

Model Solutions to 3.53 Problem Set 2

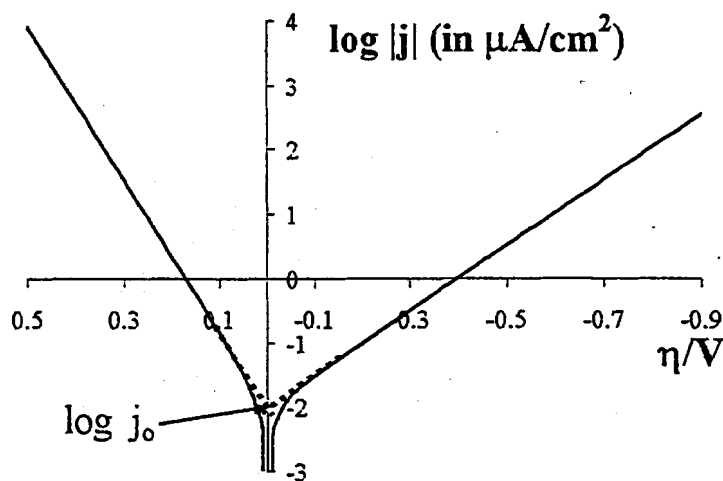
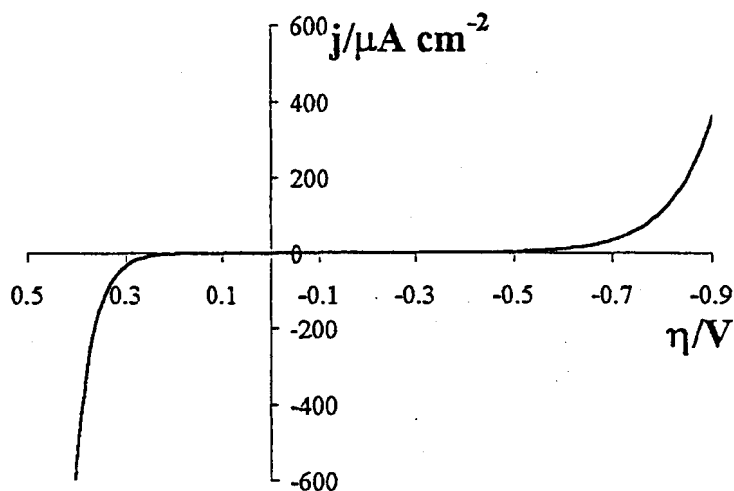
3.1. (a). From equation (3.4.6),

$$j_0 = nFk^0 C_O^{0(1-\alpha)} C_R^{0\alpha} = 9.65 \times 10^{-3} \mu\text{A}/\text{cm}^2$$

(b) and (c). Since mass transfer effects are neglected, from equation (3.4.11),

$$j = j_0 (\exp\{-\alpha n f \eta\} - \exp\{(1-\alpha) n f \eta\})$$

where $f = F/RT$. An Excel spreadsheet can be set up to calculate a j value for a given η value. Such a spreadsheet is shown below. The current density-overpotential curve for this reaction and the corresponding Tafel plot are also shown. Note that for the Tafel plot, the curves are linear for $|\eta| > 100$ mV. For less extreme overpotentials, both the anodic and cathodic terms contribute to the current and the linearization is lost.



Calculation of current density overpotential curve
Based on B&F eqn (3.4.11)

Parameters:

A(cm ²)=	1
F(C/eq)=	96485
f=F/RT(V ⁻¹)	38.94
C _O ^o (mol/cm ³)	1.00E-06
C _R ^o (mol/cm ³)	1.00E-06
E _{eq} (V)	0
alpha	0.3
k ^o (cm/s)	1.00E-07
n	1
j _o (uA/cm ²)	9.65E-03

<u>η/V</u>	<u>j/μA cm⁻²</u>	<u>log j</u>	<u>η/V</u>	<u>j/μA cm⁻²</u>	<u>log j</u>	<u>η/V</u>	<u>j/μA cm⁻²</u>	<u>log j</u>
-1.00	1142.58	3.0579	-0.48	2.63	0.4197	0.04	-0.02	-1.6447
-0.98	904.52	2.9564	-0.46	2.08	0.3182	0.06	-0.04	-1.3494
-0.96	716.06	2.8550	-0.44	1.65	0.2168	0.08	-0.08	-1.0882
-0.94	566.87	2.7535	-0.42	1.30	0.1153	0.10	-0.14	-0.8407
-0.92	448.76	2.6520	-0.40	1.03	0.0138	0.12	-0.25	-0.5991
-0.90	355.26	2.5505	-0.38	0.82	-0.0876	0.14	-0.44	-0.3601
-0.88	281.24	2.4491	-0.36	0.65	-0.1891	0.16	-0.75	-0.1223
-0.86	222.64	2.3476	-0.34	0.51	-0.2906	0.18	-1.30	0.1149
-0.84	176.25	2.2461	-0.32	0.41	-0.3920	0.20	-2.25	0.3519
-0.82	139.53	2.1447	-0.30	0.32	-0.4935	0.22	-3.88	0.5887
-0.80	110.46	2.0432	-0.28	0.25	-0.5950	0.24	-6.69	0.8255
-0.78	87.44	1.9417	-0.26	0.20	-0.6965	0.26	-11.54	1.0623
-0.76	69.23	1.8403	-0.24	0.16	-0.7980	0.28	-19.91	1.2991
-0.74	54.80	1.7388	-0.22	0.13	-0.8995	0.30	-34.34	1.5359
-0.72	43.38	1.6373	-0.20	0.10	-1.0010	0.32	-59.24	1.7726
-0.70	34.34	1.5359	-0.18	0.08	-1.1027	0.34	-102.18	2.0094
-0.68	27.19	1.4344	-0.16	0.06	-1.2046	0.36	-176.25	2.2461
-0.66	21.52	1.3329	-0.14	0.05	-1.3071	0.38	-304.02	2.4829
-0.64	17.04	1.2315	-0.12	0.04	-1.4108	0.40	-524.40	2.7197
-0.62	13.49	1.1300	-0.10	0.03	-1.5171	0.42	-904.52	2.9564
-0.60	10.68	1.0285	-0.08	0.02	-1.6294	0.44	-1560.20	3.1932
-0.58	8.45	0.9270	-0.06	0.02	-1.7553	0.46	-2691.16	3.4299
-0.56	6.69	0.8256	-0.04	0.01	-1.9153	0.48	-4641.94	3.6667
-0.54	5.30	0.7241	-0.02	0.01	-2.1808	0.50	-8006.81	3.9035
-0.52	4.19	0.6226	0.00	0.00	-15.6337			
-0.50	3.32	0.5212	0.02	-0.01	-2.0455			

3.2.

(a) Equation (3.4.29), where at 25 °C, $f = 38.92 \text{ V}^{-1}$,

$$\frac{i}{i_0} = \left(1 - \frac{i}{i_{l,c}}\right) e^{-\alpha f \eta} - \left(1 - \frac{i}{i_{l,a}}\right) e^{(1-\alpha) f \eta}$$

can be solved for i as follows. First, collect all the terms containing i .

$$i \left[\frac{1}{i_0} + \frac{e^{-\alpha f \eta}}{i_{l,c}} - \frac{e^{(1-\alpha) f \eta}}{i_{l,a}} \right] = e^{-\alpha f \eta} - e^{(1-\alpha) f \eta}$$

Then, solve for i .

$$i = \frac{e^{-\alpha f \eta} - e^{(1-\alpha) f \eta}}{\frac{1}{i_0} + \frac{e^{-\alpha f \eta}}{i_{l,c}} - \frac{e^{(1-\alpha) f \eta}}{i_{l,a}}}$$

or in current densities,

$$j = \frac{e^{-\alpha f \eta} - e^{(1-\alpha) f \eta}}{\left[\frac{1}{j_0} + \frac{e^{-\alpha f \eta}}{j_{l,c}} - \frac{e^{(1-\alpha) f \eta}}{j_{l,a}} \right]}$$

(b) For $\alpha = 0.3$, $C_R^0 = C_O^0 = 10^{-6} \text{ mol/cm}^3$, $k^0 = 10^{-7} \text{ cm/s}$, $n = 1$, and

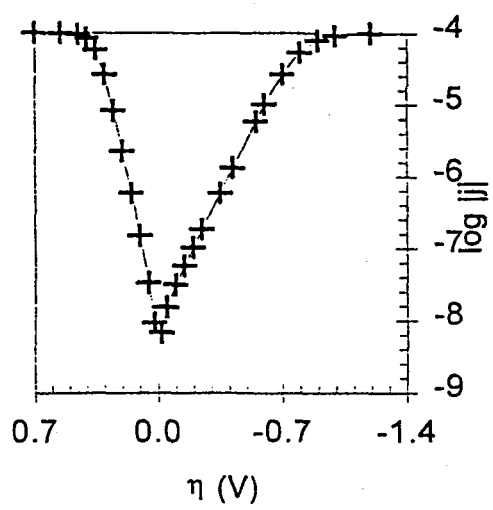
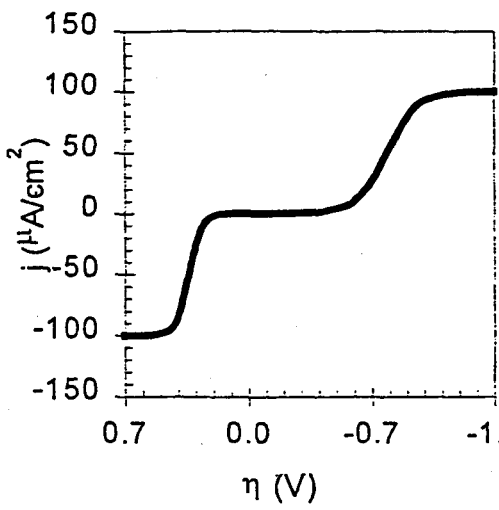
$m_O = m_R = 10^{-3} \text{ cm/s}$, the limiting current densities are calculated. From equations (1.4.9) and (1.4.17),

$$j_{l,c} = \frac{i_{l,c}}{A} = n F m_O C_O^0 = 96485 \text{ C/mol} \times 10^{-3} \text{ cm/s} \times 10^{-6} \text{ mol/cm}^3 = 1 \times 10^{-4} \text{ A/cm}^2$$

$$j_{l,a} = \frac{i_{l,a}}{A} = -n F m_R C_R^0 = -96485 \text{ C/mol} \times 10^{-3} \text{ cm/s} \times 10^{-6} \text{ mol/cm}^3 = -1 \times 10^{-4} \text{ A/cm}^2$$

From equation (3.4.6), the exchange current density, j_0 , is

$$\begin{aligned} j_0 &= \frac{i_0}{A} = F k^0 C_O^{(1-\alpha)} C_R^\alpha = 96485 \text{ C/mol} \times 10^{-7} \text{ cm/s} \times \left(10^{-6} \text{ mol/cm}^3\right)^{(1-0.3)} \times \left(10^{-6} \text{ mol/cm}^3\right)^{0.3} \\ &= 96485 \text{ C/mol} \times 10^{-7} \text{ cm/s} \times 10^{-6} \text{ mol/cm}^3 = 10^{-8} \text{ A/cm}^2 \end{aligned}$$

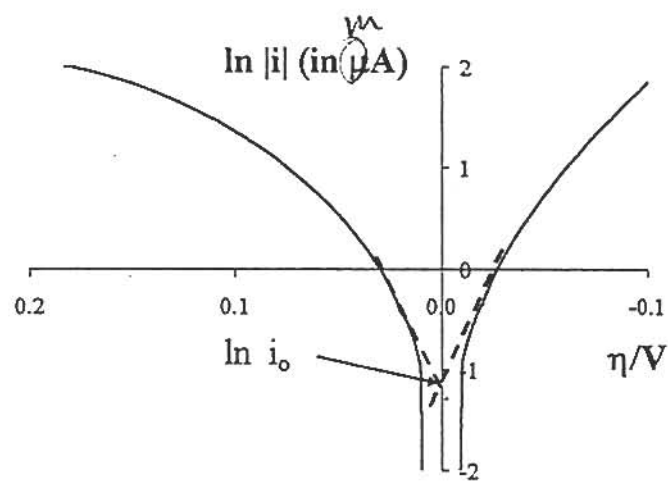
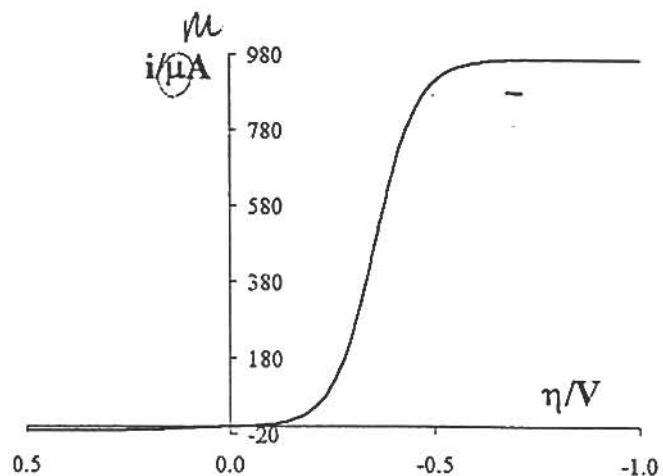


η (V)	$e^{-\alpha f \eta}$	$e^{(1-\alpha) f \eta}$	j ($\mu\text{A}/\text{cm}^2$)	$\log j $ (A/cm^2)
0.70	2.82E-04	1.92E+08	-99.995	-4.0000
0.55	1.63E-03	3.22E+06	-99.690	-4.0013
0.45	5.23E-03	2.11E+05	-95.476	-4.0201
0.40	9.37E-03	5.40E+04	-84.386	-4.0737
0.35	1.68E-02	1.38E+04	-58.056	-4.2362
0.30	3.01E-02	3.54E+03	-26.170	-4.5822
0.25	5.40E-02	9.08E+02	-8.322	-5.0798
0.20	9.68E-02	2.32E+02	-2.271	-5.6438
0.15	1.74E-01	5.95E+01	-0.590	-6.2291
0.10	3.11E-01	1.52E+01	-0.149	-6.8264
0.05	5.58E-01	3.90E+00	-0.033	-7.4755
0.02	7.92E-01	1.72E+00	-0.009	-8.0304
0.00	1.00E+00	1.00E+00	0.000	
-0.02	1.26E+00	5.80E-01	0.007	-8.1656
-0.05	1.79E+00	2.56E-01	0.015	-7.8135
-0.10	3.21E+00	6.56E-02	0.031	-7.5020
-0.15	5.76E+00	1.68E-02	0.057	-7.2409
-0.20	1.03E+01	4.30E-03	0.103	-6.9865
-0.25	1.85E+01	1.10E-03	0.185	-6.7331
-0.35	5.95E+01	7.22E-05	0.592	-6.2278
-0.42	1.35E+02	1.07E-05	1.330	-5.8761
-0.55	6.15E+02	3.11E-07	5.795	-5.2370
-0.60	1.10E+03	7.96E-08	9.933	-5.0029
-0.70	3.54E+03	5.22E-09	26.170	-4.5822
-0.80	1.14E+04	3.42E-10	53.257	-4.2736
-0.90	3.66E+04	2.25E-11	78.551	-4.1048
-1.00	1.18E+05	1.47E-12	92.170	-4.0354
-1.20	1.22E+06	6.33E-15	99.184	-4.0036
-1.40	1.26E+07	2.72E-17	99.920	-4.0003

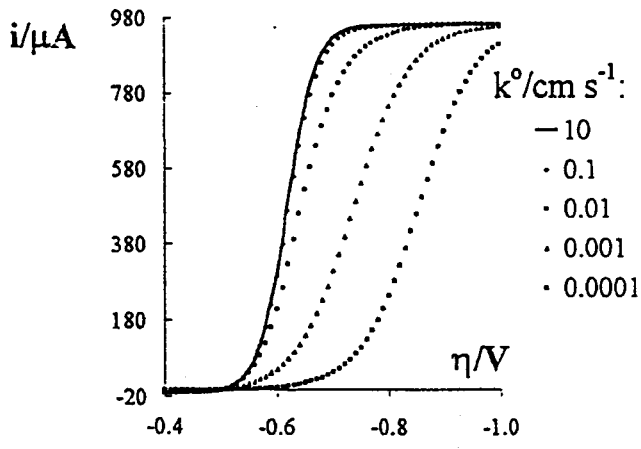
For
n 1
CO 1.00E-06
CR 1.00E-06
k0 1.00E-07
alpha 0.3
mO 1.00E-03
mR 1.00E-03

3.3. (a). All voltages are relative to NHE.

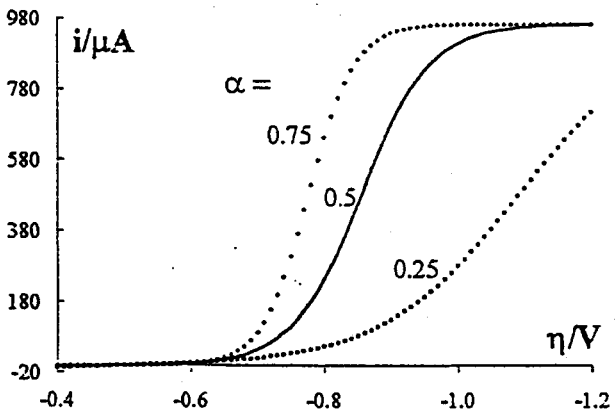
E/V	η/V	$i/\mu A$	$\ln i$ (in μA)
-1.50	-1.00	964.85	6.8720
-1.45	-0.95	964.84	6.8720
-1.40	-0.90	964.83	6.8719
-1.35	-0.85	964.79	6.8719
-1.30	-0.80	964.68	6.8718
-1.25	-0.75	964.71	6.8715
-1.20	-0.70	963.69	6.8708
-1.15	-0.65	961.78	6.8688
-1.10	-0.60	956.77	6.8636
-1.05	-0.55	943.75	6.8499
-1.00	-0.50	910.94	6.8145
-0.95	-0.45	834.17	6.7264
-0.90	-0.40	682.02	6.5251
-0.85	-0.35	459.92	6.1311
-0.80	-0.30	246.97	5.5093
-0.75	-0.25	110.91	4.7088
-0.70	-0.20	45.06	3.8079
-0.65	-0.15	17.43	2.8581
-0.60	-0.10	6.49	1.8696
-0.55	-0.05	2.10	0.7441
-0.50	0.00	0.00	$-\infty$
-0.45	0.05	-1.73	0.5486
-0.40	0.10	-3.89	1.3595
-0.35	0.15	-6.25	1.8327
-0.30	0.20	-8.01	2.0810
-0.25	0.25	-8.96	2.1926
-0.20	0.30	-9.38	2.2381
-0.15	0.35	-9.54	2.2559
-0.10	0.40	-9.61	2.2627
-0.05	0.45	-9.63	2.2652
0.00	0.50	-9.64	2.2662



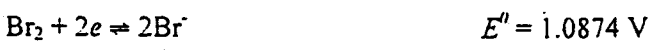
(b). k^0 values ranging from 1.0×10^{-4} to 10 cm/s were used. From the graph, one can see that for k^0 values > 0.1 cm/s under the conditions of part (a), the curves are indistinguishable from nernstian behavior.



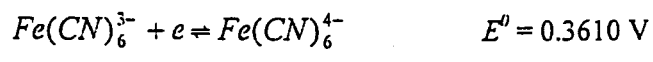
(c).



3.4. The potential is to be swept from the anodic to the cathodic background limits. Because HBr is a strong acid, $[H^+] = 1.0 \text{ M}$. The solvent/electrolyte system of water/HBr has its potential window set by the oxidation of bromine and reduction of proton.



The reduction of ferricyanide is characterized as follows.



It is given that $m_O = m_R = m$, and $\alpha = 0.5$ in all cases.

The potential is to be scanned from the anodic to the cathodic limit. Over this range, the current will be set by the oxidation of bromide, the reduction of ferricyanide, and the reduction of proton. To characterize these responses, equations must be considered for the current density when only

R is initially present (for bromide oxidation) and only O initially present (for reduction of ferricyanide and proton).

Equation (3.4.10) applies when both O and R are present in solution.

$$j = j_0 \left[\frac{C_O(0,t)}{C_O^0} \exp[-\alpha f \eta] - \frac{C_R(0,t)}{C_R^0} \exp[(1-\alpha) f \eta] \right] \tag{1}$$

$$= j_c + j_a$$

When the solution contains only O, then there will only be a cathodic current; when only R is present, only anodic current will flow. Upon substitution of equations (1.4.10) and (1.4.19),

$$\frac{C_O(0)}{C_O^0} = 1 - \frac{j}{j_{l,c}} \tag{2}$$

$$\frac{C_R(0)}{C_R^0} = 1 - \frac{j}{j_{l,a}} \tag{3}$$

into equation (1), the following expressions are found for the oxidation of bromide

$$j = -j_0 \left[\left(1 - \frac{j}{j_{l,a}} \right) \exp[(1-\alpha) f \eta] \right] \tag{4}$$

and the reduction of ferricyanide and proton.

$$j = j_0 \left[\left(1 - \frac{j}{j_{l,c}} \right) \exp[-\alpha f \eta] \right] \tag{5}$$

These are solved for j as follows.

$$j = \frac{1}{\frac{-1}{j_0 \exp[(1-\alpha) f \eta]} + \frac{1}{j_{l,a}}} = \frac{-j_{l,a} j_0 \exp[(1-\alpha) f \eta]}{j_{l,a} - j_0 \exp[(1-\alpha) f \eta]} \tag{6}$$

and

$$j = \frac{1}{\frac{1}{j_0 \exp[-\alpha f \eta]} + \frac{1}{j_{l,c}}} = \frac{j_{l,c} j_0 \exp[-\alpha f \eta]}{j_{l,c} + j_0 \exp[-\alpha f \eta]} \tag{7}$$

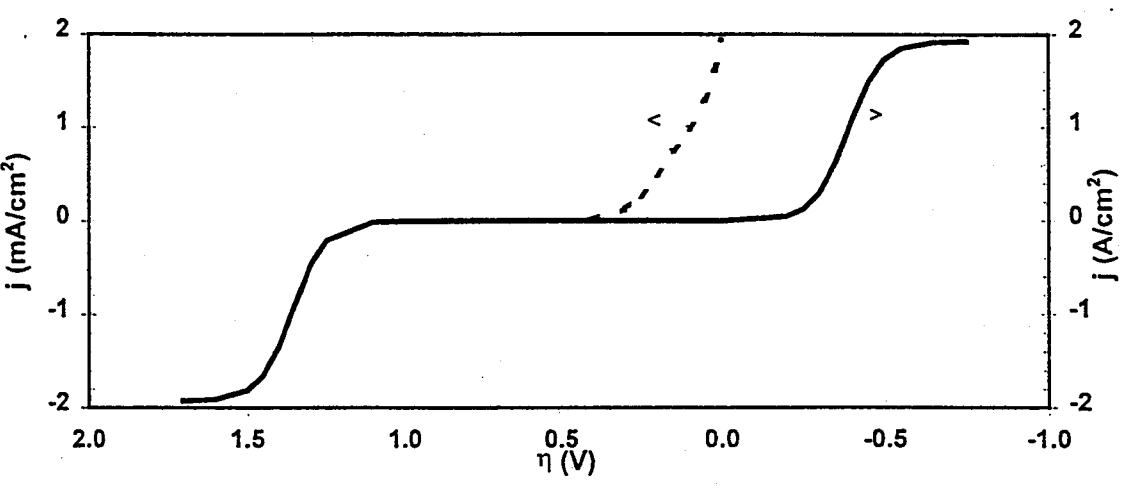
From equations (1.4.9), and (1.4.17),

$$j_{l,x} = nFmC_o^0 \tag{8}$$

$$j_{l,a} = -nFmC_r^0 \tag{9}$$

Equations (7) and (6) are used to calculate the individual current densities for reduction of ferricyanide and proton and the oxidation of bromide, respectively. The net current is the sum of the individual currents. See the spreadsheet below. The solid line shows the net current response over the whole range, between the limiting currents for proton and bromide. The contribution to the current from the ferricyanide is too small to be seen on this scale. The dotted line is on the enlarged scale, but the contribution from ferricyanide remains small. Note that this development does not include the oxidation of water, which would also contribute to the net current as the potential approached the standard potential for water oxidation, 1.23 V.

	j_0 (A)	E^0	C^* (mol/cc)	n	j_l (A)
Br ⁻	0.01	1.0874	0.001	2	-1.9297
Fe(CN) ₆ ³⁻	4.00E-05	0.361	1.00E-06	1	9.65E-04
H ⁺	0.001	0	0.001	2	1.9297

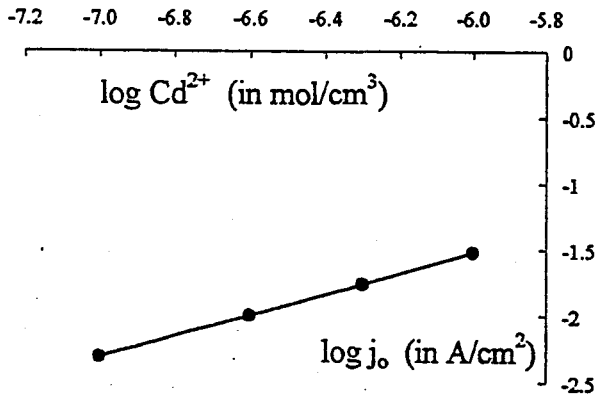


E	$j(\text{Br}^-)$	$j(\text{Fe}(\text{CN})_6^{3-})$	$j(\text{H}^+)$	$j_{\text{tot}}(\text{A}/\text{cm}^2)$	$j_{\text{tot}}(\text{mA}/\text{cm}^2)$
1.70	-1.927227632	1.93E-16	4.29E-18	-1.927227632	-1927.228
1.60	-1.912523918	1.35E-15	3.00E-17	-1.912523918	-1912.524
1.50	-1.815553319	9.46E-15	2.10E-16	-1.815553319	-1815.553
1.45	-1.654477641	2.50E-14	5.57E-16	-1.654477641	-1654.478
1.40	-1.339938699	6.62E-14	1.47E-15	-1.339938699	-1339.939
1.35	-0.891499784	1.75E-13	3.90E-15	-0.891499784	-891.500
1.30	-0.472819621	4.64E-13	1.03E-14	-0.472819621	-472.820
1.25	-0.210835919	1.23E-12	2.73E-14	-0.210835919	-210.836
1.10	-0.012694652	2.27E-11	5.05E-13	-0.012694652	-12.695
1.00	-0.001823642	1.59E-10	3.54E-12	-0.001823642	-1.824
0.80	-3.7245E-05	7.80E-09	1.73E-10	-3.7237E-05	-0.037
0.70	-5.32032E-06	5.46E-08	1.21E-09	-5.26453E-06	-0.005
0.55	-2.87232E-07	1.01E-06	2.25E-08	7.45186E-07	0.001
0.50	-1.08559E-07	2.67E-06	5.95E-08	2.61849E-06	0.003
0.40	-1.5507E-08	1.84E-05	4.16E-07	1.87708E-05	0.019
0.30	-2.21509E-09	1.15E-04	2.91E-06	0.000118328	0.118
0.25	-8.37187E-10	2.55E-04	7.71E-06	0.000262853	0.263
0.20	-3.16413E-10	4.70E-04	2.04E-05	0.000490763	0.491
0.15	-1.19587E-10	6.90E-04	5.40E-05	0.000744477	0.744
0.10	-4.51977E-11	8.39E-04	1.43E-04	0.000981707	0.982
0.05	-1.70824E-11	9.13E-04	3.78E-04	0.001290902	1.291
0.02	-9.52812E-12	9.35E-04	6.77E-04	0.001612603	1.613
0.00	-6.45624E-12	9.45E-04	9.99E-04	0.001944069	1.944
-0.20	-1.31736E-13	9.64E-04	4.78E-02	0.04875938	48.759
-0.25	-4.97894E-14	9.65E-04	1.22E-01	0.122470732	122.471
-0.30	-1.88178E-14	9.65E-04	2.91E-01	0.29226527	292.265
-0.35	-7.11213E-15	9.65E-04	6.17E-01	0.618322699	618.323
-0.40	-2.68801E-15	9.65E-04	1.07E+00	1.070988549	1070.989
-0.45	-1.01593E-15	9.65E-04	1.48E+00	1.481193647	1481.194
-0.50	-3.83967E-16	9.65E-04	1.73E+00	1.732004373	1732.004
-0.55	-1.45119E-16	9.65E-04	1.85E+00	1.850444329	1850.444
-0.65	-2.07295E-17	9.65E-04	1.92E+00	1.918782395	1918.782
-0.75	-2.96109E-18	9.65E-04	1.93E+00	1.928958503	1928.959

$m=0.01\text{cm/s}$
 $\alpha=0.5$
 $j_l/nC^*=964.85$
 Acm^2/mol

3.7.

(a). A plot of $\log j_0$ versus $\log Cd^{2+}$ is shown below.



From the discussion in Section 3.5.4 (d) and equation (3.5.41), the slope is found to be,

$$slope = 1 - \frac{n' + \alpha}{n} = 0.783$$

Thus,

$$n' + \alpha = 2 \times (1 - 0.783) = 0.434$$

The basic reaction is reduction of the cadmium ion to cadmium amalgam, where $n = 2$.



The reaction is chemically reversible. Allow that the exchange current is set solely by the RDS.

In deconvolving these mechanisms, the procedure is to propose a mechanism, derive the corresponding kinetic expressions, and determine if the experimental data are modeled by the mechanism. It is appropriate to consider several mechanisms. In this way, if only one mechanism models the data, more credence is lent to the probability that this is the correct mechanism.

It should also be noted that the number of electrons transferred in a single step is expected to be an integer.

In the following, two mechanisms are proposed: in the first, the second electron transfer is the rate determining step and in the second, the first electron transfer is the rate determining step.

Mechanism One: $n' = 1, n'' = 0$



Mechanism Two: $n' = 0, n'' = 1$



From above, for Mechanism One,

$$n' + \alpha = 0.434$$

Since $n' = 1$,

$$\alpha = 0.434 - 1 = -0.566$$

This is not an allowed value. For Mechanism Two, since $n' = 0$

$$\alpha = 0.434 - 0 = 0.434$$

This is an allowed value. Thus Mechanism Two is consistent with a slow first electron transfer and a rapid second electron transfer, with values $\alpha = 0.434$, $n' = 0$, and $n'' = 1$.

(b). k_{app}^o is found by rearranging equation (3.5.40) as follows.

$$k_{app}^o = \frac{j_o}{nFC_o^{*(1-\frac{n'+\alpha}{n})} C_R^{*(\frac{n'+\alpha}{n})}}$$

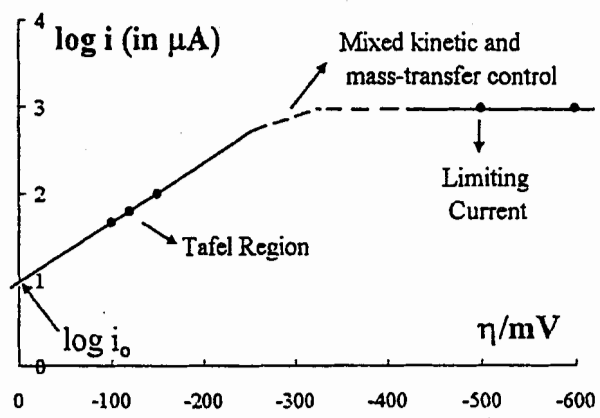
The following table shows that $k_{app}^o = 4.2 \times 10^{-2}$ cm/s for each of the Cd^{2+} concentrations.

$Cd^{2+}/mol\ cm^{-3}$	$j_o/A\ cm^{-2}$	$k_{app}^o/cm\ s^{-1}$
1.0×10^{-6}	0.0300	4.24×10^{-2}
5.0×10^{-7}	0.0173	4.20×10^{-2}
2.5×10^{-7}	0.0101	4.22×10^{-2}
1.0×10^{-7}	0.00494	4.23×10^{-2}

(c). Berzins and Delahay report values of α between 0.21 – 0.23, and a standard heterogeneous rate constant, which they call k_s , of 4.5×10^{-2} cm s⁻¹. They analyzed the data using a model for simple Butler Volmer kinetics that did not allow for any chemical steps, which might impact the current – concentration data. At the time (1955), if data of the type presented here were successfully interpreted using Butler-Volmer models, other steps in the mechanism were typically not considered.

The results presented here yield a standard rate constant comparable to that found by Berzins and Delahay, and a transfer coefficient of 0.434, which is twice that found by Berzin and Delahay. Bijl, Sluyters-Rehbach and Sluyters published a more recent paper (JEAC 435(1-2) 137-147 (1997)) wherein they analyzed the mechanism for the reduction of cadmium ion to cadmium amalgam. They reported that the first electron transfer was rate determining ($n' = 0$). They found their data were well modeled by $\alpha = 0.5$ and a standard heterogeneous rate of 0.06 cm/s, both values consistent with the data analyzed in part (a). They report the second electron transfer ($n'' = 1$) was well modeled by $\alpha = 0.5$ and a standard rate in excess of 500 cm/s.

3.11. The tabulated data show that a limiting cathodic current $i_l = 965 \mu A$ is reached at $\eta = -500$ and $\eta = -600$ mV. Comparatively large overpotentials are required to enforce this current; hence Tafel behavior should be observed for currents less than $\approx 10\%$ of the limiting current. A Tafel plot of the data is show below.



The first three points provide a Tafel line with,

$$\text{Slope} = -6.8 = -\alpha F / 2.3RT$$

Taking $T = 298$ K, leads to $\alpha = 0.40$. Extrapolation to $\eta = 0$ gives $\log i_0 = 0.98$, or $i_0 = 9.5 \mu A$. From equation (3.4.7),

$$k^o = \frac{i_0}{FAC} = \frac{9.5 \times 10^{-6} A}{96485 C/mol \times 0.1 cm^2 \times 1 \times 10^{-5} mol/cm^3} = 9.8 \times 10^{-5} cm/s$$

From equation (3.4.13),

$$R_{ct} = \frac{8.31441 J mol^{-1} K^{-1} \times 298 K}{96485 C mol^{-1} \times 9.5 \times 10^{-6} A} = 2.7 k\Omega$$

From $i_l = 965 \mu A$, and equation (1.4.9),

$$m_o = \frac{i_l}{FAC_o^*} = \frac{965 \times 10^{-6} A}{96485 C mol^{-1} \times 0.1 cm^2 \times 1.0 \times 10^{-5} mol/cm^3} = 0.010 cm/s$$

According to equation (1.4.28), the mass transfer resistance for the oxidized form is

$$R_{mii} = \frac{8.31441 J mol^{-1} K^{-1} \times 298 K}{96485 C mol^{-1} \times 965 \times 10^{-6} A} = 26.6 \Omega$$

3.12. The equation to describe the Tafel plot at large η is a rearrangement of equation (3.4.15).

$$\ln j = -\frac{\alpha F}{RT} \eta + \ln j_0 \quad (1)$$

A plot of $\ln j$ versus η yields a slope of $-\alpha F/RT$ and an intercept of $\ln j_0$. For equal concentrations of the reduced and oxidized forms of the redox probe, equation (3.4.7) is appropriate.

$$j_0 = Fk^0 C \quad (2)$$

The abscissa for the data shown in Figure 3.4.5 is E , not η . From just below equation (3.4.10),

$$\eta = E - E_{eq} \quad (3)$$

The equilibrium potential is not given. However, it can be estimated from the data in Figure (3.4.5). For a Tafel plot, there is a sharp deviation from linearity as the equilibrium potential is approached. In Figure (3.4.5), the linear region is apparent for $1.15 < E < 1.5$ V. The approach to the equilibrium potential is observed for potentials slightly greater than 1.6 V. As the highest potential recorded is for 1.62 V, let this approximate the equilibrium potential.

From the linear region, the slope is 4.86 V^{-1} and the intercept at $E = 1.62 \text{ V}$ is $\log j_0 = -4.76$. The slope yields $\alpha = 4.86 \text{ V}^{-1} \times 2.3 / 38.92 \text{ V}^{-1} = 0.29$. Note that the 2.3 is included because equation (1) is expressed in natural log and the data in Figure (3.4.5) is in \log_{10} . The intercept yields $j_0 = 1.7 \times 10^{-5} \text{ A/cm}^2 = Fk^0 C$. For $C = 1 \times 10^{-5} \text{ mol/cm}^3$, $k^0 = 1.8 \times 10^{-5} \text{ cm/s}$.

From equation (2), for $C = 1 \text{ M} = 10^{-3} \text{ mol/cm}^3$, $j_0 = 1.7 \times 10^{-3} \text{ A/cm}^2$.