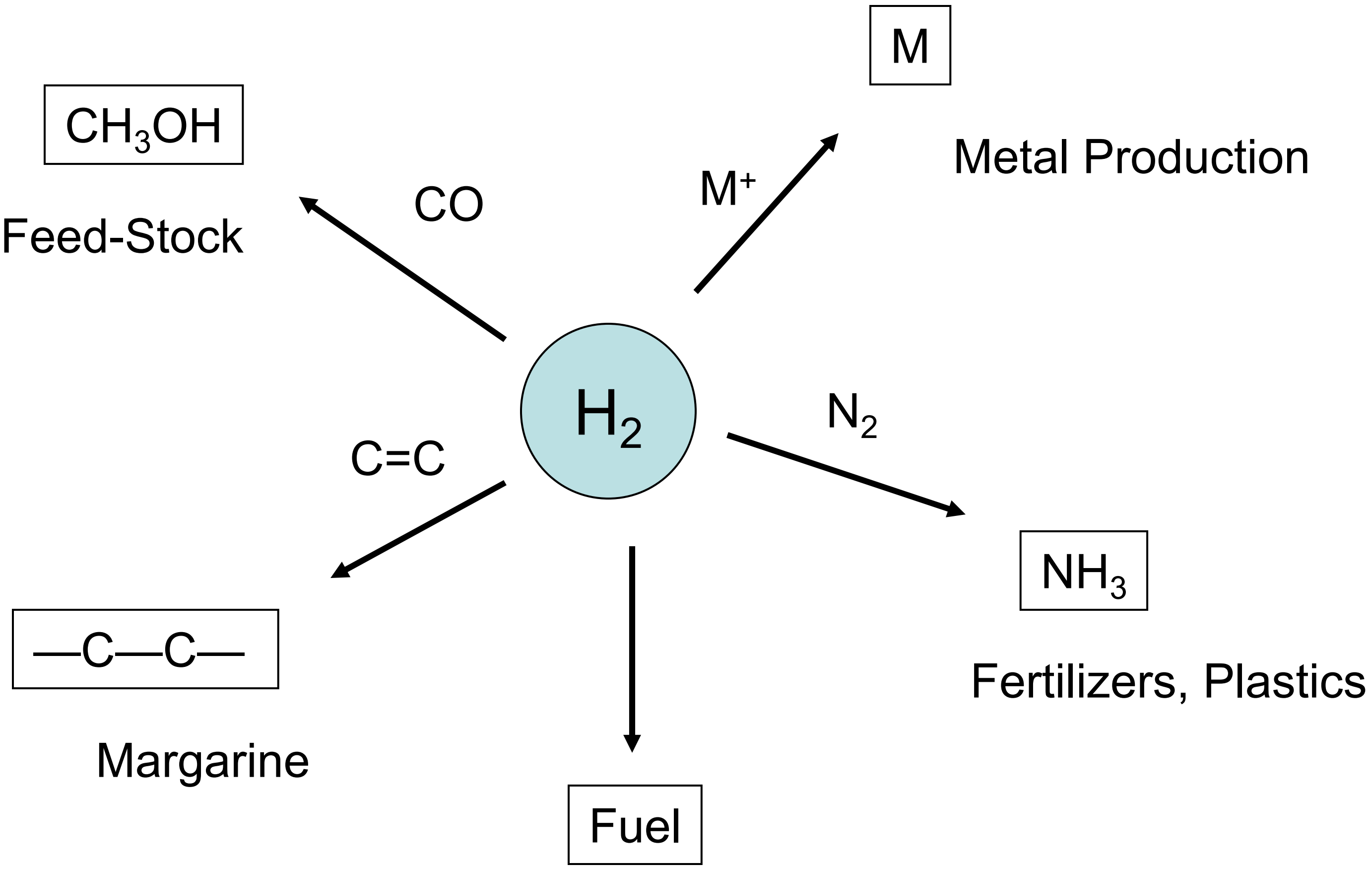
Topic 2

Hydrogen
1A: Li, Na, K, Rb, Cs, Fr
2A: Be, Mg, Ca, Sr, Ba

Industrial Applications of Hydrogen



H_2

CO

CH_3OH

Feed-Stock

M^+

M

Metal Production

N_2

NH_3

Fertilizers, Plastics

$C{=}C$

—C—C—

Margarine

Fuel

Fuel Cells, Rocket Fuel

Hydrogen

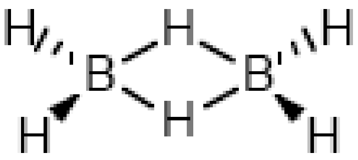
- **Hydrogen forms more compounds than any other element**

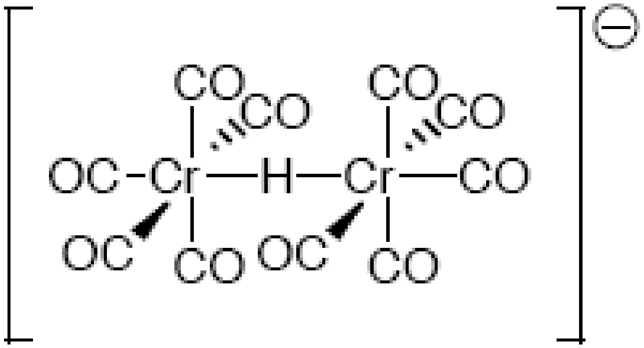
–> Three electronic possible processes:

(1) loss of a valence electron to give H^+ (proton acids)
(2) acquisition of an electron to give H^- (hydrides)
(3) formation of a covalent bond as in CH_4

Note: There are many "in between cases":

– Formation of metallic hydrides (not regarded as simple ionic hydrides)
– Formation of hydrogen bridge bonds in electron deficient compounds or transition metal complexes





– Hydrogen bonding in polar solvents

Hydrides

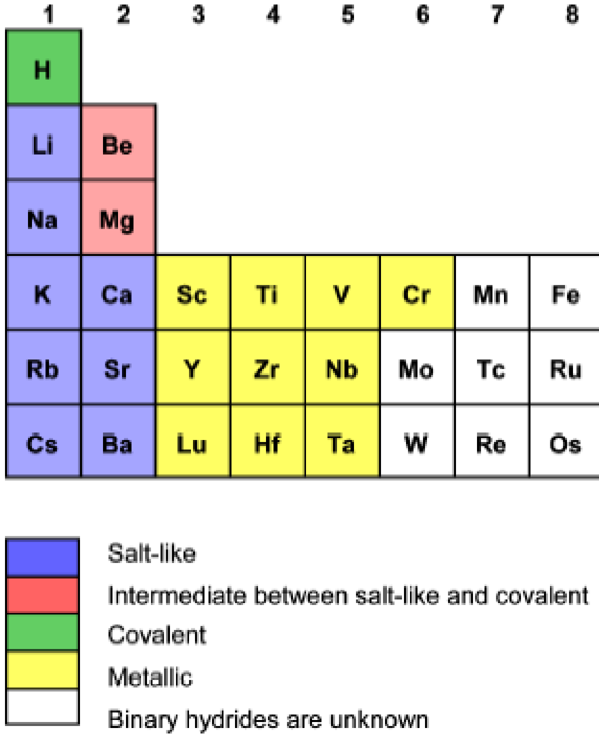
- All compounds of hydrogen could be termed “hydrides”, but not all display “hydridic” character

–> Hydridic substances react either as hydride ion (H^-) donors or clearly contain anionic hydrogen:

- “Neutral” hydrogen compounds (e.g. CH_4) have bonds with highly covalent character

- “Acidic” hydrogen compounds have highly polarized bonds which dissociate in polar solvents:

Classification of Binary Hydrides



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
🟩 H																	⬜ He
🟦 Li	🟥 Be											🟩 B	🟩 C	🟩 N	🟩 O	🟩 F	⬜ Ne
🟦 Na	🟥 Mg											🟥 Al	🟩 Si	🟩 P	🟩 S	🟩 Cl	⬜ Ar
🟦 K	🟦 Ca	🟨 Sc	🟨 Ti	🟨 V	🟨 Cr	⬜ Mn	⬜ Fe	⬜ Co	⬜ Ni	⬜ Cu	⬜ Zn	🟩 Ga	🟩 Ge	🟩 As	🟩 Se	🟩 Br	⬜ Kr
🟦 Rb	🟦 Sr	🟨 Y	🟨 Zr	🟨 Nb	⬜ Mo	⬜ Tc	⬜ Ru	⬜ Rh	🟨 Pd	⬜ Ag	⬜ Cd	🟩 In	🟩 Sn	🟩 Sb	🟩 Te	🟩 I	⬜ Xe
🟦 Cs	🟦 Ba	🟨 Lu	🟨 Hf	🟨 Ta	⬜ W	⬜ Re	⬜ Os	⬜ Ir	⬜ Pt	⬜ Au	⬜ Hg	🟩 Tl	🟩 Pb	⬜ Bi	⬜ Po	🟩 At	⬜ Rn

🟦 Salt-like
🟥 Intermediate between salt-like and covalent
🟩 Covalent
🟨 Metallic
⬜ Binary hydrides are unknown

- **Salt-like (Saline) Hydrides**: Hydrogen compounds of the highly electropositive s-block metals are nonvolatile, electrically nonconducting, crystalline solids
- **Metallic Hydrides**: d-, f- block metals form hydrides, often non-stoichiometric electrically conducting solids
- **Molecular Hydrides**: p-block (most) binary hydrogen compounds are volatile molecular compounds,

Synthesis of Hydrogen Compounds

- Direct combination of elements:

$2Na + H_2 \rightarrow 2NaH$
$N_2 + 3H_2 \rightarrow 2NH_3$
$F_2 + H_2 \rightarrow 2HF$
$Ti + H_2 \rightarrow TiH_{1.9}$

- Preparation of DiHydrogen

$Zn\ (s) + 2HCl\ (aq) \rightarrow ZnCl_2\ (aq) + H_2\ (g)$

$2\ H_2O\ (l) + 2e^- \rightarrow 2\ OH^-\ (aq) + H_2\ (g)$ [Cathode]
$2\ OH^-\ (aq) \rightarrow H_2O\ (l) + \frac{1}{2}\ O_2\ (g) + 2\ e^-$ [Anode]
$CH_4\ (g) + H_2O\ (g) \rightarrow CO\ (g) + 3\ H_2\ (g)$ [Commercial]

- Protonation of a Brønsted base

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

Synthesis of Hydrogen Compounds

- Direct combination of elements:

$2\ Li\ (l) + H_2\ (g) \rightarrow 2\ LiH\ (s)$

- Protonation of a Brønsted base

$Li_3N\ (s) + 3\ H_2O\ (l) \rightarrow 3\ LiOH\ (aq) + NH_3\ (g)$

- Metathesis (= double replacement) of a halide with a hydride

$LiAlH_4\ (s) + SiCl_4\ (l) \rightarrow LiAlCl_4\ (s) + SiH_4\ (g)$

Hydrides as Reducing Agents

- Hydrides as reducing agents

$$CaH_2\ (s) \quad + \quad H_2O \quad \rightarrow \quad Ca(OH)_2\ (s) \quad + \quad H_2\ (g)$$

Reactions of Hydrogen Compounds

- Heterolytic cleavage by hydride transfer:

$$\text{E—H} \rightarrow \text{E}^{+} + :\text{H}^{-} \qquad \text{(eqn. 1)}$$

- Homolytic cleavage:

$$\text{E—H} \rightarrow \text{E}\cdot + \text{H}\cdot \qquad \text{(eqn. 2)}$$

- Heterolytic cleavage by proton transfer:

$$\text{E—H} \rightarrow :\text{E}^{-} + \text{H}^{+} \qquad \text{(eqn. 3)}$$

Heterolytic cleavage and hydridic character (eqn. 1)

Compounds with hydridic character (i.e. can transfer a H^- ion) react vigorously with Bronsted acids and thereby evolving H_2: **(eqn 1)** :

$$\underbrace{NaH(s)} + \underset{\nwarrow}{H_2O(l)} \rightarrow NaOH(aq) + H_2(g)$$

Hydridic compound + weak proton donor (H_2O) is said to be **<u>strongly hydridic</u>**

Notes: (1) If a compound requires a strong proton donor, it is classified as **weakly hydridic** (e.g. germane, GeH_4)

(2) **Hydridic character** is most pronounced toward the left of a period where the element is most electropositive (s-block) and decreases rapidly after Group 13 (aka. Group III).

(3) **Hydrido complexes** are formed with Lewis acids from the boron group

$$2LiH + B_2H_6 \xrightarrow{R_2O} 2LiBH_4$$

Hydrido complexes are of use in simple metathesis reactions (eqn. 1)

Homolytic cleavage and radical character (eqn. 2)

- Homolytic cleavage (eqn 2) appears to occur readily for the hydrogen compounds of some p-block elements, especially the heavier elements.

- For example the use of a radical initiator (Q·, typically a peroxide) facilitates the reaction below:

$$\underset{\text{trialklystannane}}{R_3SnH} + \underset{\text{haloalkane}}{R'X} \rightarrow R'H + R_3SnX$$

Proposed Mechanism (eqn. 2)

Initiation: $R_3Sn\text{—}H + Q\cdot \rightarrow R_3Sn\cdot + QH$

Propagation: $R_3Sn\cdot + XR' \rightarrow R_3SnX + R'\cdot$

(rate-determining halogen abstraction)

$R_3SnH + R'\cdot \rightarrow R'H + R_3Sn\cdot$

Termination: $R'\cdot + R'\cdot \rightarrow R2'$

$R'\cdot + R_3Sn\cdot \rightarrow R_3SnR'$

$R_3Sn\cdot + R_3Sn\cdot \rightarrow R_3Sn\text{—}SnR_3$

(1) The order of reactivity for various haloalkanes with alkylstannanes is

$RF < RCl < RBr < RI$

(2) Fluoroalkanes do not react with R_3SnH, chloroalkanes require heat, photolysis or chemical radical initiators, and bromoalkanes and iodoalkanes react spontaneously at room temperature. This trend indicates the rate-determining step is halogen abstraction.

Trends (eqn. 2)

- Tendency toward radical reactions **increases** toward the heavier elements in each group.

- Sn—H compounds are in general **more prone** to radical reactions than Si—H compounds.

- This trend mirrors the **decrease** in E—H *bond strength* down a group and the **decrease** in the *stretching frequency*. In terms of wavenumbers:

H_2O	H_2S	H_2Se
3652 and 3756 cm-1	2611 and 2684 cm-1	2260 and 2350 cm-1

- As the E—H bond weakens, the molecular potential energy curve becomes more shallow and hence the force constant becomes smaller. The force constant is greatest when the potential well has steeply inclined walls.

Heterolytic cleavage by proton transfer (eqn. 3)

- Compounds reacting by deprotonation in this process are said to show **protic behavior**: i.e. they are **Bronsted acids**.

- Bronsted acid strength increases from left to right across a period in the p block (e.g. CH_4 to HF) and down a group (HF, HBr).

ΔG^o_f (kJ/mol) of binary s- and p-block hydrogen compounds at 25^oC

	1 II	2 III	13 IIII	14 IV	15 V	16 VI	17 VII
2	LiH (s) -68.4	BeH_2 (s) (+20)	B_2H_6 (g) +86.7	CH_4 (g) -50.7	NH_3 (g) -16.5	H_2O (l) -237.1	HF (g) -273.2
3	NaH (s) -33.5	MgH_2 (s) -35.9	AlH_3 (s) -1	SiH_4 (g) +56.9	PH_3 (g) +13.4	H_2S (g) -33.6	HCl (g) -95.3
4	KH (s) -36	CaH_2 (s) -147.2	GaH3 >0	GeH_4 (g) +113.4	AsH_3 (g) +68.9	H_2Se (g) +15.9	HBr (g) -53.5
5	RbH (s) -30	SrH_2 (s) -141	---	SnH_4 (g) +188.3	SbH_3 (g) +147.8	H_2Te (g) >0	HI (g) +1.7
6	CsH (s) -32	BaH_2 (s) -140	---	---	---	---	---

more stable

↓

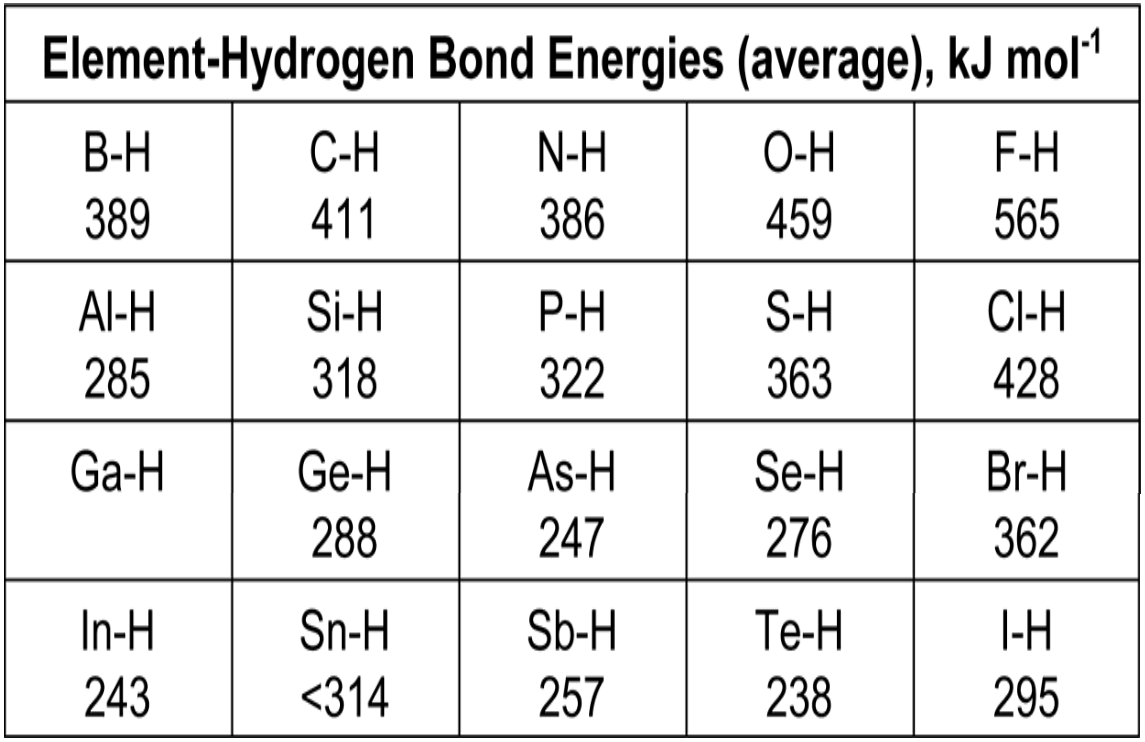
less stable

Exoergic = $\Delta G^o_f < 0$
Endoergic = $\Delta G^o_f > 0$

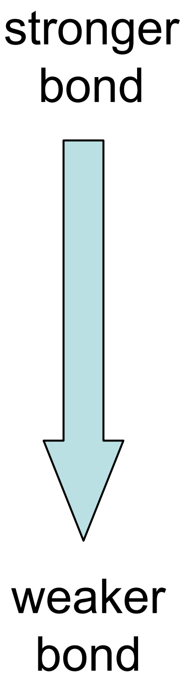
p-block: Down a group: Stability trend is largely a reflection of **decreasing E—H** bond strength (weak bonds from heavier Elements, poor overlap with diffuse s and p orbitals. Across a period: heavier members more stable from IV to VII.

J. Phys. Chem. Ref Data, 11, Suppl. 2, (1982). Values in () based on ΔH^o_f data from this source and entropy contributions estimated.

Bond Energies



Element-Hydrogen Bond Energies (average), kJ mol^{-1}				
B-H 389	C-H 411	N-H 386	O-H 459	F-H 565
Al-H 285	Si-H 318	P-H 322	S-H 363	Cl-H 428
Ga-H	Ge-H 288	As-H 247	Se-H 276	Br-H 362
In-H 243	Sn-H <314	Sb-H 257	Te-H 238	I-H 295



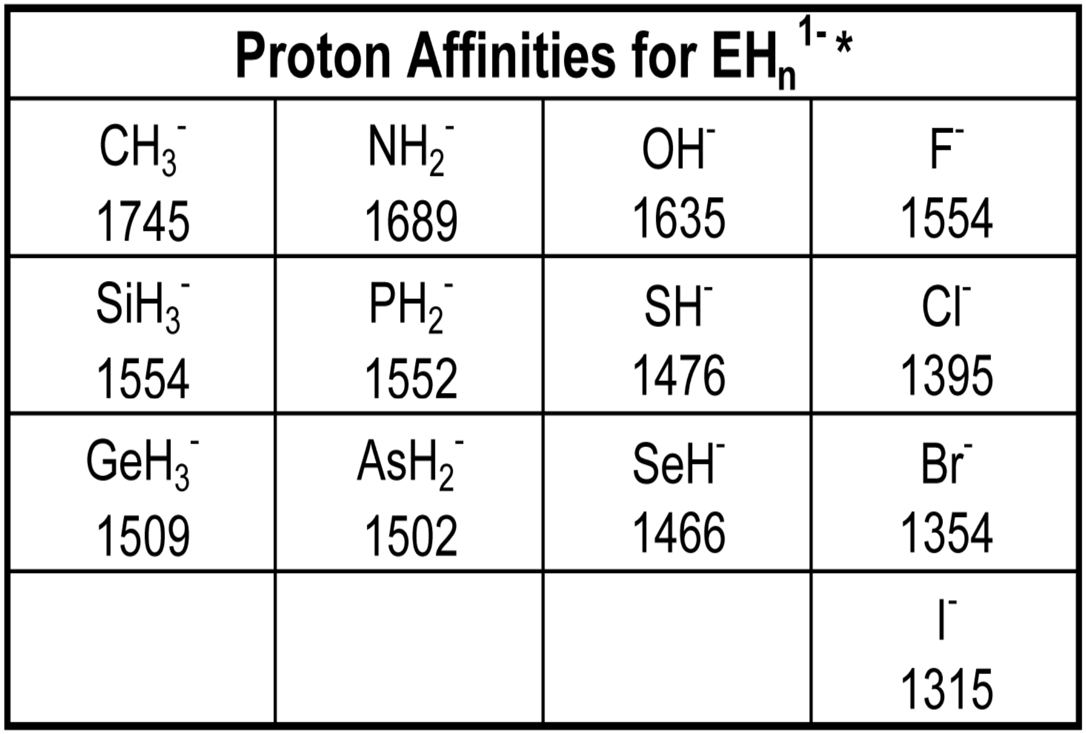
stronger
bond

weaker
bond

General trend in stability is largely a reflection of the **<u>decreasing E—H bond strength</u>** going down a group in the p-block

Proton Affinity Data

The proton affinity (A_p) is defined as the energy associated with the heterolytic cleavage of the E–H bond in the gas phase:



Proton Affinities for EH_n^{1-} *

CH_3^- 1745	NH_2^- 1689	OH^- 1635	F^- 1554
SiH_3^- 1554	PH_2^- 1552	SH^- 1476	Cl^- 1395
GeH_3^- 1509	AsH_2^- 1502	SeH^- 1466	Br^- 1354
			I^- 1315

*Proton affinity refers to the reaction E-H = H^+ + E^-; values in kJ/mol

Alkali Group Trends

	Density	Melting pt.	$\Delta H_{atomization}$
Li	0.53	180	162
Na	0.97	98	108
K	0.86	64	90
Rb	1.53	39	82
Cs	1.87	29	78

$\Delta H_{atomization}$ → energy needed to produce 1 mol of gaseous atoms of that element from the element in its normal phase at room temperature. The term is used to represent breaking of the metallic bond in metals or the overcoming of the covalent bonds and intermolecular forces in nonmetals e.g. $Cu(s) \rightarrow Cu(g)$ or $I_2(s) \rightarrow 2I(g)$

Alkalis

- All alkali metals are shiny, silver-colored metals
- (similar to metals) High electrical and thermal conductivities
- (atypical of metals) very soft, softer as go down the group, e.g. Li-cut with knife; K soft butter, low melting points e.g Cs melting at just above room temperature
- Why soft and why low melting points? Very weak metallic bonding. Most metals ΔHatomization (400-600 kJ/mol), alkalis (80-162)

Alkalis: Group Properties

- **Oxidation number** of +1
- Most compounds: **stable, ionic solids, pure elements not exist naturally**
- **Colorless compounds**, unless contain colored anion (Chromate, Permanganate)
- **Highly electropositive elements**; still bonds in compounds with nonmetals have small covalent component
- **Stabilization of Large Anions** (e.g. ions of Na thru Cs are only cations that form hydrogen carbonate salts)
- Alkalis have **very low-charge densities** compared to other metals
- All **ions are hydrated** when dissolved in water
- **Flame tests** Why useful? Alkali compounds are water soluble. Hence precipitation tests not common. The energy transfer causes electrons in the alkali atoms to be raised to excited states. Energy is released in the form of visible radiation as the e- returns to ground state

Li	Crimson
Na	Yellow
K	Lilac
Rb	Red-violet
Cs	Blue

Alkalis: Hydration Enthalpies

Ion	Hydration Enthalpy (kJ/mol)
Li+	519
Na+	406
K+	322
Rb+	301
Cs+	276

Low charge densities are reflected in the trend in hydration enthalpy among the alkalis. (see table) The values are very low (e.g. Mg^{2+} is 1920 kJ/mol), and the values decrease as radius increases down the group

Charge Density

Charge density → A measure of the polarizing power of a cation

Charge density = ion charge (number of charge units times the proton charge in coulombs) divided by the ion volume.

e.g., sodium ion (Na^+), charge +1, ionic radius 116 pm

$$\text{charge density} = \frac{1 \times (1.60\times10^{-19}\ \text{C})}{(^4/_3)\ \pi\ (1.16\times10^{-7}\text{mm})^3} = 24\ \text{C}\cdot\ \text{mm}^{-3}$$

Similarly, the charge density of the aluminum ion can be calculated to be $364\ \text{C}\cdot\ \text{mm}^{-3}$. With a much greater charge density, Al^{3+} is much more polarizing than Na^+; hence Al^{3+} more likely to favor covalency in its bonding.

Alkalis: Lithium

- Li density ½ of water. Li is the least dense of all elements that are solids at room temp. and pressure. Low density → aerospace alloys

- Bright silvery appearance → turns black rapidly with moist air

- Reactivity: Only alkali and one of very few elements to react with dinitrogen

$$6\ \mathrm{Li(s)} + \mathrm{N2} \rightarrow 2\ \mathrm{Li3N\ (s)}$$

$$\mathrm{Li3N\ (s)} + \mathrm{H2O} \rightarrow 3\ \mathrm{LiOH\ (aq)} + \mathrm{NH3\ (g)}$$

- Li liquid is most corrosive material known (produce hole in glass container, with emission of intense greenish white light.

- Li ion has most negative standard reduction potential of any element

$$\mathrm{Li+\ (aq)} + \mathrm{e-} \rightarrow \mathrm{Li\ (s)} \qquad \mathrm{Eo} = -3.05\ \mathrm{V}$$

- Industrial uses: (1) greases, lithium stearate C17H35COOLi
  (2) batteries, most common anode material in new battery technology

Alkalis: Other members

- Na: Pure Na obtained by electrolysis (Downs process)
  highest industrial demand. Uses include (1) extraction of other metals
  (e.g. rarer metals, Thorium, Zirconcium, Tantalum, Titanium)
  $$TiCl_4 (l) + 4 Na (s) \rightarrow Ti (s) + 4 NaCl (s)$$
  (2) Production of gasoline additive tetraethyllead (TEL). Banned in North America, still used in other countries to boost octane rating of cheap gas.
  $$4 NaPb (s) + 4 C_2H_5Cl (g) \rightarrow (C_2H_5)_4Pb (l) + 3 Pb (s) + 4 NaCl(s)$$

- K: Slightly radioactive (0.012% of radioactive K-40)
  $${}^{40}_{19}K \rightarrow {}^{40}_{20}Ca + {}^{0}_{-1}e$$
  $${}^{40}_{19}K + {}^{0}_{-1}e \rightarrow {}^{40}_{18}Ar$$
  Pure K too hazardous (high reactivity) for electrolytic cell) - Use LeChateliers priniciple to drive equilibrium to right (pure K gas)
  $$Na(l) + KCl \rightarrow \underline{K (g)} + NaCl (l) \qquad [rxn\ at\ 850C]$$
  bp 890C   bp 766C
  (pump green K gas away)

Alkaline Earths

(Be, Mg, Ca, Sr, Ba, Ra)

Alkaline Earths: Comparison

Alkaline Earths versus Alkalis

- harder
- denser
- less reactive

Alkaline Earths versus “typical” metals

- more reactive
- lower density

Alkaline Earths: Overview

Be: semi-metal, discussed separately

Mg, Ca, Sr, Ba: focus here

Ra: Radium member of the group, properties not as much detail

Alkaline Earths: Properties

Not drastic change compared to Radius/Density

Element	**Density (g/cm^3)**	**Melting Point (°C)**	**$\Delta H_{atomization}$**
Mg	1.74	649	149
Ca	1.55	839	177
Sr	2.63	768	164
Ba	3.62	727	175

Alkali	Ionic Radius	Alkaline Earth	Ionic Radius
Li^+	73 pm		
Na^+	116 pm	Mg^{2+}	86 pm
K^+	152 pm	Ca^{2+}	114 pm
Rb^+	166 pm	Sr^{2+}	132 pm
Cs^+	181 pm	Ba^{2+}	149 pm

- Alkaline Earths have stronger metallic bonding than alkalis →
- (1) greater ΔHatomization
  (2) higher melting boiling points
  (3) greater hardness

Alkaline Earth atomic radii smaller than corresponding Alkalis

$\Delta H_{atomization}$ → energy needed to produce 1 mol of gaseous atoms of that element from the element in its normal phase at room temperature. The term is used to represent breaking of the metallic bond in metals or the overcoming of the covalent bonds and intermolecular forces in nonmetals e.g. $Cu(s) \rightarrow Cu(g)$ or $I_2(s) \rightarrow 2I(g)$

Alkaline Earths: Reactivity

- Alkaline Earths are **Less Chemically Reactive** than Alkalis, but still more reactive than most metallic elements (e.g. Ca, Sr, Ba react with cold H2O, with Ba most vigorously)

$$Ba\ (s) + 2\ H_2O\ (l) \rightarrow Ba(OH)_2\ (aq) + H_2\ (g)$$

- Similar to Alkalis, **reactivity increases as mass increases**. Hence Mg doesn't react with cold water, but it will react slowly with hot H_2O

$$Mg\ (s) + 2\ H_2O\ (l) \rightarrow Mg(OH)_2\ (aq) + H_2\ (g)$$

- Alkaline Earths **react with nonmetals and dinitrogen**....e.g.

$$Ca\ (s) + Cl_2\ (g) \rightarrow CaCl_2\ (s)$$

$$3\ Mg\ (s) + N_2\ (g) \rightarrow Mg_3N_2\ (s)$$

Alkaline Earths: Common Features

Excluding Be from discussion (properties very different, semimetallic)

Ionic Character

1. Oxidation number of +2
2. Compounds mainly stable, colorless, ionic solids (unless colored anion)
3. Bonds of compounds mostly ionic, but covalent behavior in Mg cmpds. (Note: Covalency dominates Be chemistry)

Ion Hydration

1. Alkaline Earth salts are almost always hydrated. E.g. $CaCl_2$ can be hexa, tetra, di, monohydrates AND anhydrous.
2. As charge density of the metal decreases, so does the hydration number (number of molecules of water of crystallization)

Alkaline Earth: Hydration Number

Element	MCl_2	$M(NO_3)_2$	MSO_4
Mg	6	6	7
Ca	6	4	2
Sr	6	4	0
Ba	2	0	0

Paradoxically, the **hydroxides** of Sr and Ba are **octahydrates**

BUT

Mg and Ca are anhydrous!

Alkaline Earth Salts: Solubility Trends

In contrast with Alkali Salts, many Alkaline Earth salts are insoluble

- Alkaline Earth Soluble (mononegative anions, **Chloride & Nitrate** → soluble
- Alkaline Earth Insoluble (di, tri-negative anions, **Carbonate, Phosphate** → insoluble

BUT

- **Sulfates** change from **soluble to insoluble** down the group, but
- **Hydroxides** change from **insoluble to soluble** down the group

Nomenclature

BH_3 borane (NOT boron trihydride)
AlH_3 alane (NOT aluminum trihydride)

CH_4 methane (NOT carbon tetrahydride)
SiH_4 silane (NOT silicon tetrahydride)
GeH_4 germane (NOT germanium tetrahydride)
SnH_4 stannane (NOT tin tetrahydride)

NH_3 ammonia (NOT nitrogen trihydride)
NH_3 ammonia (NOT trihydrogen nitride)

PH_3 phosphine (NOT phosphorus trihydride)
PH_3 phosphine (NOT trihydrogen phosphide)

H_2O water (NOT dihydrogen oxide)
H_2O_2 hydrogen peroxide (NOT dihydrogen dioxide)

H_2S hydrogen sulfide (NOT dihydrogen sulfide)

Biomineralization

Biomineralization: formation of minerals by biological processes
Biominerals are grown specifically in the shape for which they are needed.

Chemical Composition	**Mineral Name**	**Occurrence and function**
$CaCO_3$	Calcite, aragonite	Exoskeletons (eggshells, corals, mollusk shells)
$Ca_5(PO_4)_3(OH)$	Hydroxyapatite	Endoskeletons (vertebrate bones and teeth)
$Ca(C_2O_4)$	Whewellite (monohydrate) Weddelite (dihydrate)	Calcium storage, passive defense in plants
$CaSO_4 \cdot 2H_2O$	Gypsum	Gravity Sensor
$SrSO_4$	Celestite	Exoskeleton (some marine unicellular organisms)
$BaSO_4$	Baryte	Gravity Sensor
$SiO_2 \cdot nH_2O$	Silica	Exoskeleton, plant defenses
Fe_3O_4	Magnetite	Magnetic sensors, teeth of certain marine organisms
$Fe(O)(OH)$	Goethite, lepidocrocite	Teeth of certain marine organisms