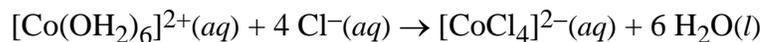# Chapter 20

PROPERTIES OF THE 3*d* TRANSITION METALS

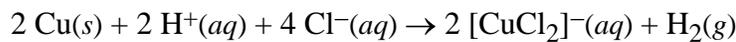## Exercises

20.1   (a) $TiCl_4(l) + O_2(g) \rightarrow TiO_2(s) + 2\ Cl_2(g)$

        (b) $Na_2Cr_2O_7(s) + S(l) \rightarrow Cr_2O_3(s) + Na_2SO_4(s)$

        (c) $Cu(OH)_2(s) \rightarrow CuO(s) + H_2O(l)$

20.3   For the earlier part of the Period 4 transition metals, the maximum oxidation number is the same as the group number (that is, the sum of the 4*s* and 3*d* electrons). For the later members, the oxidation state of +2 predominates.

20.5   Titanium(IV) chloride vaporizes readily, a characteristic of a covalent compound. Covalent behavior would be expected on the basis of the high charge density of the Ti^{4+} ion resulting in a strong attraction for the large, low charge density chloride ions (that is, covalent bond formation).

20.7   (a) $MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^- \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)$

        (b) $MnO_4^-(aq) + 2\ H_2O(l) + 3\ e^- \rightarrow MnO_2(s) + 4\ OH^-(aq)$

20.9   Iron(II) chloride is prepared under comparatively reducing conditions as a result of the hydrogen gas production:

$$Fe(s) + 2\ HCl(g) \rightarrow FeCl_2(s) + H_2(g)$$

Iron(III) chloride is prepared using highly oxidizing chlorine gas:

$$2\ Fe(s) + 3\ Cl_2(g) \rightarrow 2\ FeCl_3(s)$$

20.11 (a) Cobalt:
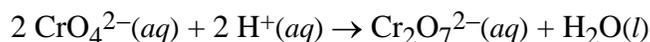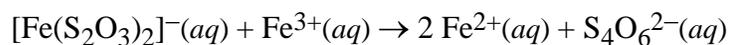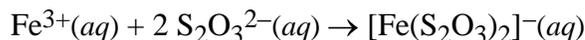
$$[Co(OH_2)_6]^{2+}(aq) + 4\ Cl^-(aq) \rightarrow [CoCl_4]^{2-}(aq) + 6\ H_2O(l)$$

(b) Copper:

$$2\ Cu(s) + 2\ H^+(aq) + 4\ Cl^-(aq) \rightarrow 2\ [CuCl_2]^-(aq) + H_2(g)$$

$$[CuCl_2]^-(aq) \rightarrow CuCl(s) + Cl^-(aq)$$

(c) Chromium:

$$2\ CrO_4{}^{2-}(aq) + 2\ H^+(aq) \rightarrow Cr_2O_7{}^{2-}(aq) + H_2O(l)$$

20.13 The two reactants are the hexaaquairon(III) ion and thiosulfate ion:

$$Fe^{3+}(aq) + 2\ S_2O_3{}^{2-}(aq) \rightarrow [Fe(S_2O_3)_2]^-(aq)$$

$$[Fe(S_2O_3)_2]^-(aq) + Fe^{3+}(aq) \rightarrow 2\ Fe^{2+}(aq) + S_4O_6{}^{2-}(aq)$$

20.15 (a) Fluoride stabilizes high oxidation states since it is a π-donor ligand. To maximize π interaction, the metal ion should have empty d orbitals and hence be in the highest possible oxidation state.

(b) The value of the crystal-field splitting, Δ, is very dependent upon oxidation state, so the nickel(IV) complex should have a very large Δ value. Thus, even though fluoride is very low in the spectrochemical series, the complex is most likely to be low spin.

20.17 $FeO_4{}^{2-}(aq) + 8\ H^+(aq) + 3\ e^- \rightarrow Fe^{3+}(aq) + 4\ H_2O(l)$

$2\ NH_3(aq) \rightarrow N_2(g) + 6\ H^+(aq) + 6\ e^-$

$2\ FeO_4{}^{2-}(aq) + 2\ NH_3(aq) + 10\ H^+(aq) \rightarrow 2\ Fe^{3+}(aq) + N_2(g) + 8\ H_2O(l)$
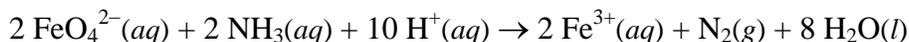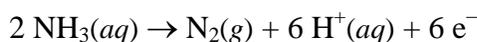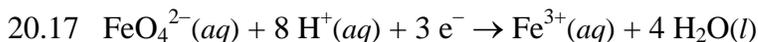
20.19 Chromium(VI) oxide. The very high charge density of the chromium metal ion will cause sufficient polarization of the electrons on the oxygens to result in covalent bond formation. Covalently bonded compounds have much lower melting points than ionic compounds (usually!).

20.21 Like aluminum and iron(III) ions, the chromium(III) ion will lose a hydrogen ion to a water molecule.

$[Cr(OH_2)_6]^{3+}(aq) + H_2O(l) \rightarrow [Cr(OH)(OH_2)_5]^{2+}(aq) + H_3O^+(aq)$

20.23 The insolubility of copper(I) chloride can be argued for reasons similar to those arguing why silver chloride is insoluble (Chapter 5). According to Fajan's Rules, cations with non-noble-gas configurations are likely to have

a more covalent character (in this case, the filled $3d$ orbitals can be polarized towards the anions). If the ionic charge in the crystal lattice is decreased by partial electron sharing, then the ion-water interaction will be less and the tendency to dissolve will, in turn, be less.
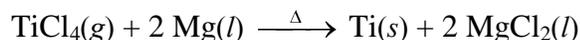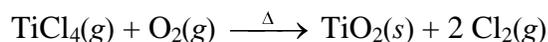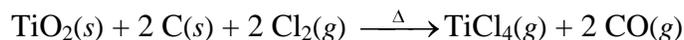
20.25 (a) In a well-aerated lake, the partial pressure of dioxygen would lead to a high positive potential, while the pH should be near neutral. FeO(OH) is the most likely species.

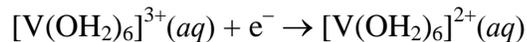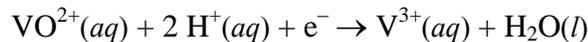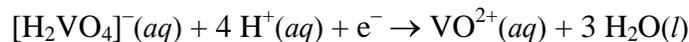(b) In acid oxidizing conditions, Fe^{3+} is the most probable species.

(c) Fe^{2+} is most likely in these acid, reducing conditions.

20.27 They both form anhydrous chlorides that react with water to release hydrogen chloride gas while their hexahydrates are water soluble. The anhydrous chlorides both function as Friedel-Craft catalysts. In the gas phase, their chlorides exist as dimers, Al_2Cl_6 and Fe_2Cl_6, respectively. On the other hand, iron(III) oxide is basic, while the oxide of aluminum is amphoteric. Also, iron(III) compounds are colored, while those of aluminum are white.
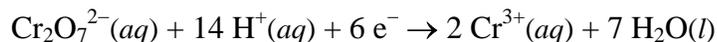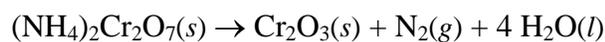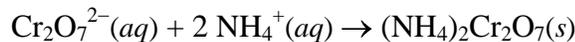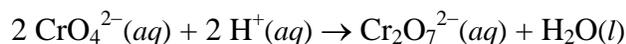
20.29 Titanium:

$$TiO_2(s) + 2\ C(s) + 2\ Cl_2(g) \xrightarrow{\Delta} TiCl_4(g) + 2\ CO(g)$$
$$TiCl_4(g) + O_2(g) \xrightarrow{\Delta} TiO_2(s) + 2\ Cl_2(g)$$
$$TiCl_4(g) + 2\ Mg(l) \xrightarrow{\Delta} Ti(s) + 2\ MgCl_2(l)$$

Vanadium:

$$[H_2VO_4]^-(aq) + 4\ H^+(aq) + e^- \rightarrow VO^{2+}(aq) + 3\ H_2O(l)$$
$$VO^{2+}(aq) + 2\ H^+(aq) + e^- \rightarrow V^{3+}(aq) + H_2O(l)$$
$$[V(OH_2)_6]^{3+}(aq) + e^- \rightarrow [V(OH_2)_6]^{2+}(aq)$$

Chromium:

$$CrO_4{}^{2-}(aq) + 2\ Ag^+(aq) \rightarrow Ag_2CrO_4(s)$$
$$CrO_4{}^{2-}(aq) + H_2O(l) \leftrightarrow HCrO_4{}^-(aq) + OH^-(aq)$$
$$2\ CrO_4{}^{2-}(aq) + 2\ H^+(aq) \rightarrow Cr_2O_7{}^{2-}(aq) + H_2O(l)$$
$$Cr_2O_7{}^{2-}(aq) + 2\ NH_4{}^+(aq) \rightarrow (NH_4)_2Cr_2O_7(s)$$
$$(NH_4)_2Cr_2O_7(s) \rightarrow Cr_2O_3(s) + N_2(g) + 4\ H_2O(l)$$
$$Cr_2O_7{}^{2-}(aq) + 14\ H^+(aq) + 6\ e^- \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)$$

$Cr_2O_7^{2-}(aq) + 2 K^+(aq) \rightarrow K_2Cr_2O_7(s)$

$K_2Cr_2O_7(s) + H_2SO_4(aq) \rightarrow 2 CrO_3(s) + K_2SO_4(aq) + H_2O(l)$

$K_2Cr_2O_7(s) + 4 NaCl(s) + 6 H_2SO_4(l) \rightarrow 2 CrO_2Cl_2(l) + 2 KHSO_4(s)$
$$+ NaHSO_4(s) + 3 H_2O(l)$$

$CrO_2Cl_2(l) + 4 OH^-(aq) \rightarrow CrO_4^{2-}(aq) + 2 Cl^-(aq) + 2 H_2O(l)$

$Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 e^- \rightarrow 2 Cr^{3+}(aq) + 7 H_2O(l)$

$2 Cr^{3+}(aq) + Zn(s) \rightarrow 2 Cr^{2+}(aq) + Zn^{2+}(aq)$

$2 Cr^{2+}(aq) + 4 CH_3COO^-(aq) + 2 H_2O(l) \rightarrow Cr_2(CH_3COO)_4(OH_2)_2(s)$

Manganese:

$MnO_4^-(aq) + e^- \rightarrow MnO_4^{2-}(aq)$

$MnO_4^{2-}(aq) + 2 H_2O(l) + 2 e^- \rightarrow MnO_2(s) + 4 OH^-(aq)$

$MnO_4^-(aq) + 2 H_2O(l) + 3 e^- \rightarrow MnO_2(s) + 4 OH^-(aq)$

$MnO_4^-(aq) + 8 H^+(aq) + 5 e^- \rightarrow Mn^{2+}(aq) + 4 H_2O(l)$

$Mn^{2+}(aq) + 2 OH^-(aq) \rightarrow Mn(OH)_2(s)$

$Mn(OH)_2(s) + OH^-(aq) \rightarrow MnO(OH)(s) + H_2O(l) + e^-$

Iron:

$[Fe(OH_2)_6]^{3+}(aq) + SCN^-(aq) \rightarrow [Fe(SCN)(OH_2)_5]^{2+}(aq) + H_2O(l)$

$[Fe(OH_2)_6]^{3+}(aq) + 4 Cl^-(aq) \leftrightarrow [FeCl_4]^-(aq) + 6 H_2O(l)$

$Fe^{3+}(aq) + 3 OH^-(aq) \rightarrow FeO(OH)(s) + H_2O(l)$

$[Fe(OH_2)_6]^{3+}(aq) + e^- \rightarrow [Fe(OH_2)_6]^{2+}(aq)$

$Fe^{3+}(aq) + 2 S_2O_3^{2-}(aq) \rightarrow [Fe(S_2O_3)_2]^-(aq)$

$[Fe(S_2O_3)_2]^-(aq) + Fe^{3+}(aq) \rightarrow 2 Fe^{2+}(aq) + S_4O_6^{2-}(aq)$

$Fe^{2+}(aq) + 2 OH^-(aq) \rightarrow Fe(OH)_2(s)$

$[Fe(OH_2)_6]^{2+}(aq) + NO(aq) \rightarrow [Fe(NO)(OH_2)_5]^{2+}(aq) + H_2O(l)$

$Fe(OH)_2(s) + OH^-(aq) \rightarrow FeO(OH)(s) + H_2O(l) + e^-$

$Fe^{2+}(aq) + 2 e^- \rightarrow Fe(s)$

$2 Fe(s) + 3 Cl_2(g) \rightarrow 2 FeCl_3(s)$

$Fe(s) + 2 HCl(g) \rightarrow FeCl_2(s) + H_2(g)$

Cobalt:

$[Co(OH_2)_6]^{3+}(aq) + e^- \rightarrow [Co(OH_2)_6]^{2+}(aq)$

$[Co(OH_2)_6]^{2+}(aq) + 4 Cl^-(aq) \rightarrow [CoCl_4]^{2-}(aq) + 6 H_2O(l)$

$Co^{2+}(aq) + 2 OH^-(aq) \rightarrow Co(OH)_2(s)$

$Co(OH)_2(s) + 2 OH^-(aq) \rightarrow Co(OH)_4^{2-}(aq)$

$Co(OH)_2(s) + OH^-(aq) \rightarrow CoO(OH)(s) + H_2O(l) + e^-$

$[Co(OH_2)_6]^{2+}(aq) + 6\ NH_3(aq) \rightarrow [Co(NH_3)_6]^{2+}(aq) + 6\ H_2O(l)$

$[Co(NH_3)_6]^{2+}(aq) \rightarrow [Co(NH_3)_6]^{3+}(aq) + e^-$

$O_2(g) + 2\ H_2O(l) + 4\ e^- \rightarrow 4\ OH^-(aq)$

Nickel:

$Ni(CO)_4(g) \rightarrow Ni(s) + 4\ CO(g)$

$Ni(s) \rightarrow Ni^{2+}(aq) + 2\ e^-$

$[Ni(OH_2)_6]^{2+}(aq) + 4\ Cl^-(aq) \rightarrow [NiCl_4]^{2-}(aq) + 6\ H_2O(l)$

$Ni^{2+}(aq) + 2\ OH^-(aq) \rightarrow Ni(OH)_2(s)$

$[Ni(OH_2)_6]^{2+}(aq) + 6\ NH_3(aq) \rightarrow [Ni(NH_3)_6]^{2+}(aq) + 6\ H_2O(l)$

Copper:

$2\ Cu(s) + 2\ H^+(aq) + 4\ Cl^-(aq) \rightarrow 2\ [CuCl_2]^-(aq) + H_2(g)$

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

$Cu(s) \rightarrow Cu^{2+}(aq) + 2\ e^-$

$[Cu(OH_2)_6]^{2+}(aq) + 4\ NH_3(aq) \rightarrow [Cu(NH_3)_4]^{2+}(aq) + 6\ H_2O(l)$

$[Cu(OH_2)_6]^{2+}(aq) + 4\ Cl^-(aq) \rightarrow [CuCl_4]^{2-}(aq) + 6\ H_2O(l)$

$Cu^{2+}(aq) + 2\ OH^-(aq) \rightarrow Cu(OH)_2(s)$

$Cu(OH)_2(s) + 2\ OH^-(aq) \rightarrow [Cu(OH)_4]^{2-}(aq)$

$Cu(OH)_2(s) \rightarrow CuO(s) + H_2O(l)$

Beyond the Basics

20.31   Addition of an anhydrous calcium compound will result in formation of the hexaaquacalcium ion. This will reduce the available mole of 'free' water and hence 'drive the reaction to the right':
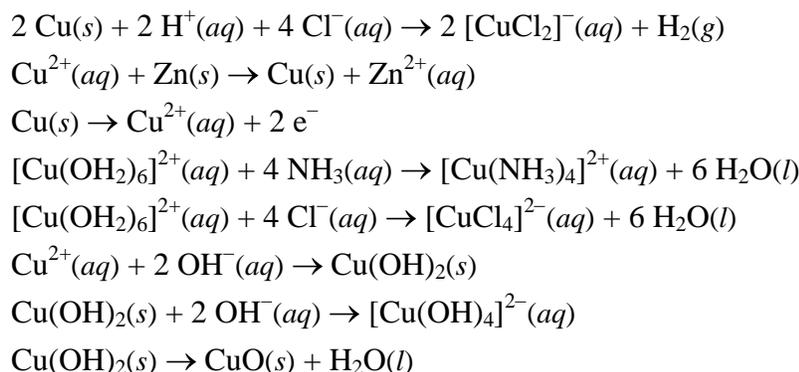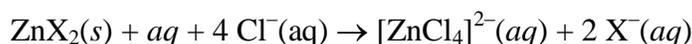
$$CaX_2(s) + aq \rightarrow [Ca(OH_2)_6]^{2+}(aq) + 2\ X^-(aq)$$

Addition of an anhydrous zinc compound results in the formation of the competing complexation of the zinc ion to give the tetrachlorozincate ion and hence 'drive the reaction to the left':

$$ZnX_2(s) + aq + 4\ Cl^-(aq) \rightarrow [ZnCl_4]^{2-}(aq) + 2\ X^-(aq)$$

20.33   Dichromate is in equilibrium with the chromate ion:

$Cr_2O_7^{2-}(aq) + H_2O(l) \rightarrow 2\ CrO_4^{2-}(aq) + 2\ H^+(aq)$
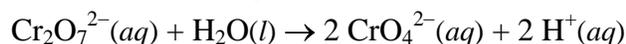
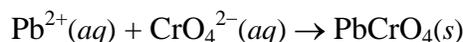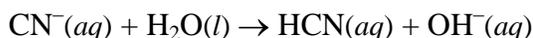The chromate then reacts with the lead ion to form insoluble lead(II) chromate (the dichromate being more soluble). As chromate ion is precipitated, more is produced, according to Le Châtelier's principle.

$$Pb^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow PbCrO_4(s)$$

20.35 (a)   A solution of cyanide ion will be basic:

$$CN^-(aq) + H_2O(l) \rightarrow HCN(aq) + OH^-(aq)$$

Thus the precipitate will probably be nickel(II) hydroxide:

$$Ni^{2+}(aq) + 2\ OH^-(aq) \rightarrow Ni(OH)_2(s)$$
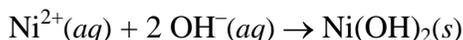
It is unlikely to be nickel(II) cyanide. Because nickel(II) chloride is soluble, nickel(II) cyanide also should be soluble (pseudohalide ion).

(b)   This should be the square planar tetracyanonickelate(II) ion:

$$Ni(OH)_2(s) + 4\ CN^-(aq) \rightarrow [Ni(CN)_4]^{2-}(aq) + OH^-(aq)$$
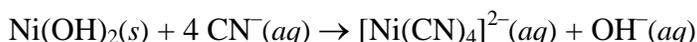
(c)   This must involve the addition of a fifth cyanide ion:

$$[Ni(CN)_4]^{2-}(aq) + CN^-(aq) \rightarrow Ni(CN)_5]^{3-}(aq)$$

20.37 (a)   The high-charge cation (Fe^{3+}) will have a lowish lattice energy when combined with a low-charge anion (ClO_4^-). Solubility depends upon the competing factors of lattice energy and ion hydration enthalpies. The lowish lattice energy results in solubility. The high-charge cation (Fe^{3+}) will have a very high lattice energy when combined with a high-charge anion (PO_4^{3-}). This will be greater than the sum of the hydration enthalpies and the compound will be insoluble.

(b)   Either: Ammonia and water are quite high in the spectrochemical series whereas phosphine and hydrogen sulfide are very low.
Or: Ammonia and water are hard bases, and the first row transition metals are mostly hard acids, while phosphine and hydrogen sulfide are soft bases.

(c)   As Fe^{3+} high spin has one electron in each orbital, there is no strong color from *d-d* transitions. The color must result from

charge transfer. Bromide is more easily reduced than chloride; thus the transition

$$Fe^{3+}Br^- \rightarrow Fe^{2+}Br^0$$
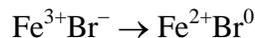
takes place at a lower energy (more in the visible region) than in the chloride compound.

20.39 Like the equivalent iron compound, this is probably nickel(II) disulfide(2−)—the disulfide ion being analogous to the dioxide(2−) ion. The sulfur oxidation state would be −1.

20.41 [A] Nickel(II) sulfide; [B] hydrogen sulfide; [C] hexaaquanickel(II) ion; [D] sulfur dioxide; [E] sulfur; [F] and [G] disulfur dichloride and sulfur dichloride; [H] hexaamminenickel(II) ion; [I] nickel(II) hydroxide; [J] nickel metal; [K] tetracarbonylnickel(0).

$NiS(s) + 2\ H^+(aq) \rightarrow Ni^{2+}(aq) + H_2S(g)$

$2\ H_2S(g) + 3\ O_2(g) \rightarrow 2\ H_2O(l) + 2\ SO_2(g)$

$2\ H_2S(g) + SO_2(g) \rightarrow 2\ H_2O(l) + 3\ S(s)$

$2\ S(s) + Cl_2(g) \rightarrow S_2Cl_2(l)$

$S(s) + Cl_2(g) \rightarrow SCl_2(l)$

$[Ni(OH_2)_6]^{2+}(aq) + 6\ NH_3(aq) \rightarrow [Ni(NH_3)_6]^{2+}(aq) + 6\ H_2O(l)$

$Ni^{2+}(aq) + 2\ OH^-(aq) \rightarrow Ni(OH)_2(s)$

$Ni^{2+}(aq) + Zn(s) \rightarrow Ni(s) + Zn^{2+}(aq)$

$Ni(s) + 4\ CO(g) \rightarrow Ni(CO)_4(l)$

20.43 Vanadium is the only transition metal whose chemistry matches the information provided.

20.45 Chromium-52 has 28 neutrons corresponding to a full neutron shell.

20.47 3+, as the shared oxygen would have an oxidation state of −2 (−1 with each chromium). The linear shape suggests there is a π-bonding Cr–O–Cr system. This would use the filled *p* orbitals on oxygen together with the part-empty d_{xy}, d_{xz}, and d_{yz} orbitals. The equivalent cobalt compound would probably have a bent Co–O–Co bond, as those *d* orbitals on cobalt are fully occupied and thus cannot be used for π bonding.
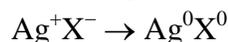
20.49   Under normal conditions, the reduction would be:

$[Fe(OH_2)_6]^{3+}(aq) + e^- \rightarrow [Fe(OH_2)_6]^{2+}(aq)$
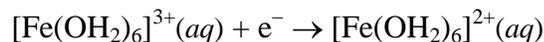
In the presence of high concentrations of chloride ion, the reaction would become:

$[FeCl_4]^-(aq) + e^- \rightarrow [FeCl_4]^{2-}(aq)$
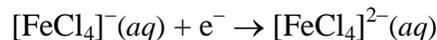
Presumably the chloride ligand has preferentially stabilized the 3+ oxidation state of the iron.

20.51   The charge transfer process can be represented as

$Ag^+X^- \rightarrow Ag^0X^0$

where X represents the halide ion. As the halide ion is more readily oxidized, the absorption of light will be of lower energy—more and more in the visible part of the spectrum. As iodide is the easiest oxidized and chloride the least, this represents the order of visible color intensity.

20.53   As calcium ion always has an oxidation state of 2+, it will replace the Mn^{2+} to give: $3Mn_2O_3 \cdot CaSiO_3$. Iron would most likely be in the Fe^{3+} oxidation state, in which case it would replace the Mn^{3+} ion to give: $3Fe_2O_3 \cdot MnSiO_3$. Titanium (as titanate) would replace the silicon in the silicate: $3Mn_2O_3 \cdot MnTiO_3$. Aluminum as Al^{3+} could replace the Mn^{3+} to give: $3Al_2O_3 \cdot MnSiO_3$, or as aluminate, it could replace silicon in silicate, though then the manganese would have to be Mn^{3+} to retain charge balance: $3Mn_2O_3 \cdot MnAlO_3$.

20.55   The ring structure suggests that there could be some form of π-bonding of the multiple-bonded ligands through the d orbitals of the nickel ion.

20.57   (a) $Fe(s) + O_2(g) \rightarrow Fe_2O_3(s)$
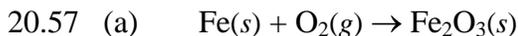
(b)   The layer of unreactive sodium silicate will coat the iron and prevent the continuation of the oxidation.

(c)   The red-hot iron would have reacted with water to give hydrogen gas.

$2\ Fe(s) + 3\ H_2O(l) \xrightarrow{\Delta} Fe_2O_3(s) + 3\ H_2(g)$

The explosion would have resulted from the hydrogen/oxygen mixture:

$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$