

# Chemistry 192

## Problem Set 7

### Spring, 2018

1. Use Table D2 to calculate the standard enthalpy change for the combustion of liquid benzene ( $\text{C}_6\text{H}_6$ ) in pure oxygen gas to produce gas phase carbon dioxide and liquid phase water.

**Answer:**  $-3267.4 \text{ kJ mol}^{-1}$

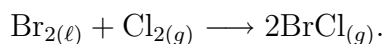
2. The enthalpy of vaporization of liquid bromine is  $29.96 \text{ kJ mol}^{-1}$  and the normal boiling point of liquid bromine is  $58.8^\circ\text{C}$ . Calculate the molar entropy change associated with the boiling of liquid bromine at its normal boiling point.

**Answer:**  $90.3 \text{ J mol}^{-1}\text{K}^{-1}$

3. The enthalpy of vaporization of ( $\text{C}_3\text{H}_8$ ) at its normal boiling point is  $19.04 \text{ kJ mol}^{-1}$ . Use Trouton's rule to estimate the normal boiling point of propane.

**Answer:**  $219. \text{ K}$

4. Use Table D2 to calculate  $\Delta G_{r,m}^\circ$  and  $K_P$  at  $298\text{K}$  for the reaction



**Answer:**  $\Delta G_{r,m}^\circ = -1960. \text{ J mol}^{-1}$ ,  $K_P = 2.2$

5. Consider the reaction



- (a) Show that if one starts with pure  $\text{PCl}_5$  and a fraction,  $\alpha$ , dissociates, the reaction quotient is given by

$$Q_P = \frac{\alpha^2}{(1 - \alpha^2)} P$$

- (b) At 250.°C the equilibrium constant for the reaction is  $K_P = 1.78$ . Calculate  $\alpha$  for  $P = 0.100$  bar and  $P = 1.00$  bar at equilibrium.

**Answer:**  $\alpha(0.100) = 0.973, \alpha(1.00) = 0.800$

- (c) Calculate  $\Delta G_{r,m}$  for an equimolar mixture at 1.00 bar pressure and 250.°C.

**Answer:**  $-7.29 \times 10^3$  J

- (d) Calculate  $\Delta G_{r,m}$  for 20.0 per cent dissociation at 250.°C and 1.00 bar pressure.

**Answer:**  $-1.63 \times 10^4$  J

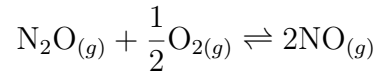
6. At 1200.K and a total pressure of 2.0 bar, the equilibrium pressures of gas phase atomic and molecular iodine associated with the equilibrium reaction



are  $P_I = 0.094$  bar and  $P_{I_2} = 1.906$  bar. Consider a mixture of molecular and atomic iodine gas at 1200.K such that  $P_{I_2} = 3.1$  bar and  $P_I = 7.3$  bar. Calculate  $\Delta G_{r,m}$  for the mixture at nonequilibrium conditions, and predict if the reaction given Eq. (1) proceeds to the left or right.

**Answer**  $8.2 \times 10^4$  J

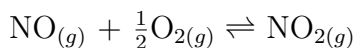
7. The pressure equilibrium constant for the gas-phase reaction



is measured at 900.K and found to be  $K_P = 0.292$ . A mixture of nitrous oxide ( $\text{N}_2\text{O}$ ), oxygen gas and nitric oxide ( $\text{NO}$ ) are placed in a container with initial partial pressures  $P_{\text{N}_2\text{O}} = 0.725$  bar,  $P_{\text{O}_2} = 0.334$  bar and  $P_{\text{NO}} = 1.11$  bar. Calculate  $\Delta G_{r,m}$  for this nonequilibrium mixture, and use the value of  $\Delta G_{r,m}$  to predict if the reaction will proceed to the right or left.

**Answer:**  $1.73 \times 10^4$  J

8. Use Table D2 of the text to calculate the equilibrium constant of the reaction



at 25.°C and 35.°C.

**Answer:**  $K_P(298) = 1.50 \times 10^6, K_P(308) = 7.10 \times 10^5$

9. The following results were obtained for the degree of dissociation,  $\alpha$ , of  $\text{CO}_2$  in the reaction



at a pressure of 1.0 bar:

T (°K)	$\alpha$
1000.	$2. \times 10^{-7}$
1400.	$1.27 \times 10^{-4}$
2000.	$1.55 \times 10^{-2}$

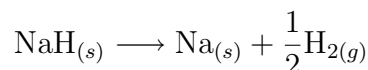
Calculate  $\Delta H_{r,m}^\circ$  for the reaction at 1400.°K.

**Answer:**  $8. \times 10^4 \text{ J mol}^{-1}$

10. The standard molar enthalpy of formation and molar Gibbs free energy of formation of solid sodium hydride (NaH) at 298K are given by

$$\Delta H_{f,m}^\circ = -56.3 \text{ J mol}^{-1} \quad \Delta G_{f,m}^\circ = -33.5 \text{ J mol}^{-1}.$$

Given the reaction



Calculate the temperature at which the pressure of hydrogen in equilibrium with  $\text{NaH}_{(s)}$  and  $\text{Na}_{(s)}$  is 0.01 bar.

**Answer:** 589.K

11. Solid ammonium chloride at 600.K is allowed to come to equilibrium with equimolar amounts of gas phase hydrogen chloride (HCl) and ammonia ( $\text{NH}_3$ ) according to the reaction



Given the table of thermodynamic data valid at 298.K

Substance	$\Delta H_{f,m}^\circ \text{ kJ mol}^{-1}$	$\Delta G_{f,m}^\circ \text{ kJ mol}^{-1}$
$\text{NH}_{3(g)}$	-45.9	-16.5
$\text{HCl}_{(g)}$	-92.3	-95.3
$\text{NH}_4\text{Cl}_{(s)}$	-314.4	-202.9

calculate the partial pressures of ammonia and hydrogen chloride gas in equilibrium with the solid ammonium chloride at 600K.

**Answer:** 0.62 bar for both gases.

12. Use the following table of thermodynamic data determined at 298.K

Substance	$\Delta H_{f,m}^\circ \text{ kJ mol}^{-1}$	$\Delta G_{f,m}^\circ \text{ kJ mol}^{-1}$
$\text{CaCO}_{3(s)}$	-1206.9	-1128.8
$\text{CaO}_{(s)}$	-634.9	-603.3
$\text{CO}_{2(g)}$	-393.5	-394.4

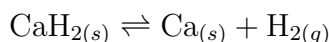
to calculate the temperature at which the pressure of carbon dioxide in equilibrium with calcium carbonate and calcium oxide according to the reaction



is  $1.00 \times 10^{-5}$  bar.

**Answer:**  $T = 7.00 \times 10^2$  K

13. The partial pressure of hydrogen gas in equilibrium with solid calcium and solid calcium hydride according to the reaction



is  $3.05 \times 10^{-1}$  bar at 1500.K and  $5.50 \times 10^{-2}$  bar at 1700. K. Calculate the partial pressure of hydrogen gas in equilibrium with solid calcium and calcium hydride at 1600.K.

**Answer:**  $P = 1.23 \times 10^{-1}$  bar

14. Use the table of thermodynamic data below valid at 298K to calculate the molar solubility of barium fluoride ( $\text{BaF}_2$ ) in water at 353K.

Substance	$\Delta H_{f,m}^\circ$ kJ mol <sup>-1</sup>	$\Delta G_{f,m}^\circ$ kJ mol <sup>-1</sup>
$\text{BaF}_{2(s)}$	-1207.	-1157.
$\text{Ba}_{(aq)}^{2+}$	-537.6	-560.8
$\text{F}_{(aq)}^-$	-332.6	-278.8

**Answer:**  $3.8 \times 10^{-3}$  M

- 15.

Substance	$\Delta H_{f,m}^\circ$ kJ mol <sup>-1</sup>	$\Delta G_{f,m}^\circ$ kJ mol <sup>-1</sup>
$\text{Ca}_3(\text{PO}_4)_{2(s)}$	-4121.	-3885.
$\text{Ca}_{(aq)}^{2+}$	-542.8	-553.6
$\text{PO}_{4(aq)}^{3-}$	-1277.	-1019.

Use the table of thermodynamic data valid at 298.K given above to calculate the temperature at which the solubility of calcium phosphate solid in water is  $1.5 \times 10^{-7}$  M.

**Answer:**  $2.8 \times 10^2$  K

16. Use the table of thermodynamic data valid at 298K given below to calculate the temperature at which the molar solubility of silver sulfate in water is 0.0200 M.

Substance	$\Delta H_{f,m}^\circ$ (kJ mol <sup>-1</sup> )	$\Delta G_{f,m}^\circ$ (kJ mol <sup>-1</sup> )	$S_m^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )
Ag <sub>2</sub> SO <sub>4(s)</sub>	-715.9	-618.4	200.4
Ag <sub>(aq)</sub> <sup>+</sup>	105.6	77.11	72.68
SO <sub>4(aq)</sub> <sup>2-</sup>	-909.3	-744.5	20.1

**Answer:** 346K

17. The molar solubility of silver sulfate in water is  $1.4 \times 10^{-2}$  M at 298 K and  $1.2 \times 10^{-2}$  M at 280 K. Calculate  $\Delta H_{r,m}^\circ$ ,  $\Delta G_{r,m}^\circ$  and  $\Delta S_{r,m}^\circ$  at 298 K for the reaction. **Answer:**  $\Delta H_m = 1.8 \times 10^4$  J mol<sup>-1</sup>,  $\Delta G_m = 2.8 \times 10^4$  J mol<sup>-1</sup>,  $\Delta S_m = -33$  J mol<sup>-1</sup>K<sup>-1</sup>