

constants:  $R=8.314$  some units =  $0.08206$  some units

$1\text{atm}=1.013\times 10^5 \text{ N m}^{-2}$

**Part 1:** Answer 7 of the following 8 questions. If you answer more than 7 cross out the one you wish not to be graded. Otherwise, only the first 7 will be graded. 10 points each.

1. What is meant by the term "minimization" in the procedure for "molecular mechanics minimization"?

2. and 3. Data:

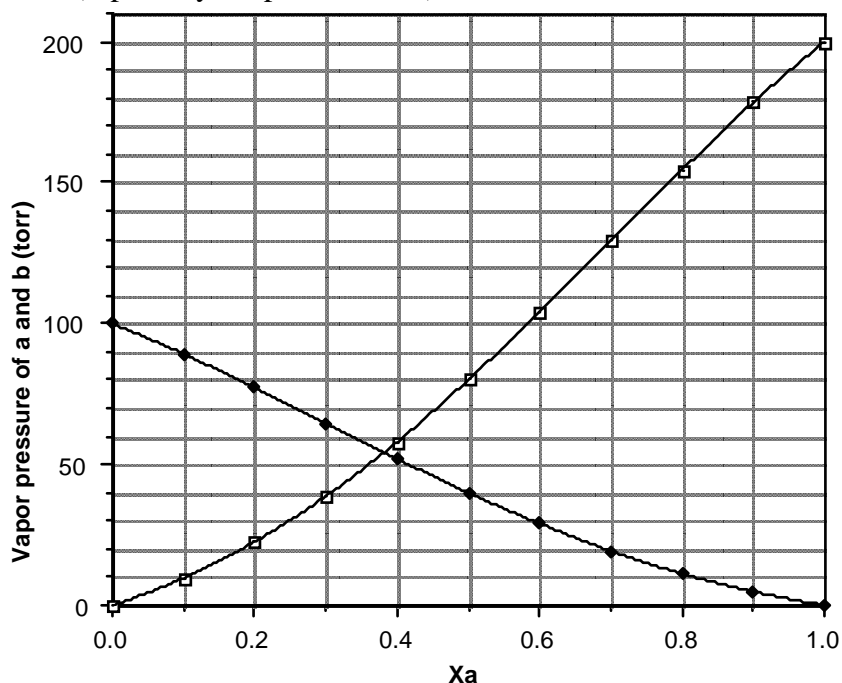
substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	all values at 298.2K
acetaldehyde	-166.4	133.3	
CO <sub>2</sub>	-393.5	394.4	
pyruvic acid	-584.5	463.4	

2. Consider the reaction: pyruvic acid  $\rightarrow$  acetaldehyde + CO<sub>2</sub> . (which is catalyzed by the enzyme pyruvate decarboxylase.) Calculate  $\Delta_r G^\circ$  for this reaction.

3. Calculate  $\Delta_r S^\circ$  for this reaction above at 298.2 K.

4. The chemical potential for pure water is  $-237.1$  kJ/mol at 298.15 K. Calculate the chemical potential for water in a solution that is 0.900 mole fraction water and 0.100 mol fraction in glycerol if the solution is an ideal-dilute solution and water is treated as the solvent.

5. The phase diagram for a binary liquid mixture of a and b is shown below. Clearly label  $P_a^\circ$ ,  $P_b^\circ$ ,  $K_a$ , and  $K_b$ . Here  $K_a$  and  $K_b$  are the Henry's Law constants and  $P_a^\circ$  and  $P_b^\circ$  are the pure vapor pressures. Draw any lines that are necessary to make your choices for these pressures clear (especially for partial credit).



6. Nitric acid hydrates have received attention as possible catalysts that bring about the Antarctic ozone hole. The sublimation of the trihydrate to nitric acid and water,  $\text{HNO}_3 \cdot 3\text{H}_2\text{O}(\text{s}) \rightarrow \text{HNO}_3(\text{g}) + 3\text{H}_2\text{O}(\text{g})$ , has a  $\Delta_{\text{sub}}G^\ominus$  of  $93.2\text{ kJ mol}^{-1}$  and a  $\Delta_{\text{sub}}H^\ominus$  of  $237\text{ kJ mol}^{-1}$  at  $220\text{K}$ . The temperature in the stratosphere is closer to  $190\text{K}$ . Calculate  $\Delta_{\text{sub}}G^\ominus$  at  $190\text{K}$ .

7. Near hydrothermal vents, organisms have been found at water temperatures in excess of  $110^\circ\text{C}$ . What pressure must be applied to water to keep it from boiling at  $110^\circ\text{C}$ ? The  $\Delta_{\text{vap}}H$  for water is  $40.66\text{ kJ mol}^{-1}$ . [Hint: find the equilibrium vapor pressure at  $110^\circ\text{C}$ .]

8. Calculate the change in chemical potential of a perfect gas that undergoes compression from 1.8 atm to 29.5 atm pressure at a constant temperature of 40°C.

**Part 2:** Answer 2 of the following 4 questions. If you answer more than 2 cross out the one you wish not to be graded. Otherwise, only the first 2 will be graded. 15 points each.

9. Calculate the changes in entropy of the system, the surroundings, and the universe when one mole of a perfect gas at 298K doubles its volume in an isothermal irreversible expansion against  $P_{\text{ext}}=0$ .

10. Pressure perturbation calorimetry has become a very useful tool in studies of protein folding. In interpreting the effects of solvation on protein conformation and folding the following

derivative is very important. Show that  $\left(\frac{\partial C_p}{\partial P}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P$

Show each step in your proof and include reasons for each step. [Hints: let  $C_p = \left(\frac{\partial H}{\partial T}\right)_P$ , change the order of differentiation and then use the thermodynamic equation of state for H.]

11. Instead of assuming that the volume of a condensed phase is constant when pressure is applied, assume only that the compressibility,  $\kappa_T$ , is constant. Starting at an initial volume of  $V_o$  and an initial pressure of  $P_o$  show that, when the pressure is changed isothermally by  $\Delta p$ ,  $G$  changes to

$\Delta G = V_o \Delta p (1 - \frac{1}{2} \kappa_T \Delta p)$  or equivalently  $\Delta G = V_o (P - P_o) - \frac{1}{2} V_o \kappa_T (P - P_o)^2$   
 where  $\Delta p = P - P_o$ . (You can end up with either formula; they are the equivalent.)

12. Show that for an isothermal change in pressure for a liquid or a solid,  $\Delta S = -\int \alpha V dP$ .

[This equation appears on your formula sheet, but you can't just say that it's on your formula sheet—you must derive it. You can, however, use any other formula on your formula sheet. Show all your work with reasons for each step. For example use phrases similar to: "since H is a state function", "from the definition of heat capacity", or "dividing by dP gives the desired result". If you use a partial derivative relationship from appendix 1, if you don't want to derive the relationship, be sure to state the rule you are using.]