2019

CHEMISTRY

(Honours)

Paper : CEMH-DC-T2

(Physical)

[CBCS]

Full Marks : 25   Time : Two Hours

The figures in the margin indicate full marks.

Group - A

1. Answer any *five* questions :   1×5=5

(a) At 298K the rate constant of a reaction is $1.6 \times 10^{-6} s^{-1}$. If the activation energy of the reaction is zero then the rate constant at 308K is —

(i) $0\ s^{-1}$

(ii) $1.6 \times 10^{-6}\ s^{-1}$

(iii) $3.2 \times 10^{-6}\ s^{-1}$

(iv) $4.8 \times 10^{-6}\ s^{-1}$

P.T.O.

(b) If $\left(\dfrac{ab}{v^2}\right)$ is negligible, the second virial coefficient 'B' in virial equation is —
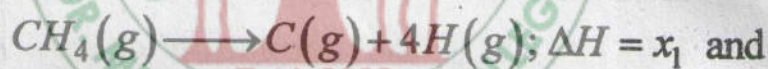
(i) $\left(b - \dfrac{a}{RT}\right)$

(ii) $\left(b + \dfrac{a}{RT}\right)$

(iii) $\left(b + \dfrac{a}{RTV}\right)$

(iv) $\left(b - \dfrac{a}{RTV}\right)$

(c) For the reactions :

$$CH_4(g) \longrightarrow C(g) + 4H(g); \Delta H = x_1 \text{ and}$$

$$C_2H_6(g) \longrightarrow 2C(g) + 6H(g); \Delta H = x_2$$

then bond energy of $C - C$ bond is,

(i) $x_1 - x_2$

(ii) $x_2 - x_1$

(iii) $x_2 + 1.5x_1$

(iv) $x_2 - 1.5x_1$

(3)

(d) For $A \longrightarrow B$, $\Delta H = 4$ kcal.mol^{-1}, $\Delta S = 11$ cal. k^{-1}.mol^{-1}. At what temperature, the reaction would be spontaneous?

    (i) 400K

    (ii) 300K

    (iii) 500K

    (iv) None of these

(e) Which is not an equation of state?

    (i) $\left(\dfrac{\partial H}{\partial P}\right)_T = V - T\left(\dfrac{\partial V}{\partial T}\right)_P$

    (ii) $\left(\dfrac{\partial U}{\partial V}\right)_T = T\left(\dfrac{\partial P}{\partial T}\right)_V - P$

    (iii) $PV = RT$

    (iv) $PV^\gamma = K$

(f) For a given $[E]_0$, enzyme concentration and low values of $[S]_0$, substrate concentration, the rate of formation of product is proportional to

    (i) $[E]_0$

    (ii) Independent of $[S]_0$

    (iii) Reached a maximum velocity

    (iv) $[S]_0$

P.T.O.

1/32-500

(4)

(g) The Maxwell Relation for the equation $dU = TdS - PdV$, is,

(i) $\left(\dfrac{\partial S}{\partial V}\right)_T = \left(\dfrac{\partial P}{\partial T}\right)_V$

(ii) $\left(\dfrac{\partial V}{\partial T}\right)_P = -\left(\dfrac{\partial S}{\partial P}\right)_T$

(iii) $\left(\dfrac{\partial T}{\partial V}\right)_S = -\left(\dfrac{\partial P}{\partial S}\right)_V$

(iv) $\left(\dfrac{\partial T}{\partial P}\right)_S = \left(\dfrac{\partial V}{\partial S}\right)_P$

(h) Carnot cycle is applicable for,

(i) Ideal gas

(ii) Gas-oil

(iii) Real gas

(iv) All substances

2. Answer any *four* questions : 2×4=8

(a) State the half life method for the determination of order of a reaction.

(b) Plot $\dfrac{dN_c}{Ndc}$ vs. c at (i) $T = 0k$. and (ii) $T = \infty K$ (symbols have their usual significance).

(c) A first order reaction never completes — Justify.

(d) Show that a van der Waals' gas behaves ideally at high temperature and low pressure.

(e) How much heat is necessary to convert 0.5kg of ice at $0°C$ to water vapour at $100°C$? Given $\Delta H_{fusion} = 80 \text{ kcal.kg}^{-1}$, $\Delta H_{vap} = 540 \text{ kcal.kg}^{-1}$, and heat capacity $= 1.00 \text{ kcal.k}^{-1}.\text{kg}^{-1}$.

(f) Show that $C_P - C_V = T\left(\dfrac{\partial P}{\partial T}\right)_V \left(\dfrac{\partial V}{\partial T}\right)_P$

(g) Find the value of $\int\limits_{0}^{\infty} e^{-x} \cdot dx$ using gamma function.

(h) Show that for an ideal gas

$$\left(\dfrac{\partial P}{\partial V}\right)_T \left(\dfrac{\partial V}{\partial T}\right)_P \left(\dfrac{\partial T}{\partial P}\right)_V = -1$$

P.T.O.

(6)

3. Answer any *two* questions : 6×2=12

   (a) (i) For the reversible adiabatic expansion of an ideal gas, show that PV^{γ} = constant.

     (ii) Two moles of an ideal monoatomic gas is heated at constant pressure from $27°C$ to $127°C$. Calculate work done (w), heat change (q), internal energy change (ΔU), change in enthalpy (ΔH) of the system in SI unit. 3+3=6

   (b) (i) Show that mixing of two ideal gases is always spontaneous. Also show that entropy change (ΔS) will be maximum when the gases are mixed in equimolar ratio.

     (ii) One mole of ice at $0°C$ is converted to vapour at $100°C$. Determine the entropy change (ΔS) of the process in *SI* unit. Given L_{fus} = 334.88 J.gm^{-1}, L_{vap} = 2247.9 J.gm^{-1}, S = 4.186 J.$gm^{-1}.k^{-1}$. 3+3=6

   (c) A substrate is simultaneously catalysed by H^+ and OH^- ions. The reaction in 1st order with restpect to the substrate concentration, $[H^+]$ and $[OH^-]$.

     (i) Depict the rate equation for the reaction.

     (ii) Mention the overall order of the reaction.

(iii) Show that the rate is minimum when

$$[H^+] = \left[\frac{k_{OH^-}}{k_{H^+}} \cdot k_W\right]^{\frac{1}{2}}$$
                                    1+1+4=6

(d) (i) Arrive at the adiabatic reversible T–V relationship.

(ii) Show that $C_P - C_V = \dfrac{\alpha^2 VT}{\beta}$ where

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \text{ and } \beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

(iii) For the reaction : $\frac{1}{2}N_2 + \frac{3}{2}H_2 = 2NH_3$,

$\Delta U(298K) = -43\,kJ/mol$. Find ΔH at 298 K assuming ideal behaviour.   2+2+2=6