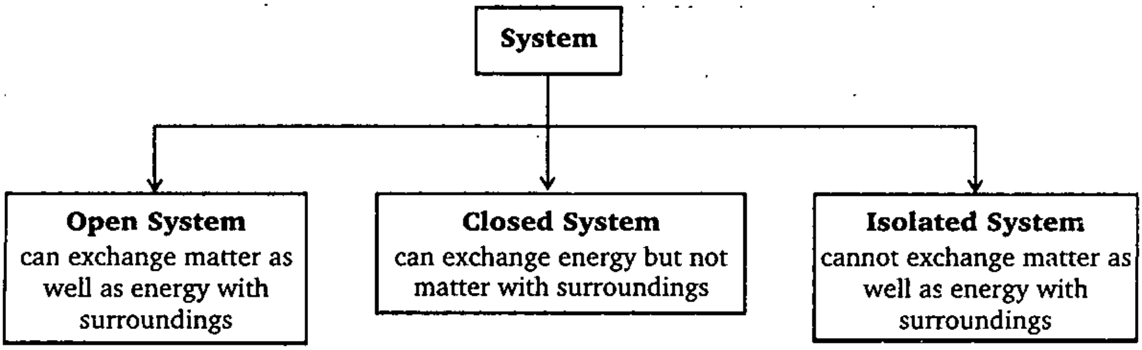
4

THERMODYNAMICS

- The subject of **Thermodynamics** deals basically with the interaction of one body with another in terms of quantities of heat & work.
- A **System** is defined as that macroscopic part of the universe which is at the moment under investigation.
- **Surroundings** are the rest of the universe outside the system.
- **Boundary** : The actual or imaginary surface that separates the system from the surroundings.


System

Open System can exchange matter as well as energy with surroundings

Closed System can exchange energy but not matter with surroundings

Isolated System cannot exchange matter as well as energy with surroundings

Thermodynamic Properties

Intensive Properties
do not depend on the amount of matter present in system
Examples : Pressure, Temperature, Density, Melting point, Boiling point etc.

Extensive Properties
depend on the amount of matter present in the system.
Examples : Mass, Volume, Heat Capacity, Enthalpy, Entropy etc.

Thermodynamic Process : The change of a system from one state to another state.

Thermodynamic Processes

Isothermal	Isobaric	Isochoric	Adiabatic	Polytropic
temperature remains constant throughout the process *i.e.,* : $dT=0$	pressure remains constant throughout the process *i.e.,* : $dP=0$	volume remains constant throughout the process *i.e.,* : $dV=0$	system cannot exchange heat with surrounding *i.e.,* : $dq=0$	PV^n= constant

- **Cyclic Process :** System undergoes a number of different processes and finally returns to its initial state.
- **REVERSIBLE PROCESS (QUASI-STATIC) & IRREVERSIBLE PROCESS :**

  A process which is carried out so slowly that the system and the surroundings are nearly in equilibrium is known as a **Reversible Process.** If this condition does not hold good, the process is said to be, **Irreversible.**

  In a reversible process the driving force is infinitesimally larger than the opposing force. If the driving force is made infinitely smaller than opposing force, the system can be brought back without producing any permanent change.
- **All natural processes are irreversible process.**

  Spontaneous Process : Proceeds on its own *i. e.*, without any external help.
- **INTERNAL ENERGY (*U*) :** The sum of all microscopic forms of energy.

  $U = U_{\text{Translational}} + U_{\text{Rotational}} + U_{\text{Vibrational}} + U_{\text{Bonding}} + U_{\text{Electronic}} + \ldots\ldots$
- U is a state function & an extensive property.
- $\Delta U = U_{\text{Final}} - U_{\text{Initial}}$; $\Delta U = q_v$
- $dU = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV$, $dU = nC_{Vm}(T_2 - T_1)$ at constant volume

Enthalpy

Chemical reactions are generally carried out at constant pressure (atmospheric pressure) so it has been found useful to define a new state function called Enthalpy (H) as :

- $H = U + PV; \Delta H = \Delta U + \Delta(PV)$; at constant pressure $\Delta H = \Delta U + P\Delta V$; combining with first law. $\Delta H = q_p$
- The difference between ΔH & ΔU becomes significant only when gases are involved (insignificant in solids and liquids)

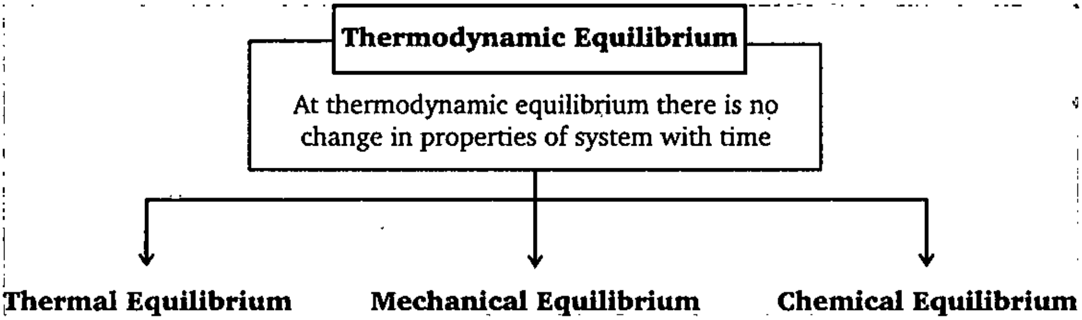
$$\Delta H = \Delta U + \Delta(PV) = \Delta U + nR\,\Delta T$$
$$\Delta H = \Delta U + (\Delta n_g)RT$$

- For a given system consider; $H = f(T,P); dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$
- For isobaric process : $dP = 0; dH = \left(\frac{\partial H}{\partial T}\right)_P dT; dH = C_P.dT; \Delta H = \int C_P.dT$
- For an ideal gas $H = f(T)$ only

  $\left(\frac{\partial H}{\partial P}\right)_T = 0$ or $dH = C_P.dT; \Delta H = \int C_P.dT$; for n moles of ideal gas $\Delta H = \int nC_P\,dT$

Kirchoff's Equation

- For chemical reactions $\int d\Delta_r H = \int \Delta_r C_p.dT$
- $\Delta_r H_{T_2} - \Delta_r H_{T_1} = \Delta_r C_p(T_2 - T_1)$
- Similarly $\Delta_r U_{T_2} - \Delta_r U_{T_1} = \Delta_r C_v(T_2 - T_1)$


Thermodynamic Equilibrium

At thermodynamic equilibrium there is no change in properties of system with time

Thermal Equilibrium **Mechanical Equilibrium** **Chemical Equilibrium**

- **ZEROTH LAW OF THERMODYNAMICS**

  Two systems in thermal equilibrium with a third system, are also in thermal equilibrium with each other.

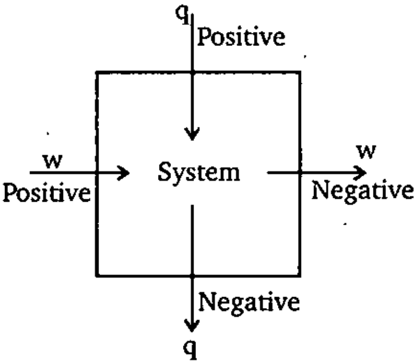
- **FIRST LAW OF THERMODYNAMICS**

  It is law of conservation of energy. Mathematically for **closed system** at rest in absence of external fields this law is written as :

  $$\Delta U = q + w$$

  Where ΔU is change in internal energy of the system, q is the transfer of heat from surroundings to the system and w is the work involved (either done on the system or by the system).

- **Sign convention according to IUPAC :**



- **HEAT :** The energy that flow into or out of a system because of a difference in temperature between the system and its surrounding.
- **TYPES OF WORK :** Two types of work normally come across in chemistry.

  1. Mechanical work (*e.g.*, *PV* work) **2.** Electric work (Non *PV* work)
- *Mechanical work* is involved when a system changes its volume in the presence of an externally applied pressure (*i.e.*, pressure volume work). It is especially important in system containing gases

$$dw = -P_{ext}\,.dV; \quad w = -\int_{V_1}^{V_2} P_{ext.}\,dV$$

- **CALCULATION OF WORK DONE IN VARIOUS PROCESS**
- **Isochoric process:**

  Since $dV = 0$ so $w = 0$

  from 1st law $\Delta U = q_v + w = q_v$
- **Isobaric process:**

$$w = -P_{ext}(V_2 - V_1)$$

& $\Delta H = q_p$

- **Isothermal process:**

  Since $dT = 0$ so $dU = 0$ for an ideal gas

  from 1st law $q + w = 0$ or $q = -w$

  If process is reversible

$$w = -nRT\ln\left(\frac{V_2}{V_1}\right) = -nRT\ln\left(\frac{P_1}{P_2}\right) \quad \text{or} \quad w = -2.303\,nRT\log\frac{V_2}{V_1} = -2.303\,nRT\log\frac{P_1}{P_2}$$

  If process is irreversible

$$w = -P_{ext}\left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right)$$

  In case of free expansion $p_{ext} = 0$ so $w = 0$
- **Adiabatic process :** $q = 0$

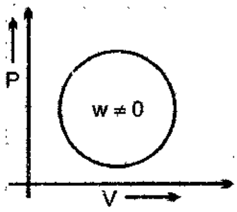
$$\Delta U = w = nC_v(T_2 - T_1) = \frac{P_2V_2 - P_1V_1}{\gamma - 1}, \text{ where } \gamma = \frac{C_P}{C_V}$$

  If process is reversible $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

If process is irreversible $\frac{T_2 - T_1}{\gamma - 1} = -P_{\text{ext}} \cdot \left(\frac{T_2}{P_2} - \frac{T_1}{P_1}\right)$

- **Cyclic process:**

  Work done = Area enclose in *PV*-diagram
  For clockwise it is –ve
  For anti-clockwise it is +ve



- Electrical work ($w = V.I.t$) is a type of non PV-work.

Heat Capacity : Between any two temperatures, the quantity of heat required to raise the temperature of the system from the lower to the higher temperature divided by the temperature difference.

- $C = dq/dT$.
- $q_v = \Delta U$
- $C_v = \left(\frac{q}{T_2 - T_1}\right)_v = \left(\frac{\Delta U}{T_2 - T_1}\right)_v$ or $C_v = (\partial U/\partial T)_v$
- $C_P = \left(\frac{\partial H}{\partial T}\right)_P$
- $C_{p,m} - C_{v,m} = R$ (for ideal gas)
- $C_{p,m}$ and $C_{v,m}$ depends on temperature even for an ideal gas. ($C = a + bT + cT^2$)
- $\gamma_{\text{mix}} = \frac{n_1 C_{p_1} + n_2 C_{p_2} + \ldots\ldots}{n_1 C_{v_1} + n_2 C_{v_2} + \ldots\ldots}$

Reversible Adiabatic process involving ideal gas

- $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$
- $TV^{\gamma-1} =$ constant
- $PV^{\gamma} =$ constant
- $T^{\gamma} P^{1-\gamma} =$ constant
- **Molar Specific heat (C_m) of ideal gas in any Reversible Polytropic Process :**

  $C_m = C_{v,m} + \frac{R}{1-x} = \frac{R}{\gamma - 1} + \frac{R}{1-x}$

Second Law of Thermodynamics

Statements :

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

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

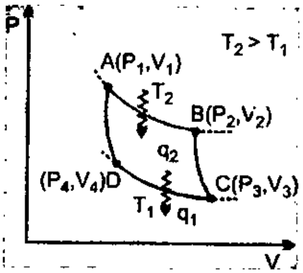
$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$ for rev. process
$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$ for irrev. process
$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0$ (In general)

(iii) Efficiency of Carnot engine working reversibly is maximum.

Carnot cycle

AB – Isothermal Reversible Expansion $w_{AB} = -nRT_2 \ln\frac{V_2}{V_1}$

BC – Adiabatic Reversible Expansion $w_{BC} = C_V(T_1 - T_2)$



CD – Isothermal Reversible Expansion $w_{CD} = -nRT_1 \ln\left(\frac{V_4}{V_3}\right)$ $T_2 > T_1$

DA – Adiabatic Reversible Expansion $w_{DA} = C_V(T_2 - T_1)$

for Carnot efficiency (η) calculation $= \frac{-w_{\text{Total}}}{q_2} = \frac{T_2 - T_1}{T_2} = \frac{q_2 - q_1}{q_2}$

Calculation of Entropy change (ΔS or ΔS_{sys})

- Ideal gas in any Reversible/Irreversible process from (P_1, V_1, T_1) to (P_2, V_2, T_2)
- $\Delta S = nC_v \ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1} = nC_p \ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2}$
- Reversible & irreversible isothermal expansion / contraction of an ideal gas

$$\Delta S = nR\ln\frac{V_2}{V_1}$$

- Isobaric heating or cooling : $\Delta S = nC_P \ln\left(\frac{T_2}{T_1}\right)$
- Isochoric heating or cooling : $\Delta S = nC_V \ln\left(\frac{T_2}{T_1}\right)$
- Adiabatic process :
- $\Delta S = nC_V \ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}$ for irreversible process

  $\Delta S = 0$ for reversible adiabatic compression and expansion.
- General reversible heating or cooling of any substance

$$\Delta S = \int_{T_1}^{T_2} \frac{dq_{\text{rev}}}{T}$$

- Reversible Phase Transformation
  - (a) $\Delta S_{\text{Fusion}} = \Delta H_{\text{Fusion}}/T_m$, T_m is normal melting point (K)
  - (b) $\Delta S_{\text{vap}} = \Delta H_{\text{vap}}/T_B$, T_B is normal boiling point (K)
  - (c) $\Delta S_{\text{sub}} = \Delta H_{\text{sub}}/T_{\text{sub}}$, T_{sub} is sublimation temperature (K)
  - (d) $\Delta S_{\text{Trans}} = \Delta H_{\text{Trans}}/T_{\text{Trans}}$, T_{Trans} is the phase transition temperature (K)
- For chemical reaction

$$\Delta_r S^\circ = \Sigma \nu_P \Delta_f S^\circ \text{ (products) } - \Sigma \nu_R \Delta_f S^\circ \text{ (reactants)}$$

Third Law of Thermodynamics

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

By virtue of the third law, the absolute value of entropy (unlike absolute value of enthalpy) for any pure substance can be calculated at room temperature.

$$S_T - S_{0K} = \int_0^T \frac{q_{\text{rev}}}{T}, \text{ since } S_{0K} = 0\,;\; S_T = \int_0^T \frac{q_{\text{rev}}}{T}$$

Absolute entropies of various substances have been tabulated and these value are used to calculate entropy changes for the reactions by the formula;

$$\Delta S^\circ = \Sigma \nu_P S_m^\circ \text{ (products) } - \Sigma \nu_R S_m^\circ \text{ (reactants)}$$

Variation of ΔS_r with temperature & pressure : $\int dS_r = \int \frac{\Delta_r C_{p,m} \cdot dT}{T}$

$$\Delta_r S_{T_2} - \Delta_r S_{T_1} = \Delta_r C_{p,m} \ln \frac{T_2}{T_1}$$

Gibbs Free Energy (*G*) and Spontaneity

- A new thermodynamic state function G, the Gibbs free energy is defined as :
- $G = H - TS$ or $\Delta G = \Delta H - T\Delta S$ (at constant temperature and pressure)
- $\Delta G < 0$ for spontaneous process
- $\Delta G = 0$ for equilibrium.

Criteria for Spontaneity

For a feasible process $\Delta S_T = \Delta S_{\text{sys}} + \Delta S_{\text{surr.}} > 0$

In absence of non *PV* work at constant T and P for a feasible process $\Delta G < 0$.

Standard Free Energy Change (ΔG°)

The free energy change for a process at a specified temperature in which the reactants in their standard state are converted to the products in their standard state. It is denoted by ΔG°.

- **Standard states :**
  - (a) Standard temperature (any specified temperature)
  - (b) For gases/solid/liquid: Standard pressure $P^\circ = 1$ bar
  - (c) For ion/substance in solution: Standard concentration $(C^\circ) = 1M$

Like the standard enthalpy of formation of an element "the standard free energy of formation of an element in its standard state is zero". And so;

- $\Delta_r G^\circ = \sum \nu_P \Delta_f G^\circ \text{ (products) } - \sum \nu_R \Delta_f G^\circ \text{ (reactants)}$

A Thermodynamic Relationship

For any reversible reaction : $\Delta G = \Delta G^\circ + RT \ln Q$.

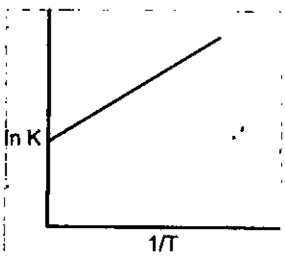
where Q is reaction quotient.

At equilibrium $\Delta G = 0$, $Q = K$

$$\Delta G^\circ = -RT \ln K, \quad \Delta G^\circ = -2.303 RT \log K_{\text{eq}}.$$

Effect of Temperature : Van't Hoff Equation

(a) $\frac{d(\ln K)}{dT} = \frac{\Delta H^\circ}{RT^2}$ (b) $\frac{d(\ln K)}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H^\circ}{R}$



If $\Delta H^\circ < 0$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ $\ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$

Integrated form $\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

- **RELATIONSHIP BETWEEN ΔG & $w_{\text{non-PV}}$**

  $dU = dq + dw_{PV} + dw_{\text{non-PV}}$

  for reversible process at constant T & P

  $dU + pdV - TdS = dw_{\text{non-PV}}$

  $dH - TdS = dw_{\text{non-PV}}$

  $(dG_{\text{system}})_{T,P} = dw_{\text{non-PV}}$

  $-(dG_{\text{system}})_{T,P} = (dw_{\text{non-PV}})_{\text{by, system}}$

  Means free energy change for a process is equal to the maximum possible work that can be derived from the process *i.e.*,

- $\Delta G^\circ = w_{\max}$ (for a reversible change at constant pressure and temperature)
- In case of a galvanic cell. $\Delta G = -nFE_{\text{cell}}$, where E_{cell} = e.m.f. of the cell ; F = Faraday constant and n = number of electrons being transferred in the chemical process
- So $\Delta G^\circ = -nFE^\circ_{\text{cell}}$, where is the standard cell potential.

THERMOCHEMISTRY

- **Enthalpy of Reaction :**

  The amount of heat evolved or absorbed when the number of moles of reactants react completely to give the products as given by the balanced chemical equation.

- **Enthalpy of formation :**

  The change in heat enthalpy when one mole of a substance is formed directly from its constituent elements at standard states.

  (i) For elements, $\Delta_f H^\circ = 0$; *e.g.*, $\Delta_f H^\circ(\text{Zn, S}) = 0$, $\Delta_f H^\circ(\text{Br}_2, l) = 0$, $\Delta_r H^\circ(\text{O}_2, g) = 0$

  (ii) If element exists in two or more allotropic forms then for most stable state $\Delta_f H^\circ = 0$

  e.g., $\Delta_f H^\circ[\text{C}(s, \text{graphite})] = 0$, $\Delta_f H^\circ\ [\text{S}(s, \text{rhombic})] = 0$

- **Enthalpy of combustion :**

  The change in enthalpy when one mole of a substance is completely burnt in oxygen.

- **Enthalpy of Transition :**

  The enthalpy change when one mole of one allotropic form changes to another.

  For example : $\text{C(graphite)} \longrightarrow \text{C(diamond)}$; $\Delta H^\circ_{\text{trs}} = 1.90\,\text{kJ mol}^{-1}$.

- **Enthalpy of fusion :**

  The change in enthalpy when one mole of a solid is completely converted into liquid state at its melting point.

- **Enthalpy of vaporisation :**
  The change in enthalpy when one mole of a liquid is completely converted into its vapours at its boiling point.
- **Enthalpy of sublimation :**
  The change in enthalpy when one mole of a solid is directly converted into vapours at sublimation temperature.
- **Enthalpy of solution :**
  The change in enthalpy when one mole of a substance is dissolved in excess of water so that further dilution does not involve any heat change.
- **Enthalpy of Dilution :**
  The change in enthalpy when a solution containing 1 mole of solute is diluted from one concentration to another.
- **Enthalpy of Hydration : (For anhydrous salt)**
  The enthalpy change when it combines with the requisite amount of water to form a new hydrated stable salt. For example, the hydration of anhydrous cupric sulphate is represented by

$$CuSO_4(s) + 5H_2O(l) \longrightarrow CuSO_4 \cdot 5H_2O(s)$$

- **Enthalpy of neutralisation :**
  Enthalpy of neutralisation is the change in enthalpy when one gram equivalent of an acid is completely neutralised by one gram equivalent of a base in dilute solutions.

$$\text{Strong acid} + \text{Strong base} \longrightarrow \text{Salt} + \text{Water}, \ \Delta H^\circ_{\text{neut}} \approx -56\,\text{kJ mol}^{-1}$$

- **Enthalpy of formation of ions :**
  The enthalpy change when one mole of aqueous ions is obtained from element in its standard state as.

$$\frac{1}{2}Cl_2(g) + aq \longrightarrow Cl^-(aq); \Delta H^\circ_r = \Delta H^\circ_r(Cl^-, aq)$$

  By convention, the standard enthalpy of formation of $H^+(aq)$ is taken to be zero.
- **Hess's law of constant heat summation :**
  The total heat change in a particular reaction is the same whether the reaction takes place in one step or in a number of steps.

  e.g., (i) $A \xrightarrow{\Delta H} B$

  (ii) $A \xrightarrow{\Delta H_1} C \xrightarrow{\Delta H_2} B$

  According to Hess's Law $\Delta H = \Delta H_1 + \Delta H_2$.
- **Enthalpy of atomisation :**
  The change in enthalpy when one mole of substance converts into gaseous atoms.
- **Bond enthalpies :**
  The average of enthalpies required to dissociate the bond present in different gaseous compounds into free atoms or radicals in the gaseous state.

  The bond enthalpy given for any particular pair of atoms is the average value of the dissociation enthalpies of the bond for a number of molecules in which the pair of atoms appears.

- **Estimation of Enthalpy of a reaction from bond Enthalpies :**

For the gaseous reaction; $C_2H_4(g) + HCl(g) \longrightarrow C_2H_5Cl(g)$

$$\Delta H = \begin{pmatrix}\text{Energy required to}\\ \text{break reactants into}\\ \text{gaseous atoms}\end{pmatrix} + \begin{pmatrix}\text{Energy released to}\\ \text{from products from the}\\ \text{gaseous atoms}\end{pmatrix}$$

- **Resonance Enthalpy :**

$$\Delta H^\circ_{\text{Resonance}} = \Delta H^\circ_{f,\text{experimental}} - \Delta H^\circ_{f,\text{calculated}}$$
$$= \Delta H^\circ_{c,\text{calculated}} - \Delta H^\circ_{c,\text{experimental}}$$

Level 1

1. Out of molar entropy (I), specific volume (II), heat capacity (III), volume (IV), extensive properties are :
(a) I, II (b) I, II, IV (c) II, III (d) III, IV

2. Out of internal energy (I), boiling point (II), pH (III) and E.M.F. of the cell (IV) intensive properties are :
(a) I, II (b) II, III, IV (c) I, III, IV (d) All of these

3. Thermodynamic equilibrium involves
(a) Chemical equilibrium (b) Mechanical equilibrium
(c) Thermal equilibrium (d) All the above simultaneously

4. Which has maximum internal energy at 290 K?
(a) Neon gas (b) Nitrogen gas (c) Ozone gas (d) Equal

5. A 10 g piece of iron ($C = 0.45\,\text{J/g}^\circ\text{C}$) at 100°C is dropped into 25 g of water ($C = 4.2\,\text{J/g}^\circ\text{C}$) at 27°C. Find temperature of the iron and water system at thermal equilibrium.
(a) 30°C (b) 33°C (c) 40°C (d) None of these

6. When freezing of a liquid takes place in a system :
(a) may have $q > 0$ or $q < 0$ depending on the liquid
(b) is represented by $q > 0$
(c) is represented by $q < 0$
(d) has $q = 0$

7. Mechanical work is specially important in systems that contain
(a) gas-liquid (b) liquid-liquid (c) solid-solid (d) amalgam

8. Determine which of the following reactions taking place at constant pressure represents system that do work on the surrounding environment
I. $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$ II. $NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$
III. $2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$
(a) I (b) III (c) II and III (d) I and II

9. Determine which of the following reactions taking place at constant pressure represent surrounding that do work on the system environment
I. $4NH_3(g) + 7O_2(g) \longrightarrow 4NO_2(g) + 6H_2O(g)$
II. $CO(g) + 2H_2(g) \longrightarrow CH_3OH(l)$
III. $C(s, \text{graphite}) + H_2O(g) \longrightarrow CO(g) + H_2(g)$
IV. $H_2O(s) \longrightarrow H_2O(l)$
(a) III, IV (b) II and III (c) II, IV (d) I and II, IV

10. A sample of liquid in a thermally insulated container (a calorimeter) is stirred for 2 hr. by a mechanical linkage to a motor in the surrounding, for this process :
(a) $w < 0;\ q = 0;\ \Delta U = 0$ (b) $w > 0;\ q > 0;\ \Delta U > 0$
(c) $w < 0;\ q > 0;\ \Delta U = 0$ (d) $w > 0;\ q = 0;\ \Delta U > 0$

11. A system undergoes a process in which $\Delta E = +300$ J while absorbing 400 J of heat energy and undergoing an expansion against 0.5 bar. What is the change in the volume (in L)?
(a) 4 (b) 5 (c) 2 (d) 3

12. An ideal gas expands against a constant external pressure of 2.0 atmosphere from 20 litre to 40 litre and absorbs 10 kJ of heat from surrounding. What is the change in internal energy of the system? (Given : 1 atm-litre =101.3 J)

(a) 4052 J (b) 5948 J (c) 14052 J (d) 9940 J

13. One mole of an ideal gas at 25°C expands in volume from 1.0 L to 4.0 L at constant temperature. What work (in J) is done if the gas expands against vacuum ($P_{external} = 0$)?

(a) -4.0×10^2 (b) -3.0×10^2 (c) -1.0×10^2 (d) Zero

14. At 25°C, a 0.01 mole sample of a gas is compressed from 4.0 L to 1.0 L at constant temperature. What is the work done for this process if the external pressure is 4.0 bar?

(a) 1.6×10^3 J (b) 8.0×10^2 J (c) 4.0×10^2 J (d) 1.2×10^3 J

15. Calculate the work done (in J) when 4.5 g of H_2O_2 reacts against a pressure of 1.0 atm at 25°C

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

(a) -1.63×10^2 (b) 4.5×10^2 (c) 3.2×10^2 (d) -6.1×10^2

16. 2 mole of zinc is dissolved in HCl at 25°C. The work done in open vessel is :

(a) −2.477 kJ (b) −4.955 kJ (c) 0.0489 kJ (d) None

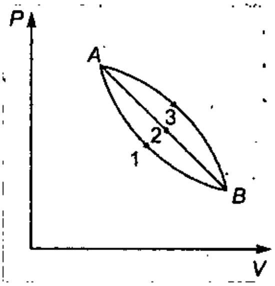
17. Temperature of 1 mole of a gas is increased by 2°C at constant pressure, work done is :

(a) R (b) $2R$ (c) $R/2$ (d) $3R$

18. A sample of an ideal gas is expanded 1 m^3 to 3 m^3 in a reversible process for which $P = KV^2$, with $K = 6 \text{ bar/m}^6$. Work done by the gas is :

(a) 5200 kJ (b) 15600 kJ (c) 52 kJ (d) 5267.6 kJ

19. A given mass of gas expands reversibly from the state A to the state B by three paths 1, 2 and 3 as shown in the figure. If w_1, w_2 and w_3 respectively be the work done by the gas along three paths then:



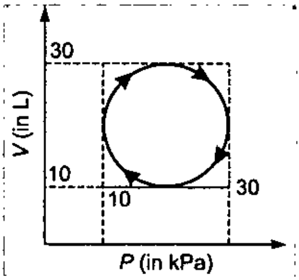
(a) $w_1 > w_2 > w_3$

(b) $w_1 < w_2 < w_3$

(c) $w_1 = w_2 = w_3$

(d) $w_2 < w_3 < w_1$

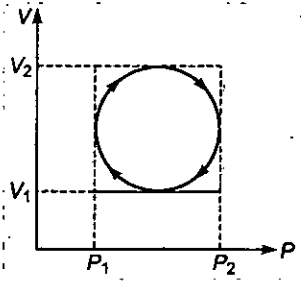
20. Heat absorbed by a system in going through a cyclic process shown in figure is :



(a) $10^7 \pi$ J (b) $10^6 \pi$ J

(c) $10^2 \pi$ J (d) $10^4 \pi$ J

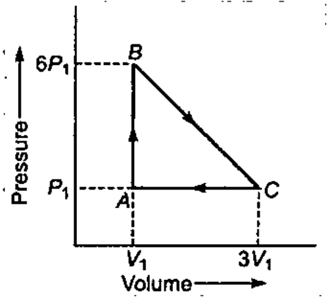
21. In the cyclic process shown in P–V diagram, the magnitude of the work done is :



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

(c) $\frac{\pi}{4}(P_2 - P_1)(V_2 - V_1)$ (d) $\pi(V_2 - V_1)^2$

22. An ideal gas is taken around the cycle $ABCA$ as shown in P–V diagram. The net work done during the cycle is equal to :



(a) $12P_1V_1$ (b) $6P_1V_1$

(c) $5P_1V_1$ (d) P_1V_1

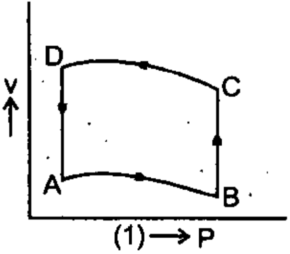
23. An ideal gas is at pressure P and temperature T in a box, which is kept in vacuum with in a large container. The wall of the box is punctured. What happens as the gas occupies entire container?

(a) It's temperature falls (b) Its temperature rises

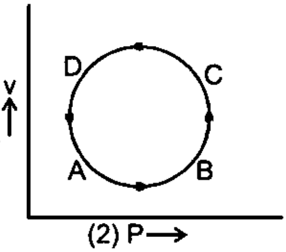
(c) Its temperature remains the same (d) Unpredictable

24. In diagrams (1 to 4), variation of volume with changing pressure is shown. A gas is taken along the path $ABCD$. The change in internal energy of the gas will be :

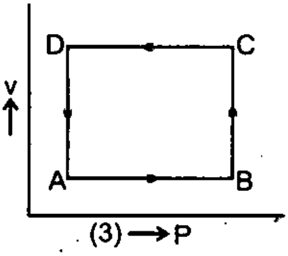
(1)



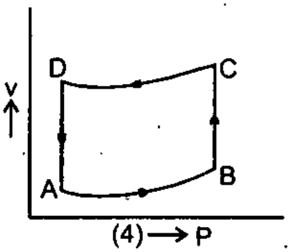
(2)



(3)



(4)



(a) Positive in all the cases (1) to (4)

(b) Positive in cases (1), (2), (3) but zero in case (4)

(c) Negative in cases (1), (2), (3) but zero in case (4)

(d) Zero in all the cases

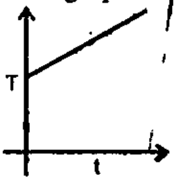
25. If the door of a refrigerator is kept open, the room in which the refrigerator is kept
(a) gets cooled
(b) gets heated
(c) neither gets cooled nor gets heated
(d) gets cooled or heated depending on the initial temperature of the room

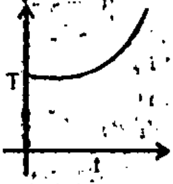
26. The temperature of an ideal gas increases in an :
(a) adiabatic expansion (b) isothermal expansion
(c) adiabatic compression (d) isothermal compression

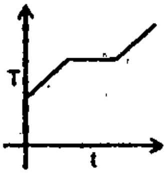
27. For two mole of an ideal gas :
(a) $C_v - C_p = R$ (b) $C_p - C_v = 2R$ (c) $C_p - C_v = R$ (d) $C_v - C_p = 2R$

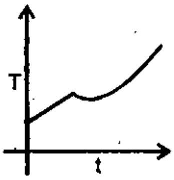
28. Which of the following expressions is true for an ideal gas ?
(a) $\left(\frac{\partial V}{\partial T}\right)_P = 0$ (b) $\left(\frac{\partial P}{\partial T}\right)_V = 0$ (c) $\left(\frac{\partial U}{\partial V}\right)_T = 0$ (d) $\left(\frac{\partial U}{\partial T}\right)_V = 0$

29. Liquefied oxygen at 1 atmosphere is heated from 50 K to 300 K by supplying heat at a constant rate. The graph that correctly shows the relationship between temperature and time is :

(a)


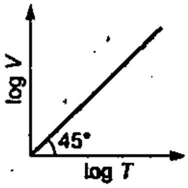
(b)


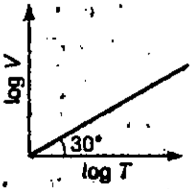
(c)


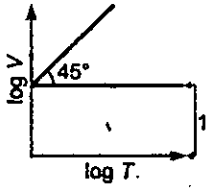
(d)


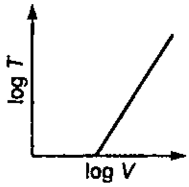
30. If w_1, w_2, w_3 and w_4 for an ideal gas are magnitude of work done in isothermal, adiabatic, isobaric and isochoric reversible expansion processes, the correct order will be :
(a) $w_1 > w_2 > w_3 > w_4$ (b) $w_3 > w_2 > w_1 > w_4$
(c) $w_3 > w_2 > w_4 > w_1$ (d) $w_3 > w_1 > w_2 > w_4$

31. For a closed container containing 100 mole of an ideal gas fitted with movable, frictionless, weightless piston operating such that pressure of gas remains constant at 8.21 atm, which graph represents correct variation of log *V* vs. log *T* where *V* is in litre and *T* in kelvin.

(a)


(b)


(c)


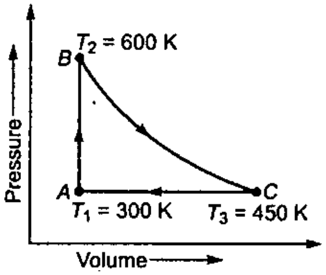
(d)


32. A gas expands against a variable pressure given by $P = \frac{20}{V}$ (where *P* in atm and *V* in L). During expansion from volume of 1 litre to 10 litre, the gas undergoes a change in internal energy of 400 J. How much heat is absorbed by the gas during expansion?
(a) 46 J (b) 4660 J (c) 5065.8 J (d) 4260 J

33. 2 mole of an ideal gas at 27°C expands isothermally and reversibly from a volume of 4 litre to 40 litre. The work done (in kJ) by the gas is :
(a) $w = -28.72$ kJ (b) $w = -11.488$ kJ
(c) $w = -5.736$ kJ (d) $w = -4.988$ kJ

34. 10 mole of ideal gas expand isothermally and reversibly from a pressure of 10 atm to 1atm at 300 K. What is the largest mass which can lifted through a height of 100 meter?
(a) 31842 kg (b) 58.55 kg (c) 342.58 kg (d) None of these

35. A heat engine carries one mole of an ideal mono-atomic gas around the cycle as shown in the figure. Select the correct option:
(a) $q_{AB} = 450\,R$ and $q_{CA} = -450\,R$
(b) $q_{AB} = 450\,R$ and $q_{CA} = -225\,R$
(c) $q_{AB} = 450\,R$ and $q_{CA} = -375\,R$
(d) $q_{AB} = 375\,R$ and $q_{CA} = -450\,R$



36. What is the final temperature of 0.10 mole monoatomic ideal gas that performs 75 cal of work adiabatically if the initial temperature is 227°C? (use $R = 2$ cal/K-mol)
(a) 250 K (b) 300 K (c) 350 K (d) 750 K

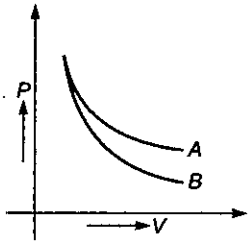
37. The work done by the gas in reversible adiabatic expansion process is :
(a) $\frac{P_2V_2 - P_1V_1}{\gamma - 1}$ (b) $\frac{nR\,(T_1 - T_2)}{\gamma - 1}$ (c) $\frac{P_2V_2 - P_1V_1}{\gamma}$ (d) None of these

38. During an adiabatic process, the pressure of gas is found to be proportional to the cube of its absolute temperature. The ratio of $(C_{p,m}/C_{v,m})$ for gas is :
(a) $\frac{3}{2}$ (b) $\frac{5}{3}$ (c) $\frac{7}{2}$ (d) $\frac{4}{3}$

39. A gas expands adiabatically at constant pressure such that $T \propto V^{-1/2}$
The value of γ $(C_{p,m}/C_{v,m})$ of the gas will be :
(a) 1.30 (b) 1.50 (c) 1.70 (d) 2

40. For a reversible adiabatic ideal gas expansion $\frac{dP}{P}$ is equal to :
(a) $\gamma \frac{dV}{V}$ (b) $-\gamma \frac{dV}{V}$ (c) $\left(\frac{\gamma}{\gamma - 1}\right)\frac{dV}{V}$ (d) $\frac{dV}{V}$

41. P–V plot for two gases (assuming ideal)during adiabatic processes are given in the Fig. Plot A and plot B should correspond respectively to:
(a) He and H_2 (b) H_2 and He
(c) He and Ne (d) H_2 and Cl_2



42. Calculate the final temperature of a monoatomic ideal gas that is compressed reversible and adiabatically from 16 L to 2 L at 300 K :
(a) 600 K (b) 1044.6 K (c) 1200 K (d) 2400 K

43. 5 mole of an ideal gas expand isothermally and irreversibly from a pressure of 10 atm to 1 atm against a constant external pressure of 1 atm. w_{irr} at 300 K is :

(a) −15.921 kJ (b) −11.224 kJ (c) −110.83 kJ (d) None of these

44. With what minimum pressure (in kPa), a given volume of an ideal gas ($C_{p,m} = 7/2\,R$), originally at 400 K and 100 kPa pressure can be compressed irreversibly adiabatically in order to raise its temperature to 600 K :

(a) 362.5 kPa (b) 275 kPa (c) 437.5 kPa (d) 550 kPa

45. The work done in adiabatic compression of 2 mole of an ideal monoatomic gas against constant external pressure of 2 atm starting from initial pressure of 1 atm and initial temperature of 300 K ($R = 2$ cal/mol-degree)

(a) 360 cal (b) 720 cal (c) 800 cal (d) 1000 cal

46. One mole of an ideal gas $\left(C_{v,m} = \frac{5}{2} R\right)$ at 300 K and 5 atm is expanded adiabatically to a final pressure of 2 atm against a constant pressure of 2 atm. Final temperature of the gas is :

(a) 270 K (b) 273 K (c) 248.5 K (d) 200 K

47. 10 litre of a non linear polyatomic ideal gas at 127°C and 2 atm pressure is suddenly released to 1 atm pressure and the gas expanded adiabatically against constant external pressure, the final temperature and volume of the gas respectively are.

(a) $T = 350\text{K}; V = 17.5\text{L}$ (b) $T = 300\text{K}; V = 15\text{L}$
(c) $T = 250\text{K}; V = 12.5\text{L}$ (d) None of these

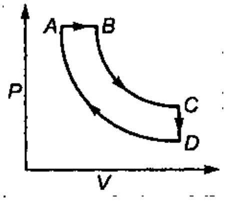
48. Calculate average molar heat capacity at constant volume of gaseous mixture contained 2 mole of each of two ideal gases $A\left(C_{v,m} = \frac{3}{2} R\right)$ and $B\left(C_{v,m} = \frac{5}{2} R\right)$:

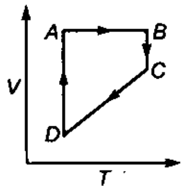
(a) R (b) $2R$ (c) $3R$ (d) $8R$

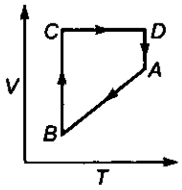
49. 0.5 mole each of two ideal gases $A\left(C_{v,m} = \frac{5}{2} R\right)$ and B ($C_{v,m} = 3R$) are taken in a container and expanded reversibly and adiabatically, during this process temperature of gaseous mixture decreased from 350 K to 250 K. Find ΔH (in cal/mol) for the process :

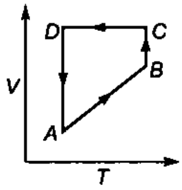
(a) $-100\,R$ (b) $-137.5\,R$
(c) $-375\,R$ (d) None of these

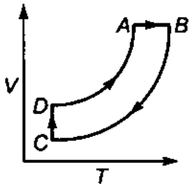
50. A cyclic process $ABCD$ is shown in P–V diagram for an ideal gas. Which of the following diagram represents the same process?



(a)


(b)


(c)


(d)


51. 36 mL of pure water takes 100 sec to evaporate from a vessel and heater connected to an electric source which delivers 806 watt. The $\Delta H_{\text{vaporization}}$ of H_2O is :
(a) 40.3 kJ/mol (b) 43.2 kJ/mol (c) 4.03 kJ/mol (d) None of these

52. For the reaction : $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$:
(a) $\Delta H = \Delta E$ (b) $\Delta H > \Delta E$ (c) $\Delta H < \Delta E$ (d) None of the above

53. Consider the reaction at 300 K

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g); \quad \Delta H^\circ = -185 \text{ kJ}$$

If 2 mole of H_2 completely react with 2 mole of Cl_2 to form HCl. What is ΔU° for this reaction?
(a) 0 (b) −185 kJ (c) 370 kJ (d) None of these

54. Which of the indicated relationship is correct for the following exothermic reaction carried out at constant pressure?

$$CO(g) + 3H_2(g) \longrightarrow CH_4(g) + H_2O(g)$$

(a) $\Delta E = \Delta H$ (b) $\Delta E > \Delta H$ (c) $w < 0$ (d) $q > 0$

55. One mole of an ideal gas undergoes a change of state (2.0 atm, 3.0 L) to (2.0 atm, 7.0 L) with a change in internal energy $(\Delta U) = 30$ L-atm. The change in enthalpy (ΔH) of the process in L-atm :
(a) 22 (b) 38 (c) 25 (d) None of these

56. What is the change in internal energy when a gas contracts from 377 mL to 177 mL under a constant pressure of 1520 torr, while at the same time being cooled by removing 124 J heat?
(a) 40.52 J (b) −83.48 J (c) −248 J (d) None of these

57. For the real gases reaction $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$; $\Delta H = -560$ kJ. In 10 litre rigid vessel at 500 K the initial pressure is 70 bar and after the reaction it becomes 40 bar. The change in internal energy is :
(a) −557 kJ (b) −530 kJ (c) −563 kJ (d) None of these

58. One mole of a non-ideal gas undergoes a change of state from (1.0 atm, 3.0 L, 200 K) to (4.0 atm, 5.0 L, 250 K) with a change in internal energy $(\Delta U) = 40$ L-atm. The change in enthalpy of the process in L-atm :
(a) 43 (b) 57 (c) 42 (d) None of these

59. Consider the reaction at 300 K

$$C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l); \ \Delta H = -3271 \text{ kJ}$$

What is ΔU for the combustion of 1.5 mole of benzene at 27°C?
(a) −3267.25 kJ (b) −4900.88 kJ (c) −4906.5 kJ (d) −3274.75 kJ

60. For the reaction; $FeCO_3(s) \longrightarrow FeO(s) + CO_2(g)$; $\Delta H = 82.8$ kJ at 25°C, what is (ΔE or ΔU) at 25°C?
(a) 82.8 kJ (b) 80.32 kJ (c) −2394.77 kJ (d) 85.28 kJ

61. At 5×10^5 bar pressure density of diamond and graphite are 3 g/cc and 2 g/cc respectively, at certain temperature 'T'. Find the value of $\Delta U - \Delta H$ for the conversion of 1 mole of graphite to 1 mole of diamond at temperature 'T' :
(a) 100 kJ/mol (b) 50 kJ/mol (c) −100 kJ/mol (d) None of these

62. Predict which of the following reaction(s) has a positive entropy change?

I. $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$

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

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

(a) I and II (b) III (c) II and III (d) II

63. Predict which of the following reaction(s) has a negative entropy change?

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

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

III. $2KClO_4(s) \longrightarrow 2KClO_3(s) + O_2(g)$

(a) III (b) II (c) I and II (d) I

64. Which of the following reactions is associated with the most negative change in entropy?

(a) $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$

(b) $C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$

(c) $C(s, \text{graphite}) + O_2(g) \longrightarrow CO_2(g)$

(d) $3C_2H_2(g) \longrightarrow C_6H_6(l)$

65. When two mole of an ideal gas $\left(C_{p,m} = \frac{5}{2}R\right)$ heated from 300 K to 600 K at constant pressure. The change in entropy of gas (ΔS) is :

(a) $\frac{3}{2}R\ln 2$ (b) $-\frac{3}{2}R\ln 2$ (c) $5R\ln 2$ (d) $\frac{5}{2}R\ln 2$

66. Which of the following expression for an irreversible process :

(a) $dS > \frac{dq}{T}$ (b) $dS = \frac{dq}{T}$ (c) $dS < \frac{dq}{T}$ (d) $dS = \frac{dU}{T}$

67. Which of the following expressions is known as Clausius inequality ?

(a) $\oint \frac{dq}{T} \le 0$ (b) $\oint \frac{ds}{T} = 0$ (c) $\oint \frac{T}{dq} \le 0$ (d) $\oint \frac{dq}{T} \ge 0$

68. In problem 65, calculate ΔS_{gas} if process is carried out at constant volume :

(a) $5R\ln 2$ (b) $\frac{3}{2}R\ln 2$ (c) $3R\ln 2$ (d) $-3R\ln 2$

69. If one mole of an ideal gas $\left(C_{p,m} = \frac{5}{2}R\right)$ is expanded isothermally at 300 until it's volume is tripled, then change in entropy of gas is :

(a) zero (b) infinity (c) $\frac{5}{2}R\ln 3$ (d) $R\ln 3$

70. In previous problem if expansion is carried out freely ($P_{ext} = 0$), then ΔS is :

(a) zero (b) infinity (c) $R\ln 3$ (d) None

71. When one mole of an ideal gas is compressed to half of its initial volume and simultaneously heated to twice its initial temperature, the change in entropy of gas (ΔS) is :

(a) $C_{p,m}\ln 2$ (b) $C_{v,m}\ln 2$ (c) $R\ln 2$ (d) $(C_{v,m} - R)\ln 2$

72. What is the change in entropy when 2.5 mole of water is heated from 27°C to 87°C? Assume that the heat capacity is constant. ($C_{p,m}(H_2O) = 4.2$ J/g-K $\ln(1.2) = 0.18$)

(a) 16.6 J/K (b) 9 J/K (c) 34.02 J/K (d) 1.89 J/K

73. Calculate standard entropy change in the reaction

$$Fe_2O_3(s) + 3H_2(g) \longrightarrow 2Fe(s) + 3H_2O(l)$$

Given : $S_m^\circ(Fe_2O_3, S) = 87.4$, $S_m^\circ(Fe, S) = 27.3$,

$S_m^\circ(H_2, g) = 130.7$, $S_m^\circ(H_2O, l) = 69.9\ JK^{-1}\ mol^{-1}$

(a) $-212.5\ JK^{-1}\ mol^{-1}$ (b) $-215.2\ JK^{-1}\ mol^{-1}$
(c) $-120.9\ JK^{-1}\ mol^{-1}$ (d) None of these

74. Calculate the entropy change (J/mol K) of the given reaction. The molar entropies [J/K-mol] are given in brackets after each substance.

$$2PbS(s)\,[91.2] + 3O_2(g)\,[205.1] \longrightarrow 2PbO(s)\,[66.5] + 2SO_2(g)\,[248.2]$$

(a) −113.5 (b) −168.3 (c) +72.5 (d) −149.2

75. Given $\Delta_r S° = -266$ and the listed [S°_m values] calculate $S°$ for $Fe_3O_4(s)$:

$$4Fe_3O_4(s)\,[\ldots\ldots] + O_2(g)\,[205] \longrightarrow 6Fe_2O_3(s)\,[87]$$

(a) +111.1 (b) +122.4 (c) 145.75 (d) 248.25

76. The entropy change for a phase transformation is :

(a) $\dfrac{\Delta U}{\gamma + dT}$ (b) $\dfrac{\Delta T}{\Delta H}$ (c) $\dfrac{\Delta H}{T}$ (d) $\dfrac{\Delta H + \Delta G}{T}$

77. What is the melting point of benzene if $\Delta H_{\text{fusion}} = 9.95\,kJ/mol$ and $\Delta S_{\text{fusion}} = 35.7\,J/K\text{-mol}$?

(a) 278.7°C (b) 278.7 K (c) 300 K (d) 298 K

78. ΔS for freezing of 10 g of $H_2O(l)$ (enthalpy of fusion is 80 cal/g) at 0°C and 1 atm is :

(a) 12.25 J/K (b) −0.244 J/K (c) −2.93 J/K (d) −12.25 J/K

79. Chloroform has $\Delta H_{\text{vaporization}} = 29.2$ kJ/mol and boils at 61.2°C. What is the value of $\Delta S_{\text{vaporization}}$ for chloroform?

(a) 87.3 J/mol-K (b) 477.1 J/mol-K (c) −87.3 J/mol-K (d) −477.1 J/mol-K

80. The entropy of vaporization of benzene is $85\ JK^{-1}\ mol^{-1}$. When 117g benzene vaporizes at it's normal boiling point, the entropy change of surrounding is :

(a) $-85\ JK^{-1}$ (b) $-85 \times 1.5\ JK^{-1}$ (c) $85 \times 1.5\ JK^{-1}$ (d) None of these

81. Identify the correct statement regarding entropy

(a) At absolute zero temperature, the entropy of perfectly crystalline substances is +ve
(b) At absolute zero temperature entropy of perfectly crystalline substance is taken to be zero
(c) At 0°C the entropy of a perfectly crystalline substance is taken to be zero
(d) At absolute zero temperature, the entropy of all crystalline substances is taken to be zero

82. Calculate ΔS for following process :

$$\underset{\text{at}\,100\text{K}}{X(s)} \longrightarrow \underset{\text{at}\,200\text{K}}{X(l)}$$

Given : Melting point of $X_{(s)} = 100\,K$; $\Delta H_{\text{Fusion}} = 20\,kJ/mol$; $C_{p,m}(X, l) = 10\,J/mol.\,K$

(a) 26.93 J/K (b) 206.93 J/K (c) 203 J/K (d) 206.93 kJ/K

83. For a perfectly crystalline solid $C_{p,m} = aT^3$, where a is constant. If $C_{p,m}$ is 0.42 J/K mol at 10 K, molar entropy at 20 K is :

(a) 0.42 J/K mol (b) 0.14 J/K mol (c) 1.12 J/K mol (d) zero

84. Consider the following spontaneous reaction $3X_2(g) \rightarrow 2X_3(g)$. What are the sign of ΔH, ΔS and ΔG for the reaction?

(a) +ve, +ve, +ve (b) +ve, −ve, −ve (c) −ve, +ve, −ve (d) −ve, −ve, −ve

85. For the reaction $2H(g) \longrightarrow H_2(g)$, the sign of ΔH and ΔS respectively are :

(a) +, − (b) +, + (c) −, + (d) −, −

86. Consider the following reaction.

$$C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(g)$$

signs of $\Delta H, \Delta S$ and ΔG for the above reaction will be

(a) +, –, + (b) –, +, – (c) –, +, + (d) +, +, –

87. Consider the following reaction at temperature T:

$$CH_2{=}CH_2(g) + Cl_2(g) \longrightarrow ClCH_2CH_2Cl(g)$$

$$\Delta_r H^\circ = -217.5 \text{ kJ/mol}, \quad \Delta_r S^\circ = -233.9 \text{ J/K-mol}$$

Reaction is supported by :

(a) entropy (b) enthalpy (c) both (a) & (b) (d) neither

88. For a process to be spontaneous at constant T and P :

(a) $(\Delta G)_{\text{system}}$ must be negative (b) $(\Delta G)_{\text{system}}$ must be positive

(c) $(\Delta S)_{\text{system}}$ must be positive (d) $(\Delta S)_{\text{system}}$ must be negative

89. For a reaction to occur spontaneously :

(a) ΔS must be negative (b) $(-\Delta H + T\,\Delta S)$ must be positive

(c) $\Delta H + T\Delta S$ must be negative (d) ΔH must be negative

90. Which of the following conditions regarding a chemical process ensures its spontaneity at all temperature?

(a) $\Delta H > 0, \Delta G < 0$ (b) $\Delta H < 0, \Delta S > 0$ (c) $\Delta H < 0, \Delta S < 0$ (d) $\Delta H > 0, \Delta S < 0$

91. The free energy change $\Delta G = 0$, when

(a) the system is at equilibrium

(b) catalyst is added

(c) reactants are initially mixed thoroughly

(d) the reactants are completely consumed

92. Which of the following conditions will always lead to a non-spontaneous change?

(a) ΔH and ΔS both +ve (b) ΔH is –ve and ΔS is +ve

(c) ΔH and ΔS both –ve (d) ΔH is +ve and ΔS is –ve

93. Suppose that a reaction has $\Delta H = -40$ kJ and $\Delta S = -50$ J/K. At what temperature range will it change from spontaneous to non-spontaneous?

(a) 0.8 K to 1 K (b) 799 K to 800 K (c) 800 K to 801 K (d) 799 K to 801 K

94. For isothermal expansion in case of an ideal gas :

(a) $\Delta G = \Delta S$ (b) $\Delta G = \Delta H$ (c) $\Delta G = -T.\Delta S$ (d) None of these

95. What is the normal boiling point of mercury?

Given : ΔH_f° (Hg, l) = 0; S° (Hg, l) = 77.4 J/K-mol

ΔH_f° (Hg, g) = 60.8 kJ/mol; S° (Hg, g) = 174.4 J/K-mol

(a) 624.8 K (b) 626.8 K (c) 636.8 K (d) None of these

96. 18 gm of ice is converted into water at 0°C and 1 atm. The entropies of $H_2O(s)$ and $H_2O(l)$ are 38.2 and 60 J/mol K respectively. The enthalpy change for this conversion is :

(a) 5951.4 J/mol (b) 595.14 J/mol (c) –5951.4 J/mol (d) None of these

97. Using the listed [ΔG°_f values] calculate ΔG° for the reaction :

$3H_2S(g)\,[-33.6] + 2HNO_3(l)\,[-80.6] \longrightarrow 2NO(g)\,[+86.6] + 4H_2O(l)\,[-237.1] + 3S(s)\,[0.0]$

(a) −513.0 (b) −1037.0 (c) +433.4 (d) +225.0

98. From the following ΔH° and ΔS° values, predict which of reactions I, II, and III would be spontaneous at 25°C.

	ΔH° (kJ)	ΔS° (J/K)
I.	+10.5	+30
II.	+1.8	−113
III.	−126	+84

(a) III (b) I (c) II and III (d) I and II

99. Calculate ΔH_f° for UBr_4 from the ΔG° of reaction and the S° values.

$U(s) + 2Br_2(l) \longrightarrow UBr_4(s)$; $\Delta G^\circ = -788.6$ kJ; S° (J/K-mol) 50.3, 152.3, 242.6

(a) −822.1 kJ/mol (b) −841.2 kJ/mol (c) −775.6 kJ/mol (d) −804.3 kJ/mol

100. The entropies of $H_2(g)$ and $H(g)$ are 130.6 and 114.6 J mol^{-1} K^{-1} respectively at 298 K. Using the data given below calculate the bond energy of H_2 (in kJ/mol) :

$$H_2(g) \longrightarrow 2H(g);\ \Delta G^\circ = 406.6\ \text{kJ}$$

(a) 377.2 (b) 436.0 (c) 425.5 (d) 430.5

101. Consider the ΔG_f° and ΔH_f° (kJ/mol) for the following oxides. Which oxide can be most easily decomposed to form the metal and oxygen gas?

(a) ZnO ($\Delta G^\circ = -318.4$, $\Delta H^\circ = -348.3$) (b) Cu_2O ($\Delta G^\circ = -146.0$, $\Delta H^\circ = -168.8$)

(c) HgO ($\Delta G^\circ = -58.5$, $\Delta H^\circ = -90.8$) (d) PbO ($\Delta G^\circ = -187.9$, $\Delta H^\circ = -217.3$)

102. Which of the following option is correct ?

(a) $\left[\dfrac{\partial \ln K_p}{\partial T}\right] = \dfrac{\Delta H^\circ}{RT^2}$ (b) $\dfrac{\partial \ln K}{\partial T} = \dfrac{E_a}{RT^2}$

(c) $\left[\dfrac{\partial \ln K_p}{\partial T}\right] = \dfrac{\Delta U}{RT^2}$ (d) All of these

103. Calculate ΔG° (kJ/mol) at 127°C for a reaction with $K_{\text{equilibrium}} = 10^5$:

(a) −38.294 (b) −16.628 (c) − 9.16 (d) None of these

104. When reaction is carried out at standard states then at the equilibrium :

(a) $\Delta H^\circ = 0$ (b) $\Delta S^\circ = 0$

(c) equilibrium constant $K = 0$ (d) equilibrium constant $K = 1$

105. At 25°C, ΔG° for the process $H_2O(l) \rightleftharpoons H_2O(g)$ is 8.6 kJ. The vapour pressure of water at this temperature, is nearly :

(a) 24 torr (b) 285 torr (c) 32.17 torr (d) 100 torr

106. For the auto-ionization of water at 25°C, $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$ equilibrium constant is 10^{-14}.

What is ΔG° for the process?

(a) $\simeq 8 \times 10^4$ J (b) $\simeq 3.5 \times 10^4$ J (c) $\simeq 10^4$ J (d) None of these

107. The molar entropies of HI(g), H(g) and I(g) at 298 K are 206.5, 114.6, and 180.7 J mol^{-1} K^{-1} respectively. Using the $\Delta G°$ given below, calculate the bond energy of HI.

$$\text{HI}(g) \longrightarrow \text{H}(g) + \text{I}(g); \quad \Delta G° = 271.8 \text{ kJ}$$

(a) 282.4 (b) 298.3 (c) 290.1 (d) 315.4

108. Hess's law states that :

(a) the standard enthalpy of an overall reaction is the sum of the enthalpy changes in individual reactions.

(b) enthalpy of formation of a compound is same as the enthalpy of decomposition of the compound into constituent elements, but with opposite sign.

(c) at constant temperature the pressure of a gas is inversely h proportional to its volume

(d) the mass of a gas dissolved per litre of a solvent is proportional to the pressure of the gas in equilibrium with the solution

109. An imaginary reaction $X \longrightarrow Y$ takes place in three steps

$X \longrightarrow A, \Delta H = -q_1$; $\quad B \longrightarrow A, \Delta H = -q_2$; $\quad B \longrightarrow Y, \Delta H = -q_3$

If Hess' law is applicable, then the heat of the reaction ($X \rightarrow Y$) is :

(a) $q_1 - q_2 + q_3$ (b) $q_2 - q_3 - q_1$ (c) $q_1 - q_2 - q_3$ (d) $q_3 - q_2 - q_1$

110. The enthalpy change for a reaction does not depend upon :

(a) the physical states of reactants and products

(b) use of different reactants for the same product

(c) the number of intermediate reaction steps

(d) the differences in initial or final temperatures of involved substances

111. The standard enthalpy of formation of gaseous H_2O at 298 K is −241.82 kJ/mol. Calculate $\Delta H°$ at 373 K given the following values of the molar heat capacities at constant pressure :

$H_2O(g) = 33.58 \text{ JK}^{-1} \text{ mol}^{-1}$; $H_2(g) = 29.84 \text{ JK}^{-1} \text{ mol}^{-1}$; $O_2(g) = 29.37 \text{ JK}^{-1} \text{ mol}^{-1}$

Assume that the heat capacities are independent of temperature :

(a) −242.6 kJ/mol (b) −485.2 kJ/mol (c) −121.3 kJ/mol (d) −286.4 kJ/mol

112. Which of the following value of ΔH_f° represent that the product is least stable ?

(a) $-94.0 \text{ kcal mol}^{-1}$ (b) $-231.6 \text{ kcal mol}^{-1}$ (c) $+21.4 \text{ kcal mol}^{-1}$ (d) $+64.8 \text{ kcal mol}^{-1}$

113. For which of the following substances the enthalpy of formation in the standard state is zero ?

(a) Sucrose (b) Ethanol (c) Aluminium (d) Calcium chloride

114. Calculate the standard enthalpy of reaction for the following reaction using the listed enthalpies of reaction :

$$3\text{Co}(s) + 2\text{O}_2(g) \longrightarrow \text{Co}_3\text{O}_4(s)$$
$$2\text{Co}(s) + \text{O}_2(g) \longrightarrow 2\text{CoO}(s); \quad \Delta H_1^{\circ} = -475.8 \text{ kJ}$$
$$6\text{CoO}(s) + \text{O}_2(g) \longrightarrow 2\text{Co}_3\text{O}_4(s); \Delta H_2^{\circ} = -355.0 \text{ kJ}$$

(a) −891.2 kJ (b) −120.8 kJ (c) +891.2 kJ (d) −830.8 kJ

115. From given following equations and $\Delta H°$ values, determine the enthalpy of reaction at 298 K for the reaction :

$$\text{C}_2\text{H}_4(g) + 6\text{F}_2(g) \longrightarrow 2\text{CF}_4(g) + 4\text{HF}(g)$$
$$\text{H}_2(g) + \text{F}_2(g) \longrightarrow 2\text{HF}(g); \quad \Delta H_1^{\circ} = -537 \text{ kJ}$$

$$C(s) + 2F_2(g) \longrightarrow CF_4(g);\quad \Delta H_2^\circ = -680\text{ kJ}$$

$$2C(s) + 2H_2(g) \longrightarrow C_2H_4(g);\quad \Delta H_3^\circ = 52\text{ kJ}$$

(a) −1165 (b) −2486 (c) +1165 (d) +2486

116. Given :

$C(\text{diamond}) + O_2 \longrightarrow CO_2;\ \Delta H = -395\text{ kJ}$

$C(\text{graphite}) + O_2 \longrightarrow CO_2;\ \Delta H = -393\text{ kJ}$

The enthalpy of formation of diamond from graphite is

(a) +2.0 kJ (b) −1.5 kJ (c) −788 kJ (d) 788 kJ

117. Which of the following equations represents a reaction that provides the enthalpy of formation of CH_3Cl?

(a) $C(s) + HCl(g) + H_2(g) \longrightarrow CH_3Cl(g)$

(b) $C(s) + 3H(g) + Cl(g) \longrightarrow CH_3Cl(g)$

(c) $C(s) + 3/2H_2(g) + 1/2Cl_2(g) \longrightarrow CH_3Cl(g)$

(d) $CH_4(g) + Cl_2(g) \longrightarrow CH_3Cl(g) + HCl(g)$

118. Use the given standard enthalpies of formation (in kJ/mol) to determine the enthalpy of reaction of the following reaction :

$$NH_3(g) + 3F_2(g) \longrightarrow NF_3(g) + 3HF(g)$$

$$\Delta H_f^\circ (NH_3, g) = -46.2;\quad \Delta H_f^\circ (NF_3, g) = -113.0;\quad \Delta H_f^\circ (HF, g) = -269.0$$

(a) −335.8 kJ/mol (b) −873.8 kJ/mol (c) −697.2 kJ/mol (d) −890.4 kJ/mol

119. The standard enthalpy of formation of octane (C_8H_{18}) is −250 kJ/mol. Calculate the enthalpy of combustion of C_8H_{18}. The enthalpy of formation of $CO_2(g)$ and $H_2O(l)$ are −394 kJ/mol and −286 kJ/mol respectively :

(a) − 5200 kJ/mol (b) − 5726 kJ/mol (c) − 5476 kJ/mol (d) − 5310 kJ/mol

120. Determine the enthalpy of formation of $B_2H_6(g)$ in kJ/mol of the following reaction :

$$B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(s) + 3H_2O(g);$$

Given : $\Delta_r H^\circ = -1941$ kJ/mol; $\Delta H_f^\circ (B_2O_3, s) = -1273$ kJ/mol;

$\Delta H_f^\circ (H_2O, g) = -241.8$ kJ/mol

(a) −75.6 (b) +75.6 (c) −57.4 (d) −28.4

121. Consider the following reactions :

$$C(s) + O_2(g) \longrightarrow CO_2(g) + x\text{ kJ}$$

$$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) + y\text{ kJ}$$

The heat of formation of $CO(g)$ is :

(a) $-(x + y)$ kJ/mol (b) $(x - y)$ kJ/mol (c) $(y - x)$ kJ/mol (d) None of these

122. If $\Delta_f H^\circ (C_2H_4)$ and $\Delta_f H^\circ (C_2H_6)$ are x_1 and x_2 kcal mol^{-1}, then heat of hydrogenation of C_2H_4 is :

(a) $x_1 + x_2$ (b) $x_1 - x_2$ (c) $x_2 - x_1$ (d) $x_1 + 2x_2$

123. What amount of energy (kJ) is released in the combustion of 5.8 g of $C_4H_{10}(g)$?

$$2C_4H_{10}(g) + 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(l);\quad \Delta H^\circ = -5756\text{ kJ}$$

(a) 575.6 (b) 287.8 (c) 182 (d) 57.56

124. The enthalpy of the reaction forming PbO according to the following equation is 438 kJ. What heat energy (kJ) is released in formation of 22.3 g PbO(*s*)?

(Atomic weights : Pb = 207, O = 16.0)

$$2Pb(s) + O_2(g) \longrightarrow 2PbO(s)$$

(a) 21.9 (b) 28.7 (c) 14.6 (d) 34.2

125. The fat, $C_{57}H_{104}O_6(s)$, is metabolized via the following reaction. Given the enthalpies of formation, calculate the energy (kJ) liberated when 1.0 g of this fat reacts.

$$C_{57}H_{104}O_6(s) + 80O_2(g) \longrightarrow 57CO_2(g) + 52H_2O(l)$$

$\Delta_f H°(C_{57}H_{104}O_6, s) = -70870$ kJ/mol; $\Delta_f H°(H_2O, l) = -285.8$ kJ/mol;

$\Delta_f H°(CO_2, g) = -393.5$ kJ/mol

(a) – 37.98 (b) – 40.4 (c) – 33.4 (d) – 30.2

126. The heat of formation of $NH_3(g)$ is –46 kJ mol^{-1}. The ΔH (in kJ mol^{-1}) of the reaction, $2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$ is :

(a) 46 (b) –46 (c) 92 (d) –92

127. Consider the following reaction:

$$H_2O(l) \longrightarrow H_2O(g); \ \Delta H_1 = 44 \text{ kJ}$$

$$2CH_3OH(l) + 3O_2(g) \longrightarrow 4H_2O(l) + 2CO_2(g); \ \Delta H_2 = -1453 \text{ kJ}$$

What is the value of ΔH for second reaction if water vapour instead of liquid water is formed as product?

(a) –1409 kJ (b) –1629 kJ (c) –1277 kJ (d) None of these

128. The standard enthalpy change for the following reaction is 436.4 kJ :

$$H_2(g) \longrightarrow H(g) + H(g)$$

What is the $\Delta_f H°$ of atomic hydrogen (H)?

(a) 872.8 kJ/mol (b) 218.2 kJ/mol (c) – 218.2 kJ/mol (d) – 436.9 kJ/mol

129. Determine enthalpy of formation for $H_2O_2(l)$, using listed enthalpies of reaction :

$$N_2H_4(l) + 2H_2O_2(l) \longrightarrow N_2(g) + 4H_2O(l); \quad \Delta_r H_1^\circ = -818 \text{ kJ/mol}$$

$$N_2H_4(l) + O_2(g) \longrightarrow N_2(g) + 2H_2O(l); \quad \Delta_r H_2^\circ = -622 \text{ kJ/mol}$$

$$H_2(g) + 1/2\,O_2(g) \longrightarrow H_2O(l); \quad \Delta_r H_3^\circ = -285 \text{ kJ/mol}$$

(a) –383 kJ/mol (b) –187 kJ/mol (c) –498 kJ/mol (d) None of these

130. Heat of combustion of ethanol at constant pressure and at temperature *T* K is found to be $-q$ J mol^{-1}. Hence, heat of combustion (in J mol^{-1}) of ethanol at the same temperature at constant volume will be :

(a) $RT - q$ (b) $-(q + RT)$ (c) $q - RT$ (d) $q + RT$

131. Stearic acid $[CH_3(CH_2)_{16}CO_2H]$ is a fatty acid, the part of fat that stores most of the energy. 1.0 g of stearic acid was burned in a bomb calorimeter. The bomb had a heat capacity of 652 J/°C. If the temperature of 500 g water ($c = 4.18$ J/g °C) rose from 25.0 to 39.3°C, how much heat was released when the stearic acid was burned? [Given C_p $(H_2O) = 4.18$ J/g°C]

(a) 39.21 kJ (b) 29.91 kJ (c) 108 kJ (d) 9.32 kJ

132. Gasoline has an enthalpy of combustion 24000 kJ/ gallon. When gasoline burns in an automobile engine, approximately 30% of the energy released is used to produce mechanical work. The remainder is lost as heat transfer to the engine's cooling system. As a start on estimating how much heat transfer is required, calculate what mass of water could be heated from 25°C to 75°C by the combustion of 1.0 gallon of gasoline in an automobile?

(Given : C $(H_2O) = 4.18$ J/g°C)

(a) 34.45 kg (b) 80.383 kg (c) 22 kg (d) 224 kg

133. A 0.05 L sample of 0.2 M aqueous hydrochloric acid is added to 0.05 L of 0.2 M aqueous ammonia in a calorimeter. Heat capacity of entire calorimeter system is 480 J/K. The temperature increase is 1.09 K. Calculate $\Delta_r H^\circ$ in kJ/mol for the following reaction :

$$HCl(aq.) + NH_3(aq.) \longrightarrow NH_4Cl(aq.)$$

(a) −52.32 (b) −61.1 (c) −55.8 (d) −58.2

134. A coffee cup calorimeter initially contains 125 g of water, at a temperature of 24.2°C. 8 g of ammonium nitrate (NH_4NO_3), also at 24.2°C, is added to the water, and the final temperature is 18.2°C. What is the heat of solution of ammonium nitrate in kJ/mol? The specific heat capacity of the solution is 4.2 J/°C g.

(a) 33.51 kJ/mol (b) 39.5 kJ/mol (c) 32.2 kJ/mol (d) 37.3 kJ/mol

135. Read following statement(s) carefully and select the right option :

(I) The enthalpy of solution of $CaCl_2 \cdot 6H_2O$ in a large volume of water is endothermic to the extent of 3.5 kcal/mol. If $\Delta H = -23.2$ kcal for the reaction,

$$CaCl_2(s) + 6H_2O(l) \longrightarrow CaCl_2.6H_2O(s)$$

then heat of solution of $CaCl_2$ (anhydrous) in a large volume of water is − 19.7 kcal/mol

(II) For the reaction $2Cl(g) \rightarrow Cl_2(g)$; the sign of ΔH and ΔS are negative.

(a) statement I and II both are wrong (b) both are correct

(c) only I is correct (d) only II is correct

136. If the enthalpy of formation and enthalpy of solution of $HCl(g)$ are −92.3 kJ/mol and −75.14 kJ/mol respectively then find enthalpy of formation of $Cl^-(aq)$:

(a) −17.16 kJ/mol (b) −167.44 kJ/mol (c) 17.16 kJ/mol (d) None of these

137. At 25°C, 1 mole of $MgSO_4$ was dissolved in water, the heat evolved was found to be 91.2 kJ. One mole of $MgSO_4 \cdot 7H_2O$ on dissolution gives a solution of the same composition accompanied by an absorption of 13.8 kJ. The enthalpy of hydration, *i.e.*, ΔH for the reaction

$$MgSO_4(s) + 7H_2O(l) \longrightarrow MgSO_4 \cdot 7H_2O(s) \text{ is :}$$

(a) −105 kJ/mol (b) −77.4 kJ/mol (c) 105 kJ/mol (d) None of these

138. The enthalpies of neutralization of a weak base AOH and a strong base BOH by HCl are −12250 cal/mol and −13000 cal/mol respectively. When one mole of HCl is added to a solution containing 1 mole of AOH and 1 mole of BOH, the enthalpy change was −12500 cal/ mol. In what ratio is the acid distribution between AOH and BOH?

(a) 2 : 1 (b) 2 : 3 (c) 1 : 2 (d) None of these

139. The magnitude of enthalpy change for neutralization of the reaction ;

$MgO(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2O(l)$ (Given $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$; −57 kJ/mol) will be :

(a) less that 57 kJ mol^{-1} (b) -57 kJ mol^{-1}
(c) greater than 57 kJ mol^{-1} (d) 57 kJ mol^{-1}

140. Enthalpy of neutralization of HCl by NaOH is -55.84 kJ/mol and by NH_4OH is -51.34 kJ/mol. The enthalpy of ionization of NH_4OH is :
(a) 107.18 kJ/mol (b) 4.5 kJ/mol (c) -4.5 kJ/mol (d) None of these

141. Which of the following reaction is endothermic ?
(a) $CaCO_3 \longrightarrow CaO + CO_2$ (b) $Fe + S \longrightarrow FeS$
(c) $NaOH + HCl \longrightarrow NaCl + H_2O$ (d) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

142. Which of the following is not correct ?
(a) Dissolution of NH_4Cl in excess of water is an endothermic process
(b) Neutralisation is always exothermic
(c) The absolute value of enthalpy (H) can be determined experimentally
(d) The heat of reaction at constant volume is denoted by ΔE

143. Substance $A_2B(g)$ can undergoes decomposition to form two set of products :

$$A_2B(g) \begin{cases} \longrightarrow A_2(g) + B(g); & \Delta H^\circ = 40 \text{ kJ/mol} \\ \longrightarrow A(g) + AB(g); & \Delta H^\circ = 50 \text{ kJ/mol} \end{cases}$$

If the molar ratio of $A_2(g)$ to $A(g)$ is 5 : 3 in a set of product gases, then the energy involved in the decomposition of 1 mole of $A_2B(g)$ is :
(a) 48.75 kJ/mol (b) 43.73 kJ/mol (c) 46.25 kJ/mol (d) None of these

144. Boron can undergo the following reactions with the given enthalpy changes :

$$2B(s) + \frac{3}{2}O_2(g) \longrightarrow B_2O_3(s); \quad \Delta H = -1260 \text{ kJ}$$

$$2B(s) + 3H_2(g) \longrightarrow B_2H_6(g); \ \Delta H = 30 \text{ kJ}$$

Assume no other reactions are occurring.

If in a container (operating at constant pressure) which is isolated from the surrounding, mixture of H_2 (gas) and O_2 (gas) are passed over excess of B(s), then calculate the molar ratio ($O_2 : H_2$) so that temperature of the container do not change :
(a) 15 : 3 (b) 42 : 1 (c) 1 : 42 (d) 1 : 84

145. The enthalpy change for the following reaction is 368 kJ. Calculate the average O—F bond energy.

$$OF_2(g) \longrightarrow O(g) + 2F(g)$$

(a) 184 kJ/mol (b) 368 kJ/mol (c) 536 kJ/mol (d) 736 kJ/mol

146. The enthalpy change for the reaction, $C_2H_6(g) \longrightarrow 2C(g) + 6H(g)$ is X kJ. The bond energy of C—H bond is :
(a) $\frac{X}{2}$ (b) $\frac{X}{3}$ (c) $\frac{X}{6}$ (d) data insufficient

147. The table given below lists the bond dissociation energy (E_{diss}) for single covalent bonds formed between C and atoms A, B, D, E.

Bond	E_{diss} (kcal mol^{-1})
C — A	240
C — B	382
C — D	276
C — E	486

Which of the atoms has smallest size ?

(a) D (b) E (c) A (d) D

148. Calculate P—Cl bond enthalpy

Given : $\Delta_f H$ (PCl_3, g) = 306 kJ/mol; $\Delta H_{atomization}$ (P, s) = 314 kJ/mol;

$\Delta_f H$ (Cl, g) = 121 kJ/mol

(a) 123.66 kJ/mol (b) 371 kJ/mol (c) 19 kJ/mol (d) None of these

149. Calculate the enthalpy for the following reaction using the given bond energies (kJ/mol) :

(C—H = 414; H—O = 463; H—Cl = 431, C—Cl = 326; C—O = 335)

$$CH_3—OH(g) + HCl(g) \longrightarrow CH_3—Cl(g) + H_2O(g)$$

(a) −23 kJ/mol (b) −42 kJ/mol (c) −59 kJ/mol (d) −511 kJ/mol

150. Based on the values of B.E. given, $\Delta_f H°$ of $N_2H_4(g)$ is :

Given : N—N = 159 kJ mol^{-1}; H—H = 436 kJ mol^{-1}

N≡N = 941 kJ mol^{-1}; N—H = 398 kJ mol^{-1}

(a) 711 kJ mol^{-1} (b) 62 kJ mol^{-1} (c) −98 kJ mol^{-1} (d) −711 kJ mol^{-1}

Level 2

1. A heating coil is immersed in a 100 g sample of $H_2O(l)$ at 1 atm and 100°C in a closed vessel. In this heating process, 60% of the liquid is converted in to gaseous form at constant pressure of 1 atm. Densities of liquid and gaseous water under these conditions are 1000 kg/m^3 and 0.60 kg/m^3 respectively. Magnitude of the work done for the process is :
(a) 4997 J (b) 4970 J (c) 9994 J (d) None of these

2. A rigid and insulated tank of 3 m^3 volume is divided into two compartments. One compartment of volume of 2 m^3 contains an ideal gas at 0.8314 MPa and 400 K and while the second compartment of volume 1 m^3 contains the same gas at 8.314 MPa and 500 K. If the partition between the two compartments is ruptured, the final temperature of the gas is :
(a) 420 K (b) 450 K (c) 480 K (d) None of these

3. What is the value of change in internal energy at 1 atm in the process?

$$H_2O\,(l,\,323\text{ K}) \longrightarrow H_2O\,(g,\,423\text{ K})$$

Given : $C_{v,m}\,(H_2O, l) = 75.0\text{ JK}^{-1}\text{ mol}^{-1}$; $C_{p,m}\,(H_2O, g) = 33.314\text{ JK}^{-1}\text{ mol}^{-1}$

ΔH_{vap} at 373 K = 40.7 kJ/mol

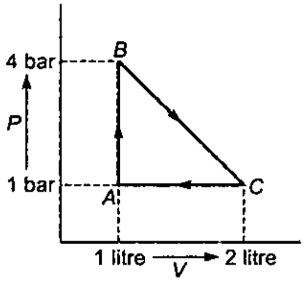
(a) 42.91 kJ/mol (b) 43086 kJ/mol (c) 42.6 kJ/mol (d) 49.6 kJ/mol

4. For an ideal gas $\frac{C_{p,m}}{C_{v,m}} = \gamma$. The molecular mass of the gas is M, its specific heat capacity at constant volume is :
(a) $\frac{R}{M(\gamma-1)}$ (b) $\frac{M}{R(\gamma-1)}$ (c) $\frac{\gamma RM}{\gamma-1}$ (d) $\frac{\gamma R}{M(\gamma-1)}$

5. 1 mole of an ideal gas $A\,(C_{v,m} = 3R)$ and 2 mole of an ideal gas B are $\left(C_{v,m} = \frac{3}{2}R\right)$ taken in a container and expanded reversible and adiabatically from 1 litre to 4 litre starting from initial temperature of 320 K. ΔE or ΔU for the process is :
(a) $-240\,R$ (b) $240\,R$ (c) $480\,R$ (d) $-960\,R$

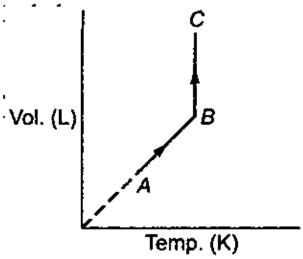
6. Calculate the work done by the system in an irreversible (single step) adiabatic expansion of 2 mole of a polyatomic gas ($\gamma = 4/3$) from 300 K and pressure 10 atm to 1 atm :
(a) $-227\,R$ (b) $-205\,R$ (c) $-405\,R$ (d) None of these

7. One mole of an ideal gas is carried through the reversible cyclic process as shown in figure. The max. temperature attained by the gas during the cycle :
(a) $\frac{7}{6R}$ (b) $\frac{12}{49R}$
(c) $\frac{49}{12R}$ (d) None of these



8. Two moles of a triatomic linear gas (neglect vibration degree of freedom) are taken through a reversible process ideal starting from A as shown in figure.

The volume ratio $\frac{V_B}{V_A} = 4$. If the temperature at A is $-73°C$, then:



(i) Work done by the gas in AB process is :

(a) 6.16 kJ (b) 308.3 kJ
(c) 9.97 kJ (d) 0 J

(ii) Total enthalpy change in both steps is :

(a) $3000\,R$ (b) $4200\,R$ (c) $2100\,R$ (d) 0

9. A gas $\left(C_{v,m} = \frac{5}{2}R\right)$ behaving ideally was allowed to expand reversibly and adiabatically from 1 litre to 32 litre. It's initial temperature was 327°C. The molar enthalpy change (in J/mol) for the process is :

(a) $-1125\,R$ (b) -675 (c) $-1575\,R$ (d) None of these

10. Two mole of an ideal gas is heated at constant pressure of one atmosphere from 27°C to 127°C. If $C_{v,m} = 20 + 10^{-2}\,T\ \text{JK}^{-1}\ \text{mol}^{-1}$, then q and ΔU for the process are respectively :

(a) 6362.8 J, 4700 J (b) 3037.2 J, 4700 J (c) 7062.8 J, 5400 J (d) 3181.4 J, 2350 J

11. 10 mole of an ideal gas is heated at constant pressure of one atmosphere from 27°C to 127°C. If $C_{\ ,m} = 21.686 + 10^{-3}\,T$, then ΔH for the process is :

(a) 3000 J (b) 3350 J (c) 3700 J, (d) 30350

12. For polytropic process PV^n = constant, molar heat capacity (C_m) of an ideal gas is given by :

(a) $C_{v,m} + \frac{R}{(n-1)}$ (b) $C_{v,m} + \frac{R}{(1-n)}$ (c) $C_{v,m} + R$ (d) $C_{p,m} + \frac{R}{(n-1)}$

13. 2 mole of an ideal monoatomic gas undergoes a reversible process for which $PV^2 = C$. The gas is expanded from initial volume of 1 L to final volume of 3 L starting from initial temperature of 300 K. Find ΔH for the process :

(a) $-600\,R$ (b) $-1000\,R$ (c) $-3000\,R$ (d) None of these

14. Calculate ΔS for 3 mole of a diatomic ideal gas which is heated and compressed from 298 K and 1 bar to 596 K and 4 bar: [Given: $C_{v,m}$ (gas) $= \frac{5}{2}R$; $\ln(2) = 0.70$; $R = 2$ cal K^{-1} mol^{-1}]

(a) -14.7 cal K^{-1} (b) $+14.7$ cal K^{-1} (c) -4.9 cal K^{-1} (d) 6.3 cal K^{-1}

15. One mole of an ideal monoatomic gas at 27°C is subjected to a reversible isoentropic compression until final temperature reaches to 327°C. If the initial pressure was 1.0 atm then find the value of ($\ln P_2$): (Given : $\ln 2 = 0{:}7$)

(a) 1.75 atm (b) 0.176 atm (c) 1.0395 atm (d) 2.0 atm

16. Two mole of an ideal gas is expanded irreversibly and isothermally at 37°C until its volume is doubled and 3.41 kJ heat is absorbed from surrounding. ΔS_{total} (system + surrounding) is :

(a) -0.52 J/K (b) 0.52 J/K (c) 22.52 J/K (d) 0

17. For a perfectly crystalline solid $C_{p,m} = aT^3 + bT$, where a and b are constant. If $C_{p,m}$ is 0.40 J/K mol at 10 K and 0.92 J/K mol at 20 K, then molar entropy at 20 K is :

(a) 0.92 J/K mol (b) 8.66 J/K mol (c) 0.813 J/K mol (d) None of these

18. Which of the following statement(s) is/are correct?

Statement (i) : The entropy in isolated system with P–V work only, is always maximized at equilibrium.

Statement (ii) : It is possible for the entropy of a close system to decrease substantially in an irreversible process.

Statement (iii) : Entropy can be created but not destroyed.

Statement (iv) : ΔS_{system} is zero for reversible process in an isolated system.

(a) Statement i, ii, iii (b) Statement ii, iv
(c) Statement i, ii, iv (d) All of these

19. Combustion of sucrose is used by aerobic organisms for providing energy for the life sustaining processes. If all the capturing of energy from the reaction is done through electrical process (non P–V work) then calculate maximum available energy which can be captured by combustion of 34.2 gm of sucrose

Given : $\Delta H_{\text{combustion}}$ (sucrose) $= -6000$ kJ mol^{-1}

$\Delta S_{\text{combustion}} = 180$ J/K-mol and body temperature is 300 K

(a) 600 kJ (b) 594.6 kJ (c) 5.4 kJ (d) 605.4 kJ

20. For the hypothetical reaction

$$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$$

$\Delta_r G^\circ$ and $\Delta_r S^\circ$ are 20 kJ/mol and -20 JK^{-1} mol^{-1} respectively at 200 K.

If $\Delta_r C_p$ is 20 JK^{-1} mol^{-1} then $\Delta_r H^\circ$ at 400 K is :

(a) 20 kJ/mol (b) 7.98 kJ/mol (c) 28 kJ/mol (d) None of these

21. Calculate $\Delta_f G^\circ$ for (NH_4Cl, s) at 310 K.

Given : $\Delta_f H^\circ$ (NH_4Cl, s) $= -314.5$ kJ/mol; $\Delta_r C_p = 0$

$S^\circ_{N_2(g)} = 192$ JK^{-1} mol^{-1}; $S^\circ_{H_2(g)} = 130.5$ JK^{-1} mol^{-1};

$S^\circ_{Cl_2(g)} = 233$ JK^{-1} mol^{-1}; $S^\circ_{NH_4Cl(s)} = 99.5$ JK^{-1} mol^{-1}

All given data at 300 K.

(a) -198.56 kJ/mol (b) -426.7 kJ/mol (c) -202.3 kJ/mol (d) None of these

22. Using listed informations, calculate $\Delta_r G^\circ$ (in kJ/mol) at 27°C

$$Co_3O_4(s) + 4CO(g) \longrightarrow 3Co(s) + 4CO_2(g)$$

Given : At 300 K ΔH°_f (kJ/mol) $-891, -110.5, 0.0, -393.5$

S° (J/K-mol) 102.5, 197.7, 30.0, 213.7

(a) -214.8 (b) -195.0 (c) -200.3 (d) -256.45

23. Fixed mass of an ideal gas contained in a 24.63 L sealed rigid vessel at 1 atm is heated from -73°C to 27°C. Calculate change in Gibb's energy if entropy of gas is a function of temperature as $S = 2 + 10^{-2}\,T$ (J/K): (Use 1 atm L = 0.1 kJ)

(a) 1231.5 J (b) 1281.5 J (c) 781.5 J (d) 0

24. The molar heat capacities at constant pressure (assumed constant with respect to temperature) of A, B and C are in ratio of 3 : 1.5 : 2.0. The enthalpy change for the exothermic reaction $A + 2B \longrightarrow 3C$ at 300 K and 310 K is ΔH_{300} and ΔH_{310} respectively then :

(a) $\Delta H_{300} > \Delta H_{310}$
(b) $\Delta H_{300} < \Delta H_{310}$
(c) $\Delta H_{300} = \Delta H_{310}$
(d) if $T_2 > T_1$ then $\Delta H_{310} > \Delta H_{300}$ and if $T_2 < T_1$ then $\Delta H_{310} < \Delta H_{300}$

25. Determine $\Delta U°$ at 300 K for the following reaction using the listed enthalpies of reaction :

$$4CO(g) + 8H_2(g) \longrightarrow 3CH_4(g) + CO_2(g) + 2H_2O(l)$$
$$C\text{ (graphite)} + 1/2\,O_2(g) \longrightarrow CO(g);\ \Delta H_1° = -110.5\text{ kJ}$$
$$CO(g) + 1/2\,O_2(g) \longrightarrow CO_2(g);\ \Delta H_2° = -282.9\text{ kJ}$$
$$H_2(g) + 1/2\,O_2(g) \longrightarrow H_2O(l);\ \Delta H_3° = -285.8\text{ kJ}$$
$$C\text{ (graphite)} + 2H_2(g) \longrightarrow CH_4(g);\ \Delta H_4° = -74.8\text{ kJ}$$

(a) −653.5 kJ (b) −686.2 kJ (c) −747.4 kJ (d) None of these

26. Calculate $\Delta_f H°$ (in kJ/mol) for Cr_2O_3 from the $\Delta_r G°$ and the $S°$ values provided at 27°C

$$4Cr(s) + 3O_2(g) \longrightarrow 2Cr_2O_3(s);\quad \Delta_r G° = -2093.4\text{ kJ/mol}$$
$$S°\text{ (J/K mol)} : S°(Cr, s) = 24;\ S°(O_2, g) = 205;\ S°(Cr_2O_3, s) = 81$$

(a) −2258.1 kJ/mol (b) −1129.05 kJ/mol (c) −964.35 kJ/mol (d) None of these

27. Calculate the heat produced (in kJ) when 224 gm of CaO is completely converted to $CaCO_3$ by reaction with CO_2 at 27°C in a container of fixed volume.

Given : $\Delta H_f°(CaCO_3, s) = -1207$ kJ/mol; $\Delta H_f°(CaO, s) = -635$ kJ/mol

$\Delta H_f°(CO_2, g) = -394$ kJ/mol; [Use $R = 8.3\ K^{-1}\ mol^{-1}$]

(a) 702.04 kJ (b) 721.96 kJ (c) 712 kJ (d) 721 kJ

28. When 1.0 g of oxalic acid ($H_2C_2O_4$) is burned in a bomb calorimeter whose heat capacity is 8.75 kJ/K, the temperature increases by 0.312 K. The enthalpy of combustion of oxalic acid at 27°C is :

(a) −245.7 kJ/mol (b) −244.452 kJ/mol (c) −246.947 kJ/mol (d) None of these

29. Enthalpy of neutralization of H_3PO_3 acid is −106.68 kJ/mol using NaOH. If enthalpy of neutralization of HCl by NaOH is −55.84 kJ/mol. Calculate $\Delta H_{\text{ionization}}$ of H_3PO_3 into its ions :

(a) 50.84 kJ/mol (b) 5 kJ/mol (c) 2.5 kJ/mol (d) None of these

30. The enthalpy of neutralization of a weak monoprotic acid (HA) in 1 *M* solution with a strong base is −55.95 kJ/mol. If the unionized acid is required 1.4 kJ/mol heat for it's complete ionization and enthalpy of neutralization of the strong monobasic acid with a strong monoacidic base is −57.3 kJ/mol. What is the % ionization of the weak acid in molar solution ?

(a) 1% (b) 3.57% (c) 35.7% (d) 10%

31. Determine C—C and C—H bond enthalpy (in kJ/mol)

Given : $\Delta_f H°(C_2H_6, g) = -85$ kJ/mol, $\Delta_f H°(C_3H_8, g) = -104$ kJ/mol

$\Delta_{sub}H°(C, s) = 718$ kJ/mol, B.E. (H—H) = 436 kJ/mol

(a) 414, 345 (b) 345, 414 (c) 287, 404.5 (d) None of these

32. Consider the following data : $\Delta_f H°(N_2H_4, l) = 50$ kJ/mol, $\Delta_f H°(NH_3, g) = -46$ kJ/mol

B.E. (N—H) = 393 kJ/mol and B.E. (H—H) = 436 kJ/mol,

$\Delta_{vap} H(N_2H_4, l) = 18$ kJ/mol

The N—N bond energy in N_2H_4 is :

(a) 226 kJ/mol (b) 154 kJ/mol (c) 190 kJ/mol (d) None of these

33. What is the bond enthalpy of Xe—F bond?

$$XeF_4(g) \longrightarrow Xe^+(g) + F^-(g) + F_2(g) + F(g)\,; \quad \Delta_r H = 292 \text{ kcal/mol}$$

Given : Ionization energy of Xe = 279 kcal/mol

B.E. (F—F) = 38 kcal/mol, Electron affinity of F = 85 kcal/mol

(a) 24 kcal/mol (b) 34 kcal/mol (c) 8.5 kcal/mol (d) None of these

34. If enthalpy of hydrogenation of $C_6H_6(l)$ into $C_6H_{12}(l)$ is −205 kJ and resonance energy of $C_6H_6(l)$ is − 152 kJ/ mol then enthalpy of hydrogenation of  is

Assume ΔH_{vap} of $C_6H_6(l)$, $C_6H_8(l)$, $C_6H_{12}(l)$ all are equal :

(a) −535.5 kJ/mol (b) −238 kJ/mol (c) −357 kJ/mol (d) − 119 kJ/mol

35. The enthalpy of combustion of propane (C_3H_8) gas in terms of given data is :

Bond energy (kJ/mol)

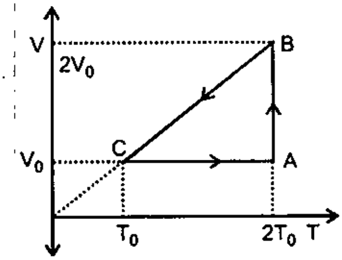
$\varepsilon_{C—H}$	$\varepsilon_{O=O}$	$\varepsilon_{C=O}$	$\varepsilon_{O—H}$	$\varepsilon_{C—C}$
$+x_1$	$+x_2$	$+x_3$	$+x_4$	x_5

Resonance energy of CO_2 is $-z$ kJ/mol and $\Delta H_{vaporization}$ [$H_2O(l)$] is y (kJ/mol)

(a) $8x_1 + 2x_5 + 5x_2 - 6x_3 - 8x_4 - 4y - 3z$ (b) $6x_1 + x_5 + 5x_2 - 3x_3 - 4x_4 - 4y - 3z$

(c) $8x_1 + 2x_5 + 5x_2 - 6x_3 - 8x_4 - y - z$ (d) $8x_1 + x_5 + 5x_2 - 6x_3 - 8x_4 - 4y + 3z$

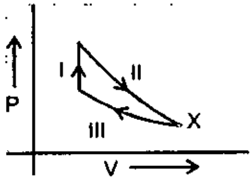
36. The efficiency of an ideal gas with adiabatic exponent 'γ' for the shown cyclic process would be



(a) $\dfrac{(\gamma-1)(2\ln 2-1)}{1+(\gamma-1)2\ln 2}$ (b) $\dfrac{(\gamma-1)(1-2\ln 2)}{(\gamma-1)2\ln 2-1}$

(c) $\dfrac{(2\ln 2+1)(\gamma-1)}{(\gamma-1)2\ln 2+1}$ (d) $\dfrac{(2\ln 2-1)}{\gamma/(\gamma-1)}$

37. Initially one mole of ideal gas $\left(C_v = \dfrac{5}{2}R\right)$ at 1.0 atm and 300 K is put through the following cycle :



Step-I : Heating to twice its initial pressure at constant volume.

Step-II : Adiabatic expansion to its initial temperature.

Step-III : Isothermal compression back to 1.00 atm.

What is the volume at state X ?

(a) 40.4 L (b) 65.0 L (c) 139 L (d) 4.35 L

38. What is the enthalpy of neutralization of HF against a strong base ?

Given : $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l); \Delta_r H^\circ = -56$ kJ/mol

$\Delta_r H^\circ(\text{HF}, aq) = -329$ kJ/mol ; $\Delta_r H^\circ(H_2O, l) = -285$ kJ/mol

$\Delta_r H^\circ(F^-, aq) = -320$ kJ/mol

(a) −17 kJ/mol (b) −38 kJ/mol (c) −47 kJ/mol (d) −43 kJ/mol

39. The molar heat capacities of Iodine vapour and solid are 7.8 and 14 cal/mol respectively if enthalpy of sublimation of iodine is 6096 cal/mole at 200°C, then what is ΔU (internal energy change) at 250°C in cal/mol

(a) 5360 (b) 4740 (c) 6406 (d) None of these

40. For the reaction takes place at certain temperature $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$. If equilibrium pressure is $3X$ bar then $\Delta_r G^\circ$ would be

(a) $-RT \ln 9 - 3RT \ln X$ (b) $RT \ln 4 - 3RT \ln X$

(c) $-3RT \ln X$ (d) None of these

Level 3

PASSAGE 1

The first law of thermodynamics for a closed system is $dU = dq + dw$, where $dw = dw_{pv} + dw_{\text{non-pv}}$. The most kind of $w_{\text{non-pv}}$ is electrical work. As per IUPAC convention work done on the system is positive.

1. A system generates 50 J of electrical energy, has 150 J of pressure-volume work done on it by the surroundings while releasing 300 J of heat energy. What is the change in the internal energy of the system?
(a) –500 (b) –100 (c) –300 (d) –200

2. A system generates 50 J of electrical energy and delivers 150 J of pressure-volume work against the surroundings while releasing 300 J of heat energy. What is the change in the internal energy of the system?
(a) –100 (b) –400 (c) –300 (d) –500

PASSAGE 2

If the boundary of system moves by an infinitesimal amount, the work involved is given by $dw = -P_{\text{ext}}\, dV$

for irreversible process $w = -P_{\text{ext}}\, \Delta V$ (where $\Delta V = V_f - V_i$)

for reversible process $P_{\text{ext}} = P_{\text{int}} \pm dP \simeq P_{\text{int}}$

so for reversible isothermal process $w = -nRT \ln \dfrac{V_f}{V_i}$

2 mole of an ideal gas undergoes isothermal compression along three different paths :

(i) reversible compression from $P_i = 2$ bar and $V_i = 8$ L to $P_f = 20$ bar

(ii) a single stage compression against a constant external pressure of 20 bar, and

(iii) a two stage compression consisting initially of compression against a constant external pressure of 10 bar until $P_{\text{gas}} = P_{\text{ext}}$, followed by compression against a constant pressure of 20 bar until $P_{\text{gas}} = P_{\text{ext}}$.

1. Work done (in bar-L) on the gas in reversible isothermal compression is :
(a) 9.212 (b) 36.848 (c) 18.424 (d) None of these

2. Work done on the gas in single stage compression is :
(a) 36 (b) 72 (c) 144 (d) None of these

3. Total work done on the gas in two stage compression is :
(a) 40 (b) 80 (c) 160 (d) None of these

4. Order of magnitude of work is :
(a) $w_1 > w_2 > w_3$ (b) $w_3 > w_2 > w_1$ (c) $w_2 > w_3 > w_1$ (d) $w_1 = w_2 = w_3$

PASSAGE 3

Standard Gibb's energy of reaction ($\Delta_r G^\circ$) at a certain temperature can be computed as $\Delta_r G^\circ = \Delta_r H^\circ - T.\Delta_r S^\circ$ and the change in the value of $\Delta_r H^\circ$ and $\Delta_r S^\circ$ for a reaction with temperature can be computed as follows :

$$\Delta_r H^\circ_{T_2} - \Delta_r H^\circ_{T_1} = \Delta_r C^\circ_p (T_2 - T_1)$$

$$\Delta_r S^\circ_{T_2} - \Delta_r S^\circ_{T_1} = \Delta_r C^\circ_p \ln\left(\frac{T_2}{T_1}\right)$$

$$\Delta_r G^\circ = \Delta_r H^\circ - T.\Delta_r S^\circ$$

and by $\Delta_r G^\circ = -RT \ln K_{eq}$.

Consider the following reaction : $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

Given : $\Delta_f H^\circ (CH_3OH, g) = -201$ kJ/mol; $\Delta_f H^\circ (CO, g) = -114$ kJ/mol

$S^\circ (CH_3OH, g) = 240$ J/K-mol ; $S^\circ (H_2, g) = 29\ JK^{-1}\ mol^{-1}$

$S^\circ (CO, g) = 198$ J/mol-K ; $C^\circ_{p,m} (H_2) = 28.8$ J/mol-K

$C^\circ_{p,m} (CO) = 29.4$ J/mol-K; $C^\circ_{p,m} (CH_3OH) = 44$ J/mol-K

and $\ln\left(\frac{320}{300}\right) = 0.06$, all data at 300 K

1. $\Delta_r S^\circ$ at 300 K for the reaction is :
(a) 152.6 J/K-mol (b) 181.6 J/K-mol (c) −16 J/K-mol (d) None of these

2. $\Delta_r H^\circ$ at 300 K for the reaction is :
(a) −87 kJ/mol (b) 87 kJ/mol (c) −315 kJ/mol (d) −288 kJ/mol

3. $\Delta_r S^\circ$ at 320 K is :
(a) 155.18 J/mol-K (b) 150.02 J/mol-K (c) 172 J/mol-K (d) None of these

4. $\Delta_r H^\circ$ at 320 K is :
(a) −288.86 kJ/mol (b) −289.1 kJ/mol (c) −87.86 kJ/mol (d) None of these

5. $\Delta_r G^\circ$ at 320 K is :
(a) −48295.2 kJ/mol (b) −240.85 kJ/mol (c) 240.85 kJ/mol (d) −81.91 kJ/mol

PASSAGE 4

Enthalpy of neutralization is defined as the enthalpy change when 1 mole of acid/base is completely neutralized by base/acid in dilute solution.

For strong acid and strong base neutralization net chemical change is

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l); \quad \Delta_r H^\circ = -55.84 \text{ kJ/mol}$$

$\Delta H^\circ_{\text{ionization}}$ of aqueous solution of strong acid and strong base is zero.

When a dilute solution of a weak acid or base is neutralized, the enthalpy of neutralization is some what less because of the absorption of heat in the ionization of the weak acid or base, for weak acid/base

$$\Delta H^\circ_{\text{neutralization}} = \Delta H^\circ_{\text{ionization}} + \Delta_r H^\circ \quad (H^+ + OH^- \rightarrow H_2O)$$

1. If enthalpy of neutralization of CH_3COOH by HCl is –49.86 kJ/mol then enthalpy of ionization of CH_3COOH is :
   (a) 5.98 kJ/mol (b) –5.98 kJ/mol (c) 105.7 kJ/mol (d) None of these
2. What is $\Delta H°$ for complete neutralization of strong diacidic base $A(OH)_2$ by HNO_3?
   (a) –55.84 kJ (b) –111.68 kJ (c) 55.84 kJ/mol (d) None of these
3. Under the same conditions how many mL of 0.1 M NaOH and 0.05 M H_2A (strong diprotic acid) solution should be mixed for a total volume of 100 mL produce the highest rise in temperature :
   (a) 25 : 75 (b) 50 : 50 (c) 75 : 25 (d) 66.66 : 33.33

PASSAGE 5

Gibbs Helmholtz equation relates the enthalpy, entropy and free energy change of the process at constant pressure and temperature as

$$\Delta G = \Delta H - T\Delta S \qquad \text{(at constant P, T)}$$

In General the magnitude of ΔH does not change much with the change in temperature but the term $T\Delta S$ changes appreciably. Hence in some process spontaneity is very much dependent on temperature and such processes are generally known as entropy driven process.

1. For the reaction at 298 K; $A_2B_4 \longrightarrow 2AB_2$
   $\Delta H = 2\text{kJ}$ and $\Delta S = 20\,\text{J/K}$ at constant P and T, the reaction will be
   (a) spontaneous and entropy driven (b) Spontaneous and enthalpy driven
   (c) Non spontaneous (d) At equilibrium
2. When $CaCO_3$ is heated to a high temperature it decomposes into CaO and CO_2, However it is quite stable at room temperature. It can be explained by the fact that
   (a) ΔH_r dominates the terms $T\Delta S$ at high temperature
   (b) The term $T\Delta S$ dominates the ΔH_r at high temperature
   (c) At high temperature both ΔS_r and ΔH_r becomes negative
   (d) Thermodynamics can not say anything about spontaneity
3. The Dissolution of $CaCl_2 \cdot 6H_2O$ in a large volume of water is endothermic to the extent of 3.5 Kcal mol^{-1} and ΔH for the reaction is –23.2 kcal mol^{-1}.

   $$CaCl_2(s) + 6H_2O(l) \longrightarrow CaCl_2 \cdot 6H_2O(s)$$

   Select the correct statement
   (a) $\Delta H_{\text{Solution}}$ for anhydrous $CaCl_2$ is –19.7 kcal/mol and the process is enthalpy driven
   (b) $\Delta H_{\text{Solution}}$ for anhydrous $CaCl_2$ is –19.7 kcal/mol and the process is entropy driven
   (c) Dissolution of $CaCl_2 \cdot 6H_2O$ in water is enthalpy driven process
   (d) The $\Delta_r S$ the reaction $CaCl_2(s) + 6H_2O(l) \longrightarrow CaCl_2 \cdot 6H_2O(s)$ is negative

ONE OR MORE ANSWERS IS/ARE CORRECT

1. Identify the intensive quantities from the following :
(a) Enthalpy (b) Temperature (c) Pressure (d) Mass

2. Identify the extensive quantities from the following :
(a) Gibb's energy (b) Entropy (c) Refractive index (d) Specific heat

3. Identify the state functions from the following :
(a) Heat (b) Work (c) Enthalpy (d) Enthalpy change

4. Which of the following statements is/are correct as per IUPAC sign convention?
(a) The work done by the system on the surrounding is negative
(b) The work done by the surrounding on the system is positive
(c) The heat absorbed by the system from the surrounding is positive
(d) The heat absorbed by the surrounding from the system is positive

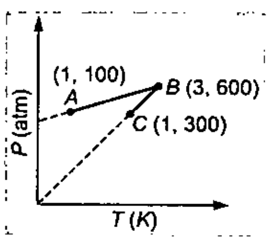
5. In an isothermal irreversible expansion of an ideal gas as per IUPAC sign convention :
(a) $\Delta U = 0$ (b) $\Delta H = 0$ (c) $w = -nRT \ln \frac{P_1}{P_2}$ (d) $w = -q$

6. In reversible isothermal ideal gas expansion :
(a) $w = 0$ (b) $U_1 = U_2$ (c) $H_1 = H_2$ (d) $q = nRT \ln \frac{V_2}{V_1}$

7. An adiabatic process is that process in which :
(a) energy is transferred as heat
(b) no energy is transfer as heat
(c) $\Delta U = w$
(d) the temp. of gas increases in a reversible adiabatic compression

8. In adiabatic process, the work involved during expansion or compression of an ideal gas is given by :
(a) $nC_v\Delta T$ (b) $\frac{nR}{\gamma - 1}(T_2 - T_1)$
(c) $-nRP_{ext}\left[\frac{T_2P_1 - T_1P_2}{P_1P_2}\right]$ (d) $-2.303\, RT \log \frac{V_2}{V_1}$

9. One mole of an ideal gas is subjected to a two step reversible process (A—B and B—C). The pressure at A and C is same. Mark the correct statement(s) :
(a) Work involved in the path AB is zero
(b) In the path AB work will be done on the gas by the surrounding
(c) Volume of gas at $C = 3\times$ volume of gas at A
(d) Volume of gas at B is 16.42 litres



10. Assume ideal gas behaviour for all the gases considered and neglect vibrational degrees of freedom. Separate equimolar samples of Ne, O_2, CO_2 and SO_2 were subjected to a two process as mentioned. Initially all are at same state of temperature and pressure.

Step I ⟶ All undergo reversible adiabatic expansion to attain same final volume, which is double the original volume thereby causing the decreases in their temperature.

Step II ⟶ After step I all are given appropriate amount of heat isochorically to restore the original temperature.

Mark the correct option(s) :

(a) Due to step I only, the decrease in temperature will be maximum for Ne

(b) During step II, heat given will be minimum for SO_2

(c) There will be no change in internal energy for any of the gas after both the steps of process are competed

(d) The P–V graph of O_2 and CO_2 will be same

11. Which of the following is/are correct?

(a) $\Delta H = \Delta U + \Delta (PV)$ when P and V both changes

(b) $\Delta H = \Delta U + P\Delta V$ when pressure is constant

(c) $\Delta H = \Delta U + V\Delta P$ when volume is constant

(d) $\Delta H = \Delta U + P\Delta V + V\Delta P$ when P and V both changes

12. $\Delta H < \Delta E$ for the reaction(s) :

(a) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ (b) $Ag_2O(s) \longrightarrow 2Ag(s) + \frac{1}{2}O_2(g)$

(c) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$ (d) $C(s) + O_2(g) \longrightarrow CO_2(g)$

13. Which of the following conditions may lead to a non-spontaneous change?

(a) ΔH and ΔS both + ve (b) $\Delta H = -$ve; $\Delta S = +$ ve

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

14. For a process to be spontaneous :

(a) $(\Delta G_{\text{system}})_{T,p} = 0$ (b) $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$

(c) $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} < 0$ (d) $(\Delta G_{\text{system}})_{T,p} < 0$

15. The normal boiling point of a liquid 'X' is 400 K. Which of the following statement is true about the process $X(l) \longrightarrow X(g)$?

(a) at 400 K and 1 atm pressure $\Delta G = 0$ (b) at 400 K and 2 atm pressure $\Delta G = +$ ve

(c) at 400 K and 0.1 atm pressure $\Delta G = -$ve (d) at 410 K and 1 atm pressure $\Delta G = +$ ve

16. When ice melts at 1°C :

(a) an increase in entropy (b) a decrease in enthelpy

(c) a decrease in free energy (d) process is spontaneous

17. The value of $\Delta H_{\text{transition}}$ of C (graphite) ⟶ C (diamond) is 1.9 kJ/mol at 25°C entropy of graphite is higher than entropy of diamond. This implies that :

(a) C (diamond) is more thermodynamically stable than C (graphite) at 25°C

(b) C (graphite) is more thermodynamically stable than C (diamond) at 25°C

(c) diamond will provide more heat on complete combustion at 25°C

(d) $\Delta G_{\text{transition}}$ of C (diamond) ⟶ C (graphite) is –ve

18. Which of the following statement(s) is/are false?

(a) All adiabatic processes are isoentropic (or isentropic) processes

(b) When $(\Delta G_{\text{system}})_{T,p} < 0$; the reaction must be exothermic

(c) $dG = VdP - SdT$ is applicable for closed system, both PV and non-PV work

(d) The heat of vaporisation of water at 100°C is 40.6 kJ/mol. When 9 gm of water vapour condenses to liquid at 100°C of 1 atm, then $\Delta S_{\text{system}} = 54.42$ J/K

19. Which of the following statement(s) is/are true?

(a) $\Delta E = 0$ for combustion of $C_2H_6(g)$ in a sealed rigid adiabatic container

(b) $\Delta_f H^\circ$ (S, monoclinic) $\neq 0$

(c) If dissociation energy of $CH_4(g)$ is 1656 kJ/mol and $C_2H_6(g)$ is 2812 kJ/mol, then value of C—C bond energy will be 328 kJ/mol

(d) If $\Delta H_f(H_2O, g) = -242$ kJ/mol; $\Delta H_{\text{vap}}(H_2O, l) = 44$ kJ/mol then, $\Delta_f H^\circ(OH^-, aq.)$ will be −142 kJ/mol

20. From the following data, mark the option(s) where ΔH is correctly written for the given reaction.

Given : $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l);\ \Delta H = -57.3$ kJ

$$\Delta H_{\text{solution}} \text{ of } HA(g) = -70.7 \text{ kJ/mol}$$

$$\Delta H_{\text{solution}} \text{ of } BOH(g) = 20 \text{ kJ/mol}$$

$\Delta H_{\text{ionization}}$ of HA = 15 kJ/mol and BOH is a strong base.

	Reaction	**ΔH_r (kJ/mol)**
(a)	$HA(aq) + BOH(aq) \longrightarrow BA(aq) + H_2O$	−42.3
(b)	$HA(g) + BOH(g) \longrightarrow BA(aq) + H_2O$	−93
(c)	$HA(g) \longrightarrow H^+(aq) + A^-(aq)$	−55.7
(d)	$B^+(aq) + OH^-(aq) \longrightarrow BOH(aq)$	−20

21. Select correct statement(s)

(a) An adiabatic system can exchange energy with its surroundings.

(b) A thermodynamic property which is intensive is additive.

(c) Work done may be zero in a cyclic process.

(d) For a simple compressible substance, the relation $dq - P.dv = 0$ is true for any cycle involving mechanical work only.

22. For an isolated system, the entropy :

(a) Either increases or remains constant
(b) Either decreases or remains constant
(c) Can never decrease
(d) Can never increase

23. The normal boiling point of a liquid X is 400 K. ΔH_{vap} at normal boiling point is 40 kJ/mol. Select correct statement(s) :

(a) $\Delta S_{\text{Vaporisation}} < 100$ J/mol.K at 400 K and 2 atm

(b) $\Delta S_{\text{Vaporisation}} < 10$ J/mol.K at 400 K and 1 atm

(c) $\Delta G_{\text{Vaporisation}} < 0$ at 410 K and 1 atm

(d) $\Delta U = 43.32$ kJ/mol.K at 400 K and 1 atm

24. Select incorrect statement(s)

(a) A closed system with all adiabatic boundaries must be an isolated system

(b) Total heat exchange in a cyclic process may be zero

(c) Entropy of a closed system is maximum at equilibrium

(d) Molar Gibb's Energy is an extensive property

25. Select correct statement(s) for the reaction $H_2O(g) + CO(g) \longrightarrow H_2(g) + CO_2(g)$

Substance	$CO(g)$	$CO_2(g)$	$H_2O(g)$	$H_2(g)$
$\Delta_f H^\circ_{400}$ (kcal mol^{-1})	-25	-95	-55	0
S°_{400} (cal mol^{-1}K^{-1})	45	50	40	30

(a) Reaction is enthalpy driven
(b) Reaction is entropy driven
(c) Reaction is spontaneous at 400 K
(d) Reaction is non-spontaneous at 400 K

MATCH THE COLUMN

Column-I and Column-II contains four entries each. Entries of Column-I are to be matched with some entries of column-II. One or more than one entries of Column-I may have the matching with the same entries of Column-II.

1.

Column-I	Column-II
(A) Reversible cooling of an ideal gas at constant volume	(P) $w = 0; q < 0; \Delta U < 0$
(B) Reversible isothermal expansion of an ideal gas	(Q) $w < 0; q > 0; \Delta U > 0$
(C) Adiabatic expansion of non-ideal gas into vacuum	(R) $w = 0; q = 0; \Delta U = 0$
(D) Reversible melting of sulphur at normal melting point	(S) $w < 0; q > 0; \Delta U = 0$

2.

Column-I	Column-II
(A) Adiabatic process	(P) $q = 0$
(B) Isothermal process	(Q) $\Delta H = 0$
(C) Isoenthalpic process	(R) $\Delta T = 0$
(D) Isoentropic process	(S) $\Delta S = 0$

3.

Column-I	Column-II
(A) Reversible isothermal expansion of an ideal gas	(P) $w = -2.303\, nRT \log\left(\frac{V_2}{V_1}\right)$
(B) Reversible adiabatic compression of an ideal gas	(Q) $PV^\gamma = \text{constant}$
(C) Irreversible adiabatic expansion of an ideal gas	(R) $w = \frac{nR}{(\gamma - 1)}(T_2 - T_1)$
(D) Irreversible isothermal compression of an ideal gas	(S) $\Delta H = 0$

4.

Column-I	Column-II
(A) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ in a closed system	(P) $\Delta H < \Delta U$
(B) $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ in a closed system	(Q) $\Delta H = \Delta U \neq 0$
(C) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ in a closed system	(R) $\Delta H > \Delta U$
(D) $CO(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g)$ in an isolated system	(S) $\Delta U = 0$

5.

Column-I (Process)	Column-II (Entropy Change)
(A) Reversible isothermal compression of an ideal gas	(P) $\Delta S_{\text{system}} > 0$
(B) Isothermal free expansion ($P_{\text{ext}} = 0$) of an ideal gas	(Q) $\Delta S_{\text{system}} < 0$
(C) Reversible adiabatic expansion of an ideal gas	(R) $\Delta S_{\text{system}} = 0$
(D) Reversible ideal gas expansion	(S) Information insufficient

6.

Column-I (Process)	Column-II (Entropy change)
(A) Reversible isothermal ideal gas expansion	(P) $\Delta S_{\text{surrounding}} = 0$
(B) Reversible adiabatic ideal gas compression	(Q) $\Delta S_{\text{surrounding}} < 0$
(C) Adiabatic free expansion ($P_{\text{ext}} = 0$) of an ideal gas	(R) $\Delta S_{\text{surrounding}} > 0$
(D) Irreversible isothermal ideal gas compression	(S) $\Delta S_{\text{system}} = 0$

7.

Column-I	Column-II
(A) $(\Delta G_{\text{system}})_{T,P} = 0$	(P) Process is in equilibrium
(B) $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$	(Q) Process is nonspontaneous
(C) $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} < 0$	(R) Process is spontaneous
(D) $(\Delta G_{\text{system}})_{T,P} > 0$	(S) System is unable to do useful work

8.

Column-I	Column-II
(A) $(\Delta G_{\text{system}})_{T,P}$	(P) $nR \ln\left(\frac{V_2}{V_1}\right)$
(B) Work done in reversible isothermal ideal gas expansion	(Q) $nRT \ln\left(\frac{P_2}{P_1}\right)$
(C) ΔG for reversible isothermal expansion of an ideal gas	(R) $-nFE$
(D) ΔS_{gas} for isothermal expansion of an ideal gas	(S) $nR \ln\left(\frac{P_1}{P_2}\right)$

9.

Column-I	Column-II
(A) Heating of an ideal gas at constant pressure	(P) $\Delta H = nC_{p,m}\,\Delta T \neq 0$
(B) Compression of liquid at constant temperature	(Q) $\Delta U = 0$
(C) Reversible process for an ideal gas at constant temperature	(R) $\Delta G = V\,\Delta P$
(D) Adiabatic free expansion of an ideal gas	(S) $\Delta G = nRT \ln\left(\frac{P_2}{P_1}\right)$

10.

Column-I	Column-II
(Sign of ΔH and ΔS respectively)	(Nature of reaction)
(A) − & −	(P) Spontaneous only at low temperature
(B) − & +	(Q) Spontaneous only at high temperature
(C) + & +	(R) Spontaneous at all temperature
(D) + & −	(S) Non-spontaneous at all temperature

11.

Column-I	Column-II
(A) Reversible adiabatic compression	(P) $\Delta S_{\text{system}} > 0$
(B) Reversible vaporisation of liquid	(Q) $\Delta S_{\text{system}} < 0$
(C) $2N(g) \rightarrow N_2(g)$	(R) $\Delta S_{\text{surrounding}} < 0$
(D) $MgCO_3(s) \xrightarrow{\Delta} MgO(s) + CO_2(g)$	(S) $\Delta S_{\text{surrounding}} = 0$

12.

Column-I	Column-II
(A) $H^+(aq)$	(P) $\Delta_f H° = 0$
(B) $H(g)$	(Q) $\Delta_f H° \neq 0$
(C) $H_2(g)$	(R) $\Delta_f G° = 0$
(D) C (*s*, diamond)	(S) $\Delta_f S° < 0$

13.

Column-I (Partial derivative)	Column-II (Thermodynamic variable)
(A) $\left(\frac{\partial U}{\partial T}\right)_V$	(P) C_P
(B) $\left(\frac{\partial H}{\partial T}\right)_P$	(Q) C_V
(C) $\left(\frac{\partial G}{\partial T}\right)_P$	(R) $-S$
(D) $\left(\frac{\partial G}{\partial P}\right)_T$	(S) V

14.

Column-I	Column-II
(A) $C(s, \text{graphite}) + O_2(g) \rightarrow CO_2(g)$	(P) $\Delta H°_{\text{combustion}}$
(B) $C(s, \text{graphite}) \rightarrow C(g)$	(Q) $\Delta H°_{\text{formation}}$
(C) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$	(R) $\Delta H°_{\text{atomization}}$
(D) $CH_4(g) \rightarrow C(g) + 4H(g)$	(S) $\Delta H°_{\text{sublimation}}$

15.

Column-I	Column-II
(A) $O_2(g)$	(P) $\Delta_f H° = +\text{ve}$; $\Delta_f S° = +\text{ve}$
(B) $O_3(g)$	(Q) $\Delta_f H° = -\text{ve}$; $\Delta_f S° = -\text{ve}$
(C) $Br_2(g)$	(R) $\Delta_f H° = +\text{ve}$; $\Delta_f S° = -\text{ve}$
(D) $H_2O(l)$	(S) $\Delta_f H° = 0$; $\Delta_f S° = 0$

ASSERTION-REASON TYPE QUESTIONS

Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason).

Examine the statements carefully and mark the correct answer according to the instructions given below :

(A) If both the statements are TRUE and STATEMENT-2 is the correct explanation of STATEMENT-1

(B) If both the statements are TRUE but STATEMENT-2 is NOT the correct explanation of STATEMENT-1

(C) If STATEMENT-1 is TRUE and STATEMENT-2 is FALSE

(D) If STATEMENT-1 is FALSE and STATEMENT-2 is TRUE

1. **STATEMENT-1 :** Heat and work are "definite quantities".
   STATEMENT-2 : Heat and work are not properties of a system their values depend on the path of the process and vary accordingly.
2. **STATEMENT-1 :** There is no change in internal energy for an ideal gas at constant temperature.
   STATEMENT-2 : Internal energy of an ideal gas is a function of temperature only.
3. **STATEMENT-1 :** The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.
   STATEMENT-2 : The volume occupied by the molecules of an ideal gas is zero.
4. **STATEMENT-1 :** ΔH and ΔE are the same for the reaction, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$,
   STATEMENT-2 : All reactants and products are gases where all gases are ideal.
5. **STATEMENT-1 :** The magnitude of the work involved in an isothermal expansion is greater than that involved in an adiabatic expansion.
   STATEMENT-2 : P–V curve (P on y-axis and V on x-axis) decrease more rapidly for reversible adiabatic expansion compared to reversible isothermal expansion starting from same initial state.
6. **STATEMENT-1 :** Entropy change in reversible adiabatic expansion of an ideal gas is zero.
   STATEMENT-2 : The increase in entropy due to volume increase just componsate the decrease in entropy due to fall in temperature.
7. **STATEMENT-1 :** There cannot be chemical equilibrium in an open system.
   STATEMENT-2 : There is no fixed mass in an open system.
8. **STATEMENT-1 :** The standard free energy changes of all spontaneously occuring reactions are negative.
   STATEMENT-2 : The standard free energies of the elements in their standard states at 1 bar and 298 K are taken as zero.
9. **STATEMENT-1 :** Enthalpy and entropy of any elementary substance in the standard states are taken as zero.

STATEMENT-2 : At absolute zero, particles of the perfectly crystalline substance become completely motionless.

10. **STATEMENT-1 :** A reaction which is spontaneous and accompanied by decrease of randomness must be exothermic.
STATEMENT-2 : All exothermic reactions are accompanied by decrease of randomness.

11. **STATEMENT-1 :** Many endothermic reactions that are not spontaneous at room temperatures become spontaneous at high temperature.
STATEMENT-2 : ΔH° of the endothermic reaction increases with increase in temperature.

12. **STATEMENT-1 :** Decrease of free energy during the process under constant temperature and pressure provides a measure of its spontaneity.
STATEMENT-2 : A spontaneous change must have +ve sign of ΔS_{system}.

13. **STATEMENT-1 :** $|\Delta_f H|$ of $(H_2O, l) > |\Delta_f H|$ of (H_2O, g)
STATEMENT-2 : $\Delta H_{\text{condensation}}$ is negative.

14. **STATEMENT-1 :** All combustion reactions are exothermic.
STATEMENT-2 : Enthalpies of products are greater than enthalpies of reactants $(\Sigma\, \nu_p \Delta_f H(P) > \Sigma\, \nu_R \Delta_f H(R))$

15. **STATEMENT-1 :** Enthalpy of neutralization of CH_3COOH by NaOH is less than that of HCl by NaOH.
STATEMENT-2 : Enthalpy of neutralization of CH_3COOH is less because of the absorption of heat in the ionization process.

16. **STATEMENT-1 :** Internal energy of a real gas may change during expansion at constant temperature.
STATEMENT-2 : Internal energy of a real gas is a function of temperature and volume.

17. **STATEMENT-1 :** Work is a state function which is expressed in joule.
STATEMENT-2 : Work appears only at the boundary of the system.

18. **STATEMENT-1 :** The expansion of a gas into an evacuated space takes place non-spontaneously.
STATEMENT-2 : A process in which all steps cannot be retraced by themselves is called a spontaneous process.

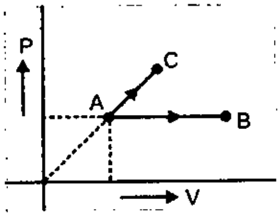
SUBJECTIVE PROBLEMS

1. A perfect gas undergoes a reversible adiabatic expansion from (300 K, 200 atm) to (90 K, 10 atm). Find the atomicity of gas.
2. 5 mole of an ideal gas at temp. T are compressed isothermally from 12 atm. to 24 atm. Calculate the value of $10r$

Where, $$r = \frac{\text{Work done along reversible process}}{\text{Work done along single step irreversible process}}$$ (Given : ln 2 = 0.7)

3. A diatomic ideal gas is expanded according to $PV^3 = \text{constant}$, under very high temperature (Assume vibration mode active). Calculate the molar heat capacity of gas (in cal / mol K) in this process.

4. A heat engine is operating between 500K to 300K and it absorbs 10 kcal of heat from 500K reservoir reversibly per cycle. Calculate the work done (in kcal) per cycle.
5. In a carnot cycle involving ideal non-linear triatomic gas, if during adiabatic expansion volume increases from 2L to 16L and heat absorbed during isothermal expansion is 8 kcal, then calculate magnitude of work done by carnot engine (in kcal).
6. Molar heat capacities at constant pressure for A, B and C are 3, 1.5 and 2 J/K mol. The enthalpy of reaction and entropy of reaction, $A + 2B \longrightarrow 3C$ are 20 kJ/mol and 20 J/K mol at 300K. Calculate ΔG (in kJ / mol) for the reaction ,
$$\frac{1}{2}A + B \longrightarrow \frac{3}{2}C$$
7. Standard molar enthalpy of combustion of glucose is −2880 kJ. If only 25% of energy is available for muscular work and 1.0 km walk consumes 90 kJ of energy, what maximum distance (in km) a person can walk after eating 90 g of glucose.
8. Given $C_2H_2(g) + H_2(g) \longrightarrow C_2H_4(g)$: $\Delta H^\circ = -175\,kJ\,mol^{-1}$
$\Delta H^\circ_{f(C_2H_4,g)} = 50\,kJ\,mol^{-1}$; $\Delta H^\circ_{f(H_2O,l)} = -280\,kJ\,mol^{-1}$; $\Delta H^\circ_{f(CO_2 g)} = -390\,kJ\,mol^{-1}$
If ΔH° is enthalpy of combustion (in kJ mol^{-1}) of $C_2H_2(g)$, then calculate the value of $\left|\frac{\Delta H^\circ}{280}\right|$.
9. The integral enthalpies of solution of anhydrous $CuSO_4(s)$ and hydrated $CuSO_4 \cdot 5H_2O(s)$ are −70 kJ and 10 kJ per mol respectively. Determine the magnitude of enthalpy of hydration of 0.1 mole anhydrous $CuSO_4(s)$ as
$CuSO_4(s) + 5H_2O(l) \longrightarrow CuSO_4 \cdot 5H_2O(s)$
10. If enthalpy of neutralisation of HCl by NaOH is $-57\,kJ\,mol^{-1}$ and with NH_4OH is $-50\,kJ\,mol^{-1}$. Calculate enthalpy of ionisation of $NH_4OH(aq)$.
11. Lattice energy of NaCl(s) is $-790\,kJ\,mol^{-1}$ and enthalpy of hydration is $-785\,kJ\,mol^{-1}$. Calculate enthalpy of solution of NaCl(s).
12. x g sample of NH_4NO_3 is decomposed in a Bomb calorimeter. The temperature of calorimeter increase by 4°C. The heat capacity of the system is 1.25 kJ/°C. Calculate the value of x. Given molar heat of decomposition of NH_4NO_3 is $400\,kJ\,mol^{-1}$.
13. A heat engine operating between 227°C and 77°C absorbs 10 kcal of heat from the 227°C reservoir reversibly per cycle. Calculate total work done (in kcal) in two cycles.
14. Calculate work done in chemical reaction (in kcal)
$A(s) + 3B(g) \longrightarrow C(l)$ at 227°C at 1 atm in closed vessel.
15. One mole ideal monoatomic gas is heated according to path AB and AC.
If temperature of state B and state C are equal.
Calculate $\frac{q_{AC}}{q_{AB}} \times 10$.



ANSWERS

Level 1

1. (d)	2. (b)	3. (d)	4. (c)	5. (a)	6. (c)	7. (a)	8. (c)	9. (d)	10. (d)
11. (c)	12. (b)	13. (d)	14. (d)	15. (a)	16. (b)	17. (b)	18. (a)	19. (b)	20. (c)
21. (c)	22. (c)	23. (c)	24. (d)	25. (b)	26. (c)	27. (b)	28. (c)	29. (c)	30. (d)
31. (a)	32. (c)	33. (b)	34. (b)	35. (c)	36. (a)	37. (a)	38. (a)	39. (b)	40. (b)
41. (b)	42. (c)	43. (b)	44. (b)	45. (b)	46. (c)	47. (a)	48. (b)	49. (c)	50. (c)
51. (a)	52. (b)	53. (d)	54. (b)	55. (b)	56. (b)	57. (b)	58. (b)	59. (b)	60. (b)
61. (a)	62. (c)	63. (c)	64. (d)	65. (c)	66. (a)	67. (a)	68. (c)	69. (d)	70. (c)
71. (d)	72. (c)	73. (b)	74. (b)	75. (c)	76. (c)	77. (b)	78. (d)	79. (a)	80. (b)
81. (b)	82. (b)	83. (c)	84. (d)	85. (d)	86. (b)	87. (b)	88. (a)	89. (b)	90. (b)
91. (a)	92. (d)	93. (d)	94. (c)	95. (b)	96. (a)	97. (a)	98. (a)	99. (a)	100. (b)
101. (c)	102. (d)	103. (a)	104. (d)	105. (a)	106. (a)	107. (b)	108. (a)	109. (b)	110. (c)
111. (a)	112. (d)	113. (c)	114. (a)	115. (b)	116. (a)	117. (c)	118. (b)	119. (c)	120. (c)
121. (c)	122. (c)	123. (b)	124. (a)	125. (a)	126. (c)	127. (c)	128. (b)	129. (b)	130. (a)
131. (a)	132. (b)	133. (a)	134. (a)	135. (b)	136. (b)	137. (a)	138. (a)	139. (c)	140. (b)
141. (a)	142. (c)	143. (b)	144. (d)	145. (a)	146. (d)	147. (b)	148. (a)	149. (a)	150. (b)

Level 2

1. (c)	2. (c)	3. (c)	4. (a)	5. (d)	6. (c)	7. (c)	8. i (c), ii (b)	9. (c)	10. (a)
11. (d)	12. (b)	13. (b)	14. (d)	15. (a)	16. (b)	17. (c)	18. (d)	19. (d)	20. (a)
21. (a)	22. (d)	23. (c)	24. (c)	25. (d)	26. (b)	27. (a)	28. (d)	29. (b)	30. (b)
31. (b)	32. (c)	33. (b)	34. (d)	35. (a)	36. (a)	37. (c)	38. (c)	39. (b)	40. (d)

Level 3

Passage–1 1. (d) 2. (d)

Passage–2 1. (b) 2. (c) 3. (b) 4. (c)

Passage–3 1. (c) 2. (a) 3. (d) 4. (c) 5. (d)

Passage–4 1. (a) 2. (b) 3. (b)

Passage–5 1. (a) 2. (b) 3. (a)

One or More Answers is/are Correct

1. (b,c)	2. (a,b)	3. (c)	4. (a,b,c)	5. (a,b,d)
6. (b,c,d)	7. (b,c,d)	8. (a,b,c)	9. (c,d)	10. (a,c,d)
11. (a,b,c)	12. (a,c)	13. (a,c,d)	14. (b,d)	15. (a,b,c)
16. (a,c,d)	17. (b,c,d)	18. (a,b,c,d)	19. (a,b,c)	20. (a,b,c)
21. (a,c,d)	22. (a,c)	23. (a,c)	24. (a,c,d)	25. (a,c)

Match the Column

1. $A \rightarrow P$; $B \rightarrow S$; $C \rightarrow R$; $D \rightarrow Q$

2. $A \rightarrow P$; $B \rightarrow R$; $C \rightarrow Q$; $D \rightarrow S$

3. $A \rightarrow P, S$; $B \rightarrow Q, R$; $C \rightarrow R$; $D \rightarrow S$

4. $A \rightarrow R$; $B \rightarrow Q$; $C \rightarrow P$; $D \rightarrow S$

5. $A \rightarrow Q$; $B \rightarrow P$; $C \rightarrow R$; $D \rightarrow S$

6. $A \rightarrow Q$; $B \rightarrow P, S$; $C \rightarrow P$; $D \rightarrow R$

7. $A \rightarrow P, S$; $B \rightarrow R$; $C \rightarrow Q, S$; $D \rightarrow Q, S$

8. $A \rightarrow R$; $B \rightarrow Q$; $C \rightarrow Q$; $D \rightarrow P, S$

9. $A \rightarrow P$; $B \rightarrow R$; $C \rightarrow Q, S$; $D \rightarrow Q, S$

10. $A \rightarrow P$; $B \rightarrow R$; $C \rightarrow Q$; $D \rightarrow S$

11. $A \rightarrow S$; $B \rightarrow P, R$; $C \rightarrow Q$; $D \rightarrow P, R$

12. A → P, R; B → Q; C → P, R; D → Q, S
13. A → Q; B → P; C → R; D → S
14. A → P, Q; B → Q, R, S; C → P; D → R
15. A → S; B → R; C → P; D → Q

Assertion-Reason Type Questions

1. (D) **2.** (A) **3.** (B) **4.** (B) **5.** (A) **6.** (A) **7.** (A) **8.** (B) **9.** (D) **10.** (C)
11. (B) **12.** (C) **13.** (A) **14.** (C) **15.** (A) **16.** (A) **17.** (D) **18.** (D)

Subjective Problems

1.	1	**2.**	7	**3.**	6	**4.**	4	**5.**	4	**6.**	7	**7.**	4	**8.**	5	**9.**	8	**10.**	7
11.	5	**12.**	1	**13.**	6	**14.**	3	**15.**	8										

Hints and Solutions

Level 1

5. (a) Heat lost by iron + Heat gained by water = 0

$10 \times 0.45(T - 373) + 25 \times 4.2 \times (T - 300) = 0$

$T = 303\text{ K}$ or $30°\text{C}$

9. (d) $w = -P_{ext}.\Delta V = -\Delta n_g RT$ and Δn_g is –ve for I and III

also $\quad \Delta V = -$ ve for IV

12. (b) $\Delta U = q + w$

$= 10 \times 1000 - 2 \times (20) \times 101.3 = 5948\text{ J}$

16. (b) $w = -P.\Delta V = -n_{H_2}$

$RT = -\dfrac{2 \times 8.314 \times 298}{1000}$

$= -4.955\text{ kJ}$

18. (a) $\int dw = -\int P.dV$

$\Rightarrow \quad w_{rev} = -\int 6.V^2 dV$

$= -6\left[\dfrac{V_2^3}{3} - \dfrac{V_1^3}{3}\right]$ bar. m^3;

$w = -5200\text{ kJ}$

so, work done by the gas is 5200 kJ.

20. (c) For cyclic process : $dU = 0$

$\therefore \quad -w = q$

Net work done by system = Area of the circle

21. (c) Process direction in V–P diagram is clockwise so process direction in P–V diagram is anti-clockwise.

Net work done by system = Area of the circle

$= \pi \times \dfrac{(P_2 - P_1)}{2}.\dfrac{(V_2 - V_1)}{2}$

22. (c) Work done in the cyclic process

= Area bounded $(ABCA) = 5P_1V_1$

31. (a) $V = \dfrac{nRT}{P} = \dfrac{100 \times 0.0821 \times T}{8.21} = T$

$\therefore \quad \log V = \log T$

32. (c) $\int dw = \int -P.dV$

$\Rightarrow \quad w = -\int 20 \cdot \dfrac{dV}{V} = -20 \ln \dfrac{V_2}{V_1}$

$w = -46.06\text{ L atm} = -4665.8\text{ J}$

$\Delta U = q + w \Rightarrow 400 = q - 4665.8$

$q = 5065.8\text{ J}$

34. (b) $w = -nRT \ln \dfrac{P_1}{P_2}$

$= -10 \times 8.314 \times 300 \ln \dfrac{10}{1}$

$= -57441.42\text{ J}$

$w = -mgh$

$\therefore \quad m \times 9.81 \times 100 = 57441.42$

$m = 58.55\text{ kg}$

35. (c) At constant volume $\Delta U = q_v = nC_{vm}\,\Delta T$

at constant pressure $\Delta H = q_p = nC_{p,m}\,\Delta T$

36. (a) $\quad \Delta U = w$

$\Rightarrow \quad -75 = 0.1 \times \dfrac{3}{2} \times 2[T_2 - 500]$

$T_2 = 250\text{ K}$

38. (a) $T^{\frac{\gamma}{1-\gamma}}.P =$ constant or $P \propto T^{\frac{\gamma}{\gamma-1}}$

$\because \quad P \propto T^3$

$\therefore \quad \dfrac{\gamma}{\gamma - 1} = 3; \quad \gamma = \dfrac{3}{2}$

39. (b) $T \propto \dfrac{1}{\sqrt{V}}$; $TV^{1/2} =$ constant

For adiabatic process,

$TV^{\gamma-1} =$ constant

$\therefore \quad \gamma - 1 = \dfrac{1}{2}, \quad \gamma = \dfrac{3}{2}$

40. (b) $PV^\gamma =$ constant, $P \cdot \gamma\, V^{\gamma-1} \cdot dV + V^\gamma \cdot dP = 0$

$\therefore \quad \dfrac{dP}{P} = -\gamma \cdot \dfrac{dV}{V}$

41. (b) $PV =$ constant for isothermal process

$PV^\gamma =$ constant for adiabatic process so more value of γ, more decrease in pressure.

42. (c) $T . V^{\gamma-1}$ = constant

$$\therefore \quad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$\Rightarrow \quad T_2 = 300 \times \left(\frac{16}{2}\right)^{\frac{5}{3}-1}$$

$$= 1200 \text{ K}$$

43. (b) $\int dw = -\int P_{\text{ext}} \cdot dV$

$$\therefore \quad w_{\text{irr}} = -P_{\text{ext}}\left[\frac{nRT}{P_2} - \frac{nRT}{P_1}\right]$$

$$w_{\text{irr}} = -1 \times (5 \times 8.314 \times 300) \times \left[1 - \frac{1}{10}\right]$$

$$w_{\text{irr}} = -11.224 \text{ kJ}$$

44. (b) For an adiabatic irreversible compression, $\Delta U = w$

$$\therefore \; nC_{v,m}(T_2 - T_1) = -P_{\text{ext}}(V_2 - V_1)$$

here $P_{\text{ext}} = P_2$

$$nC_{v,m}(T_2 - T_1) = -P_2\left[\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right]$$

$$\Rightarrow \; \frac{5}{2}R\,(T_2 - T_1) = -P_2 \times R\left[\frac{T_2}{P_2} - \frac{T_1}{P_1}\right]$$

$$\Rightarrow \quad P_2 = 275 \text{ kPa}$$

46. (c) $\because \quad q = 0 \qquad \therefore \quad \Delta U = w$

$$\Rightarrow nC_{v,m}(T_2 - T_1) = -P_{\text{ext}}\left[\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right]$$

$$\therefore \quad C_{v,m}[T_2 - T_1] = P_{\text{ext}} \cdot R\left[\frac{T_1}{P_1} - \frac{T_2}{P_2}\right]$$

$$\Rightarrow \frac{5}{2}R\,[T_2 - 300] = 2 \times R\left[\frac{300}{5} - \frac{T_2}{2}\right]$$

$$\Rightarrow \quad T_2 = 248.5 \text{ K}$$

47. (a) $\Delta U = w$

$$n \times \frac{R}{\gamma - 1}(T_2 - T_1) = -P_{\text{ext}}\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)$$

$$3(T_2 - T_1) = -1\left(\frac{T_2}{1} - \frac{T_1}{2}\right)$$

$$3T_2 - 3T_1 = -T_2 + \frac{T_1}{2}$$

$$4T_2 = \frac{7T_1}{2}$$

$$T_2 = \frac{7T_1}{8} = \frac{7 \times 400}{8} = 350 \text{ K}$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \Rightarrow \frac{2 \times 10}{400} = \frac{1 \times V_2}{350} \Rightarrow V_2 = 17.5 \text{ L}$$

48. (b) Average $C_{v,m} = \dfrac{n_1C_{v,m_1} + n_2C_{v,m_2}}{n_1 + n_2}$

$$= \frac{2 \times \frac{3}{2}R + 2 \times \frac{5}{2}R}{2 + 2} = 2R$$

49. (c) $\Delta H = (n_1C_{p,m_1} + n_2C_{p,m_2})\,\Delta T$

$$= \left(0.5 \times \frac{7}{2}R + 0.5 \times 4\,R\right)(-100)$$

$$= -375\,R$$

51. (a) 1 watt = 1 J/sec

Total heat supplied for 36 mL H_2O

$$= 806 \times 100$$

$$= 80600 \text{ J}$$

$$\Delta H_{\text{vap}} = \frac{80600}{36} \times 18$$

$$= 40300 \text{ J or } 40.3 \text{ kJ/mol}$$

53. (d) $\Delta n_g = 0 \quad \therefore \quad \Delta H° = \Delta U°$

For 2 mole $\Delta U° = -370$ kJ

55. (b) At constant pressure, $\Delta H = \Delta U + P \cdot \Delta V$

$$= 30 + 2 \times 4$$

$$= 38 \text{ atm-L}$$

56. (b) $\Delta H = \Delta U + P \cdot \Delta V$

$$\Rightarrow \; -124 = \Delta U + \frac{1520}{760} \times (177 - 377) \times 10^{-3} \times 101.3$$

$$\Delta U = -83.48 \text{ J}$$

57. (b) At constant volume $\Delta H = \Delta U + V\Delta P$

$$\Rightarrow \; -560 = \Delta U + 10 \times (-30) \times 0.1$$

$$\Delta U = -530 \text{ kJ}$$

58. (b) When both P and V are changing

$$\Delta H = \Delta U + \Delta(PV)$$

$$= \Delta U + (P_2V_2 - P_1V_1)$$

$$\Delta H = 40 + (20 - 3)$$

$$= 57 \text{ L-atm}$$

59. (b) For 1 mole of combustion of benzene

$$\Delta n_g = -1.5$$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\Rightarrow \; -3271 = \Delta U - \frac{1.5 \times 8.314 \times 300}{1000}$$

$$\Rightarrow \quad \Delta U = -3267.25 \text{ kJ}$$

For 1.5 mole of combustion of benzene

$$\Delta U = -3267.25 \times 1.5$$

$$= -4900.88 \text{ kJ}$$

60. (b) $\Delta H = \Delta E + \Delta n_g RT$

$$\Rightarrow\ 82.8 = \Delta E + \frac{1 \times 8.314 \times 298}{1000}$$

$$\Rightarrow\ \Delta E = 80.32$$

61. (a) C (graphite) $\longrightarrow$ C (diamond)

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

$$V_m \text{ (diamond)} = \frac{12}{3} \text{ mL}$$

$$V_m \text{ (graphite)} = \frac{12}{2} \text{ mL}$$

$$\Delta H - \Delta U = (500 \times 10^3 \times 10^5 \text{ N/m}^2) \left(\frac{12}{3} - \frac{12}{2}\right) \times 10^{-6}$$

$$= -100 \text{ kJ/mol}$$

$$\Delta U - \Delta H = +100 \text{ kJ/mol}$$

62. (c) Δn_g is +ve

65. (c) $\Delta S = nC_{p,m} \ln \frac{T_2}{T_1}$

$$= 2 \times \frac{5}{2} R \ln \frac{600}{300}$$

$$= 5R \ln 2$$

68. (c) $\Delta S_{gas} = nC_{v,m} \ln \frac{T_2}{T_1}$

$$= 2 \times \left(\frac{5}{2} - 1\right) R \ln 2$$

$$= 3R \ln 2$$

70. (c) ΔS will be same because entropy is a state function.

71. (d) $\Delta S = nC_{v,m} \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$

$$= C_{v,m} \ln 2 + R \ln \left(\frac{1}{2}\right)$$

$$\Delta S = (C_{v,m} - R) \ln 2$$

72. (c) $\Delta S = nC_{p,m} \ln \frac{T_2}{T_1}$

$$= 2.5 \times 18 \times 4.2 \ln \left(\frac{360}{300}\right)$$

$$= 34.02 \text{ J/K}$$

73. (b) $\Delta_r S° = \Sigma\, \nu_P S°$ (Products) $- \Sigma\, \nu_R S°$ (Reactants)

$$= (2 \times 27.3 + 3 \times 69.9) - (87.4 + 3 \times 130.7)$$

$$= -215.2 \text{ JK}^{-1} \text{ mol}^{-1}$$

77. (b) at M.P. $\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T}$

$$\Rightarrow\ T = \frac{\Delta H}{\Delta S} = \frac{9.95 \times 1000}{35.7} = 278.7 \text{ K}$$

78. (d) $\Delta S_{freezing} = -\frac{\Delta H_{fusion}}{T}$

$$\Rightarrow\ \Delta S = -\frac{80 \times 10}{273}$$

$$= -2.93 \text{ cal/K} = -12.25 \text{ J/K}$$

80. (b) $n_{C_6H_6} = \frac{117}{78} = 1.5$

$$\Delta S_{system} = 1.5 \times 85 \text{ J/K}$$

$$\therefore\ \Delta S_{surrounding} = -1.5 \times 85 \text{ J/K}$$

83. (c) $0.42 = a\,(10)^3 \ \Rightarrow\ a = 0.42 \times 10^{-3}$

$$S_m = \int_0^{20} \frac{C_{p,m}}{T}\, dT$$

$$= \int_0^{20} aT^2 dT = \frac{a}{3}[20^3 - 0]$$

$$= 1.12 \text{ J/K-mol}$$

87. (b) For $\Delta_r G°$ – ve, $\Delta_r H°$ should be –ve and $\Delta S°$ should be +ve

89. (b) $(\Delta G)_{system} = \Delta H - T \cdot \Delta S$

and $\Delta H - T \cdot \Delta S < 0$

94. (c) For ideal gas isothermal expansion $\Delta H = 0$

$$\therefore\ \Delta G = -T \cdot \Delta S$$

where $\Delta S = nR \ln \left(\frac{V_2}{V_1}\right)$

95. (b) $\text{Hg}(l) \rightleftharpoons \text{Hg}(g)$,

$$\Delta_r S° = 174.4 - 77.4 = 97 \text{ J/K-mol}$$

$$\because\ \Delta G° = \Delta H° - T \cdot \Delta S° = 0$$

$$T = \frac{\Delta H°}{\Delta S°}$$

$$= \frac{60.8 \times 1000}{97} = 626.8 \text{ K}$$

96. (a) At equilibrium $\therefore$ $\Delta H = T \cdot \Delta S$

$$H_2O(s) \longrightarrow H_2O(l)$$

$$\Delta S = S_{H_2O(l)} - S_{H_2O(s)} = 21.8 \text{ J/mol-K}$$

$$\Delta H = 273 \times (21.8) = 5951.4 \text{ J/mol}$$

105. (a) At equilibrium $\Delta G° = -RT \ln K_{eq}$

where $K_{eq} = (P_{H_2O}/P°)$ and $P° = 1$ bar

106. (a) $\Delta G° = -RT \ln K_w$

$$= -8.314 \times 298 \times 2.303\,(-14)$$

$$\simeq 80000 \text{ J}$$

111. (a) $\Delta_r C_p° = -10.945$ for

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(g)$$

According to Kirchhoff's law

$$\Delta_r H°_{T_2} - \Delta_r H°_{T_1} = \Delta_r C°_p [T_2 - T_1]$$

$\Delta_r H^\circ_{T_2} - (241.82) = [-10.94 \text{ J } (373-298)/100]$

$\Rightarrow \quad \Delta_r H_{T_2} = -242.6$ kJ/mol

114. (a) $\Delta H^\circ = \frac{3}{2} \times \Delta H_1^\circ + \frac{\Delta H_2^\circ}{2}$

$= -713.7 - 177.5$

$= -891.2$ kJ

115. (b) $\Delta H^\circ = 2 \times \Delta H_1^\circ + 2 \times \Delta H_2^\circ - \Delta H_3^\circ$

119. (c) $C_8H_{18}(g) + \frac{25}{2} O_2(g) \rightarrow 8CO_2(g) + 9H_2O(l)$

$\Delta_r H^\circ = 8 \times (-394) + 9 \times (-286) - (-250)$

$= -5476$ kJ/mol

121. (c) $C(s) + O_2(g) \longrightarrow CO_2(g)$;

$\Delta_r H_1 = -x$ kJ/mol ...(1)

$CO(g) + 1/2\, O_2(g) \longrightarrow CO_2(g)$

$\Delta_r H_2 = -y$ kJ/mol ...(2)

Equation (1) – (2)

$C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g)$

$\Delta_f H = (y - x)$ kJ/mol

125. (a) $\Delta_r H^\circ = 57 \times (-393.5) + 52 \times (-285.8) - (-70870)$

$= -33578.9$ kJ/mol

$= -\frac{33578.9}{884} = -37.98$ kJ/mol

129. (b) For $H_2(g) + O_2(g) \longrightarrow H_2O_2(l)$

$\Delta_f H^\circ (H_2O_2, l) = \Delta_r H_3{}^\circ + \frac{\Delta_r H_2^\circ}{2} - \frac{\Delta_r H_1^\circ}{2}$

131. (a) $-q_{\text{reaction}} = q_{\text{bomb}} + q_{\text{water}}$

$q_{\text{reaction}} = (C\ (\text{bomb}) + (m_{\text{water}} \times c))\, \Delta T$

$= (652 + 500 \times 4.18) \times 14.3$

$= 39210$ J or 39.21 kJ

132. (b) $q = m \times c \times \Delta T$, $m = q/(c \times \Delta T)$

$= (24 \times 10^6 \times 0.7)/(4.18 \times 50)$

$= 80383$ g or 80.383 kg

133. (a) m mole of acid $= 0.05 \times 0.2 = 0.01$

$\Delta_r H^\circ = -\frac{480 \times 1.09}{0.01 \times 1000} = -52.32$ kJ/mol

134. (a) $\Delta H_{\text{solution}} = \frac{(125+8) \times 4.2 \times 6}{8} \times 80$

$= 33516$ J/mol or 33.51 kJ/mol

136. (b) $HCl(g) + aq \longrightarrow H^+(aq.) + Cl^-(aq.)$;

$\Delta_r H = -75.14$

$-75.14 = \Delta_f H\, (H^+, aq) + \Delta_f H\, (Cl^-, g) - \Delta_f H\, (HCl, g)$

$\because \quad \Delta_f H\, (H^+, aq) = 0$

$\Delta_f H\, (Cl^-, aq) = -75.14 - 92.3$

$= -167.44$ kJ/mol

137. (a) Given that

$MgSO_4(s) + nH_2O \longrightarrow MgSO_4\,(nH_2O)$;

$\Delta_r H_1 = -91.2$ kJ/mol ...(i)

$MgSO_4 \cdot 7H_2O(s) + (n-7)H_2O \longrightarrow MgSO_4\,(nH_2O)$

$\Delta_r H_2 = 13.8$ kJ/mol ...(ii)

Equation (i) – (ii)

or $\Delta H_{\text{hyd}} = \Delta_r H_1 - \Delta_r H_2$

$= -91.2$ kJ/mol $- 13.8$ kJ/mol

$= -105$ kJ/mol

138. (a) $-12250x - 13000\,(1-x) = -12500$

$750x = 500 \Rightarrow x = 2/3$ and $y = 1/3$

So, $\frac{x}{y} = \frac{2}{1}$

140. (b) $\Delta H_{\text{neut.}}$

$= \Delta H_{\text{ionization}} + \Delta_r H\, (H^+ + OH^- \rightarrow H_2O)$

$\Rightarrow \quad -51.34 = x - 55.84$

So, $\Delta H_{\text{ionization}}$ or $x = 4.5$ kJ/mol

143. (b) $\Delta_r H = \frac{5}{8} \times 40 + \frac{3}{8} \times 50 = 43.75$ kJ/mol

144. (d) No. of moles of O_2 required to supplied 30 kJ heat to second reaction

$= \frac{30}{1260} \times \frac{3}{2} = \frac{1}{28}$

So $n_{O_2} : n_{H_2} = \frac{1}{28} : 3$ or $1 : 84$

148. (a) $P(s) + \frac{3}{2} Cl_2(g) \longrightarrow PCl_3(g)$

$306 = (314 + 3 \times 121) - [\text{B. E. } (P—Cl) \times 3]$;

B.E. (P—Cl) $= 123.66$ kJ/mol

150. (b) $N_2(g) + 2H_2(g) \longrightarrow N_2H_4(g)$

$\Delta_f H\, (N_2H_4, g)$

$= (941 + 2 \times 436) - (159 + 4 \times 398)$

$= 1813 - 1751 = 62$ kJ mol^{-1}

Level 2

1. (c) $w = -P_{\text{ext}}(V_f - V_i)$

$$= -10^5\left(\frac{60\times10^{-3}}{0.60} + \frac{40\times10^{-3}}{1000} - \frac{100\times10^{-3}}{1000}\right)$$

$$= -10^5\,(100\times10^{-3} + 0.04\times10^{-3} - 0.1\times10^{-3})$$

$$|w| = 9994\ \text{J}$$

2. (c) Mole of the gas in the first compartment

$$n_1 = \frac{P_1V_1}{RT_1} = \frac{0.8314\times10^6\times2}{8.314\times400} = 500$$

Similarly, $n_2 = 2000$

The tank is rigid and insulated hence $w = 0$ and $q = 0$ therefore $\Delta U = 0$

Let T_f and P_f denote the final temperature and pressure respectively

$$\Delta U = n_1C_{V,m}[T_f - T_1] + n_2C_{V,m}[T_f - T_2] = 0$$

$$500\,(T_f - 400) + 2000\,(T_f - 500) = 0$$

$$T_f = 480\ \text{K}$$

3. (c)

$$\begin{tikzcd}
H_2O\,(l, 323\,K) \arrow[r, "\Delta U_1"] & H_2O\,(l, 373\,K) \arrow[d, "\Delta U_2"] \\
H_2O\,(g, 323\,K) & H_2O\,(g, 373\,K) \arrow[l, "\Delta U_3"']
\end{tikzcd}$$

$$C_{V,m}(H_2O, g) = 33.314 - 8.314 = 25\ \text{J/K mol}$$

$$\Delta U_2 = \Delta H_2 - \Delta n_gRT = 37.6$$

$$\Delta U_{\text{total}} = \Delta U_1 + \Delta U_2 + \Delta U_3$$

$$= C_{v,m}(l)\cdot\Delta T + \Delta V_{\text{vap.}} + C_{v,m}(g)\,\Delta T$$

$$= \frac{75\times50}{1000} + 37.6 + \frac{25\times50}{1000}$$

$$= 42.6\ \text{kJ/mol}$$

4. (a) $\because \dfrac{C_{p,m}}{C_{V,m}} = \gamma$ and $C_{p,m} - C_{V,m} = R$

$$\therefore\quad C_{V,m} = \frac{R}{\gamma-1}$$

$$C_{V,m} = \frac{C_V}{n} \quad\text{and}\quad C_V = m\cdot c_V$$

$$\therefore\quad \frac{R}{\gamma-1} = \frac{m\cdot c_V}{m}\times M$$

$$\therefore\quad c_V = \frac{R}{(\gamma-1)M}$$

5. (d) Av. $C_{V,m} = \dfrac{n_1C_{V,m_1} + n_2C_{V,m_2}}{n_1 + n_2} = 2R$

for adiabatic process $dU = dW$

$$\frac{dT}{T} = -\frac{R}{C_{V,m}}\left(\frac{dV}{V}\right)$$

$$n_1C_{V,m_1}\,dT + n_2C_{V,m_2}\,dT = -(n_1RT + n_2RT)\times\frac{dV}{V}$$

$$\ln\frac{T_2}{T_1} = -\frac{1}{2}\ln\left(\frac{V_2}{V_1}\right)$$

$$\Rightarrow\quad T_2 = 320\times\left(\frac{1}{4}\right)^{1/2} = 160\ \text{K}$$

$$\Delta U = (n_1C_{V,m_1} + n_2C_{V,m_2})\,\Delta T = -960\,R$$

6. (c) $2\times C_{V,m}(T_2 - T_1) = -1\left(\dfrac{2RT_2}{1} - \dfrac{2RT_1}{10}\right)$

$$\gamma = \frac{4}{3} = \frac{C_{p,m}}{C_{V,m}}$$

and $C_{p,m} = C_{V,m} + R \quad\therefore\quad C_{V,m} = 3R;$

$$3R\,(T_2 - 300) = -RT_2 + \frac{R\times300}{10}$$

$$T_2 = 232.5\ \text{K}$$

$$w = \Delta U = 2\times3R\,(300 - 232.5)$$

$$\Rightarrow\quad w = -405\,R$$

7. (c) Max. temp. attained by gas in between B to C

According to equation of straight line

$$\frac{P-4}{1-4} = \frac{V-1}{2-1}$$

$$\Rightarrow\quad P - 4 = -3V + 3$$

$$\Rightarrow\quad P = 7 - 3V$$

For 1 mole gas

$$\frac{RT}{V} = 7 - 3V;\quad RT = 7V - 3V^2 \qquad \ldots(1)$$

$$R\frac{dT}{dV} = 7 - 6V = 0$$

$V = \dfrac{7}{6}$ put in Eq. (1)

$$RT = \left(7 - 3\times\frac{7}{6}\right)\times\frac{7}{6}$$

$$\Rightarrow\quad T = \frac{49}{12R}$$

8. (i) (c) $w = -P\cdot\Delta V = -nR\Delta T = -2\times8.314\times600 = -9.97\ \text{kJ}$

(ii) (b) $\Delta H_{\text{total}} = \Delta H_{AB} + \Delta H_{BC} = nC_{p,m}\,\Delta T + 0$

$$= 2\times\frac{7}{2}\times R\times(800 - 200)$$

$$= 4200\,R$$

9. (c) $\dfrac{T_2}{T_1} = \left(\dfrac{V_1}{V_2}\right)^{\gamma - 1}$

$$T_2 = T_1 \cdot \left(\frac{1}{32}\right)^{\frac{7}{5}-1} = 600 \cdot \left(\frac{1}{2^5}\right)^{\frac{2}{5}}$$

$$= 600(0.5)^2 = 150\text{ K}$$

$$\Delta H_m = \frac{7}{2} R \times (150 - 600) = -1575\, R$$

10. (a) $w = -nR\,\Delta T = -2 \times 8.314 \times 100$

$$= -1662.8\text{ J}$$

$$\Delta U = n \int C_{v,\,m}\, dT$$

$$= 2 \times \int (20 + 10^{-2}\, T)\, dT$$

$$= 2 \times 20 \times (T_2 - T_1) + 2 \times 10^{-2} \times \frac{(T_2^2 - T_1^2)}{2}$$

$$= 4700\text{ J}$$

$$4700 = q - 1662.8$$

$$\therefore \quad q = 6362.8\text{ J}$$

11. (d) $C_{p,\,m} = (21.686 + 8.314 + 10^{-3} T)$

$$= 30 + 10^{-3} T$$

$$\int \Delta H = \int nC_{p,\,m}\, \Delta T$$

$$= 10 \times \int (30 + 10^{-3} T) \cdot dT$$

$$\Delta H = 10 \times 30\,(T_2 - T_1) + \frac{10^{-3}}{2} \times [T_2^2 - T_1^2] \times 10$$

$$= 30350\text{ J}$$

12. (b) $dU = dq + dw$

$$nC_{v,\,m} \cdot dT = nC_m \cdot dT - P \cdot dV$$

$$C_m = C_{v,\,m} + \frac{P \cdot dV}{n \cdot dT} \qquad \ldots(1)$$

$$PV^n = K \quad \text{and} \quad PV = nRT$$

$$\therefore \quad KV^{1-n} = nRT$$

$$K\,(1-n)\,V^{-n} \cdot dV = nR\,dT$$

$$\frac{dV}{dT} = \frac{nR}{K\,(1-n)\,V^{-n}} \qquad \ldots(2)$$

from Eqs. (1) and (2)

$$C_m = C_{v,\,m} + \frac{R}{(1-n)}$$

13. (b) $P_2 V_2^2 = P_1 V_1^2$

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^2$$

$$\text{Now,} \quad \frac{T_2}{T_1} = \frac{P_2 V_2}{P_1 V_1} = \frac{V_1}{V_2} = \frac{1}{3}$$

$$\therefore \quad T_2 = \frac{300}{3} = 100\text{ K}$$

$$\Delta H = nC_{p,\,m}\, \Delta T$$

$$= 2 \times \frac{5}{2} R \times (-200\text{ K}) = 1000\text{ R}$$

14. (d) $\Delta S = nC_{p,\,m} \ln \dfrac{T_2}{T_1} + nR \ln \dfrac{P_1}{P_2}$

$$= 3 \times \frac{7}{2} R \ln \left(\frac{596}{298}\right) + 3R \ln \frac{1}{4}$$

$$= -6.3\text{ cal K}^{-1}$$

15. (a) For isoentropic process $\Delta S_{\text{system}} = 0$

$$\therefore \quad nC_{p,\,m} \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} = 0$$

$$\Rightarrow \quad \ln (P_2) = \frac{5}{2} \times \ln \left(\frac{600}{300}\right)$$

$$= 1.75\text{ atm}$$

16. (b) $\Delta S_{\text{system}} = nR \ln \dfrac{V_2}{V_1}$

$$= 2 \times R \times \ln 2$$

$$= 11.52\text{ J/K}$$

$$\Delta S_{\text{surrounding}} = -\frac{3.41 \times 1000}{310}$$

$$= -11\text{ J/K}$$

$$\Delta S_{\text{total}} = +11.52 - 11$$

$$= +0.52\text{ J/K}$$

17. (c) $0.40 = aT_1^3 + bT_1$

$$0.40 = a \times (1000) + b \times 10$$

$$0.4 = 1000a + 10b \qquad \ldots(1)$$

$$0.92 = aT_2^3 + bT_2$$

$$\Rightarrow \quad 0.92 = a \times 8000 + 20b \qquad \ldots(2)$$

from Eqs. (1) and (2)

$$a = 2 \times 10^{-5}, \quad b = 0.038$$

$$S_m = \int \frac{aT^3 + bT}{T} \cdot dT$$

$$= \frac{a[T_2^3 - T_1^3]}{3} + b[T_2 - T_1]$$

$$= 0.813\text{ J/K-mol}$$

19. (d) No. of moles of sucrose $= \dfrac{34.2}{342} = 0.1$

$-(\Delta G)_{T,\,P} =$ useful work done by the system

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

$$= +(6000 \times 0.1) + \frac{180 \times 0.1 \times 300}{1000}$$

$$= 605.4\text{ kJ}$$

20. (a) $\Delta G^\circ_{200} = \Delta H^\circ_{200} - T\, \Delta S^\circ_{200}$

$$\Delta H^\circ_{200} = 20 - 4 = 16\text{ kJ/mol}$$

$\Delta H^\circ_{T_2} = \Delta H^\circ_{T_1} + \Delta C_P [T_2 - T_1]$

$\Delta H^\circ_{400} = \Delta H^\circ{}_{200} + \dfrac{20 \times 200}{1000}$ kJ/mol

$= 16 + 4 = 20$ kJ/mol

21. (a) $\Delta_f S^\circ$ (NH_4Cl, s) at 300 K

$= S^\circ_{NH_4Cl(s)} - \left[\dfrac{1}{2} S^\circ_{N_2} + 2S^\circ_{H_2} + \dfrac{1}{2} S^\circ_{Cl_2}\right]$

$= -374 \text{ JK}^{-1} \text{ mol}^{-1}$

$\because \quad \Delta_r C_P = 0$

$\therefore \quad \Delta_f S^\circ_{310} = \Delta_f S^\circ_{300}$

$= -374 \text{ JK}^{-1} \text{ mol}^{-1}$

$\Delta_f H^\circ_{310} = \Delta_f H^\circ_{300} = -314.5$

$\Delta_f G^\circ_{310} = \Delta_f H^\circ - 310\, \Delta S^\circ$

$= -314.5 - \dfrac{310\,(-374)}{1000}$

$= -198.56$ kJ/mol

22. (d) $\Delta_r H^\circ = 3 \cdot \Delta_f H^\circ (CO, s) + 4\, \Delta_f H^\circ (CO_2, g)$
$- \Delta_f H^\circ (Co_3O_4, s) - 4 \cdot \Delta_f H^\circ (CO, g)$

$\Delta_r H^\circ = -241$ kJ/mol

$\Delta_r S^\circ = 3 \times 30 + 4 \times 213.7 - 102.5 - 4 \times 197.7$

$= 51.5$ J/K-mol

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

$= -241 - \dfrac{300 \times 51.5}{1000}$

$= -256.45$ kJ/mol

23. (c) At constant volume, $\dfrac{P_1}{T_1} = \dfrac{P_2}{T_2}$

$\Rightarrow \quad P_2 = 1 \times \dfrac{300}{200} = \dfrac{3}{2}$

and $\quad V_1 = 24.63$ L

for single phase

$\because \quad dG = Vdp - S\,dT$

$\Delta G = V \cdot \Delta P - \int (2 + 10^{-2}\, T) \cdot dT$

$= 1231.5 - 200 - \dfrac{10^{-2} \times 50{,}000}{2}$

$= 781.5$ J

24. (c) $\because \Delta_r C_p = 0, \qquad \therefore \ \Delta H_{300} = \Delta H_{310}$

25. (d) $\Delta H^\circ = -3\, \Delta H^\circ_1 + \Delta H^\circ_2 + 2\, \Delta H^\circ_3 + 3\, \Delta H^\circ_4$

$= -747.4$ kJ

$\Delta H^\circ = \Delta U^\circ + \Delta n_g\, RT$; where $\Delta n_g = -8$

$-747.4 = \Delta U^\circ - \dfrac{8 \times 8.314 \times 300}{1000}$

$\Delta U^\circ = -727.44$ kJ

26. (b) $\Delta_r G^\circ = \Delta_r H^\circ - T \times \Delta_r S^\circ$

$\Delta_r S^\circ = 2 \times 81 - 4 \times 24 - 3 \times 205$ J/mol

$\therefore \quad \Delta_r H^\circ = -2258.1$ kJ/mol

$\Delta_r H^\circ = 2 \times \Delta_f H^\circ (Cr_2O_3, s)$

$\therefore \quad \Delta_f H^\circ (Cr_2O_3, s) = -\dfrac{2258.1}{2}$

$= -1129.05$ kJ/mol

27. (a) $CaO(s) + CO_2(g) \longrightarrow CaCO_3(s)$

$\Delta_f H^\circ = \Delta H^\circ_f (CaCO_3) - \Delta H^\circ_f (CaO) - \Delta H^\circ_f (CO_2)$

$= -1207 - (-635) - (-394)$

$= -178$ kJ/mol

$\therefore \Delta E = \Delta H - \Delta n_g\, RT$

$\Delta E = -178 - \dfrac{(-1) \times 8.3 \times 300}{1000}$

$= -175.51$ kJ

$n_{CaO} = \dfrac{224}{56} = 4$

$\therefore \quad q_v = n \cdot \Delta_r E = 4 \times (-175.51)$

$= -702.04$ kJ

28. (d) $H_2C_2O_4(l) + \frac{1}{2} O_2(g) \rightarrow H_2O(l) + 2CO_2(g)$;

$\Delta n_g = 3/2$

$\Delta U_c = -\dfrac{0.312 \times 8.75}{1} \times 90$

$= -245.7$ kJ/mol

$\Delta H = \Delta U + \Delta n_g RT$

$= -245.7 + \frac{3}{2} \times \dfrac{8.314 \times 300}{1000}$

$= -246.947$ kJ/mol

29. (b) $H_3PO_3 \longrightarrow 2H^+ + HPO_3^{2-}$; $\Delta_r H = ?$

$2H^+ + 2OH^- \longrightarrow 2H_2O$;

$\Delta_r H = -55.84 \times 2 = -111.68$

$-106.68 = \Delta_{\text{ion}} H - 55.84 \times 2$

$\Delta_{\text{ion}}\, H = 5$ kJ/mol

30. (b) $HA \longrightarrow H^+ + A^-$; $\Delta_r H = 1.4$ kJ/mol

$\Delta H_{\text{neutralization}} = \Delta H_{\text{ionization}} + \Delta_r H$
$(H^+ + OH^- \rightarrow H_2O)$

$-55.95 = \Delta H_{\text{ionization}} - 57.3$

$\Delta H_{\text{ionization}}$ for 1 M HA $= 1.35$ kJ/mol

% heat utilized by 1 M acid for ionization

$= \dfrac{1.35}{1.4} \times 100 = 96.43\%$

so, acid is $100 - 96.43 = 3.57\%$ ionized

31. (b) $2C(s) + 3H_2(g) \longrightarrow C_2H_6(g)$

$$\Delta_f H^\circ = \begin{bmatrix} 2\times\Delta_{sub}H\,(C, s) \\ 3\times B.E.\,(H—H) \end{bmatrix} - \begin{bmatrix} B.E.\,(C—C) \\ + 6\times B.E.\,(C—H) \end{bmatrix}$$

$$-85 = 2\times 718 + 3\times 436 - (x + 6y)$$

$$x + 6y = 2829 \qquad \ldots(1)$$

Similarly, for $C_3H_8(g)$

$$2x + 8y = 4002 \qquad \ldots(2)$$

from Eqs. (1) and (2)

$x = 345$ kJ/mol; $y = 414$ kJ/mol

32. (c) $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$

Let B.E. of N≡N is x

$$-46 = \frac{x}{2} + \frac{3}{2}\times 436 - 3\times 393 \Rightarrow x = 958$$

$N_2H_4(l) \longrightarrow N_2(g) + 2H_2(g)$;

$\Delta_r H = -50$ kJ/mol

$$\Delta_r H = \begin{bmatrix} \Delta_{vap}H\,(N_2H_4, l) \\ + 4\times B.E.\,(N—H) \\ + B.E.\,(N—N) \end{bmatrix} - \begin{pmatrix} B.E.\,(N\equiv N) \\ + 2\,B.E.\,(H—H) \end{pmatrix}$$

$$-50 = (18 + 4\times 393 + y) - (958 + 2\times 436)$$

$$-50 = (1590 + y) - (1830)$$

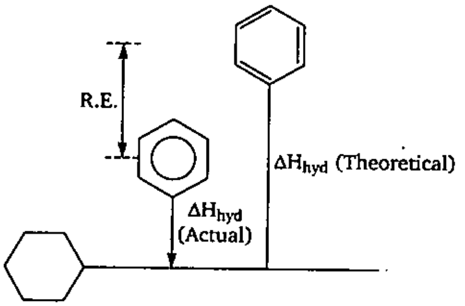
B. E. (N—N) or $y = 190$ kJ/mol

33. (b) $\Delta_r H$ = [Heat supplied] − [Heat evolved]

$$292 = [4x + 279] - [38 + 85]$$

$\Rightarrow \quad x = 34$ kcal/mol

34. (d) Theoretical heat of hydrogenation of benzene = (Actual heat of hydrogenation) + (Resonance energy)



$$= -205 - 152 = -357$$

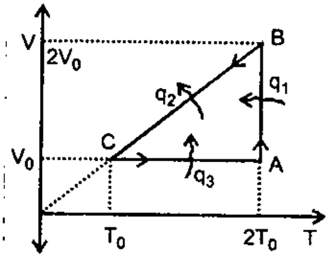
Enthalpy of hydrogenation of 

$= \frac{-357}{3} = -$ **119 kJ/mol**

35. (a) $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$

$$\Delta_C H = \begin{bmatrix} 8\times B.E.\,(C—H) \\ + 2\times B.E.\,(C—C) \\ + 5\times B.E.\,(O{=}O) \end{bmatrix} - \begin{bmatrix} 6\times B.E.\,(C{=}O) \\ + 8\times B.E.\,(O—H) \\ + 3\times|R.E.|\text{ of }CO_2 \\ + 4\times\Delta_{vap}H\,(H_2O) \end{bmatrix}$$

36. (a)



AB process

$$0 = q_1 + w_1$$

$$= q_1 - nR(2T_0)\ln 2$$

BC process $\Delta U_2 = q_2 + w_2$

$$\frac{nR}{(\gamma-1)}(T_0 - 2T_0) = q_2 - \left(\frac{nRT_0}{V_0}\right)\cdot(V_0 - 2V_0)$$

CA process

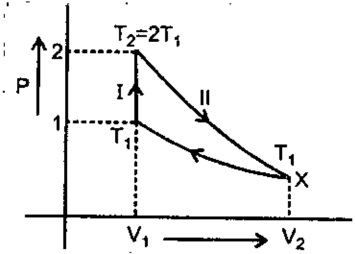
$$\Delta U_3 = q_3 + w_3$$

$$\frac{nR}{(\gamma-1)}(2T_0 - T_0) = q_3 + 0$$

$$\text{Efficiency} = \frac{\text{Total work done}}{\text{Total heat absorbed}} = \frac{w_1 + w_2}{q_1 + q_3}$$

$$= \frac{(-2RT_0\ln 2) + (nRT_0)}{(2RT_0\ln 2) + \left(\frac{nRT_0}{\gamma-1}\right)}$$

37. (c) $V_1 = 24.63\,L \quad T_1 = 300\,K; T_2 = 600\,K$



For path (II)

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

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

$$\frac{600}{300} = \left(\frac{V_2}{V_1}\right)^{\frac{7}{5}-1}$$

$$(2)^{5/2} = \frac{V_2}{V_1}$$

$$V_2 = 4\sqrt{2} \times 24.63 = 139.3\,\text{L} \approx 139\,\text{L}$$

38. (c)

$$\Delta_r H^\circ = \Delta_r H^\circ(H_2O, l) - \Delta_r H^\circ(OH^-, aq) = -229$$

$$-56 = -285 - \Delta_r H^\circ(OH^-, aq);$$

$$\Delta_r H^\circ(OH^-, aq) = -229$$

$$HF(aq) + OH^-(aq) \longrightarrow F^-(aq) + H_2O(l)$$

$$\Delta.\, H^\circ_{\text{neut}} = (-320 - 285) - (-329 - 229)$$

$$= -47 \text{ kJ/mol}$$

39. (b) $I_{2(s)} \longrightarrow I_2(g)$

$$\Delta H_2 = \Delta H_1 + \Delta C_P (T_2 - T_1)$$

$$\Delta C_P = C_P(I_{2,g}) - C_P(I_{2,s}) = -6.2 \text{ cal/mole}$$

$$\Delta H_2 = 6096 - 6.2(50) = 5786 \text{ cal/mole}$$

$$\Delta H = \Delta U + 1 \times 2 \times 523$$

$$5786 = \Delta U + 1 \times 2 \times 523$$

$$\Delta U = 5786 - 1046 = 4740 \text{ cal}$$

40. (d) $\Delta G^\circ = -RT \ln K_p;\ \ K_p = (2x)^2 X = 4X^3$

$$\Delta G^\circ = -RT \ln(4X^3)$$

$$\Delta G^\circ = -RT \ln 4 - 3RT \ln X$$

Level 3

Passage-2

1. (b) $PV = nRT \Rightarrow 2 \times 8 = 2 \times 0.080 \times T$

$$T = 100 \text{ K}$$

$$w_{\text{rev}} = -2.303 \times n \times R \times T \log \frac{P_1}{P_2}$$

$$= -2.303 \times 2 \times 0.08 \times 100 \times \log\left(\frac{1}{10}\right)$$

$$= 36.848 \text{ bar-L}$$

2. (c) $w_{\text{irr}} = -P_{\text{ext}}(V_2 - V_1)$

$$= -20\left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right)$$

$$= 144 \text{ bar-L}$$

3. (b) $w_{\text{irr (total)}} = w_1 + w_2$

$$= -10\left(\frac{nRT}{10} - \frac{nRT}{2}\right)$$

$$= -20\left(\frac{nRT}{20} - \frac{nRT}{10}\right)$$

$$= 5 \times nRT = 80 \text{ bar-L}$$

Passage-3

5. (d) $\Delta_r S^\circ = S^\circ_{CH_3OH} - S^\circ_{CO} - 2\,S^\circ_{H_2} = -\text{ J/K-mol}$

$$\Delta_r H^\circ = \Delta_f H^\circ(CH_3OH) - \Delta_f H^\circ(CO) - 2 \cdot \Delta_f H^\circ(H_2)$$

$$= -87 \text{ kJ/mol}$$

$$\Delta_r S^\circ_{320} - \Delta_r S^\circ_{300} = \Delta_r C_p [T_2 - T_1]$$

where $\Delta_r C^\circ_p = 44 - 29.4 - 2 \times 28.8$

$$= -43 \text{ J/K-mol}$$

$$\Delta_r S^\circ_{320} = -16 + (-43) \ln \frac{320}{320}$$

$$= -18.58$$

$$\Delta_r H^\circ_{320} = \Delta_r H^\circ_{300} + \Delta_r C^\circ_p [T_2 - T_1]$$

$$= -87 + \frac{(-43) \times 20}{1000}$$

$$= -87.86 \text{ kJ/mol}$$

$$\Delta_r G^\circ_{320} = \Delta_r H^\circ_{320} - T \cdot \Delta_r S^\circ_{320}$$

$$= -87.86 - \frac{320 \times (-18.58)}{1000}$$

$$= -81.91 \text{ kJ/mol}$$

Passage-4

3. (b) For max. rise in temp.; max. neutralization of H^+ and OH^- required.

- If we take equal volume, all H^+ (5 m-mole) will react with all OH^- (5 m-mole).

Passage-5

1. (a) $(\Delta G)_{PT} = 2000 - (20 \times 298)$

$$= -3960 \text{ J/mol}$$

2. (b) $CaCO_3 \longrightarrow CaO + CO_2 \quad \Delta H + \text{ve}$

Reaction becomes spontaneous at high temperature because $T\Delta S$ dominates over ΔH_{rxn}.

One or More Answers is/are Correct

6. (b,c,d) $\Delta U = 0 \quad \therefore \quad U_2 - U_1 = 0$

Similarly, $\Delta H = 0$

$$q = -w = nRT \ln \frac{V_2}{V_1}$$

9. (c,d)

At $V_A = \dfrac{1 \times R \times 100}{1} = 100\,R$

$$V_B = \frac{1 \times R \times 600}{3} = \mathbf{200\,R}$$

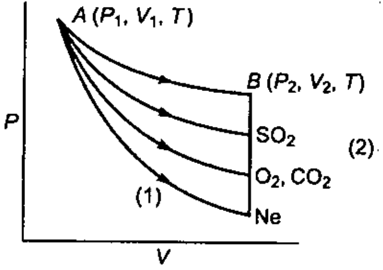
$\because$ $V_B > V_A$ so expansion of gas takes place

$$V_B = 200 \times 0.0821 = 16.42 \text{ L}$$

10. (a,c,d)

First step is adiabatic $(q = 0)$ so $\Delta U_1 = w_1$

Second step is isochoric $(w = 0)$



So, $\Delta U_2 = q_2$

$\because$ initial and final temp. are same

$\therefore$ $\Delta U_{\text{total}} = \Delta U_1 + \Delta U_2 = 0$

or $w_1 + q_2 = 0$

Max. work done by the gas, SO_2 is (area) under the curve

so, SO_2 absorbed

$\because$ $\gamma_{SO_2} < \gamma_{CO_2} = \gamma_{O_2} < \gamma_{Ne}$

so, max. decrease in temp. of Ne due to step 1.

11. (a,b,c)

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

is correct relation.

21. (a,c,d)

Work is a form of energy exchange between system and surrounding in adiabatic process.

Intensive property is not additive.

In cyclic process work may be zero.

For cyclic process

$$dU = 0 = dq + dw \Rightarrow dq - Pdv = 0$$

22. (a,c,)

Entropy of isolated system increases or remains constant but it can never decreases.

23. (a,c)

$$\Delta S_{\text{vap}} = \frac{\Delta H}{\text{B. P.}} = \frac{40 \times 1000}{400} = 100$$

(a) $P = 2\,\text{atm}$ B. P. > 400 K

$P \uparrow$ B. P. $\uparrow$ $\Delta S_{\text{vap}} < 100$

(c) $\Delta G = \Delta H - T\Delta S$

$= 40 \times 1000 - 410 \times 100 = -\text{ve}$

$\Delta G < 0$

(d) $\Delta H = \Delta U + \Delta n_g RT$

$\Delta O = \Delta U + 1 \times 8.31 \times 10^{-3} \times 400$

$\Delta U = 36.676$ kJ/mol

25. (a,c)

$\Delta_r H° = 0 - 95 + 55 + 25 = -15;$

$\Delta_r S° = 50 + 30 - 45 - 40 = -5;$

$\Delta_r G° = -15 \times 1000 + (400 \times 5) = -\text{ve}$

Subjective Problems

13. $\eta = \frac{T_2 - T_1}{T_2} = \frac{|-w_{\text{Total}}|}{q_2} \Rightarrow \frac{500 - 350}{500} = \frac{|-w_{\text{Total}}|}{10}$

Work done in one cycle = 3

Work done in two cycles = 3 × 2 = 6

14. $W = -\Delta n_g RT = \frac{-(-3) \times 2 \times 500}{1000} = 3$

15. Process AC = polytropic process $(P = KV)$

Molar Heat capacity $c_m = c_V + R/2 = 2R$

Process AB = Isobaric

$$c_m = c_p = 5R/2$$

$$\frac{q_{AC}}{q_{AB}} = \frac{\int_{T_A}^{T_C} nC_m \cdot dT}{\int_{T_A}^{T_B} n \cdot C_{p,m} \cdot dT} = \frac{2R}{\frac{5}{2}R} = 0.8 \;:$$

$$\frac{q_{AC}}{q_{AB}} \times 10 = 0.8 \times 10 = 8$$