ENGINEERING CHEMISTRY—2006

Time Allowed : 3 Hours *Full Marks : 70*

Group–A

(Multiple Choice Questions)

1. Choose the correct alternatives for any ten of the following : 10 × 1 = 10

(i) $[Co(NH_3)_5Br]\ SO_4$ and $[Co(NH_3)_5SO_4]\ Br$ are example of
(a) Geometrical (b) optical
(c) linkage (d) ionization isomers.

(ii) Free radicals take part in
(a) addition (b) substitution (c) elimination (d) disproportionate reactions.

(iii) The time required to reduce the concentration of a reactant from 0.02M to 0.01M is 15 sec and from 0.01M to 0.005M is also 15 sec. The order of the reaction is
(a) zero (b) one (c) two (d) three.

(iv) Cellulose acetate is a
(a) natural polymer (b) synthetic polymer (c) semisynthetic polymer (d) thermosetting polymer.

(v) The polydispersity index of a commercial polymer is
(a) 1.0 (b) 5.0 (c) 50.0 (d) 100.

(vi) During mixing entropy
(a) increases (b) decreases (c) remains unchanged (d) cannot be predicted.

(vii) The unit of equivalent conductance is
(a) $ohm^{-1}\ cm^2/gm\text{-}eqv$ (b) $ohm^{-1}\ m^2/gm\text{-}eqv$
(c) $ohm^{-1}\ cm^{-1}$ (d) $ohm^{-1}\ m^{-1}$.

(viii) Monomer unit presnt in natural rubber is
(a) 1, 3-butadiene (b) 2-methyl-1, 3-butadiene
(c) 2-ethyl-1, 3-butadiene (d) 2-chloro-1, 3-butadiene.

(ix) Hydrolysis of ethyl acetate follows the
(a) second order reaction kinetics
(b) first order reaction kinetics
(c) zero order reaction kinetics
(d) pseudo first order reaction.

(x) By proximate analysis we can determine
(a) the moisture content of coal only (b) the moisture content and ash content only (c) the moisture content, volatile matter, ash & fixed carbon contents of coal (d) the moisture content, volatile matter and fixed carbon of coal.

(xi) The relation between HCV and LCV will be
(a) HCV = LCV (b) HCV > LCV
(c) HCV < LCV (d) no relation exists.

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(xii) The presence of hydrogen atom attached to an aromatic ring may be identified by which of the following spectroscopies?

(a) UV-Vis (b) IR (c) NMR (d) EPR.

Ans. 1.(i)(d) ; (ii)(a) ; (iii)(b) ; (iv)(c) ; (v)(a) ; (vi)(a) ; (vii)(a) ; (viii)(b) ; (ix)(d) ; (x)(c) ; (xi)(b) ; (xii)(c).

Group-B

(Short Answer Questions)

Note : (i) Each answer should not exceed 50 words.

(ii) Write short notes on any three of the following. 3 × 5 = 15

2. (a) Prove that for an adiabatic reversible process, PV^{γ} = constant.

(b) Show that for an ideal gas $C_p - C_v = R$.

Ans. (a). Same as Question No. 2.(b), 2005

Soln. : (b). We know $C_P = \frac{dH}{dT}$ ....(i), and $C_V = \frac{dE}{dT}$ ....(ii)

[C_p = Heat capacity at constant pressure; C_v = Heat capacity at constant volume ; H = Enthalpy ; E = Internal energy]

By definition H = E + PV for one mole of an ideal gas.

or, H = E + RT (∵ PV = RT)

Differentiating w.r.t. temperature, T, we get, $\frac{dH}{dT} = \frac{dE}{dT} + R$

or, $C_p = C_v + R$ [By using equations (i) & (ii)]

$C_p - C_v = R$ **(Proved).**

3. The standard reduction potential for the electrode Sn^{4+}, Sn^{2+} is 0.16 volt and that for Fe^{3+}, Fe^{2+} electrode is 0.77 volt. Write the cell reaction and calculate the value of the equilibrium constant of the reaction at 25°C.

Ans. $S_n^{2+}/S_n^{4+}//F_e^{3+}/F_e^{2+}$

$$E^0_{cell} = E^0_{oxd^n}(\text{anode}) + E^o_{red^n}(\text{cathode})$$

$$= E^0_{Sn^{2+}/sn^{4+}} + E^0_{Fe^{3+}/Fe^{2+}}$$

$$= E^o_{Fe^{3+}/Fe^{2+}} - E^0_{sn^{4+}/sn^{2+}}$$

$$= 0.77 - 0.16 = 0.61V.$$

$Sn^{2+} - 2e \rightleftharpoons Sn^{4+}$

$Fe^{3+} + e \rightleftharpoons Fe^{2+}$

$Sn^{2+} - 2e \rightleftharpoons Sn^{4+}$

$2Fe^{3+} + 2e \rightleftharpoons 2Fe^{2+}$

$Sn^{2+} + 2Fe^{3+} \rightleftharpoons Sn^{4+} + 2Fe^{2+}$

$$E^{o}_{cell} = \frac{2\cdot303RT}{\eta F}\log k = \frac{0\cdot059}{2}\log k$$

$$0\cdot61 = \frac{0\cdot059}{2}\log k \,;\ \log k = \frac{1\cdot22}{0\cdot059} = 20\cdot67$$

$\therefore$ k = $10^{20.67}$ = 4.68 **Ans.**

4. State Kohlrausch's law of independent migration of ions ad show how this law is utilized to determine the equivalent conductance of acetic acid at infinite dilution.

Soln. : Kohlrausch's law : Same as Question No. 9.(b), 2005.

Kohlrausch's law has provided a method for finding the Λ_m^{∞} for weak electrolytes from Λ_m^{∞} measurements of strong electrolytes. Suppose we want to determine the equivalent conductance of acetic acid at infinite dilution. This value can be obtained from Λ_m^{∞} values of HCl, NaCl and CH_3COONa (all strong electrolytes). By Kohlransch's law we have :

$$\Lambda_m^{\infty}(HCl) + \Lambda_m^{\infty}(CH_3COONa) - \Lambda_m^{\infty}(NaCl)$$

$$= \left[\lambda^{\infty}(H^+) + \lambda^{\infty}(cl^-)\right] + \left[\lambda^{\infty}(CH_3COO^-) + \lambda^{\infty}(Na^+)\right] - \left[\lambda^{\infty}(Na^+) + \lambda^{\infty}(c\,l^-)\right]$$

$$= \left[\lambda^{\infty}(H^+)\right] + \lambda^{\infty}(CH_3COO^-) = \Lambda_m^{\infty}(CH_3COOH)$$

The value of Λ_m^{∞} for HCl, CH_3COONa & NaCl can be obtained by extrapolation of $\Lambda_m^{\infty} - \sqrt{c}$ graphs. So by applying Kohlrausch's we can determine the equivalent conductance of acetic acid.

5. What is entropy? What is its physical significance? Explain what you understand by internal energy of a system.

Soln. : Entropy : Entopy is a thermodynamic state quantity that is a measure of the randomness or disorder of the molecules of the system.

Physical significance : The symbol of entropy is 'S', which the change in disorder accompanying a process from start to completion is represented by ΔS. The entropy of a system is a state function and depends only out the initial and final states of the system. The change in entropy, ΔS, for any process is given by he equation,

$$\Delta S = S_{final} - S_{initial}$$

when s find > s initial, ΔS is + ve.

Internal energy : The total of all the possible kinds of energy of a system is called its internal energy. Hence internal energy of a system is a state function i.e. is independent of the path by which it is obtained.

Since the value of internal energy of a system depends on the mass of the matter contained in a system, it is classed as an extensive property.

1st laws of thermodynamics starts that the total energy of an isolated system remains constant though it may change from one form to another.

When a system is changed from state A to state B, it indergoes a change in the internal energy from E_A to E_B, so we can write

$$\Delta E = E_B - E_A$$

This energy change is brought about by the evolution or absorption of heat and / or by work being done by the system. Become the total energy of the system must remain constant.

∴ mathematical statement $\Delta E = q - w$.

w = work done by the system.

q = the amount of heat supplied to the system.

6. What is LPG? Why is it used as a domestic fuel? Define octane number of a fuel and explain how the octane number can be improved.

Soln. : LPG : Liquid Petroleum Gas (LPG) or bottled gas or refinery gas is obtained as a by-product, during the cracking of heavy oils or from natural gas. LPG is dehydrated, desulphurised and traces of odorous organic sulphides (mercaptans) are added to give waring of gas leak. Its calorific value is about 27,800 K cal/m^3.

It is used as a domestic fuel due to following reason :

(i) High efficiency and heating rate. The calorific value is roughly 3 times that natural gas and 7 times that of coal gas.

(ii) Use of well-designed, durable and neatly constructed burners ensure complete combustion with no smoke.

(iii) Needs little care for maintanance purpose.

(iv) Cleanlines in storage, handling and use.

(v) Flexibility and easy control.

(vi) Portability in steel cylinder/containers make it use in remote/isolated places.

(vii) Comparatively less health hazard.

Octane number : Same as Question 6.(b), 2004.

The Octane number of a fuel can be improved by the following way:

(i) **Reforming :** This process increases the contents of molecules having branched and aromatic ring structures. Thus, by molecular reforming, the contents of isopentane, isoctane, ethyl benzene and isopropyl benzene increases in the given fuel.

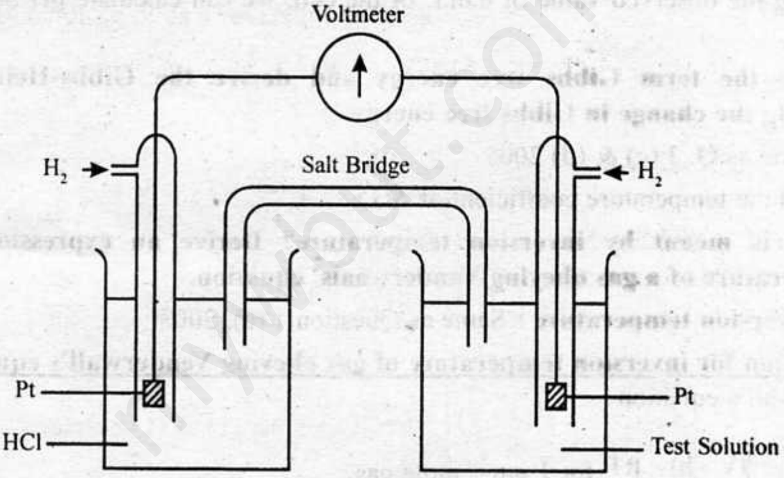
(ii) **Methyl tertiary butyl ether (MTBE) :** Can also be added to improve the octane rating of the fuel. MTBE has oxygen in the form of ether group and supplies oxygen for the combustion of the petrol in internal combustion engine thus reducing the formation of per oxy compounds.

Group–C
(Long Answer Questions)

Answer *any three* questions : 3 × 15 = 45

7. Discuss the physicochemical principle involved in the measurement of pH of an aqueous solution by using a hydrogen electrode.

Ans. A half cell is set up with the test solution as electrolyte. The emf of the cell depends on the concentration H^+ ions or pH of the solution. The emf of the half-cell is determined by coupling it with Hydrogen half-cell and measuring the emf of the complete cell.



Determination of pH with Hydrogen electrode

A standard hydrogen electrodes coupled with another hydrogen electrode which contains the aqueous solution of unknown pH. In both half cells hydrogen gas is used at 1 atm presure and 25°C. The emf of the complete cell

$Pt / H_2(1\ atm) / H^+(1M) // H^+\ (unknown) / H_2\ (1\ atm) / Pt$

is recorded experimentally.

The 2nd electrode reaction is $H^+ + e = \frac{1}{2}H_2$

The electrode potential of the 2nd half-cell is given by the Nearnst equatioh

$$E = E^0 + \frac{2 \cdot 303RT}{nF} \log \frac{\left[H^+\right]}{P_{H_2}^{\frac{1}{2}}}$$

Since $P_{H_2}^{\frac{1}{2}}=1$ and $E^0 = 0$, we have, $E = \frac{2 \cdot 303RT}{nF} \log\left[H^+\right] = \frac{2 \cdot 303RT}{nF} \cdot \log\left[H^+\right]$

Substituting the values of R, T and n (charge number of H⁺) and F (Faraday constant), the expression becomes

$$E = 0\cdot 0591 \log\left[H^+\right] = -0\cdot 059 \text{ pH} \,\ldots\ldots\ldots (1)$$

or, The e.m.f. of the cell, E cell is give as, $E_{cell} = E_{right} - E_{left}$

The left-hand electrode in the standard hydrogen electrode and its e.m.f. will be zero.

$$E_{cell} = E_{right} = -(-0.0591) \text{ pH}$$

Using equation (1) $E_{cell} = -(-0.0591 \times \text{pH}) = 0.0591 \times \text{pH}$

$$\text{or, pH} = \frac{E_{cell}}{0\cdot 059}$$

Knowing the observed value of e.m.f. of the cell, we can calculate pH of the aqueous test solution.

8. Define the term Gibbs free energy and derive the Gibbs-Helmholtz equation relating the change in Gibbs free energy.

Ans. Same as Q. 3.(c) & (d) 2005

(ΔG), and the temperature coefficient of ΔG.

9. What is meant by inversion temperature? Derive an expression for inversion temperature of a gas obeying Vanderwaals' equation.

Ans. Inversion temperature : Same as Question 1.(c), 2003.

Expression for inversion temperature of gas obeying Venderwall's equation.

Vanderwall's equation

$$\left(P = \frac{a}{V^2}\right)(V-b) = RT \text{ for 1 gm -- mole gas.}$$

Differentiating the above equation w.r. to T at constant pressure

$$\left[\left(P+\frac{a}{V^2}\right)+(V-b)\left(-\frac{2a}{V^3}\right)\right]\left(\frac{\partial V}{\partial T}\right)_P = R$$

$$\text{or, } \left(P+\frac{a}{V^2}-\frac{2a}{V^2}+\frac{2ab}{V^3}\right)\left(\frac{\partial V}{\partial T}\right)_P = R \quad \text{or, } \left(p+\frac{a}{V^2}-\frac{2a}{V^2}\right)\left(\frac{\partial V}{\partial T}\right)_P = R$$

Since a & b are small quantities and v^3 is a large quantity.

$$\therefore \frac{2ab}{v^3} \text{ can be neglected.}$$

$$\therefore \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{\left(p+\frac{a}{V^2}-\frac{2a}{V^2}\right)} = \frac{R}{\frac{RT}{V-b}-\frac{2a}{V^2}} \quad \left[\because \left(p+\frac{a}{V^2}\right)=\frac{RT}{(V-b)}\right]$$

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$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{\frac{RT}{V-b}\left[1-\frac{2a(V-b)}{RT\,V^2}\right]} = \frac{R}{\left(\frac{RT}{V-b}\right)}\cdot\left[1-\frac{2a(V-b)}{RT\,V^2}\right]^{-1} = \frac{V-b}{RT}\left[1+\frac{2a(V-b)}{RT\,V^2}\right] \text{.......(2)}$$

Here $\frac{2a(V-b)}{RT\,V^2} << 1$

Therefore expanding and neglecting the higher poners.

We know H = E + PV

dH = dE + PdV + VdP = dq + VdP = TdS + VdP

$\therefore$ dq = dE + PdV

Since in Joule – Thomson expansion work is mechanical type. Expansion of gas through porous barrier may be think of as a reversible process.

$$\left[\therefore \left(\frac{\partial S}{\partial p}\right) = -\left(\frac{\partial V}{\partial T}\right)_P\right]$$

$$\therefore \left(\frac{\partial H}{\partial P}\right)_T = T\cdot\left(\frac{\partial S}{\partial P}\right)_T + V = -T\cdot\left(\frac{\partial V}{\partial T}\right)_P + V$$

Now, $\mu = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T$ or, $\mu = \frac{1}{C_p}\left[T\cdot\left(\frac{\partial V}{\partial T}\right)_P - V\right]$ ....(i)

Therefore from equation (1) & (2) we get, $\mu = \frac{1}{C_P}\left[(V-b)\left\{1+\frac{2a(V-b)}{RTV^2}\right\} - V\right]$

$$= \frac{1}{C_P}\left[(V-b)+\frac{2a(V-b)^2}{RTV^2} - V\right] = \frac{1}{C_P}\left[\frac{2a(v-b)^2}{RTv^2} - b\right]$$

$\mu = \frac{1}{C_P}\left[\frac{2a}{RT} - b\right]$ [as b is small, therefore, $(V-b) \simeq V^2$]

Case I : If $\frac{2a}{RT} > b$

then μ = + ve, i.e. cooling effect is observed.

$\therefore$ Cooling is observed when

$\frac{2a}{RT} > b$ or, $T < \frac{2a}{Rb}$

Case II. If $\frac{2a}{RT} < b$

then $\mu = -ve$, i.e. heating effect is observed.

Therefore, heating effect is observed when

$$\frac{2a}{RT} < b \quad \text{or, } T > \frac{2a}{Rb}$$

Case III. If $\frac{2a}{RT} = b$ or, $T = \frac{2a}{Rb}$

when $\mu = 0$, i.e. no Joule – Thomson effect is observed.

i.e. at this temperature a real gas behaves ideally.

This temperature is known as inversion temperature (T_i)

i.e. $T_i = \frac{2a}{Rb}$

Its significance is that when a gas is adiabatically expanded above this temperature heating effect is observed and when temperature is below this temperature, cooling effect is observed. At this temperature no Joule–Thomson effect is found.

10. (a) What are the important products formed from the atmosphereic distillation of crude oil?

(b) How do the gasoline and diesel differ in chemical composition?

Ans. (a). Important products obtained by distillation of crude oil :

Sl. No.	Fraction's Name	Boiling temp.	Approx. composition interms of hydrocarbon containing C atoms
1	Uncondensed gas (refinery gas)	< 30°C	C_1 to C_4 (such as ethane, propane etc.) lower hydrocarbons
2.	Petroleum ether	30^0 to 70°C	C_5 to C_7
3	Gasoline or Petrol or motor spirit	40^0 to 120°C	C_5 to C_9
4	Naptha or Solvent spirit	120^0 to 180°C	C_9 to C_{10}
5	Kerosene oil	180^0 to 250°C	C_{10} to C_{16}
6	Diesel oil or fuel oil or gas oil	250^0 to 320°C	C_{10} to C_{18}
7	Heavy oil	320^0 to 400°C	C_{17} to C_{30}
8	Lubricating oil		
9	Petroleum jelly		
10	Grease		
11	Paraffin wax		

(b) Gasoline : It is a mixture of hydrocarbons (C_5 to C_8), from pentane to octane. This is highly volatile and inflamable and used as fuel for internal combustion engines. Its calorific value is about 11, 250 K cal/kg. Its thermal efficiency low.

Diesel : It is a mixture of higher hydrocarbons (C_{15} to C_{18}). It is used as a fuel for diesel engine and its calorific value is about 11,000 K cal/kg. Its thermal efficiency high (about 30–35%).

11. What are water gas and semiwater gas? How is water gas produced from coke?

Ans. Water gas : Water gas is essentially a mixture of combustible gases, CO and H_2, with a little non-combustible gases, CO_2 and N_2. The average composition of water gas is : H_2 = 51% ; CO = 41% ; N_2 = 4% ; CO_2 = 4%.

Its calorific value is about 2,800 Kcal/m^3. It's used as source of hydrogen gas, a fuel gas, an illuminating gas.

Semi water gas : It is obtained by passing a properly adjusted air and stream mixture continuously through a bed of red-hot coke so that the 'endothermic reaction' just balances the exothermic reactions. Its average composition is H_2 = 12% ; CH_4 = 3% ; CO_2 = 2 ; N_2 = 53% and CO = 30%. Its calorific value is nearly 1,700 Kcal/m^3. It is used as a fuel, source of N_2 and H_2 in the manufacture of NH_3.

Production of water gas from coke : It is made by passing alternatively steam and little air through a bed of red hot coke, maintained at about 900 to 1000°C in a reactor.

Reactions : (i) Supplied steam reacts with red-hot coke at 900 – 1000°C to form CO and H_2. The reaction is endothermic, so the temperature of bed falls.

$$\underset{\text{red-hot coke}}{C} + \underset{\text{Steam}}{H_2O} \rightarrow \underset{\text{water gas}}{CO + H_2} - 29 \text{ KCal (Endothermic)}$$

(ii) In order to raise the coke bed to 1000°C, the steam supply is temporarily cut off and air is blown in, when the following exothermic reactions occur :

$$C + O_2 \rightarrow CO_2 + 97 \text{ Kcal} ; 2C + O_2 \rightarrow 2CO + 59 \text{KCal (Exothermic)}$$

These reactions again raises the bed to about 1000°C. The cycles of steam – run and air-blown are thus repeated alternatively to maintain proper temperature.

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