2.12 Chemistry: Electrode Potentials and Transition Metals: 1-hour Pack

AQA 7405 · Calculator allowed · about 60 minutes

Total Marks

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 This question uses techniques from the required practical on measuring the emf of an electrochemical cell. A student sets up a cell using a platinum electrode dipping into a solution containing both $Fe^{3+}(aq)$ and $Fe^{2+}(aq)$ ions, connected by a salt bridge to a second platinum electrode dipping into a solution containing both $Cr^{3+}(aq)$ and $Cr^{2+}(aq)$ ions, all under standard conditions. Standard electrode potentials: $E(Fe^{3+}/Fe^{2+}) = +0.77$ V; $E(Cr^{3+}/Cr^{2+}) = -0.41$ V.

(a) Explain why a platinum electrode, rather than a strip of metal, must be used for each of these two half-cells. **(2)**

(b) Calculate the standard emf of this cell. **(1)**

(c) State which half-cell forms the positive electrode of this cell, and explain your reasoning. **(2)**

(d) The student's measured emf for this cell was 1.16 V, slightly below the theoretical value. Suggest two reasons for this discrepancy that relate specifically to this cell using platinum electrodes with ion-ion redox couples in solution (rather than solid metal electrodes). **(3)**

(Total for Question 1 is 8 marks)

© Revision Library | revisionlibrary.co.uk

2 Standard electrode potentials: $E(MnO_4^-/Mn^{2+}$, acidic) = +1.51 V; $E(O_2/H_2O)$ = +1.23 V, for the half-equation $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$.

(a) Use these data to show, by calculation, that acidified potassium manganate(VII) solution is thermodynamically capable of oxidising water to oxygen gas. **(3)**

(b) Despite this, acidified $KMnO_4$(aq) solutions can be stored and used as titrants over the timescale of a normal titration without significant decomposition. Explain this observation in terms of reaction kinetics. **(3)**

(c) Suggest why $KMnO_4$(aq) solutions are typically stored in dark (brown glass) bottles, away from direct sunlight. **(2)**

(Total for Question 2 is 8 marks)

---

3 Explain why many transition metal ion complexes are coloured, but the corresponding complexes of calcium (Ca^{2+}) and zinc (Zn^{2+}) are colourless. Your answer should refer to d-orbitals, ligands and electronic transitions.

(Total for Question 3 is 6 marks)

© Revision Library | revisionlibrary.co.uk

4 Ammonium vanadate(V) solution (containing VO_2^+ ions, yellow) is reduced by an excess of zinc metal in dilute sulfuric acid. Standard electrode potentials: $VO_2^+ + 2H^+ + e^- \rightarrow VO_2^+ + H_2O$, E = +1.00 V; $VO_2^+ + 2H^+ + e^- \rightarrow V^{3+} + H_2O$, E = +0.34 V; $V^{3+} + e^- \rightarrow V^{2+}$, E = -0.26 V; $Zn^{2+} + 2e^- \rightarrow Zn$, E = -0.76 V.

(a) State the sequence of colour changes observed as reduction proceeds from vanadium(V) to vanadium(II), naming the oxidation state and colour present at each stage. **(4)**

(b) Using the standard electrode potentials given, show by calculation that zinc metal is able to reduce VO_2^+ all the way down to V^{2+}, i.e. that each of the three reduction steps is thermodynamically feasible. **(4)**

(c) Write the overall balanced ionic equation, including state symbols, for the direct reduction of VO_2^+ to V^{2+} by zinc metal in acidic solution. **(4)**

(Total for Question 4 is 12 marks)

---

5 Copper(I) ions are unstable in aqueous solution but can be stabilised as insoluble compounds or as complex ions. Standard electrode potentials: $E(Cu^{2+}/Cu^+)$ = +0.15 V; $E(Cu^+/Cu)$ = +0.52 V.

(a) Use an appropriate calculation to show that aqueous Cu^+ ions disproportionate to form Cu^{2+} and Cu, and state which copper species is oxidised and which is reduced in this reaction. **(3)**

(b) Despite this, solid copper(I) oxide, Cu_2O, and copper(I) chloride, CuCl, are both stable compounds that do not spontaneously disproportionate. Suggest why Cu^+ is stable in these solids but not in aqueous solution. **(3)**

(c) In the presence of excess copper metal and a source of ammonia, Cu^+ can be stabilised in solution as the complex ion $[Cu(NH_3)_2]^+$, which does not readily disproportionate. Explain, in terms of the relative stabilisation of the Cu^+ and Cu^{2+} oxidation states by ligands, how forming this complex ion helps to prevent disproportionation. **(4)**

(Total for Question 5 is 10 marks)

© Revision Library | revisionlibrary.co.uk

Mark scheme · 2.12 Chemistry: Electrode Potentials and Transition Metals: 1-hour Pack

Question 1

(a) neither half-cell involves a solid metal in equilibrium with its own ion (both couples are between two different oxidation states of ions in solution), so there is no solid metal electrode available to use (oe) **M1**

(a) platinum is used because it is inert/unreactive: it does not itself take part in the reaction, but simply provides a conducting surface at which electrons can be transferred to or from the ions in solution (oe) **A1**

(a) Answer: Both couples involve only dissolved ions (no solid metal), so an inert platinum electrode is used to conduct electrons to/from the solution without itself reacting.

(b) +1.18 V cao (E cell = 0.77 - (-0.41)) **B1**

(b) Answer: +1.18 V

(c) the Fe^{3+}/Fe^{2+} half-cell is the positive electrode **B1**

(c) because it has the more positive (higher) standard electrode potential, so it is the couple that is reduced (accepts electrons) when the cell operates (oe) **B1**

(c) Answer: The Fe^{3+}/Fe^{2+} half-cell; it has the more positive E value, so it is reduced (accepts electrons from the Cr^{3+}/Cr^{2+} half-cell) when the cell operates.

(d) Cr^{2+} is a very strong reducing agent and is readily oxidised by dissolved oxygen in the air/solution before or during the measurement, reducing the effective concentration of Cr^{2+} (moving that half-cell away from standard conditions and altering its potential) (oe) **B1**

(d) surface contamination, incomplete platinisation, or slow electron-transfer kinetics at the inert platinum surface can mean true equilibrium (and hence the full theoretical potential) has not yet been established when the reading is taken (oe) **B1**

(d) small amounts of current drawn by the voltmeter (not perfectly infinite resistance) reduce the reading slightly below the true zero-current emf (oe); allow any two valid, distinct reasons specific to this system **B1**

(d) Answer: For example: Cr^{2+} is readily air-oxidised by dissolved oxygen, shifting that half-cell from standard conditions; and/or slow electron-transfer kinetics or surface contamination at the platinum electrodes mean equilibrium is not fully established when the reading is taken.

Question 2

(a) E cell = $E(MnO_4^-/Mn^{2+}) - E(O_2/H_2O)$ = 1.51 - 1.23 **M1**

(a) = +0.28 V cao **A1**

(a) positive E cell, so the reaction (MnO_4^- oxidising H_2O to O_2) is thermodynamically feasible **B1**

(a) Answer: E cell = +0.28 V, positive, so acidified $KMnO_4$ is thermodynamically capable of oxidising water to oxygen.

(b) a positive E cell value only shows that a reaction is thermodynamically feasible (energetically favourable); it gives no information about the rate at which the reaction occurs (oe) **M1**

(b) in the absence of a catalyst, this decomposition reaction has a high activation energy, so its rate at room temperature is extremely slow (oe) **M1**

(b) so, although $KMnO_4(aq)$ does very slowly decompose over long-term storage (which is why standard solutions are periodically re-standardised), this occurs far too slowly to have any measurable effect during the timescale of a single titration (oe) **A1**

(b) Answer: A positive E cell only shows the reaction is feasible, not that it is fast; with no catalyst present, the reaction has a high activation energy and is extremely slow at room temperature, so $KMnO_4(aq)$ remains usable as a titrant over the timescale of a titration, even though it very slowly decomposes over long-term storage.

(c) light (particularly UV/visible light) can provide energy that catalyses (accelerates) the decomposition reaction, e.g. by a photochemical pathway (oe) **M1**

(c) storing the solution in the dark minimises exposure to light, slowing this decomposition and keeping the concentration of the standard solution constant (accurate) for longer (oe) **A1**

(c) Answer: Light can catalyse (speed up) the decomposition of $KMnO_4(aq)$; storing it in the dark minimises this, keeping its concentration reliable for longer.

© Revision Library | revisionlibrary.co.uk

Question 3

Level 3 A coherent, logically structured explanation covering: the five d orbitals of a free/isolated metal ion are degenerate; ligands bonding to the metal ion cause the d orbitals to split into two groups of different energy; an electron can be promoted (absorbing energy) from the lower to the higher set of d orbitals (a d-d transition), and the energy absorbed corresponds to a frequency of visible light; the complementary colour (the light not absorbed) is seen; the size of the splitting (and hence the colour observed) depends on the ligand and the metal ion; Ca^{2+} and Zn^{2+} have either an empty (d0) or full (d10) d sub-shell, so no d-d transition is possible, hence they are colourless. **5-6**

Level 2 Some relevant chemistry given, e.g. describing d-orbital splitting by ligands and d-d electron transitions, but with incomplete or partly inaccurate linkage to why Ca^{2+}/Zn^{2+} complexes are specifically colourless. **3-4**

Level 1 Basic or isolated statement(s), e.g. 'transition metals have partly-filled d orbitals' or 'electrons absorb light', with little or no development of the mechanism. **1-2**

Level 0 No relevant chemistry given, or answer entirely incorrect/irrelevant. **0**

Indicative content:

- In a free (isolated, gaseous) transition metal ion, the five d orbitals are degenerate (all the same energy).
- When ligands bond to the central metal ion, they cause the d orbitals to split into two groups (sets) of different energy (e.g. a lower set of three and a higher set of two in an octahedral complex).
- An electron in the lower-energy set of d orbitals can absorb a specific quantity (quantum) of energy and be promoted into the higher-energy set; this is called a d-d transition.
- The energy absorbed corresponds to a particular frequency/wavelength of light, which for transition metal complexes typically falls within the visible region of the spectrum.
- The colour observed is the complementary colour to the light absorbed (the wavelengths not absorbed are transmitted or reflected, and this is what is seen).
- The size of the energy gap between the two sets of d orbitals (and therefore the frequency of light absorbed, and the colour seen) depends on the identity of both the ligand and the metal ion/its oxidation state.
- Ca^{2+} has an empty d sub-shell (d0), so there are no d electrons available to be promoted; Zn^{2+} has a full d sub-shell (d10), so there is no vacant d orbital for an electron to be promoted into.
- Because neither Ca^{2+} nor Zn^{2+} can undergo a d-d transition, no visible light is absorbed and their complexes are colourless.

Question 4

(a) vanadium(V), VO_2^+, yellow **B1**

(a) vanadium(IV), VO_2^+, blue **B1**

(a) vanadium(III), V^{3+}, green **B1**

(a) vanadium(II), V^{2+}, violet (lilac) **B1**

(a) Answer: Yellow VO_2^+ (V, +5) -> blue VO_2^+ (V, +4) -> green V^{3+} (V, +3) -> violet/lilac V^{2+} (V, +2).

(b) step 1: E cell = E(VO_2^+/VO_2^+) - E(Zn^{2+}/Zn) = 1.00 - (-0.76) = +1.76 V, positive so feasible **M1**

(b) step 2: E cell = E(VO_2^+/V^{3+}) - E(Zn^{2+}/Zn) = 0.34 - (-0.76) = +1.10 V, positive so feasible **M1**

(b) step 3: E cell = E(V^{3+}/V^{2+}) - E(Zn^{2+}/Zn) = -0.26 - (-0.76) = +0.50 V, positive so feasible **M1**

(b) since E(Zn^{2+}/Zn) = -0.76 V is more negative than all three vanadium E values, E cell is positive at every stage, so zinc can reduce V(+5) all the way to V(+2) cao **A1**

(b) Answer: E cell = +1.76 V, +1.10 V and +0.50 V for the three steps respectively; all positive, so zinc reduces VO_2^+ fully to V^{2+}.

(c) combined vanadium reduction half-equation: $VO_2^+ + 4H^+ + 3e^- \rightarrow V^{2+} + 2H_2O$ **M1**

(c) zinc oxidation half-equation: $Zn \rightarrow Zn^{2+} + 2e^-$ **M1**

(c) half-equations correctly scaled to balance electrons transferred (vanadium x2, zinc x3, giving 6 electrons) **M1**

(c) $2VO_2^+(aq) + 8H^+(aq) + 3Zn(s) \rightarrow 2V^{2+}(aq) + 4H_2O(l) + 3Zn^{2+}(aq)$ fully balanced with state symbols cao **A1**

(c) Answer: $2VO_2^+(aq) + 8H^+(aq) + 3Zn(s) \rightarrow 2V^{2+}(aq) + 4H_2O(l) + 3Zn^{2+}(aq)$

© Revision Library | revisionlibrary.co.uk

Question 5

(a) E cell = E(Cu^+/Cu) - E(Cu^{2+}/Cu^+) = 0.52 - 0.15 = +0.37 V **M1**

(a) positive E cell, so $2Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$ is thermodynamically feasible cao **A1**

(a) some Cu^+ is reduced to Cu (gains an electron) while the rest of the Cu^+ is oxidised to Cu^{2+} (loses an electron); i.e. Cu^+ acts as both the oxidising and reducing agent **B1**

(a) Answer: E cell = +0.37 V, positive, so $2Cu^+ \rightarrow Cu^{2+} + Cu$ is feasible; Cu^+ is simultaneously reduced (to Cu) and oxidised (to Cu^{2+}) - it disproportionates.

(b) in the solid state the Cu^+ ions are held in a fixed lattice, strongly bonded to the oxide/chloride ions (by ionic/some covalent-character bonding), rather than existing as free, mobile hydrated ions **M1**

(b) there is no mechanism for two neighbouring Cu^+ ions in a rigid solid lattice to come together and exchange an electron in the way that mobile $Cu^+(aq)$ ions can in solution (oe) **A1**

(b) so, although disproportionation may still be thermodynamically favourable overall, these solids are kinetically stable (do not disproportionate at a measurable rate) under normal conditions (oe) **A1**

(b) Answer: In Cu_2O and CuCl the Cu^+ ions are fixed in a rigid lattice rather than existing as free, mobile hydrated ions, so there is no route for neighbouring Cu^+ ions to exchange electrons; these solids are kinetically stable even though $Cu^+(aq)$ disproportionates readily.

(c) ammonia ligands form complexes with both Cu^+ and Cu^{2+}, but the two oxidation states are not stabilised to the same extent (oe) **M1**

(c) if ammonia complexation stabilises Cu^+ (lowers its energy/makes $[Cu(NH_3)_2]^+$ have a much larger stability constant) more than it stabilises Cu^{2+}, then converting Cu^+ to Cu^{2+} (as required for disproportionation) becomes energetically less favourable than in the uncomplexed aqua-ion system (oe) **M1**

(c) this effectively raises the relevant electrode potential for the Cu^{2+}/Cu^+ couple, reducing (or reversing the sign of) E cell for the disproportionation reaction, so it is no longer thermodynamically favourable, and free $Cu^+(aq)$ is removed from solution as the stable complex (oe) **A1**

(c) this implies that the stability constant of $[Cu(NH_3)_2]^+$ (the Cu^+ ammine complex) is much larger than that of the corresponding Cu^{2+} ammine complex, relative to their aqua ions (oe) **A1**

(c) Answer: Ammonia stabilises Cu^+ (as $[Cu(NH_3)_2]^+$) much more strongly than it stabilises Cu^{2+}, so oxidising Cu^+ to Cu^{2+} becomes less favourable once both are complexed; this effectively changes the relevant electrode potential enough that disproportionation is no longer feasible, implying the Cu^+ ammine complex has a disproportionately large stability constant compared with the Cu^{2+} ammine complex.

© Revision Library | revisionlibrary.co.uk