BITS-PILANI, K. K. Birla Goa Campus

Physical Chemistry I (CHEM F211), Semester I 2022-23

Comprehensive Examination: 26/12/22, FN (Closed Book), Maximum Marks: 80 Duration: 3 hrs

Instructions: Answer all parts and steps of a question together and write the final answers in the main answer sheet in boxes as per format given wherever applicable. Use only pen for answering.

Useful Data: R = 82.06 $cm^3 atm mol^{-1}$ ≡ 8.314 $JK^{-1}mol^{-1}$, P^o = 1 bar = 750 torr, 1 atm = 760 torr = 1.01325 × 10^5 Pa, Avogadro Number = 6.023 × 10^{23}, Atomic Mass (g/mol): Ar-40, C-12, H-1, 0^0C ≡ 273.15 K, 1F = 96485 C/mol

Q.1 For the cell at 25 ºC and 1 bar **: Pt|Ag|AgCl(s) | HCl(aq) ‖ Hg_2Cl_2(s) | Hg | Pt' ,**
ξ^o values for the left and right half cells are 0.2222 and 0.2680 V respectively.

(a) Find the **emf** if the HCl molality is 0.100 mol/kg.

(b) For this cell, $(\partial \xi/\partial T)_P$ = 0.338 mV/K at 25 ºC and 1 bar. Find **ΔHº, ΔGº** (both in **kJ/mol**) and **ΔSº** (**kJ/mol.K**) for the cell reaction at 25 ºC. [**3** + **6** = **9**]

ξ (V)	**ΔH° (kJ/mol)**	**ΔS° (kJ/mol.K)**	**ΔG° (kJ/mol)**

Q.2 For a 0.02 mol/kg $MgCl_2$(aq) solution at 25 ºC.

(a) Calculate ($\nu_\pm$).

(b) Calculate the ionic strength I_m of the solution.

(c) Use Davies equation to calculate $\gamma_\pm$ for the solution. **[2 + 2 + 3 = 7]**

$\nu_\pm$	I_m	$\gamma_\pm$

Q.3 For the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ in the range from 298 K to 900 K, the standard equilibrium constant (K_P^o) is expressed as a function of temperature (T in Kelvin (K)) as:

$$K_P^o = a \times \left(T/_K\right)^b \times e^{-\left(\frac{c}{T/K}\right)}$$

***a* = 1.09 × 10^13^, *b* = −1.304, *c* = 7307**. Answer the following questions: .

(a) Calculate K_P^o at **400 K** and **800 K**.

(b) Find **Δ*H*º (in J/mol)**, assuming enthalpy is constant.

(c) Find **Δ*G*º (in J/mol)** and **Δ*S*º (J/mol.K)** at **400 K**. **[2 + 2 + 4 + 2 + 2 = 12]**

K_P^o **(400K)**	K_P^o **(800K)**	**Δ*H*º (J/mol)**	**Δ*G*º (J/mol)@400K**	**Δ*S*º (J/mol.K) @400K**

Q.4 The normal melting point of NaCl is 801ºC. Given the specific enthalpy of fusion of NaCl as 492.6 J/g, the density of the solid NaCl as 2.165 g/cm^3 and the density of liquid NaCl as 1.733 g/cm^3.

(a) Calculate the change in volume (**Δ*V*** in **cm^3**) and increase in pressure (**Δ*P*** in **atm**) that is needed to raise the normal melting point of 5g of NaCl by 2ºC?

(b) Find P_2 **(in atm)** if P_1 corresponds to pressure at normal fusion transition and the entropy of fusion **(Δ_{fus}S** in **J/K)** at the normal fusion temperature**.** **[4 + 4 = 8]**

[P.T.O.]

Q.5 The vapor pressure of benzene for the liquid-vapor region is given as a function of *T*:

$$ln(P/torr) = -\frac{4110}{T/K} + 18.33$$

Answer the following using the above equation:

(a) Find the normal boiling point (***T_{nbp}*** in **K**).
(b) Find the equilibrium vapor pressure (***P*** in **torr**) when benzene boils at 40°C.
(c) Calculate the molar enthalpy of vaporization (***$\Delta_{vap}H_m$*** in **J/mol**) of liquid benzene and the molar entropy (***$\Delta_{vap}S_m$*** in **J/mol.K**) during vaporization at its normal boiling point. Assume constant enthalpy of vaporization. **[2 + 2 + 4 = 8]**

$T_{nbp}(K)$	***P*** (torr) @ 40°C	***$\Delta_{vap}H_m$*** (J/mol)	***$\Delta_{vap}S_m$*** (J/mol.K)

Q.6 For ethane, critical constants are P_C = 48.2 atm, T_C = 305.4 K. Calculate the pressure (***P*** in **atm**) exerted by 50 g of C_2H_6 in a 500 cm^3 vessel at 50^0C using the following equations of state:

(a) Ideal gas equation (b) Van der Waal's equation and (c) Virial equation given that virial coefficients for ethane B = −157 cm^3/mol, C = 9650 cm^6/mol^2 at 50^0C. **[3 + 7 + 5 = 15]**

Q.7 For 88 g of a hypothetical hydrocarbon gas A of molar mass 44 g/mol occupying a volume of 160 cm^3 at a temperature of 320 K, calculate the pressure (***P*** in **atm**) using:

(a) the Redlich-Kwong (R-K) state equation. [Useful information: Use Redlich-Kwong (R-K) constants of A as: ***a*** = 1.074×10^8 $cm^6 atm K^{1/2} mol^{-2}$, ***b*** = 50 cm^3/mol].

(b) the given compressibility factor Z = 0.8. **[5 + 3 = 8]**

Q.8 Argon (Ar) considered as perfect gas, answer the following:

(a) For 15 g of Ar in a container, find the number of molecules of gas ***(dN_v)*** within the speed interval 200 m/s to 200.001 m/s at 340 K and 1 atm. (Molar mass of Ar = 40 g/mol). **[5]**

(b) Calculate the temperature (***T*** in **K**) at which the molecular speed distribution function (G(v)) of Ar gas at 200 m/s and 800 m/s are equal considering the same infinitesimal thicknesses of 0.001 m/s. **[4]**

(c) Calculate the mean free path (***λ*** in **m**) of Ar, given the collision diameter (*d*) as 5×10^{-10}m (5Å), at 340 K and 1 atm. **[4]**

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