Model Solutions to 3.53 Problem Set 4

6.3. To plot the potential data from Table 6.3.1 (current functions for irreversible charge transfer), the following equation, based on footnote b under the table and assuming that $D_O = D_R$, was used

$$E - E^{o'} = \frac{RT}{\alpha F}\left[\text{Dimensionless\_Potential} - \ln\left(\frac{\sqrt{\pi D_O \alpha F v / RT}}{k^o} \right) \right] \qquad (1)$$

Three values of k^o were used: 10^{-5}, 10^{-7}, and 10^{-9} cm/s. The current function used was $\pi^{1/2} \chi(bt)$ as given in the table.

Comparison to a reversible reaction was made by plotting the reversible linear sweep voltammogram on the same graph. The potential data from Table 6.2.1 (current functions for reversible charge transfer) was plotted based on the following equation assuming that $D_O = D_R$.

$$E - E^{o'} = \frac{RT}{nF} \times \text{Dimensionless\_Potential} \qquad (2)$$

The current function $\pi^{1/2} \chi(\sigma t)$ was used.

The Excel spreadsheet and the resulting graph are shown below.

alpha	0.5		
T(K)	298.15		
v(V/s)	0.1		
D(m2/s)	1.00E-09		
F(C/mol)	96485		
R(J/molK)	8.31441		
ko(m/s)	1.00E-07	1.00E-09	1.00E-11
PI	3.1415926		

$\pi^{1/2}\chi 0$

ko=10-5 cm/s
ko=10-7 cm/s
ko=10-9 cm/s
Reversible
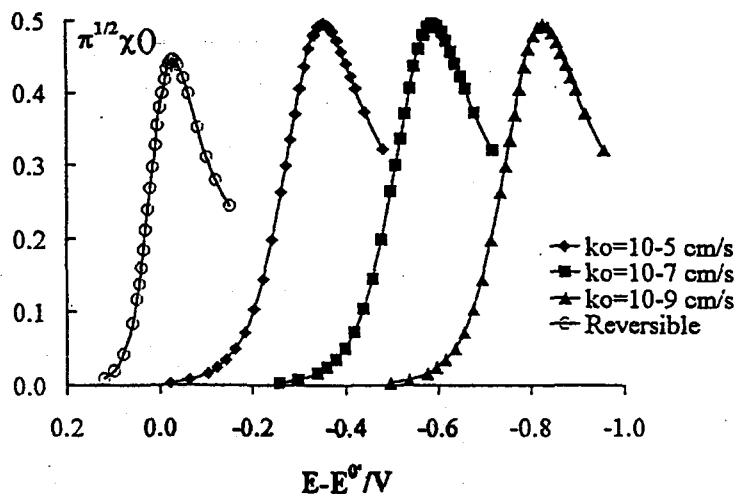
$E - E^{o'} / V$

E(no dim)	Irreversible $k^\circ=10^{-5}$ cm/s E-Eo'(V)	$k^\circ=10^{-7}$ cm/s E-Eo'(V)	$k^\circ=10^{-9}$ cm/s E-Eo'(V)	PI1/2*x(bt)	Reversible E(no dim)	E-Eo'(V)	PI1/2x(st)
6.230	-2.22E-02	-2.59E-01	-4.95E-01	0.0030	4.670	1.20E-01	0.009
5.450	-6.23E-02	-2.99E-01	-5.36E-01	0.0080	3.890	9.99E-02	0.020
4.670	-1.02E-01	-3.39E-01	-5.76E-01	0.0160	3.110	7.99E-02	0.042
4.280	-1.22E-01	-3.59E-01	-5.96E-01	0.0240	2.340	6.01E-02	0.084
3.890	-1.42E-01	-3.79E-01	-6.16E-01	0.0350	1.950	5.01E-02	0.117
3.500	-1.62E-01	-3.99E-01	-6.36E-01	0.0500	1.750	4.50E-02	0.138
3.110	-1.83E-01	-4.19E-01	-6.56E-01	0.0730	1.560	4.01E-02	0.160
2.720	-2.03E-01	-4.39E-01	-6.76E-01	0.1040	1.360	3.49E-02	0.185
2.340	-2.22E-01	-4.59E-01	-6.95E-01	0.1450	1.170	3.01E-02	0.211
1.950	-2.42E-01	-4.79E-01	-7.15E-01	0.1990	0.970	2.49E-02	0.240
1.560	-2.62E-01	-4.99E-01	-7.35E-01	0.2640	0.780	2.00E-02	0.269
1.360	-2.72E-01	-5.09E-01	-7.46E-01	0.3000	0.580	1.49E-02	0.298
1.170	-2.82E-01	-5.19E-01	-7.55E-01	0.3370	0.390	1.00E-02	0.328
0.970	-2.92E-01	-5.29E-01	-7.66E-01	0.3720	0.190	4.88E-03	0.355
0.780	-3.02E-01	-5.39E-01	-7.76E-01	0.4060	0.000	0.00E+00	0.380
0.580	-3.13E-01	-5.49E-01	-7.86E-01	0.4370	-0.190	-4.88E-03	0.400
0.390	-3.22E-01	-5.59E-01	-7.96E-01	0.4620	-0.390	-1.00E-02	0.418
0.190	-3.33E-01	-5.69E-01	-8.06E-01	0.4800	-0.580	-1.49E-02	0.432
0.000	-3.42E-01	-5.79E-01	-8.16E-01	0.4920	-0.780	-2.00E-02	0.441
-0.190	-3.52E-01	-5.89E-01	-8.25E-01	0.4960	-0.970	-2.49E-02	0.445
-0.210	-3.53E-01	-5.90E-01	-8.26E-01	0.4958	-1.109	-2.85E-02	0.446
-0.390	-3.62E-01	-5.99E-01	-8.36E-01	0.4930	-1.170	-3.01E-02	0.446
-0.580	-3.72E-01	-6.09E-01	-8.45E-01	0.4850	-1.360	-3.49E-02	0.443
-0.780	-3.82E-01	-6.19E-01	-8.56E-01	0.4720	-1.560	-4.01E-02	0.438
-0.970	-3.92E-01	-6.29E-01	-8.65E-01	0.4570	-1.950	-5.01E-02	0.421
-1.170	-4.02E-01	-6.39E-01	-8.76E-01	0.4410	-2.340	-6.01E-02	0.399
-1.360	-4.12E-01	-6.49E-01	-8.85E-01	0.4230	-3.110	-7.99E-02	0.353
-1.560	-4.22E-01	-6.59E-01	-8.96E-01	0.4060	-3.890	-9.99E-02	0.312
-1.950	-4.43E-01	-6.79E-01	-9.16E-01	0.3740	-4.670	-1.20E-01	0.280
-2.720	-4.82E-01	-7.19E-01	-9.55E-01	0.3230	-5.840	-1.50E-01	0.245

For the reversible reaction, shown by the open circles, a peak current, i_p, and various values related to the peak potential, E_p, can be calculated from given data for α, T, v, n, and D_O, through the use of equations (6.2.18), (6.2.20), (6.2.21), and (6.2.22).

$$\frac{i_p}{AC_O^*} = 0.4463\left(\frac{F^3}{RT}\right)^{1/2} n^{3/2} D_O^{1/2} v^{1/2} = 269 \text{ A cm mol}^{-1} \tag{3}$$

$$E_p - E^{o'} = -28.5 \text{ mV at } 25\,°C \tag{4}$$

$$|E_p - E_{p/2}| = 56.5 \text{ mV} \tag{5}$$

Equation (4) demonstrates where a reversible wave would appear on the potential axis relative to the formal potential, whereas equation (5) is an indication of the steepness of the reversible linear sweep voltammogram.

In contrast, equations (6.3.8), (6.3.10), and (6.3.11) demonstrate that i_p and $|E_p - E_{p/2}|$ are dependent on α but independent of k^0, whereas $E_p - E^{o'}$ is dependent on both α and k^o.

$$\frac{i_p}{AC_O^*} = (2.99 \times 10^5)(\alpha D_O v)^{1/2} = 211 \text{ A cm mol}^{-1} \tag{6}$$

$$E_p - E^{o'} = -0.389 \text{ V for } k^o = 10^{-5} \text{ cm/s}$$

$$= -0.625 \text{ V for } k^o = 10^{-7} \text{ cm/s} \tag{8}$$

$$= -0.862 \text{ V for } k^o = 10^{-9} \text{ cm/s}$$

$$| E_p - E_{p/2} | = \frac{47.7}{\alpha} \text{ mV at 25 °C} = 95.4 \text{ mV} \tag{9}$$

Thus, an irreversible voltammogram is less steep than a reversible voltammogram and moves progressively more negative along the potential axis as k^o becomes smaller in magnitude. The shape of the wave remains the same in this case since only k^o changes.

6.4.   The expression for the peak current in cyclic voltammetry under reversible conditions is given by equation (6.2.18).

$$\frac{i_p(v)}{\sqrt{v}} = 0.4463 \sqrt{\frac{F}{RT}} F n^{3/2} A D_O^{1/2} C_O^* \tag{6.2.18}$$

For chronoamperometry under mass transport limited conditions, the Cottrell equation (equation (5.2.11)) applies.

$$i(t)\sqrt{t} = \frac{nFAC_O^* D_O^{1/2}}{\sqrt{\pi}} \tag{5.2.11}$$

Experimental data for cyclic voltammetry and chronoamperometry on a single system will yield both $i_p(v)/\sqrt{v}$ and $i(t)\sqrt{t}$. The ratio of these two parameters yields an expression for determining n without knowing A, D_O, and C_O^*.

$$\frac{\dfrac{i_p(v)}{\sqrt{v}}}{i(t)\sqrt{t}} = \frac{0.4463 \sqrt{\dfrac{F}{RT}} F n^{3/2} A D_O^{1/2} C_O^*}{\dfrac{nFAC_O^* D_O^{1/2}}{\sqrt{\pi}}} = 0.4463 \sqrt{\frac{\pi F}{RT}} n^{1/2}$$

The above ratio is equal to $4.935 n^{1/2}$ at 298 K.

A similar procedure is not suitable for determining n for irreversible reactions, but does allow the transfer coefficient, α, to be determined. For an irreversible system at 298 K, where the rate determining step proceeds by a single electron transfer but the overall process proceeds by n electrons, equation (6.3.8) is appropriate. For comments on the incorporation of n in equation (6.3.8), see the text on page 236 just before the start of Section 6.4.

$$\frac{i_p(v)}{\sqrt{v}} = \left(2.99 \times 10^5\right) n \sqrt{\alpha} A D_O^{1/2} C_O^* \tag{6.3.8}$$

Combination with the Cottrell equation yields the following, which allows the determination of α for irreversible electron transfers independent of n, A, D_O, and C_O^*. The right-most term applies at 298 K.

$$\frac{\frac{i_p(v)}{\sqrt{v}}}{i(t)\sqrt{t}} = \frac{\left(2.99\times10^5\right)\sqrt{\alpha}AD_O^{1/2}C_O^*}{\dfrac{nFAD_O^{1/2}C_O^*}{\sqrt{\pi}}} = \frac{\left(2.99\times10^5\right)\sqrt{\pi\alpha}}{nF} = 5.49\frac{\sqrt{\alpha}}{n}$$

6.5. (a). This problem deals with a reversible reaction in which equation (6.2.19) holds, where A is expressed in units of cm^2, D_O in cm^2/s, C_O^* in mol/cm^3, v in V/s and i_p in A. Thus, $A = 2.73$ mm$^2 = 2.73\times10^{-2}$ cm^2, $C_O^* = 2.27\times10^{-3}$ $M = 2.27\times10^{-6}$ mol/cm^3, $v = 0.500$ V/min $= 8.33\times10^{-3}$ V/s, $i_p = 8.19\times10^{-6}$ A, and $n = 2$. Solving equation (6.2.19) for $D_O^{1/2}$ leads to

$$D_O^{1/2} = \frac{i_p}{\left(2.69\times10^5\right)\times n^{3/2}\times A\times C_O^*\times v^{1/2}}$$

$$= \frac{8.19\times10^{-6}}{(2.69\times10^5)\times2^{3/2}\times(2.73\times10^{-2})\times(2.27\times10^{-6})\times(8.33\times10^{-3})^{1/2}} = 1.90\times10^{-3}\, cm/s^{1/2}$$

$$D_O = 3.62\times10^{-6}\ cm^2/s$$

(b). This problem is solved by taking the ratio of the peak currents given by equation (6.2.19) at the two values of v.

$$i_{p,v=100} = \sqrt{\frac{v_{v=100}}{v_{v=8.33\times10^{-3}}}}\times i_{p,v=8.33\times10^{-3}} = \sqrt{\frac{0.100}{8.33\times10^{-3}}}\times8.19\,\mu A = 28.4\,\mu A$$

(c). As in part b, this problem is solved by taking the ratio of the peak currents given by equation (6.2.19) at the two values of C_O^* and v.

$$i_{p,v=50,C=8.2} = \frac{C_{0.8.2}^*}{C_{0.2.27}^*}\times\sqrt{\frac{v_{50}}{v_{8.33}}}\times i_{p,v=8.33,C=2.27} = \frac{8.2}{2.27}\times\sqrt{\frac{50}{8.33}}\times8.19\,\mu A = 72.5\,\mu A$$

6.9. From the cyclic voltammogram given in Figure 6.10.4, the first wave appears reversible while the second wave looks chemically irreversible.

First Wave
From Section (6.5.1), for a reversible system, $i_{pa}/i_{pc} = 1$, independent of scan rate, and $\Delta E_p = 59/n$ mV at 25 °C. From Section 6.2.2, equation (6.2.20) demonstrates that E_p is independent of scan rate and equation (6.2.19) de..onstrates that $i_p/v^{1/2} = $ constant. Thus, for the tabulated numbers given for the first wave of the cyclic voltammogram, the quantities $i_{pc}/v^{1/2}$, i_{pa}/i_{pc}, and ΔE_p, as a function of v are of interest.

v/mV s^{-1}	$i_{pc}/v^{1/2}$	i_{pa}/i_{pc}	ΔE_p/mV
430	0.39	1.0	60
298	0.39	1.0	60
203	0.36	1.0	60
91	0.36	1.0	60
73	0.35	0.97	60

From coulometry, the first reduction step involves one electron. $\Delta E_p = 60$ mV suggests the first wave is a nernstian one electron reaction. Since $i_{pa}/i_{pc} \approx 1$, the product is stable. Thus, letting A = azotoluene, the first wave is

$$A + e \rightleftarrows A^{\cdot-} \tag{1}$$

Since $E_{pc} = -1.42$ V vs. SCE, then, from equation (6.2.20)

$$E_{1/2} = E_p + 1.109 \times \frac{RT}{nF} = -1.42V + 1.109 \times \frac{8.31441 Jmol^{-1}K^{-1} \times 298.15K}{1 equivmol^{-1} \times 96485 Cequiv^{-1}}$$

$$= -1.39 \text{ V vs SCE} \tag{2}$$

From equation (6.2.19)

$$\frac{i_p}{v^{1/2}} = (2.69 \times 10^5)n^{3/2}AD_O^{1/2}C_O^* \tag{3}$$

From the table, the average value of $i_{pc}/v^{1/2}$ is

$$\frac{i_{pc}}{v^{1/2}} = 0.37 \ \mu A \ s^{1/2}/(mV)^{1/2} \times (10^3 \ mV/V)^{1/2} \times 10^{-6} \ A/\mu A = 1.17 \times 10^{-5} \ A \ (s/V)^{1/2} \tag{4}$$

$$A = 1.54mm^2 \times \frac{cm^2}{100mm^2} = 1.54 \times 10^{-2} cm^2 \tag{5}$$

$$C_O^* = 0.68 \times 10^{-3} M = 0.68 \frac{mol}{m^3} = 0.68 \frac{mol}{m^3} \times \left(\frac{m}{10^2}\right)^3 = 6.8 \times 10^{-7} \frac{mol}{cm^3} \tag{6}$$

Rearranging equation (2) for $D_O^{1/2}$ leads to

$$D_O^{1/2} = \frac{i_p}{v^{1/2}} \times \frac{1}{(2.69 \times 10^5)n^{3/2}AC_O^*} \tag{7}$$

$$= \frac{1.17 \times 10^{-5}}{(2.69 \times 10^5)(1)^{3/2}(1.54 \times 10^{-2})(6.8 \times 10^{-7})} = 4.15 \times 10^{-3} \frac{cm}{s^{1/2}}$$

$$D_O = D_A = 1.73 \times 10^{-5} \ cm^2/s = 1.7 \times 10^{-5} \ cm^2/s \tag{8}$$

Second Wave

For the second wave, $i_{pc(2)} \approx i_{pc(1)}$. Thus, $n = 1$, and the reaction can be written

$$A^{\cdot-} + e \rightarrow A^{2-} \tag{9}$$

The product, A^{2-}, is not stable and undergoes some reaction, e.g. protonation, since no reverse current is found for the second wave. $E_{pc(2)}$ shifts to more negative values with increasing v, indicating some kinetic limitations on the reaction. These kinetic effects prevent fixing $E^{o'}$ for this reaction, but it is probably near -2.0 V vs. SCE.