Chemistry 192
Problem Set 7
Spring, 2018

1. Use Table D2 to calculate the standard enthalpy change for the combusion of liquid benzene (C_6H_6) in pure oxygen gas to produce gas phase carbon dioxide and liquid phase water.
   Answer: -3267.4 kJ mol^{-1}

2. The enthalpy of vaporization of liquid bromine is 29.96 kJ mol^{-1} and the normal boiling point of liquid bromine is 58.8°C. Calculate the molar entropy change associated with the boiling of liquid bromine at its normal boiling point.
   Answer: 90.3 J mol^{-1}K^{-1}

3. The enthalpy of vaporization of (C_3H_8) at its normal boiling point is 19.04 kJ mol^{-1}. Use Trouton's rule to estimate the normal boiling point of propane.
   Answer: 219. K

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

$$\mathrm{Br}_{2(\ell)} + \mathrm{Cl}_{2(g)} \longrightarrow 2\mathrm{BrCl}_{(g)}.$$

   Answer: $\Delta G^\circ_{r,m} = -1960.\ \mathrm{J\ mol}^{-1}, K_P = 2.2$

5. Consider the reaction

   $\mathrm{PCl}_{5(g)} \longrightarrow \mathrm{PCl}_{3(g)} + \mathrm{Cl}_{2(g)}$

   (a) Show that if one starts with pure PCl_5 and a fraction, α, 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 α 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: -7.29×10^3 J

(d) Calculate $\Delta G_{r,m}$ for 20.0 per cent dissociation at 250.°C and 1.00 bar pressure.
Answer: -1.63×10^4 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

$$I_{2(g)} \rightleftharpoons 2I_{(g)} \tag{1}$$

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 nonequilibrum conditions, and predict if the reaction given Eq. (1) proceeds to the left or right.
Answer 8.2×10^4 J

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

$$N_2O_{(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

is measured at 900.K and found to be $K_P = 0.292$. A mixture of nitrous oxide (N_2O), oxygen gas and nitric oxide (NO) are placed in a container with initial partial pressures $P_{N_2O} = 0.725$ bar, $P_{O_2} = 0.334$ bar and $P_{NO} = 1.11$ 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: 1.73×10^4 J

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

$NO_{(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons NO_{2(g)}$

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, α, of CO_2 in the reaction

$CO_{2(g)} \longrightarrow CO_{(g)} + \frac{1}{2}\, O_{2(g)}$

at a pressure of 1.0 bar:

T (°K)	α
1000.	2. x 10^{-7}
1400.	1.27 x 10^{-4}
2000.	1.55 x 10^{-2}

Calculate $\Delta H^\circ_{r,m}$ for the reaction at 1400.°K.
Answer: $8. \times 10^4$ 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

$$\Delta H^\circ_{f,m} = -56.3 \text{ J mol}^{-1} \qquad \Delta G^\circ_{f,m} = -33.5 \text{ J mol}^{-1}.$$

Given the reaction

$$\mathrm{NaH}_{(s)} \longrightarrow \mathrm{Na}_{(s)} + \frac{1}{2}\mathrm{H}_{2(g)}$$

Calculate the temperature at which the pressure of hydrogen in equilibrium with $\mathrm{NaH}_{(s)}$ and $\mathrm{Na}_{(s)}$ 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 (NH_3) according to the reaction

$$\mathrm{NH_4Cl}_{(s)} \rightleftharpoons \mathrm{NH}_{3(g)} + \mathrm{HCl}_{(g)}.$$

Given the table of thermodynamic data valid at 298.K

Substance	$\Delta H^\circ_{f,m}$ kJ mol^{-1}	$\Delta G^\circ_{f,m}$ kJ mol^{-1}
$\mathrm{NH}_{3(g)}$	-45.9	-16.5
$\mathrm{HCl}_{(g)}$	-92.3	-95.3
$\mathrm{NH_4Cl}_{(s)}$	-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	$\Delta H^\circ_{f,m}$ kJ mol^{-1}	$\Delta G^\circ_{f,m}$ kJ mol^{-1}
$\mathrm{CaCO}_{3(s)}$	-1206.9	-1128.8
$\mathrm{CaO}_{(s)}$	-634.9	-603.3
$\mathrm{CO}_{2(g)}$	-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

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

is 1.00×10^{-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

$$CaH_{2(s)} \rightleftharpoons Ca_{(s)} + H_{2(g)}$$

is 3.05×10^{-1} bar at 1500.K and 5.50×10^{-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 (BaF_2) in water at 353K.

Substance	$\Delta H^\circ_{f,m}$ kJ mol^{-1}	$\Delta G^\circ_{f,m}$ kJ mol^{-1}
$BaF_{2(s)}$	-1207.	-1157.
$Ba^{2+}_{(aq)}$	-537.6	-560.8
$F^-_{(aq)}$	-332.6	-278.8

Answer: 3.8×10^{-3} M

15.

Substance	$\Delta H^\circ_{f,m}$ kJ mol^{-1}	$\Delta G^\circ_{f,m}$ kJ mol^{-1}
$Ca_3(PO_4)_{2(s)}$	-4121.	-3885.
$Ca^{2+}_{(aq)}$	-542.8	-553.6
$PO^{3-}_{4(aq)}$	-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 1.5×10^{-7} M.
Answer: 2.8×10^2 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	$\Delta H^\circ_{f,m}$ (kJ mol^{-1})	$\Delta G^\circ_{f,m}$ (kJ mol^{-1})	S°_m (J mol^{-1}K^{-1})
$Ag_2SO_{4(s)}$	-715.9	-618.4	200.4
$Ag^+_{(aq)}$	105.6	77.11	72.68
$SO^{2-}_{4(aq)}$	-909.3	-744.5	20.1

Answer: 346K

17. The molar solubility of silver sulfate in water is 1.4×10^{-2} M at 298 K and 1.2×10^{-2} M at 280 K. Calculate $\Delta H^\circ_{r,m}, \Delta G^\circ_{r,m}$ and $\Delta S^\circ_{r,m}$ at 298 K for the reaction. **Answer**: $\Delta H_m = 1.8 \times 10^4$J mol^{-1}, $\Delta G_m = 2.8 \times 10^4$ J mol^{-1}, $\Delta S_m = -33$ J mol^{-1}K^{-1}