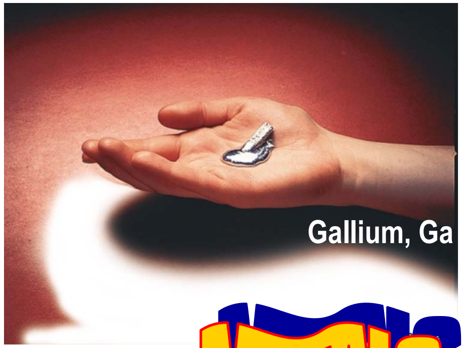
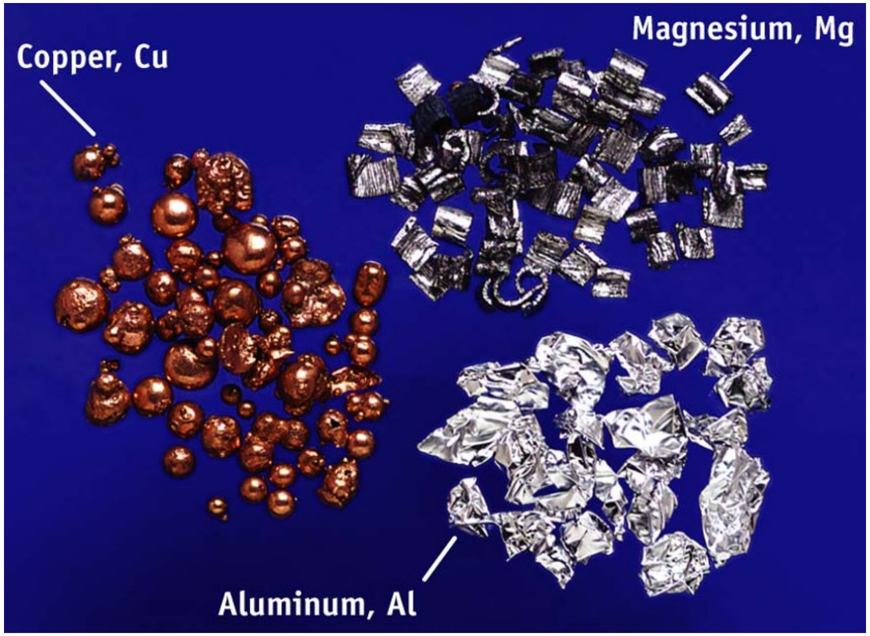


METALS



CHEMISTRY 1000

NONMETALS

Topic #2: The Chemical Alphabet

Fall 2020

Dr. Susan Findlay

See Exercises 10.1 to 10.4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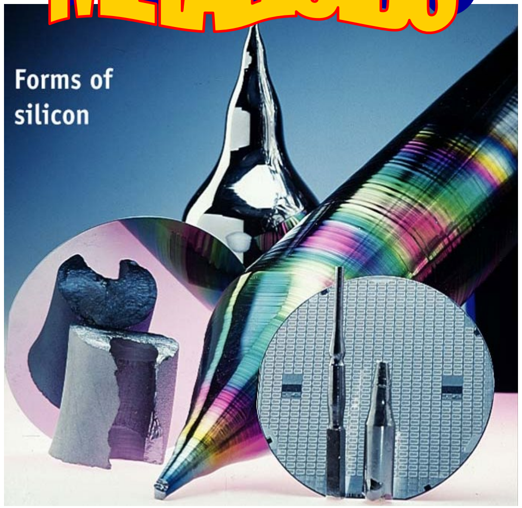
Forms of Carbon

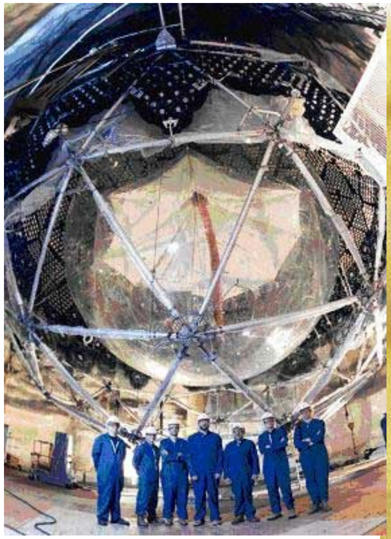
METALLOIDS

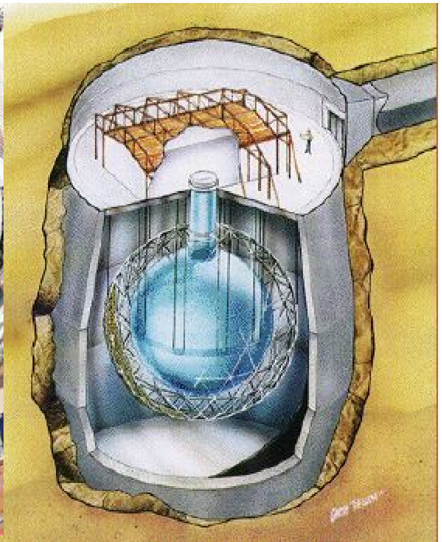


Hydrogen (The "Groupless" Element)

- Hydrogen has three isotopes: **protium** (^{1}H, 99.985%), **deuterium** (^{2}D, 0.015%) and **tritium** (^{3}T, ~10^{-15}%). Of these, only tritium is radioactive.

- While the physical properties of most elements don't change significantly between the isotopes, this is not the case for hydrogen. D_2O melts at 3.8 °C, boils at 101.4 °C and is ~10% denser than H_2O – hence the name "heavy water". The main use of D_2O is to slow down neutrons in nuclear reactors. Approximately 1000 tons of D_2O is also being used as part of a neutrino detector at the Sudbury Neutrino Observatory (SNO) in Ontario.





Hydrogen (The “Groupless” Element)

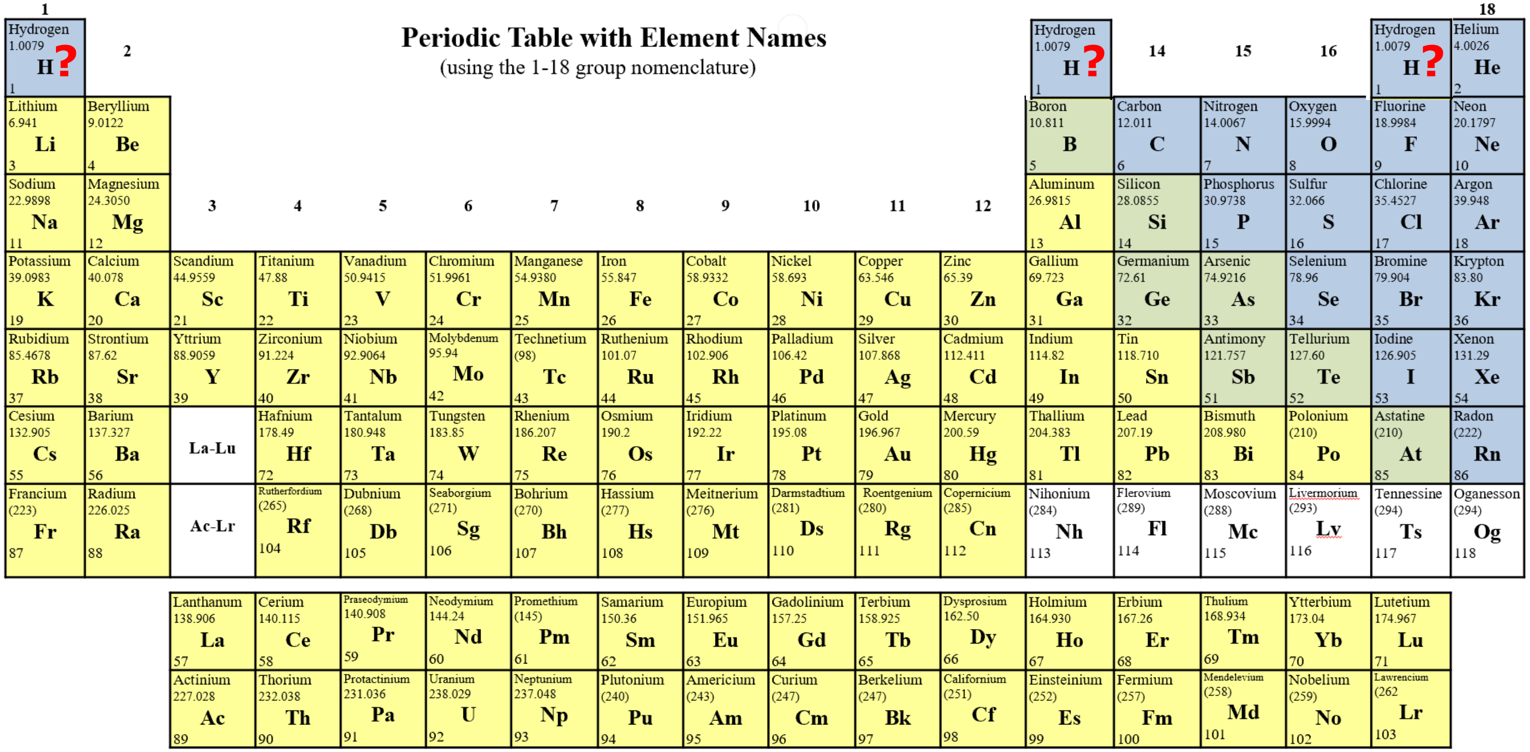
- ^{3}T is used as a radioactive tracer in medicine as it emits low energy β radiation which does relatively little tissue damage.

- The commercial value of ^{3}T, however, is that it is the fuel for the “hydrogen bomb”. As such, it has been aggressively produced from ^{6}Li – so much so that commercially available lithium has a slightly higher average atomic mass than naturally occurring lithium!

- ^{3}T decays to ^{3}He, a rare but very useful isotope. It has an even lower boiling point than the common ^{4}He – and is therefore of immense value for use in extreme low-temperature apparati for cryogenic physics.

Hydrogen (The “Groupless” Element)

- Hydrogen stands alone! *To convey this, some periodic tables leave it floating adrift above the other elements.*
- In some respects, it behaves like the alkali metals but, in others, it behaves more like a halogen – and its electronegativity falls between the values for boron and carbon!



Periodic Table with Element Names
(using the 1-18 group nomenclature)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Hydrogen 1.0079 **H**? 1												Hydrogen 1.0079 **H**? 1				Hydrogen 1.0079 **H**? 1	Helium 4.0026 **He** 2
Lithium 6.941 **Li** 3	Beryllium 9.0122 **Be** 4											Boron 10.811 **B** 5	Carbon 12.011 **C** 6	Nitrogen 14.0067 **N** 7	Oxygen 15.9994 **O** 8	Fluorine 18.9984 **F** 9	Neon 20.1797 **Ne** 10
Sodium 22.9898 **Na** 11	Magnesium 24.3050 **Mg** 12											Aluminum 26.9815 **Al** 13	Silicon 28.0855 **Si** 14	Phosphorus 30.9738 **P** 15	Sulfur 32.066 **S** 16	Chlorine 35.4527 **Cl** 17	Argon 39.948 **Ar** 18
Potassium 39.0983 **K** 19	Calcium 40.078 **Ca** 20	Scandium 44.9559 **Sc** 21	Titanium 47.88 **Ti** 22	Vanadium 50.9415 **V** 23	Chromium 51.9961 **Cr** 24	Manganese 54.9380 **Mn** 25	Iron 55.847 **Fe** 26	Cobalt 58.9332 **Co** 27	Nickel 58.693 **Ni** 28	Copper 63.546 **Cu** 29	Zinc 65.39 **Zn** 30	Gallium 69.723 **Ga** 31	Germanium 72.61 **Ge** 32	Arsenic 74.9216 **As** 33	Selenium 78.96 **Se** 34	Bromine 79.904 **Br** 35	Krypton 83.80 **Kr** 36
Rubidium 85.4678 **Rb** 37	Strontium 87.62 **Sr** 38	Yttrium 88.9059 **Y** 39	Zirconium 91.224 **Zr** 40	Niobium 92.9064 **Nb** 41	Molybdenum 95.94 **Mo** 42	Technetium (98) **Tc** 43	Ruthenium 101.07 **Ru** 44	Rhodium 102.906 **Rh** 45	Palladium 106.42 **Pd** 46	Silver 107.868 **Ag** 47	Cadmium 112.411 **Cd** 48	Indium 114.82 **In** 49	Tin 118.710 **Sn** 50	Antimony 121.757 **Sb** 51	Tellurium 127.60 **Te** 52	Iodine 126.905 **I** 53	Xenon 131.29 **Xe** 54
Cesium 132.905 **Cs** 55	Barium 137.327 **Ba** 56	La-Lu	Hafnium 178.49 **Hf** 72	Tantalum 180.948 **Ta** 73	Tungsten 183.85 **W** 74	Rhenium 186.207 **Re** 75	Osmium 190.2 **Os** 76	Iridium 192.22 **Ir** 77	Platinum 195.08 **Pt** 78	Gold 196.967 **Au** 79	Mercury 200.59 **Hg** 80	Thallium 204.383 **Tl** 81	Lead 207.19 **Pb** 82	Bismuth 208.980 **Bi** 83	Polonium (210) **Po** 84	Astatine (210) **At** 85	Radon (222) **Rn** 86
Francium (223) **Fr** 87	Radium 226.025 **Ra** 88	Ac-Lr	Rutherfordium (265) **Rf** 104	Dubnium (268) **Db** 105	Seaborgium (271) **Sg** 106	Bohrium (270) **Bh** 107	Hassium (277) **Hs** 108	Meitnerium (276) **Mt** 109	Darmstadtium (281) **Ds** 110	Roentgenium (280) **Rg** 111	Copernicium (285) **Cn** 112	Nihonium (284) **Nh** 113	Flerovium (289) **Fl** 114	Moscovium (288) **Mc** 115	Livermorium (293) **Lv** 116	Tennessine (294) **Ts** 117	Oganesson (294) **Og** 118

Lanthanum 138.906 **La** 57	Cerium 140.115 **Ce** 58	Praseodymium 140.908 **Pr** 59	Neodymium 144.24 **Nd** 60	Promethium (145) **Pm** 61	Samarium 150.36 **Sm** 62	Europium 151.965 **Eu** 63	Gadolinium 157.25 **Gd** 64	Terbium 158.925 **Tb** 65	Dysprosium 162.50 **Dy** 66	Holmium 164.930 **Ho** 67	Erbium 167.26 **Er** 68	Thulium 168.934 **Tm** 69	Ytterbium 173.04 **Yb** 70	Lutetium 174.967 **Lu** 71
Actinium 227.028 **Ac** 89	Thorium 232.038 **Th** 90	Protactinium 231.036 **Pa** 91	Uranium 238.029 **U** 92	Neptunium 237.048 **Np** 93	Plutonium (240) **Pu** 94	Americium (243) **Am** 95	Curium (247) **Cm** 96	Berkelium (247) **Bk** 97	Californium (251) **Cf** 98	Einsteinium (252) **Es** 99	Fermium (257) **Fm** 100	Mendelevium (258) **Md** 101	Nobelium (259) **No** 102	Lawrencium (262 **Lr** 103

Hydrogen (The “Groupless” Element)

- Because of its electron configuration (______), hydrogen can achieve a “noble gas”-like electron configuration by *either* gaining an electron, losing an electron *or* sharing an electron:

Hydrogen (The “Groupless” Element)

- The H – H bond in hydrogen is extremely strong (436 kJ/mol), so H_2 is a relatively unreactive molecule. Even thermodynamically favoured reactions of hydrogen often require a catalyst to break the strong H – H bond. Hydrogen does, however, react with exothermically with oxygen and with fluorine:

Hydrogen (The “Groupless” Element)

- Because the H – H bond is so strong, it is not difficult to make hydrogen gas. You have made H_2 several different ways in the Chemistry 1000 lab:

Hydrogen (The "Groupless" Element)

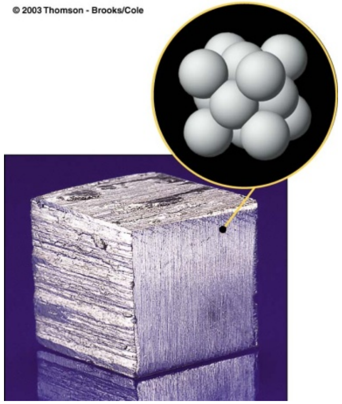
- Industrially, most hydrogen is produced by the **catalytic steam reformation of hydrocarbons**. Methane gas (CH_4 – the main component of natural gas) reacts with steam at 900 to $1000\ °C$ to give carbon monoxide (CO) and hydrogen (H_2):

- The carbon monoxide reacts with more steam at 400 to $500\ °C$ in the presence of calcium oxide (CaO):

- The method that gives the purest hydrogen is electrolysis of water, but the electricity required for this process is prohibitively expensive for large-scale production in most countries.

Hydrogen (The "Groupless" Element)

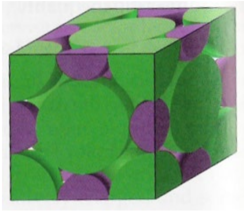
- There are three general classes of hydrogen compounds:
  - **Ionic hydrides** in which hydrogen combines with elements from groups 1-2 (except beryllium) to form ionic compounds:



  - **Metallic hydrides** (also called *interstitial compounds*) in which elements from groups 3-10 "absorb" hydrogen. The hydrogen atoms fill holes in the metallic lattice, distorting its structure if enough hydrogen is absorbed.
  - **Covalent hydrogen compounds** in which hydrogen combines with elements from groups 11-17 (or beryllium) to form covalent molecules:

Ionic Hydrides

- Most ionic hydrides have a crystal structure like either NaCl (for alkali metal hydrides) or CaF_2 (for the metal dihydrides). Unlike most ionic compounds, the cations form the main lattice as they are typically larger than the hydride anions:



- Ionic hydrides are strong bases, reacting with acids (even those as weak as water):
- Ionic hydrides are typically sold as grey powders suspended in mineral oil. The oil protects them from reacting with moisture in the air though it must be washed off *(with solvent)* if an accurate amount is to be weighed. If an ionic hydride is not stored properly, it turns white. What has happened?

(c) The reaction of CaH_2 and water. The products are hydrogen gas and $Ca(OH)_2$.

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Metallic Hydrides

- The hydrogen in metallic hydrides can act as either “H^+” or “H^-”:

- Transition metals are often used as catalysts for reactions in which hydrogen is added to a double bond (e.g. hydrogenating vegetable oil to make margarine). The hydrogen first reacts with the transition metal to make a metallic hydride (more reactive than hydrogen gas).
- The ratio of hydrogen : metal atoms in a metallic hydride is often fractional – not every hole in the lattice contains a hydrogen atom.

Covalent Hydrogen Compounds

- Most of the “everyday” compounds containing hydrogen are covalent hydrogen compounds.
  - When hydrogen is covalently bonded to a less electronegative element, it has a partial negative charge and may act as a hydride:
  - When hydrogen is covalently bonded to an element with similar electronegativity, it is fairly neutral and tends not to be reactive:
  - When hydrogen is covalently bonded to a more electronegative element, it has a partial positive charge and may act as an acid:

Acids and Bases

- There are three main classification systems for acids and bases.
  - You are already familiar with Arrhenius acids and bases:
    - Arrhenius acid:
    - Arrhenius base:
  - The Brønsted definitions of acids and bases are broader, applying in solvents other than just water:
    - Brønsted acid:
    - Brønsted base:
  - Lewis acids and bases are defined a bit differently:
    - Lewis acid:
    - Lewis base:

Acids and Bases

- The three definitions are not mutually exclusive. Arrhenius acids are often Brønsted acids too. Arrhenius bases are often Brønsted bases too.

- To see how the electron pairs referenced in the Lewis acid/base definitions fit in, consider the electron flow in a reaction between a hydroxide ion (OH^-) and hydrofluoric acid (HF):

Lewis Acids and Bases

- Why do we call a Lewis acid an acid if it doesn't necessarily generate H^+?
  - H^+ is the ultimate Lewis acid. What happens when it reacts with Lewis bases like:
    - Ammonia (NH_3)
    - Water (H_2O)
    - Cyanide (CN^-)

Lewis Acids and Bases

- Now, look at the reactions of those same Lewis bases with a more typical Lewis acid like BCl_3:
  - Ammonia (NH_3)
  - Water (H_2O)
  - Cyanide (CN^-)

Lewis Acids and Bases

- What properties are required for something to be a Lewis base?

Lewis Acids and Bases

- What properties are required for something to be a Lewis acid?

- As such, all transition metal cations act as Lewis acids when they are dissolved in water:

hydrated metal cation = “aqua complex”

Brønsted Acids and Bases

- Since H^+ is the ultimate Lewis acid, it acts as a Lewis acid in water. As such, there isn't really such a thing as $H^+_{(aq)}$. It's much closer to $H(OH_2)_4^+$ or $H_9O_4^+$.
- **To remind us that $\boldsymbol{H^+_{(aq)}}$ is <u>always</u> surrounded by water molecules, we often write $\boldsymbol{H_3O^+_{(aq)}}$.**
- Thus, when we write a chemical equation for the reaction between a strong acid and a strong base, we get:

We can see that H_3O^+ is serving as a proton donor and OH^- is serving as a proton acceptor – just like in the Brønsted definition of acid-base chemistry.

Brønsted Acids and Bases

- A "strong acid" is any acid that is fully converted to H_3O^+ in water:
- A "strong base" is any base that is fully converted to OH^- in water.

Brønsted Acids and Bases

- When comparing strengths of acids, we refer to their pK_a values.
- $pK_a = -logK_a$ where K_a is the equilibrium constant for the dissociation of the acid into H^+ and its conjugate base:
- Acids with lower pK_a values are stronger while acids with higher pK_a values are weaker.
- “Strong acids” have pK_a values that are negative.

Brønsted Acids and Bases

pK$_a$

H_2O (pK$_a$ = 14)

WEAK ACIDS

HCO_3^{-1} (pK$_a$ = 10.3)

H_2CO_3 (pK$_a$ = 6.4)

CH_3CO_2H (pK$_a$ = 4.7)

HF (pK$_a$ = 3.1)

Citric acid (pK$_a$ = 3.1)

H_3PO_4 (pK$_a$ = 2.15)

H_3O^+ (pK$_a$ = 0) ←This includes all aqueous solutions of HCl, HBr, HI, HNO_3, $HClO_4$ and H_2SO_4

Pure HNO_3 (pK$_a$ = -1)

STRONG ACIDS

Pure H_2SO_4 (pK$_a$ = -6)

Pure HCl (pK$_a$ = -7)

Pure HI (pK$_a$ = -10)

Aqua Complexes as Acids

- With a pK_a of 0, a hydrated proton is an excellent acid, defining the line between the strong and weak acids. How do the other aqua complexes compare?

Cation	**pK_a**	**Approximate pH of a 1 M solution**
$Na(OH_2)_6^+$	14.2	7
$Ag(OH_2)_6^+$	12	6.0
$Mg(OH_2)_6^{2+}$	11.4	5.7
$Al(OH_2)_6^{3+}$	5	2.5
$Ti(OH_2)_6^{4+}$	-4	0

Aqua Complexes as Acids

- What factors affect how easily the aqua complex gives up H^+?

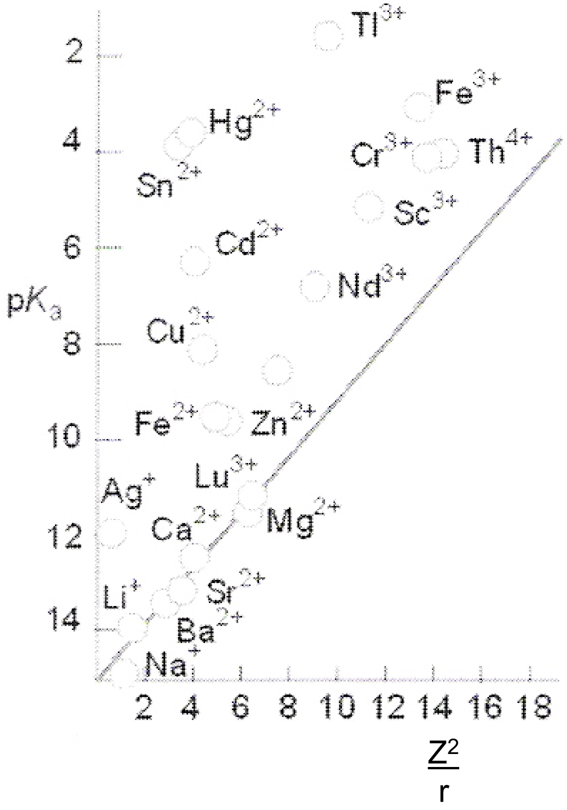
Aqua Complexes as Acids

- If we plot pK_a versus $\frac{z^2}{r}$ for a variety of aqua complexes, we see that there is a correlation. If we only look at those metals with low electronegativity values (□ 1.5), we can approximate:

$$pK_a = 15.14 - 88.16\,pm\frac{z^2}{r}$$

- If we introduce an empirical "fudge factor", we get a more accurate – if more complex – formula:

$$\boxed{pK_a = 15.14 - 88.16\,pm\left(\frac{z^2}{r} + 0.0960\,pm^{-1}(\chi_{Pauling} - 1.50)\right)}$$



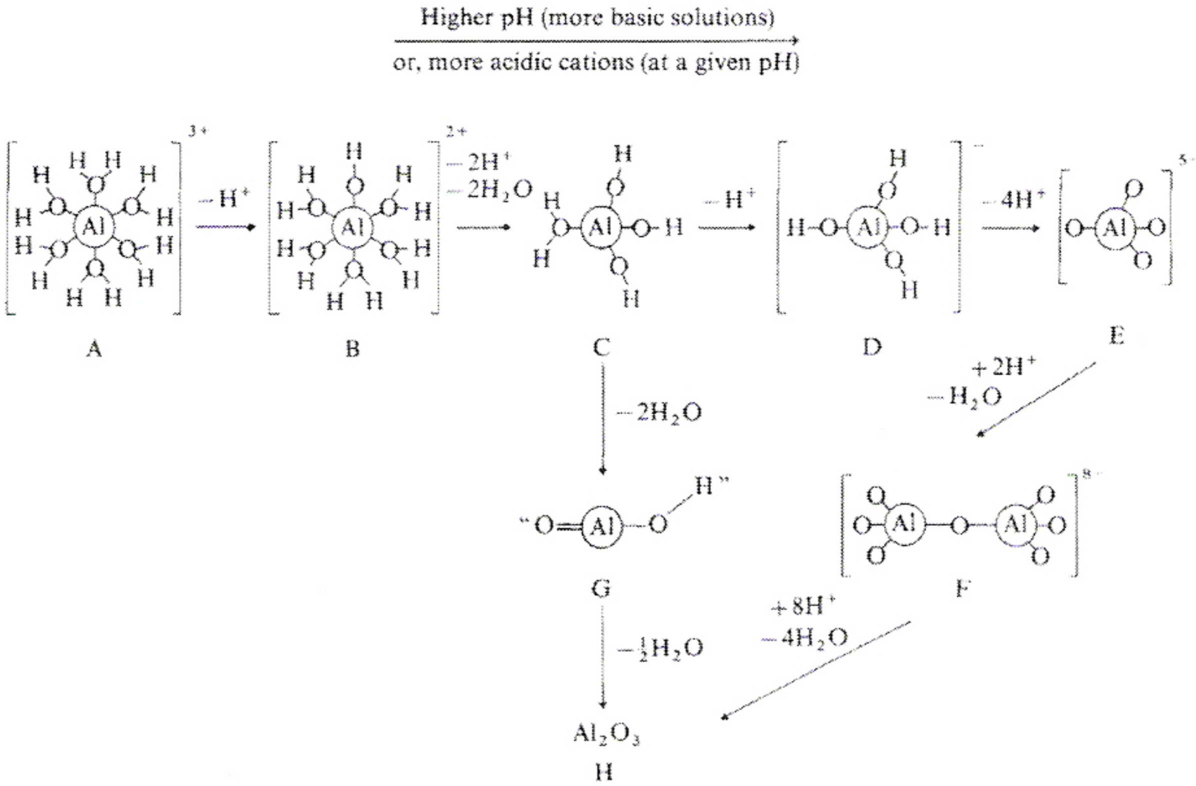
Aqua Complexes as Acids

- Recall what happens when a metal cation is hydrated:
  - The cation accepts electrons from oxygen *(Lewis acid-base rxn).*
  - This aqua complex will give up H^+ if reacted with a strong enough base *(Brønsted acid-base rxn).*

- In aqueous solutions, the most abundant – if weak – base is water. Aqua complexes with pK_a values below 14 will react to some extent with water, giving an acidic solution.
- At higher pH values, OH^- will also be available in significant concentrations and can further deprotonate the aqua complex.

Aqua Complexes as Acids

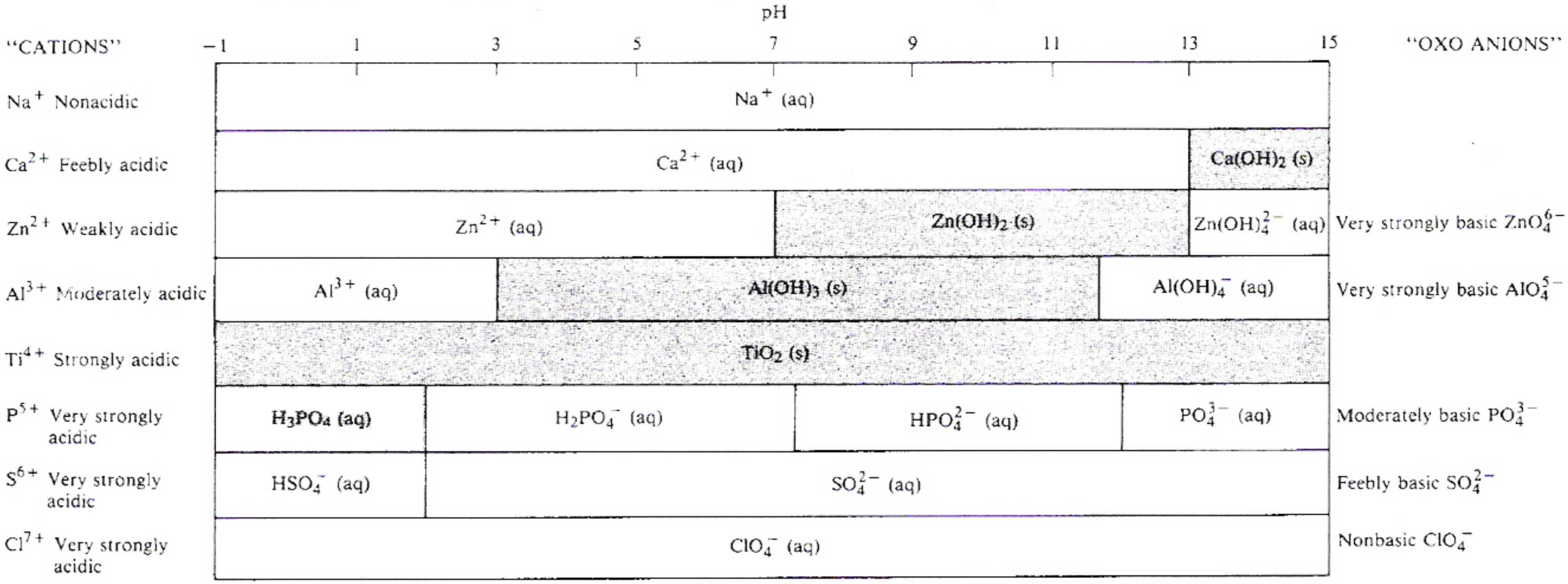
- So, this tells us what, exactly? Consider what happens when we add a base to a solution of an acidic aqua complex:



As more base is added, more protons are removed. Which of the species in the diagram above would you expect to be soluble in water, and which will be more stable as solid lattices?

Aqua Complexes as Acids

- We can see from this diagram that the dominant species of aluminum (hydrated cation, hydroxide or oxide) depends on how much base is present in solution – as determined by the pH. This is true of most elements; the diagram below shows the predominant species of each element in 0.001 M aqueous solutions of varying pH (but fixed oxidation state).

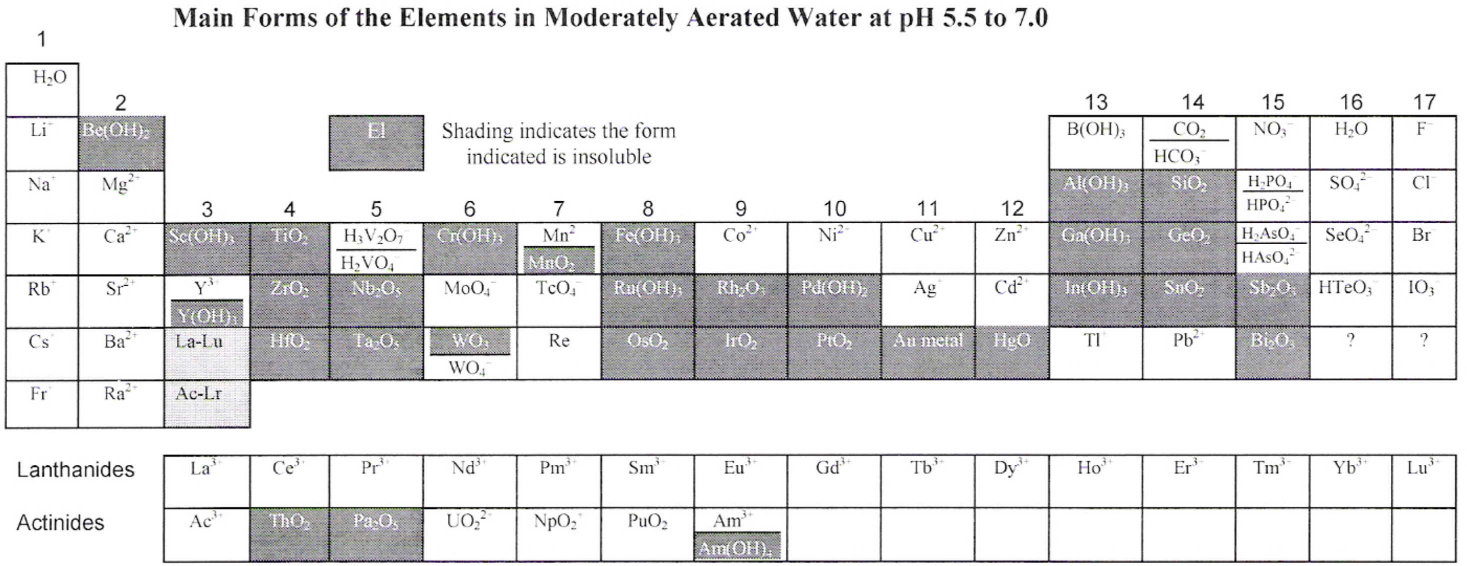


Aqua Complexes as Acids

- In nature, water is never completely pure. It always contains some dissolved ions which keep it within a constant pH range. Looking at the distribution diagram, we can see which elements are soluble (and therefore bioavailable) in different pH ranges:
  - Titanium is never soluble, so remains fixed in the soil or minerals.
  - Sodium is always soluble, so is always bioavailable – as are phosphates which are essential nutrients for plants.
  - Calcium is soluble under all but the most basic conditions.
  - Aluminum is soluble at low and high pH, but not between 3 and 11. This means that when a lake becomes acidified (pH 2 to 4), it dissolves significantly more aluminum than normal. It is believed that this is why fish die in acid lakes. When they absorb lake water through their gills, its pH is raised to the physiological pH of 7.5. The $\mathrm{Al}(OH_2)_6^{3+}$ which had been soluble at low pH reacts with the hydroxide ions available at the higher pH, forming a gelatinous gel of hydrated aluminum hydroxide. This gel precipitates on the gills, and the fish can no longer breathe, so it dies.

Aqua Complexes as Acids

- Most aerated fresh water (except for that polluted by acid rain) has a pH between 5.5 and 7. The table below shows the dominant species of each element within that pH range:



Main Forms of the Elements in Moderately Aerated Water at pH 5.5 to 7.0

▨ El — Shading indicates the form indicated is insoluble

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
H_2O																
Li^+	▨ $Be(OH)_2$											$B(OH)_3$	CO_2 HCO_3^-	NO_3^-	H_2O	F^-
Na^+	Mg^{2+}											▨ $Al(OH)_3$	▨ SiO_2	$H_2PO_4^-$ HPO_4^{2-}	SO_4^{2-}	Cl^-
K^+	Ca^{2+}	▨ $Sc(OH)_3$	▨ TiO_2	$H_3V_2O_7^-$ $H_2VO_4^-$	▨ $Cr(OH)_3$	Mn^2 ▨ MnO_2	▨ $Fe(OH)_3$	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	▨ $Ga(OH)_3$	▨ GeO_2	$H_2AsO_4^-$ $HAsO_4^{2-}$	SeO_4^{2-}	Br^-
Rb^+	Sr^{2+}	Y^{3+} ▨ $Y(OH)_3$	▨ ZrO_2	▨ Nb_2O_5	MoO_4^-	TcO_4^-	▨ $Ru(OH)_3$	▨ Rh_2O_3	▨ $Pd(OH)_2$	Ag^+	Cd^{2+}	▨ $In(OH)_3$	▨ SnO_2	▨ Sb_2O_3	$HTeO_3^-$	IO_3^-
Cs^+	Ba^{2+}	La-Lu	▨ HfO_2	▨ Ta_2O_5	▨ WO_3 WO_4^-	Re	▨ OsO_2	▨ IrO_2	▨ PtO_2	▨ Au metal	▨ HgO	Tl^+	Pb^{2+}	▨ Bi_2O_3	?	?
Fr^+	Ra^{2+}	Ac-Lr														

Lanthanides	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Pm^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}
Actinides	Ac^{3+}	▨ ThO_2	▨ Pa_2O_5	UO_2^{2+}	NpO_2^+	PuO_2	Am^{3+} ▨ $Am(OH)_3$								

- Recognize that many environmental scientists, nutritionists, etc. refer to all compounds containing an element by the element's name. When you're told that calcium is good for your bones, it's not actually intended that you should eat calcium metal! "Calcium levels" in the blood are a combination of the aqua complex, other complexes and calcium salts.