

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

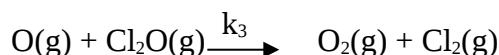
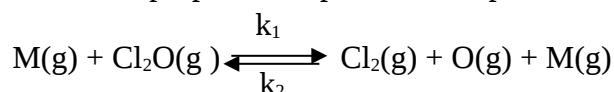
Date: December 05, 2016

Time: Afternoon

Useful data: $1 \text{ a.m.u.} = 1.67 \times 10^{-27} \text{ kg}$; $h = 6.626 \times 10^{-34} \text{ Js}$; $\hbar = 1.054 \times 10^{-34} \text{ Js}$

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 $75.315 \text{ J K}^{-1} \text{ mol}^{-1}$ and $(30.09 + 0.00883T) \text{ J K}^{-1} \text{ mol}^{-1}$, respectively and latent heat of vaporization is $0.414 \times 10^5 \text{ J mol}^{-1}$. **[10]**

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



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 $d[\text{Cl}_2\text{O}]/dt$ 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:

$\Delta_{\text{fus}}H = 7 \text{ kJ mol}^{-1}$; and $\Delta_{\text{fus}}S = 25 \text{ J mol}^{-1}\text{K}^{-1}$.

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, $40 \text{ J mol}^{-1}\text{K}^{-1}$ and $70 \text{ J mol}^{-1}\text{K}^{-1}$, 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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