BITS Pilani, Pilani Campus; Semester-I, 2016-17

CHEM G553 : Advanced Physical Chemistry

Comprehensive Examination Part-II (Open book)

Duration: 120 min Max. Total Marks: 48

Date: December 05, 2016 **Time: Afternoon**

Useful data: 1 a.m.u.=1.67×10^{-27} kg; h=6.626×10^{-34} Js; ħ=1.054×10^{-34} Js

1. Compute the change in the entropy when 20 g of water at 25°C are converted into water vapour at 200°C under constant atmospheric pressure. The specific heats of liquid water and water vapor are 75.315 J $K^{-1}mol^{-1}$ and (30.09 + 0.00883T) J K^{-1} mol^{-1}, respectively and latent heat of vaporization is 0.414 x10^5 J mol^{-1}. **[10]**

2. A reaction mechanism was proposed for photo-decomposition of Cl_2O as under:

$$M(g) + Cl_2O(g) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Cl_2(g) + O(g) + M(g)$$

$$O(g) + Cl_2O(g) \xrightarrow{k_3} O_2(g) + Cl_2(g)$$

Where M is a molecule that can exchange energy with the reacting Cl_2O molecule through collision but does not react. Derive the rate law for $d[Cl_2O]/dt$ assuming that the intermediate O(g) concentration can be treated by the steady state approximation. **[10]**

3. For some pure substance, the thermodynamic the following data was obtained:
$\Delta_{fus}H$ = 7 kJ mol^{-1}; and $\Delta_{fus}S$ = 25 J $mol^{-1}K^{-1}$.
Calculate the melting point of the substance at the given pressure. Which phase of the substance will be more stable at 273 K if the molar entropies of the solid and the liquid phases are, respectively, 40 J $mol^{-1}K^{-1}$ and 70 J $mol^{-1}K^{-1}$, at the given pressure and within the given range of temperatures. (Justify with the proper calculation). **[10]**

4. Which d-type orbitals would you choose to form d^2sp^3 hybrid orbitals oriented equal and opposite along the three coordinate axes? Assuming that the pure d-type, p-type and s-type atomic orbitals are mutually orthonormal, obtain the expression for the mutually orthonormal d^2sp^3 hybrid orbitals. **[4+6]**

5. Write a short note (two-three sentences only) for each of the following: **[2+2+2+2]**
(a) NMR Chemical Shift (b) Chemical potential (c) Angular nodes of a hydrogenic wavefunction (d) Azeotropic liquid mixture

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