for the process is: **(IIT 2004)**

(a) 11.4 (b) −11.4
(c) 0 (d) 4.8

6. The enthalpy of vaporisation of a liquid is 30 kJ mol^{-1} and entropy of vaporisation is 75 J mol^{-1} K^{-1}. The boiling point of the liquid at 1 atm is: **(IIT 2004)**

(a) 250 K (b) 400 K
(c) 450 K (d) 600 K

7. When one mole of monoatomic ideal gas T K undergoes reversible adiabatic change under a constant external pressure of 1 atm changes volume from 1 litre to 2 litre. The final temperature in kelvin would be: **(IIT 2005)**

(a) $\frac{T}{(2)^{2/3}}$ (b) $T + \frac{2}{3 \times 0.081}$

(c) T (d) $T - \frac{3}{2 \times 0.0821}$

8. The direct conversion of A to B is difficult, hence it is carried out as:

$$A \longrightarrow C \longrightarrow D \longrightarrow B$$

Given, $\Delta S_{(A \to C)} = 50\, eU$; $\Delta S_{(C \to D)} = 30\, eU$; $\Delta S_{(B \to D)} = 20\, eU$; where eU is entropy unit. Thus change in entropy in $(A \to B)$ is: **(IIT 2006)**

(a) 100 eU (b) 60 eU
(c) − 100 eU (d) − 60 eU

9. For the reaction : $H_2O_{(l)}$ (1 bar, 373 K) $\longrightarrow H_2O_{(g)}$ (1 bar, 373 K), the correct set of thermodynamic parameters is: **(IIT 2007)**

(a) $\Delta G = 0, \Delta S = +$ ve (b) $\Delta G = 0, \Delta S = -$ ve
(c) $\Delta G = +$ ve, $\Delta S = 0$ (d) $\Delta G = -$ ve, $\Delta S = +$ ve

10. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and w for the process will be: ($R = 8.314$ J/mol K) (ln 7.5 = 2.01) **[JEE (Main) 2013]**

(a) $q = -208$ J, $w = +208$ J (b) $q = +208$ J, $w = +208$ J
(c) $q = +208$ J, $w = -208$ J (d) $q = -208$ J, $w = -208$ J

11. For the process

$H_2O(l) \longrightarrow H_2O(g)$

at $T = 100°$C and 1 atmosphere pressure, the correct choice is: **[JEE (Advanced-II) 2014]**

(a) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surrounding}} > 0$
(b) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surrounding}} < 0$
(c) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surrounding}} > 0$
(d) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surrounding}} < 0$

12. One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings (ΔS_{surr}) in JK^{-1} is:

(1 L atm = 101.3 J) **[JEE (Advanced) I 2016]**

(a) 5.763 (b) 1.013
(c) − 1.013 (d) − 5.763

13. ΔU is equal to: **[JEE (Main) 2017]**

(a) Isochoric work (b) Isobaric work
(c) Adiabatic work (d) Isothermal work

14. The standard state Gibbs free energies of formation of C (graphite) and C (diamond) at $T = 298$ K are

$\Delta_f G°$ [C (graphite)] = 0 kJ mol^{-1}

$\Delta_f G°$ [C (diamond)] = 2.9 kJ mol^{-1}

The standard state means that the pressure should be 1 bar, and substance should be pure at a given temperature. The conversion of graphite [C(graphite)] to diamond [C(diamond)] reduces its volume by 2×10^{-6} m^{3}mol^{-1}. If C(graphite) is converted to C(diamond) isothermally at T = 298 K, the pressure at which C(graphite) is in equilibrium with C(diamond), is:

[JEE (Advanced) II 2017]

[Useful information : 1 J = 1 kg m^2s^{-2}; 1 Pa = 1 kg $m^{-1}s^{-2}$; 1 bar = 10^5 Pa]

(a) 14501 bar (b) 29001 bar
(c) 58001 bar (d) 1450 bar

SOLUTIONS (Previous Year Problems)

1. (a) $\left(\frac{\delta H}{\delta T}\right)_P = \left(\frac{\delta U}{\delta T}\right)_P + P\left(\frac{\Delta V}{\Delta T}\right)_P$

Now $PV = RT$

or $(V \times 1) \cdot V = RT$ $\left[\because \frac{P}{V} = 1\, l\, \text{atm}^{-1}\right]$

or $V^2 = RT$

or $2V\left(\frac{\delta V}{\delta T}\right)_P = \frac{R}{1}$

or $\left(\frac{\delta V}{\delta T}\right)_P = \frac{R}{2V \times (1\,\text{atm}\, l^{-1})}$

$\therefore\ C_p = C_v + \frac{P \times R}{2V} = \frac{3}{2}R + \frac{R}{2} = 2R$ $\left(\because \frac{P}{V} = 1\right)$

2. (a) Work is not a state function. State functions are P, T, V, U, H, S, etc. State functions are path independent.

3. (c) During reversible process, the internal equilibrium is disturbed only infinitesimally small and in the limit, it is not disturbed at all. Thus, system and surroundings remain in equilibrium.

4. (c)

$$\begin{aligned} H &= U + PV \\ \Delta H &= \Delta U + \Delta(PV) \\ &= \Delta U + P_1(V_2 - V_1) + V_2(P_2 - P_1) \\ &= 30 + 2(5-3) + 5 \times (4-2) \\ &= 44 \text{ L-atm} \end{aligned}$$

5. (c) For 1 mole $\Delta H = \Delta U + P\Delta V$

$$\begin{aligned} &= C_v(T_2 - T_1) + R(T_2 - T_1) \\ \Delta H &= (C_v + R)(T_2 - T_1) \\ &= (C_v + R)\Delta T \end{aligned}$$

$\because\ \Delta T = 0$ $\therefore \Delta H = 0$

6. (b) $\Delta S = \frac{\Delta H_{\text{vap.}}}{T}$

$\therefore\ T = \frac{\Delta H_{\text{vap.}}}{\Delta S} = \frac{30 \times 10^3}{75} = 400\text{ K}$

7. (a) $TV^{\gamma-1} = K$

$\therefore\ T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$ $\left(\gamma = \frac{5}{3}\right)$

$T_1V_1^{2/3} = T_2V_2^{2/3}$

or $T_1(1)^{2/3} = T_2(2)^{2/3}$

or $T_2 = \frac{T_1}{(2)^{2/3}} = \frac{T}{(2)^{2/3}}$

8. (b)

$$\begin{aligned} \Delta S_{A\to B} &= \Delta S_{A\to C} + \Delta S_{C\to D} + \Delta S_{D\to B} \\ &= 50 + 30 - 20 = 60\, eU \end{aligned}$$

$(\Delta S_{B\to D} = 20,\ \therefore\ \Delta S_{D\to B} = -20)$

9. (a) $S_{(g)} > S_{(l)}$ and the process is spontaneous at 100°C and is in equilibrium. Thus $\Delta G = 0$

10. (c) The given process is isothermal, hence $\Delta U = 0$

$\therefore\ q = -w$

$\because\ q = 208\text{ J}$

$\therefore\ w = -208\text{ J}$ (*i. e.* work done by the system)

11. (b) At 100°C and 1 atmosphere pressure, water shows equilibrium in two phases as $H_2O(l) \rightleftharpoons H_2O(g)$ and thus for equilibrium $\Delta S_{\text{total}} = 0$ and

$\therefore\ \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = 0$

For change of liquid to gases state, ΔS_{sys} is +ve and therefore $\Delta S_{\text{surr.}}$ will be – ve.

$\therefore\ \Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surrounding}} < 0$

12. (c) $\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} = -\frac{q_{\text{sys}}}{T} = \frac{W_{\text{sys}}}{T}$

($\because$ Isothermal expansion $\Rightarrow \Delta U = 0$)

$$\begin{aligned} \Delta S_{\text{surr}} &= \frac{-P_{\text{ext}}(V_f - V_i)}{T} = \frac{-3(2-1)}{300}\text{ L atm K}^{-1} \\ &= -0.01\text{ L atm K}^{-1} = -0.01 \times 101.3\text{ JK}^{-1} \\ &= -1.013\text{ JK}^{-1} \end{aligned}$$

Note : The temperature of surroundings has been assumed to be 300 K.

13. (c) For adiabatic process, $q = 0$

From 1st law of thermodynamics, $\Delta U = W$

14. (a)

$$\begin{aligned} \Delta G^\circ &= \Delta V \cdot \Delta P \\ &= 2 \times 10^{-6}\Delta P \end{aligned}$$

or $\Delta P = \frac{\Delta G^\circ}{\Delta V} = \frac{29 \times 10^3 \times 10^6}{2}\text{ Pa}$

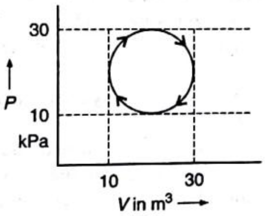
$$\begin{aligned} \Delta P &= 1.45 \times 10^9\text{ Pa} = \frac{1.45 \times 10^9}{10^5}\text{ bar} \\ &= 1.45 \times 10^4\text{ bar} \end{aligned}$$

$P_F - 1 = 14500\text{ bar}$

or $P_F = 14501\text{ bar}$

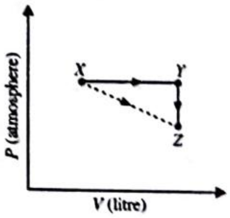
OBJECTIVE PROBLEMS (More Than One Answer Correct)

1. Select the correct statement :
   (a) There is a natural asymmetry between converting work to heat and converting heat to work.
   (b) No process is possible in which the sole results is the absorption of heat from a reservoir and its complete conversion into work.
   (c) For every chemical reaction at equilibrium standard change in Gibbs free energy is zero.
   (d) A constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy.
2. Which of the following are intensive properties?
   (a) Heat capacity (b) Refractive index
   (c) Specific volume (d) Entropy
3. Which of the following are extensive properties?
   (a) Elevation in b. pt. (b) b. pt.
   (c) f.pt. (d) E° of cell
4. Which one is not correct for a cyclic process as shown in figure?



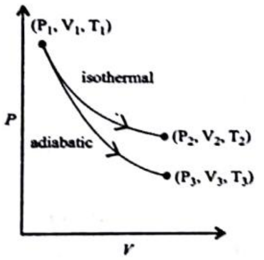
   (a) $dU = 0$ (b) $q = -w$
   (c) 314 J (d) 31.4 J
5. If w_1, w_2, w_3 and w_4 are work done in isothermal, adiabatic, isobaric and isochoric reversible expansion for an ideal gas then :
   (a) $w_3 > w_1$ (b) $w_1 > w_2$
   (c) $w_2 > w_4$ (d) $w_4 > w_2$
6. Average value of poisson's ratio for a mixture of 2 mole of each gas A and B is 1.66, then :
   (a) gases are monoatomic
   (b) gases are diatomic
   (c) average molar heat capacity at constant volume is 4 cal
   (d) average molar heat capacity at constant V is 3 cal
7. A reaction attains equilibrium state under standard conditions, then :
   (a) equilibrium constant $K = 0$
   (b) equilibrium constant $K = 1$
   (c) $\Delta G^\circ = 0$ and $\Delta H^\circ = T\Delta S^\circ$
   (d) $\Delta G = 0$ and $\Delta H = T\Delta S$
8. The poisson's ratio for O_2 is 1.4. Which are correct for O_2?
   (a) $C_v = 5$ cal (b) $c_v = 0.156$ cal
   (c) $C_p = \frac{R\gamma}{\gamma - 1}$ (d) $C_v = \frac{\cdot R}{(\gamma - 1)}$
9. Select the correct statements :
   (a) The magnitude of work involved in an intermediate irrversible expansion is less than that involved in reversible expansion
   (b) Heat absorbed during intermediate reversible expansion is more than that in intermediate reversible expansion
   (c) The magnitude of work involved in an intermediate reversible compression is more than that involved in intermediate irreversible compression
   (d) Heat released during intermediate irrversible compression is more than that in intermediate reversible compression
10. Select the correct statements for the equilibrium under standard conditions
    $H_2O_{(s)} \rightleftharpoons H_2O_{(l)};\ \Delta S_1^\circ$
    $H_2O_{(l)} \rightleftharpoons H_2O_{(v)};\ \Delta S_2^\circ$
    $H_2O_{(s)} \rightleftharpoons H_2O_{(v)};\ \Delta S_3^\circ$
    (a) $\Delta S_1^\circ > \Delta S_2^\circ$ (b) $\Delta S_2^\circ >>> \Delta S_1^\circ$
    (c) $\Delta S_3^\circ > \Delta S_2^\circ$ (d) $\Delta S_3^\circ > \Delta S_1^\circ$
11. A cyclic process is completed by process 1 and process 2. If ΔQ and ΔW represent heat supplied and work done respectively. ΔU_1 and ΔU_2 are the changes in internal energy of two process then:
    (a) $\Delta U_1 = \Delta U_2$ (b) $\Delta U_1 = -\Delta U_2$
    (c) $\Delta Q = \Delta W$ (d) $\Delta Q = -\Delta W$
12. For a reaction to be spontaneous in neither direction regarding the closed system:
    (a) $(\Delta G)_{T,P} = 0$ (b) $(\Delta G)_{T,P} = -\text{ve}$
    (c) $(\Delta S)_{U,V} = 0$ (d) $(\Delta S)_{U,V} = +\text{ve}$
13. Which of the following are not path dependent:
    (a) Work (b) Internal energy
    (c) Heat change (d) Entropy
14. Identify the intensive quantities from the following:
    (a) Enthalpy (b) Temperature
    (c) Volume (d) Refrative index
15. Among the following, the state function(s) is (are) : **(IIT 2009)**
    (a) Internal energy
    (b) Irreversible expansion work
    (c) Molar enthalpy
    (d) Reversible expansion work
16. Among the following the intensive property (properties) are: **(IIT 2010)**
    (a) Molar conductivity (b) Electromotive force
    (c) Resistance (d) Heat capacity

17. For an ideal gas, consider only P - V work in going from an initial state X to the final state Z. The final state Z can be reached by either of the two paths shown in the figure. Which of the following choice(s) is (are) correct? [take ΔS as change in entropy and w as work done] **(IIT 2012)**



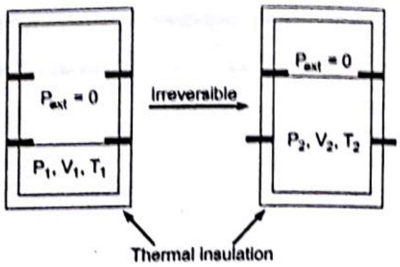
(a) $\Delta S_{x \to z} = \Delta S_{x \to y} + \Delta S_{y \to z}$
(b) $w_{x \to z} = w_{x \to y} + w_{y \to z}$
(c) $w_{x \to y \to z} = w_{x \to y}$
(d) $\Delta S_{x \to y \to z} = \Delta S_{x \to y}$

18. The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is (are) correct? **(IIT 2012)**



(a) $T_1 = T_2$
(b) $T_3 > T_1$
(c) $w_{\text{isothermal}} > w_{\text{adiabatic}}$
(d) $\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$

19. An ideal gas in a thermally insulated vessel at internal pressure $= P_1$, volume $= V_1$ and absolute temperature $= T_1$ expands irreversibly against zero external pressure, as shown in the diagram. The final internal pressure, volume and absolute temperature of the gas are P_2, V_2 and T_2, respectively. For this expansion,



[JEE (Advanced-I) 2014]

(a) $q = 0$ (b) $T_2 = T_1$
(c) $P_2V_2 = P_1V_1$ (d) $P_2V_2^{\gamma} = P_1V_1^{\gamma}$

20. An ideal gas is expanded from (P_1, V_1, T_1) to (P_2, V_2, T_2) under different conditions. The correct statement(s) among the following is (are): **[JEE (Advanced-I) 2017]**

(a) The work done on the gas is maximum when it is compressed irreversibly from (P_2, V_2) to (P_1, V_1) against constant pressure P_1
(b) The work done on the gas is less when it is expanded reversibly from V_1 to V_2 under adiabatic conditions as compared to that when expanded reversibly from V_1 to V_2 under isothermal conditions
(c) The change in internal energy of the gas (i) zero, if it is expanded reversibly with $T_1 = T_2$, and (ii) positive, if it is expanded reversibly under adiabatic conditions with $T_1 \neq T_2$
(d) If the expansion is carried out freely, it is simultaneously both isothermal as well as adiabatic

21. For a reaction taking place in a container in equilibrium with its surroundings, the effect of temperature on its equilibrium constant K in terms of change in entropy is described by: **[JEE (Advanced-II) 2017]**

(a) with increase in temperature, the value of K for exothermic reaction decreases because the entropy change of the system is positive
(b) with increase in temperature, the value of K for endothermic reaction increases because unfavourable change in entropy of the surroundings decreases
(c) with increase in temperature, the value of K for exothermic reaction decreases because favourable change in entropy of the surroundings decreases
(d) with increase in temperature, the value of K for endothermic reaction increases because the entropy change of the system is negative

SOLUTIONS (More Than One Answer Correct)

1. (b,d) $\Delta G = -$ ve for spontaneous process and $\Delta G^\circ \neq 0$ at equilibrium. Statement (b) represents carnot theorem.
2. (b,c,d) Mass independent properties are intensive.
3. (a) Mass dependent properties are extensive.
4. (a,b,c) For a cyclic process $dU = 0$

$\therefore\ q = \Delta U + (-w), \qquad q = -w$

Also, w = area covered by sphere

$$= \pi r^2 = \pi \times \left[\frac{(V_2 - V_1)}{2}\right]^2 = \frac{\pi \times (20)^2}{2^2}$$

$$= 100\pi = 100 \times 3.14 = 314\ \text{J}$$

5. (a,b,c) The correct order is : $w_3 > w_1 > w_2 > w_4$

6. (a,d) γ for monoatomic is 1.66 $\therefore\ C_v = \frac{3R}{2}, C_p = \frac{5}{2}R$

$$C_{vM} = \frac{2\times\frac{3R}{2} + 2\times\frac{3R}{2}}{4} = \frac{3}{2}R \qquad \therefore \quad C_v = 3\,\text{cal}$$

$$\therefore \quad C_{pM} = \frac{2\times\frac{5R}{2} + 2\times\frac{5R}{2}}{4} = \frac{5}{2}R \qquad \therefore \quad C_p = 5\,\text{cal}$$

7. (b,c,d) $\Delta G^\circ = 0$ at equilibrium under standard state. Also, at eq. $\Delta G = 0$

$\therefore \qquad \Delta H^\circ - T\Delta S^\circ = 0$

Also, $\qquad \Delta G^\circ = 2.303\,RT \ln K$

$\therefore \qquad K = 1$

8. (a,b,c,d) $\qquad \frac{C_p}{C_v} = 1.4 = \gamma$

$$C_p - C_v = R$$

$\therefore\ \gamma C_v - C_v = R\ \therefore C_v = \frac{R}{\gamma - 1}$ and similarly $C_p - \frac{C_p}{\gamma} = R$

$\therefore \qquad C_v = \frac{2}{0.4} = 5\,\text{cal}\ \ \therefore\ C_p \frac{\gamma . R}{(\gamma - 1)}$

Also, $\qquad c_v = \frac{2}{0.4 \times 32} = 0.156\,\text{cal}$

9. (a,b,c,d) These are mathematically established facts. For details consult **Concepts of Physical Chemistry by Dr. P. Bahadur,** Prakash Publications Muzaffarnagar.
10. (b,c,d) $H_2O_{(s)}$ has more ordered arrangement. Also,

$$\Delta S_2^\circ = S^\circ_{H_2O_{(v)}} - S^\circ_{H_2O_{(l)}}$$

$$\Delta S_0^1 = S^\circ_{H_2O_{(l)}} - S^\circ_{H_2O_{(s)}}$$

$\therefore \quad S^\circ_{H_2O_{(v)}}$ is maximum and this $\Delta S_2^\circ >>> \Delta S_1^\circ$

11. (a, c) For a cyclic process $\Delta U = 0 \qquad \therefore\ \Delta U_1 = -\Delta U_2$

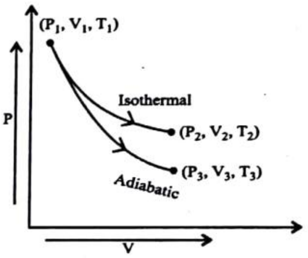
and $\quad \Delta Q = \Delta U + \Delta w$

$\therefore \quad \Delta Q = \Delta w$

12. (a, c) For a reaction to be spontaneous in neither direction $(\Delta G)_{T,P}, (\Delta S)_{U,V}$ and $(\Delta U)_{S,V}$ should be zero.
13. (b, d) Internal energy and entropy are path independent.
14. (b, d) These are mass independent.
15. (a,c) Work is not state function.
16. (a,b) An intensive property is one for which a system in fixed state is divided into two parts, the property of each part in that state shows same value. These are mass independent. Resistance and heat capacity are mass dependent.
17. (a,c) $\Delta S_{x-z} = \Delta S_{x\to y} + \Delta S_{y\to z}$ [entropy (S) being a state function, and thus additive property]

$W_{x\to y\to z} = W_{x\to y}$ (work done in $Y \to Z$ is zero because it is an isochoric process)

18. (a,c,d)



$T_1 = T_2$ because process is isothermal.

Work done in adiabatic process is less than in isothermal process because area covered by isothermal curve is more than the area covered by the adiabatic curve.

In adiabatic process work of expansion is done on the cost of internal energy hence it decrease while in isothermal process temperature remains constant and thus no change in internal energy. Therefore $\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$

19. (a,b,c)

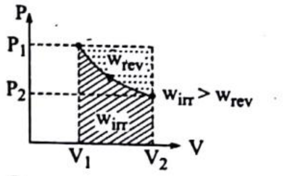
For thermally insulated container, $q = 0$ and for free expansion, $W = 0$ and $\Delta U = 0$

So, $\qquad T_1 = T_2$

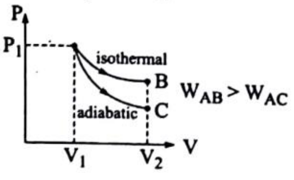
Also, $\qquad P_1V_1 = P_2V_2$

20. (a,b,d)

(a)



(b)



(c) (i) $\Delta U = nC_v\Delta T = 0$ (isothermal hence $\Delta T = 0$)

(ii) $\Delta U = q + w = -\text{ve}$ ($q = 0, w$ is negative, as work done by the system $\Delta U = nC_v\Delta T$, ΔU can be negative only when $\Delta T = -\text{ve}$

(d) $q = 0$ (adiabatic), $w = 0$ (free expansion)

$\Delta U = 0$ and $\Delta T = 0$ (isothermal)

21. (b,c)

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

at equilibrium $\Delta G = 0$

$$\therefore \quad \Delta S = T\Delta S$$

$$\Delta S_{\text{Surr}} = +\frac{\Delta H_{\text{Surr}}}{T_{\text{Surr}}}$$

For endothermic reaction ($\Delta H_{\text{sys}} = +\text{ve}$) and $\Delta H_{\text{Surr}} = -\text{ve}$, if T_{Surr} increases, $\Delta S_{\text{Surr}} = -\text{ve}$ or entropy of surrounding decreases *i.e.*, unfavourable change.

For exothermic reaction ($\Delta H_{\text{sys}} = -\text{ve}$), if T_{surr} increases, $\Delta S_{\text{surr}} = +\text{ve}$ or entropy of surrounding increases. Thus, favourable change

Also, for $\Delta S_{\text{sys}} = \dfrac{\Delta H_{\text{sys}}}{T_{\text{sys}} \text{ or } T_{\text{surr}}}$ (in equilibrium)

For exothermic reaction $\Delta H_{\text{sys}} = -\text{ve}$

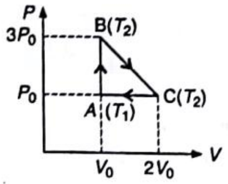
$\therefore \quad \Delta S_{\text{sys}} = -\text{ve}$

For endothermic reaction $\Delta H_{\text{sys}} = +\text{ve}$

$\therefore \quad \Delta S_{\text{sys}} = +\text{ve}$

COMPREHENSION BASED PROBLEMS

Comprehension 1 : One mole of an ideal monoatomic gas is taken round cyclic process $ABCA$ as shown in figure. Calculate.



[1] The work done by the gas.

(a) P_0V_0 (b) $-P_0V_0$
(c) $2P_0V_0$ (d) $-2P_0V_0$

[2] The heat rejected by the gas in the path CA the heat absorbed by the gas in the path AB respectively.

(a) $\frac{5}{2}P_0V_0, 3P_0V_0$ (b) $3P_0V_0, \frac{5}{2}P_0V_0$
(c) $5P_0V_0, 3P_0V_0$ (d) $3P_0V_0, 5P_0V_0$

[3] The net heat absorbed by the gas in the path BC.

(a) $\frac{P_0V_0}{3}$ (b) $\frac{P_0V_0}{2}$
(c) P_0V_0 (d) $2P_0V_0$

[4] The maximum temperature attained by the gas during the cycle.

(a) $3T_1$ (b) $2T_1$
(c) $4T_1$ (d) $5T_1$

Comprehension 2: The change in internal energy (U) can be brought about in two ways :

(i) Either by allowing the heat to flow into the system or out of the system

(ii) By doing work on the system or the work done by the system

Using the symbol q to represent heat transferred to system and using work done by the system $-w$, we can represent the internal energy change of a system Δu, as :

$$q = \Delta U + (-w) \quad \text{(First law of thermodynamics)}$$

If the reaction is carried out in a closed container with constant volume, so that $\Delta V = 0$

Hence, $q_v = \Delta U$

On the other hand, if a reaction is carried out in open vessel that keeps the pressure constant and allows the volume of the system to change freely. In such case, $\Delta V \neq 0$ and $-w = P \cdot \Delta V$.

Hence, $q_p = \Delta U + P\Delta V$

Also $q_p = q_v + \Delta n_g RT$

As reactions carried out at constant pressure are so common, the heat change for such process is given a special symbol ΔH, called the enthalpy change of the reaction. The enthalpy (H) of the system is the name given to the quantity ($U + PV$).

[1] In which of the following cases ΔH and ΔU are not equal to each other?

(a) The reaction involves no gaseous reactant and product
(b) The number of mole of gaseous reactants and gaseous products are not equal to each other
(c) The number of mole of gaseous reactants and gaseous products are equal to each other
(d) The process is carried out in closed vessel

[2] The latent heat of vaporization of liquid at 500 K and 1 atmospheric pressure is 10.0 kcal/mol. What will be the change in internal energy of 3 mole of the liquid at the same temperature and pressure?

(a) 27.0 kcal (b) 13.0 kcal
(c) –27.0 kcal (d) –13.0 kcal

[3] A mixture of 2 mole of carbon monoxide and one mole of oxygen in a closed vessel is ignited to get carbon dioxide. If ΔH is the enthalpy change and ΔU is the change in internal energy, then :

(a) $\Delta H > \Delta U$ (b) $\Delta H < \Delta U$
(c) $\Delta H = \Delta U$ (d) Not definite

[4] A piston exerting a pressure of 1.0 atmosphere rests on the surface of water at 100°C. The pressure is reduced to smaller extent and as a result 10 g of water evaporates and absorbs 22.2 kJ of heat. The change in internal energy is :

(a) 18.24 kJ (b) 20.477 kJ
(c) 22.05 kJ (d) 23.923 kJ

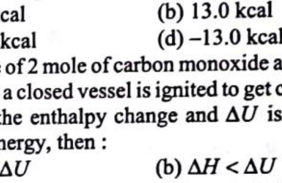
[5] A system is provided 50 kJ energy and work done on the system is 100 J. The change in internal energy is :

(a) 150 J (b) 50 kJ
(c) 50.1 kJ (d) 49.9 kJ

[6] One mole of a gas is allowed to expand freely in vacuum at 300 K. The work done during the process is :

(a) 300 J (b) 300 kJ
(c) zero (d) nothing can be said

Comprehension 3 : A fixed mass 'm' of a gas is subjected to transformation of states from K to L to M to N and back to K as shown in the figure.



[1] The pair of isochoric processes among the transformation of states is : **[JEE (Advanced) 2013]**

(a) K to L and L to M (b) L to M and N to K
(c) L to M and M to N (d) M to N and N to K

[2] The succeeding operations that enable this transformation of states are :

[JEE (Advanced) II 2013]

(a) Heating, cooling, heating, cooling
(b) Cooling, heating, cooling, heating
(c) Heating, cooling, cooling, heating
(d) Cooling, heating, heating, cooling

SOLUTIONS

Comprehension 1

Path AB is isochoric ($w_1 = 0$), path BC is isothermal ($w_2 = -ve$), path CA is isobaric ($w_3 = +ve$)

[1] (b) Total work done by gas $(w) = w_1 + w_2 + w_3$

$$= 0 - \frac{1}{2}[(P_B + P_C) \times (V_C - V_B)] + P_A(V_C - V_A)$$

$$= 0 - \frac{1}{2}[4P_0 \times V_0] + P_0(2V_0 - V_0)$$

$$= -2P_0V_0 + P_0V_0 = \boldsymbol{-P_0V_0}$$

Also, $w_2 = -2P_0V_0$
and $w_3 = P_0V_0$

[2] (a) Also, **For the path AB, *i.e.*, isochoric**

$$q_1 = n \times C_v \times (T_B - T_A) = 1 \times \frac{3}{2}R\left[\frac{P_BV_B - P_AV_A}{R}\right]$$

$$= \frac{3}{2}[3P_0V_0 - P_0V_0] = \boldsymbol{+3P_0V_0}$$

For the path CA, *i.e.*, isobaric

$$q_3 = n \times C_p(T_A - T_B) = 1 \times \frac{5}{2}R\left[\frac{P_AV_A - P_BV_B}{R}\right]$$

$$= \frac{5}{2}[P_0V_0 - 2P_0V_0]$$

$$q_3 = -\frac{5}{2}\boldsymbol{P_0V_0}$$

[3] (b) Also net heat absorbed $= 3P_0V_0 - \frac{5}{2}P_0V_0 = \frac{P_0V_0}{2}$

$$\therefore \quad q_{\text{net}} = \frac{\boldsymbol{P_0V_0}}{\boldsymbol{2}}$$

[4] (a) Also, $\frac{P_0V_0}{T_1} = \frac{3P_0V_0}{T_2} \quad \therefore \quad T_2 = 3T_1$

Comprehension-2

[1] (b) If $\Delta n_g = 0$ then only $\Delta H = \Delta U$

[2] (a) $3H_2O(l) \longrightarrow 3H_2O(g)$; $\Delta n_g = 3$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\therefore \quad \Delta U = \Delta H - \Delta n_g RT$$

$$= 10 \times 3 - 3 \times 2 \times 10^{-3} \times 500 = 27 \text{ kcal}$$

[3] (b) $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$

$$\Delta n_g = 2 - 3 = -1$$

$$\Delta H = \Delta U + \Delta n_g RT = \Delta U - RT$$

Hence, $\Delta H < \Delta U$

[4] (b) $\Delta H = \Delta U + P\Delta V = \Delta U + \Delta n_g RT$

$$\therefore \quad \Delta U = \Delta H - \Delta n_g RT$$

$$= 22.2 - \frac{10}{18} \times 8.314 \times 10^{-3} \times 373$$

$$= 20.477 \text{ kJ}$$

[5] (c) $q = \Delta U + (-W)$

or $\Delta U = q + (W)$ where W is work done on the system

$$= 50 \times 10^{-3} + 100 = 50.100 \text{ J} = 50.1 \text{ kJ}$$

[6] (c) $W = -P_{\text{ext}}(V_2 - V_1) = -0 \times (V_2 - V_1) = 0$

($P_{\text{ext}} = 0$ if expansion in vacuum)

Comprehension-3

[1] (b) For a given mass of gas (constant n) volume increases from K to L at constant P due to heating *i.e.* isobaric process. Pressure decreases from L to M at constant V due to cooling *i.e.* **isochoric process.** Volume decreases from M to N at constant P due to cooling *i.e.* **isobaric process.** Pressure increases from N to K at constant V due to heating *i.e.* **isochoric process.** Thus isochoric process (constant V) are L to M and N to K.

[2] (c) Follow answer 1.

STATEMENT EXPLANATION PROBLEMS

In each sub question given below a statement (S) and explanation (E) is given. Choose the correct answers from the codes (a), (b), (c) and (d) given for each question:

(a) S is correct but E is wrong
(b) S is wrong but E is correct
(c) Both S and E are correct and E is correct explanation of S
(d) Both S and E are correct but E is not correct explanation of S

1. S : Work and internal energy are not state functions.
E : The sum of $q + w$ is state function.

2. S : Internal energy of a system is an extensive property.
E : The internal energy of a system depends upon the amount and physical state of the substance.

3. S : The change in internal energy and change in heat enthalpy does not depend upon the path by which changes are brought in.
E : Both ΔU and ΔH are path independent as U and H are state functions.

4. S : Both work and heat are manifested by an effect on the surroundings.
E : Work done by/on the system and ΔH appear only at the boundary of system.

5. S : The zeroth law of thermodynamics was known before I law of thermodynamics.
E : The zeroth law concerning thermal equilibrium was appeared after three laws (I, II and III) of thermodynamics and thus was named as zeroth law.

6. S : The entropies of CO, NO, N_2O, $Cl_2(s)$ are not zero at absolute zero.
E : These are exceptions to III law of thermodynamics.

7. S : Phase transition involves change in internal energy only.
E : Phase transition occurs at constant pressure.

8. S : The change in entropy during melting of ice is negligible in comparison to change in entropy during vaporisation.
E : The volume occupied by solid and liquid is too less in comparison to volume occupied by gas.

9. S : The SI unit of entropy is $J\,K^{-1}mol^{-1}$.
E : $\Delta S = \frac{q_{rev}}{T}$.

10. S : Whole of work can be converted to heat but whole heat cannot be converted to work.
E : Conversion of work into heat by friction and II law of thermodynamics are respectively responsible for statement.

11. S : For $H_2(g) + O_2(g) \longrightarrow H_2O_2(l); \Delta H = -187.6$ kJ mol^{-1}, the word stability for H_2O_2 represents energetic stability and not kinetic stability.
E : The reaction does not occur spontaneously.

12. S : $\Delta_f H^\circ$ for white phosphorus has been taken to be zero, whereas black phosphorus is most stable allotrope of phosphorus and this is only exception.
E : The reference standard state of white phosphorus is taken despite the fact that this form not being the most stable allotrope but simply the most reproducible form of phosphorus.

13. S : Two bodies at thermal equilibrium may or may not have equal heat.
E : Two bodies at thermal equilibrium have same temperature.

14. S : Energy can neither be created nor destroyed.
E : Total energy of the universe is constant.

15. S : The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.
E : The volume occupied by the molecules of an ideal gas is zero.

16. S : A non-spontaneous endothermic reaction at room temperature may be spontaneous at high temperature.
E : At high temperature $T\Delta S$ becomes more than ΔH.

17. S : Neither q nor W is state function but $q + W$ is state function.
E : ΔU is state function.

18. S : Fall of water as rain drops from clouds is spontaneous.
E : During the process entropy increases.

19. S : There is a natural asymmetry between converting work to heat and converting heat to work.
E : No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work. **[IIT 2008]**

ANSWERS (Statement Explanation Problems)

1. (d) w and q are state functions, whereas $\Delta U = q + w$ is state function.

2. (c) Reason is correct explanation for statement.

3. (c) Reason is correct explanation for statement.

4. (c) —do—

5. (b) The reason is also an explanation for the name Zeroth law.

6. (d) Both are facts.

7. (b) Phase transition occurs at constant P and thus change is referred as ΔH.

8. (c) Reason is correct explanation for statement. $\Delta S_{\text{vap}} = S_{\text{vap}} - S_{\text{liq}}$ and $\Delta S_{\text{fus}} = S_{(L)} - S_{(S)}$ $\Delta S_{\text{vap}} >>> \Delta S_{\text{fus}}$. Gaseous state has more disordered system.

9. (c) $\Delta S = \frac{q_{\text{rev}}}{T}$, thus, unit is J $K^{-1}\text{mol}^{-1}$.

10. (c) Reason is correct explanation for statement.

11. (c) —do—

12. (c) —do—

13. (d) Both are facts.

14. (d) Both are facts.

15. (d) $q = \Delta U - W$. For isothermal expansion $\Delta U = 0$. Also $W = 0$, because $W = P \times \Delta V$ and $P = 0$; Also volume occupied by molecules is zero for ideal gas. Thus, both assertion and reason are correct, but this is not an explanation for assertion.

16. (c) For a spontaneous reaction $\Delta G = -\text{ve}$ and $\Delta G = \Delta H - T\Delta S$, if $\Delta H = +\text{ve}, \Delta G$ will be negative when $T\Delta S > \Delta H$.

17. (c) Explanation is correct reason for statement.

18. (c) Explanation is correct reason for statement.

19. (c) Statement represents II law of thermodynamics which is an arguement for statement.

MATCHING TYPE PROBLEMS

Type I : Only One Match Is Possible

1.

List A		List B
A. Kirchoff's equation	(a)	$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)$
B. Claussues Clapeyron equation	(b)	$\frac{d \ln K_P}{dT} = \frac{\Delta H^\circ}{RT^2}$
C. van't Hoff isochore	(c)	$\frac{d \ln P}{dT} = \frac{\Delta H^\circ}{RT^2}$
D. Gibbs Helmholtz equation	(d)	$\frac{\partial(\Delta G)}{\partial T} = \Delta C_P$

Type II : More Than One Match Are Possible

2.

List A	List B
A. $H_2O(l) \xrightarrow{\text{1 atm, 20 K}} H_2O(s)$	1. $\Delta rG = +ve$
B. $H_2O(l) \xrightarrow{\text{1 atm, 363 K}} H_2O(g)$	2. $\Delta rS = +ve$
C. $H_2O(l) \xrightarrow{\text{1 atm, 373 K}} H_2O(g)$	3. $\Delta rH = -ve$
D. $H_2O(g) \xrightarrow{\text{1 atm 273 K}} H_2O(l)$	4. $\Delta rH = +ve$

3.

List A	List B
A. Work	1. Boundary phenomenon
B. Heat	2. Path function
C. Temperature	3. Intensive property
D. $q+w$	4. Extensive property

4.

Reaction	At equilibrium
A. $H_2O(l) \rightleftharpoons H_2O(v)$	a. $\Delta G = 0$
B. $H_2O(s) \rightleftharpoons H_2O(v)$	b. $\Delta S_{\text{Total}} = 0$
C. $H_2O(s) \rightleftharpoons H_2O(l)$	c. $Q = K_P$
	d. $\Delta H = +ve$
	e. $\Delta H = -ve$
	f. $\Delta V = +ve$
	g. $\Delta V = -ve$

5.

List A	List B
(A) Cyclic rule	1. $-P_{ext} \times \Delta V$
(B) Work done in reversible isothermal process	2. $\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_v = -1$
(C) Work done in isobaric process	3. $nRT \ln \frac{P_1}{P_2}$
(D) Work done during free expansion	4. $nRT \ln \frac{V_1}{V_2}$
(E) Work done in adiabatic reversible process	5. $-nR\,(T_{\text{final}} - T_{\text{initial}})$
(F) Work done in adiabatic irreversible process	6. Zero
	7. $\frac{nR}{r-1}(T_{\text{final}} - T_{\text{initial}})$
	8. $-nC_v \cdot T_{\text{initial}}\left[1-\left(\frac{P_2}{P_1}\right)^{R/C_P}\right]$
	9. $-P_{ext} \times R\left[\frac{P_1T_2 - P_2T_1}{P_1P_2}\right]$

6.

Thermodynamic Functions	Dependent
A. Internal energy	(a) Temperature
B. Heat enthalpy	(b) Mass
C. Entropy	(c) Pressure
D. Gibbs energy	(d) Volume
E. Work	(e) State

7.

List A	List B
A. Raw egg → Boiled egg	(a) $\Delta S_T = +ve$
B. $Pd + H_2 \rightleftharpoons$ absorbed gas	(b) $\Delta S = -ve$
C. $\text{Water}_{(l)} \underset{\text{1 atm}}{\overset{\text{373 K}}{\rightleftharpoons}} \text{Water}_{(g)}$	(c) $\Delta G^\circ = -ve$
D. $\text{Water}_{(s)} \underset{\text{1 atm}}{\overset{0^\circ C}{\rightleftharpoons}} \text{Water}_{(l)}$	(d) $\Delta G = 0$

8. Match the thermodynamic processes given under Column-I with the expressions given under Column-II.

Column-I	Column-II
(A) Freezing of water at 273 K and 1 atm	(P) $q = 0$
(B) Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions	(Q) $w = 0$
(C) Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container	(R) $\Delta S_{sys} < 0$
(D) Reversible heating of $H_2(g)$ at 1 atm from 300 K to 600 K followed by reversible cooling to 300 K at 1 atm	(S) $\Delta U = 0$
	(T) $\Delta G = 0$

[JEE (Advanced I) 2015]

Type III : Only One Match From Each List

9.

List A	List B	List C
1. Trouton's rule	a. $\Delta S^{\circ}_{vap} = \frac{\Delta H^{\circ}_V}{T_b}$	(i) Entropy of vaporisation
2. Kirchoff's equation	b. $\left(\frac{\partial \Delta_H}{\partial T}\right)_P = C_p$	(ii) Reaction enthalpy
3. Joule-Thomson effect	c. $\left(\frac{\partial T}{\partial P}\right)_H = \mu$	(iii) Inversion temperature
4. Polymeri-sation	d. $\overline{M}_n = \frac{\Sigma n_i m_i}{\Sigma n_i}$	(iv) Glass transition temperature
5. Ideal gas	e. $\left(\frac{\partial E}{\partial V}\right)_T = 0$	(v) Hypothetical concept
6. Sublimation of ice	f. $\Delta H_{sub} = \Delta H_f + \Delta H_V$	(vi) Hoar frost

ANSWERS

1. A – d; B – c; C – b; D – a
2. A – 3; B – 1, 2, 4; C – 2,4; D – 2,4
3. A – 1, 2, 4; B – 1, 2, 4; C – 3; D – 3
4. A – a, b, c, d, f; B – a, b, c, d, f; C – a, b, c, d, g
5. A – 2; B – 1, 3, 4; C – 1, 5; D – 1, 6; E – 1, 7, 8;. F – 1, 5, 9
6. A – a, b, d, e; B – a, b, c, e; C – a, b, c, d, e; D – a, b, c, d, e; E – a, c, d
7. A – a, c; B – b, c, d; C – a, c, d; D – b, c, d
8. A – R, T; B – P, Q, S; C – P, Q, S; D – P, Q, S, T
9. 1 – a – i; 2 – b – ii; 3 – c – iii; 4 – d – iv; 5 – e – v; 6 – f – vi