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

Max. Marks: 70 **11 Oct 2023** **Duration: 1hr 30 min.**

Instructions to the student:

1) There are five questions 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) Data required are available in Text and/or Reference books. However, for quick reference the following constant values 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 .
Relative Atomic Masses: Ar = 39.95;

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1. (a) Consider a two-level system of energy separation equivalent to 300 cm^{-1}. What is the temperature of the system when the population of the upper state is one-half that of the lower state? **[4]**

(b) Calculate the translational partition function at (i) 300 K and (ii) 3000 K of an Ar atom in a cubic box of side 1.00 cm. **[4]**

(c) Consider 1 mol. of an ideal gas of relative molar mass 2 and at 298 K. Write an expression for enthalpy (H) in terms of canonical partition function. Given that the translational partition function $\mathfrak{z}_{tr} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2}.V$, write an expression for the change in enthalpy when volume is changed from V_1 to V_2. **[6]**

2. (a) For Ar(g) $S°_{m,298}$ = 154.8 J mol^{-1} K^{-1} and $U°_{m,298}$ **-** $U°_{m,0}$ =3718 J mol^{-1}. Calculate ln Z, Z and $\mathfrak{z}$ for 1 mole of the ideal gas Ar at 25 °C and 1 bar. **[6]**

(b) For $^1H^{35}Cl$, the rotational constant is B_0 = 3.1779 x 10^{11} s^{-1}. Calculate the ratio of the J = 3 to J = 0 populations at 500 K. **[4]**

c) For N_2 the fundamental vibration wavenumber is $\widetilde{\nu_0} = 2329.8\ cm^{-1}$. For 1.000 mol of N_2(g), calculate the number of molecules in the v = 0 level and in the v = 1 level at 800 °C. **[4]**

3. (a) The gas phase decomposition of acetic acid at 1189 K proceeds by way of two parallel reactions:

(1) $CH_3COOH \rightarrow CH_4 + CO_2$ $k_1 = 3.74\ s^{-1}$
(2) $CH_3COOH \rightarrow H_2C{=}C{=}O + H_2O$ $k_2 = 4.65\ s^{-1}$

What is the maximum percentage yield of the ketene CH_2CO obtainable at this temperature? **[4]**

(b) The first order reaction 2A → 2B + C is 35% complete after 350 s at 300 K. (i) Find k and k_A. (ii) How long will it take for the same 35% completion at 320 K if the activation energy is 50 kJ/mol? **[6]**

(c) Deduce an expression for the time it takes for the concentration of a substance to fall to one-fifth (1/5) of its initial value in an nth-order reaction (n#1). **[4]**

4. (a) The effective rate constant for a unimolecular gaseous reaction that follows Lindemann mechanism is **1.7 x 10^{-3}** s^{-1} at 1.09 kPa and **2.2 x 10^{-4}** mol dm^{-3} s^{-1} at 25 Pa. Find (i) the rate constant for the activation step in the mechanism, (ii) the ratio (k_2/k_{-1}). **[6]**

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4. (b) Which molecule(s) among the following molecules can decompose by unimolecular process suggested in Lindemann mechanism?

C_2H_6, H_2, CO, I_2, N_2, acetone. **[4]**

(c) Consider addition polymerization reaction of polyethylene formation; Assume the termination occurs only by addition. Assume the Degree of Polymerization (DP) is 3000 at a particular concentration of monomer and that of initiator; What will be the new values of DP if (i) both the monomer and initiator concentrations are doubled, (ii) monomer concentration is doubled but initiator concentration is reduced to half the original value? **[4]**

5. (a) The following mechanism has been proposed for the thermal decomposition of acetaldehyde (ethanal):

$$CH_3CHO \xrightarrow{k_a} CH_3\bullet + CHO\bullet$$

$$CH_3\bullet + CH_3CHO \xrightarrow{k_b} CH_4 + CH_2CHO\bullet$$

$$CH_2CHO\bullet \xrightarrow{k_c} CO + CH_3\bullet$$

$$CH_3\bullet + CH_3\bullet \xrightarrow{k_d} CH_3CH_3$$

The rate constants for the four steps are (**k_a, k_b, k_c and k_d**). Find an expression for the rate of formation of methane and rate of disappearance of acetaldehyde. **[8]**

(b) Consider the following mechanism:

(1) $AH + B \rightarrow BH^+ + A^-$

(2) $A^- + BH^+ \rightarrow AH + B$

(3) $A^- + AH \rightarrow$ product

Derive the rate law for the formation of the product using steady state approximation. Use the notations for rate constants as k_1, k_2, k_3 respectively for the steps (1), (2) and (3) **[6]**