DAY SIX

Chemical Thermodynamics

Learning & Revision for the Day

- Fundamental of Thermodynamics
- Types of Processes
- Concept of Work
- Heat
- First Law of Thermodynamics
- Entropy Change (ΔS)
- Second Law of Thermodynamics
- Third Law of Thermodynamics
- Gibb's Free Energy (ΔG)

The laws of thermodynamics deal with the energy changes of macroscopic systems involving a large number of molecules rather than microscopic systems containing a few molecules.

Fundamentals of Thermodynamics

Some basic terms and concepts commonly used in thermodynamics are briefly explained below:

System and Surroundings

System is a part of universe under observation and the part of the universe except system is called **surroundings**. System basically a specific portion which is considered under thermodynamic studies.

Thus, system and the surrounding together constitute the universe, i.e.

$$\text{universe} = \text{system} + \text{surroundings}$$

On the basis of exchange of mass and energy, systems are of three types:

1. **Open System** In which energy and matter both can be exchanged with surroundings.
2. **Closed System** In which only energy can be exchanged with surroundings.
3. **Isolated System** In which neither matter nor energy can be exchanged with surroundings.

Extensive and Intensive Properties

Properties used to define the state of a system are extensive and intensive properties.

1. **Intensive Properties** Those properties that depend on nature of matter but do not depend on quantity of the matter, e.g. pressure, temperature, specific heat, melting point etc.

2. **Extensive Properties** Those properties that depend on quantity of the matter present in the system, e.g. internal energy, heat, total moles, volume, enthalpy, entropy, free energy etc.

   Force is extensive property but pressure is intensive property.

State and Path Functions

1. **State Functions** Those functions which depend only on the state of the system and not on how it is reached. e.g. pressure, volume, temperature, ΔH, ΔE etc.
2. **Path Functions** The functions that depend upon the path followed are called path functions, e.g. work done, heat etc.

Types of Processes

The state of a variable can be changed by means of a thermodynamic process. These are of the following types :

1. **Adiabatic Process** In which system does not exchange heat with its surrounding, i.e. $dQ = 0$.
2. **Isothermal Process** In which temperature remains fixed, i.e. $dT = 0$.
3. **Isobaric Process** In which change of state is brought about at constant pressure, i.e. $dp = 0$.
4. **Isochoric Process** In which volume of the system remains constant, i.e. $dV = 0$.
5. **Cyclic Process** This is the process in which a system undergoes a number of different states and finally returns to its initial state. For such a process, change in internal energy and enthalpy is zero, i.e. $dE = 0$ and $dH = 0$.
6. **Reversible Process** In this process, (quasistatic system), change taken place is infinitesimally slow and their direction at any point can be reversed by infinitesimal change in the state of the system. Reversible process is an ideal process and here, every intermediate state is in equilibrium with others, if any.
7. **Irreversible Process** This process, is the one which cannot be reversed. In this process, amount of energy increases. All natural processes are irreversible in nature.

NOTE

- If macroscopic properties like temperature, pressure, etc., do not change with the time, the system is said to be in **thermodynamic equilibrium**.
- If the two systems are in thermal equilibrium with a third system, they must be in thermal equilibrium with each other. This law is known as **zeroth law of thermodynamics**.

  The law defines the temperature as the property which determines, whether the body is in thermal equilibrium or not.

Concept of Work

- The work is said to be done when gas expands or contracts against the external pressure. Work done is a path function not a state function as depends upon the path followed.

$$W = -p_{ext} \times \Delta V$$

For expansion $W = -p_{ext}(V_2 - V_1)$ [Here, $V_2 > V_1$]

For compression $W = -p_{ext}(V_2 - V_1)$ [Here, $V_2 < V_1$]

- Maximum work done for reversible isothermal process

$$W_{rev} = -2.303\, nRT \log \frac{V_2}{V_1}$$

where, V_2 = final volume, V_1 = initial volume

Also, $W_{rev} = -2.303 nRT \log \dfrac{p_1}{p_2}$

Maximum work done for irreversible isothermal expansion

(i) **Intermediate expansion**

$$p_{ext} < p_{gas}, W_{irr} = \int_{V_1}^{V_2} p_{ext}\, dV$$

$$W = -p_{ext}(V_2 - V_1)$$

(ii) **Free expansion** If gas expands in vacuum, $p_{ext} = 0$, therefore, $W = 0$

Sign Convention

(i) If W is positive — work done on the system

(ii) If W is negative — work done by the system

Heat

It is defined as the quantity of energy, which flows between system and surroundings on account of temperature difference. It is also a path function, i.e. depends upon the path followed.

Sign Convention

(i) If q is positive — heat is supplied to the system

(ii) If q is negative — heat is lost by the system

Internal Energy (E or U)

- It is the total energy within the substance. It is equal to the sum of translational energy, vibrational energy, potential energy etc. We can only determine the change in internal energy.

  i.e. $\Delta U = U_2 - U_1$
- At constant temperature, internal energy change (ΔE) will be zero. Internal energy depends on temperature, pressure, volume and quantity of matter.

First Law of Thermodynamics

According to this law, energy can neither be created nor destroyed although it may be converted from one form to another.

- Mathematical form of first law of thermodynamics,

$$\Delta E = q + W$$

- Both W and q are not state functions but quantity $W + q$ is a state function.

Enthalpy

- The total heat content of a system at constant pressure is called the enthalpy of the system. It is the sum of internal energy and the product of pressure-volume work.
- It is an extensive quantity, state function and represented by the symbol H.

  The equation is

$$H = E + pV$$

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

$$\Delta H = \Delta E + \Delta n_g RT$$

where, ΔH = enthalpy change

Δn_g = gaseous moles of products − gaseous moles of reactants

- If $\Delta n_g = 0$, then $\Delta H = \Delta U$; If $\Delta n_g > 0$ then $\Delta H > \Delta U$ and if $\Delta n_g < 0$ then, $\Delta H < \Delta U$.
- For reaction involving solids and liquids only, $\Delta H = \Delta E$. Enthalpy also changes, when a substance undergoes phase transition.

Heat Capacity

Heat capacity (C) of a system is defined as the amount of heat required to raise the temperature of the system by 1°C.

$$C = \frac{q}{\Delta T}$$

- If the system consists of a single substance or a solution and weighs 1 mol, the heat capacity of the system is referred as **molar heat capacity** (C_m).
- If the system consists of a single substance or a solution and weights 1 g, the heat capacity of the system is referred as **specific heat of the system** (C_s).

$$q = C \times m \times \Delta T$$

where, m = mass of substance,

C = specific heat capacity

and ΔT = temperature difference.

There are two types of heat capacities based on the conditions such as volume and pressure.

1. **Heat Capacity at Constant Pressure** (C_p) The heat capacity of a substance measured when the gaseous system is at constant pressure.

$$C_p = \left(\frac{q}{\Delta T}\right)_p \quad \text{or} \quad C_p = \frac{dH}{dT}$$

2. **Heat Capacity at Constant Volume** (C_V) The heat capacity of a substance measured when the gaseous system is at constant volume.

$$C_V = \left(\frac{q}{\Delta T}\right)_V \quad \text{or} \quad C_V = \frac{dV}{dT}$$

- Relationship between C_p and C_V is given as $C_p - C_V = R$ (R is the molar gas constant.)

$$C_p - C_V = \frac{R}{M}$$

- For monoatomic gas the molar heat capacity at constant volume, $C_V = \left(\frac{3}{2}\right)R$
- For monoatomic gas molar heat capacity at constant pressure,

$$C_p = \left(\frac{3}{2}\right)R + R = \left(\frac{5}{2}\right)R$$

- Poisson's ratio, $\gamma = \frac{C_p}{C_V} = \left(\frac{5}{3}\right) = 1.66$

  $\gamma = 1.66$ for monoatomic gases (like He, Ar)

  $\gamma = 1.40$ for diatomic gases (like H_2, O_2, CO)

  $\gamma = 1.33$ for triatomic gases (like H_2O, O_3)
- Work done in reversible adiabatic expansion

  Work done $= C_V\Delta T = C_V \times (T_2 - T_1)$

NOTE The molar heat capacity for any process is given by

$$C = C_V + \frac{R}{1-\gamma}$$

when, pV^{γ} = constant

Kirchhoff's Equation

According to Kirchhoff's equation, the partial derivatives of the change of enthalpy (or of internal energy) during a reaction, with respect to temperature at constant pressure (or volume) equals to the change in heat capacity at constant pressure (or volume).

$$\Delta C_p = \frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} \quad \text{and} \quad \Delta C_V = \frac{\Delta E_2 - \Delta E_1}{T_2 - T_1}$$

where, $\Delta C_p = \Sigma C_p$ of products $- \Sigma C_p$ of reactants

$\Delta C_V = \Sigma C_V$ of products $- \Sigma C_V$ of reactants

Entropy Change (ΔS)

Entropy is the measurement of randomness or disorder of the molecules. A process which proceeds at its own without any outside help is termed as spontaneous process. The total entropy change (ΔS_{total}) for the system and surrounding of a spontaneous process is always positive,

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0.$$

- Entropy is a state function and depends only on initial and final states of the system.

  i.e. $\Delta S = S_{\text{final}} - S_{\text{initial}}$
- Unit of entropy is joule per Kelvin per mole.
- For a reversible change at constant temperature

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

  q_{rev} = heat absorbed or evolved at absolute temperature T. If $\Delta S > 0$, heat is absorbed and if $\Delta S < 0$, heat is evolved.
- For a spontaneous isothermal expansion

  $$\Delta S = 2.303\, nR \log \frac{V_2}{V_1}$$
- The change of matter from one state to another is called **phase transition.**

  The entropy changes at the time of phase transition are as follows:

  (i) $\Delta S_{\text{melting}} = \dfrac{\Delta H_{\text{fusion}}}{T_m}$; ($T_m$ = melting point of substance)

  (ii) $\Delta S_{\text{vaporisation}} = \dfrac{\Delta H_{\text{vaporisation}}}{T_b}$; ($T_b$ = boiling point of substance)

  (iii) $\Delta S_{\text{sublimation}} = \dfrac{\Delta H_{\text{sublimation}}}{T_{\text{sub}}}$; ($T_{\text{sub}}$ = sublimation temperature)

Second Law of Thermodynamics

The second law of thermodynamics tells us whether a given process can occur spontaneously and to what extent, it also helps us to calculate maximum fraction of heat that can be converted into work in a given process. The second law states that the entropy of the universe is continuously increasing and tends to a maximum.

For an irreversible process,

$$dS > \frac{dq}{T}$$

$$\therefore \quad dS \geq \frac{dq}{T}$$

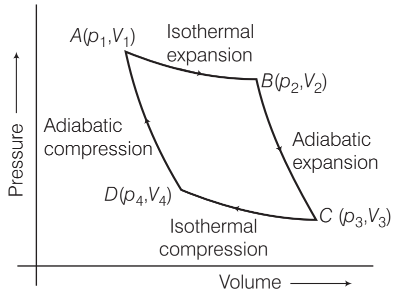
This is the mathematical statement of the second law of thermodynamics.

Carnot Engine

Carnot in 1824 gave an imaginary reversible cycle which demonstrates the maximum conversion of heat into work. He actually proposed a theoretical heat engine to show that its efficiency was based upon the temperatures, between which it operated.

A Carnot cycle comprises four operations or processes:

(i) Isothermal reversible expansion
(ii) Adiabatic reversible expansion
(iii) Isothermal reversible compression
(iv) Adiabatic reversible compression



Carnot cycle

- Net work done in 1 cycle is

  $$W = RT_2 \ln \frac{V_2}{V_1} + RT_1 \ln \frac{V_4}{V_3}$$
- Net heat absorbed in the whole cycle is

  $$q = R(T_2 - T_1) \ln \frac{V_2}{V_1}$$
- Efficiency of a heat engine (denoted by η) in a Carnot cycle is given

  $$\eta = \frac{W}{q_2} = \frac{T_2 - T_1}{T_2} = 1 - \frac{T_1}{T_2}$$
- The above relation was stated in the form of Carnot theorem by Carnot, i.e. "Every perfect engine working reversibly between the same temperature limits has the same efficiency, whatever be the working substance."

Third Law of Thermodynamics

- This law was proposed by German chemist Walther Nernst. According to this law, "The entropy of a perfectly crystalline substance approaches zero as the absolute zero of temperature is approached".
- It forms the basis from which entropies at other temperatures can be measured, $\lim_{T \to 0} S = 0$

Gibbs Free Energy (ΔG)

- The maximum amount of energy available to a system, during a process that can be converted into useful work is called free energy or Gibbs free energy.
- Under standard conditions of temperature (i.e. at 298 K) and pressure (i.e. 1 atm), the free energy change for a process in which reactants in their standard state is converted into products in their standard state is called standard free energy change (i.e. $\Delta G°$).
- The changes in the Gibbs energy of a system as a function of temperature can be calculated by the equation known as Gibbs Helmholtz Equation.

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

where, ΔG = Gibbs free energy (measurement of useful work)

- The following cases are considered for ΔG.
  (i) $\Delta G > 0$, for non-spontaneous process
  (ii) $\Delta G < 0$, for spontaneous process
  (iii) $\Delta G = 0$, at equilibrium

Criteria for Spontaneity

- In the determination of spontaneity, Gibbs energy criteria is better than entropy criteria because Gibbs energy refers to the system only while entropy refers to both system and surroundings.
- For negative value of ΔG several conditions exist which plays an important role in deciding the spontaneity of the process.

ΔS	ΔH	ΔG	**Spontaneity of a Process**
+	−	Negative at all temperatures.	Spontaneous at all temperatures.
−	−	Negative at all temperatures.	Spontaneous at low temperature but non-spontaneous at high temperature.
+	+	Positive at low temperature and negative at high temperature.	Spontaneous at high temperature.
+	+	Positive at all temperature.	Non-spontaneous at all temperature.

Relation between Gibbs Energy Change and Equilibrium Constant

Relation between Gibbs free energy with reaction quotient and equilibrium constant are as follows :

- $\Delta G = \Delta G° + 2.303\, RT \log Q$
  where, Q = reaction quotient
- At equilibrium, $\Delta G = 0$
  $\therefore \quad \Delta G° = -2.303\, RT \log K$
  K = equilibrium constant
- $\Delta G° = -nE°_{\text{cell}}F$
  where, n = number of electrons lose or gained,
  $E°_{\text{cell}}$ = standard electrode potential,
  1F = 96500 C
- Efficiency of the fuel cell $= \Delta G / \Delta H \times 100$

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 Which of the following statement is correct?

(a) The presence of reacting species in a covered beaker is an example of open system
(b) There is an exchange of energy as well as matter between the system and the surroundings in a closed system
(c) The presence of reactants in a closed vessel made up of copper is an example of a closed system
(d) The presence of reactants in a thermos flask or any other closed insulated vessel is an example of a closed system

2 The pressure-volume work for an ideal gas can be calculated by using the expression $W = -\int_{V_i}^{V_f} p_{ex} dV$. The work can also be calculated from the pV – plot by using the area under the curve within the specified limits. When an ideal gas is compressed (a) reversibly or (b) irreversibly from volume V_i to V_t. Choose the correct option.

(a) $W_{(\text{reversible})} = W_{(\text{irreversible})}$
(b) $W_{(\text{reversible})} < W_{(\text{irreversible})}$
(c) $W_{(\text{reversible})} > W_{(\text{irreversible})}$
(d) $W_{(\text{reversible})} = W_{(\text{irreversible})} + p_{ex}\Delta V$

3 An ideal gas expands in volume from 1×10^{-3} m^3 to 1×10^{-2} m^3 at 300 K against a constant pressure of 1×10^5 N/m^2. The work done is

(a) –900 J
(b) –900 kJ
(c) 270 kJ
(d) 900 kJ

4 When 1 mole of a gas is heated at constant volume, temperature is raised from 298 K to 308 K. Heat supplied to the gas is 500 J. Then, which statement is correct?

(a) $q = -W = 500$ J, $\Delta E = 0$
(b) $q = W = 500$ J, $\Delta E = 0$
(c) $q = \Delta E = 500$ J, $W = 0$
(d) $\Delta E = 0$, $q = W = -500$ J

5 In an adiabatic process, no transfer of heat takes place between system and surroundings. Choose the correct option for free expansion of an ideal gas under adiabatic condition from the following.

(a) $q = 0, \Delta T \neq 0, W = 0$
(b) $q \neq 0, \Delta T = 0, W = 0$
(c) $q = 0, \Delta T = 0, W = 0$
(d) $q = 0, \Delta T < 0, W \neq 0$

6 1 mole of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 L to 10 L. The ΔE for this process is ($R = 2$ cal K^{-1} mol^{-1})

(a) 270 cal
(b) zero
(c) 10 L atm
(d) 181.7 cal

7 ΔU is equal to →JEE Main 2017

(a) isochoric work
(b) isobaric work
(c) adiabatic work
(d) isothermal work

8 A piston filled with 0.04 mole of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and W for the process will be [$R = 8.314$ J/mol K) (ln 7.5 = 2.01) →JEE Main 2013

(a) $q = -208$ J, $W = -208$ J
(b) $q = -208$ J, $W = +208$ J
(c) $q = +208$ J, $W = +208$ J
(d) $q = +208$ J, $W = -208$ J

9 Latent heat of vaporisation of a liquid at 500 K and 1 atm pressure is 10.0 kcal/mol. What will be the change in internal energy (ΔE) of 3 moles of liquid at same temperature?

(a) 30 kcal
(b) –54 kcal
(c) 27.0 kcal
(d) 50 kcal

10 ($\Delta H - \Delta E$) for the formation of carbon monoxide (CO) from its elements at 298 K is ($R = 8.314$ JK^{-1} mol^{-1})

(a) –2477.57 J mol^{-1}
(b) 2477.57 J mol^{-1}
(c) –1238.78 J mol^{-1}
(d) 1238.78 J mol^{-1}

11 Consider the reaction,
$N_2 + 3H_2 \longrightarrow 2NH_3$ carried out at constant temperature and pressure. If ΔH and ΔE are the enthalpy and internal energy changes for the reaction, which of the following expressions is true?

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

12 The combustion of benzene (l) gives $CO_2(g)$ and $H_2O(l)$. Given that heat of combustion of benzene at constant volume is –3263.9 kJ mol^{-1} at 25° C; heat of combustion (in kJ mol^{-1}) of benzene at constant pressure will be ($R = 8.314$ JK^{-1} mol^{-1}) →JEE Main 2018

(a) 4152.6
(b) –452.46
(c) 3260
(d) –3267.6

13 Heat required to raise the temperature of 1 mole of a substance by 1°C is called

(a) specific heat
(b) molar heat capacity
(c) water equivalent
(d) specific gravity

14 The molar heat capacity of water at constant pressure is 75 J $K^{-1}mol^{-1}$. When 1.0 kJ of heat is supplied to 100 g of water, which is free to expand, the increase in temperature of water is

(a) 1.2 K
(b) 2.4 K
(c) 4.8 K
(d) 6.8 K

15 For two moles of an ideal gas

(a) $(C_p - C_V) = 2R$
(b) $(C_p - C_V) = 0$
(c) $(C_p - C_V) = R$
(d) $(C_p - C_V) = R/2$

16 The heat of sublimation of iodine is 24 cal g^{-1} at 50°C. If specific heat of solid iodine and its vapours are 0.055 and 0.031 cal g^{-1} respectively, the heat of sublimation of iodine at 100°C is

(a) 22.8 cal g^{-1}
(b) 25.2 cal g^{-1}
(c) –22.8 cal g^{-1}
(d) –25.2 cal g^{-1}

17 What will be the change of entropy $\Delta_r S°$ at 298 K for the reaction, in which urea is formed from NH_3 and CO_2?

$$2NH_3(g) + CO_2(g) \longrightarrow NH_2CONH_2(aq) + H_2O(l)$$

[Given, the standard entropy of $NH_2CONH_2(aq)$, $CO_2(g)$, $NH_3(g)$ and $H_2O(l)$ are 174.0, 213.7, 192.3 and 69.9 JK mol^{-1} respectively]

(a) 200 JK^{-1} mol^{-1}
(b) –35.44 JK^{-1} mol^{-1}
(c) –354.4 JK^{-1} mol^{-1}
(d) 425.2 JK^{-1} mol^{-1}

18 2 moles of an ideal gas at 27°C are expanded reversibly from 2 L to 20 L. Find entropy change (in cal/mol K). ($R = 2$ cal/mol K)

(a) 0
(b) 4
(c) 9.2
(d) 92.0

19 For an isolated system, $\Delta E = 0$, then

(a) $\Delta S = 0$
(b) $\Delta S < 0$
(c) $\Delta S > 0$
(d) the value of ΔS cannot be predicted

20 When 1.8 g of steam at the normal boiling point of water is converted into water, at the same temperature, enthalpy and entropy changes respectively will be [Given, ΔH_{vap} for water = 40.8 kJ mol^{-1}]

(a) –8.12 kJ, 11.89 JK^{-1}
(b) 10.25 kJ, 12.95 JK^{-1}
(c) –4.08 kJ, – 10.93 JK^{-1}
(d) 10.93 kJ, –4.08 JK^{-1}

21 Which of the following does not have zero entropy even at absolute zero?

$CO, CO_2, NaCl, NO$

(a) CO, CO_2 (b) CO, NO
(c) CO_2, NaCl (d) NaCl

22. The enthalpy of vaporisation of liquid diethyl ether $(C_2H_5)_2O$, is 26.0 kJ mol^{-1} at its boiling point (35°C). What will be the ΔS for conversion of liquid to vapour and vapour to liquid respectively?

(a) $+84.41$ and -84.41 JK^{-1} mol^{-1}
(b) $+80.90$ and -68.83 JK^{-1} mol^{-1}
(c) -84.41 and $+90.63$ JK^{-1} mol^{-1}
(d) $+68.83$ and -84.41 JK^{-1} mol^{-1}

23 The direct conversion of A to B is difficult, hence it is carried out by the following shown path

$$\begin{tikzcd} C \arrow[r] & D \arrow[d] \\ A \arrow[u] & B \end{tikzcd}$$

Given, $\Delta S_{(A \to C)} = 50$ eu

$\Delta S_{(C \to D)} = 30$ eu

$\Delta S_{(B \to D)} = 20$ eu

where, eu is entropy unit, then $\Delta S_{(A \to B)}$ is

(a) + 100 eu (b) + 60 eu
(c) − 100 eu (d) − 60 eu

24 Match the following and choose the correct option.

	Column I		Column II
A.	Entropy of vaporisation	1.	decreases
B.	K for spontaneous process	2.	is always +ve
C.	Crystalline solid state	3.	lowest entropy
D.	ΔE in adiabatic expansion of ideal gas	4.	$\frac{\Delta H_{vap}}{T_b}$

Codes

	A	B	C	D		A	B	C	D
(a)	2,4	2	3	1	(b)	3	1,2	4	2
(c)	2	4	1	3	(d)	3,4	2	1	2

25 The entropy change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of 10 dm^3 to a volume of 100 dm^3 at 27°C is ➞ AIEEE 2011

(a) 38.3 J mol^{-1} K^{-1}
(b) 35.8 J mol^{-1} K^{-1}
(c) 32.3 J mol^{-1} K^{-1}
(d) 42.3 J mol^{-1} K^{-1}

26 A Carnot engine operates between temperature T and 400 K ($T > 400$ K). If efficiency of engine is 25%, the temperature T is

(a) 666.0 K (b) 498.5 K
(c) 533.3 K (d) 500.0 K

27 In view of the signs of $\Delta_r G°$ for the following reactions

$$PbO_2 + Pb \longrightarrow 2PbO, \ \Delta_r G° < 0$$
$$SnO_2 + Sn \longrightarrow 2SnO, \ \Delta_r G° > 0$$

(a) For lead + 4, for tin + 2 (b) For lead + 2 , for tin + 2
(c) For lead + 4, for tin + 4 (d) For lead + 2, for tin + 4

28 When the heat of a reaction at constant pressure is -2.5×10^3 cal and entropy change for the reaction is 7.4 cal deg^{-1}, it is predicted that the reaction at 25°C is

(a) reversible (b) spontaneous
(c) non-spontaneous (d) irreversible

29 At 1 atm pressure, $\Delta S = 75$ J K^{-1} mol^{-1}; $\Delta H = 30$ kJ mol^{-1}. The temperature of the reaction at equilibrium is

(a) 400 K (b) 330 K (c) 200 K (d) 110 K

30 For a particular reversible reaction at temperature T, ΔH and ΔS were found to be both positive. If T_e is the temperature at equilibrium, the reaction would be spontaneous when ➞ AIEEE 2010

(a) $T_e > T$ (b) $T > T_e$
(c) T_e is 5 times T (d) $T = T_e$

31 For the process,

$$H_2O(l)\,(1 \text{ bar}, 273 \text{ K}) \rightarrow H_2O(g)\,(1 \text{ bar}, 373 \text{ K}),$$

The correct set of thermodynamic parameters is

(a) $\Delta G = 0, \Delta S = +ve$ (b) $\Delta G = 0, \ \Delta S = -ve$
(c) $\Delta G = +ve, \Delta S = 0$ (d) $\Delta G = -ve, \Delta S = +ve$

32 Considering entropy (S) as a thermodynamic parameter, the criterion for the spontaneity of any process is

(a) $\Delta S_{system} + \Delta S_{surrounding}$ be +ve
(b) ΔS_{system} be zero
(c) $\Delta S_{system} - \Delta S_{surrounding}$ be + ve
(d) $\Delta S_{surrounding}$ be zero

33 For a reaction, $M_2O(s) \longrightarrow 2M(s) + \frac{1}{2}O_2(g)$, $\Delta H = 30$ kJ mol^{-1} and $\Delta S = 0.07$ kJ K^{-1} mol^{-1} at 1 atm. The temperature upto which the reaction would not be spontaneous is

(a) $T < 400.08$ K (b) $T < 273.15$ K
(c) $T < 428.57$ K (d) $T < 473.50$ K

34 For the process, $H_2O(l) \longrightarrow H_2O(g)$ at $T = 100$ °C and 1 atmosphere pressure, the correct choice is ➞ JEE Main 2014

(a) $\Delta S_{system} > 0$ and $\Delta S_{Surrounding} > 0$
(b) $\Delta S_{system} > 0$ and $\Delta S_{Surrounding} < 0$
(c) $\Delta S_{system} < 0$ and $\Delta S_{Surrounding} > 0$
(d) $\Delta S_{system} < 0$ and $\Delta S_{Surrounding} < 0$

35 The incorrect expression among the following is ➞ AIEEE 2012

(a) $\frac{\Delta G_{system}}{\Delta S_{total}} = -T$

(b) In isothermal process, $W_{reversible} = -nRT \ln \frac{V_f}{V_i}$

(c) $\ln K = \frac{\Delta H° - T\Delta S°}{RT}$

(d) $K = e^{-\Delta G°/RT}$

36 The value of $\log_{10} K_C$ for a reaction $A \rightleftharpoons B$ is

[Given, $\Delta_r H^\circ_{298\,\text{K}} = -54.07$ kJ mol^{-1},

$\Delta_r S^\circ_{298\,\text{K}} = 10$ JK^{-1} mol^{-1} and $R = 8.314$ JK^{-1} mol^{-1}

and $2.303 \times 8.314 \times 298 = 5705$]

(a) 5 (b) 10
(c) 95 (d) 100

37 For a spontaneous reaction, the ΔG, equilibrium constant (K) and E°_{cell} will be respectively

(a) $-$ ve, > 1, $-$ ve (b) $-$ ve, < 1, $-$ ve
(c) $+$ ve, > 1, $-$ ve (d) $-$ ve, > 1, $+$ ve

38 In a fuel cell, methanol is used as fuel and oxygen gas is used as an oxidiser. The reaction is

$$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

At 298 K standard Gibb's energies of formation for $CH_3OH(l)$, $H_2O(l)$ and CO_2 (g) are -166.2, -237.2 and -394.4 kJ mol^{-1}, respectively. If standard enthalpy of combustion of methanol is -726 kJ mol^{-1}, efficiency of the fuel cell will be ➞ AIEEE 2009

(a) 80% (b) 87%
(c) 90% (d) 97%

Direction (Q.Nos. 39 and 40) *In the following questions assertion followed by a reason is given. Choose the correct answer out of the following choices.*

(a) Both Assertion and Reason are correct statements and Reason is correct explanation of Assertion.
(b) Both Assertion and Reason are correct statements but Reason is not correct explanation of Assertion.
(c) Assertion is correct statements but Reason is wrong statement.
(d) Both Assertion and Reason are wrong.

39 **Assertion** (A) Spontaneous process is an irreversible process and may only be reversed by some external agency.

Reason (R) Decrease in enthalpy is a contributory factor for spontaneity.

40 **Assertion** (A) The thermodynamic function which determines the spontaneity of a process is the free energy. For a process to be spontaneous, the change in free energy must be negative.

Reason (R) The change in free energy is related to the change in enthalpy and change in entropy. The change in entropy for a process must be always positive if it is spontaneous.

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

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

(a) $(T_f)_{\text{irrev}} > (T_f)_{\text{rev}}$
(b) $T_f > T_i$ for reversible process, but $T_f = T_i$ for irreversible process
(c) $(T_f)_{\text{rev}} > (T_f)_{\text{irrev}}$
(d) $T_f = T_i$ for both reversible and irreversible processes

2. When one mole of monoatomic ideal gas at T K undergoes adiabatic change under a constant external pressure of 1 atm, changes volume from 1 L to 2 L. The final temperature in Kelvin would be

(a) $\dfrac{T}{2^{2/3}} Z$ (b) $T + \dfrac{2}{3 \times 0.0821}$
(c) T (d) $T - \dfrac{2}{3 \times 0.0821}$

3. Water is brought to boil under a pressure of 1.0 atm. When an electric current of 0.50 A from a 12 V supply is passed for 300 s through a resistance in thermal contact with it, it is found that 0.798 g of water is vaporised. Calculate the molar internal energy change at boiling point (373.15 K).

(a) 37.5 kJ mol^{-1} (b) 3.75 kJ mol^{-1}
(c) 42.6 kJ mol^{-1} (d) 4.26 kJ mol^{-1}

4. 1 mole of CO_2 gas at 300 K is expanded under adiabatic conditions such that its volume becomes 27 times. What is work done? ($\gamma = 1.33$ and $C_V = 6$ cal mol^{-1} for CO_2)

(a) 900 cal (b) 1000 cal (c) 1200 cal (d) 1400 cal

5. A monoatomic ideal gas undergoes a process in which the ratio of p to V at any instant is constant and equals to 1. What is the molar heat capacity of the gas?

(a) $4R/2$ (b) $3R/2$
(c) $5R/2$ (d) Zero

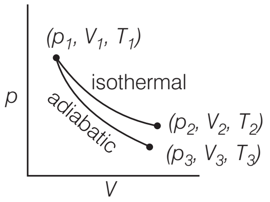
6. $CaCO_3$ exists in two forms calcite and aragonite. The conversion of 1 mole of calcite to aragonite is accompanied by internal energy change equal to + 0.21 kJ. Given that the densities of calcite and aragonite are 2.71 cm^{-3} and 2.73 g cm^{-3} respectively. The enthalpy change at the pressure of 1.0 bar will be

(a) 200.72 J mol^{-1} (b) 309.72 J mol^{-1}
(c) 209.72 J mol^{-1} (d) 315.00 J mol^{-1}

7 Identify the correct statement regarding a spontaneous process.

(a) For a spontaneous process in an isolated system, the change in entropy is positive
(b) Endothermic processes are never spontaneous
(c) Exothermic processes are always spontaneous
(d) Lowering of energy in the reaction process is the only criteria for spontaneity

8 The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement is incorrect?



(a) $T_1 = T_2$ (b) $T_3 > T_1$
(c) $W_{(\text{isothermal})} > W_{(\text{adiabatic})}$ (d) $\Delta E_{(\text{isothermal})} > \Delta E_{(\text{adiabatic})}$

9 A gas present in a cylinder, fitted with a frictionless piston, expands against a constant pressure of 1 atm from a volume of 2 litre to a volume of 6 litre. In doing so, it absorbs 800 J heat from surroundings. The increase in internal energy of process is

(a) 305.85 J (b) 394.95 J
(c) 405.83 J (d) –463.28 J

10 In an irreversible process taking place at constant T and p and in which only pressure volume work is being done, the change in Gibbs free energy (ΔG) and change in entropy (ΔS), satisfy the criteria

(a) $(\Delta S)_{V,E} < 0, (\Delta G)_{T,p} < 0$ (b) $(\Delta S)_{V,E} > 0, (\Delta G)_{T,p} < 0$
(c) $(\Delta S)_{V,E} = 0, (\Delta G)_{T,p} = 0$ (d) $(\Delta S)_{V,E} = 0, (\Delta G)_{T,p} > 0$

11 A reaction is non-spontaneous at the freezing point of water but is spontaneous at the boiling point of water, then

	ΔH	ΔS
(a)	+ ve	+ ve
(b)	– ve	– ve
(c)	– ve	+ ve
(d)	+ ve	– ve

12 One mole of a liquid (1 bar, 100 mL) is taken in an adiabatic container and the pressure increases steeply to 100 bar. Then at constant pressure of 100 bar, volume decreases by 1 mL. ΔU and ΔH will be respectively.

(a) 10 J, 10 J
(b) 10 J, 0
(c) 0, 10 J
(d) 5 J, 10 J

13 Standard entropy of X_2, Y_2 and XY_3 are 60, 40 and 50 $JK^{-1}\,mol^{-1}$ respectively. For the reaction,

$$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \longrightarrow XY_3, \ \Delta H = -30\text{ kJ}$$

to be at equilibrium, the temperature will be

(a) 750 K (b) 1000 K
(c) 1250 K (d) 500 K

14 For an isomerisation reaction $A \rightleftharpoons B$, the temperature dependence of equilibrium constant is given by

$$\log_e K = 4.0 - \frac{2000}{T}$$

The value of $\Delta S°$ at 300 K is therefore,

(a) $4R$ (b) $5R$
(c) $400R$ (d) $2000R$

15 1 kg block of ice at 0°C is placed into a perfectly insulated, sealed container that has 2 kg of water also at 0°C. The water and ice completely fill the container is flexible. After sometime one can except that

(a) the water will freeze so that the mass of the ice will increase
(b) the ice will melt so that the mass of ice will decrease
(c) both the amount of water and the amount of ice will remain constant
(d) both the amount of water and the amount of ice will decrease

ANSWERS

SESSION 1

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

SESSION 2

1 (a) **2** (d) **3** (a) **4** (c) **5** (a) **6** (c) **7** (a) **8** (b) **9** (b) **10** (b)
11 (a) **12** (b) **13** (a) **14** (a) **15** (b)

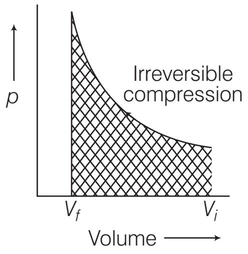
Hints and Explanations

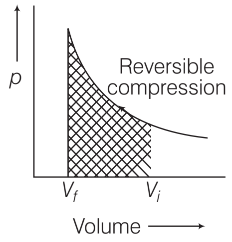
SESSION 1

1 For a closed vessel made up of copper, no matter can exchange between the system and the surrounding but energy exchange can occur through its walls.

Presence of reaction species in a covered beaker-closed system and exchange of matter as well as energy-open system. Presence of reactant in a closed vessel is a closed system and presence of reactant flask is an isolated system.

2





As the area under the curve is more in irreversible compression than the area under curve of reversible compression. Thus, $W_{\text{irreversible}} > W_{\text{reversible}}$.

3 Work done due to change in volume against constant pressure is

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

$$= -1\times10^5\ \text{N/m}^2\,(1\times10^{-2} - 1\times10^{-3})\ \text{m}^3$$

$$= -900\ \text{Nm} = -900\ \text{J}$$

4 At constant volume, $p\Delta V = 0$, i.e. $W = 0$

From first law of thermodynamics,

$$\Delta E = q + W$$

$$\therefore \quad q = \Delta E$$

5 In free expansion, $W = 0$ while in adiabatic process, $q = 0$.

$$\Delta U = q + W = 0$$

This suggests that internal energy remains constant. Therefore, $\Delta T = 0$. Expansion of an ideal gas under adiabatic conditions in a vacuum leads to no absorption/evolution of heat.

Thus, no external work is done for the separation of gaseous molecules.

6 For isothermal process, $\Delta T = 0$, then

$$\Delta E = 0$$

7 According to first law of thermodynamics,

$$\Delta U = q + W = q - p\Delta V$$

In isochoric process ($\Delta V = 0$),

$$\Delta U = q$$

In isobaric process ($\Delta p = 0$),

$$\Delta U = q$$

In adiabatic process ($q = 0$)

$$\Delta U = W$$

In isothermal process $\Delta T = 0$ and $\Delta U = 0$

$\therefore$ ΔU is equal to adiabatic work.

8 As the process is carrying out at constant temperature, therefore this type of expansion is called **isothermal reversible expansion**, for which, $\Delta U = 0$. Hence, $q = -W$

i.e. heat absorbed by the system is equal to the work done by the system.

Thus, $\quad q = +208$ J

$\qquad\quad W = -208$ J

9 $\Delta H = \Delta E + \Delta n_g RT$

Given, $\Delta H = 30$ kcal for 3 mol

$$\Delta n_g = 3$$

because, liquid $\rightleftharpoons$ vapour

$$30 = \Delta E + 3\times2\times500\times10^{-3}$$

$$\Delta E = 27\ \text{kcal}$$

10 $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$

$$\Delta n_g = 1 - \frac{1}{2} = \frac{1}{2}$$

$$\Delta H - \Delta E = \Delta n_g RT$$

$$= \frac{1}{2}\times 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}\times 298\ \text{K}$$

$$= 1238.78\ \text{J mol}^{-1}$$

11 According to relationship of ΔH and ΔE,

$$\Delta H = \Delta E + \Delta n_g RT$$

ΔH = enthalpy change (at constant pressure)

ΔE = internal energy change (at constant volume)

(given reaction is exothermic)

(Δn_g = moles of gaseous products − moles of gaseous reactants)

For the reaction,

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

$$\Delta n_g = 2 - 4 = -2$$

Thus, $\quad \Delta H = \Delta E - 2RT$

$\Rightarrow \quad \Delta H < \Delta E$

Numerical value of $\Delta H < \Delta E$ in exothermic reaction and when $\Delta n_g < 0$.

12 Calculate the heat of combustion with the help of following formula,

$$\Delta H_p = \Delta U + \Delta n_g RT$$

where, ΔH_p = Heat of combustion at constant pressure

ΔU = Heat at constant volume (It is also called ΔE)

Δn_g = Change in number of moles (In gaseous state

R = Gas constant

T = Temperature

From the equation,

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

Change in the number of gaseous moles, i.e.

$$\Delta n_g = 6 - \frac{15}{2} = -\frac{3}{2} \text{ or } -1.5$$

Now, we have Δn_g and other values given in the question are

$$\Delta U = -3263.9\ \text{kJ/mol}$$

$$T = 25^\circ\ \text{C}$$

$$= 273 + 25 = 298\ \text{K}$$

$$R = 8.314\ \text{JK}^{-1}\text{mol}^{-1}$$

So, $\Delta H_p = (-3263.9) + (-1.5)\times 8.314 \times 10^{-3}\times 298$

$$= -3267.6\ \text{kJ mol}^{-1}$$

13 The amount of heat required to raise the temperature of one mole of substance through 1°C is called molar heat capacity.

$$C = \frac{q}{T_2 - T_1}$$

14

$$Q = mC\Delta T$$

$$1000 = \frac{100}{18}\times75\times\Delta T$$

$$\Delta T = 2.4\ \text{K}$$

15 The equation, $C_p - C_V = nR$

2 moles of an ideal gas is equal to

$$C_p - C_V = 2R$$

16 Using Kirchhoff's equation,

$$\Delta C_p = \frac{\Delta H_2 - \Delta H_1}{T_2 - T_1}$$

$$\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$$

$$\Delta H_2 - 24 = (0.031 - 0.055)(100 - 50)$$

$$\Delta H_2 = 22.8 \text{ cal g}^{-1}$$

17 For the given change,

$$\Delta_r S^\circ = \Sigma n_P S_P^\circ - \Sigma n_R S_R^\circ$$

$$= S^\circ_{NH_2CONH_2} + S^\circ_{H_2O}$$

$$- [2 \times S^\circ_{NH_3} + S^\circ_{CO_2}]$$

$$= 174.0 + 69.9 - [2 \times 192.3 + 213.7]$$

$$= -354.4 \text{ JK}^{-1} \text{ mol}^{-1}$$

18 $\Delta S = 2.303 nR \log \frac{V_2}{V_1}$

$$= 2.303 \times 2 \times 2 \log \frac{20}{2} = 9.2$$

19 For an isolated system,

$\Delta H = \Delta E + p\Delta V$ or $T\Delta S = \Delta E + p\Delta V$

But $\Delta E = 0$

$\therefore \quad T\Delta S = p\Delta V$

$$\Delta S = \frac{p\Delta V}{T} > 0$$

20 $\Delta H_{\text{condensation}}$ for 1.8 g of steam

$$= (-40.8) \times \frac{1.8}{18} = -4.08 \text{ kJ}$$

$$\Delta S = \frac{\Delta H}{T_b} = \frac{-4.08 \times 10^3}{373.15}$$

$$= -10.93 \text{ JK}^{-1}$$

21 CO and NO molecules in solid states at 0 K adopt a nearly random arrangement indicating a positive value of entropy. It is due to their dipole moment which results in disorder.

22 $\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T} = \frac{26 \times 10^3}{308}$

$$= +84.41 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{\text{cond}} = \frac{\Delta H_{\text{cond}}}{T} \quad [\because \Delta H_{\text{cond}} = -26 \text{ kJ}]$$

$$= -\frac{26 \times 10^3}{308} = -84.41 \text{ JK}^{-1}\text{mol}^{-1}$$

23

$$\begin{array}{lcr} & & \Delta S \\ A \to C & = & 50 \text{ eu} \\ C \to D & = & 30 \text{ eu} \\ D \to B & = & -20 \text{ eu} \\ \hline \underline{A \to B} & & \underline{60 \text{ eu}} \end{array}$$

24 A → (2, 4), B → (2), C → (3), D → (1)

$A \to$ Entropy of vaporisation is always positive, i.e. $\frac{\Delta H_{\text{vap}}}{T_b}$

$B \to \Delta G^\circ = -RT \ln K$

If K is +ve, then, $\Delta G^\circ = -$ve, i.e. spontaneous process.

$C \to$ Crystalline state is most orderly arranged state of particles, thus lowest entropy.

$D \to$ During adiabatic expansion of an ideal gas, $q = 0$ thus, $\Delta E = W$ i.e.

Work done at the cost of internal energy which decreases when $q = 0$.

25 Entropy change for n moles of isothermal expansion of an ideal gas from volume V_1 to volume V_2 is

$$\Delta S = 2.303 \, nR \log \frac{V_2}{V_1}$$

$$= 2.303 \times 2 \times 8.3143 \log \frac{100}{10}$$

$$= 38.296 \text{ J mol}^{-1} \text{ K}^{-1}$$

26 $\eta \text{ (efficiency)} = \frac{T_2 - T_1}{T_2}$

$$\Rightarrow \quad 0.25 = \frac{T - 400}{T}$$

$$\therefore \quad T = 533.3 \text{ K}$$

27

$$PbO_2 + Pb \longrightarrow 2PbO$$

Oxidation state $+4$ $\quad 0$ $\quad +2$

Since, $\Delta G^\circ < 0$, i.e. it is negative. Therefore, the reaction is spontaneous in the forward direction. This suggest that Pb^{2+} is more stable than Pb^{4+}.

$$SnO_2 + Sn \longrightarrow 2SnO$$

Oxidation state $+4$ $\quad 0$ $\quad +2$

Since, $\Delta_r G^\circ > 0$, i.e. it is positive, therefore, the reaction is non-spontaneous in the forward direction. But it will be spontaneous in the backward direction. This suggests that Sn^{4+} will be more stable than Sn^{2+}. These facts are also supported by the inert pair effect down the group.

28 Heat at constant pressure means enthalpy, i.e.

$$\Delta H = -2.5 \times 10^3 \text{ cal}$$

$$\Delta S = 7.4 \text{ cal deg}^{-1}$$

$$T = 298 \text{ K}$$

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

$$= -2.5 \times 10^3 - 298 \times 7.4$$

$$= -4705 \text{ cal}$$

As, $\Delta G = -$ ve

Hence, the process is spontaneous.

29 $\Delta G = \Delta H - T\Delta S$

At equilibrium, $\Delta G = 0$

$$T = \frac{\Delta H}{\Delta S} = \frac{30 \times 10^3}{75} = 400 \text{ K}$$

30 $\Delta G = \Delta H - T\Delta S$

At equilibrium, $\Delta G = 0$

$$\therefore \quad T_e = \Delta H / \Delta S$$

For a reaction to be spontaneous ΔG should be negative, so this implies $\Delta H < T\Delta S$.

$$\frac{\Delta H}{\Delta S} < T; T_e < T$$

Therefore, T should be greater than T_e.

31 $H_2O(l)$ and $H_2O(g)$ both exist together at same temperature and pressure,

$$H_2O(l) \rightleftharpoons H_2O(g)$$

In the state of equilibrium, $\Delta G = 0$ and conversion of liquid into gas increases the disorderness.

Hence, entropy $\Delta S = +$ve

32 For a spontaneous process,

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

be positive.

33 For a non-spontaneous reaction,

$$\Delta G = + \text{ ve}$$

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

$\therefore \Delta H - T\Delta S$ should be +ve or $\Delta H > T\Delta S$

which is possible if $T < \frac{\Delta H}{\Delta S}$

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

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

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

$$T < 428.57 \text{ K}$$

34 Total entropy change of universe is zero. At 100°C and 1 atmosphere pressure,

$$H_2O(l) \rightleftharpoons H_2O(g)$$

is at equilibrium.

For equilibrium, $\Delta S_{\text{total}} = 0$

and $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = 0$

As we know, during conversion of liquid to gas, entropy of system increases, in a similar manner entropy of surroundings decreases.

$$\therefore \quad \Delta S_{\text{system}} > 0$$

and $\quad \Delta S_{\text{surrounding}} < 0$

Hence, (b) is the correct choice.

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

For a system, total entropy change

$$= \Delta S_{\text{total}}$$

$$\Delta H_{\text{total}} = 0$$

$$\therefore \quad \Delta G_{\text{system}} = -T\Delta S_{\text{total}}$$

$$\therefore \quad \frac{\Delta G_{\text{system}}}{\Delta S_{\text{total}}} = -T$$

(b) For isothermal reversible process,

$$\Delta E = 0$$

By first law of thermodynamics

$$\Delta E = q + W$$

$$\therefore \quad W_{\text{reversible}} = -q = -\int_{V_i}^{V_{f'}} p\,dV$$

$$W_{\text{reversible}} = -nRT \ln \frac{V_f}{V_i}$$

(c) $\Delta G = \Delta H^\circ - T\Delta S^\circ = -RT \log K$

$$\log K = -\left(\frac{\Delta H^\circ - T\Delta S^\circ}{RT}\right)$$

(d) $\Delta G^\circ = -RT \log K$

$$\therefore \quad \log K = -\frac{\Delta G^\circ}{RT}$$

$$\therefore \quad K = e^{-\Delta G^\circ / RT}$$

36 $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -2.303\, RT \log_{10} K$

$$\therefore \quad -2.303\, RT \log_{10} K = \Delta H^\circ - T\Delta S^\circ$$

i.e. $-2.303 \times 8.314 \times 298 \times \log_{10} K$

$$= [-54.07 \times 1000] - [298 \times 10]$$

$$-5705 \log_{10} K = -54070 - 2980$$

$$-5705 \log_{10} K = -57050$$

or $\log_{10} K = 10$

37 The standard free energy related to equilibrium constant, K as

$$\Delta G^\circ = -2.303\, RT \log K_{eq}$$

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

If a cell reaction is spontaneous (proceeding in forward side), it means

$$K_{eq} > 1 \text{ and } E^\circ_{\text{cell}} = +\text{ ve}$$

Thus, $\Delta G^\circ = -\text{ ve}$

38 Percentage efficiency of the fuel cell

$$= \frac{\Delta G}{\Delta H} \times 100$$

The concerned reaction is

$$CH_3OH(l) + \frac{3}{2} O_2(g) \longrightarrow CO_2(g) + 2H_2O(l);$$

$$\Delta G_r = [\Delta G_f(CO_2, g) + 2\Delta G_f(H_2O, l)] - [-\Delta G_f(CH_3OH, l) - \frac{3}{2}\Delta G_f(O_2, g)]$$

$$= -394.4 + 2(-237.2) - (-166.2) - 0$$

$$= -394.4 - 474.4 + 166.2$$

$$= -702.6 \text{ kJ mol}^{-1}$$

Percentage efficiency

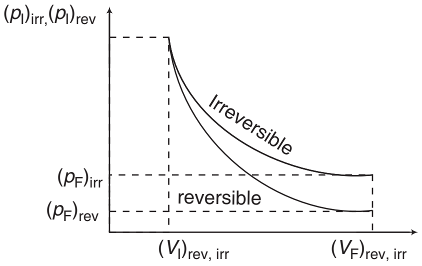
$$= \frac{702.6}{726} \times 100 = 96.78\% \approx 97\%$$

39 Spontaneous processes are accompanied by decrease in energy and increase in randomness.

40 Reason is the correct explanation for Assertion.

SESSION 2

1. The pV diagram for the reversible and irreversible expansion of an ideal gas is shown below :



From ideal gas equation

$$p = \frac{nRT}{V}$$

For final condition of temperature, pressure and volume

$$p_F = \frac{nRT_f}{V_f}$$

From the curve it is seen that

$$(p_F)_{irr} > (p_F)_{rev} \text{ or } (T_F)_{irr} > (T_f)_{rev}$$

2 For adiabatic change, $\Delta E = \Delta W$

$$\Delta E = nC_V(T_2 - T)$$

$$\Delta W = -p(V_2 - V_t)$$

$$nC_V(T_2 - T) = -p(V_2 - V_t) = -1(2 - 1)$$

$$n \times \frac{R}{(\gamma - 1)} \times (T_2 - T) = -1$$

For monoatomic gas $n = 1, \gamma = \frac{5}{3}$,

$R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$

$$1 \times \frac{0.0821}{(5/3) - 1} \times (T_2 - T) = -1$$

$$T_2 = T - \frac{2}{3 \times 0.0821}$$

3 $\Delta H = \text{work done} = i \times V \times t$

$$= 0.50 \text{ A} \times 12 \text{ V} \times 300 \text{ s}$$

$$= 1800 \text{ J} = +1.8 \text{ kJ}$$

Molar enthalpy of vaporisation,

$$\Delta H_m = \frac{\Delta H}{\text{moles of } H_2O} = \frac{\Delta H}{n_{H_2O}}$$

$$= \frac{1.8 \text{ kJ}}{\frac{0.798}{18}} = 40.6 \text{ kJ mol}^{-1}$$

$$\Delta H_m = \Delta E_m + \Delta n_g RT$$

$$\Delta H_m = \Delta E_m + RT$$

$[\Delta n_g = 1 \text{ for } H_2O(l) \rightleftharpoons H_2O(g)]$

Molar internal energy change,

$$\Delta E_m = \Delta H_m - RT$$

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

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

4 For adiabatic condition, $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$

$$\frac{T_2}{T_1} = \left(\frac{1}{27}\right)^{1.33 - 1} \Rightarrow \left(\frac{1}{27}\right)^{0.33}$$

$$= \left(\frac{1}{27}\right)^{1/3} = \frac{1}{3}$$

$$T_2 = 300 \times \frac{1}{3} = 100 \text{ K}$$

Thus, $T_2 < T_1$, hence cooling takes place due to expansion under adiabatic condition.

$$\Delta E = q + W = W$$

($\because q = 0$ for adiabatic change.)

Sign of W is negative because the gas expands.

$$W = -\Delta E = -C_V(T_2 - T_1)$$

$$= -6(100 - 300) = 1200 \text{ cal}$$

5. The molar heat capacity for any process is given by following expression,

$C = C_V + \frac{R}{1-\gamma}$ when $pV^\gamma = \text{constant}$

and $C_p / C_V = \gamma$

Here, $\frac{p}{V} = 1$, i.e. pV^{-1} constant

$$C = \frac{3}{2}R + \frac{R}{1-(-1)} = \frac{3}{2}R + \frac{R}{2} = \frac{4}{2}R$$

6 $\Delta H = \Delta U + p\Delta V$

Here, $\Delta U = +0.21 \text{ kJ mol}^{-1}$

$$= 0.21 \times 10^3 \text{ J mol}^{-1}$$

$$= 210 \text{ J mol}^{-1}$$

$$p = 1 \text{ bar} = 10^5 \text{ Pa}$$

ΔV = Molar volume of aragonite – Molar volume of calcite

$$= \frac{100}{2.93} - \frac{100}{2.71} \text{ cm}^3 \text{ mol}^{-1}$$

($\because$ Molar mass of $CaCO_3 = 100 \text{ g mol}^{-1}$)

$$= 100\left(\frac{1}{2.93} - \frac{1}{2.71}\right)$$

$$= 100 \times \left(\frac{0.22}{2.93 \times 2.71}\right)$$

$$= 2.77 \text{ cm}^3 \text{ mol}^{-1}$$

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

$$\therefore \Delta H = 210 \times 10^5 \ (-2.77 \times 10^{-6})$$

$$= 210 - 0.277 \text{ J}$$

$$= 209.72 \text{ J mol}^{-1}$$

7 For spontaneous process

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + S_{\text{surr}} > 0$$

For an isolated system $\Delta S_{\text{surr}} = 0$
Hence, $\Delta S_{\text{sys}} > 0$.

8 (a) Since, change of state (p_1, V_1, T_1) to (p_2, V_2, T_2) is isothermal therefore, $T_1 = T_2$ (correct statement)

(b) Since, change of state (p_1, V_1, T_1) to (p_3, V_3, T_3) is an adiabatic expansion, it brings about cooling of gas, therefore, $T_3 < T_1$. Thus, it is incorrect.

(c) Work done is given by the area under the curve of p-V diagram. As obvious from the given diagram, magnitude of area under the isothermal curve is greater than that under adiabatic curve, hence $W_{\text{isothermal}} > W_{\text{adiabatic}}$ (correct statement).

(d) $\Delta E = nC_V \Delta T$

In isothermal process, $\Delta E = 0$ as

$$\Delta T = 0$$

In adiabatic process,

$$\Delta E = nC_V \ (T_3 - T_1) < 0 \text{ as } T_3 < T_1$$

$$\Delta E_{\text{isothermal}} > \Delta E_{\text{adiabatic}}$$

(correct statement)

9 Work is done against constant pressure and thus, irreversible.

Given, $\Delta V = 6 - 2 = 4 \text{ L}$ and $p = 1$ atm

$$W = -\ p \times dV$$

$$= -1 \times 4 \text{ L atm}$$

$$= -\frac{1 \times 4 \times 1.987}{0.0821} \text{ cal}$$

$$(\because 0.0821 \text{ L atm} = 1.987 \text{ cal})$$

$$= -\ 96.81 \text{ cal}$$

$$= -\ 96.81 \times 4.184 \text{ J} = -405.04 \text{ J}$$

From first law of thermodynamics,

$$q = \Delta E - W$$

$$\Delta E = q + W = 800 + (-405.04)$$

$$= 394.95 \text{ J}$$

10 For an irreversible process to be spontaneous,

$(\Delta S)_{V,E}$ (change in entropy)

$$= +\text{ ve} > 0$$

$\Rightarrow (\Delta G)_{T,p}$ (change in Gibbs free energy)

$$= -\text{ ve} < 0$$

11 For spontaneity, $\Delta G = -$ ve

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

ΔH, for endothermic process + ve

At lower temperature,

$$T\Delta S = +\text{ve}$$

At lower temperature, $T\Delta S$ will be less than ΔH.

Hence, $\Delta G = +$ve

But at high temperature, $T\Delta S$ will be greater than ΔH.

Hence, $\Delta G = -$ ve, spontaneous.

12 As the process is carried out under adiabatic conditions, $q_p = 0$. But by definition $q_p = \Delta H$.

Hence, $\Delta H = 0$

Further, at constant pressure of 100 bar, volume has decreased by 1 mL, therefore, work of contraction

$$= p\Delta V = 100 \text{ bar} \times 1 \text{ mL}$$

$$= (100 \times 10^5 \text{ Nm}^{-2})(10^{-6} \text{ m}^3)$$

$$= 10 \text{ J}$$

During adiabatic process, work done

= change in internal energy

Hence, $\Delta U = 10$ J

13 $\Delta_r S^\circ = S^\circ_{XY_3} - \left[\frac{1}{2} S^\circ_{X_2} + \frac{3}{2} S^\circ_{Y_2}\right]$

$$= 50 - \left[\frac{1}{2} \times 60 + \frac{3}{2} \times 40\right]$$

$$= 50 - (30 + 60) = -\ 40 \text{ JK}^{-1} \text{ mol}^{-1}$$

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

(At equilibrium, $\Delta_r G^\circ = 0$)

$\therefore$

$$T = \frac{\Delta_r H^\circ}{\Delta_r S^\circ} = \frac{-30{,}000 \text{ J mol}^{-1}}{-40 \text{ JK}^{-1} \text{ mol}^{-1}} = 750 \text{ K}$$

14 $\Delta G = \Delta H - T\Delta S$

Also, $\Delta G = -2.303\, RT \log K$

Variation of K with temperature is given by $\log K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$

Given, $\log K = 4.0 - \frac{2000}{T}$

On comparing, $\frac{\Delta S^\circ}{R} = 4$ or

$\Delta S^\circ = 4\,R$

15 In accordance to second law of thermodynamics, if an irreversible process occurs in a closed system, the entropy of that system always increases, it never decreases. As the ice is more ordered then water, i.e. it has less entropy. Therefore, the ice will melt so that the mass of the ice will decrease.