Time: $2\frac{1}{4}$ hours

Chemistry 217
Chemical Dynamics
Final Exam

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NAME: _____

USEFUL INFORMATION

Planck's constant $h = 6.626 \times 10^{-34}$ J s

Speed of light: $c = 2.998 \times 10^{8}$ m s^{-1}

Avogadro's number: $N_A = 6.023 \times 10^{23}$ molec/mol

1 nm $\equiv 10^{-9}$ m

Gas constant: $R = 0.08206\ \ell$ atm/mol K $= 8.314$ J/mol K

Boltzmann's contant $k = 1.380 \times 10^{-23}$ J/molec K

Faraday's constant $\mathcal{F} = 96.485$ C/mol

Einstein relation $u = \frac{z\mathcal{F}D}{RT}$

1.	/24
2.	/44
3.	/20
4.	/30
5.	/25
6.	/27
7.	/30
Total	/200

Good Luck

1. (24 pts) (9.8.7) Three *independent* parts:

- **A.** Define the phenomenon of adsorption. Then explain (briefly) the main differences between physisorption and chemisorption.

- **B.** Sketch (qualitatively) two plots: the first one showing the dependence of the viscosity coefficient η of an ideal gas on temperature; the second one showing the dependence of η on pressure.

- **C.** Explain (not more than two sentences) the principle of cyclic voltammetry.
  Then sketch a linear sweep cyclic voltammogram, along with a plot showing the time variation of the sweeping potential.

2. (44 pts) (16,28)

- **A.** Derive an expression of the concentration overpotential η^c (in polarography) as a function of the current density flown j. Express the limiting current density j_L in terms of the model parameters.

- **B.** The ionic conductivity of Fe^{2+} is 40 S cm^2 mol^{-1}. The limiting current at a platinum electrode of area 40 cm^2 dipping into a solution of iron (II) chloride at 25°C was measured at various concentrations. the results are given in the following table:

$[FeCl_2]$ (M)	0.250	0.125	0.063	0.031
I (mA)	215	107	49	23

Make an appropriate plot of these data to calculate the thickness of the diffusion layer (use Graph 1).

3. (20 pts) The mechanism of the pyrolysis of acetaldehyde at 520°C and 0.2 bar is:

$$CH_3CHO \xrightarrow{k_1} CH_3 + CHO$$

$$CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + CH_3CO$$

$$CH_3CO \xrightarrow{k_3} CO + CH_3$$

$$CH_3 + CH_3 \xrightarrow{k_4} C_2H_6$$

Show that the rate of product formation has the form:

$$\frac{d[P]}{dt} = k[CH_3CHO]^{3/2}.$$

Determine the composite rate constant k.

4. (30 pts) (13,17) Two *independent* parts:

- **A.** For the gaseous reaction $A + B \rightarrow P$, the reactive cross-section obtained from the experimental value of the pre-exponential factor is 9.2×10^{-22} m^2. The collision cross-sections of A and B estimated from the transport properties are 0.95 and 0.65 nm^2 respectively. Calculate the steric factor P for the reaction.

- **B.** A sample of gaseous acetone is irradiated with monochromatic light having a wavelength of 313 nm. Light of this wavelength decomposes the acetone according to the equation:

$$(CH_3)_2CO \rightarrow C_2H_6 + CO.$$

The reaction cell used has a volume of 59 cm^3. The acetone vapor absorbs 91.5 % of the incident energy. During the experiment the following data are obtained: Temperature of reaction = 56.7°C; initial pressure = 102.16 kPa; final pressure = 104.42 kPa; time of radiation = 7 h; incident energy = 48.1×10^{-4} J s^{-1}.
Calculate the quantum yield.

5. (25 pts) An extended Michaelis-Menten mechanism for enzyme kinetics is

$$E + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} X \underset{k_4}{\overset{k_3}{\rightleftharpoons}} E + P$$

Show that the rate of product formation is given by:

$$\frac{d[P]}{dt} = \frac{(k_3/K_S)[S] - (k_2/K_P)[P]}{1 + [S]/K_S + [P]/K_P}[E]_o,$$

where

$$K_S = \frac{k_2 + k_3}{k_1}, \quad K_P = \frac{k_2 + k_3}{k_4},$$

are the two *Michaelis* constants.

6. (27 pts) The rate constant of a bimolecular reaction in the gas phase is given by the empirical relation:

$$k = 2.05 \times 10^{13} e^{-8681(K)/T} \quad M^{-1} s^{-1}.$$

Evaluate the energy, enthalpy and entropy of activation. Derive your expressions starting from:

$$k = \frac{kT}{h} \frac{RT}{p^\circ} e^{-\Delta G^{\neq}/RT}.$$

7. (30 pts) The hydrolysis of a certain ester has been studied at $25°C$ and found to be first order in the ester. The hydrolysis reaction is:

$$RCOOR' + H_2O \rightarrow RCOOH + R'OH.$$

The extent of hydrolysis was measured by titrating the acid formed after different intervals of time with a solution of NaOH. The data are as follows:

t (h)	0	1.0	3.0	5.0	9.0	12	∞
v (cm^3)	0.035	0.295	0.715	1.055	1.505	1.725	2.197

Make an appropriate plot of the data to extract the rate contant of the above reaction (use Graph 2).