

Chem 155  
Thermodynamics  
Quantum Chemistry  
Molecular Orbital Theory  
Transition-Metal Complexes  
Chemical Kinetics

Final Exam  
December 13, 2002



Name \_\_\_\_\_

Full credit will be given to correct answers only when ALL the necessary steps are shown.  
DO NOT GUESS THE ANSWER.

This is a closed book and closed notes exam, and you are responsible to be sure that your exam has no missing pages (9 pages).

If you consider that there is not enough information to solve a problem, you have to specify the missing information and describe the problem solving procedure.

*Whoever thinks a faultless  
piece to see  
Thinks what ne'er was, nor is,  
nor e'er shall be.*

- Alexander Pope,  
An Essay on Criticism

**Honor Statement**

I have neither give nor received aid in this examination.

Full signature \_\_\_\_\_

**Problem 1 (10 points)**

List the condition(s) under which each of the following equations can be applied. If no conditions are required, write "none."

$$w = -P\Delta V$$

CONSTANT PRESSURE

$$\bar{S}^{\circ} = 0 \text{ (third law of thermodynamics)}$$

PURE CRYSTALLINE SUBSTANCE AT 0K

$$\Delta H = \Delta U + \Delta(PV) \quad \text{none}$$

$$\Delta S = n\bar{C}_P \ln \frac{T_2}{T_1}$$

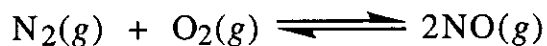
$\bar{C}_P$  INDEPENDENT OF T

$$E = E^{\circ} - \frac{RT}{vF} \ln Q$$

none

**Problem 2 (10 points)**

Consider the reaction



Given that  $K_p$  for the reaction at  $25^\circ\text{C}$  is  $4.0 \times 10^{-31}$ , calculate the standard Gibbs energy of formation ( $\Delta_f \bar{G}^\circ$ ) for NO. ( $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ )

$$\begin{aligned}\Delta G_{\text{rxn}}^\circ &= -RT \ln K \\ &= -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K}) \ln [4.0 \times 10^{-31}] \\ &= 1.7 \times 10^5 \text{ J mol}^{-1}\end{aligned}$$

↳ 2 sig figs

$$\begin{aligned}\Delta G_f^\circ &= \frac{1}{2} \Delta G_{\text{rxn}}^\circ \\ &= 8.7 \times 10^4 \text{ J mol}^{-1}\end{aligned}$$

**Problem 3 (15 points)**

A galvanic cell using  $\text{Cu}^{2+}/\text{Cu}$  and  $\text{Sn}^{2+}/\text{Sn}$  half-cells initially operates under standard-state conditions at  $25^\circ\text{C}$  and each cell compartment has a volume of 245 mL. The cell delivers 0.15 A for 54.0 hours.

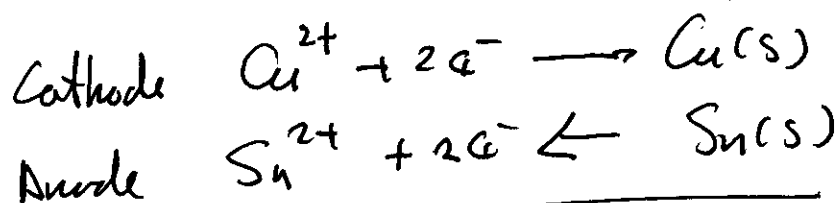
- (a) How many grams of Cu are deposited at the cathode?  
 (b) What is the emf (E) of the cell?

(Hint: The standard reduction potentials are:  $\text{Cu}^{2+}/\text{Cu} = 0.34 \text{ V}$  and  $\text{Sn}^{2+}/\text{Sn} = -0.14 \text{ V}$ .

$1 \text{ C} = 1 \text{ A} \times 1 \text{ s}$ . Charge on 1 mole of electrons = 96,500 C. Molar mass of Cu = 63.55 g.)

$$Q = It = 0.15 (54.0 \times 60 \times 60) \\ = 29160 \text{ C}$$

$$\# \text{ of moles of } e^- \rightarrow = \frac{29160}{96500} = 0.302 \text{ mol}$$



$$E^\circ = 0.34 \text{ V} - (-0.14 \text{ V}) = 0.48 \text{ V}$$

$$\text{Amount of Cu deposited} = \frac{1}{2} (\# \text{ of moles of } e^-) \\ = 0.151 \text{ mol.}$$

$$\text{a) Mass} = 63.55 \frac{\text{g}}{\text{mol}} \times 0.151 \text{ mol} = 9.60 \text{ g}$$

$$\text{b) } E = E^\circ - \frac{RT}{nF} \ln K = 0.48 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{[\text{Sn}^{2+}]}{[\text{Cu}^{2+}]} \\ = 0.46 \text{ V} \checkmark$$

**Problem 4 (20 points)**

Consider butadiene,  $H_2C=CH-CH=CH_2$ , which has four  $\pi$  electrons. Although butadiene is not a linear molecule, we shall assume for simplicity that the  $\pi$  electrons in butadiene move along a straight line whose length can be estimated as equal to two C=C bond lengths of 0.135 nm, plus one C-C bond, or 0.154 nm, plus the distance of a carbon atom radius at each end, or another 0.154 nm.

- Calculate the energy difference between the Highest Occupied Energy Level and the Lowest Unoccupied Energy Level.
- Calculate the wavelength of a photon with such energy.

FOR PARTICLE IN A BOX  $E_n = \frac{h^2}{8mL^2} n^2$

SINCE WE HAVE 4 electrons  
WE FILL THE FIRST TWO ENERGY LEVELS

TRANSITION  $n=2 \rightarrow n=3$

$$\Delta E = E_3 - E_2 = \frac{h^2}{8mL} [3^2 - 2^2]$$

$$\Delta E = \frac{5h^2}{8mL} = \frac{5 \times (6.6260 \times 10^{-34} \text{ Js})^2}{8(9.109 \times 10^{-31} \text{ kg})(0.578 \times 10^{-9} \text{ m})^2}$$

$$L = [2(0.135) + 0.154 + 0.154] \text{ nm}$$

0.270 + 0.308

$$L = 0.578 \text{ nm}$$

$$\Delta E = \frac{9.01 \times 10^{-68} \text{ J} (\text{kg} \frac{\text{m}^2}{\text{s}^2}) \text{ s}^2}{10^{-49} \text{ kg m}^2}$$

$$\Delta E = 9.01 \times 10^{-19} \text{ J} = 5.62 \text{ eV}$$

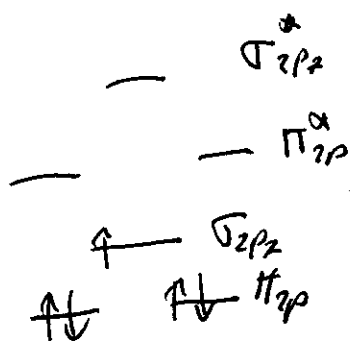
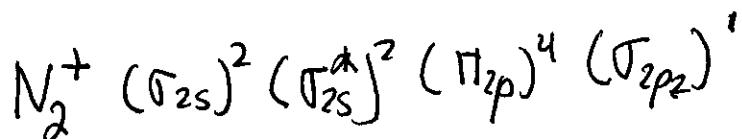
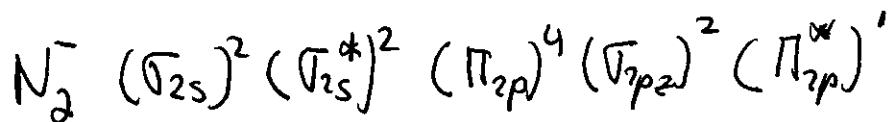
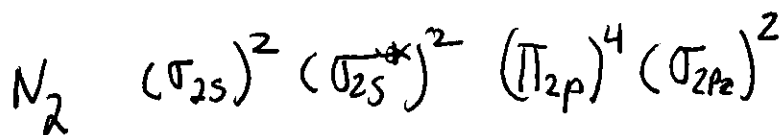
$$\Delta E = h\nu = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{\Delta E} = \frac{6.6260 \times 10^{-34} \text{ J s} \times 2.997 \times 10^8 \text{ m s}^{-1}}{9.01 \times 10^{-19} \text{ J}}$$

$$\lambda = 2.28 \times 10^{-7} \text{ m}$$

$$\lambda = 228 \text{ nm}$$

**Problem 5 (20 points)**

Using Molecular Orbital Theory describe as thorough as possible the following diatomic molecules:  $N_2$ ,  $N_2^+$ , and  $N_2^-$ . Include the relative properties such as stability.



$$BO \quad N_2^+ \quad 2\frac{1}{2}$$

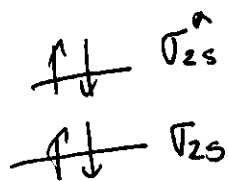
$$N_2 \quad 3$$

$$N_2^- \quad 2\frac{1}{2}$$

$N_2$  diamagnetic

$N_2^+$ ,  $N_2^-$  paramagnetic

$N_2$  MORE STABLE THAN  $N_2^+$  AND  $N_2^-$



**Problem 6 (20 points)**

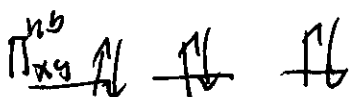
Using Crystal Field theory predict the number of unpaired electrons in the following complexes:

Weak Field Ligands:  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  
Strong Field Ligands: en,  $\text{NH}_3$

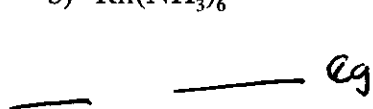
a)  $\text{Co}(\text{en})_3^{2+}$  octahedral; en STRONG FIELD  $\Rightarrow$  LOW SPIN  
 $\text{Co}^{2+} \rightarrow 7 \text{ d electrons}$



**1 UNPAIRED  $e^-$**

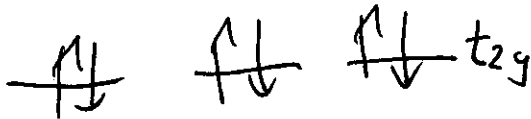


b)  $\text{Rh}(\text{NH}_3)_6^{3+}$  octahedral;  $\text{NH}_3$  STRONG FIELD  $\Rightarrow$  LOW SPIN



$\text{Rh}^{3+} \rightarrow 6 \text{ d } e^-$

**NO UNPAIRED  $e^-$**



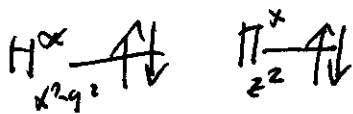
c)  $\text{CoBr}_4^{2-}$  Tetrahedral structure

$\text{Br}^-$  WEAK FIELD  $\Rightarrow$  HIGH SPIN

$\text{Co}^{2+} 7 e^-$



**3 UNPAIRED  $e^-$**



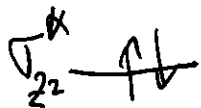
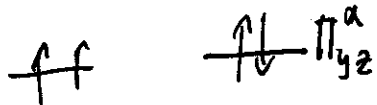
d)  $\text{Pt}(\text{NH}_3)_4^{2+}$  Square planar

$\text{NH}_3$  STRONG FIELD  $\Rightarrow$  LOW SPIN

$\text{Pt}^{2+} \rightarrow 8 \text{ d electrons}$

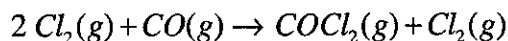


**NO UNPAIRED  $e^-$**



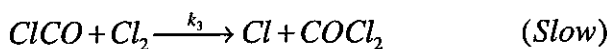
**Problem 7 (20 points)**

In the following reaction we use an isotopic chlorine mixture of 50%  $^{35}\text{Cl}_2$  and 50%  $^{37}\text{Cl}_2$



In the products, we find 25%  $\text{CO}^{35}\text{Cl}_2$ , 50%  $\text{CO}^{35}\text{Cl}^{37}\text{Cl}$  and 25%  $\text{CO}^{37}\text{Cl}_2$ . Thus Cl is an intermediate.

We propose the following mechanism



where M is a host inert gas like argon.

a) What is the rate law predicted by this mechanism?

b) What is the value of the rate constant as a function of  $K_1$ ,  $K_2$ , and  $k_3$ ?

a) THE SLOW STEP CONTROLS THE OVERALL RXN

$$r = k_3 [\text{Cl}_2] [\text{ClCO}]$$

BOTH FAST RXN REACH EQUILIBRIUM

$$K_1 = \frac{[\text{Cl}]^2}{[\text{Cl}_2]}$$

$$K_2 = \frac{[\text{ClCO}]}{[\text{Cl}][\text{CO}]}$$

$$[\text{Cl}] = \sqrt{K_1} \sqrt{[\text{Cl}_2]}$$

$$[\text{ClCO}] = K_2 [\text{Cl}][\text{CO}]$$

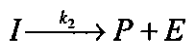
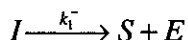
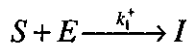
$$r = k_3 K_2 \sqrt{K_1} [\text{CO}] [\text{Cl}_2]^{3/2}$$

b)  $k = k_3 K_2 \sqrt{K_1}$

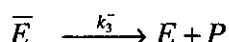
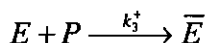


**Problem 8 (20 points)**

In glycolysis, glucose is phosphorylated with the help of hexokinase. It is known that the product, glucose-6-phosphate, binds to hexokinase and inhibits the enzyme. In class we studied a simple enzymatic reaction. Here we want to include an inhibitory step in the mechanism and obtain the rate of the reaction. We will assume that we have ATP in excess so we can propose the following mechanism:



Now the inhibition



where  $\bar{E}$  is an inactive form of the enzyme.

a) Write down the rate of change equations for I and  $\bar{E}$ .

b) If we assume that the amount of enzyme remains constant, we can consider the following equation:

$$E_0 = E + I + \bar{E}$$

Using the Steady State Approximation in a), find I and  $\bar{E}$  as functions of E. Use the previous expressions and the conservation of enzyme to find E as a function of S, P and constants like  $E_0$ .

c) Now we can find the rate of the reaction by finding first

$$r = \frac{dP}{dt} = k_3 I - k_3^+ E \cdot P + k_3^- \bar{E} \stackrel{=0}{=} k_3 I = k_3 \frac{S \cdot E}{K_M} = \frac{k_3 E_0 S}{K_M + S + K_M K_3 P}$$

Make sure that your final result is expressed as a function of S, P and constants.

$$a) \quad \frac{dI}{dt} = k_1^+ S \cdot E - k_1^- I - k_2 I \approx 0$$

$$\frac{d\bar{E}}{dt} = k_3^+ E \cdot P - k_3^- \bar{E} \approx 0$$

$$b) \quad I = \frac{k_1^+ S \cdot E}{k_2 + k_1^-} \quad \bar{E} = \frac{k_3^+ P \cdot E}{k_3^-} \quad ; \quad E_0 = E + \frac{S \cdot E}{K_M} + K_3 P \cdot E$$

$$E = \frac{K_M E_0}{K_M + S + K_M K_3 P}$$