Columbia University in the City of New York New York, N.Y. 10027

Chemistry C2407x
Final Exam
December 17, 2002

Total Points: 300
2002
George Flynn
3 Hours
All questions are not weighted equally. I have attempted to order the questions from the least difficult to the most difficult, but "beauty is in the eye of the beholder", so skip around to find the problems that are easiest for you. Good luck!

Please print your name in the boxes provided and sign where indicated. Tear off this sheet and pass it to the right for the proctors to pick up.

| Print your last name: |
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| Print your first name: |

Signature: $\qquad$

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| Print your last name: |
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Do not write anything else on this page. Answer the questions in the spaces provided on the following pages.

| 1 a | 2 a | 3 a | 4 a | 5 a | 6 a |
| :--- | :--- | :--- | :--- | :--- | :--- |
|  |  |  |  |  |  |
| 1 b | 2 b | 3 b | 4 b | 5 b | 6 b |
|  |  |  |  |  |  |
| 1 c | 2 c | 3 c | 4 c | 5 c | 6 c |
|  |  |  |  |  |  |
| 1 d | 2 d | 3 d | 4 d | 5 d | 6 d |
|  |  |  |  |  |  |
| 1 e | 2 e |  | 4 e |  |  |
|  | 2 f |  |  |  |  |

Print your name here:
Problem 1 (45 points) (Looks like Oxtoby problem 7.57) Suppose that 7 moles of Xenon gas are confined by a movable, frictionless piston in a cylinder at a pressure of seven atmospheres and a temperature of 300 ${ }^{\circ} \mathrm{K}$. The gas is cooled at this constant pressure of 7 atmospheres until the temperature reaches $200^{\circ} \mathrm{K}$. Xenon is a monatomic, ideal gas.
a) (10 points) Determine w, the work done on the system. Show reasoning clearly.
b) (10 points) Determine q, the heat absorbed by the system. Show reasoning clearly.

Print your name here:
c) (5 points) Determine $\square \mathrm{E}$, the energy change for the system. Show reasoning clearly.
d) (5 points) Determine $\square \mathrm{H}$, the enthalpy change for the system. Show reasoning clearly.

Print your name here:
e) (15 points) Determine $\square S$, the entropy change for the system. Show reasoning clearly.

Print your name here:
Problem 2: (55 points) Consider the chemical transformation:

$$
2 \mathrm{HCl}(\mathrm{~g})=\mathrm{Cl}_{2}(\mathrm{~g})+\mathrm{H}_{2}(\mathrm{~g})
$$

and the data:

|  | $\square \mathrm{H}_{\mathrm{f}}^{\circ}\left(25^{\circ} \mathrm{C}\right)$ | $\mathrm{S}^{\circ}\left(25^{\circ} \mathrm{C}\right)$ | $\square \mathrm{G}_{\mathrm{f}}^{\circ}\left(25^{\circ} \mathrm{C}\right)$ | $\mathrm{C}_{\mathrm{p}}\left(25^{\circ} \mathrm{C}\right)$ |
| :--- | :--- | :--- | :--- | :--- |
|  | $(\mathrm{kJ} / \mathrm{mole})$ | $\left(\mathrm{J} / \mathrm{K}^{\circ} \mathrm{mole}\right)$ | $(\mathrm{kJ} / \mathrm{mole})$ | $\left(\mathrm{J} / \mathrm{K}^{\circ} \mathrm{mole}\right.$ |
| $\mathrm{HCl}(\mathrm{g})$ | -92.31 | 186.8 | -95.30 | 29.12 |
| $\mathrm{Cl}_{2}(\mathrm{~g})$ |  | 222.96 |  | 33.91 |
| $\mathrm{H}_{2}(\mathrm{~g})$ |  |  |  | 28.82 |

Note: Missing entries in the table are not necessarily zero. a)( 5 points) Calculate $\mathrm{HH}^{\circ}{ }_{298}$ for this reaction. Show all reasoning clearly.
b)(5 points) Calculate $\square \mathrm{G}^{\circ}{ }_{298}$ for this reaction. Show all reasoning clearly.

## Print your name here:

c)(10 points) Calculate $\square S^{\circ} 298$ for this reaction. Show all reasoning clearly.
d)(10 points) Assuming all the gases involved in this reaction are ideal gases, calculate $\square^{\circ}{ }_{298}$ for this reaction. Show all reasoning clearly.

Print your name here:
e)(15 points) Compute the absolute entropy [ $\mathrm{S}^{\circ}{ }_{298}$ ] for $\mathrm{H}_{2}(\mathrm{~g})$ at 298 K . Show all reasoning clearly.
f)(10 points) Compute the equilibrium constant for the reaction at 298 K. Show all reasoning clearly.

Print your name here:
Problem 3 (50 points) Acetic Acid is a weak acid:
$\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{H}_{2} \mathrm{O}=\mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$
Phenolphthalein is a popular indicator with a $\mathrm{pK}_{\mathrm{a}}$ of 8.0 :
PhenH(colorless) $+\mathrm{H}_{2} \mathrm{O}=$ Phen $^{-}$(red) $+\mathrm{H}_{3} \mathrm{O}^{+}$
A sample is prepared by dissolving 1.00 moles of acetic acid in enough water to make one liter of solution. The pH of the resulting solution is measured with a meter and found to be 2.38. A drop of phenolphthalein is added to follow the solution pH . The phenolphthalein does not affect the concentration of $\mathrm{H}_{3} \mathrm{O}^{+}$because there is such a small amount of it.

However, the color of phenolphthalein is, of course, affected by the concentration of $\mathrm{H}_{3} \mathrm{O}^{+}$.
a) (10 points) What is the acid ionization constant, $K_{2}$, for acetic acid? Show reasoning clearly.

Print your name here:
b) (10 points) What is the color of this solution? A good answer to this question will include a quantitative measure of the ratio [ $\left.\left.\mathrm{Phen}^{-(r e d}\right)\right] /$ [PhenH(colorless)]. Show all reasoning clearly.
c) ( 15 points) What is the pH for this mixture if 0.35 moles of NaOH ( a strong base) is added to the solution without changing the volume? Show reasoning clearly.

Print your name here:
d) ( 15 points) What is the pH for this mixture if another 0.65 moles of NaOH (a strong base) is added to the solution of part c without changing the volume? Show reasoning clearly.

Print your name here: Problem 4: (55 Points) [Oxtoby problem16.2; looks like homework problem Oxtoby 16.1] When one electron is added to an oxygen molecule, a superoxide ion $\left(\mathrm{O}_{2}^{-}\right)$is formed. The addition of two electrons gives a peroxide ion $\left(\mathrm{O}_{2}{ }^{2-}\right)$. Removal of an electron from $\mathrm{O}_{2}$ leads to $\mathrm{O}_{2}{ }^{+}$. The molecular orbital filling order for these species is the same as that for $\mathrm{O}_{2}$. In what follows, you are reminded that the atomic configuration of the oxygen atom is $\mathrm{O}\left(1 \mathrm{~s}^{2} 2 \mathrm{~s}^{2} 2 \mathrm{p}^{4}\right)$.
a) (15 points) Construct the energy correlation diagram for $\mathrm{O}_{2}$ - Show all reasoning clearly.

Print your name here:
b)(15 points) Give the molecular electron configuration for each of the following species: $\mathrm{O}_{2}{ }^{+}, \mathrm{O}_{2}, \mathrm{O}_{2}{ }^{-}, \mathrm{O}_{2}{ }^{2-}$. Show reasoning clearly.
c) (10 points) Give the bond order for each of the following species: $\mathrm{O}_{2}{ }^{+}, \mathrm{O}_{2}, \mathrm{O}_{2}^{-}, \mathrm{O}_{2}^{2-}$. Show all reasoning clearly.

Print your name here:
d) (10 points) Give the number of unpaired electrons for each of the following species: $\mathrm{O}_{2}{ }^{+}, \mathrm{O}_{2}, \mathrm{O}_{2}^{-}, \mathrm{O}_{2}{ }^{2-}$. Show all reasoning clearly.
e) (5 points) Predict the order of increasing bond dissociation energy among the species. Show reasoning clearly.

## Print your name here:

Problem 5 (50 points) The graph on the next page shows data (initial rate in units of $\mathrm{mM} / \mathrm{min}$ and substrate concentration in $\mathrm{mM}=10^{-3} \mathrm{M}$ ) for the enzyme catalyzed decomposition of the pesticide paraoxon by the enzyme organophosphorus hydrase. The data is presented as a "Lineweaver-Burke" plot of $1 / \mathrm{V}$ (where V is the initial rate) versus $1 /[\mathrm{S}]$ (where [S] is the substrate concentration). Dots represent actual data points, and the solid curve through the points is the best fit straight line to these points. The intercept of this plot and its value are clearly marked with a dotted line. Other dotted lines are provided to aid in reading data off the graph. Use data obtained from the graph to answer the following questions, assuming the decomposition of paraoxon substrate by organophosphorus hydrase obeys Michaelis-Menten kinetics. Watch your units carefully!
a)(15 points) Determine the numerical value (including units) of the kinetic rate constant $\mathrm{k}_{2}$ if the total enzyme concentration is $5 \times 10^{-6} \mathrm{M}$. Show all reasoning clearly by using formulas from the free formula sheet.

Print your name here:
b)(15 points) What is the numerical value (including units) of $\mathrm{K}_{\mathrm{M}}$, the Michaelis-Menten constant for this system. Show all reasoning clearly using formulas from the free formula sheet.

Print your name here:
c)(10 points) If the total enzyme concentration is halved to $2.5 \times 10^{-6} \mathrm{M}$, give the numerical value (including units) for the maximum initial rate at infinite substrate concentration and the value of $\mathrm{K}_{\mathrm{M}}$, the Michaelis-Menten constant. Show all reasoning clearly using formulas from the free formula sheet.
d) ( 10 points) If the total enzyme concentration is halved to $2.5 \times 10^{-6} \mathrm{M}$, as in part (c), give the numerical value (including units) for the substrate concentration, $[S]_{1 / 2}$, at which the initial rate will reach half of its maximum value as determined in part (c). Show all reasoning clearly using formulas from the free formula sheet.

## Print your name here:

Problem 6 ( 45 points) In the year 2020 you are traveling aboard the starship Columbia when you accidentally go through a "wormhole" and come out in a strange "alternate" universe called Alterland. In this alternate universe the laws of physics and chemistry that you learned in your beloved 2407 chemistry course at Columbia, 18 years earlier, are somewhat altered. For example, the Equipartition Theorem in Alterland can be stated:

Kinetic Energy=kT per degree of freedom per atom or molecule
but the kinetic energy of an atom is still $(1 / 2) \mathrm{m}\left(\mathrm{C}_{\mathrm{rms}}\right)^{2}$
a)(10 points) Determine the kinetic energy of 1 mole of Helium gas at 300 K in Alterland. Show all reasoning clearly.

Print your name here:
b) (10 points) If the atomic weight of He is $0.004 \mathrm{Kg} / \mathrm{mole}$, determine the root mean square speed of a He atom at 300 K in Alterland. Show all reasoning clearly.
c)(5 points) Derive an expression for the constant volume heat capacity, $\mathrm{C}_{\mathrm{V}}$, for ideal monatomic gases like He , Ne, Xe in Alterland. Show all reasoning clearly.

Print your name here:
d)(10 points) Derive an expression for the constant pressure heat capacity, $\mathrm{C}_{\mathrm{P}}$, for ideal monatomic gases like He , Ne , Xe in Alterland. Using the results of part (c) above, determine the ratio of $\mathrm{C}_{\mathrm{p}} / \mathrm{C}_{\mathrm{V}}$ for monatomic atoms like He etc in Alterland. Show all reasoning clearly.
e)(10 points) Determine the ratio of $\mathrm{C}_{\mathrm{p}} / \mathrm{C}_{\mathrm{V}}$ for linear diatomics like $\mathrm{N}_{2}, \mathrm{O}_{2}$ in Alterland. Show reasoning clearly.

The End!

