CHEM 323
Fall 2008
Post-Exam 3
Due December 12, 2008 at 5:00 PM

Name: _____

Instructions
Fill in only the answers below. Attach your work to these cover pages, but do not include the questions. Sign the affidavit at the bottom of the second page. A link to the full contest rules is posted on the *Announcements* section of the class web page.

1a. K = _____

b. Relationship between *p*H and *p*D: _____

2a. ΔG = _____

ΔH = _____

ΔS = _____

b. $\gamma_{\pm}$ = _____

3. Rate Law: rate =

k = _____

4a. k = _____ at low ionic strength

b. k = _____ at high ionic strength

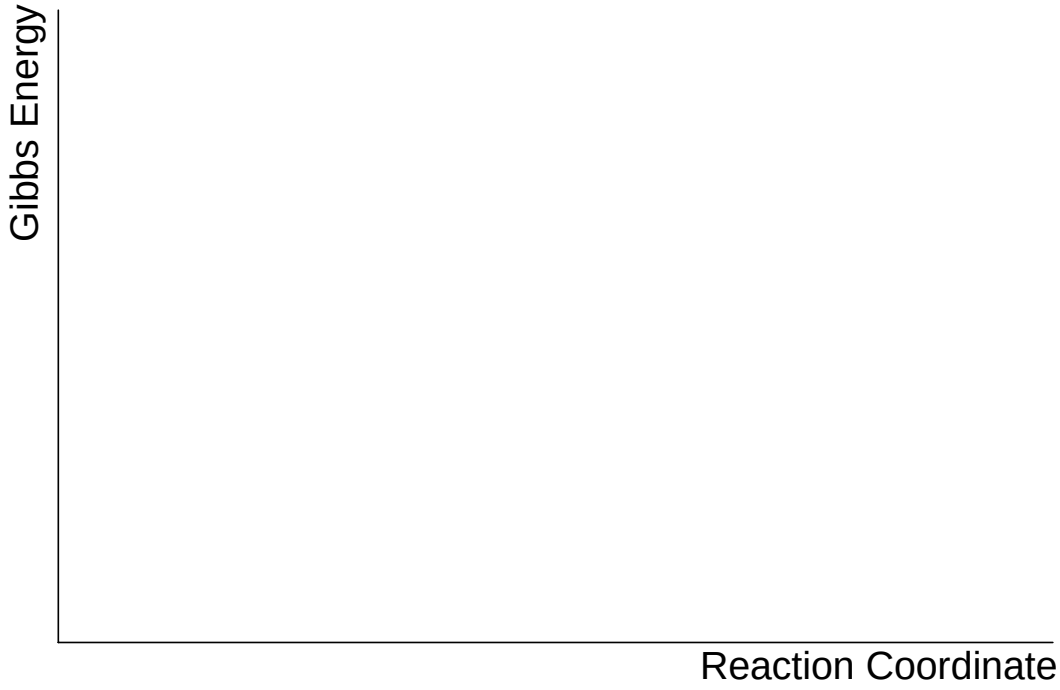
5a. $\Delta^{\ddagger}S$ = _____

b. $\Delta^{\ddagger}H$ = _____

6. $[Ca(HEDTA)]^{2-}$ = _____

7a. Rate Law: rate =

b.



8a. E_a = _____

b. T = _____

By my signature below I attest that I have abided by all the rules set forth on the web page.

_____ _____

Signature Date

Instructor Use Only!

Number correct	
Work included	
Instructions followed	
Total	

DO NOT TURN THESE QUESTIONS IN WITH THE ANSWER SHEET

1a. The reaction $2\ D^+\ (aq) + 2\ e^-$ $\rightleftharpoons$ $D_2\ (g)$ defines the D^+/D_2 redox couple. The standard reduction potential for the D^+/D_2 redox couple is -3.40 mV at 25.0 °C. Calculate *K* for the reaction: $2\ H^+\ (aq) + D_2\ (g)$ $\rightleftharpoons$ $2\ D^+\ (aq) + H_2\ (g)$.

b. Derive an equation that relates *p*D to *p*H in terms of *K* for the reaction in part *a* (you don't need a numerical value for *K* to do this).

2. The following galvanic cell has a measured cell potential of +1.015 V versus SHE at 25.0 °C. It was also found that $\left(\frac{\partial E}{\partial T}\right)_p = -4.02x10^{-4}\ \mathrm{V \cdot K^{-1}}$ at that temperature.

$$\mathrm{Zn\ (s)\ |\ ZnCl_2\ (aq,\ 0.555\ m)\ |\ AgCl\ (s)\ |Ag\ (s)}$$

a. Determine ΔG, ΔH and ΔS for this cell at 25.0 °C.

b. Using the Nernst equation for this cell written in terms of the $ZnCl_2$ molality and $\gamma_\pm$, determine $\gamma_\pm$ for the ions in this cell. You are given that E^0 for the Zn/Zn^{2+} redox couple is -0.7618 V while E^0 for the AgCl/Ag redox couple is +0.22233 V.

3. The following table gives the initial rate of reaction for the reaction $OCl^- + I^- \rightarrow OI^- + Cl^-$ in aqueous solution at various reactant concentrations. What is the rate law for the reaction and what is the value of the rate constant?

$[OCl^-]$ (M)	$[I^-]$ (M)	$[OH^-]$ (M)	$\frac{d[IO^-]}{dt}$ $(M^{-1}\cdot s^{-1})$
0.0017	0.0017	1.00	$1.75x10^{-4}$
0.0034	0.0017	1.00	$3.50x10^{-4}$
0.0017	0.0034	1.00	$3.50x10^{-4}$
0.0017	0.0017	0.500	$3.50x10^{-4}$

4. The equilibrium constant for the reaction $[Co(NH_3)_5(H_2O)]^{3+} + Br^-$ $\rightleftharpoons$ $[Co(NH_3)_5Br]^{3+} + H_2O$ is 0.37 and the rate constant for the back reaction is $6.3x10^{-6}\ s^{-1}$, both values at 25.0 °C. Calculate the rate constant for the forward reaction a) at low ionic strength ($I \approx 0$) and b) in 0.1 M $NaClO_4$.

5. Calculate $\Delta^{\ddagger}S$ and $\Delta^{\ddagger}H$ for the first-order decomposition of N_2O_5 at high pressure given that $k = 3.35x10^{-5}\ s^{-1}$ at 25.0 °C and $k = 0.0048\ s^{-1}$ at 65 °C.

6. The ligand N-(2-hydroxyethyl)ethylenedinitrilotriacetic acid (HEDTA) binds metals as the tetraanion ($HEDTA^{4-}$). At a certain temperature, *p*H and ionic strength HEDTA binds Pb^{2+} with log $K = 15.6$ and under identical conditions it binds Ca^{2+} with log $K = 8.1$. A solution, which has a total concentration of 0.100 M in both HEDTA and Ca^{2+}, is at equilibrium. Sufficient $Pb(NO_3)_2$ is added to the solution so as to bring the $[Pb^{2+}]$ to 0.100 M (assume no volume change). What will be the concentration of $[Ca(HEDTA)]^{2-}$ when the system returns to equilibrium? Assume that no other equilibria occur and activity effects can be ignored.

7a. Derive the rate law from the following mechanism assuming that the second step is rate determining, but the first step is <u>not</u> a rapid pre-equilibrium.

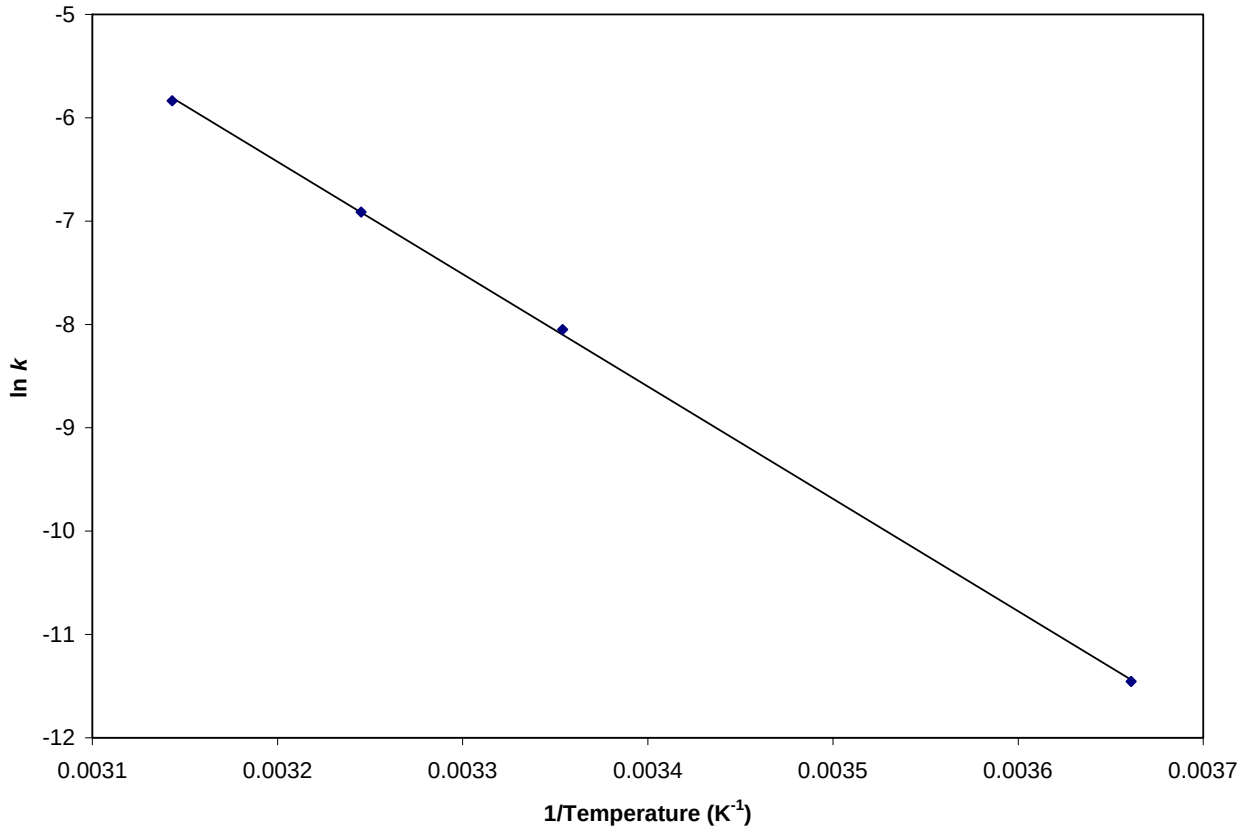
$$O_3 + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O + M$$

$$O_3 + O \xrightarrow{k_2} 2\,O_2$$

b. Given that $\Delta_f G^0$ (O_3, g) = +163.2 kJ/mole, draw a qualitative reaction profile for this mechanism in the space provided on the answer sheet. Label the important thermodynamic and kinetic features that are present (e. g., intermediate, E_a, etc.).

8. The hydrolysis of 2-chlorononane in 80% ethanol is first-order in 2-chlorononane. The temperature dependence of the rate constant, k (in units of s^{-1}), was obtained and the data was graphed as shown below. The best-fit line through the data had a slope of $(-1.08 \pm 0.01)\times10^4$ K and an intercept of 28.4 ± 0.4.

a. What is the activation energy for this reaction?



b. At what temperature will the half-life of this first-order reaction be 10.00 days? You are given the expression $t_{1/2} = \dfrac{\ln 2}{k}$, where $t_{1/2}$ is the half-life.