

## SOLVED EXAMPLES

**Ex. 1** During 200J work done on the system, 140 J of heat is given out. Calculate the change in internal energy.

**Sol.**  $w = 200 \text{ J}$ ;  $q = -140 \text{ J}$ ;

$\therefore q = \Delta E + (-w)$ ; where  $-w$  is work done by the system

$$\Delta E = q + w$$

$$\Delta E = -140 + 200 = +60 \text{ J}$$

**Ex. 2** A gas absorbs 200 J of heat and expands against the external pressure of 1.5 atm from a volume of 0.5 litre. Calculate the change in internal energy.

**Sol.**  $w = -P\Delta V = -1.5 \times (1.0 - 0.5) = -0.75 \text{ litre atm}$

$$= -0.75 \times 101.3 \text{ J} = -75.975 \text{ J}$$

$\therefore 1 \text{ litre atm} = 101.3 \text{ J}$

Now,  $\Delta E = 200 - 75.975 = +124.025 \text{ J}$

**Ex. 3** Two litre of  $\text{N}_2$  at  $0^\circ\text{C}$  and 5 atm pressure are expanded isothermally against a constant external pressure of 1 atm until the pressure of gas reaches 1 atm. Assuming gas to be ideal, calculate work of expansion.

**Sol.** Since the external pressure is greatly different from the pressure of  $\text{N}_2$  and thus, process is irreversible.

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

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

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

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

$\therefore P_1 V_1 = P_2 V_2$

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

$\therefore w = -1 \times (10 - 2) = -8 \text{ litre atm}$

$$\therefore = -\frac{8 \times 1.987}{0.0821} \text{ calorie} = -\frac{8 \times 1.987 \times 4.184}{0.0821} \text{ J} = -810.10 \text{ joule}$$

**Ex. 4** The enthalpy of vaporisation of liquid diethyl ether  $(\text{C}_2\text{H}_5)_2\text{O}$ , is  $26.0 \text{ kJ mol}^{-1}$  at its boiling point ( $35.0^\circ\text{C}$ ). Calculate  $\Delta S$  for conversion of: (a) liquid to vapour, and (b) vapour to liquid at  $35^\circ\text{C}$ .

**Sol.** (a)  $\Delta S_{\text{vap.}} = \frac{\Delta H_{\text{vap.}}}{T} = \frac{26 \times 10^3}{308} = +84.41 \text{ JK}^{-1} \text{ mol}^{-1}$

(b)  $\Delta S_{\text{cond.}} = \frac{\Delta H_{\text{cond.}}}{T} = -\frac{26 \times 10^3}{308}$  ( $\therefore H_{\text{cond}} = -26 \text{ kJ}$ )  
 $= -84.41 \text{ JK}^{-1} \text{ mol}^{-1}$

**Ex. 5** Calculate the free energy change when 1 mole of NaCl is dissolved in water at  $25^\circ\text{C}$ . Lattice energy of NaCl =  $777.8 \text{ kJ mol}^{-1}$ ;  $\Delta S$  for dissolution =  $0.043 \text{ kJ mol}^{-1}$  and hydration energy of NaCl =  $-774.1 \text{ kJ mol}^{-1}$ .

**Sol.**  $\Delta H_{\text{dissolution}} = \text{Lattice energy} + \text{Hydration energy}$   
 $= 777.8 - 774.1 = 3.7 \text{ kJ mol}^{-1}$

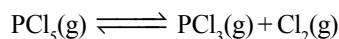
Now  $\Delta G = \Delta H - T\Delta S$

$$= 3.7 - 298 \times 0.043 = 3.7 - 12.814$$

$$\Delta G = -9.114 \text{ kJ mol}^{-1}$$

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**Ex. 6** The equilibrium constant for the reaction given below is  $2.0 \times 10^{-7}$  at 300 K. Calculate the standard free energy change for the reaction;



Also, calculate the standard entropy change if  $\Delta H^\circ = 28.40 \text{ kJ mol}^{-1}$ .

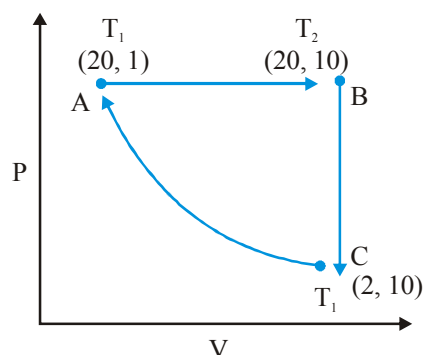
**Sol.**  $\Delta G^\circ = -2.303 \times 8.314 \times 300 \log [2.0 \times 10^{-7}]$   
 $= +38479.8 \text{ J mol}^{-1} = +38.48 \text{ kJ mol}^{-1}$

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

$$\therefore \Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{28.40 - 38.48}{300}$$

$$= -0.0336 \text{ kJ} = -33.6 \text{ JK}^{-1}$$

**Ex. 7** One mole of a perfect monoatomic gas is put through a cycle consisting of the following three reversible steps :



(CA) Isothermal compression from 2 atm and 10 litres to 20 atm and 1 litre.

(AB) Isobaric expansion to return the gas to the original volume of 10 litres with T going from  $T_1$  to  $T_2$ .

(BC) Cooling at constant volume to bring the gas to the original pressure and temperature.

The steps are shown schematically in the figure shown.

(a) Calculate  $T_1$  and  $T_2$ .

(b) Calculate  $\Delta E$ ,  $q$  and  $w$  in calories, for each step and for the cycle.

**Sol.** We know,

Path CA – Isothermal compression

Path AB – Isobaric expansion

Path BC – Isochoric change

Let  $V_i$  and  $V_f$  are initial volume and final volume at respective points,

For temperature  $T_1$  (For C) :  $PV = nRT_1$

$$2 \times 10 = 1 \times 0.0821 \times T_1$$

$$\therefore T_1 = 243.60 \text{ K}$$

For temperature  $T_2$  (For C and B) :  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$$\frac{2 \times 10}{T_1} = \frac{20 \times 10}{T_2}$$

$$\therefore \frac{T_2}{T_1} = 10$$

$$\therefore T_2 = 243.60 \times 10 = 2436.0 \text{ K}$$

**Path CA:**  $w = +2.303 nRT_1 \log \frac{V_i}{V_f}$   
 $= 2.303 \times 1 \times 2 \times 243.6 \log \frac{10}{1}$   
 $= +1122.02 \text{ cal}$

$\Delta E = 0$  for isothermal compression ; Also  $q = w$

**Path AB:**  $w = -P(V_f - V_i)$   
 $= -20 \times (10 - 1) = -180 \text{ litre atm}$   
 $= \frac{-180 \times 2}{0.0821} = -4384.9 \text{ cal}$

**Path BC:**  $w = -P(V_f - V_i) = 0$  ( $\because V_f - V_i = 0$ )

since volume is constant for monoatomic gas heat change at constant volume  $= q_v = \Delta E$ .

Thus for path BC  $q_v = C_v \times n \times \Delta T = \Delta E$

$\therefore q_v = \frac{3}{2} R \times 1 \times (2436 - 243.6)$

$q_v = \frac{3}{2} \times 2 \times 1 \times 2192.4 = 6577.2 \text{ cal}$

Since process involves cooling  $\therefore q_v = \Delta E = -6577.2 \text{ cal}$

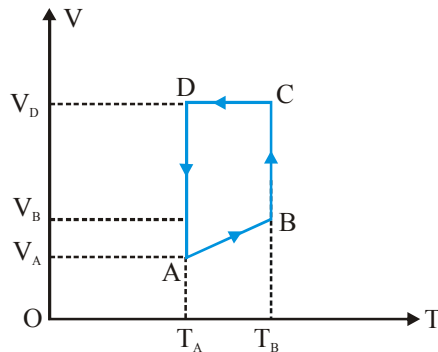
Also in path AB, the internal energy in state A and state C is same. Thus during path AB, an increase in internal energy equivalent of change in internal energy during path BC should take place. Thus  $\Delta E$  for path AB  $= +6577.2 \text{ cal}$

Now  $q$  for path AB  $= \Delta E - w_{AB} = 6577.2 + 4384.9 = 10962.1 \text{ cal}$

**Cycle:**  $\Delta E = 0$  ;  $q = -w = -[w_{\text{Path CA}} + w_{\text{Path AB}} + w_{\text{Path BC}}]$   
 $= -[+1122.02 + -4384.9 + 0]$

$\therefore q = -w$   
 $= +3262.88 \text{ cal}$

**Ex. 8** A monoatomic ideal gas of two moles is taken through a cyclic process starting from A as shown in figure. The volume ratios are  $\frac{V_B}{V_A} = 2$  and  $\frac{V_D}{V_A} = 4$ . If the temperature  $T_A$  at A is  $27^\circ\text{C}$ , calculate :



- (a) The temperature of the gas at point B.
- (b) Heat absorbed or released by the gas in each process.
- (c) The total work done by the gas during complete cycle.

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**Sol.** For the given cyclic process,

$$\frac{V_B}{V_A} = 2, \quad \frac{V_D}{V_A} = 4, \quad T_A = 300 \text{ K}$$

(a) For isobaric process AB

$$\frac{V_A}{T_A} = \frac{V_B}{T_B}$$

$$\therefore T_B = T_A \times \frac{V_B}{V_A} = 300 \times 2 = 600 \text{ K}$$

(b) The following process are there in complete cycle

- (i) A → B Isobaric expansion                      (ii) B → C Isothermal expansion  
 (iii) C → D Isochoric compression              (iv) D → A Isothermal compression

For (i)  $q_{A \rightarrow B} = +n \times C_p \times \Delta T = +2 \times \frac{5}{2} \times R \times 300 = +1500 \times 2 = +3000 \text{ cal}$       ( $R = 2 \text{ cal}$ )

(ii)  $q_{B \rightarrow C} = \Delta E - w$       ( $\Delta E = 0$ )

$$\therefore q_{B \rightarrow C} = \Delta E - w = + \int P dV = +nRT \ln \frac{V_D}{V_B} = +2 \times 2 \times 600 \ln \frac{4}{2} = +1.663 \times 10^3 \text{ cal}$$

(iii)  $q_{C \rightarrow D} = n \times C_v \times \Delta T = 2 \times \frac{3}{2} \times 2 \times -300 = -1800 \text{ cal}$

(iv)  $q_{D \rightarrow A} = +nRT_A \ln \frac{V_A}{V_D} = +2 \times 2 \times 300 \ln \frac{1}{4} = -2 \times 2 \times 300 \times 1.386 = -1.663 \times 10^3 \text{ cal}$

$$\therefore Q = q_{A \rightarrow B} + q_{B \rightarrow C} + q_{C \rightarrow D} + q_{D \rightarrow A} = 3000 + 1663 - 1800 - 1663 = 1200 \text{ cal}$$

(c) Since the process ABCDA is a cyclic process

$$\therefore \Delta E = 0 \text{ or } Q = \Delta E - Q = -w \text{ or } Q = -1200 \text{ cal}$$

i.e., work done on the system = 1200 cal

**Ex. 9** Calculate the work done when 50 g of iron reacts with hydrochloric acid in :

- (i) a closed vessel of fixed volume, (ii) an open beaker at 25°C.

**Sol.** We know,

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

(ii) The  $H_2$  gas formed drives back the atmosphere hence.

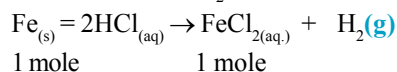
$$w = -P_{\text{ext}} \cdot \Delta V$$

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

$$\therefore \Delta V = \frac{nRT}{P_{\text{ext}}}$$

or  $w = -P_{\text{ext}} \cdot \frac{nRT}{P_{\text{ext}}} = -nRT$

where n is the number of mole of  $H_2$  gas obtained from n mole of  $Fe_{(s)}$ .



$$\therefore n = \frac{50}{56} = 0.8929 \text{ mole}$$

$$\therefore w = -0.8929 \times 8.314 \times 298 = -2212.22 \text{ J}$$

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

**Ex. 10** The internal energy change in the conversion of 1.0 mole of the calcite form of  $\text{CaCO}_3$  to the aragonite form is +0.21 kJ. Calculate the enthalpy change when the pressure is 1.0 bar; given that the densities of the solids are  $2.71 \text{ g cm}^{-3}$  and  $2.93 \text{ g cm}^{-3}$  respectively.

**Sol.**

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

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

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

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

$$= \left( \frac{100}{2.93} - \frac{100}{2.71} \right) \text{ cm}^3 \text{ mol}^{-1} \text{ of CaCO}_3$$

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

$$\therefore \Delta H = 0.21 \times 10^3 - 1 \times 10^5 \times 2.77 \times 10^{-6} = 209.72 \text{ J} = 0.20972 \text{ kJ mol}^{-1}$$

**Ex. 11** For a reaction  $\text{M}_2\text{O}(\text{s}) \rightarrow 2\text{M}(\text{s}) + \frac{1}{2} \text{O}_2(\text{g})$ ;  $\Delta H = 30 \text{ kJ mol}^{-1}$  and  $\Delta S = 0.07 \text{ kJ K}^{-1} \text{ mol}^{-1}$  at 1 atm. Calculate upto which temperature, the reaction would not be spontaneous.

**Sol.** Given, for the change,  $\Delta H = 30 \times 10^3 \text{ J mol}^{-1}$ ,  $\Delta S = 70 \text{ JK}^{-1} \text{ mol}^{-1}$

For a non-spontaneous reaction

$$\Delta G = +ve$$

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

$$\therefore \Delta H - T\Delta S \text{ should be } +ve$$

**or**  $\Delta H > T\Delta S$

**or**  $T < \frac{\Delta H}{\Delta S} \Rightarrow T < \frac{30 \times 10^3}{70} \Rightarrow T < 428.57 \text{ K}$

**Ex. 12** Predict whether the entropy change of the system in each of the following process is positive or negative.

- |  |   |
|--|---|
| (a) $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ | (b) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$         |
| (c) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$     | (d) $\text{HCl}(\text{g}) + \text{NH}_3(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$ |
| (e) $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$ | (f) Cooling of $\text{N}_2(\text{g})$ from $20^\circ\text{C}$ to $-50^\circ\text{C}$          |

**Sol.** Gaseous substances generally possess more entropy than solids. So whenever the products contain more moles of a gas than the reactants, the entropy change is probably positive. And hence,  $\Delta S$  is

- |  |              |
|--|--------------|
| (a) positive   | (b) negative |
| (c) small, the sign of $\Delta S$ is impossible to predict | (d) negative |
| (e) negative   | (f) negative |

[Note : For a given substance at a given temperature,  $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$ ]

**Ex. 13** Calculate the boiling point of bromine from the following data :

$\Delta H^\circ$  and  $\Delta S^\circ$  values of  $\text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{g})$  are  $30.91 \text{ kJ/mole}$  and  $93.2 \text{ J/mol. K}$  respectively. Assume that  $\Delta H$  and  $\Delta S$  do not vary with temperature.

**Sol.** Consider the process :  $\text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{g})$

The b.p. of a liquid is the temperature at which the liquid and the pure gas coexist at equilibrium at 1 atm.

$$\therefore \Delta G = 0$$

As it is given that  $\Delta H$  and  $\Delta S$  do not change with temperature

$$\Delta H = \Delta H^\circ = 30.91 \text{ kJ}$$

$$\Delta S = \Delta S^\circ = 93.2 \text{ J/K} = 0.0932 \text{ kJ/K}$$

We have,  $\Delta G = \Delta H - T\Delta S = 0$

$$\therefore T = \frac{\Delta H}{\Delta S} = \frac{30.91}{0.0932} = 331.6 \text{ K.}$$

This is the temperature at which the system is in equilibrium, that is, the b.p of bromine.

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**Ex. 14** The efficiency of the Carnot engine is  $1/6$ . On decreasing the temperature of the sink by  $65\text{K}$ , the efficiency increases to  $1/3$ . Find the temperature of the source and the sink.

**Sol.** We have,

$$\eta = \frac{T_2 - T_1}{T_2}, \text{ where } T_1 \text{ and } T_2 \text{ are the temperatures of sink and source respectively.}$$

$$\therefore \eta = \frac{T_2 - T_1}{T_2} = \frac{1}{6} \quad \dots\dots\dots\text{(i)}$$

Now the temperature of the sink is reduced by  $65\text{ K}$ .

$$\therefore \text{temp. of the sink} = (T_1 - 65)$$

$$\therefore \eta = \frac{T_2 - (T_1 - 65)}{T_2} = \frac{1}{3} \quad \dots\dots\dots\text{(ii)}$$

On solving eqns. (i) and (ii), we get,

$$T_1 = 325\text{ K}$$

$$T_2 = 390\text{ K}$$

**Ex. 15** (a) One mole of an ideal gas expands isothermally and reversibly at  $25^\circ\text{C}$  from a volume of  $10\text{ litres}$  to a volume of  $20\text{ litres}$ .

(i) What is the change in entropy of the gas ?

(ii) How much work is done by the gas ?

(iii) What is  $q(\text{surroundings})$  ?

(iv) What is the change in the entropy of the surroundings ?

(v) What is the change in the entropy of the system plus the surroundings ?

(b) Also answer the questions (i) to (v) if the expansion of the gas occurs irreversibly by simply opening a stopcock and allowing the gas to rush into an evacuated bulb of  $10\text{-L}$  volume.

**Sol.** (i)  $\Delta S = 2.303nR \log \frac{V_2}{V_1} = 2.303 \times 1 \times 8.314 \times \log \frac{20}{10} = 5.76\text{ J/K.}$

(A) (ii)  $w_{\text{rev}} = 2.303 nRT \log \frac{V_2}{V_1}$   
 $= -2.303 \times 1 \times 8.314 \times 298 \times \log \frac{20}{10} = -1718\text{ J.}$

(iii) For isothermal process,  $\Delta E = 0$  and heat is absorbed by the gas,

$$q_{\text{rev}} = \Delta E - W = 0 - (-1718) = 1718\text{ J}$$

$$\therefore q_{\text{surr}} = 1718\text{ J. } (\because \text{process is reversible})$$

(iv)  $\Delta S_{\text{surr}} = -\frac{1718}{298} = -5.76\text{ J/K.}$

As entropy of the system increases by  $5.76\text{ J}$ , the entropy of the surrounding decreases by  $5.76\text{ J}$ , since the process is carried out reversibly.

(v)  $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$  ..... for reversible process.

(b) (i)  $\Delta S = 5.76\text{ J/K}$ , which is the same as above because  $S$  is a state function.

(ii)  $w = 0$ . ( $\because p_{\text{ext}} = 0$ )

(iii) No heat is exchanged with the surroundings.

(iv)  $\Delta S_{\text{surr}} = 0$

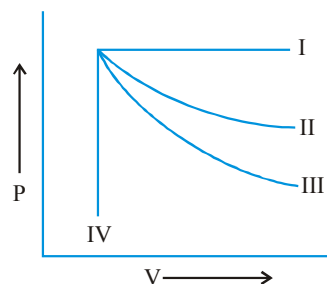
(v) The entropy of the system plus surroundings increases by  $5.76\text{ J/K}$ , as we expect entropy to increase in an irreversible process.

## Exercise # 1

[Single Correct Choice Type Questions]

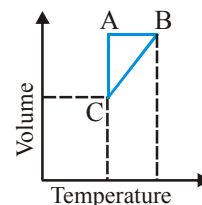
- Out of boiling point (I), entropy (II), pH (III) and e.m.f. of a cell (IV), intensive properties are :  
 (A) I, II (B) I, II, III (C) I, III, IV (D) All of the above
- If a refrigerator's door is opened, then we get  
 (A) Room heated (B) Room cooled  
 (C) More amount of heat is passed out (D) No effect on room
- Warming ammonium chloride with sodium hydroxide in a test tube is an example of :  
 (A) Closed system (B) Isolated system (C) Open system (D) None of these
- In thermodynamics, a process is called reversible when -  
 (A) surroundings and system change into each other  
 (B) there is no boundary between system and surroundings  
 (C) the surroundings are always in equilibrium with the system  
 (D) the system changes into the surroundings spontaneously
- A gaseous system changes from state A ( $P_1, V_1, T_1$ ) to B ( $P_2, V_2, T_2$ ), B to C ( $P_3, V_3, T_3$ ) and finally from C to A. The whole process may be called :  
 (A) Reversible process (B) Cyclic process  
 (C) Isobaric process (D) Spontaneous process

6.



The plots between P and V which represent adiabatic and isothermal process respectively :

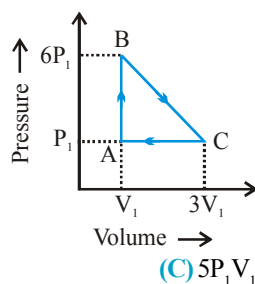
- (A) I, IV (B) II, III (C) III, II (D) IV, I
- Five moles of a gas is put through a series of changes as shown graphically in a cyclic process the A  $\rightarrow$  B, B  $\rightarrow$  C and C  $\rightarrow$  A respectively are  
 (A) Isochoric, Isobaric, Isothermal  
 (B) Isobaric, Isochoric, Isothermal  
 (C) Isothermal, Isobaric, Isochoric  
 (D) Isochoric, Isothermal, Isobaric



- Determine which of the following reactions at constant pressure represent surrounding that do work on the system  
 I  $4\text{NH}_3(\text{g}) + 7\text{O}_2(\text{g}) \longrightarrow 4\text{NO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$   
 II  $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \longrightarrow \text{CH}_3\text{OH}(\ell)$   
 III  $\text{C}(\text{s, graphite}) + \text{H}_2\text{O}(\text{g}) \longrightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$   
 IV  $\text{H}_2\text{O}(\text{s}) \longrightarrow \text{H}_2\text{O}(\ell)$   
 (A) III, IV (B) II and III (C) II, IV (D) I and II, IV

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9. An electric heater of resistance 6 ohm is run for 10 minutes on a 120 volt line. The work done in this period of time is  
 (A)  $7.2 \times 10^3 \text{J}$  (B)  $14.4 \times 10^5 \text{J}$  (C)  $43.2 \times 10^4 \text{J}$  (D)  $28.8 \times 10^4 \text{J}$
10. Two moles of an ideal gas expand spontaneously in vacuum. The work done is  
 (A) 2 Joule (B) 4 Joule (C) Zero (D) Infinite
11. A thermodynamic system goes from states (i)  $P_1, V$  to  $2P_1, V$  (ii)  $P, V_1$  to  $P, 2V_1$ . Then work done in the two cases is  
 (A) Zero, Zero (B) Zero,  $-PV_1$  (C)  $-PV_1$ , Zero (D)  $-PV_1, -P_1V_1$
12. Mechanical work is specially important in system that contain  
 (A) Solid-liquid (B) Liquid-Liquid (C) Solid-Solid (D) Gases
13. An ideal gas is taken around the cycle ABCA as shown in P-V diagram. The net work done by the gas during the cycle is equal to :



- (A)  $12P_1V_1$  (B)  $6P_1V_1$  (C)  $5P_1V_1$  (D)  $P_1V_1$
14. The work done in ergs for the reversible expansion of one mole of an ideal gas from a volume of 10 litres to 20 litres at  $25^\circ\text{C}$  is  
 (A)  $-2.303 \times 298 \times 0.082 \log 2$  (B)  $-298 \times 10^7 \times 8.31 \times 2.3031 \log 2$   
 (C)  $-2.303 \times 298 \times 0.082 \log 0.5$  (D)  $-8.31 \times 10^7 \times 298 \times 2.303 \log 0.5$
15. Which has maximum internal energy at 290 K ?  
 (A) Neon gas (B) Nitrogen gas (C) Ozone gas (D) All have equal value
16. For the real gases reaction  $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{CO}_2(\text{g})$ ;  $\Delta H = -560 \text{ kJ}$ . 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)  $-557 \text{ kJ}$  (B)  $-530 \text{ kJ}$  (C)  $-563 \text{ kJ}$  (D) None of these
17. A piece of zinc at a temperature of  $20^\circ\text{C}$  weighing 65.38 g is dropped into 180 g of boiling water ( $T = 100^\circ\text{C}$ ). The specific heat of zinc is  $0.4 \text{ J g}^{-1} \text{C}^{-1}$  and that of water is  $4.2 \text{ J g}^{-1} \text{C}^{-1}$ . What is the final common temperature reached by both the zinc and water ?  
 (A)  $97.3^\circ\text{C}$  (B)  $33.4^\circ\text{C}$  (C)  $80.1^\circ\text{C}$  (D)  $60.0^\circ\text{C}$
18. 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)  $w > 0$ ;  $q = 0$ ;  $\Delta U > 0$
19. A system absorb 600J of heat and work equivalent to 300J on its surroundings. The change in internal energy is :  
 (A) 300J (B) 400J (C) 500J (D) 600J
20. For the reaction of one mole of zinc dust with one mole of sulphuric acid in a bomb calorimeter,  $\Delta U$  and  $w$  correspond to  
 (A)  $\Delta U < 0$ ,  $w = 0$  (B)  $\Delta U = 0$ ,  $w < 0$  (C)  $\Delta U > 0$ ,  $w = 0$  (D)  $\Delta U < 0$ ,  $w > 0$



21. In a closed insulated container, a liquid is stirred with a paddle to increase its temperature. In this process, which of the following is true  
 (A)  $\Delta E = W = Q = 0$     (B)  $\Delta E \neq 0, Q = W = 0$     (C)  $\Delta E = W \neq 0, Q = 0$     (D)  $\Delta E = Q \neq 0, W = 0$
22. In an isochoric process the increase in internal energy is  
 (A) Equal to the heat absorbed    (B) Equal to the heat evolved  
 (C) Equal to the work done    (D) Equal to the sum of the heat absorbed and work done
23. The temperature of the system decreases in an  
 (A) Adiabatic compression    (B) Isothermal compression  
 (C) Isothermal expansion    (D) Adiabatic expansion
24. 1 mole of  $\text{NH}_3$  gas at  $27^\circ\text{C}$  is expanded in reversible adiabatic condition to make volume 8 times ( $\gamma = 1.33$ ). Final temperature and work done respectively are :  
 (A) 150 K, 900 cal    (B) 150 K, 400 cal    (C) 250 K, 1000 cal    (D) 200 K, 800 cal
25. In an adiabatic expansion of an ideal gas  
 (A)  $W = -\Delta E$     (B)  $W = \Delta E$     (C)  $\Delta E = 0$     (D)  $W = 0$
26. A vessel contains 100 litres of a liquid X. Heat is supplied to the liquid in such a fashion that, Heat given = change in enthalpy. The volume of the liquid increases by 2 litres. If the external pressure is one atm, and 202.6 Joules of heat were supplied then, [U - total internal energy]  
 (A)  $\Delta U = 0, \Delta H = 0$     (B)  $\Delta U = +202.6\text{ J}, \Delta H = +202.6\text{ J}$   
 (C)  $\Delta U = -202.6\text{ J}, \Delta H = -202.6\text{ J}$     (D)  $\Delta U = 0, \Delta H = +202.6\text{ J}$
27. One mole of non-ideal gas undergoes a change of state (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
28. A certain mass of gas is expanded from (1L, 10 atm) to (4L, 5 atm) against a constant external pressure of 1 atm. If initial temperature of gas is 300 K and the heat capacity of process is  $50\text{ J}^\circ\text{C}$ . Then the enthalpy change during the process is (1L atm  $\simeq$  100 J)  
 (A)  $\Delta H = 15\text{ kJ}$     (B)  $\Delta H = 15.7\text{ kJ}$     (C)  $\Delta H = 14.4\text{ kJ}$     (D)  $\Delta H = 14.7\text{ kJ}$
29. Consider the reaction at 300 K  
 $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{HCl}(\text{g}); \quad \Delta H^\circ = -185\text{ kJ}$   
 If 2 mole of  $\text{H}_2$  completely react with 2 mole of  $\text{Cl}_2$  to form HCl. What is  $\Delta U^\circ$  for this reaction ?  
 (A) 0    (B)  $-185\text{ kJ}$     (C)  $370\text{ kJ}$     (D)  $-370\text{ kJ}$
30. For the isothermal expansion of an ideal gas  
 (A) E and H increases    (B) E increases but H decreases  
 (C) H increases but E decreases    (D) E and H are unaltered
31. A system containing real gas changes its state from state-1 to state-2.  
 State-1 (2 atm, 3L, 300 K)  
 State-2 (5 atm, 4L, 500 K)  
 If change in internal energy = 30 L atm then calculate change in enthalpy.  
 (A) 44 L atm    (B) 35 L atm    (C) 40 L atm    (D) None of these
32. Mixing of non-reacting gases is generally accompanied by  
 (A) Decrease in entropy    (B) Increase in entropy  
 (C) Change in enthalpy    (D) Change in free energy

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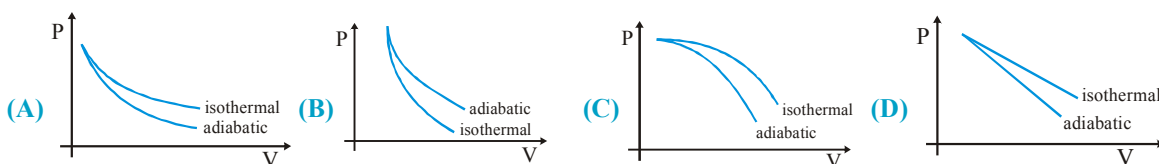
33. Which of the following reactions is associated with the most negative change in entropy ?  
 (A)  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{SO}_3(\text{g})$  (B)  $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_6(\text{g})$   
 (C)  $\text{C}(\text{s, graphite}) + \text{O}_2 \longrightarrow \text{CO}_2(\text{g})$  (D)  $3\text{C}_2\text{H}_2(\text{g}) \longrightarrow \text{C}_6\text{H}_6(\ell)$
34. Predict which of the following reaction (s) has a positive entropy change ?  
 I.  $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \longrightarrow \text{AgCl}(\text{s})$   
 II.  $\text{NH}_4\text{Cl}(\text{s}) \longrightarrow \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$   
 III.  $2\text{NH}_3(\text{g}) \longrightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$   
 (A) I and II (B) III (C) II and III (D) II
35. Which one of the following has  $\Delta S^\circ$  greater than zero  
 (A)  $\text{CaO}(\text{s}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{CaCO}_3(\text{s})$  (B)  $\text{NaCl}(\text{aq}) \rightleftharpoons \text{NaCl}(\text{s})$   
 (C)  $\text{NaNO}_3(\text{s}) \rightleftharpoons \text{Na}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$  (D)  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
36. For the gas - phase decomposition,  $\text{PCl}_5(\text{g}) \xrightarrow{\Delta} \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ :  
 (A)  $\Delta H < 0, \Delta S < 0$  (B)  $\Delta H > 0, \Delta S > 0$  (C)  $\Delta H > 0, \Delta S < 0$  (D)  $\Delta H < 0, \Delta S > 0$
37. When 2 moles of an ideal gas  $\left( C_{p,m} = \frac{5}{2}R \right)$  heated from 300 K to 600 K at constant volume, the change in entropy of gas  $\Delta S_{\text{gas}}$  is :  
 (A)  $5R \ln 2$  (B)  $\frac{3}{2}R \ln 2$  (C)  $3R \ln 2$  (D)  $-3R \ln 2$
38. 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 ( $\Delta S$ ) is :  
 (A)  $C_{p,m} \ln 2$  (B)  $C_{v,m} \ln 2$  (C)  $R \ln 2$  (D)  $(C_{v,m} - R) \ln 2$
39. 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 ( $\Delta S$ ) is :  
 (A)  $\frac{3}{2}R \ln 2$  (B)  $-\frac{3}{2}R \ln 2$  (C)  $5R \ln 2$  (D)  $\frac{5}{2}R \ln 2$
40. If one mole of an ideal gas  $\left( C_{p,m} = \frac{5}{2}R \right)$  is expanded isothermally at 300 K until its volume is tripled, then change in entropy of gas is :  
 (A) zero (B) infinity (C)  $\frac{5}{2}R \ln 3$  (D)  $R \ln 3$
41. The entropy change when two moles of ideal monoatomic gas is heated from 200 to 300°C reversibly and isochorically ?  
 (A)  $\frac{3}{2}R \ln \left( \frac{300}{200} \right)$  (B)  $\frac{5}{2}R \ln \left( \frac{573}{273} \right)$  (C)  $3R \ln \left( \frac{573}{473} \right)$  (D)  $\frac{3}{2}R \ln \left( \frac{573}{473} \right)$
42. 1 mole of an ideal gas at 25°C is subjected to expand reversibly and adiabatically to ten times of its initial volume. Calculate the change in entropy during expansion (in  $\text{J k}^{-1} \text{mol}^{-1}$ )  
 (A) 19.15 (B) -19.15 (C) 4.7 (D) zero
43. 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. ( $C_{p,m}(\text{H}_2\text{O}) = 4.2 \text{ J/g-K} \ln(1.2) = 0.18$ )  
 (A) 16.6 J/K (B) 9 J/K (C) 34.02 J/K (D) 1.89 J/K
44. 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.  $\Delta S_{\text{total}}$  (system + surrounding) is :  
 (A) -0.52 J/K (B) 0.52 J/K (C) 22.52 J/K (D) 0

45. Given  $\Delta_r S^\circ = -266$  and the listed [ $S_m^\circ$  values] calculate  $S^\circ$  for  $\text{Fe}_3\text{O}_4(\text{s})$  :
- $$4\text{Fe}_3\text{O}_4(\text{s}) [\text{.....}] + \text{O}_2(\text{g}) [205] \longrightarrow 6\text{Fe}_2\text{O}_3(\text{s}) [87]$$
- (A) +111.1 (B) +122.4 (C) 145.75 (D) 248.25
46.  $\text{C}_2\text{H}_6(\text{g}) + 3.5 \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{g})$   
 $\Delta S_{\text{vap}}(\text{H}_2\text{O}, \ell) = x_1 \text{ cal K}^{-1}$  (boiling point =  $T_1$ )  
 $\Delta H_f(\text{H}_2\text{O}, \ell) = x_2$   
 $\Delta H_f(\text{CO}_2) = x_3$   
 $\Delta H_f(\text{C}_2\text{H}_6) = x_4$   
Hence,  $\Delta H$  for the reaction is -  
(A)  $2x_3 + 3x_2 - x_4$  (B)  $2x_3 + 3x_2 - x_4 + 3x_1T_1$   
(C)  $2x_3 + 3x_2 - x_4 - 3x_1T_1$  (D)  $x_1T_1 + X_2 + X_3 - x_4$
47. Calculate the total entropy change for the transition at 368 K of 1 mol of sulphur from the monoclinic to the rhombic solid state and  $\Delta H = -401.7 \text{ J mol}^{-1}$  for the transition. Assume the surroundings to be an ice-water. Both at  $0^\circ\text{C}$  :  
(A)  $-1.09 \text{ JK}^{-1}$  (B)  $1.47 \text{ JK}^{-1}$  (C)  $0.38 \text{ JK}^{-1}$  (D) None of these
48. When reaction is at standard state at equilibrium, then :  
(A)  $\Delta H^\circ = 0$  (B)  $\Delta S^\circ = 0$   
(C) equilibrium constant  $K = 0$  (D) equilibrium constant  $K = 1$
49. What is the free energy change ( $\Delta G$ ) when 1.0 mole of water at  $100^\circ\text{C}$  and 1 atm pressure is converted into steam at  $100^\circ\text{C}$  and 1 atm pressure ?  
(A) 80 cal (B) 540 cal (C) 620 cal (D) Zero
50. 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)  $\Delta H > 0, \Delta S < 0$
51. A reaction has  $\Delta H = -33 \text{ kJ}$  and  $\Delta S = -58 \frac{\text{J}}{\text{K}}$ . This reaction would be :  
(A) spontaneous at all temperatures (B) non-spontaneous at all temperatures  
(C) spontaneous above a certain temperature (D) spontaneous below a certain temperature
52. The enthalpy change for a given reaction at 298 K is  $-x \text{ J mol}^{-1}$  ( $x$  being positive). If the reaction occurs spontaneously at 298 K, the entropy change at that temperature  
(A) can be negative but numerically larger than  $x/298$   
(B) can be negative but numerically smaller than  $x/298$   
(C) cannot be negative  
(D) cannot be positive
53. Consider the  $\Delta G_f^\circ$  and  $\Delta H_f^\circ$  (kJ/mol) for the following oxides. Which oxide can be most easily decomposed to form the metal and oxygen gas ?  
(A)  $\text{ZnO}$  ( $\Delta G^\circ = -318.4, \Delta H^\circ = -348.3$ ) (B)  $\text{Cu}_2\text{O}$  ( $\Delta G^\circ = -146.0, \Delta H^\circ = -168.8$ )  
(C)  $\text{HgO}$  ( $\Delta G^\circ = -58.5, \Delta H^\circ = -90.8$ ) (D)  $\text{PbO}$  ( $\Delta G^\circ = -187.9, \Delta H^\circ = -217.3$ )
54. If  $\Delta G = -177 \text{ K cal}$  for (1)  $2 \text{Fe}(\text{s}) + \frac{3}{2} \text{O}_2(\text{g}) \longrightarrow \text{Fe}_2\text{O}_3(\text{s})$   
and  $\Delta G = -19 \text{ K cal}$  for (2)  $4 \text{Fe}_2\text{O}_3(\text{s}) + \text{Fe}(\text{s}) \longrightarrow 3 \text{Fe}_3\text{O}_4(\text{s})$   
What is the Gibbs free energy of formation of  $\text{Fe}_3\text{O}_4(\text{s})$  ?  
(A) +229.6 kcal/mol (B) -242.3 kcal/mol (C) -727 kcal/mol (D) -229.6 kcal/mol

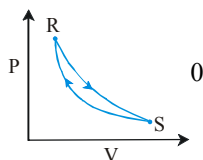
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55. For a reaction  $A(g) \rightleftharpoons B(g)$  at equilibrium. The partial pressure of B is found to be one fourth of the partial pressure of A. The value of  $\Delta G^\circ$  of the reaction  $A \rightarrow B$  is  
 (A)  $RT \ln 4$  (B)  $-RT \ln 4$  (C)  $RT \log 4$  (D)  $-RT \log 4$
56. Identify the state function among the following  
 (A)  $q$  (B)  $q - w$  (C)  $q/w$  (D)  $q + w$
57. In which one of the following sets, all the properties belong to same category (all extensive or all intensive)?  
 (A) Mass, volume, pressure (B) Temperature, pressure, volume  
 (C) Heat capacity, density, entropy (D) Enthalpy, internal energy, volume.
58. Which one of the following statement is false :  
 (A) work is a state function  
 (B) temperature is a state function  
 (C) change in the state is completely defined when the initial and final states are specified  
 (D) work appears at the boundary of the system.

59. The correct figure representing isothermal and adiabatic expansions of an ideal gas from a particular initial state is



60. Consider the cyclic process  $R \rightarrow S \rightarrow R$  as shown in the Fig. You are told that one of the path is adiabatic and the other one isothermal. Which one of the following is(are) true?



- (A) Process  $R \rightarrow S$  is isothermal (B) Process  $S \rightarrow R$  is adiabatic  
 (C) Process  $R \rightarrow S$  is adiabatic (D) Such a graph is not possible
61. Match the entries of column I with appropriate entries of column II and choose the correct option out of the four options (A), (B), (C) and (D).

**Column I**

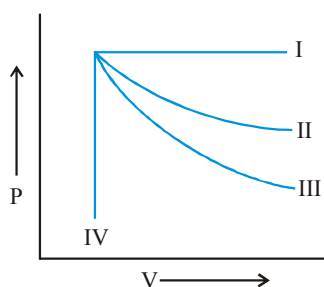
- (X) Isothermal  
 (Y) Isobaric  
 (Z) Adiabatic  
 (W) Isochoric

**Column II**

- (p)  $\Delta T = 0$   
 (q)  $\Delta V = 0$   
 (r)  $\Delta P = 0$   
 (s)  $q = 0$

- (A) X-p, Y-q, Z-r, W-x (B) X-p, Y-r, Z-s, W-q (C) X-s, Y-p, Z-r, W-q (D) X-s, Y-p, Z-q, W-r

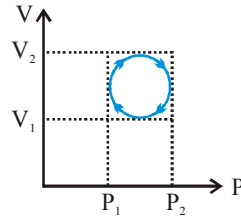
- 62.



The plots between P and V which represent isochoric and isobaric process respectively :

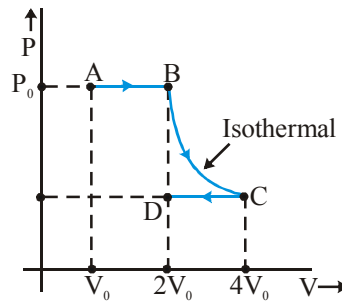
- (A) I, II (B) IV, I (C) I, IV (D) II, III

63. 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)  $\pi (V_2 - V_1)^2$

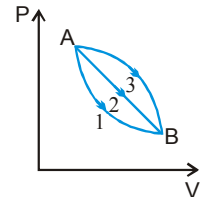
64. Work for the following process ABCD on a monoatomic gas is :



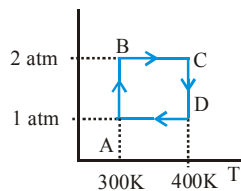
- (A)  $w = -2 P_0 V_0 \ln 2,$  (B)  $w = -2 P_0 V_0 \ln 2,$   
 (C)  $w = -P_0 V_0 (1 + \ln 2),$  (D)  $w = -P_0 V_0 \ln 2,$

65. A given mass of gas expands 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)  $w_2 < w_3 < w_1$



66. Two moles of Helium gas undergo a reversible cyclic process as shown in figure. Assuming gas to be ideal, what is the net work involved in the cyclic process ?



- (A)  $-100 R/n4$  (B)  $+100R/n4$  (C)  $+200R/n4$  (D)  $-200R/n4$

67. Select the correct set of statement/s :

- I. Work done by the surrounding in case of infinite stage expansion is more than single stage expansion  
 II. Irreversible work is always greater than reversible work. (with sign)  
 III. On an ideal gas in case of single stage expansion and compression system as well as surrounding are restored back to their original states  
 IV. If gas is in thermodynamic equilibrium is taken from state A to state B, by four successive single stage expansions. Then we can plot 4 points on the P-V indicator diagram.

- (A) II (B) I, II, III, IV (C) II, IV (D) I, II, IV

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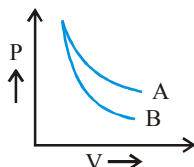
68. 50 L of a certain liquid is confined in a piston system at the external pressure 100 atm. This pressure is suddenly released and liquid is expanded against the constant atmospheric pressure, volume of the liquid increases by 1 L and the final pressure on the liquid is 10 atm. Find the workdone.
- (A) 1L.atm                      (B) 5 L.atm                      (C) 500 L.atm                      (D) 50 L.atm
69. The increase in internal energy of 1 kg of water at  $100^{\circ}\text{C}$  when it is converted into steam at the same temperature and at 1 atm (100 k Pa) will be [The density of water and steam are  $1000\text{ kg/m}^3$  &  $0.6\text{ kg/m}^3$  respectively. The latent heat of vapourisation of water is  $2.25 \times 10^6\text{ J/kg}$ .]
- (A)  $2.08 \times 10^6\text{ J}$                       (B)  $4 \times 10^7\text{ J}$                       (C)  $3.27 \times 10^8\text{ J}$                       (D)  $5 \times 10^9\text{ J}$
70. Consider a classroom that is roughly  $5\text{ m} \times 10\text{ m} \times 3\text{ m}$ . Initially  $t = 27^{\circ}\text{C}$  and  $P = 1\text{ atm}$ . There are 50 people in an insulated class losing energy to the room at the average rate of 150 watt per person. How long can they remain in class if the body temperature is  $42^{\circ}\text{C}$  and person feels uncomfortable above this temperature. Heat capacity of air =  $(7/2)R$ .
- (A) 4.34 minutes                      (B) 5.91 minutes                      (C) 6.86 minutes                      (D) 7.79 minutes

## Exercise # 2

## Part # I

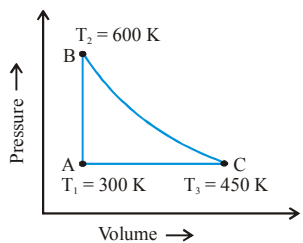
## [Multiple Correct Choice Type Questions]

1. In an isothermal expansion of a gaseous sample, the correct relation is : (consider  $w$  (work) with sign according to new IUPAC convention)  
[The reversible and irreversible processes are carried out between same initial and final states.]  
(A)  $w_{\text{rev}} > w_{\text{irrev}}$       (B)  $w_{\text{irrev}} > w_{\text{rev}}$       (C)  $q_{\text{rev}} < q_{\text{irrev}}$       (D)  $\Delta E_{\text{rev}} = \Delta E_{\text{irrev}}$
2. If  $x$  and  $y$  are extensive properties then, which one is correct ?  
(A)  $(x + y)$  is an extensive variable      (B)  $(x/y)$  is an intensive variable  
(C)  $(dx/dy)$  is an intensive variable      (D)  $(x - y)$  is an intensive variable
3. Choose the correct statement :  
(A) system and surrounding are always separated by a real or imaginary boundary.  
(B) perfectly isolated system can never be created.  
(C) in reversible process, energy change in each step can be reversed.  
(D) irreversible process is also called quasi-equilibrium state.
4. P-V plot for two gases (assuming ideal) during adiabatic processes are given in the figure. Plot A and plot B should correspond respectively to :



- (A) He and  $H_2$       (B)  $H_2$  and He      (C)  $SO_3$  and  $CO_2$       (D)  $N_2$  and Ar
5. During the isothermal expansion of an ideal gas :  
(A) The internal energy remains unaffected      (B) The temperature remains constant  
(C) The enthalpy remains unaffected      (D) The enthalpy increases
6. 0.5 mole each of two ideal gases A ( $C_{v,m} = \frac{5}{2}R$ ) 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 and 250 K. Then for the process :  
(A)  $\Delta U = -100 R$       (B)  $\Delta U = -275 R$       (C)  $\Delta H = -375 R$       (D)  $\Delta H = -300 R$
7. When some potential difference  $V$  is applied across a resistance  $R$  then the work by the electrical field on the charge  $q$  to flow through the circuit in time  $t$  will be :  
(A)  $qV$       (B)  $Vit$       (C)  $i^2Rt$       (D)  $\frac{V^2t}{R}$
8. When a liquid solidifies, generally, there is :  
(A) Decrease in enthalpy      (B) Decrease in entropy      (C) Increase in enthalpy      (D) Increase in entropy
9. Choose the correct statement (s) :  
(A) Temperature, enthalpy and entropy are state functions  
(B) For reversible and irreversible both isothermal expansion of an ideal gas, change in internal energy and enthalpy is zero  
(C) for a reaction in which  $\Delta n_2 = 0$ , entropy change is not always zero  
(D) The entropy change associated with reversible isothermal expansion of an ideal gas is equal to  $2.303 R \log_{10} \frac{P_1}{P_2}$
10. One mole of an ideal diatomic gas ( $C_v = 5 \text{ cal}$ ) was transformed from initial  $25^\circ\text{C}$  and 1 L to the state when temperature is  $100^\circ\text{C}$  and volume 10 L. Then for this process ( $R = 2 \text{ calories/mol/K}$ ) (take calories as unit of energy and kelvin for temp)  
(A)  $\Delta H = 525$       (B)  $\Delta S = 5 \ln \frac{373}{298} + 2 \ln 10$   
(C)  $\Delta E = 525$       (D)  $\Delta G$  of the process can not be calculated using given information.

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11. In previous problem if expansion is carried out freely ( $P_{\text{ext}} = 0$ ), then :  
 (A)  $W = 0$  (B)  $W = RT \ln 3$  (C)  $\Delta S = R \ln 3$  (D)  $Q = RT \ln 3$
12. For isothermal expansion in case of an ideal gas :  
 (A)  $\Delta H = 0$  (B)  $\Delta E = 0$  (C)  $\Delta G = -T \Delta S$  (D)  $T_{\text{final}} = T_{\text{initial}}$
13. In which of the following entropy increases :  
 (A) Rusting of iron (B) Melting of ice  
 (C) Crystallisation of sugar from solution (D) Vaporisation of camphor
14. 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  $\Delta G = +ve$
15. A heat engine carries one mole of an ideal mono-atomic gas around the cycle as shown in the figure, the amount of heat added in the process AB and heat removed in the process CA are :  
 (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  $q_{CA} = -450 R$
- 
16. 1 mole of an ideal gas A ( $C_{v,m} = 3R$ ) and 2 mole of an ideal gas B are ( $C_{v,m} = \frac{3}{2}R$ ) taken in a container and expanded reversibly and adiabatically from 1 litre to 4 litre starting from initial temperature of 320 K.  $\Delta E$  or  $\Delta U$  for the process is  
 (A)  $-240 R$  (B)  $-240 R$  (C)  $480 R$  (D)  $-960 R$
17. In an isobaric process, the ratio of heat supplied to the system ( $dQ$ ) and work done by the system ( $dW$ ) for diatomic gas is  
 (A) 1 : 1 (B) 7 : 2 (C) 7 : 5 (D) 5 : 7
18. Ice – Water mass ratio is maintained as 1 : 1 in a given system containing water in equilibrium with ice at constant pressure. If  $C_p(\text{ice}) = C_p(\text{water}) = 4.18 \text{ J mol}^{-1} \text{ K}^{-1}$  molar heat capacity of such a system is  
 (A) Zero (B) Infinity (C)  $4.182 \text{ JK}^{-1} \text{ mol}^{-1}$  (D)  $75.48 \text{ JK}^{-1} \text{ mol}^{-1}$
19. Two mole of an ideal gas is heated at constant pressure of one atmosphere from  $27^\circ\text{C}$  to  $127^\circ\text{C}$ . If  $C_{v,m} = 20 + 10^{-2} T \text{ JK}^{-1} \text{ mol}^{-1}$ , then  $q$  and  $\Delta U$  for the process are respectively :  
 (A) 6362.8 J, 4700 J (B) 3037.2 J, 4700 J (C) 7062.8, 5400 J (D) 3181.4 J, 2350 J
20. A system is provided 50 joule of heat and the change in internal energy during the process is 60 J. work done on the system is :  
 (A) -10 J (B) 10 J (C) 110 J (D) -110 J
21. Which one of the following equations does not correctly represent the first law of thermodynamics for the given process ?  
 (A) Isothermal process :  $q = -w$  (B) Cyclic process :  $q = -w$   
 (C) Adiabatic process :  $\Delta E = q$  (D) Expansion of a gas into vacuum :  $\Delta E = q$
22. A gas expands adiabatically at constant pressure such that  $T \propto V^{-1/2}$ . The value of  $\gamma$  ( $C_{p,m}/C_{v,m}$ ) of the gas will be :  
 (A) 1.30 (B) 1.50 (C) 1.70 (D) 2



23. The magnitudes of enthalpy changes for irreversible adiabatic expansion of a gas from 1L to 2L is  $\Delta H_1$  and for reversible adiabatic expansion for the same expansion is  $\Delta H_2$ . Then  
 (A)  $\Delta H_1 > \Delta H_2$   
 (B)  $\Delta H_1 < \Delta H_2$   
 (C)  $\Delta H_1 = \Delta H_2$ , enthalpy being a state function ( $\Delta H_1 = \Delta H_2$ )  
 (D)  $\Delta H_1 = \Delta E_1$  &  $\Delta H_2 = \Delta E_2$  where  $\Delta E_1$  &  $\Delta E_2$  are magnitudes of change in internal energy of gas in these expansions respectively.
24. A new fluoro-carbon of molar mass  $102 \text{ g mol}^{-1}$  was placed in an electrically heated vessel. When the pressure was 650 torr, the liquid boiled at  $77^\circ\text{C}$ . After the boiling point had been reached, it was found that a current of 0.25 A from a 12.0 volt supply passed for 600 sec vaporises 1.8g of the sample. The molar enthalpy & internal energy of vaporisation of new fluoro-carbon will be :  
 (A)  $\Delta H = 102 \text{ kJ/mol}$ ,  $\Delta E = 99.1 \text{ kJ/mol}$  (B)  $\Delta H = 95 \text{ kJ/mol}$ ,  $\Delta E = 100.3 \text{ kJ/mol}$   
 (C)  $\Delta H = 107 \text{ kJ/mol}$ ,  $\Delta E = 105.1 \text{ kJ/mol}$  (D)  $\Delta H = 92.7 \text{ kJ/mol}$ ,  $\Delta E = 97.4 \text{ kJ/mol}$
25. An athlete is given 100 g of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) of energy equivalent to 1560 kJ. He utilises 50 percent of this gained energy in the event. In order to avoid storage of energy in the body, the weight of water he would need to perspire is- (The enthalpy of evaporation of water is  $44 \text{ kJ/mole}$ .)  
 (A) 319 gm (B) 422 gm (C) 293 gm (D) 378 gm
26. One mole of an ideal gas ( $C_{v,m} = \frac{5}{2}R$ ) 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
27. 10 litres of a monoatomic ideal gas at  $0^\circ\text{C}$  and 10 atm pressure is suddenly released to 1 atm pressure and the gas expands adiabatically against this constant pressure. The final temperature and volume of the gas respectively are.  
 (A)  $T = 174.9 \text{ K}$ ,  $V = 64 \text{ L}$  (B)  $T = 153 \text{ K}$ ,  $V = 57 \text{ L}$  (C)  $T = 165.4 \text{ K}$ ,  $V = 78.8 \text{ L}$  (D)  $T = 161.2 \text{ K}$ ,  $V = 68.3 \text{ L}$
28. The work done in adiabatic compression of 2 mole of an ideal monoatomic gas by constant external pressure of 2 atm starting from initial pressure of 1 atm and initial temperature of 300 K ( $R = 2 \text{ cal/mol-degree}$ )  
 (A) 360 cal (B) 720 cal (C) 800 cal (D) 1000 cal
29. There are two samples of same gas initially under similar initial state. Gases of both the samples are expanded. I<sup>st</sup> sample using reversible isothermal process and II<sup>nd</sup> sample using reversible adiabatic process till final pressures of both the samples becomes half of initial pressure. Then :  
 (A) Final volume of I<sup>st</sup> sample < final volume of II<sup>nd</sup> sample  
 (B) Final volume of II<sup>nd</sup> sample < final volume of I<sup>st</sup> sample  
 (C) Final volumes will be equal  
 (D) Information is insufficient
30. In the above problem :  
 (A) work done by gas in I<sup>st</sup> sample > work done by gas in II<sup>nd</sup> sample  
 (B) work done by gas in II<sup>nd</sup> sample > work done by gas in I<sup>st</sup> sample  
 (C) work done by gas in I<sup>st</sup> sample = work done by gas in II<sup>nd</sup> sample  
 (D) none of these
31. One mole of an ideal diatomic gas ( $C_v = 5 \text{ cal}$ ) was transformed from initial  $25^\circ\text{C}$  and 1 L to the state when temperature is  $100^\circ\text{C}$  and volume 10 L. The entropy change of the process can be expressed as ( $R = 2 \text{ calories/mol/K}$ )  
 (A)  $3 \ln \frac{298}{373} + 2 \ln 10$  (B)  $5 \ln \frac{373}{298} + 2 \ln 10$  (C)  $7 \ln \frac{373}{298} + 2 \ln \frac{1}{10}$  (D)  $5 \ln \frac{373}{298} + 2 \ln \frac{1}{10}$

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32. For a perfectly crystalline solid  $C_{p,m} = aT^3 + bT$ , where  $a$  and  $b$  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
33. Calculate the entropy change (J/mol K) of the given reaction. The molar entropies [J/K-mol] are given in brackets after each substance.  

$$2\text{PbS}(s) [91.2] + 3\text{O}_2(g) [205.1] \longrightarrow 2\text{PbO}(s) [66.5] + 2\text{SO}_2(g) [248.2]$$
 (A) -113.5      (B) -168.3      (C) +72.5      (D) -149.2
34. Which of the following statement (s) is/are correct?  
 Statement (i) : The entropy of isolated system with P-V work only, is always maximized at equilibrium.  
 Statement (ii) : It is possible for the entropy of close system to decrease substantially in an irreversible process.  
 Statement (iii) : Entropy can be created but not destroyed.  
 Statement (iv) :  $\Delta S_{\text{system}}$  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
35. During winters, moisture condenses in the form of dew and can be seen on plant leaves and grass. The entropy of the system in such cases decreases as liquids possess lesser disorder as compared to gases. With reference to the second law, which statement is **correct**, for the above process?  
 (A) The randomness of the universe decreases  
 (B) The randomness of the surroundings decreases  
 (C) Increase in randomness of surroundings equals to the decrease in randomness of system  
 (D) The increase in randomness of the surroundings is greater as compared to the decrease in randomness of the system.
36. 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 g of sucrose  
 Given :  $\Delta H_{\text{combustion}}(\text{sucrose}) = -6000 \text{ kJ mol}^{-1}$   
 $\Delta S_{\text{combustion}} = 180 \text{ J/K - mol}$  and body temperature is 300 K  
 (A) 600 kJ      (B) 594.6 kJ      (C) 5.4 kJ      (D) 605.4 kJ
37. For the hypothetical reaction  

$$\text{A}_2(g) + \text{B}_2(g) \rightleftharpoons 2\text{AB}(g)$$
 If  $\Delta_r G^\circ$  and  $\Delta_r S^\circ$  are 20 kJ/mol and  $-20 \text{ JK}^{-1} \text{ mol}^{-1}$  respectively at 200 K.  
 $\Delta_r C_p$  is  $20 \text{ JK}^{-1} \text{ mol}^{-1}$  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
38. Given the following data :
- | Substance    | $\Delta H^\circ$ (kJ/mol) | $S^\circ$ (J/mol K) | $\Delta G^\circ$ (kJ/mol) |
|--------------|---------------------------|---------------------|---------------------------|
| FeO(s)       | -266.3                    | 57.49               | -245.12                   |
| C (Graphite) | 0                         | 5.74                | 0                         |
| Fe(s)        | 0                         | 27.28               | 0                         |
| CO(g)        | -110.5                    | 197.6               | -137.15                   |
- Determine at what temperature the following reaction is spontaneous ?  

$$\text{FeO}(s) + \text{C}(\text{Graphite}) \longrightarrow \text{Fe}(s) + \text{CO}(g)$$
 (A) 298 K  
 (B) 668 K  
 (C) 964 K  
 (D)  $\Delta G^\circ$  is +ve, hence the reaction will never be spontaneous

Each question has 5 choices (A), (B), (C), (D) and (E) out of which only one is correct.

(A) Statement-1 is true, Statement-2 is true and Statement-2 is correct explanation for Statement-1

(B) Statement-1 is true, Statement-2 is true and Statement-2 is not correct explanation for Statement-1

(C) Statement-1 is true, Statement-2 is false

(D) Statement-1 is false, Statement-2 is true

(E) Both Statements are false

1. **Statement-1** : When a gas at high pressure expands against vacuum, the magnitude of work done is maximum.  
**Statement-2** : Work done in expansion depends upon the pressure inside the gas and increase in volume.
2. **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.
3. **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 compensates the decrease in entropy due to fall in temperature.
4. **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.
5. **Statement-1** : The standard free energy changes of all spontaneously occurring 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.
6. **Statement-1** : Many endothermic reactions that are not spontaneous at room temperature become spontaneous at high temperature.  
**Statement-2** :  $\Delta H^\circ$  of the endothermic reaction increases with increase in temperature.
7. **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 positive sign of  $\Delta S_{\text{system}}$ .
8. **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.
9. **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.

**Exercise # 3**

Part # I

[Matrix Match Type Questions]

1. **Column-I**
- (A) Reversible isothermal expansion of an ideal gas
  - (B) Reversible adiabatic compression of an ideal gas
  - (C) Irreversible adiabatic expansion of an ideal gas
  - (D) Irreversible isothermal compression of an ideal gas
- Column-II**
- (p)  $w = -2.303 nRT \log \left( \frac{V_2}{V_1} \right)$
  - (q)  $PV^\gamma = \text{constant}$
  - (r)  $w = \frac{nR}{(\gamma - 1)} (T_2 - T_1)$
  - (s)  $\Delta H = 0$
2. **Column I**
- (A) A process carried out infinitesimally slowly
  - (B) A process in which no heat enters or leaves the system
  - (C) A process carried out at constant temperature
  - (D) A process in equilibrium
  - (E)  $A(s) \longrightarrow A(g)$
  - (F) Cyclic process
- Column II**
- (p) Adiabatic
  - (q)  $\Delta G = 0$
  - (r) Sublimation
  - (s)  $\Delta E = 0, \Delta H = 0$
  - (t) Reversible
  - (u) Isothermal
3. **Column - I**
- (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)  $(\Delta G_{\text{system}})_{T,P} > 0$
- Column - II**
- (p) Process is in equilibrium
  - (q) Process is nonspontaneous
  - (r) Process is spontaneous
  - (s) System is unable to do useful work
4. **Column - I**
- (A) Reversible adiabatic compression
  - (B) Reversible vaporisation of liquid
  - (C)  $2N(g) \longrightarrow N_2(g)$
  - (D)  $MgCO_3(s) \xrightarrow{\Delta} MgO(s) + CO_2(g)$
- Column - II**
- (p)  $\Delta S_{\text{system}} > 0$
  - (q)  $\Delta S_{\text{system}} < 0$
  - (r)  $\Delta S_{\text{surrounding}} < 0$
  - (s)  $\Delta S_{\text{surrounding}} = 0$
5. **Column-I (Process of reaction)**
- (A) For the process  
 $H_2O_{(l)} \rightleftharpoons H_2O_{(s)}$ ,  $\Delta H$  &  $\Delta S$  are
  - (B) For the endothermic reaction  
 $2A_{(s)} + \frac{1}{2} O_{2(g)} \rightleftharpoons A_2O_{(s)}$  at 298 K,  
 $\Delta S$  &  $\Delta G$  are
  - (C)  $C(\text{diamond}) \rightleftharpoons C(\text{graphite})$ , favourable conditions for formation of diamond are high pressure and high temperature then  $\Delta H_f$  of diamond and  $\Delta S_f$  of graphite from diamond are
  - (D) For the given reaction  
 $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ ,  $E_{a(\text{forward})} = 57.2 \text{ kJ}$   
and  $E_{a(\text{backward})} = 3.2 \text{ kJ}$ ,  $\Delta H$  &  $\Delta S$  for the given reaction
- Column-II (Positive, negative)**
- (p) -ve, +ve
  - (q) +ve, -ve
  - (r) +ve, +ve
  - (s) -ve, -ve

## Comprehension # 1

A mixture of hydrogen gas and the theoretical amount of air at 25°C and a total pressure of 1 atm, is exploded in a closed rigid vessel. If the process occurs under adiabatic condition then using the given datas answer the questions that follow :

Given  $C_p(N_2) = 8.3 \text{ cal deg}^{-1} \text{ mol}^{-1}$   $C_p[H_2O(g)] = 11.3 \text{ cal deg}^{-1} \text{ mol}^{-1}$ ;  $\Delta H_f[H_2O(g)] = -57.8 \text{ Kcal}$  [Take air as 80%  $N_2$ , 20%  $O_2$  by volume]

- The value of  $C_p$  of  $N_2$  &  $H_2O$  in the order are (in cal.  $\text{deg}^{-1} \text{ mol}^{-1}$ )  
 (A) 8.3, 8.3                      (B) 8.3, 11.3                      (C) 11.3, 11.3                      (D) 11.3, 8.3
- What will be the maximum temperature attained if the process occurs in adiabatic container.  
 (A)  $\cong 2940 \text{ K}$                       (B)  $\cong 2665 \text{ K}$                       (C)  $\cong 1900 \text{ K}$                       (D)  $\cong 298 \text{ K}$
- What will be the final pressure in atm.  
 (A)  $\cong 8.5$                       (B)  $\cong 7.6$                       (C)  $\cong 5.46$                       (D)  $\cong 0.85$
- If at initial temperature  $T_1, E_1$  is initial energy & at higher final temperature  $T_2, E_2$  is the final internal energy, then which option is true.  
 (A)  $E_1 > E_2$                       (B)  $E_2 > E_1$   
 (C)  $E_1 = E_2$                       (D) can't be compared from the given data

## Comprehension # 2

A gaseous sample is generally allowed to do only expansion/compression type of work against its surroundings. The work done in case of an irreversible expansion (in the intermediate stages of expansion/compression the states of gases are not defined). The work done can be calculated using

$$dw = -P_{\text{ext}} dV$$

while in case of reversible process the work done can be calculated using

$dw = -PdV$  where P is pressure of gas at some intermediate stages. Like for an isothermal

reversible process. Since  $P = \frac{nRT}{V}$ , so

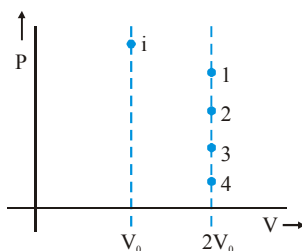
$$w = \int dw = - \int_{V_i}^{V_f} \frac{nRT}{V} \cdot dV = -nRT \ln \left( \frac{V_f}{V_i} \right)$$

Since  $dw = -PdV$  so magnitude of work done can also be calculated by calculating the area under the PV curve of the reversible process in PV diagram.

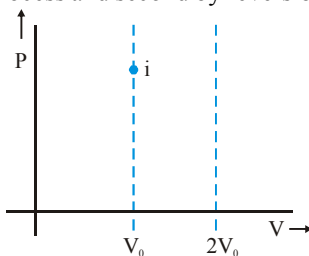
- An ideal gaseous sample at initial state i ( $P_0, V_0, T_0$ ) is allowed to expand to volume  $2V_0$  using two different process; in the first process the equation of process is  $PV^2 = K_1$  and in second process the equation of the process is  $PV = K_2$ . Then,  
 (A) work done in first process will be greater than work in second process (magnitude wise)  
 (B) The order of values of work done can not be compared unless we know the value of  $K_1$  and  $K_2$ .  
 (C) value of work done (magnitude) in second process is greater in above expansion irrespective of the value of  $K_1$  and  $K_2$ .  
 (D) I<sup>st</sup> process is not possible
- There are two samples of same gas initially under similar initial state. Gases of both the samples are expanded. I<sup>st</sup> sample using reversible isothermal process and II<sup>nd</sup> sample using reversible adiabatic process till final pressures of both the samples becomes half of initial pressure, then  
 (A) Final volume of I<sup>st</sup> sample < final volume of II<sup>nd</sup> sample  
 (B) Final volume of II<sup>nd</sup> sample < final volume of I<sup>st</sup> sample  
 (C) final volumes will be equal  
 (D) Information is insufficient

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3. In the above problem  
 (A) work done by gas in I<sup>st</sup> sample > work done by gas in II<sup>nd</sup> sample  
 (B) work done by gas in II<sup>nd</sup> sample > work done by gas in I<sup>st</sup> sample  
 (C) work done by gas in I<sup>st</sup> sample = work done by gas in II<sup>nd</sup> sample  
 (D) none of these
4. If four identical samples of an ideal gas initially at similar state ( $P_0, V_0, T_0$ ) are allowed to expand to double their volumes by four different process.  
 I : by isothermal irreversible process  
 II : by reversible process having equation  $P^2 V = \text{constant}$   
 III : by reversible adiabatic process  
 IV : by irreversible adiabatic expansion against constant external pressure.  
 Then, in the graph shown the final state is represented by four different points then, the correct match can be



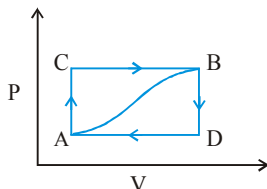
- (A) 1 - I, 2 - II, 3 - III, 4 - IV  
 (B) 1 - II, 2 - I, 3 - IV, 4 - III  
 (C) 2 - III, 3 - II, 4 - I, 1 - IV  
 (D) 3 - II, 1 - I, 3 - IV, 4 - III
5. Two samples (initially under same states) of an ideal gas are first allowed to expand to double their volume using irreversible isothermal expansion against constant external pressure, then samples are returned back to their original volume first by reversible adiabatic process and second by reversible process having equation  $PV^2 = \text{constant}$  then



- (A) final temperature of both samples will be equal  
 (B) final temperature of first sample will be greater than of second sample  
 (C) final temperature of second sample will be greater than of first sample  
 (D) none of these.

### Comprehension # 3

When a system is taken from state A to state B along path ACB as shown in figure below, 80 J of heat flows into the system and the system does 30 J of work.



1. How much heat flows into the system along path ADB if the work done by the system is 10 J :  
 (A) 40 J  
 (B) 60 J  
 (C) 80 J  
 (D) 100 J

2. When the system is returned from state B to A along the curved path, the work done on the system is 20 J. Does the system absorb or liberate heat and by how much ?  
 (A) -70 J ; heat is liberated. (B) -60 J ; heat is liberated.  
 (C) +70 J ; heat is absorbed. (D) +60 J ; heat is absorbed.
3. If  $E_D - E_A = -40\text{J}$ , the heat absorbed in the processes AD and DB are respectively :  
 (A)  $q_{AD} = 30\text{ J}$  and  $q_{DB} = -90\text{ J}$  (B)  $q_{AD} = -60\text{ J}$  and  $q_{DB} = 30\text{ J}$   
 (C)  $q_{AD} = 30\text{ J}$  and  $q_{DB} = 90\text{ J}$  (D)  $q_{AD} = -30\text{ J}$  and  $q_{DB} = 90\text{ J}$

### Comprehension # 4

#### Dependence of Spontaneity on Temperature :

For a process to be spontaneous, at constant temperature and pressure, there must be decrease in free energy of the system in the direction of the process, i.e.  $\Delta G_{P,T} < 0$ .  $\Delta G_{P,T} = 0$  implies the equilibrium condition and  $\Delta G_{P,T} > 0$  corresponds to non-spontaneity.

Gibbs-Helmholtz equation relates the free energy change to the enthalpy and entropy changes of the process as :

$$\Delta G_{P,T} = \Delta H - T\Delta S \quad \dots(1)$$

The magnitude of  $\Delta H$  does not change much with the change in temperature but the entropy factor  $T\Delta S$  changes appreciably. Thus, spontaneity of a process depends very much on temperature.

For endothermic process, both  $\Delta H$  and  $\Delta S$  are positive. The energy factor, the first factor of equation, opposes the spontaneity whereas entropy factor favours it. At low temperature the favourable factor  $T\Delta S$  will be small and may be less than  $\Delta H$ ,  $\Delta G$  will have positive value indicating the nonspontaneity of the process. On raising temperature, the factor  $T\Delta S$  increases appreciably and when it exceeds  $\Delta H$ ,  $\Delta G$  would become negative and the process would be spontaneous.

For an exothermic process, both  $\Delta H$  and  $\Delta S$  would be negative. In this case the first factor of eq. 1 favours the spontaneity whereas the second factor opposes it. At high temperature, when  $T\Delta S > \Delta H$ ,  $\Delta G$  will have positive value, showing thereby the non-spontaneity of the process. However, on decreasing temperature, the factor  $T\Delta S$  decreases rapidly and when  $T\Delta S < \Delta H$ ,  $\Delta G$  becomes negative and the process occurs spontaneously. Thus, an exothermic process may be spontaneous at low temperature and non-spontaneous at high temperature.

1. When  $\text{CaCO}_3$  is heated to a high temperature, it undergoes decomposition into  $\text{CaO}$  and  $\text{CO}_2$  whereas it is quite stable at room temperature. The most likely explanation of it, is  
 (A) The enthalpy of reaction ( $\Delta H$ ) overweighs the term  $T\Delta S$  at high temperature.  
 (B) The term  $T\Delta S$  overweighs the enthalpy of reaction at high temperature.  
 (C) At high temperature, both enthalpy of reaction and entropy change become negative.  
 (D) None of these.
2. For the reaction at  $25^\circ\text{C}$ ,  $\text{X}_2\text{O}_4 (\ell) \longrightarrow 2\text{XO}_2 (\text{g})$   
 $\Delta H = 2.1\text{ Kcal}$  and  $\Delta S = 20\text{ cal K}^{-1}$ . The reaction would be  
 (A) spontaneous (B) non-spontaneous (C) at equilibrium (D) unpredictable
3. For the reaction at  $298\text{ K}$ ,  $2\text{A} + \text{B} \longrightarrow \text{C}$   
 $\Delta H = 100\text{ kcal}$  and  $\Delta S = 0.050\text{ kcal K}^{-1}$ . If  $\Delta H$  and  $\Delta S$  are assumed to be constant over the temperature range, above what temperature will the reaction become spontaneous ?  
 (A)  $1000\text{ K}$  (B)  $1500\text{ K}$  (C)  $2000\text{ K}$  (D)  $2500\text{ K}$
4. A reaction has a value of  $\Delta H = -40\text{ kcal}$  at  $400\text{ K}$ . Above  $400\text{ K}$ , the reaction is spontaneous, below this temperature, it is not. The values of  $\Delta G$  and  $\Delta S$  at  $400\text{ K}$  are respectively  
 (A)  $0, -0.1\text{ cal K}^{-1}$  (B)  $0, 100\text{ cal K}^{-1}$   
 (C)  $-10\text{ kcal}, -100\text{ cal K}^{-1}$  (D)  $0, -100\text{ cal K}^{-1}$

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5. The enthalpy change for a certain reaction at 300 K is  $-15.0 \text{ K cal mol}^{-1}$ . The entropy change under these conditions is  $-7.2 \text{ cal K}^{-1} \text{ mol}^{-1}$ . The free energy change for the reaction and its spontaneous/non-spontaneous character will be  
 (A)  $-12.84 \text{ kcal mol}^{-1}$ , spontaneous (B)  $12.84 \text{ kcal mol}^{-1}$ , non-spontaneous  
 (C)  $-17.16 \text{ kcal mol}^{-1}$ , spontaneous (D) None of these

### Comprehension # 5

Entropy is a state function and its value depends on two or three variables temperature (T), Pressure (P) and volume (V). Entropy change for an ideal gas having number of moles (n) can be determined by the following equation.

$$\Delta S = 2.303 nC_v \log \left( \frac{T_2}{T_1} \right) + 2.303 nR \log \left( \frac{V_2}{V_1} \right)$$

$$\Delta S = 2.303 nC_p \log \left( \frac{T_2}{T_1} \right) + 2.303 nR \log \left( \frac{P_1}{P_2} \right)$$

Since free energy change for a process or a chemical equation is a deciding factor of spontaneity, which can be obtained by using entropy change ( $\Delta S$ ) according to the expression,  $\Delta G = \Delta H - T\Delta S$  at a temperature T.

1. What would be the entropy change involved in thermodynamic expansion of 2 moles of a gas from a volume of 5 L to a volume of 50 L at  $25^\circ\text{C}$  [Given  $R = 8.3 \text{ J/mole-K}$ ]  
 (A)  $38.23 \text{ J/K}$  (B)  $26.76 \text{ J/K}$  (C)  $20 \text{ J/K}$  (D)  $28.23 \text{ J/K}$
2. An isobaric process having one mole of ideal gas has entropy change  $23.03 \text{ J/K}$  for the temperature range  $27^\circ\text{C}$  to  $327^\circ\text{C}$ . What would be the molar specific heat capacity ( $C_v$ )?  
 (A)  $\frac{10}{\log 2} \text{ J/K mol}$  (B)  $\frac{10}{\log 2} - 8.3 \text{ J/K mol}$  (C)  $10 \times \log 2 \text{ J/K mol}$  (D)  $10 \log 2 + 8.3 \text{ J/K mol}$
3. For a reaction  $\text{M}_2\text{O(s)} \longrightarrow 2\text{M(s)} + \frac{1}{2}\text{O}_2\text{(g)}$ ;  $\Delta H = 30 \text{ kJ/mol}$  and  $\Delta S = 0.07 \text{ kJ/K-mol}$  at 1 atm. Calculate upto which temperature the reaction would not be spontaneous.  
 (A)  $T > 428.6 \text{ K}$  (B)  $T > 300.8 \text{ K}$  (C)  $T < 300.8 \text{ K}$  (D)  $T < 428.6 \text{ K}$

### Comprehension # 6

Standard Gibb's energy of reaction ( $\Delta_r G^\circ$ ) at a certain temperature can be computed as  $\Delta_r G^\circ = \Delta_r H^\circ - T \cdot \Delta_r S^\circ$  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 :

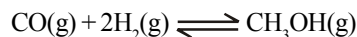
$$\Delta_r H^\circ_{T_2} - \Delta_r H^\circ_{T_1} = \Delta_r C_p^\circ (T_2 - T_1)$$

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

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

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

Consider the following reaction :



Given:  $\Delta_f H^\circ(\text{CH}_3\text{OH, g}) = -201 \text{ kJ/mol}$ ;  $\Delta_f H^\circ(\text{CO, g}) = -114 \text{ kJ/mol}$

$S^\circ(\text{CH}_3\text{OH, g}) = 240 \text{ J/mol-K}$ ;  $S^\circ(\text{H}_2, \text{g}) = 29 \text{ JK}^{-1} \text{ mol}^{-1}$

$S^\circ(\text{CO, g}) = 198 \text{ J/mol-K}$ ;  $C_{p,m}^\circ(\text{H}_2) = 28.8 \text{ JK}^{-1} \text{ mol}^{-1}$

$C_{p,m}^\circ(\text{CO}) = 29.4 \text{ J/mol-K}$ ;  $C_{p,m}^\circ(\text{CH}_3\text{OH}) = 44 \text{ J/mol-K}$

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

### Comprehension # 7

An ideal gas, having ratio of specific heat  $\gamma$  undergoes a process in which its internal energy relates to the volume as  $U = \alpha\sqrt{V}$ , where  $\alpha$  is a constant. If the gas is expanded from volume  $V_1$  to  $V_2$ .

1. The work performed by gas is :  
 (A)  $2\alpha(\gamma - 1)[\sqrt{V_2} - \sqrt{V_1}]$   
 (B)  $\alpha(\gamma - 1)[\sqrt{V_2} - \sqrt{V_1}]$   
 (C)  $2\alpha(\gamma - 1)[V_2 - V_1]$   
 (D)  $\alpha(\gamma - 1)[V_2 - V_1]$
2. If the ideal gas is diatomic and its increase in internal energy is 100 J then the work performed by gas is : (Ignore vibrational degree of freedom)  
 (A) 80 J      (B) 180 J      (C) 100 J      (D) 20 J
3. In the above question, the heat supplied to gas is :  
 (A) 80 J      (B) 180 J      (C) 100 J      (D) 20 J

## Exercise # 4

## [Subjective Type Questions]

1. In which of the following changes at constant pressure is work done by system on surrounding ? By the surrounding on system ?

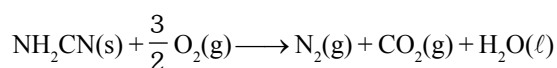
Initial state	→	Final state
(i) $\text{H}_2\text{O}(\text{g})$	→	$\text{H}_2\text{O}(\ell)$
(ii) $\text{H}_2\text{O}(\text{s})$	→	$\text{H}_2\text{O}(\text{g})$
(iii) $\text{H}_2\text{O}(\ell)$	→	$\text{H}_2\text{O}(\text{s})$
(iv) $3\text{H}_2(\text{g}) + \text{N}_2(\text{g})$	→	$2\text{NH}_3(\text{g})$
(v) $\text{CaCO}_3(\text{s})$	→	$\text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

2. The gas is cooled and loses 65 J of heat. The gas contracts as it cools and work done on the system equal to 20 J which is exchanged with the surroundings. What are q, w and  $\Delta E$  ?
3. The enthalpy of combustion of glucose is  $-2808 \text{ kJ mol}^{-1}$  at  $25^\circ\text{C}$ . How many grams of glucose do you need to consume [Assume wt = 62.5 Kg].

- (a) To climb a flight of stairs rising through 3m.  
 (b) To climb a mountain of altitude 3000 m ?

Assume that 25% of enthalpy can be converted to useful work.

4. What is  $\Delta E$  when 2.0 mole of liquid water vaporises at  $100^\circ\text{C}$  ? The heat of vaporisation, ( $\Delta H_{\text{vap}}$ ) of water at  $100^\circ\text{C}$  is  $40.66 \text{ kJ mol}^{-1}$ .
5. If 1.0 kcal of heat is added to 1.2 L of  $\text{O}_2$  in a cylinder of constant pressure of 1 atm, the volume increases to 1.5 L. Calculate  $\Delta E$  and  $\Delta H$  of the process.
6. When the following reaction was carried out in a bomb calorimeter,  $\Delta E$  is found to be  $-742.7 \text{ kJ/mol}$  of  $\text{NH}_2\text{CN}(\text{s})$  at 298 K.



Calculate  $\Delta H_{298}$  for the reaction.

7. When 1 mole of ice melt at  $0^\circ\text{C}$  and at constant pressure of 1 atm. 1440 calories of heat are absorbed by the system. The molar volumes of ice and water are 0.0196 and 0.0180 litre respectively. Calculate  $\Delta H$  and  $\Delta E$  for the reaction.
8. Water expands when it freezes. Determine amount of work in joules, done when a system consisting of 1.0 L of liquid water freezes under a constant pressure of 1.0 atm and forms 1.1 L of ice.
9. One mole of solid Zn is placed in excess of dilute  $\text{H}_2\text{SO}_4$  at  $27^\circ\text{C}$  in a cylinder fitted with a piston. Find the value of  $\Delta E$ , q and w for the process if the area of piston is  $500 \text{ cm}^2$  and it moves out by 50 cm against a pressure of 1 atm during the reaction. The heat given to surrounding is 36.5 kJ.



10. Five moles of an ideal gas at 300K, expanded isothermally from an initial pressure of 4 atm to a final pressure of 1 atm against a cont. ext. pressure of 1 atm. Calculate q, w,  $\Delta U$  &  $\Delta H$ . Calculate the corresponding value of all if the above process is carried out reversibly.

11. 1 mole of CO<sub>2</sub> gas at 300 K is expanded under reversible adiabatic condition such that its volume becomes 27 times.  
 (a) What is final temperature  
 (b) What is work done.  
 Given  $\gamma = 1.33$  and  $C_v = 25.08 \text{ J mol}^{-1} \text{ K}^{-1}$  for CO<sub>2</sub>.

12. A sample of a fluorocarbon was allowed to expand reversibly and adiabatically to twice its volume. In the expansion the temperature dropped from 298.15 to 248.44 K. Assume the gas behaves perfectly. Estimate the value of  $C_{v,m}$ .

13. Find the work done when one mole of the gas is expanded reversibly and isothermally from 5 atm to 1 atm at 25°C ?

14. One mole of an ideal monoatomic gas is carried through the cycle of the given figure consisting of step A, B and C and involving state 1, 2 and 3. Fill in the blank space in the table given below assuming reversible steps.

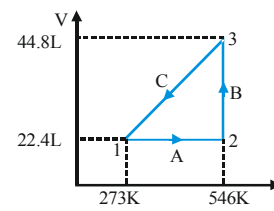


Table-1			
State	P	V	T
1			
2			
3			

Step	Name of process	q	w	$\Delta E$	$\Delta H$
A					
B					
C					
overall					

15. The standard enthalpy of formation of water liquid is  $-285.76 \text{ kJ}$  at 298 K. Calculate the value at 373K. The molar heat capacities at constant pressure ( $C_p$ ) in the given temperature range of H<sub>2</sub>(g), O<sub>2</sub>(g) and H<sub>2</sub>O(l) are respectively 38.83, 29.16 and  $75.312 \text{ JK}^{-1} \text{ mol}^{-1}$ .

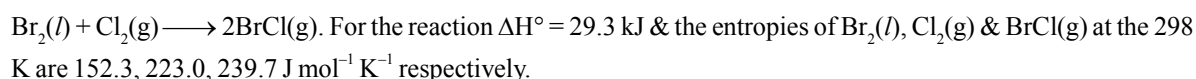
16. Methane (Considered to be an ideal gas) initially at 25°C and 1 bar pressure is heated at constant pressure until the volume has doubled. The variation of the molar heat capacity with absolute temperature is given by  $C_p = 22.34 + 48.1 \times 10^{-3} T$ . where  $C_p$  is in  $\text{JK}^{-1} \text{ mol}^{-1}$ . Calculate molar (a)  $\Delta H$  (b)  $\Delta U$ .

17. One mole of NaCl(s) on melting absorbed 30.5 kJ of heat and its entropy is increased by  $28.8 \text{ JK}^{-1}$ . What is the melting point of sodium chloride ?

18. Oxygen is heated from 300 K to 600 K at a constant pressure of 1 bar. What is the increases in molar entropy? The molar heat capacity in  $\text{JK}^{-1} \text{ mol}^{-1}$  for the O<sub>2</sub> is.

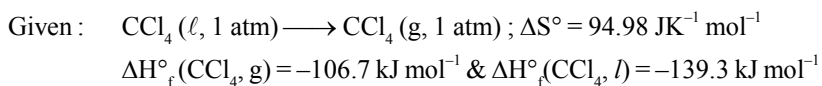
$$C_p = 25.5 + 13.6 \times 10^{-3} T - 42.5 \times 10^{-7} T^2$$

19. Calculate the free energy change at 298 K for the reaction :

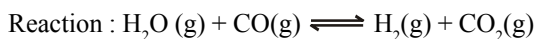


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20. Using the data given below, establish that the vaporization of  $\text{CCl}_4(l)$  at 298K to produce  $\text{CCl}_4(g)$  at 1 atm pressure does not occur spontaneously.



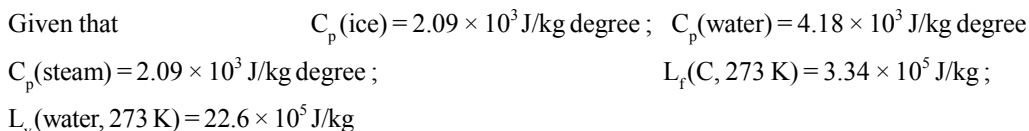
21. From the given table answer the following questions :



- (ii) Calculate  $\Delta_r H_{298}^\circ$  (ii) Calculate  $\Delta_r G_{298}^\circ$   
 (iii) Calculate  $\Delta_r S_{298}^\circ$  (iv) Calculate  $\Delta_r E_{298}^\circ$   
 (v) Calculate  $S_{298}^\circ[\text{H}_2\text{O}(g)]$

	CO(g)	CO <sub>2</sub> (g)	H <sub>2</sub> O(g)	H <sub>2</sub> (g)
$\Delta H_{298}^\circ$ (-kCal/mole)	-26.42	-94.05	-57.8	0
$\Delta G_{298}^\circ$ (-kCal/mole)	-32.79	-94.24	-54.64	0
$S_{298}^\circ$ (-Cal/kmole)	47.3	51.1	?	31.2

22. The increase in entropy of 1 kg of ice at 200 K which is heated to 400 K (super heated steam) at constant atmospheric pressure, will be :



23. Calculate workdone in adiabatic compression of one mole of an ideal gas (monoatomic) from an initial pressure of 1 atm to final pressure of 2 atm. Initial temperature = 300 K

- (a) If process is carried out reversibly.  
 (b) If process is carried out irreversible against 2 atm external pressure.

Compute the final volume reached by gas in two cases.

24. 20.0 dm<sup>3</sup> of an ideal gas (diatomic  $C_{v,m} = 5R/2$ ) at 673 K and 0.7 MPa expands until pressure of the gas is 0.2 MPa. Calculate q, w,  $\Delta U$  and  $\Delta H$  for the process if the expansion is :

- (i) Isothermal and reversible  
 (ii) Adiabatic and reversible  
 (iii) Isothermal and adiabatic  
 (iv) Against 0.2 MPa and adiabatic  
 (v) Against 0.2 MPa and isothermal.

25. One mole of an ideal gas is expanded isothermally at 298 K until its volume is tripled. Find the values of  $\Delta S_{\text{gas}}$  and  $\Delta S_{\text{total}}$  under the following conditions.

- (i) Expansion is carried out reversibly.  
 (ii) Expansion is carried out irreversibly where 836.6 J of heat is less absorbed than in (i)  
 (iii) Expansion is free.

26. 10 g of neon initially at a pressure of 506.625 kPa and temperature of 473 K expand adiabatically to a pressure of 202.65 kPa. Calculate entropy change of the system and total entropy change for the following ways of carrying out this expansion.
- (i) Expansion is carried out reversibly.
  - (ii) Expansion occurs against a constant external pressure of 202.65 kPa.
  - (iii) Expansion is free expansion.
27. Pressure over 1000 mL of a liquid is gradually increases from 1 bar to 1001 bar under adiabatic conditions. If the final volume of the liquid is 990 mL, calculate  $\Delta U$  and  $\Delta H$  of the process, assuming linear variation of volume with pressure.
28. One mole of ideal monoatomic gas was taken through reversible isochoric heating from 100 K to 1000 K. Calculate  $\Delta S_{\text{system}}$ ,  $\Delta S_{\text{surr}}$ , and  $\Delta S_{\text{total}}$  in
- (i) when the process carried out reversibly
  - (ii) when the process carried out irreversibly (one step)
29. Fixed amount of an ideal gas contained in a sealed rigid vessel ( $V = 24.6$  litre) at 1.0 bar is heated reversibly from  $27^\circ\text{C}$  to  $127^\circ\text{C}$ . Determine change in Gibb's energy (in Joule) if entropy of gas  $S = 10 + 10^{-2} T$  (J/K).
30. A 32 g sample of  $\text{CH}_4$  gas initially at 101.325 kPa and 300 K is heated to 550 K.  $C_{p,m}/\text{JK}^{-1}\text{mol}^{-1} = 12.552 + 8.368 \times 10^{-2} T/\text{K}$ . Assuming  $\text{CH}_4$  behaves ideally, compute  $w$ ,  $q$ ,  $\Delta U$  and  $\Delta H$  for (a) an isobaric reversible process and (b) an isochoric reversible process.
31. At 298 K,  $\Delta H^\circ_{\text{combustion}}(\text{sucrose}) = -5737 \text{ kJ/mol}$  &  $\Delta G^\circ_{\text{combustion}}(\text{sucrose}) = -6333 \text{ kJ/mol}$ . Estimate additional non-PV work that is obtained by raising temperature to 310 K. Assume  $\Delta_r C_p = 0$  for this temperature change.
32. Compute  $\Delta_r G$  for the reaction  $\text{H}_2\text{O}(\ell, 1 \text{ atm}, 323 \text{ K}) \rightarrow \text{H}_2\text{O}(\text{g}, 1 \text{ atm}, 323 \text{ K})$   
 Given that :  $\Delta_{\text{vap}} H$  at 373 K =  $40.639 \text{ kJmol}^{-1}$ ,  $C_p(\text{H}_2\text{O}, \ell) = 75.312 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  
 $C_p(\text{H}_2\text{O}, \text{g}) = 33.305 \text{ J K}^{-1} \text{ mol}^{-1}$ .
33. (a) An ideal gas undergoes a single state expansion against a constant opposing pressure from  $(P_1, V_1, T)$  to  $(P_2, V_2, T)$ . What is the largest mass  $m$  which can be lifted through a height  $h$  in this expansion ?
- (b) The system (a) restored to its initial state by a single state compression. What is the smallest mass  $m'$  which must fall through the height  $h$  to restore system?
- (c) What is the net mass lowered through height  $h$  in the cyclic transformation in (a) and (b) ?

Exercise # 5

Part # I [Previous Year Questions] [AIEEE/JEE-MAIN]

- An ideal gas expands in volume from  $1 \times 10^{-3} \text{ m}^3$  to  $1 \times 10^{-2} \text{ m}^3$  at 300 K against a constant pressure of  $1 \times 10^5 \text{ Nm}^{-2}$ . The work is : [AIEEE 2004]  
 (A)  $-900 \text{ J}$  (B)  $-900 \text{ kJ}$  (C)  $270 \text{ kJ}$  (D)  $+900 \text{ kJ}$
- Consider the reaction,  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$ ; carried out at constant temperature and pressure. If  $\Delta H$  and  $\Delta U$  are enthalpy change and internal energy change respectively, which of the following expressions is true ? [AIEEE 2005]  
 (A)  $\Delta H = 0$  (B)  $\Delta H = \Delta U$  (C)  $\Delta H < \Delta U$  (D)  $\Delta H > \Delta U$
- For a spontaneous reaction the  $\Delta G$ , equilibrium constant (K) and  $E_{\text{cell}}^\circ$  will be respectively [AIEEE 2005]  
 (A)  $-ve, > 1, +ve$  (B)  $+ve, > 1, -ve$  (C)  $-ve, < 1, -ve$  (D)  $-ve, > 1, -ve$
- 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 statements is correct ? [AIEEE 2006]  
 (A)  $T_f > T_i$  for reversible process but  $T_f = T_i$  for irreversible process  
 (B)  $(T_f)_{\text{rev}} = (T_f)_{\text{irrev}}$   
 (C)  $T_f = T_i$  for both reversible and irreversible processes  
 (D)  $(T_f)_{\text{irrev}} > (T_f)_{\text{rev}}$
- Assuming that water vapour is an ideal gas, the internal energy change ( $\Delta U$ ) when 1 mol of water is vapourised at 1 bar pressure and  $100^\circ\text{C}$ , (Given : Molar enthalpy of vapourization of water at 1 bar and  $373 \text{ K} = 41 \text{ kJ mol}^{-1}$  and  $R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$ ) will be : [AIEEE 2007]  
 (A)  $37.904 \text{ kJ mol}^{-1}$  (B)  $41.00 \text{ kJ mol}^{-1}$  (C)  $4.100 \text{ kJ mol}^{-1}$  (D)  $3.7904 \text{ mol}^{-1}$
- Identify the correct statement regarding a spontaneous process : [AIEEE 2007]  
 (A) Exothermic processes are always spontaneous.  
 (B) Lowering of energy in the reaction process is the only criterion for spontaneity.  
 (C) For a spontaneous process in an isolated system, the change in entropy is positive.  
 (D) Endothermic processes are never spontaneous.
- In conversion of lime-stone to lime,  $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$  the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  are  $+179.1 \text{ kJ mol}^{-1}$  and  $160.2 \text{ J/K}$  respectively at  $298 \text{ K}$  and 1 bar. Assuming that  $\Delta H^\circ$  and  $\Delta S^\circ$  do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is : [AIEEE 2007]  
 (A)  $845 \text{ K}$  (B)  $1118 \text{ K}$  (C)  $1008$  (D)  $1200 \text{ K}$
- Standard entropy of  $\text{X}_2$ ,  $\text{Y}_2$  and  $\text{XY}_3$  are  $60$ ,  $40$  and  $50 \text{ JK}^{-1} \text{ mol}^{-1}$ , respectively. [AIEEE 2008]  
 For the reaction,  $\frac{1}{2} \text{X}_2 + \frac{3}{2} \text{Y}_2 \rightarrow \text{XY}_3$ ,  $\Delta H = -30 \text{ kJ}$ . To be at equilibrium the temperature will be :  
 (A)  $500 \text{ K}$  (B)  $750 \text{ K}$  (C)  $1000 \text{ K}$  (D)  $1250 \text{ K}$
- In a fuel cell methanol is used as fuel and oxygen gas is used as an oxidizer. The reaction is [AIEEE 2009]  

$$\text{CH}_3\text{OH}(\ell) + \frac{3}{2} \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\ell)$$
 At  $298 \text{ K}$ , standard Gibb's energies of formation for  $\text{CH}_3\text{OH}(\ell)$ ,  $\text{H}_2\text{O}(\ell)$  and  $\text{CO}_2(\text{g})$  are  $-166.2$ ,  $-237.2$  and  $-394.4 \text{ kJ mol}^{-1}$  respectively. If standard enthalpy of combustion of methanol is  $-726 \text{ kJ mol}^{-1}$ , efficiency of the fuel cell will be  
 (A)  $87\%$  (B)  $90\%$  (C)  $97\%$  (D)  $80\%$
- For a particular reversible reaction at temperature  $T$ ,  $\Delta H$  and  $\Delta S$  were found to be both  $+ve$ . 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)  $T = T_e$

11. The entropy change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of 10 dm<sup>3</sup> to a volume of 100 dm<sup>3</sup> at 27°C is : [AIEEE 2011]

(A) 38.3 J mol<sup>-1</sup> K<sup>-1</sup>      (B) 35.8 J mol<sup>-1</sup> K<sup>-1</sup>      (C) 32.3 J mol<sup>-1</sup> K<sup>-1</sup>      (D) 42.3 J mol<sup>-1</sup> K<sup>-1</sup>

12. In view of the signs of  $\Delta_r G^\circ$  for the following reactions :



which oxidation states are more characteristics for lead and tin ? [AIEEE 2011]

(A) For lead +2, for tin +2      (B) For lead +4, for tin +4  
 (C) For lead +2, for tin +4      (D) For lead +4, for tin +2

13. The incorrect expression among the following is : [AIEEE 2012]

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

(B) In isothermal process,  $w_{\text{reversible}} = -nRT \ln \frac{V_f}{V_i}$

(C)  $\ln K = \frac{\Delta H^\circ - T\Delta S^\circ}{RT}$

(D)  $K = e^{-\Delta G^\circ/RT}$

14. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and w for the process will be:

(R = 8.314 J/mol K) (ln 7.5 = 2.01) [JEE 2013, (Mains)]

(R = 8.314 J/mol K) (ln 7.5 = 2.01)

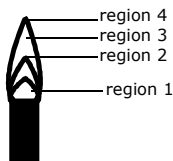
(A) q = +208 J, w = -208 J      (B) q = -208 J, w = -208 J  
 (C) q = -208 J, w = +208 J      (D) q = +208 J, w = +208 J

15. The heats of combustion of carbon and carbon monoxide are -393.5 and -283.5 kJ mol<sup>-1</sup> respectively. The heat of formation (in kJ) of carbon monoxide per mole is: [JEE 2016, (Mains)]

(A) 676.5      (B) -676.5      (C) -110.5      (D) 110.5

16. The hottest region of Bunsen flame shown in the figure below is: [JEE 2016, (Mains)]

(A) region 2  
 (B) region 3  
 (C) region 4  
 (D) region 1

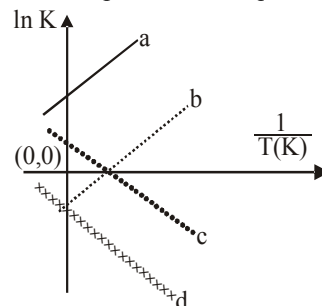


17.  $\Delta U$  is equal to :

(A) Isochoric work      (B) Isobaric work      (C) Adiabatic work      (D) Isothermal work [JEE 2017, (Mains)]

18. Which of the following lines correctly show the temperature dependence of equilibrium constant, K, for an exothermic reaction ? [JEE 2018, (Mains)]

(A) b and c  
 (B) c and d  
 (C) a and d  
 (D) a and b



19. The combustion of benzene (l) gives CO<sub>2</sub>(g) and H<sub>2</sub>O(l). Given that heat of combustion of benzene at constant volume is -3263.9 kJ mol<sup>-1</sup> at 25°C; heat of combustion (in kJ mol<sup>-1</sup>) of benzene at constant pressure will be :

(R = 8.314 JK<sup>-1</sup> mol<sup>-1</sup>) [JEE MAIN 2018]

(A) -452.46      (B) 3260      (C) -3267.6      (D) 4152.6

- 2 moles of ideal gas is expanded isothermally & reversibly from 1 litre to 10 litre. Find the enthalpy change in  $\text{kJ mol}^{-1}$ . [JEE 2004]  
 (A) 0 (B) 11.7 (C) -11.7 (D) 25
- There is 1 mol liquid (molar volume 100 ml) in an adiabatic container initial, pressure being 1 bar Now the pressure is steeply increased to 100 bar, and the volume decreased by 1 ml under constant pressure of 100 bar. Calculate  $\Delta H$  and  $\Delta E$ . [Given 1 bar =  $10^5 \text{ N/m}^2$ ] [JEE 2004]
- $\Delta H = 30 \text{ kJ mol}^{-1}$ ,  $\Delta S = 75 \text{ J/k/mol}$ . Find boiling temperature at 1 atm. [JEE 2004]  
 (A) 400 K (B) 300 K (C) 150 K (D) 425 K
- Spontaneous adsorption of a gas on a solid surface is exothermic process because [JEE 2004]  
 (A) enthalpy of the system increases. (B) entropy increases.  
 (C) entropy decreases. (D) free energy change increases.
- For the reaction :  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$   
 (i) In a mixture of 5 mol  $\text{NO}_2$  and 5 mol  $\text{N}_2\text{O}_4$  and pressure of 20 bar. Calculate the value of  $\Delta G$  for the reaction. Given  $\Delta G_f^\circ(\text{NO}_2) = 50 \text{ kJ/mol}$ ,  $\Delta G_f^\circ(\text{N}_2\text{O}_4) = 100 \text{ kJ/mol}$  and  $T = 298 \text{ K}$ .  
 (ii) Predict the direction in which the reaction will shift, in order to attain equilibrium  
 [Given at  $T = 298 \text{ K}$ ,  $2.303 RT = 5.7 \text{ kJ/mol}$ .] [JEE 2004]
- One mole of an ideal monoatomic gas at temperature  $T$  and volume 1L expands to 2L against a constant external pressure of one atm under adiabatic conditions, then final temperature of gas will be : [JEE 2005]  
 (A)  $T + \frac{2}{3 \times 0.0821}$  (B)  $T - \frac{2}{3 \times 0.0821}$  (C)  $\frac{T}{2^{5/3-1}}$  (D)  $\frac{T}{2^{5/3+1}}$
- The ratio of  $P$  to  $V$  at any instant is constant and is equal to 1, for a monoatomic ideal gas under going a process. What is the molar heat capacity of the gas. [JEE 2006]  
 (A)  $\frac{3R}{2}$  (B)  $\frac{4R}{2}$  (C)  $\frac{5R}{2}$  (D) 0
- The given reaction  

$$2\text{CO} + \text{O}_2 \longrightarrow 2\text{CO}_2 \quad \Delta H = -560 \text{ kJ}$$

2moles      1 mole

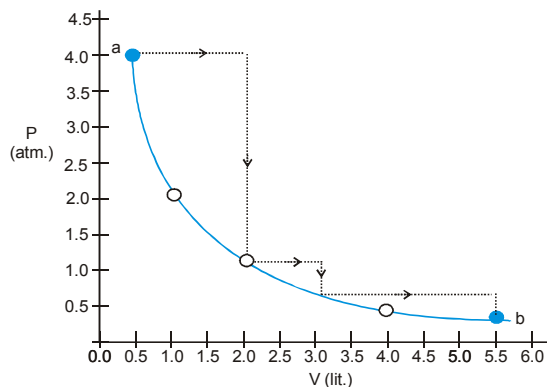
 is carried out in one litre container, if the pressure in the container gets changes from 70 atm to 40 atm as reaction gets completed. Calculate  $\Delta U$  of the reaction. [1L atm = 0.1 kJ] [JEE 2006]
- The direct conversion of A to B is difficult, hence it is carried out by the following shown path:  

$$\begin{array}{ccc} & \text{C} & \longrightarrow & \text{D} \\ & \uparrow & & \downarrow \\ \text{A} & & & \text{B} \end{array}$$

$$\Delta S(\text{A} \longrightarrow \text{C}) = 50; \quad \Delta S(\text{C} \longrightarrow \text{D}) = 30; \quad \Delta S(\text{B} \longrightarrow \text{D}) = +20$$
 The entropy change for the process  $\text{A} \longrightarrow \text{B}$  is [JEE 2006]  
 (A) 100 (B) -60 (C) -100 (D) +60
- The value of  $\log_{10} K$  for a reaction  $\text{A} \rightleftharpoons \text{B}$  is :  
 (Given :  $\Delta_r H_{298\text{K}}^\circ = -54.07 \text{ kJ mol}^{-1}$ ,  $\Delta_r S_{298\text{K}}^\circ = 10 \text{ JK}^{-1} \text{ mol}^{-1}$  and  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ;  $2.303 \times 8.314 \times 298 = 5705$ ) [JEE 2007]  
 (A) 5 (B) 10 (C) 95 (D) 100



11. For the process  $\text{H}_2\text{O}(\ell)$  (1 bar, 373 K)  $\rightarrow$   $\text{H}_2\text{O}(\text{g})$  (1 bar, 373 K), the correct set of thermodynamic parameters is : [JEE 2007]  
 (A)  $\Delta G = 0, \Delta S = +ve$       (B)  $\Delta G = 0, \Delta S = -ve$       (C)  $\Delta G = +ve, \Delta S = 0$       (D)  $\Delta G = -ve, \Delta S = +ve$
12. **Statement-1** : For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero.  
**Statement-2** : At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy. [JEE 2008]  
 (A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.  
 (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1  
 (C) Statement-1 is True, Statement-2 is False  
 (D) Statement-1 is False, Statement-2 is True
13. **Statement-1** : There is a natural asymmetry between converting work to heat and converting heat to work.  
**Statement-2** : No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work. [JEE 2008]  
 (A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.  
 (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1  
 (C) Statement-1 is True, Statement-2 is False  
 (D) Statement-1 is False, Statement-2 is True
14. Among the following, the state function(s) is(are) : [JEE 2009]  
 (A) Internal energy      (B) Irreversible expansion work  
 (C) Reversible expansion work      (D) Molar enthalpy
15. Among the following, the intensive property is (properties are) : [JEE 2010]  
 (A) molar conductivity      (B) electromotive force  
 (C) resistance      (D) heat capacity
16. One mole of an ideal gas is taken from **a** and **b** along two paths denoted by the solid and the dashed lines as shown in the graph below. If the work done along the solid line path is  $w_s$  and that along the dotted line path is  $w_d$ , then the integer closest to the ratio  $w_d / w_s$  is : [JEE 2010]

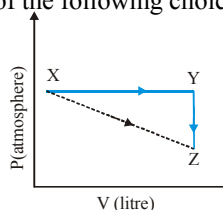


17. Match the transformation in **column I** with appropriate options in **column II**. [JEE 2011]
- | Column I   | Column II                  |
|--|----------------------------|
| (A) $\text{CO}_2(\text{s}) \longrightarrow \text{CO}_2(\text{g})$                          | (p) phase transition       |
| (B) $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ | (q) allotropic change      |
| (C) $2\text{H} \bullet \longrightarrow \text{H}_2(\text{g})$                               | (r) $\Delta H$ is positive |
| (D) $\text{P}_{(\text{white, solid})} \longrightarrow \text{P}_{(\text{red, solid})}$      | (s) $\Delta S$ is positive |
|  | (t) $\Delta S$ is negative |

# CHEMISTRY FOR JEE MAIN & ADVANCED

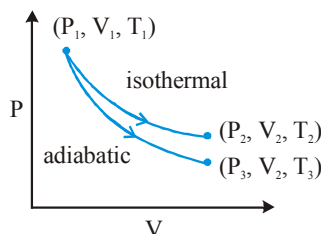
18. For an ideal gas, consider only P-V work in going from an initial state X to the final state Z. The final state Z can be reached by either of the two paths shown in the figure. Which of the following choice(s) is (are) correct? [take  $\Delta S$  as change in entropy and  $w$  as work done]. [JEE 2012]

- (A)  $\Delta S_{x \rightarrow z} = \Delta S_{x \rightarrow y} + \Delta S_{y \rightarrow z}$   
 (B)  $w_{x \rightarrow z} = w_{x \rightarrow y} + w_{y \rightarrow z}$   
 (C)  $w_{x \rightarrow y \rightarrow z} = w_{x \rightarrow y}$   
 (D)  $\Delta S_{x \rightarrow y \rightarrow z} = \Delta S_{x \rightarrow y}$

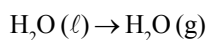


19. The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is (are) correct? [JEE 2012]

- (A)  $T_1 = T_2$   
 (B)  $T_3 > T_1$   
 (C)  $w_{\text{isothermal}} > w_{\text{adiabatic}}$   
 (D)  $\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$



20. For the process [JEE 2015]



at  $T = 100^\circ\text{C}$  and 1 atmosphere pressure, the correct choice is :

- (A)  $\Delta S_{\text{system}} > 0$  and  $\Delta S_{\text{surroundings}} > 0$       (B)  $\Delta S_{\text{system}} > 0$  and  $\Delta S_{\text{surroundings}} < 0$   
 (C)  $\Delta S_{\text{system}} < 0$  and  $\Delta S_{\text{surroundings}} > 0$       (D)  $\Delta S_{\text{system}} < 0$  and  $\Delta S_{\text{surroundings}} < 0$

21. One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings ( $\Delta S_{\text{sur}}$ ) in  $\text{J K}^{-1}$  is (1 L atm = 101.3 J) [JEE 2016]

- (A) 5.763      (B) 1.013      (C) -1.013      (D) -5.763

22. An ideal gas is expanded from  $(p_1, V_1, T_1)$  to  $(p_2, V_2, T_2)$  under different conditions. The correct statement(s) among the following is(are)

- (A) the work done by the gas is less when it is expanded reversibly from  $V_1$  to  $V_2$  under adiabatic conditions as compared to that when expanded reversibly from  $V_1$  to  $V_2$  under isothermal conditions.  
 (B) The change in internal energy of the gas is (i) zero, if it is expanded reversibly with  $T_1 = T_2$ , and (ii) positive, if it is expanded reversibly under adiabatic conditions with  $T_1 \neq T_2$   
 (C) If the expansion is carried out freely, it is simultaneously both isothermal as well as adiabatic  
 (D) The work done on the gas is maximum when it is compressed irreversibly from  $(p_2, V_2)$  to  $(p_1, V_1)$  against constant pressure  $p_1$  [JEE 2017]

23. The standard state Gibbs free energies of formation of C(graphite) and C(diamond) at  $T = 298 \text{ K}$  are

$$\Delta_f G^\circ[\text{C}(\text{graphite})] = 0 \text{ kJ mol}^{-1}$$

$$\Delta_f G^\circ[\text{C}(\text{diamond})] = 2.9 \text{ kJ mol}^{-1}$$

The standard state means that the pressure should be 1 bar, and substance should be pure at a given temperature. The conversion of graphite [C(graphite)] to diamond [C(diamond)] reduces its volume by  $2 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ . If C(graphite) is converted to C(diamond) isothermally at  $T = 298 \text{ K}$ , the pressure at which C(graphite) is in equilibrium with C(diamond), is [Useful information :  $1 \text{ J} = \text{kg m}^2 \text{ s}^{-2}$ ;  $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$ ;  $1 \text{ bar} = 10^5 \text{ Pa}$ ] [JEE 2017]

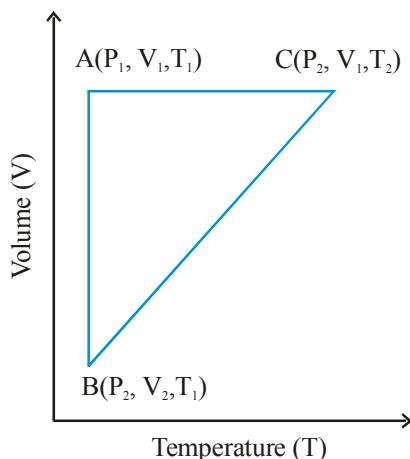
- (A) 29001 bar      (B) 58001 bar      (C) 14501 bar      (D) 1450 bar

24. For a reaction taking place in a container in equilibrium with its surroundings, the effect of temperature on its equilibrium constant  $K$  in terms of change in entropy is described by [JEE 2017]

- (A) With increase in temperature, the value of  $K$  for endothermic reaction increases because unfavourable change in entropy of the surroundings decreases  
 (B) With increase in temperature, the value of  $K$  for exothermic reaction decreases because favourable change in entropy of the surroundings decreases  
 (C) With increase in temperature, the value of  $K$  for exothermic reaction decreases because the entropy change of the system is positive  
 (D) With increase in temperature, the value of  $K$  for endothermic reaction increases because the entropy change of the system is negative

25. A reversible cyclic for an ideal gas is shown below. Here, P, V, and T, are pressure, volume and temperature, respectively. The thermodynamic parameters q, w, H and U are heat, work, enthalpy and internal energy, respectively.

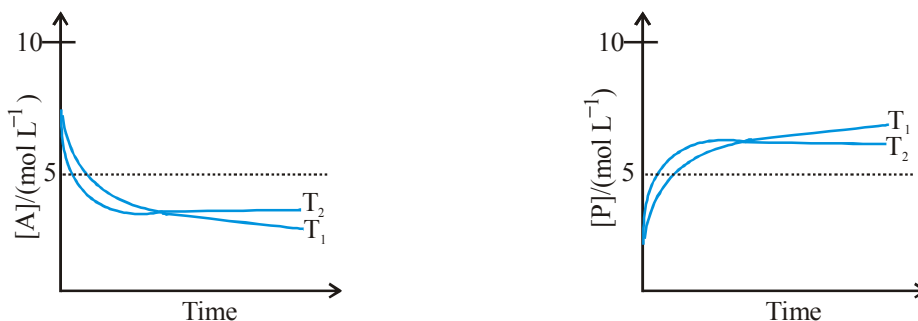
[JEE(ADVANCED) 2018]



The correct option (s) is (are)

- (A)  $q_{AC} = \Delta U_{BC}$  and  $W_{AB} = P_2(V_2 - V_1)$       (B)  $W_{BC} = P_2(V_2 - V_1)$  and  $q_{BC} = \Delta U_{AC}$   
 (C)  $\Delta H_{CA} < \Delta U_{CA}$  and  $q_{AC} = \Delta U_{BC}$       (D)  $q_{BC} = \Delta H_{AC}$  and  $\Delta H_{CA} > \Delta U_{CA}$
26. For a reaction,  $A \rightleftharpoons P$ , the plots of [A] and [P] with time at temperature  $T_1$  and  $T_2$  are given below.

[JEE(ADVANCED) 2018]



If  $T_2 > T_1$ , the correct statement(s) is (are)

(Assume  $\Delta H^0$  and  $\Delta S^0$  are independent of temperature and ratio of  $\ln K$  at  $T_1$  to  $\ln K$  at  $T_2$  is greater than  $\frac{T_2}{T_1}$ . Here H, S, G and K are enthalpy, entropy, Gibbs energy and equilibrium constant, respectively.)

- (A)  $\Delta H^0 < 0$ ,  $\Delta S^0 < 0$       (B)  $\Delta G^0 < 0$ ,  $\Delta H^0 > 0$       (C)  $\Delta G^0 < 0$ ,  $\Delta S^0 < 0$       (D)  $\Delta G^0 < 0$ ,  $\Delta S^0 > 0$

MOCK TEST

SECTION - I: STRAIGHT OBJECTIVE TYPE

- Warming ammonium chloride with sodium hydroxide in a test tube is an example of :  
 (A) Closed system      (B) Isolated system      (C) Open system      (D) None of these
- A gaseous system changes from state A ( $P_1, V_1, T_1$ ) to B ( $P_2, V_2, T_2$ ), B to C ( $P_3, V_3, T_3$ ) and finally from C to A. The whole process may be called :  
 (A) Reversible process      (B) Cyclic process  
 (C) Isobaric process      (D) Spontaneous process
- An electric heater of resistance 6 ohm is run for 10 minutes on a 120 volt line. The work done in this period of time is  
 (A)  $7.2 \times 10^3 \text{ J}$       (B)  $14.4 \times 10^5 \text{ J}$       (C)  $43.2 \times 10^4 \text{ J}$       (D)  $28.8 \times 10^4 \text{ J}$
- Determine which of the following reactions at constant pressure represent surrounding that do work on the system  
 I       $4\text{NH}_3(\text{g}) + 7\text{O}_2(\text{g}) \longrightarrow 4\text{NO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$   
 II       $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \longrightarrow \text{CH}_3\text{OH}(\ell)$   
 III       $\text{C}(\text{s, graphite}) + \text{H}_2\text{O}(\text{g}) \longrightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$   
 IV       $\text{H}_2\text{O}(\text{s}) \longrightarrow \text{H}_2\text{O}(\ell)$   
 (A) III, IV      (B) II and III      (C) II, IV      (D) I and II, IV
- 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)  $w > 0; q = 0; \Delta U > 0$
- In an isochoric process the increase in internal energy is  
 (A) Equal to the heat absorbed      (B) Equal to the heat evolved  
 (C) Equal to the work done      (D) Equal to the sum of the heat absorbed and work done
- Which of the following reactions is associated with the most negative change in entropy ?  
 (A)  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{SO}_3(\text{g})$       (B)  $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_6(\text{g})$   
 (C)  $\text{C}(\text{s, graphite}) + \text{O}_2 \longrightarrow \text{CO}_2(\text{g})$       (D)  $3\text{C}_2\text{H}_2(\text{g}) \longrightarrow \text{C}_6\text{H}_6(\ell)$
- For the gas - phase decomposition,  $\text{PCl}_5(\text{g}) \xrightleftharpoons{\Delta} \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$  :  
 (A)  $\Delta H < 0, \Delta S < 0$       (B)  $\Delta H > 0, \Delta S > 0$       (C)  $\Delta H > 0, \Delta S < 0$       (D)  $\Delta H < 0, \Delta S > 0$
- In previous problem calculate  $\Delta S_{\text{gas}}$  if process is carried out at constant volume :  
 (A)  $5R \ln 2$       (B)  $\frac{3}{2} R \ln 2$       (C)  $3R \ln 2$       (D)  $-3R \ln 2$
- 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 ( $\Delta S$ ) is :  
 (A)  $C_{p,m} \ln 2$       (B)  $C_{v,m} \ln 2$       (C)  $R \ln 2$       (D)  $(C_{v,m} - R) \ln 2$
- The enthalpy change for a given reaction at 298 K is  $-x \text{ J mol}^{-1}$  ( $x$  being positive). If the reaction occurs spontaneously at 298 K, the entropy change at that temperature  
 (A) can be negative but numerically larger than  $x/298$   
 (B) can be negative but numerically smaller than  $x/298$   
 (C) cannot be negative  
 (D) cannot be positive

12. A reaction has  $\Delta H = -33 \text{ kJ}$  and  $\Delta S = -58 \frac{\text{J}}{\text{K}}$ . This reaction would be :
- (A) spontaneous at all temperatures                      (B) non-spontaneous at all temperatures  
(C) spontaneous above a certain temperature            (D) spontaneous below a certain temperature

### SECTION - II : MULTIPLE CORRECT ANSWER TYPE

13. Choose the correct statement :
- (A) system and surrounding are always separated by a real or imaginary boundary.  
(B) perfectly isolated system can never be created.  
(C) in reversible process, energy change in each step can be reversed.  
(D) irreversible process is also called quasi-equilibrium state.
14. In an isothermal expansion of a gaseous sample, the correct relation is : (consider  $w$  (work) with sign according to new IUPAC convention)  
[The reversible and irreversible processes are carried out between same initial and final states.]
- (A)  $w_{\text{rev}} > w_{\text{irrev}}$                       (B)  $w_{\text{irrev}} > w_{\text{rev}}$                       (C)  $q_{\text{rev}} < q_{\text{irrev}}$                       (D)  $\Delta E_{\text{rev}} = \Delta E_{\text{irrev}}$
15. During the isothermal expansion of an ideal gas :
- (A) The internal energy remains unaffected                      (B) The temperature remains constant  
(C) The enthalpy remains unaffected                                  (D) The enthalpy increases
16. When a liquid solidifies, generally, there is :
- (A) Decrease in enthalpy    (B) Decrease in entropy  
(C) Increase in enthalpy    (D) Increase in entropy
17. Choose the correct statement (s) :
- (A) Temperature, enthalpy and entropy are state functions  
(B) For reversible and irreversible both isothermal expansion of an ideal gas, change in internal energy and enthalpy is zero  
(C) for a reaction in which  $\Delta n_g = 0$ , entropy change is not always zero  
(D) The entropy change associated with reversible isothermal expansion of an ideal gas is equal to  $2.303 R \log_{10} \frac{P_1}{P_2}$
18. One mole of an ideal diatomic gas ( $C_v = 5 \text{ cal}$ ) was transformed from initial  $25^\circ\text{C}$  and 1 L to the state when temperature is  $100^\circ\text{C}$  and volume 10 L. Then for this process ( $R = 2 \text{ calories/mol/K}$ ) (take calories as unit of energy and kelvin for temp)
- (A)  $\Delta H = 525$     (B)  $\Delta S = 5 \ln \frac{373}{298} + 2 \ln 10$   
(C)  $\Delta E = 525$     (D)  $\Delta G$  of the process can not be calculated using given information

### SECTION - III : ASSERTION AND REASON TYPE

Each question has 5 choices (A), (B), (C), (D) and (E) out of which only one is correct.

- (A) Statement-1 is true, Statement-2 is true and Statement-2 is correct explanation for Statement-1  
(B) Statement-1 is true, Statement-2 is true and Statement-2 is not correct explanation for Statement-1  
(C) Statement-1 is true, Statement-2 is false  
(D) Statement-1 is false, Statement-2 is true  
(E) Both Statements are false
19. **Statement-1** : When a gas at high pressure expands against vacuum, the magnitude of work done is maximum.  
**Statement-2** : Work done in expansion depends upon the pressure inside the gas and increase in volume.

20. **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.
21. **Statement-1** : The standard free energy changes of all spontaneously occurring 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.
22. **Statement-1** : Many endothermic reactions that are not spontaneous at room temperature become spontaneous at high temperature.  
**Statement-2** :  $\Delta H^\circ$  of the endothermic reaction increases with increase in temperature.
23. **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 positive sign of  $\Delta S_{\text{system}}$ .

### SECTION - IV : COMPREHENSION TYPE

Read the following comprehensions carefully and answer the questions.

#### Comprehension # 1

A gaseous sample is generally allowed to do only expansion/compression type of work against its surroundings. The work done in case of an irreversible expansion (in the intermediate stages of expansion/compression the states of gases are not defined). The work done can be calculated using

$$dw = -P_{\text{ext}} dV$$

while in case of reversible process the work done can be calculated using

$dw = -PdV$  where P is pressure of gas at some intermediate stages. Like for an isothermal

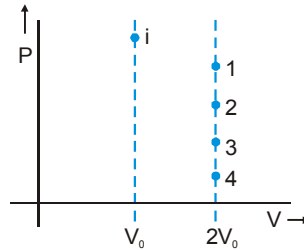
reversible process. Since  $P = \frac{nRT}{V}$ , so

$$w = \int dw = - \int_{V_i}^{V_f} \frac{nRT}{V} \cdot dV = -nRT \ln \left( \frac{V_f}{V_i} \right)$$

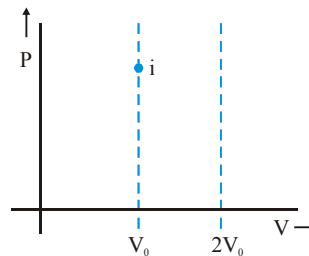
Since  $dw = -PdV$  so magnitude of work done can also be calculated by calculating the area under the PV curve of the reversible process in PV diagram.

24. An ideal gaseous sample at initial state i ( $P_0, V_0, T_0$ ) is allowed to expand to volume  $2V_0$  using two different process; in the first process the equation of process is  $PV^2 = K_1$  and in second process the equation of the process is  $PV = K_2$ . Then,  
 (A) work done in first process will be greater than work in second process (magnitude wise)  
 (B) The order of values of work done can not be compared unless we know the value of  $K_1$  and  $K_2$ .  
 (C) value of work done (magnitude) in second process is greater in above expansion irrespective of the value of  $K_1$  and  $K_2$ .  
 (D) I<sup>st</sup> process is not possible
25. There are two samples of same gas initially under similar initial state. Gases of both the samples are expanded. I<sup>st</sup> sample using reversible isothermal process and II<sup>nd</sup> sample using reversible adiabatic process till final pressures of both the samples becomes half of initial pressure, then  
 (A) Final volume of I<sup>st</sup> sample < final volume of II<sup>nd</sup> sample  
 (B) Final volume of II<sup>nd</sup> sample < final volume of I<sup>st</sup> sample  
 (C) final volumes will be equal  
 (D) Information is insufficient

26. In the above problem  
 (A) work done by gas in I<sup>st</sup> sample > work done by gas in II<sup>nd</sup> sample  
 (B) work done by gas in II<sup>nd</sup> sample > work done by gas in I<sup>st</sup> sample  
 (C) work done by gas in I<sup>st</sup> sample = work done by gas in II<sup>nd</sup> sample  
 (D) none of these
27. If four identical samples of an ideal gas initially at similar state ( $P_0, V_0, T_0$ ) are allowed to expand to double their volumes by four different process.  
 I : by isothermal irreversible process  
 II : by reversible process having equation  $P^2 V = \text{constant}$   
 III : by reversible adiabatic process  
 IV : by irreversible adiabatic expansion against constant external pressure.  
 Then, in the graph shown the final state is represented by four different points then, the correct match can be



- (A) 1 - I, 2 - II, 3 - III, 4 - IV  
 (B) 1 - II, 2 - I, 3 - IV, 4 - III  
 (C) 2 - III, 3 - II, 4 - I, 1 - IV  
 (D) 3 - II, 1 - I, 3 - IV, 4 - III
28. Two samples (initially under same states) of an ideal gas are first allowed to expand to double their volume using irreversible isothermal expansion against constant external pressure, then samples are returned back to their original volume first by reversible adiabatic process and second by reversible process having equation  $PV^2 = \text{constant}$  then



- (A) final temperature of both samples will be equal  
 (B) final temperature of first sample will be greater than of second sample  
 (C) final temperature of second sample will be greater than of first sample  
 (D) none of these.

SECTION - V : MATRIX - MATCH TYPE

29.

Column-I

Column-II

- (A) Reversible isothermal expansion of an ideal gas  
 (B) Reversible adiabatic compression of an ideal gas  
 (C) Irreversible adiabatic expansion of an ideal gas  
 (D) Irreversible isothermal compression of an ideal gas

- (p)  $w = -2.303 nRT \log \left( \frac{V_2}{V_1} \right)$   
 (q)  $PV^\gamma = \text{constant}$   
 (r)  $w = \frac{nR}{(\gamma - 1)} (T_2 - T_1)$   
 (s)  $\Delta H = 0$

- | 30. | Column I   | Column II                        |
|-----|--|----------------------------------|
|     | (A) A process carried out infinitesimally slowly           | (p) Adiabatic                    |
|     | (B) A process in which no heat enters or leaves the system | (q) $\Delta G = 0$               |
|     | (C) A process carried out at constant temperature          | (r) Sublimation                  |
|     | (D) A process in equilibrium                               | (s) $\Delta E = 0, \Delta H = 0$ |
|     | (E) $A(s) \longrightarrow A(g)$                            | (t) Reversible                   |
|     | (F) Cyclic process   | (u) Isothermal                   |

**SECTION - VI : SUBJECTIVE TYPE**

31. The molar enthalpy of vaporization of benzene at its boiling point (353 K) is  $30.84 \text{ kJ mol}^{-1}$ . What is the molar internal energy change? For how long would a 12 V source need to supply a 0.5 A current in order to vaporise 7.8 g of the sample at its boiling point ?
32. Calculate change in internal energy when 4 kJ of work is done on the system and 1 kJ of heat is given out by the system.
33. A gas expands against a variable pressure given by  $P = \frac{20(L - \text{atm})}{V}$ . 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 ?
34. A sample of 4 mol  $\text{O}_2$  is originally confined in 20L at 270K and then undergoes adiabatic expansion against a constant pressure of 600 Torr until the volume has increased by a factor of 3. Calculate q, w,  $\Delta T$ ,  $\Delta U$  and  $\Delta H$ . (The final pressure of the gas is not necessarily 600 Torr).



## ANSWER KEY

## EXERCISE - 1

1. C 2. A 3. C 4. C 5. B 6. C 7. A 8. D 9. B 10. C 11. B 12. D 13. C  
 14. B 15. C 16. B 17. A 18. D 19. A 20. A 21. C 22. A 23. D 24. A 25. B 26. D  
 27. B 28. B 29. D 30. D 31. A 32. B 33. D 34. C 35. C 36. B 37. C 38. D 39. C  
 40. D 41. C 42. D 43. C 44. B 45. C 46. B 47. C 48. D 49. D 50. B 51. D 52. B  
 53. C 54. B 55. A 56. D 57. D 58. A 59. A 60. D 61. B 62. B 63. C 64. A 65. B  
 66. A 67. A 68. A 69. A 70. B

## EXERCISE - 2 : PART # I

1. B,D 2. A,B,D 3. A,B,C 4. C,D 5. A,B,C 6. B,C 7. A,B,C,D 8. A,B  
 9. A,B,C,D 10. A,B,D 11. A,C 12. A,B,C,D 13. A,B,D 14. A,B,C 15. C 16. D 17. B 18.  
 B 19. A 20. B 21. C 22. B 23. B 24. A 25. A 26. C 27. A 28. B 29. B 30. A 31. B  
 32. D 33. B 34. D 35. D 36. D 37. A 38. C

## PART # II

1. D 2. A 3. A 4. D 5. B 6. B 7. C 8. B 9. C

## EXERCISE - 3 : PART # I

1.  $A \rightarrow (p, s), B \rightarrow (q, r), C \rightarrow (r), D \rightarrow (s)$  2.  $A \rightarrow (t), B \rightarrow (p), C \rightarrow (u), D \rightarrow (q), (E) \rightarrow (r), (F) \rightarrow (q, s)$   
 3.  $A \rightarrow (p, s), B \rightarrow (r), C \rightarrow (q, s), D \rightarrow (q, s)$  4.  $A \rightarrow (s), B \rightarrow (p, r), C \rightarrow (q), D \rightarrow (p, r)$   
 5.  $A \rightarrow (s), B \rightarrow (p), C \rightarrow (r), D \rightarrow (r)$

## PART # II

- Comprehension # 1 : 1. B 2. A 3. A 4. C  
 Comprehension # 2 : 1. C 2. B 3. A 4. B 5. C  
 Comprehension # 3 : 1. B 2. A 3. D  
 Comprehension # 4 : 1. B 2. A 3. C 4. D 5. A  
 Comprehension # 5 : 1. A 2. B 3. D  
 Comprehension # 6 : 1. C 2. A 3. D 4. C 5. D  
 Comprehension # 7 : 1. A 2. A 3. B

## EXERCISE - 5 : PART # I

1. A 2. C 3. A 4. D 5. A 6. C 7. B 8. B 9. C 10. B 11. A 12. C 13. C  
 14. A 15. C 16. A 17. C 18. D 19. C

## PART # II

1. A 2.  $\Delta H = 0 \text{ J}, \Delta E = 10 \text{ J}$  3. A 4. C 5. (i)  $\Delta G = -5700 \text{ J/mol}$  (ii) backward shifting  
 6. B 7. B 8.  $\Delta H = \Delta U + \Delta(PV)$  So,  $\Delta U = \Delta H - \Delta(PV) = -560 - [40 - 70] (\text{L atm}) = (-560 + 30 \times 0.1) \text{ kJ} = -557 \text{ kJ}$ .  
 9. D 10. B 11. A 12. D 13. A 14. A,D 15. A,B 16.2 17.  $(A-p, r, s); (B-r, s); (C-t); (D-p, q, t)$   
 18. A,C 19. A, D 20. B 21. C 22. A, C, D 23. C 24. A, B, C 25. B, C 26. A, C

## MOCK TEST

1. C 2. B 3. B 4. D 5. D 6. A 7. D 8. B 9. C 10. D 11. B 12. D 13. A,B,C  
 14. B,D 15. A,B,C 16. A,B 17. A,B,C,D 18. A,B,D 19. D 20. A 21. B 22. B 23. C 24. C  
 25. B 26. A 27. B 28. C 29.  $A \rightarrow (p, s), B \rightarrow (q, r), C \rightarrow (r), D \rightarrow (s)$  30.  $A \rightarrow (t), B \rightarrow (p), C \rightarrow (u), D \rightarrow (q),$   
 $E \rightarrow (r), F \rightarrow (q, s)$