26

a) Compile ud contast the models proPosed lor elecuical double laye. at the elect.ode-soLution interph6e,
(50 maks)
b) DEw a labeled electical equivalent circujt for m electochemical cell
(10 mdks)

c) Describe the electro€pillary cwes Outtine the ioforution which ce be obtained from electocappilary cwes?
(40 milks)

a) Explain the following:
i Cyclic volmetry is typicatly Perfomed in ihe presence of a)tge excess of m ined electrolyte md in the absence ofmy mecbmicd disturbance in the solution
(15 mdks)

li Clssy carbon electrode is a befter choice over a Pt electode for preliminary electochemical iirvestigation of an inorgmic redox system in an aqueow acidic soturjon (10 maks)

b) A well-defned rcversible cyclic voltmogram (CV) at troud -0 75 V was obhined for a O2/O., coqle at a glassy cilbon elechode for m orygen satuated non-aqueous solution Potential scming was perfomed from +0 0 V to _1 00 V

i Draw a labelled CV for the 02/0lcoqle
(10 mdks)

ii Ninhyd.ine was founcl to scavange superoxide radical anion Draw and explain tie chmge in shape of CVs lot lhe O2/O; couple, before md aier ach successive addition of ninhydrine to the solulion
(20 Eeks)
iii How do you experimentally prove, in CVs obhined for the above reaction' that tle electron-tufer rate is diffusion @nfolled dd the electoch€mica'l
reversibilily
(20 mdks)

c) A 5iriillified e.qution for the peak cment in at 25 oC fot a loblly reveEible couple is'given by, i.p=(2.69 x l1s)n3/2AD1/2v1/2ci.From the CVs recorded at different sce rates fo. a solution of Ru(NH.)!+,a Rmdles-Sevcik gEph of i' against v//2 Ms drawn using ip daE for ihe reduction cyc]e The linee pd ofthe graph had a gradient of 6 09 xlorA (V s-r)-ra at 25 'C, md the working et€ctrode &ea wd 0 45 cm2.

i Calculate the diffusion coefficient D of of R/(M3)?+ in the electolyte
(15 IMks)
ii Il tle CV is recorded ior one-electron rcduction of Ru(NH3):+at a Pt microelbctrode, dEwthe shaPe ofCV
(l 0 m{ko

PaEe Z af 4

2?

a) The molecule AB is elecronically excited ro AB' Briefly describe four Processes by which fie excited molecule AB+ could lose the excibtion energy
(15 meks)
b) Use the Eranck-Condon prirciple to explainlhe following obse.vations

i Fluorescence or phosphorescence from orgaic molecules in solution gene.ally occurs from the lowest excited singlet (SL) or triptet (Tr) $ate, irespective of the energy ofthe electronic stale jnitially exciLed

ii Iniensjty of vibratioDal fine strucLure (vo + ro) is higher thm (,r r vo) You nay use potential energy vs internuclear dishce Plots for the itlusration
(20 maks)
c)
i Wlat is memt by the qMntum yield ofa photochemical reaclion?
(10 milks)
ii For the gas phase photoreaction HI + hv + b H)+ t/211, the quzilum yield at 254 m is lound to be bc 2 0 Suggest a reaction scheme to cxplain this resultju$ifying both the steps you include and those you omit

(20 ntrks)
iii State the factors contributing b fluorescence behavior
(15 nilk,

d) Briefly discuss,
i photoinduced electron umsfer
ii excitation energy kansfer
with two applications ftom each
(20 mdks)

a) Give afrlropriate mechmisms md the product (P) for three of the following

plotoctemical rdsfomations,a h,

- "

V
-,

H- -H --I.
L/ lN (254 nm)

(3 x20 mtrks)

b) Considerins the deactivation processes of the singlet excited shte in the absence and presence ofa quencher, derive the Stern_yolmer equation which exp.€sses the ratio of (he fluorescence quantm yields in the presence and absence ofa quencher
(30 mtrks)

c) Discuss the two applications ofSt€rtr'Volmer equation jn chemistry
(10 mdks)

-

END-