

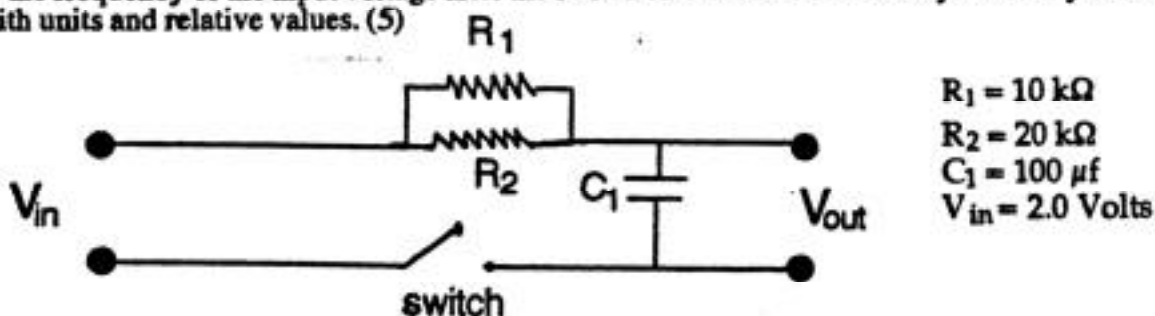
Please answer all questions in a blue exam book and make sure you write your name on the front. Good Luck!!!

1). A recent graduate of this department was able to secure (miraculously!!) a job as an "analytical chemist" with a large Fortune 200 company. He/she was assigned to develop a method to determine low levels of lead (Pb) and cadmium (Cd) in various petroleum products. Recalling all the electrochemistry he/she learned as a student in Chem 447, the former student decided to try D.C. and normal pulse polarographic techniques (with DME working electrode) that required a prior decomposition of the sample (weighed accurately) and then redissolution of the residue in 50 ml of 0.1 M HNO_3 . This procedure produced a sample containing all the original lead and cadmium in the form of Pb^{2+} and Cd^{2+} . Assuming that the concentrations of lead and cadmium in the final 50 ml solution of acid were 1.5×10^{-5} and 3.0×10^{-5} M, respectively, sketch the D.C. polarogram you would expect to observe (current vs. E_{DME}) for this sample if the reference electrode used was Ag/AgCl with 1 M KCl as the reference electrolyte. Make sure you label your potential axis with specific values of potential. Also, briefly explain why it would be necessary to thoroughly purge the sample with nitrogen or argon before recording the polarogram (10).

2). Please answer the following questions True or False (3 points each):

- Alkaline error observed with a pH glass electrode is due to high levels of hydroxide ions interacting with the surface of the glass membrane.
- For the reduction of an electroactive species at a small area micro-stationary electrode at constant applied potential, the current will always decrease rapidly with time (e.g. $t^{-1/2}$), even if the solution is well stirred.
- In highly acidic samples, the pH measured by glass electrode with a Ag/AgCl reference (with 0.1M KCl as reference electrolyte) is likely to be falsely high due to the error caused by the liquid junction potential.
- Johnson noise is sometimes called dark current noise since it occurs even in the absence of any currents flowing through the circuits of a typical analytical instrument.
- When using a three electrode potentiostat to do electrochemistry, the reference electrode is often placed close to the working electrode so that more current can flow between these two electrodes.
- The sensitivity of an analytical method is synonymous with detection limits, provided that the response signal is linearly related to analyte concentration.

3). (a) For the following circuit, sketch the ratio of output voltage to input voltage as a function of the frequency of the input voltage after the switch is closed. Make sure you label your axes with units and relative values. (5)



(b) For the same circuit shown above, when operated in the d.c. mode, determine the current flow in the circuit one second after the switch is closed. (5)

4). Briefly explain how signal averaging can be used to enhance signal to noise ratios and why such improvements are often seen in fourier transform based analytical instruments. (10)

5). Another former undergraduate student of this department was fortunate enough to land a prestigious faculty position at a small liberal arts college following 5 years of graduate studies in Analytical Chemistry and another Big Ten school. The former student was asked to develop a new instrumental analysis laboratory course and he/she decided to include an ion-selective membrane electrode experiment (measurement of potassium ions in gatorade using a polymer membrane potassium selective electrode) because of the low cost of these relatively simple devices. To further reduce the cost of setting up the laboratory, the former student decided to buy 10 digital Simpson multimeters (at \$367/ea) rather than more expensive pH/mV meters to measure cell potentials originating from ion-selective electrode/reference electrode cells. The new professor thought he/she really made a wise move until he found out that the cell potentials measured by the new multimeters in given solutions of potassium ions (see attached description of the meter) were not what he expected based on the equations he learned way back in Chem 447. Given the specifications for this multimeter, explain why his/hers measured values were far from the actual calculated cell potential values. Also, rather than returning these cheap multimeters and buying more expensive pH/mV meters, suggest (draw) an operational amplifier circuit that the assistant professor could use that would, when used in conjunction with the Simpson multimeters, solve his/her problem. (10)

6). Neglecting liquid junction potentials, assuming unity activity coefficients, and given that the glass membrane exhibits a potentiometric selectivity coefficient of $K_{H,Na} = 10^{-10}$, calculate the absolute cell potential of the following pH electrode-based galvanic cell when the sample is a 10^{-2} M NaOH : (7)

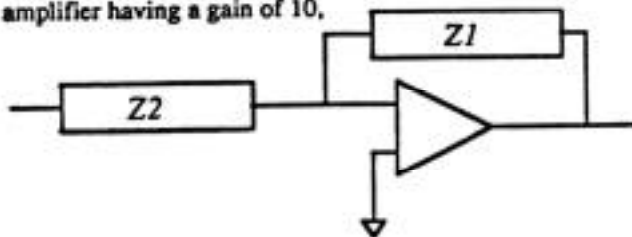
$\text{Hg}/\text{Hg}_2\text{Cl}_2(\text{s}), \text{KCl} (1\text{M})/ \text{sample} / \text{glass membrane} / \text{buffer, pH } 7.0, \text{NaCl} (0.1\text{M}), \text{AgCl}(\text{s})/\text{Ag}$

Also, If this cell were allowed to discharge spontaneously, which electrode (Ag or Hg) would be the true cathode of the cell? (3)

7). When is it desirable to use an internal standard type analytical procedure rather than a conventional calibration curve type method. (5)

8). The following multiple choice questions were extracted from a recent graduate level qualifier exam. Please indicate the letter next to the correct answer for each question in your exam booklet. (3 points each)

a) A general diagram for an operational amplifier circuit is shown below. If it were to be used as an inverting amplifier having a gain of 10,



- (A) Z_1 and Z_2 must both be resistors. $Z_2 = 10 Z_1$
 (B) Z_1 and Z_2 must both be resistors. $Z_1 = 10 Z_2$
 (C) Z_1 must be a capacitor, Z_2 a resistor. $Z_1 = 10 Z_2$
 (D) Z_2 must be a capacitor, Z_1 a resistor. $Z_2 = 10 Z_1$
 (E) Z_1 and Z_2 must both be capacitors. $Z_1 = 10 Z_2$

b) Identify the *true* statement concerning the cell
 $\text{Pt, H}_2 (1 \text{ atm}) \mid \text{H}^+ (1 \text{ M}) \parallel \text{Ag}^+ (1 \text{ M}) \mid \text{Ag}$

- (A) If an external wire were connected, electrons would flow from the silver electrode to the platinum electrode.
 (B) Allowing the cell to discharge would result in a decrease in pH in the left compartment.
 (C) Allowing the cell to discharge would result in silver metal being oxidized to silver ions.
 (D) Oxidation occurs at the electrode in the right compartment.
 (E) No spontaneous reaction will occur in this cell as it is configured.

c) If a diffusion current of $10.0 \mu\text{A}$ were observed for the reduction wave of 0.100 mM Pb^{2+} , what current would be expected for the reduction wave of 0.200 mM Tl^+ ?

- (A) $40.0 \mu\text{A}$ (B) $20.0 \mu\text{A}$ (C) $10.0 \mu\text{A}$
 (D) $5.0 \mu\text{A}$ (E) $2.5 \mu\text{A}$

d) Given the following standard potentials, what is the spontaneous cell reaction and the expected voltage if all ions are at unit activity?

$$E_{\text{Zn}^{2+}, \text{Zn}}^{\circ} = -0.763 \text{ V} \quad E_{\text{Cu}^{2+}, \text{Cu}}^{\circ} = +0.337 \text{ V}$$

- (A) $\text{Zn}^{2+} + \text{Cu} = \text{Zn} + \text{Cu}^{2+}$ 1.100 V
 (B) $\text{Cu}^{2+} + \text{Zn} = \text{Cu} + \text{Zn}^{2+}$ 1.100 V
 (C) $\text{Cu}^{2+} + \text{Zn}^{2+} = \text{Cu} + \text{Zn}$ -0.426 V
 (D) $\text{Cu}^{2+} + \text{Zn} = \text{Cu} + \text{Zn}^{2+}$ 0.426 V
 (E) $\text{Zn}^{2+} + \text{Cu} = \text{Zn} + \text{Cu}^{2+}$ -1.100 V

e) Concentration polarization can best be minimized by

- (A) only increasing the temperature.
 (B) only increasing the rate of stirring.
 (C) only decreasing the temperature.
 (D) only decreasing the rate of stirring.
 (E) both increasing the temperature and the rate of stirring.

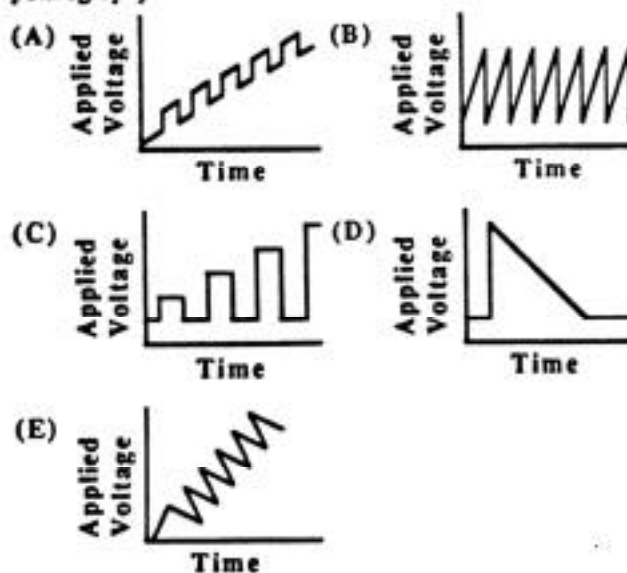
f) Modulation of an instrumental signal permits

- (A) separation of the signal from "dc" or zero frequency.
 (B) placement of the signal in a relatively noise-free frequency region.
 (C) the use of phase-lock amplifiers.
 (D) selective amplification of signals at the modulation frequency.
 (E) all of the above.

g) In a potentiometric titration, detection of the end point can be improved by

- (A) integrating the area under the curve.
 (B) lengthening the volume axis of the graph.
 (C) displaying the curve on an oscilloscope.
 (D) plotting a first or second derivative curve.
 (E) changing to another reference electrode.

h) Which of the following voltage sweep programs (applied voltage plotted against time) is used for differential pulse polarography?



i) A three-electrode potentiostat is used

- (A) to adjust the flow of mobile phase in an electrochemical detector used in reverse-phase liquid chromatography.
- (B) to compensate for the resistance of the solution between the indicator and reference electrodes in an electrochemical cell.
- (C) to measure the current during an amperometric titration.
- (D) to adjust the drop rate from a dropping-mercury electrode in a polarograph.
- (E) for none of the applications listed above.