19.1: Occurrence, Preparation, and Properties of Transition Metals and Their Compounds

Q19.1.1

Write the electron configurations for each of the following elements:

a. Sc
b. Ti
c. Cr
d. Fe
e. Ru

S19.1.1

a. Sc: [Ar]4s^23d^1
b. Ti: [Ar]4s^23d^2
c. Cr: [Ar]4s^13d^5
d. Fe: [Ar]4s^23d^6
e. Ru: [Kr]5s^14d^7 (anomalous configuration)

Q19.1.2

Write the electron configurations for each of the following elements and its ions:

a. Ti
b. Ti^{2+}
S19.1.2

- a. \([\text{Ar}]4s^2\ 3d^2\)
- b. \([\text{Ar}]3d^2\)
- c. \([\text{Ar}]3d^1\)
- d. \([\text{Ar}]\)

Q19.1.3

Write the electron configurations for each of the following elements and its 3+ ions:

- a. La
- b. Sm
- c. Lu

La: \([\text{Xe}]6s^2\ 5d^1\), La\(^{3+}\): \([\text{Xe}]\);
Sm: \([\text{Xe}]6s^2\ 4f^6\), Sm\(^{3+}\): \([\text{Xe}]4f^5\);
Lu: \([\text{Xe}]6s^2\ 4f^{14}5d^1\), Lu\(^{3+}\): \([\text{Xe}]4f^{14}\)

Q19.1.4

Why are the lanthanoid elements not found in nature in their elemental forms?

Q19.1.5

Which of the following elements is most likely to be used to prepare La by the reduction of La\(_2\)O\(_3\): Al, C, or Fe? Why?

S19.1.5

Al is used because it is the strongest reducing agent and the only option listed that can provide sufficient driving force to convert La(III) into La.

Q19.1.6

Which of the following is the strongest oxidizing agent: \(\text{V}_2\text{O}_4\), \(\text{Cr}_2\text{O}_7^{2-}\), or \(\text{Mn}_2\text{O}_7\)?

S19.1.6

\(\text{Mn}_2\text{O}_7\)
Q19.1.7
Which of the following elements is most likely to form an oxide with the formula MO$_3$: Zr, Nb, or Mo?

S19.1.7
Mo

Q19.1.8
The following reactions all occur in a blast furnace. Which of these are redox reactions?

a. \(\text{\ce{3Fe2O3(s) + CO(g) -> 2Fe3O4(s) + CO2(g)}}\)

b. \(\text{\ce{Fe3O4(s) + CO(g) -> 3FeO(s) + CO2(g)}}\)

c. \(\text{\ce{FeO(s) + CO(g) -> Fe(l) + CO2(g)}}\)

d. \(\text{\ce{C(s) + O2(g) -> CO2(g)}}\)

e. \(\text{\ce{C(s) + CO2(g) -> 2CO(g)}}\)

f. \(\text{\ce{CaCO3(s) -> CaO(s) + CO2(g)}}\)

g. \(\text{\ce{CaO(s) + SiO2(s) -> CaSiO3(l)}}\)

S19.1.8
a, b, c, d, e

Q19.1.9
Why is the formation of slag useful during the smelting of iron?

S19.1.9
The CaSiO$_3$ slag is less dense than the molten iron, so it can easily be separated. Also, the floating slag layer creates a barrier that prevents the molten iron from exposure to O$_2$, which would oxidize the Fe back to Fe$_2$O$_3$.

Q19.1.10
Would you expect an aqueous manganese(VII) oxide solution to have a pH greater or less than 7.0? Justify your answer.

S19.1.10
In relation to the Lewis acid-base theory, the Lewis acid accepts lone pair electrons; thus, it is also known as the electron pair acceptor. This may be any chemical species. Acids are substances that must be lower than 7. Therefore, oxides of manganese is most likely going to become more acidic in (aq) solutions if the oxidation number increases.
Q19.1.11
Iron(II) can be oxidized to iron(III) by dichromate ion, which is reduced to chromium(III) in acid solution. A 2.5000-g sample of iron ore is dissolved and the iron converted into iron(II). Exactly 19.17 mL of 0.0100 M Na$_2$Cr$_2$O$_7$ is required in the titration. What percentage of the ore sample was iron?

S19.1.11
2.57%

Q19.1.12
How many cubic feet of air at a pressure of 760 torr and 0 °C is required per ton of Fe$_2$O$_3$ to convert that Fe$_2$O$_3$ into iron in a blast furnace? For this exercise, assume air is 19% oxygen by volume.

Q19.1.13
Find the potentials of the following electrochemical cell:

Cd | Cd$^{2+}$ ($M = 0.10$) || Ni$^{2+}$ ($M = 0.50$) | Ni

S19.1.13
0.167 V

Q19.1.14
A 2.5624-g sample of a pure solid alkali metal chloride is dissolved in water and treated with excess silver nitrate. The resulting precipitate, filtered and dried, weighs 3.03707 g. What was the percent by mass of chloride ion in the original compound? What is the identity of the salt?

Q19.1.15
The standard reduction potential for the reaction \(\ce{[Co(H2O)6]^3+}(aq)+\ce{e^-} \rightarrow \ce{[Co(H2O)6]^2+}(aq)\) is about 1.8 V. The reduction potential for the reaction \(\ce{[Co(NH3)6]^3+}(aq)+\ce{e^-} \rightarrow \ce{[Co(NH3)6]^2+}(aq)\) is +0.1 V. Calculate the cell potentials to show whether the complex ions, [Co(H$_2$O)$_6$]$^{2+}$ and/or [Co(NH$_3$)$_6$]$^{2+}$, can be oxidized to the corresponding cobalt(III) complex by oxygen.

S19.1.15
\(E^o = -0.6\) V, \(E^o\) is negative so this reduction is not spontaneous. \(E^o = +1.1\) V
Q19.1.16

Predict the products of each of the following reactions. (Note: In addition to using the information in this chapter, also use the knowledge you have accumulated at this stage of your study, including information on the prediction of reaction products.)

a. \(\ce{MnCO3}(s)+\ce{HI}(aq)\)
b. \(\ce{CoO}(s)+\ce{O2}(g)\)
c. \(\ce{La}(s)+\ce{O2}(g)\)
d. \(\ce{V}(s)+\ce{VCl4}(s)\)
e. \(\ce{Co}(s)+\ce{xS}(\ce{F2}(g))\)
f. \(\ce{CrO3}(s)+\ce{CsOH}(aq)\)

Q19.1.17

Predict the products of each of the following reactions. (Note: In addition to using the information in this chapter, also use the knowledge you have accumulated at this stage of your study, including information on the prediction of reaction products.)

a. \(\ce{Fe}(s)+\ce{H2SO4}(aq)\)
b. \(\ce{FeCl3}(aq)+\ce{NaOH}(aq)\)
c. \(\ce{Mn(OH)2}(s)+\ce{HBr}(aq)\)
d. \(\ce{Cr}(s)+\ce{O2}(g)\)
e. \(\ce{Mn2O3}(s)+\ce{HCl}(aq)\)
f. \(\ce{Ti}(s)+\ce{xS}(\ce{F2}(g))\)

S19.1.17

a. \(\ce{Fe}(s)+\ce{2H3O+}(aq)+\ce{SO4^2-}(aq)\rightarrow\ce{Fe^2+}(aq)+\ce{SO4^2-}(aq)+\ce{H2}(g)+\ce{2H2O}(l))\)
b. \(\ce{FeCl3}(aq)+\ce{3Na+}(aq)+\ce{3OH-}(aq)+\ce{Fe(OH)3}(s)+\ce{3Na+}(aq)+\ce{3Cl+}(aq)\)
c. \(\ce{Mn(OH)2}(s)+\ce{2H3O+}(aq)+\ce{2Br-}(aq)\rightarrow\ce{Mn^2+}(aq)+\ce{2Br-}(aq)+\ce{4H2O}(l))\)
d. \(\ce{4Cr}(s)+\ce{3O2}(g)\rightarrow\ce{2Cr2O3(s))}\)
e. \(\ce{Mn2O3(s)+6H3O+}(aq)+\ce{6Cl-}(aq)\rightarrow\ce{2MnCl3(s)+9H2O(l))}\)
\(\ce{Ti(F2(g)+\ce{TiF4(g))}\)

Q19.1.18

Describe the electrolytic process for refining copper.

S19.1.18

The electrolytic process for refining copper is to extract the copper through the process of electrolysis.
Predict the products of the following reactions and balance the equations.

a. Zn is added to a solution of Cr$_2$SO$_4$$_3$ in acid.
b. FeCl$_2$ is added to a solution containing an excess of Cr$_2$O$_7^{2-}$ in hydrochloric acid.
c. Cr$^{2+}$ is added to Cr$_2$O$_7^{2-}$ in acid solution.
d. Mn is heated with CrO$_3$.
e. CrO is added to 2HNO$_3$ in water.
f. FeCl$_3$ is added to an aqueous solution of NaOH.

In acid solution between pH 2 and pH 6, Cr$_2$O$_7^{2-}$ forms H$_r$CrO$_4^{-}$, which is in equilibrium with dichromate ion. The reaction is $\ce{2HCrO4-}(aq)?\ce{Cr2O7^2-}(aq)+\ce{H2O}(l)$. At other acidic pHs, the reaction is $\ce{3Cr^2+}(aq)+\ce{CrO4^2-}(aq)+\ce{8H3O+}(aq)?\ce{4Cr^3+}(aq)+\ce{12H2O}(l)$;

d. $\ce{8CrO3}(s)+\ce{9Mn}(s)?\ce{4Cr2O3}(s)+\ce{3Mn3O4}(s)$;
e. $\ce{CrO}(s)+\ce{2H3O+}(aq)+\ce{2NO3-}(aq)?\ce{Cr^2+}(aq)+\ce{2NO3-}(aq)+\ce{3H2O}(l)$;
f. $\ce{FeCl3}(s)+\ce{3NaOH}(aq)?\ce{Fe(OH)3}(s)+\ce{3Na+}(aq)+\ce{3Cl-}(aq)$

What is the gas produced when iron(II) sulfide is treated with a nonoxidizing acid?

Predict the products of each of the following reactions and then balance the chemical equations.

a. Fe is heated in an atmosphere of steam.
b. NaOH is added to a solution of Fe(NO$_3$)$_3$.
c. FeSO$_4$ is added to an acidic solution of KMnO$_4$.
d. Fe is added to a dilute solution of H$_2$SO$_4$.
e. A solution of Fe(NO$_3$)$_2$ and HNO$_3$ is allowed to stand in air.
f. FeCO$_3$ is added to a solution of HClO$_4$.
g. Fe is heated in air.
c. $\text{2CrO}_4^{-2}(aq) + \text{2H}^+(aq) \rightarrow \text{2CrO}_4^{-2}(aq) + \text{2H}_2O(l)$

d. $\text{6Fe}^{2+}(aq) + \text{Cr}_2\text{O}_7^{2-}(aq) + \text{14H}^+(aq) \rightarrow \text{6Fe}^{3+}(aq) + \text{2Cr}^{3+}(aq) + \text{7H}_2O(l)$

e. $\text{Fe}(s) + \text{2H}^+(aq) + \text{SO}_4^{2-}(aq) \rightarrow \text{Fe}^{2+}(aq) + \text{SO}_4^{2-}(aq) + \text{H}_2(g) + \text{2H}_2O(l)$

f. $\text{4Fe}^{2+}(aq) + \text{O}_2(g) + \text{4HNO}_3(aq) \rightarrow \text{4Fe}^{3+}(aq) + \text{2H}_2O(l) + \text{4NO}_3^{-}(aq)$

g. $\text{FeCO}_3(s) + \text{2HClO}_4(aq) \rightarrow \text{Fe(ClO}_4)_2(aq) + \text{H}_2O(l) + \text{CO}_2(g)$

h. $\text{3Fe}(s) + \text{2O}_2(g) \rightarrow \text{Fe}_3\text{O}_4(s)$

Q19.1.22

Balance the following equations by oxidation-reduction methods; note that three elements change oxidation state.

$\text{Co(NO}_3)_2(s) \rightarrow \text{Co}_2\text{O}_3(s) + \text{NO}_2(g) + \text{O}_2(g)$

Q19.1.23

Dilute sodium cyanide solution is slowly dripped into a slowly stirred silver nitrate solution. A white precipitate forms temporarily but dissolves as the addition of sodium cyanide continues. Use chemical equations to explain this observation. Silver cyanide is similar to silver chloride in its solubility.

S19.1.23

As CN$^-$ is added,

$\text{Ag}^+(aq) + \text{CN}^-(aq) \rightarrow \text{AgCN}(s)$

As more CN$^-$ is added,

$\text{Ag}^+(aq) + \text{2CN}^-(aq) \rightarrow [\text{Ag(CN)}_2]^{-}(aq)$

$\text{AgCN}(s) + \text{CN}^-(aq) \rightarrow [\text{Ag(CN)}_2]^{-}(aq)$

Q19.1.24

Predict which will be more stable, $\text{[CrO}_4]^{2-}$ or $\text{[WO}_4]^{2-}$, and explain.

S19.1.24

$\text{[CrO}_4]^{2-}$ is more stable because Chromium is in the 3d orbital while Tungsten is in the 4d orbital, which has a higher energy level and makes it less stable.
Q19.1.25

Give the oxidation state of the metal for each of the following oxides of the first transition series. (Hint: Oxides of formula $M_3O_4$ are examples of mixed valence compounds in which the metal ion is present in more than one oxidation state. It is possible to write these compound formulas in the equivalent format $MO\cdot M_2O_3$, to permit estimation of the metal’s two oxidation states.)

a. $Sc_2O_3$
b. $TiO_2$
c. $V_2O_5$
d. $CrO_3$
e. $MnO_2$
f. $Fe_3O_4$
g. $Co_3O_4$
h. $NiO$
i. $Cu_2O$

Q19.2.1

Indicate the coordination number for the central metal atom in each of the following coordination compounds:

a. $[Pt(H_2O)_2Br_2]$
b. $[Pt(NH_3)(py)(Cl)(Br)]$ (py = pyridine, $C_5H_5N$)
c. $[Zn(NH_3)Cl_2]$
d. $[Zn(NH_3)(py)(Cl)(Br)]$
e. $[Ni(H_2O)Cl_2]$tf. $[Fe(en)_2(CN)_2]^+$ (en = ethylenediamine, $C_2H_8N_2$)

S19.1.25

$Sc^{3+}$; $Ti^{4+}$; $V^{5+}$; $Cr^{6+}$; $Mn^{4+}$; $Fe^{2+}$ and $Fe^{3+}$; $Co^{2+}$ and $Co^{3+}$; $Ni^{2+}$; $Cu^+$

19.2: Coordination Chemistry of Transition Metals

Q19.2.1

Indicate the coordination number for the central metal atom in each of the following coordination compounds:

a. $[Pt(H_2O)_2Br_2]$
b. $[Pt(NH_3)(py)(Cl)(Br)]$ (py = pyridine, $C_5H_5N$)
c. $[Zn(NH_3)Cl_2]$
d. $[Zn(NH_3)(py)(Cl)(Br)]$
e. $[Ni(H_2O)Cl_2]$tf. $[Fe(en)_2(CN)_2]^+$ (en = ethylenediamine, $C_2H_8N_2$)

S19.2.1

a. The 2 aqua and the 2 bromo ligands form a total of 4 coordinate covalent bonds and as a result coordination number is 4.
b. The ammine, pyridine, chloro and bromo each form one coordinate covalent bond that gives a total of 4 and hence $CN=4$
c. two ammine and two chloro ligands give a total of 4 coordinate covalent bonds and a $CN = 4$. 
d. one ammine, a pyrimidine, a chloro and a bromo ligand give a total of 4 covalent bonds, resulting in \( \text{CN} = 4 \).

e. 4 aqua ligands and 2 chloro ligands form a total of 6 coordinate covalent bonds and a \( \text{CN} = 6 \)

f. ethylenediamine is a bidentate ligand that forms two coordinate covalent bonds and along with two cyano ligands it forms a total of 6 bonds. hence has a \( \text{CN} = 6 \)

**Q19.2.2**

Give the coordination numbers and write the formulas for each of the following, including all isomers where appropriate:

a. tetrahydroxozincate(II) ion (tetrahedral)

b. hexacyanopalladate(IV) ion

c. dichloraurate ion (note that *aurum* is Latin for "gold")

d. diaminedichloroplatinum(II)

e. potassium diaminetetrachlorochromate(III)

f. hexaaminecobalt(III) hexacyanochromate(III)

g. dibromobis(ethylenediamine) cobalt(III) nitrate

**S19.2.2**

a. 4, \([\text{Zn(OH)}_4]^{2-}\);

b. 6, \([\text{Pd(CN)}_6]^{2-}\);

c. 2, \([\text{AuCl}_2]^{-}\);

d. 4, \([\text{Pt(NH}_3)_2\text{Cl}_2]^{-}\);

e. 6, \([\text{K(Cr(NH}_3)_2\text{Cl}_4}]^{-}\);

f. 6, \([\text{Co(NH}_3)_6][\text{Cr(CN)}_6]\);

g. 6, \([\text{Co(en)}_2\text{Br}_2]\text{NO}_3\)

**Q19.2.3**

Give the coordination number for each metal ion in the following compounds:

a. \([\text{Co(CO}_3]_3]^{3-}\) (note that \(\text{CO}_3^{2-}\) is bidentate in this complex)

b. \([\text{Cu(NH}_3]_4]^{2+}\)

c. \([\text{Co(NH}_3]_4\text{Br}_2][\text{SO}_4]_3\)

d. \([\text{Pt(NH}_3]_4][\text{PtCl}_4]\)

e. \([\text{Cr(en)}_3]([\text{NO}_3])_3\)

f. \([\text{Pd(NH}_3]_2\text{Br}_2]\) (square planar)

g. \(\text{K}_3[\text{Cu(Cl)}_5]\)

h. \([\text{Zn(NH}_3]_2\text{Cl}_2]\)
Q19.2.4

Sketch the structures of the following complexes. Indicate any cis, trans, and optical isomers.

a. \([Pt(H_2O)_2Br_2]\) (square planar)
b. \([Pt(NH_3)(py)(Cl)(Br)]\) (square planar, \(py = \text{pyridine, } C_5H_5N\))
c. \([Zn(NH_3)_3Cl]^+\) (tetrahedral)
d. \([Pt(NH_3)_3Cl]^+\) (square planar)
e. \([Ni(H_2O)_4Cl_2]\)
f. \([Co(C_2O_4)_2Cl_2]^{3-}\) (note that \(\text{C}_2\text{O}_4^{2-}\) is the bidentate oxalate ion, \(\text{−O}_2\text{CCO}_2^{-}\))

S19.2.4

a. \([Pt(H_2O)_2Br_2]\):

\[
\begin{align*}
\text{cis} & : & \text{trans} & :
\end{align*}
\]

b. \([Pt(NH_3)(py)(Cl)(Br)]\):

\[
\begin{align*}
\text{Br} & : & \text{pt} & : & \text{Cl} & : & \text{py} & : & \text{NH}_3
\end{align*}
\]

c. \([Zn(NH_3)_3Cl]^+\) :

\[
\begin{align*}
\text{Cl} & : & \text{Zn} & : & \text{NH}_3 & : & \text{NH}_3 & : & \text{NH}_3
\end{align*}
\]

d. \([Pt(NH_3)_3Cl]^+\) :
Q19.2.5

Draw diagrams for any cis, trans, and optical isomers that could exist for the following (en is ethylenediamine):

a. \([\text{Co}(\text{en})_2(\text{NO}_2)\text{Cl}]^+\)

b. \([\text{Co}(\text{en})_2\text{Cl}_2]^+\)

c. \([\text{Pt}(\text{NH}_3)_2\text{Cl}_4]\)

d. \([\text{Cr}(\text{en})_3]^{3+}\)

e. \([\text{Pt}(\text{NH}_3)_2\text{Cl}_2]\)

Q19.2.6

Name each of the compounds or ions given in Exercise Q19.2.3, including the oxidation state of the metal.
a. tricarbonatocobaltate(III) ion;
b. tetraaminecopper(II) ion;
c. tetraaminedibromocobalt(III) sulfate;
d. tetraamineplatinum(II) tetrachloroplatinate(II);
e. tris-(ethylenediamine)chromium(III) nitrate;
f. diaminedibromopalladium(II);
g. potassium pentachlorocuprate(II);
h. diaminedichlorozinc(II)

Name each of the compounds or ions given in Exercise Q19.2.5.

Specify whether the following complexes have isomers.

a. tetrahedral $[\text{Ni(CO)}_2\text{(Cl)}_2]$  
   The two Cl ligands can be *cis* or *trans*. When they are *cis*, there will also be an optical isomer.

Predict whether the carbonate ligand $\text{CO}_3^{2-}$ will coordinate to a metal center as a monodentate, bidentate, or tridentate ligand.

$\text{CO}_3^{2-}$ will coordinate to a metal center as a monodentate ligand.

Draw the geometric, linkage, and ionization isomers for $[\text{CoCl}_5\text{CN}][\text{CN}]$. 

19.3: Spectroscopic and Magnetic Properties of Coordination Compounds

Q19.3.1
Determine the number of unpaired electrons expected for \([\text{Fe(NO}_2)_6]^{3-}\) and for \([\text{FeF}_6]^{3-}\) in terms of crystal field theory.

Q19.3.2
Draw the crystal field diagrams for \([\text{Fe(NO}_2)_6]^{4-}\) and \([\text{FeF}_6]^{2-}\). State whether each complex is high spin or low spin, paramagnetic or diamagnetic, and compare \(\Delta_{\text{oct}}\) to \(P\) for each complex.

S19.3.2

Q19.3.3
Give the oxidation state of the metal, number of \(d\) electrons, and the number of unpaired electrons predicted for \([\text{Co(NH}_3)_6]Cl_3\).
Q19.3.4

The solid anhydrous solid CoCl₂ is blue in color. Because it readily absorbs water from the air, it is used as a humidity indicator to monitor if equipment (such as a cell phone) has been exposed to excessive levels of moisture. Predict what product is formed by this reaction, and how many unpaired electrons this complex will have.

S19.3.4

[Co(H₂O)₆]Cl₂ with three unpaired electrons.

Q19.3.5

Is it possible for a complex of a metal in the transition series to have six unpaired electrons? Explain.

Q19.3.6

How many unpaired electrons are present in each of the following?

a. [CoF₆]³⁻ (high spin)
b. [Mn(CN)₆]³⁻ (low spin)
c. [Mn(CN)₆]⁴⁻ (low spin)
d. [MnCl₆]⁴⁻ (high spin)
e. [RhCl₆]³⁻ (low spin)

S19.3.6

4; 2; 1; 5; 0

Q19.3.7

Explain how the diphosphate ion, [O₃P=O−PO₃]⁴⁻, can function as a water softener that prevents the precipitation of Fe²⁺ as an insoluble iron salt.

Q19.3.8

For complexes of the same metal ion with no change in oxidation number, the stability increases as the number of electrons in the t₂⁰ orbitals increases. Which complex in each of the following pairs of complexes is more stable?

a. [Fe(H₂O)₆]²⁺ or [Fe(CN)₆]⁴⁻
b. [Co(NH₃)₆]³⁺ or [CoF₆]³⁻
c. [Mn(CN)₆]⁴⁻ or [MnCl₆]⁴⁻
S19.3.8

\[ \text{[Fe(CN)₆]^{4-}; [Co(NH₃)₆]^{3+}; [Mn(CN)₆]^{4-}} \]

Q19.3.9

Trimethylphosphine, P(CH₃)₃, can act as a ligand by donating the lone pair of electrons on the phosphorus atom. If trimethylphosphine is added to a solution of nickel(II) chloride in acetone, a blue compound that has a molecular mass of approximately 270 g and contains 21.5% Ni, 26.0% Cl, and 52.5% P(CH₃)₃ can be isolated. This blue compound does not have any isomeric forms. What are the geometry and molecular formula of the blue compound?

Q19.3.10

Would you expect the complex [Co(en)₃]Cl₃ to have any unpaired electrons? Any isomers?

S19.3.10

The complex does not have any unpaired electrons. The complex does not have any geometric isomers, but the mirror image is nonsuperimposable, so it has an optical isomer.

Q19.3.11

Would you expect the Mg₃[Cr(CN)₆]₂ to be diamagnetic or paramagnetic? Explain your reasoning.

Q19.3.12

Would you expect salts of the gold ion, Au⁺, to be colored? Explain.

S19.3.12

No. Au⁺ has a complete 5d sublevel.

Q19.3.13

[CuCl₄]²⁻ is green. [Cu(H₂O)₆]²⁺ is blue. Which absorbs higher-energy photons? Which is predicted to have a larger crystal field splitting?