Chemistry 117
Problem Set 3

This problem set is due to the box outside 210A Noyes no later than 2:30 p.m. on Feb 15, 2017.

1. The following double-step chronocoulometric data was reported by Anson in 1966 for the reduction of Cd^{2+} at a dropping Hg electrode. (By the way, 1F means 1M in today's language.)

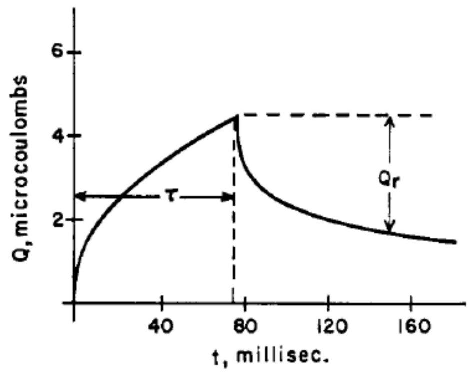


Figure 3. Charge-time curve for double potential-step chronocoulometry with 1 m*M* $Cd(NO_3)_2$ in 1 *F* $NaNO_3$

The potential was stepped from −200 to −800 to −200 mv. vs. S.C.E. Electrode area was 0.032 sq. cm.

From Anson, F.C., *Anal. Chem.* **1966**, *38* (1), 54-57.
DOI: 10.1021/ac60233a014

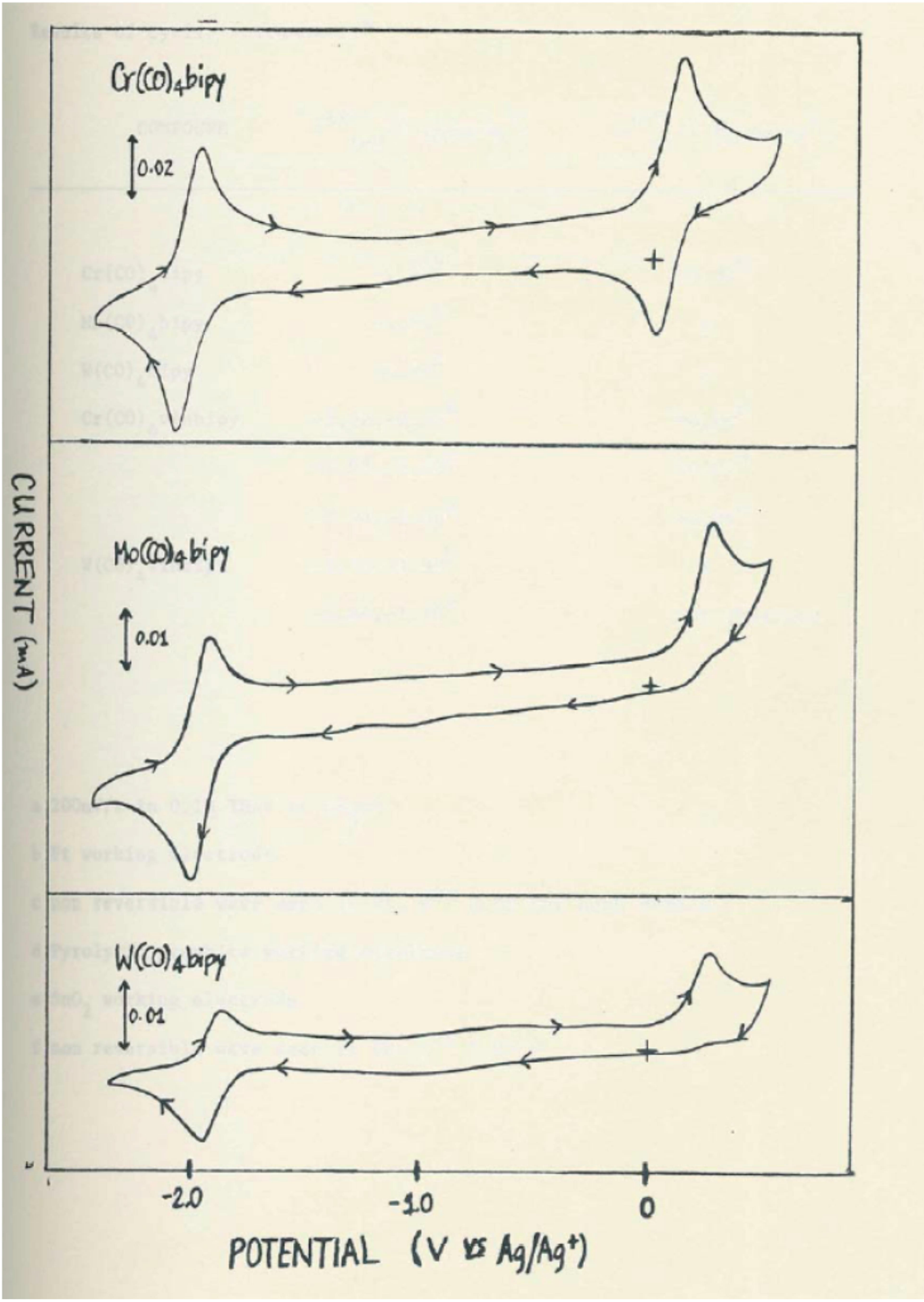
a) Based on the first step, is this a mass-transport-limited process?

b) Does the reduction of Cd involve an adsorption process at mercury?

c) How many coulombs per square centimeter are required to completely charge the double layer?

2. Do the following problems in Bard and Faulkner: 6.9 and 6.12 (the quasi-reversible case).

3. The cyclic voltammetry data shown on the next page were obtained using a Pt working electrode with a scan rate of 100 mV/s in CH_3CN containing 0.1 M tetrabutylammonium perchlorate supporting electrolyte. The three compounds employed are of the form $[M(CO)_4bpy]$ where M=Cr, Mo, or W, and bpy is 2,2'-bipyridine. All three complexes are initially neutral. The scan direction is shown on the CVs. All scans start at -1.0 V versus Ag/Ag^+. The little "+" sign indicates the origin.
   a) What specifically is reduced? What is the oxidation wave associated with? Draw a simple MO scheme (a pseudo-octahedral crystal-field splitting diagram with the bpy π^* orbital added will do) and show the electron configurations for the oxidation states present in the CVs.
   b) For $[Mo(CO)_4bpy]$ what is the diffusion-limited reduction current?
   c) Estimate the double-layer capacitance in the middle panel.
   d) In the absence of a scan-rate dependence, is it likely that the reduction wave is reversible?
   e) Speculate why the Cr complex's oxidation wave appears different from the oxidation wave for the Mo and W complexes.
   f) Scan-rate data for the reductive wave of the chromium complex is shown on page 3. (This is real data.) Assign a mechanism to this wave. Speculate about the specific chemistry that is occurring.


Cr(CO)4bipy
0.02
Mo(CO)4bipy
0.01
W(CO)4bipy
0.01
CURRENT (mA)
-2.0
-1.0
0
POTENTIAL (V vs Ag/Ag+)

Scan Rate (mV/s)	Peak Current (mA)	Peak Current Ratio (anodic/cathodic)
5		0.54
10	10.5	0.55
20	15.8	0.63
30	20.3	0.67
40	24.4	0.66
50	27.6	0.64
150	52.9	0.69
200	66.1	0.69
250	74.5	----
300	79.3	0.71
350	88.8	0.72
400	92.0	0.72
450	101.4	0.69
500	108.9	0.71
550	113.1	0.70