Q1: For the processes, $Cu^{2+}(aq.) + e^- \rightarrow Cu^{+}(aq.)\ E = 0.15V$

$Cu^{2+}(aq.) + 2e^- \rightarrow Cu(s)\ E = 0.336V$

Therefore, E for the process, $Cu^{+}(aq.) + e^- \rightarrow Cu(s)$

Ans: Eqn (1) can be re-written as

Cu^{+} (aq) → Cu^{2+}(aq) + e^- , $E^o_{Cu^+/Cu^{2+}}$ = -0.15 V, $\Delta G_4 = -nFE_4^o$ = -1 x F x -0.15 = +0.15F

Cu^{2+}(aq) + 2e^- → Cu (s), $E^o_{Cu^{2+}/Cu}$ = +0.336 V, , $\Delta G_2 = -nFE_2^o$ = -2 x F x +0.336 = -0.672F

Adding eqn (4) and eqn (2),

Cu^{+} (aq) + e^- → Cu (s), $E^o_{Cu^+/Cu}$

$\Delta G_3 = -nFE_3^o$

=> $\Delta G_3 = \Delta G_4 + \Delta G_2$ = 0.15F + (-0.672F) = -0.522F

=> $-nFE_3^o$ = -0.522F

=>-1x F xE_3^o = -0.522F

=>E_3^o = +0.522 V

Electrode Potential (E^o_{el}) and Nernst Equation

Nernst equation can also be applied for half cell reactions.
The electrode potential of half cells also deviate from the standard electrode potentials when the electrolyte concentration is not 1M or temperature is not 298K.
Taking the example of the reduction reaction:

$$M^{n+}_{(aq)} + ne^- \rightarrow M_{(s)}$$

If $E^o_{M^{n+}/M}$ is the standard reduction potential, then Nernst equation can be applied as:

$$\mathbf{E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{RT}{nF} \ln Q_c}$$

-

$$\mathbf{=> E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}}$$

$$\mathbf{=> E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}}$$

$$\mathbf{=> E_{M^{n+}/M} = E^o_{M^{n+}/M} + \frac{RT}{nF} \ln [M^{n+}]}$$

M (s) → M^{n+} (aq) + ne^-

$E_{M/Mn+} = E_{M/Mn+}{}^o - (RT/nF) \ln [M^{n+}]/[M] =$
$= E_{M/Mn+}{}^o - (RT/nF) \ln [M^{n+}]$

Q2. A zinc electrode is dipped in a 0.1 M solution of $ZnSO_4$ at 25°C. Assuming that salt is dissociated to 20% at this dilution. Calculate the electrode potential. $E^{\circ}_{Zn^{+2}/Zn} = -0.76V$

$Zn \longrightarrow Zn^{+2} + 2e$

Ans:

$ZnSO_4\ (aq) \rightarrow Zn^{2+}\ (aq) + 2e^-$

At t = 0	0.1 M	0	0
	(100 %)	(0%)	(0%)

At t = t, 20% dissociated

80%	20%

Concentration of Zn^{2+} after 20% dissociation of $ZnSO_4$ = (20 x 0.1)/100 M = 0.02 M

Applying the Nernst equation,

$$E_{Zn/Zn^{2+}} = E^{o}_{Zn/Zn^{2+}} - \frac{RT}{nF} \ln \frac{[Zn^{2+}]}{[Zn]}$$

Q3. The standard cell potential for the reaction, $Zn(s)+Cu^{2+}(aq)\rightarrow Zn^{2+}+Cu(s)$, at 25°C is 0.5 V. The standard free energy (in kJ) is:

(a) –24.1 (b) –48.25 (c) –96.5 (d) –193.0

Q4. Consider the cell:

$Zn\,|\,Zn^{2+}(a=0.01)\,||\,Fe^{3+}(a=0.001), Fe^{2+}(a=0.01)\,|\,Pt$

$E_{cell} = 1.71V$ at 25°C for the above cell. The equilibrium constant for the reaction:

$Zn + 2Fe^{3+} \rightleftharpoons Zn^{2+} + 2Fe^{2+}$ at 25°C would be close to

a = Activity coefficient

Q5. Given the standard potential for the following half-cell reaction at 298K,

$Cu^{+}(aq)+e^{-}\longrightarrow Cu(s)$ $E_0 = 0.52V$

$Cu^{2+}(aq)+e^{-}\longrightarrow Cu^{+}(aq)$ $E_0 = 0.16V$

Calculate the $\Delta G^0(kJ)$ for the reaction,

$2Cu^{+}(aq)\longrightarrow Cu(s)+Cu^{2+}$

At anode

$Zn \rightarrow Zn^{2+} + 2e^-$

At cathode

$2Fe^{3+} + 2e^- \rightarrow 2Fe^{2+}$

Net cell reaction

$Zn + 2Fe^{3+} \rightarrow Zn^{2+} + 2Fe^{2+}$

$E^o_{cell} = -\{RT/nF\} \ln K_c$

$\Rightarrow \ln K_c = \{-nFE^o_{cell}\}/RT$

$\Rightarrow 2.303 \log K_c = (-2 \times 96500 \times 1.71)/(8.314 \times 298)$

$\Rightarrow \log K_c = (-2 \times 96500 \times 1.71)/(8.314 \times 298 \times 2.303)$