Redox & Electrochemistry

Answers and Explanations

1. A

Redox is an accounting system. The valence electrons in a molecular, atomic or ionic species are all assigned to an element. Electrons within a covalent bond are assigned to the more electronegative element. This accounting system provides a useful way to keep track of how electrons shift from their old neighborhoods in the reagents to their new neighborhoods in the products. An electron which before was in the vicinity of a lithium atom now finds itself in the vicinity of a fluorine atom. It has fallen down into a well. An oxidizing agent (oxidant, oxidizer) is a substance that has the ability to oxidize other substances — in other words to accept their electrons.

2. D

There are two tracks you can choose from in assigning oxidation numbers. You can use the rules for assigning oxidation numbers, or if you know or are given the structural formula, you can think of each bond as a tug of war and assign the electrons brought to the bonds to the more electronegative element.

In our molecule, each chlorine has brought seven valence electrons to share with oxygen in covalent bonding. Although they are both very electronegative elements, oxygen is more electronegative than chlorine (3.5 vs. 3.0), so the electrons chlorine brought to these bonds become oxygen's property in terms of redox accounting. The bond is only slightly polar, but we say those electrons are oxygen's. That's redox accounting. Oxygen has gained and chlorine has lost. Chlorine's oxidation number here is +7.

Alternatively, we could have used rules. One of our rules is that the oxidation number of oxygen is almost always −2. Another rule is that the sum of oxidation numbers in an electrically neutral molecule is 0. We have seven oxygens. $7 \times -2 = -14$, so the two chlorines must be +7 each. Rules might be confusing though, because another rule is that the oxidation number of chlorine is almost always −1. One of the exceptions is that when it is bonded to oxygen.

3. B

In the reaction, copper's oxidation number changes from +2 to 0. Iron's oxidation number changes from 0 to +2. Copper is reduced and iron is oxidized. Copper is the oxidizing agent and iron is the reducing agent.

4. A

In most reactions with O_2, the oxygen atoms gain electron control over electrons brought by less electronegative elements to the reaction. In many reactions with H_2 hydrogen atoms lose electrron control to more electronegative atoms. However, hydrogen's electronegativity is actually pretty respectable (2.1), so H_2 will not be readily oxidized by any metal.

5. D

It's very important to understand that hydrogen in its +1 oxidation state, such as in water or with H^+ ions, can perform as a decent oxidizing agent. It's easy to forget in the world of organic chemistry, where everything is oxidizing hydrogen, that hydrogen, itself, actually has a respectable electronegativity (2.1), especially compared to metals. If a very reactive, ie. low electronegativity, metal such as lithium is exposed to water, a vigorous reaction will result in which hydrogen oxidizes lithium.

$$2Li\ (s) + 2\,H_2O \rightharpoonup 2LiOH\ (aq) + H_2\ (g)$$

The other metals of our answer choices are among the more electronegative transition metals. They are too electronegative to be oxidized by hydrogen.

6. B

Potassium permanganate is widely used as a strong oxidizing agent. The manganese atom has a high positive reduction potential. In a +7 oxidation state, its valence shell is all oxygen's property in $KMnO_4$. The manganese atom is reduced (+7 to +2) when potassium permanganate oxidizes a substrate, such as oxidation of acetaldehyde to acetic acid below.

$$5\,CH_3CHO + 2\,KMnO_4 + 3\,H_2SO_4 \rightharpoonup$$
$$5\,CH_3COOH + 3\,H_2O + K_2SO_4 + 2\,MnSO_4$$

7. B

A representative reaction of the type mentioned in the question stem would be sodium metal reacting with aluminum chloride to produce sodium chloride and aluminum. Aluminum oxidizes the sodium.

$$3\ Na(s) + AlCl_3(aq) \rightarrow 3\ NaCl(aq) + Al(s)$$

With electronegativity of 1.61, you would not normally expect to see aluminum oxidizing anything, but sodium's electronegativity is even lower, 0.93. In a tug-of-war with sodium over electrons, aluminum wins.

In other words, sodium is a great reducing agent. The best, most precise way to say that something is a powerful reducing agent is to say that its oxidized form, here sodium ion, has a large negative standard reduction potential.

$$Na^+(aq) + e^- \rightarrow Na(s) \quad E^0 = -2.71V$$

This means that if you were removing electrons from a standard hydrogen electrode and trying to put them onto sodium ions, the electrons would have a long uphill climb to get there, 2.71 joules to climb up for every coulomb of electrons.

Think of the standard hydrogen electrode as the ground floor of a house. Some other places an electron might find itself are like the roof of the house. These are reducing agents like sodium, lithium or potassium. Reducing agents have negative standard reduction potential. Electrons have an uphill climb to get to these from the hydrogen electrode. Some other places are like the basement of the house, such as fluorine or oxygen. These are oxidizing agents. Oxidizing agents have positive standard reduction potential.

Aluminum itself has a substantial negative standard reduction potential.

$$Al^{3+}(aq) + 3e^- \rightarrow Al(s) \quad E^0 = -1.66V$$

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Even though aluminum itself is a decent reducing agent, it will oxidize sodium because the trip for an electron from sodium to aluminum is downhill -2.71V to -1.66V.

8. B

Balancing by oxidation number method begins by determining the change in oxidation states of all of the individual species in the reaction and then balancing the increase with the decrease. The oxidation number decrease (minus 6 total), in chromium, is balanced with the increase, in chlorine (+6), when the coefficients are as follows.

$$Cr_2O_7^{2-} + 6Cl^- \rightarrow 2Cr^{3+} + 3Cl_2$$

The above is sufficient to answer the question, but let's look at the finished balanced reaction after inclusion of water and hydrogen ions.

$$14H^+ + Cr_2O_7^{2-} + 6Cl^- \rightarrow 2Cr^{3+} + 3Cl_2 + 7H_2O$$

Though balancing redox reactions ia a classic Chem 101 problem, it's not a typical MCAT exercise. It's important to see and understand how this kind of thing works. It's important to understand that the oxidation number increase in a redox reaction must be matched by an oxidation number decrease.

9. C

Disproportionation is a redox reaction in which one compound of intermediate oxidation state converts to two compounds, one of higher and one of lower oxidation states. As an example, phosphorous acid disproportionates upon heating to give phosphoric acid and phosphine.

$$4\ H_3PO_3 \rightarrow 3\ H_3PO_4 + PH_3$$

The reaction in the problem is the reverse of a disproportionation. A substance is formed, N_2, in an intermediate oxidation state from precursors of lower and higher oxidation states. The reverse of disproportionation is called comproportionation.

10. B

Fluorine is an example of a substance with a large positive standard reduction potential. It is a powerful oxidizing agent.

$$F_2 + 2e^- \rightarrow 2\ F^- \quad E^0 = +2.87V$$

This means that if you removed electrons from a standard hydrogen electrode and gave them to fluorine, the electrons would fall down into a deep well of binding energy, 2.87 joules for every coulomb of electrons.

11. A

Oxidation always occurs at the anode, whether the cell is electrolytic or galvanic. The reaction occurring in an electrolytic cell is non-spontaneous. An external voltage is being applied to make the reaction occur. What this means is that the electrons are being pushed uphill by the voltage, the overall cell potential being negative. Uphill for electrons is the journey from a positive potential to a negative potential. The external voltage is pulling the electrons out from the positive anode, where oxidation is occurring, and pushing them up onto the negative cathode, where reduction is occurring.

12. C

Oxidation always occurs at the anode, whether the cell is electrolytic or galvanic. The reaction occurring in an electrolytic cell is spontaneous. Electrons are falling downhill. The overall cell potential is positive. Downhill for electrons is the journey from a negative anode, where oxidation is occurring, to a positive cathode, where reduction is occurring.

13. D

Electrolysis of brine (concentrated NaCl) will oxidize Cl^- ions at the anode forming Cl_2. The only other possible reductant would be the oxygen in water (hydrogen and sodium are already oxidized). Oxygen is generally more electron greedy than chlorine. In other words, it has a higher positive standard reduction potential than chlorine, so the voltage will pull the electrons from chloride preferentially over oxygen. Therefore, the anode half reaction is as follows.

$$2\ Cl^-(aq) \rightharpoonup Cl_2(g) + 2e^-$$

At the cathode, the question of whether hydrogen or sodium will be reduced is easy. Sodium ions have a big negative standard reduction potential while hydrogen, of course, has a standard reduction potential of zero. It's the ground floor we compare everything to. Compared to hydrogen, sodium ions are a place it takes 2.71 joules of energy to move a coulomb of electrons to from a standard hydrogen electrode.

$$Na^+(aq) + e^- \rightharpoonup Na(s) \quad E^0 = -2.71V$$

Compared to sodium, in other words, hydrogen is a very respectable oxidizing agent, so hydrogen is reduced at the cathode, not sodium.

$$2\ H_2O + 2e^- \rightharpoonup 2\ OH^-\ (aq) + H_2(g)$$

In summary, electrolysis of brine produces chlorine gas at the anode and hydrogen gas at the cathode. As the reaction progresses, the solution forms concentrated sodium hydroxide.

14. C

The standard reduction potential represents the path that electrons would take from a standard hydrogen electrode to reduce a particular oxidant. The standard reduction potential of Zn^{2+} tells us that for hydrogen to reduce Zn^{2+} ions, electrons would need to travel uphill from hydrogen to –0.762 V. To reduce Ag^+ the electrons would travel downhill, though, from hydrogen to +0.800 V.

If you think about it, these two standard reduction potentials respectively have given us the two legs of the journey all the way from Zn (the reductant in our cell) to Ag^+ (the oxidant). Instead of going uphill to Zn^{2+}, we imagine going in the reverse, downhill instead from Zn to hydrogen. Instead of uphill to Zn^{2+}, downhill to hydrogen would be a change in the +0.762 V direction, and then from hydrogen to Ag^+, which would be another +0.800 V, so our cell potential is approximately 1.6V (0.762 V + 0.800 V). Don't let this be complicated. The electrons are falling from –0.762 V to +0.800 V.

The way you say this imaginary path as a formula is as follows.

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

15. D

One of the fundamental conceptual leaps we make into electrochemistry is to conceive of the free energy change in a chemical reaction as the journey of electrons through a potential difference. Instead of joules per mole we think in terms of joules per coulomb, or volts, as electrons transfer from the reductant to the oxidant. Underlying both conceptual frameworks is the fundamental reality that internal energy change in chemical reactions derive from the electrostatic potential energy differences as valence electrons find themselves within the new structural configurations of the product. Electrons were adjacent to a carbon atom and now they are in a covalent bond being pulled towards an oxygen nucleus, for example. For an oxidation-reduction reaction, we can convert a cell potential into a free energy change by using the Faraday unit for conversion of moles of electrons into Coulombs.

$$1\,F = 96{,}500\text{ C mol}^{-1}$$

$$\Delta G = -nFE$$

A very important equation in chemical thermodynamics describes how the free energy change of a reaction, ΔG, depends on both the standard free energy change, $\Delta G°$, and the reaction quotient, Q.

$$\Delta G = \Delta G° + RT \ln Q$$

In other words, whether a reaction is spontaneous in the forward or reverse direction depends not only on how the free energies of the product and reagent would compare, $\Delta G°$, if they were both present in equal concentration. It also depends on what their concentrations actually are in the beaker, the reaction quotient, Q. A reaction with a negative standard free energy change, spontaneous forward if product and reagent are in equal concentration, may even run in the reverse direction if there is a high concentration of product and very little reagent.

We can convert this equation into a form which is convenient for electrochemistry. This new form of our thermodynamics equation is called the Nernst equation.

$$\Delta G = \Delta G° + RT \ln Q$$

$$-nFE_{\text{cell}} = -nFE°_{\text{cell}} + RT \ln Q$$

$$E_{\text{cell}} = E°_{\text{cell}} - \frac{RT}{nF} \ln Q$$

$$E_{\text{cell}} = E°_{\text{cell}} - \frac{0.0592V}{n} \ln Q$$

The actual cell potential depends not only on how the standard reduction potentials of the product and reagent sides of the reaction compare, $E°$, the cell potential if they were both present in equal concentration. The cell potential also depends on what their concentrations actually are in the electrochemical cell, which is given by the reaction quotient, Q.

As a redox reaction proceeds towards equilibrium , $Q \longrightarrow \boldsymbol{K}$, the free energy change approaches zero, $\Delta G \longrightarrow 0$, and, equivalently, the cell potential approaches zero, $E_{\text{cell}} \longrightarrow 0$.

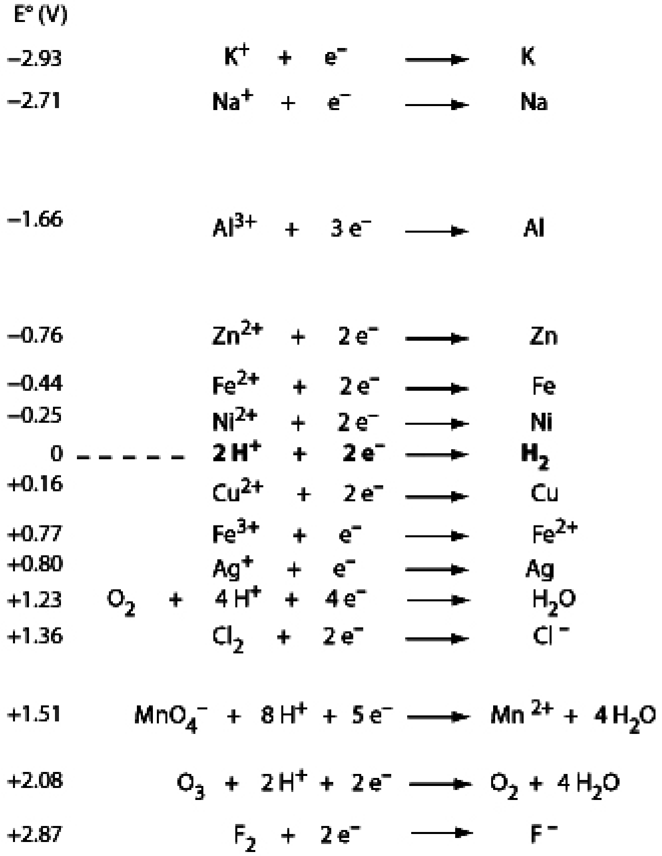
In summary, a dead battery is a chemical reaction that has attained the equilibrium state.

16. D

The evidence presented in the question stem is consistent with the relative standard reduction potentials of copper, zinc, and aluminum. On the table of standard reduction potentials below, we can see that aluminum metal is a stronger reducing agent than zinc metal which, in turn, is a stronger reducing agent than copper metal, and, equivalently, a copper ion is a stronger oxidizing agent than a zinc ion, which, in turn, is a stronger oxidizing agent than an aluminum ion. The standard reduction potential of a substance tells you the energy involved in reduction of the substance by the standard hydrogen electrode. The more negative the standard reduction potential, the more uphill the trip electrons must take in terms of potential energy. The more positive the standard reduction potential, the further downhill the electrons are falling from hydrogen to carry out the reduction of the substance.

In the question stem, we were told that placing metallic zinc into a solution of 1M $CuCl_2$ will result in a layer of copper being deposited on the zinc. When metal ions are reduced, they 'plate out' as pure metal. This happens spontaneously because zinc is a stronger reducing agent than copper (choice I), ie. it has a more negative reduction potential than copper; copper has a more positive reduction potential than zinc (choice II).

Additionally, we were told that placing an aluminum rod in a 1M solution of $ZnCl_2$ will result in metallic zinc being deposited on the aluminum. This tells us that aluminum has a more negative reduction potential than zinc. If aluminum has a more negative reduction potential than zinc and zinc has a more negative reduction potential than copper, aluminum must through transitive principle have a more negative reduction potential than copper. It follows that copper ions would spontaneously oxidize aluminum.



E° (V)	
−2.93	$K^+ + e^- \rightarrow K$
−2.71	$Na^+ + e^- \rightarrow Na$
−1.66	$Al^{3+} + 3e^- \rightarrow Al$
−0.76	$Zn^{2+} + 2e^- \rightarrow Zn$
−0.44	$Fe^{2+} + 2e^- \rightarrow Fe$
−0.25	$Ni^{2+} + 2e^- \rightarrow Ni$
0	$2H^+ + 2e^- \rightarrow H_2$
+0.16	$Cu^{2+} + 2e^- \rightarrow Cu$
+0.77	$Fe^{3+} + e^- \rightarrow Fe^{2+}$
+0.80	$Ag^+ + e^- \rightarrow Ag$
+1.23	$O_2 + 4H^+ + 4e^- \rightarrow H_2O$
+1.36	$Cl_2 + 2e^- \rightarrow Cl^-$
+1.51	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
+2.08	$O_3 + 2H^+ + 2e^- \rightarrow O_2 + 4H_2O$
+2.87	$F_2 + 2e^- \rightarrow F^-$

17. C

It's unlikely to have a version of this type of problem on the MCAT involving extensive quantitative work, but you need to know how to get through a basic form. The key to relating the chemical stoichiometry of a redox reaction to DC current parameters is the conversion factor known as *the Faraday*.

$$1\,F = 96{,}500\text{ C mol}^{-1}$$

A mole of electrons is the same as 96,500 coulombs of electric charge.

We're making 50g of Al (s). The atomic weight of Al is 27g mol^{-1}. Let's start rolling out conversion factors. This gets us to moles of aluminum.

$$50\text{g Al}\left(\frac{1\text{ mol Al}}{27\text{ g Al}}\right)$$

Aluminum in Al_2O_3 is in the +3 oxidation state. To plate out 1 mole of aluminum requires 3 moles of electrons.

$$Al^{3+} + 3e^- \rightharpoonup Al$$

This gets us to moles of electrons.

$$50\text{g Al}\left(\frac{1\text{ mol Al}}{27\text{ g Al}}\right)\left(\frac{3\text{ mol e}^-}{1\text{ mol Al}}\right)$$

Now the Faraday to get to electric charge.

$$50\text{g Al}\left(\frac{\text{mol Al}}{27\text{ g Al}}\right)\left(\frac{3\text{ mol e}^-}{\text{mol Al}}\right)\left(\frac{96{,}500\text{ C}}{\text{mol e}^-}\right)$$

We were given that the current employed is 10,000A. If 1,000 coulombs flow per second, there is one second per 1,000 coulombs.

$$50\text{g Al}\left(\frac{\text{mol Al}}{27\text{ g Al}}\right)\left(\frac{3\text{ mol e}^-}{\text{mol Al}}\right)\left(\frac{96{,}500\text{ C}}{\text{mol e}^-}\right)\left(\frac{1\text{ s}}{1{,}000\text{ C}}\right)$$

At the start, you don't need to see the whole solution to your foothold with a problem like this. Feel your way. We've worked through conversion factors all the way from grams of aluminum to the time required. Our answers are well spaced, so let's call $^{50}/_{27}$ ~ 2 and 96,500 ~ 100,000.

$$50\cancel{\text{g Al}}\left(\frac{\cancel{\text{mol Al}}}{27\,\cancel{\text{g Al}}}\right)\left(\frac{3\,\cancel{\text{mol e}^-}}{\cancel{\text{mol Al}}}\right)\left(\frac{96{,}500\,\cancel{\text{C}}}{\cancel{\text{mol e}^-}}\right)\left(\frac{1\text{ s}}{1{,}000\,\cancel{\text{C}}}\right)$$

~ 600s

18. D

NAD^+ oxidizes $FADH_2$. It is an oxidizing agent. Oxidation by NAD^+ always involves a two electron transfer in the form of a hydride (H^-).

Note that even though a hydrogen is transfered, it is not a proton transfer, but a hydride transfer. NAD^+ is not acting as a Brønsted base.

19. A

In lipoamide disulfide, each sulfur has one covalent bond to a carbon and one to a sulfur. Sulfur is slightly more electronegative than carbon (2.6 to 2.5), so the electron that carbon brought to that bond are assigned in redox accounting to sulfur. In lipoamide disulfide the oxidation state of sulfur is therefore –1.

In the dithiol form of lipoamide, each sulfur has one covalent bond to a carbon and one to a hydrogen. Sulfur is more electronegative than both carbon and hydrogen, so each of the electrons those respective atoms brought to these bonds are now sulfur's property. In the dithiol form the oxidation state of sulfur is therefore –2.

Not only in the context of lipoamide, but also regarding disulfide bridges in proteins and other important contexts such as the activity of glutathione, it's very important in biochemistry to recognize the disulfide form as the oxidized form and the dithiol as the reduced form.

20. C

As a result of the reactions of the pyruvate dehydrogenase complex, a pair of electrons that had been the property of carbon (originally within the nutrient molecule glucose) have become the property of nicotinamide. Between pyruvate and NADH, the pair of electrons were passed first to the two sulfurs of lipoamide, which then passed them to the flavin of FAD. FAD then passed them to NADH. Subsequent to completion of the mechanism, both lipoamide and FAD have returned to their initial oxidized state. In the net mechanism, carbon has been oxidized and NAD^+ reduced.

21. A

For of lipoamide disulfide to have a standard reduction potential of –0.29V means we would need to be pushing electrons uphill to NAD^+ at –0.32V, if the concentrations the reagents and products were all equal. In other words, the standard cell potential of a lipoamide/NAD cell would be –0.03V.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$-0.03\text{V} = (-0.32\text{V}) - (-0.29\text{V})$$

The reaction would not be spontaneous forward in that case. A negative standard cell potential corresponds to a positive standard free energy change.

$$\Delta G^\circ = -nFE^\circ$$

However, just as the actual free energy change not only depends on the standard free energy change but also the reaction quotient, so does the cell potential, which we can see in the Nernst equation.

$$\Delta G = \Delta G^\circ + RT\ln Q$$

$$-nFE_{\text{cell}} = -nFE^\circ_{\text{cell}} + RT\ln Q$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF}\ln Q$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592V}{n}\ln Q$$

For the dihydrolipoyl dehydrogenase mechanism to be spontaneous forward, the reaction quotient must be a fraction. The product of the concentrations of the reagents [NAD^+][lipoamide thiol] must be greater than the product of the concentrations of the reaction products [NADH][lipoamide disulfide].

22. C

Although a carbon of pyruvate is oxidized through the mechanism of the pyruvate dehydrogenase enzyme, at this stage of the overall pyruvate dehydrogenase complex there has not yet been any net movement of electrons from the nutrient carbons to the electron shuttling coenzymes. The carboxyl carbon has lost an electron which the original carbonyl carbon of pyruvate has gained, so this is a type of disproportionation in which one carbon converts to a higher oxidation state and one to a lower oxidation state.