

## CHAPTER

# 4

# Thermodynamics

## EXERCISE I (JEE MAIN)

### Basics

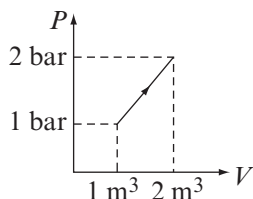
1. A thermodynamic property is that physical quantity
  - (a) which is used in thermochemistry.
  - (b) which obeys all the laws of thermodynamics.
  - (c) which is used to define a state of the system.
  - (d) which is used in measuring thermal change.
2. Which of the following is not a thermodynamic property of a system?
  - (a)  $H$
  - (b)  $P$
  - (c)  $E$
  - (d)  $w$
3. Which of the following is the best container for gas during isothermal process?
  - (a) Glass vessel
  - (b) Wood vessel
  - (c) Copper vessel
  - (d) Thermos flask
4. The internal energy of an ideal gas increases during an isothermal process when the gas is
  - (a) expanded by adding more molecules to it.
  - (b) expanded by adding more heat to it.
  - (c) expanded against zero pressure.
  - (d) compressed by doing work on it
5. Maximum work can a gas do, if it is allowed to expand isothermally against
  - (a) vacuum
  - (b) high pressure of surrounding
  - (c) low pressure of surrounding
  - (d) atmospheric pressure
6. The internal energy change when a system goes from state A to B is 40 kJ/mol. If the system goes from A to B by a reversible path and returns to state A by an irreversible path, what would be the net change in internal energy?
  - (a) 40 kJ
  - (b) >40 kJ
  - (c) <40 kJ
  - (d) Zero
7. A system is said to be in thermodynamic equilibrium with surrounding if
  - (a) it is only in thermal equilibrium with surrounding.
  - (b) it is in both thermal and chemical equilibrium with surrounding.
  - (c) it is in thermal, chemical as well as mechanical equilibrium with the surrounding.
  - (d) it is in thermal and mechanical equilibrium, but not in chemical equilibrium with surrounding.

8. If a closed system has adiabatic boundaries, then at least one boundary must be
    - (a) permeable
    - (b) imaginary
    - (c) movable
    - (d) fixed
  9. Which of the following pair does show the extensive properties?
    - (a) temperature and pressure
    - (b) viscosity and surface tension
    - (c) refractive index and specific heat
    - (d) volume and heat capacity
  10. Which of the following statement is correct?
    - (a) Heat is thermodynamic property of system.
    - (b) Work is thermodynamic property of system.
    - (c) Work done by a conservative force is path function.
    - (d) Heat involved in chemical reaction is path independent physical quantity.
  11. Which of the following statement is incorrect?
    - (a) Only a state function may be expressed as difference in its value at two states in any process.
    - (b) A process cannot be defined on the basis of initial and final states of the system.
    - (c) In a cyclic process, the internal energy of the system remains throughout constant.
    - (d) During irreversible process, the equation  $PV = nRT$  is not applicable to ideal gas.
  12. For an isothermal process, the essential condition is
    - (a)  $\Delta T = 0$
    - (b)  $\Delta H = 0$
    - (c)  $\Delta U = 0$
    - (d)  $dT = 0$
  13. Which of the following is correct?
    - (a) An ideal gas always obeys the equation:  $PV^\gamma = \text{constant}$  in adiabatic process.
    - (b) An ideal gas always obeys the equation:  $PV^x = \text{constant}$  in polytropic process.
    - (c) In a polytropic process, the heat capacity of the system remains same throughout.
    - (d) In all the cyclic process,  $w_{\text{net}}$  by the system is non-zero.
  14. Which of following is incorrect about reversible process?
    - (a) System remains always in thermodynamic equilibrium.
    - (b) The process is extremely slow.
    - (c) The process may be reversed at any stage only by making infinitesimally small change in opposite direction.
    - (d) Reversible processes may be performed in finite time.
  15. The law of equipartition of energy is applicable to the system whose constituents are
    - (a) in random motion
    - (b) in orderly motion
    - (c) moving with constant speed
    - (d) in rest
- 

## First Law of Thermodynamics

16. A system absorbs 20 kJ heat and does 10 kJ of work. The internal energy of the system
  - (a) increases by 10 kJ
  - (b) decreases by 10 kJ
  - (c) increases by 30 kJ
  - (d) decreases by 30 kJ
17. The volume of a system becomes twice its original volume on the absorption of 300 cal of heat. The work done on the surrounding was found to be 200 cal. What is  $\Delta U$  for the system?
  - (a) 500 cal
  - (b) 300 cal
  - (c) 100 cal
  - (d) -500 cal

18. A system absorbs 100 kJ heat in the process shown in the figure. What is  $\Delta U$  for the system?



- (a) -50 kJ (b) +50 kJ  
(c) +150 kJ (d) -150 kJ
19. In a given process on an ideal gas,  $dw = 0$  and  $dq < 0$ . Then for the gas,  
(a) the temperature will decrease  
(b) the volume will increase  
(c) the pressure will remain constant  
(d) the temperature will increase
20. Five moles of an ideal gas is expanded isothermally from  $5 \text{ dm}^3$  to  $5 \text{ m}^3$  at 300 K. Which of the following is incorrect about the gas?  
(a) No heat is absorbed or rejected by the gas.  
(b) There is no change in internal energy of the gas.  
(c) There is no change in enthalpy of the gas.  
(d) Pressure of the gas will decrease by 1000 times.
21. One mole of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 L to 10 L. The change in internal energy,  $\Delta U$ , for the gas in this process is  
(a) 163.7 cal (b) zero  
(c) 1381.1 cal (d) 9 L-atm
22. Five moles of an ideal gas expand isothermally and reversibly from an initial pressure of 100 atm to a final pressure of 1 atm at  $27^\circ\text{C}$ . The work done by the gas is ( $\ln 100 = 4.6$ )  
(a) 2760 cal  
(b) 6000 cal  
(c) 0  
(d) 13,800 cal
23. The work done in the isothermal reversible expansion of argon gas at  $27^\circ\text{C}$  from 4 l to 16 l was equal to 4200 cal. What is the amount of argon subjected to such an expansion? ( $\text{Ar} = 40$ ,  $\ln 4 = 1.4$ )  
(a) 5.0 g  
(b) 20.0 g  
(c) 200.0 g  
(d) 48.1 g
24. The minimum work which must be done to compress 16 g of oxygen isothermally, at 300 K from a pressure of  $1.01325 \times 10^3 \text{ N/m}^2$  to  $1.01325 \times 10^5 \text{ N/m}^2$  is ( $\ln 100 = 4.6$ ,  $R = 8.3 \text{ J/K-mol}$ )  
(a) 5727 J  
(b) 11.454 kJ  
(c) 123.255 kJ  
(d) 1232.55 J
25. For a reversible process at  $T = 300 \text{ K}$ , volume of the ideal gas is increased from 1 L to 10 L. If the process is isothermal, the  $\Delta H$  of the process is  
(a) 11.47 kJ  
(b) 4.98 kJ  
(c) 0  
(d) -11.47 kJ
26. The magnitude of work done by one mole of a van der Waals gas, during its isothermal reversible expansion from volume  $V_1$  to  $V_2$  at temperature  $T \text{ K}$ , is  
(a)  $RT \ln \left( \frac{V_2}{V_1} \right)$   
(b)  $RT \ln \left( \frac{V_2 - b}{V_1 - b} \right)$   
(c)  $RT \ln \left( \frac{V_2 - b}{V_1 - b} \right) + a \left( \frac{1}{V_2} - \frac{1}{V_1} \right)$   
(d)  $RT \ln \left( \frac{V_2 - b}{V_1 - b} \right) - a \left( \frac{1}{V_2} - \frac{1}{V_1} \right)$

27. An ideal gas undergoes isothermal expansion from (10 atm, 1 L) to (1 atm, 10 L) either by path-I (infinite stage expansion) or by path-II (first against 5 atm and then against 1 atm). The value of  $\left(\frac{q_{\text{path-I}}}{q_{\text{path-II}}}\right)$  is
- (a)  $\frac{2.303}{1.3}$  (b)  $\frac{1.3}{2.303}$   
 (c)  $\frac{1.0}{13 \times 2.303}$  (d)  $13 \times 2.303$
28. An ideal gas is expanded irreversibly from 5 L to 10 L against a constant external pressure of 1 bar. The value of heat involved ( $q$ ) in this isenthalpic process is
- (a) 0 (b) +500 J  
 (c) +5 J (d) -500 J
29. The work done in an adiabatic change of fixed amount of an ideal gas depends on change in
- (a) volume (b) pressure  
 (c) temperature (d) density
30. In the reversible adiabatic expansion of an ideal monoatomic gas, the final volume is 8 times the initial volume. The ratio of final temperature to initial temperature is
- (a) 8:1 (b) 1:4  
 (c) 1:2 (d) 4:1
31. One mole of monoatomic ideal gas at  $T$  K is expanded from 1 L to 2 L adiabatically under a constant external pressure of 1 atm. The final temperature of the gas in Kelvin is
- (a)  $T$   
 (b)  $\frac{T}{2^{\left(\frac{5}{3}-1\right)}}$   
 (c)  $T - \frac{2}{3 \times 0.0821}$   
 (d)  $T + \frac{3}{2 \times 0.0821}$
32. Two moles of an ideal gas  $\left(C_{v,m} = \frac{5}{2}R\right)$  was compressed adiabatically against constant pressure of 2 atm, which was initially at 350 K and 1 atm. The work done on the gas in this process is
- (a) 250R (b) 500R  
 (c) 125R (d) 300R
33. Two moles of an ideal gas ( $\gamma = 1.4$ ) was allowed to expand reversibly and adiabatically from 1 L, 527°C to 32 L. The molar enthalpy change of the gas is
- (a) -4200R (b) -2100R  
 (c) -1500R (d) -3000R
34. Equal moles of He, H<sub>2</sub>, CO<sub>2</sub> and SO<sub>3</sub> gases are expanded adiabatically and reversibly from the same initial state to the same final volume. The magnitude of work is maximum for (Assume ideal behaviour of gases and all the degree of freedoms are active.)
- (a) He (b) H<sub>2</sub>  
 (c) CO<sub>2</sub> (d) SO<sub>3</sub>
35. An ideal monoatomic gas initially at 300 K expands adiabatically into vacuum to double its volume. The final temperature of gas is
- (a) 300 K  
 (b)  $300 \times (0.5)^{2/3}$  K  
 (c)  $300 \times (2)^{2/3}$  K  
 (d) 600 K
36. Temperature of one mole of an ideal gas is increased by one degree at constant pressure. Work done by the gas is
- (a)  $R$  (b)  $2R$   
 (c)  $R/2$  (d)  $3R$
37. What is the change in internal energy when a gas contracts from 325 ml to 125 ml at a constant pressure of 2 bar, while at the same time being cooled by removing 124 J heat?
- (a) -524 J (b) -84 J  
 (c) -164 J (d) +84 J

38. Two moles of an ideal gas [ $C_{v,m}$  ( $\text{J K}^{-1} \text{mol}^{-1}$ ) =  $20 + 0.01T(\text{K})$ ] is heated at constant pressure from  $27^\circ\text{C}$  to  $127^\circ\text{C}$ . The amount of heat absorbed by the gas is  
 (a) 1662.8 J (b) 4700 J  
 (c) 6362.8 J (d) 3037.2 J
39. A monoatomic gas expands isobarically. The percentage of heat supplied that increases the thermal energy and that involved in doing work for expansion is  
 (a) 50:50 (b) 60:40  
 (c) 40:60 (d) 75:25
40. The maximum high temperature molar heat capacity at constant volume to be expected for acetylene which is a linear molecule is  
 (a) 9 cal/deg-mole  
 (b) 12 cal/deg-mole  
 (c) 19 cal/deg-mole  
 (d) 14 cal/deg-mole
41. Molar heat capacity of water in equilibrium with ice at constant pressure is  
 (a) zero  
 (b) infinity  
 (c) 40.45 kJ/K-mol  
 (d) 75.48 J/K-mol
42. For which of the following ideal gas,  $C_{v,m}$  is independent of temperature?  
 (a) He (b)  $\text{H}_2$   
 (c) CO (d)  $\text{SO}_2$
43. If one mole of a monoatomic gas ( $\gamma = 5/3$ ) is mixed with one mole of a diatomic gas ( $\gamma = 7/5$ ), the value of  $\gamma$  for the mixture is  
 (a) 1 (b) 1.5  
 (c) 2 (d) 3.0
44. When an ideal diatomic gas is heated at a constant pressure, the fraction of heat energy supplied which increase the internal energy of the gas is  
 (a)  $\frac{2}{5}$  (b)  $\frac{3}{5}$   
 (c)  $\frac{5}{7}$  (d)  $\frac{3}{7}$
45. A gas is heated at constant pressure. The fraction of heat absorbed used in doing work is  
 (a)  $\frac{1}{\gamma}$  (b)  $1 - \frac{1}{\gamma}$   
 (c)  $\gamma - 1$  (d)  $\gamma$
46. An ideal gas undergoes a process in which its pressure and volume are related as  $PV^n = \text{constant}$ , where  $n$  is a constant. The molar heat capacity for the gas in this process will be zero if  
 (a)  $n = \gamma$  (b)  $n = \gamma - 1$   
 (c)  $n = \gamma + 1$  (d)  $n = 1 - \gamma$
47. An ideal gas ( $\gamma = 1.5$ ) undergoes a change in state such that the magnitude of heat absorbed by the gas is equal to the magnitude of work done by the gas. The molar heat capacity of the gas in this process is  
 (a)  $2R$  (b)  $R$   
 (c)  $3R$  (d)  $1.5R$
48. A quantity of 70 calories of heat is required to raise the temperature of 2 mole of an ideal gas at constant pressure from  $40^\circ\text{C}$  to  $50^\circ\text{C}$ . The amount of heat required to raise the temperature of the same gas through the same range at constant volume is  
 (a) 90 calorie  
 (b) 70 calorie  
 (c) 50 calorie  
 (d) 30 calorie
49. During an adiabatic process, the pressure of a gas is found to be proportional to cube of its absolute temperature. The Poisson's ratio of gas is  
 (a)  $3/2$  (b)  $7/2$   
 (c)  $5/3$  (d)  $9/7$
50. A diatomic ideal gas initially at 273 K is given 100 cal heat due to which system did 210 J work. Molar heat capacity of the gas for the process is (1 cal = 4.2 J)  
 (a)  $\frac{3}{2}R$  (b)  $\frac{5}{2}R$   
 (c)  $\frac{5}{4}R$  (d)  $5R$

51. An ideal monoatomic gas undergoes a reversible process:  $\frac{P}{V} = \text{constant}$ , from (2 bar, 273 K) to 4 bar. The value of  $\frac{\Delta U}{w}$  for this process is

(a) +3.0 (b) -3.0  
(c) -1.5 (d) +1.5

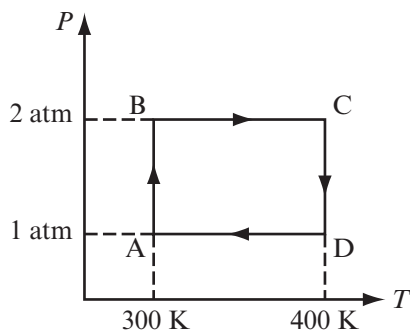
52. The work done by one mole of an ideal gas in the reversible process:  $PV^3 = \text{constant}$ , from (1 atm, 300 K) to  $2\sqrt{2}$  atm is

(a)  $150R$  (b)  $300R$   
(c)  $75R$  (d)  $600R$

53. 2 moles of an ideal monoatomic gas undergoes reversible expansion from (4 L, 400 K) to 8 L such that  $TV^2 = \text{constant}$ . The change in enthalpy of the gas is

(a)  $-1500R$  (b)  $-3000R$   
(c)  $+1500R$  (d)  $+3000R$

54. Two moles of helium gas undergoes a cyclic process as shown in the figure. Assuming ideal behaviour of gas, the net work done by the gas in this cyclic process is



(a) 0 (b)  $100R \ln 2$   
(c)  $100R \ln 4$  (d)  $200R \ln 4$

55. One mole of an ideal gas undergoes the following cyclic process:

- Isochoric heating from  $(P_1, V_1, T_1)$  to double temperature.
- Isobaric expansion to double volume.

(iii) Linear expansion (on  $P$ - $V$  curve) to  $(P_1, 8V_1)$ .

(iv) Isobaric compression to initial state.

If  $T_1 = 300$  K, the magnitude of net work done by the gas in the cyclic process is

(a) 2400 cal  
(b) 1200 cal  
(c) 4800 cal  
(d) 3600 cal

56. One mole of a non-ideal gas undergoes a change of state (2 atm, 3 L, 95 K)  $\rightarrow$  (4 atm, 5 L, 245 K) with a change in internal energy,  $\Delta U = 30.0$  L-atm. The change in enthalpy ( $\Delta H$ ) of the process in L-atm is

(a) 40.0  
(b) 42.3  
(c) 44.0

(d) undefined, because pressure is not constant

57. The normal boiling point of water is  $100^\circ\text{C}$ . At  $100^\circ\text{C}$

- the average kinetic energy of molecules in vapour is greater than that of liquid water.
- the average potential energy of molecules in vapour is greater than that of liquid water.
- the molar internal energy is same for vapour and liquid water.
- water boils at any pressure.

58. The latent heat of vaporization of a liquid at 500 K and 1 atm pressure is 10 kcal/mol. What will be the change in internal energy if 3 moles of the liquid changes to vapour state at the same temperature and pressure?

(a) 27 kcal  
(b) 13 kcal  
(c) -27 kcal  
(d) -13 kcal

59. A quantity of 1 g of water on evaporation at atmospheric pressure forms  $1671 \text{ cm}^3$  of steam. Heat of vaporization is  $540 \text{ cal/g}$ . The approximate increase in internal energy is
- 250 cal
  - 500 cal
  - 1000 cal
  - 1500 cal
60. At 500 kbar and  $T \text{ K}$ , the densities of graphite and diamond are 2.0 and  $3.0 \text{ g/cm}^3$ , respectively. The value of  $(\Delta H - \Delta U)$  for the conversion of 1 mole of graphite into diamond at 500 kbar and  $T \text{ K}$  is
- 100 kJ
  - 100 kJ
  - 1000 kJ
  - 1000 kJ

## Second and Third Law of Thermodynamics, Entropy

61. The efficiency of the reversible heat engine is  $\eta_r$  and that of irreversible heat engine is  $\eta_i$ . Which of the following relation is correct?
- $\eta_r = \eta_i$
  - $\eta_r > \eta_i$
  - $\eta_r < \eta_i$
  - $\eta_i$  may be less than, greater than or equal to  $\eta_r$ , depending on the gas.
62. For which of the following process,  $\Delta S$  is negative?
- $\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$
  - $\text{N}_2(\text{g}, 1 \text{ atm}) \rightarrow \text{N}_2(\text{g}, 8 \text{ atm})$
  - $2\text{SO}_3(\text{g}) \rightarrow 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$
  - $\text{C}(\text{graphite}) \rightarrow \text{C}(\text{diamond})$
63.  $\Delta S$  will be highest for the reaction
- $\text{Ca}(\text{s}) + 1/2 \text{O}_2(\text{g}) \rightarrow \text{CaO}(\text{s})$
  - $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
  - $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
  - $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$
64. Entropy decrease during
- crystallization of sucrose from solution
  - rusting of iron
  - melting of ice
  - vaporization of camphor
65. Change in entropy is negative for
- Bromine (l)  $\rightarrow$  Bromine (g)
  - $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$
  - $\text{N}_2(\text{g}, 10 \text{ atm}) \rightarrow \text{N}_2(\text{g}, 1 \text{ atm})$
  - $\text{Fe}(1 \text{ mol}, 400 \text{ K}) \rightarrow \text{Fe}(1 \text{ mol}, 300 \text{ K})$
66. When a substance is heated, its entropy increases. The increase will be maximum at
- $0^\circ\text{C}$
  - the melting point
  - the boiling point
  - $100^\circ\text{C}$
67. An isolated system comprises the liquid in equilibrium with vapours. At this stage, the molar entropy of the vapour is
- less than that of liquid
  - more than that of liquid
  - equal to zero
  - equal to that of liquid
68. According to second law of thermodynamics, heat is partly converted into useful work and part of it
- becomes electrical energy
  - is always wasted
  - increases the weight of the body
  - becomes K.E.



69. Choose the substance which has higher possible entropy (per mole) at a given temperature.
- solid carbon dioxide
  - nitrogen gas at 1 atm
  - nitrogen gas at 0.01 atm
  - nitrogen gas at 0.00001 atm
70. The change that does not increase entropy
- evaporation of liquid
  - condensation
  - sublimation
  - melting of solid
71. Ammonium chloride when dissolved in water leads to cooling sensation. The dissolution of  $\text{NH}_4\text{Cl}$  at constant temperature is accompanied by
- increase in entropy
  - decrease in entropy
  - no change in entropy
  - no change in enthalpy
72. When the value of entropy is greater, then the ability for work is
- maximum
  - minimum
  - medium
  - none of these
73. When one mole of an ideal gas is compressed to half of its initial volume and simultaneously heated to twice its temperature, the change in entropy is
- $C_v \ln 2$
  - $C_p \ln 2$
  - $R \ln 2$
  - $(C_v - R) \ln 2$
74. What is the entropy change when 3.6 g of liquid water is completely converted into vapours at 373 K? The molar heat of vaporization is 40.85 kJ/mol.
- 218.9 J/K
  - 2.189 J/K
  - 21.89 J/K
  - 0.2189 J/K
75. The entropy change in the fusion of one mole of a solid melting at 300 K (latent heat of fusion, 2930 J/mol) is
- 9.77 J/K-mol
  - 10.73 J/K-mol
  - 2930 J/K-mol
  - 108.5 J/K-mol
76. Oxygen gas weighing 64 g is expanded from 1 atm to 0.25 atm at 30°C. What is the entropy change, assuming the gas to be ideal? ( $\ln 4 = 1.4$ ,  $R = 8.3 \text{ J/K-mol}$ )
- 23.24 J/K
  - 34.86 J/K
  - 46.48 J/K
  - 11.62 J/K
77. Two moles of an ideal monoatomic gas is heated from 27°C to 627°C, reversibly and isochorically. The entropy of gas
- increases by  $2R \ln 3$
  - increases by  $3R \ln 3$
  - decreases by  $2R \ln 3$
  - decreases by  $3R \ln 3$
78. One mole of an ideal monoatomic gas undergoes adiabatic free expansion from 2 to 20 dm<sup>3</sup>, 300 K. The value of  $\Delta S$  for the gas is
- 0
  - $+R \ln 10$
  - $-R \ln 10$
  - $+1.5 R \ln 10$
79. The standard molar entropy of an ideal gas ( $\gamma = \frac{4}{3}$ ) is 2.5 cal/K-mol at 25°C and 1 bar. The standard molar entropy of the gas at 323°C and 1 bar is
- undefined
  - $R \ln 2$
  - $R \ln 4$
  - $R \ln 8$
80. Given the following entropy values (in J/K-mol) at 298 K and 1 atm  $\text{H}_2(\text{g}) = 130.6$ ,  $\text{Cl}_2(\text{g}) = 223.0$  and  $\text{HCl}(\text{g}) = 186.7$ . The entropy change (in J/K-mol) for the reaction:  $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$ , is
- +540.3
  - +727.0
  - 166.9
  - +19.8



## Gibbs Free Energy Function

81. The  $\Delta G$  in the process of melting of ice at  $-15^\circ\text{C}$  is

(a) less than zero  
(b) greater than zero  
(c) equal to zero  
(d) none of these

82. For a system in equilibrium,  $\Delta G = 0$  under conditions of constant

(a) temperature and pressure  
(b) temperature and volume  
(c) pressure and volume  
(d) energy and volume

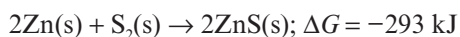
83. One mole of ice is converted into water at 273 K and 1 atm. The entropies of  $\text{H}_2\text{O}(\text{s})$  and  $\text{H}_2\text{O}(\text{l})$  are 38.0 and 58.0 J/K-mol, respectively. The enthalpy change for the conversion is

(a) 5460 kJ/mol  
(b) 5460 J/mol  
(c) -5460 J/mol  
(d) 20 J/mol

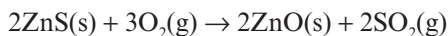
84. The solubility of  $\text{NaCl}(\text{s})$  in water at 298 K is about 6 moles per litre. Suppose you add 1 mole of  $\text{NaCl}(\text{s})$  to a litre of water. For the reaction:  $\text{NaCl}(\text{s}) + \text{H}_2\text{O} \rightarrow \text{NaCl}(\text{aq})$

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

85. The values of  $\Delta G$  are very important in metallurgy. The  $\Delta G$  values for the following reactions at 1000 K are given as:



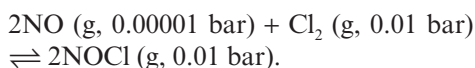
The  $\Delta G$  for the reaction:



will be

(a) -357 kJ (b) -731 kJ  
(c) -773 kJ (d) -229 kJ

86. The following reaction is at equilibrium at 298 K



$\Delta G^\circ$  for the reaction is

(a) -45.65 kJ (b) -28.53 kJ  
(c) -22.82 kJ (d) -57.06 kJ

87. What is the free energy change,  $\Delta G$ , when 1.0 mole of water at  $100^\circ\text{C}$  and 1 atm pressure is converted into steam at  $100^\circ\text{C}$  and 1 atm pressure?

(a) 540 cal (b) -9800 cal  
(c) 9800 cal (d) 0 cal

88. The enthalpy and entropy change for a chemical reaction are -2500 cal and +7.4 cal/K, respectively. The nature of reaction at 298 K is

(a) Spontaneous  
(b) Reversible  
(c) Irreversible  
(d) Non-spontaneous

89. A spontaneous reaction is impossible if

(a) both  $\Delta H$  and  $\Delta S$  are negative  
(b)  $\Delta H$  and  $\Delta S$  are positive  
(c)  $\Delta H$  is negative and  $\Delta S$  is positive  
(d)  $\Delta H$  is positive and  $\Delta S$  is negative

90. For a reversible reaction, if  $\Delta G^\circ = 0$ , the equilibrium constant of the reaction should be equal to

(a) Zero (b) 1  
(c) 2 (d) 10

**Answer Keys – Exercise I****Basics**

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

**First Law of Thermodynamics**

16. (a) 17. (c) 18. (a) 19. (a) 20. (a) 21. (b) 22. (d) 23. (c) 24. (a) 25. (c)  
26. (c) 27. (a) 28. (b) 29. (c) 30. (b) 31. (c) 32. (b) 33. (b) 34. (d) 35. (a)  
36. (a) 37. (b) 38. (c) 39. (b) 40. (c) 41. (b) 42. (a) 43. (b) 44. (c) 45. (b)  
46. (a) 47. (b) 48. (d) 49. (a) 50. (d) 51. (b) 52. (a) 53. (a) 54. (c) 55. (a)  
56. (c) 57. (b) 58. (a) 59. (b) 60. (b)

**Second and Third Law of Thermodynamics, Entropy**

61. (b) 62. (b) 63. (b) 64. (a) 65. (d) 66. (c) 67. (b) 68. (b) 69. (d) 70. (b)  
71. (a) 72. (b) 73. (d) 74. (c) 75. (a) 76. (a) 77. (b) 78. (b) 79. (d) 80. (d)

**Gibbs Free Energy Function**

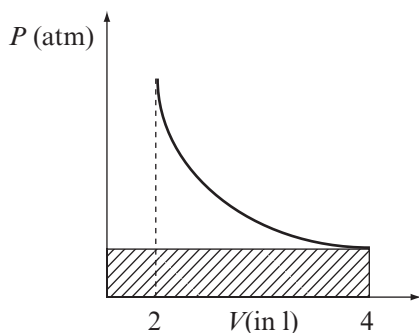
81. (b) 82. (a) 83. (b) 84. (b) 85. (b) 86. (a) 87. (d) 88. (a) 89. (d) 90. (b)
-

## 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 =  $4.2 \text{ J/K-g}$ .
  - $29.76^\circ\text{C}$
  - $2.976 \text{ K}$
  - $2.976 \times 10^4^\circ\text{C}$
  - $0.029^\circ\text{C}$
- 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
  - $-nRT \sum_{i=1}^{i=P-1} \left( \frac{1}{P+1-i} \right)$
  - $-nRT \sum_{i=1}^{i=P} \left( \frac{1}{P+1-i} \right)$
  - $-nRT \sum_{i=1}^{i=P} \left( \frac{i}{P+1-i} \right)$
  - $-nRT \sum_{i=1}^{i=P-1} \left( \frac{i}{P+1-i} \right)$

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
- Magnitude of work done in the first process will be greater than that in the second process.
  - Magnitude of work done in the second process will be greater than that in the first process.
  - Work done in both the processes cannot be compared without knowing the relation between  $K_1$  and  $K_2$ .
  - 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?
- zero
  - 60%
  - 50%
  - 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)
- 49.26
  - 98.52
  - 78.63
  - 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
- 4.2 J/K-mol
  - +4.2 J/K-mol
  - 12.47 J/K-mol
  - 20.78 J/K-mol
11. The molar heat capacity at 25°C should be close to 27 J/K-mol for all of the given elements except
- Pt
  - W
  - Ne
  - 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  $P_2/P_1$ ?
- 32
  - 64
  - 128
  - 256
13. How many times a diatomic gas should be expanded adiabatically so as to reduce the RMS speed to half?
- 8
  - 16
  - 32
  - 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
- $C_A = C_B$
  - $C_A > C_B$
  - $C_A < C_B$
  - both, undefined
15. One mole of oxygen is heated from 0°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
- $32 \times 0.22 \times 27.3 \times 4.2$  J
  - $16 \times 0.22 \times 27.3 \times 4.2$  J
  - $\frac{32 \times 0.22 \times 27.3}{4.2}$  J
  - $\frac{16 \times 0.22 \times 27.3}{4.2}$  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 ( $C_{p,m} = 5$  cal/K-mol) at 300 K and vessel B contains 3 moles of  $\text{SO}_2$  gas ( $C_{p,m} = 8$  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)  $227.5^\circ\text{C}$   
(c) 455 K (d)  $455^\circ\text{C}$
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)  $RT_0 \ln\left(\frac{V_2}{V_1}\right) - \alpha C_{p,m}(V_2 - V_1)$

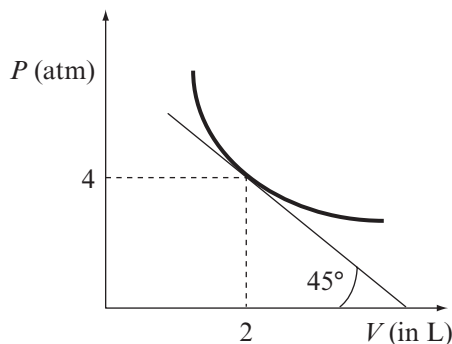
25. The average degree of freedom per molecule for a gas is 6. The gas performs 25 J of work when it expands at constant pressure. What is the amount of heat absorbed by the gas?

(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:

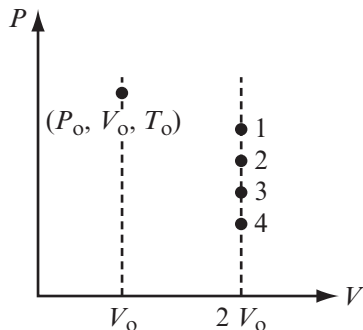
Process I: Isothermal reversible process

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

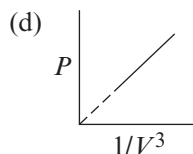
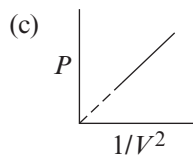
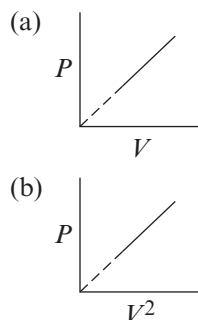
Process III: Reversible adiabatic process

Process IV: Irreversible adiabatic expansion against constant external pressure.

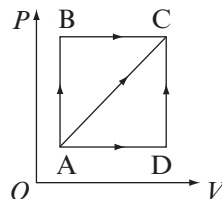
If the final states of gases are shown by different points in the graph represented, then match each point with the correct process:



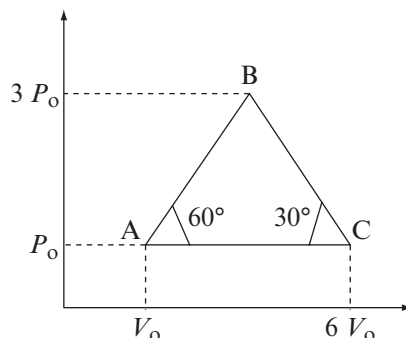
- (a) I – 1, II – 2, III – 3, IV – 4  
 (b) I – 2, II – 1, III – 4, IV – 3  
 (c) I – 4, II – 3, III – 2, IV – 1  
 (d) I – 2, II – 1, III – 3, IV – 4
33. For an ideal gas subjected to different processes as shown in the graphs, select the graph which will involve greatest amount of heat exchange if 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
39. A cylinder with thermally insulated walls contains an insulated portion which can

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?
- $\frac{\gamma P_0}{\alpha(\gamma-1)}$
  - $\frac{\gamma P_0}{\alpha(\gamma+1)}$
  - $\frac{\alpha P_0}{\gamma+1}$
  - $\frac{\alpha P_0}{\gamma-1}$
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
- $C \cdot \ln \left[ \frac{(T_2 - T_1)^2}{4T_1 T_2} + 1 \right]$
  - $C \cdot \ln \left[ \frac{(T_2 - T_1)^2}{4T_1 T_2} \right]$
  - $C \cdot \ln \left[ \frac{(T_2 + T_1)^2}{4T_1 T_2} + 1 \right]$
  - $C \cdot \ln \left[ \frac{(T_2 + T_1)^2}{4T_1 T_2} - 1 \right]$
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  $\text{A}(\text{g})$ , 6 moles of  $\text{B}(\text{g})$  and 3 moles of  $\text{C}(\text{g})$ . 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  
 $\text{H}_2\text{O}(\text{g}, 0.04 \text{ atm}, 27^{\circ}\text{C}) \rightarrow \text{H}_2\text{O}(\text{l}, 0.04 \text{ atm}, 27^{\circ}\text{C})$   
 (a) 0 (b)  $R \times 300 \times \ln \frac{1}{25}$   
 (c)  $R \times 300 \times \ln 25$  (d)  $300R$

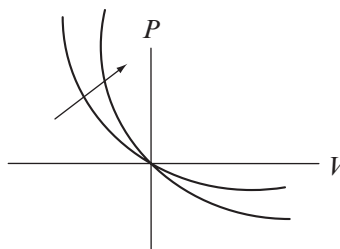
## Section B (One or More than One Correct)

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?

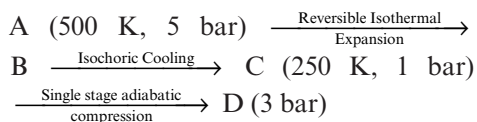
- (a)  $(-w_{\text{rev}}) - (-w_{\text{irr}}) > 0$  for isothermal expansion.
- (b)  $w_{\text{rev}} > w_{\text{irr}}$  for isothermal compression.
- (c) Heat rejected in isothermal process is greater in  $(n-1)^{\text{th}}$  stage as compared to  $n^{\text{th}}$  stage work.
- (d) Arrow shown in the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

- The pressure at B is 2.0 bar.
  - The temperature at D is 450 K.
  - $\Delta H_{CD} = 1000R$
  - $\Delta U_{BC} = 375R$
13. Which of the following is true for reversible adiabatic process involving an ideal gas?
- Gas with higher  $\gamma$  has high magnitude of slope in a  $P$  ( $y$ -axis) v/s  $T$  ( $x$ -axis) curve.
  - Gas with higher  $\gamma$  has high magnitude of slope in a  $V$  ( $y$ -axis) v/s  $T$  ( $x$ -axis) curve.
  - Gas with higher  $\gamma$  has high magnitude of slope in a  $P$  ( $y$ -axis) v/s  $V$  ( $x$ -axis) curve.
  - 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
- $\Delta T = 0$
  - $\Delta P = 0$
  - $q = 0$
  - $\Delta U = 0$
15. For a process to occur under isothermal conditions, the essential condition(s) is/are
- $\alpha T = 0$
  - $\alpha P = 0$
  - $q = 0$
  - $\alpha U = 0$
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.

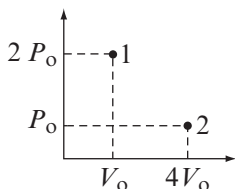
**Step I:** All undergo reversible adiabatic expansion to attain same final volume, which is double the original volume thereby causing the decrease in their temperature.

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

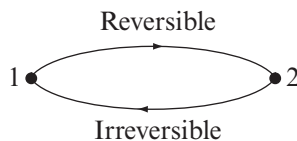
Which of the following is/are correct statement(s)?

- Due to Step I only, the decrease in temperature will be maximum for Ne.
  - During Step II, heat given will be maximum for CH<sub>4</sub>.
  - There will be no change in internal energy for any gas after both the steps of process are completed.
  - 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?
- The specific heat capacity of substance is greater in the solid state than in liquid state.
  - The specific heat capacity of a substance is greater in gaseous state than in the liquid state.
  - The latent heat of vaporization of a substance is greater than that of fusion.
  - 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?
- N<sub>2</sub>
  - N<sub>2</sub>O
  - CO
  - 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)  $\Delta H = \frac{2\gamma P_0 V_0}{\gamma - 1}$       (b)  $\Delta U = \frac{3P_0 V_0}{\gamma - 1}$   
 (c)  $\Delta H = -P_0 V_0$       (d)  $\Delta U = -3P_0 V_0$
20. Which of the following statement(s) is/are incorrect?
- 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.
  - 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.
  - 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.
  - 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?
- Combustion of methane gas in an adiabatic rigid container will cause no change in temperature of the system.
  - It is possible to have both adiabatic reversible and adiabatic irreversible processes between two states.
  - 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.
  - $P-V$  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?
- In expansion, more work is done by the gas in isothermal process.
  - In compression, more work is done on the gas in adiabatic process.
  - In expansion, the final temperature of gas will be higher in isothermal process.
  - 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?
- 75 J
  - 85 J
  - 90 J
  - 70 J
24. For the cyclic process given below, which of the following relations are correct?



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

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.

- What is the molar heat capacity of gas in this process?  
 (a)  $C_{v,m}$  (b)  $-C_{v,m}$   
 (c)  $C_{p,m}$  (d)  $-C_{p,m}$
- 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)  $T \cdot V^{\gamma} = \text{constant}$
- 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.

- The work performed by the gas is  
 (a) 8.60 kJ (b) 0.60 kJ  
 (c) 16.60 kJ (d) 4.60 kJ
- The value of  $\gamma$  for the gas is  
 (a) 0.6 (b) 0.16  
 (c) 1.6 (d) 2.2

## 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.

- 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)  $\frac{15\alpha(\gamma+1)V_0^2}{2(\gamma-1)}$
- 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)  $\frac{15\alpha(\gamma+1)V_0^2}{2(\gamma-1)}$
- 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)  $R\alpha \cdot \Delta T$   
 (c)  $R \cdot \Delta T / (1 - \alpha)$  (d)  $R \cdot \Delta T / \alpha$
14. What is the molar heat capacity of the gas in the process?
- (a)  $\frac{R(1 + \alpha)}{\gamma - 1}$  (b)  $\frac{R\alpha}{\gamma - 1}$   
 (c)  $\frac{R}{\gamma - 1} + R(1 - \alpha)$  (d)  $\frac{R}{\gamma - 1} + \frac{R}{1 - \alpha}$
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  $\Delta U$ ?
- (a)  $\Delta U \left( 1 + \frac{\gamma - 1}{\alpha} \right)$  (b)  $\Delta U \left( 1 - \frac{\gamma - 1}{\alpha} \right)$   
 (c)  $\Delta U \left( 1 + \frac{\alpha}{\gamma - 1} \right)$  (d)  $R \cdot \Delta U \left( 1 + \frac{\gamma - 1}{\alpha} \right)$
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)  $\frac{R}{\gamma - 1} - \frac{R}{\alpha}$

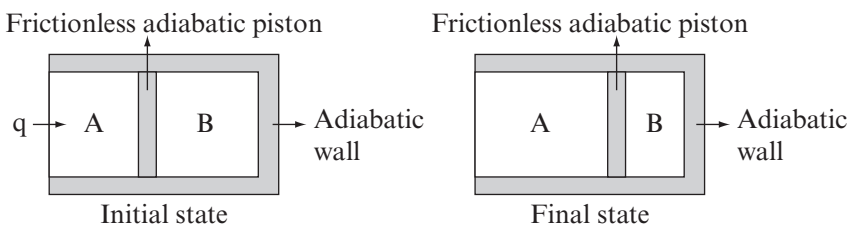
### Comprehension VII

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

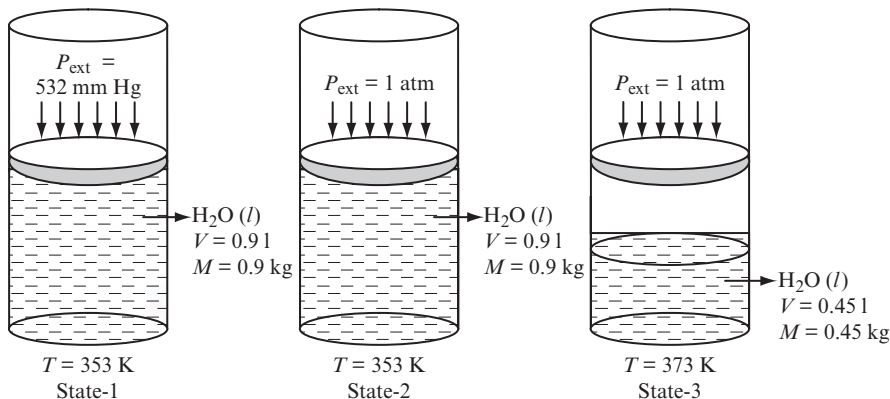
The vapour pressure of water at 353 K is 532 mm Hg. The external pressure on  $\text{H}_2\text{O}(\text{l})$  taken in a cylinder fitted with frictionless movable piston initially containing 0.9 L (= 0.9 kg) of  $\text{H}_2\text{O}(\text{l})$  at 353 K is increased to 1 atm at the constant temperature. 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  $\text{H}_2\text{O}(\text{l}) = 4.2 \text{ J}^\circ\text{C}^{-1}\text{g}^{-1}$

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

1 L-atm = 100 J

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



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

### 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.

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

### 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) $N_2(g) + O_2(g) \rightarrow 2NO(g)$	(P) $\Delta S \approx 0$
(B) $2KI(aq) + HgI_2(aq) \rightarrow K_2[HgI_4](aq)$	(Q) $\Delta S < 0$
(C) $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$	(R) $\Delta H > 0$
(D) $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$	(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) $q = 0$

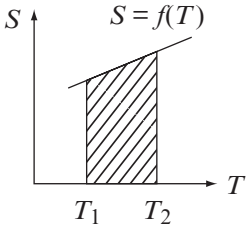
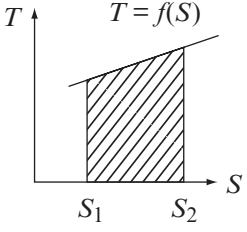
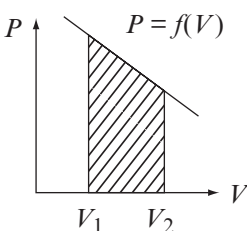
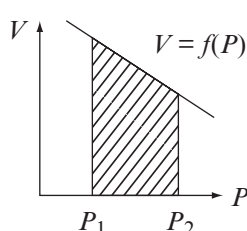
## 8. Match Column I with Column II

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) $A_2(g) \rightarrow B(g) + C(g)$ , $E_{\text{a(forward)}} = 50 \text{ kJ/mol}$ , $E_{\text{a(backward)}} = 40 \text{ kJ/mol}$ , $\Delta H$ 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  $2.0 \text{ J}$
- 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 Gibb's 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:  $X \rightleftharpoons Y$ , 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 a 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.

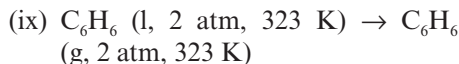
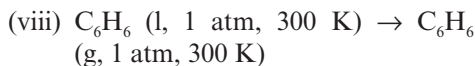
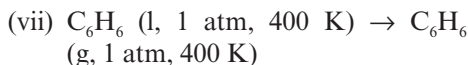
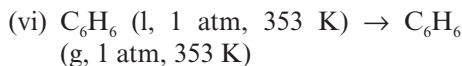
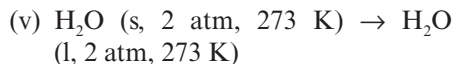
19. Select the conditions which represent the criteria for spontaneity of a process in a closed system, from the following given conditions:

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)
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