

10 Equilibrium electrochemistry

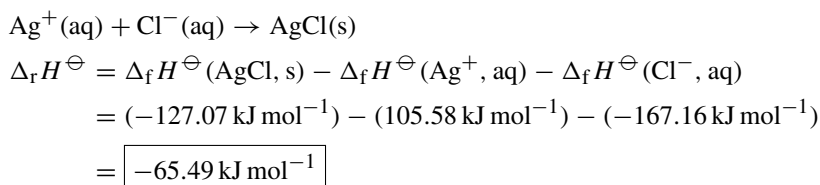
Solutions to exercises

Discussion questions

- E10.1(b)** The Debye–Hückel theory is a theory of the activity coefficients of ions in solution. It is the coulombic (electrostatic) interaction of the ions in solution with each other and also the interaction of the ions with the solvent that is responsible for the deviation of their activity coefficients from the ideal value of 1. The electrostatic ion–ion interaction is the stronger of the two and is fundamentally responsible for the deviation. Because of this interaction there is a build up of charge of opposite sign around any given ion in the overall electrically neutral solution. The energy, and hence, the chemical potential of any given ion is lowered as a result of the existence of this ionic atmosphere. The lowering of the chemical potential below its ideal value is identified with a non-zero value of $RT \ln \gamma_{\pm}$. This non-zero value implies that γ_{\pm} will have a value different from unity which is its ideal value. The role of the solvent is more indirect. The solvent determines the dielectric constant, ϵ , of the solution. Looking at the details of the theory as outlined in *Justification 10.2* we see that ϵ enters into a number of the basic equations, in particular, Coulomb’s law, Poisson’s equation, and the equation for the Debye length. The larger the dielectric constant, the smaller (in magnitude) is $\ln \gamma_{\pm}$.
- E10.2(b)** The potential difference between the electrodes in a working electrochemical cell is called the **cell potential**. The cell potential is not a constant and changes with time as the cell reaction proceeds. Thus the cell potential is a potential difference measured under non-equilibrium conditions as electric current is drawn from the cell. **Electromotive force** is the zero-current cell potential and corresponds to the potential difference of the cell when the cell (not the cell reaction) is at equilibrium.
- E10.3(b)** The pH of an aqueous solution can in principle be measured with any electrode having an emf that is sensitive to $H^+(aq)$ concentration (activity). In principle, the hydrogen gas electrode is the simplest and most fundamental. A cell is constructed with the hydrogen electrode being the right-hand electrode and any reference electrode with known potential as the left-hand electrode. A common choice is the saturated calomel electrode. The pH can then be obtained from eqn 10.43 by measuring the emf (zero-current potential difference), E , of the cell. The hydrogen gas electrode is not convenient to use, so in practice glass electrodes are used because of ease of handling.

Numerical exercises

- E10.4(b)** $NaCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + NaNO_3(aq)$
NaCl, AgNO₃ and NaNO₃ are strong electrolytes; therefore the net ionic equation is



- E10.5(b)** $PbS(s) \rightleftharpoons Pb^{2+}(aq) + S^{2-}(aq)$

$$K_S = \prod_j a_j^{\nu_j}$$

Since the solubility is expected to be low, we may (initially) ignore activity coefficients. Hence

$$K_S = \frac{b(Pb^{2+})}{b^\ominus} \times \frac{b(S^{2-})}{b^\ominus} \quad b(Pb^{2+}) = b(S^{2-}) = S$$

$$K_S = \frac{S^2}{(b^\ominus)^2}$$

$$S = (K_S)^{1/2} b^\ominus$$

Use $\ln K_S = \frac{-\Delta_r G^\ominus}{RT}$ to obtain K_S

$$\begin{aligned}\Delta_r G^\ominus &= \Delta_f G^\ominus(\text{S}^{2-}, \text{aq}) + \Delta_f G^\ominus(\text{Pb}^{2+}, \text{aq}) - \Delta_r G^\ominus(\text{PbS}, \text{s}) \\ &= (+85.8 \text{ kJ mol}^{-1}) + (-24.43 \text{ kJ mol}^{-1}) - (-98.7 \text{ kJ mol}^{-1}) \\ &= 160.07 \text{ kJ mol}^{-1}\end{aligned}$$

$$\ln K_S = \frac{-160.07 \times 10^3 \text{ J mol}^{-1}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} = -64.61$$

$$K_S = e^{-64.61} = 8.7 \times 10^{-29}$$

$$K_S = \frac{S^2}{b^\ominus{}^2} \quad S = (K_S)^{1/2} b^\ominus = (8.735 \times 10^{-29})^{1/2} = \boxed{9.3 \times 10^{-15} \text{ mol kg}^{-1}}$$

E10.6(b) The ratio of hydration Gibbs energies is

$$\frac{\Delta_{\text{hyd}} G^\ominus(\text{NO}_3^-)}{\Delta_{\text{hyd}} G^\ominus(\text{Cl}^-)} = \frac{r(\text{Cl}^-)}{r(\text{NO}_3^-)} = \frac{181 \text{ pm}}{189 \text{ pm}} = 0.958$$

We have $\Delta_{\text{hyd}} G^\ominus(\text{Cl}^-) = -379 \text{ kJ mol}^{-1}$ [Exercise 10.6a]

$$\text{So } \Delta_{\text{hyd}} G^\ominus(\text{NO}_3^-) = (0.958) \times (-379 \text{ kJ mol}^{-1}) = \boxed{-363 \text{ kJ mol}^{-1}}$$

E10.7(b) $I = \frac{1}{2} \sum_i (b_i/b^\ominus) z_i^2$ [10.18]

and for an M_pX_q salt, $b_+/b^\ominus = pb/b^\ominus$, $b_-/b^\ominus = qb/b^\ominus$, so

$$I = \frac{1}{2}(pz_+^2 + qz_-^2)b/b^\ominus$$

$$\text{(a) } I(\text{MgCl}_2) = \frac{1}{2}(1 \times 2^2 + 2 \times 1)b/b^\ominus = 3b/b^\ominus$$

$$\text{(b) } I(\text{Al}_2(\text{SO}_4)_3) = \frac{1}{2}(2 \times 3^2 + 3 \times 2^2)b/b^\ominus = 15b/b^\ominus$$

$$\text{(c) } I(\text{Fe}_2(\text{SO}_4)_3) = \frac{1}{2}(2 \times 3^2 + 3 \times 2^2)b/b^\ominus = 15b/b^\ominus$$

E10.8(b) $I = I(\text{K}_3[\text{Fe}(\text{CN})_6]) + I(\text{KCl}) + I(\text{NaBr}) = \frac{1}{2}(3 + 3^2) \frac{b(\text{K}_3[\text{Fe}(\text{CN})_6])}{b^\ominus} + \frac{b(\text{KCl})}{b^\ominus} + \frac{b(\text{NaBr})}{b^\ominus}$
 $= (6) \times (0.040) + (0.030) + (0.050) = \boxed{0.320}$

Question. Can you establish that the statement in the comment following the solution to Exercise 10.8a (in the *Student's Solutions Manual*) holds for the solution of this exercise?

E10.9(b) $I = I(\text{KNO}_3) = \frac{b}{b^\ominus}(\text{KNO}_3) = 0.110$

Therefore, the ionic strengths of the added salts must be 0.890.

$$\text{(a) } I(\text{KNO}_3) = \frac{b}{b^\ominus}, \quad \text{so } b(\text{KNO}_3) = 0.890 \text{ mol kg}^{-1}$$

$$\text{and } (0.890 \text{ mol kg}^{-1}) \times (0.500 \text{ kg}) = 0.445 \text{ mol KNO}_3$$

$$\text{So } (0.445 \text{ mol}) \times (101.11 \text{ g mol}^{-1}) = \boxed{45.0 \text{ g KNO}_3} \text{ must be added.}$$

$$(b) \quad I(\text{Ba}(\text{NO}_3)_2) = \frac{1}{2}(2^2 + 2 \times 1^2) \frac{b}{b^\ominus} = 3 \frac{b}{b^\ominus} = 0.890$$

$$b = \frac{0.890}{3} b^\ominus = 0.296\bar{7} \text{ mol kg}^{-1}$$

$$\text{and } (0.296\bar{7} \text{ mol kg}^{-1}) \times (0.500 \text{ kg}) = 0.148\bar{4} \text{ mol Ba}(\text{NO}_3)_2$$

$$\text{So } (0.148\bar{4} \text{ mol}) \times (261.32 \text{ g mol}^{-1}) = \boxed{38.8 \text{ g Ba}(\text{NO}_3)_2}$$

$$\text{E10.10(b)} \quad I(\text{Al}_2(\text{SO}_4)_3) = \frac{1}{2}((2 \times 3^3) + (3 \times 2^2)) b/b^\ominus = 15b/b^\ominus$$

$$I(\text{Ca}(\text{NO}_3)_2) = \frac{1}{2}(2^2 + 2) b/b^\ominus = 3b/b^\ominus$$

$$3(0.500 \text{ mol kg}^{-1}) = 15(b(\text{Al}_2(\text{SO}_4)_3))$$

$$b(\text{Al}_2(\text{SO}_4)_3) = \frac{3}{15} (0.500 \text{ mol kg}^{-1}) = \boxed{0.100 \text{ mol kg}^{-1}}$$

$$\text{E10.11(b)} \quad \gamma_{\pm} = (\gamma_+^p \gamma_-^q)^{1/s} \quad s = p + q$$

For $\text{Al}_2(\text{SO}_4)_3$ $p = 2$, $q = 3$, $s = 5$

$$\boxed{\gamma_{\pm} = (\gamma_+^2 \gamma_-^3)^{1/5}}$$

E10.12(b) Since the solutions are dilute, use the Debye–Hückel limiting law

$$\log \gamma_{\pm} = -|z_+ z_-| A I^{1/2}$$

$$I = \frac{1}{2} \sum_i z_i^2 (b_i/b^\ominus) = \frac{1}{2} \{1 \times (0.020) + 1 \times (0.020) + 4 \times (0.035) + 2 \times (0.035)\}$$

$$= 0.125$$

$$\log \gamma_{\pm} = -1 \times 1 \times 0.509 \times (0.125)^{1/2} = -0.1799\bar{6}$$

$$(\text{For NaCl}) \gamma_{\pm} = 10^{-0.1799\bar{6}}$$

$$= \boxed{0.661}$$

$$\text{E10.13(b)} \quad I(\text{CaCl}_2) = \frac{1}{2}(4 + 2) b/b^\ominus = 3b/b^\ominus$$

$$\log \gamma_{\pm} = -2 \times 1 \times 0.509 \times (0.300)^{1/2} = -0.557\bar{6}$$

$$\gamma_{\pm} = 10^{-0.557\bar{6}} = 0.277\bar{0} = 0.277$$

$$\text{Error} = \frac{0.524 - 0.277}{0.524} \times 100 \text{ per cent} = \boxed{47.1 \text{ per cent}}$$

E10.14(b) The extended Debye–Hückel law is $\log \gamma_{\pm} = -\frac{A|z_+ z_-| I^{1/2}}{1 + B I^{1/2}}$

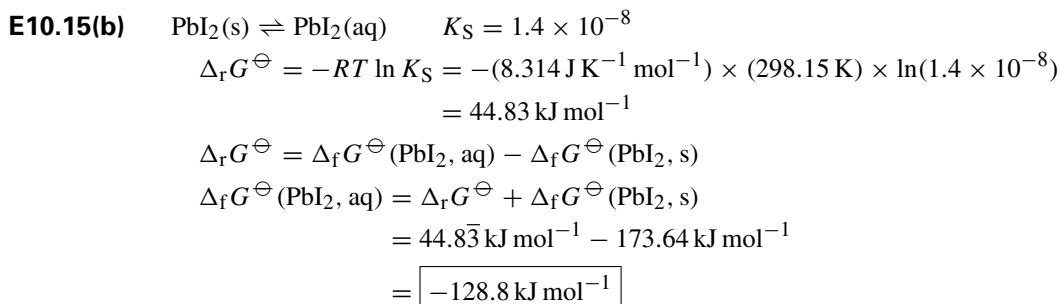
Solving for B

$$B = -\left(\frac{1}{I^{1/2}} + \frac{A|z_+ z_-|}{\log \gamma_{\pm}} \right) = -\left(\frac{1}{(b/b^\ominus)^{1/2}} + \frac{0.509}{\log \gamma_{\pm}} \right)$$

Draw up the following table

$b/(\text{mol kg}^{-1})$	5.0×10^{-3}	10.0×10^{-3}	50.0×10^{-3}
γ_{\pm}	0.927	0.902	0.816
B	1.32	1.36	1.29

$$B = \boxed{1.3}$$



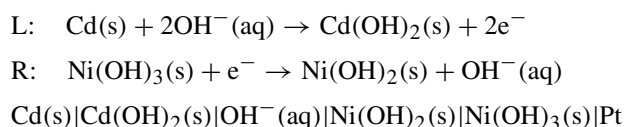
E10.16(b) The Nernst equation may be applied to half-cell potentials as well as to overall cell potentials.

$$E(\text{H}^+/\text{H}_2) = \frac{RT}{F} \ln \frac{a(\text{H}^+)}{(f_{\text{H}_2}/p^\ominus)^{1/2}}$$

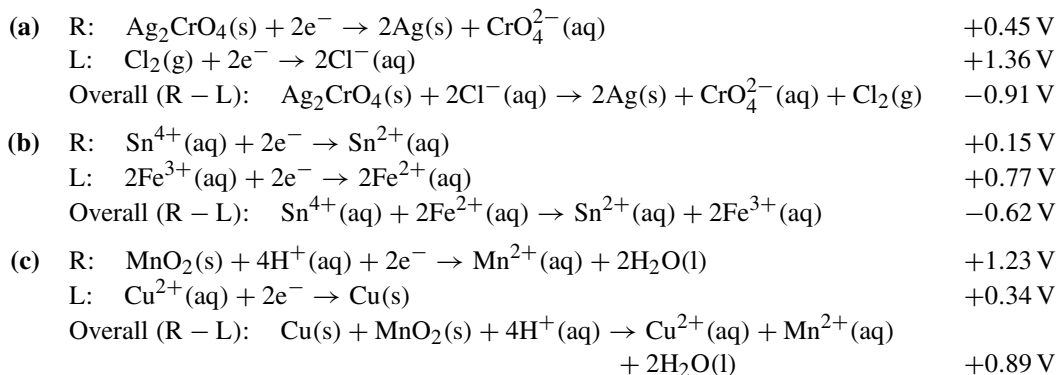
$$\Delta E = E_2 - E_1 = \frac{RT}{F} \ln \frac{a_2(\text{H}^+)}{a_1(\text{H}^+)} [f_{\text{H}_2} \text{ is constant}] = \frac{RT}{F} \ln \frac{\gamma_{\pm} b_2}{\gamma_{\pm} b_1}$$

$$= (25.7 \text{ mV}) \times \ln \left[\frac{(0.830) \times (5.0 \times 10^{-2})}{(0.929) \times (5.0 \times 10^{-3})} \right] = \boxed{+56.3 \text{ mV}}$$

E10.17(b) Identify electrodes using species with the desired oxidation states.

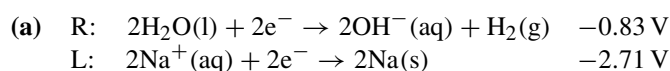


E10.18(b) The cell notation specifies the right and left electrodes. Note that for proper cancellation we must equalize the number of electrons in half-reactions being combined.

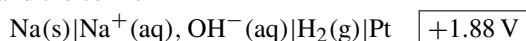


Comment. Those cells for which $E^\ominus > 0$ may operate as spontaneous galvanic cells under standard conditions. Those for which $E^\ominus < 0$ may operate as nonspontaneous electrolytic cells. Recall that E^\ominus informs us of the spontaneity of a cell under standard conditions only. For other conditions we require E .

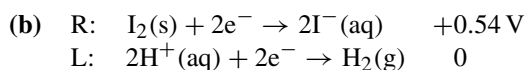
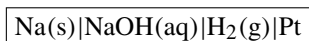
E10.19(b) The conditions (concentrations, etc.) under which these reactions occur are not given. For the purposes of this exercise we assume standard conditions. The specification of the right and left electrodes is determined by the direction of the reaction as written. As always, in combining half-reactions to form an overall cell reaction we must write half-reactions with equal number of electrons to ensure proper cancellation. We first identify the half-reactions, and then set up the corresponding cell.



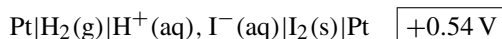
and the cell is



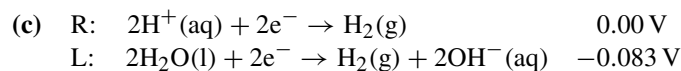
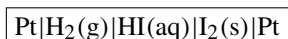
or more simply



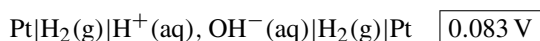
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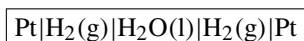
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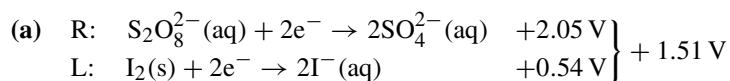
Comment. All of these cells have $E^\ominus > 0$, corresponding to a spontaneous cell reaction under standard conditions. If E^\ominus had turned out to be negative, the spontaneous reaction would have been the reverse of the one given, with the right and left electrodes of the cell also reversed.

E10.20(b) See the solutions for Exercise 10.18(b), where we have used $E^\ominus = E_R^\ominus - E_L^\ominus$, with standard electrode potentials from Table 10.7.

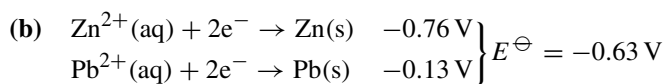
E10.21(b) See the solutions for Exercise 10.19(b), where we have used $E^\ominus = E_R^\ominus - E_L^\ominus$, with standard electrode potentials from Table 10.7.

E10.22(b) In each case find $E^\ominus = E_R^\ominus - E_L^\ominus$ from the data in Table 10.7, then use

$$\Delta_r G^\ominus = -\nu F E^\ominus \quad [10.32]$$

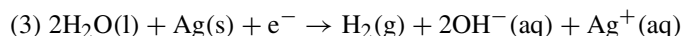


$$\Delta_r G^\ominus = (-2) \times (96.485 \text{ kC mol}^{-1}) \times (1.51 \text{ V}) = \boxed{-291 \text{ kJ mol}^{-1}}$$



$$\Delta_r G^\ominus = (-2) \times (96.485 \text{ kC mol}^{-1}) \times (-0.63 \text{ V}) = \boxed{+122 \text{ kJ mol}^{-1}}$$

E10.23(b) (a) A new half-cell may be obtained by the process (3) = (1) – (2), that is



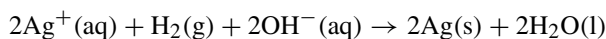
But, $E_3^\ominus \neq E_1^\ominus - E_2^\ominus$, for the reason that the reduction potentials are intensive, as opposed to extensive, quantities. Only extensive quantities are additive. However, the $\Delta_r G^\ominus$ values of the half-reactions are extensive properties, and thus

$$\begin{aligned} \Delta_r G_3^\ominus &= \Delta_r G_1^\ominus - \Delta_r G_2^\ominus \\ -\nu_3 F E_3^\ominus &= -\nu_1 F E_1^\ominus - (-\nu_2 F E_2^\ominus) \end{aligned}$$

Solving for E_3^\ominus we obtain

$$E_3^\ominus = \frac{\nu_1 E_1^\ominus - \nu_2 E_2^\ominus}{\nu_3} = \frac{(2) \times (-0.828 \text{ V}) - (1) \times (0.799 \text{ V})}{1} = \boxed{-2.455 \text{ V}}$$

(b) The complete cell reactions is obtained in the usual manner. We take (2) \times (2) – (1) to obtain



$$E^\ominus(\text{cell}) = E_R^\ominus - E_L^\ominus = E_2^\ominus - E_1^\ominus = (0.799 \text{ V}) - (-0.828 \text{ V}) = \boxed{+1.627 \text{ V}}$$

Comment. The general relation for E^\ominus of a new half-cell obtained from two others is

$$E_3^\ominus = \frac{\nu_1 E_1^\ominus \pm \nu_2 E_2^\ominus}{\nu_3}$$

E10.24(b) (a) $E = E^\ominus - \frac{RT}{\nu F} \ln Q \quad \nu = 2$

$$Q = \prod_j a_j^{\nu_j} = a_{\text{H}^+}^2 a_{\text{Cl}^-}^2 \quad [\text{all other activities} = 1]$$

$$= a_+^2 a_-^2 = (\gamma_+ b_+)^2 \times (\gamma_- b_-)^2 \quad \left[b \equiv \frac{b}{b^\ominus} \text{ here and below} \right]$$

$$= (\gamma_+ \gamma_-)^2 \times (b_+ b_-)^2 = \gamma_\pm^4 b^4 \quad [16, b_+ = b, b_- = b]$$

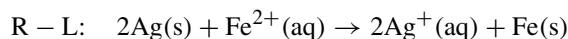
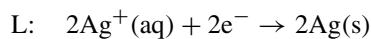
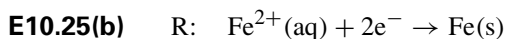
$$\text{Hence, } E = E^\ominus - \frac{RT}{2F} \ln(\gamma_\pm^4 b^4) = \boxed{E^\ominus - \frac{2RT}{F} \ln(\gamma_\pm b)}$$

(b) $\Delta_r G = -\nu F E [10.32] = -(2) \times (9.6485 \times 10^4 \text{ C mol}^{-1}) \times (0.4658 \text{ V}) = \boxed{-89.89 \text{ kJ mol}^{-1}}$

(c) $\log \gamma_\pm = -|z_+ z_-| A I^{1/2} [19] = -(0.509) \times (0.010)^{1/2} [I = b \text{ for HCl(aq)}] = -0.0509$
 $\gamma_\pm = 0.889$

$$\begin{aligned} E^\ominus &= E + \frac{2RT}{F} \ln(\gamma_\pm b) = (0.4658 \text{ V}) + (2) \times (25.693 \times 10^{-3} \text{ V}) \times \ln(0.889 \times 0.010) \\ &= \boxed{+0.223 \text{ V}} \end{aligned}$$

The value compares favourably to that given in Table 10.7.



$$E^\ominus = E_{\text{R}}^\ominus - E_{\text{L}}^\ominus = (-0.44 \text{ V}) - (0.80 \text{ V}) = \boxed{-1.24 \text{ V}}$$

$$\Delta_{\text{r}}G^\ominus = -\nu FE^\ominus = -2 \times (9.65 \times 10^4 \text{ C mol}^{-1}) \times (-1.24 \text{ V})$$

$$= \boxed{+239 \text{ kJ mol}^{-1}}$$

$$\Delta_{\text{r}}H^\ominus = 2\Delta_{\text{f}}H^\ominus(\text{Ag}^+, \text{aq}) - \Delta_{\text{f}}H^\ominus(\text{Fe}^{2+}, \text{aq}) = [(2) \times (105.58) - (-89.1)] \text{ kJ mol}^{-1}$$

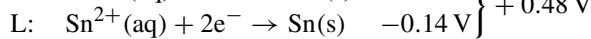
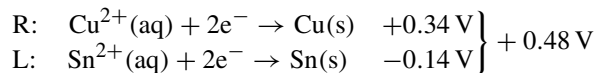
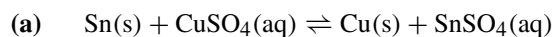
$$= \boxed{+300.3 \text{ kJ mol}^{-1}}$$

$$\left(\frac{\partial \Delta_{\text{r}}G^\ominus}{\partial T}\right)_p = -\Delta_{\text{r}}S^\ominus = \frac{\Delta_{\text{r}}G^\ominus - \Delta_{\text{r}}H^\ominus}{T} \quad [\Delta_{\text{r}}G^\ominus = \Delta_{\text{r}}H^\ominus - T\Delta_{\text{r}}S^\ominus]$$

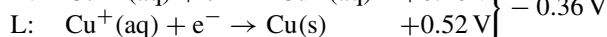
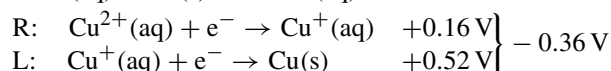
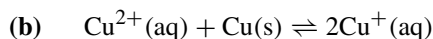
$$= \frac{(239 - 300.3) \text{ kJ mol}^{-1}}{298.15 \text{ K}} = -0.206 \text{ kJ mol}^{-1} \text{ K}^{-1}$$

Therefore, $\Delta_{\text{r}}G^\ominus(308 \text{ K}) \approx (239) + (10 \text{ K}) \times (-0.206 \text{ K}^{-1}) \text{ kJ mol}^{-1} \approx \boxed{+237 \text{ kJ mol}^{-1}}$

E10.26(b) In each case $\ln K = \frac{\nu FE^\ominus}{RT}$ [10.36]

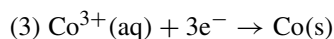


$$\ln K = \frac{(2) \times (0.48 \text{ V})}{25.693 \text{ mV}} = +37.4, \quad K = \boxed{1.7 \times 10^{16}}$$

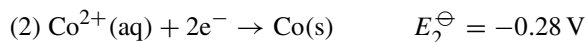
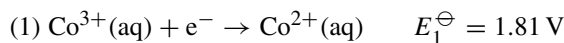


$$\ln K = \frac{-0.36 \text{ V}}{25.693 \text{ mV}} = -14.0, \quad K = \boxed{8.2 \times 10^{-7}}$$

E10.27(b) We need to obtain E^\ominus for the couple



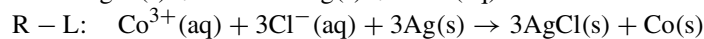
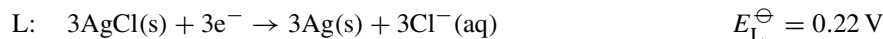
from the values of E^\ominus for the couples



We see that (3) = (1) + (2); therefore (see the solution to Exercise 10.23(b))

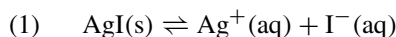
$$E_3 = \frac{\nu_1 E_1^\ominus + \nu_2 E_2^\ominus}{\nu_3} = \frac{(1) \times (1.81 \text{ V}) + (2) \times (-0.28 \text{ V})}{3} = 0.42 \text{ V}$$

Then,



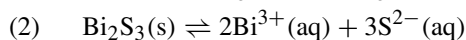
$$E^{\ominus} = E_{\text{R}}^{\ominus} - E_{\text{L}}^{\ominus} = (0.42 \text{ V}) - (0.22 \text{ V}) = \boxed{+0.20 \text{ V}}$$

E10.28(b) First assume all activity coefficients are 1 and calculate K_{S}° , the ideal solubility product constant.



$S(\text{AgI}) = b(\text{Ag}^{+}) = b(\text{I}^{-})$ because all stoichiometric coefficients are 1.

$$\text{Thus } K_{\text{S}}^{\circ} = \frac{b(\text{Ag}^{+})b(\text{I}^{-})}{b^{\ominus 2}} = \frac{S^2}{b^{\ominus 2}} = (1.2 \times 10^{-8})^2 = \boxed{1.44 \times 10^{-16}}$$



$$b(\text{Bi}^{3+}) = 2S(\text{Bi}_2\text{S}_3)$$

$$b(\text{S}^{2-}) = 3S(\text{Bi}_2\text{S}_3)$$

$$K_{\text{S}}^{\circ} = \frac{(b(\text{Bi}^{3+}))^2 \times (b(\text{S}^{2-}))^3}{b^{\ominus 5}} = \frac{(2S)^2 \times (3S)^3}{b^{\ominus 5}} = 108 \left(\frac{S}{b^{\ominus}} \right)^5$$

$$= \boxed{1.13 \times 10^{-97}}$$

For AgI, $K_{\text{S}} = \gamma_{\pm}^2 K_{\text{S}}^{\circ}$

$$\log \gamma_{\pm} = -|z_{+}z_{-}|AI^{1/2} \quad A = 0.509$$

$$I = Sb^{\ominus}, \quad |z_{+}z_{-}| = 1 \quad \text{so}$$

$$\log \gamma_{\pm} = -(0.509) \times (1.2 \times 10^{-8})^{1/2} = -5.58 \times 10^{-5}$$

$$\gamma_{\pm} = 0.9999$$

$$K_{\text{S}} = (0.9999)^2 K_{\text{S}}^{\circ} = 0.9997 K_{\text{S}}^{\circ}$$

For Bi_2S_3 , $I = 15b/b^{\ominus} = 15Sb^{\ominus}$, $|z_{+}z_{-}| = 6$

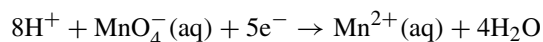
$$\text{so } \log \gamma_{\pm} = -(0.509) \times (6) \times [15(1.6 \times 10^{-20})]^{1/2} = -1.496 \times 10^{-9}$$

$$\gamma_{\pm} = 1.0$$

$$K_{\text{S}} = \gamma_{\pm}^5 K_{\text{S}}^{\circ} = K_{\text{S}}^{\circ}$$

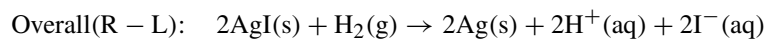
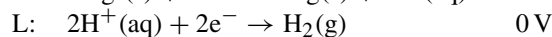
Neglect of activity coefficients is not significant for AgI and Bi_2S_3 .

E10.29(b) The Nernst equation applies to half-reactions as well as whole reactions; thus for



$$E = E^{\ominus} - \frac{RT}{5F} \ln \frac{a(\text{Mn}^{2+})}{a(\text{MnO}_4^{-})a(\text{H}^{+})^8}$$

E10.30(b) R: $2\text{AgI}(\text{s}) + 2\text{e}^{-} \rightarrow 2\text{Ag}(\text{s}) + 2\text{I}^{-}(\text{aq}) \quad -0.15 \text{ V}$



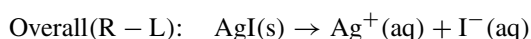
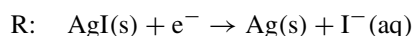
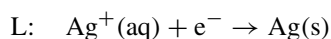
$$Q = a(\text{H}^{+})^2 a(\text{I}^{-})^2 \quad \nu = 2$$

Assume $a(\text{H}^{+}) = a(\text{I}^{-})$, $Q = a(\text{H}^{+})^4$

$$E = E^\ominus - \frac{RT}{2F} \ln a(\text{H}^+)^4 = E^\ominus - \frac{2RT}{F} \ln a(\text{H}^+) = E^\ominus + 2 \times (2.303) \times \left(\frac{RT}{F}\right) \times \text{pH}$$

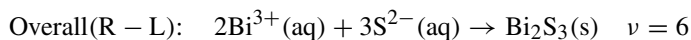
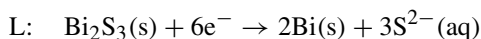
$$\text{pH} = \left(\frac{F}{2 \times (2.303RT)}\right) \times (E - E^\ominus) = \frac{E + 0.15 \text{ V}}{0.1183 \text{ V}} = \frac{1.15 \text{ V}}{0.1183 \text{ V}} = \boxed{9.72}$$

E10.31(b) The electrode reactions are



Since the cell reaction is a solubility equilibrium, for a saturated solution there is no further tendency to dissolve and so $E = \boxed{0}$

E10.32(b) R: $2\text{Bi}^{3+}(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Bi}(\text{s})$



$$\ln K = \frac{\nu F E^\ominus}{RT}$$

$$= \frac{6(0.96 \text{ V})}{(25.693 \times 10^{-3} \text{ V})}$$

$$= 22\bar{4}$$

$$K = \text{e}^{22\bar{4}}$$

It is convenient to give the solution for **(b)** first.

(b) $K_S = K^{-1} = \text{e}^{-22\bar{4}} \approx \boxed{10^{-98}}$, since the cell reaction is the reverse of the solubility equilibrium.

$$\text{(a)} \quad K_S \approx 10^{-98} = \left[\frac{b}{b^\ominus}(\text{Bi}^{3+})\right]^2 \times \left[\frac{b}{b^\ominus}(\text{S}^{2-})\right]^3 = (2S)^2 \times (3S)^3 = 108S^5$$

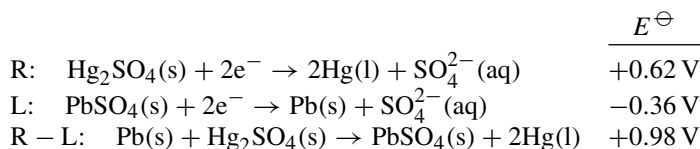
$$S = \left(\frac{10^{-98}}{108}\right)^{1/5} \approx \boxed{10^{-20} \text{ mol L}^{-1}}$$

Solutions to problems

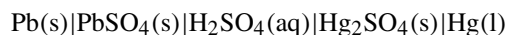
Solutions to numerical problems

P10.1

We require two half-cell reactions, which upon subtracting one (left) from the other (right), yields the given overall reaction (Section 10.4). The half-reaction at the right electrode corresponds to reduction, that at the left electrode to oxidation, though all half-reactions are listed in Table 10.7 as reduction reactions.



Hence, a suitable cell would be



or, alternatively,



For the cell in which the only sources of electrolyte are the slightly soluble salts, PbSO_4 and Hg_2SO_4 , the cell would be



The potential of this cell is given by the Nernst equation [10.34].

$$E = E^\ominus - \frac{RT}{\nu F} \ln Q \quad [10.34]; \quad \nu = 2$$

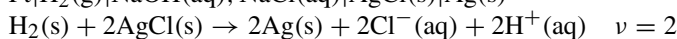
$$Q = \frac{a_{\text{Pb}^{2+}} a_{\text{SO}_4^{2-}}}{a_{\text{Hg}_2^{2+}} a_{\text{SO}_4^{2-}}} = \frac{K_S(\text{PbSO}_4)}{K_S(\text{Hg}_2\text{SO}_4)}$$

$$\begin{aligned} E &= (0.98 \text{ V}) - \frac{RT}{2F} \ln \frac{K_S(\text{PbSO}_4)}{K_S(\text{Hg}_2\text{SO}_4)} \\ &= (0.98 \text{ V}) - \left(\frac{25.693 \times 10^{-3} \text{ V}}{2} \right) \times \ln \left(\frac{1.6 \times 10^{-8}}{6.6 \times 10^{-7}} \right) \end{aligned}$$

[Table 10.6, 4th Edition, or *CRC Handbook*]

$$= (0.98 \text{ V}) + (0.05 \text{ V}) = \boxed{+1.03 \text{ V}}$$

P10.6



$$E = E^\ominus - \frac{RT}{2F} \ln Q, \quad Q = a(\text{H}^+)^2 a(\text{Cl}^-)^2 \quad [f/p^\ominus = 1]$$

$$= E^\ominus - \frac{RT}{F} \ln a(\text{H}^+) a(\text{Cl}^-) = E^\ominus - \frac{RT}{F} \ln \frac{K_w a(\text{Cl}^-)}{a(\text{OH}^-)} = E^\ominus - \frac{RT}{F} \ln \frac{K_w \gamma_{\pm} b(\text{Cl}^-)}{\gamma_{\pm} b(\text{OH}^-)}$$

$$= E^\ominus - \frac{RT}{F} \ln \frac{K_w b(\text{Cl}^-)}{b(\text{OH}^-)} = E^\ominus - \frac{RT}{F} \ln K_w - \frac{RT}{F} \ln \frac{b(\text{Cl}^-)}{b(\text{OH}^-)}$$

$$= E^\ominus + (2.303) \frac{RT}{F} \times \text{p}K_w - \frac{RT}{F} \ln \frac{b(\text{Cl}^-)}{b(\text{OH}^-)} \quad \left(\text{p}K_w = -\log K_w = \frac{-\ln K_w}{2.303} \right)$$

$$\text{Hence, } \text{p}K_w = \frac{E - E^\ominus}{2.303 RT/F} + \frac{\ln \left(\frac{b(\text{Cl}^-)}{b(\text{OH}^-)} \right)}{2.303} = \frac{E - E^\ominus}{2.303 RT/F} + 0.05114$$

$$E^\ominus = E_{\text{R}}^\ominus - E_{\text{L}}^\ominus = E^\ominus(\text{AgCl}, \text{Ag}) - E^\ominus(\text{H}^+/\text{H}_2) = +0.22 \text{ V} - 0 \text{ [Table 10.7]}$$

We then draw up the following table with the more precise value for $E^\ominus = +0.2223 \text{ V}$ [Problem 10.8]

$\theta/^\circ\text{C}$	20.0	25.0	30.0
E/V	1.04774	1.04864	1.04942
$\frac{2.303RT}{F}$ V	0.05819	0.05918	0.06018
$\text{p}K_w$	14.23	14.01	13.79

$$\frac{d \ln K_w}{dT} = \frac{\Delta_r H^\ominus}{RT^2} \quad [9.26]$$

$$\text{Hence, } \Delta_r H^\ominus = -(2.303)RT^2 \frac{d}{dT}(\text{p}K_w)$$

$$\text{then with } \frac{d \text{p}K_w}{dT} \approx \frac{\Delta \text{p}K_w}{\Delta T}$$

$$\Delta_r H^\ominus \approx -(2.303) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})^2 \times \frac{13.79 - 14.23}{10 \text{ K}}$$

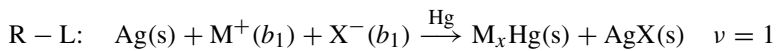
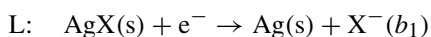
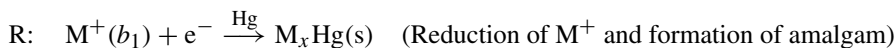
$$= \boxed{+74.9 \text{ kJ mol}^{-1}}$$

$$\Delta_r G^\ominus = -RT \ln K_w = 2.303RT \times \text{p}K_w = \boxed{+80.0 \text{ kJ mol}^{-1}}$$

$$\Delta_r S^\ominus = \frac{\Delta_r H^\ominus - \Delta_r G^\ominus}{T} = \boxed{-17.1 \text{ J K}^{-1} \text{ mol}^{-1}}$$

See the original reference for a careful analysis of the precise data.

P10.7 The cells described in the problem are back-to-back pairs of cells each of the type



$$Q = \frac{a(\text{M}_x\text{Hg})}{a(\text{M}^+)a(\text{X}^-)}$$

$$E = E^\ominus - \frac{RT}{F} \ln Q$$

For a pair of such cells back to back,



$$E_R = E^\ominus - \frac{RT}{F} \ln Q_R \quad E_L = E^\ominus - \frac{RT}{F} \ln Q_L$$

$$E = \frac{-RT}{F} \ln \frac{Q_L}{Q_R} = \frac{RT}{F} \ln \frac{(a(\text{M}^+)a(\text{X}^-))_L}{(a(\text{M}^+)a(\text{X}^-))_R}$$

(Note that the unknown quantity $a(\text{M}_x\text{Hg})$ drops out of the expression for E .)

$$a(\text{M}^+)a(\text{X}^-) = \left(\frac{\gamma_+ b_+}{b^\ominus}\right) \left(\frac{\gamma_- b_-}{b^\ominus}\right) = \gamma_\pm^2 \left(\frac{b}{b^\ominus}\right)^2 \quad (b_+ = b_-)$$

With L = (1) and R = (2) we have

$$E = \frac{2RT}{F} \ln \frac{b_1}{b_2} + \frac{2RT}{F} \ln \frac{\gamma_\pm(1)}{\gamma_\pm(2)}$$

Take $b_2 = 0.09141 \text{ mol kg}^{-1}$ (the reference value), and write $b = \frac{b_1}{b^\ominus}$

$$E = \frac{2RT}{F} \left(\ln \frac{b}{0.09141} + \ln \frac{\gamma_\pm}{\gamma_\pm(\text{ref})} \right)$$

For $b = 0.09141$, the extended Debye–Hückel law gives

$$\log \gamma_{\pm}(\text{ref}) = \frac{(-1.461) \times (0.09141)^{1/2}}{(1) + (1.70) \times (0.09141)^{1/2}} + (0.20) \times (0.09141) = -0.273\bar{5}$$

$$\gamma_{\pm}(\text{ref}) = 0.532\bar{8}$$

$$\text{then } E = (0.05139 \text{ V}) \times \left(\ln \frac{b}{0.09141} + \ln \frac{\gamma_{\pm}}{0.5328} \right)$$

$$\ln \gamma_{\pm} = \frac{E}{0.05139 \text{ V}} - \ln \frac{b}{(0.09141) \times (0.5328)}$$

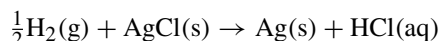
We then draw up the following table

$b/(\text{mol}/\text{kg}^{-1})$	0.0555	0.09141	0.1652	0.2171	1.040	1.350
E/V	-0.0220	0.0000	0.0263	0.0379	0.1156	0.1336
γ	0.572	0.533	0.492	0.469	0.444	0.486

A more precise procedure is described in the original references for the temperature dependence of E^{\ominus} (Ag, AgCl, Cl^{-}), see Problem 10.10.

P10.10

The method of the solution is first to determine $\Delta_r G^{\ominus}$, $\Delta_r H^{\ominus}$, and $\Delta_r S^{\ominus}$ for the cell reaction



and then, from the values of these quantities and the known values of $\Delta_f G^{\ominus}$, $\Delta_f H^{\ominus}$, and S^{\ominus} for all the species other than $\text{Cl}^{-}(\text{aq})$, to calculate $\Delta_f G^{\ominus}$, $\Delta_f H^{\ominus}$, and S^{\ominus} for $\text{Cl}^{-}(\text{aq})$.

$$\Delta_r G^{\ominus} = -\nu F E^{\ominus}$$

At 298.15 K (25.00°C)

$$E^{\ominus}/\text{V} = (0.23659) - (4.8564 \times 10^{-4}) \times (25.00) - (3.4205 \times 10^{-6}) \times (25.00)^2 + (5.869 \times 10^{-9}) \times (25.00)^3 = +0.22240 \text{ V}$$

Therefore, $\Delta_r G^{\ominus} = -(96.485 \text{ kC mol}^{-1}) \times (0.22240 \text{ V}) = -21.46 \text{ kJ mol}^{-1}$

$$\Delta_r S^{\ominus} = - \left(\frac{\partial \Delta_r G^{\ominus}}{\partial T} \right)_p = \left(\frac{\partial E^{\ominus}}{\partial T} \right)_p \times \nu F = \nu F \left(\frac{\partial E^{\ominus}}{\partial \theta} \right)_p \frac{^{\circ}\text{C}}{\text{K}} \quad [d\theta/^{\circ}\text{C} = dT/\text{K}] \quad (\text{a})$$

$$\begin{aligned} \left(\frac{\partial E^{\ominus}}{\partial \theta} \right)_p &= (-4.8564 \times 10^{-4} / ^{\circ}\text{C}) - (2) \times (3.4205 \times 10^{-6} \theta / (^{\circ}\text{C})^2) \\ &\quad + (3) \times (5.869 \times 10^{-9} \theta^2 / (^{\circ}\text{C})^3) \end{aligned}$$

$$\left(\frac{\partial E^{\ominus}}{\partial \theta} \right)_p = (-4.8564 \times 10^{-4}) - (6.8410 \times 10^{-6} (\theta / ^{\circ}\text{C})) + (1.7607 \times 10^{-8} (\theta / ^{\circ}\text{C})^2)$$

Therefore, at 25.00°C,

$$\left(\frac{\partial E^{\ominus}}{\partial \theta} \right)_p = -6.4566 \times 10^{-4} \text{ V}/^{\circ}\text{C}$$

and

$$\left(\frac{\partial E^{\ominus}}{\partial T} \right)_p = (-6.4566 \times 10^{-4} \text{ V}/^{\circ}\text{C}) \times (^{\circ}\text{C}/\text{K}) = -6.4566 \times 10^{-4} \text{ V K}^{-1}$$

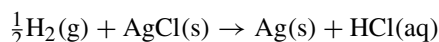
Hence, from equation (a)

$$\Delta_r S^\ominus = (-96.485 \text{ kC mol}^{-1}) \times (6.4566 \times 10^{-4} \text{ V K}^{-1}) = -62.30 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{and } \Delta_r H^\ominus = \Delta_r G^\ominus + T \Delta_r S^\ominus$$

$$= -(21.46 \text{ kJ mol}^{-1}) + (298.15 \text{ K}) \times (-62.30 \text{ J K}^{-1} \text{ mol}^{-1}) = -40.03 \text{ kJ mol}^{-1}$$

For the cell reaction



$$\Delta_r G^\ominus = \Delta_f G^\ominus(\text{H}^+) + \Delta_f G^\ominus(\text{Cl}^-) - \Delta_f G^\ominus(\text{AgCl})$$

$$= \Delta_f G^\ominus(\text{Cl}^-) - \Delta_f G^\ominus(\text{AgCl}) \quad [\Delta_f G^\ominus(\text{H}^+) = 0]$$

$$\text{Hence, } \Delta_f G^\ominus(\text{Cl}^-) = \Delta_r G^\ominus + \Delta_f G^\ominus(\text{AgCl}) = [(-21.46) - (109.79)] \text{ kJ mol}^{-1}$$

$$= \boxed{-131.25 \text{ kJ mol}^{-1}}$$

$$\text{Similarly, } \Delta_f H^\ominus(\text{Cl}^-) = \Delta_r H^\ominus + \Delta_f H^\ominus(\text{AgCl}) = (-40.03) - (127.07) \text{ kJ mol}^{-1}$$

$$= \boxed{-167.10 \text{ kJ mol}^{-1}}$$

For the entropy of Cl^- in solution we use

$$\Delta_r S^\ominus = S^\ominus(\text{Ag}) + S^\ominus(\text{H}^+) + S^\ominus(\text{Cl}^-) - \frac{1}{2} S^\ominus(\text{H}_2) - S^\ominus(\text{AgCl})$$

with $S^\ominus(\text{H}^+) = 0$. Then,

$$S^\ominus(\text{Cl}^-) = \Delta_r S^\ominus - S^\ominus(\text{Ag}) + \frac{1}{2} S^\ominus(\text{H}_2) + S^\ominus(\text{AgCl})$$

$$= (-62.30) - (42.55) + \left(\frac{1}{2}\right) \times (130.68) + (96.2) = \boxed{+56.7 \text{ J K}^{-1} \text{ mol}^{-1}}$$

P10.12 (a) From $\left(\frac{\partial G}{\partial p}\right)_T = V$ [5.10]

$$\text{we obtain } \left(\frac{\partial \Delta_r G}{\partial p}\right)_T = \Delta_r V$$

Substituting $\Delta_r G = -\nu FE$ [10.32] yields

$$\boxed{\left(\frac{\partial E}{\partial p}\right)_{T,n} = -\frac{\Delta_r V}{\nu F}}$$

(b) The plot (Fig. 10.1) of E against p appears to fit a straight line very closely. A linear regression analysis yields

$$\text{Slope} = \boxed{2.840 \times 10^{-3} \text{ mV atm}^{-1}},$$

$$\text{standard deviation} = 3 \times 10^{-6} \text{ mV atm}^{-1}$$

$$\text{Intercept} = 8.5583 \text{ mV,}$$

$$\text{standard deviation} = 2.8 \times 10^{-3} \text{ mV}$$

$$R = 0.99999701 \quad (\text{an extremely good fit})$$

From $\Delta_r V$

$$\left(\frac{\partial E}{\partial p}\right)_{T,n} = -\frac{(-2.666 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})}{1 \times 9.6485 \times 10^4 \text{ C mol}^{-1}}$$

$$\text{Since } J = V C = \text{Pa m}^3, C = \frac{\text{Pa m}^3}{V} \text{ or } \frac{\text{m}^3}{C} = \frac{V}{\text{Pa}}$$

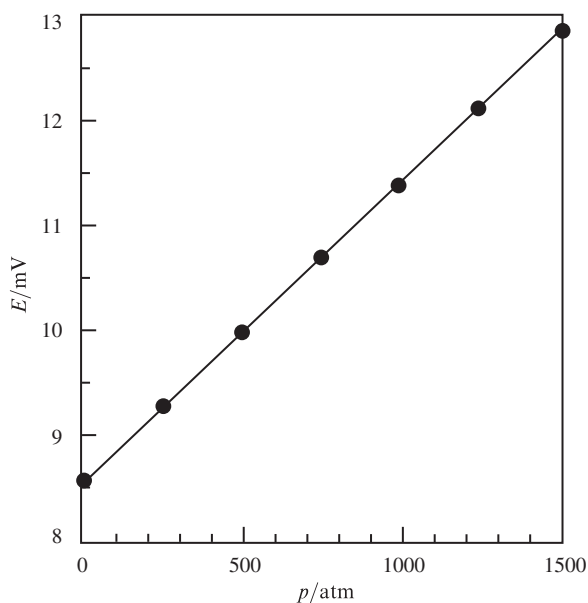


Figure 10.1

Therefore

$$\begin{aligned} \left(\frac{\partial E}{\partial p}\right)_{T,n} &= \left(\frac{2.66\bar{6} \times 10^{-6}}{9.648\bar{5} \times 10^4}\right) \frac{\text{V}}{\text{Pa}} \times \frac{1.01325 \times 10^5 \text{ Pa}}{\text{atm}} = 2.80 \times 10^{-6} \text{ V atm}^{-1} \\ &= \boxed{2.80 \times 10^{-3} \text{ mV atm}^{-1}} \end{aligned}$$

This compares closely to the result from the potential measurements.

(c) A fit to a second-order polynomial of the form

$$E = a + bp + cp^2$$

yields

$$\begin{aligned} a &= 8.5592 \text{ mV}, & \text{standard deviation} &= 0.0039 \text{ mV} \\ b &= 2.835 \times 10^{-3} \text{ mV atm}^{-1}, & \text{standard deviation} &= 0.012 \times 10^{-3} \text{ mV atm}^{-1} \\ c &= 3.02 \times 10^{-9} \text{ mV atm}^{-2}, & \text{standard deviation} &= 7.89 \times 10^{-9} \text{ mV atm}^{-1} \\ R &= 0.99999711 \end{aligned}$$

This regression coefficient is only marginally better than that for the linear fit, but the uncertainty in the quadratic term is > 200 per cent.

$$\left(\frac{\partial E}{\partial p}\right)_T = b + 2cp$$

The slope changes from $\left(\frac{\partial E}{\partial p}\right)_{\min} = b = 2.835 \times 10^{-3} \text{ mV atm}^{-1}$

to $\left(\frac{\partial E}{\partial p}\right)_{\max} = b + 2c(1500 \text{ atm}) = 2.836 \times 10^{-3} \text{ mV atm}^{-1}$

We conclude that the linear fit and constancy of $\left(\frac{\partial E}{\partial p}\right)$ are very good.

(d) We can obtain an order of magnitude value for the isothermal compressibility from the value of c .

$$\begin{aligned}\frac{\partial^2 E}{\partial p^2} &= -\frac{1}{\nu F} \left(\frac{\partial \Delta_r V}{\partial p} \right)_T = 2c \\ (\kappa_T)_{\text{cell}} &= -\frac{1}{V} \left(\frac{\partial \Delta_r V}{\partial p} \right)_T = \frac{2\nu c F}{V} \\ (\kappa_T)_{\text{cell}} &= \frac{2(1) \times (3.02 \times 10^{-12} \text{ V atm}^{-2}) \times (9.6485 \times 10^4 \text{ C mol}^{-1}) \times \left(\frac{82.058 \text{ cm}^3 \text{ atm}}{8.3145 \text{ J}} \right)}{\left(\frac{1 \text{ cm}^3}{0.996 \text{ g}} \right) \times \left(\frac{18.016 \text{ g}}{1 \text{ mol}} \right)} \\ &= \boxed{3.2 \times 10^{-7} \text{ atm}^{-1}} \quad \text{standard deviation} \approx 200 \text{ per cent}\end{aligned}$$

where we have assumed the density of the cell to be approximately that of water at 30°C.

Comment. It is evident from these calculations that the effect of pressure on the potentials of cells involving only liquids and solids is not important; for this reaction the change is only $\sim 3 \times 10^{-6} \text{ V atm}^{-1}$. The effective isothermal compressibility of the cell is of the order of magnitude typical of solids rather than liquids; other than that, little significance can be attached to the calculated numerical value.

P10.15 The equilibrium is

$$K = \frac{a(\text{H}_2\text{O})^4 a(\text{V}_4\text{O}_{12}^{-4})}{a(\text{H}_2\text{VO}_4^-)^4} \approx \frac{\gamma(\text{V}_4\text{O}_{12}^{-4}) b(\text{V}_4\text{O}_{12}^{-4})}{\gamma(\text{H}_2\text{VO}_4^-)^4 b(\text{H}_2\text{VO}_4^-)^4}$$

Let x be $b(\text{H}_2\text{VO}_4^-)$; then $b(\text{V}_4\text{O}_{12}^{-4}) = (0.010 - x)/4$. Then the equilibrium equation can be expressed as

$$x^4 \left(\frac{K \gamma(\text{H}_2\text{VO}_4^-)^4}{\gamma(\text{V}_4\text{O}_{12}^{-4})} \right) = (0.010 - x)/4$$

which can be solved numerically once the constants are determined. The activity coefficients are

$$\log \gamma(\text{H}_2\text{VO}_4^-) = -\frac{0.5373}{2} = -0.269 \quad \text{so} \quad \gamma(\text{H}_2\text{VO}_4^-) = 0.538$$

$$\text{and } \log \gamma(\text{V}_4\text{O}_{12}^{-4}) = -\frac{0.5373(4^2)}{2} = -1.075 \quad \text{so} \quad \gamma(\text{V}_4\text{O}_{12}^{-4}) = 0.0842$$

The equation is

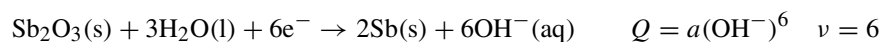
$$x^4 (2.5 \times 10^6) = (0.010 - x)/4$$

Its solution is

$$x = \boxed{0.0048 \text{ mol kg}^{-1}} = b(\text{H}_2\text{VO}_4^-)$$

$$\text{and } b(\text{V}_4\text{O}_{12}^{-4}) = 0.010 - (0.010 - 0.0048)/4 = \boxed{0.0013 \text{ mol kg}^{-1}}$$

P10.18 The reduction reaction is



Therefore

$$(a) \quad E = E^\ominus - \frac{RT}{6F} \ln a(\text{OH}^-)^6 = E^\ominus - \frac{RT}{F} \ln a(\text{OH}^-) = \boxed{E^\ominus + \frac{2.303RT}{F} \text{pOH}}$$

$$[\ln a(\text{OH}^-) = 2.303 \log a(\text{OH}^-) = -2.303 \text{pOH}]$$

(b) Since $\text{pOH} + \text{pH} = \text{p}K_w$

$$E = E^\ominus + \frac{2.303RT}{F}(\text{p}K_w - \text{pH})$$

(c) The change in potential is

$$\Delta E = \frac{2.303RT}{F}(\text{pOH}_f - \text{pOH}_i) = (59.17 \text{ mV}) \times (\text{pOH}_f - \text{pOH}_i)$$

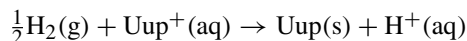
$$\text{pOH}_f = -\log(0.050\gamma_{\pm}) = -\log 0.050 - \log \gamma_{\pm} = -\log 0.050 + A\sqrt{(0.050)} = 1.41\bar{5}$$

$$\text{pOH}_i = -\log(0.010\gamma_{\pm}) = -\log 0.010 - \log \gamma_{\pm} = -\log 0.010 + A\sqrt{(0.010)} = 2.05\bar{1}$$

$$\text{Hence, } \Delta E = (59.17 \text{ mV}) \times (1.41\bar{5} - 2.05\bar{1}) = \boxed{-37.6 \text{ mV}}$$

P10.19

We need to obtain $\Delta_r H^\ominus$ for the reaction



We draw up the thermodynamic cycle shown in Fig. 10.2.

Data are obtained from Table 13.4, 14.3, 2.6, and 2.6b. The conversion factor between eV and kJ mol^{-1} is

$$1 \text{ eV} = 96.485 \text{ kJ mol}^{-1}$$

The distance from A to B in the cycle is given by

$$\begin{aligned} \Delta_r H^\ominus = x &= (3.22 \text{ eV}) + \left(\frac{1}{2}\right) \times (4.5 \text{ eV}) + (13.6 \text{ eV}) - (11.3 \text{ eV}) - (5.52 \text{ eV}) - (1.5 \text{ eV}) \\ &= 0.75 \text{ eV} \end{aligned}$$

$$\begin{aligned} \Delta_r S^\ominus &= S^\ominus(\text{Uup, s}) + S^\ominus(\text{H}^+, \text{aq}) - \frac{1}{2}S^\ominus(\text{H}_2, \text{g}) - S^\ominus(\text{Uup}^+, \text{aq}) \\ &= (0.69) + (0) - \left(\frac{1}{2}\right) \times (1.354) - (1.34) \text{ meV K}^{-1} = -1.33 \text{ meV K}^{-1} \end{aligned}$$

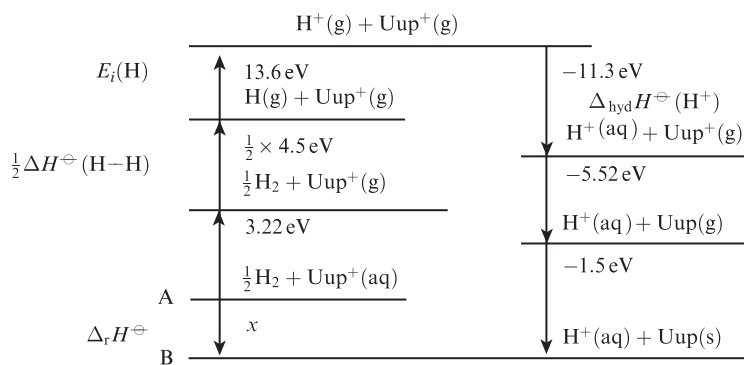


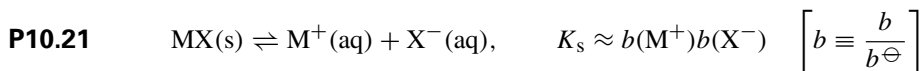
Figure 10.2

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T \Delta_r S^\ominus = (0.75 \text{ eV}) + (298.15 \text{ K}) \times (1.33 \text{ meV K}^{-1}) = +1.1\bar{5} \text{ eV}$$

which corresponds to $\boxed{+111 \text{ kJ mol}^{-1}}$

The electrode potential is therefore $\frac{-\Delta_r G^\ominus}{\nu F}$, with $\nu = 1$, or $\boxed{-1.1\bar{5} \text{ V}}$

Solutions to theoretical problems



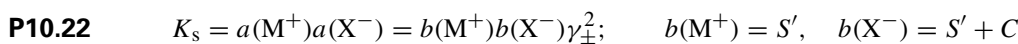
$$b(\text{M}^+) = S, \quad b(\text{X}^-) = S + C$$

$$K_s = S(S + C), \quad \text{or} \quad S^2 + CS - K_s = 0$$

which solves to $S = \frac{1}{2}(C^2 + 4K_s)^{1/2} - \frac{1}{2}C$ or $S = \frac{1}{2}C \left(1 + \frac{4K_s}{C^2} \right)^{1/2} - \frac{1}{2}C$

If $4K_s \ll C^2$,

$$S \approx \frac{1}{2}C \left(1 + \frac{2K_s}{C^2} \right) - \frac{1}{2}C \left[(1+x)^{1/2} \approx 1 + \frac{1}{2}x + \dots \right] \approx \frac{K_s}{C}$$



$$\log \gamma_{\pm} = -AI^{1/2} = -AC^{1/2} \quad \ln \gamma_{\pm} = -2.303AC^{1/2}$$

$$\gamma_{\pm} = e^{-2.303AC^{1/2}} \quad \gamma_{\pm}^2 = e^{-4.606AC^{1/2}}$$

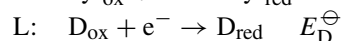
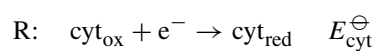
$$K_s = S'(S' + C) \times e^{-4.606AC^{1/2}}$$

We solve $S'^2 + S'C - \frac{K_s}{\gamma_{\pm}^2} = 0$

to get $S' = \frac{1}{2} \left(C^2 + \frac{4K_s}{\gamma_{\pm}^2} \right)^{1/2} - \frac{1}{2}C \approx \frac{K_s}{C\gamma_{\pm}^2}$ [as in Problem 10.21]

Therefore, since $\gamma_{\pm}^2 = e^{-4.606AC^{1/2}}$ $S' \approx \frac{K_s e^{-4.606AC^{1/2}}}{C}$

P10.25 The half-reactions involved are:



The overall cell reaction is:



(a) The Nernst equation for the cell reaction is

$$E = E - \frac{RT}{F} \ln \frac{[\text{cyt}_{\text{red}}][\text{D}_{\text{ox}}]}{[\text{cyt}_{\text{ox}}][\text{D}_{\text{red}}]}$$

at equilibrium, $E = 0$; therefore

$$\ln \frac{[\text{cyt}_{\text{red}}]_{\text{leq}}[\text{D}_{\text{ox}}]_{\text{leq}}}{[\text{cyt}_{\text{ox}}]_{\text{leq}}[\text{D}_{\text{red}}]_{\text{leq}}} = \frac{F}{RT} (E_{\text{cyt}}^\ominus - E_{\text{D}}^\ominus)$$

$$\ln \left(\frac{[\text{D}_{\text{ox}}]_{\text{leq}}}{[\text{D}_{\text{red}}]_{\text{leq}}} \right) = \ln \left(\frac{[\text{cyt}]_{\text{ox}}}{[\text{cyt}]_{\text{red}}} \right) + \frac{F}{RT} (E_{\text{cyt}}^\ominus - E_{\text{D}}^\ominus)$$

Therefore a plot of $\ln \left(\frac{[\text{D}_{\text{ox}}]_{\text{leq}}}{[\text{D}_{\text{red}}]_{\text{leq}}} \right)$ against $\ln \left(\frac{[\text{cyt}]_{\text{ox}}}{[\text{cyt}]_{\text{red}}} \right)$ is linear with a slope of one and an intercept of $\frac{F}{RT} (E_{\text{cyt}}^\ominus - E_{\text{D}}^\ominus)$

(b) Draw up the following table:

$\ln\left(\frac{[D_{\text{ox}}]_{\text{eq}}}{[D_{\text{red}}]_{\text{eq}}}\right)$	-5.882	-4.776	-3.661	-3.002	-2.593	-1.436	-0.6274
$\ln\left(\frac{[\text{cyt}_{\text{ox}}]_{\text{eq}}}{[\text{cyt}_{\text{red}}]_{\text{eq}}}\right)$	-4.547	-3.772	-2.415	-1.625	-1.094	-0.2120	-0.3293

The plot of $\ln\left(\frac{[D_{\text{ox}}]_{\text{eq}}}{[D_{\text{red}}]_{\text{eq}}}\right)$ against $\ln\left(\frac{[\text{cyt}_{\text{ox}}]_{\text{eq}}}{[\text{cyt}_{\text{red}}]_{\text{eq}}}\right)$ is shown in Fig. 10.3. The intercept is -1.2124 . Hence

$$\begin{aligned} E_{\text{cyt}}^{\ominus} &= \frac{RT}{F} \times (-1.2124) + 0.237 \text{ V} \\ &= 0.0257 \text{ V} \times (-1.2124) + 0.237 \text{ V} \\ &= \boxed{+0.206 \text{ V}} \end{aligned}$$

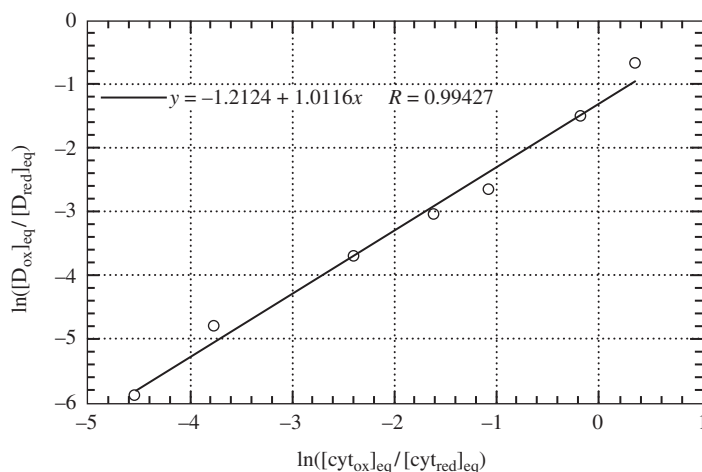


Figure 10.3

Solutions to application

P10.27

(a) $\text{molality}_{\text{H}_2\text{SO}_4} = b(d) = a(d - d_{25}) + c(d - d_{25})^2$

where d is density in g cm^{-3} at 25°C , $a = 14.523 \text{ mol kg}^{-1}(\text{g cm}^{-3})^{-1}$,
 $c = 25.031 \text{ mol kg}^{-1}(\text{g cm}^{-3})^{-2}$, and $d_{25} = 0.99707 \text{ g cm}^{-3}$.

For 1 kg solvent ($m_{\text{H}_2\text{O}} = 1 \text{ kg}$):

$$\text{mass \%}_{\text{H}_2\text{SO}_4} = \left(\frac{m_{\text{H}_2\text{SO}_4}}{m_{\text{H}_2\text{SO}_4} + m_{\text{H}_2\text{O}}} \right) 100 = \frac{b \times 100}{b + \frac{m_{\text{H}_2\text{O}}}{m_{\text{H}_2\text{SO}_4} m_{\text{H}_2\text{O}}}}$$

$$\text{mass \%}_{\text{H}_2\text{SO}_4}(d) = \frac{100 \times b(d)}{b(d) + \frac{1}{m_{\text{H}_2\text{SO}_4}}} \text{ where } m_{\text{H}_2\text{SO}_4} = 0.09807 \text{ kg mol}^{-1}$$

an equation for the solution molarity is deduced with a unit analysis.

$$\text{molarity}_{\text{H}_2\text{SO}_4}(d) = b(d) \times \left(1 - \frac{\text{mass \%}_{\text{H}_2\text{SO}_4}(d)}{100} \right) d \times \left(\frac{10^3 \text{ cm}^3}{\text{L}} \right) \left(\frac{\text{kg}}{10^3 \text{ g}} \right)$$

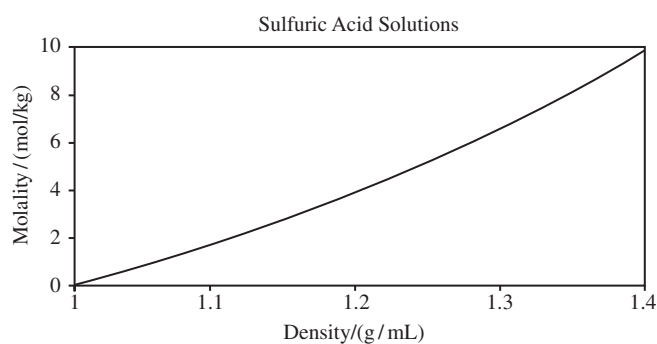


Figure 10.4(a)

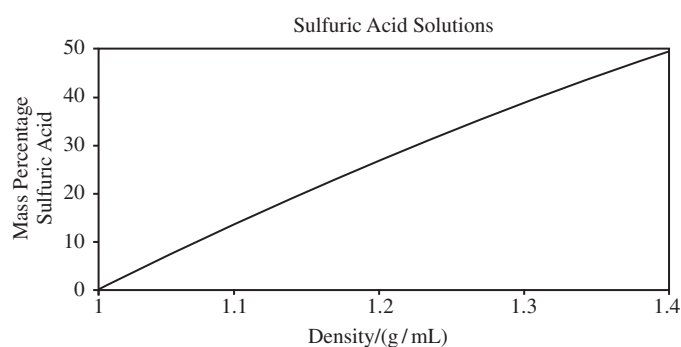


Figure 10.4(b)

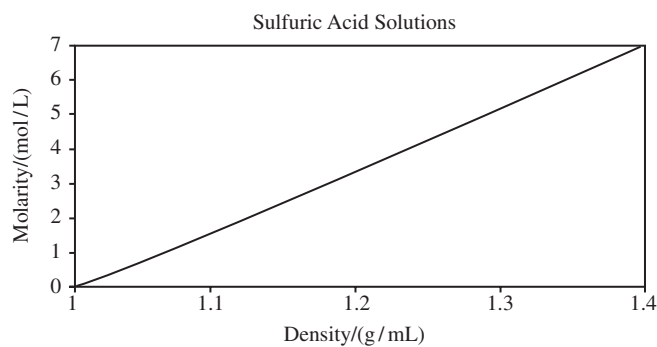
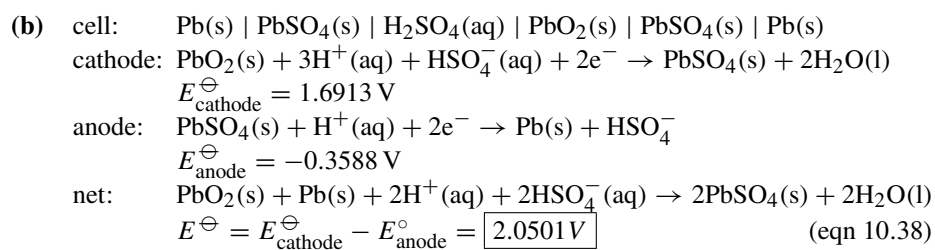


Figure 10.4(c)



$$\Delta_r G^\ominus = -\nu F E^\ominus = -(2)(9.64853 \times 10^4 \text{ C mol}^{-1})(2.0501 \text{ V})$$

$$= -3.956 \times 10^5 \text{ C V mol}^{-1} = -3.956 \times 10^5 \text{ J mol}^{-1} = \boxed{-395.6 \text{ kJ mol}^{-1}}$$

$\Delta_f H^\ominus$ values of Table 2.6 and the *CRC Handbook of Chemistry and Physics* are used in the $\Delta_r H^\ominus$ calculation.

$$\begin{aligned}\Delta_r H^\ominus &= 2\Delta_f H^\ominus(\text{PbSO}_4) + 2\Delta_f H^\ominus(\text{H}_2\text{O}(\text{l})) - \Delta_f H^\ominus(\text{PbO}_2) - \Delta_f H^\ominus(\text{Pb}) \\ &\quad - 2\Delta_f H^\ominus(\text{H}^+) - 2\Delta_f H^\ominus(\text{HSO}_4^-) \\ &= 2(-919.94 \text{ kJ mol}^{-1}) + 2(-285.83 \text{ kJ mol}^{-1}) - (-277.4 \text{ kJ mol}^{-1}) \\ &\quad - 2(-887.34 \text{ kJ mol}^{-1})\end{aligned}$$

$$\Delta_r H^\ominus = \boxed{-359.5 \text{ kJ mol}^{-1}}$$

$$\begin{aligned}\Delta_r S^\ominus &= \frac{\Delta_r H^\ominus - \Delta_r G^\ominus}{T} = \frac{-359.5 \text{ kJ mol}^{-1} - (-395.6 \text{ kJ mol}^{-1})}{298.15 \text{ K}} \\ &= \boxed{121 \text{ J K}^{-1} \text{ mol}^{-1}} \quad (\text{eqn 4.39})\end{aligned}$$

$$\begin{aligned}E^\ominus(15^\circ\text{C}) &= E^\ominus(25^\circ\text{C}) + \Delta E^\ominus = E^\ominus(25^\circ\text{C}) + \frac{\Delta_r S^\ominus}{\nu F} \Delta T \quad (\text{eqn 10.45}) \\ &= 2.0501 \text{ V} + \frac{(121 \text{ J K}^{-1} \text{ mol}^{-1})}{2(96485 \text{ C mol}^{-1})} (10 \text{ K}) \\ &= 2.0501 \text{ V} + 0.006 \text{ V} = \boxed{2.0507 \text{ V}}\end{aligned}$$

The temperature difference makes a negligibly small difference in the cell potential.

When $Q = 6.0 \times 10^{-5}$,

$$\begin{aligned}E &= E^\ominus - \frac{RT}{\nu F} \ln Q \quad (\text{eqn 10.34}) \\ &= 2.0501 \text{ V} - \frac{(8.31451 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{2(96485 \text{ C mol}^{-1})} \ln(6.0 \times 10^{-5}) \\ &= \boxed{2.1750 \text{ V}}\end{aligned}$$

- (c) The general form of the reduction half-reaction is: $\text{ox} + \nu e^- + \nu_{\text{H}}\text{H}^+ + a\text{A} \rightarrow \text{red} + x\text{X}$ using eqn 10.34,

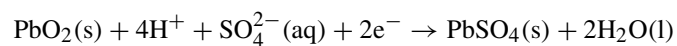
$$\begin{aligned}E &= E^\ominus - \frac{RT}{\nu F} \ln Q = E^\ominus - \frac{RT}{\nu F} \ln \left(\frac{a_{\text{red}} a_{\text{X}}^x}{a_{\text{ox}} a_{\text{H}^+}^{\nu_{\text{H}}} a_{\text{A}}^a} \right) \\ &= E^\ominus - \frac{RT}{\nu F} \ln \left(\frac{1}{a_{\text{H}^+}^{\nu_{\text{H}}}} \right)\end{aligned}$$

(all species other than acids are at unit activity in a Pourboix diagram)

$$\begin{aligned}&= E^\ominus + \frac{\nu_{\text{H}} RT}{\nu F} \ln a_{\text{H}^+} = E^\ominus + \frac{\nu_{\text{H}} RT \ln^{(10)}}{\nu F} \log a_{\text{H}^+} \\ &= E^\ominus - \frac{\nu_{\text{H}}}{\nu} \left(\frac{RT \ln^{(10)}}{F} \right) \text{pH} \quad (\text{eqn 9.29})\end{aligned}$$

$$\boxed{E = E^\ominus - (0.05916 \text{ V}) \left(\frac{\nu_{\text{H}}}{\nu} \right) \text{pH}}$$

For the $\text{PbO}_2 \mid \text{PbSO}_4$ couple,



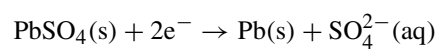
$$E^\ominus = 1.6913 \text{ V}, \nu_{\text{H}} = 4, \nu = 2$$

$$E = 1.6913 \text{ V} - (0.11832 \text{ V})\text{pH}$$

$$\text{For pH} = 5, \boxed{E = 1.0997 \text{ V}}$$

$$\text{For pH} = 8, \boxed{E = 0.7447 \text{ V}}$$

For the PbSO_4/Pb couple,



Since $\nu_{\text{H}} = 0$, $\boxed{E = E^\ominus = -0.3588 \text{ V}}$ at all pH values in the Pourboix diagram.