CHAPTER

# 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, then 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 the surroundings, if
  - (a) it is only in thermal equilibrium with the surrounding.
  - (b) it is in both thermal and chemical equilibrium with the 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 the 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 a 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 statement is correct?
  - (a) An ideal gas always obeys the equation  $PV^{\gamma} =$  constant in adiabatic process.

#### **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?



- (b) An ideal gas always obeys the equation  $PV^x =$  constant in polytropic process.
- (c) In a polytropic process, the heat capacity of the system remains same throughout.
- (d) In all the cyclic process,  $w_{net}$  by the system is non-zero.
- **14.** Which of following is incorrect about reversible process?
  - (a) System always remains 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.

(a) $-50 \text{ kJ}$	(b) $+50 \text{ kJ}$
(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 dm<sup>3</sup> to 5 m<sup>3</sup> 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°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°C from 4L to 16 L was equal to 4200 cal. What is the amount of argon subjected to such an expansion? (Ar = 40,  $\ln 4 = 1.4$ )

(a) 5.0 g	(b)	20.0 g
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- (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  $1.01325 \times 10^3$  N/m<sup>2</sup> to  $1.01325 \times 10^5$  N/m<sup>2</sup> is (ln100 = 4.6, R = 8.3 J/K-mol)

(a)	5727 J	(b)	11.454 k.
(c)	123.255 kJ	(d)	1232.55 J

**25.** For a reversible process at T = 300 K, the volume of the ideal gas is increased from 1 L to 10 L. If the process is isothermal, then  $\Delta H$  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 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  $\left(a_{\text{metr},\text{L}}\right)$ 

$$\left(\frac{1}{q_{\text{path}-II}}\right) \text{ is}$$
(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) 250*R* (b) 500*R*
- (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,  $H_2$ ,  $CO_2$  and  $SO_3$  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)	$H_2$
(c)	$CO_2$	(d)	$SO_3$

**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)	$300 \times (0.5)^{2/3} \text{ K}$
(c)	$300 \times (2)^{2/3} \text{ K}$	(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)	<i>R</i> /2	(d)	3 <i>R</i>

**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  $[C_{v,m} (/JK^{-1}mol^{-1}) = 20 + 0.01T(/K)]$  is heated at constant pressure from 27°C to 127°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.** The 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) H <sub>2</sub>
(c) CO	(d) SO <sub>2</sub>

- 43. If one mole of a monoatomic gas ( $\gamma = 5/3$ ) is mixed with one mole of a diatomic gas ( $\gamma = 7/5$ ), then 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 a heated at a constant pressure, the fraction of heat energy supplied which increases 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) γ

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 on the gas. The molar heat capacity of the gas in this process is

(a) 2 <i>R</i>	(b) <i>R</i>
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(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°C to 50°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
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- (c) 50 calorie (d) 30 calorie
- **49.** During an adiabatic process, the pressure of a gas is found to be proportional to the 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. The 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, where  $\frac{P}{V}$  = 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 on one mole of an ideal gas in the reversible process:  $PV^3$  = constant, from (1 atm,

300 K) to  $2\sqrt{2}$  atm is

(a)	150 <i>R</i>	(b)	300 <i>R</i>
(c)	75 <i>R</i>	(d)	600R

**53.** 2 moles of an ideal monoatomic gas undergoes reversible expansion from (4 L, 400 K) to 8 L such that  $TV^2$  = 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 magnitude of net work done by the gas in this cyclic process is



- **55.** One mole of an ideal gas undergoes the following cyclic process.
  - (i) Isochoric heating from  $(P_1, V_1, T_1)$  to double temperature.
  - (ii) 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, then 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°C. At 100°C
  - (a) the average kinetic energy of molecules in vapour is greater than that of liquid water.
  - (b) the average potential energy of molecules in vapour is greater than that of liquid water.
  - (c) the molar internal energy is same for vapour and liquid water.
  - (d) 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 cal/g. The approximate increase in internal energy is (1L atom = 24 cal)

#### 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?
  - (a)  $\eta_r = \eta_1$
  - (b)  $\eta_r > \eta_1$
  - (c)  $\eta_r < \eta_1$
  - (d)  $\eta_1$  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?
  - (a)  $H_2(g) \rightarrow 2H(g)$
  - (b)  $N_2(g, 1 \text{ atm}) \rightarrow N_2(g, 8 \text{ atm})$
  - (c)  $2SO_3(g) \rightarrow 2SO_2(g) + O_2(g)$
  - (d) C (Diamond)  $\rightarrow$  C (Graphite)
- **63.**  $\Delta S$  will be highest for which of the following reaction ?
  - (a)  $Ca(s) + 1/2 O_2(g) \rightarrow CaO(s)$
  - (b)  $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
  - (c)  $C(s) + O_2(g) \rightarrow CO_2(g)$
  - (d)  $N_2(g) + O_2(g) \rightarrow 2NO(g)$
- 64. Entropy of universe decreases during
  - (a) crystallization of sucrose from unsaturated solution.
  - (b) rusting of iron.
  - (c) melting of ice at  $0^{\circ}$ C and 1 atm.
  - (d) vaporization of camphor above normal sublimation temperature and 1 atm.
- **65.** Change in entropy is negative for
  - (a) Bromine (l)  $\rightarrow$  Bromine (g)
  - (b)  $C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$
  - (c)  $N_2(g, 10 \text{ atm}) \rightarrow N_2(g, 1 \text{ atm})$
  - (d) Fe (1 mol, 400 K)  $\rightarrow$  Fe (1 mol, 300 K)

- (a) 250 cal (b) 500 cal (c) 1000 cal (d) 1500 cal
- 60. At 500 kbar and T K, the densities of graphite and diamond are 2.0 and 3.0 g/cm<sup>3</sup>, respectively. The value of  $(\Delta H - \Delta U)$  for the conversion of 1 mole of graphite into diamond at 500 kbar and T K is
  - (a) 100 kJ (b) -100 kJ(c) 1000 kJ (d) -1000 kJ
- **66.** When a substance is heated, its entropy increases. The increase will be maximum at
  - (a) 0°C
  - (b) the melting point
  - (c) the boiling point
  - (d) 100°C
- **67.** An isolated system comprises of the liquid in equilibrium with vapours. At this stage, the molar entropy of the vapour is
  - (a) less than that of liquid.
  - (b) more than that of liquid.
  - (c) equal to zero.
  - (d) equal to that of liquid.
- **68.** According to second law of thermodynamics, heat is partly converted into useful work and part of it
  - (a) becomes electrical energy.
  - (b) is always wasted.
  - (c) increases the weight of the body.
  - (d) becomes K.E.
- **69.** Choose the substance which has higher possible entropy (per mole) at a given temperature.
  - (a) Solid carbon dioxide
  - (b) Nitrogen gas at 1 atm.
  - (c) Nitrogen gas at 0.01 atm.
  - (d) Nitrogen gas at 0.00001 atm.
- **70.** The change that does not increase entropy is
  - (a) evaporation of liquid
  - (b) condensation
  - (c) sublimation
  - (d) melting of solid

- 71. Ammonium chloride when dissolved in water leads to cooling sensation. The dissolution of  $NH_4Cl$  at constant temperature is accompanied by
  - (a) increase in entropy.
  - (b) decrease in entropy.
  - (c) no change in entropy.
  - (d) no change in enthalpy.
- **72.** When the value of entropy is greater, then the ability for work is
  - (a) maximum (b) minimum
  - (c) medium (d) 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
  - (a)  $C_{V,m} \ln 2$  (b)  $C_{P,m} \ln 2$ (c)  $R \ln 2$  (d)  $(C_{V,m} - R) \ln 2$
- **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.

(a)	219.0 J/K	(b)	2.190 J/K
(c)	21.90 J/K	(d)	109.5 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

(a)	9.77 J/K-mol	(b)	10.73 J/K-mol
(c)	2930 J/K-mol	(d)	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,

#### **Gibbs Free Energy Function**

- **81.** The  $\Delta G$  in the process of melting of ice at  $-15^{\circ}$ C and 1 atm, 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.

assuming the gas to be ideal? ( $\ln 4 = 1.4$ , R = 8.3 J/K-mol)

(a)	23.24 J/K	(b)	)	34.86 J/K
(c)	46.48 J/K	(d)	)	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
  - (a) increases by  $2R \ln 3$
  - (b) increases by  $3R \ln 3$
  - (c) decreases by  $2R \ln 3$
  - (d) 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
  - (a) 0 (b)  $+R \ln 10$ (c)  $-R \ln 10$  (d)  $+1.5 R \ln 10$
- **79.** The standard molar entropy of an ideal gas  $\left(\gamma = \frac{4}{3}\right)$  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 (ln 2 = 0.7)
  - (a) undefined (b)  $4R \ln 2$ (c) 5.6 cal/K-mol (d) 8.1 cal/K-mol
- 80. Given the following entropy values (in J/K-mol) at 298 K and 1 atm  $H_2(g) = 130.6$ ,  $Cl_2(g) = 223.0$  and HCl(g) = 186.7. The entropy change (in J/K-mol) for the reaction  $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$  is
  - (a) +540.3(b) +727.0(c) -166.9(d) +19.8
- 83. One mole of ice is converted into water at 273 K and 1 atm. The entropies of  $H_2O$  (s) and  $H_2O$  (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 NaCl(s) in water at 298 K is about 6 moles per litre. Suppose you add 1 mole of NaCl(s) to a litre of water. For the reaction:

 $NaCl(s) + H_2O \rightarrow NaCl(aq)$ 

- (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 follows.

$$S_2(s) + 2O_2(g) \rightarrow 2SO_2(g); \Delta G = -544 \text{ kJ}$$

 $2Zn(s) + S_2(s) \rightarrow 2ZnS(s); \Delta G = -293 \text{ kJ}$ 

 $2Zn(s) + O_2(g) \rightarrow 2ZnO(s); \Delta G = -480 \text{ kJ}$ 

The  $\Delta G$  for the reaction

 $2ZnS(s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g)$ 

will be

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

86. The following reaction is at equilibrium at 298 K

2NO (g, 0.00001 bar) +  $Cl_2$  (g, 0.01 bar)  $\rightleftharpoons$  2NOCl (g, 0.01 bar).

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

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

**87.** What is the free energy change,  $\Delta G$ , when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°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) never occurring
  - (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



# EXERCISE II (JEE ADVANCED)

# Section A (Only one Correct)

- 1. Which of the following gas possess the largest internal energy?
  - (a) 2 moles of He gas occupying 1000 L at 300 K.
  - (b) 56 kg of nitrogen at 107 Pa and 300 K.
  - (c) 8 g of oxygen at 8 atm and 300 K.
  - (d) 2000 mole of argon occupying 40000 L at 900 K.
- 2. A gas expands reversibly in a piston cylinder device from  $V_1$  to  $V_2$ , the process being described by PV = a + bV, where P is in Nm<sup>-2</sup>, V is in m<sup>3</sup> and a and b are constants. The work done in the process (w) is

(a) 
$$a \log_{e} \left( \frac{V_{1}}{V_{2}} \right) + b(V_{2} - V_{1})$$
  
(b)  $-a \log_{e} \left( \frac{V_{2}}{V_{1}} \right) - b(V_{2} - V_{1})$   
(c)  $-a \log_{e} \left( \frac{V_{1}}{V_{2}} \right) - b(V_{2} - V_{1})$   
(d)  $a \log_{e} \left( \frac{V_{2}}{V_{1}} \right) + b(V_{2} - V_{1})$ 

3. 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 J/K-g.

(a)	29.76°C	(b)	2.976 K
(c)	$2.976 \times 10^{4}$ °C	(d)	0.029°C

4. The heat capacity of liquid water is 75.6 J/K-mol, while the enthalpy of fusion of ice is 6.0 kJ/mol. What is the smallest number of ice cubes at 0°C each containing 9.0 g of water needed to cool 500 g of liquid water from 20°C to 0°C?

(a)	1	(b)	7
(c)	14	(d)	21

5. 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 it 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

(a) 
$$\frac{T_1T_2(P_1V_1 + P_2V_2)}{P_1V_1T_2 + P_2V_2T_1}$$
 (b)  $\frac{P_1V_1T_1 + P_2V_2T_2}{P_1V_1 + P_2V_2}$ 

(c) 
$$\frac{P_1V_1T_2 + P_2V_2T_1}{P_1V_1 + P_2V_2}$$
 (d)  $\frac{T_1T_2(P_1V_1 + P_2V_2)}{P_1V_1T_1 + P_2V_2T_2}$ 

6. 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

(a) 
$$-nRT \sum_{i=1}^{i=P-1} \left(\frac{1}{P+1-i}\right)$$
  
(b)  $-nRT \sum_{i=1}^{i=P} \left(\frac{1}{P+1-i}\right)$   
(c)  $-nRT \sum_{i=1}^{i=P} \left(\frac{i}{P+1-i}\right)$   
(d)  $-nRT \sum_{i=1}^{i=P-1} \left(\frac{i}{P+1-i}\right)$ 

- 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  $PV = K_2$ .
  - (a) Magnitude of work done in the first process will be greater than that in the second process.
  - (b) Magnitude of work done in the second process will be greater than that in the first process.
  - (c) Work done in both the processes cannot be compared without knowing the relation between  $K_1$  and  $K_2$ .
  - (d) First process is impossible.

8. If a triatomic non-linear gas is heated isothermally, then what percentage of the heat energy is used to increase the internal energy?

(a)	zero	(b)	60%
(c)	50%	(d)	100%

- **9.** A student is calculating the work done by 2 mole of an ideal gas in a reversible isothermal expansion shown in the figure. By mistake he calculated the area of the shaded area in the *PV* graph shown, as work and answered the magnitude of work equal to 49.26 L-atm. What is the correct magnitude of work done by the gas in L-atm? (R = 0.0821 L-atm/K-mol)
  - (a) 49.26 (b) 98.52



- **10.** In a certain polytropic process, the volume of argon was increased 4 times. Simultaneously, the pressure decreased 8 times. The molar heat capacity of argon in this process, assuming the gas to be ideal, is
  - (a) -4.2 J/K-mol (b) +4.2 J/K-mol (c) 12.47 J/K-mol (d) 20.78 J/K-mol
- **11.** The molar heat capacity at 25°C should be close to 27 J/K-mol for all of the given elements except

(a)	Pt	(b)	W
(c)	Ne	(d)	Sr

12. The pressure and density of a diatomic gas ( $\gamma = 7/5$ ) change from ( $P_1$ ,  $d_1$ ) to ( $P_2$ ,  $d_2$ ) adiabatically. If  $d_2/d_1 = 32$ , then what is the value of  $P_2/P_1$ ?

(a)	32	(b)	64
(c)	128	(d)	256

**13.** How many times a diatomic gas should be expanded adiabatically so as to reduce the RMS speed to half?

(a)	8	(b)	16
~ ~			

(c) 32 (d) 64

- 14. Work done by a sample of an ideal gas in a process A is double the work done in another process B. The temperature rises through the same amount in the two processes. If  $C_A$  and  $C_B$  are the molar heat capacities for the two processes, then
  - (a)  $C_{\rm A} = C_{\rm B}$  (b)  $C_{\rm A} > C_{\rm B}$ (c)  $C_{\rm A} < C_{\rm B}$  (d) Both, undefined
- **15.** One mole of oxygen is heated from 0°C at constant pressure till its volume is increased by 10%. The specific heat of oxygen, under these conditions, is 0.22 cal/g-K. The amount of heat required is
  - (a)  $32 \times 0.22 \times 27.3 \times 4.2$  J
  - (b)  $16 \times 0.22 \times 27.3 \times 4.2 \text{ J}$

(c) 
$$\frac{32 \times 0.22 \times 27.3}{4.2}$$
 J  
(d)  $\frac{16 \times 0.22 \times 27.3}{4.2}$  J

16. Heat energy of 743 J is needed to raise the temperature of 5 moles of an ideal gas by 2 K at constant pressure. How much heat energy is needed to raise the temperature of the same mass of the gas by 2 K at constant volume? (R = 8.3 J/K-mol) (a) 826 J (b) 743 J

(a)	826 J	(b)	743.
		( <b>4</b> )	

- (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 SO<sub>2</sub> 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? (R = 0.08 L-atm/K-mol)
  - (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 final temperature will be

(a)	300 K	(b)	227.5°C
(c)	455 K	(d)	455°C

- 23. If all degree of freedom of a three-dimensional N-atomic gaseous molecules is excited, then  $C_{\rm P}/C_{\rm V}$  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  $V_2$ , then 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)	$100 \mathrm{J}$

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



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

(d) 1.33R

- (1) Reversible isothermal
- (2) Reversible adiabatic
- (3) Irreversible adiabatic under a constant external pressure.

Then

(c) 3.5R

- (a) Final temperature of gas will be highest at the end of second 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 third 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, such as 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°C. What will happen to the gas if it is adiabatically expanded at 50°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 the 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  $P^2V$  = 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.



**33.** For an ideal gas subjected to different processes as shown in the graphs, select the graph which will involve the 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?



- 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 the gas volume isothermally under the piston  $\eta$  times by slowly raising the piston? The friction of the piston against the cylinder walls is negligibly small.
  - (a)  $RT(\eta 1 \ln \eta)$
  - (b)  $RT(1 \eta + \ln \eta)$
  - (c)  $RT \ln \eta$
  - (d)  $-RT \ln \eta$
- 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 the volume of one part of gas isothermally  $\eta$  times when compared to that of the other by slowly moving the piston?

(a) 
$$P_{o}V_{o} \ln \eta$$
  
(b)  $P_{o}V_{o} \ln \frac{(\eta+1)^{2}}{4\eta}$   
(c)  $P_{o}V_{o} \ln \frac{(\eta-1)^{2}}{4\eta}$   
(d)  $2P_{o}V_{o} \ln \eta$ 

**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

(a) 1:1:1 (b	b) 2:2:1
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(c)  $2: 2\sqrt{2}: 1$  (d)  $1: 2\sqrt{2}: 2$ 

**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  $P_o$ ,  $T_o$ and  $V_o$ , respectively. By means of heating the coil, heat is supplied slowly to the gas in one chamber (A) until its pressure becomes  $27P_o/8$ . If the value of  $\gamma$  is 1.5, then find the heat supplied to the gas in chamber A.

(a)	$5P_{0}V_{0}/4$	(b)	$19P_{\rm o}V_{\rm o}/2$
(c)	$15P_{0}V_{0}/2$	(d)	$15P_{0}V_{0}/4$

- 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 thermal 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?
  - (a) The piston ends up 0.4H above its initial position.
  - (b) The piston ends up 0.6H above its initial position.
  - (c) The piston ends at its initial position.
  - (d) The piston ends up 0.4H below its initial position.
- **41.** Three lawn chairs, one made up of aluminium (heat capacity = 0.90 J/K-g), one of iron (heat capacity = 0.45 J/K-g) and one of tin (heat capacity = 0.60 J/K-g) are painted of the same colour. On a sunny day, which chair will be hotter to sit?

(a) Iron chair	(b)	Tin chair
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- (c) Aluminium chair (d) All are same
- **42.** One mole of a real gas is subjected to a process from (2 bar, 30 L, 300 K) to (2 bar, 40 L, 500 K). The molar heat capacity of gas at constant volume

and constant pressure are 25 and 40 J/K-mol, respectively. What is the change in internal energy of the gas in this process?

(a)	5000 J	(b)	6000 J
(c)	8000 J	(d)	10,000 J

**43.** A real gas is subjected to an adiabatic process from (2 bar, 40 L, 300 K) to (4 bar, 30 L, 300 K) against a constant pressure of 4 bar. The enthalpy change for the process is

J

(a)	zero	(b)	6000 J
(c)	8000 J	(d)	10,000

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 the 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°C, the efficiency increases to 1/3. The temperature of source is

(a)	117°C	(b)	52°C
(c)	390°C	(d)	1755°C

**47.** A Carnot engine operates between 327°C and 117°C. If it absorbs 120 cal heat per cycle from the source, then 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 J/K	(b)	100 J/K
(c)	20 J/K	(d)	180 J/K

52. Molar heat capacity of  $CD_2O$  (deuterated form of formaldehyde) vapour at constant pressure is vapour 14 cal/K-mol. The entropy change associated with the cooling of 3.2 g of  $CD_2O$ vapour from 1000 K to 900 K at constant pressure is (assume ideal gas behaviour for  $CD_2O$ ) [ln 0.9 = -0.1]

(a)	+0.14 cal/K	(b) -0.14 cal/K
(c)	-1.4 cal/K	(d) $+1.4$ cal/K

**53.** An amount of 2 mole of CO was in the small cubical container of length (l = a) at 57°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 J/K	(b) $-34.58 \text{ J/K}$
(c)	-11.53 J/K	(d) +11.53 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 is (ln 2 = 0.7)

(a)	4.2 cal/K	(b)	7.0 cal/K
(c)	2.1 cal/K	(d)	3.5 cal/K

55. The molar entropy of a constant volume sample of neon at 500 K if it is 46.2 cal/K-mol at 250 K is  $(\ln 2 = 0.7)$ 

(a)	2.1 cal/K-mol	(b) 44.1 cal/K-mol
(c)	48.3 cal/K-mol	(d) 46.2 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 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°C to 927°C. If the initial pressure of gas was 1 bar, then the final pressure of gas becomes

(a)	4 bar	(b)	8 bar
(c)	32 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 to bereversible. The entropy change of the gas in this process is  $(\ln 3 = 1.1)$ 

(a)	-1.1 cal/K	(b)	+1.1 cal/K
(c)	-2.2 cal/K	(d)	+2.2 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)

(a)	-11.64 J/K	(b)	+11.64 J/K
(c)	-34.92 J/K	(d)	+34.92 J/K

61. Each of the vessels 1 and 2 contain 1.2 moles of gaseous helium. The ratio of the volume of vessels 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 difference of gas entropies in these vessels,  $S_2 - S_1$  (ln 2 = 0.7).

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

a) 
$$\frac{(n-\gamma)R}{(n-1)(\gamma-1)} \ln \tau$$
 (b)  $\frac{(n-1)(\gamma-1)}{(n-\gamma)R} \ln \tau$ 

(c) 
$$\frac{(n-\gamma)R}{(\gamma-1)} \ln \tau$$
 (d)  $\frac{(n-\gamma)R}{(n-1)} \ln \tau$ 

- **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  $(\ln 2 = 0.7)$ 
  - (a) +11.2 cal/K (b) -11.2 cal/K (c) +5.6 cal/K (d) -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?

(a) 
$$\frac{\gamma . P_o}{\alpha(\gamma - 1)}$$
 (b)  $\frac{\gamma . P_o}{\alpha(\gamma + 1)}$ 

(c) 
$$\frac{\alpha . P_{o}}{\gamma + 1}$$
 (d)  $\frac{\alpha . P_{o}}{\gamma - 1}$ 

**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  $T = T_o$  at  $V = V_{o, \text{ then}}$  the volume dependence of the gas on temperature in this process is

(a) 
$$T = T_{o} + \ln V$$
 (b)  $T = T_{o} + \frac{R}{a} . \ln \frac{V_{o}}{V}$   
(c)  $T = T_{o} + \frac{R}{a} . \ln \frac{V}{V_{o}}$  (d)  $V = V_{o} + \frac{a}{R} . \ln \frac{T}{T_{o}}$ 

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.

(a) 
$$S = \frac{a.T^3}{3}$$
 (b)  $S = aT^3$   
(c)  $\frac{a.T^2}{2}$  (d)  $\frac{a.T}{3}$ 

**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

(a) -10.0 J/K	(b)	+10.0 J/K
(c) $-57.8 \text{ J/K}$	(d)	+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, then the  $\Delta S_{\text{mix}}$  is (ln 2 = 0.7, ln 3 = 1.1, ln 7 = 1.95)

(a)	+3.33 kcal/K	(b)	-1.0 kcal/K
(c)	+1.0 kcal/K	(d)	+1.33 kcal/K

69. Two blocks of copper metal are of the 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

(a) 
$$C \cdot \ln \left[ \frac{(T_2 - T_1)^2}{4T_1T_2} + 1 \right]$$
  
(b)  $C \cdot \ln \left[ \frac{(T_2 - T_1)^2}{4T_1T_2} \right]$   
(c)  $C \cdot \ln \left[ \frac{(T_2 + T_1)^2}{4T_1T_2} + 1 \right]$   
(d)  $C \cdot \ln \left[ \frac{(T_2 + T_1)^2}{4T_1T_2} - 1 \right]$ 

70. Assuming ideal gas behaviour, the  $\Delta S$  for the isothermal mixing of 0.8 mole N<sub>2</sub> and 0.2 mole of O<sub>2</sub> is (ln 2 = 0.7, ln 10 = 2.3)

(a)	+0.96 cal/K	(b)	+0.32 cal/K
(c)	-0.96 cal/K	(d)	-0.32 cal/K

**71.** If all the following gases are in monoatomic form, then which of the following has greater entropy?

(a) <i>H</i>	(b) N
(c) O	(d) Cl

**72.** Which of the following would be expected to have the largest entropy per mole?

(a)	$SO_2Cl_2(s)$	(b)	$SO_2Cl_2(l)$
(c)	$SO_2Cl_2(g)$	(d)	$SO_2(g)$

- **73.** The enthalpy of formation steadily changes from -17.89 Kcal/mol to -49.82 Kcal/mol as we go from CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> to C<sub>8</sub>H<sub>18</sub>. The value of  $\Delta G$  however shows opposite trend from -12.12 Kcal/mol for CH<sub>4</sub> to 4.14 Kcal/mol for C<sub>8</sub>H<sub>18</sub>. Why?
  - (a) As the number of carbon atoms increases, the number of possible isomers increases. This reverses the expected trend of  $\Delta G$  values.
  - (b) 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.
  - (c) In the formation of  $C_nH_{2n+2}$  from *n* carbon atoms and (n + 1) hydrogen molecules there is a large decrease in entropy. This is reflected in the  $\Delta G$  values.
  - (d) No simple reason is possible.
- 74. An amount of 5 mole  $H_2O(1)$  at 100°C and 1 atm is converted into  $H_2O(g)$  at 100°C and 5 atm.  $\Delta G$  for the process is

(a) zero	(b) 1865 ln 5 cal
(c) 3730 ln 5 cal	(d) $-3730 \ln 5$ 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?

(a) zero	(b) +1200 cal
(c) $-1200$ cal	(d) 4 cal

76. A reaction at 300 K with  $\Delta G^{\circ} = -1743$  J consists of 3 moles of A(g), 6 moles of B(g) and 3 moles of C(g). If A, B and C are in equilibrium in one liter vessel, then the reaction should be (ln 2 = 0.7, R = 8.3 J/K-mol)

(a) $A + B \rightleftharpoons C$	(b) $A \rightleftharpoons B + 2C$
(c) $2A \rightleftharpoons B + C$	(d) $A + B \rightleftharpoons 2C$

77. The vapour pressures of water and ice at  $-10^{\circ}$ C are 0.28 and 0.26 Pa, respectively. What is the molar free energy change for the process?

 $H_2O(l, -10^{\circ}C, 0.28 \text{ Pa}) \rightarrow H_2O(s, -10^{\circ}C, 0.26 \text{ Pa})$ 

(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°C expands against vacuum from 1.2 dm<sup>3</sup> to 2.4 dm<sup>3</sup>. The change in free energy of the gas,  $\Delta G$ , is (R = 0.08 bar- L/K-mol, ln 2 = 0.7)
  - (a) 0 (b) -64 bar-l
  - (c) +84 J (d) -84 J
- **79.** For a reaction  $A \rightleftharpoons B$  carried out at 27°C, the ratio of equilibrium concentrations of the 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°C. The free energy change for the following process is

 $H_2O(g, 0.04 \text{ atm}, 27^{\circ}C) \rightarrow H_2O(l, 0.04 \text{ atm}, 27^{\circ}C)$ 

- (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 both independent from amount and path
  - (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>> 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) Adiabatic free expansion of any gas is also isothermal.
  - (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)  $(-w_{rev}) (-w_{irr}) > 0$  for isothermal expansion.
  - (b)  $w_{rev} > w_{irr}$  for isothermal compression.
  - (c) Heat rejected in isothermal process is greater in (n-1)th stage as compared to *n*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°C to 17°C. Which of the following is/are true?

(a) q = 0 (b)  $\Delta H = 0$ (c)  $\Delta H = -600$  cal (d)  $\Delta U = -600$  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, then 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.

A (500 K, 5 bar)  $\xrightarrow{\text{Reversible isothermal}} B$  $\xrightarrow{\text{Isochoric cooling}} C(250 \text{ K}, 1 \text{ bar}) \xrightarrow{\text{Single stage adiabatic}} O(3 \text{ bar})$ 

The correct statement(s) is/are

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

(a) $\Delta T = 0$	(b) $\Delta P = 0$
(c) $q = 0$	(d) $\Delta U = 0$

**15.** For a process to occur under isothermal conditions, the essential condition(s) is/are

(a)	dT = 0	(b)	$d\mathbf{P} = 0$
(c)	q = 0	(d)	dU = 0

16. Assume ideal gas behaviour for all the gases considered and vibrational degrees of freedom to be active. Separate equimolar samples of Ne,  $O_2$ ,  $SO_2$  and  $CH_4$  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 the same final volume, which is double the original volume thereby causing decrease in their temperature.

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

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

- (a) Due to Step I only, the decrease in temperature will be maximum for Ne.
- (b) During Step II, heat given will be maximum for  $CH_4$ .
- (c) There will be no change in internal energy for any gas after both the steps of process are completed.
- (d) The P-V graph of CH<sub>4</sub> and SO<sub>2</sub> will be the same for overall process.
- 17. Which of the following statement(s) is/are incorrect?
  - (a) The specific heat capacity of substance is greater in the solid state than in liquid state.
  - (b) The specific heat capacity of a substance is greater in gaseous state than in the liquid state.
  - (c) The latent heat of vaporization of a substance is greater than that of fusion.
  - (d) The internal energy of an ideal gas is a function of its temperature.
- **18.** For which of the following gases, the difference in specific heats at constant pressure and at constant volume is equal to 0.04545 cal/gm?

(a) 
$$N_2$$
 (b)  $N_2O$ 

(c) CO (d)  $CO_2$ 

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

$$2 P_{o} = 1$$

$$P_{o} = 1$$

$$P_{o} = 1$$

$$P_{o} = 1$$

$$P_{o} = 1$$

(a) 
$$\Delta H = \frac{2\gamma P_o V_o}{\gamma - 1}$$
 (b)  $\Delta U = \frac{3P_o V_o}{\gamma - 1}$ 

(c) 
$$\Delta H = -P_{o}V_{o}$$
 (d)  $\Delta U = -3P_{o}V_{o}$ 

- **20.** Which of the following statement(s) is/are incorrect?
  - (a) For a closed system at rest with no fields, the sum of q + w has the same value for every process that goes from a given state 1 to a given state 2.
  - (b) If a closed system at rest in the absence of external fields undergoes an adiabatic process that has w = 0, then the temperature of system must remain constant.
  - (c) A change in state from state 1 to state 2 produces a greater increase in entropy of the system when carried out irreversible than when carried out reversibly.
  - (d) The change in entropy of the system for an adiabatic process in a closed system must be zero.
- **21.** Which of the following statement(s) is/are incorrect?
  - (a) Combustion of methane gas in an adiabatic rigid container will cause no change in temperature of the system.
  - (b) It is possible to have both adiabatic reversible and adiabatic irreversible processes between two states.
  - (c) For a reaction involving only ideal gases and occurring at constant temperature, there will not be any change in the internal energy of the system.
  - (d) P-V work is always non-zero when there is some change in the volume of system.
- **22.** Which of the following statement(s) is/are correct regarding reversible adiabatic and isothermal processes for an ideal gas, starting from the same initial state to the same final volume?
  - (a) In expansion, more work is done by the gas in isothermal process.
  - (b) In compression, more work is done on the gas in adiabatic process.
  - (c) In expansion, the final temperature of gas will be higher in isothermal process.
  - (d) In compression, the final temperature of gas will be higher in adiabatic process.
- **23.** A heat engine is operating in between 500 K and 400 K. If the engine absorbs 100 J heat per cycle, then which of the following is impossible amount of heat rejected by the engine per cycle?

(a) 75 J	(b) 85 J
(c) 90 J	(d) 70 J

24. For the cyclic process given below, which of the following relations are correct?



(c) 
$$\Delta S_{\text{cycle}} = 0 = \int_{1}^{2} \frac{\delta q_{\text{rev}}}{T} + \int_{2}^{1} \frac{\delta q_{\text{irr}}}{T}$$
  
(d)  $\Delta S_{\text{cycle}} = 0 > \left(\int_{1}^{2} \frac{\delta q_{\text{rev}}}{T} + \int_{2}^{1} \frac{\delta q_{\text{irr}}}{T}\right)$ 

- **25.** For which of the following process  $\Delta S_{sys}^{o}$  is positive?
  - (a) The dissolution of ammonium nitrate in water.
  - (b) The expansion of a sample of chlorine into a larger volume.
  - (c) The decomposition of mercuric oxide.
  - (d) The rusting of iron.
- 26. Any process will be spontaneous at constant pressure and temperature when
  - (a)  $\Delta S_{\text{system}} = +\text{ve}$  (b)  $\Delta S_{\text{univ.}} = +\text{ve}$

(c)  $\Delta G_{\rm sys} = -ve$ (d)  $\Delta G_{\text{univ}} = +\text{ve}$ 

- 27. Which of the following statement(s) is/are incorrect?
  - (a) Entropy is a measure of unavailable energy.
  - (b) Decrease in free energy of the system represents the unavailable energy of the system.
  - (c) Complete conversion of heat into work is not possible in a reversible isothermal expansion of ideal gas.
  - (d) Complete conversion of heat into work is

# 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 $-50^{\circ}$ C.

- 1. What is the change in internal energy of gas?
  - (a) -1400 cal (b) -600 cal
  - (c) -1000 cal (d) Zero
- 2. What is the change in enthalpy of gas?
  - (a) -1400 cal (b) -600 cal
  - (c) -1000 cal (d) Zero

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 nonspontaneous at high temperature?
  - (a) Dissociation of  $PCl_5(g)$  into  $PCl_3(g)$  and  $Cl_2(g)$ .
  - (b) Formation of  $H_2O(1)$  from  $H_2(g)$  and  $O_2(g)$ .
  - (c) Formation of  $H_2O(g)$  from  $H_2(g)$  and  $O_2(g)$ .
  - (d) 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
  - (a)  $\Delta S_{\text{vap}} > 100 \text{ J/K-mol}$  at 350 K and 0.5 atm.
  - (b)  $\Delta G_{\text{vap}} < 0$  at 350 K and 0.5 atm.
  - (c)  $\Delta S_{\text{vap}} > 100 \text{ J/K-mol}$  at 350 K and 2.0 atm.
  - (d)  $\Delta G_{\text{vap}} > 0$  at 350 K and 2.0 atm.
- **30.** Select the correct statement(s).
  - (a) In a reversible process,  $\Delta G$  is always zero in a closed system.
  - (b) In a reversible process,  $\Delta S_{univ}$  is always zero in a closed system.
  - (c) In a reversible process,  $\Delta S_{sys}$  is always zero in a closed system.
  - (d) In a reversible process,  $\Delta S_{sys}$  is always zero in an isolated system.

- (a) 600 J
- (b) 600 cal
- (c) 1000 cal
- (d) Zero
- 3. What is the magnitude of work done by the gas?

#### **Comprehension II**

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

- **4.** What is the molar heat capacity of gas in this process?
  - (a)  $C_{v,m}$  (b)  $-C_{v,m}$ (c)  $C_{Pm}$  (d)  $-C_{Pm}$
- 5. What is the relation between *T* and *V* of gas in this process?
  - (a)  $T \cdot V^{2(\gamma 1)} = \text{Constant}$
  - (b)  $T \cdot V^{\gamma 1} = \text{Constant}$

(c)  $T \cdot V^{(\gamma - 1)/2} = \text{Constant}$ (d)  $T \cdot V^{\gamma} = \text{Constant}$ 

6. What is the magnitude of work performed by one mole of the gas when its volume increases 8 times if the initial temperature of the gas is 300 K?  $C_{v,m}$  for the gas is 1.5*R*.

(a)	900 cal	(b)	450 cal
(c)	1247.7 cal	(d)	623.8 cal

#### **Comprehension III**

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

7.	The work performed by the	e gas is	9.	The value of $\gamma$ for the gas i	S	
	(a) 8.60 kJ	(b) 0.60 kJ		(a) 0.6	(b)	0.16
	(c) 16.60 kJ	(d) 4.60 kJ		(c) 1.6	(d)	2.2
8.	The increment of its intern	nal energy (in kJ) is				
	(a) 1.0	(b) 1.6				

#### **Comprehension IV**

(c) 2.2

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

**10.** What is the in the increment of the internal energy of the gas?

(d) 2.0

(a)  $\frac{15\alpha V_0^2}{\gamma - 1}$  (b)  $\frac{\alpha V_0^2}{\gamma - 1}$ 

(c) 
$$\frac{15\alpha V_0^2}{2}$$
 (d)  $\frac{15\alpha(\gamma+1)V_0^2}{2(\gamma-1)}$ 

- **11.** What is the magnitude of work performed by the gas?
  - (a)  $\frac{15\alpha V_0^2}{\gamma 1}$  (b)  $\frac{\alpha V_0^2}{\gamma 1}$  (d)  $\frac{15\alpha(\gamma + 1)V_0^2}{2(\gamma 1)}$ (c)  $\frac{15\alpha V_0^2}{2}$  (d)  $\frac{15\alpha(\gamma + 1)V_0^2}{2(\gamma - 1)}$

**12.** What is the molar heat capacity of the gas in the process?

(a) 
$$\frac{R(\gamma+1)}{2(\gamma-1)}$$

b) 
$$\frac{\alpha V_0^2}{\gamma - 1}$$

(

(c) 
$$\frac{R(\gamma-1)}{2(\gamma+1)}$$

#### **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)  $R\cdot\alpha\cdot\Delta T$
  - (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)  $\frac{R}{\gamma-1} + \frac{R}{1-\alpha}$ 

#### **Comprehension VI**

An ideal gas with the adiabatic exponent  $\gamma$  undergoes a process in which its internal energy relates to the volume as  $U = a V^{\alpha}$ , 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)  $\frac{R.\Delta U}{\alpha(\gamma-1)}$  (b)  $\frac{\Delta U}{\alpha(\gamma-1)}$
  - (c)  $\frac{\Delta U.(\gamma 1)}{\alpha}$  (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  $\Delta U$ ?

- 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)  $\alpha < \gamma$

- (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
  - (c) 1/32 attil (d) 1/120 attil
- **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.



#### **Comprehension IX**

The vapour pressure of water at 353 K is 532 mm Hg. The external pressure on  $H_2O$  (l) taken in a cylinder fitted with frictionless movable piston initially containing 0.9 L (= 0.9 kg) of  $H_2O$  (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  $H_2O$  (l) is evaporated to form  $H_2O$  (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.

Specific heat of H<sub>2</sub>O (l) = 4.2 J/°C-g  $\Delta H_{vap}$  at 373 K and 1 atm = +40 kJ/mol

1 L-atm = 100 J

R = 8 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 (d) 74.6
  - (c) 1001 (d) 74.6

27.	Total change in enthalpy (i to State-3 is	n kJ) going from State-1	28.	What is the magnitude State-1 to State-3?	of work done (in J) in going
	(a) 75.6	(b) 1075.6		(a) Zero	(b) 74.6
	(c) 1001	(d) 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	30.	The change in inter	nal energy of gas in the process
	(a) 800 K	(b) 200 K		BC is	
	(c) 400 K	(d) 100 K		(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 the answer as follows.

- (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, ΔU = 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 compression is less in reversible compression than in irreversible compression against a constant external pressure.

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

**9.** Statement I: For the same mole of  $SO_2$  and  $O_2$  gases, more heat is needed for  $SO_2$  gas than  $O_2$  gas for the same increase in the temperature of the gas at constant pressure.

**Statement II:**  $SO_2$  gas, being triatomic, has higher heat capacity than the diatomic  $O_2$  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.

### Section E (Column Match)

**1.** Match the columns

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

**2.** Match the columns

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

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

- Statement I: An exothermic process, nonspontaneous 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,  $\Delta S_{surr} = 0$ . Statement II: Entropy is a state function.
- 3. Match the columns

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

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

**4.** Match the columns (Given process does not include chemical reaction and phase change).

5. Match the columns (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) $dU = n \cdot C_{v,m} \cdot dT +$	(Q) Van der Waals gas
$n^2 a \frac{\mathrm{d}V}{V^2}$	
(C) $dU = n^2 a \frac{dV}{V^2}$	<ul><li>(R) Van der Waals gas in isothermal process</li></ul>
	(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 the columns.

Column I	Column II
(A) Reversible isothermal expansion of an ideal gas	(P) $\Delta S_{sys} = \Delta S_{surr} = \Delta S_{total} = 0$
<ul><li>(B) Reversible adiabatic expansion of an ideal gas</li></ul>	(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 the columns.

9.

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

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).



# Section F (Subjective)

# Single-digit Integer Type

- 1. 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/°C; density of water = 1.0 g cm<sup>-3</sup> and external pressure = 1 bar. If the magnitude of work for this process is X J, then the value of  $\frac{X}{6 \times 10^{-4}}$  is
- 2. The final volume (in L) of one mole of an ideal gas initially at 27°C and 8.21 atm pressure, if it absorbs 420 cal of heat during a reversible isothermal expansion is ( $\ln 2 = 0.7$ )
- 3. A balloon containing air at  $27^{\circ}$ 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  $10^7$  J) is
- 4. A quantity of 8 g oxygen gas is expanded isothermally at 27°C from 2 dm<sup>3</sup> to 8 dm<sup>3</sup> at a constant external pressure of 4 bar. If the magnitude of work done in this process is used in lifting a body of mass 40 kg, the height (in metre) up to which the body can be lifted is ( $g = 10 \text{ ms}^{-2}$ )
- 5. 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 cal/K-mol) for the process is
- 6. What amount of heat (in J) is to be transferred to nitrogen in the isobaric heating process for that gas to perform the work 2.0 J?
- 7. Ten 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
- **8.** 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  $C_{\rm v,m}$  for this gas (in cal/K-mol) is (ln 5 = 1.6)

- 9. The number of degrees of freedom of molecules in a gas whose molar heat capacity is 29 J/mol-K in the process PT = constant is
- **10.** 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
- **11.** 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 cal/K-mol) in this process is
- 12. 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
- 13. At 298 K, the standard enthalpy of combustion of sucrose is -5737 kJ mol<sup>-1</sup> and the standard Gibb's energy of the reaction is -6333 kJ mol<sup>-1</sup>. The additional (non-expansion) work (in kJ) that may be obtained by raising the temperature to 29°C is
- 14. The diamonds are formed from graphite under very high pressure. Calculate the equilibrium pressure (in  $10^4$  bar) at which graphite is converted into diamond at 25°C. The densities of graphite and diamond are 2.4 and 3.6 g/cm<sup>3</sup>, respectively, and are independent of pressure.  $\Delta G^{\circ}$  for the conversion of graphite into diamond is 5.0 kJ/ mol.
- 15. The standard entropy change (in cal/K-mol) for the reaction:  $X \rightleftharpoons Y$ , if the value of  $\Delta H^\circ = 7.5$  kcal/mol and  $K_C = e^{-10}$  at 300 K.

# Four-digit Integer Type

- 1. One mole of a Van der Waals gas expands reversibly and isothermally at 27°C from 2 L to 20 L. The magnitude of work done (in J) if  $a = 1.42 \times 10^{12}$  dynes cm<sup>4</sup>/mole and b = 30 ml/mole.
- 2. One mole of an non-ideal gas undergoes a change of state from (2.0 atm, 3.0 L, 95 K) to (4.0 atm, 5.0 L, 245 K) with a change in internal energy, ΔU = 30.0 L-atm. The enthalpy change (ΔH) of the process in L-atm is
- 3. The internal energy change in the conversion of 1 mole of the calcite form of  $CaCO_3$  to the aragonite form is +0.21 kJ. The enthalpy change (in J) in the conversion at 2.7 bar is (The densities of the solids calcite and aragonite are 2.7 g cm<sup>-3</sup> and 3.0 g cm<sup>-3</sup>, respectively.)
- 4. A system undergoes a certain change in state by path I and the corresponding heat absorbed and work done are 10 kcal and 0 erg, respectively. For the same change in state by path II, the respective quantities are 11 kcal and 0.5  $w_{max}$ , where  $w_{max}$  represents the work done if the changes were reversibly carried out. The magnitude of  $w_{max}$ , in J, is (1 cal = 4.2 J)
- 5. The internal energy of a gas is given by U=1.5 PV. It expands from 100 to 200 cm<sup>3</sup> against a constant pressure of  $1.0 \times 10^5$  Pa. The heat absorbed (in KJ) by the gas in the process is
- 6. 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 cm<sup>2</sup>. The cylinder is closed by a light frictionless piston. The gas is heated slowly in a process during which a total of 42 J heat is given to the gas. If the temperature rises through 2°C, then find the distance moved by the piston (in cm). Atmospheric pressure = 100 kPa.
- 7. Only at extremely high pressure does  $\Delta H \Delta U$  for condensed state reactions becomes significantly different than zero. Determine the pressure (in bar) at which  $\Delta H \Delta U$  is equal to -1.0 kJ for the reaction, C(graphite)  $\rightarrow$  C(diamond). For graphite and diamond, the densities are 2.4 and 3.6 g/ml, respectively.
- **8.** The melting point of a certain substance is 70°C, its normal boiling point is 450°C, its enthalpy of

fusion is 30 cal/g, its enthalpy of vaporization is 45 cal/g, and its specific heat is 0.215 cal/g-K. The heat required (in cal) to convert 10 g of the substance from the solid state at 70°C to vapour at  $450^{\circ}$ C is

- 9. When an electric current of 0.50 A from a 12 V supply is passed for  $\frac{1805}{6}$  sec through a resistance in thermal contact with water maintained at 1 atm and 373 K, it is found that 0.9 g of water is vaporized. The molar internal energy change (in kJ/mol) of water is (Take 8.314 × 373 = 3100)
- 10. A volume of 100 ml of a liquid contained in an adiabatic container at a pressure of 1 bar. The pressure is steeply increased 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°C till its volume is doubled. It is then adiabatically compressed to its original volume. The magnitude of total work done (in J) by the gas is (ln 2 = 0.7,  $2^{0.4} = \frac{4}{3}$ , R = 8.3 J/K-mol)
- 13. Consider a classroom that is roughly 8.21 m × 10 m×3 m. Initially, T=290 K and P=1 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 L-atm/K-mol = 8.3 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 ( $\ln 2 = 0.7$ )
- 16. Calculate  $\Delta S_{univ}$  (in J/K) for the chemical reaction: C(Graphite) + 2H<sub>2</sub>(g)  $\rightarrow$  CH<sub>4</sub>(g);  $\Delta H^{o}_{300} = -75.0$  kJ. The standard entropies of C (Graphite), H<sub>2</sub>(g) and CH<sub>4</sub>(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.

 $Al_2O_3(Solution) + 3C(Graphite) \rightarrow 2 Al(l) + 3CO(g); \Delta G^{\circ} = 600 \text{ kJ}$ 

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°C (body temperature)? The standard entropy and enthalpy of reaction are +200 J/K-mol and -2808 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.	$(\mathrm{d}G)_{P,T} > 0$
2.	$(\Delta S)_{\text{universe}} > 0$
3.	$(dU)_{S,V} > 0$
4.	$(\mathrm{d}H)_{S,P} < 0$
5.	$(\mathrm{d}S)_{U,V} < 0$
6.	$(\mathrm{d}S)_{H,P} > 0$

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

20. Consider the following phase transitions.

(i)	$H_2O$	(s,	1	atm,	273	K)	$\rightarrow$	$H_2O$
	( <i>l</i> , 1 at	tm, 2	73 F	()				
(ii)	$H_2O$	(s,	1	atm,	300	K)	$\rightarrow$	$H_2O$

- (l, 1 atm, 300 K)  $(iii) \text{ H}_2\text{O} \quad (s, 1 \text{ atm}, 200 \text{ K}) \rightarrow \text{ H}_2\text{O}$  (l, 1 atm, 200 K)
- (iv) H<sub>2</sub>O (s, 0.5 atm, 273 K)  $\rightarrow$  H<sub>2</sub>O (*l*, 0.5 atm, 273 K)
- (v) H<sub>2</sub>O (s, 2 atm, 273 K)  $\rightarrow$  H<sub>2</sub>O (*l*, 2 atm, 273 K)
- (vi)  $C_6H_6$  (*l*, 1 atm, 353 K)  $\rightarrow C_6H_6$ (g, 1 atm, 353 K)
- (vii)  $C_6H_6$  (*l*, 1 atm, 400 K)  $\rightarrow C_6H_6$ (g, 1 atm, 400 K)
- (viii)  $C_6H_6$  (*l*, 1 atm, 300 K)  $\rightarrow C_6H_6$ (g, 1 atm, 300 K)
- (ix)  $C_6H_6$  (*l*, 2 atm, 323 K)  $\rightarrow C_6H_6$ (g, 2 atm, 323 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 follows.

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** 

## **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) 39. (b) 41. (b) 42. (a) 45. (b) 36. (a) 37. (b) 38. (c) 40. (c) 43. (b) 44. (c) 51. (b) 52. (a) 46. (a) 47. (b) 48. (d) 49. (a) 50. (d) 53. (a) 54. (c) 55. (a) 56. (c) 58. (a) 60. (b) 57. (b) 59. (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	3. (b)	84.	(b)	85.	(b)	86.	(a)	87.	(d)	88.	(a)	89.	(d)	90.	(b)
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# Answer Keys

## 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. (c)	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), (c)	10. (a), (c)	11. (a), (b), (c)	12. (a), (b), (c)
13. (c), (d)	14. (c)	15. (a)	16. (a), (b), (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)		

# **Exercise II**

**Exercise** I

#### **Section C**

Compreh	ension I		Comprehension VII
1. (c)	2. (a)	3. (d)	19. (b) 20. (a) 21. (b)
Compreh	ension II		Comprehension VIII
4. (b)	5. (c)	6. (a)	22. (d) 23. (a) 24. (b)
Compreh	ension III		Comprehension IX
7. (b)	8. (a)	9. (c)	25. (c) 26. (c) 27. (b) 28. (b)
Compreh	ension IV		Comprehension X
10. (a)	11. (c)	12. (a)	29. (c) 30. (a)
Compreh	ension V		
13. (a)	14. (c)	15. (c)	
Compreh	ension VI		
16. (c)	17. (a)	18. (c)	

#### 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)

16. (0169)

17. (0300)

1.  $A \rightarrow P, R, S, T; B \rightarrow P, Q, R, S; C \rightarrow Q, R, S, T; D \rightarrow P, Q, R, T$ 2.  $A \rightarrow Q$ ;  $B \rightarrow Q$ , S;  $C \rightarrow Q$ , S;  $D \rightarrow P$ 3.  $A \rightarrow P, R, S; B \rightarrow Q, R, S; C \rightarrow Q, R, S; D \rightarrow R, S$ 4.  $A \rightarrow P, Q, R, S; B \rightarrow R, S; C \rightarrow Q$ 5.  $A \rightarrow P, S; B \rightarrow Q, R, S; C \rightarrow R$ 6.  $A \rightarrow P, R; B \rightarrow Q, S; C \rightarrow R; D \rightarrow Q, S$ 7.  $A \rightarrow Q$ ;  $B \rightarrow P$ , S;  $C \rightarrow R$ , S 8.  $A \rightarrow P, S; B \rightarrow P, R, S; C \rightarrow Q; D \rightarrow R, S$ 9.  $A \rightarrow P, S, R; B \rightarrow P, R; C \rightarrow P; D \rightarrow Q, R, S$ 10.  $A \rightarrow S; B \rightarrow P; C \rightarrow Q; D \rightarrow R$ Section F (Subjective) Single-digit Integer Type 7. (3) 1. (6) 2. (6) 3. (1) 4. (6) 5. (6) 6. (7) 8. (5) 9. (3) 12. (5) 13. (8) 11. (6) 14. (3) 15. (5) Four-digit Integer Type 1. (5713) 2. (0044) 3. (0209) 4. (8400) 5. (0025) 6. (0020) 7. (6000) 8. (1567) 9. (0033) 10. (1990) 11. (1500) 12. (0332) 13. (0500) 14. (1900) 15. (3120)

18. (2870)

19. (0012)

20. (2349)

10. (9)



# HINTS AND EXPLANATIONS

# EXERCISE I (JEE MAIN)

#### **Basics**

- 1. Theory based
- 2. Work cannot be defined at a particular state of system.
- **3.** For isothermal process, the container must be a good conductor of heat.
- **4.** Internal energy of ideal gas depends on the temperature as well as quantity of gas.
- 5. Greater the external pressure, greater will be the magnitude of work done by the gas.
- 6. Internal energy is a state function.

$$\Delta U_{net} = \Delta U_{AB} + \Delta U_{BA} = (U_B - U_A) + (U_A - U_B) = 0.$$

- 7. Theory based
- **8.** A closed system should exchange energy with the surrounding. If heat exchange is not possible, then energy must be exchanged as work.
- 9. Theory based

#### **First Law of Thermodynamics**

- **16.**  $\Delta U = q + w = (+20) + (-10) = +10$  J.
- 17.  $\Delta U = q + w = (+300) + (-200) = 100$  cal.

(Work is done by the system)

18. 
$$W = -1 \times \frac{1+2}{2} = -1.5$$
 bar · m<sup>3</sup> =  $\frac{-1.5 \times 1000 \times 100}{1000}$  kJ  
= -150 kJ  
and q = +100 kJ  
∴ ΔU = q + w = -50 kJ

- **19.** As the system rejects heat, the temperature will decrease.
- **20.** As the system is doing work but its internal energy is not changing, the system must absorb heat.

- 10. Hess's law of constant heat summation.
- 11. During cyclic process, the internal energy of system may change but  $\Delta U_{net} = 0$ .



For the process,  $\Delta T = 0$  but during the process, temperature is changing and hence, the process is not isothermal.

13.  $PV^{\gamma}$  = Constant or  $PV^{x}$  = Constant, are valid only when the gas is ideal, the process is reversible and  $C_{v,m}$  is temperature independent.

For a cyclic process,  $w_{net}$  may or may not be zero.

- 14. A true reversible process takes infinite time.
- 15. Theory based
- **21.**  $\Delta U = n.C_{v,m} \Delta T = 0$  (as  $\Delta T = 0$ )

22. 
$$w = -nRT \ln \frac{P_1}{P_2} = -5 \times 2 \times 300 \times \ln \frac{100}{1}$$
  
= -13800 cal.

23. 
$$w = -nRT \ln \frac{V_2}{V_1} \Rightarrow -4200 = -\frac{w}{40} \times 2 \times 300 \times \ln \frac{16}{4}$$
  
 $\therefore w = 200 \text{ g.}$ 

24. For minimum work in compression, the process must be reversible.

$$w = -nRT \cdot \ln \frac{P_1}{P_2} = -\frac{16}{32} \times 8.3 \times 300 \times \ln \frac{1.01325 \times 10^3}{1.01325 \times 10^{25}}$$
  
= +5727 J

**25.** 
$$\Delta H = n \cdot C_{P,m} \cdot \Delta T = 0$$
 (as  $\Delta T = 0$ )

26. 
$$W = -\int_{V_1}^{V_2} P_{ext} \cdot dv = -\int_{V_2}^{V_2} P \cdot dv$$
 (For reversible process)  
$$= -\int_{V_1}^{V_2} \left( \frac{nRT}{V - nb} - \frac{an^2}{V^2} \right) \cdot dV$$
$$= -\left[ nRT \cdot \ln \frac{V_2 - nb}{V_1 - nb} + an^2 \left( \frac{1}{V_2} - \frac{1}{V_1} \right) \right]$$

**27.** For both paths,  $\Delta U = 0$ , as  $\Delta T = 0$ .

$$\frac{q_{path-I}}{q_{path-II}} = \frac{-w_{path-I}}{-w_{path-II}} = \frac{PV \cdot \ln \frac{V_2}{V_1}}{(P \cdot \Delta V)_1 + (P \cdot \Delta V)_2}$$
$$= \frac{10 \times 1 \times \ln \left(\frac{10}{1}\right)}{5(2-1) + 1(10-2)} = \frac{10 \times 2.303}{13}$$

**28.**  $\Delta H = 0 \Rightarrow \Delta U = 0 \Rightarrow q = -w$ 

and 
$$w = -P_{ert}(V_2 - V_1) = -1$$
 bar (10 L - 5 L)  
= -5 Lbar = -500 J

**29.** For adiabatic process:

$$q = 0 \Longrightarrow w = \Delta U = n \cdot C_{v,m} \cdot \Delta T$$

**30.** 
$$T_1 \cdot V_1^{\gamma - 1} = T_2 \cdot V_2^{\gamma - 1} \Longrightarrow \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1} = \left(\frac{1}{8}\right)^{5/3 - 1}$$
$$= \frac{1}{4}$$

**31.** 
$$q = 0 \Rightarrow \Delta U = w \Rightarrow n \cdot C_{v,m} \cdot (T_2 - T_1)$$
  
=  $-P_{ert} \cdot (V_2 - V_1)$ 

or 
$$1 \times \frac{3}{2}R \times (T_2 - T) = -1 \text{ atm} \times (2 \text{ L} - 1 \text{ L})$$
  
 $\therefore T_2 = T - \frac{2}{3 \times 0.0821}$ 

32. 
$$w = \Delta U \Rightarrow -P_{ext}(V_2 - V_1) = n \cdot C_{v,m}(T_2 - T_1)$$

or 
$$-P_2\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right) = n \times \frac{5}{2}R(T_2 - T_1)$$
  
or  $-\left(T_2 - T_1 \cdot \frac{P_2}{P_1}\right) - \frac{5}{2}(T_2 - T_1)$ 

or 
$$-\left(T_2 - 350 \times \frac{2}{1}\right) = \frac{5}{2}(T_2 - 350) \Rightarrow T_2 = 450 \text{ K.}$$
  
Now,  $w = \Delta U = n \cdot C_{v,m}(T_2 - T_1)$   
 $= 2 \times \frac{5}{2} R \times (450 - 350) = 500R$   
33.  $T_1 V_1^{\gamma - 1} = T_2 \cdot V_2^{\gamma - 1} \Rightarrow T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$   
 $= 800 \times \left(\frac{1}{32}\right)^{\frac{\gamma}{5} - 1} = 200 \text{ K}$   
 $\therefore \Delta H = n \cdot C_{P,m} \cdot (T_2 - T_1) = 1 \times \frac{7}{2} R \times (200 - 800)$   
 $= -2100 \text{ R}$ 

34. P



**35.** Adiabatic free expansion of an ideal gas is also isothermal.

$$36. \quad w = -P \cdot \Delta V = -nR \cdot \Delta T = -1 \times R \times 1 = -R$$

**37.** 
$$q = -124$$
 J and

$$w = -P \cdot \Delta V = -2 \text{ bar } (125 - 325) \text{ ml}$$
  
= +400 bar-ml  
=  $\frac{400}{1000} \times 100 = 40 \text{ J}.$ 

: 
$$\Delta U = q + w = (-124) + 40 = -84$$
 J.

**38.** 
$$q_P = n \cdot \int_{T_1}^{T_2} C_{P,m} \cdot dT = 2 \times \int_{T_1=300\text{K}}^{T_2=400\text{K}} (28.314 \quad 0.01 \quad \cdot dT)$$
  
=  $2 \left[ 28.314 (T_2 - T_1) + \frac{0.01}{2} (T_2^2 - T_1^2) \right] = 6362.8 \text{ J}$ 

**39.** 
$$\frac{\Delta U}{-w} = \frac{n \cdot C_{v,m} \cdot \Delta T}{nR \cdot \Delta T} = \frac{3}{2}$$
  
**40.** 
$$C_{v,m} = 3 \times \frac{1}{2}R + 2 \times \frac{1}{2}R + (3 \times 4 - 5) \times R = \frac{19}{2}R$$

- **41.** For isothermal changes,  $C_m = \frac{q}{N \cdot \Delta t}$  = Infinite.
- **42.** Monoatomic gases have only translational degree of freedom.

43. 
$$\gamma_{mix} = 1 + \frac{(n_1 + n_2) \cdot R}{n_1 \cdot C_{\nu,m,1} + n_2 \cdot C_{\nu,m,2}}$$
  
$$= 1 + \frac{(1+1) \times R}{1 \times \frac{R}{5} - 1} + 1 \times \frac{R}{\frac{7}{5} - 1}$$
$$= 1.5$$

44. 
$$\frac{\Delta U}{q_P} = \frac{C_{v,m}}{C_{p,m}} = \frac{\frac{5}{2}R}{\frac{7}{2}R} = \frac{5}{7}$$

**45.** 
$$\frac{-w}{q_p} = \frac{nR \cdot \Delta T}{n \cdot C_{p,m} \cdot \Delta T} = \frac{R}{\left(\frac{\gamma \cdot R}{\gamma - 1}\right)} = 1 - \frac{1}{\gamma}$$

46. 
$$C_m = \frac{R}{\gamma - 1} + \frac{R}{1 - n} = 0 \Rightarrow \gamma - 1 = -(1 - n) \Rightarrow n = \gamma.$$

47. 
$$q = \Delta U - w$$
 and from the question,  $q = |w| = w$   
or  $2q = \Delta U$ 

or 
$$2 \cdot n \cdot C_m \cdot \Delta T = n \cdot C_{v,m} \cdot \Delta T \Rightarrow C_m = \frac{C_{v,m}}{2}$$
  
 $= \frac{1}{2} \times \frac{R}{1.5 - 1} = R$   
**48.**  $C_{p,m} = \frac{q_p}{n \cdot \Delta T} = \frac{70}{2 \times 10} = \frac{7}{2}$  cal  
 $\therefore C_{v,m} = \frac{7}{2} - 2 = \frac{3}{2}$  cal  
Now,  $q_v = n \cdot C_{v,m} \cdot \Delta T$   
 $= 2 \times \frac{3}{2} \times 10 = 30$  cal  
**49.**  $P \propto T^3 \Rightarrow P \alpha \left(\frac{PV}{nR}\right)^3 \Rightarrow PV^{3/2} = \text{Constant}$   
 $\Rightarrow \gamma = \frac{3}{2}$   
**50.**  $\Delta U = q + w = 100 + \left(-\frac{210}{4.2}\right) = 50$  cal  $= n \cdot c_{v,m} \cdot \Delta T$   
and  $q = 100$  cal  $= n \cdot c_m \cdot \Delta T$ 

$$\therefore \frac{50}{100} = \frac{n \cdot C_{v,m} \cdot \Delta T}{n \cdot C_m \cdot \Delta T} \Longrightarrow C_m = 2C_{v,m} = 2 \times \frac{5}{2}R = 5R$$

51. 
$$P \cdot V^{-1} = K \Rightarrow x = -1$$
  
Now,  $\frac{\Delta U}{w} = \frac{n \cdot C_{v,m} \cdot \Delta T}{\left(\frac{n \cdot R \cdot \Delta T}{x - 1}\right)} = -2 \cdot \frac{C_{v,m}}{R} = -2 \times \frac{\frac{3}{2}R}{R}$   
 $= -3.$ 

52. 
$$P_1 = 1 \text{ atm}, V_1 = V \text{ L}, T_1 = 300 \text{ K}$$
  
 $P_2 = 2\sqrt{2} \text{ atm}, V_2 = V_1 \cdot \left(\frac{P_1}{P_2}\right)^{\frac{1}{3}} = V_1 \left(\frac{1}{2^{\frac{3}{2}}}\right)^{\frac{1}{3}} = \frac{V_1}{\sqrt{2}}$   
;  $T_2 = \frac{P_2 V_2 \cdot T_1}{P_1 V_1}$   
or  $T_2 = \frac{2\sqrt{2}}{1} \times \frac{1}{\sqrt{2}} \times 300 = 600 \text{ K}$   
Now,  $w = \frac{-nR(T_2 - T_1)}{1 - x} = -\frac{1 \times R \times (600 - 300)}{1 - 3}$   
 $= +150R.$ 

53. 
$$T_1 V_1^2 = T_2 V_2^2 \Rightarrow T_2 = T_1 \cdot \left(\frac{V_1}{V_2}\right)^2 = 400 \times \left(\frac{4}{8}\right)^2$$
  
= 100 K  
Now,  $\Delta H = n \cdot C_{p,m} \cdot (T_2 - T_1) = 2 \times \frac{5}{2} R \times (100 - 400)$ 

= -1500R

54. 
$$w_{AB} = -nRT \cdot \ln \frac{P_1}{P_2} = -2 \times R \times 300 \times \ln \frac{1}{2}$$
  
= +600R \cdot \ln 2  
$$w_{BC} = -nR(T_2 - T_1) = -2 \times R \times (400 - 300)$$
  
= -200R  
$$w_{CD} = -nRT \ln \frac{P_1}{P_2} = -2 \times R \times 400 \times \ln \frac{2}{1}$$
  
= -800R \cdot \ln 2  
$$w_{DA} = -nR(T_2 - T_1) = -2 \times R \times (300 - 400)$$
  
= +200R  
$$\therefore w_{net} = w_{AB} + w_{BC} + w_{CD} + w_{DA} = -200R \cdot \ln 2$$
  
= -100R \cdot \ln 4



- 56.  $\Delta H = \Delta U + \Delta (PV) = \Delta U + (P_2V_2 P_1V_1)$ = 30.0 L-atm + (4×5-2×3) L-atm = 44.0 L-atm
- **57.** As the intermolecular distance increases against intermolecular attraction, the potential energy increases.

**58.** 
$$q = n \cdot L_m = 3 \times 10 = 30$$
 kcal

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

- **61.** Reversible heat engine is always more efficient than irreversible heat engine.
- **62.** Entropy increases with increase in mole of gases as well as volume of gas (decrease in pressure).
- 63. Entropy increases with increase in mole of gases.
- **64.** In all spontaneous process, entropy of universe increases but for system at equilibrium, entropy of universe becomes constant.
- 65. Entropy decreases on decreasing temperature.
- 66. Entropy: Solid < Liquid << Gas
- 67. Entropy: Solid < Liquid << Gas
- **68.** Efficiency is never 100%.
- **69.** Entropy of gas is greater and it increases with the increase in volume (decrease in pressure).
- 70. Entropy: Solid < Liquid << Gas
- 71. As  $\Delta H = +ve$  but the process is spontaneous, it is possible only when  $\Delta S$  is also +ve.

$$w = -P(V_{\text{vap}} - V_{\text{liq}}) \approx -P \cdot V_{\text{vap}} = -nRT$$
$$= -3 \times \frac{2}{1000} \times 500$$
$$= -3 \text{ kcal}$$
$$\therefore \Delta U = q + w = 27 \text{ kcal}$$

**59.** q = 540 cal

$$w = -P(V_{vap} - V_{liq}) = -1 \text{ atm}(1671 - 1) \text{ cm}^{3}$$
  
=  $-\frac{1670}{1000}$ L-atm =  $-1.670 \times 101.3$  J  
=  $-\frac{1.670 \times 101.3}{4.184}$  cal ≈  $-40$  cal  
 $\therefore \Delta U = q + w \approx 500$  cal

60. 
$$\Delta H - \Delta U = P \cdot \Delta V = P(V_{\text{diamond}} - V_{\text{graphite}})$$
  
=  $500 \times 10^3 \times 10^5 \frac{N}{m^2} \left(\frac{12}{3.0} - \frac{12}{2.0}\right) \times 10^{-6} \text{ m}^3$   
=  $-100 \text{ kJ}$ 

72. Entropy measures unavailable energy, i.e., energy which can't be converted into useful work.

73. 
$$\Delta S = n \cdot C_{v,m} \cdot \ln \frac{T_2}{T_1} + nR \cdot \ln \frac{V_2}{V_1}$$
$$= 1 \times C_{v,m} \times \ln 2 + 1 \times R \times \ln \frac{1}{2} = (C_{v,m} - R) \cdot \ln 2$$

74. 
$$\Delta S = \frac{\Delta H_{vap}}{B.P.} = \frac{\frac{40.85}{18} \times 3.6 \times 1000}{373} = 21.9 \text{ J/K}$$

10.05

**75.** 
$$\Delta S = \frac{\Delta H_{fus}}{M.P.} = \frac{2930}{300} = 9.77 \,\text{J/K.mol}$$

76.  $\Delta S = nR \cdot \ln \frac{P_1}{P_2} = \frac{64}{32} \times 8.3 \times \ln \frac{1}{0.25} = 23.24 \text{ J/K}$ 

77. 
$$\Delta S = n \cdot C_{v,m} \cdot \ln \frac{T_2}{T_1} = 2 \times R \times \ln \frac{900}{300} = 2R \cdot \ln 3$$

78. 
$$\Delta S = nR \ln \frac{V_2}{V_1} = 1 \times R \times \ln \frac{20}{2} = R \cdot \ln 10$$

(Adiabatic free expansion is also isothermal)

79. 
$$S_2 - S_1 = n \cdot C_{p,m} \cdot \ln \frac{T_2}{T_1}$$
  
or  $S_2 - 2.5 = 1 \times 4R \cdot \ln \frac{596}{298} = 4R \cdot \ln 2$ 

# **Gibbs Free Energy Function**

- **81.** Melting of ice at  $-15^{\circ}$  C and 1 atm is a non-spontaneous process and hence,  $\Delta G = +ve$ .
- 82.  $\Delta G_{T,P} = 0$
- 83.  $\Delta S = S_{water} S_{ice} = 58.0 38.0 = 20$  J/K.mol

Now,  $\Delta H = T \cdot \Delta S = 273 \times 20 = 5460$  J/mol.

- **84.** Amount is less than saturation and hence, NaCl will dissolve spontaneously.
- **85.**  $\Delta_r G = [(-480) + (-544)] [(-293)] = -731 \text{ kJ}$

:. 
$$S_2 = 2.5 + 4 \times 2 \times 0.7 = 8.1$$
 cal/K.mol

80. 
$$\Delta_r S = (2 \times S_{m,HCl}) - (S_{m,H_2} + S_{m,Cl_2})$$
  
=  $(2 \times 186.7) - (130.6 + 223.0)$   
=  $+19.8$  J/K.mol

86. 
$$\Delta G^{\circ} = -RT \cdot \ln K_P^{\circ} = -RT \cdot \ln \frac{P_{\text{NOCl}}^2}{P_{\text{NO}}^2 \cdot P_{\text{Cl}_2}}$$
  
=  $-8.314 \times 298 \times \ln \frac{(0.01)^2}{(0.00001)^2 \times 0.01}$   
=  $+45.65 \text{ kJ}$ 

- 87. For equilibrium condition,  $\Delta G = 0$
- 88.  $\Delta G = \Delta H T \cdot \Delta S = (-2500) 298 \times (+7.4) = -ve$  $\Rightarrow$  Spontaneous
- 89.  $\Delta H = +ve$ ,  $\Delta S = -ve$ , then  $\Delta G = +ve$  always
- **90.**  $\Delta G^{\circ} = RT \cdot \ln K_{eq} = 0 \Longrightarrow K_{eq} = 1$

# EXERCISE II (JEE ADVANCE)

#### Section A (Only one Correct)

$$1. \quad U = n \times \frac{f}{2} R \times T$$

For larger U, n, f, T, should be higher.

2. 
$$w = -\int_{V_1}^{V_2} P \cdot dv = -\int_{V_1}^{V_2} \left(\frac{a}{V} + b\right) dv$$
  
=  $-a \ln \frac{V_2}{V_1} - b(V_2 - V_1)$ 

- 3.  $q = m.s.\Delta T$   $\Rightarrow 10 \times 10^6 = 80 \times (4.2 \times 10^3) \times \Delta T$   $\Rightarrow \Delta T = 29.76 K$  $= 29.76^\circ C$
- 4. Heat lost by water = Heat gained by ice or,  $500 \times \frac{75.6}{18} \times 20 = (N \times 9) \times \frac{6000}{18}$  $\Rightarrow N = 14$
- 5. Let  $T_1 > T_2$ . Now, heat lost by gas (1) = Heat gained by gas (2) or,  $n_1 \cdot C_m \cdot (T_1 - T_f) = n_2 \cdot C_m \cdot (T_f - T_2)$ or,  $\frac{P_1 V_1}{R T_1} \cdot (T_1 - T_f) = \frac{P_2 V_2}{R T_2} (T_f - T_2)$  $\Rightarrow T_f = \frac{T_1 T_2 (P_1 V_1 + P_2 V_2)}{P_1 V_1 T_2 + P_2 V_2 T_1}$ 6.  $w = -P_{\text{ext}} (V_2 - V_1)$  $= -P_2 \left( \frac{nRT}{P_2} - \frac{nRT}{P_1} \right)$  $= -nRT \left( 1 - \frac{P_2}{P_1} \right) = -nRT \left( 1 - \frac{P_1 - 1}{P_1} \right)$

$$=-nRT \times \frac{1}{P_1}$$

Now, 
$$w_{\text{total}} = w_1 + w_2 + \dots + w_f$$
  
= $\left(-nRT \times \frac{1}{P}\right) + \left(-nRT \times \frac{1}{P-1}\right)$   
+ $\dots + \left(-nRT \times \frac{1}{2}\right)$   
= $-nRT \sum_{i=1}^{i=P-1} \left(\frac{1}{P+1-i}\right)$ 

7. 
$$w_{1} = -\int_{V_{1}}^{V_{2}} P \cdot dV = -\int_{V_{0}}^{2V_{0}} \frac{K_{1}}{2V^{2}} \cdot dV = +\frac{K_{1}}{2} \left[ \frac{1}{2V_{0}} - \frac{1}{V_{0}} \right]$$
$$= -\frac{K_{1}}{4V_{0}}$$
$$= -\frac{2P_{0}V_{0}^{2}}{4V_{0}} = -\frac{P_{0}V_{0}}{2} = -0.5P_{0}V_{0}$$
$$w_{2} = -\int_{V_{1}}^{V_{2}} P \cdot dV = -\int_{V_{0}}^{2V_{0}} \frac{K_{1}}{V} \cdot dV = -K_{2} \ln \frac{2V_{0}}{V_{0}}$$
$$= -P_{0}V_{0} \times 0.7$$

- 8. As  $\Delta T = 0$ ,  $\Delta U = 0$
- 9. Area =  $P_2 \times \Delta V \Rightarrow P_2 \times 4 = 49.26$  *L*-atom Now, correct work,  $w = -nRT \cdot \ln \frac{V_2}{V_1} = -P_2V_2 \cdot \ln \frac{4}{2}$ = -49.26 × 0.693 = -34.137 *L*-atom
- **10.**  $PV^x$  = Constant

$$\Rightarrow P_1 V_1^x = P_2 V_2^x$$
  
$$\Rightarrow \frac{P_1}{P_2} = \left(\frac{V_2}{V_1}\right)^x \Rightarrow 8 = 4^x \Rightarrow x = \frac{3}{2}$$
  
Now,  $C_m = C_{v_1 m} + \frac{R}{1-x} = \frac{3R}{2} + \frac{R}{1-\frac{3}{2}} = -\frac{R}{2}$ 

- 11. Dulong and Petit's law is applicable only for solid element. (Molar heat capacity  $\approx 6.4$  cal/K-mol = 26.8 J/K-mol).
- 12.  $P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$  $\Rightarrow \frac{P_1}{d_1^{\gamma}} = \frac{P_2}{d_2^{\gamma}}$   $\Rightarrow \frac{P_2}{P_1} = \left(\frac{d_2}{d_1}\right)^{\gamma} = (32)^{7/5} = 128$

13. 
$$\frac{U_{rms}, 2}{U_{rms}, 1} = \frac{1}{2} = \sqrt{\frac{T_2}{T_1}} \Rightarrow \frac{1}{4}$$

Now, 
$$T V^{r-1} = \text{Constant}$$
  

$$\Rightarrow \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{r-1} \Rightarrow \frac{1}{4} = \left(\frac{V_1}{V_2}\right)^{7/5-1}$$

$$\therefore V_2 = 32 V_1$$

- 14.  $|w_A| = 2 \times |w_B|$  But  $\Delta U_A = \Delta U_B$ , Hence  $q_A > q_B$ or,  $(C_A \cdot \Delta T) > (C_B \cdot \Delta T) \Rightarrow C_A > C_B$
- **15.**  $q = n \cdot C_m \cdot \Delta T = 1 \times (0.22 \times 32) \times (273 \times 1.1 273) \times 4.2 \text{ J}$

16. 
$$\frac{q_V}{q_P} = \frac{n \cdot C_{V,m} \cdot \Delta T}{n \cdot C_{P,m} \cdot \Delta T} = \frac{1}{\gamma}$$
  
 $\Rightarrow q_V = \frac{1}{\left(\frac{74.3}{66}\right)} \times 793 = 660 \text{ J}$   
 $(C_{P,m} = \frac{743}{5 \times 2} = 74.3 \Rightarrow C_{V,m} = 74.3 - 8.3 = 66.0)$ 

17. Isothermal: 
$$P \cdot V = P_i \times \frac{V}{n} \Rightarrow P_i = n \cdot P$$
  
Adiabatic:  $P \cdot V^r = P_a \times \left(\frac{V}{n}\right)^{\gamma} \Rightarrow P_a = n^{\gamma} \cdot P$   
 $\therefore \frac{P_i}{P_a} = \frac{n \cdot P}{n^{\gamma} \cdot P} = n^{1-\gamma}$   
18.  $\Delta U = n \cdot C_{V,m} \cdot (T_2 - T_1) = n \cdot \frac{R}{\gamma - 1} \cdot \left(\frac{P \cdot 2V}{nR} - \frac{P \cdot V}{nR}\right)$   
 $= \frac{PV}{\gamma - 1}$ 

- 19. K.E. =  $\Delta U \Rightarrow \frac{1}{2} \times \frac{(n \times 40)}{1000} \times (100)^2$ =  $n \times \frac{8.314}{(1.5-1)} \times \Delta T$  $\therefore \Delta T = 12.03 K$
- **20.** For minimum pressure, compression should be irreversible.

$$\Delta U = w \Rightarrow n \cdot \frac{R}{\gamma - 1} \cdot (T_2 - T_1) = -P_{ext}(V_2 - V_1)$$
$$= -P_2 \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)$$

or, 
$$\frac{T_2 - T_1}{\gamma - 1} = -\left(T_2 - T_2 \cdot \frac{P_2}{P_1}\right)$$
  
 $\Rightarrow \frac{700 - 400}{1.4 - 1} = -\left(700 - 400 \times \frac{P_2}{100}\right)$   
 $\therefore P_2 = 362.5 \text{ kPa}$   
21.  $q = (n \cdot C_{V,m} \cdot \Delta T)_{Ne} + (n \cdot C_{V,m} \cdot \Delta T)_{SO_3}$   
or,  $12 \times 10^3 = 2 \times 3 \times (T_f - 300) + 3 \times 6 \times (T_f - 400)$   
 $\Rightarrow T_f = 875 \text{ K}$   
Now,  $P_{\text{final}} = \frac{nRT}{V} = \frac{5 \times 0.08 \times 875}{10} = 35 \text{ atm}$   
22. Free expansion is isothermal.  
23.  $C_{V,m} = 3 \times \frac{1}{2}R + 3 \times \frac{1}{2}R + (3N - 6) \times R = (3N - 3)R$   
 $\therefore \gamma = \frac{C_P}{C_V} = 1 + \frac{R}{C_{V,m}} = 1 + \frac{1}{3N - 3}$   
24.  $C_m = C_{V,m} + \frac{P \cdot dV}{dT} = C_{V,m} + \frac{P}{\alpha} = C_{V,m} + \frac{RT}{V \cdot \alpha}$   
 $= C_{V,m} + \frac{R(T_0 + \alpha V)}{V\alpha}$   
 $= C_{P,m} + \frac{RT_0}{V\alpha}$   
Now,  $q = \int_{T_1}^{T_2} C_m \cdot dT = \int_{V_1}^{V_2} C_m \cdot (\alpha \cdot dV)$   
 $= \int_{V_1}^{V_2} \left(C_{P,m} \cdot \alpha + \frac{RT_0}{V}\right) dV$   
 $= \alpha \cdot C_{P,m} (V_2 - V_1) + RT_0 \cdot \ln \frac{V_2}{V_1}$   
25.  $w = -25 \text{ J} = -nR \cdot \Delta T$   
 $\Delta U = n \cdot C_{V,m} \cdot \Delta T = n \cdot \left(\frac{6}{2}R\right) \cdot \Delta T = 75J$   
 $\therefore q = \Delta U - w = 100 \text{ J}$ 

26. 
$$C_m = C_{V,m} + \frac{K}{1-x} = \frac{5K}{2} + \frac{K}{1-\frac{5}{2}} = \frac{5K}{6}$$
  
 $\therefore q = n \cdot C_m \cdot \Delta T = 1 \times \frac{5R}{6} \times 26 = 180 \cdot 14J$ 

27. 
$$PV^x = K \Rightarrow \frac{dP}{dV} = -x \cdot \frac{P}{V} \Rightarrow -1 = -x \times \frac{4}{2} \Rightarrow x = \frac{1}{2}$$
  
 $\therefore C_m = C_{V,m} + \frac{R}{1-x} = \frac{3R}{2} + \frac{R}{1-\frac{1}{2}} = 3.5R$ 



**30.** Boyle temperature,  $T_B = 20 + 273 = 293$  K Inversion temperature,  $T_i = 2 \times T_B = 586$  K = 313° C > 50° C

31.  $V_0 \qquad V_0 \\ Mono \qquad Di \\ Initial \\ \hline V_1 \qquad \frac{3}{4} V_0 \\ Mono \qquad Di \\ \hline \end{array}$ 

Monoatomic :  $P_1 \cdot V_0^{5/3} = P_2 \cdot V_1^{5/2}$ 

Diatomic : 
$$P_1 \cdot V_0^{7/5} = P_2 \cdot \left(\frac{3}{4}V_0\right)^{7/5}$$
  
 $\therefore \frac{V_1}{V_0} = \left(\frac{3}{4}\right)^{\frac{21}{25}}$ 



**33.** For greater heat exchange, heat capacity should be high.

$$C_m = C_{V,m} + \frac{R}{1-x}$$
 for  $PV^x = \text{Constant}$ 

34. 
$$q_{ABC} = 600 + 200 = 800 \text{ J}$$
  
 $w_{AB} = 0 \text{ and } w_{BC} = -\left(8 \times 10^4 \times \frac{N}{m^2}\right)$   
 $(5 \times 10^{-3} - 2 \times 10^{-3})m^2$   
 $= -240 \text{ J}$   
 $\therefore \Delta U_{AC} = \Delta U_{ABC} = q_{ABC} + w_{ABC}$   
 $= 800 + (-240) = 560 \text{ J}$ 



$$AB: P = \sqrt{3}V + C_1$$
  
$$P_0 = \sqrt{3}V_0 + C_1$$
 (1)

and 
$$3P_0 = \sqrt{3}V_B + C_1$$
 (2)

$$BC: P = -\frac{1}{\sqrt{3}}V + C_2$$

$$P_0 = -\frac{1}{\sqrt{3}} \cdot 6V_0 + C_2 \tag{3}$$

$$3P_0 = -\frac{1}{\sqrt{3}} \cdot V_B + C_2 \tag{4}$$

From equation (1), (2), (3) and (4),  $V_B = \frac{9}{4}V_0$ 

Now, 
$$\frac{T_B}{T_A} = \frac{3P_0 \cdot \frac{9}{4}V_0}{P_0 \cdot V_0} = \frac{27}{4}$$

36.

$$P_{0}$$

$$F$$

$$F$$

$$P_{i} = P_{0}$$

$$P_{f} = P$$

$$dw = F \cdot dx = (P_{0} - P)A \cdot dx = (P_{0} - P) \cdot dV$$

$$\therefore w = \int_{V}^{\eta V} \left(P_{0} - \frac{nRT}{V}\right) dV$$

$$= P_{0}(\eta V - V) - RT \cdot \ln \frac{V \cdot \eta}{V}$$

$$P_0 V(\eta - 1) - \operatorname{RT.ln} \eta = \operatorname{RT} [\eta - 1 - \ln \eta]$$

37.

$$\begin{array}{c|c} T_0 & T_0 \\ (P_0, V_0) \twoheadrightarrow (P_1, \eta \cdot V) \end{array} & (P_0, V_0) \twoheadrightarrow (P_2, V) \end{array}$$

Work performed on the piston

$$= -\left[\int_{V_0}^{\eta V} P_1 \cdot dV + \int_{V_0}^{V} P_2 \cdot dV\right] \text{ and } (V + \eta \cdot V) = 2V_0$$
$$= P_0 V_0 \cdot \ln \frac{(\eta + 1)^2}{4\eta}$$

**38.** Isothermal :  $P_A \cdot V = P \cdot (2V) \Rightarrow P_A = 2P$ Adiabatic :  $P_B \cdot V^{1.5} = P \cdot (2V)^{1.5} \Rightarrow P_A = 2\sqrt{2} P$ Isobaric :  $P_C = P$  $\therefore P_A : P_B : P_C = 2 : 2\sqrt{2} : 1$ 

**39.** 
$$A \qquad T_0 \\ (P_0, V_0, T_0) \\ P_f = \frac{27P_0}{8} \qquad P_f = \frac{27P_0}{8}$$

Chamber 
$$B: P_0 \cdot V_0^{\gamma} = \frac{27P_0}{8} \cdot V_B^{\gamma}$$

$$\therefore V_{B} = \frac{4V_{0}}{9} \Rightarrow T_{B} = \frac{3}{2}T_{0}$$
  
and  $V_{A} = 2V_{0} - \frac{4V_{0}}{9} = \frac{14V_{0}}{9} \Rightarrow T_{A} = \frac{21}{4}T_{0}$   
Now,  $q_{A} = \Delta U_{A} + \Delta U_{B} = n \cdot C_{V,m} \cdot (T_{A} - T_{0})$   
 $+ n \cdot C_{V,m} \cdot (T_{B} - T_{0})$   
 $= \frac{P_{0}V_{0}}{R \cdot T_{0}} \cdot 2R \cdot \left[ \left( \frac{21}{4}T_{0} - T_{0} \right) + \left( \frac{3}{2}T_{0} - T_{0} \right) \right]$   
 $= \frac{19}{2} \cdot P_{0}V_{0}$ 

40.



After 1st step, the process is irreversible adiabatic. Hence,  $\Delta U = w$ 

$$n \cdot C_{V,m} \cdot (T_2 - T_1) = -P_{\text{ext}}(V_2 - V_1)$$
  
or,  $n \cdot \frac{3}{2} R \left( \frac{P_1 \cdot V_2}{nR} - \frac{P_1 V_1}{nR} \right) = -P_1 [V_2 - (V_1 + A \cdot H)]$   
 $\therefore V_2 = V_1 + 0.4 H.A \Rightarrow x = 0.4 H$ 

(The final pressure of gas after 2nd step will remain same as initial, beginning of processes.)

**41.** Smaller the heat capacity larger is  $\Delta T$ .

**43.** 
$$q = 0 \Rightarrow \Delta U = w = -P_{\text{ext}} \cdot (V_2 - V_1) = -4 \times (30 - 40)$$
  
= 40 *l*-bar  
Now,  $\Delta H = \Delta U + \Delta (PV) = 40 + (4 \times 30 - 2 \times 40)$ 

$$= 80 L$$
-atom  $= 8000 J$ 

44. 
$$\Delta U = 0$$
$$\Delta H = \Delta U + \Delta (PV) = 0 + B (P_2 - P_1)$$
$$= B \cdot \frac{RT}{V_2 - B} - \frac{RT}{V_1 - B}$$

$$= 2 \times 8.314 \times 400 \left( \frac{1}{22 - 2} - \frac{1}{12 - 2} \right) = -332.56 \text{ J}$$

45. 
$$\Delta U_{1} = n \cdot C_{V,m} \cdot (T_{2} - T_{1})$$

$$\Delta H_{1} = \Delta U_{1} + V \cdot \Delta P = 1 \times C_{V,m} \times (T_{2} - T_{1}) + V_{1}(P_{2} - P_{1})$$
Now, 
$$\Delta U_{2} = w_{2} = -P_{\text{ext}} (V_{2} - V_{1}) = -P_{3}(V_{2} - V_{1})$$

$$\Delta H_{2} = \Delta U_{2} + \Delta (PV) = -P_{3}(V_{2} - V_{1}) + (P_{3}V_{2} - P_{2}V_{1})$$

$$\therefore \Delta H_{\text{total}} = \Delta H_{1} + \Delta H_{2} = C_{V}(T_{2} - T_{1}) + V_{1}(P_{3} - P_{1})$$

46. 
$$\eta = 1 - \frac{T_C}{T_H}$$
  
 $\frac{1}{6} = 1 - \frac{T_C}{T_H}$  and  $\frac{1}{3} = 1 - \frac{T_C - 65}{T_H} \Rightarrow T_H = 390 \text{ K}$   
 $= 117^{\circ} \text{ C}$ 

**47.** 
$$\frac{|q_{\rm rej}|}{q_{\rm abs}} = \frac{T_C}{T_H} \Rightarrow |q_{\rm rej}| = \frac{390}{600} \times 120 = 78 \text{ cal}$$

$$48. \quad \left(1 - \frac{T_C - \Delta T}{T_H}\right) > \left(1 - \frac{T_C}{T_H + \Delta T}\right)$$

**49.** 
$$T_H \cdot V_2^{\gamma - 1} = T_C \cdot V_3^{\gamma - 1}$$
  
 $\Rightarrow \frac{T_C}{T_M} = \left(\frac{V_2}{V_3}\right)^{\gamma - 1} = \left(\frac{1}{2.75}\right)^{1.4 - 1} = \frac{1}{1.5}$   
 $\therefore \eta = 1 - \frac{T_C}{T_H} = \frac{1}{3}$ 

50.



$$T_2 \cdot V_1^{\gamma - 1} = T_3 \cdot V_2^{\gamma - 1}$$
  
and  $T_1 \cdot V_1^{\gamma - 1} = T_4 \cdot V_2^{\gamma - 1}$   
$$\therefore \ \frac{T_2}{T_1} = \frac{T_3}{T_4} \Rightarrow \frac{T_2 - T_1}{T_1} = \frac{T_3 - T_4}{T_4}$$

$$\eta = 1 - \frac{|q_{\text{rej}}|}{q_{\text{abs}}} = 1 - \frac{n \cdot C_{V,m}(T_3 - T_4)}{n \cdot C_{V,m}(T_2 - T_1)} = 1 - \frac{T_4}{T_1}$$
$$= 1 - \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$$
$$= 1 - \left(\frac{1}{10}\right)^{\frac{\gamma}{5} - 1} = -0.6$$

51. 
$$\Delta S_{\text{unit}} = \Delta S_{\text{Source}} + \Delta S_{\text{Heat engine}} + \Delta S_{\text{Sink}}$$
  
=  $-\frac{40 \times 10^3}{500} + 0 + \frac{30 \times 10^3}{300} = +20 \text{J/K}$   
52.  $\Delta S = n \cdot C_{Pm} \cdot \ln \frac{T_2}{m}$ 

$$= \frac{3.2}{32} \times 14 \times \ln \frac{900}{1000} = -0.14 \text{ cal/K}$$

53. 
$$\Delta S = nR \cdot \ln \frac{V_2}{V_1}$$
  
= 2×8.314× $\ln \frac{(2a)^3}{a^3}$  = 34.58 J/K

54. 
$$\Delta S = n \cdot C_{P,m} \cdot \ln \frac{T_2}{T_1}$$
  
=  $1 \times \frac{5R}{2} \times \ln \frac{1000}{250} = 7.0 \text{ cal/K}$ 

55. 
$$\Delta S = n \cdot C_{V,m} \cdot \ln \frac{T_2}{T_1}$$
  
 $S_{500 K} - 46.2 = 1 \times \frac{3R}{2} \times \ln \frac{500}{250}$   
 $\therefore S_{500 K} = 48.3 \text{ Ccal/K-mol}$ 

56. 
$$\Delta S = nR \cdot \ln \frac{V_2}{V_1}$$
  
 $\Rightarrow -5.0 = \frac{10^5 \times (15 \times 10^{-3})}{300} \times \ln \frac{V_2}{15} \Rightarrow V_2 = 5.4 \text{ L}$ 
63.

57. 
$$\Delta S_{\text{Surr}} = -\frac{1.5 \times 10^3}{300} = -5 \text{ J/K}$$
  
Now, 
$$\Delta S_{\text{unit}} = \Delta S_{\text{Sys}} + \Delta S_{\text{Surr}} = 5.51 + (-5)$$
$$= + 0.51 \text{ J/K}$$
  
Hence, the process is irreversible.

58. 
$$\Delta S = n \cdot C_{P,m} \cdot \ln \frac{T_2}{T_1} + nR \cdot \ln \frac{P_1}{P_2}$$
  
or, 
$$0 = n \times \frac{5}{2}R \times \ln \frac{1200}{300} + nR \times \ln \frac{1}{P_2}$$
$$\Rightarrow P_2 = 32 \text{ bar}$$

59. 
$$\Delta S = \Delta S_{\text{adiabatic}} + \Delta S_{\text{isobaric}} = 0 + n \cdot C_{P,m} \cdot \ln \frac{T_2}{T_1}$$
$$= \frac{1.6}{4} \times \frac{5R}{2} \times \ln \frac{1}{3} = -2.2 \text{ cal/K}$$

60. 
$$\Delta S = n \cdot C_{V,m} \cdot \ln \frac{T_2}{T_1} + nR \cdot \ln \frac{V_2}{V_1}$$
$$= n \cdot C_{V,m} \cdot \ln \frac{P_2}{P_1} + n \cdot C_{P,m} \cdot \ln \frac{V_2}{V_1}$$
$$= 2 \times \frac{R}{1.5 - 1} \times \ln \frac{1}{4} + 2 \times \frac{1.5R}{1.5 - 1} \times \ln 2$$
$$= -11.64 \text{ J/K}$$

61. 
$$S_2 - S_1 = n \cdot C_{V,m} \cdot \ln \frac{T_2}{T_1} + nR \cdot \ln \frac{V_2}{V_1}$$
  
=  $1.2 \times \frac{3R}{2} \times \ln \frac{1}{2} + 1.2 \times R \times \ln 2$   
= -0.84 cal/K

62. 
$$\Delta S = n \cdot C_{V,m} \cdot \ln \frac{T_2}{T_1} + nR \cdot \ln \frac{V_2}{V_1}$$
$$= 1 \times \frac{R}{\gamma - 1} \times \ln \frac{T_2}{T_1} + 1 \times R \times \ln \left(\frac{T_1}{T_2}\right)^{1/n - 1}$$
(as  $T. V^{n - 1}$  = Constant)
$$R \cdot \ln \frac{T_2}{T_1} \left[\frac{1}{\gamma - 1} - \frac{1}{n - 1}\right]$$

$$= \frac{(n-\gamma)R}{(n-1)(\gamma-1)} \cdot \ln \tau$$

63. 
$$\Delta S = n \cdot C_{V,m} \cdot \ln \frac{P_2}{P_1} + n \cdot C_{P,m} \cdot \ln \frac{V_2}{V_1}$$
$$= 2 \times \frac{3R}{2} \times \ln 2 + 2 \times \frac{5R}{2} \times \ln 2$$
$$= + 11.2 \text{ cal/K}$$

64. 
$$dS = \frac{n \cdot C_{V,m} \cdot dT + P \cdot dV}{T}$$
  
For maximum entropy,  $\frac{dS}{dV} = 0$ 

or, 
$$n \cdot C_{V,m} \frac{dT}{dV} + P = 0$$
 (1)

Now, 
$$P = \frac{RT}{V} = P_0 - \alpha V \Rightarrow \frac{dT}{dV} = \frac{1}{R}(P_0 - 2\alpha V)$$
(2)

From (1) and (2),

$$1 \times \frac{R}{\gamma - 1} \times \frac{1}{R} (P_0 - 2\alpha V) + (P_0 - \alpha V) = 0$$
  
$$\therefore V = \frac{\gamma \cdot P_0}{\alpha(\gamma + 1)}$$

65. 
$$dS = C_{V,m} \cdot \frac{dT}{T} + P \cdot \frac{dV}{T} = a \cdot dT + C_{V,m} \cdot \frac{1}{T} \cdot dT$$
  
or, 
$$\int_{V_0}^{V} \frac{R}{V} \cdot dV = a \cdot \int_{T_0}^{T} dT \Rightarrow R \cdot \ln \frac{V}{V_0} = a(T - T_0)$$
  
$$\therefore T = T_0 + \frac{R}{a} \cdot \ln \frac{V}{V_0}$$

66. 
$$\int_0^S dS = \int_0^T C \cdot \frac{dT}{T} = \int_0^T T^3 \cdot \frac{dT}{T} \Longrightarrow S = \frac{aT^3}{3}$$

**67.** 
$$\Delta S = \Delta S_A + \Delta S_B = -\frac{12000}{600} + \frac{12000}{400} = +10 \text{ J/K}$$

68. Heat lost by alloy = Heat gained by water or  $4 \times 4 \times (800 - T) = 4 \times 1.0 \times (T - 300)$  $\Rightarrow T = 700 \text{ K}$ 

(As date is not given for vaporization of water)

Now, 
$$\Delta S_{\text{mix}} = \Delta S_{\text{alloy}} + \Delta S_{\text{water}}$$
  
=  $4 \times 4 \times \ln \frac{700}{800} + 4 \times 1 \times \ln \frac{700}{300}$   
= 1.0 K cal/K

**69.** Final temperature of both blocks =  $\frac{T_1 + T_2}{2}$ 

$$\therefore \Delta S = \Delta S_1 + \Delta S_2 = C \cdot \ln \frac{(T_1 + T_2)/2}{T_1} + C \cdot \ln \frac{(T_1 + T_2)/2}{T_2}$$
$$= C \cdot \ln \frac{(T_1 + T_2)^2}{4T_1 T_2}$$

70. 
$$\Delta S = -R[n_1 \cdot \ln x_1 + n_2 \cdot \ln x_2]$$
  
=  $-R[0.8 \times \ln 0.8 + 0.2 \times \ln 0.2]$   
=  $+ 0.96$  Cal/K.

- 71. Larger molar mass, greater is the molar entropy.
- **72.** Greater the number of atoms, greater is the molar entropy.

73. 
$$nC(s) + (n + 1) H_2(g) \rightarrow C_n H_{2n+2}(g)$$
  
with increase in *n*, the decrease in entropy increases.

74. H<sub>2</sub>O (*l*, 1 atm, 100°C) 
$$\xrightarrow{(1)}$$
 H<sub>2</sub>O (*g*, 1 atm,  
100°C)  $\xrightarrow{(2)}$  H<sub>2</sub>O (*g*, 5 atm, 100°C)  
 $\Delta G_1 = 0 \text{ and } \Delta G_2 = nRT \ln \frac{P_2}{P_1} = 5 \times 2 \times 373 \times \ln \frac{5}{1}$   
= 3730 ln 5 Cal  
75.  $q = \Delta U - w = 0 - \left(-nRT \cdot \ln \frac{P_1}{P_2}\right) = nRT \cdot \ln \frac{P_1}{P_2}$ 

5. 
$$q = \Delta U - w = 0 - \left(\frac{-nKT \cdot \ln P_2}{P_2}\right) = nKT \cdot \ln P_2$$
  
=  $-\Delta G$   
 $\therefore \Delta G = -q = -(-1200) = +1200$  cal

76. 
$$\Delta G^{\circ} = -RT \cdot \ln K_{eq}$$
$$\Rightarrow -1743 = -8.3 \times 300 \times \ln K_{eq}$$
$$\therefore K_{eq} = 2$$

Now, (a) 
$$K_{eq} = \frac{3}{3 \times 6}$$
  
(b)  $K_{eq} = \frac{6 \times 3^2}{3}$   
(c)  $K_{eq} = \frac{6 \times 3}{3^2}$   
(d)  $K_{eq} = \frac{3^2}{3 \times 6}$ 

77.

$$H_2O(l, -10^{\circ}C, 0.28 \text{ Pa}) \longrightarrow H_2O(s, -10^{\circ}C, 0.26 \text{ Pa})$$
$$\downarrow \Delta G_1 = 0 \qquad \uparrow \Delta G_3 = 0$$

$$\mathrm{H}_{2}\mathrm{O}(g,-10^{\circ}\mathrm{C},0.28\,\mathrm{Pa}) \xrightarrow{\Delta G_{2}} \mathrm{H}_{2}\mathrm{O}(g,-10^{\circ}\mathrm{C},0.26\,\mathrm{Pa})$$

$$\Delta G_2 = nRT \ln \frac{P_2}{P_1} = 1 \times R \times 263 \times \ln \frac{0.26}{0.28}$$
$$\therefore \Delta G = \Delta G_1 + \Delta G_2 + \Delta G_3 = 263 R \ln \frac{13}{14}$$

78. Free expansion is isothermal

$$\Delta G = nRT \ln \frac{P_2}{P_1} = nRT \ln \frac{V_2}{V_1}$$
$$= 10^5 \times (1.2 \times 10^{-3}) \times \ln \frac{1.2}{2.4} = -84 \text{ J}$$

79.  $\Delta G_1^{\circ} = -RT \cdot \ln K_1 \text{ and } \Delta G_2^{\circ} = -RT \cdot \ln K_2$ Now,  $\Delta G_2^{\circ} - \Delta G_1^{\circ} = -RT[\ln K_2 - \ln K_1]$  $= -RT [\ln e^4]$  $= -2 \times 300 \times 4 = -2400 \text{ cal}$ 

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

- 1. Theory based
- 2. Theory based
- **3.** For isolated system, there should not be any mass and energy transfer with surroundings.



- 5. The internal energy of real gas may change on changing the volume of gas. Change in physical state also changes the physical state.
- 6. Theory based
- 7. Theory based
- **8.** Option (c) should be changed with (c) adiabatic free expansion of any gas is also isothermal.

9. 
$$w_{rev} - w_{irr} = (-P \cdot dV) - (-P_{ext} \cdot dV)$$
  
=  $(P_{ext} - P) \cdot dV$  = negative, always and  $q_{rev} - q_{irr}$  = positive, always

$$w = \Delta U = n \cdot C_{V,m} \cdot (T_2 - T_1) = 4 \times \frac{3}{2} R \times (290 - 320)$$
$$= -360 \text{ cal}$$
$$\Delta H = \gamma \cdot \Delta U = \frac{5}{3} \times (-360) = -600 \text{ cal}$$

**80.** At 0.04 atom, the system is in equilibrium.

11. Theory based

12. Process 
$$BC: \frac{P_B}{T_B} = \frac{P_C}{T_C} \Rightarrow \frac{P_B}{500} = \frac{1}{250} \Rightarrow P_B = 2$$
 bar

and 
$$\Delta U_{BC} = n \cdot C_{V_{1}m} (T_C - T_B)$$
  
= 2×1.5 R×(250 - 500)  
= -750 R

Process 
$$CD$$
:  $\Delta U = w$   
 $\Rightarrow n \cdot C_{V_1m}(T_D - T_C)$   
 $= -P_{\text{ext}}(V_D - V_C)$   
or,  $n \times 1.5R \times (T_D - T_C)$   
 $= -P_D \left( \frac{nRT_D}{P_D} - \frac{nRT_C}{P_C} \right)$   
 $\Rightarrow T_D = 450 \text{ K}$   
and  $\Delta H_{CD} = n \cdot C_{P_1m} \cdot (T_D - T_C)$   
 $= 2 \times 2.5 R \times (450 - 250)$   
 $= 1000 \text{ R}$ 

13. 
$$PV^{\gamma} = K_1$$
  
 $\Rightarrow P = K_1 \cdot V^{-\gamma}$   
 $\Rightarrow \frac{dP}{dV} = K_1 \cdot (-\gamma) \cdot V^{-\gamma - 1}$   
 $= -\gamma \cdot \frac{P}{V}$ 

The gas having higher  $\gamma$  will have higher magnitude of slope of *P* vs. *V* curve.

Now, 
$$n \cdot \frac{R}{\gamma - 1} \cdot dT = -P \cdot dV = -\frac{nRT}{V} \cdot dV$$
  
or,  $\frac{dV}{dT} = -\frac{1}{\gamma - 1} \cdot \frac{V}{T}$ 

**10.** q = 0

Gas having higher  $\gamma$  will have lower magnitude of slope of V vs. T curve.

Now, 
$$n \cdot C_{V,m} \cdot dT = -P \cdot dV = -[nRdT - V \cdot dP]$$
  
or,  $n \cdot C_{P,m} \cdot dT = -V \cdot dP \Rightarrow \frac{n \cdot \gamma R}{\gamma - 1} \cdot dT = \frac{nRT}{P} \cdot dP$   
 $\therefore \frac{dP}{dT} = \frac{\gamma}{\gamma - 1} \cdot \frac{P}{T}$ 

Gas having higher  $\gamma$  will have lower magnitude of slope of *P* vs. *T* curve.

**14.** 
$$q = 0$$

**15.** dT = 0



Here,  $\gamma$  decreases on increasing degree of freedoms. As final pressure is minimum for Ne, its final temperature is minimum (decrease in temperature is maximum).

Now, for overall process,  $\Delta T = 0 \Rightarrow \Delta U_{\text{total}} = 0$ or,  $\Delta U_I + \Delta U_{II} = 0 \Rightarrow (0 + w_I) + (q_{II} + 0) = 0$  $\therefore q_{II} = -w_I = \text{maximum for CH}_4$ 

- 17. Theory based
- **18.**  $C_{P,m} C_{V,m} = R$

$$\Rightarrow S_P - S_V = \frac{R}{M} = 0.04545$$
  
$$\therefore M = 44 \text{ gm/mol}$$

**19.** 
$$q = 0 \Rightarrow \Delta U = w = -P_0(4V_0 - V_0) = -3P_0V_0$$
  
Now,  $\Delta H = \Delta U + \Delta (PV) = (-3P_0V_0) + (P_0 \cdot 4V_0 - 2P_0 \cdot V_0)$   
 $= -P_0 \cdot V_0$ 

- 20. Theory based
- 21. Theory based



**23.** In reversible cycle, heat rejected is minimum. For reversible cycle,

► V

$$\left|q_{\text{rej}}\right| = \frac{T_C}{T_H} \times q_{\text{abs}} = \frac{400}{500} \times 100 = 80 \text{ J}$$

24. 
$$dS = \frac{q_{\text{rev}}}{T}$$
 and  $\oint dS = 0$ 

- 25. In rusting, moles of gas decreases.
- 26. Theory based.
- **27.**  $\Delta U = 0 \Rightarrow q = -w$
- 28. For a process to be spontaneous at low temperature and non-spontaneous at high temperature,  $\Delta H$  = negative and  $\Delta S$  = negative.

**29.** 
$$(\Delta S_{\text{Vap}})_{350 \, K, 1 \, \text{atm}} = \frac{35 \times 10^3}{350} = 100 \frac{J}{K \, \text{mol}}$$

On increasing pressure at constant temperature entropy decreases.

$$(\Delta G_{\text{Vap}})_{350 \text{ K}, 1 \text{ atm}} = 0$$

On increasing pressure at constant temperature energy increases.

30. Theory based.

# Section C (Comprehensions)

#### **Comprehension I**

1. 
$$\Delta U = n \cdot C_{V_1 m} \cdot (T_2 - T_1) = 4 \times \frac{5}{2} R \times (-50 - 0)$$
  
= -1000 cal

2. 
$$\Delta H = \gamma \cdot \Delta U = \frac{7}{5} \times (-1000) = -1400$$
 cal  
3.  $w = 0$  (V = Constant)

# **Comprehension II**

$$\begin{aligned} \mathbf{4.} \quad q &= -\Delta U \Rightarrow n \cdot C_{V,m} \cdot \Delta T = -n \cdot C_{V,m} \cdot \Delta T \\ &\Rightarrow C_m = -C_{V,m} \end{aligned}$$

5. 
$$C_m = C_{V,m} + \frac{R}{1-x}$$
  
 $\Rightarrow -C_{V,m} = C_{V,m} + \frac{R}{1-x} \Rightarrow -2 \cdot \frac{R}{\gamma - 1} = \frac{R}{1-x}$ 

 $\therefore x = \frac{\gamma + 1}{2}$ Now,  $T \cdot V^{x-1} = \text{Constant} \Rightarrow T \cdot V^{(\gamma - 1)/2} = \text{Constant}$ 6.  $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1/2} \Rightarrow \frac{T_2}{300} = \left(\frac{1}{8}\right)^{\left(\frac{5}{3} - 1\right)/2} \Rightarrow T_2 = 150 \text{ K}$   $\therefore w = -\frac{nR(T_2 - T_1)}{1 - x} = -\frac{1 \times 2(150 - 300)}{1 - \left(\frac{5}{3} + 1\right)/2}$  = -900 cal

# **Comprehension III**

7.  $w = -nR \cdot \Delta T = -1 \times 8.314 \times 72 = -598.6 \text{ J}$ = - 0.6 kJ

8. 
$$\Delta U = q + w = 1.6 + (-0.6) = 1.0 \text{ kJ}$$
  
9.  $\gamma = \frac{\Delta H}{\Delta U} = \frac{1.6}{1.0} = 1.6$ 

# **Comprehension IV**

10. 
$$V_2 = 4 V_0 \Rightarrow P_2 = 4 P_0$$
  
As  $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$   
 $\Rightarrow \frac{P_0V_0}{T_0} = \frac{4P_0 \cdot 4P_0}{T_2}$   
 $\Rightarrow T_2 = 16T_0$ 

Now, 
$$\Delta U = n \cdot C_{V,m} \cdot \Delta T = n \times \frac{R}{\gamma - 1} \times (16.T_0 - T_0)$$
  
 $= \frac{15P_0V_0}{\gamma - 1} = \frac{15\alpha V_0^2}{\gamma - 1}$   
11.  $w = \frac{nR(T_2 - T_1)}{1 - x} = \frac{nR \times 15T_0}{1 - (-1)} = \frac{15\alpha V_0^2}{2}$   
12.  $C_m = C_{V_1m} + \frac{R}{1 - x} = \frac{R}{\gamma - 1} + \frac{R}{1 - (-1)} = \frac{(\gamma + 1)R}{2(\gamma - 1)}$ 

# **Comprehension V**

13. 
$$P = a \cdot T^{\alpha} = a \cdot \left(\frac{PV}{nR}\right)^{\alpha}$$
$$\Rightarrow P \cdot V^{\frac{\alpha}{\alpha - 1}} = \text{Constant}$$
$$\therefore w = \frac{nR \cdot \Delta T}{x - 1} = \frac{1 \times R \cdot \Delta T}{\frac{\alpha}{\alpha - 1} - 1} = R(\alpha - 1) \cdot \Delta T$$
$$14. \quad C_m = C_{V,m} + \frac{R}{1 - x} = \frac{R}{\gamma - 1} + \frac{R}{1 - \frac{\alpha}{\alpha - 1}}$$
$$= \left[\frac{1}{\gamma - 1} + (1 - \alpha)\right] \cdot R$$

15.  $\frac{1}{\gamma - 1} + (1 - \alpha) < 0$  $\Rightarrow \alpha > \frac{\gamma}{\gamma - 1}$ 

#### **Comprehension VI**

16. 
$$U = \alpha \cdot V^{\alpha} = n \cdot C_{V,m} \cdot T$$
  
 $\Rightarrow T \cdot V^{-\alpha} = \text{Constant}$   
As  $T \cdot V^{x-1} = \text{Constant}$   
 $\Rightarrow x - 1 = -\alpha$   
17.  $q = \Delta U - w = \Delta U + \frac{(\gamma - 1) \cdot \Delta U}{\alpha} = \Delta U \left[ 1 + \frac{\gamma - 1}{\alpha} \right]$   
18.  $C_m = \frac{R}{\gamma - 1} + \frac{R}{1 - x} = \frac{R}{\gamma - 1} + \frac{R}{\alpha}$ 

### **Comprehension VII**

**19.** 
$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$
  
 $\Rightarrow P_2 = 1 \times \left(\frac{320}{10}\right)^{7/5} = 128 \text{ atm}$   
**20.**  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$   
 $\Rightarrow T_2 = 1200 \text{ K}$   
**21.**  $w = n \cdot C_{V,m} \cdot \Delta T = \frac{1 \times 0.32}{0.082 \times 300} \times \left(\frac{5}{2} \times 8.314\right) \times (1200 - 300)$   
 $= 243.3 \text{ J}$ 

# **Comprehension VIII**

22.  $P_1 V_1^{\gamma} = P_2 V_2^{\gamma} \Rightarrow P_2 = 1 \times (8)^{5/3} = 32 \text{ atm}$ 23. For A:  $P_1 = 1 \text{ atm}$ ,  $P_2 = 32 \text{ atm}$   $V_1 = VL$ ,  $V_2 = V + \frac{7}{8}V = \frac{15}{8}VL$   $T_1 = 27.3 \text{ K};$   $T_2 = ?$ Now,  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$  $\Rightarrow T_2 = 1638 \text{ K}$ 

24. 
$$\Delta H_A = n \cdot C_{P,m} \cdot \Delta T = \frac{1 \times 22.4}{0.082 \times 27.3} \times \left(\frac{5}{2} \times 2\right) \times (1638 - 27.3)$$
  
= 80535 cal

# **Comprehension IX**

25.  $\Delta U = 0$   $\Delta H = \Delta U + V \cdot \Delta P = 0.9L \times \left(1 - \frac{532}{760}\right) \text{atm} = 0.27$  L -atm = 27 J26.  $\Delta U_{1 \to 2} = 0$   $\Delta U_{2 \to 3} = \Delta U \text{ for temperature increase } + \Delta U \text{ for vaporization of water.}$   $= m.s. \cdot \Delta T + (q + w)$  $= \left(900 \times \frac{4.2}{1000} \times 20\right) + \left(\frac{450}{18} \times 40\right)$ 

27. 
$$\Delta H_{1\to3} = \Delta H_{1\to2} + q_{2\to3}$$
  
=  $27J + \begin{pmatrix} \frac{450}{18} \times 40 \text{ kJ} + 900 \\ \times \frac{4.2}{1000} \times 20 \text{ kJ} \end{pmatrix}$   
= 1075.573 kJ

**28.**  $w_{1\to 2} = 0$ 

$$w_{2\to 3} = -\frac{450}{18} \times \frac{8}{1000} \times 373 = -74.6 \text{ kJ}$$

= 1001 kJ

 $+\left(-\frac{450}{18}\times\frac{8}{1000}\times373\right)$ 

# **Comprehension X**

**29.** 
$$T_A > T_B < T_C < T_D = T_A$$
  
From question :  $\frac{T_A}{T_B} = 4$  and  $T_A = 800$  K  
 $\Rightarrow T_B = 200$ K  
Also,  $V_A > V_B > V_C = V_D$   
From equation :  $\frac{V_A}{V_C} = 8\sqrt{2}$  and  $\frac{V_A}{V_B} = \frac{T_A}{T_B} = 4$ 

For process BC :  $T_B \cdot V_B^{\gamma - 1} = T_C \cdot V_C^{\gamma - 1}$ 

$$\Rightarrow T_{C} = T_{B} \cdot \left(\frac{V_{B}}{V_{C}}\right)^{r-1}$$
  
= 200 ×  $\left(\frac{8\sqrt{2}}{4}\right)^{\frac{5}{3}-1} = 400$  K  
**30.**  $\Delta U_{BC} = C_{V,m} \cdot (T_{C} - T_{B}) = 1 \times \frac{3}{2} R \times (400 - 200)$ 

= 2.4942 kJ

- 1. q = 0 because  $\Delta U = 0$  and w = 0
- 2. Enthalpy of ideal gas is independent from pressure.
- 3. For non-ideal gas, U = f(T, V)
- 4. In adiabatic free expansion,  $\Delta T = 0$



 $P_2$ 

 $V_1$ 

- 7. Magnitude of work in adiabatic process depends on change in temperature.
- **8.** Magnitude of work in adiabatic process depends on change in temperature.
- 9.  $q_P = n \cdot C_{P,m} \cdot \Delta T$
- 10. Endothermic reactions may also be spontaneous.
- **11.** At high temperature, process may become entropy driven.
- **12.** At low temperature, process may become enthalpy driven.
- 13. If  $\Delta G$  = negative and  $\Delta S$  = negative,  $\Delta H$  must be negative and  $\Delta G = \Delta H T \cdot \Delta S$ .
- 14. Theory based

V

 $V_2$ 

15.  $\Delta S_{\rm sys} = 0$  but  $\Delta S_{\rm univ} = +ve$ 

#### Section E (Column Match)

- 1. Theory based
- 2. Theory based
- 3. Theory based
- 4. For ideal gas, H = f(T) but in general, H = f(T, P)

5. 
$$U = f(T,V) \Rightarrow dU = \left(\frac{\partial U}{\partial T}\right)_V \cdot dT + \left(\frac{\partial U}{\partial V}\right)_T \cdot dV$$
  
 $\left(\frac{\partial U}{\partial T}\right)_V = n \cdot C_{V,m} \text{ and } \left(\frac{\partial U}{\partial V}\right)_T = T \cdot \left(\frac{\partial P}{\partial T}\right)_V - P$   
6.  $N_2(g) + O_2(g) \rightarrow 2NO(g); \Delta H = \text{Positive}, \Delta S \approx 0$   
 $2 \text{ KI}(aq) + \text{HgI}_2(aq) \rightarrow \text{K}_2[\text{HgI}_4](aq);$   
 $\Delta H = \text{Negative}, \Delta S \approx \text{Negative}$   
 $PCl_5(g) \rightarrow PCl_3(g) + Cl_2; \Delta H = \text{Positive}, \Delta S \approx \text{Positive},$ 

NH<sub>3</sub> (g) + HCl (g)  $\rightarrow$  NH<sub>9</sub>Cl (s);  $\Delta H$  = Negative,  $\Delta S$  = Negative

7. (A)  $\Delta H = 0$ ,  $\Delta U = 0$ ,  $\Delta S_{\text{total}} = 0$ ,  $\Delta S_{\text{Sys}} = \text{Positive}$ 

- (B) q = 0,  $\Delta S_{\text{Sys}} = 0$ ,  $\Delta S_{\text{total}} = 0$ ,  $\Delta S_{\text{surr}} = 0$ (C) q = 0,  $\Delta S_{\text{surr}} = 0$ ,  $\Delta S_{\text{total}} = \text{Positive}$ .
- 8. (A)  $\Delta H$  = Negative,  $\Delta V = \pm Ve$ 
  - (B)  $\Delta H = \pm Ve, \Delta S = -Ve, \Delta G = \Delta H T, \Delta S$   $= +Ve, \text{ if } \Delta H = +Ve$   $= \pm Ve, \text{ if } \Delta H = -Ve$ (C)  $\Delta H = Ea_f - Ea_b = 10 \text{ kJ / mol} = +Ve$   $\Delta S = +Ve$   $\therefore \Delta G = \Delta H - T \Delta S = -Ve, \text{ at high temperature}$ (D)  $\Delta H = +Ve, \Delta S \approx 0 \Rightarrow \Delta G \approx \Delta H$
- 9. (A) Solid  $\rightleftharpoons$  Liquid ;  $\Delta G = 0$ ,  $\Delta S =$  Positive,  $\Delta V \approx 0$  $\Rightarrow \Delta H \approx \Delta U$ 
  - (B) Liquid  $\rightleftharpoons$  Vapour :  $\Delta G = 0$ ,  $\Delta S =$  Positive,
  - (C) Triple point is equilibrium condition.
  - (D) Melting at boiling point is spontaneous.
- $10. \quad dG = V \cdot dP S \cdot dT$

4.

5.

$$\Rightarrow (dG)_T = V \cdot dP$$
 and  $(dG)_P = -S \cdot dT$ 

# Section F (Subjective)

# Single-digit Integer Type

1. 
$$w = -P_{\text{ext}} (V_2 - V_1)$$
  
 $= -P_{\text{ext}} [V_0(1 + \gamma \cdot t_2) - V_0(1 + \gamma \cdot t_1)]$   
 $= -P_{\text{ext}} \cdot V_0 \cdot \gamma \cdot (t_2 - t_1)$   
 $-\left(10^5 \frac{N}{m^2}\right) \times (18 \times 10^{-6} \text{ m}^3) \times \frac{0.0002}{^{\circ}\text{C}} \times 10^{\circ}\text{C}$   
 $= 0.0036 \text{ J}$   
2.  $q = \Delta U - w = 0 - \left(-nRT \ln \frac{V_2}{V_1}\right)$ 

or, 
$$420 = 1 \times 2 \times 300 \times \ln \frac{V_2}{\left(\frac{1 \times 0.082 \times 300}{8.21}\right)}$$
  

$$\Rightarrow V_2 = 6 L$$

3. 
$$P = K \cdot l$$
  
For initial condition, 1 bar =  $K \times 1$  m  
 $\Rightarrow K = 1$  bar/m  
And,  $V = \frac{4}{3}\pi r^3 = \frac{\pi}{6}l^3$ 

$$\Rightarrow dV = \frac{\pi}{2}l^2 \cdot dl$$
  
Now,  $w = -\int_{V_1}^{V_2} P \cdot dV = -\int_{l_1}^{l_2} (K \cdot l) \cdot \left(\frac{\pi}{2}l^2 dl\right)$   
 $= -\frac{K\pi}{2} \cdot \frac{l_2^4 - l_1^4}{4}$   
 $= -10^5 \frac{N/m^2}{m} \times \frac{\pi}{2} \times \frac{(4^4 - 1^4)m^4}{4} \approx -1 \times 10^7 \text{ J}$   
 $-w = mgh \Rightarrow P_{\text{ext}} (V_2 - V_1) = mgh$   
 $= \left(4 \times 10^5 \frac{N}{m^2}\right) \times (8 - 2) \times 10^{-3} m^3 = 40 \times 10 \times h$   
 $\Rightarrow h = 6 \text{ m}$   
 $\frac{q}{\Delta U} = \frac{n \cdot C_m \cdot \Delta T}{n \cdot C_{V,m} \cdot \Delta T} = \frac{Q}{Q - \frac{Q}{2}}$   
 $\Rightarrow \frac{C_m}{\frac{3}{2}R} = 2$   
 $\Rightarrow C_m = 6 \text{ cal/K mole}$ 

6. 
$$\frac{q}{w} = \frac{n \cdot C_{P,m} \cdot \Delta T}{-nR \cdot \Delta T}$$
$$\Rightarrow \frac{q}{-2} = \frac{\frac{7}{2}R}{-R}$$
$$\Rightarrow q = 7 \text{ J}$$
7. 
$$q = q_1 + q_2 = \Delta U_1 + \Delta H_2 = n \cdot C_{V,m} \cdot \left(\frac{300}{2} - 300\right)$$
$$+ n \cdot C_{P,m} \cdot \left(300 - \frac{300}{2}\right)$$
$$= n \cdot R \cdot \frac{300}{2} = 10 \times 2 \times \frac{300}{2} = 3000 \text{ cal}$$

$$= n \cdot R \cdot \frac{300}{2} = 10 \times 2 \times \frac{300}{2} = 3000 \text{ cal}$$

- 8. State I  $\xrightarrow{\text{Isothermal}}$  State II  $\xrightarrow{\text{Isochoric}}$  $T_1 = 273 \text{ K}$   $T_2 = 273 \text{ K}$   $T_3 = 5 \times 273 \text{ K}$  $V_1 = V$   $V_2 = 5 V$   $V_3 = 5 V$  $P_1 = P_0$   $P_2 = \frac{P}{5}$   $P_3 = P$  $q_{\text{total}} = nRT \cdot \ln \frac{V_2}{V_1} + n \cdot C_{V_1m} \cdot (T_3 - T_2)$ 
  - or,  $80 \times 10^3 = 3 \times 8.314 \times 273 \times \ln 5 + 3 \times C_{V,m} \times 4$  $\times 273$
  - $\therefore C_{V,m} \approx 21 \text{ J/K-mol} = 5 \text{ cal/K-mol}$
- 9.  $PT = \text{Constant} \Rightarrow P \cdot V^{1/2} = \text{Constant}$

Now,  $C_m = C_{V_1m} + \frac{R}{1-x} \Rightarrow 29 = f \times \frac{8.314}{2} + \frac{8.314}{1-\frac{1}{2}}$  $\Rightarrow f \approx 3$ 10.  $\frac{u_2}{u_1} = 2 = \sqrt{\frac{T_2}{300}} \Rightarrow T_2 = 1200 \text{ K}$  $\Rightarrow T_2 = 1200 \text{ K}$ Now,  $q_V = n \cdot C_{V,m} \cdot (T_2 - T_1)$  $=\frac{56}{28} \times \left(\frac{5}{2} \times 2\right) \times (1200 - 300)$ = 9000 cal

11. 
$$Z_{w} = \frac{1}{4} \cdot u_{aV} \cdot N^{*} = \frac{1}{4} \cdot \sqrt{\frac{8RT}{\pi M}} \cdot \frac{PN_{A}}{RT} = \text{Constant}$$
  
or,  $\frac{P}{\sqrt{T}} = \text{Constant} \Rightarrow P \cdot V^{-1} = \text{Constant}$   
 $\therefore C_{m} = C_{V_{1}m} + \frac{R}{1-x} = \frac{5}{2}R + \frac{R}{1-(-1)} = 3R$   
 $= 6 \text{ cal/K mol}$   
12.  $\Delta G = V \cdot \Delta P$ 

$$= \left(\frac{13}{0.78} \times 10^{-6} \,\mathrm{m}^3\right) (3001 - 1) \times 10^5 \,\frac{\mathrm{N}}{\mathrm{m}^2}$$
$$= 5000 \,\mathrm{J}$$

13. 
$$\Delta G_1 = \Delta H - T_1 \cdot \Delta S \text{ and } \Delta G_2 = \Delta H - T_2 \cdot \Delta S$$
$$\therefore (-\Delta G_2) - (-\Delta G_1) = (T_2 - T_1) \cdot \Delta S = (T_2 - T_1) \times \frac{\Delta H - \Delta G_1}{T_1}$$
$$= (302 - 298) \times \frac{(-5737) - (-6333)}{208} = 8 \text{ kJ}$$

298

14. Graphite 
$$\rightleftharpoons$$
 Diamond;  $\Delta G^{\circ} = 5.0 \text{ kJ}$   $P = 1 \text{ bar}$   
 $\Delta G = 0$   $P = ?$   
Now,  $\Delta G_2 - \Delta G_1 = (V_P - V_G) (P_2 - P_1)$   
or,  $0 - 5000 = \left[\left(\frac{12}{3.6} - \frac{12}{2.4}\right) \times 10^{-6}\right] \times (P_2 - 10^5)$   
 $\Rightarrow 3 \times 10^9 \frac{\text{N}}{\text{m}^2}$ 

15. 
$$\Delta G^{\circ} = -RT \cdot \ln K_{eq} = -2 \times 300 \times \ln (e^{-10}) = +6000 \text{ cal}$$
  
Now,  $\Delta S^{\circ} = \frac{\Delta H^{\circ} - \Delta G^{\circ}}{T} = \frac{7500 - 6000}{300}$   
= 5 cal/k-mol

# Four-digit Integer Type

1. 
$$w = -\left[nRT\ln\frac{V_2 - nb}{V_1 - nb} + an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right)\right]$$
  
$$= -\left[\frac{1 \times 8.314 \times 300 \times \ln\left(\frac{20 - 1 \times 0.03}{2 - 1 \times 0.03}\right)}{+1.42 \times 10^{12} \times 1^2 \times \left(\frac{1}{20} - \frac{1}{2}\right) \times 10^{-10}}\right]$$
$$= -5713.16 \text{ J}$$

- 2.  $\Delta H = \Delta U + \Delta (PV) = 30 + (4 \times 5 2 \times 3) = 44$  *L*-atm
- 3. Calcite  $\rightarrow$  Aragonite  $\Delta H = \Delta U + P \cdot \Delta V$   $\Delta V = 210 \text{ J} + \left(2.7 \times 10^5 \frac{\text{N}}{\text{m}^2}\right) \left(\frac{100}{3} - \frac{100}{2.7}\right) \times 10^{-6} \text{ m}^3$ = 209 J
- 4.  $\Delta U = (q + w)_{\text{path I}} = (q + w)_{\text{path II}}$ or, 10 × 10<sup>3</sup> × 4.2 J + 0 = (11 × 10<sup>3</sup> × 4.2 J) + (-0.5 w\_{\text{max}}) ∴  $w_{\text{max}} = 8400$  J
- 5. H = U + PV = 2.5 PV  $\therefore \Delta H = 2.5 \times 10^5 \frac{\text{N}}{\text{m}^2} \times (200 - 100) \times 10^{-3} \text{m}^3$ = 25 kJ
- 6.  $q = \Delta U w = 1.5 \ nR \cdot \Delta T + P_{\text{ext}} \cdot A \cdot \Delta l$   $42 = 1.5 \times 1 \times 8.314 \times 2 + 100 \times 10^3 \times 8.5 \times 10^{-4} \times \Delta l$  $\therefore \Delta l \approx 0.2 \ m$
- 7.  $\Delta H \Delta U = P(V_D V_G)$ ⇒  $-1000 = P\left[\frac{12}{3.6} - \frac{12}{2.4}\right] \times 10^{-6}$ ∴  $P = 6000 \times 10^5 Pa$
- 8. Solid (70°C)  $\xrightarrow{1}$  Liquid (70°C)  $\xrightarrow{2}$ Liquid (450°C)  $\xrightarrow{3}$  Vapour (450°C)  $q = q_1 + q_2 + q_3 = 30 \times 10 + 10 \times 0.215 \times 380$  $+ 10 \times 45 = 1567$  cal

9. 
$$q = 12 \times 0.5 \times \frac{1805}{6} = 1805 \text{ J}$$
  
 $w = -P \cdot (V_g - V_l) = -P \cdot V_g = -nRT$   
 $= -\frac{0.9}{18} \times 8.314 \times 373 = -155 \text{ J}$ 

$$\therefore \Delta U = q + w = 1805 + (-155) = 1650 \text{ J (for } 0.9 \text{ g)}$$
$$= \frac{1650}{0.9} \times 18 \times 10^{-3} = 33 \text{ kJ}$$

**10.** 
$$q = \Delta U - w = 0 \Rightarrow \Delta U = w = -P_{ext} (V_2 - V_1)$$
  
= -100(-1) = 100 bar-ml  
Now,  $\Delta H = \Delta U + \Delta P V = 100 + (100 \times 99 - 1 \times 100)$   
= 9900 bar-ml = 990 J

11. 
$$q = \Delta U - w = 0 \Rightarrow \Delta U = w$$
  
 $= \frac{1}{2} \times 10 \times 1000 \text{ bar-ml}$   
 $= 500 \text{ J}$   
1001 bar  
1 bar  
1 bar  
990 1000  $V(\text{ml})$ 

12. For adiabatic process:

$$T_{2} = T_{1} \cdot \left(\frac{V_{1}}{V_{2}}\right)^{\gamma-1} = 300 \times (2)^{1.4-1} = 400 \text{ K}$$
  
Now,  $w = w_{1} + w_{2}$   
 $= \left(-nRT \cdot \ln \frac{V_{2}}{V_{1}}\right) + [nC_{V,m} \cdot (T_{2} - T_{1})]$   
 $= [-1 \times 8.3 \times 300 \times \ln 2] + \left[1 \times \frac{8.3}{1.4 - 1} \times (400 - 300)\right]$   
 $= 332 \text{ J}$ 

13. 
$$q = n \cdot C_{V,m} \cdot \Delta T$$
  
or,  $50 \times 166 \times$ 
$$t = \frac{1 \times 8.21 \times 10 \times 2.9 \times 10^3}{0.0821 \times 290} \times \frac{5 \times 8.3}{2} \times 20$$
$$\therefore t = 500 \text{ sec}$$

14. 
$$\Delta U = 3 \times 1.5 R \times 100 + 2 \times 2.5 R \times 100 = 1900$$
 cal



Path AB (Adiabatic):

$$P_2 = P_1 \cdot \left(\frac{T_1}{T_2}\right)^{\frac{1}{1-1}} = 64 \times \left(\frac{1200}{300}\right)^{\frac{1}{3-1}} = 2 \text{ atm}$$

Now,  $w_{\text{total}} = w_{AB} + w_{BC}$ 

$$= n \cdot C_{V,m} \cdot \Delta T + \left(-nRT \ln \frac{P_B}{P_C}\right)$$
$$= 1 \times \frac{3}{2}R \times (300 - 1200) - 1 \times R \times 300 \times \ln \frac{2}{1}$$
$$= -3120 \text{ cal}$$

16. 
$$\Delta S^{\circ} = S_{CH_4} - (S_{grap} + 2 \times S_{H_2})$$
  
= 186.2 - (6.0 + 2 × 130.6)  
= -81 J/K  
Now,  $\Delta G^{\circ} = \Delta H^{\circ} - T \cdot \Delta S^{\circ} = -T \cdot \Delta S_{univ}$   
or, (-75 × 10<sup>3</sup>) - 300 × (-81) = -300 ×  $\Delta S_{univ}$   
 $\Rightarrow \Delta S_{univ} = 169$  J/K

17. 
$$(-mgh) \times N = (-\Delta G^{\circ})$$
  
or  $50 \times 10 \times 2 \times N = \frac{600 \times 10^3}{2 \times 27} \times 27 \Rightarrow N = 300$ 

**18.** 
$$(-\Delta G) = -(\Delta H - T \cdot \Delta S)$$
  
=  $\left[ (-2808) - 310 \times \frac{200}{1000} \right] = 2870 \text{ kJ}$ 

**19.** 
$$2 + 4 + 6 = 12$$

**20.** 
$$a = 2$$
 (i, vi)  
 $b = 3$  (ii, v, vii)  
 $c = 4$  (iii, iv, viii, ix)  
 $d = 9$  (all)