# CHEM 132A LEC A (40758)



# Final Exam (Fall Qtr 2017) - LETTER SIZE

8194 (3848)

Assigned Se	at#:
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## <u>Instructions to Instructor:</u>

Do not alter this coversheet in ANY way. Substantial delays and additional fees may apply.

#### <u>Instructions to Student:</u>

- 1. Clearly print your Last Name, First Name and the Date
- 2. Clearly print your Student ID number in the boxes provided. Use large, dark numbers. These numbers are captured automatically during the scanning process.
- 3. Bubble in each number of your Student ID completely. The bubbles are used only if your written ID number is not captured.
- 4. Write your Name and Student ID number in the upper right corner of all following pages of your exam.

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1. (20 points)

a.

For **many** biologically important reactions the rate of the reaction doubles if the temperature is increased by 10K from 298K to 308K. Calculate the activation energy for a reaction for which this is true.

b.

A radioactive isotope commonly used in biotracer studies of phosphorous metabolism is  $^{32}$ P, which has a decay half-life of 14.3 days. Suppose we have been doing experiments with  $^{32}$ P and accumulate waste material that is showing a radioactive decay rate of 3.7 x  $10^7$  decays per second. The radiation safety officer of the University rules that it is not safe to dispose of this waste material until the decay rate has decreased to 3.7 x  $10^2$  decays per second. Until the rate has decreased sufficiently, it must be stored in a lead container in our laboratory. How many days must we store the waste in the lead container before it is safe to dispose of it?

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# 2. 30 points

The overall reaction  $O_2NNH_2(aq) = N_2O(aq) + H_2O(l)$  occurs in water solution by the set of elementary steps shown below. Determine the rate law that is consistent with this mechanism.

$$\begin{array}{ccc} O_2NNH_2 \xrightarrow{k_1} O_2NNH^- + H^+ & \text{fast equilibrium} \\ O_2NNH^- \xrightarrow{k_2} N_2O + OH^- & \text{slow} \\ H^+ + OH^- \xrightarrow{k_3} H_2O & \text{fast} \end{array}$$

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### 3. 30 points

The table below shows the results from four experiments that were done to discover how the initial rate of consumption of  $BrO_3^-(aq)$  ions varies as the concentrations of the reactants are changed in the following reaction:

$$BrO_3^-(aq) + 5Br^-(aq) + 6H_3O^+(aq) = 3Br_2(aq) + 9H_2O(I)$$

The data were collected at 300 K.

Experiment	Initial	Initial	Initial	Initial Rate
number	[BrO <sub>3</sub> -(aq)]M	[Br-(aq)]M	$[H_3O^+(aq)]M$	(M•sec <sup>-1</sup> )
1	0.10	0.10	0.10	1.2 x 10 <sup>-3</sup>
2	0.20	0.10	0.10	2.4 x 10 <sup>-3</sup>
3	0.10	0.30	0.10	3.5 x 10 <sup>-3</sup>
4	0.20	0.10	0.15	5.5 x 10 <sup>-3</sup>

a. Determine the order of the reaction with respect to each reactant. Indicate which pair of experiments you used to arrive at each of your answers.

h

Write the rate law for the reaction in terms of  $\frac{d[Br_2]}{dt}$  = ?

and calculate the rate constant at 300K. Indicate clearly what data you use from the table above to calculate the rate constant.

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# 4. First and Second Law (30 Points)

For all of the following parts of question 4 assume the only type of work available to the system is PV work.

#### Ideal Gas:

1 mole of an ideal gas is heated from  $T_1$  to  $T_2$  in a a rigid container (constant volume). This process is done reversibly. Calculate the heat (q), work (w), change in Internal Energy  $\Delta U$ , and the change in Entropy  $\Delta S$  associated with the process.

### Nonideal Gas:

Consider 1 mole of a gas that can be described using the following Equation of State.

$$P = \frac{RT}{V_m} \left( 1 + \frac{B}{V_m} \right)$$

The gas undergoes a reversible isothermal expansion from  $V_1$  to  $V_2$ .

Assume the Internal Energy is only a function of temperature and the parameter B is a constant.

Calculate the heat (q), work (w), change in Internal Energy ( $\Delta U$ ), and the change in the Entropy ( $\Delta S$ ) due to the expansion.

4 (continued) Adiabatic Process:
A ideal gas undergoes an adiabatic compression in which the initial volume ( $V_1$ ) drops to half its original value.
The pressure of the gas increases by a factor of 4 during this process.
What is the specific heat ratio, $\gamma$ ? (Recall: $\gamma = \frac{C_P}{C_V}$ )
Free Expansion: A gas expands into a vacuum from an initial volume ( $V_1$ ) to a final volume ( $V_2$ ). There is no change in temperature during this process.
Does Entropy of the system increase, decrease, or stay the same? Justify your answer.
What is the work for this process? Justify your answer.
Is this a reversible or irreversible process? Justify your answer.

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### 5 Combustion (30 points)

Consider the combustion of benzene gas under constant pressure conditions (1atm) and a temperature of 370K.

The balanced combustion reaction is given below.

Using the provided data, calculate  $\Delta H_{rxn}$  (370K).

$$2C_6H_6(g) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(I)$$

The following experimental data is available:

For benzene (liquid):

$$\Delta H_f^o(298) = 49 \text{kJ mol}^{-1}$$

$$\Delta H_{vap}^o = 33.9 \text{kJ mol}^{-1}$$

Boiling Point = 353.2K

Cp(benzene liquid) = 136.1J mol<sup>-1</sup> K<sup>-1</sup>

Cp(benzene gas) =  $81.67 \text{J mol}^{-1} \text{ K}^{-1}$ 

For O<sub>2</sub>(gas):

$$\Delta H_f^o(298) = 0$$

 $Cp = 29.355 \text{J mol}^{-1} \text{ K}^{-1}$ 

For CO<sub>2</sub>(gas):

 $\Delta H_f^o(298) = -393.51 \text{kJ mol}^{-1}$ 

 $Cp = 37.11J \text{ mol}^{-1} \text{ K}^{-1}$ 

For H<sub>2</sub>O(liquid):

 $\Delta H_f^o(298) = -285.83 \text{kJ mol}^{-1}$ 

 $Cp = 75.291 \text{J mol}^{-1} \text{K}^{-1}$ 

Use the following blank page to show your work if needed.

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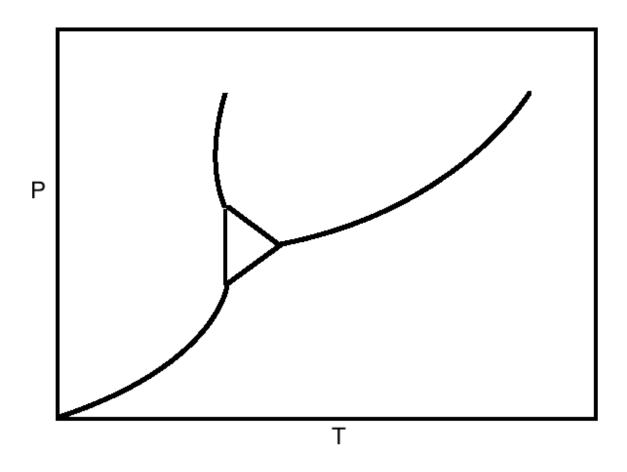
5. Extra page for your work

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## 6. Phase Diagram (30 points)

Single Component Phase Diagram



In this question we will characterize the phase diagram (above) of a single component system. This phase diagram contains two different solid phases ( $\alpha$ , and  $\beta$ ).

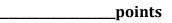
The  $\alpha$  phase is more stable at lower temperatures.

Label the above phase diagram (write on the graph).

Be sure to Label all of the physical phases in the system.

Label the transitions occurring at each phase line.

And for each phase, phase line, and triple point, make a statement about the associated chemical potentials.



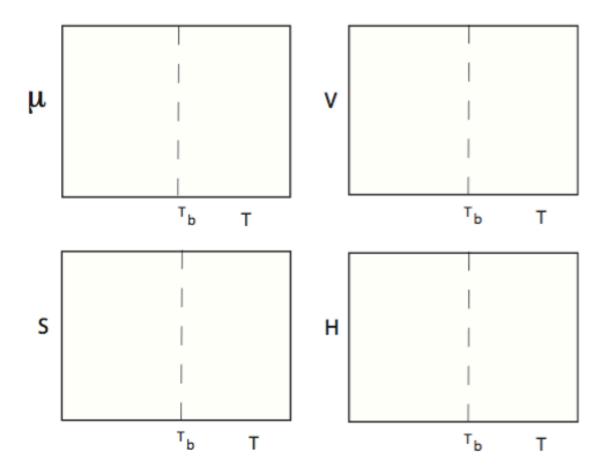
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# 6 (continued)

First-Order Phase Transitions

In the graphs below sketch the indicated molar quantities as a function of temperature ( $T_b$  is the boiling temperature).



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### 7. Flux (30 points)

Dimensions:

In general, what are the physical dimensions of flux? Please draw a simple picture to help illustrate your answer.

Flux in Thermodynamics

During lecture we discussed various transport properties of interest to chemical systems. The various types of flux (J) are usually proportional to a spatial derivative.

$$J(Some Property) = c \frac{d}{dz} f(x, y, z)$$

Where the coefficient c relates the proportionality.

These coefficients are well-known and can be tabulated for various materials.

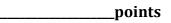
The function f is the variable that is actually changing during the flux.

Given the three following transport coefficients, please write down the analogous Fick's Law equation.

To do this you will need to define the type of flux that is associated with the transport coefficient, and the physical variable that is changing during that flux.

Be sure to define all symbols used, and briefly explain each type of flux in words.

- 1. The Diffusion Coefficient (D)
- 2. The Thermal Conductivity Coefficient (κ)
- 3. The Viscosity Coefficient ( $\eta$ ).



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## 7. (continued)

### Collision Flux

For a perfect gas the collision flux (Z<sub>w</sub>) can be shown to be

$$\mathsf{Z}_{\mathsf{w}} = \frac{P}{\sqrt{2\pi m k_B T}}$$

Where P is the pressure of the gas, m is the mass,  $k_B$  is Boltzmann's constant, and T is the temperature of the gas.

Using dimensional analysis show that this equation is reasonable (i.e. show the units of each side of the equation are consistent).

**Note:** The units of  $k_B$  are  $\frac{kg m^2}{s^2 K}$ , and a Newton (the unit of force) is  $\frac{kg m}{s^2}$ .

#### Collisions

Consider some gas at a pressure P, exposed to a rectangular surface.

Determine the number of collisions that occur with the surface over the time interval t (simplify as much as possible).