Birla Institute of Technology & Science Pilani
Pilani Campus
I Semester 2023-2024
CHEM F312 Physical Chemistry IV
Comprehensive Examination
(Open Book)

Max. Marks: 70 **11 December 2023** **Duration: 3 hrs.**

Instructions to the student:

1) There are seven questions (two pages) in total; answer all the questions.
2) Start answering each question on a fresh page and answer all parts of a question together.
3) Write brief answers to the point with proper justification.
4) Mobile phones, lap-tops etc. are to be switched off and kept away from you.
5) Open book test. Textbook, Ref. books, class notes, and printed slides are allowed. However, exchange of these materials is not allowed.
6) Any unfair means, if identified, will be sternly dealt with.
7) Data required are available in Text and/or Reference books. However, for quick reference the following constant values and conversions are given.

DATA:

R = 8.3145 J mol^{-1} K^{-1}; **R**= 0.0820575 L atm K^{-1} mol^{-1}; **k = k_B** = 1.38065 x 10^{-23} J K^{-1} **k = k_B** = 0.69509 cm^{-1} K^{-1};
Avogadro's Number = **N_A** = 6.022142 x 10^{23} mol^{-1}; **h** = 6.626069 x 10^{-34} J s; **e** = 1.60216 x 10^{-19} C;
m_e = 9.10938 x 10^{-31} kg; **F** = 96485.34 C mol^{-1}; **c** = 2.99792458 x 10^8 m s^{-1}; **ε_0** = 8.854188 x 10^{-12} C^2 N^{-1} m^{-2};
g = 9.807 m s^{-2}; 1 **calorie** = 4.184 J; **1 erg** = 10^{-7} J; **1 dyn (dyne)** = 10^{-5} N .

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1. **(a)** Write the statistical-mechanical formula for Gibbs Energy (G) in terms of the canonical partition function. **[1]**

(b) Consider a system having four energy levels. Assuming the degeneracy of the levels being (1, 2, 3 and 4) with the corresponding energy values of (0, 1, 2, and 3) x 10^{-23} J respectively, calculate the value of the partition function at 300 K. What is the value of the partition function at 300 K if the energy values are (0, 1, 2, and 3) x 10^{-19} J? **[4]**

(c) In a two-level energy system at 400 K, the population of the upper state is found to be one-third of the lower state. Find out the energy separation between the levels in cm^{-1}. **[3]**

(d) For a homonuclear diatomic molecule the fundamental vibrational frequency is ν_0 = 6.0 x 10^{13} Hz. Calculate the ratio of the v = 2 to v = 1 populations at 3000 °C. **[2]**

2. **(a)** The first three steps in the decay of ^{238}U are

$$^{238}\mathrm{U} \xrightarrow[4.5 \times 10^9\ \mathrm{y}]{\alpha} {}^{234}\mathrm{Th} \xrightarrow[24.1\ \mathrm{d}]{\beta} {}^{234}\mathrm{Pa} \xrightarrow[1.14\mathrm{m}]{\beta} {}^{234}\mathrm{U}$$

If we start with pure ^{238}U, what fraction will be ^{234}Th after 1 year? (Assume 1y = 365 days & 1 month = 30 days) **[3]**

(b) The gas phase reaction $2Cl_2O + 2N_2O_5 \rightarrow 2NO_3Cl + 2NO_2Cl + O_2$ has the rate law $r = k[N_2O_5]$. Devise a mechanism consistent with the rate law. **[2]**

(c) Consider the following hypothetical mechanism for the thermal decomposition of acetone:

Reaction	**Activation Energy(kJ/mol)**
$CH_3COCH_3 \xrightarrow{k_1} 2CH_3 + CO$	**290**
$CH_3 + CH_3COCH_3 \xrightarrow{k_2} CH_4 + CH_2COCH_3$	**63**
$CH_2COCH_3 \xrightarrow{k_3} CH_3 + CH_2CO$	**200**
$CH_3 + CH_2COCH_3 \xrightarrow{k_4} CH_3COC_2H_5$	**33**

(i) What is(are) the principal product(s) predicted by this mechanism?
(ii) Find an expression for the rate of formation of methane in terms of the concentration of the reactant.
(iii) What is the overall activation energy for the reaction? **[1 + 2 + 2 = 5]**

3. **(a)** For the HBr formation mechanism (Eq. 16.88 of Text Book / lecture 16 – slide 9), write expressions for **d[Br_2]/dt** and **d[Br]/dt** in terms of concentrations and rate constants (do not eliminate intermediates). **[4]**

(b) Consider the elementary reaction $A \rightleftharpoons 2C$. **(i)** If the system in this equilibrium is subjected to a small perturbation find an expression for the relaxation time. (ii) Given $\mathbf{k_f = 1.0 \times 10^{14}\ s^{-1}}$, $\mathbf{k_b = 2 \times 10^{13}\ mol^{-1}\ dm^3\ s^{-1}}$ and the **relaxation time = 0.5×10^{-14} s**, find out the equilibrium concentration of A. **[3 + 3 = 6]**

4. **(a)** The enzyme catalyzed conversion of a substrate at 25 °C has a Michaelis Constant of **0.046** mol dm^{-3}. The rate of the reaction is **1.04×10^{-3}** mol $dm^{-3}s^{-1}$ when the substrate concentration is **0.105** mol dm^{-3}. What is the maximum rate of this reaction? **[3]**

(b) The non-dissociative adsorption of a gas is described by the Langmuir isotherm with **b = 0.60 kPa^{-1}** at 25 °C. Calculate the pressure at which the fractional surface coverage is **0.30**. **[2]**

(c) Suppose it is known that ozone adsorbs on a particular surface in accord with a Langmuir isotherm. How could you use the pressure dependence of the fractional coverage to distinguish between adsorption (i) without dissociation (ii) with dissociation into $O+O_2$ (iii) with dissociation into O+O+O? **[5]**

5. **(a) (i)** Using Collision theory calculate the pre-exponential factor for the elementary reaction A + B → C + D at 500 K. Assume the radii of A and B are **0.4 and 0.6 nm** respectively. (Rel. Mol. Mass of A and B are **60 and 70** respectively). **(ii)** calculate the steric factor, if the experimental value of pre-exponential factor is **1.0×10^6 mol^{-1} dm^3 s^{-1}**. **[3]**

(b) Consider the reaction **H + H → H_2**. Explain why 75% of the collisions of one hydrogen with another hydrogen are nonproductive according to quantum mechanics. **[2]**

(c) In the context of Transition State Theory, explain precisely the following **(i)** transition state **and (ii)** reaction coordinate. **[2]**

(d) Consider the H + H_2 reaction as per transition state theory; How will you explain the variety of structures of the supermolecule near CDS (Consider PE surface as a function of two distances and one angle)? **[3]**

6. **(a)** The electric dipole moment of HCl is 3.57×10^{-30} Cm and its bond length is 0.13 nm. If we pretend that the molecule consists of charges δ and –δ separated at the ends of the molecule find δ. **[2]**

(b) In the tetragonal crystal system identify the point groups which will show ferroelectric phenomena. **[3]**

(c) Assuming formic acid and acetic acid have the same solubility in water, find out the ratio of solubility of acetic acid to that of formic acid in octanol. **[3]**

(d) The polarizability volume of H_2O is 1.48×10^{-24} cm^3; calculate the dipole moment of the molecule (in addition to the permanent dipole moment) induced by an applied electric field of strength 15.0 kV m^{-1}. **[2]**

7. **(a)** Calculate the pressure inside a bubble of gas in water at 20 °C, if the pressure of the water is 760 torr and the bubble radius is 0.030 cm. The surface tension of water is 73 dyn/cm at 20 °C. **[2]**

(b) Show by a diagram the structure of reverse micelle. **[2]**

(c) Calculate the total surface area of a colloidal dispersion of 1.0 cm^3 of silver in which each silver particle is a sphere of radius 25 nm. **[3]**

(d) Surface tension of ethyl acetate at 0 °C is 26.5 mN/m, and its critical temperature is 523.2 K. Estimate its surface tension at 50 °C and compare with experimental value of 20.2 mN/m. **[3]**
