General Chemistry

Principles and Modern Applications

Petrucci • Harwood • Herring

8th Edition

Chapter 22: Main-Group Elements I: Metals

Philip Dutton
University of Windsor, Canada
N9B 3P4

Contents

Group 1: The Alkali Metals

TABLE 22.1 Group 1 Elements: Abundances

	ppm*	Rank
Li	18	35
Na	22,700	7
K	18,400	8
Rb	78	23
Cs	2.6	46
Fr	Trace	—

*Grams per 1000 kg of solid crust.

Spodumene $LiAl(SiO_3)_2$

Important Li source;

The Alkali Metals

- Discoveries are recent.
  - Sodium and potassium (1807) by electrolysis.
  - Cesium (1860) and rubidium (1861) from emission spectra.
  - Francium (1939) from actinium radioactive decay.
- Most salts are water soluble.
  - Natural brines are good sources.
  - Natural deposits allow mining of solids.

TABLE 22.2 Some Properties of the Group 1 (Alkali) Metals

	Li	Na	K	Rb	Cs
Atomic number	3	11	19	37	55
Valence-shell electron configuration	$2s^1$	$3s^1$	$4s^1$	$5s^1$	$6s^1$
Atomic (metallic) radius, pm	152	186	227	248	265
Ionic (M^+) radius, pm	59	99	138	149	170
Electronegativity	1.0	0.9	0.8	0.8	0.8
First ionization energy, kJ mol^{-1}	520.2	495.8	418.8	403.0	375.7
Electrode potential $E°$, V[a]	−3.040	−2.713	−2.924	−2.924	−2.923
Melting point, °C	180.54	97.81	63.65	39.05	28.4
Boiling point, °C	1347	883.0	773.9	687.9	678.5
Density, g/cm^3 at 20 °C	0.534	0.971	0.862	1.532	1.873
Hardness[b]	0.6	0.4	0.5	0.3	0.2
Electrical conductivity[c]	17.1	33.2	22.0	12.4	7.76
Flame color	Carmine	Yellow	Violet	Bluish red	Blue
Principal visible emission lines, nm	610.671	589	405.767	780.795	456.459

[a] For the reduction $M^+(aq) + e^- \longrightarrow M(s)$.
[b] Hardness measures the ability of substances to scratch, abrade, or indent one another. On the Mohs scale, ten minerals are ranked by hardness, ranging from that of talc (0) to diamond (10). Other values: wax (0 °C), 0.2; asphalt, 1–2; fingernail, 2.5; copper, 2.5–3; iron, 4–5; chromium, 9. Each substance can scratch only other substances with hardness values lower than its own.
[c] On a scale relative to silver as 100.

Production and Use

Electrolysis: $2\ NaCl(l) \rightarrow 2\ Na(l) + Cl_2(g)$ at 600 °C

Sodium as a reducing agent:

$$KCl(l) + Na(l) \rightarrow NaCl(l) + K(g) \text{ at } 850\ °C$$

$$TiCl_4 + 4\ Na \xrightarrow{\Delta} Ti + 4\ NaCl$$

All group 1 metals are strong reducing agents and, thus, their cations are difficult to reduce:

$$2\ M(s) + 2\ H_2O(l) \rightarrow 2\ M^+(aq) + 2\ OH^-(aq) + H_2(g)$$

Sodium Sulfate and Carbonates

$$H_2SO_4(\text{conc. aq}) + NaCl(s) \xrightarrow{\Delta} NaHSO_4(s) + HCl(g)$$

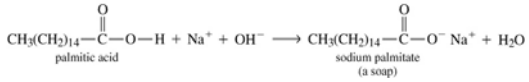
$$NaHSO_4(s) + NaCl(s) \xrightarrow{\Delta} Na_2SO_4(s) + HCl(g)$$

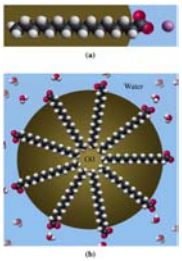
$$Na^+ + Cl^- + NH_3 + CO_2 + H_2O \rightarrow NaHCO_3(s) + NH_4 + Cl^-$$

All ions are present in saturated NaCl solution and the following salts could precipitate out: NaCl, NH_4Cl, NH_4HCO_3, and $NaHCO_3$;

$$2\ NaHCO_3(s) \xrightarrow{\Delta} Na_2CO_3(s) + H_2O(g) + CO_2$$

Detergents and Soaps





Like
Dissolves
Like

22-2 Group 2: The Alkaline Earth Metals

Emerald is based on the mineral beryl: $3BeO{\cdot}Al_2O_3{\cdot}6SiO_2$

TABLE 22.3 Group 2 Elements: Abundances

	ppm*	Rank
Be	2	51
Mg	27,640	6
Ca	46,600	5
Sr	384	15
Ba	390	14
Ra	Trace	—

*Grams per 1000 kg of solid crust.

Group 2

- Principle forms:
  - carbonates, sulfates and silicates
- Oxides and hydroxides only sparingly soluble.
  - Basic or "alkaline"
- Compounds do not decompose on heating.
  - Therefore named "earths"
- Heavier Group II elements are more reactive and are similar to Group I (also in other respects).

TABLE 22.4 Some Properties of the Group 2 (Alkaline Earth) Metals

	Be	Mg	Ca	Sr	Ba
Atomic number	4	12	20	38	56
Atomic (metallic) radius, pm	111	160	197	215	222
Ionic (M^{2+}) radius, pm	27	72	100	113	136
Electronegativity	1.5	1.2	1.0	1.0	0.9
First ionization energy, kJ mol^{-1}	899.4	737.7	589.7	549.5	502.8
Electrode potential $E°$, V[a]	−1.85	−2.356	−2.84	−2.89	−2.92
Melting point, °C	1278	648.8	839	769	729
Boiling point, °C	2970[b]	1090	1483.6	1383.9	1637
Density, g/cm^3 at 20 °C	1.85	1.74	1.55	2.54	3.60
Hardness[c]	~ 5	2.0	1.5	1.8	~2
Electrical conductivity[c]	39.7	35.6	40.6	6.90	3.20
Flame color	None	None	Orange–red	Scarlet	Green

[a] For the reduction $M^{2+}(aq) + 2\ e^- \longrightarrow M(s)$.
[b] Boiling point at 5 mmHg pressure.
[c] See footnotes of Table 22.2.

Decomposition of $CaCO_3$ (lime)

In the lime rotary kiln:

$$CaCO_3 \xrightarrow{\Delta} CaO(s) + CO_2(g)$$

burnt lime
or
quicklime

In the lime slaker:

$$CaO + H_2O \rightarrow Ca(OH)_2(s)$$

slaked lime

$$Ca(OH)_2(s) + CO_2(g) \xrightarrow{aq} CaCO_3(s) + H_2O$$

carbonation

Limestone

Stalactites and Stalagmites

$CO_2 + H_2O \rightarrow H_3O^+ + HCO_3^-$

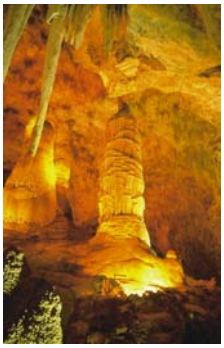
$K_{a1} = 4.4 \times 10^{-7}$

$HCO_3^- + H_2O \rightarrow H_3O^+ + CO_3^{2-}$

$K_{a2} = 4.7 \times 10^{-11}$

$CaCO_3(s) + H_2O(l) + CO_2(g) \rightarrow$

$Ca(HCO_3)_2(aq) \quad K_{eq} = 2.6 \times 10^{-5}$



Group 2 Halides and Sulfates

$M + X_2 \rightarrow MX_2$; X = F, Cl, Br, I

$MgSO_4$		Na_2SO_4
$CaSO_4$	versus	K_2SO_4
$SrSO_4$		Rb_2SO_4
$BaSO_4$		Cs_2SO_4
$2^+ + 2^-$		$1^+ + 2^-$

22-3 Ions in Natural Waters: Hard Water

- Rainwater is not chemically pure water.
  - Contains dissolved atmospheric gases.
  - Once on the ground it may pick up a few to about 1000 ppm of dissolved substances.
  - If the water contains ions capable of forming a precipitate we say that the water is *hard.*
- Hardness may be permanent or temporary.

Temporary Hard Water

- Contains HCO_3^- ion.
  - When heated gives CO_3^{2-}, CO_2 and H_2O.
  - The CO_3^{2-} reacts with multivalent ions to form precipitates. (for example $CaCO_3$, $MgCO_3$)
- Soften water by precipitating the multivalent ions using slaked lime.

22-4 Group 13 Metals: Aluminum, Gallium, Indium and Thallium

TABLE 22.5 Some Properties of the Group 13 Metals

	Al	Ga	In	Tl
Atomic number	13	31	49	81
Atomic (metallic) radius, pm	143	122	163	170
Ionic (M^{3+}) radius, pm	53	62	79	88
Electronegativity	1.5	1.6	1.7	1.8
First ionization energy, kJ mol^{-1}	577.6	578.8	558.3	589.3
Electrode potential $E°$, V[a]	−1.676	−0.56	−0.34	+0.72
Melting point, °C	660.37	29.78	156.17	303.55
Boiling point, °C	2467	2403	2080	1457
Density, g/cm^3 at 20 °C	2.698	5.907	7.310	11.85
Hardness[b]	2.75	1.5	1.2	1.25
Electrical conductivity[b]	59.7	9.1	19.0	8.82

[a] For the reduction $M^{3+}(aq) + 3\,e^- \longrightarrow M(s)$.
[b] See footnotes of Table 22.2.

Uses

- Aluminum is most important.
  - Third most abundant element, 8.3% by mass of crust.
  - Lightweight alloys.
  - Easily oxidized to Al^{3+}.

$2\ Al(s) + 6\ H^+(aq) \rightarrow 2\ Al^{3+}(aq) + 3\ H_2(g)$

$2\ Al(s) + 3/2\ O_2(g) \rightarrow Al_2O_3(s) \quad \Delta H = -1676$ kJ

The thermite reaction (used in on-site welding of large objects):

$2\ Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + Fe(s)$

Oxidation States

- Al almost exclusively 3+.
- Al_2O_3 is an amphoteric oxide

$Al_2O_3(s) + 6\ H^+(aq) \rightarrow 2\ Al^{3+} + 3\ H_2O$

$Al_2O_3(s) + 2\ OH^-(aq) + 3\ H_2O(l) \rightarrow 2\ [Al(OH)_4]^-(aq)$

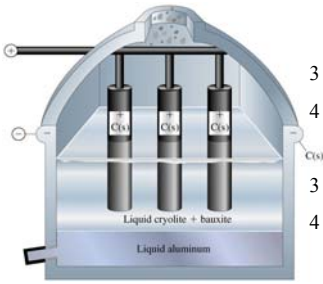
Purification of Bauxite

ppt $Fe(OH)_3$ with OH^- and filter

Make $Al(OH)_4^-$ acidic with CO_2

Precipitated $Al(OH)_3$

Production of Aluminum



$3\ C(s) + 2\ O^{2-} \rightarrow CO_2(g) + 4\ e^-$

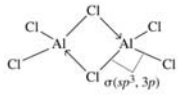
$4\ Al^{3+} + 3e^- \rightarrow Al(l)$

overall

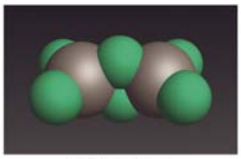
$3\ C(s) + 4\ Al^{3+} + 6\ O^{2-} \rightarrow 4\ Al(l) + 3\ CO_2(g)$

$Na_3AlF_6 + Al_2O_3$

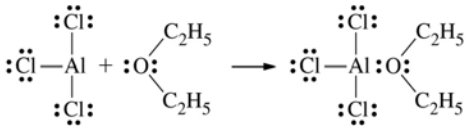
Aluminum Halides



Bonding scheme



Space-filling model



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