

## Review Sheet for Final Exam

To study for the exam, we suggest you look through the past review sheets, exams and homework assignments, and identify the topics that you most need to work on. To help with this, the table given below lists the topics covered in the course and the exam and review sheet questions on each of these topics. Once you've identified your weak spots, you can do practice problems etc. to get more comfortable with that material. To prepare for the multiple-choice questions, you may want to look back over the concept tests used in lecture. This may be especially useful for qualitative topics such as LeChatelier's principle.

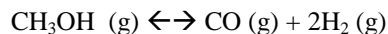
We've also provided three long questions that are designed to help you see the connections between the various topics, and help you tie everything together into a coherent whole. The topics covered by these problems are shown in the last column of the table.

The questions on the exam will have a format similar to those on the hour exams. The exam will be about twice the length of an hour exam, and you will be given 3 hours.

Topic	Review 1	Exam 1	Review 2	Exam 2	Review 3	Exam 3	Final Review
The meaning of the quantities listed in appendix D, and how to determine $\Delta H$ , $\Delta S$ , $\Delta G$ and $K$ for a chemical reaction from this data. This includes inverse problems such as determining $\Delta H_f^\circ$ of a molecule from its heat of combustion.	1,3,7b	1a,b					1c, 2a, 2i, 3a
How to estimate $\Delta H$ of a chemical reaction from the standard bond enthalpies of Table 7.3	5,7a	3					1a
How to guess the sign of $\Delta S$ for chemical reactions, based on chemical grounds. In particular, the entropy of a gas is much larger than that of a liquid which, in turn, is much larger than that of a solid. Also, if the number of gas molecules increases in a reaction, then $\Delta S > 0$ for that reaction.	11,12, 13	5b,c					1b
The meaning of $\Delta H$ , $\Delta S$ and $\Delta G$ . For instance, given $\Delta H$ , $\Delta S$ and $\Delta G$ for a reaction, you should be able to tell if the reaction is entropy driven, enthalpy driven, neither or both.	7c-f, 14	1c,d					
How to solve heat transfer problems. For instance, you may be asked to find the final (equilibrium) temperature when a hot object is placed in contact with a cold object. You may also be asked to calculate the heat generated by a chemical reaction and the effect that this has on the temperature of the system, be it a gas mixture or a solution.	2,3,4, 7g	4					2i
How to calculate entropy of vaporization.	6						
Know the difference between $C_v$ and $C_p$ , both in terms of the numerical values for ideal gases ( $3/2 R$ and $5/2 R$ ), and the reason why $C_p$ of a gas is greater than $C_v$ . You should know that for water, $C_p = C_v = 1 \text{ cal/(g K)}$	15	5a,d					
Know basic thermodynamic definitions, such as state function, heat of formation, standard entropy, heat and work, reversible processes, enthalpy vs. energy, adiabatic process.	10,17, 18	5e					
Basic thermodynamics of an ideal gas							
When reactions are added together, know how to calculate $\Delta H$ , $\Delta S$ , $\Delta G$ , $K$ and $E_{\text{cell}}^\circ$ for the combined reaction.	9,16					3	3c

Relation between $K$ , $\Delta G^\circ$ and $E^\circ_{\text{cell}}$	8a	2a					1f, 2b
Compare $K$ to $Q$ to determine direction of a reaction	8b	2b					1g
Solve equilibrium problems involving one reaction							1h
LeChatelier's principle			1-5,16	4			1d,e 2c
Reactions between strong acids and bases			6,7	1			
Determine who wins in a fight for protons			8,15				
pH of a weak acid solutions			9a				
Hydrolysis reactions			9b,10				2e
Titration of weak acid with strong base and titration of weak base with strong acid			9c,11,12,13	2			2f,g,h
Buffer solutions			9d,e	3a,b			2d,h
pH indicators			14	3c			
Buffers based on polyprotic acids							
Titration of a polyprotic acid							
Calculation of solubility from $K_{\text{sp}}$						5a	3b
Common ion effect					2b,3	5b	3b
Selective precipitation of ions						2	
Complex ion formation					2c	3,4	3c
pH dependent solubility					4,5		
Definition of initial rate					7	6	
Definition of order of a reaction, and how to determine it from initial rates					7	6	
First order reactions and half-lives							1i
Determining rate-laws from mechanisms							1k
Steady-state approximation					8	7	1k
Relation between rate and activation energy					6		1j
Voltaic (or Galvanic) cells: calculation of cell potential via Nernst equation, identification of cathode and anode							3d
Electrolytic cell, and use of Faraday constant							3e

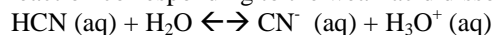
1) Consider the reaction:



- Using the bond enthalpies of Table 7.3, estimate  $\Delta H$  for this reaction. (Assume the CO bond in carbon monoxide has a bond enthalpy of 1075kJ/mol)
- Do you expect  $\Delta S$  to be  $>0$ ,  $<0$ , or nearly 0 for this reaction
- Using the data of appendix D, calculate  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$  for this reaction at 298°K.
- A system containing the gases  $\text{CH}_3\text{OH}$ ,  $\text{CO}$ , and  $\text{H}_2$  is at equilibrium. When the temperature is increased, will the amount of  $\text{CO}$  increase or decrease?
- A system containing the gases  $\text{CH}_3\text{OH}$ ,  $\text{CO}$ , and  $\text{H}_2$  is at equilibrium. If the total pressure is raised by decreasing the volume of the container, will the number of moles of  $\text{CO}$  increase or decrease?
- Calculate  $K$  for this reaction at 250°K.
- You find a system at 250°K, where the partial pressures of the above gases are  $P_{\text{CH}_3\text{OH}} = 0.20\text{atm}$ ,  $P_{\text{CO}} = 0.85\text{atm}$ ,  $P_{\text{H}_2} = 0.78\text{atm}$ . As the system approaches equilibrium, will the partial pressure of  $\text{H}_2$  increase or decrease?
- For the system in part g, what are the partial pressures of  $\text{CH}_3\text{OH}$ ,  $\text{CO}$ , and  $\text{H}_2$  at equilibrium?
- A cylinder with volume of 1 liter is filled with 1atm of  $\text{CH}_3\text{OH}$  at 25°K. Five minutes later, the pressure has risen to 1.5atm. Assuming the forward reaction  $[\text{CH}_3\text{OH (g)} \rightarrow \text{CO (g)} + 2\text{H}_2 \text{ (g)}]$  is first order, what is the half-life for this first-order process? (Ignore any changes in temperature.)
- When the temperature is raised from 25°K to 50°K, the half-life of the forward reaction obtained in part (i) decreases by a factor of 2. What is the activation energy for this process?
- We will now consider the reverse reaction,  $\text{CO (g)} + 2\text{H}_2 \text{ (g)} \rightarrow \text{CH}_3\text{OH (g)}$ . Derive the rate law for each of these mechanisms:
  - $$\begin{array}{ll} \text{CO} + \text{H}_2 \rightarrow \text{H}_2\text{CO} & \text{(slow)} \\ \text{H}_2\text{CO} + \text{H}_2 \rightarrow \text{CH}_3\text{OH} & \text{(fast)} \end{array}$$
  - $$\begin{array}{ll} \text{CO} + \text{H}_2 \leftrightarrow \text{H}_2\text{CO} & \text{(fast equilibrium)} \\ \text{H}_2\text{CO} + \text{H}_2 \rightarrow \text{CH}_3\text{OH} & \text{(slow)} \end{array}$$
  - $$\begin{array}{ll} \text{CO} + \text{H}_2 \leftrightarrow \text{H}_2\text{CO} & \text{(fast)} \\ \text{H}_2\text{CO} + \text{H}_2 \rightarrow \text{CH}_3\text{OH} & \text{(fast)} \end{array}$$

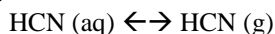
(for this third mechanism, derive the rate by applying the steady-state approximation to  $\text{H}_2\text{CO}$ )

2) Consider the reaction corresponding to the weak-acid dissociation of hydrocyanic acid



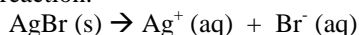
- Using the data of appendix D, calculate  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$  for this reaction at 298°K.
- Based on your results from part a, what is the  $\text{pK}_a$  of  $\text{HCN}$  at 298°K? at 350°K?
- When the temperature of the solution is raised, what happens to the  $\text{pH}$ ? (throughout this problem, assume that  $K_w = 1.0 \times 10^{-14}$ , and is independent of temperature)
- How many moles of  $\text{NaOH}$  would you add to 100ml of a 0.01M  $\text{HCN}$  solution to make a buffer with  $\text{pH} = 9.0$  at 25°K. (Assume that adding solid  $\text{NaOH}$  does not change the volume of the solution, and that the  $\text{HCN}$  remains in solution and does not escape as a gas.)
- When 0.050 mole of  $\text{NaCN}$  is added to 100ml of water, what is the  $\text{pH}$  of the resulting solution at 25°K.
- You have 50.0ml of a solution that contains  $\text{HCN}$  with an unknown concentration. You titrate it with 0.100M  $\text{NaOH}$  and it takes 72.3ml to reach the equivalence point. What was the concentration of the original solution?
- At the equivalence point in part f, is the solution equivalent to: (i) a solution made by mixing equal amounts of  $\text{HCN}$  and  $\text{NaCN}$  or (ii) a solution made by dissolving  $\text{NaCN}$  in water.

- h) Group the following solutions into those that have equal pH.
- 1) 1M HCN + 0.5M NaOH
  - 2) 1M HCN + 1M NaOH
  - 3) 1M HCN + 1.5M NaOH
  - 4) 1M NaCN + 0.5M HCl
  - 5) 1M NaCN + 1M HCl
  - 6) 1M NaCN + 1.5M HCl
  - 7) 0.5M HCN + 0.5M NaCN
  - 8) 2M NaOH + 1M HCl + 1M HCN
  - 9) 1M NaCN
  - 10) 1M HCN
- i) If 0.050 mole of NaCN and 0.050 moles of a strong acid are added to 100ml of water at 25.0°C, what is the temperature of the solution at the end of the reaction? (assume that the HCN remains in solution and does not escape as gas)
- j) Consider the reaction:

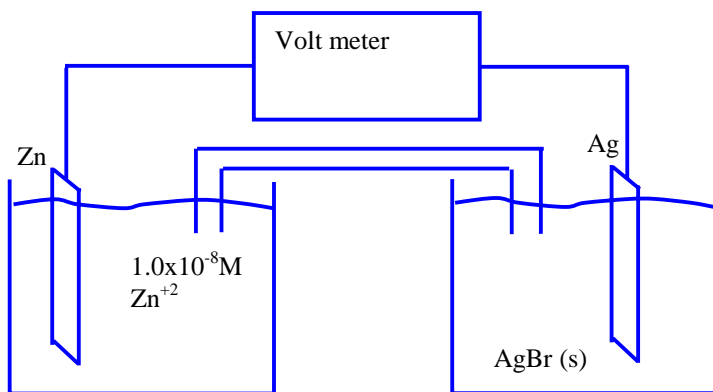


Using data from the appendix D, calculate K for this reaction at 25°C. Just looking at K, and without doing detailed calculations, do you think significant amounts of HCN gas will leave the solution in part i. (This is the reaction used in the gas chamber.)

- 3) Consider the reaction:



- a) From the data in appendix D and  $K_{sp}$  from table 11.3, calculate  $\Delta G_f^\circ$  ( $\Delta G_f^\circ = \Delta H_f^\circ + TS^\circ$ ) of AgBr at 25°C.
- b) What is the solubility of AgBr in water at 25°C? In 1.0M NaBr at 25°C?
- c) What is the solubility of AgBr in 1.0M  $\text{NH}_3$ , at 25°C?
- d) Someone builds the following experimental set-up (I would call it an electrochemical cell, but I'm not guaranteeing that the anode is correctly placed on the right.) The cell with the Ag electrode has solid AgBr at the bottom (so that it is a saturated solution.) What is the reading on the volt meter? What is the anode and what is the cathode? Is the positive side the Zn or the Ag electrode?



- e) A electro-plating device (an electrolytic cell) is being used to plate silver onto a large and gaudy cup. If a current of 3.0 amps is applied for 1hour, how many grams of silver have been deposited on the cup?

Solutions (Please watch the web site, <http://ir.chem.cmu.edu/chem106/> for corrections).

1a) 106 kJ/mole

1b)  $\Delta S > 0$

1c)  $\Delta H = 90.14 \text{ kJ/mol}$ ;  $\Delta S = 219 \text{ J/mole K}$ ;  $\Delta G = 24.84 \text{ kJ/mole}$

1d) CO increases

1e) CO will decrease

1f)  $K = 274.9$

1g)  $\text{H}_2$  increases

1h)  $\text{CH}_3\text{OH} = 0.0053 \text{ atm}$ ;  $\text{CO} = 1.05 \text{ atm}$ ;  $\text{H}_2 = 1.18 \text{ atm}$

1i) 12 minutes

1j) 22 kJ/mole

1k) (1)  $\text{rate} = k[\text{CO}][\text{H}_2]$

(2)  $\text{rate} = (k_2 k_1/k_{-1}) [\text{H}_2]^2[\text{CO}]$

(3)  $\text{rate} = (k_2 k_1[\text{CO}][\text{H}_2]^2) / (k_{-1} + k_2[\text{H}_2])$

2a)  $\Delta H = 43.5 \text{ kJ/mol}$ ,  $\Delta S = -30.6 \text{ J/mol K}$ ,  $\Delta G = 52.6 \text{ kJ/mol}$

2b)  $\text{pK}_a = 9.22$  at 298K and 8.09 at 350K

2c) pH decreases

2d)  $3.8 \times 10^{-4}$  moles

2e) 11.5

2f) 0.145M

2g) ii - pure NaCN

2h) 1-4-7, 2-8-9, 5-10

2i) 30 degrees C

2j)  $K = 0.13$

3a) -131.3 kJ/mol

3b)  $8.8 \times 10^{-7} \text{ M}$ ,  $7.7 \times 10^{-13} \text{ M}$

3c)  $3.6 \times 10^{-3} \text{ M}$

3d) 0.34V, Zn is the anode, Ag is the cathode, The Ag electrode is positive

3e) 12.1g of Ag.