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## **Class Room Problems**

**Problems 1** A certain electric motor produced 15 kJ of energy each second as mechanical work and lost 2 kJ as heat to the surroundings. What is the change in the internal energy of the motor and its power supply each second ?

Sol.

**Problems 3** Work done in expansion of an ideal gas from 4 litre to 6 litre against a constant external pressure of 2.5 atm was used to heat up 1 mole of water at 293 K. If specific heat of water is 4.184 J  $g^{-1}$  K $^{-1}$  what is the final tempeature of water ? **Sol.** 

**Problems 2** The internal energy change in the conversion of 1.0 mole of the calcite form of  $CaCO_3$  to the aragonite form is +0.21 kJ. Calculate the enthalpy change when the pressure is 1.0 bar; given that the densities of the solid are 2.71 g cm<sup>-3</sup> and 2.93 g cm<sup>-3</sup> respectively.



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**Problems 5** Water is boiled under a pressure of 1.0 atm. When an electric current of 0.50 A from a 12 V supply is passed for 300 s through a resistance in thermal contact with it, it is found that 0.789 g of water is vaporized. Calculate the molar internal energy and enthalpy changes at boiling point (373.15 K.)

Sol.

**Problems 4** 10 g of argon gas is compressed isothermally and reversibly at a temperature of 27°C from 10 L of 5L. Calculate q, W,  $\Delta U$  and  $\Delta H$  for this process. R = 2.0 cal K<sup>-1</sup> mol<sup>-1</sup>,  $\log_{10} 2 = 0.30$ , Atomic wt. of Ar = 40. **Sol.** 



**Problem 6** An aeroplane weighing 63,000 kg flies up from sea level to a height of 8000 metre. Its engine run with pure normal octane ( $C_8H_{18}$ ) has a 30% of efficiency. Calculate the fuel cost of the flight, if octane sells at Rs 3/- per litre. Given density of octane = 0.705 g mL<sup>-1</sup>, heat of combustion of octane = 1300 kcal mol<sup>-1</sup> (g = 981 cm/sec<sup>2</sup>)



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Sol.

**Problem 8** For a reaction at 25°C enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ ) are  $-11.7 \times 10^3$  J mol<sup>-1</sup> and -105 J mol<sup>-1</sup> K<sup>-1</sup> respectively. Find out whether this reaction is spontaneous or not ? **Sol.** 

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**Problem 7**A lead bullet weighing 18.0 g and travelling at 500 m/s is embedded in a wooden block of 1.00 kg. If both the bullet and the block were initially at 25.0°C, what is the final temperature of block containing bullet? Assume no temperature loss to the surroundings. (Heat capacity of wood = 0.5 kcal/kg-K; heat capacity of lead = 0.030 kcal/kg-K)

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**Problem 10** Derive a relation showing reversible work of expansion from volume  $V_1$  to  $V_2$  by 'n' moles of a real gas obeying van der Waals' equation at temperature T where volume occupied by molecules may be taken as negligible in comparison to total volume of gas.

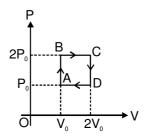
Sol.

**Problems 9** Calculate the entropy change when 1 kg of water is heated from 27°C to 200°C forming super heated steam under constant pressure. Given specific heat of water = 4180 J/kg-K and specific heat of steam = 1670 + 0.49 T J/kg-K and latent heat of vaporization =  $23 \times 10^5$  J/kg

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**Problem 11** Find out the work done in the given graph. Also draw the corresponding T-V curve and P-T curve.

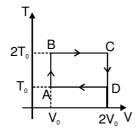


Sol.

**Problem 13** P-T curve of a cyclic process is shown. Find out the work done by the gas in the given process if number of moles of the gas are n.

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**Problem 12** T-V curve of cyclic process is shown below, number of moles of the gas n find the total work done during the cycle.



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**Problem 15** 1 gm water at  $100^{\circ}$ C is heated to convert into steam at  $100^{\circ}$ C at 1 atm. Find out change in internal energy of water. It is given that volume of 1 gm water at  $100^{\circ}$ C = 1 cc. volume of 1 gm steam at  $100^{\circ}$ C = 1671 cc. Latent heat of vaporization = 540 cal/g. (Mechanical equivalent of heat J = 4.2 J/cal.) **Sol.** 

**Problem 14** Consider the cyclic process ABCA on a sample of 2.0 mol of an ideal gas as shown in figure. The temperatures of the gas at A and B are 300 K and 500 K respectively. A total of 1200 J heat is withdrawn from the sample in the process. Find the work done by the gas in part BC. Take R = 8.3 J/mol-K.

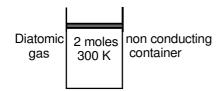
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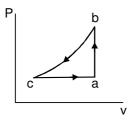
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**Problem 16** Two moles of a diatomic gas at 300 K are kept in a nonconducting container enclosed by a piston. Gas is now compressed to increase the temperature from 300 K to 400 K. Find work done by the gas



Sol.

**Problem 17** A sample of an ideal gas is taken through the cyclic process abca (figure. It ab-sorbs 50 J of heat during the part ab, no heat during bc and reflects 70 J of heat during ca. 40 J of work is done on the gas during the part bc.(a) Find the internal energy of the gas at b and c if it is 1500 J at a. (b) Calculate the work done by the gas during the part ca.





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**Problem 18** The internal energy of a monatomic ideal gas is  $1.5 \, \text{nRT}$ . One mole of helium is kept in a cylinder of cross-section  $8.5 \, \text{cm}^2$ . The cylinder is closed by a light frictionless piston. The gas is heated slowly in a process during which a total of 42 J heat is given to the gas. If the temperature rises through  $2^{\circ}\text{C}$ , find the distance moved by the piston. Atmospheric pressure =  $100 \, \text{kPa}$ .

Sol.

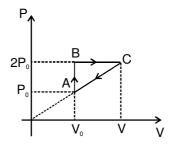
**Problem 19** A sample of an ideal gas has pressure  $p_0$ , volume  $v_0$  and temperature  $T_0$ . It is isothermally expanded to twice its original volume. It is then compressed at constant pressure to have the original volume  $V_0$ . Finally, the gas is heated at constant volume to get the original temperature. (a) Show the process in a V - T diagram (b) Calculate the heat absorbed in the process.





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**Problem 20** A sample of ideal gas (f = 5) is heated at constant pressure. If an amount 140 J of heat is supplied to the gas, find (a) the change in internal energy of the gas (b) the work done by the gas. **Sol.** 



- (i) Volume at C?
- (ii) Maximum temperature?
- (iii)Total heat given to gas?
- (iv) is heat rejected by the gas, if yes how much heat is rejected ?
- (v) Find out the efficiency

Sol.

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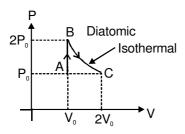
**Problem 21** n moles of a diatomic gas has undergone a cyclic process ABC as shown in figure. Temperature at A is  $T_{\rm o}$ .

Find

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**Problem 22** P-V curve of a diatomic gas is shown in the figure. Find the total heat given to the gas in the process AB and BC



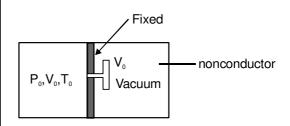
Sol.

**Problem 23** A quantity of air is kept in a container having walls which are slightly conducting. The initial temperature and volume are 27°C (equal to the temperature of the surrounding) and 800 cm³ respectively. Find the rise in the temperature if the gas is compressed to 200 cm³ (a) in a short time (b) in a long time. Take  $\gamma = 1.4$ . **Sol.** 

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**Problem 24** A monoatomic gas is enclosed in a nonconducting cylinder having a piston which can move freely. Suddenly gas is compressed to 1/8 of its initial volume. Find the final pressure and temperature if initial pressure and temperature are  $P_0$  and  $T_0$  respectively.



Sol.



**Problem 25** A nonconducting cylinder having volume  $2V_0$  is partitioned by a fixed nonconducting wall in two equal part. Partition is attached with a valve. Right side of the partition is a vaccum and left part is filled with a gas having pressure and temperature  $P_0$  and  $T_0$  respectively. If valve is opened find the final pressure and temperature of the two parts.



## **Exercise - I**

# (only one option is correct)

Sol.

**1.**Out of boiling point (I), entropy (II), pH (III) and density (IV), Intensive properties are :

(A) I, II

(B) I, II, III

(C) I, III, IV

(D) All of these

Sol.

2. Consider the reaction at 300 K

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) \Delta H^\circ = -185 \text{ kJ}$$

If 3 mole of  $H_2$  completely react with 3 mole of  $Cl_2$  to form HCl. What is  $\Delta U^o$  for this reaction ?

(A) 0

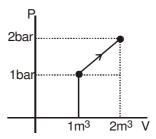
(B) -185 kJ

(C) 555 kJ

(D) None of these

Sol.

**4.** What is  $\Delta U$  for the process described by figure. Heat supplied during the process q = 100 kJ.



(A) + 50 kJ

(B) -50 kJ

(C) -150 kJ

(D) + 150 kJ

Sol.

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**3.** Ethyl chloride (C<sub>2</sub>H<sub>5</sub>Cl), is prepared by reaction of ethylene with hydrogen chloride:

$$C_2H_4(g) + HCI(g) \rightarrow C_2H_5cI(g) \Delta H = -72.3 \text{ kJ}$$

What is the value of  $\Delta E$  (in kJ), if 70 g of ethylene and 73 g of HCl are allowed to react at 300 K.

(A) -69.8

(B) -180.75

(C) -174.5

(D) -139.6

- **5.**One mole of ideal gas is allowed to expand reversibly and adiabatically from a temperature of 27°C. If the work done by the gas in the process is 3 kJ, the final temperature will be equal to  $(C_v = 20 \text{ J/K mol})$
- (A) 100 K
- (B) 450 K
- (C) 150 K
- (D) 400 K

- **7.**The heat capacity of liquid water is 75.6 J/mol K, 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) None of these

Sol.

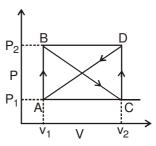
**6.** What is the change in internal energy when a gas contracts from 377 ml to 177 ml under a constant pressure of 1520 torr, while at the same time being cooled by removing 124 J heat?

[Take: (1 L atm) = 100 J]

- (A) -24 J
- (B) 84 J
- (C) -164 J (D) -248 J

Sol.

**8.**An ideal gas is taken around the cycle ABCDA as shown in figure. The net work done during the cycle is equal to :



- (A) zero
- (B) positive
- (C) negative
- (D) we cannot predict

Sol.

- **9.** Molar heat capacity of water in equilibrium with ice at costant pressure is
- (A) zero
- (B) ∞
- (C) 40.45 kJ K<sup>-1</sup> mol<sup>-1</sup>
- (D) 75.48 JK<sup>-1</sup> mol<sup>-1</sup>

Sol.

- **11.** A diatomic ideal gas initially at 273 K is given 100 cal heat due to which system did 209 J work. Molar heat capcity ( $C_m$ ) of gas for the process is :
- (A)  $\frac{3}{2}$ R

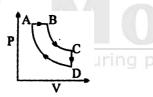
(B)  $\frac{5}{2}$ R

(C)  $\frac{5}{4}$ R

(D) 5 R

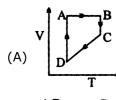
Sol.

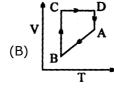
**10.** A cyclic process ABCD is shown in PV diagram for an ideal gas. Which of the following diagram represents the same process?

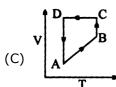


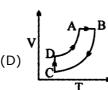
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12. One mole of an ideal monoatomic gas expanded irreversibly in two stage expansion.

State-1 (8.0 bar, 4.0 litre, 300 K)

State-2 (2.0 bar, 16 litre, 300 K)

State-3 (1.0 bar, 32 litre, 300 K)

Total heat absorbed by the gas in the process is:

- (A) 116 J
- (B) 40 J
- (C) 4000 J
- (D) None of these

Sol.

**14.** A gas ( $C_{v,m} = \frac{5}{2}R$ ) behaving ideally was allowed to

expand reversibly and adiabaticaly from 1 litre to 32 litre. It's initial temperature was 327°C. The molar enthalpy change (in J/mole) for the process is

- (A) -1125 R
- (B) -575 R
- (C) -1575 R
- (D) None of these

Sol.

15. What is the net work done (in calories) on 1 mole f monoatomic ideal gas in a process described by 1,2,3,4 in given V-T graph.

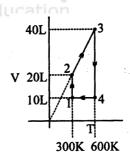
Use: R = 2cal/mole K

13. For an ideal monoatomic gas during any process T = kV, find out the molar heat capacity of the gas during the process. (Assume vibrational degree of freedom to be active)

- (A)  $\frac{5}{2}$ R

- (B) 3R (C)  $\frac{7}{2}$  (D) 4R

Sol.



ln 2 = 0.7

- (A) -600 cal
- (B) -660 cal
- (C) + 660 cal
- (D) +600 cal

17. An insulated container of gas has two chambers separated by an insulating partition. One of the chambers has volume  $V_1$  and contains ideal gas at pressure  $P_1$  and temperature  $T_1$ . The other chambers has volume v<sub>2</sub> and contains ideal gas at pressure P<sub>2</sub> and temperature T<sub>2</sub>. If the partion 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)  $\frac{T_1T_2(P_1V_1 + P_2V_2)}{P_1V_1T_1 + P_2V_2T_2}$

Sol.

**16.** Two moles of an ideal gas  $(C_v = \frac{5}{2}R)$  was compressed adiabatically against constant pressure of 2 atm. Which was initially at 350 K and 1 atm pressure. The work involve in the process is equal to (A) 250 R (B) 300 R (C) 400 R (D) 500 R Sol.



- **18.** The maximum efficiency of a heat engine operating between 100°C and 25°C is
- (A) 20.11%
- (B) 22.2%
- (C) 25.17%
- (D) None

**19.** A heat engine operating between 227°C and 27°C absorbs 2 Kcal of heat from the 227°C reservoir reversibly per cycle. The amount of work done in one cycle is :

(A) 0.4 Kcal (B) 0.8 Kcal (C) 4 Kcal (D) 8 Kcal **Sol.** 

and B are the same then the temperautre  $T_2$  is (A) 680 K (B) 640 K (C) 600 K (D) None **Sol.** 

21. For the reaction at 300 K

A(g) + B(g)  $\rightarrow$  C(g)  $\Delta$ E = - 3.0 kcal ;  $\Delta$ S = -10.0 cal/K value of  $\Delta$ G is

(A) -600 cal (B) -6600 cal(C) -6000 cal (D) None **Sol.** 

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**20.** A reversible heat engine A (based on carnot cycle) absorbs heat from a reservoir at 1000 K and rejects heat to a reservoir at  $T_2$ . A second reversible engine B absorbs, the same amount of heat as rejected by the engine A, from the reservoir at  $T_2$  and rejects energy to a reservoir at 360 K. If the efficiencies of engines A

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- 22. The entropy change when two moles of ideal monoatomic gas is heated from 200 to 300°C reversibly and isochorically
- (A)  $\frac{3}{2}$ R In  $\left(\frac{300}{200}\right)$ 
  - (B)  $\frac{5}{2}$ RIn $\left(\frac{573}{273}\right)$
- (C)  $3Rln\left(\frac{573}{473}\right)$  (D)  $\frac{3}{2}Rln\left(\frac{573}{473}\right)$

Sol.

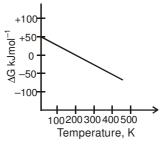
- **23.** What is the free energy change ( $\Delta G$ ) when 1.0 mole of water at 100° C and 1 pressure is converted into steam at 100°C and 1 atm pressure?
- (A) 80 cal
- (B) 540 cal (C) 620 cal (D) zero

Sol.

- **24.** What if 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 2 atm pressure?
- (A) zero cal
- (B) 540 cal
- (C) 517.13 cal
- (D) 510 cal

Sol.

25. What can be concluded about the values of  $\Delta H$ and  $\Delta S$  from this graph?



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

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Sol.

**27.** Pressure of 10 moles of an ideal gas is changed from 2 atm to 1 at against constant external pressure without change in temperature. If surrounding temperature (300K) and pressure (1 atm) always remains constant then calculate total entropy change  $(\Delta S_{\text{system}} + \Delta S_{\text{surrounding}})$  for given process.

[Given :  $\ell$ n2 = 0.70 and R = 8.0 J/mol/K]

(A) 56 J/K

(B) 14 J/K

(C) 16 J/K

(D) None of these

Sol.

**26.** If  $\Delta H_{\text{vaporisation}}$  of substance X ( $\it{l}$ ) (molar mass : 30 g/mol) is 300 J/g at it's boiling point 300 K, then molar entropy change for revesible condensation process is

(A) 30 J/mol.K

(B) -300 J/mol K

(C) -30 J/mol K

(D) None of these

Sol.

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**28.** The enthalpy of tetramerization of X in gas phase  $(4X(g) \rightarrow X_4(g))$  is -100 kJ/mol at 300 K. The enthalpy of vaporisation for liquid X and  $X_4$  are respectively 30 kJ/mol and 72 kJ/mol respectively.  $\Delta S$  for tetramerization of X in liquid phase is -125 J/K mole at 300 K. What is the  $\Delta G$  at 300 K for tetramerization of x in liquid phase.

(A) -52 kJ/mol

(B) -89.5 kJ/mol

(C) -14.5 kJ/mol

(D) None of these



**30.** Standard entropy of  $X_2$ ,  $Y_2$  and  $XY_3$  are 60, 40 and 50 JK<sup>-1</sup> mol<sup>-1</sup>, respectively. For the reaction,

 $\frac{1}{2} X_2 + \frac{3}{2} Y_2 \rightarrow X Y_3$  ,  $\Delta H \, = \, -30$  kJ to be at equilibrium,

the temperature will be

(A) 1250 K (B) 500 K

Sol.

- (C) 750 K (D) 1000 K

29. The change in entropy of 2 moles of an ideal gas upon iosthermal expansion at 243.6 K from 20 litre until the pressure becomes 1 atm, is:

- (A) 1.385 cal/K
- (B) -1.2 cal/k
- (C) 1.2 cal/K
- (D) 2.77 cal/K

Sol.

31. When two equal sized pieces of the same metal at different temperatures  $T_h$  (hot piece) and  $T_c$  (cold piece) are brought into contact into thermal contact and isolate from it's surrounding. The total change in entropy of system is given by

- $\begin{array}{ll} \text{(A)} & \text{CIn} \frac{T_c + T_h}{2T_c} & \text{(B)} & \text{CIn} \frac{T_2}{T_1} \\ \\ \text{(C)} & \text{CIn} \, \frac{(T_c + T_h)^2}{2T_h.\,T_c} & \text{(D)} & \text{CIn} \, \frac{(T_c + T_h)^2}{4T_h.\,T_c} \\ \end{array}$

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Sol.

**33. Statement-1:** Due to adiabatic free expansion, temperature of a real gas always increases

**Statement-II:** If a real gas is at inversion temperature then no change in temperature is observed in adiabatic free expansion.

- (A) Statement-I is true, statement-II is true and statement-II is correct explanation for statement-I
- (B) Statement-I is true, statement-II is true and statement-II is NOT correct explanation for statement-I
- (C) Statement-I is true, statement-II is false.
- (D) Statement-I is false, statement-II is true. **Sol.**

**34. Statement-1:** 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.

- (A) Statement-I is true, statement-II is true and statement-II is correct explanation for statement-I
- (B) Statement-I is true, statement-II is true and statement-II is NOT the correct explanation for statement-I
- (C) Statement-I is false, statement-II is true.
- (D) Statement-I is true, statement-II is false. **Sol.**

#### **Assertion Reason:**

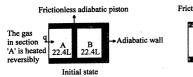
**32. Statement-1:** There is no change in enthalpy of an ideal gas during compression at constant temperautre.

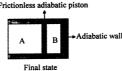
**Statement-II:** Enthalpy of an ideal gas is a function of temperature and pressure.

- (A) Statement-I is true, statement-II is true and statement-II is correct explanation for statement-I
- (B) Statement-I is true, statement-II is true and statement-II is NOT the correct explanation for statement-I
- (C) Statement-I is false, statement-II is true.
- (D) Statement-I is true, statement-II is false. **Sol.**

#### **COMPREHENSION-I**

A cylindrical container of volume 44.8 litres is containing equal no. of moles (in integer no.) of an ideal monoatomic gas in two sections A and B separated by an adiabatic frictionless piston as shown in figure. The initial temperature and pressure of gas in both section is 27.3 K and 1 atm. Now gas is section 'A' is slowly heated till the volume of section B becomes (1/8)<sup>th</sup> of initial volume.





Given: R = 2 cal/mol-K,  $C_{v,m}$  of monoatomic gas =  $\frac{3}{2}$  R, At 1 atm & 0°C ideal gas occupy 22.4 litre.

**35.** What will be the final pressure in container B.

(A) 2 atm (B) 8 atm (C) 16 atm (D) 32 atm **Sol.** 

**37.** Change in enthalpy for section A in Kcal. (A) 48.3 (B) 80.53 (C) 4.83 (D) 8.05 **Sol.** 

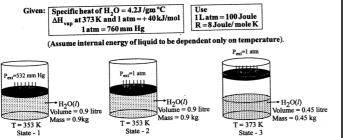


**36.** Final temperature in container A will be (A) 1638 K (B) 6988 K (C) 3274 K (D) 51 K **Sol.** 



#### **COMPREHENSION - 2**

The vapour pressure of  $H_2O(l)$  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. Temperature remained constant. Now, heat is supplied keeping pressure constant till 0.45 L of H<sub>2</sub>O (l) = (0.45 kg) is evaporated to form H<sub>2</sub>O (g) at 373 K. Carefully observe the diagrams provided and from given data, answer the following questions.



**38.**  $\Delta H$  when system is taken from state 1 to state 2 (Joule)?

(A) zero (B) 0.27

(C) 27 (D) 90

Sol.

40. Total change in enthalpy going from state 1 to state 3 (kJ)?

(A)75.6

Sol.

(B) 1075.6 (C) 1001

(D) 74.6

**39.** Total change in  $\Delta U$  going from state 1 to 3 (kJ)?

(A) 75.6

Sol.

(B) 1075.6 (C) 1001

(D) 74.6

**41.** What is the work done in going state 1 to state 3 to in Joules.

(A) zero

(B) 45

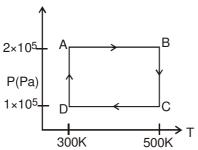
(C) 90

(D) 31.5

43. The work done involved in taking it from D to A is (A) -414 R (B) +414 R (C) -690 R (D) +690 R Sol.

#### **COMPREHENSION-3**

Two moles of helium gas are taken over the cycle ABCDA, as shown in the P-T diagram.



**42.** Assuming the gas to be ideal the work done by the gas in taking it from A to B is -

(A) 200 R

- (B) 300 R
- (C) 400 R
- (D) 500 R

Sol.

44. The net work done involved in the cycle ABCDA is (A) zero (B) 276 R (C) 1076 R (D) 1904 R Sol.

## Match the column:

45. Match Column-I with Column-II

Column - I (Ideal Gas) Column-II (Related equation)

- (A) Reversible isothermal (P) W =  $2.303 \text{ nRT log } (P_2/P_1)$ process
- (B) Reversible adiabatic
- (Q) W =  $nC_{v.m} (T_2 T_1)$
- process (C) Irreversible adiabatic (R) PV = nRT
- (D) Irreversible isothermal (S)  $W = -\int_{0}^{\infty} P_{ext.} dV$ process

46. Match the column - I with column-II

Note that column - I may have more than one matching options in column-II

#### Column-I

#### Column-II

- (A) Reversible adiabatic (P)  $\Delta S_{\text{system}} > 0$ compression
- (B) Reversible vaporisation(Q)  $\Delta S_{\text{system}} < 0$
- (C) Free expansion of (R)  $\Delta S_{\text{surroudning}} < 0$ ideal gas in vacuum
- (D) Dissociation of
- (S)  $\Delta S_{\text{surrounding}} = 0$
- $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ Sol.

48. Column - I may have more than one matching options in column-II

#### Column-I

### Column-II

- (A) Reversible condensation
- of vapour

- (P)  $\Delta S_{\text{system}} > 0$
- (B) Irreversible adiabatic
- compression of an ideal gas
- (Q)  $\Delta S_{\text{system}} < 0$
- (C) Isothermal free
- expansion of an ideal
- (R)  $\Delta S_{\text{surroudning}} < 0$
- gas in vaccum
- (D) Reversible adiabatic expansion of an ideal gas
- (S)  $\Delta S_{\text{surrounding}} = 0$

Sol.

#### 47. Column I Column-II

- (A) For the process
- $A(l) \rightarrow A(s)$ ,  $\Delta H \& \Delta V$  may be
- (P) -ve, +ve
- (B)  $A_2(s) + B_2(g) \rightleftharpoons C_2(s) + D_2(s)$  (Q) +ve, -ve

ΔH & ΔG may be

- (C) For the given reaction (R) +ve, +ve
- $A_2(g) \rightleftharpoons B_2(g) + C_2(g), E_{a(forward)} = 50 \text{ kJ/mol}$
- at very high temperature ΔH & ΔG are
- (D) For the given reaction
- (S) -ve, -ve
- $A(g) \Longrightarrow B(g)$ , at very low temperature ΔH & ΔG may be

Sol.

49. Column-I Column-II (Related to process) (Related to system)

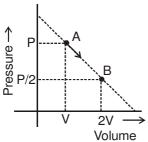
(D) Melting at normal boiling point (S)  $\Delta H \simeq \Delta U$ 

- (A) Fusion at melting point
- (P)  $\Delta G = 0$
- (B) Vapourisation at boiling point
- (Q)  $\Delta G < 0$
- (C) Condensation at triple point
- (R)  $\Delta S > 0$

# **Exercise - II**

# (One or more than one option correct)

**1.**An ideal gas is taken from state A (Pressure P, Volume V) to the state B (Pressure P/2, Volume 2V) along a straight line path in PV diagram as shown in the adjacent figure.



Select the correct statement (s) among the following

- (A) The work done by gas in the process A to B exceeds the work that would be done by it if the system were taken from A to B along the isotherm.
- (B) In the T-V diagram, the path AB become part of parabola.
- (C) In the P-V diagram, the path AB becomes a part of hyperbola.
- (D) In going from A to B, the temperature T of the gas first increases to a maximum value then decreases.

Sol.

- **2.**The normal boiling point of a liquid 'A' is 350 K.  $\Delta H_{vap}$  at normal boiling point is 35 kJ/mole. Pick out the correct statement (s). (Assume  $\Delta H_{vap}$  to be independent of pressure).
- (A)  $\Delta S_{\mbox{\tiny vaporisation}} >$  100 J/K mole at 350 K and 0.5 atm
- (B)  $\Delta S_{\text{vaporisation}}^{\phantom{i}}$  < 100 J/K mole at 350 K and 0.5 atm
- (C)  $\Delta S_{\text{vaporisation}} <$  100 J/K mole at 350 K and 2 atm
- (D)  $\Delta S_{\text{vaporisation}} = 100 \text{ J/K}$  mole at 350 K and 2 atm

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3. Which of the following statement(s) is/are false:

(A) 
$$\Delta_r S$$
 for  $\frac{1}{2} N_2(g) \rightarrow N(g)$  is positive

- (B)  $\Delta G_{\text{system}}$  is always zero for a reversible process in a closed system  $_{\text{BSE}}$  [SAT]NTSE
- (C)  $\Delta G^o$  for an ideal gas is a function of temperature and pressure
- (D) entropy of a closed system is always maximized at equilibrium

- 4. Which statement is/are correct:
- (A) Final temperature in reversible adiabatic expansion is lesser than in irrevesible adiabatic expansion.
- (B) When heat is supplied to an ideal gas in an isothermal process, kinetic energy of gas will increase
- (C) When an ideal gas is subjected to adiabatic expansion it gets cooled
- (D) Entropy increases in atomisation of dihydrogen Sol.

- **5.** Which is /are correct statement.
- (A)  $\rm W_{adiabatic} > \rm W_{isothermal}$  in an ideal gas compression from same intial state to same final volume
- (B) The volume of  $\gamma \left( \gamma = \frac{C_p}{C_v} \right)$  remains constant for

diatomic gas at all temperature

- (C) Entropy increases when an ideal gas expanded isothermally.
- (D)  $\Delta_r H \& \Delta_r S$  both are +ve for the decomposition of  $MgCO_3(s)$ .

Sol.

(A) The pressure at B is 2.0 bar

(B) The temperature at D is 450 K

(C)  $\Delta H_{CD} = 1000 \text{ R}$ 

(D)  $\Delta U_{BC} = 375 \text{ R}$ 

Sol.



7. In isothermal ideal gas compression

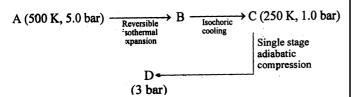
(A) w is +ve\_OLYMPIADS

(B) ∆H is zero

(C)  $\Delta S_{gas}$  is +ve (D)  $\Delta G$  is +ve

Sol.

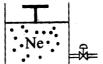
**6.** Two moles of an ideal gas  $(C_{v,m} = 3/2 \text{ R})$  is subjected to following change of state.



The correct statement is/are:

8.A piston cyclinder device initially contains 0.2 m<sup>3</sup> neon (assume ideal) at 200 kPa inside at T<sub>1</sub>°C. A valve is now opened and neon is allowed to escape until the volume reduces to half the initial v

At the same time heat transfer with outside at T, ° C ensures a constant temperature inside.



(A) ΔU must be zero

Select correct statement(s) for given process

- (B) ∆U may not be zero
- (C) q may be +ve
- (D) q may be -ve

Sol.

- **10.** Which of the following statement(s) is/are correct (A) Reversible isothermal compression of an ideal gas represents the limiting minimum value of the workdone (|w|) by the surrounding on the system.
- (B) In an irreversible process, the cyclic integral of work is not zero.
- (C) For thermodynamic changes in adiabatic process

$$T^{\left(\frac{C_{P,m}}{R}\right)}.$$
 P = constant

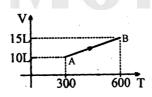
(D) Work done by 1 mole of a real (vander waals) gas

$$W = -RT \ln \frac{V_2 - b}{V_1 - b} - a \left[ \frac{V_1 \times V_2}{V_2 - V_1} \right]$$

Sol.

- 9. If one mole monoatomic ideal gas was taken through process AB as shown in figure, the select correct option
- (A)  $W_{AB} = -1496.52 J$
- (B)  $q_{AB} = 5237.82 J$
- (C)  $\Delta H_{AB} = 3741.3 \text{ J}$

(D)  $\Delta S_{AB}$  is +ve



## **Exercise - III**

# **Subjective Level-I**

## First law: Heat (q), work (w) and $\Delta U$ , $\Delta H$

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

 $\begin{array}{lll} \text{Initial state} & & \text{Final state} \\ \text{(i)} \ H_2\text{O}(g) & & \rightarrow H_2\text{O} \ (\textit{l}) \\ \text{(ii)} \ H_2\text{O} \ (s) & & \rightarrow H_2\text{O}(g) \\ \text{(iii)} \ H_2\text{O}(\textit{l}) & & \rightarrow H_2\text{O}(s) \\ \text{(iv)} \ 3H_2(g) + N_2(g) & & \rightarrow 2\text{NH}_3(g) \\ \text{(v)} \ \text{CaCO}_3(s) & & \rightarrow \text{CaO}(s) + \text{CO}_2(g) \end{array}$ 

Sol.

- **4.**The enthalpy of combustion of glucose is -2808 KJ mol<sup>-1</sup> at 25°C. How many grams of glucose do you need to consume [Assume wt = 62.5 Kg]
- (a) to climb a flight of stairs rising through 3M
- (b) to climb a mountain of altitude 3000 M?

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

Sol.

**2.**The gas is cooled and loses 65 J of heat. The gas contracts as it cools and work done on the system equal to 20 J is exchanged with the surroundings. What are q, w and  $\Delta E$ ?

Sol.

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**3.**The enthalpy change for the reaction of 50 ml of ethylene with 50.0 ml of  $H_2$  at 1.5 atm pressure is  $\Delta H = -0.31$  KJ. What is the  $\Delta E$ .

**5.** What is  $\Delta E$  when 2.0 mole of liquid water vaporises at 100°? The heat of vaporisation,  $\Delta H$  vap. of water at 100° C is 40.66 KJ mol<sup>-1</sup>.

Sol.

**7.** When the following reaction was carried out in a bomb calorimeter,  $\Delta E$  is found to be -742.7kJ/mol of NH<sub>2</sub>CN(s) at 298 K.

$$NH_2CN(s) + \frac{3}{2}O_2(g) \rightarrow N_2(g) + CO_2(g) + H_2O(l)$$

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

Sol.

**6.**If 1.0 kcal of heat is added to 1.2 L of  $O_2$  in a cylinder of constant pressure of 1 atm, the volume increases to 1.5 L. Calculate  $\Delta E$  and  $\Delta H$  of the process. **Sol.** 

**8.**When 1 mole of ice melt at 0°C and at constant pressure of 1 atm. 1440 calories of heat are absorbed by the system. The molar volumes of ice and water are 0.0196 and 0.0180 litre respectively. Calculate  $\Delta H$  and  $\Delta E$  for the reaction.

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Sol.

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**9.** Water expands when it freezes. Determine amount of work in joules, done when a system consisting of 1.0 L of liquid water freezes under a constant pressure of 1.0 atm and forms 1.1 L of ice. **Sol.** 

**11.** One mole of solid Zn is placed in excess of dilute  $H_4SO_4$  at 27°C in a cylinder fitted with a piston. Find the value of  $\Delta E$ , q and w for the process if the area of piston is 500 cm² and it moves out by 50 cm against a pressure of 1 atm during the reaction. The heat given to surrounding is 36.5 KJ.

$$Zn(s) + 2H^+ (aq) \rightleftharpoons Zn^{2+} (aq) + H_2(g)$$
  
Sol.

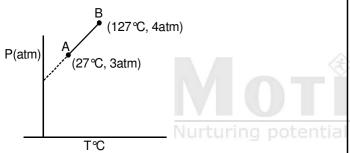
**10.** Lime is made commercially by decomposition of limestone  $CaCO_3$ . What is the change in internal energy when 1.00 mole of solid  $CaCO_3$  (V = 34.2 ml) absorbs 177.9 kJ of heat and decomposes at 25°C against a pressure of 1.0 atm to give solid CaO. (Volume = 16.9 ml) and  $CO_2$  (g) (V = 24.4 L) **Sol.** 



**12.** Two mole of ideal diatomic gas ( $C_{v,m} = 5/2$  R) at 300 K and 5 atm expanded irreversly & adiabatically to a final pressure of 2 atm against a constant pressure of 1 atm. Calculate q, w,  $\Delta H$  &  $\Delta U$ . **Sol.** 

**14.** Calculate the max. work done by system in an irreversible (single step) adiabatic expansion of 1 mole of a polyatmic gas ( $\gamma = 1.33$ ) from 300 K and pressure 10 atm to 1 atm. **Sol.** 

- **13.** 4 moles of an ideal gas ( $C_{v, m} = 15 \text{ JK}^{-1} \text{ mol}^{-1}$ ) is subjected to the following process represented on P T graph from the data given. Find out
- (a) The process is isochoric or not



(b) Calculate q, w,  $\Delta U$  &  $\Delta H$  for the process. **Sol.** 

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- **15.**1 mole of CO<sub>2</sub> gas at 300 K is expanded under reversible adiabatic condition such that its volume becomes 27 time.
- (a) What is the final temperature
- (b) What is work done
- Given  $\gamma = 1.33$  and  $C_v = 25.08$  J mol $^{-1}$  K $^{-1}$  for  $CO_2$

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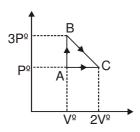
**17.** A sample of a fluorocarbon was allowed to expand to expand reversibly and adiabatically to twice its volume. In the expansion the temperature dropped from 298.15 K to 248.44 K. Assume the gas behaves perfectly Estimate the value of  $C_{_{v.m.}}$ 

**16.** Three moles of a ideal gas at 200K and 2.0 atm pressure undergo reversible adiabatic compression until the temperature becomes 250 K for the gas  $C_v$  is 27.5 JK<sup>-1</sup> mol<sup>-1</sup> in this temperature range. Calculate q, w,  $\Delta U$ ,  $\Delta H$  and final V and final P. **Sol.** 

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



- **19.** One mole of ideal monoatomic gas is carried through the reversible cyclic process as shown in figure. Calculate .
- (a) work done by the gas.
- (b) The heat changed by the gas in path CA and AB.
- (c) Net heat absorbed by the gas in the path BC.



(d) The max. temperature attained by the gas during the cycle.

Sol.

**20.** One mole of an ideal monoactomic gas is carried through the reversible cycle of the given figure consisting of step A, B and C and involving state 1, 2 and 3.

Fill in the blank space in the table given below assuming

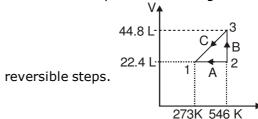


Table-1					
State	Р	V	Т		
1					
2					
3					

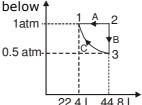
Step	Name of process	q	w	ΔE	ΔH
Α					
В					
С					

Sol.



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**21.** One mole of an ideal monoatomic gas is put through reversible path as shown in figure. Fill in the blank in the table given below **†** 



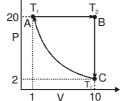
State	Р	٧	T
1			
2			
3			

Step	Name of process	q	w	Е	Н
Α					
В					
С					
	cyclic				

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

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

(AB) Isobaric expansion to return the gas to the original volume of 10 litres



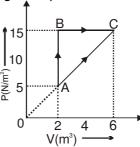
with T going from  $T_1$  to  $T_2$ .

(BC) Cooling at constant volume to bring the gas to original pressure and temperature. The steps are shown schematically in the figure shown.

- (a) Calculate  $T_1$  and  $T_2$
- (b) Calculate  $\Delta E$ , q and w in calories, for each step and for the cycle.

Sol.

- **23.** The given figure shows a change of state A to state C by two paths ABC and AC for a an ideal gas. Calculate the : IT-JEE | ALEEE
- (a) Path along which work done is least.
- (b) Internal energy at C if the internal energy of gas at A is 10 J and amount of heat supplied to change its state to C through the path AC is 200 J.



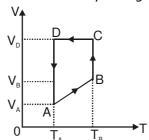
(c) Amount of heat supplied to the gas to go from A to B, if internal energy change of gas is 10 J.

Sol.

**24.** A monoatomic ideal gas of two moles is taken through a reversible cyclic process starting from A as shown in figure. The volume ratios are  $\frac{V_B}{V_A} = 2$  and

 $\frac{V_D}{V_A}$  = 4 . If the temperature  $T_A$  at A is 27°C, calculate (a) The temperature of the gas at point B.

(b) Heat absorbed or released by the gas in each



process.

(c) The total work done by the gas during complete cycle.

## Kirchoff's Rule : Variation of Enthalpy with Temperature

**25.** The standard enthalpy of formation of water liquid is -285.76 kJ at 298 K. Calculate the value of  $\Delta_{F}H^{o}$  at 373 K. The molar heat capacities at constant pressure  $_{(c_p)}$  in the given temperature range of  $H_2(g)$ ,  $O_2(g)$  and  $H_2O$  (l) are respectively 38.83, 29.16 and 75.312 JK<sup>-1</sup> mol<sup>-1</sup>.

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Sol.

# Second & third law & Entropy change in thermodynamic processes

**27.** One mole of NaCl (s) on melting absorbed 30.5 KJ of heat and its entropy is increased by  $28.8~\rm JK^{-1}$ . What is the melting point of sodium chloride ? **Sol.** 

**26.** Methane (considered to be an idela gas) initially at 25°C and 1 bar pressure is heated at constant pressure until the volume has doubled. The variation of the molar heat capacity with absolute temperature is given by

 $C_p = 22.34 + 48.1 \times 10^{-3} \, T$  where  $C_p$  in JK<sup>-1</sup> mol<sup>-1</sup>. Calculate molar (a)  $\Delta H(b) \, \Delta U$ . **Sol.** 

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**28.** Oxygen is heated from 300 to 600 at a constant pressure of 1 bar. What is the increase in molar entropy ? The molar heat capacity in JK<sup>-1</sup> mol<sup>-1</sup> for the  $O_2$  is  $C_p = 25.5 + 13.6 \times 10^{-3} \, \text{T} - 42.5 \times 10^{-7} \, \text{T}^2$  **Sol.** 

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**30.** Calculate the entropy of a substance at 600 K using the following data.

- (i) Heat capacity of solid from 0 K to normal melting point 200 K  $C_{P_{Pm}}(s) = 0.035 \, T$  JK $^{-1}$  mol $^{-1}$
- (ii) Enthalpy of fusion =  $7.5 \, kJ \, mol^{-1}$ ,
- (iii) Enthalpy of vaporisation = 30 kJ mol<sup>-1</sup>.
- (iii) Heat capacity of liquid from 200 K to normal boiling point 300 K  $C_{P.m}$  ( $\ell$ ) = 60 + 0.016 T JK<sup>-1</sup>mol<sup>-1</sup> (iv) Heat capacity of gas from 300 K to 600 K at 1 atm  $C_{P.m}$  (g) = 50.0 JK<sup>-1</sup>mol<sup>-1</sup>. **Sol.**

**29.** A heat engine absorbs 760 kJ heat from a source at 380 K. It rejects (i) 650 kJ, (ii) 560 kJ, (iii) 504 kJ of heat to sink at 280 K. State which of these represent a reversible, an irreversible and an impossible cycle. **Sol.** 



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#### **Gibb's Function**

**31.** Calculate the free energy change at 298 K for the reaction;

 $Br_2(l) + Cl_2(g) \rightarrow 2BrCl(g)$ . For the reaction  $\Delta H^0 = 29.3$ 

kJ & the entropies of  $Br_2(l), Cl_2(g)$  & BrCl(g) at the 298 K are 152.3, 223.0, 239.7 J  $mol^{-1}$  K<sup>-1</sup> respectively. **Sol.** 

**33.** Animals operate under conditions of constant pressure and most of the processes that maintain life are electrical (in a broad sense). How much energy is available for sustaining this type of muscular and nervous activity from the combustion of 1 mol of glucose molecules under standard conditions at  $37^{\circ}$ C (blood temperature)? The entropy change is +182.4 JK<sup>-1</sup> for the reaction as stated.

 $\Delta H_{combustion[glucose]} = -2808\,KJ$ 

Sol.

**32.** Using the data given below, establish that the vaporization of  $CCl_4(l)$  298 K to produce  $CCl_4(g)$  at 1atm pressure does not occur spontaneously.

Given:  $CCl_4(l, 1atm) \rightarrow CCl_4(g 1 atm)$ ; potentia

 $\Delta S^{\circ} = 94.98 \text{ JK}^{-1} \text{ mol}^{-1}$ 

 $\Delta H_{f}^{0}$  (CCl<sub>4</sub>,g) = -106.7 kJ mol<sup>-1</sup>

&  $\Delta H_{f}^{0}$  (CCl<sub>4</sub>, l) = -139.3 kJ mol<sup>-1</sup>

Sol.



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 $Reaction: \ H_2O(g) + CO(g) \Longrightarrow \ H_2(g) + CO_2(g)$ 

- (i) Calculate  $\Delta_{\rm r} H_{298}^{^{\rm c}}$  (ii) Calculate  $\Delta_{\rm r} \ G_{298}^{^{\rm c}}$
- (iii) Calculate  $\Delta_{\rm r}\,{\sf S}_{298}^{\circ}$  (iv) Calculate  $\Delta_{\rm r}\,{\sf E}_{298}^{\circ}$
- (v) Calculate  $S_{298}^{\circ}[H_2O(g)]$

Sol.

**34.** At 298 K,  $\Delta H^{\circ}_{combustion}$  (sucrose) = -5737 KJ/mol,

$$\Delta G^{\circ}_{combustion}$$
 (sucrose) = -6333 KJ/mol.

Estimate additional non-PV work that is obtained by raising temperature to 310 K.

Assume  $\Delta_r C_P = 0$  for this temperature change Sol.



#### 35. From the given table answer the following questions

	CO(g)	CO <sub>2</sub> (g)	H <sub>2</sub> O(g)	H <sub>2</sub> (g)
ΔH° <sub>298</sub> (-KCal/mole)	-26.42	-94.05	-57.8	0
ΔG° <sub>298</sub> (-KCal/mole)	-32.79	-94.24	-54.64	0
S° <sub>298</sub> (-Cal/Kmole)	47.3	51.1	?	31.2

### **Exercise - IV**

- **1.**Calculate workdone in adiabatic compression of one mole of an ideal gas (monoatomic) from an initial pressure of 1atm to final pressure of 2 atm. Initial temperature = 300 K.
- (a) If process is carried out reversibly
- (b) If process is carried out irreversible against 2 atm external pressure.

Compute the final volume reached by gas in two cases and describe the work graphically.

**2.**0.5 mole each of two ideal gases  $A\left(C_v = \frac{3}{2}R\right)$  and

$$B\left(C_v = \frac{5}{2}R\right)$$
 are taken in a container and expanded

reversibly and adiabatically from V = 1 L to V = 4 L starting from initial temperature T = 300 K.

Find  $\Delta H$  for the process in (cal/mol).

- **3.**20.0 dm³ of an ideal gas (diatomic  $C_{v,m} = 5R/2$ ) at 673 K and 0.7 MPa expands until pressure of the gas is 0.2 MPa. Calculate q, w,  $\Delta U$  and  $\Delta H$  for the process if the expansion is :
- (i) Isothermal and reversible
- (ii) Adiabatic and reversible
- (iii) Isothermal and adiabatic
- (iv) Against 0.2 MPa and adiabatic
- (v) Against 0.2 MPa and isothermal.
- **4.** One mole of a ideal monoatomic gas ( $C_{v.m} = 1.5 \text{ R}$ ) is subjected to the following sequence of steps :
- (a) The gas is heated reversibly at constant pressure of 101.325 kPa from 298 K to 373 K.
- (b) Next, the gas is expanded reversibly and isothermally to double its volume.
- (c) Finally, the gas is cooled reversibly and adiabatically to  $308\ K.$

Calculate q, w,  $\Delta U$  and  $\Delta H$  for the overall process.

### **Subjective Level-II**

- **5.**2 mole of an ideal gas undergoes isothermal compression along three different paths
- (i) reversible compression from  $P_i = 2$  bar and  $V_i = 4$  L to  $P_f = 20$  bar
- (ii) a single stage compression against a constant external pressure of 20 bar, and
- (iii) a two stage compression consisting initially of compression against a constant external pressure of 10 bar until  $P_{gas} = P_{ext}$ , followed by compression against a constant pressure of 20 bar until  $P_{gas} = P_{ext}$ .

Calculate the work (in bar. L) for each of these processes and for which of the irreversible processes is the magnitude of the work greater  $?[Given: R = 0.08 \, bar.L/mole.K]$ 

**6.**Calculate the heat of vaporisation of water per gm at 25°C and 1 atm.

Given  $\Delta H_f^0[H_2O(l)] = -285.57 \text{ kJ/mol}$ 

$$\Delta H_f^0[H_2O(g)] = -241.6 \text{ kJ/mol}$$

Comment why  $\Delta H_{vap}(25^{\circ}C) > \Delta H_{vap}(100^{\circ}C)$ 

**7.**Given:  $\Delta_{\text{vap}}$  H at 373 K = 40.639 kJ mol<sup>-1</sup>,

 $C_{0}(H_{2}O, l) = 75.312 \text{ J K}^{-1} \text{ mol}^{-1},$ 

 $C_p(H_2O, g) = 33.305 \text{ J K}^{-1} \text{ mol}^{-1}.$ 

Pressure over 1000 ml of a liquid is gradually increases from 1 bar to 1001 bar under adiabatic conditions. If the final volume of the liquid is 990 ml, calculate  $\Delta U$  and  $\Delta H$  of the process, assuming linear variation of volume with pressure.

**8.** (a) An ideal gas undergoes a single stage expansion against a constant opposing pressure from  $(P_1, V_1, T)$  to  $(P_2, V_2, T)$ . What is the largest mass m which mass m which can be lifted through a height h in this expansion?

- (b) The system in (a) restored to initial state by a single compression. What is the smallest mass 'm' which must fall through the height h to restore the system? (c) What is the net mass lowered through height h in the cycle transformation in (a) and (b)?
- **9.**The vapour pressure of  $H_2O(\mathit{l})$  at 353 K is 532 mm Hg. The external pressure on  $H_2O(\mathit{l})$  taken in a cyclinder fitted with frictionless movable piston initially containing 0.9 L (= 0.9 kg) of  $H_2O(\mathit{l})$  at 353 K is increased to 1 atm. Temperature remained constant. Now, heat is supplied keeping pressure constant till 0.45 L of  $H_2O(\mathit{l})$  (= 0.45 kg) is evaporated to form  $H_2O(\mathit{g})$  at 373 K. Carefully observe the diagrams provided and from given data, answer the following questions.
- (a) $\Delta H$  when system is taken from state 1 to state 2 (Joule)?
- (b) Total change in  $\Delta U$  going from state 1 to 3 (kJ)?
- (c)Total change in enthalpy going from state 1 to state 3 (kJ) ?

Given: Specific heat of H<sub>2</sub>O = 4.2 J/gm °C

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

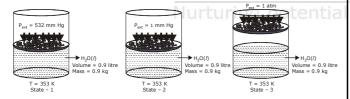
1 atm = 760 mm Hg

Use

1 L atm = 100 Joule

R = 8 Joule/mole K

(Assume internal energy of liquid to be dependent only on temperature).



**10.** Derive a mathematical expression for the work done on the surrounding when a gas that has the equation of state PV = nRT -  $\frac{n^2a}{V}$  expands reversibly from V<sub>i</sub> to V<sub>f</sub> at constant temperature.

- **11.** Calculate  $\Delta S_f^o$  at 298 K of ; (i) NaCl(s) , (ii) NH<sub>4</sub>Cl (s) & diamond The values of S° of Na, Cl<sub>2</sub>, NaCl, NH<sub>4</sub>Cl, N<sub>2</sub>, H<sub>2</sub>, diamond & graphite are 51, 223, 72, 95, 192, 131, 2.43 & 5.69 JK<sup>-1</sup> mol<sup>-1</sup> respectively.
- **12.** One mole of an ideal gas is expanded isothermally at 298 K until its volume is tripled. Find the values of  $\Delta S_{qas}$  and  $\Delta S_{total}$  under the following conditions.
- (i) Expansion is carried out reversibly.
- (ii) Expansion is carried out irreversibly where 836.8 J of heat is less absorbed than in (i)
- (iii) Expansion is free.
- **13.** The enthalpy change for vapourization of liquid 'A' at 200 K and 1 atm is 22 kJ/mol. Find out  $\Delta S_{\text{vapourisation}}$  for liquid 'A' at 200 K ? The normal Boiling point of liquid 'A' is 300 K.

A(l) [200 K, 1 atm]  $\rightarrow$  A(g) [200 K, 1 atm]

**Given :**  $C_{p,m}(A,g) = 30 \text{ J/mol-K}, C_{p,m}(A, l) = 40 \text{ J/mol-K}$ 

**Use:**  $\ln(3/2) = 0.405$ 

**14.** Pressure of 10 moles of an ideal gas is changed from 2 atm to 1 atm against constant external pressure without change in temperature. If surrounding temperature (300 K) and pressure (1 atm) always remains constant then calculate total entropy change  $(\Delta S_{\text{system}} + \Delta S_{\text{surrounding}})$  for given process.

[Use :  $\ell$ n2 = 0.70 and R = 8.0 J/mol/K]

**15.** Compute, Δ.G for the reaction

 $H_2O(l, 1 \text{ atm, } 323 \text{ K}) \rightarrow H_2O(g, 1 \text{ atm, } 323 \text{ K})$ 

Given that,  $\Delta_{\text{vap}}$  H at 373 K = 40.639 kJ mol<sup>-1</sup>, C<sub>p</sub> (H<sub>2</sub>O, l) = 75.312 J K<sup>-1</sup> mol<sup>-1</sup>,

 $C_p(H_2O, g) = 33.305 \text{ J K}^{-1} \text{ mol}^{-1}.$ 

### **Exercise - V**

JEE-Problems

**1.**Among the following, the state function(s) is (are)

(A) Internal energy

[JEE 2009]

(B) Irreversible expansion work

(C) Reversible expansion (D) Molar enthalpy

(C) -100 e.u. Sol.

(A) + 100 e.u.

(B) -60 e.u.(D) +60 e.u.

 $\Delta S (B \rightarrow D) = 20 \text{ e.u.}$  where e.u. is entropy unit.

Then the entropy change for the process  $\Delta S$  (A  $\rightarrow$  B) is:

[JEE 2006]

**2. Statement-I:** There is a natural asymmetry between converting work to heat and converting heat to work.

Statement-II: No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.

(A) Statement-I is True, Statement-II is True, **Statement-II** is a correct explanation for **Statement-I** 

(B) Statement-I is True, Statement-II is True, Statement-II is NOT a correct explanation for Statement-I (C) Statement-I is True, Statement-

**3.** For the process  $H_2O(l)$  (1 bar, 373 K)  $\rightarrow$   $H_2O$  (q) (1

bar, 373 K), the correct set of thermodynamic

(D) **Statement-I** is False, **Statement-II** is True Sol. [JEE 2008]

> 5. The molar heat capacity of a monoatomic gas for which the ratio of pressure and volume is one.

(A) 4/2 RSol.

(B) 3/2 R

(C) 5/2 R

(D) zero [JEE 2006]

(A)  $\Delta G = 0$ ,  $\Delta S = +ve$ 

parametes is

(C)  $\Delta G = +ve$ ,  $\Delta S = 0$ 

(B)  $\Delta G = 0$ ,  $\Delta S = -ve$ 

(D)  $\Delta G = -ve$ ,  $\Delta S = +ve$ Sol.

[JEE 2007]

**4.**A process A → B is difficult to occur directly instead it takes place in the three successive steps.

$$\Delta S (A \rightarrow C) = 50 \text{ e.u.}$$

$$\Delta S (C \rightarrow D) = 30 \text{ e.u.}$$



**6.**One mole of monoatomc ideal gas expands adiabatically at initial temp. T against a constant external pressure of 1 atm from one litre to two litre. Find out the final temp. (R = 0.0821 litre.)atm K<sup>-1</sup> mol<sup>-1</sup>):

(A) T (B) 
$$\frac{T}{(2)^{5/3-1}}$$
 (C)  $T - \frac{2}{3 \times 0.0821}$  (D)  $T + \frac{2}{3 \times 0.0821}$  **Sol.** [JEE 2005]

Sol. [JEE 2004]

- **7.**Two mole of an ideal gas is expanded isothermally and reversibly from 1 litre to 10 litre at 300 K. The enthalpy change (in kJ) for the process is (A) 11.4 kJ (B) -11.4 kJ (C) 0 kJ (D) 4.8 kJ Sol. [JEE 2004]
- 9. One mol of non-ideal gas undergoes change of state (2.0 atm, 3.0 L, 95 K) to (4.0 atm, 5.01, 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 (A) 40.0 (B) 42.3 (C) 44.0 (D) not defined, because pressure is not constant [JEE 2002] Sol.

8. The enthalpy of vapourization of a liquid is 30 kJ mol<sup>-1</sup> and entropy of vapourization is 75 J mol<sup>-1</sup> K. The boiling point of the liquid at 1 atm is (C) 450 K (D) 600 K

- 10. Which of the following statement is false?
- (A) Work is a state function
- (B) Temperature is a state function
- (C) Change of state is completely defined when initial and final states are specified.
- (D) Work appears at the boundary of the system **Sol.** [JEE 2001]

#### 11. For the reaction.

 $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$ ;  $\Delta H = -560 \text{ kJ mol}^{-1}$ 

In one litre vessel at 500 K the initial pressure is 70 atm and after the reaction it becomes 40 atm at constant volume of one litre. Calculate change in internal energy. All the above gases show significant deviation from ideal behaviour. (1 L atm =  $0.1 \, \text{kJ}$ ) Sol. [JEE 2006]

- **13.** Two moles of a perfect gas undergoes the following processes : [JEE 2002]
- (a) a reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L);
- (b) a reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L);
- (c) a reversible isothermal compression from (0.5 atm, 40.0L) to (1.0 atm, 20.0 L);
- (i) Sketch with labels each of the processes on the same P-V diagram.
- (ii) Calculate the total work (w) and the total heat change (q) involved in the above processes.
- (iii) What will be the values of  $\Delta U$ ,  $\Delta H$  and  $\Delta S$  for the overall process ?

Sol.

Nurturing potentia through education

**12.** One mole of a liquid (1 bar, 100 ml) is taken in an adiabatic container and the pressure increases steeply to 100 bar. Then at a constant pressure of 100 bar, volume decreases by 1 ml. Find  $\Delta U$  and  $\Delta H$  **Sol.** [JEE 2004]

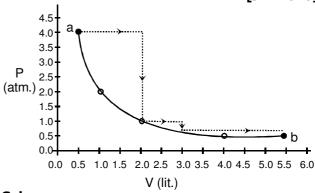


**14.** Show that the reaction  $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$  at 300 K is spontaneous and exothermic, when the standard entropy is -0.094 kJ mol<sup>-1</sup>K<sup>-1</sup>. The standard Gibbs free energies of formation for  $CO_2$  and CO are -394.4 and -137.2 kJ mol<sup>-1</sup>, respectively.

Sol. (JEE 2001)

**15.** A sample of argon gas at 1 atm pressure and 27° expands reversibly and adiabatically from 1.25 dm $^3$  to 2.50 dm $^3$ . Calculate the enthalpy change in this process.  $C_{v,m}$  for argon is 12.48 JK $^{-1}$  mol $^{-1}$ . **Sol.** [JEE 2000]

**16.** One mole of an ideal gas is taken from a to b along two paths denoted by the solid and the dashed lines as shown in the graph below. If the work done along the solid line path is  $w_s$  and that along the dotted line path is  $w_d$ , then integer closest to the ratio  $w_d/w_5$  is **[JEE 2010]** 



Sol.

**17.** Match the transformations in **Column-I** with appropriate options in **Column-II**. [JEE 2011]

#### Column-I

#### Column-II

- (A)  $CO_2(s) \rightarrow CO_2(g)$
- (P) Phase transition
- (B)  $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ 
  - (Q) allotropic change
- (C)  $2H^{\bullet} \rightarrow H_2(g)$  The parameter (R)  $\Delta H$  is positive

(D)  $P_{\text{(white.solid)}} \rightarrow P_{\text{(red, solid)}}$ (S)  $\Delta S$  is positive

ough education (T) ΔS is negative

Sol.

## **ANSWER-KEY**

### **Exercise-I**

1. С **2.** D

**3.** D

**4.** B **12.** C **5.** C

6. В **7.** C

8. A

9.

**10.** C

**11.** D

**13.** A

14. С **15.** C

**16.** D

**17.** A

18. A

**19.** B

**20.** C 21. A 22. C **23.** D

24. C

**25**. A

**26.** C

**27.** C

28. C

**29.** D

30. С **31.** D

**32.** D

**33.** D

**34.** D

**35.** D

**36.** A

**37.** B

38.

**39.** C

**40.** B

**41.** B

**42.** C

**43.** B

С

**44.** B

**45.** (A)  $\rightarrow$  P,R,S, (B)  $\rightarrow$  Q,R,S, (C)  $\rightarrow$  Q,R,S, (D)  $\rightarrow$  R,S

**46.** (A)  $\rightarrow$  S, (B)  $\rightarrow$  P,R (C)  $\rightarrow$  P,S, (D)  $\rightarrow$  P, R

**47.** (A)  $\rightarrow$  P,S, (B)  $\rightarrow$  P,R,S, (C)  $\rightarrow$  Q, (D)  $\rightarrow$  R,S

**48.** (A)  $\rightarrow$  Q, (B)  $\rightarrow$  P,S, (C)  $\rightarrow$  P,S, (D)  $\rightarrow$  S

**49.** (A)  $\rightarrow$  P,S,R (B)  $\rightarrow$  R, (C)  $\rightarrow$  P, (D)  $\rightarrow$  Q,R,S

### **Exercise-II**

A,B,D

**2.** A,C

3. B,C,D

**4.** A,C,D

**5.** A,C,D

6. A,B,C **7.** A,B,D

B,C,D

9. A,B,D

**10.** A,B

#### **Exercise-III**

(i) w, (ii) -w, (iii) -w, (iv) w, (v) -w1.

**2.** q = -65 J; w = 20 J;  $\Delta E = -45 J$ 

-0.3024 kJ 3.

4. (a) 0.47 gm, (b) 0.47 kg

**5.**  $\Delta E = 75.11 \text{ kJ}$ 

 $\Delta E = 0.993$  kcal,  $\Delta H = 1$  kcal 6.

7. -741.5 kJ

**8.**  $\Delta H \cong \Delta E = 1440$  calories

-10 J 9.

**10.**  $q = 177.9 \text{ kJ}, w = -2.5 \text{ kJ}; \Delta E = 175.4 \text{ kJ}$ 

**11.**  $\Delta E = -39.03 \text{ KJ/mole}$ ; q = -36.5 kJ; w = -2.53 kJ

**12.**  $\Delta U = W = -1247.1$ ;  $\Delta H = -1745.94$  J

**13.** (i) yes (ii) W = 0;  $Q = \Delta E = 6000 \text{ J}$ ;  $\Delta H = 9325.6 \text{ J}$ 

14. -1.683 kJ

**15.**  $T_2 = 100 \text{ K}$ ; w = 5.016 KJ

**16.** q = 0 ; w =  $\Delta U$  = 4.12 KJ;  $\Delta H$  = 5.37 KJ;  $V_r$  = 11.8 dm³ ; P = 5.21 atm

17.  $C_{v.m} = 31.6 \, J K^{-1} \, mol^{-1}$ 

**18.** w = -3.988 kJ

**19.**  $W = -P_0V_0$ ;  $q_{CA} = -\frac{5}{2}P^{\circ}V^{\circ}$ ;  $q_{AB} = 3P^{\circ}V^{\circ}$ ;  $q_{BC} = \frac{1}{2}P^{\circ}V^{\circ}T_{max} = \frac{25}{8}\left(\frac{P^{\circ}V^{\circ}}{P}\right)$ 

		i able - 1				
	State	Р	V	T		
20.	1	1 atm	22.4	273		
	2	2 atm	22.4	546		
	3	1 atm	44.8	546		

Step	Name of process	q	W	ΔΕ	ΔΗ
Α	Isochoric	3/2 R(273)	0	3/2 R (273)	5/2 R (273)
В	Isothermal	546 R In 2	–546 R In 2	0	0
С	Isobaric	-5/2 R (273)	R (273)	-3/2 R (273)	-5/2 R (273)

Ρ ٧ State Т 22.4 273 1 atm 21. 2 1 44.8 546 0.5 44.8 273

_					
Step	Name of process	q	w	ΔΕ	ΔН
Α	Isobaric	5/2 R(273)	– R (273)	3/2 R (273)	5/2 R (273)
В	Isochoric	-3/2 R (273)	0	-3/2 R (273)	-5/2 R (273)
С	Isothermal	–273 R ln 2	273 R In 2	0	0
	Cyclic	R(273) – 273 R In 2	– R (273) – Rln 2	0	0

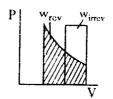
- **22.** (a)  $T_1 = 243.60 \text{ K}$ ;  $T_2 = 2436.0 \text{ K}$ , (b)  $\Delta E = 0$ ; q = -w = +3262.88 cal
- 23. (a) AC, (b) 170 J, (c) 10 J
- **24.** (a) 600 K, (b)  $q_{AB} = 3000 \text{ cal}$ ;  $q_{BC} = 1663 \text{ cal}$ ;  $q_{CD} = -1800 \text{ cal}$ ;  $q_{DA} = -1663 \text{ cal}$ ; Total q = 1200 cal, (c) w = -1200 cal
- **25.**  $\Delta H_{373}^{\circ} (H_2O(l)) = -284.11 \text{ kJ}$  **26.** (a) 13.064 kJ mol<sup>-1</sup>, (b) 10.587 kJ mol<sup>-1</sup>
- **27.** T = 1059 K
- 28. 21.18 JK-1 mol-1
- 29. (i) irreversible, (ii) reversible, (iii) impossible (Where Faith Counts the Success)
- **30.** 205.08 JK<sup>-1</sup> mol<sup>-1</sup>
- **31.** –1721.8 J
- **32.**  $\Delta G^{\circ} = 4.3 \text{ kJ mol}^{-1}$
- 33. -2864.5 KJ

- **34.** 24 kJ/mol
- 35. (i) -9.83 Kcal/mole. (ii) -6.81 Kcal/mole, (iii) -10.13 Cal/Kmole, (iv) -9.83 Kcal/mole
  - (v) +45.13 Cal/Kmole

### **Exercise-IV**

(a)  $T_2 = 395.8$ ;  $V_2 = 16.24 L$ ;  $W_{rev} = 1194.72 J$ ,

(b) 
$$V_2' = 17.24 L$$
;  $T_2' = 420 K$ ,  $W_{irrev} = 1496.52 J$ 



- 2. - 900 calories
- 3. (i) q = -w = 17.54 kJ,  $\Delta U = 0$  and  $\Delta H = 0$ ; (ii) q = 0,  $w = \Delta U = -10.536 \text{ kJ}$  and  $\Delta H = -14.75 \text{ kJ}$ (iii) q = 0, w = 0,  $\Delta U = 0$  and  $\Delta H = 0$  (iv) q = 0;  $\Delta U = w = -7.14$  KJ;  $\Delta H = -9.996$  KJ, (v)  $q = -w = 10.0 \text{ KJ}, \Delta U = \Delta H = 0$
- (a)  $q = \Delta H = 1558.88$ ,  $\Delta U = 935.33$ ;  $w = -P(\Delta U) = -623.55 \text{ J mol}^{-1}$ 
  - (b) w = -2149.7;  $\Delta U \& \Delta H = 0$ , q = -w
  - (c) q = 0, w = -810.62,  $\Delta H = -1351.03$  Jmol<sup>-1</sup>

for overall process q = 3708.59; w = -3583.88,  $\Delta U = 124.71$ ;  $\Delta H = 207.85$ 

- 5. (i) 18.424 bar. L; (ii) 72 bar. L; (iii) 40 bar L. Magnitude of work is maximum in single stage compression
- 6.  $\Delta H_{van}(25 \,^{\circ}\text{C}) = 43.97 \,\text{kJ/mol} = 2.433 \,\text{kJ/gm}, \Delta H_{van}(100 \,^{\circ}\text{C}) = 40.62 \,\text{KJ/mol} \,(\text{given})$
- 7.  $\Delta U = 501 \text{ J}; \Delta H = 99.5 \text{ kJ}$
- (a)  $m = \frac{nRT}{gh} \left( 1 \frac{P_2}{P_1} \right)$ , (b)  $m' = \frac{nRT}{gh} \left( \frac{P_1}{P_2} 1 \right)$  (c)  $m' m = \frac{nRT}{gh} \left( \frac{(P_1 P_2)^2}{P_1 P_2} \right)$
- (a) 27 Joule, (b) 1001 kJ, (c) 1075.627 kJ
- **10.**  $w = -nRT / n \frac{V_f}{V_i} n^2 a \left( \frac{1}{V_f} \frac{1}{V_i} \right)$

# **Exercise-V**

(Where Faith Counts the Success)

- 1. A,D
- **2**. A
- **3.** A
- D
- **5.** A
- 6. С
- **7.** C

- В
- 9. C
- 10. A
- 11. -557 kJ/mol
- **12.**  $\Delta U = 0.1$  litre atm,  $\Delta H = 9.9$  litre atm
- **13.** (ii) -w = q = 620.77 J, (iii)  $\Delta H = 0$ ,  $\Delta U = 0$ ,  $\Delta S = 0$
- **14.**  $\Delta H^{\circ} = -285.4 \text{ kj/mol}, \Delta G^{\circ} = -257.2 \text{ kj/mol}$
- **15.** ∆H ≃ −115 J
- **16.** 0002

17. A-PRS, B-RS, C-T, D-QR