

Q6.41 Suppose now that the cell represented by cell diagram 6.15 is set up such that the concentration of $\text{Ni}^{2+}(\text{aq})$ ions is 1.0 mol dm^{-3} , and the concentration of $\text{X}^{+}(\text{aq})$ ions is 0.1 mol dm^{-3} . What assumptions or approximations would you have to make in order to calculate the cell emf at 298.15 K under these conditions? Select *two* items from the key.

KEY for Q6.41

- A For an element in its reference state, $\Delta G_f^\ominus = 0$.
- B ΔH_m^\ominus for the overall cell reaction does not vary with temperature.
- C A solution in which the concentration of $\text{Ni}^{2+}(\text{aq})$ ions is 1.0 mol dm^{-3} behaves ideally.
- D ΔS_m^\ominus for the overall cell reaction does not vary with temperature.
- E In the half-cell on the left-hand side of cell diagram 6.15, the activity of $\text{X}^{+}(\text{aq})$ is unity.
- F In the half-cell on the left-hand side of cell diagram 6.15, the mean ionic activity coefficient, γ_{\pm} , of the electrolyte is unity.

Q6.42 Given the necessary assumptions and approximations, what is your estimate of the emf at 298.15 K of the cell represented by cell diagram 6.15 under the conditions specified in question Q6.41? Select from the key the value that is closest to your answer.

KEY for Q6.42

- | | |
|-----------|-----------|
| A +0.50 V | E -0.04 V |
| B +0.38 V | F -0.16 V |
| C +0.16 V | G -0.86 V |
| D +0.04 V | H -0.98 V |

Q6.43 This question is concerned with Figure 6.6 (*overleaf*), which shows plots of overall cell potential versus current density at 298.15 K for a set of hypothetical self-driving cells, labelled 1 to 4. All four cells have the following characteristics: emf, $E = 2.5 \text{ V}$; electrodes, each of area $A = 40 \text{ cm}^2$; $\alpha_{\text{ox,an}} = \alpha_{\text{red,ca}} = 0.5$; $i_{\text{e,ca}} = i_{\text{e,an}}$; $i_{\text{L,ca}} = i_{\text{L,an}}$. Examine the statements in the key and select *two* that are **correct**.

KEY for Q6.43

- A The exchange current densities of the electrode reactions ($i_{\text{e,ca}} = i_{\text{e,an}}$) are larger in cell 3 than in cell 1.
- B The limiting current densities of the electrode reactions ($i_{\text{L,ca}} = i_{\text{L,an}}$) are higher in cell 4 than in cell 1.
- C The internal resistance, R_{cell} , of cell 1 is greater than that of cell 2.
- D Under particular conditions, the power output of cell 2 can exceed the power output of cell 3.
- E In cell 1, if the overpotential at the cathode, η_{ca} , is due *solely* to the kinetics of the electrode reaction, and $i_{\text{e,ca}} = i_{\text{e,an}} = 10 \text{ A m}^{-2}$, then the value of η_{ca} is approximately 283 mV when a current of 10 A is drawn from the cell.
- F If the internal resistance, R_{cell} , of cell 2 is due *solely* to the electrical resistance of the electrolyte between the electrodes, then it should be possible to reduce the value of R_{cell} by operating the cell at a higher temperature.