Final Exam – Fall 2018

BCH 341 - Physical Chemistry with a Biological Focus
Professor Jeff Yarger

Oct 1-3, 2018

DUE Wed. Oct 3, 2018 by 11:59 PM (UTC-7). Turn in completed exam as a single PDF document into the assignment link on ASU Canvas. Please make sure the completed exam is organized, self-contained and legible.

Name: ____ (as recorded on ASU Blackboard)

ASU Email: ________________________________ ASU ID: _____________________________

There are 12 physical biochemistry problems on this comprehensive final exam. Pick 10 problems to work on this examination. The exam is worth a total of 300 points. Each multicomponent problem is worth 30 points. Please write 'skip' on the two questions you want to omit and not be graded. IF you do NOT indicate (by writing 'skip' or 'omit') which two problems you want omitted from evaluation, then the first 10 problems will be graded (even if a student has worked problems 11 and 12).

The problems are designed to evaluate student's knowledge and ability to solve biochemical problems in the primary areas of thermodynamics and kinetics. Each exam problem is worth 30 points for a total of 300 points. The majority of the points for each problem are given for the setup and systematic step by step method (logic) used to solve each problem. Most final solutions are numerical. However, the numerical answer alone is not sufficient to receive credit for solving the problem. A detailed methodology is required. An example of a common problem solving methodology is (i) restate the problem or question; (ii) define or sketch the system; (iii) express the relevant principles, laws, postulates, axioms in a form suitable to the system and/or process; (iv) determine what properties are involved and how to find values for them (write down the principle equations or tables); (v) describe the process in terms of the changes in system properties (typically involves sorting the information into initial property values, final property values and transfer properties); (vi) substitute the known property values and process relations into the principle equations; (vii) calculate the desired quantities (answers) and check their reasonableness (and associated units). This represents one general method used for general problem solving in the biological, chemical and physical sciences. However, it is by no means unique or universal. Problem solving in the area of biochemistry and physical chemistry can take on many paths and methods. The evaluation does not depend on the exact path or method, just on its logical consistency and its ability to follow step-by-step the path, equations, mathematics and calculations used to solve each problem. The final numeric answer is roughly worth 10%, the other 90% of the points come from evaluating a student's methodology and ability to show a consistent logical path (typically mathematically) to solving each problem.

This is a long-winded way of telling students to show all work in solving each problem. Also, be organized and legible when you show your step-by-step work for solving each problem.

Total Points (300 possible): _________

1. The Van der Waals equation of state is one of the most common used to understand the behavior of real gases. **(i)** Determine the critical temperature (T_c) and critical pressure (P_c) for carbon dioxide. **(ii)** Make a P-V Plot (Pressure vs Volume Graph) and show isotherms of the equation of state 20°C above, 20°C below and at the critical temperature. **(iii)** Graph the same three isotherms that were plotted in part (ii) but using the ideal gas law. **(iv)** Write a paragraph that explains the differences between the idea gas law equation of state and the Van der Waals equation of state for the 3 isotherms plotted in parts (ii) and (iii). **(v)** Under what P-V conditions does carbon dioxide gas start to differ significantly from ideal behavior?

2. (i) Derive an analytical expression for the thermal expansion coefficient (α), the isothermal compressibility (κ_T), and $\left(\frac{\partial U}{\partial V}\right)_T$ for gases which obey the Van der Waals equation of state. Being able to express equations (expressions) in simple form is very helpful and can often add much insight to our fundamental understanding. Hence, simplify these expressions for the thermal expansion coefficient (α), the isothermal compressibility (κ_T), and $\left(\frac{\partial U}{\partial V}\right)_T$ as much as possible to get full credit. **(ii)** Show how the α, κ_T, and $\left(\frac{\partial U}{\partial V}\right)_T$ of a Van der Waals equation of state gas differs from that of an ideal equation of state gas.

3. (i) As accurately as possible, calculate the change in energy and entropy for the process of taking an ice cube (you can assume a typical ice cube is 1 in^3) out of your freezer at -30°C and heating at atmospheric pressure to a final state of steam at 180°C. As a reminder, to calculate thermodynamics as accurately as possible, do NOT assume ideal behavior or that the heat capacities are independent of temperature. Instead, use the temperature dependent heat capacities, which are very well known for all forms of H_2O. It can really help to look at this problem graphically through plots of the energy and entropy as a function of temperature (over the range covered in the problem, 30°C to 180°C). **(ii)** Graphically represent this thermodynamic problem with full credit given to clear, understandable graphically representations (typically 2D plots, but use whatever you feel is the best and most clear graphical representation) of the problem and associated solution. **(iii)** Graphically show the results for this same problem where you assume ideal behavior and temperature independent heat capacities of ice, water and steam.

4. When you put water in your freezer to make ice, it is common for this water to ‘supercool’ before freezing into ice. A ‘supercooled liquid’ is defined as a liquid that has a temperature below its freezing point. Let’s look more closely at the thermodynamics of this common process that happens in your freezer. **(i)** Calculate the change in enthalpy (ΔH) and entropy (ΔS) for the process of taking 10.0 ml supercooled liquid water (H_2O (*l*)) at a temperature of -15°C (initial state of the system) and having it crystalize into ice (H_2O (*s*)) with a final temperature of -15°C. It can really help to look at this problem graphically through plots of the enthalpy and entropy as a function of temperature. **(ii)** Graphically represent this thermodynamic problem with full credit given to clear, understandable graphically representations (typically 2D plots, but use whatever you feel is the best and most clear graphical representation) of the problem and associated solution.

5. The sequestration of carbon dioxide is critical to reducing greenhouse emissions. Taking a lesson from planet earth, which stored carbon dioxide as alkali and alkaline earth metal carbonates over geological time scales, let's determine which alkali or alkaline earth metal oxide most stably stores carbon dioxide as a carbonate. So, consider the decomposition of group I (alkali) and group II (alkali earth) solid carbonate, to form solid metal oxides and gaseous carbon dioxide. **(i)** Calculate the temperature at which the decomposition is thermodynamically favorable under standard pressure conditions. **(ii)** Which of the group I and group II carbonates would you pick to most stability sequester carbon dioxide? **(iii)** Plot the change in Gibbs free energy versus temperature for the various group I and group II carbonates to graphically show the stability of these carbonate.

6. The concentrations of the principal ions in a sample of intracellular fluid are 50.0 *mM* for potassium hydrogen phosphate, 80.0 *mM* for sodium chloride, 15.0 *mM* for magnesium chloride, and 15.0 *mM* for calcium sulfate. Calculate the ionic strength of the intracellular fluid. Show all work or preferably just share your google sheet or spreadsheet (e.g., excel, numbers, calc) where you program it to do this calculation in a general way (where you can change the concentration of any of the above compounds and have the spreadsheet automatically recalculate the ionic strength).

7. Carbon dioxide (CO_2) readily dissolves in water and a small percentage of the dissolved CO_2 is converted to what we might call the hydrated form and undergoes standard acid-base chemistry as carbonic acid. This is a very important process to understand in light of the importance of ocean environment and global warming. **(i)** Calculate the solubility of carbon dioxide in the earth's oceans. State all assumptions used in your calculations. **(ii)** What are the concentrations of all the species associated with the dissolution of atmospheric CO_2 into room temperature water? (This is a very practical problem and can provide a lot of insight into environmental biochemistry associated with global warming and ocean acidification)

8. (i) As accurately and with as much graphic illustration as possible, make a plot of the concentrations of aspartic acid species as a function of pH (over the pH range 0-14). **(ii)** What are the concentrations of <u>all species</u> in a 100.0 mM solution of aspartic acid at a pH of 7.4? Show all work or preferably just share your google sheet or spreadsheet (e.g., excel, numbers, calc) where you program it to calculate the concentration of all species at any input value for the pH and overall starting aspartic acid solution concentration.

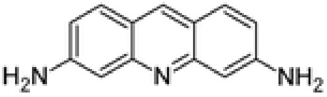
9. The potassium ion concentration inside a nerve cell is much larger than the concentration outside it. The potential difference across the cell membrane was measured to be a steady state of 89 mV. **(i)** What is the ratio of the concentration of potassium ions inside and outside the cell? State all assumptions explicitly. **(ii)** Is this calculated ratio consistent with intracellular and extracellular concentrations observed in cells? **(iii)** Show how hydrolysis of ATP under common inter- and intra-cellular potassium ion concentrations has an affinity for the active transport of potassium ions. Furthermore, show or explain how this is linked to sodium ion transport.

10. Consider the following sequential reaction scheme:

$$A \xrightarrow{k_A} I \xrightarrow{k_I} P$$

(i) Plot the concentration profiles ([A], [I] and [P] versus time) for the above sequential reaction where the rate constant for A→I is 0.5 inverse seconds and twice the rate of I→P (i.e., $k_A = 2k_I = 0.5\ s^{-1}$).
(ii) Determine the time at which [I] is at a maximum for the above sequential reaction, i.e., $k_A = 2k_I = 0.5\ s^{-1}$.

11. Proflavine has been used as a bacterial disinfectant and topical antiseptic. However, its use has been limited because it is also a mutagenic compound arising from its ability



to intercalate between nucleic-acid base pairs in DNA. Although the monomeric form of proflavin can intercalate, the dimer cannot. The monomer and dimer forms of proflavine exist in equilibrium in solution:

$$2M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M_2$$

and it has been determined under certain room temperature conditions that the dimerization rate constant (k_1) was 3.0×10^7 $M^{-1}s^{-1}$ and the rate constant for dissociation of the dimer back to monomers (k_{-1}) was 4.0×10^6 s^{-1}. In addition, the apparent rate constant for the relaxation of this system toward equilibrium is equal to:

$$k_{-1} + 4k_1[M]_{eq}$$

If 5.0 millimolar (mM) of monomer is present at equilibrium, **(i)** what is the equilibrium constant for the dimerization reaction, and **(ii)** the concentration of dimer present at equilibrium?

12. Find and read a paper in the scientific literature that sounds interesting to you. It needs to be a scientific paper in which experimental or theoretical kinetics (non-equilibrium thermodynamics) is a central theme component. **(i)** Record the reference (citation) to this scientific paper. **(ii)** Summarize the purpose of the paper and why it was worthwhile in one paragraph. **(iii)** List the kinetic parameters determined and what methods were used to measure or compute the kinetics presented in the paper.

Extra Credit (30 pts). The primary active pharmaceutical ingredients (API) in hemp or cannabis plants and associated extracts is the general class of chemical compounds called cannabinoids. The most notable cannabinoid in hemp is cannabidiol (CBD). The majority of cannabinoids produced from the hemp plant are found in a carboxylic acid form. This includes CBD, which is actually found as cannabidiolic acid (CBDA) in living hemp plants. The process of going from CBDA to CBD is decarboxylation. To date, the thermodynamics and kinetics of decarboxylation in CBD has not been studied rigorously. However, the great thing about thermodynamics of such a common reaction, like decarboxylation, is that it is still possible to estimate the expected thermodynamics energies based on computational analysis, arithmetic methods or based on comparison to decarboxylation reaction trends in similar classes of compounds. Using one or more of the methods mentioned above (or a novel method of your own choosing), **(i)** calculate as many thermodynamic parameters associated with CBD, CBDA and the decarboxylation of CBDA. Most important and practically, estimate the temperature at which you would expect decarboxylation of CBDA to be thermodynamically favorable. **(ii)** Decarboxylation reactions in organic compounds are known to often have high activation barriers. Hence, the thermodynamics can often be hindered by kinetics. Suggest one or more potential catalysis that would potentially speed up this reaction.