Ch 20 Chemistry of Metals

The majority of elements, about 88% are metals.

We concentrate on:
1. IA alkali metals: Na; K
2. IIA alkaline earth metals: Mg; Ca
3. the transition metals: Cr; Mn; Fe; Co; Ni; Cu; Zn

Content:

§ 20-1 Meallurgy (冶金學)

The processes by which metals are extracted from their ores fall within the science of metallurgy.

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The chemical reactions involved depend on the type of ore.
chloride ores: electrolysis.
oxide ores: electrolysis for active metal oxides and less active oxides reduced by carbon.
sulfide ores: heating with air or pure oxygen.

§ Chloride ores:

Sodium metal is obtained by electrolysis of molten sodium chloride.

Anode: $2\ Cl^-(\mathbf{l}) \longrightarrow Cl_2(g) + 2\ e^-$

Cathode: $2\ Na^+(\mathbf{l}) + 2\ e^- \longrightarrow 2\ Na(\mathbf{l})$

$$2\ NaCl(\mathbf{l}) \longrightarrow 2\ Na(\mathbf{l}) + Cl_2(g)$$

The cell is operated at about 600℃ to keep the electrolyte molten; calcium chloride is added to the lower molting point.

Ex. 20.1: Taking ΔH^o and ΔS^o for the reaction

$$2\ \mathrm{NaCl}(\mathbf{l}) \longrightarrow 2\ \mathrm{Na}(\mathbf{l}) + \mathrm{Cl}_2(g)$$

to be +820 kJ and +0.180 kJ/k, respectively, calculate

a). ΔG^o at the electrolysis temperature, 600℃.

b). the voltage required to carry out the electrolysis.

Ans: (a) $\Delta G^o = \Delta \mathrm{H^o} - \mathrm{T}\Delta \mathrm{S^o}$

$= (+820) - (873) \cdot (+0.1800)$

$= +663$ kJ

(b) $\Delta G^o = -\ \mathrm{n\ F\ E^o}$

$$\mathrm{E^o} = -\frac{\Delta G^o}{n\ \mathrm{F}} = -\frac{663\times10^3}{2\cdot(9.648\times10^4)} = -3.44\ \mathrm{V}$$

§ Oxide ores: Al from Al_2O_3; Fe from Fe_2O_3

Oxides of very active metals such as calcium or aluminum are reduced by electrolysis.

§ Al from Bauxite ore: (鋁礦砂)

$$2\ \mathrm{Al_2O_3}(\mathbf{l}) \longrightarrow 4\ \mathrm{Al}(\mathbf{l}) + 3\ \mathrm{O_2(g)}$$

Cryolite (冰晶石); Na_3AlF_6, is added to Al_2O_3 to produce a mixture melting at about 1000℃. ⇒ 助熔劑

About 30 kJ of electrical energy is consumed per gram of aluminum formed.

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The high energy requirement explains in large part the volume of recycling aluminum cans.

With less active metals, a chemical reducing agent can be used to reduce a metal cation to the element. The most common reducing agent in metallurgical processes is carbon, in the form of coke or, more exactly, carbon monoxide formed from the coke.

§ Fe from Hematite ore: (赤鐵礦)

Several different reactions occur:

1. Conversion of carbon to carbon monoxide.

$$2C(s) \longrightarrow 2CO(g) \qquad \Delta H = -221\ kJ$$

2. Reduction of Fe^{3+} ions to Fe.

$$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(\mathbf{l}) + 3CO_2(g)$$

3. Forming of slag. 溶渣; $CaSiO_3$ 偏矽酸鈣

$$CaCO_3(s) \xrightarrow{800^oC} CaO(s) + CO_2(g)$$
$$CaO(s) + SiO_2 \longrightarrow CaSiO_3(\mathbf{l})$$

The product that comes out of the blast furnace, called “pig iron” (生鐵) Is highly impure. On the average, it contains about 4% carbon along with lesser amount of Si, Mg and P.

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To make steel from pig iron, the carbon content must be lower below 2%.

Ex. 20.2: Write the balanced equations for the reduction of each of the following oxide ores by carbon monoxide.

a). ZnO b). MnO_2 c). Fe_3O_4

$$Ans: \ a).\ ZnO(s) + CO(g) \longrightarrow Zn(s) + CO_2(g)$$
$$b).\ MnO_2(s) + 2CO(g) \longrightarrow Mn(s) + 2CO_2(g)$$
$$c).\ Fe_3O_4 + 4CO(g) \longrightarrow 3Fe(s) + 4CO_2(g)$$

§ Sulfide ores:

Sulfide ores, after preliminary treatment, most often undergo roasting, that is, heating with air or pure oxygen then reduced by CO.

Ex: ZnS:

$$2ZnS(s) + 3O_2(g) \longrightarrow 2ZnO(s) + 2SO_2(g)$$

Then ZnO can be reduced to the metal with carbon.

$$ZnO(s) + C(s) \longrightarrow Zn(s) + CO(g)$$

§ Cinnabar 辰砂, the sulfide ore of mercury; HgS

$$HgS(s) + O_2(g) \longrightarrow Hg(s) + SO_2(g)$$

§ Chalcocite 輝銅礦, Cu_2S copper(II) sulfide.

$$Cu_2S(s) + O_2(g) \longrightarrow 2Cu(s) + SO_2(g)$$

The solid produced is called “blister copper” (泡銅). It has irregular appearance due to air bubbles that enter the copper while it is still molten. Copper is then purified by electrolysis.

Anode: blister copper.

$$Cu(s, \text{ impure}) \longrightarrow Cu^{2+}(aq) + 2e^-$$

Cathode: a piece of pure copper.

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s, \text{pure})$$

Net equation: $Cu(s, \text{ impure}) \longrightarrow Cu(s, \text{pure})$

Electrolyte: 0.5 to 1.0 M $CuSO_4$, adjusted to pH= 0 (1.0M) with sulfuric acid.

Thus the net effect of electrolysis is to transfer copper metal from the impure blister copper used as one electrode to the pure copper sheet used as the other electrode. Electrolytic copper is 99.95% pure.

Ex. 20.3: A major ore of bismuth (III) sulfide, Bi_2S_3. By roasting in air, it is converted to the corresponding oxide. Sulfur oxide is a by-product. What volume of SO_2 at 25℃ and 1.00 atm, is formed from one metric ton (10^6 g) of ore containing 1.25% Bi_2S_3？

Ans:

$$2Bi_2S_3(s) + 9O_2(g) \longrightarrow 2Bi_2O_3(s) + 6SO_2(g)$$

$$MM_{Bi_2S_3} = 514.2 \text{ g/mol}$$

$$n_{Bi_2S_3} = \frac{1.25\% \cdot 10^6}{514.2} = 24.3 \text{ mol}$$

$$n_{SO_2} = 24.3 \cdot \frac{9}{2} = 72.9 \text{ mol}$$

$$V_{SO_2} = \frac{nRT}{P} = \frac{72.9 \cdot 0.0821 \cdot 298}{1.00} = 1.78 \times 10^3 \text{ L}$$

§ **Native** metals; Au

A few very unreactive metals, notably silver and gold, are found in native in element form, mixed with large amount of rocky material.

Nowadays, the ore is treated with very dilute (0.01M) sodium cyanide (NaCN) solution.

$$4Au(s) + 8CN^-(aq) + O_2(g) + 2H_2O(\mathbf{l}) \longrightarrow 4Au(CN)_2^-(aq) + 4OH^-(aq)$$

Metallic gold is recovered from solution by adding zinc.

$$Zn(s) + 2Au(CN)_2^-(aq) \longrightarrow Zn(CN)_4^{2-}(aq) + 2Au(s)$$

The gold in the complex is reduced to the metal.

§ 20-2 Reactions of the Alkali and Alkaline Earth Metals

The metals in Group 1 and 2 are among the most reactive of all elements. The high reactivity is due to low ionization energy and high E^o_{ox} values.

IA and IIA metals are commonly stored under dry mineral oil or kerosene to prevent them from reacting with oxygen or water vapor in the air.

Table 20.1 Reactions of the Alkali and Alkaline Earth Metals

Reactant	Product	Comments
	Alkali Metals (M)	
$H_2(g)$	$MH(s)$	On heating in hydrogen gas
$X_2(g)$	$MX(s)$	X = F, Cl, Br, I
$N_2(g)$	$M_3N(s)$	Only Li reacts; product contains N^{3-} ion
$S(s)$	$M_2S(s)$	On heating
$O_2(g)$	$M_2O(s)$	Li; product is an oxide (O^{2-} ion)
	$M_2O_2(s)$	Na; product is a peroxide (O_2^{2-} ion)
	$MO_2(s)$	K, Rb, Cs; product is a superoxide (O_2^- ion)
$H_2O(l)$	$H_2(g)$, M^+, OH^-	Violent reaction with Na, K
	Alkaline Earth Metals (M)	
$H_2(g)$	$MH_2(s)$	All except Be; heating required
$X_2(g)$	$MX_2(s)$	Any halogen
$N_2(g)$	$M_3N_2(s)$	All except Be; heating required
$S(s)$	$MS(s)$	On heating
$O_2(g)$	$MO(s)$	All; product contains O^{2-} ion
	$MO_2(s)$	Ba; product contains O_2^{2-} ion
$H_2O(l)$	$H_2(g)$, M^{2+}, OH^-	Ca, Sr, Ba

Ex. 20.4: Write the balanced equations for the reaction of

a). sodium with hydrogen？

b). barium with oxygen？

Ans:

$$a).\ 2Na^{+}(s) + H_2(g) \longrightarrow 2NaH(s)$$

$$b).\ 2Ba(s) + O_2(g) \longrightarrow 2BaO(s)$$ 氧化鋇

$$Ba(s) + O_2(g) \longrightarrow BaO_2(s)$$ 過氧化鋇

§ Reactions with hydrogen

IA: $2M + H_2(g) \longrightarrow 2M^{+}H^{-}$

IIA: $M + H_2(g) \longrightarrow M^{2+}H^{-}$ (Be無法反應)

MH and MH_2 are white crystalline solids, they are often referred to as saline hydrides because of their physical resemblance to NaCl. Chemically, they behave quite differently from NaCl; for example they react with water to produce hydrogen gas.

$$NaH(s) + H_2O(\mathbf{l}) \longrightarrow H_2(g) + Na^{+}(aq) + OH^{-}(aq)$$

$$CaH_2(s) + H_2O(\mathbf{l}) \longrightarrow 2H_2(g) + Ca^{2+}(aq) + 2OH^{-}(aq)$$

Saline hydrides can serve as compact, portable sources of hydrogen gas for inflating life rafts and balloons.

§ Reaction with water:

IA: $2M + 2H_2O(\mathbf{l}) \longrightarrow H_2(g) + 2M^{+}(aq) + 2OH^{-}(aq)$

violent reaction with Na, K

IIA: $M + H_2O(\mathbf{l}) \longrightarrow H_2(g) + M^{2+}(aq) + OH^{-}(aq)$ M: Ca, Sr, Ba

例外: $Mg + H_2O(g) \longrightarrow MgO(s) + H_2(g)$

§ Reaction with oxygen:

IA:

$$M + O_2(g) \longrightarrow M_2O \quad \text{M: Li}$$
$$M_2O_2 \quad \text{M: Na}$$
$$MO_2 \quad \text{M: K; Rb; Cs}$$

IIA:

$$M + O_2(g) \longrightarrow MO \quad \text{M: Be; Mg; Ca; Sr; Ba; Ra}$$
$$MO_2 \quad \text{M: Ba}$$

The oxides of these metals react with water to form hydroxides.

$$Li_2O(s) + H_2O(l) \longrightarrow 2LiOH(s)$$
$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s)$$
$$Na_2O_2(s) + H_2O(l) \longrightarrow 2Na^+(aq) + OH^-(aq) + H_2O_2(aq)$$
$$4KO_2(s) + 2H_2O(l) \longrightarrow 4KOH(s) + 3O_2(g)$$

KO is used in self-contained breathing devices for firefighters and miners.

Ex. 20.5: Consider the compounds strontium hydride (SrH_2), radium peroxide (RaO_2), cesium superoxide (CsO_2).

a). give the formulas of these compounds.

b). write equations for the formation of these compounds from the elements.

c). write equations for the reaction of strontium hydride (SrH_2) and radium peroxide (RaO_2) with water.

Ans:

a). storntium hydride: SrH_2

radium peroxide: RaO_2

cesium superoxide: CsO_2

b). $Sr(s) + H_2(g) \longrightarrow SrH_2(s)$

$Ra(s) + O_2(g) \longrightarrow RaO_2(s)$

$Cs(s) + O_2(g) \longrightarrow CsO_2(s)$

c). $SrH_2(s) + 2H_2O(l) \longrightarrow 2H_2(g) + Sr^{2+}(aq) + 2OH^-(aq)$

$RaO_2(s) + 2H_2O(l) \longrightarrow 2H_2O_2(g) + Ra^{2+}(aq) + 2OH^-(aq)$

§ 20-3 Redox Chemistry of the Transition Metals

Transition metals typically show several different oxidation numbers in their compounds.

Cu: +1, +2

Fe: +2. +3

Co: +2. +3

Mn: +2,+4,+7

§ Reaction of the transitional metals with oxygen:

過渡金屬氧化物中過渡金屬之氧化數大多爲 +2, 例外: Cu_2O: +1; $Co_3O_4 = Co^{2+}O \cdot Co_2^{3+}O_3$.

一般過渡金屬氧化物, 多直接由過渡金屬與氧作用生成. 例外:

$$Ag_2O: \quad 2Ag^+(aq) + 2OH^-(aq) \longrightarrow Ag_2O(s) + H_2O(\mathbf{l})$$
$$CoO: \quad CoCO_3(s) \longrightarrow CoO(s) + CO_2(g)$$

§ 123 compound: $Y_1Ba_2Cu_3O_x$ x: 6.5 to 7.2 $\Rightarrow$ superconductor

These compounds on cooling to about 100 K (-173℃), their electrical resistance drops to zero.

$\Downarrow$

Superconductor

§ Reaction of transitional metals with acids:

Any metal with a positive standard oxidation voltage, $E^o_{ox} > 0$, can be oxidized by the H^+ ions present in a 1 M solution of a strong acid.

$\Downarrow$

$E^o_{ox} \uparrow \Rightarrow$ reactivity $\uparrow$

Ex:

$$Ni(s) + 2H^+(aq) \longrightarrow Ni^{2+}(aq) + H_2(g)$$
$$Fe(s) + 2H^+(aq) \longrightarrow Fe^{2+}(aq) + H_2(g)$$

Ex. 20.6: Write the balanced equations for the reactions, if any, at standard conditions of
a). chromium with hydrochloric acid.
b). silver with nitric acid.

Ans:

a).

$$\mathrm{Cr(s)} \longrightarrow \mathrm{Cr^{2+}}(aq) + 2\mathrm{e^-} \qquad E^o_{ox} = +0.912\ \mathrm{V}$$

$$2H^+(aq) + 2\mathrm{e^-} \longrightarrow \mathrm{H_2}(g) \qquad E^o_{red} = +0.000\ \mathrm{V}$$

$$\mathrm{Cr(s)} + 2\mathrm{H^+}(aq) \longrightarrow \mathrm{Cr^{2+}}(aq) + \mathrm{H_2(g)} \qquad E^o = +0.912\ \mathrm{V}$$

b).

$$3\cdot[\ \mathrm{Ag(s)} \longrightarrow \mathrm{Ag^+}(aq) + \mathrm{e^-}\ ] \qquad E^o_{ox} = -0.799\ \mathrm{V}$$

$$NO_3^-(aq) + 4\mathrm{H^+}(aq) + 3\mathrm{e^-} \longrightarrow \mathrm{NO(g)} + 2\mathrm{H_2}O \qquad E^o_{red} = +0.964\ \mathrm{V}$$

$$3\mathrm{Ag(s)} + \mathrm{NO_3^-}(aq) + 4\mathrm{H^+}(aq) \longrightarrow 3\mathrm{Ag^+}(aq) + \mathrm{NO(g)} + 2\mathrm{H_2O} \qquad E^o = +0.165\ \mathrm{V}$$

Gold is not oxidized by nitric acid, it can be brought into solution in aqua regia, a 1 : 3 mixture by volume of 12 M HCl and 16 M HNO_3.

$$Au(s) + 4\mathrm{H^+}(aq) + 4\mathrm{Cl^-}(aq) + \mathrm{NO_3^-}(aq) \longrightarrow \mathrm{AuCl_4^-}(aq) + \mathrm{NO(g)} + 2\mathrm{H_2}O(\mathbf{l})$$

§ Equilibria between different cations of a transition metal

Several transitional metals form more than one cation.

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It is possible to decide on the relative stabilities of different transition metal cations in water solution.

Cations for which E^o_{red} is large, positive number are readily reduced and hence tend to unstable in water solution.

∴ Mn^{3+} cations are never found in water solution.

§ Disproportionate 歧化

In water solution, copper (I) salts disproportionate, undergoing reduction (to copper metal) and oxidation (to Cu^{2+}) at the same time.

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

$E^{o} = +0.518\ V + (-0.161\ V)$

$= +0.357\ V$

Table 20.4:

Ex. 20.7: Using Table 20.4, find

a). three different cations, in addition to Mn^{3+}, that react with H_2O form $O_2(g)$ (E^{o}_{ox} H_2O = -1.229 V).

b). another cation, in addition to Cu^{+}, that disproportionates in water.

c). two other cations, in addition to Cr^{2+} and Fe^{2+}, that are oxidized by $O_2(g)$ dissolved in water (E^{o}_{red} O_2 = +1.229 V).

Ans:

a). $E^{o}_{red} > 1.229$ V 者 $\Rightarrow$ $\therefore$ Co^{3+} $E^{o}_{red} = +1.953$ V

Au^{3+} $E^{o}_{red} = +1.400$ V

Au^{+} $E^{o}_{red} = +1.695$ V

b). $E^{o}_{red} + E^{o}_{ox} > 0$ 者 $\Rightarrow$ $\therefore$ Au^{+} $E^{o}_{red} + E^{o}_{ox} = +1.695\ V + (-1.400)$

$= +0.295$ V

c). $E^{o}_{ox} < +1.229$ V 者 $\Rightarrow$ $\therefore$ Cu^{+} $E^{o}_{ox} = -0.161$ V

Hg_2^{2+} $E^{o}_{ox} = -0.908$ V

§ Oxoanions of the transition metals (CrO_4^{2-}, $Cr_2O_7^{2-}$, MnO_4^{-})

Oxidiation number:

CrO_4^{2-} chromate ion Cr: +6

v $Cr_2O_7^{2-}$ dichromate ion Cr: +6

MnO_4^{-} permanganate ion Mn: +7

The chromate ion is a stable in basic or neutral solution; in acid, it is converted to the dichromate ion.

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

yellow red

$KMnO_4$: a very powerful oxidizing agent.