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

Chemistry 217
Chemical Dynamics
Final Exam

June 20, 1997
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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

Volmer-Butler equation $j = j_\circ \left[e^{(1-\alpha) f \eta} - e^{-\alpha f \eta} \right]$

$$q^\circ_{t,m} = \left(\frac{2\pi m k T}{h^2} \right)^{3/2} V^\circ_m, \quad q^\circ_r = \frac{8\pi^2 I_{AB} k T}{h^2 \sigma}, \quad q^\circ_v = \frac{1}{1 - e^{-\frac{h\nu}{kT}}}$$

1.	/40
2.	/28
3.	/25
4.	/31
5.	/52
6.	/24
Total	/200

Good Luck

1. (40 pts) (10,8,10,12) Four independent parts:

- **A.** Give a clear and concise definition of each of the following expressions or concepts:

  – Limit cycle

  – Kinetic salt effect

  – Branching elementary step

  – Exchange current density

- **B.** An ionic species X with a a diffusion coeffiecient D_x and mobility u_x undergoes a chemical reaction whose scheme is known to be:

$$X + 2Y \xrightarrow{k} Z$$

$$Z + Y \xrightarrow{k'} X.$$

An electric field $\vec{E}$ is applied across the solution; and the solution is subject to a turbulent convective flow whose velocity may be averaged to $\vec{v}$.
Write out the evolution equation for the species X (in three-dimensional space), illustrating the coupling of transport to chemical reactions.

- **C.** An effusion cell has a circular hole which is 2.50 mm in diameter. If the molar mass of the solid in the cell is 260 g mol^{-1} and its vapor pressure is 0.835 Pa at 400 K, by how much will the mass of the solid decrease in a period of 2.00 hours?

- **D.** In an experiment to measure the quantum efficiency of a photochemical reaction, the absorbing substance was exposed to 490 nm light from a 100 W source for 45 minutes. The intensity of the transmitted light was 40% of the intensity of the incident light. As a result of irradiation, 0.344 mol of the absorbing substance decomposed. Determine the quantum yield.

2. (28 pts) Using the Eyring equation, show that the calculation of the rate constant for a bimolecular gaseous chemical reaction involving structureless atoms (A and B), yields an expression identical to the one obtained from collision theory.

3. (25 pts) Consider the scheme of reactions:

$$A \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} B \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} C \underset{k_3'}{\overset{k_3}{\rightleftharpoons}} D$$

Derive an equation for the rate of product formation $d[D]/dt$ under the following conditions:

1. Steady-state approximation for the intermediates.
2. $[A]$ is maintained at a fixed value $[A]_o$.
3. The product D is removed as soon as it is formed.

4. (31 pts) (3.28) A chemical reaction $A \rightarrow P$ is observed to have the rate law $d[P]/dt = k[A]^2[P]$.

- **A.** What can readily be said about the mechanism of this reaction?

- **B.** Derive an integrated rate law for the above reaction, given that A and P have initial concentrations $[A]_o$ and $[P]_o$ respectively.

HINT:

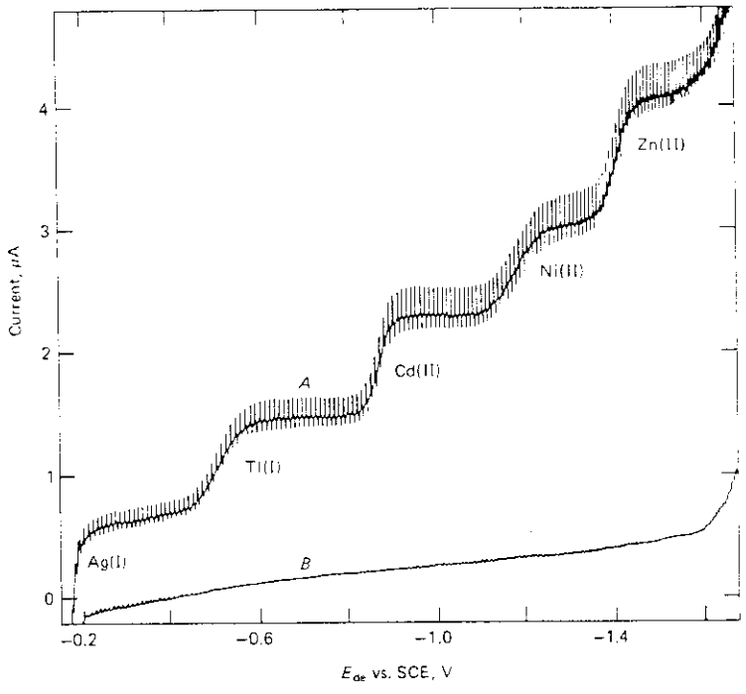
$$\frac{1}{(a-x)^2(p+x)} = \frac{\alpha}{(a-x)^2} + \frac{\beta}{(a-x)} + \frac{\gamma}{(p+x)}$$

5. (52 pts) (18,14.20)

- **A.** Derive the polagrography relation expressing current density j in response to a concentration overpotential η.

- **B.** Sketch a reversible cyclic voltammogram for a couple, followed by a corresponding potential versus time plot representing the various stages of the linear sweep.
  Then explain how E° for the couple is determined from the voltammogram.

- C. Consider the following polarogram of a solution 0.1 mM in each of silver (I), thallium (I), cadmium (II), nickel (II), and zinc (II) ions.



Determine the diffusion-limited current (i_L) and the half-wave potential ($E_{1/2}$) for each of those ions. Record your results in the Table below:

	Ag^+	Tl^+	Cd^{++}	Ni^{++}	Zn^{++}
$E_{1/2}$ (V)					
i_L (μA)					

6. (24 pts) In a flow study of the reaction between O atoms and Cl_2 (J. N. Bradley, D. A. Whytock, and T. A. Zaleski, *J. Chem. Soc. Faraday Trans.* I, 1251 (1973)) at high chlorine pressures, plots of $\ln [O]_\circ/[O]$ (where $[O]_\circ$ is the oxygen concentration at zero chlorine pressure) against distances along the flow tube, gave straight lines.

Given that the flow velocity is 6.66 ms^{-1} and the data below, find graphically the rate coefficient for the reaction: $O + Cl_2 \rightarrow ClO + Cl$.

ℓ (cm)	$\ln [O]_\circ/[O]$
0	0.27
2	0.31
4	0.34
6	0.38
8	0.45
10	0.46
12	0.50
14	0.55
16	0.56
18	0.60

$[O]_\circ = 3.3 \times 10^{-8}$ M,

$[Cl_2] = 2.54 \times 10^{-7}$ M.