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| **DEPARTMENT OF CHEMISTRY****FOURAH BAY COLLEGE****UNIVERSITY OF SIERRA LEONE**CHEM 311**PHYSICAL ANALYTICAL CHEMISTRY II****Unit 2 – Electroanalytical Techniques****CONTINUOUS ASSESSMENT****ASSIGNMENT**This assignment must be submitted no later than 2 pm on Friday March 23rd 2018You must submit this cover sheet with your assignment.Name: ……………………………………………………Admission No. ………………..Note: Unit 2 Continuous Assessment is worth 10% of the total marks for CHEM312Your score will be divided into three parts:Lecture and Tutorial Attendance 10%Assignment 40%Test 50% |

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| **1.** | (a) | Name the electroanalytical method used to obtain the following graphs:1. potential vs volume of titrant
2. current vs volume of titrant
3. current vs potential
4. potential vs time
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|  | (b) | Sketch a typical graph for each method |
|  | (c) | Briefly explain the principles behind each method |
|  | (d) | Describe the instrumentation used for each method[25] |
| **2.** | What is the difference between a polarograph and a polarogram? Draw diagrams to show the main features of each.[5] |
| **3.** | Describe the main features of a dropping mercury electrode and explain why it is useful in polarography. [5] |
| **4.** | (a) | What is meant by the term “diffusion-limited current” |
|  | (b) | In the presence of a supporting electrolyte, the flux due to diffusion is given by **fM = DM**$\frac{d[M]}{dx}$Hence derive an expression linking the current at an electrode to the concentration gradient, in the presence of a supporting electrolyte. |
|  | (c) | Fick’s Law of diffusion relates the concentration gradient to the rate of change of concentration as follows: $\frac{dC}{dt}=D\frac{d^{2}C}{dx^{2}}$This equation can be solved to show that $\frac{d[M]}{dx}$ = $\frac{\left[M\right]}{\sqrt{πDt}}$ when [M] has reduced to zero at the electrode.Hence derive an expression for the diffusion current ID |
|  | (d) | Derive an expression for the surface area of mercury at the dropping electrode in terms of the flow rate m, the density of mercury and the time. |
|  | (e) | Hence show that ID is proportional to $D\_{M}^{\frac{1}{2}}m^{\frac{2}{3}}τ^{\frac{1}{6}}[M]$ |
|  | (f) | Discuss some of the limitations of the Ilkovic equation.[25] |
| **5.** | (a) | For the equation O + ne 🡪 R, use the Nernst equation to write an expression for the potential E at the electrode in terms of Eo, n, [O]e and [R]e |
|  | (b) | Show that [O]e = $\frac{I\_{D}-I}{k\sqrt{D\_{o}}}$ and that [R]e = $\frac{I}{k\sqrt{D\_{r}}}$ |
|  | (c) | Hence show that $V\_{\frac{1}{2}}$ = E0 + $\frac{RT}{nF}$ln$\sqrt{\frac{D\_{r}}{D\_{o}}}$ |
|  | (d) | Discuss the validity of the approximation that $V\_{\frac{1}{2}}$ = E0.[10] |

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| **6.** | (a) | Write an equation for the formation of the complex ion [MLp]x+py and hence write an expression for the stability constant Kstab of the complex |
|  | (b) | The value of E1/2 for a complex ion can be shown to be E1/2 = Eo - $\frac{RT}{nF}$lnKstab - $\frac{pRT}{nF}$ln[Ly]  |
|  |  | (i) | Explain the meaning of the terms in this expression |
|  |  | (ii) | Show how the expression can be used to deduce values for p and Kstab[5] |
| **7.** | (a) | Draw three different shapes of curves obtained in amperometric titrations; in each case, suggest a possible titrand and titrant which could give each type of curve and explain the shape of the curves obtained.[5] |
| **8.** | (a) | What is the difference between an amperometric titration and a potentiometric titration? |
|  | (b) | In potentiometric titrations, a graph of ΔE/ΔV against V is more useful than a graph of E against V. Explain why, and sketch the shape of a graph of ΔE/ΔV against V.[5] |

**TOTAL 85 MARKS**