

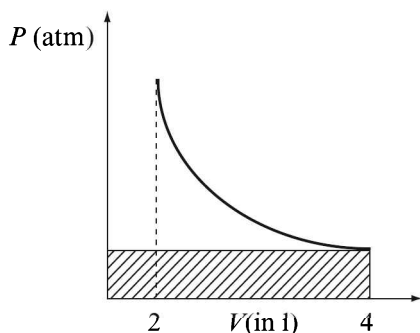
## EXERCISE II (JEE ADVANCED)

### Section A (Only one Correct)

- Which of the following gas possess the largest internal energy?
  - 2 moles of He gas occupying 1000 L at 300 K
  - 56 kg of nitrogen at 107 Pa and 300 K
  - 8 g of oxygen at 8 atm and 300 K
  - 1000 mole of argon occupying 40000 L at 900 K
- A gas expands in a piston cylinder device from  $V_1$  to  $V_2$ , the process being described by  $PV = a + bV$ , where  $P$  is in  $\text{Nm}^{-2}$ ,  $V$  is in  $\text{m}^3$  and  $a$  and  $b$  are constants. The work done in the process is
  - $a \log_e \left( \frac{V_1}{V_2} \right) + b(V_2 - V_1)$
  - $-a \log_e \left( \frac{V_2}{V_1} \right) - b(V_2 - V_1)$
  - $-a \log_e \left( \frac{V_1}{V_2} \right) - b(V_2 - V_1)$
  - $a \log_e \left( \frac{V_2}{V_1} \right) + b(V_2 - V_1)$
- An average human produces about 10 MJ of heat each day through metabolic activity. If a human body were an isolated system of mass 80 kg with the heat capacity of water, what temperature rise would the body experience? Heat capacity of water =  $4.2 \text{ J/K-g}$ .
  - 29.76°C
  - 2.976 K
  - $2.976 \times 10^4$ °C
  - 0.029°C
- The heat capacity of liquid water is  $75.6 \text{ J/K-mol}$ , while the enthalpy of fusion of ice is  $6.0 \text{ kJ/mol}$ . What is the smallest number of ice cubes at  $0^\circ\text{C}$ , each containing 9.0 g of water, needed to cool 500 g of liquid water from  $20^\circ\text{C}$  to  $0^\circ\text{C}$ ?
  - 1
  - 7
  - 14
  - 21
- An insulated container of gas has two chambers separated by an insulating partition. One of the chambers has volume  $V_1$  and contains an ideal gas at pressure  $P_1$  and temperature  $T_1$ . The other chamber has volume  $V_2$  and contains the same ideal gas at pressure  $P_2$  and temperature  $T_2$ . If the partition is removed without doing any work on the gas, the final equilibrium temperature of the gas in the container will be
  - $\frac{T_1 T_2 (P_1 V_1 + P_2 V_2)}{P_1 V_1 T_2 + P_2 V_2 T_1}$
  - $\frac{P_1 V_1 T_1 + P_2 V_2 T_2}{P_1 V_1 + P_2 V_2}$
  - $\frac{P_1 V_1 T_2 + P_2 V_2 T_1}{P_1 V_1 + P_2 V_2}$
  - $\frac{T_1 T_2 (P_1 V_1 + P_2 V_2)}{P_1 V_1 T_1 + P_2 V_2 T_2}$
- The work involved ( $w$ ) in an isothermal expansion of  $n$  moles of an ideal gas from an initial pressure of ' $P$ ' atm to final pressure of 1 atm in number of steps such that in every step the constant external pressure exactly 1 atm less than the initial pressure of gas is maintained, is given as
  - $-nRT \sum_{i=1}^{i=P-1} \left( \frac{1}{P+1-i} \right)$
  - $-nRT \sum_{i=1}^{i=P} \left( \frac{1}{P+1-i} \right)$
  - $-nRT \sum_{i=1}^{i=P} \left( \frac{i}{P+1-i} \right)$
  - $-nRT \sum_{i=1}^{i=P-1} \left( \frac{i}{P+1-i} \right)$

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7. An ideal gaseous sample at initial state ( $P_o, V_o, T_o$ ) is allowed to expand to volume  $2V_o$  using two different processes. For the first process, the equation of process is  $2PV^2 = K_1$  and for the second process, the equation of the process is  $PV = K_2$ . Then
  - (a) Magnitude of work done in the first process will be greater than that in the second process.
  - (b) Magnitude of work done in the second process will be greater than that in the first process.
  - (c) Work done in both the processes cannot be compared without knowing the relation between  $K_1$  and  $K_2$ .
  - (d) First process is impossible.
8. If a triatomic non-linear gas is heated isothermally, what percentage of the heat energy is used to increase the internal energy?
  - (a) zero
  - (b) 60%
  - (c) 50%
  - (d) 100%
9. A student is calculating the work done by 2 mole of an ideal gas in a reversible isothermal expansion shown in the figure. He by mistake calculated the area of the shaded area in the  $PV$  graph shown, as work and answered the magnitude of work equal to 49.26 L-atm. What is the correct magnitude of work done by the gas, in l-atm? ( $R = 0.0821$  L-atm/K-mol)
  - (a) 49.26
  - (b) 98.52
  - (c) 78.63
  - (d) 34.14
10. In a certain polytropic process the volume of argon was increased 4 times. Simultaneously, the pressure decreased 8 times. The molar heat capacity of argon in this process, assuming the gas to be ideal, is
  - (a)  $-4.2$  J/K-mol
  - (b)  $+4.2$  J/K-mol
  - (c)  $12.47$  J/K-mol
  - (d)  $20.78$  J/K-mol
11. The molar heat capacity at  $25^\circ\text{C}$  should be close to  $27$  J/K-mol for all of the given elements except
  - (a) Pt
  - (b) W
  - (c) Ne
  - (d) Sr
12. The pressure and density of a diatomic gas ( $\gamma = 7/5$ ) change from  $(P_1, d_1)$  to  $(P_2, d_2)$  adiabatically. If  $d_2/d_1 = 32$ , then what is the value of  $P_2/P_1$ ?
  - (a) 32
  - (b) 64
  - (c) 128
  - (d) 256
13. How many times a diatomic gas should be expanded adiabatically so as to reduce the RMS speed to half?
  - (a) 8
  - (b) 16
  - (c) 32
  - (d) 64
14. Work done by a sample of an ideal gas in a process A is double the work done in another process B. The temperature rises through the same amount in the two processes. If  $C_A$  and  $C_B$  are the molar heat capacities for the two processes, then
  - (a)  $C_A = C_B$
  - (b)  $C_A > C_B$
  - (c)  $C_A < C_B$
  - (d) both, undefined
15. One mole of oxygen is heated from  $0^\circ\text{C}$ , at constant pressure, till its volume increased by 10%. The specific heat of oxygen, under these conditions, is  $0.22$  cal/g-K. The amount of heat required is
  - (a)  $32 \times 0.22 \times 27.3 \times 4.2$  J
  - (b)  $16 \times 0.22 \times 27.3 \times 4.2$  J
  - (c)  $\frac{32 \times 0.22 \times 27.3}{4.2}$  J
  - (d)  $\frac{16 \times 0.22 \times 27.3}{4.2}$  J



16. Heat energy of 743 J is needed to raise the temperature of 5 moles of an ideal gas by 2 K at constant pressure. How much heat energy is needed to raise the temperature of the same mass of the gas by 2K at constant volume?
- (a) 826 J (b) 743 J  
(c) 660 J (d) 600 J
17. When an ideal gas at pressure,  $P$ , temperature,  $T$  and volume,  $V$ , is isothermally compressed to  $V/n$ , its pressure becomes  $P_i$ . If the gas is compressed adiabatically to  $V/n$ , its pressure becomes  $P_a$ . The ratio of  $P_i/P_a$  is
- (a) 1 (b)  $n$   
(c)  $n^\gamma$  (d)  $n^{(1-\gamma)}$
18. If the ratio  $C_p/C_v = \gamma$ , the change in internal energy of the mass of a gas, when volume changes from  $V$  to  $2V$  at constant pressure,  $P$ , is
- (a)  $\frac{R}{\gamma-1}$  (b)  $PV$   
(c)  $\frac{PV}{\gamma-1}$  (d)  $\frac{\gamma PV}{\gamma-1}$
19. A thermally insulated vessel containing a gas whose molar mass is equal to 40 and ratio of specific heats is 1.5, moves with a velocity 100 m/s. Find the gas temperature increment (in °C) resulting from the sudden stoppage of the vessel.
- (a) 12 (b) 24  
(c) 36 (d) 48
20. With what minimum pressure must a given volume of an ideal gas ( $\gamma = 1.4$ ), originally at 400 K and 100 kPa, be adiabatically compressed in order to raise its temperature up to 700 K?
- (a) 708.9 kPa (b) 362.5 kPa  
(c) 1450 kPa (d) 437.4 kPa
21. Two rigid adiabatic vessels A (volume = 4 L) and B (volume = 6 L), which initially contains two gases at different temperatures, are connected by a pipe of negligible volume. The vessel A contains 2 moles of Ne gas ( $C_{p,m} = 5 \text{ cal/K-mol}$ ) at 300 K and vessel B contains 3 moles of  $\text{SO}_2$  gas ( $C_{p,m} = 8 \text{ cal/K-mol}$ ) at 400 K. What is the final pressure (in atm) when the valve is opened and 12 kcal heat is supplied through it to the vessels?
- (a) 3.5 (b) 7  
(c) 35 (d) 70
22. A container of volume  $1 \text{ m}^3$  is divided into two equal parts by a partition. One part has an ideal diatomic gas at 300 K and the other part has vacuum. The whole system is isolated from the surrounding. When the partition is removed, the gas expands to occupy the whole volume. Its temperature will be
- (a) 300 K (b) 227.5°C  
(c) 455 K (d) 455°C
23. If all degree of freedom of a three dimensional N-atomic gaseous molecule is excited, then  $C_p/C_v$  ratio of gas should be
- (a) 1.33 (b)  $1 + \frac{1}{3N-3}$   
(c)  $1 + \frac{1}{N}$  (d)  $1 + \frac{1}{3N-2}$
24. One mole of an ideal gas undergoes a reversible process:  $T = T_0 + \alpha V$ , where  $T_0$  and  $\alpha$  are constants. If its volume increases from  $V_1$  to  $V_2$ , the amount of heat transferred to the gas is
- (a)  $C_{p,m}RT_0 \ln\left(\frac{V_2}{V_1}\right)$   
(b)  $\alpha C_{p,m} \frac{V_2 - V_1}{RT_0} \ln\left(\frac{V_2}{V_1}\right)$   
(c)  $\alpha C_{p,m}(V_2 - V_1) + RT_0 \ln\left(\frac{V_2}{V_1}\right)$   
(d)  $RT_0 \ln\left(\frac{V_2}{V_1}\right) - \alpha C_{p,m}(V_2 - V_1)$

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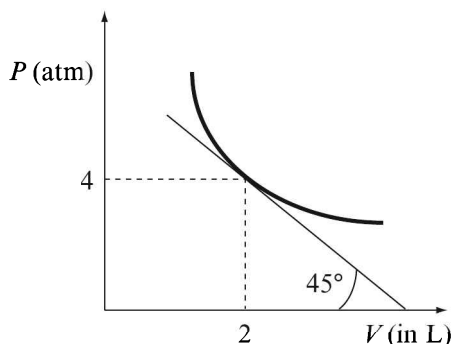
25. The average degree of freedom per molecule for a gas is 6. The gas performs 25 J of work when it expands at constant pressure. What is the amount of heat absorbed by the gas?

(a) 25 J (b) 50 J  
(c) 75 J (d) 100 J

26. One mole of an ideal monoatomic gas is heated in a process  $PV^{5/2} = \text{constant}$ . By what amount heat is absorbed in the process in  $26^\circ\text{C}$  rise in temperature?

(a) 100 J (b) 180 J  
(c) 200 J (d) 208 J

27. What is the heat capacity of the ideal monoatomic gas undergoing the process shown in the figure?



(a)  $1.5R$  (b)  $2.5R$   
(c)  $3.5R$  (d)  $1.33R$

28. A sample of ideal gas is compressed from initial volume of  $2V_0$  to  $V_0$  using three different processes

- (1) reversible isothermal
- (2) reversible adiabatic
- (3) irreversible adiabatic under a constant external pressure.

Then

- (a) final temperature of gas will be highest at the end of 2<sup>nd</sup> process.
- (b) magnitude of enthalpy change of sample will be highest in isothermal process.

- (c) final temperature of gas will be highest at the end of 3<sup>rd</sup> process.

- (d) final pressure of gas will be highest at the end of second process.

29. An ideal gas expands from volume  $V_1$  to  $V_2$ . This may be achieved by any of the three processes: isobaric, isothermal and adiabatic. Which of the following statement is not true for  $\Delta E$ ?

- (a)  $\Delta E$  is the least in the adiabatic expansion.

- (b)  $\Delta E$  is the greatest in the adiabatic expansion.

- (c)  $\Delta E$  is the greatest in the isobaric process.

- (d)  $\Delta E$  in isothermal process lies in-between the value obtained under isobaric and adiabatic process.

30. Inversion temperature is defined as the temperature above which a gas gets warm up and below which, the gas become cooler, when expanded adiabatically. Boyle temperature for a gas is  $20^\circ\text{C}$ . What will happen to the gas if it is adiabatically expanded at  $50^\circ\text{C}$ ?

- (a) Heating

- (b) Cooling

- (c) Neither heating nor cooling

- (d) First cooling then heating

31. An adiabatic cylinder fitted with an adiabatic piston at the right end of cylinder, is divided into two equal halves with a monoatomic gas on left side and diatomic gas on right side, using an impermeable movable adiabatic wall. If the piston is pushed slowly to compress the diatomic gas to  $\frac{3}{4}$ th of its original volume. The ratio of new volume of monoatomic gas to its initial volume would be

(a)  $\left(\frac{4}{3}\right)^{\frac{25}{21}}$

(b)  $\left(\frac{7}{5}\right)^{\frac{3}{4}}$

(c)  $\left(\frac{3}{4}\right)^{\frac{21}{25}}$

(d)  $\frac{3}{4}$

32. If four identical samples of an ideal gas initially at same state ( $P_o$ ,  $V_o$ ,  $T_o$ ) are allowed to expand to double their volumes by the following processes:

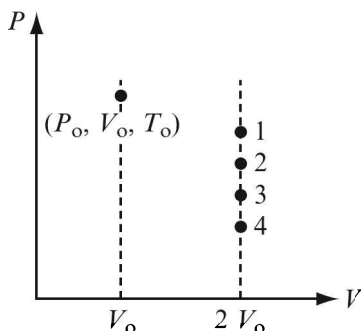
Process I: Isothermal reversible process

Process II: Reversible process  $P^2V = \text{constant}$

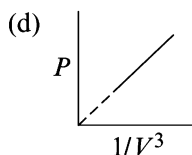
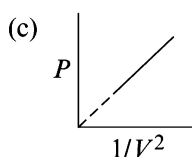
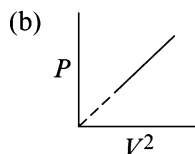
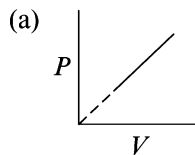
Process III: Reversible adiabatic process

Process IV: Irreversible adiabatic expansion against constant external pressure.

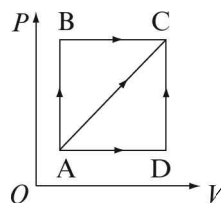
If the final states of gases are shown by different points in the graph represented, then match each point with the correct process:



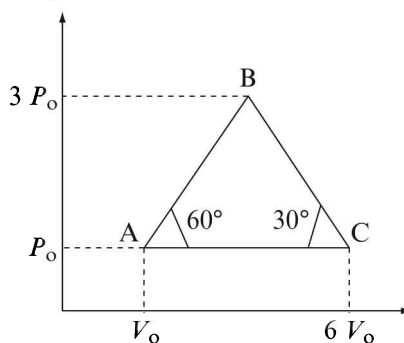
- (a) I – 1, II – 2, III – 3, IV – 4  
 (b) I – 2, II – 1, III – 4, IV – 3  
 (c) I – 4, II – 3, III – 2, IV – 1  
 (d) I – 2, II – 1, III – 3, IV – 4
33. For an ideal gas subjected to different processes as shown in the graphs, select the graph which will involve greatest amount of heat exchange if the initial and final temperatures are same in all?



34. A thermodynamic process is shown in the following figure. The pressure and volumes corresponding to some points in the figure are:  $P_A = 3 \times 10^4$  Pa,  $P_B = 8 \times 10^4$  Pa,  $V_A = 2 \times 10^{-3}$  m<sup>3</sup>,  $V_D = 5 \times 10^{-3}$  m<sup>3</sup>. In the process AB, 600 J of heat is added to the system and in BC, 200 J of heat is added to the system. The change in internal energy of the system in the process AC would be



- (a) 560 J  
 (b) 800 J  
 (c) 600 J  
 (d) 640 J
35. Two moles of an ideal monoatomic gas undergoes a cyclic process ABCA as shown in the figure. What is the ratio of temperature at B and A?



- (a) 1:1  
 (b) 3:2  
 (c) 27:4  
 (d) 9:2

36. One mole of a certain ideal gas is contained under a weightless piston of a vertical cylinder at a temperature  $T$ . The space over the piston opens into the atmosphere. What work has to be performed in order to increase isothermally the gas volume under the piston  $n$  times by slowly raising the piston? The friction of the piston against the cylinder walls is negligibly small.
- $RT(n - 1 - \ln n)$
  - $RT(1 - n + \ln n)$
  - $RT \ln n$
  - $-RT \ln n$
37. A piston can freely move inside a horizontal cylinder closed from both ends. Initially, the piston separates the inside space of the cylinder into two equal parts each of volume  $V_0$ , in which an ideal gas is contained under the same pressure  $P_0$  and at the same temperature. What work has to be performed in order to increase isothermally the volume of one part of gas  $\eta$  times compared to that of the other by slowly moving the piston?
- $P_0 V_0 \ln \eta$
  - $P_0 V_0 \ln \frac{(\eta+1)^2}{4\eta}$
  - $P_0 V_0 \ln \frac{(\eta-1)^2}{4\eta}$
  - $2P_0 V_0 \ln \eta$
38. Three samples A, B and C of the same ideal gas ( $\gamma = 1.5$ ) have equal volumes and temperatures. The volume of each sample is doubled, the process being isothermal for A, adiabatic for B and isobaric for C. If the final pressures are equal for the three samples, then the ratio of their initial pressures is
- 1:1:1
  - 2:2:1
  - $2:2\sqrt{2}:1$
  - $1:2\sqrt{2}:2$
39. A cylinder with thermally insulated walls contains an insulated portion which can slide freely. The partition divides the cylinder into two chambers containing equal moles of the same gas, the initial pressure, temperature and volume being  $P_0$ ,  $T_0$  and  $V_0$ , respectively. By means of heating coil, heat is supplied slowly to the gas in one chamber until its pressure becomes  $27P_0/8$ . If the value of  $\gamma$  is 1.5, find the heat supplied to the gas in chamber A.
- $5P_0 V_0/4$
  - $19P_0 V_0/2$
  - $15P_0 V_0/2$
  - $15P_0 V_0/4$
40. A portion of helium gas in a vertical cylindrical container is in thermodynamic equilibrium with the surroundings. The gas is confined by a movable heavy piston. The piston is slowly elevated by a distance  $H$  from its equilibrium position and then kept in the elevated position long enough for the thermodynamic equilibrium to be re-established. After that, the container is insulated and then the piston is released. After the piston comes to rest, what is the new equilibrium position of the piston with respect to initial position?
- The piston ends up  $0.4H$  above its initial position
  - The piston ends up  $0.6H$  above its initial position
  - The piston ends at its initial position
  - The piston ends up  $0.4H$  below its initial position
41. Three lawn chairs, one made up of aluminium (heat capacity =  $0.90 \text{ J/K-g}$ ), one of iron (heat capacity =  $0.45 \text{ J/K-g}$ ) and one of tin (heat capacity =  $0.60 \text{ J/K-g}$ ) are painted of the same colour. On a sunny day which chair will be hotter to sit?
- Iron chair
  - tin chair
  - aluminium chair
  - all, same

42. One mole of a real gas is subjected to a process from (2 bar, 30 L, 300 K) to (2 bar, 40 L, 500 K). The molar heat capacity of gas at constant volume and constant pressure are 25 and 40 J/K-mol, respectively. What is the change in internal energy of the gas in this process?  
 (a) 5000 J (b) 6000 J  
 (c) 8000 J (d) 10,000 J
43. A real gas is subjected to an adiabatic process from (2 bar, 40 L, 300 K) to (4 bar, 30 L, 300 K) against a constant pressure of 4 bar. The enthalpy change for the process is  
 (a) zero  
 (b) 6000 J  
 (c) 8000 J  
 (d) 10,000 J
44. The equation of state for one mole of a gas is  $PV = RT + BP$ , where  $B$  is a constant, independent of temperature. The internal energy of fixed amount of gas is function of temperature only. If one mole of the above gas is isothermally expanded from 12 L to 22 L at a constant external pressure of 1 bar at 400 K, then the change in enthalpy of the gas is approximately ( $B = 2$  L/mol)  
 (a) 0 (b)  $-3.32$  J  
 (c)  $-332$  J (d)  $-166$  J
45. One mole of a real gas is subjected to heating at constant volume from ( $P_1, V_1, T_1$ ) state to ( $P_2, V_1, T_2$ ) state. Then it is subjected to irreversible adiabatic compression against constant external pressure of  $P_3$  atm, till the system reaches final state ( $P_3, V_2, T_3$ ). If the constant volume molar heat capacity of real gas is  $C_V$ , then the correct expression for  $\Delta H$  from State 1 to State 3 is  
 (a)  $C_V(T_3 - T_1) + (P_3V_1 - P_1V_1)$   
 (b)  $C_V(T_2 - T_1) + (P_3V_2 - P_1V_1)$   
 (c)  $C_V(T_2 - T_1) + (P_3V_1 - P_1V_1)$   
 (d)  $C_P(T_2 - T_1) + (P_3V_1 - P_1V_1)$
46. The efficiency of a Carnot cycle is  $1/6$ . On decreasing the temperature of the sink by  $65^\circ\text{C}$ , the efficiency increases to  $1/3$ . The temperature of source is  
 (a)  $117^\circ\text{C}$   
 (b)  $52^\circ\text{C}$   
 (c)  $390^\circ\text{C}$   
 (d)  $1755^\circ\text{C}$
47. A Carnot engine operates between  $327^\circ\text{C}$  and  $117^\circ\text{C}$ . If it absorbs 120 cal heat per cycle from the source, the heat rejected per cycle to the sink is  
 (a) 120 cal (b) 42 cal  
 (c) 78 cal (d) 90 cal
48. In which case will the efficiency of a Carnot cycle be higher: when the hot body temperature is increased by  $\Delta T$ , or when the cold body temperature is decreased by the same magnitude?  
 (a) same in both  
 (b) on decreasing the temperature of cold body  
 (c) on increasing the temperature of hot body  
 (d) depends on the initial temperature of cold and hot bodies
49. An ideal gas ( $\gamma = 1.40$ ) is used in a Carnot cycle as a working substance. The efficiency of the cycle, if as a result of an adiabatic expansion the gas volume increases 2.75 times, is  $[(1.5)^{2.5} = 2.75]$   
 (a)  $\frac{100}{3}\%$  (b)  $\frac{200}{3}\%$   
 (c) 50% (d) 25%
50. What is the efficiency of a cycle consisting of two isochoric and two adiabatic lines, if the volume of the ideal gas changes 10 times within the cycle? The working substance is nitrogen.  $[(10)^{0.4} = 2.5]$   
 (a) 40%  
 (b) 25%  
 (c) 60%  
 (d) 75%

51. A reversible heat engine absorbs 40 kJ of heat at 500 K and performs 10 kJ of work rejecting the remaining amount to the sink at 300 K. The entropy change for the universe is  
 (a)  $-80 \text{ J/K}$   
 (b)  $100 \text{ J/K}$   
 (c)  $20 \text{ J/K}$   
 (d)  $180 \text{ J/K}$
52. Molar heat capacity of  $\text{CD}_2\text{O}$  (deuterated form of formaldehyde) vapour at constant pressure is vapour  $14 \text{ cal/K-mol}$ . The entropy change associated with the cooling of 3.2 g of  $\text{CD}_2\text{O}$  vapour from 1000 K to 900 K at constant pressure is (assume ideal gas behaviour for  $\text{CD}_2\text{O}$ ) [ $\ln 0.9 = -0.1$ ]  
 (a)  $+0.14 \text{ cal/K}$   
 (b)  $-0.14 \text{ cal/K}$   
 (c)  $-1.4 \text{ cal/K}$   
 (d)  $+1.4 \text{ cal/K}$
53. An amount of 2 mole of CO was in the small cubical container of length, ( $l = a$ ) at  $57^\circ\text{C}$ . The gas was taken out completely from the small container and put into large container ( $l = 2a$ ) at the same temperature. What is the change in entropy, if it is assumed that the process is reversible and gas is behaving as an ideal gas?  
 (a)  $34.58 \text{ J/K}$   
 (b)  $-34.58 \text{ J/K}$   
 (c)  $-11.53 \text{ J/K}$   
 (d)  $+11.53 \text{ J/K}$
54. The change in entropy accompanying the heating of one mole of helium gas ( $C_{v,m} = 3R/2$ ), assumed ideal, from a temperature of 250 K to a temperature of 1000 K at constant pressure. ( $\ln 2 = 0.7$ )  
 (a)  $4.2 \text{ cal/K}$   
 (b)  $7.0 \text{ cal/K}$   
 (c)  $2.1 \text{ cal/K}$   
 (d)  $3.5 \text{ cal/K}$
55. The molar entropy of a constant volume sample of neon at 500 K if it is  $46.2 \text{ cal/K-mol}$  at 250 K, is ( $\ln 2 = 0.7$ )  
 (a)  $2.1 \text{ cal/K-mol}$   
 (b)  $44.1 \text{ cal/K-mol}$   
 (c)  $48.3 \text{ cal/K-mol}$   
 (d)  $46.2 \text{ cal/K-mol}$
56. A sample of perfect gas that initially occupies 15.0 L at 300 K and 1.0 bar is compressed isothermally. To what volume must the gas be compressed to reduce its entropy by  $5.0 \text{ J/K}$ ? [ $\ln 0.36 = -1.0$ ,  $\ln 2.7 = 1.0$ ]  
 (a) 5.4 L (b) 8.22 L  
 (c) 40.5 L (d) 5.56 L
57. A system undergoes a process in which the entropy change is  $+5.51 \text{ JK}^{-1}$ . During the process, 1.50 kJ of heat is added to the system at 300 K. The correct information regarding the process is  
 (a) the process thermodynamically reversible.  
 (b) the process is thermodynamically irreversible.  
 (c) the process may or may not be thermodynamically reversible.  
 (d) the process must be isobaric.
58. Consider a reversible isentropic expansion of 1 mole of an ideal monoatomic gas from  $27^\circ\text{C}$  to  $927^\circ\text{C}$ . If the initial pressure of gas was 1 bar, the final pressure of gas becomes  
 (a) 4 bar (b) 8 bar  
 (c) 0.125 bar (d) 0.25 bar
59. A quantity of 1.6 g helium gas is expanded adiabatically 3.0 times and then compressed isobarically to the initial volume. Assume ideal behaviour of gas and both the processes reversible. The entropy change of the gas in this process is ( $\ln 3 = 1.1$ )  
 (a)  $-1.1 \text{ cal/K}$  (b)  $+1.1 \text{ cal/K}$   
 (c)  $-2.2 \text{ cal/K}$  (d)  $+2.2 \text{ cal/K}$



60. The entropy change of 2.0 moles of an ideal gas whose adiabatic exponent  $\gamma = 1.50$ , if as a result of a certain process, the gas volume increased 2.0 times while the pressure dropped 4.0 times, is ( $\ln 2 = 0.7$ )
- 11.64 J/K
  - +11.64 J/K
  - 34.92 J/K
  - +34.92 J/K
61. Each of the vessels 1 and 2 contain 1.2 moles of gaseous helium. The ratio of the vessels volumes is  $V_2/V_1 = 2.0$ , and the ratio of the absolute temperature of helium in them is  $T_1/T_2 = 2.0$ . Assuming the gas to be ideal, find the different of gas entropies in these vessels,  $S_2 - S_1$ . ( $\ln 2 = 0.7$ )
- 0.84 cal/K
  - 4.2 cal/K
  - 0.84 cal/K
  - 4.2 cal/K
62. One mole of an ideal gas with the adiabatic exponent ' $\gamma$ ' goes through a polytropic process as a result of which the absolute temperature of the gas increases  $\tau$ -fold. The polytropic constant equals  $n$ . The entropy increment of the gas in this process is
- $\frac{(n-\gamma)R}{(n-1)(\gamma-1)} \ln \tau$
  - $\frac{(n-1)(\gamma-1)}{(n-\gamma)R} \ln \tau$
  - $\frac{(n-\gamma)R}{(\gamma-1)} \ln \tau$
  - $\frac{(n-\gamma)R}{(n-1)} \ln \tau$
63. The expansion process of 2.0 moles of argon proceeds so that the gas pressure increases in direct proportion to its volume. The entropy change of the gas in this process if its volume increases 2.0 times, is
- +11.2 cal/K
  - 11.2 cal/K
  - +5.6 cal/K
  - 5.6 cal/K
64. An ideal gas with the adiabatic exponent  $\gamma$  goes through a process:  $P = P_0 - \alpha V$ , where  $P_0$  and  $\alpha$  are positive constants and  $V$  is the volume. At what volume will the gas entropy have the maximum value?
- $\frac{\gamma \cdot P_0}{\alpha(\gamma-1)}$
  - $\frac{\gamma \cdot P_0}{\alpha(\gamma+1)}$
  - $\frac{\alpha \cdot P_0}{\gamma+1}$
  - $\frac{\alpha \cdot P_0}{\gamma-1}$
65. One mole of an ideal gas undergoes a reversible process in which the entropy of the gas changes with absolute temperature  $T$  as:  $S = aT + C_{v,m} \ln T$ , where  $a$  is a positive constant. If  $T = T_0$  at  $V = V_0$ , the volume dependence of the gas on temperature in this process is
- $T = T_0 + \ln V$
  - $T = T_0 + \frac{R}{a} \cdot \ln \frac{V_0}{V}$
  - $T = T_0 + \frac{R}{a} \cdot \ln \frac{V}{V_0}$
  - $V = V_0 + \frac{a}{R} \cdot \ln \frac{T}{T_0}$
66. At very low temperature, the heat capacity of crystals is equal to  $C = aT^3$ , where  $a$  is a constant. Find the entropy of a crystal as a function of temperature in this temperature interval.
- $S = \frac{aT^3}{3}$
  - $S = aT^3$
  - $\frac{aT^2}{2}$
  - $\frac{aT}{3}$
67. The entropy change accompanying the transfer of 12,000 J of heat from a body A at 327°C to a body B at 127°C is
- 10.0 J/K
  - +10.0 J/K
  - 57.8 J/K
  - +57.8 J/K

68. A piece of alloy weighing 4 kg and at a temperature of 800 K is placed in 4 kg of water at 300 K. If the specific heat capacity of water is 1.0 cal/K-g and that of alloy is 4 cal/K-g, the  $\Delta S_{\text{mix}}$  is ( $\ln 2 = 0.7$ ,  $\ln 3 = 1.1$ ,  $\ln 7 = 1.95$ )
- +3.33 kcal/K
  - 1.0 kcal/K
  - +1.0 kcal/K
  - +1.33 kcal/K
69. Two blocks of copper metal are of same size (heat capacity = C) but at different temperatures  $T_1$  and  $T_2$ . These blocks are brought together and allowed to attain thermal equilibrium. The entropy change of system is
- $C \cdot \ln \left[ \frac{(T_2 - T_1)^2}{4T_1T_2} + 1 \right]$
  - $C \cdot \ln \left[ \frac{(T_2 - T_1)^2}{4T_1T_2} \right]$
  - $C \cdot \ln \left[ \frac{(T_2 + T_1)^2}{4T_1T_2} + 1 \right]$
  - $C \cdot \ln \left[ \frac{(T_2 + T_1)^2}{4T_1T_2} - 1 \right]$
70. Assuming ideal gas behaviour, the  $\Delta S$  for the isothermal mixing of 0.8 mole  $\text{N}_2$  and 0.2 mole of  $\text{O}_2$  is ( $\ln 2 = 0.7$ ,  $\ln 10 = 2.3$ )
- +0.96 cal/K
  - +0.32 cal/K
  - 0.96 cal/K
  - 0.32 cal/K
71. If all the following gases are in monoatomic form, which has greater entropy?
- H
  - N
  - O
  - Cl
72. Which of the following would be expected to have the largest entropy per mole?
- $\text{SO}_2\text{Cl}_2(\text{s})$
  - $\text{SO}_2\text{Cl}_2(\text{l})$
  - $\text{SO}_2\text{Cl}_2(\text{g})$
  - $\text{SO}_2(\text{g})$
73. The enthalpy of formation steadily changes from -17.89 Kcal/mol to -49.82 Kcal/mol as we go from  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$  to  $\text{C}_8\text{H}_{18}$ . The value of  $\Delta G$  however shows opposite trend, from -12.12 Kcal/mol for  $\text{CH}_4$  to 4.14 Kcal/mol for  $\text{C}_8\text{H}_{18}$ . Why?
- As the number of carbon atoms increases the number of possible isomers increases. This reverses the expected trend of  $\Delta G$  values.
  - The increase in the number of C-C bonds in relation to the number of C-H bonds modifies the trend of  $\Delta G$  values in relation to  $\Delta H$  values.
  - In the formation of  $\text{C}_n\text{H}_{2n+2}$  from  $n$  carbon atoms and  $(n + 1)$  hydrogen molecules there is a large decrease in entropy. This is reflected in the  $\Delta G$  values.
  - No simple reason possible.
74. An amount of 5 mole  $\text{H}_2\text{O}(\text{l})$  at  $100^\circ\text{C}$  and 1 atm is converted into  $\text{H}_2\text{O}(\text{g})$  at  $100^\circ\text{C}$  and 5 atm.  $\Delta G$  for the process is
- zero
  - $1865 \ln 5$  cal
  - $3730 \ln 5$  cal
  - $-3730 \ln 5$  cal
75. Heat liberated by a given amount of an ideal gas undergoing reversible isothermal process is 1200 cal at 300 K. What is the Gibbs free energy change of the gas in this process?
- zero
  - +1200 cal
  - 1200 cal
  - 4 cal
76. A reaction at 300 K with  $\Delta G^\circ = -1743$  kJ consist of 3 moles of A(g), 6 moles of B(g) and 3 moles of C(g). If A, B and C are in equilibrium in one liter vessel, then the reaction should be ( $\ln 2 = 0.7$ ,  $R = 8.3$  J/K-mol)
- $\text{A} + \text{B} \rightleftharpoons \text{C}$
  - $\text{A} \rightleftharpoons \text{B} + 2\text{C}$
  - $2\text{A} \rightleftharpoons \text{B} + \text{C}$
  - $\text{A} + \text{B} \rightleftharpoons 2\text{C}$

77. The vapour pressures of water and ice at  $-10^{\circ}\text{C}$  are 0.28 and 0.26 Pa, respectively. What is the free energy change for the process?
- $\text{H}_2\text{O}$  (l,  $-10^{\circ}\text{C}$ , 0.28 Pa, 1 mole)  
 $\rightarrow \text{H}_2\text{O}$  (s,  $-10^{\circ}\text{C}$ , 0.26 Pa, 1 mole)
- (a)  $R \times 263 \times \ln \frac{14}{13}$   
 (b)  $R \times 263 \times \ln \frac{13}{14}$   
 (c)  $R \times 10 \times \ln \frac{13}{14}$   
 (d)  $R \times 10 \times \ln \frac{14}{13}$
78. A definite mass of a monoatomic ideal gas at 1 bar and  $27^{\circ}\text{C}$  expands against vacuum from  $1.2 \text{ dm}^3$  to  $2.4 \text{ dm}^3$ .
- The change in free energy of the gas,  $\Delta G$ , is ( $R = 0.08 \text{ bar} \cdot \text{L/K} \cdot \text{mol}$ ,  $\ln 2 = 0.7$ )
- (a) 0 (b)  $-64 \text{ bar} \cdot \text{L}$   
 (c)  $+84 \text{ J}$  (d)  $-84 \text{ J}$
79. For a reaction:  $\text{A} \rightleftharpoons \text{B}$ , carried out at  $27^{\circ}\text{C}$ , the ratio of equilibrium concentrations of product to reactant changes by a factor of  $e^4$  for every
- (a) 1.2 kcal rise in  $\Delta G^{\circ}$   
 (b) 1.2 kcal fall in  $\Delta G^{\circ}$   
 (c) 2.4 kcal rise in  $\Delta G^{\circ}$   
 (d) 2.4 kcal fall in  $\Delta G^{\circ}$
80. The vapour pressure of water is 0.04 atm at  $27^{\circ}\text{C}$ . The free energy change for the following process is
- $\text{H}_2\text{O}$  (g, 0.04 atm,  $27^{\circ}\text{C}$ )  $\rightarrow \text{H}_2\text{O}$  (l, 0.04 atm,  $27^{\circ}\text{C}$ )
- (a) 0 (b)  $R \times 300 \times \ln \frac{1}{25}$   
 (c)  $R \times 300 \times \ln 25$  (d)  $300R$

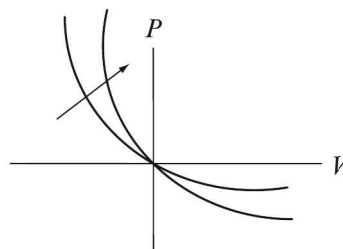
## Section B (One or More than One Correct)

1. Which of the following physical quantities are independent from amount and path, both?
- (a) Internal energy  
 (b) Temperature  
 (c) Molar heat exchanged at constant volume  
 (d) Molar heat exchanged at constant pressure
2. Which of the following sets does show the intensive properties?
- (a) temperature and pressure  
 (b) viscosity and surface tension  
 (c) refractive index and specific heat  
 (d) volume and heat capacity
3. For an isolated system, the wall/boundary separating the system from surrounding must be
- (a) rigid  
 (b) impermeable  
 (c) adiabatic  
 (d) diathermal
4. An ideal gas is taken reversibly from state A ( $P, V$ ) to the state B ( $0.5 P, 2 V$ ) along a straight line in  $PV$  diagram. Which of the following statement(s) is/are correct regarding the process?
- (a) The work done by gas in the process A to B exceeds the work that would be done by it if the same change in state were performed isothermally.  
 (b) In the  $T-V$  diagram, the path AB becomes a part of parabola.  
 (c) In the  $P-T$  diagram, the path AB becomes a part of hyperbola.  
 (d) On going from A to B, the temperature of the gas first increases to a maximum value and then decreases.

5.  $\Delta E$  must be zero for
  - (a) cyclic process
  - (b) isothermal ideal gas expansion
  - (c) isothermal real gas expansion
  - (d) isothermal change in physical state
6. Select the correct option(s):
  - (a) Molar internal energy is an intensive property.
  - (b) Ideal gases produce more work in an isothermal reversible expansion as compared to van der Waals gases, assuming ( $V \gg nb$ ).
  - (c) Reversible process can be reversed at any point in the process by making infinitesimal change.
  - (d) Less heat is absorbed by the gas in the reversible isothermal expansion as compared to irreversible isothermal expansion to the same final volume.
7. Which of the following statement(s) is/are true?
  - (a)  $C_{v,m}$  is independent of temperature for a perfect gas.
  - (b) If neither heat nor matter can enter or leave a system, the system must be isolated.
  - (c)  $\oint dF = 0$ , where  $F = U, H, G, S$ .
  - (d) A process in which the final temperature equals to the initial temperature must be an isothermal process.
8. Which of the following statement(s) is/are incorrect?
  - (a)  $\Delta E = q + w$  for every thermodynamic system at rest in the absence of external field.
  - (b) A thermodynamic process is specified by specifying the initial and final state of the system.
  - (c) If neither heat nor matter can enter or leave a system, the system must be isolated.
  - (d) For every cyclic process, the final state of the surroundings is the same as the initial state of surroundings.

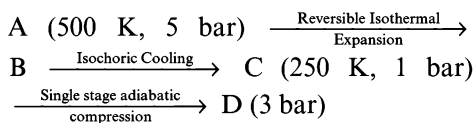
9. Which of the following statement(s) is/are true for ideal gas?

- (a)  $(-w_{\text{rev}}) - (-w_{\text{irr}}) > 0$  for isothermal expansion.
- (b)  $w_{\text{rev}} > w_{\text{irr}}$  for isothermal compression.
- (c) Heat rejected in isothermal process is greater in  $(n-1)^{\text{th}}$  stage as compared to  $n^{\text{th}}$  stage work.
- (d) Arrow shown in the graph below indicates the decreasing value of  $\gamma$ .



10. An amount of 4 moles of an ideal monoatomic gas expands adiabatically and reversibly by which its temperature decreases from  $47^\circ\text{C}$  to  $17^\circ\text{C}$ . Which of the following is/are true?
  - (a)  $q = 0$
  - (b)  $\Delta H = 0$
  - (c)  $\Delta H = -600 \text{ cal}$
  - (d)  $\Delta U = -600 \text{ cal}$
11. Which of the following statement(s) is/are correct regarding ideal gas?
  - (a) If all the gas molecules are assumed to be rigid spheres of negligible volume, the only possible molecular motion is translational.
  - (b) In polyatomic molecules, the motion of each atom is independent to the motion of other atoms of the same molecule and the net motion of the molecule is the resultant of motion of all the constituent atoms.
  - (c) Kinetic and potential energies are independent modes to describe the energy of a particle.
  - (d) All polyatomic molecules have two rotational degrees of freedom.

12. Two moles of an ideal gas ( $C_{v,m} = 1.5R$ ) is subjected to the following changes in states:



The correct statement(s) is/are

- (a) The pressure at B is 2.0 bar.
  - (b) The temperature at D is 450 K.
  - (c)  $\Delta H_{CD} = 1000R$
  - (d)  $\Delta U_{BC} = 375R$
13. Which of the following is true for reversible adiabatic process involving an ideal gas?
- (a) Gas with higher  $\gamma$  has high magnitude of slope in a  $P$  ( $y$ -axis) v/s  $T$  ( $x$ -axis) curve.
  - (b) Gas with higher  $\gamma$  has high magnitude of slope in a  $V$  ( $y$ -axis) v/s  $T$  ( $x$ -axis) curve.
  - (c) Gas with higher  $\gamma$  has high magnitude of slope in a  $P$  ( $y$ -axis) v/s  $V$  ( $x$ -axis) curve.
  - (d) Gas with higher  $\gamma$  has low magnitude of slope in a  $P$  ( $y$ -axis) v/s  $T$  ( $x$ -axis) curve.
14. For a process to occur under adiabatic conditions, the essential condition(s) is/are
- (a)  $\Delta T = 0$
  - (b)  $\Delta P = 0$
  - (c)  $q = 0$
  - (d)  $\Delta U = 0$
15. For a process to occur under isothermal conditions, the essential condition(s) is/are
- (a)  $\alpha T = 0$
  - (b)  $\alpha P = 0$
  - (c)  $q = 0$
  - (d)  $\alpha U = 0$
16. Assume ideal gas behaviour for all the gases considered and vibrational degrees of freedom to be active. Separate equimolar samples of Ne, O<sub>2</sub>, SO<sub>2</sub> and

CH<sub>4</sub> gases were subjected to a two-step process as mentioned. Initially all are at the same temperature and pressure.

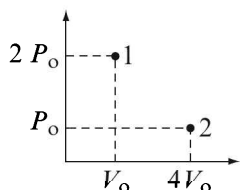
**Step I:** All undergo reversible adiabatic expansion to attain same final volume, which is double the original volume thereby causing the decrease in their temperature.

**Step II:** After Step I, all are given appropriate amount of heat isochorically to restore the original temperature.

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

- (a) Due to Step I only, the decrease in temperature will be maximum for Ne.
  - (b) During Step II, heat given will be maximum for CH<sub>4</sub>.
  - (c) There will be no change in internal energy for any gas after both the steps of process are completed.
  - (d) The  $P$ - $V$  graph of CH<sub>4</sub> and SO<sub>2</sub> will be same for overall process.
17. Which of the following statement(s) is/are incorrect?
- (a) The specific heat capacity of substance is greater in the solid state than in liquid state.
  - (b) The specific heat capacity of a substance is greater in gaseous state than in the liquid state.
  - (c) The latent heat of vaporization of a substance is greater than that of fusion.
  - (d) The internal energy of an ideal gas is a function of its temperature.
18. For which of the following gases, the difference in specific heats at constant pressure and at constant volume is equal to 0.04545 cal?
- (a) N<sub>2</sub>
  - (b) N<sub>2</sub>O
  - (c) CO
  - (d) CO<sub>2</sub>

19. A liquid is adiabatically compressed from state – I to state – II, suddenly by a single step, as shown in the figure then

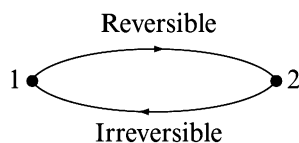


- (a)  $\Delta H = \frac{2\gamma P_o V_o}{\gamma - 1}$       (b)  $\Delta U = \frac{3P_o V_o}{\gamma - 1}$   
 (c)  $\Delta H = -P_o V_o$       (d)  $\Delta U = -3P_o V_o$
20. Which of the following statement(s) is/are incorrect?
- (a) For a closed system at rest with no fields, the sum of  $q + w$  has the same value for every process that goes from a given state 1 to a given state 2.  
 (b) If a closed system at rest in the absence of external fields undergoes an adiabatic process that has  $w = 0$ , then the temperature of system must remain constant.  
 (c) A change in state from state 1 to state 2 produces a greater increase in entropy of the system when carried out irreversible than when carried out reversibly.  
 (d) The change in entropy of the system for an adiabatic process in a closed system must be zero.

21. Which of the following statement(s) is/are incorrect?
- (a) Combustion of methane gas in an adiabatic rigid container will cause no change in temperature of the system.  
 (b) It is possible to have both adiabatic reversible and adiabatic irreversible processes between two states.  
 (c) For a reaction involving only ideal gases and occurring at constant

temperature, there will not be any change in the internal energy of the system.

- (d)  $P-V$  work is always non-zero when there is some change in the volume of system.
22. Which of the following statement(s) is/are correct regarding reversible adiabatic and isothermal processes for an ideal gas, starting from the same initial state to the same final volume?
- (a) In expansion, more work is done by the gas in isothermal process.  
 (b) In compression, more work is done on the gas in adiabatic process.  
 (c) In expansion, the final temperature of gas will be higher in isothermal process.  
 (d) In compression, the final temperature of gas will be higher in adiabatic process.
23. A heat engine is operating in between 500 K and 400 K. If the engine absorbs 100 J heat per cycle, then which of the following is impossible amount of heat rejected by the engine per cycle?
- (a) 75 J      (b) 85 J  
 (c) 90 J      (d) 70 J
24. For the cyclic process given below, which of the following relations are correct?



- (a)  $\Delta S = S_2 - S_1 = \int_1^2 \frac{\delta q_{\text{rev}}}{T}$   
 (b)  $\Delta S = S_1 - S_2 = \int_2^1 \frac{\delta q_{\text{irr}}}{T}$   
 (c)  $\Delta S_{\text{cycle}} = 0 = \int_1^2 \frac{\delta q_{\text{rev}}}{T} + \int_2^1 \frac{\delta q_{\text{irr}}}{T}$   
 (d)  $\Delta S_{\text{cycle}} = 0 > \left( \int_1^2 \frac{\delta q_{\text{rev}}}{T} + \int_2^1 \frac{\delta q_{\text{irr}}}{T} \right)$

25. For which of the following process  $\Delta S^\circ$  is positive?
- The dissolution of ammonium nitrate in water
  - The expansion of a sample of chlorine into a larger volume
  - The decomposition of mercuric oxide
  - The resting of iron
26. Any process will be spontaneous at constant pressure and temperature when
- $\Delta S_{\text{system}} = +ve$
  - $\Delta S_{\text{univ.}} = +ve$
  - $\Delta G_{\text{sys}} = -ve$
  - $\Delta G_{\text{univ.}} = +ve$
27. Which of the following statement(s) is/are incorrect?
- Entropy is a measure of unavailable energy.
  - Decrease in free energy of the system represents the unavailable energy of the system.
  - Complete conversion of heat into work is not possible in a reversible isothermal expansion of ideal gas.
  - Complete conversion of heat into work is not possible in an irreversible isothermal expansion of ideal gas.
28. Which of the following processes are expected to be spontaneous at low temperature and non-spontaneous at high temperature?
- Dissociation of  $\text{PCl}_5(\text{g})$  into  $\text{PCl}_3(\text{g})$  and  $\text{Cl}_2(\text{g})$
  - Formation of  $\text{H}_2\text{O}(\text{l})$  from  $\text{H}_2(\text{g})$  and  $\text{O}_2(\text{g})$
  - Formation of  $\text{H}_2\text{O}(\text{g})$  from  $\text{H}_2(\text{g})$  and  $\text{O}_2(\text{g})$
  - Freezing of water
29. The normal boiling point of a liquid is 350 K and  $\Delta H_{\text{vap}}$  is 35 kJ/mol. Assume that  $\Delta H_{\text{vap}}$  is independent from temperature and pressure. The correct statement(s) is/are
- $\Delta S_{\text{vap}} > 100 \text{ J/K-mol}$  at 350 K and 0.5 atm
  - $\Delta G_{\text{vap}} < 0$  at 350 K and 0.5 atm
  - $\Delta S_{\text{vap}} > 100 \text{ J/K-mol}$  at 350 K and 2.0 atm
  - $\Delta G_{\text{vap}} > 0$  at 350 K and 2.0 atm
30. Select the correct statement(s)
- In a reversible process,  $\Delta G$  is always zero in a closed system.
  - In a reversible process,  $\Delta S_{\text{univ}}$  is always zero in a closed system.
  - In a reversible process,  $\Delta S_{\text{sys}}$  is always zero in a closed system.
  - In a reversible process,  $\Delta S_{\text{sys}}$  is always zero in an isolated system.

## Section C (Comprehensions)

### Comprehension I

An amount of 4 mole of hydrogen gas is taken in a vessel at STP and the vessel is sealed. Now the gas is cooled to  $-50^\circ\text{C}$ .

- What is the change in internal energy of gas?
  - 600 J
  - 600 cal
  - 1000 cal
  - zero
- What is the change in enthalpy of gas?
  - 1400 J
  - 600 cal
  - 1000 cal
  - zero
- What is the magnitude of work done by the gas?
  - 600 J
  - 600 cal
  - 1000 cal
  - zero

## Comprehension II

An ideal gas ( $C_p/C_v = \gamma$ ) is expanded so that the amount of heat transferred to the gas is equal to the decrease in its internal energy.

4. What is the molar heat capacity of gas in this process?
    - (a)  $C_{v,m}$
    - (b)  $-C_{v,m}$
    - (c)  $C_{p,m}$
    - (d)  $-C_{p,m}$
  5. What is the relation between  $T$  and  $V$  of gas in this process?
    - (a)  $T \cdot V^{2(\gamma-1)} = \text{constant}$
    - (b)  $T \cdot V^{\gamma-1} = \text{constant}$
    - (c)  $T \cdot V^{(\gamma-1)/2} = \text{constant}$
    - (d)  $T \cdot V^{\gamma} = \text{constant}$
  6. What is the magnitude of work performed by one mole of the gas when its volume increases 8 times if the initial temperature of the gas is 300 K?  $C_{v,m}$  for the gas is  $1.5R$ .
    - (a) 900 cal
    - (b) 450 cal
    - (c) 1247.7 cal
    - (d) 623.8 cal
- 

## Comprehension III

As a result of the isobaric heating by  $\Delta T = 72$  K, one mole of a certain ideal gas obtains an amount of heat  $Q = 1.60$  kJ.

7. The work performed by the gas is
    - (a) 8.60 kJ
    - (b) 0.60 kJ
    - (c) 16.60 kJ
    - (d) 4.60 kJ
  8. The increment of its internal energy (in kJ) is
    - (a) 0.6
    - (b) 0.16
    - (c) 1.6
    - (d) 2.2
  9. The value of  $\gamma$  for the gas is
    - (a) 1
    - (b) 10
    - (c) 2
    - (d) 20
- 

## Comprehension IV

An ideal gas whose adiabatic exponent equals  $\gamma$  is expanded according to the law  $P = \alpha V$ , where  $\alpha$  is a constant. The initial volume of the gas is equal to  $V_0$ . As a result of expansion, the volume increases 4 times.

10. What is the increment of the internal energy of the gas?
    - (a)  $\frac{15\alpha V_0^2}{\gamma-1}$
    - (b)  $\frac{\alpha V_0^2}{\gamma-1}$
    - (c)  $\frac{15\alpha V_0^2}{2}$
    - (d)  $\frac{15\alpha(\gamma+1)V_0^2}{2(\gamma-1)}$
  11. What is the magnitude of work performed by the gas?
    - (a)  $\frac{15\alpha V_0^2}{\gamma-1}$
    - (b)  $\frac{\alpha V_0^2}{\gamma-1}$
    - (c)  $\frac{15\alpha V_0^2}{2}$
    - (d)  $\frac{15\alpha(\gamma+1)V_0^2}{2(\gamma-1)}$
  12. What is the molar heat capacity of the gas in the process?
    - (a)  $\frac{R(\gamma+1)}{2(\gamma-1)}$
    - (b)  $\frac{\alpha V_0^2}{\gamma-1}$
    - (c)  $\frac{R(\gamma-1)}{2(\gamma+1)}$
    - (d)  $\frac{15\alpha(\gamma+1)V_0^2}{2(\gamma-1)}$
-



### Comprehension V

One mole of an ideal gas whose adiabatic exponent equals  $\gamma$  undergoes a process in which the gas pressure relates to the temperature as  $p = aT^\alpha$ , where  $a$  and  $\alpha$  are constants.

13. What is the magnitude of work performed by the gas if its temperature is increased by  $\Delta T$ ?
- (a)  $R(1 - \alpha) \cdot \Delta T$  (b)  $\frac{R\alpha}{\gamma - 1}$   
 (c)  $R \cdot \alpha \cdot \Delta T$  (d)  $\frac{R}{\gamma - 1} + R(1 - \alpha)$   
 (e)  $R \cdot \Delta T / (1 - \alpha)$  (f)  $\frac{R}{\gamma - 1} + \frac{R}{1 - \alpha}$   
 (g)  $R \cdot \Delta T / \alpha$
14. What is the molar heat capacity of the gas in the process?
15. At what value of  $\alpha$  will the heat capacity be negative?
- (a)  $\alpha < -1$  (b)  $\alpha < 0$   
 (c)  $\alpha > \frac{\gamma}{\gamma - 1}$  (d)  $\alpha < \gamma$

### Comprehension VI

An ideal gas with the adiabatic exponent  $\gamma$  undergoes a process in which its internal energy relates to the volume as  $U = a \cdot V^\alpha$ , where  $a$  and  $\alpha$  are constants.

16. What is the magnitude of work performed by the gas to increase its internal energy by  $\Delta U$ ?
- (a)  $\frac{R \cdot \Delta U}{\alpha(\gamma - 1)}$  (b)  $\frac{\Delta U}{\alpha(\gamma - 1)}$   
 (c)  $\frac{\Delta U \cdot (\gamma - 1)}{\alpha}$  (d)  $\frac{\Delta U \cdot \alpha}{(\gamma - 1)}$
17. What amount of heat is to be transferred to this gas to increase its internal energy by  $\Delta U$ ?
18. What is the molar heat capacity of the gas in this process?
- (a)  $\frac{R}{\alpha(\gamma - 1)}$  (b)  $\frac{R}{\alpha + \gamma - 1}$   
 (c)  $\frac{R}{\gamma - 1} + \frac{R}{\alpha}$  (d)  $\frac{R}{\gamma - 1} - \frac{R}{\alpha}$

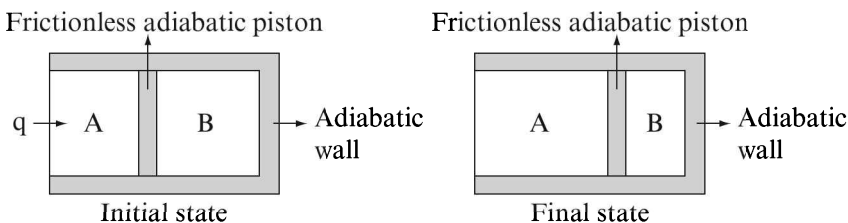
### Comprehension VII

The adiabatic compression of a mixture of 2 volumes of Hydrogen and 1 volume of oxygen from 320 ml to 10 ml caused explosion. The initial pressure and temperature of the gaseous mixture were 1 atm and 27°C.

19. What is the pressure of the gaseous mixture at the moment of explosion?
- (a) 32 atm (b) 128 atm  
 (c) 1/32 atm (d) 1/128 atm
20. What is the temperature of the gaseous mixture at the moment of explosion?
- (a) 1200 K (b) 300 K  
 (c) 75 K (d) 3023.8 K
21. What is the magnitude of maximum work performed by the gaseous mixture before explosion?
- (a) 145.87 J (b) 243.12 J  
 (c) 2400 J (d) 0

## Comprehension VIII

A cylindrical container of volume 44.8 L is containing equal number of moles of an ideal monoatomic gas in two sections A and B, separated by an adiabatic frictionless piston as shown in the figure. The initial temperature and pressure of gas in both section is 27.3 K and 1 atm. Now, gas in section A is slowly heated till the volume of section B becomes one-eighth of the initial volume.



22. What will be the final pressure of gas in Section B?  
 (a) 2 atm (b) 8 atm (c) 16 atm (d) 32 atm
23. What is the final temperature of gas in Section A?  
 (a) 1638 K (b) 6988 K (c) 3274 K (d) 51 K
24. The change in enthalpy of gas in Section A is  
 (a) 48.3 kcal (b) 80.53 kcal (c) 4.83 kcal (d) 8.05 kcal

## Comprehension IX

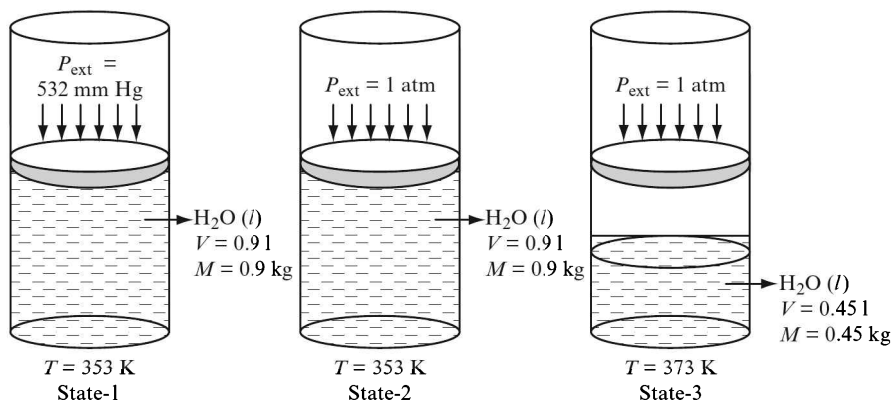
The vapour pressure of water at 353 K is 532 mm Hg. The external pressure on  $\text{H}_2\text{O}(\text{l})$  taken in a cylinder fitted with frictionless movable piston initially containing 0.9 L (= 0.9 kg) of  $\text{H}_2\text{O}(\text{l})$  at 353 K is increased to 1 atm at the constant temperature. Then, heat is supplied keeping the pressure constant till 0.45 L of  $\text{H}_2\text{O}(\text{l})$  is evaporated to form  $\text{H}_2\text{O}(\text{g})$  at 373 K. Assume the internal energy of liquid to be dependent only on temperature. Answer the following questions by carefully observing the diagrams and the data provided. Given:

Specific heat of  $\text{H}_2\text{O}(\text{l}) = 4.2 \text{ J/}^\circ\text{C-g}$

$\Delta H_{\text{vap}}$  at 373 K and 1 atm = +40 kJ/mol

1 L-atm = 100 J

$R = 8 \text{ J/K-mol}$



- |   |   |
|---|---|
| <p>25. <math>\Delta H</math> (in J), when system is taken from State 1 to State 2, is<br/>         (a) zero (b) 0.27<br/>         (c) 27 (d) 90</p> <p>26. Total change in <math>\Delta U</math> (in kJ) going from State 1 to State 3 is<br/>         (a) 75.6 (b) 1075.6<br/>         (c) 1001 (d) 74.6</p> | <p>27. Total change in enthalpy (in kJ) going from State 1 to State 3 is<br/>         (a) 75.6 (b) 1075.6<br/>         (c) 1001 (d) 74.6</p> <p>28. What is the work done (in J) in going State 1 to State 3?<br/>         (a) zero (b) 74.6<br/>         (c) 90 (d) 31.5</p> |
|---|---|
- 

### Comprehension X

One mole of a monoatomic ideal gas is used as a working substance in an engine working in the following reversible cycle: process AB = isobaric compression; process BC = adiabatic compression; process CD = isochoric heating; process DA = isothermal expansion. The ratio of maximum to minimum volume and temperature during the cycle is  $8\sqrt{2}$  and 4, respectively. The maximum temperature in the cycle is 800 K.

- |   |  |
|---|--|
| <p>29. The temperature of gas at state 'C' is<br/>         (a) 800 K (b) 200 K<br/>         (c) 400 K (d) 100 K</p> | <p>30. The change in internal energy of gas in the process BC is<br/>         (a) 2.49 kJ (b) -2.49 kJ<br/>         (c) 4.16 kJ (d) -4.16 kJ</p> |
|---|--|
- 

### Section D (Assertion – Reason)

The following questions consist of two statements. Mark

- (a) If both statements are CORRECT, and **Statement II** is the CORRECT explanation of **Statement I**.  
 (b) If both statements are CORRECT, and **Statement II** is NOT the CORRECT explanation of **Statement I**.  
 (c) If **Statement I** is CORRECT, but **Statement II** is INCORRECT.  
 (d) If **Statement I** is INCORRECT, but **Statement II** is CORRECT.

1. **Statement I:** The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.

**Statement II:** The volume occupied by the molecules of an ideal gas is negligible.

2. **Statement I:** There is no change in enthalpy of an ideal gas during compression at constant temperature.

**Statement II:** Enthalpy of an ideal gas is a function of temperature and pressure.

3. **Statement I:** The temperature of a non-ideal gas does not change in adiabatic free expansion.

**Statement II:** In adiabatic free expansion of ideal as well non-ideal gas,  $q = w = \Delta U = 0$ .

4. **Statement I:** Due to adiabatic expansion, the temperature of an ideal gas always decreases.

**Statement II:** For an adiabatic process,  $\Delta U = w$ .

5. **Statement I:** The magnitude of work done by an ideal gas in adiabatic reversible expansion from the same initial pressure and volume to the same final volume is less than that in isothermal reversible process.

**Statement II:** If an ideal gas is expanded reversibly from the same initial pressure and volume to the same final volume, then the final pressure in adiabatic process is less than that in the isothermal process.

6. **Statement I:** The magnitude of work done by an ideal gas in reversible adiabatic expansion from the same initial volume to the same final pressure and volume is greater than that in reversible isothermal process.

**Statement II:** If an ideal gas is expanded reversibly from the same initial volume to the same final pressure and volume, then the initial pressure is greater in adiabatic process than that in isothermal process.

7. **Statement I:** The final temperature of an ideal gas in adiabatic expansion is less in reversible expansion than in irreversible expansion against a constant external pressure.

**Statement II:** The magnitude of work done by an ideal gas in adiabatic expansion is more in reversible process than that in irreversible process.

8. **Statement I:** The final temperature of an ideal gas in adiabatic expansion is less in reversible compression than in irreversible compression against a constant external pressure.

**Statement II:** The magnitude of work done by an ideal gas in adiabatic compression is more in irreversible process than that in reversible process.

9. **Statement I:** For the same mole of  $\text{SO}_2$  and  $\text{O}_2$  gases, more heat is needed for  $\text{SO}_2$  gas than  $\text{O}_2$  gas for the same increase in the temperature of the gas.

**Statement II:**  $\text{SO}_2$  gas, being triatomic, has higher heat capacity than the diatomic  $\text{O}_2$  gas.

10. **Statement I:** Decrease in free energy causes spontaneous reaction.

**Statement II:** Spontaneous reactions are invariably exothermic.

11. **Statement I:** Many endothermic reactions that are not spontaneous at room temperature become spontaneous at high temperature.

**Statement II:** Entropy of the system increases with increase in temperature.

12. **Statement I:** An exothermic process, non-spontaneous at high temperature, may become spontaneous at low temperature.

**Statement II:** With decrease in temperature, randomness (entropy) decreases.

13. **Statement I:** A reaction which is spontaneous and accompanied by decrease of randomness must be exothermic.

**Statement II:** All exothermic reactions are accompanied by decrease of randomness.

14. **Statement I:** The endothermic reactions are favoured at lower temperatures and the exothermic reactions are favoured at higher temperatures.

**Statement II:** When a system in equilibrium is disturbed by changing the temperature, it will tend to adjust itself so as to overcome the effect of change.

15. **Statement I:** For an irreversible cyclic process in a closed system,  $\Delta S_{\text{surr}} = 0$ .

**Statement II:** Entropy is a state function.

## Section E (Column Match)

## 1. Match the column

Column I (Process)	Column II (Type of boundary possible)
(A) Isochoric	(P) Rigid
(B) Isothermal	(Q) Non-rigid
(C) Isobaric	(R) Impermeable
(D) Adiabatic	(S) Diathermal
	(T) Insulated
	(U) Thermostatic

## 2. Match the column

Column I	Column II
(A) Change in internal energy	(P) Independent from the quantity of system
(B) Heat	(Q) Depends on the quantity of system
(C) Work done by a gas	(R) State function
(D) Molar heat capacity at constant volume	(S) Path function

## 3. Match the column

Column I (Ideal gas)	Column II (Related equations)
(A) Reversible isothermal process	(P) $w = nRT \ln \frac{P_2}{P_1}$
(B) Reversible adiabatic process	(Q) $w = nC_{v,m}(T_2 - T_1)$
(C) Irreversible adiabatic process	(R) $PV = nRT$
(D) Irreversible isothermal process	(S) $w = -\int_{V_1}^{V_2} P_{\text{ext}} \cdot dV$

## 4. Match the column: (Given process does not include chemical reaction and phase change)

Column I (Relation)	Column II (Applicable to)
(A) $\Delta H = \Delta U + \Delta(PV)$	(P) Any matter undergoing any process.
(B) $\Delta H = n \cdot C_{p,m} \cdot \Delta T$	(Q) Isochoric process involving any substance.
(C) $q = \Delta U$	(R) Ideal gas, under any process.
	(S) Ideal gas under isothermal process.

5. Match the column (assume  $C_{v,m}$  is independent of temperature)

Column I	Column II
(A) $dU = n \cdot C_{v,m} \cdot dT$	(P) Ideal gas
(B) $dU = n \cdot C_{v,m} \cdot dT + n^2 a \frac{dV}{V^2}$	(Q) van der Waals gas
(C) $dU = n^2 a \frac{dV}{V^2}$	(R) van der Waals gas in isothermal process
	(S) van der Waals gas in isochoric process

## 6. Match the process of Column I with entropy or enthalpy change in Column II

Column I	Column II
(A) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$	(P) $\Delta S \approx 0$
(B) $2\text{KI}(\text{aq}) + \text{HgI}_2(\text{aq}) \rightarrow \text{K}_2[\text{HgI}_4](\text{aq})$	(Q) $\Delta S < 0$
(C) $\text{PCl}_5(\text{g}) \rightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$	(R) $\Delta H > 0$
(D) $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$	(S) $\Delta H < 0$

## 7. Match Column I with Column II

Column I	Column II
(A) Reversible isothermal expansion of an ideal gas	(P) $\Delta S_{\text{sys}} = \Delta S_{\text{surr}} = \Delta S_{\text{total}} = 0$
(B) Reversible adiabatic expansion of an ideal gas	(Q) $\Delta H = \Delta U = \Delta S_{\text{total}} = 0$
(C) Adiabatic free expansion	(R) $\Delta S_{\text{total}} > 0$
	(S) $q = 0$

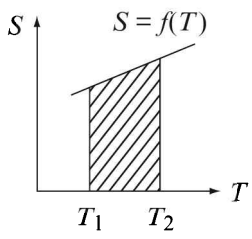
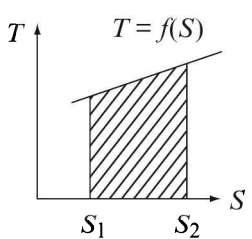
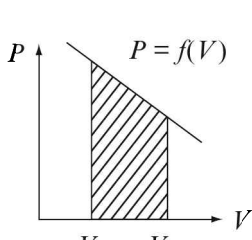
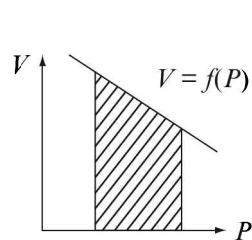
## 8. Match Column I with Column II

Column I	Column II
(A) For the process: $A(l) \rightarrow A(s)$ , $\Delta H$ and $\Delta V$ may be	(P) -ve, +ve
(B) $A_2(s) + B_2(g) \rightarrow C_2(s) + D_2(s)$ , $\Delta H$ and $\Delta G$ may be	(Q) +ve, -ve
(C) $A_2(g) \rightarrow B(g) + C(g)$ , $E_{a(\text{forward})} = 50 \text{ kJ/mol}$ , $E_{a(\text{backward})} = 40 \text{ kJ/mol}$ , $\Delta H$ and $\Delta G$ at very high temperature are	(R) +ve, +ve
(D) $A(g) \rightarrow B(g)$ , $\Delta H$ and $\Delta G$ at very low temperature are	(S) -ve, -ve

## 9. Match Column I with Column II

Column I	Column II
(A) Fusion at melting point	(P) $\Delta G = 0$
(B) Vaporization at boiling point	(Q) $\Delta G < 0$
(C) Condensation at triple point	(R) $\Delta S > 0$
(D) Melting at normal boiling point	(S) $\Delta H \approx \Delta U$

## 10. Match Column I (graph) with the physical quantity in Column II (area shown in the graph represents the magnitude of)

Column I	Column II
(A) 	(P) $q$
(B) 	(Q) $w$
(C) 	(R) $(\Delta G)_T$
(D) 	(S) $(\Delta G)_P$

## Section F (Subjective)

### Single-digit Integer Type

- As 1 mole of liquid water is heated from 288 to 298 K, it expands slightly against the atmosphere. Given coefficient of cubic expansion of water is  $0.0002/^{\circ}\text{C}$ ; density of water =  $1.0 \text{ g cm}^{-3}$  and external pressure = 1 bar. If the magnitude of work for this process is  $X \text{ J}$ , then the value of  $\frac{X}{6 \times 10^{-4}}$  is
- The final volume (in L) of one mole of an ideal gas initially at  $27^{\circ}\text{C}$  and 8.21 atm pressure, if it absorbs 420 cal of heat during a reversible isothermal expansion, is
- A balloon containing air at  $27^{\circ}\text{C}$  and 1 bar initially is filled with air further, isothermally and reversibly till the pressure is 4 bar. If the initial diameter of the balloon is 1 m and the pressure at each stage is proportional to diameter of balloon, the magnitude of work done (in  $10^7 \text{ J}$ ) is
- A quantity of 8 g oxygen gas is expanded isothermally at  $27^{\circ}\text{C}$  from  $2 \text{ dm}^3$  to  $8 \text{ dm}^3$  at a constant external pressure of 4 bar. If the magnitude of work done in this process is used in lifting body of mass 40 kg, the height (in meter) up to which the body can be lifted is ( $g = 10 \text{ ms}^{-2}$ )
- An amount  $Q$  of heat is added to a monoatomic ideal gas in a process in which the gas performs a work  $Q/2$  on its surrounding. The molar heat capacity of gas (in  $\text{cal/K-mol}$ ) for the process is
- What amount of heat (in J) is to be transferred to nitrogen in the isobaric heating process for that gas to perform the work 2.0 J?
- Five moles of a certain ideal gas at a temperature 300 K was cooled isochorically so that the gas pressure reduced 2.0 times. Then, as a result of the isobaric process, the gas expanded till its temperature got back to the initial value. The total amount of heat absorbed (in Kcal) by the gas in this process is
- Three moles of an ideal gas being initially at a temperature 273 K was isothermally expanded 5.0 times its initial volume and then isochorically heated so that the pressure in the final state became equal to that in the initial state. The total amount of heat transferred to the gas during the process equals 80 kJ. The value of  $C_{v,m}$  for this gas (in  $\text{cal/K-mol}$ ) is
- The number of degrees of freedom of molecules in a gas whose molar heat capacity is  $29 \text{ J/mol-K}$  in the process:  $PT = \text{constant}$  is
- A quantity of 56 g of nitrogen gas is enclosed in a rigid vessel at a temperature 300 K. The amount of heat (in kcal) has to be transferred to the gas to increase the root mean square velocity of its molecules 2.0 times is
- A gas consisting of rigid diatomic molecules was expanded in a polytropic process so that the rate of collisions of the molecules against the vessel's wall did not change. The molar heat capacity of the gas (in  $\text{cal/K-mol}$ ) in this process is
- The increase in Gibbs free energy (in kJ) of 13 g of ethanol (density =  $0.78 \text{ g cm}^{-3}$ ), when the pressure is increased isothermally from 1 bar to 3001 bar, is
- At 298 K, the standard enthalpy of combustion of sucrose is  $-5737 \text{ kJ mol}^{-1}$  and the standard Gibbs energy of the reaction is  $-6333 \text{ kJ mol}^{-1}$ . The additional (non-expansion) work (in kJ) that may be obtained by raising the temperature to  $29^{\circ}\text{C}$  is

14. The diamonds are formed from graphite under very high pressure. Calculate the equilibrium pressure (in  $10^5$  bar) at which graphite is converted into diamond at  $25^\circ\text{C}$ . The densities of graphite and diamond are  $2.4$  and  $3.6\text{ g/cm}^3$ , respectively, and are independent of pressure.  $\Delta G^\circ$  for the conversion of graphite into diamond is  $5.0\text{ kJ/mol}$ .
15. The standard entropy change (in  $\text{cal/K-mol}$ ) for the reaction:  $\text{X} \rightleftharpoons \text{Y}$ , if the value of  $\Delta H^\circ = 7.5\text{ kcal/mol}$  and  $K_c = e^{-10}$  at  $300\text{ K}$ .

### Four-digit Integer Type

- One mole of a van der Waals gas expands reversibly and isothermally at  $27^\circ\text{C}$  from  $2\text{ L}$  to  $20\text{ L}$ . The magnitude of work done (in  $\text{J}$ ) if  $a = 1.42 \times 10^{12}\text{ dynes cm}^4/\text{mole}$  and  $b = 30\text{ ml/mole}$ .
- One mole of an non-ideal gas undergoes a change of state from  $(2.0\text{ atm}, 3.0\text{ L}, 95\text{ K})$  to  $(4.0\text{ atm}, 5.0\text{ L}, 245\text{ K})$  with a change in internal energy,  $\Delta U = 30.0\text{ L-atm}$ . The enthalpy change ( $\Delta H$ ) of the process in  $\text{L-atm}$  is
- The internal energy change in the conversion of  $1\text{ mole}$  of the calcite form of  $\text{CaCO}_3$  to the aragonite form is  $+0.21\text{ kJ}$ . The enthalpy change (in  $\text{J}$ ) in the conversion at  $2.7\text{ bar}$  is (The densities of the solids calcite and aragonite are  $2.7\text{ g cm}^{-3}$  and  $3.0\text{ g cm}^{-3}$ , respectively.)
- A system undergoes a certain change in state by path I and the corresponding heat absorbed and work done are  $10\text{ kcal}$  and  $0\text{ erg}$ , respectively. For the same change in state by path II, the respective quantities are  $11\text{ kcal}$  and  $0.5 w_{\text{max}}$ , where  $w_{\text{max}}$  represents the work done if the changes were reversibly carried out. The magnitude of  $w_{\text{max}}$ , in  $\text{J}$ , is ( $1\text{ cal} = 4.2\text{ J}$ )
- The internal energy of a gas is given by  $U = 1.5 PV$ . It expands from  $100$  to  $200\text{ cm}^3$  against a constant pressure of  $1.0 \times 10^5\text{ Pa}$ . The heat absorbed (in  $\text{J}$ ) by the gas in the process is
- The internal energy of a monoatomic ideal gas is  $1.5 nRT$ . One mole of helium is kept in a cylinder of cross section  $8.5\text{ cm}^2$ . The cylinder is closed by a light frictionless piston. The gas is heated slowly in a process during which a total of  $42\text{ J}$  heat is given to the gas. If the temperature rises through  $2^\circ\text{C}$ , find the distance moved by the piston (in  $\text{cm}$ ). Atmospheric pressure =  $100\text{ kPa}$ .
- Only at extremely high pressure does  $\Delta H - \Delta U$  for condensed state reactions becomes significantly different than zero. Determine the pressure (in  $\text{bar}$ ) at which  $\Delta H - \Delta U$  is equal to  $-1.0\text{ kJ}$  for the reaction,  $\text{C}(\text{graphite}) \rightarrow \text{C}(\text{diamond})$ . For graphite and diamond, densities are  $2.25$  and  $3.51\text{ g/ml}$ , respectively.
- The melting point of a certain substance is  $70^\circ\text{C}$ , its normal boiling point is  $450^\circ\text{C}$ , its enthalpy of fusion is  $30\text{ cal/g}$ , its enthalpy of vaporization is  $45\text{ cal/g}$ , and its specific heat is  $0.215\text{ cal/g-K}$ . The heat required (in  $\text{cal}$ ) to convert  $10\text{ g}$  of the substance from the solid state at  $70^\circ\text{C}$  to vapour at  $450^\circ\text{C}$  is
- When an electric current of  $0.50\text{ A}$  from a  $12\text{ V}$  supply is passed for  $\frac{1805}{6}\text{ sec}$  through a resistance in thermal contact with water maintained at  $1\text{ atm}$  and  $373\text{ K}$ , it is found that  $0.9\text{ g}$  of water is vaporized. The molar internal energy change (in  $\text{kJ/mol}$ ) of water is (Take  $8.314 \times 373 = 3100$ )



10. A volume of 100 ml of a liquid contained in an isolated container at a pressure of 1 bar. The pressure is steeply increases to 100 bar by which the volume of liquid is decreased by 1 ml. The change in enthalpy,  $\Delta H$ , of the liquid is (Answer as 'abcd', where  $a = 1$ , if  $\Delta H$  is +ve and  $a = 2$ , if  $\Delta H$  is - ve, and 'bcd' is the magnitude of  $\Delta H$ , in J)
11. Pressure over 1000 ml of a liquid is gradually increased from 1 bar to 1001 bar under adiabatic conditions. If the final volume of the liquid is 990 ml and there is linear variation of volume with pressure, the value of  $\Delta U$  of the process is (Answer as 'abcd', where  $a = 1$ , if  $\Delta U$  is +ve and  $a = 2$ , if  $\Delta U$  is - ve, and 'bcd' is the magnitude of  $\Delta U$ , in J)
12. One mole of an ideal gas ( $\gamma = 1.4$ ) is expanded isothermally at  $27^\circ\text{C}$  till its volume is doubled. It is then adiabatically compressed to its original volume. The magnitude of total work done by the gas is
13. Consider a classroom that is roughly  $8.21\text{ m} \times 10\text{ m} \times 3\text{ m}$ . Initially  $T = 290\text{ K}$  and  $P = 1\text{ atm}$ . There are 50 people in the class, each losing energy to the room at the average rate of 166 W. Assume that the walls, ceiling, floor, and furniture are perfectly insulated and do not absorb any heat. Also assume that all the doors and windows are tightly closed to prevent any exchange of air from surrounding. How long (in sec) will the physical chemistry examination last if the professor (Mr Neeraj Kumar) has foolishly agreed to dismiss the class when the air temperature in the room reaches body temperature, 310 K? For air,  $C_{p,m} = 7R/2$ . ( $R = 0.0821\text{ L-atm/K-mol} = 8.3\text{ J/K-mol}$ )
14. Three moles of an ideal gas ( $C_{p,m} = 2.5R$ ) and 2 moles of another ideal gas ( $C_{p,m} = 3.5R$ ) are taken in a vessel and compressed reversibly and adiabatically. In this process, the temperature of gaseous mixture increased from 300 K to 400 K. The increase in internal energy of gaseous mixture (in cal) is
15. One mole of an ideal monoatomic gas initially at 1200 K and 64 atm is expanded to a final state at 300 K and 1 atm. To achieve the above change, a reversible path is constructed that involve an adiabatic expansion in the beginning followed by an isothermal expansion to the final state. The magnitude of net work done by the gas (in cal) is
16. Calculate  $\Delta S_{\text{univ}}$  (in J/K) for the chemical reaction:  $\text{C}(\text{graphite}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g})$ ;  $\Delta H^\circ_{300} = -75.0\text{ kJ}$ . The standard entropies of C (graphite),  $\text{H}_2(\text{g})$  and  $\text{CH}_4(\text{g})$  are 6.0, 130.6 and 186.2 J/K-mol, respectively.
17. An athlete in the weight room lifts a 50 kg mass through a vertical distance of 2.0 m. The mass is allowed to fall through the 2.0 m distance while coupled to an electrical generator. The electrical generator produces an equal amount of electrical work, which is used to produce aluminium by Hall electrolytic process.  

$$\text{Al}_2\text{O}_3(\text{solution}) + 3\text{C}(\text{graphite}) \rightarrow 2\text{Al}(\text{l}) + 3\text{CO}(\text{g}); \Delta G^\circ = 600\text{ kJ}$$

How many times must the athlete lift the 50 kg mass to provide sufficient Gibbs energy to produce 27 g Al? ( $g = 10\text{ m/s}^2$ )
18. How much energy (in kJ) is available for sustaining muscular and nervous activity from the combustion of 1.0 mole of glucose molecules under standard conditions at  $37^\circ\text{C}$  (body temperature)? The standard entropy and enthalpy of reaction are  $+200\text{ J/K-mol}$  and  $-2808\text{ kJ/mol}$ , respectively.

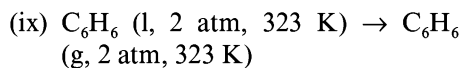
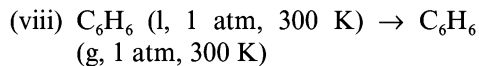
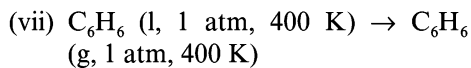
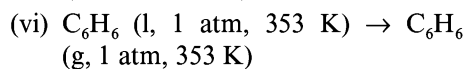
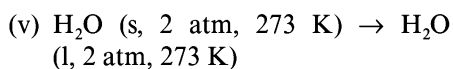
19. Select the conditions which represent the criteria for spontaneity of a process in a closed system, from the following given conditions:

Serial Number	Conditions
1.	$(dG)_{P,T} > 0$
2.	$(\Delta S)_{\text{universe}} > 0$
3.	$(dU)_{S,V} > 0$
4.	$(dH)_{S,P} < 0$
5.	$(dS)_{U,V} < 0$
6.	$(dS)_{H,P} > 0$

(Answer by adding the serial numbers of the correct conditions.)

20. Consider the following phase transitions:

- (i)  $\text{H}_2\text{O}$  (s, 1 atm, 273 K)  $\rightarrow$   $\text{H}_2\text{O}$  (l, 1 atm, 273 K)
- (ii)  $\text{H}_2\text{O}$  (s, 1 atm, 300 K)  $\rightarrow$   $\text{H}_2\text{O}$  (l, 1 atm, 300 K)
- (iii)  $\text{H}_2\text{O}$  (s, 1 atm, 200 K)  $\rightarrow$   $\text{H}_2\text{O}$  (l, 1 atm, 200 K)
- (iv)  $\text{H}_2\text{O}$  (s, 0.5 atm, 273 K)  $\rightarrow$   $\text{H}_2\text{O}$  (l, 0.5 atm, 273 K)



The normal freezing point of water is 273 K and the normal boiling point of benzene is 353 K.

Now, a four-digit number 'abcd' is defined as:

Digit 'a': number of phase transitions for which  $\Delta S_{\text{total}} = 0$

Digit 'b': number of phase transitions for which  $\Delta S_{\text{total}} > 0$

Digit 'c': number of phase transitions for which  $\Delta S_{\text{total}} < 0$

Digit 'd': number of phase transitions for which  $\Delta H > 0$

Determine the number 'abcd'.

## Answer Keys – Exercise II

### Section A (Only one Correct)

- |         |         |         |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (d)  | 2. (b)  | 3. (a)  | 4. (c)  | 5. (a)  | 6. (a)  | 7. (b)  | 8. (a)  | 9. (d)  | 10. (a) |
| 11. (c) | 12. (c) | 13. (c) | 14. (b) | 15. (a) | 16. (c) | 17. (d) | 18. (c) | 19. (a) | 20. (b) |
| 21. (c) | 22. (a) | 23. (b) | 24. (c) | 25. (d) | 26. (b) | 27. (c) | 28. (c) | 29. (b) | 30. (b) |
| 31. (c) | 32. (b) | 33. (a) | 34. (a) | 35. (c) | 36. (a) | 37. (b) | 38. (c) | 39. (b) | 40. (a) |
| 41. (a) | 42. (b) | 43. (c) | 44. (c) | 45. (c) | 46. (a) | 47. (c) | 48. (b) | 49. (a) | 50. (c) |
| 51. (c) | 52. (b) | 53. (a) | 54. (b) | 55. (c) | 56. (a) | 57. (b) | 58. (b) | 59. (c) | 60. (a) |
| 61. (c) | 62. (a) | 63. (a) | 64. (b) | 65. (c) | 66. (a) | 67. (b) | 68. (c) | 69. (a) | 70. (a) |
| 71. (d) | 72. (c) | 73. (c) | 74. (c) | 75. (b) | 76. (c) | 77. (b) | 78. (d) | 79. (d) | 80. (a) |

### Section B (One or More than one Correct)

- |                  |                  |                  |                       |
|------------------|------------------|------------------|-----------------------|
| 1. (b), (c), (d) | 2. (a), (b), (c) | 3. (a), (b), (c) | 4. (a), (b), (d)      |
| 5. (a), (b)      | 6. (a), (b), (c) | 7. (c)           | 8. (a), (b), (c), (d) |

- |                        |                        |                   |                   |
|------------------------|------------------------|-------------------|-------------------|
| 9. (a), (b), (c)       | 10. (a), (c)           | 11. (a), (b), (c) | 12. (a), (b), (c) |
| 13. (d)                | 14. (c)                | 15. (a)           | 16. (a), (c)      |
| 17. (a), (b)           | 18. (b), (d)           | 19. (c), (d)      | 20. (b), (c), (d) |
| 21. (a), (b), (c), (d) | 22. (a), (b), (c), (d) | 23. (a), (d)      | 24. (a), (d)      |
| 25. (a), (b), (c)      | 26. (b), (c)           | 27. (b), (c), (d) | 28. (b), (c), (d) |
| 29. (a), (b), (d)      | 30. (b), (d)           |                   |                   |

## Section C

### Comprehension I

1. (c)    2. (a)    3. (d)

### Comprehension II

4. (b)    5. (c)    6. (a)

### Comprehension III

7. (b)    8. (a)    9. (c)

### Comprehension IV

10. (a)    11. (c)    12. (a)

### Comprehension V

13. (a)    14. (c)    15. (c)

### Comprehension VI

16. (c)    17. (a)    18. (c)

### Comprehension VII

19. (b)    20. (a)    21. (b)

### Comprehension VIII

22. (d)    23. (a)    24. (b)

### Comprehension IX

25. (c)    26. (c)    27. (b)    28. (b)

### Comprehension X

29. (c)    30. (a)

## Section D (Assertion – Reason)

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

## Section E (Column Match)

- $A \rightarrow P, R, S, T, U; B \rightarrow P, Q, R, S, U; C \rightarrow Q, R, S, T, U; D \rightarrow P, Q, T$
- $A \rightarrow Q; B \rightarrow Q, S; C \rightarrow Q, S; D \rightarrow P, R$
- $A \rightarrow P, R, S; B \rightarrow Q, R, S; C \rightarrow Q, R, S; D \rightarrow R, S$
- $A \rightarrow P, Q, R, S; B \rightarrow R, S; C \rightarrow Q$
- $A \rightarrow P, S; B \rightarrow Q, R, S; C \rightarrow R$
- $A \rightarrow P, R; B \rightarrow Q, S; C \rightarrow R; D \rightarrow Q, S$
- $A \rightarrow Q; B \rightarrow P, S; C \rightarrow R, S$
- $A \rightarrow P, S; B \rightarrow P, R, S; C \rightarrow Q; D \rightarrow R, S$
- $A \rightarrow P, S, R; B \rightarrow P, R; C \rightarrow P; D \rightarrow Q, R, S$
- $A \rightarrow S; B \rightarrow P; C \rightarrow Q; D \rightarrow R$

**Section F (Subjective)**

**Single-digit Integer Type**

- |         |         |         |         |         |        |        |        |        |         |
|---------|---------|---------|---------|---------|--------|--------|--------|--------|---------|
| 1. (6)  | 2. (6)  | 3. (1)  | 4. (6)  | 5. (6)  | 6. (7) | 7. (3) | 8. (5) | 9. (3) | 10. (9) |
| 11. (6) | 12. (5) | 13. (8) | 14. (3) | 15. (5) |        |        |        |        |         |

**Four-digit Integer Type**

- |            |            |            |            |            |
|------------|------------|------------|------------|------------|
| 1. (5778)  | 2. (0044)  | 3. (0209)  | 4. (8400)  | 5. (0025)  |
| 6. (0020)  | 7. (5071)  | 8. (1567)  | 9. (0033)  | 10. (1990) |
| 11. (1501) | 12. (3714) | 13. (0500) | 14. (1900) | 15. (3120) |
| 16. (0169) | 17. (0300) | 18. (2870) | 19. (0012) | 20. (2439) |
-

## EXERCISE II (JEE ADVANCED)

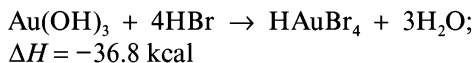
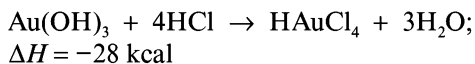
### Section A (Only one Correct)

- In a flask, colourless  $\text{N}_2\text{O}_4$  is in equilibrium with brown coloured  $\text{NO}_2$ . At equilibrium, when the flask is heated at 373 K, the brown colour deepens and on cooling it becomes less coloured. The change in enthalpy for this reaction is  
 (a) negative (b) positive  
 (c) zero (d) unpredictable
- $2\text{MnO}_4^- + 16\text{H}^+ + 10\text{Cl}^- \rightarrow 2\text{Mn}^{2+} + 5\text{Cl}_2(\text{g}) + 8\text{H}_2\text{O}$   
 Above reaction is endothermic and hence the actual temperature of the reaction vessel (isolated from the surrounding) may be different from that expected. Given that the initial temperature of the reaction vessel was used in the calculations, how would, this affect the predicted value of moles of  $\text{Cl}_2$  ( $n$ ), according to equation:  $n = PV/RT$   
 (a) It would be greater than the actual value  
 (b) It would be less than the actual value  
 (c) It would be the same as the actual value  
 (d) This cannot be determined from the information given
- The molar heat capacities of A, B and C are in the ratio 1:2:3. The enthalpy change for the reaction  $\text{A} + \text{B} \rightarrow \text{C}$  at temperature  $T_1$  is  $\Delta H_1$ . Assuming that the heat capacities do not change with temperature, the enthalpy change,  $\Delta H_2$ , at temperature,  $T_2$  ( $T_2 > T_1$ ) will be  
 (a) greater than  $\Delta H_1$   
 (b) equal to  $\Delta H_1$   
 (c) less than  $\Delta H_1$   
 (d) greater or less than  $\Delta H_1$ , depending on the values of  $T_2$  and  $T_1$ .
- The specific heats of iodine vapours and solid are 0.031 and 0.055 cal/g, respectively. If the enthalpy of sublimation of iodine is 24 cal/g at 200°C, then the enthalpy of sublimation of iodine at 250°C should be  
 (a) 24 cal/g  
 (b) 22.8 cal/g  
 (c) 26.4 cal/g  
 (d) 20.8 cal/g
- A quantity that cannot be directly measured is  
 (a) heat of formation of  $\text{H}_2\text{O}(\text{l})$   
 (b) heat of formation of  $\text{CH}_4(\text{g})$   
 (c) latent heat of fusion of ice  
 (d) heat of combustion of ethyl alcohol
- Which of the following gas will liberate maximum heat on combustion, per gram?  
 (a) Methane  
 (b) Ethane  
 (c) Acetylene  
 (d) Ethylene
- Ethyl chloride is prepared by reaction of ethylene with hydrogen chloride as:  

$$\text{C}_2\text{H}_4(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{Cl}(\text{g});$$

$$\Delta H = -72.3 \text{ kJ}$$
 What is the value of  $\Delta U$  (in kJ) if 70 g of ethylene and 73 g of HCl are allowed to react?  
 (a) -69.8  
 (b) -180.75  
 (c) -174.5  
 (d) -139.6

8. Reactions involving gold have been of particular interest to a chemist. Consider the following reactions:



In an experiment, there was absorption of 0.44 kcal when one mole of  $\text{HAuBr}_4$  was mixed with 4 moles of  $\text{HCl}$ . What is the percentage conversion of  $\text{HAuBr}_4$  into  $\text{HAuCl}_4$ ?

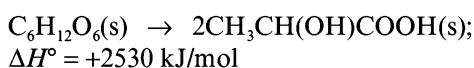
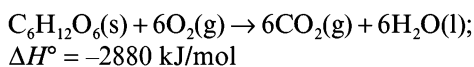
- (a) 0.5%  
(b) 0.6%  
(c) 5%  
(d) 50%
9. When carbon is burnt in a definite amount of oxygen, the product will be  $\text{CO}$ , if excess amount of carbon is present and the product will be  $\text{CO}_2$  if excess amount of  $\text{O}_2$  is present. The enthalpies of formation of  $\text{CO(g)}$  and  $\text{CO}_2\text{(g)}$  are  $-75$  and  $-95$  kcal/mol, respectively. In which of the following case, the amount of heat evolved will be maximum?
- (a) 10 moles of carbon and 4.5 moles of  $\text{O}_2$   
(b) 24 g of carbon and 64 g of  $\text{O}_2$   
(c) 4 moles of carbon and 3.5 moles of  $\text{O}_2$   
(d) 30 g of carbon and 80 g of  $\text{O}_2$
10. The standard molar enthalpies of formation of trinitrotoluene(l),  $\text{CO}_2\text{(g)}$  and  $\text{H}_2\text{O(l)}$  are 65,  $-395$  and  $-285$  kJ/mol, respectively. The density of trinitrotoluene is 1.816 g/ml. Trinitrotoluene can be used as rocket fuel, with the gases resulting from its combustion streaming out of the rocket to give the required thrust. What is

the enthalpy density for the combustion reaction of trinitrotoluene?

- (a)  $-28.34$  MJ/l  
(b)  $-28.34$  kJ/l  
(c)  $-27.30$  MJ/l  
(d)  $-8.59$  MJ/l
11. When 1 g-equivalent of strong acid reacts with strong base, heat released is 13.5 kcal. When 1 g-equivalent  $\text{H}_2\text{A}$  is completely neutralized against strong base, 13 kcal is released. When 1 g-equivalent  $\text{B(OH)}_2$  is completely neutralized against strong acid, 10 kcal heat is released. What is the enthalpy change when 1 mole of  $\text{H}_2\text{A}$  is completely neutralized by  $\text{B(OH)}_2$ .
- (a)  $-27$  kcal  
(b)  $-10$  kcal  
(c)  $-20$  kcal  
(d)  $-19$  kcal
12. The enthalpy change for the reaction,  $\text{NaOH(aq)} + \text{HCl(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$  is  $-57$  kJ. Predict the value of the enthalpy change in the following reaction:
- $$\text{Ba(OH)}_2\text{(aq)} + \text{H}_2\text{SO}_4\text{(aq)} \rightarrow \text{BaSO}_4\text{(s)} + 2\text{H}_2\text{O(l)}$$
- (a)  $-57$  kJ  
(b)  $-76$  kJ  
(c)  $-114$  kJ  
(d)  $-200$  kJ
13. The enthalpy of neutralization of a strong monobasic acid by a strong monoacidic base is  $-13,700$  cal. A certain monobasic weak acid is 10% ionized in a molar solution. If the enthalpy of ionization of the weak acid is  $+400$  cal/mole, what is the enthalpy of neutralization of one molar solution of the weak acid?
- (a)  $-13,700$  cal  
(b)  $-13,340$  cal  
(c)  $-13,660$  cal  
(d)  $-13,300$  cal

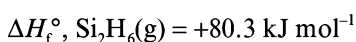
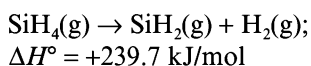
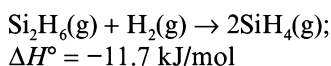
## 5.14 ■ Chapter 5

14. In biological cells that have a plentiful supply of  $O_2$ , glucose is oxidized completely to  $CO_2$  and  $H_2O$  by a process called aerobic oxidation. Muscle cells may be deprived of  $O_2$  during vigorous exercise and, in that case, one molecule of glucose is converted to two molecules of lactic acid,  $CH_3CH(OH)COOH$ , by a process called anaerobic glycolysis.



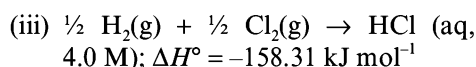
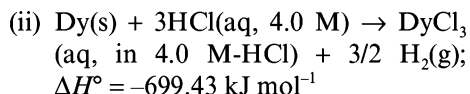
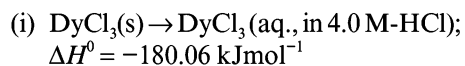
Which of the following statements is true regarding aerobic oxidation and anaerobic glycolysis with respect to energy change as heat?

- Aerobic oxidation has biological advantage over anaerobic glycolysis by 5410 kJ/mol.
  - Aerobic oxidation has biological advantage over anaerobic glycolysis by 350 kJ/mol
  - Anaerobic glycolysis has biological advantage over aerobic oxidation by 5410 kJ/mol.
  - Anaerobic glycolysis has biological advantage over aerobic oxidation by 350 kJ/mol.
15. The intermediate  $SiH_2$  is formed in the thermal decomposition of silicon hydrides. Calculate  $\Delta H_f^\circ$  of  $SiH_2$  from the following reactions:



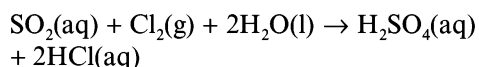
- 353 kJ/mol
- 321 kJ/mol
- 198 kJ/mol
- 274 kJ/mol

16. Study the following thermodynamic data given by E. H. P. Cordfunke, A. S. Booji and M. Y. Furkalionk.



What is  $\Delta H_f^\circ$  of  $\text{DyCl}_3(s)$  from these data?

- $-248.58 \text{ kJ mol}^{-1}$
  - $-994.30 \text{ kJ mol}^{-1}$
  - $-3977.2 \text{ kJ mol}^{-1}$
  - $-1469.2 \text{ kJ mol}^{-1}$
17. The enthalpies of formation of  $SO_2(g)$ ,  $H_2O(l)$ ,  $HCl(g)$  and  $H_2SO_4(l)$  are  $-70.97$ ,  $-68.32$ ,  $-22.1$  and  $-188.84 \text{ (kJ mol}^{-1}\text{)}$ . The enthalpies of solution of  $SO_2$ ,  $H_2SO_4$  and  $HCl$  in dilute solution are  $-8.56$ ,  $-22.05$  and  $-17.63 \text{ (kJ mol}^{-1}\text{)}$ , respectively. What is the enthalpy change for the reaction?



- $-74.18 \text{ kcal}$
- $-78.97 \text{ kcal}$
- $-43.71 \text{ kcal}$
- $-87.14 \text{ kcal}$

18. The enthalpy of neutralization of a strong acid by a strong base is  $-57.32 \text{ kJ mol}^{-1}$ . The enthalpy of formation of water is  $-285.84 \text{ kJ mol}^{-1}$ . The enthalpy of formation of aqueous hydroxyl ion is
- $+228.52 \text{ kJ/mol}$
  - $-114.26 \text{ kJ/mol}$
  - $-228.52 \text{ kJ/mol}$
  - $+114.2 \text{ kJ/mol}$

19.  $\Delta H_f^\circ$  for  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$  are  $-94.0$  and  $-68.0$  kcal/mol.  $\Delta H_f^\circ$  for the propanoic acid is one-third of the enthalpy of combustion of the acid and has the same sign as the latter.  $\Delta H_f^\circ$  of propanoic acid is
- $-364.5$  kcal/mol
  - $-729.0$  kcal/mol
  - $-121.5$  kcal/mol
  - $-243.0$  kcal/mol

20. The enthalpy change when  $x$  g of phenol dissolves in  $y$  g of  $\text{CHCl}_3$  is given below at a certain temperature:

$x$	$Y$	$\Delta H$ (kcal)
0.632	135.9	$-0.021$
1.569	148.69	$-0.041$

Calculate the enthalpy of dilution per mole of phenol, when the second solution is diluted to the concentration of the first by addition of  $\text{CHCl}_3$ .

- $-0.38$  kcal/mol
  - $-0.67$  kcal/mol
  - $+0.38$  kcal/mol
  - $+0.76$  kcal/mol
21. Consider the equations:



$$\Delta H = -14.7 \text{ kcal}$$



$$\Delta H = -0.522 \text{ kcal}$$

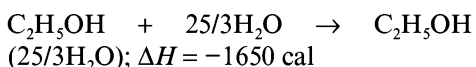
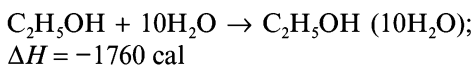
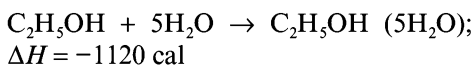
$\Delta H$  for the neutralization of  $\text{HCl}$  and  $\text{NaOH}$  is  $-13.75$  kcal/eq. The enthalpy of ionization of  $\text{CH}_3\text{CH}(\text{OH})\text{CHClCOOH}$  is

- $+0.492$  kcal/mol
- $-0.249$  kcal/mol
- $+0.294$  kcal/mol
- $-0.429$  kcal/mol

22. The enthalpies of formation of  $\text{FeO}(\text{s})$  and  $\text{Fe}_2\text{O}_3(\text{s})$  are  $-65.0$  and  $-197.0$  kcal/mol, respectively. A mixture of the two oxides contains  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$  in the mole ratio 2:1. If by oxidation it is changed in to a 1:2 mole ratio mixture, how much of thermal energy will be released per mole of the initial mixture?

- 13.4 kcal
- 67 kcal
- 47.2 kcal
- 81 kcal

23. Calculate the heat effect produced when a solution of 1 mole of ethanol in 5 moles of water is mixed with a solution of 2 moles of ethanol in 20 moles of water. Given that,



- 310 cal is absorbed
- 310 cal is released
- 103.33 cal is absorbed
- 103.33 cal is released

24. A solution was prepared by dissolving 7.45 g of  $\text{KCl}$  in 200 g of  $\text{H}_2\text{O}$  in a calorimeter with a water equivalent of 25 g. The temperature of the water had reduced from  $28^\circ\text{C}$  to  $25^\circ\text{C}$ .  $\Delta H$  (in kJ/mol) for dissolving  $\text{KCl}$  in water is (Specific heat capacity of water is  $4.2 \text{ J/K-g}$ .)

- +2.52
- +2.835
- +25.2
- +28.35



25. In an ice calorimeter, a chemical reaction is allowed to occur in thermal contact with an ice-water mixture at  $0^{\circ}\text{C}$ . Any heat liberated by the reaction is used to melt some ice; the volume change of the ice-water mixture indicates the amount of melting. When solutions containing 1.0 millimole each of  $\text{AgNO}_3$  and  $\text{NaCl}$  were mixed in such a calorimeter, both solutions having been pre-cooled to  $0^{\circ}\text{C}$ , 0.20 g of ice melted. Assuming complete reaction in this experiment, what is  $\Delta H$  for the reaction:  $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$ ? Latent heat of fusion of ice at  $0^{\circ}\text{C}$  is 80 cal/g.
- (a) -16 kcal (b) +16 kcal  
(c) -16 cal (d) +16 cal
26. A volume of 4.0 l of a mixture of ethane and methane gases on complete combustion at 300 K produced 6.0 l of carbon dioxide. Find out the amount of heat evolved on burning 1 l of gaseous mixture. The heats of combustion of ethylene and methane are -1573 and -890 kJ per mole, respectively, at 300 K.
- (a) 4926 kJ (b) 2000 kJ  
(c) 1231.5 kJ (d) 200 kJ
27. A quantity of 0.3 g of carbon was converted into  $\text{CO}_2$  producing 2400 cal of heat. When 0.6 g of carbon was converted to CO, 1400 cal of heat were produced. What will be the heat produced when 0.7 g of CO is converted to  $\text{CO}_2$ ?
- (a) 1700 cal (b) 1633.33 cal  
(c) 700 cal (d) 1000 cal
28. Assume that for a domestic hot water supply, 160 kg of water per day must be heated from  $10^{\circ}\text{C}$  to  $60^{\circ}\text{C}$  and gaseous fuel propane,  $\text{C}_3\text{H}_8$ , is used for this purpose. What volume of propane gas at STP would have to be used for heating domestic water, with efficiency of 40%? Heat of combustion of propane is -500 kcal/mol and specific heat capacity of water is 1.0 cal/K-g.
- (a) 896 L (b) 908 L  
(c)  $896 \text{ m}^3$  (d)  $908 \text{ m}^3$
29. As a 0.1 mole sample of solid  $\text{NH}_4\text{Cl}$  was dissolved in 50 ml of water, the temperature of the solution decreased. A small electrical immersion heater restored the temperature of the system by passing 0.125 A from a 15 V power supply for a period of 14 min.  $\Delta H$  for the process:  $\text{NH}_4\text{Cl}(\text{s}) \rightarrow \text{NH}_4\text{Cl}(\text{aq})$  is
- (a) -15.75 kJ  
(b) +15.75 kJ  
(c) -787.5 J  
(d) +787.5 J
30. The thermochemical equation for the dissociation of hydrogen gas into atoms may be written as:  $\text{H}_2 \rightarrow 2\text{H}$ ;  $\Delta H = 432.0 \text{ kJ}$ . What is the ratio of the energy yield on combustion of hydrogen atoms to steam to the yield on combustion of an equal mass of hydrogen molecules to steam? Heat of formation of steam is -240.0 kJ/mol.
- (a) 2.80  
(b) 1.80  
(c) 0.8  
(d) 2.40
31. The most exothermic 'ordinary' chemical reaction for a given mass of reactants is  $2\text{H}(\text{g}) \rightarrow \text{H}_2(\text{g})$ ;  $\Delta E = 103 \text{ kcal}$ . The theoretical decrease in mass on combination of 2.0 moles of hydrogen atoms to form 1.0 mole of hydrogen molecules, assuming that the energy is released only due to decrease in mass of the system, is
- (a)  $4.8 \times 10^{-12} \text{ kg}$   
(b)  $4.8 \times 10^{-12} \text{ g}$   
(c)  $2.4 \times 10^{-12} \text{ kg}$   
(d)  $9.6 \times 10^{-12} \text{ kg}$

32. Calculate the enthalpy of formation (in kcal/mol) of gaseous HCl using following data:

Substance	NH <sub>3</sub> (g)	HCl(g)	NH <sub>4</sub> Cl(s)
Heat of formation	-11	X	-75
Heat of solution	-8.5	-17.5	+3.9 kcal

and,  $\text{NH}_3(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{NH}_4\text{Cl}(\text{aq}); \Delta H = -12 \text{ kcal}$

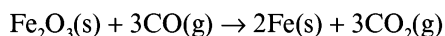
- (a) -44.2 (b) -22.1  
(c) -11.05 (d) -28.7
33. Two bars of different metals are heated to 60°C and then immersed in identical, insulated containers each containing 200 g of water at 20°C. Will the metal with higher or lower atomic mass cause a greater temperature rise in water?  
(a) Lower atomic mass  
(b) Higher atomic mass  
(c) Same for both  
(d) Cannot be predicted
34. From the following data, calculate the enthalpy change (in kJ/mol) for the combustion of cyclopropane(g) at 298 K. The enthalpy of formation of CO<sub>2</sub>(g), H<sub>2</sub>O(l) and propene(g) are -394, -286 and 20 kJ/mol, respectively. The enthalpy of isomerization of cyclopropane(g) to propene(g) is -33 kJ/mol.  
(a) -2073 (b) -2093  
(c) -2060 (d) -2027
35. The reaction of zinc metal with hydrochloric acid was used to produce 1.5 moles of hydrogen gas at 298 K and 1 atm pressure. The magnitude work done in pushing back the atmosphere is  
(a) 596 cal (b) 894 cal  
(c) 447 cal (d) 298 cal
36. The molar enthalpy of vaporization of benzene at its boiling point (353 K) is 7.4 kcal/mol. The molar internal energy change of vaporization is  
(a) 7.4 kcal/mol (b) 8.106 kcal/mol  
(c) 6.694 kcal/mol (d) 62.47 kcal/mol
37. Determine the standard enthalpy of reaction:  $\text{C}_3\text{H}_8(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g}) + \text{CH}_4(\text{g})$ , using the given enthalpies under standard conditions:

Compound	H <sub>2</sub> (g)	CH <sub>4</sub> (g)	C <sub>2</sub> H <sub>6</sub> (g)	C (graphite)
$\Delta H^\circ$ (kJ/mol)	-285.8	-890.0	-1560.0	-393.5

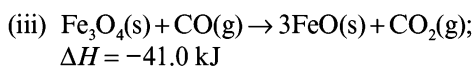
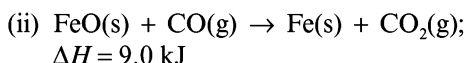
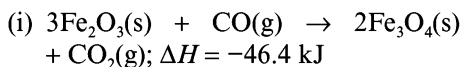
The standard enthalpy of formation of C<sub>3</sub>H<sub>8</sub>(g) is -103.8 kJ/mol

- (a) -55.7 kJ  
(b) +55.7 kJ  
(c) -2060.4 kJ  
(d) +2060.4 kJ
38. The enthalpy of formation of KCl(s) from the following data is  
(i)  $\text{KOH}(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{KCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}); \Delta H = -13.7 \text{ kcal}$   
(ii)  $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}); \Delta H = -68.4 \text{ kcal}$   
(iii)  $\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{Cl}_2(\text{g}) + \text{aq} \rightarrow \text{HCl}(\text{aq}); \Delta H = -39.3 \text{ kcal}$   
(iv)  $\text{K}(\text{s}) + \frac{1}{2} \text{O}_2(\text{g}) + \frac{1}{2} \text{H}_2(\text{g}) + \text{aq} \rightarrow \text{KOH}(\text{aq}); \Delta H = -116.5 \text{ kcal}$   
(v)  $\text{KCl}(\text{s}) + \text{aq} \rightarrow \text{KCl}(\text{aq}); \Delta H = +4.4 \text{ kcal}$   
(a) +105.5 kcal/mol  
(b) -105.5 kcal/mol  
(c) -13.7 kcal/mol  
(d) -18.1 kcal/mol

39. Calculate  $\Delta H$  for the following reaction at 298 K:

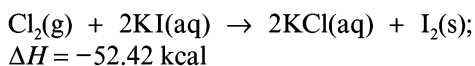
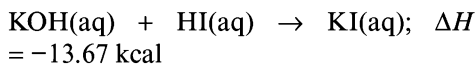
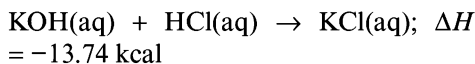
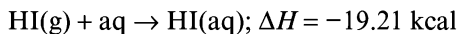
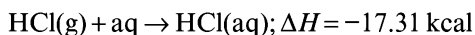
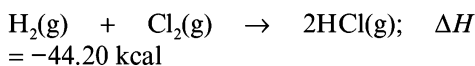


from the following thermochemical equations:



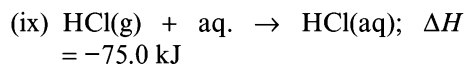
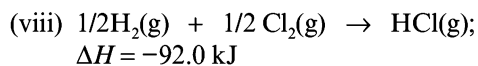
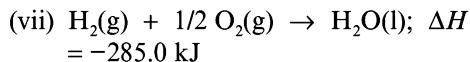
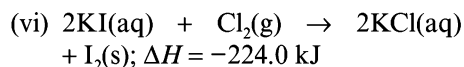
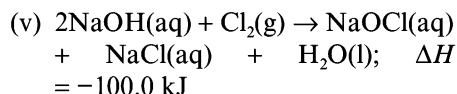
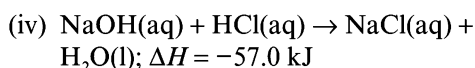
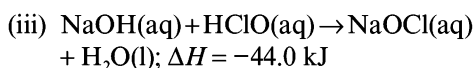
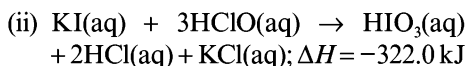
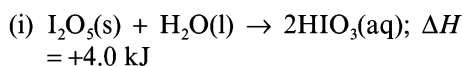
- (a)  $-24.8 \text{ kJ}$  (b)  $+24.8 \text{ kJ}$   
(c)  $-17.97 \text{ kJ}$  (d)  $+17.97 \text{ kJ}$

40. Calculate the enthalpy of formation (in kcal/mol) of HI(g) from the following data:



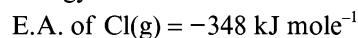
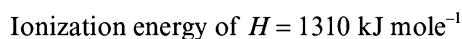
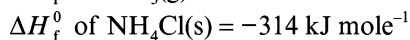
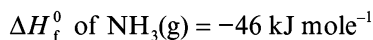
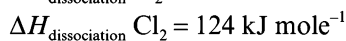
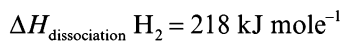
- (a)  $+19.21$  (b)  $-32.87$   
(c)  $+5.94$  (d)  $+7.82$

41. Calculate the enthalpy of formation of  $\text{I}_2\text{O}_5(\text{s})$  from the following data:



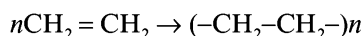
- (a)  $-173.0 \text{ kJ}$  (b)  $+173.0 \text{ kJ}$   
(c)  $-154.0 \text{ kJ}$  (d)  $+154.0 \text{ kJ}$

42. Calculate proton affinity of  $\text{NH}_3(\text{g})$  from the following data:



- (a)  $-818 \text{ kJ mole}^{-1}$   
(b)  $-718 \text{ kJ mole}^{-1}$   
(c)  $-318 \text{ kJ mole}^{-1}$   
(d)  $-418 \text{ kJ mole}^{-1}$

43. The polymerization of ethylene to linear polyethylene is represented by the reaction:



where  $n$  has a large integral value. Given that the average enthalpies of bond dissociation for C=C and C-C at 298 K are +590 and +331 kJ/mol, respectively, the enthalpy of polymerization per mole of ethylene at 298 K is

- (a)  $-72 \text{ kJ}$   
(b)  $+259 \text{ kJ}$   
(c)  $-259 \text{ kJ}$   
(d)  $-849 \text{ kJ}$

44. The enthalpy of formation of liquid methyl alcohol in kJ/mol, using the following data (in kJ/mol):

Heat of vaporization of liquid methyl alcohol = 38.

Heat of formation of gaseous atoms from the elements in their standard states: H, 218; C, 715; O, 249.

Average bond energies: C–H, 415; C–O, 356; O–H, 463.

- (a) –190 (b) –702  
(c) –626 (d) –266

45. The strain energy (in kJ/mol) of cyclopropane from the following data:

$\Delta_f H$  [C<sub>3</sub>H<sub>6</sub>(g)] = 53.0 kJ/mol;  $\Delta_f H$  [C(g)] = 715.0 kJ/mol;  $\Delta_f H$  [H(g)] = 218.0 kJ/mol

BE (C–C) = 356.0 kJ/mol; BE (C–H) = 408.0 kJ/mol.

- (a) 770 kJ (b) 116 kJ  
(c) 240 kJ (d) 346 kJ

46. Standard enthalpy of formation of gaseous ethane, ethene and benzene from gaseous atoms are –2839, –2275 and –5506 kJ/mol, respectively. The bond enthalpy of C–H bond is 412 kJ/mol. The magnitude of resonance energy of benzene, compared with one Kekule structure is

- (a) 24 kJ (b) 52 kJ  
(c) 2524 kJ (d) 152 kJ

47. Find the bond energy of S–S bond from the following data:

C<sub>2</sub>H<sub>5</sub>–S–C<sub>2</sub>H<sub>5</sub>(g);  $\Delta H_f^\circ$  = –148 kJ,

C<sub>2</sub>H<sub>5</sub>–S–S–C<sub>2</sub>H<sub>5</sub>(g);  $\Delta H_f^\circ$  = –202 kJ,

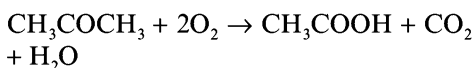
S(g);  $\Delta H_f^\circ$  = 222 kJ

- (a) 276 kJ/mol  
(b) 128 kJ/mol  
(c) 168 kJ/mol  
(d) 222 kJ/mol

48. Given the bond dissociation enthalpy of CH<sub>3</sub>–H bond as 103 kcal/mol and the enthalpy of formation of CH<sub>4</sub>(g) as –18 kcal/mol, find the enthalpy of formation of methyl radical. The dissociation energy of H<sub>2</sub>(g) into H (atoms) is 103 kcal/mol.

- (a) –33.5 kcal/mol  
(b) 33.5 kcal/mol  
(c) 18 kcal/mol  
(d) –9 kcal/mol

49. Calculate the enthalpy of the following homogeneous gaseous reaction:



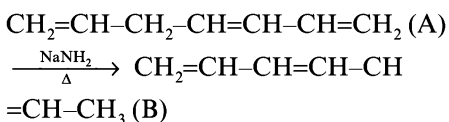
from the following data:

Bond energies (kJ/mol): C–H = 414; C–C = 348; C=O = 580; C–O = 354; O=O = 610; O–H = 462;

Magnitude of resonance energies (kJ/mol): COOH = 118; CO<sub>2</sub> = 140.

- (a) 348 kJ  
(b) 168 kJ  
(c) –168 kJ  
(d) –348 kJ

50. What is the enthalpy change for the isomerization reaction:

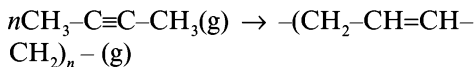


Magnitude of resonance energies of A and B are 50 and 70 kJ/mol, respectively.

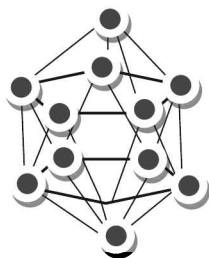
Enthalpies of formation of A and B are –2275.2 and –2839.2 kJ/mol, respectively.

- (a) –584 kJ  
(b) –564 kJ  
(c) –544 kJ  
(d) –20 kJ

51. The bond enthalpies of C–C, C=C and C≡C bonds are 348, 610 and 835 kJ/mol, respectively, at 298 K and 1 bar. The enthalpy of polymerization per mole of 2-Butyne at 298 K and 1 bar, as shown below, is



- (a) –123 kJ (b) –132 kJ  
(c) –139 kJ (d) –37 kJ
52. The enthalpies of combustion of formaldehyde and paraformaldehyde (a polymer of formaldehyde) are –134 and –732 kcal/mol, respectively. The enthalpy of polymerization per mole of paraformaldehyde is –72 kcal. The molecular formula of paraformaldehyde is
- (a) CH<sub>2</sub>O (b) C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>  
(c) C<sub>3</sub>H<sub>6</sub>O<sub>3</sub> (d) C<sub>4</sub>H<sub>8</sub>O<sub>4</sub>
53. Boron exists in different allotropic forms. All allotropic form contains icosahedral units (icosahedral is a regular shape with 12 corners and 20 faces) with boron atoms at all 12 corners and all bonds are equivalent. Calculate the heat evolved at constant pressure (in kJ/mole) of boron atom undergoing the above change if the bond dissociation enthalpy of B–B bond is 300 kJ/mol.



- (a) 500 (b) 750  
(c) 1500 (d) 900

54. Butane exists in various conformations in nature. At any given instant, the probability that a given butane molecule is in anti, gauche, eclipsed and fully eclipsed conformation is 0.7, 0.2, 0.06 and 0.04, respectively. If the molar enthalpy of combustion of natural butane is –690 kcal/mol at 25°C, then calculate the enthalpy of combustion of butane if all the butane molecules are in gauche conformation.

- (a) –690 kcal/mol  
(b) –689 kcal/mol  
(c) –691 kcal/mol  
(d) –692 kcal/mol
55. For an ionic solid MX<sub>2</sub>, where X is monovalent, the enthalpy of formation of the solid from M(s) and X<sub>2</sub>(g) is 1.5 times the electron gain enthalpy of X(g). The first and second ionization enthalpies of the metal (M) are 1.2 and 2.8 times of the enthalpy of sublimation of M(s). The bond dissociation enthalpy of X<sub>2</sub>(g) is 0.8 times the first ionization enthalpy of metal and it is also equal to one-fifth of the magnitude of lattice enthalpy of MX<sub>2</sub>. If the electron gain enthalpy of X(g) is –96 kcal/mol, then what is the enthalpy of sublimation (in kcal/mol) of the metal (M)?
- (a) 41.38  
(b) 52.5  
(c) 48.0  
(d) 38.27

**Section B (One or More than one Correct)**

- Which of the following is/are endothermic reaction(s)?
  - Combustion of methane
  - Decomposition of water
  - Dehydrogenation of ethane to ethylene
  - Conversion of graphite to diamond
- The enthalpy change for the following process would be expected to be a negative for
  - $\text{Na}^+(\text{g}) + \text{e}^- \rightarrow \text{Na}(\text{g})$
  - $\text{F}(\text{g}) + \text{e}^- \rightarrow \text{F}^-(\text{g})$
  - $\text{Na}^+(\text{g}) + \text{F}^-(\text{g}) \rightarrow \text{NaF}(\text{s})$
  - $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$
- For which of the following substance(s), the standard enthalpy of formation is/are zero?
  - C (graphite)
  - $\text{O}_3(\text{g})$
  - $\text{I}_2(\text{g})$
  - $\text{Br}_2(\text{l})$
- Which of the following is/are endothermic compound(s)?
  - $\text{NO}(\text{g})$
  - $\text{CO}_2(\text{g})$
  - $\text{CO}(\text{g})$
  - $\text{NH}_3(\text{g})$
- Among the following the reaction for which  $\Delta H = \Delta E$ , is
  - $\text{PCl}_5(\text{g}) \rightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
  - $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$
  - $\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{g})$
  - $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$
- $\Delta H$  of which of the following reaction(s) may be directly taken as enthalpy of combustion of the concerned substance?
  - $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
  - $2\text{C}_2\text{H}_6(\text{g}) + 7\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$
  - $\text{C}_3\text{H}_8(\text{g}) + 7/2 \text{O}_2(\text{g}) \rightarrow 3\text{CO}(\text{g}) + 4\text{H}_2\text{O}(\text{l})$
  - $1/2 \text{N}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \rightarrow \text{NO}(\text{g})$
- Which of the following reaction(s) is/are endothermic?
  - $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$
  - $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
  - $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$
  - $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$
- A volume of 100 ml of 0.5 N- $\text{H}_2\text{SO}_4$  solution is neutralized with 200 ml of 0.2 M- $\text{NH}_4\text{OH}$  in a constant pressure calorimeter which resulted  $1.4^\circ\text{C}$  rise in temperature. The heat capacity of the calorimeter system is  $1.5 \text{ kJ}/^\circ\text{C}$ . Some useful thermochemical equations are:
 
$$\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O} + 57 \text{ kJ}$$

$$\text{CH}_3\text{COOH} + \text{NH}_4\text{OH} \rightarrow \text{CH}_3\text{COONH}_4 + \text{H}_2\text{O} + 48.1 \text{ kJ}$$
 Which of the following statements are correct?
  - Enthalpy of neutralization of HCl vs.  $\text{NH}_4\text{OH}$  is  $-52.5 \text{ kJ/mol}$ .
  - Enthalpy of dissociation (ionization) of  $\text{NH}_4\text{OH}$  is  $4.5 \text{ kJ/mol}$
  - Enthalpy of dissociation (ionization) of  $\text{CH}_3\text{COOH}$  is  $4.6 \text{ kJ/mol}$
  - $\Delta H$  for  $2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}^+(\text{aq}) + 2\text{OH}^-(\text{aq})$  is  $114 \text{ kJ}$ .
- From the following data at  $25^\circ\text{C}$ , which of the following statement(s) is/are correct?
 
$$1/2 \text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \rightarrow \text{OH}(\text{g}); \Delta H^\circ = 42 \text{ kJ}$$

$$\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}); \Delta H^\circ = -242 \text{ kJ}$$

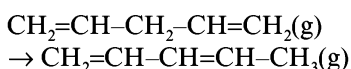
$$\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g}); \Delta H^\circ = 436 \text{ kJ}$$

$$\text{O}_2(\text{g}) \rightarrow 2\text{O}(\text{g}); \Delta H^\circ = 495 \text{ kJ}$$
  - $\Delta_f H^\circ$  for the reaction  $\text{H}_2\text{O}(\text{g}) \rightarrow 2\text{H}(\text{g}) + \text{O}(\text{g})$  is  $925.5 \text{ kJ}$
  - $\Delta_f H^\circ$  for the reaction  $\text{OH}(\text{g}) \rightarrow \text{H}(\text{g}) + \text{O}(\text{g})$  is  $502 \text{ kJ}$
  - Enthalpy of formation of  $\text{H}(\text{g})$  is  $-218 \text{ kJ/mol}$
  - Enthalpy of formation of  $\text{OH}(\text{g})$  is  $42 \text{ kJ/mol}$

10. Which of the following molecules will have different values of standard molar enthalpy of formation, one calculated using bond energy concept and other calculated calorimetrically?

(a)  $C_2H_6$   
 (b) 1,3-Butadiene  
 (c) 1,4-Cyclohexadiene  
 (d)  $N_2O$

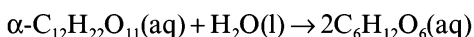
11. Consider the following isomerization process:



Which of the following statement(s) is/are true regarding this process?

(a) The process is exothermic.  
 (b) Enthalpy change of reaction = Resonance enthalpy of product.  
 (c) The magnitude of enthalpy of combustion of product is less than that of reactant.  
 (d) The magnitude of enthalpy of hydrogenation of product is greater than that of reactant.

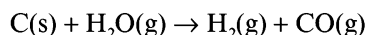
12.  $\alpha$ -maltose can be hydrolysed to glucose according to the following reaction:



The standard enthalpy of formation of  $H_2O(l)$ ,  $C_6H_{12}O_6(aq)$  and  $\alpha-C_{12}H_{22}O_{11}(aq)$  are  $-285$ ,  $-1263$  and  $-2238$  kJ/mol, respectively. Which of the following statement(s) is/are true?

(a) The hydrolysis reaction is exothermic.  
 (b) Heat liberated in combustion of 1.0 mole of  $\alpha$ -maltose is smaller than the heat liberated in combustion of 2.0 mole of glucose.  
 (c) Increase in temperature will increase the degree of hydrolysis of  $\alpha$ -maltose.  
 (d) Enthalpy of reaction will remain the same even if solid  $\alpha$ -maltose is taken in the reaction.

13. In certain areas where coal is cheap, artificial gas is produced for house hold use by the 'water gas' reaction:



Assume that coke is 100% carbon. Given  $\Delta H_c$  (kcal/mol) at  $25^\circ C$ :  $H_2(g) = -68.0$ ;  $CO(g) = -68.0$ ;  $C(s) = -94.0$ . Select the correct option(s):

(a) The maximum heat obtainable at  $25^\circ C$  from the combustion of 1.2 kg of coke is 9400 kcal.  
 (b) The maximum heat obtainable at  $25^\circ C$  from burning water gas produced from 1.2 kg of coke is 13,600 kcal.  
 (c) The maximum heat obtainable at  $25^\circ C$  from burning 1.2 kg of water gas is 5440 kcal.  
 (d) The maximum heat obtainable at  $25^\circ C$  from burning water gas or burning the same mass of coke will be same.

14. At 300 K, the standard enthalpies of formation of  $C_6H_5COOH(s)$ ,  $CO_2(g)$  and  $H_2O(l)$  are  $-408$ ,  $-393$  and  $-286$  kJ/mol, respectively. The enthalpy of combustion of benzoic acid(s) at 300 K is

(a)  $-3201$  kJ/mol, at constant pressure  
 (b)  $-3199.76$  kJ/mol, at constant pressure  
 (c)  $-3201$  kJ/mol, at constant volume  
 (d)  $-3199.76$  kJ/mol, at constant volume

15. For the reaction,  $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ ;  $\Delta H = -35.0$  kcal at 300 K. If 6.0 moles of NO reacts with 3.0 moles of  $O_2$  at constant pressure of 1.0 atm and temperature 300 K to form  $NO_2$ , then the correct statement(s) is/are

(a) the magnitude of work done by the system is 1.8 kcal  
 (b) the amount of heat released by the reaction is 35 kcal  
 (c) the internal energy of system decreased by 103.2 kcal  
 (d) the internal energy of system decreased by 106.8 kcal

## Section C (Comprehensions)

### Comprehension I

Study the following thermochemical equations:

- (a)  $\text{N}_2\text{O}(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{N}_2\text{H}_4(\text{l}); \Delta H = -75.56 \text{ kcal}$   
 (b)  $4\text{N}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{NH}_3(\text{g}) + 3\text{N}_2\text{O}(\text{g}); \Delta H = +241.35 \text{ kcal}$   
 (c)  $\text{N}_2\text{H}_4(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{NH}_3(\text{g}) + 1/2 \text{ O}_2(\text{g}); \Delta H = +34.18 \text{ kcal}$   
 (d)  $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2(\text{g}) + 1/2 \text{ O}_2(\text{g}); \Delta H = +68.32 \text{ kcal}$

- The enthalpy of combustion (in kcal/mol) of liquid  $\text{N}_2\text{H}_4$  is  
 (a) -129.4  
 (b) +129.4  
 (c) -148.84  
 (d) +148.84
  - The enthalpy of formation (in kcal/mol) of liquid  $\text{N}_2\text{H}_4$  is  
 (a) +36.6  
 (b) +48.8  
 (c) +12.2  
 (d) +24.4
  - Ammonia can be obtained according to reaction (b) or (c). Which of the following is correct regarding these reactions, for the same mass of ammonia formed?  
 (a) More mass of reactants is needed for reaction (c)  
 (b) Less mass of reactants is needed for reaction (b)  
 (c) More heat is needed for reaction (b)  
 (d) More heat is needed for reaction (c)
- 

### Comprehension II

The integral enthalpy of solution of one mole of  $\text{H}_2\text{SO}_4$  in  $n$  mole of water is given by the equation

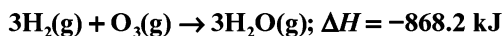
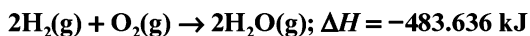
$$\Delta H = -\frac{75n}{(n+1.8)} \text{ kJ/mol. Determine } \Delta H \text{ for the following solutions:}$$

- Solution I:** 1 mole of  $\text{H}_2\text{SO}_4$  dissolved in 5 moles of water.  
 (a) -64.66 kJ  
 (b) -66.18 kJ  
 (c) -208.33 kJ  
 (d) -55.15 kJ
  - Solution III:** 1 mole of  $\text{H}_2\text{SO}_4$  dissolved in large excess of water.  
 (a) Indeterminate  
 (b) zero  
 (c) -750 kJ  
 (d) -75 kJ
  - Solution IV:** Solution I + 5 moles of water.  
 (a) -63.56 kJ  
 (b) -55.15 kJ  
 (c) +8.41 kJ  
 (d) -8.41 kJ
  - Solution II:** 1 mole of  $\text{H}_2\text{SO}_4$  dissolved in 10 moles of water.  
 (a) -69.44 kJ  
 (b) -63.56 kJ  
 (c) -416.67 kJ  
 (d) -58.59 kJ
  - Solution V:** solution II + large excess of water.  
 (a) Indeterminate  
 (b) -63.56 kJ  
 (c) -11.44 kJ  
 (d) -75 kJ
-



## Comprehension III

Study the following thermochemical equations:



- |   |   |
|---|---|
| <p>9. Which oxidizing agent will generate the greatest amount of energy for 1 mole of <math>\text{H}_2(\text{g})</math>?</p> <p>(a) <math>\text{O}_2(\text{g})</math>                                      (b) <math>\text{O}_3(\text{g})</math><br/>         (c) <math>\text{H}_2\text{O}_2(\text{g})</math>                                  (d) all, same</p> <p>10. Which oxidizing agent will generate the greatest amount of energy for 1 g of oxidizing agent?</p> <p>(a) <math>\text{O}_2(\text{g})</math><br/>         (b) <math>\text{O}_3(\text{g})</math><br/>         (c) <math>\text{H}_2\text{O}_2(\text{g})</math><br/>         (d) all, same</p> | <p>11. Which of the reaction will generate the greatest amount of energy on a total mass basis of reactants?</p> <p>(a) <math>\text{H}_2-\text{O}_2</math><br/>         (b) <math>\text{H}_2-\text{O}_3</math><br/>         (c) <math>\text{H}_2-\text{H}_2\text{O}_2</math><br/>         (d) all, same</p> |
|---|---|
- 

## Comprehension IV

The thermal effects of reactions in liquid  $\text{NH}_3$  at  $-33^\circ\text{C}$  were measured by observing the quantity of liquid  $\text{NH}_3$  vaporized by the process of interest. The heat of vaporization of  $\text{NH}_3$  at  $-33^\circ\text{C}$  is 320.0 cal/g. When 0.98 g of  $\text{NH}_4\text{Br}$  was dissolved in 20 g of liquid  $\text{NH}_3$ , 0.25 g of  $\text{NH}_3$  was vaporized. ( $\text{Br} = 80$ )

- |  |   |
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| <p>12. The molar heat of solution of <math>\text{NH}_4\text{Br}</math> in liquid <math>\text{NH}_3</math> at this concentration is</p> <p>(a) +80.0 cal<br/>         (b) - 80.0 cal<br/>         (c) - 8.0 kcal<br/>         (d) +8.0 kcal</p> <p>13. When 0.49 g of <math>\text{NH}_4\text{Br}</math> was dissolved in 20 g of liquid <math>\text{NH}_3</math> containing an equimolar amount of <math>\text{KNH}_2</math>, 0.80 g of</p> | <p>ammonia was vaporized. The <math>\Delta H</math> for the reaction:</p> $\text{NH}_4^+(\text{NH}_3, \text{l}) + \text{NH}_2^-(\text{NH}_3, \text{l}) \rightarrow 2\text{NH}_3(\text{l})$ <p>at 240 K is</p> <p>(a) -256.0 cal<br/>         (b) +256.0 cal<br/>         (c) +51.2 kcal<br/>         (d) -51.2 kcal</p> |
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**Comprehension V**

Use the data (all values are in kJ per mole at 25°C) given below to answer the following:

Enthalpy of formation of  $\text{CH}_3\text{CN} = +88.0$

Enthalpy of formation of  $\text{C}_3\text{H}_8 = -85.0$

Enthalpy of sublimation of graphite = 719.0

Enthalpy of dissociation of nitrogen = 948.0

Enthalpy of dissociation of hydrogen = 435.0

Bond enthalpies: C–H = 414.0; C–N = 378.0; N–H = 426.0

- |  |   |
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| <p>14. The bond enthalpy of C–C bond (kJ/mol) is</p> <p>(a) 250.0                      (b) 335.0</p> <p>(c) 223.33                    (d) 248.5</p>                                  | <p>16. The enthalpy of hydrogenation of <math>\text{CH}_3\text{CN}</math> (kJ/mol) is</p> <p>(a) –288.5</p> <p>(b) +288.5</p> <p>(c) –89.5</p> <p>(d) +89.5</p> |
| <p>15. The bond enthalpy of <math>\text{C}\equiv\text{N}</math> bond (kJ/mol) is</p> <p>(a) 987.5                      (b) 811.5</p> <p>(c) 899.5                      (d) 890.0</p> |   |
- 

**Comprehension VI**

An intimate mixture of hydrogen gas and the theoretical amount of air at 25°C and a total pressure of 1 atm, is exposed in a closed rigid vessel. If the process occurs under adiabatic condition, then using the following data, answer the following questions:

Given: (i)  $C_{p,m} = 8.3 \text{ cal/K-mol}$  (ii)  $C_{p,m} = 11.3 \text{ cal/K-mol}$  (iii)  $\Delta_r H [\text{H}_2\text{O(g)}] = -57.8 \text{ kcal}$  (iv) Air contains 20%  $\text{O}_2$  and 80%  $\text{N}_2$ , by volume

- |  |  |
|--|--|
| <p>17. The values of <math>C_{p,m}</math> of <math>\text{N}_2(\text{g})</math> and <math>\text{H}_2\text{O(g)}</math> (in cal/K-mol) should be</p> <p>(a) 8.3, 8.3</p> <p>(b) 8.3, 11.3</p> <p>(c) 11.3, 11.3</p> <p>(d) 11.3, 8.3</p> | <p>19. What will be the final pressure (approximately)?</p> <p>(a) 8.5 atm</p> <p>(b) 7.6 atm</p> <p>(c) 5.46 atm</p> <p>(d) 0.85 atm</p>  |
| <p>18. What will be the maximum temperature (approximately) attained if the process occurs in adiabatic container?</p> <p>(a) 2940 K</p> <p>(b) 2665 K</p> <p>(c) 1900 K</p> <p>(d) 298 K</p>  | <p>20. If at initial temperature, <math>T_1</math>, <math>E_1</math> is the internal energy and at higher temperature <math>T_2</math>, <math>E_2</math> is the internal energy, then</p> <p>(a) <math>E_1 &gt; E_2</math></p> <p>(b) <math>E_1 &lt; E_2</math></p> <p>(c) <math>E_1 = E_2</math></p> <p>(d) Unpredictable</p> |
-

## Comprehension VII

When 0.1 mole of  $C_8H_{18}(l)$  at 300 K is completely burned at constant pressure in some oxygen gas at 300 K, yielding as products gaseous  $H_2O$ ,  $CO$  and  $CO_2$  at 800 K, the process yielding 87.3 kcal of heat to the surrounding. Given:

$$\Delta_f H \text{ (kcal/mol): } C_8H_{18}(l) = -74.0, CO_2(g) = -94.0, CO(g) = -26.5, H_2O(g) = -58.0$$

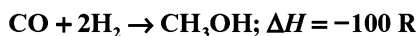
Molar heat capacity at constant pressure (cal/K-mol):  $CO(g) = 7.0$ ,  $CO_2(g) = 8.0$ ,  $H_2O(g) = 6.0$

Assume that all  $\Delta_f H$  are independent of temperature.

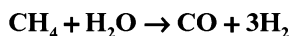
21. The value of  $\Delta_c H$  of  $C_8H_{18}(l)$  is (in kcal/mol)  
 (a) +1200.0 (b) +660.0  
 (c) -1200.0 (d) -660.0
22. The value of  $\Delta_r H$  for the reaction:  
 $C_8H_{18}(l) + \frac{17}{2} O_2(g) \rightarrow 8CO_2(g) + 9H_2O(g)$   
 is (in kcal/mol)  
 (a) +1200.0  
 (b) +660.0  
 (c) -1200.0  
 (d) -660.0
23. How many moles of  $CO_2$  are produced?  
 (a) 0.1 (b) 0.8  
 (c) 0.4 (d) 0.05
24. How many moles of  $H_2O$  are produced?  
 (a) 0.1 (b) 0.9  
 (c) 0.45 (d) 1.8
25. What is the magnitude work done by the system?  
 (a) 1.03 kcal (b) 2.06 kcal  
 (c) 0.96 kcal (d) 5.7 kcal

## Comprehension VIII

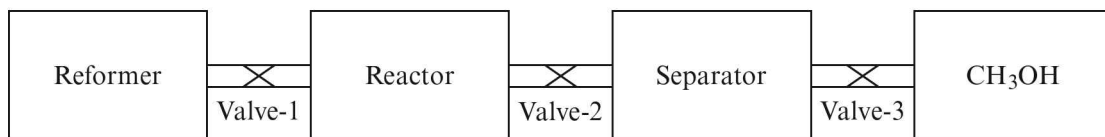
A factory is producing methanol based on the reaction:



Hydrogen and carbon monoxide are obtained by the reaction:



Three units of factory, namely, reformer (for the production of  $H_2$  and  $CO$ ), reactor (for the production of methanol from  $CO$  and  $H_2$ ) and separator (to separate  $CH_3OH$  from  $CO$  and  $H_2$ ) are schematically shown in the figure:



The flow of methanol from Valve-3 is 1000 mol/sec. The factory is so designed that  $2/3^{rd}$  of the  $CO$  is converted to  $CH_3OH$ . Assume that the reformer reaction goes to completion.

26. What is the flow of  $CO$  and  $H_2$  at valve-1?  
 (a)  $CO = 1500 \text{ mol/sec}$ ;  $H_2 = 2000 \text{ mol/sec}$   
 (b)  $CO = 1500 \text{ mol/sec}$ ;  $H_2 = 3000 \text{ mol/sec}$   
 (c)  $CO = 1000 \text{ mol/sec}$ ;  $H_2 = 2000 \text{ mol/sec}$   
 (d)  $CO = 1500 \text{ mol/sec}$ ;  $H_2 = 4500 \text{ mol/sec}$
27. What is the flow of  $CO$  and  $H_2$  at valve-2?  
 (a)  $CO = 500 \text{ mol/sec}$ ;  $H_2 = 1000 \text{ mol/sec}$   
 (b)  $CO = 500 \text{ mol/sec}$ ;  $H_2 = 2500 \text{ mol/sec}$
- (c)  $CO = 500 \text{ mol/sec}$ ;  $H_2 = 2000 \text{ mol/sec}$   
 (d)  $CO = 500 \text{ mol/sec}$ ;  $H_2 = 1500 \text{ mol/sec}$
28. Amount of energy released in methanol reactor in one minute is  
 (a) 12,000 kcal  
 (b) 1200 kcal  
 (c) 6000 kcal  
 (d) 600 kcal

### Comprehension IX

When 12 g of carbon reacted with oxygen to form CO and CO<sub>2</sub> at 298 K and constant pressure, 72.0 kcal of heat was liberated and no carbon remained. Heat of formation of CO and CO<sub>2</sub> are -26.0 and -94.0 kcal/mole, respectively.

- |                           |   |
|---------------------------|---|
| 29. Moles of CO formed is | 30. Mass of oxygen reacted with carbon is |
| (a) 0.4                   | (a) 16 g                                  |
| (b) 0.5                   | (b) 32 g                                  |
| (c) 0.6                   | (c) 24 g                                  |
| (d) 1.0                   | (d) 22.4 g                                |
- 

### Comprehension X

The bond dissociation enthalpy of the first H-S bond in hydrogen sulphide is 376.0 kJ/mol. The enthalpies of formation of H<sub>2</sub>S(g) and S(g) are -20.0 and 277.0 kJ/mol, respectively. The bond dissociation enthalpy of H-H bond is 436.0 kJ/mol.

- |   |  |
|---|--|
| 31. The enthalpy of formation of the free radical HS is | 32. The bond dissociation enthalpy of the free radical HS is |
| (a) 138 kJ/mol  | (a) 138 kJ/mol   |
| (b) -138 kJ/mol   | (b) 276 kJ/mol   |
| (c) -10 kJ/mol  | (c) 357 kJ/mol   |
| (d) 357 kJ/mol  | (d) 376 kJ/mol   |
- 

### Comprehension XI

For the reaction at 25°C,  $X_2O_4(l) \rightarrow 2XO_2(g)$ ,  $\Delta E^\circ = 2.1$  kcal and  $\Delta S^\circ = 20$  cal/K.

- |  |                                    |
|--|------------------------------------|
| 33. $\Delta G^\circ$ for the reaction is | 34. The reaction is                |
| (a) -2.7 kcal                            | (a) spontaneous and exergonic      |
| (b) -9.25 kcal                           | (b) non-spontaneous and exergonic  |
| (c) +2.7 kcal                            | (c) spontaneous and endergonic     |
| (d) +9.25 kcal                           | (d) non-spontaneous and endergonic |
- 

### Section D (Assertion – Reason)

The following questions consist of two statements. Mark

- If both statements are CORRECT, and **Statement II** is the CORRECT explanation of **Statement I**.
- If both statements are CORRECT, and **Statement II** is NOT the CORRECT explanation of **Statement I**.
- If **Statement I** is CORRECT, but **Statement II** is INCORRECT.
- If **Statement I** is INCORRECT, but **Statement II** is CORRECT.

- Statement I:** On increasing the temperature, enthalpy of reaction may increase, decrease or remain constant.

**Statement II:** On changing the temperature, the enthalpies of reactants and products may change to same or different extent depending on their heat capacities.

- Statement I:** Standard enthalpy of isomerization of an enantiomer into the other is zero.

**Statement II:** The two enantiomers of any chiral compound have the same enthalpy of formation.

3. **Statement I:** Heat evolved in the neutralization of either 1 mole of HCl or 1 mole of  $\text{H}_2\text{SO}_4$  with NaOH is same.

**Statement II:** Both, HCl and  $\text{H}_2\text{SO}_4$  are strong acids.

4. **Statement I:** When a salt is dissolved in water, the temperature of solution decreases.

**Statement II:** Solubility of any salt in water may be endothermic or exothermic.

5. **Statement I:** If 5 ml of an acid solution is completely neutralized by adding 5 ml of a base solution, the temperature of solution increases by  $x^\circ\text{C}$ . If 20 ml of the same acid solution is completely neutralized by adding 20 ml of the same base solution, the temperature of solution increases by  $4x^\circ\text{C}$ .

**Statement II:** Heat liberated in the second case will be four times the heat liberated in the first case.

6. **Statement I:** The solubility of any gas in any liquid is an exothermic process.

**Statement II:** All the gases are highly soluble in any liquid.

7. **Statement I:** For all the salts completely soluble in water, the magnitude of sum of

enthalpies of hydration of ions is greater than the magnitude of lattice enthalpy of the salt.

**Statement II:** If the magnitude of sum of enthalpies of hydration of ions is less than the lattice enthalpy of the salt, the salt is completely insoluble in water.

8. **Statement I:** The magnitude of enthalpy of combustion of diamond is greater than that of graphite.

**Statement II:** Graphite is thermodynamically more stable form of carbon than diamond.

9. **Statement I:** The magnitude of enthalpy of combustion of 2-Butene is less than that of 1-Butene.

**Statement II:** 2-Butene is thermodynamically more stable than 1-Butene.

10. **Statement I:** Enthalpy changes are positive when  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and salt like NaCl, KCl, etc., which do not form hydrates is dissolved in water. But enthalpy changes are negative when anhydrous salts capable of forming hydrates are dissolved in water.

**Statement II:** The difference in the behaviour is due to large difference in the molecular masses of hydrated and anhydrous salts. The substance with large molecular mass usually show positive enthalpy changes on dissolutions.

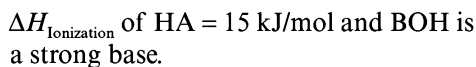
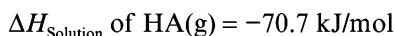
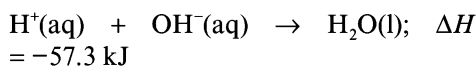
## Section E (Column Match)

1. Match Column I with Column II

Column I (Reaction)	Column II (Process)
(A) $\text{C(s)} + \frac{1}{2} \text{O}_2\text{(g)} \rightarrow \text{CO(g)}$	(P) Combustion
(B) $\text{CO(g)} + \frac{1}{2} \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$	(Q) Neutralization
(C) $\text{NaOH(aq)} + \text{HCl(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$	(R) Process of formation
(D) $\text{H}_2\text{(g)} + \frac{1}{2} \text{O}_2\text{(g)} \rightarrow \text{H}_2\text{O(l)}$	(S) Used in fuel cell

## 2. Match the following

Column I (Reaction)	Column II (Relation)
(A) $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$	(P) $\Delta H = \Delta U + RT$
(B) $2\text{N}_2\text{O}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$	(Q) $\Delta H = \Delta U$
(C) $\text{H}_2(\text{g}) + \text{I}_2(\text{s}) \rightarrow 2\text{HI}(\text{g})$	(R) $\Delta H = \Delta U - 2RT$
(D) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$	(S) $\Delta H = \Delta U - RT$

3. Column I contains some chemical reactions and Column II contains some  $\Delta H$  values (in kJ). Match the correct  $\Delta H$  in Column II for the chemical reaction in Column I, with the help of the following thermochemical equations given:

Column I (Chemical reactions)	Column II ( $\Delta H$ values in kJ)
(A) $\text{HA}(\text{aq}) + \text{BOH}(\text{aq}) \rightarrow \text{BA}(\text{aq}) + \text{H}_2\text{O}$	(P) -42.3
(B) $\text{HA}(\text{g}) + \text{BOH}(\text{g}) \rightarrow \text{BA}(\text{aq}) + \text{H}_2\text{O}$	(Q) -93
(C) $\text{HA}(\text{g}) \rightarrow \text{H}^+(\text{aq}) + \text{A}^-(\text{aq})$	(R) -55.7
(D) $\text{B}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{BOH}(\text{aq})$	(S) 0

## 4. Carefully observe the given diagrams which indicate standard enthalpy of

formation of different states of one mole of Mg and two moles of Cl atoms and match the entries in Column I and II provided.

+ 2600	.....	$[\text{Mg}^{2+}(\text{g}) + 2\text{Cl}(\text{g})]$
+ 2360	.....	$[\text{Mg}^{2+}(\text{g}) + \text{Cl}_2(\text{g})]$
+ 1870	.....	$[\text{Mg}^{2+}(\text{g}) + 2\text{Cl}^-(\text{g})]$
+ 1110	.....	$[\text{Mg}^{2+}(\text{g}) + 2\text{Cl}^-(\text{aq})]$
+ 170	.....	$[\text{Mg}(\text{g}) + \text{Cl}_2(\text{g})]$
0	.....	$[\text{Mg}(\text{s}) + \text{Cl}_2(\text{g})]$
- 640	.....	$[\text{MgCl}_2(\text{s})]$
- 790	.....	$[\text{Mg}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq})]$

Energy (kJ) ↑                      States of Mg and Cl<sub>2</sub>

Column I	Column II
(A) $\Delta_f H [\text{Mg}^{2+}(\text{aq})]$	(P) -1900 kJ/mol
(B) $\Delta_f H [\text{Cl}^-(\text{aq})]$	(Q) +460 kJ/mol
(C) $\Delta H_{\text{Hydration}} [\text{Mg}^{2+}(\text{g})]$	(R) -625 kJ/mol
(D) Lattice enthalpy of $\text{MgCl}_2(\text{s})$	(S) +2510 kJ/mol

## 5. Match the columns

Column I	Column II ( $\Delta H$ is also known as)
(A) $\text{C}(\text{graphite}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$	(P) $\Delta H_{\text{formation}}$
(B) $\text{C}(\text{graphite}) \rightarrow \text{C}(\text{g})$	(Q) $\Delta H_{\text{combustion}}$
(C) $\text{HCl}(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{Cl}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$	(R) $\Delta H_{\text{atomization}}$
	(S) $\Delta H_{\text{neutralization}}$

## 6. Match the columns

Column I	Column II
(A) Sb(s)	(P) $\Delta_f H^\circ = +ve$ , $\Delta_f S^\circ = +ve$
(B) O <sub>3</sub> (g)	(Q) $\Delta_f H^\circ = 0$ , $\Delta_f S^\circ = 0$
(C) I <sub>2</sub> (g) (R)	(R) $\Delta_f H^\circ = +ve$ , $\Delta_f S^\circ = -ve$
(D) CO(g)	(S) $\Delta_f H^\circ = -ve$ , $\Delta_f S^\circ = +ve$

## 7. Match the columns

Column I	Column II
(A) $2\text{HCl(g)} \rightarrow \text{H}_2\text{(g)} + \text{Cl}_2\text{(g)}$	(P) $\Delta H = +ve$ , $\Delta S = +ve$
(B) $2\text{O}_3\text{(g)} \rightarrow 3\text{O}_2\text{(g)}$	(Q) $\Delta H = -ve$ , $\Delta S = +ve$
(C) $\text{MgCO}_3\text{(g)} \rightarrow \text{MgO(s)} + \text{CO}_2\text{(g)}$	(R) $\Delta H = -ve$ , $\Delta S = -ve$
(D) $2\text{NO}_2\text{(g)} \rightarrow \text{N}_2\text{O}_4\text{(g)}$	(S) $\Delta H = +ve$ , $\Delta S \approx +ve$

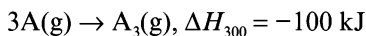
## 8. Match the column

Column I	Column II
(A) $\text{H}_2\text{(g)} + \text{Cl}_2\text{(g)} \rightarrow 2\text{HCl(g)}$	(P) $\Delta H = \Delta U$
(B) $2\text{C(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{CO(g)}$	(Q) $\Delta H > \Delta U$
(C) $\text{PCl}_5\text{(g)} \rightarrow \text{PCl}_3\text{(g)} + \text{Cl}_2\text{(g)}$	(R) $\Delta H < \Delta U$
(D) $\text{C}_2\text{H}_4\text{(g)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)} + 2\text{H}_2\text{O(l)}$	(S) $ \Delta H  >  \Delta U $
	(T) $ \Delta H  <  \Delta U $

## 9. Match the columns

Column I	Column II
(A) $\text{C(diamond)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$	(P) $\Delta_f H^\circ = \Delta_c H^\circ$
(B) $\text{C(graphite)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$	(Q) $\Delta_f H^\circ = \Delta_f H^\circ$
(C) $\text{H}_2\text{(g)} \rightarrow 2\text{H(g)}$	(R) $\Delta_f H^\circ = \Delta_{\text{atomization}} H^\circ$
(D) $\text{CH}_4\text{(g)} \rightarrow \text{C(g)} + 4\text{H(g)}$	(S) $\Delta_f H^\circ = \Delta_{\text{bond}} H^\circ$

## 10. Some thermochemical details are given as:



The standard boiling points of A(l) and A<sub>3</sub>(l) are 300 K and 400 K, respectively.

Molar heat capacities at constant pressure (in J/K·mol): A(l) = 40; A(g) = 20; A<sub>3</sub>(l) = 50; A<sub>3</sub>(g) = 30

Match the columns on the basis of these details:

Column I	Column II
(A) $\text{A(l)} \rightarrow \text{A(g)}, \Delta_{\text{vap}} H_{400}$	(P) -103 kJ/mol
(B) $\text{A}_3\text{(l)} \rightarrow \text{A}_3\text{(g)}, \Delta_{\text{vap}} H_{300}$	(Q) +23 kJ/mol
(C) $3\text{A(l)} \rightarrow \text{A}_3\text{(l)}, \Delta H_{300}$	(R) +52 kJ/mol
(D) $3\text{A(l)} \rightarrow \text{A}_3\text{(l)}, \Delta H_{400}$	(S) -77 kJ/mol

## Section F (Subjective)

### Single-digit Integer Type

- Volumes of 50 ml of 1 M-NaOH and 50 ml of 1 M-HCl both at the same temperature were mixed in a calorimeter of very small heat capacity. A temperature rise of 411 K was recorded. In a second experiment, the HCl was replaced by 50 ml of 1 M-HCOOH. The temperature rise was 321 K. The enthalpy of ionization (in kcal/mol) of HCOOH is
- The heat evolved on combustion of 1 g of starch,  $(C_6H_{10}O_5)_x$ , into  $CO_2(g)$  and  $H_2O(l)$  is 4.6 kcal. Heat of formation of  $CO_2(g)$  and  $H_2O(l)$  are  $-94.2$  and  $-68.4$  kcal/mol, respectively. The magnitude of standard enthalpy of formation of 1 g of starch (in kcal) is
- In order to get maximum calorific output, a burner should have an optimum fuel to oxygen ratio which corresponds to 3 times as much oxygen as is required theoretically for complete combustion of the fuel. A burner which has been adjusted for methane as fuel (with 'X' l/hr of methane and '6X' l/hr of oxygen) is to be adjusted for butane. In order to get same calorific output, what should be the supply of oxygen (in l/hr) with 1 l/hr supply of butane? Assume that losses due to incomplete combustion, etc., are the same for both fuels and that the gases behave ideally. Enthalpies of combustion; methane =  $-800$  kJ/mol; butane =  $-3120$  kJ/mol.
- The enthalpy of neutralization of monobasic acid in decinormal solution by a dilute solution of KOH is  $-12,200$  cal. The enthalpy of neutralization of strong acid by strong base is  $-13,700$  cal. Assuming that the acid is 25% dissociated in decinormal solution, the enthalpy of dissociation of the acid (in kcal/mole) is
- A volume of 1.642 l sample of a mixture of methane gas and oxygen measured at 298 K and 1.192 atm, was allowed to react at constant pressure in a calorimeter which together with its content had a heat capacity of 1260 cal/K. The complete combustion of methane to carbon dioxide and water caused a temperature rise in calorimeter 0.667 K. The volume per cent of methane in original mixture is (Given the heat of combustion of methane is  $-210$  kcal/mole)
- A solution of 6.3 g of haemoglobin (molar mass = 64,000 g/mol) in 25 ml of solution shows a temperature rise of  $0.03^\circ C$  for complete oxygenation. Each mole of haemoglobin binds 4 moles of oxygen. If the heat capacity of the solution is 4.2 J/K-ml, the amount of heat released per mole of oxygen bound (in kJ) is
- Two solutions, initially at  $25^\circ C$ , were mixed in an insulated bottle. One contained 200 ml of 0.4 M weak monoprotic acid solution. The other contained 100 ml of a solution having 0.5 mole NaOH per litre. After mixing, the temperature rose to  $26^\circ C$ . Assume that the densities of both the solutions are 1.0 g/ml and that their specific heat capacities are all 1.0 cal/g-K. The amount of heat evolved (in kcal) in the neutralization of 1 mole of the acid is
- In solid  $NH_3$ , each  $NH_3$  molecule has six other  $NH_3$  molecules as nearest neighbours. The enthalpy of sublimation of  $NH_3(s)$  at its melting point is 30.4 kJ/mol and estimated value of enthalpy of sublimation of  $NH_3(s)$ , where there were no hydrogen bonds, is 15.4 kJ/mol. What is the average strength of hydrogen bonds in solid  $NH_3$  in kJ/mol?



- When 3.0 g graphite is burnt in limited supply of oxygen at 298 K and 1 bar, 7.5 kcal heat is released. No solid is left and the gaseous product formed is not absorbed in aqueous KOH solution. When 4.0 g graphite is burnt in excess supply of oxygen at 298 K and 1 bar, 32 kcal heat is released. No solid residue is left and the gaseous product formed is absorbed completely in aqueous KOH solution. When 4.0 g  $\text{CO}_2(\text{g})$  is decomposed completely into  $\text{CO}(\text{g})$  and  $\text{O}_2(\text{g})$  at 29 K and 1 bar, the enthalpy of system increases (in kcal) by
- The enthalpies of neutralization of a weak acid HA and a weak acid HB by NaOH are  $-6900$  cal/equivalent and  $-2900$  cal/equivalent, respectively. When one equivalent of NaOH is added to a solution containing one equivalent of HA and one equivalent of HB, the enthalpy change was  $-3900$  cal. If the base is distributed between HA and HB in the ratio 1 :  $x$ , the value of ' $x$ ' is

### Four-digit Integer Type

- The heat of total cracking of hydrocarbons,  $\Delta H_{\text{TC}}$  is defined as  $\Delta H$  at 298.15 K and 101.325 kPa for the process:  

$$\text{C}_n\text{H}_m + \left(2n - \frac{m}{2}\right) \text{H}_2(\text{g}) \rightarrow n\text{CH}_4(\text{g})$$

The values of  $\Delta H_{\text{TC}}$  is  $-65.2$  kJ for  $\text{C}_2\text{H}_6$  and  $-87.4$  kJ for  $\text{C}_3\text{H}_8$ . Calculate  $\Delta H$  (in kJ) for  

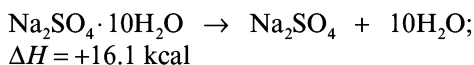
$$\text{CH}_4(\text{g}) + \text{C}_3\text{H}_8(\text{g}) \rightarrow 2\text{C}_2\text{H}_6(\text{g})$$
- An athlete takes 20 breaths per minute at room temperature. The air inhaled in each breath is 164.2 ml which contains 20% oxygen by volume, while exhaled air contains 10% oxygen by volume. Assuming that all the oxygen consumed is used for converting glucose into carbon dioxide and water, how much heat is produced (in kJ) in the body in one hour? Body temperature is 310 K and enthalpy of combustion of glucose is  $-2820$  kJ/mol at 310 K.
- The heat of combustion of glycogen is about 432 kJ/mol of carbon. Assume that average rate of heat loss by an adult male is 150 W. If we were to assume that all the heat comes from the oxidation of glycogen, how many units of glycogen (1 mole carbon per unit) must be oxidized per day to provide for this heat loss?
- Only gases remains after 15.0 g of carbon is treated with 20 l of air at 380 K and 8.21 atm pressure. (Assume 19% by volume oxygen, 80% nitrogen, 1% carbon dioxide). Determine the amount of heat evolved (in kcal) under constant pressure. Enthalpies of formation of  $\text{CO}_2(\text{g})$  and  $\text{CO}(\text{g})$  are  $-96.0$  and  $-26.0$  kcal/mol, respectively.
- Ethanol was oxidized to acetic acid in a catalyst chamber at  $18^\circ\text{C}$ . What should be rate of removal of heat (in kcal/hr) to maintain the reaction chamber at  $18^\circ\text{C}$  with the feed rate of 2.3 kg ethanol per hour, along with excess oxygen to the system at  $18^\circ\text{C}$ , with a 40 mole per cent yield based on ethanol. The enthalpies of formation of  $\text{H}_2\text{O}(\text{l})$ ,  $\text{C}_2\text{H}_5\text{OH}(\text{l})$  and  $\text{CH}_3\text{COOH}(\text{l})$  are, respectively,  $-68$ ,  $-66$  and  $-118$  kcal/mol.
- The carbon dioxide exhaled in the breath of astronaut is often removed from the spacecrafts by reaction with lithium hydroxide.  

$$2\text{LiOH}(\text{s}) + \text{CO}_2(\text{g}) \rightarrow \text{Li}_2\text{CO}_3(\text{s}) + \text{H}_2\text{O}(\text{l})$$

Assume that each astronaut requires 2100 kcal of energy per day. Further

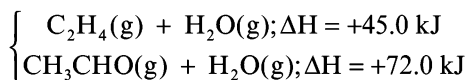
assume that this energy is obtained only from the combustion of glucose into to  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$ . The standard enthalpies of formation of glucose,  $\text{CO}_2$  and water are  $-1280$ ,  $-395$  and  $-285$   $\text{kJ/mol}$ , respectively. The minimum mass (in g) of  $\text{LiOH}$  required per astronaut per day to react completely with all the  $\text{CO}_2$  produced is

7. The reversible reaction:



goes completely to the right at temperature above  $32.4^\circ\text{C}$  and remains completely on the left below this temperature. This system has been used in some solar houses for heating at night with the energy absorbed from the sun's radiation during the day. How many litres of fuel gas could be saved per night by the reversal of the dehydration of a fixed charge of  $100 \text{ kg Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ? Assume that the fuel value of the gas is  $10,000 \text{ kcal/m}^3$ .

8. Ethanol can undergo decomposition to form two sets of products:



If the molar ratio of  $\text{C}_2\text{H}_4(\text{g})$  to  $\text{CH}_3\text{CHO}(\text{g})$  in the product is  $8:1$ , the heat absorbed in decomposition of  $2.5$  mole of ethanol(g) (in kJ) is

9. A slice of banana weighing  $2.5 \text{ g}$  was burnt in a bomb calorimeter and produced a temperature rise of  $3.0 \text{ K}$ . In the same calorimeter, combustion of a  $0.305 \text{ g}$  sample of benzoic acid produced a temperature rise of  $4.0 \text{ K}$ . The heat of combustion of benzoic acid at constant volume is  $-800 \text{ kcal/mol}$ . If an average

banana weighs  $125 \text{ g}$ , how many calories can be obtained from one average banana?

10. The enthalpy of formation of liquid water at  $25^\circ\text{C}$  is  $-286 \text{ kJ}$ . Given  $C_p = 75.4 \text{ J/K-mol}$  for  $\text{H}_2\text{O}(\text{l})$  and  $33.4 \text{ J/K-mol}$  for  $\text{H}_2\text{O}(\text{g})$  and that the molar enthalpy of vaporization of liquid water at  $125^\circ\text{C}$  is  $40.8 \text{ kJ/mol}$ . The enthalpy of dissociation (in  $\text{kJ/mol}$ ) of  $\text{H}_2\text{O}(\text{g})$  into  $\text{H}_2$  and  $\text{O}_2$  gases at  $25^\circ\text{C}$  is
11. For the hypothetical reaction:  $2\text{B}(\text{g}) \rightarrow \text{B}_2(\text{g})$ ;  $\Delta C_p [\text{J/K}^{-1}] = 2.0 \times 10^{-2} \text{ T/K}$  and  $\Delta H_{300} = -40.0 \text{ kJ/mol}$ . Estimate the absolute temperature at which  $\Delta H = 0$  for this reaction.
12. The value of heat of combustion per  $\text{CH}_2$  unit of cyclopropane is  $-697 \text{ kJ/mol}$ . Calculate its strain energy. Given: the heats of formation of  $\text{C}(\text{g})$ ,  $\text{H}(\text{g})$ , carbon dioxide and water are  $715$ ,  $218$ ,  $-393$  and  $-285 \text{ kJ/mol}$ , respectively, and  $\text{C-C}$  and  $\text{C-H}$  bond energies are  $356$  and  $408 \text{ kJ/mol}$ , respectively.
13. The hydrogen bond between  $\text{F}^-$  and  $\text{CHCOOH}$  is very strong and its strength may be analysed by setting up a Born-Haber cycle with the following data (in  $\text{kJ/mol}$ ): Lattice energy of  $\text{KF} \cdot \text{CH}_3\text{COOH}$ ,  $734$ ; enthalpy of vaporization of  $\text{CH}_3\text{COOH}$ ,  $20$ ; enthalpy of solution of  $\text{KF}$ ,  $35$ ; solvation energy of  $\text{K}^+(\text{g})$ ,  $-325$ ; solvation energy of  $\text{F}^-$ ,  $-389$ ; enthalpy of formation of  $\text{KF} \cdot \text{CH}_3\text{COOH}(\text{s})$  from  $\text{KF}(\text{s})$  and  $\text{CH}_3\text{COOH}(\text{l})$ ,  $-25$ . Find the energy of the hydrogen bond between  $\text{F}^-$  and  $\text{CH}_3\text{COOH}$  in the gas phase (in  $\text{kJ/mol}$ ).
14. Find the bond enthalpy (in  $\text{kJ/mol}$ ) of 'three centre two electron bond' in  $\text{B}_2\text{H}_6$  from the following data:  $\Delta_f H^\circ [\text{BH}_3(\text{g})] = 100 \text{ kJ/mol}$ ;  $\Delta_f H^\circ [\text{B}_2\text{H}_6(\text{g})] = 36 \text{ kJ/mol}$ ;  $\Delta H_{\text{Atomization}} [\text{B}(\text{s})] = 565 \text{ kJ/mol}$ ;  $\Delta H_{\text{Atomization}} [\text{H}_2(\text{g})] = 436 \text{ kJ/mol}$ .

15. Calculate the enthalpy change (in kcal) for the reaction:  $\text{XeF}_4 \rightarrow \text{Xe}^+ + \text{F}^- + \text{F}_2 + \text{F}$ . The average Xe – F bond enthalpy is 34 kcal/mol, first ionization enthalpy of Xe is 279 kcal/mol, electron gain enthalpy of fluorine is –85 kcal/mol and bond dissociation enthalpy of  $\text{F}_2$  is 38 kcal/mol.

16. Calculate  $\Delta H_{\text{vap}}$  [ $\text{CH}_3\text{COOH}(\text{l})$ ] in kJ/mol from the following data:

$\Delta H_{\text{Solution}}$  [ $\text{KF} \cdot \text{CH}_3\text{COOH}(\text{s})$ ] in glacial acetic acid = –3 kJ/mol




$\Delta H_{\text{Solution}}$  [ $\text{KF}(\text{s})$ ] in glacial acetic acid = +35 kJ/mol

The strength of H-bond between  $\text{F}^-(\text{g})$  and  $\text{CH}_3\text{COOH}(\text{g})$  = +46 kJ/mol

Lattice enthalpy of  $\text{KF} \cdot \text{CH}_3\text{COOH}(\text{s})$  = +734 kJ/mol

Lattice enthalpy of  $\text{KF}(\text{s})$  = +797 kJ/mol

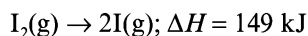
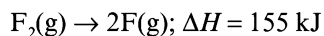
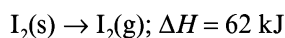
17. Estimate  $\Delta_f H^\circ$  [Pyridine(l)] (in kJ/mol) from the given data:

Compound	$\Delta_f H^\circ$ (kJ/mol)
$\text{CH}_2 = \text{N} - \text{CH}_3(\text{g})$	+44
$\text{CH}_3 - \text{NH} - \text{CH}_3(\text{g})$	–18
 (g)	–37
 (g)	–156
 N – H (g)	–50

Magnitude of resonance energy of pyridine = 125 kJ/mol

$\Delta H_{\text{vap}, 298 \text{ K}}$  [Pyridine(l)] = 40 kJ/mol

18. The standard molar enthalpies of formation of  $\text{IF}_3(\text{g})$  and  $\text{IF}_5(\text{g})$  are –470 kJ and –847 kJ, respectively. Valence shell electron-pair repulsion theory predicts that  $\text{IF}_5(\text{g})$  is square pyramidal in shape in which all I – F bonds are equivalent while  $\text{IF}_3(\text{g})$  is T-shaped (based on trigonal-bipyramidal geometry) in which I – F bonds are of different lengths. It is observed that the axial I – F bonds in  $\text{IF}_3$  are equivalent to the I – F bonds in  $\text{IF}_5$ . Calculate the equatorial I – F bond strength (in kJ/mol) in  $\text{IF}_3$ . Some other details given are:



19. The standard molar enthalpies of formations of  $\text{H}_2\text{O}(\text{l})$  and  $\text{H}_2\text{O}_2(\text{l})$  are –286 and –188 kJ/mol, respectively. Molar enthalpies of vaporization of  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$  are 44 and 53 kJ, respectively. The bond dissociation enthalpy of  $\text{O}_2(\text{g})$  is 498 kJ/mol. Calculate the bond dissociation enthalpy (in kJ/mol) of O – O bond in  $\text{H}_2\text{O}_2$ , assuming that the bond dissociation enthalpy of O – H bond is same in both  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$ .

20. Enthalpy of the reaction:  $\text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq}) \rightarrow \text{AgBr}(\text{s})$  is –84.54 kJ. Magnitude of enthalpies of formation of  $\text{Ag}^+(\text{aq})$  and  $\text{Br}^-(\text{aq})$  is in 8:9 ratio but their signs are opposite. Enthalpy of formation of  $\text{AgBr}$  is –99.54 kJ/mol. The magnitude of enthalpy of formation of  $\text{Ag}^+(\text{aq})$  (in kJ/mol) is

## Answer Keys – Exercise II

### Section A (Only one Correct)

- |         |         |         |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (b)  | 2. (b)  | 3. (b)  | 4. (b)  | 5. (b)  | 6. (a)  | 7. (d)  | 8. (c)  | 9. (c)  | 10. (a) |
| 11. (d) | 12. (d) | 13. (b) | 14. (a) | 15. (d) | 16. (b) | 17. (a) | 18. (c) | 19. (a) | 20. (b) |
| 21. (d) | 22. (a) | 23. (b) | 24. (d) | 25. (a) | 26. (d) | 27. (a) | 28. (b) | 29. (b) | 30. (a) |
| 31. (a) | 32. (b) | 33. (a) | 34. (b) | 35. (b) | 36. (c) | 37. (a) | 38. (b) | 39. (a) | 40. (c) |
| 41. (a) | 42. (b) | 43. (a) | 44. (d) | 45. (b) | 46. (b) | 47. (a) | 48. (b) | 49. (d) | 50. (d) |
| 51. (a) | 52. (b) | 53. (b) | 54. (c) | 55. (a) |         |         |         |         |         |

### Section B (One or More than one Correct)

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

### Section C

#### Comprehension I

1. (c)    2. (c)    3. (c)

#### Comprehension II

4. (d)    5. (b)    6. (d)  
7. (d)    8. (c)

#### Comprehension III

9. (c)    10. (b)    11. (b)

#### Comprehension IV

12. (c)    13. (d)

#### Comprehension V

14. (b)    15. (c)    16. (a)

#### Comprehension VI

17. (b)    18. (a)    19. (a)    20. (c)

#### Comprehension VII

21. (c)    22. (d)    23. (c)  
24. (b)    25. (b)

#### Comprehension VIII

26. (d)    27. (b)    28. (a)

#### Comprehension IX

29. (c)    30. (d)

#### Comprehension X

31. (a)    32. (c)

#### Comprehension XI

33. (a)    34. (a)

### Section D (Assertion – Reason)

1. (a)    2. (a)    3. (d)    4. (d)    5. (d)    6. (c)    7. (c)    8. (a)    9. (a)    10. (c)

### Section E (Column Match)

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

- 4.  $A \rightarrow Q; B \rightarrow R; C \rightarrow P; D \rightarrow S$
- 5.  $A \rightarrow P, Q; B \rightarrow P, R; C \rightarrow S$
- 6.  $A \rightarrow Q; B \rightarrow R; C \rightarrow P; D \rightarrow S$
- 7.  $A \rightarrow S; B \rightarrow Q; C \rightarrow P; D \rightarrow R$
- 8.  $A \rightarrow P; B \rightarrow Q, T; C \rightarrow Q, S; D \rightarrow R, T$
- 9.  $A \rightarrow P; B \rightarrow P, Q; C \rightarrow R, S; D \rightarrow R$
- 10.  $A \rightarrow Q; B \rightarrow R; C \rightarrow S; D \rightarrow P$

**Section F (Subjective)**

**Single-digit Integer Type**

1. (3)    2. (1)    3. (5)    4. (2)    5. (5)    6. (8)    7. (6)    8. (5)    9. (6)    10. (3)

**Four-digit Integer Type**

- |            |            |            |            |            |
|------------|------------|------------|------------|------------|
| 1. (0043)  | 2. (0564)  | 3. (0030)  | 4. (0085)  | 5. (2400)  |
| 6. (0216)  | 7. (0500)  | 8. (0120)  | 9. (0075)  | 10. (0241) |
| 11. (0700) | 12. (0120) | 13. (0060) | 14. (0455) | 15. (0292) |
| 16. (0021) | 17. (0085) | 18. (0272) | 19. (0142) | 20. (0120) |
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