### **THERMODYNAMICS**

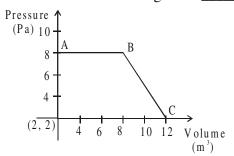
**1.** For the reaction;

$$A(l) \rightarrow 2B(g)$$

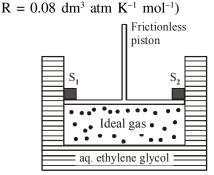
 $\Delta U = 2.1 \text{ kcal}$ ,  $\Delta S = 20 \text{ cal } K^{-1} \text{ at } 300 \text{ K}$ 

Hence  $\Delta G$  in kcal is\_\_\_\_\_.

2. The magnitude of work done by a gas that undergoes a reversible expansion along the path ABC shown in the figure is \_\_\_\_\_



- 3. At constant volume, 4 mol of an ideal gas when heated from 300 K to 500K changes its internal energy by 5000 J. The molar heat capacity at constant volume is \_\_\_\_\_.
- **4.** The true statement amongst the following is:
  - (1) Both  $\Delta S$  and S are functions of temperature.
  - (2) S is not a function of temperature but  $\Delta S$  is a function of temperature.
  - (3) Both S and  $\Delta$ S are not functions of temperature.
  - (4) S is a function of temperature but  $\Delta S$  is not a function of temperature.
- 5. A cylinder containing an ideal gas (0.1 mol of  $1.0 \text{ dm}^3$ ) is in thermal equilibrium with a large volume of 0.5 molal aqueous solution of ethylene glycol at its freezing point. If the stoppers  $S_1$  and  $S_2$  (as shown in the figure) are suddenly withdrawn, the volume of the gas in litres after equilibrium is achieved will be\_\_\_\_. (Given,  $K_f$  (water) = 2.0 K kg mol<sup>-1</sup>,



- **6.** Five moles of an ideal gas at 1 bar and 298 K is expanded into vacuum to double the volume. The work done is:-
  - (1)  $C_v(T_2 T_1)$
- (2)  $-RT \ln V_2/V_1$
- (3)  $-RT(V_2 V_1)$
- (4) zero
- 7. For one mole of an ideal gas, which of these statements must be true?
  - (a) U and H each depends only on temperature
  - (b) Compressibility factor z is not equal to 1
  - (c)  $C_{P,m} C_{Vm} = R$
  - (d)  $dU = C_V dT$  for any process
  - (1) (a), (c) and (d)
- (2) (b), (c) and (d)
- (3) (c) and (d)
- (4) (a) and (c)
- **8.** For a dimerization reaction,

$$2 A(g) \rightarrow A_2(g)$$

at 298 K,  $\Delta U^{\odot}$ , = - 20kJ mol<sup>-1</sup>,  $\Delta S^{\odot}$  = -30 J

 $K^{-1}$  mol<sup>-1</sup>, then the  $\Delta G^{\odot}$  will be \_\_\_\_\_J.

9. The internal energy change (in J) when 90g of water undergoes complete evaporation at 100°C is \_\_\_\_.

(Given :  $\Delta H_{\text{vap}}$  for water at 373 K = 41 kJ/mol, R = 8.314 JK<sup>-1</sup> mol<sup>-1</sup>)

10. The Gibbs energy change (in J) for the given reaction at  $[Cu^{2+}] = [Sn^{2+}] = 1$  M and 298K is:  $Cu(s) + Sn^{2+}$  (aq.)  $\rightarrow Cu^{2+}$  (aq.) + Sn(s);

$$(E^0_{Sn^{2+}|Sn} = -0.16V, \, E^0_{Cu^{2+}|Cu} = 0.34V, \,$$

Take  $F = 96500 \text{ C mol}^{-1}$ 

**11.** The variation of equilibrium constant with temperature is given below:

## Temperature

#### **Equilibrium constant**

$$T_1 = 25^{\circ}C$$

$$K_1 = 100$$

 $T_2 = 100^{\circ}C$ 

$$K_2 = 100$$

The values of  $\Delta H^o$ ,  $\Delta G^o$  at  $T_1$  and  $\Delta G^o$  at  $T_2$  (in kJ mol<sup>-1</sup>) respectively, are close to

[Use  $R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$ ]

- (1) 0.64, -5.71 and -14.29
- (2) 28.4, -7.14 and -5.71
- (3) 28.4, -5.71 and -14.29
- (4) 0.64, -7.14 and -5.71

#### 2

#### **SOLUTION**

- 1. NTA Ans. (-2.70 to -2.71)
- Sol.  $A(\ell) \longrightarrow 2B(g)$

$$\Delta U$$
 = 2.1 Kcal ,  $\Delta S =$  20 cal  $K^{-1}~$  at 300 K

$$\Delta H = \Delta U + \Delta n_{g}RT$$

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

$$\Delta G = \Delta U + \Delta n_{\sigma} RT - T\Delta S$$

$$=2.1+\frac{2\times2\times300}{1000}-\frac{300\times20}{1000}$$

$$(R = 2 \text{ cal } K^{-1} \text{ mol}^{-1})$$

$$= 2.1 + 1.2 - 6 = -2.70 \text{ Kcal/mol}$$

- 2. NTA Ans. (48.00)
- Sol. Area enclosed under

$$P V curve = 48 = 48 Joule$$

- 3. NTA Ans. (6.25)
- **Sol.** For ideal gas:

$$\Delta U = nC_V[T_2 - T_1] \Rightarrow 5000 = 4 \times C_V[500 - 300]$$

$$\Rightarrow$$
  $C_v = \frac{5000}{800} = 6.25 \text{ J mole}^{-1} \text{ K}^{-1}$ 

4. NTA Ans. (1)

**Sol.** ds = 
$$\int \frac{q_{rev.}}{T}$$

5. NTA Ans. (2.17 to 2.23)

**Sol.** 
$$0 - T_f' = 2 \times 0.5 = 1$$

$$T_f' = -1^{\circ}C = 272 \text{ K}$$

for gas 
$$P = \frac{0.1 \times 0.08 \times 272}{1}$$

$$P = 2.176 \text{ atm}$$

$$P_1V_1 = P_2V_2$$

$$2.176 \times 1 = 1 \times V_2$$

$$V_2 = 2.176$$
 litre

- 6. Official Ans. by NTA (4)
- **Sol.** As the expansion is done in vaccum that is in absence of  $p_{ext}$  so

$$W = zero$$

- 7. Official Ans. by NTA (1)
- **Sol.** For ideal Gas

$$\# U = f(T), H = f(T)$$

$$\# Z = 1$$

$$\# C_P - C_V = R$$

$$\# dU = C_V dT$$

# 8. Official Ans. by NTA (-13538.00) Official Ans. by ALLEN (-13537.57)

**Sol.** 
$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$= (\Delta U^{\circ} + \Delta n_{g}RT) - T\Delta S^{\circ}$$

$$= \left[ \left\{ -20 + (-1)\right\} \frac{8.314}{1000} \times 298 \right\} - \frac{298}{1000} \times (-30) \right] \text{kJ}$$

$$= -13.537572 \text{ kJ}$$

$$= -13537.57$$
 Joule

9. Official Ans. by NTA (189494.00) Official Ans. by ALLEN (189494.39)

**Sol.** 
$$H_2O(\ell) \rightleftharpoons H_2O(g)$$
 90 gm of  $H_2O$   
 $\Delta H = \Delta U + \Delta n_g RT$   $\Rightarrow$  5 moles of  $H_2O$   
 $5 \times 41000 J = \Delta U + 1 \times 8.314 \times 373 \times 5$ 

10. Official Ans. by NTA (96500.00)

 $\Delta U = 189494.39$  Joule

**Sol.** 
$$\Delta G = \Delta G^{\circ} + RT \ln \left[ \frac{Sn^{+2}}{Cu^{+2}} \right]$$

= 
$$-2 \times 96500 [(-0.16) - 0.34] + RT ln  $\left(\frac{1}{1}\right)$   
=  $96500 J$$$

#### 11. Official Ans. by NTA (3)