Chemistry 113C, Spring 2009
Take-home Final Exam

The exams will be collected in Webb 1100 on Wednesday June 10,
between 9:00AM and 9:30AM.

If you want to work in a group, you may do so
BUT YOU MUST write your own report.

name

perm number

Staple this page to your report. Put your initials or name on each page.

Grading

Problem	**Possible points**	**Actual points**
1a	10	
1b	30	
1c	20	
1d	50	
1e	20	
1f	100	
1g	100	
2	50	
3	30	
TOTAL	**410**	

1. You have a cubic container of side L = 1 cm and you introduce in it 4.0×10^{-11} moles of a gas consisting of atoms. These gas atoms interact with the walls of the container with the potential energy

$$V(z) = 4\,\varepsilon\,[(\sigma/z)^{12}-(\sigma/z)^{6}] \qquad (1)$$

where

$$\varepsilon = 0.4 \text{ eV}$$

and

$$\sigma = 2.8 \text{ Angstroms.}$$

Here z is the coordinate in the direction perpendicular to the surface of the wall. The potential attracts the atoms to the wall and as a consequence some of the atoms stick to the wall and some will exist inside the cube. The atoms stuck to the wall (which we call the adsorbed atoms) move freely in directions parallel to the wall and do not interact with each other. The atoms inside the cube do not interact with each other either.

a) (10 points) The motion of the adsorbed atoms in the direction perpendicular to the wall can be approximated by a harmonic oscillator. Calculate the frequency of this oscillator.

b) (30 points) Calculate the partition function of the adsorbed atom (hint: the atoms move like in a gas in the direction parallel to the surface (i.e. a two dimensional gas) and oscillate in the direction perpendicular to it). The spin of the nucleus and the electronic spin are both zero.

c) (20 points) Derive formulae for the energy, the heat capacity, and the chemical potential of the adsorbed atoms.

d) (50 points) Calculate the number of atoms N_s adsorbed on the surface of the cube when they are in equilibrium with the atoms inside the cube. If you do not use Mathematica, calculate N_s for the temperature T = 298 K. If you use Mathematica, plot N_s versus T. (Hint: pay attention to the zero of energy when you calculate the partition function of the oscillator.)

e) (20 points) What is the pressure of the gas in the container after the atoms in it have equilibrated with the adsorbed atoms?

f) (100 points) Use transition state theory to show that the rate of desorption (the rate with which the adsorbed atoms leave the surface) is given by

$$\left(\frac{dN_s}{dt}\right)_d = -k_d\, N_s$$

and calculate the rate constant k_d. Take the dividing surface at z = 6 Angstroms, where the potential V(z) is zero.

g) (100 points) Assume that the rate of adsorption is given by

$$\left(\frac{dN_s}{dt}\right)_a = -k_a\, A\, P$$

where P is the pressure of the gas inside the cube. Use the detailed balance to connect the adsorption rate constant k_a to the desorption rate constant k_d, the equilibrium concentration N_s, and the pressure of the gas at equilibrium.

2. (50 points) The dissociation of dicyclopentadiene was studied by performing measurements of a quantity A that is proportional to the concentration of dicyclopentadiene. The values of A measured at different times are

A	1.85	2.04	2.34	2.70	3.83	5.28
t/sec	524	620	752	876	1188	1452

Use these data to determine the rate equation and the rate constant.

3. (30 points) Consider the reaction

$$H_2O(\ell) + Cr_2O_7^{2-}(aq) \rightarrow 2\ CrO_4^{2-}(aq) + 2\ H^+(aq)$$

in which a dichromate is converted into a chromate. You start the reaction initially by dissolving the bichromate in water. You know the initial concentration of the bichromate. The counter ion for the bichromate is Na^+ but this does not participate in the reaction. You can measure how the concentration of the $Cr_2O_7^{2-}(aq)$ ion changes in time by using light absorption. Show how you can use these measurements to calculate the time evolution of the pH of the solution. (Recall that $pH = -\log_{10} [H^+]$ where $[H^+]$ is the concentration of the protons.)