

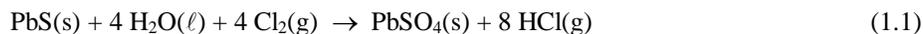
\* While I prefer you turn in a hard copy of the worksheet, I will accept scanned copies sent to my email address, joensj@fiu.edu

Section: (circle one)      M,W,F                      Tu,Tr

Exam 1 is Friday, September 23 (for the M,W,F class) and Thursday, September 22 (for the T,R class) in class. It will cover material from Chapters 13 and 14 of Burdge.

For problems involving calculations you must show your work for credit.

1) Consider the following chemical reaction.



Thermochemical data relevant to the reaction are given below (for  $T = 298. \text{ K}$ ).

Substance	$\Delta H^\circ_f$ (kJ/mole)	$\Delta G^\circ_f$ (kJ/mole)	$S^\circ$ (J/mole·K)
$\text{Cl}_2(g)$	0.0	0.0	223.0
$\text{HCl}(g)$	- 92.3	- 95.3	187.0
$\text{H}_2\text{O}(\ell)$	- 285.8	- 237.2	69.9
$\text{PbS}(s)$	- 94.3	- 92.7	91.2
$\text{PbSO}_4(s)$	- 918.4	- 811.2	147.3

a) Using the values for  $\Delta G^\circ_f$  in the above table, find  $\Delta G^\circ_{\text{rxn}}$  for reaction 1.1 at  $T = 298. \text{ K}$ ?

$$\begin{aligned} \Delta G^\circ_{\text{rxn}} &= [ \Delta G^\circ_f(\text{PbSO}_4(s)) + 8 \Delta G^\circ_f(\text{HCl}(g)) ] - [ \Delta G^\circ_f(\text{PbS}(s)) + 4 \Delta G^\circ_f(\text{H}_2\text{O}(\ell)) + 4 \Delta G^\circ_f(\text{Cl}_2(g)) ] \\ &= [ (- 811.2) + 8 (- 95.3) ] - [ (- 92.7) + 4 (- 237.2) + 4 (0.0) ] \\ &= [ - 1573.6 ] - [ - 1041.5 ] = - 532.1 \text{ kJ/mol} \end{aligned}$$

b) As found in Worksheet 3, the change in enthalpy and entropy for reaction 1.1 at  $T = 298. \text{ K}$  are  $\Delta H^\circ_{\text{rxn}} = - 419.3 \text{ kJ/mol}$  and  $\Delta S^\circ_{\text{rxn}} = 380.5 \text{ J/mol}\cdot\text{K}$ . Using those results and eq 1.2

$$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T \Delta S^\circ_{\text{rxn}} \quad (1.2)$$

find  $\Delta G^\circ_{\text{rxn}}$ . Show that you get the same value for  $\Delta G^\circ_{\text{rxn}}$  using eq 1.2 as found in part a of the problem.

From eq 1.2

$$\begin{aligned} \Delta G^\circ_{\text{rxn}} &= \Delta H^\circ_{\text{rxn}} - T \Delta S^\circ_{\text{rxn}} = (- 419.3 \text{ kJ/mol}) - (298. \text{ K}) (380.5 \text{ J/mol}\cdot\text{K}) (1 \text{ kJ}/1000. \text{ J}) \\ &= (- 419.3 \text{ kJ/mol}) - ( 113.4 \text{ kJ/mol}) = - 532.7 \text{ kJ/mol} \end{aligned}$$

This is the same answer as in part a ( $- 532.1 \text{ kJ/mol}$ ) to within roundoff error. If you have a choice, it is much easier to find  $\Delta G^\circ_{\text{rxn}}$  the way we did in part a, as it is a shorter calculation.

c) Based on your answer in part a, is reaction 1.1 spontaneous for standard conditions? Justify your answer.

Yes. Since  $\Delta G^\circ_{\text{rxn}} < 0$ , the reaction is spontaneous for standard conditions and  $T = 298. \text{ K}$ .

2) For each of the following pairs of substances indicate the one with the larger value for  $S^\circ$  (absolute entropy).



For the same molecule, entropy is larger in the gas phase than in the liquid phase. For similar molecules in the same phase, the larger molecule has the higher value for entropy. Entropy increases as you go from a solid to a solution.

3) State the Third Law of thermodynamics.

The Third Law of thermodynamics says that the absolute entropy of a pure substance is exactly  $0.0 \text{ J/mol}\cdot\text{K}$  at absolute zero ( $T = 0.0 \text{ K}$ ).

4) For a particular chemical reaction  $\Delta H^\circ_{\text{rxn}} > 0$  and  $\Delta S^\circ_{\text{rxn}} > 0$ . Based on this, which of the following statements concerning the reaction (for standard conditions) is correct?

- a) The reaction is always spontaneous
- b) The reaction is never spontaneous
- D** c) The reaction is spontaneous at low temperatures, but not at high temperatures
- d) The reaction is spontaneous at high temperatures, but not at low temperatures
- e) Cannot tell from the information given

$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T \Delta S^\circ_{\text{rxn}}$ . We may assume both  $\Delta H^\circ_{\text{rxn}}$  and  $\Delta S^\circ_{\text{rxn}}$  are approximately independent of temperature. For low values of  $T$ ,  $\Delta G^\circ_{\text{rxn}} \cong \Delta H^\circ_{\text{rxn}}$  (since if  $T$  is small then  $T \Delta S^\circ_{\text{rxn}}$  will also be small). Since  $\Delta H^\circ_{\text{rxn}}$  is positive,  $\Delta G^\circ_{\text{rxn}}$  will also be positive, and so the reaction will not be spontaneous at low temperatures. As  $T$  gets larger,  $T \Delta S^\circ_{\text{rxn}}$  becomes larger. Since  $\Delta S^\circ_{\text{rxn}}$  is positive, the value for  $\Delta G^\circ_{\text{rxn}}$  decreases as  $T$  increases, and eventually  $\Delta G^\circ_{\text{rxn}}$  will become less than zero, making the reaction spontaneous at high values for  $T$ .

5) Using the data given below, estimate the value for  $T_b^\circ$ , the normal boiling point, for  $\text{GeCl}_4(\ell)$

Substance	$\Delta H^\circ_f(\text{kJ/mole})$	$\Delta G^\circ_f(\text{kJ/mole})$	$S^\circ(\text{J/mole}\cdot\text{K})$
$\text{GeCl}_4(\ell)$	- 531.8	- 462.7	245.6
$\text{GeCl}_4(\text{g})$	- 495.8	- 457.3	347.7



The normal boiling point corresponds to the boiling point for when the pressure is 1 atm.

$$\Delta H^\circ_{\text{rxn}} = \Delta H^\circ_f(\text{GeCl}_4(\text{g})) - \Delta H^\circ_f(\text{GeCl}_4(\ell)) = [ (- 495.8) - (- 531.8) ] = 36.0 \text{ kJ/mol}$$

$$\Delta S^\circ_{\text{rxn}} = S^\circ(\text{GeCl}_4(\text{g})) - S^\circ(\text{GeCl}_4(\ell)) = [ (347.7) - (245.6) ] = 102.1 \text{ J/mol}\cdot\text{K}$$

$$\text{So } T_{\text{eq}} = T_b^\circ \cong \frac{\Delta H^\circ_{\text{rxn}}}{\Delta S^\circ_{\text{rxn}}} = \frac{36.0 \text{ kJ/mol} (1000. \text{ J/1 kJ})}{102.1 \text{ J/mol}\cdot\text{K}} = 352.6 \text{ K} = 79.4 \text{ }^\circ\text{C}$$

The experimental value for the normal boiling point of  $\text{GeCl}_4$  is  $T_b^\circ = 86.5 \text{ }^\circ\text{C}$ , and so our approximation is off by about  $7 \text{ }^\circ\text{C}$ . I guess that is why we say it is approximate.