Question 1

$\overset{0}{Pb_{(s)}} \mid \overset{+2\;-2}{PbSO_{4(s)}} \mid \overset{+2\;-2}{MgSO_{4(aq)}}\ (15.0\,mmol/kg) \mid \overset{0}{Mg_{(s)}}$

a)

LS: $Pb_{(s)} + SO_4^{2-}{}_{(aq)} \longrightarrow PbSO_{4(s)} + 2e^-$ $\quad = -0.36$

RS: $Mg^{+2}_{(aq)} + 2e^- \longrightarrow Mg_{(s)}$ $\quad = -2.36$

overall: $Pb_{(s)} + SO_4^{2-}{}_{(aq)} + Mg^{2+}{}_{(aq)} \longrightarrow PbSO_{4(s)} + Mg_{(s)}$

b)

$E = -2.08V$

$\gamma_{\pm}\ MgSO_4 = ?$

$Mg^{2+} \quad SO_4^{2-}$

$$I = \tfrac{1}{2}\left[(Mg^{2+})(2)^2 + (SO_4^{2-})(-2)^2\right]$$
$$= \tfrac{1}{2}\left[(0.015)(4) + (0.015)(4)\right]$$
$$= 0.06\ mol/kg$$

$$\log \gamma_{\pm} = -A\,|z_+ z_-|\,\sqrt{I}$$
$$= -0.5092\,|(2)(2)|\,\sqrt{0.06}$$
$$= -0.4987$$
$$\gamma_{\pm} = 0.317$$

c)

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{\nu F}\ln Q$$
$$= E^{\circ}(R) - E^{\circ}(L) - \frac{RT}{2F}\ln\left(\frac{1}{(\gamma_{\pm} MgSO_4)\left(\frac{b_{MgSO_4}}{b^{\circ}}\right)}\right)$$
$$= (-2.36) - (-0.36) - \frac{(8.314)(298.15)}{2(96485)} \times \ln\left(\frac{1}{(0.015)(0.317)}\right)$$
$$= (-2) - (0.012846)(5.3486)$$
$$= -2.07$$

$\therefore$ difference

$= \text{theoretical} - \text{measured}$

$= -2.08 - (-2.07)$

$\boxed{\Delta = -0.01}$

Question 2

Ksp for AgBr?

$Ag_{(s)} \mid Ag^+_{(aq)} \,\|\, Br^-_{(aq)} \mid AgBr_{(s)} \mid Ag_{(s)}$

LS: $Ag_{(s)} \longrightarrow Ag^+_{(aq)} + e^-$ $\quad E^{\circ} = 0.80$

RS: $AgBr_{(s)} + e^- \longrightarrow Br^-_{(aq)} + Ag_{(s)}$ $\quad E^{\circ} = 0.0713$

$Ag_{(s)} + AgBr_{(s)} \longrightarrow Ag^+_{(aq)} + Br^-_{(aq)} + Ag_{(s)}$

$$E^{\circ} = E^{\circ}(RS) - E^{\circ}(LS)$$
$$= 0.0713 - 0.80$$
$$= -0.7287$$

$$\Delta G = -\nu F E^{\circ}$$
$$= -(1)(96485\ \tfrac{C}{mol})(-0.7287)$$
$$= 70308.62\ J/mol$$
$$= 70.3\ kJ/mol$$

$$\Delta G = -RT\ln K_{sp}$$
$$K_{sp} = e^{-\Delta G/RT}$$
$$= e^{-70300/(8.314)(298.15)}$$
$$K_{sp} = 4.82 \times 10^{-13}$$

Question 3

A) $Co^{3+} + e^- \longrightarrow Co^{2+}$ $\quad E^\circ = 1.81$

B) $Co^{3+} + 3e^- \longrightarrow Co$

$$\left[\begin{array}{lll} Co^{3+} + e^- \longrightarrow Co^{2+} & E^\circ = 1.81 \\ Co^{2+} + 2e^- \longrightarrow Co & E^\circ = -0.28 \end{array}\right]$$

$$E^\circ = \frac{2(-0.28) - (1)(1.81)}{3}$$

$$E^\circ = -0.79$$

∴ a $1e^-$ reduction of Co^{3+} will be favored. This is because when $E^\circ > 0$, the half cell has a greater tendency to be reduced. When $E^\circ < 0$, the half cell has a lower tendency to be reduced.