Total No. of printed pages = 8

3 (Sem 1) CHM M1

2015

CHEMISTRY

(Major)

Paper : 1.1

Full Marks – 60

Time – Three hours

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

1. (a) What type of thermodynamic system is a human body ? 1

(b) Give a statement of the first law of thermodynamics. 1

(c) At a very low temperature heat capacity of a solid is given by $C_p = aT^3$. What is the change in enthalpy of the solid when it is heated from 0 to temperature T ? 2

[Turn over

2. (a) Calculate the change in entropy when 25 kJ of energy is transferred reversibly and isothermally as heat to a large block of iron at 500 K. 1

(b) Inversion temperature of nitrogen gas is 621K. When a sample of nitrogen gas is allowed to expand at 298 K through a porous barrier from high pressure to low pressure under adiabatic condition, the gas exhibits which one of the following effects ? 1

(i) Heating effect

(ii) Cooling effect

(iii) Neither heating effect nor cooling effect

(iv) Magnetic effect

(c) Write physical significance of the criterion $dG_{T,P} \leq 0$. 2

3. (a) The rate law for the reaction $2A + B \rightarrow 2C + 3D$ was reported as $\frac{d[C]}{dt} = k[A][B][C]$.

Express the rate law in terms of the reaction rate. 1

(b) Which one of the following terms represents the slope of the straight line obtained by plotting ln k against $1/T$. 1

(a) ln A (b) ln E_α

(c) $-E_\alpha/R$ (d) ln A/R

(c) A catalyst does not affect the position of equilibrium. Explain. 2

4. Answer any *two* : 3×2=6

(a) For a system which can do only expansion work, show that $\Delta H = q_p$.

(b) The standard enthalpy of the reaction

$$H_2(g)+\frac{1}{2}O_2(g)\rightarrow H_2O(g)$$

at 298K is $-241.82\ \text{kJ mol}^{-1}$.

Estimate standard enthalpy of the reaction at 100°C.

Given the following values of molar heat capacities at constant pressure :

$H_2O(g)$ 33.58 J K^{-1};

$H_2(g)$ 28.84 J K^{-1};

$O_2(g)$ 29.37 JK^{-1}

Assume that the heat capacities are independent of temperature.

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

where $\gamma = \frac{C_{p,m}}{C_{v,m}}$

5. Answer any *two* : 3×2=6

(a) Derive an expression for Clausius inequality and mention its physical significance.

(b) State Nernst heat theorem. Show how we can arrive at the third law of thermodynamics from this theorem.

(c) For an ideal gas show that

$$\mu = \mu_0 + RT \ln\left(\frac{p}{p^0}\right)$$

where p^0 is the standard pressure.

6. Answer any *two* : 3×2=6

(a) What is a rate-determining step ? The reaction mechanism

$$A_2 \rightleftharpoons A + A \text{ (fast)}$$

$$A + B \rightarrow P \text{ (slow)}$$

involves an intermediate A. Deduce the rate law for the reaction using rate-determining step approximation.

(b) Discuss either the half-life method or the isolation method for the determination of order of a reaction.

(c) Calculate the concentration of a non-competitive inhibitor ($K_I = 2.9 \times 10^{-4}$ mol dm^{-3}) needed to yield a 90% inhibition of an enzyme-catalyzed reaction.

7. Answer any *two* : 5×2=10

(a) Define Joule-Thomson coefficient. Obtain the following expression for Joule-Thomson coefficient

$$\mu_{JT} = \frac{1}{C_p}\left[\left(\frac{dU}{dV}\right)_T\left(\frac{dV}{dP}\right)_T + \left(\frac{d(PV)}{dP}\right)_T\right].$$

Show that $\mu_{JT} = 0$ for an ideal gas.

(b) One mole of a certain gas obeys the equation of state $p(V - b) = RT$ (where b is a constant) and has a constant molar heat capacity $C_{v,m}$ which is independent of temperature. For one mole of the gas, find ΔU, w, q and ΔH for isothemal and isobaric reversible process.

(c) One mole of chlorine gas undergoes adiabatic free expansion from 1 dm^3 to 10 dm^3. If the initial temperature of the gas is 273K, calculate T_{final}, q, w, ΔU and ΔH consider the gas as a van der Waals gas.

Given : $a = 655\ dm^3\ kPa\ mol^{-2}$, $b = 0.055\ dm^3\ mol^{-1}$, $C_{v,m} = 33.91\ J\ K^{-1}\ mol^{-1}$.

8. Answer any *two* : 5×2=10

(a) Calculate the change in entropies of the system and the surroundings, and the total change in entropy, when the volume of a sample of argon gas of mass 21g at 298K and 1.50 bar increases from 1.20 dm^3 to 4.60 dm^3 in

(a) an isothermal reversible expansion,

(b) an isothermal irreversible expansion against zero external pressure.

(Molar mass of Ar = 40g mol^{-1}) 5

(b) (i) Derive the expressions

$$\left(\frac{dG}{dT}\right)_p = -S \text{ and } \left(\frac{dG}{dP}\right)_p = V.$$

(ii) Calculate the standard reaction Gibbs energy for $CO(g)+\frac{1}{2}O_2(g) \rightarrow CO_2(g)$ at 25°C. Given that standard Gibbs energy of formation of $CO_2(g)$, $CO(g)$ are -394.4 and -137.2 kJ mol^{-1} respectively. 3+2=5

(c) (i) Discuss the effect of temperature and pressure on the following equilibrium :

$N_2(g)+O_2(g) \rightleftharpoons 2NO(g)$; $\Delta_r H = -180.75$ kJ mol^{-1}.

(ii) Deduce Gibbs-Helmholtz equation to show the variation of Gibbs energy with temperature. 2+3=5

9. Answer any *two* : 5×2=10

(a) For the competing irreversible first order reactions 5

$$A \xrightarrow{k_1} C$$

$$A \xrightarrow{k_2} D$$

find expressions for the molar concentrations of A, C and D at time t. Plot [A], [C] and [D] against time t for $k_1=2k_2$. Give one example of such reactions.

(b) The elementary steps proposed for the chain reaction between $H_2(g)$ and $Br_2(g)$ are 5

$$Br_2 \xrightarrow{k_1} 2\,Br$$

$$Br + H_2 \xrightarrow{k_2} HBr + H$$

$$Br_2 + H \xrightarrow{k_3} HBr + Br$$

$$H + HBr \xrightarrow{k_4} H_2 + Br$$

$$Br + Br \xrightarrow{k_5} Br_2$$

Derive a rate law for the reaction.

(c) For enzyme catalysis is derive the Michaelis Menten equation. Modify this equation fo[r] high concentration of the substrate. Give a[n] expression for the turnover number of a[n] enzyme catalyst. 5