Chemistry 217
Chemical Dynamics
Time: $2\frac{1}{2}$ *hours*

June 29, 1996
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Final Exam

NAME: ______________________

Gas constant R=8.314 J mol^{-1} K^{-1}

Avogadro's Number $N_o = 6.023 \times 10^{23}$ mol^{-1}

Proton charge $e = 1.602 \times 10^{-19}$ J

Vacuum permittivity $\varepsilon_o = 8.854 \times 10^{-12}$ $J^{-1}C^2m^{-1}$

Factorization of the quadratic equation: $ax^2 + bx + c = a(x - x')(x - x'')$, where x' and x'' are the roots. Product of the roots $p = c/a$.

Debye-Hückel constant for water at 298 K, $A = 0.509$ $M^{-1/2}$

1.	/18
2.	/21
3.	/18
4.	/20
5.	/40
6.	/20
7.	/15
8.	/20
9.	/28
Total	/200

Good Luck

1. (18 pts) Three independent parts

- **a.** Give the SI unit for the following physical quantities:

  ⋆ Diffusion coefficient

  ⋆ Thermal conductivity coefficient

  ⋆ Electrical conductivity coefficient (6 pts)

  ⋆ Viscosity coefficient

  ⋆ Ionic mobility

- **b.** Discuss briefly the dependence of ionic mobility on hydrodynamic radius. Then explain why is the trend in group I broken in the case of H^+. (5 pts)

- **c.** Predict the effect of ionic strength on the rate constant of the following reaction in aqueous solution: (7 pts)

$$A^+ \quad + \quad B^{2+} \quad \longrightarrow \quad X^{3+}.$$

2. (21 pts)

- **a.** A conductivity cell when standardized with 0.0100 M KCl was found to have a resistance of 189 Ω. With 0.0100 M ammonia solution the resistance was 2460 Ω. Calculate the base dissociation constant of ammonia. (15 pts)

  <u>GIVEN</u>: $\lambda(K^+)$=73.5 Ω^{-1} cm^2 mol^{-1}; $\lambda(Cl^-)$=76.4 Ω^{-1} cm^2 mol^{-1}; $\lambda(NH_4^+)$=73.4 Ω^{-1} cm^2 mol^{-1}; $\lambda(OH^-)$=198.6 Ω^{-1} cm^2 mol^{-1}.

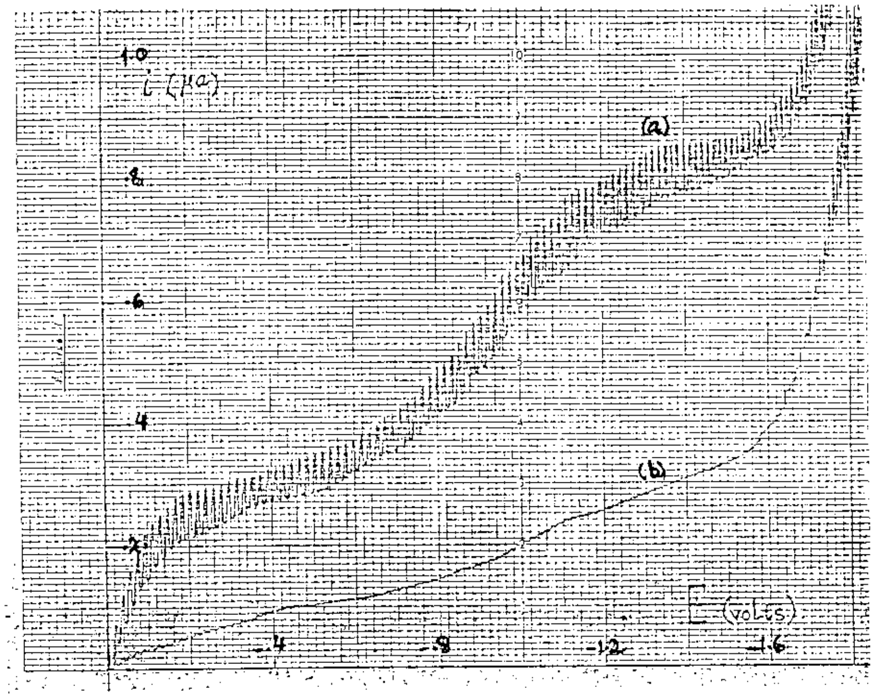
  <u>HINT</u>: For KCl, use $\Lambda(c) \approx \Lambda^\circ$.

- **b.** Using the Debye-Hückel limiting law, show that the thermodynamic pK_b (i.e. using activities) for ammonia can be determined from the intercept of a plot of pK_c (using concentrations) versus $\sqrt{c}$. What is the slope of this plot at 298 K?

  Then explain how you can determine the mean activity coefficient for ammonium hydroxide at a given concentration. (6 pts)

  <u>HINT</u>: Take the activity coefficient of a neutral molecule to be unity.

3. (18 pts) The following polarogram shows polarographic waves for O_2 in acidic medium (the first two waves).



NOTE: Consider only curve (a); ignore curve (b).

The first wave is for $O_2 \rightarrow H_2O_2$

The second wave is for $H_2O_2 \rightarrow H_2O$

Write the two half-reactions, and determine from the graph the half-wave potential and the diffusion-limited current for each of them.

4. (20 pts) The Arrhenius factor for the reaction Na + Cl_2 $\rightarrow$ NaCl + Cl was found to be 4.60×10^{11} $M^{-1}s^{-1}$ at 628 K.

- **a.** Estimate the steric factor for this reaction as predicted by the Collision Theory. Take $R(\text{Na})+R(\text{Cl}_2)=350$ *pm*.
  Comment on the result obtained. (8 pts)

- **b.** To account for the the steric factor, a "harpoon mechanism" was proposed for the above reaction, involving a sodium ion and a chlorine molecule-ion. Calculate the steric factor predicted by this mechanism, given that $IE(\text{Na})=496$ kJ/mol and $EA(\text{Cl}_2^-)=230$ kJ/mol.
  Compare your result with that of part **a.** (12 pts)

5. (40 pts) Consider the following chemical reaction scheme:

$$A + B \underset{k'}{\overset{k}{\rightleftharpoons}} X.$$

Let $[A]_\circ = [B]_\circ = a_\circ$, and call x_e the equilibrium concentration of the product X.

- **a.** Show that the integrated rate law can be written in the form:

$$\frac{x_e}{a_\circ^2 - x_e^2} \ln \frac{x_e(a_\circ^2 - x x_e)}{a_\circ^2(x_e - x)} = kt.$$

where x is the concentration of product at time t. (20 pts)
<u>HINT</u>: the physical solution of $dx/dt = 0$ is the equilibrium concentration x_e. The other root of the quadratic equation can be expressed in terms of x_e.

- **b.** The following experimental data were taken in a kinetic run at 628 K.

x (M)	t (s)
0	0
0.00162	500
0.00277	1000
0.00368	1500
0.00431	2000
0.00478	2500
0.00518	3000
0.00547	3500
0.00650	∞

Using the graph sheet (1) provided, make an appropriate plot of these data to determine the rate constants k and k'. (20 pts)
<u>HINT</u>: Use the result of part **a.**

6. (20 pts) When an inhibitor I is added to a single substrate enzyme system, the mechanism is sometimes:

$$
\begin{array}{ccc}
 & \mathrm{S} & \\
 & + & \\
\mathrm{I} + & \mathrm{E} & \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} \ \mathrm{EI} \\
k_{-1} & \uparrow\downarrow & k_1 \\
 & \mathrm{ES} & \\
 & \downarrow & k_2 \\
 & \mathrm{E} + \mathrm{P} &
\end{array}
$$

- **a.** This is known as a *competitive* mechanism. Explain why. (2 pts)

- **b.** Assume that the substrate and inhibitor are present in large excess of the enzyme. Apply the steady-state approximation and obtain the rate of product formation v in terms of: [S], [I], $[\mathrm{E}]_o$, k_2, the Michaelis constant K_M, and K_i the equilibrium constant for the inhibition step. (18 pts)

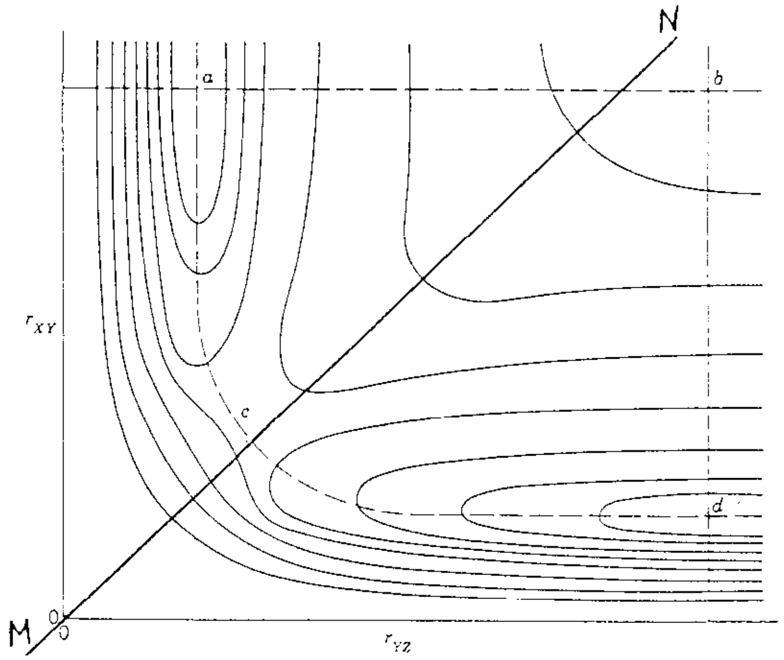
7. (15 pts) Consider the scheme of autocatalytic reaction steps:

$$A + X \rightarrow 2X$$

$$2A + X \rightarrow P$$

Assuming the concentration of A remains constant, determine the condition under which the reaction system becomes unstable to oscillations.

8. (20 pts) Consider the following potential energy contour diagram for the linear XYZ system:



- **a.** Sketch the molecular approach for the reaction showing clearly r_{XY} and r_{YZ}. (2 pts)

- **b.** What can you say about the energy of each of the points a, b, c and d? (8 pts)

- **c.** Sketch (on the diagram) the following trajectories:
  - Z approaching an XY molecule with r_{XY} remaining constant (label A).
  - Z approaching an XY molecule with r_{XY} gradually increasing as r_{YZ} is decreasing (label B).
  - A path through the saddle point (label C).
  - An unsuccessful trajectory (label D). (6 pts)

- **d.** Draw the curve obtained by cutting a vertical cross-section along the line MN. (4 pts)

9. (28 pts) CORROSION DYNAMICS

Consider a cell in which the current is activation controled. The cell anode undergoes corrosion when connected in a closed circuit to a battery of emf E' and a resistance R.

- **a.** Show that the current for maximum power can be estimated by plotting $\ln I/I_\circ$ and $c_1 - c_2 I$ against I (where $I_\circ = \sqrt{AA'j_\circ j'_\circ}$ and c_1 and c_2 are constants to be determined), and looking for the intersection point of the two curves. (10 pts)

- **b.** Using graph sheet (2), construct the plot of interest to determine the current for maximum power I_{max}, using the following data:
  Electrode reaction: M $\rightleftharpoons M^{2+} + 2e^-$ (i.e. z=2)
  $E' = 1.10\ V$ $j_\circ = j'_\circ = 1.00\ mA\ cm^{-2}$ $R = 3.80\ \Omega$
  $A = A' = 5.00\ cm^2$ $f = 1/25.69\ \ mV^{-1}$.
  Use values of I= 110, 112, 114, 116, 118 and 120 mA for your points. (18 pts)