

2013

CHEMISTRY

(Major)

Paper : 1.1

Full Marks : 60

Time : 2½ hours

*The figures in the margin indicate full marks
for the questions*

1. (a) Internal energy of n mol of a monatomic gas at temperature T is given by

$$U = U(0) + \frac{3}{2} nRT$$

where $U(0)$ is the internal energy at 0 K.
What is the constant volume heat capacity of the gas? 1

- (b) Which of the following laws gives a formal definition of 'temperature'? 1
- (i) Kirchhoff's law
 - (ii) Hess's law
 - (iii) Third law of thermodynamics
 - (iv) Zeroth law of thermodynamics

- (c) Give the mathematical formulation of the first law of thermodynamics and explain the sign convention. 2
2. (a) State the second law of thermodynamics in terms of entropy. 1
- (b) Consider the following gas phase reaction equilibrium :
- $$2\text{NO}_2 (\text{g}) \rightarrow \text{N}_2\text{O}_4 (\text{g}); \Delta H < 0$$
- Decomposition of N_2O_4 can be favoured by which one of the following? 1
- (i) Lowering the temperature
- (ii) Increasing the pressure
- (iii) Introducing an inert gas at constant volume
- (iv) Introducing an inert gas at constant pressure
- (c) Calculate the entropy change for 1.00 mol of water undergoing reversible vaporization at 100°C . Enthalpy of vaporization of water at 100°C is $40.656 \text{ kJ mol}^{-1}$. 2
3. (a) Rate of formation of C in the reaction $2\text{A} + \text{B} \rightarrow 2\text{C} + 3\text{D}$ is $1.0 \text{ mol L}^{-1} \text{ s}^{-1}$. What is the rate of the reaction? 1

(b) Order of the catalytic decomposition reaction of phosphine (PH_3) on hot tungsten at high pressure is

(i) 1

(ii) 2

(iii) 0

(iv) 3 (Choose the correct one) 1

(c) Give one example each of consecutive and concurrent elementary reactions. 2

4. Answer any two : $3 \times 2 = 6$

(a) Discuss the Born-Haber cycle, taking a suitable example.

(b) The standard enthalpy of combustion of propane gas is $-2220 \text{ kJ mol}^{-1}$ and the standard enthalpy of vaporization of the liquid propane is $+15 \text{ kJ mol}^{-1}$. Calculate (i) the standard enthalpy and (ii) the standard internal energy of combustion of the liquid.

(c) Derive the following fundamental equations of thermodynamics :

(i) $dU = T dS - p dV$

(ii) $dH = T dS + V dp$

(iii) $dG = V dp - S dT$

5. Answer any two :

3×2=6

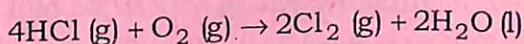
(a) For a reversible process occurring in a closed system, entropy change is defined as $ds = \frac{dq_{\text{rev}}}{T}$. Can we adapt

this definition as $ds_{\text{surr}} = \frac{dq_{\text{surr}}}{T_{\text{surr}}}$ to

calculate entropy change in the surroundings? Justify your answer.

(b) For isothermal irreversible free expansion of a perfect gas from V_1 to V_2 , show that total entropy change of the universe is always greater than zero.

(c) Calculate the standard Gibbs' energy of the reaction



at 298 K using the following data :

$$\Delta_f H^\circ (\text{HCl, g}) = -92.31 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ (\text{H}_2\text{O, l}) = -285.83 \text{ kJ mol}^{-1}$$

$$S_m^\circ (\text{HCl, g}) = 186.91 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$S_m^\circ (\text{H}_2\text{O, l}) = 69.91 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$S_m^\circ (\text{Cl}_2, \text{g}) = 223.07 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$S_m^\circ (\text{O}_2, \text{g}) = 205.1 \text{ JK}^{-1} \text{ mol}^{-1}$$

6. Answer any two :

3×2=6

- (a) For a zero-order reaction $A \rightarrow P$, find an expression for the variation of concentration of A with time. Using this expression, draw a diagram to show how $[A]$ will change with time.
- (b) Discuss the mode of action of a homogeneous catalyst, taking a suitable example.
- (c) The activation energy of a certain uncatalyzed reaction at 300 K is 76 kJ mol^{-1} . The activation energy is lowered to 57 kJ mol^{-1} by the use of a catalyst. By what factor is the rate of the reaction increased in the presence of catalyst?

7. Answer any two :

5×2=10

- (a) A sample consisting of 2.00 mol He is expanded isothermally at 0°C from 22.4 L to 31.7 L, (i) reversibly and (ii) against a constant external pressure equal to the final pressure of the gas. For the two processes, calculate q , w , ΔU and ΔH .

- (b) Discuss the variation of internal energy with temperature under various conditions of volume and pressure deriving the appropriate relations.
- (c) Show that Joule-Thomson coefficient of a van der Waals' gas is given by

$$\mu = \frac{1}{C_p} \left[\frac{2a}{RT} - b \right]$$

Hence obtain an expression for the inversion temperature.

8. Answer any two :

5×2=10

- (a) For the ideal gas reaction equilibrium $A \rightleftharpoons B$, derive the relation

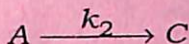
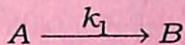
$$\Delta_r G^\circ = - RT \ln K$$

- (b) Derive Gibbs-Duhem equation and show that intensive variables of a system are not independent.
- (c) For reversible adiabatic expansion of n mol of a perfect gas, find expressions for w , ΔU and ΔH and show that $TV^\gamma = \text{constant}$.

9. Answer any two :

5×2=10

(a) For the concurrent elementary reactions



show that

$$(i) \ln \frac{[A]_0}{[A]} = (k_1 + k_2)t$$

where $[A]_0$ is the concentration of A at time $t = 0$.

$$(ii) \frac{[B]}{[C]} = \frac{k_1}{k_2}$$

(b) For the Michaelis-Menten mechanism of

enzyme action $E + S \xrightleftharpoons[k_{-1}]{k_1} ES \xrightarrow{k_2} P$, the

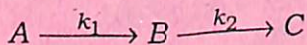
rate law is given by $v = \frac{k_2 [E]_0 [S]_0}{[S]_0 + K_M}$,

where $K_M = \frac{k_2 + k_{-1}}{k_1}$ is Michaelis

constant. Answer the following questions :

(i) Show that enzyme reaction is of first-order and zero-order with respect to low and high initial concentration of S respectively.

- (ii) What type of graph is expected between the rate and $[S]_0$?
- (iii) Show that if $k_2 \ll k_{-1}$, K_M represents the dissociation constant for ES .
- (c) For the consecutive first-order elementary reaction



concentration of B is given by

$$[B] = [A]_0 \left(\frac{k_1}{k_2 - k_1} \right) \{ e^{-k_1 t} - e^{-k_2 t} \}$$

At what time will product B be present in greatest concentration? Calculate the maximum concentration of B .
