

14.7: Chapter 14 Problems

An underlined problem number or problem-part letter indicates that the numerical answer appears in Appendix I.

14.1

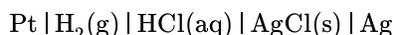
The state of a galvanic cell without liquid junction, when its temperature and pressure are uniform, can be fully described by values of the variables T , p , and ξ . Find an expression for dG during a reversible advancement of the cell reaction, and use it to derive the relation $\Delta_r G_{\text{cell}} = -zFE_{\text{cell, eq}}$ (Eq. 14.3.8). (Hint: Eq. 3.8.8.)

14.2

Before 1982 the standard pressure was usually taken as 1 atm. For the cell shown in Fig. 14.1, what correction is needed, for a value of $E_{\text{cell, eq}}^\circ$ obtained at 25 °C and using the older convention, to change the value to one corresponding to a standard pressure of 1 bar? Equation 14.3.15 can be used for this calculation.

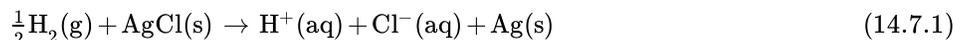
14.3

Careful measurements (Roger G. Bates and Vincent E. Bower, *J. Res. Natl. Bur. Stand. (U.S.)*, **53**, 283–290, 1954) of the equilibrium cell potential of the cell



yielded, at 298.15 K and using a standard pressure of 1 bar, the values $E_{\text{cell, eq}}^\circ = 0.22217 \text{ V}$ and $dE_{\text{cell, eq}}^\circ/dT = -6.462 \times 10^{-4} \text{ V K}^{-1}$. (The requested calculated values are close to, but not exactly the same as, the values listed in Appendix H, which are based on the same data combined with data of other workers.)

(a) Evaluate $\Delta_r G^\circ$, $\Delta_r S^\circ$, and $\Delta_r H^\circ$ at 298.15 K for the reaction



(b) Problem 12.18 showed how the standard molar enthalpy of formation of the aqueous chloride ion may be evaluated based on the convention $\Delta_f H^\circ(\text{H}^+, \text{aq}) = 0$. If this value is combined with the value of $\Delta_r H^\circ$ obtained in part (a) of the present problem, the standard molar enthalpy of formation of crystalline silver chloride can be evaluated. Carry out this calculation for $T = 298.15 \text{ K}$ using the value $\Delta_f H^\circ(\text{Cl}^-, \text{aq}) = -167.08 \text{ kJ mol}^{-1}$ (Appendix H).

(c) By a similar procedure, evaluate the standard molar entropy, the standard molar entropy of formation, and the standard molar Gibbs energy of formation of crystalline silver chloride at 298.15 K. You need the following standard molar entropies evaluated from spectroscopic and calorimetric data:

$$\begin{aligned} S_m^\circ(\text{H}_2, \text{g}) &= 130.68 \text{ J K}^{-1} \text{ mol}^{-1} & S_m^\circ(\text{Cl}_2, \text{g}) &= 223.08 \text{ J K}^{-1} \text{ mol}^{-1} \\ S_m^\circ(\text{Cl}^-, \text{aq}) &= 56.60 \text{ J K}^{-1} \text{ mol}^{-1} & S_m^\circ(\text{Ag}, \text{s}) &= 42.55 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned} \quad (14.7.2)$$

14.4

The standard cell potential of the cell



has been determined over a range of temperature (G. Faita, P. Longhi, and T. Mussini, *J. Electrochem. Soc.*, **114**, 340–343, 1967). At $T = 298.15 \text{ K}$, the standard cell potential was found to be $E_{\text{cell, eq}}^\circ = 1.13579 \text{ V}$, and its temperature derivative was found to be $dE_{\text{cell, eq}}^\circ/dT = -5.9863 \times 10^{-4} \text{ V K}^{-1}$.

(a) Write the cell reaction for this cell.

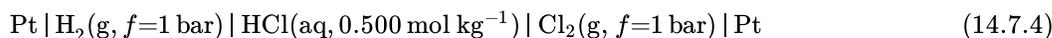
(b) Use the data to evaluate the standard molar enthalpy of formation and the standard molar Gibbs energy of formation of crystalline silver chloride at 298.15 K (Note that this calculation provides values of quantities also calculated in Prob. 14.3 using independent data.)

14.5

Use data in Sec. 14.3.3 to evaluate the solubility product of silver chloride at 298.15 K

14.6

The equilibrium cell potential of the galvanic cell



is found to be $E_{\text{cell, eq}} = 1.410 \text{ V}$ at 298.15 K . The standard cell potential is $E_{\text{cell, eq}}^\circ = 1.360 \text{ V}$.

(a) Write the cell reaction and calculate its thermodynamic equilibrium constant at 298.15 K .

(b) Use the cell measurement to calculate the mean ionic activity coefficient of aqueous HCl at 298.15 K and a molality of $0.500 \text{ mol kg}^{-1}$.

14.7

Consider the following galvanic cell, which combines a hydrogen electrode and a calomel electrode:



(a) Write the cell reaction.

(b) At 298.15 K , the standard cell potential of this cell is $E_{\text{cell, eq}}^\circ = 0.2680 \text{ V}$. Using the value of $\Delta_f G^\circ$ for the aqueous chloride ion in Appendix H, calculate the standard molar Gibbs energy of formation of crystalline mercury(I) chloride (calomel) at 298.15 K .

(c) Calculate the solubility product of mercury(I) chloride at 298.15 K . The dissolution equilibrium is $\text{Hg}_2\text{Cl}_2(\text{s}) \rightleftharpoons \text{Hg}_2^{2+}(\text{aq}) + 2 \text{Cl}^-(\text{aq})$. Take values for the standard molar Gibbs energies of formation of the aqueous ions from Appendix H.

14.8

Table 14.1 lists equilibrium cell potentials obtained with the following cell at 298.15 K (Albert S. Keston, *J. Am. Chem. Soc.*, **57**, 1671–1673, 1935):



Use these data to evaluate the standard electrode potential of the silver-silver bromide electrode at this temperature to the nearest millivolt. (Since the electrolyte solutions are quite dilute, you may ignore the term $Ba\sqrt{m_B}$ in Eq. 14.5.2.)

14.9

The cell diagram of a mercury cell can be written



(a) Write the electrode reactions and cell reaction with electron number $z = 2$.

(b) Use data in Appendix H to calculate the standard molar reaction quantities $\Delta_r H^\circ$, $\Delta_r G^\circ$, and $\Delta_r S^\circ$ for the cell reaction at 298.15 K .

(c) Calculate the standard cell potential of the mercury cell at 298.15 K to the nearest 0.01 V .

(d) Evaluate the ratio of heat to advancement, $\delta q / d\xi$, at a constant temperature of 298.15 K and a constant pressure of 1 bar , for the cell reaction taking place in two different ways: reversibly in the cell, and spontaneously in a reaction vessel that is not part of an electrical circuit.

(e) Evaluate $dE_{\text{cell, eq}}^\circ / dT$, the temperature coefficient of the standard cell potential.

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