

\* 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

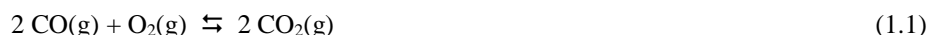
Section: (circle one)      M,W,F                      Tu,Tr

For problems involving calculations you must show your work for credit. Unless otherwise stated, you may assume  $T = 25.0\text{ }^{\circ}\text{C}$ .

1) The data below are given at  $T = 25.0\text{ }^{\circ}\text{C}$ , and may be of use in doing the following problem.

substance	$\Delta H^{\circ}_f$ (kJ/mol)	$\Delta G^{\circ}_f$ (kJ/mol)	$S^{\circ}$ (J/mol·K)
CO(g)	- 110.5	- 137.3	197.9
CO <sub>2</sub> (g)	- 393.5	- 394.4	213.6
O <sub>2</sub> (g)	0.0	0.0	205.0

Consider the reaction



a) Give the expression for K, the thermodynamic equilibrium constant, for the above reaction.

$$K = \frac{(p_{\text{CO}_2})^2}{(p_{\text{CO}})^2 (p_{\text{O}_2})}$$

b) Using the thermochemical data above, find the numerical value for K at  $T = 25.0\text{ }^{\circ}\text{C}$ .

$$\begin{aligned} \Delta G^{\circ}_{\text{rxn}} &= [ 2 \Delta G^{\circ}_f(\text{CO}_2\text{(g)}) ] - [ 2 \Delta G^{\circ}_f(\text{CO(g)}) + \Delta G^{\circ}_f(\text{O}_2\text{(g)}) ] \\ &= [ 2 (- 394.4) ] - [ 2 (- 137.3) + (0.0) ] = - 514.2 \text{ kJ/mol} \end{aligned}$$

$$\text{But } \ln K = - \frac{\Delta G^{\circ}_{\text{rxn}}}{RT} = - \frac{(- 514.2 \text{ kJ/mol}) (1000. \text{ J/kJ})}{(8.314 \text{ J/mol}\cdot\text{K}) (298. \text{ K})} = + 207.5$$

$$K = e^{207.5} = 1.4 \times 10^{90}$$

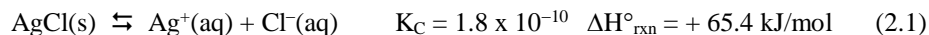
c) Typical partial pressures of CO, CO<sub>2</sub>, and O<sub>2</sub> in the lower atmosphere are  $p_{\text{CO}} = 1.0 \times 10^{-7}$  atm,  $p_{\text{CO}_2} = 4.1 \times 10^{-4}$  atm, and  $p_{\text{O}_2} = 0.21$  atm. Based on your answer in b, are CO, CO<sub>2</sub> and O<sub>2</sub> in equilibrium in the lower atmosphere? Justify your answer.

Using the information given we can find the value for Q

$$Q = \frac{(p_{\text{CO}_2})^2}{(p_{\text{CO}})^2 (p_{\text{O}_2})} = \frac{(4.1 \times 10^{-4})^2}{(1.0 \times 10^{-7})^2 (0.21)} = 8.0 \times 10^7$$

If we were at equilibrium then  $Q = K$  would occur. The further away Q is from K, the further from equilibrium we are. In this case, Q is about  $10^{82}$  smaller than K, so we are very far from equilibrium. This actually tells us something useful about the atmosphere. If the atmosphere was in equilibrium the value for  $p_{\text{CO}}$  would be very close to zero (in fact, it would be  $p_{\text{CO}} \cong 8 \times 10^{-49}$  atm). The actual partial pressure of CO is much larger than this. That means there must be new CO introduced into the atmosphere at a much faster rate than equilibrium occurs.

2) For nominally insoluble ionic compounds a small amount of the compound will usually dissolve in water. As an example, consider the solubility reaction for silver chloride (AgCl).



Consider 1.000 of an aqueous solution of silver chloride in equilibrium with solid silver chloride. For each of the following changes, indicate whether the number of moles of  $\text{Ag}^+(\text{aq})$  will increase, stay the same, or decrease (circle your answer).

a) Add 0.100 moles of NaCl(s), a soluble ionic compound, to the solution.

moles  $\text{Ag}^+(\text{aq})$  increases                      moles  $\text{Ag}^+(\text{aq})$  stays the same                      **moles  $\text{Ag}^+(\text{aq})$  decreases**

b) Add 2.00 g of solid silver chloride to the solution.

moles  $\text{Ag}^+(\text{aq})$  increases                      **moles  $\text{Ag}^+(\text{aq})$  stays the same**                      moles  $\text{Ag}^+(\text{aq})$  decreases

c) Change the temperature of the solution from  $T = 25.0^\circ\text{C}$  to  $T = 50.0^\circ\text{C}$ .

**moles  $\text{Ag}^+(\text{aq})$  increases**                      moles  $\text{Ag}^+(\text{aq})$  stays the same                      moles  $\text{Ag}^+(\text{aq})$  decreases

In a, since NaCl is soluble, adding NaCl(s) produces  $\text{Na}^+(\text{aq})$  and  $\text{Cl}^-(\text{aq})$ , and so the reaction will shift from right to left to get rid of some of the  $\text{Cl}^-$  (and also decrease the  $\text{Ag}^+$  concentration). b is tricky.  $K = [\text{Ag}^+][\text{Cl}^-]$ . Since AgCl(s) does not appear in the expression for K, changing the amount of AgCl(s) has no effect on equilibrium. For c, since the reaction is endothermic, we can think of heat as a reactant. Increasing the temperature increases the “heat” that is available, and so the system will shift from left to right to get rid of some heat, causing  $\text{Ag}^+$  to increase. If the reaction had been exothermic ( $\Delta H^\circ_{\text{rxn}} < 0$ ) then heat would be a product of the reaction, and increasing temperature would cause the reaction to shift from right to left.

3) The major industrial source of hydrogen gas is from the chemical reaction of methane with water.



A system initially has the following partial pressures of gases:  $p_{\text{CH}_4} = 2.00 \text{ atm}$  and  $p_{\text{H}_2\text{O}} = 0.0100 \text{ atm}$ . There is initially no CO or  $\text{H}_2$  in the system.

a) What is the partial pressure of  $\text{H}_2(\text{g})$  in the system when equilibrium is reached?

$$K_p = \frac{(p_{\text{CO}})(p_{\text{H}_2})^3}{(p_{\text{CH}_4})(p_{\text{H}_2\text{O}})} = 1.0 \times 10^{-68}$$

	Initial	Change	Equilibrium
CO	0	x	x
$\text{H}_2$	0	3x	3x
$\text{CH}_4$	2.00	-x	2.00 - x
$\text{H}_2\text{O}$	0.0100	-x	0.100 - x

Substituting into the expression for  $K_p$  gives

$$K_p = \frac{(x)(3x)^3}{(2.00 - x)(0.0100 - x)} = 1.0 \times 10^{-68}$$

Let's try assuming  $x \ll 0.0100$  Then

$$\frac{(x)(3x)^3}{(2.00)(0.0100)} = \frac{27x^4}{0.0200} = 1.0 \times 10^{-68}$$

So  $x^4 = \frac{(1.0 \times 10^{-68})(0.0200)}{(27)} = 7.4 \times 10^{-72}$

$$x = (7.4 \times 10^{-72})^{1/4} = 1.6 \times 10^{-18} \quad \text{Note that the assumption that } x \ll 0.0100 \text{ turned out to be a good assumption.}$$

So at equilibrium,  $(p_{H_2}) = 3x = 3(1.6 \times 10^{-18}) = 4.9 \times 10^{-18} \text{ atm}$

b) Based on your answer in a, is it likely that this reaction for producing  $H_2(g)$  is carried out at  $T = 25.0 \text{ }^\circ\text{C}$ ? Justify your answer.

This is such a small amount of hydrogen present at equilibrium that this reaction would not be a practical way of generating hydrogen gas at  $T = 25. \text{ }^\circ\text{C}$ . Since it says in the problem that this reaction is the major industrial source of  $H_2(g)$ , that strongly suggests the reaction is run at a much higher temperature. Note that most chemical reactions are faster at high temperatures than at low temperatures, and so that would also help in generating hydrogen gas. In fact, this reaction is usually run at high temperatures ( $T = 650 \text{ }^\circ\text{C}$  to  $950 \text{ }^\circ\text{C}$ ) and high pressures, with an added catalyst to make the reaction faster.

If assuming  $x \ll 0.0100$  turned out to not be a good assumption then you would have to use a different method to find  $x$  for this problem. There are methods for doing this (successive approximation would work), but if you were not able to assume  $x$  is small this would not be a fair question, as solving it would make use of math skills you are not required to have for this class.