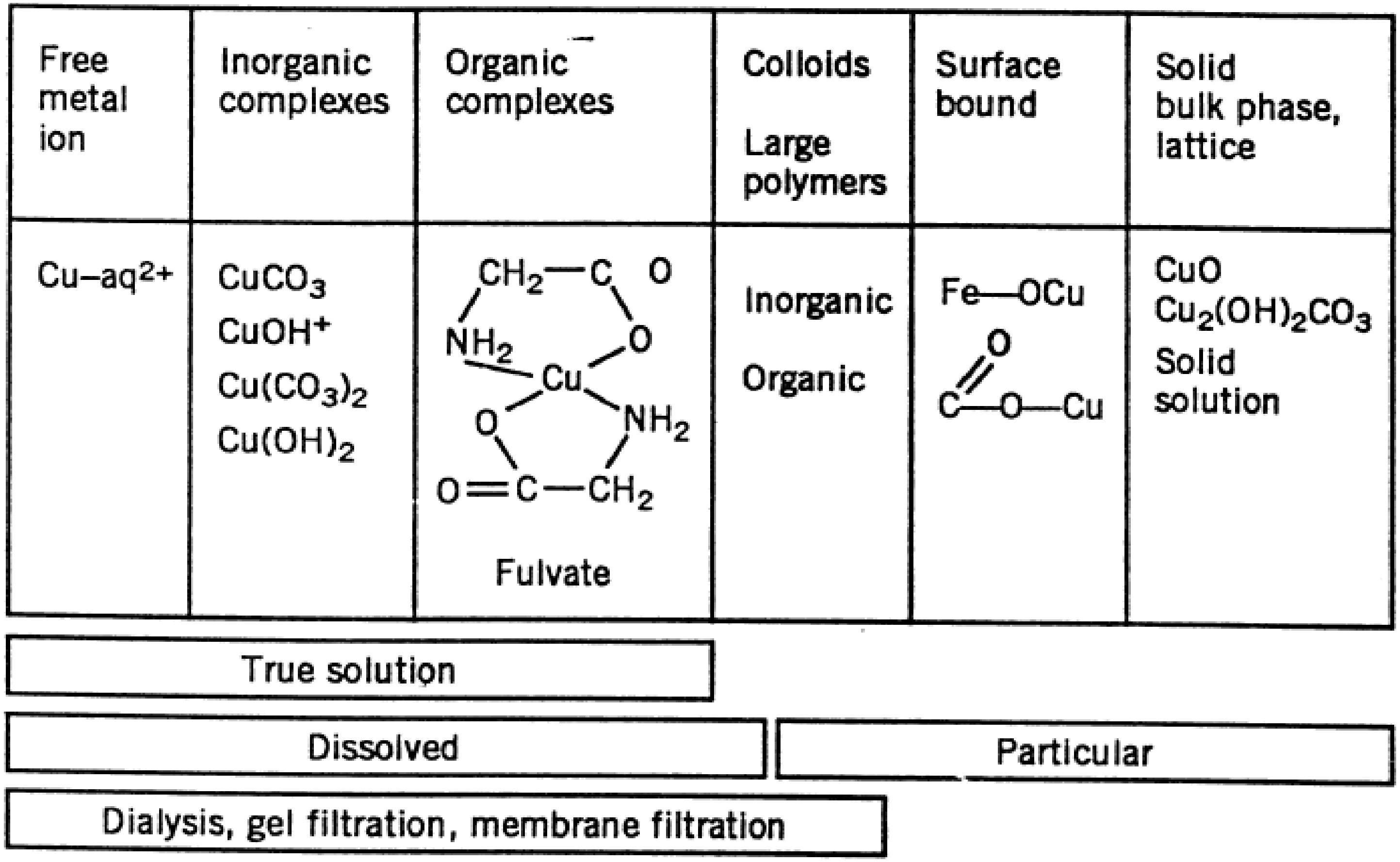
The make-up of a natural solution



Free metal ion	Inorganic complexes	Organic complexes	Colloids Large polymers	Surface bound	Solid bulk phase, lattice
Cu–aq^{2+}	$CuCO_3$ $CuOH^+$ $Cu(CO_3)_2$ $Cu(OH)_2$	Fulvate	Inorganic Organic	Fe—OCu O C—O—Cu	CuO $Cu_2(OH)_2CO_3$ Solid solution

True solution

Dissolved

Particular

Dialysis, gel filtration, membrane filtration

Figure 6.1. Forms of occurrence of metal species.

http://eps.mcgill.ca/~courses/c220/

The make-up of a natural solution

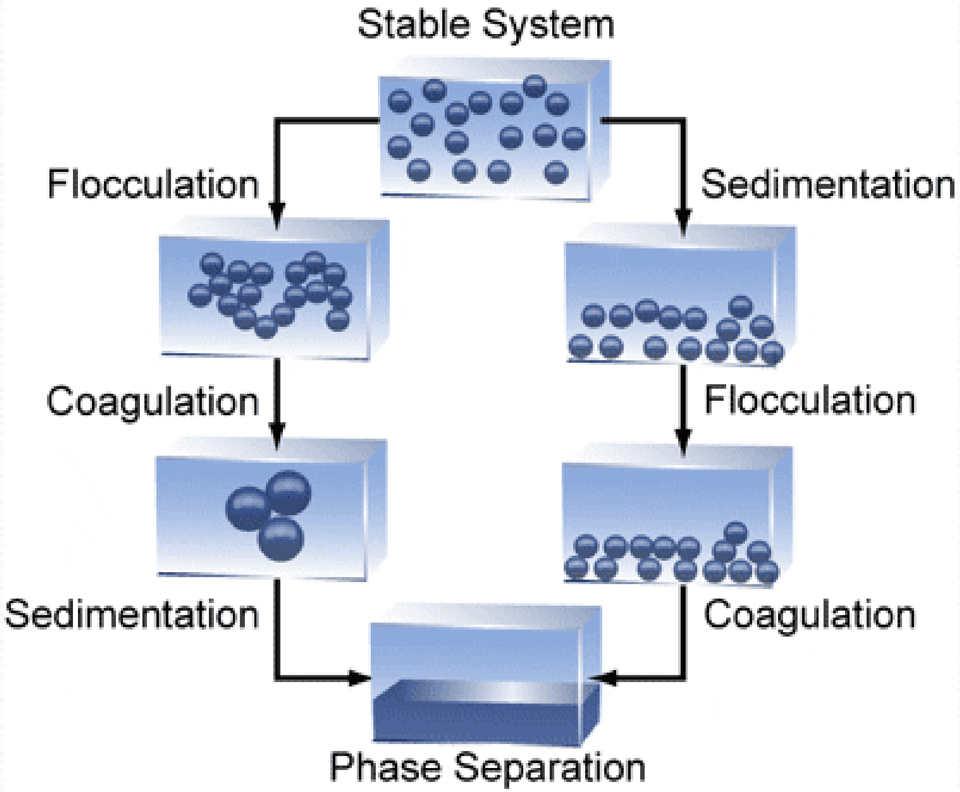
I – Particulate or solids

II- Colloidal material

III – Truly dissolved

  - a) non-associated (free)
  - b) associated (complexed)
    - i) Weak electrolytes
    - ii) Complexes
    - iii) Ion-pairs

Colloids



Stable System

Flocculation

Sedimentation

Coagulation

Flocculation

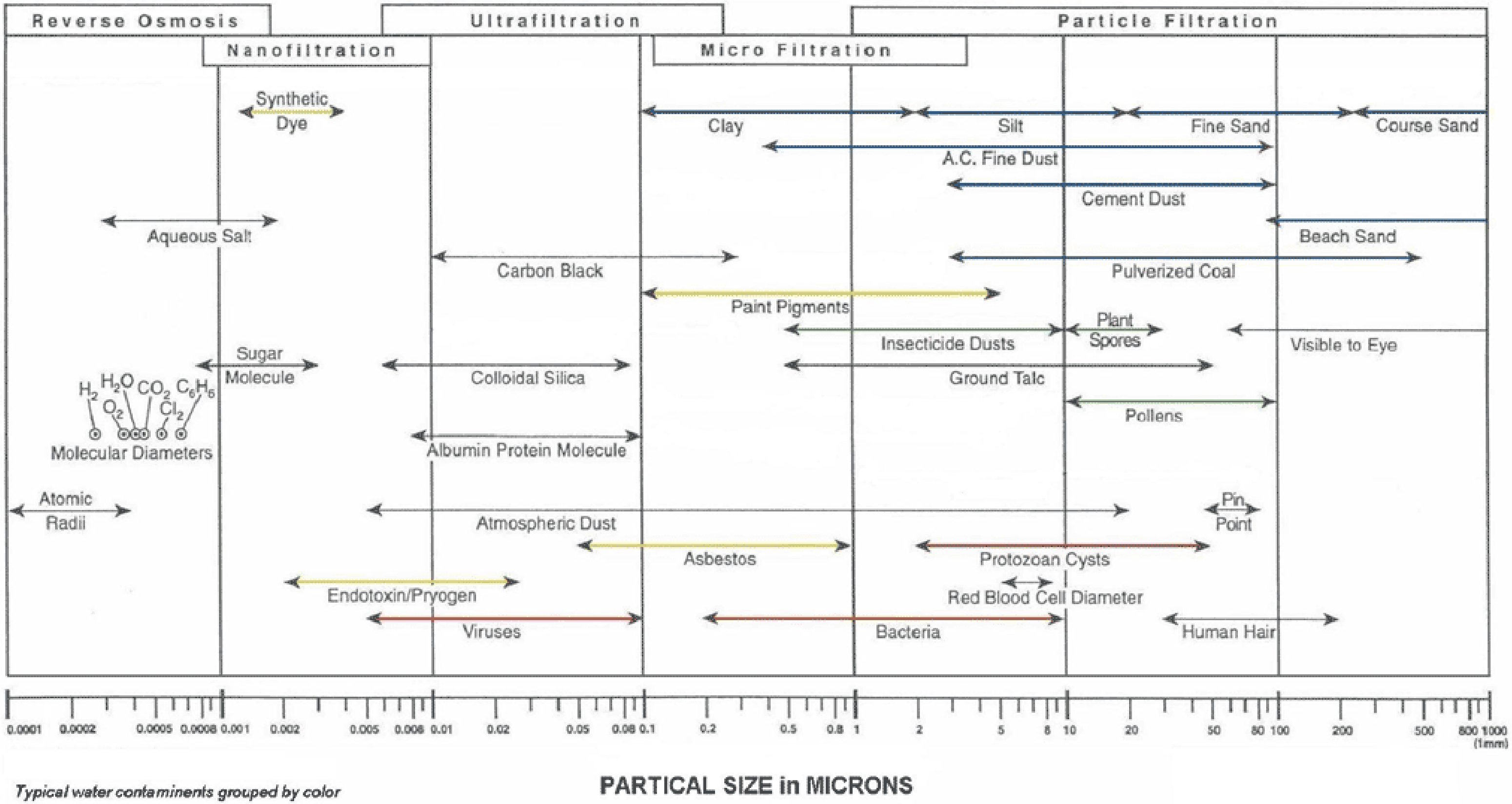
Sedimentation

Coagulation

Phase Separation

Operational definition of the dissolved fraction

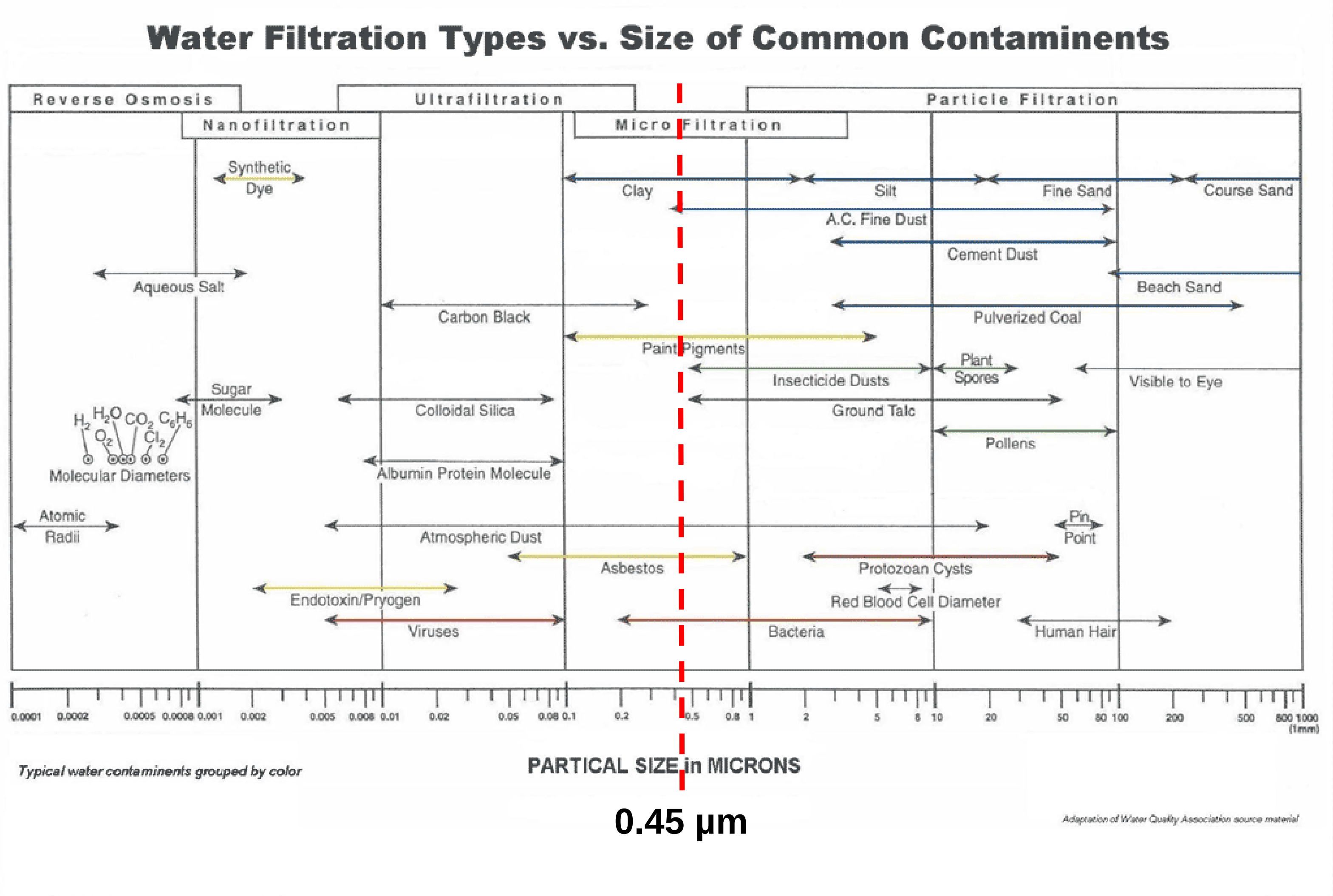
Water Filtration Types vs. Size of Common Contaminents



Typical water contaminents grouped by color

Adaptation of Water Quality Association source material

Operational definition of the dissolved fraction



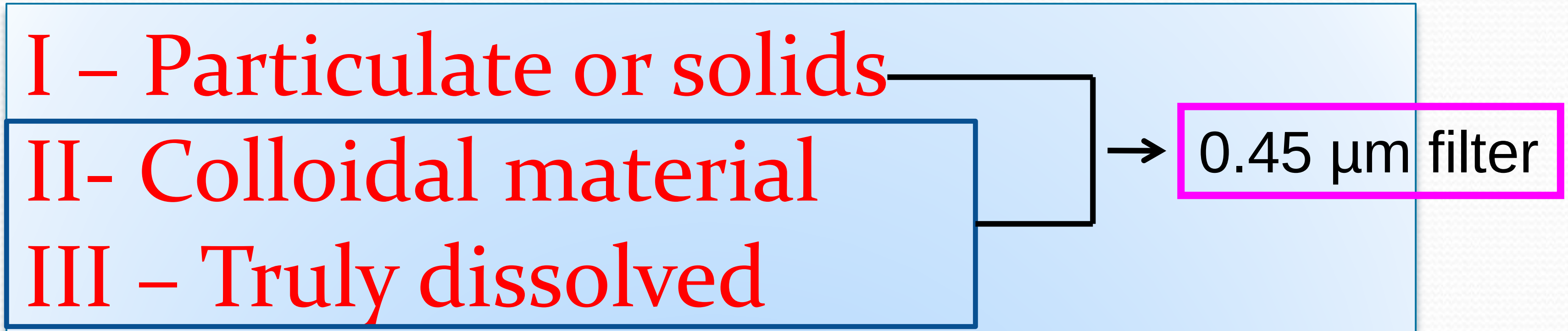
Water Filtration Types vs. Size of Common Contaminents

Typical water contaminents grouped by color

0.45 µm

Adaptation of Water Quality Association source material

The make-up of a natural solution



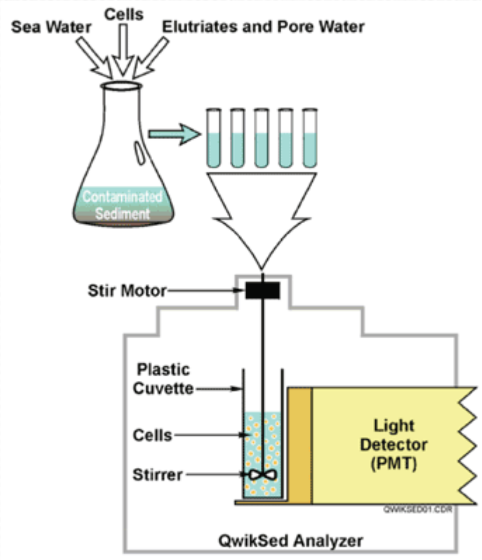
I – Particulate or solids

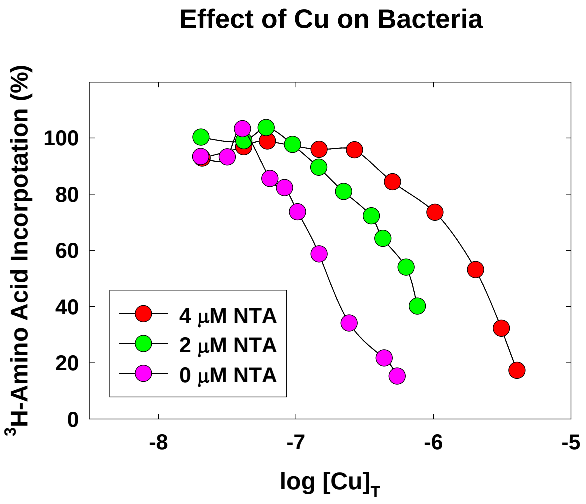
II- Colloidal material

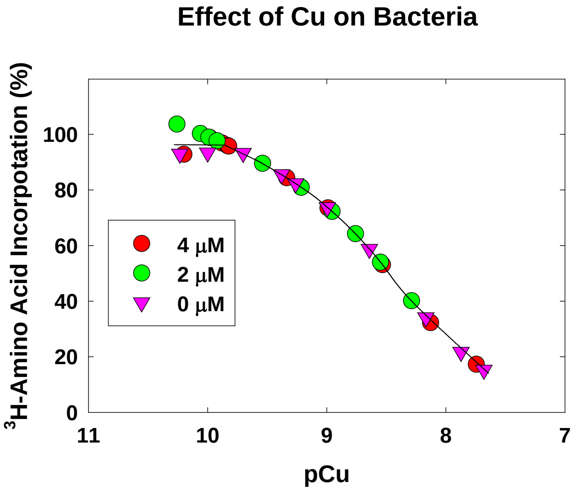
III – Truly dissolved

- a) non-associated (free)
- b) associated (complexed)
    - i) Weak electrolytes
    - ii) Complexes
    - iii) Ion-pairs

Free vs complexed solutes
(bio-assay)



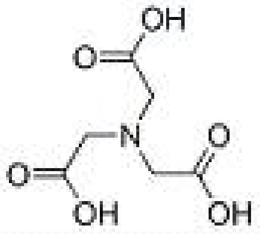




||

-log a$_{(Cu^{2+})}$

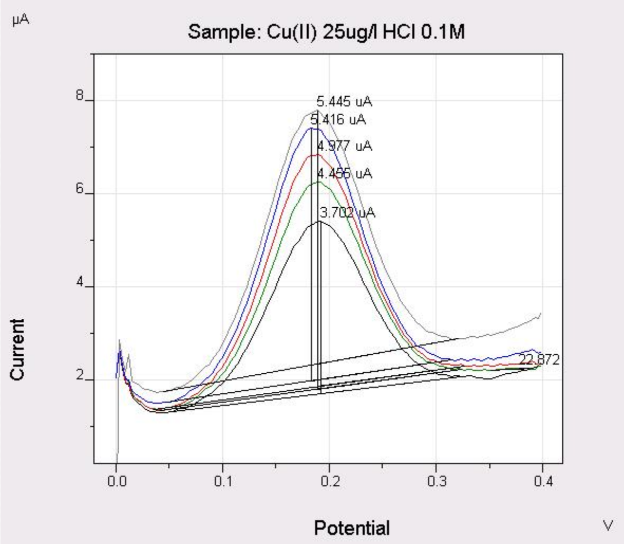
NTA – nitrilotriacetic acid

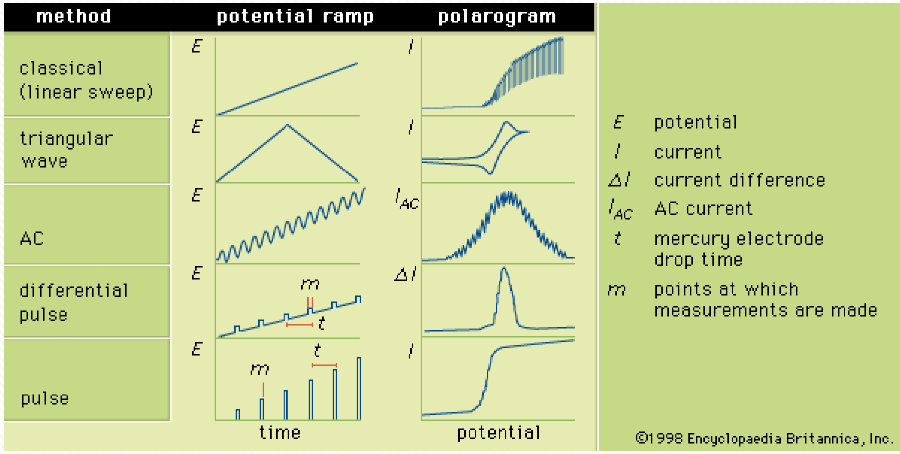


Free vs complexed solutes

Potentiometry/
Ion specific electrodes

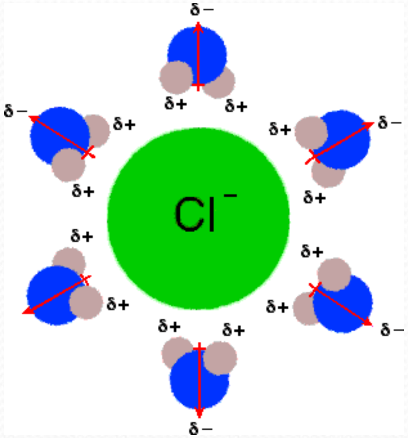
Polarography

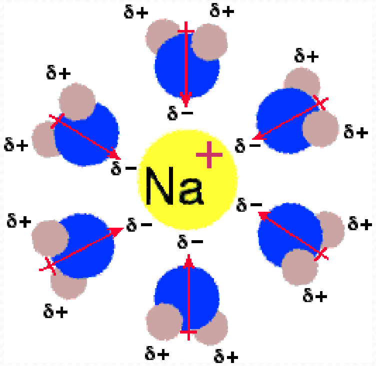




Non-associated electrolytes

Presumed to exist in the form of simple cations and anions, all of which are probably solvated.

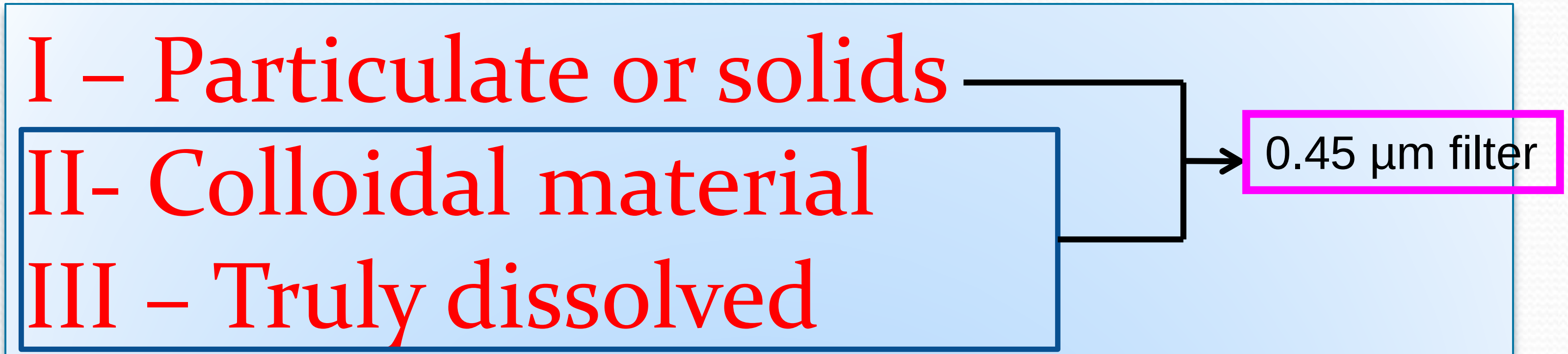




Free ion

Included in this category are elements that do not exhibit strong covalent bonding or electrostatic association between oppositely charged ions. This behavior is typical of the alkali metal ions: Li^+, Na^+, K^+, Rb^+, Cs^+.

The make-up of a natural solution



I – Particulate or solids

II- Colloidal material

III – Truly dissolved

0.45 µm filter

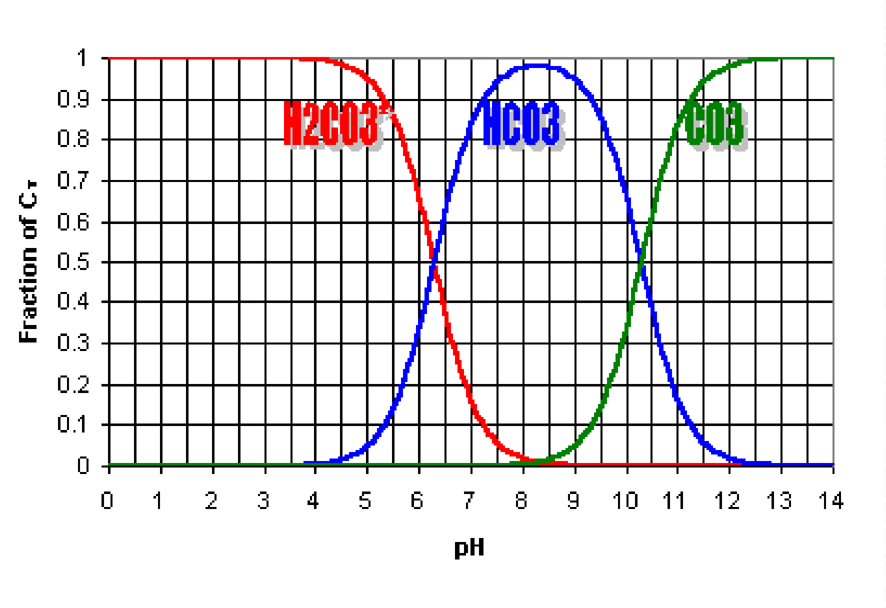
- a) non-associated (free)
- b) associated (complexed)
  - i) Weak electrolytes
  - ii) Complexes
  - iii) Ion-pairs

Associated electrolytes
(weak electrolytes)

Solutes that can exist as undissociated molecules in equilibrium with their ions. This group includes substances that might be regarded as weak acids or bases, such as H_2CO_3 and H_3BO_3, for which the dissociation is pH dependent.

$CO_{2(g)} + H_2O \leftrightarrow H_2CO_3$
$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$
$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$

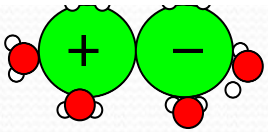
$$K°_1 = \frac{(H_+)\,(HCO_3^-)}{(H_2CO_3^*)} = 10^{-6.38} \text{ or } pK°_1 = 6.38$$



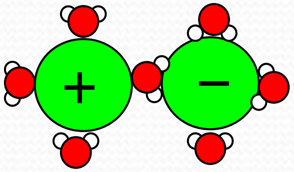
Associated electrolytes
(ion-pairs/outer-sphere complexes)

Ion-pairs result from purely electrostatic attraction between oppositely charged ions.

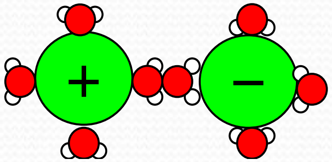
ex: $Cd^{2+} + Cl^{-} \leftarrow\rightarrow CdCl^{+}$ (positive ion pair)
$Hg^{2+} + 3Cl^{-} \leftarrow\rightarrow HgCl_3^{-}$ (negative ion pair)
$Mg^{2+} + SO_4^{2-} \leftarrow\rightarrow MgSO_4^{o}$ (neutral ion pair)



Contact ion-pair



Solvent-shared ion-pair



Solvent-separated ion-pair

Associated electrolytes
(ion-pairs /stability)

$$Mg^{2+} + SO_4^{2-} \leftrightarrow MgSO_4^o$$

$$K^o(MgSO_4^o) = \frac{(MgSO_4^o)}{(Mg^{2+})\,(SO_4^{2-})} = \frac{[MgSO_4^o]}{[Mg^{2+}]_F\,[SO_4^{2-}]_F} \quad \frac{\gamma(MgSO_4^o)}{\gamma_F(Mg^{2+})\,\gamma_F(SO_4^{2-})}$$

$$= K^*(MgSO_4^o) \times \frac{\gamma(MgSO_4^o)}{\gamma_F(Mg^{2+})\,\gamma_F(SO_4^{2-})}$$

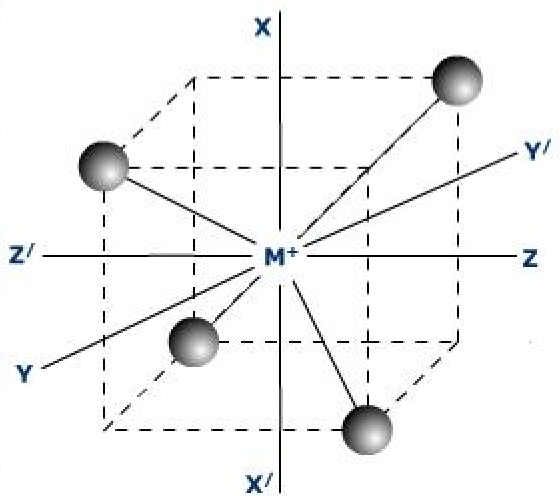
$$= 165 \text{ at } 25^oC \text{ and } I = 0$$

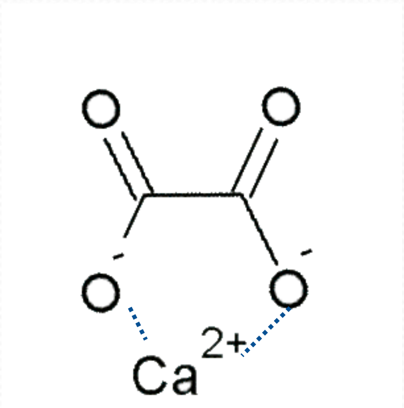
Ion-pairs are transient species held by strictly electrostatic interactions, most often between ions that have not shed their hydration layer. Nevertheless, the nature of the complexes can change with changes in T and P.

As temperature increases, the dielectric constant of water decreases so that ion-solvent interactions become weaker. As a consequence, a solvent-separated ion-pair may develop into a solvent-shared ion-pair, into a contact ion-pair and eventually into an inner-sphere complex.

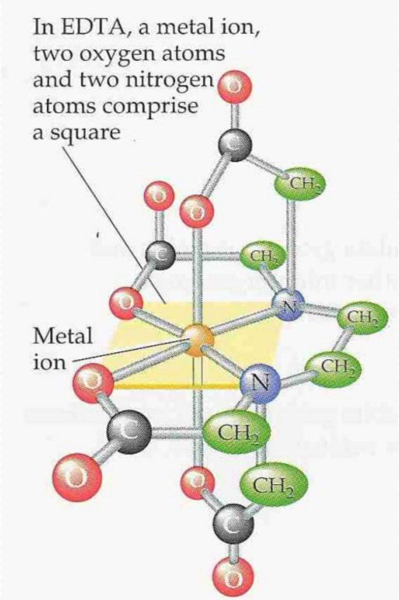
Associated electrolytes
(true or inner-sphere complexes)

Formed by interaction between a cationic species and ligands (organic or inorganic), and for which covalent bonding is typically important.
The number of linkages attaching ligands to a central atom is known as the coordination number.
Complexes in which the ligand attaches itself to the central atom through two or more bonds are known as chelates or multidentate complexes.





Calcium oxalate


In EDTA, a metal ion, two oxygen atoms and two nitrogen atoms comprise a square

Metal ion

Associated electrolytes

(true complexes /stability)

	Sequential		Global/cumulative constant
$M + L \leftarrow\rightarrow ML$	$K_1 = \frac{[ML]}{[M]\,[L]}$	$=$	$\beta_1 =$ global constant
$ML + L \leftarrow\rightarrow ML_2$	$K_2 = \frac{[ML^2]}{[ML]\,[L]}$	&	$\beta_2 = \frac{[ML^2]}{[M]\,[L]^2}$
. . .			
$ML_{n-1} + L \leftarrow\rightarrow ML_n$	$K_{n+1} = \frac{[ML_n]}{[ML_{n-1}]\,[L]}$	&	$\beta_n = \frac{[ML_n]}{[M]\,[L]^n}$

or $\beta_n = K_1K_2 \ldots K_n = [ML_n]/[M][L]^n = \prod K_i$

and $\Sigma M = [M] + [M]\,\Sigma\,\beta_i\,[L]^i$ and $\Sigma L = [L] + [M]\,\Sigma\,\beta_i\,[L]^i$

Associated electrolytes

(true complex formation involving a proton exchange)

Sequential Global constant

$M + HL \leftrightarrow ML + H^+ \quad {}^*K_1 = \frac{[ML]\,[H^+]}{[M]\,[HL]} = {}^*\beta_1 =$ global constant

$$ML + HL \leftrightarrow ML_2 + H^+ \quad {}^*K_2 = \frac{[ML^2]\,[H^+]}{[ML]\,[HL]} \quad \& \quad {}^*\beta_2 = \frac{[ML^2]\,[H^+]^2}{[M]\,[HL]^2}$$

. . .

$$ML_{n-1} + HL \leftrightarrow ML_n + H^+ \quad {}^*K_n = \frac{[ML_n]\,[H^+]}{[ML_{n-1}]\,[HL]} \quad \& \quad {}^*\beta_{n+1} = \frac{[ML_n]\,[H^+]^n}{[M]\,[HL]^n}$$

or $\quad {}^*\beta_n = {}^*K_1 {}^*K_2 \ldots {}^*K_n = [ML_n]\,[H^+]^n/[M][L]^n = \prod {}^*K_i$

and $\quad \Sigma M = [M] + [M]\, \Sigma\, {}^*\beta_i\, [HL]^i\, /[H^+]^i$

and $\quad \Sigma L = [L] + [M]\, \Sigma\, {}^*\beta_i\, [HL]^i/[H^+]^i$

Associated electrolytes

(polynuclear complexes)

Some complexes can contain more than one metal cation. They are typically uncommon in natural waters because they are only stable at very high metal concentrations. The general reaction for the formation of these polynuclear complexes is written as:

$$mM + nL \leftarrow\rightarrow M_mL_n$$

for which: $ß_{mn} = [M_mL_n]/[M]^m [L]^n$

or if written in terms of proton-metal exchange:

$$mM + nHL \leftarrow\rightarrow M_mL_n + nH^+$$

for which: $*ß_{mn} = [M_mL_n] [H^+]^n/[M]^m [HL]^n$

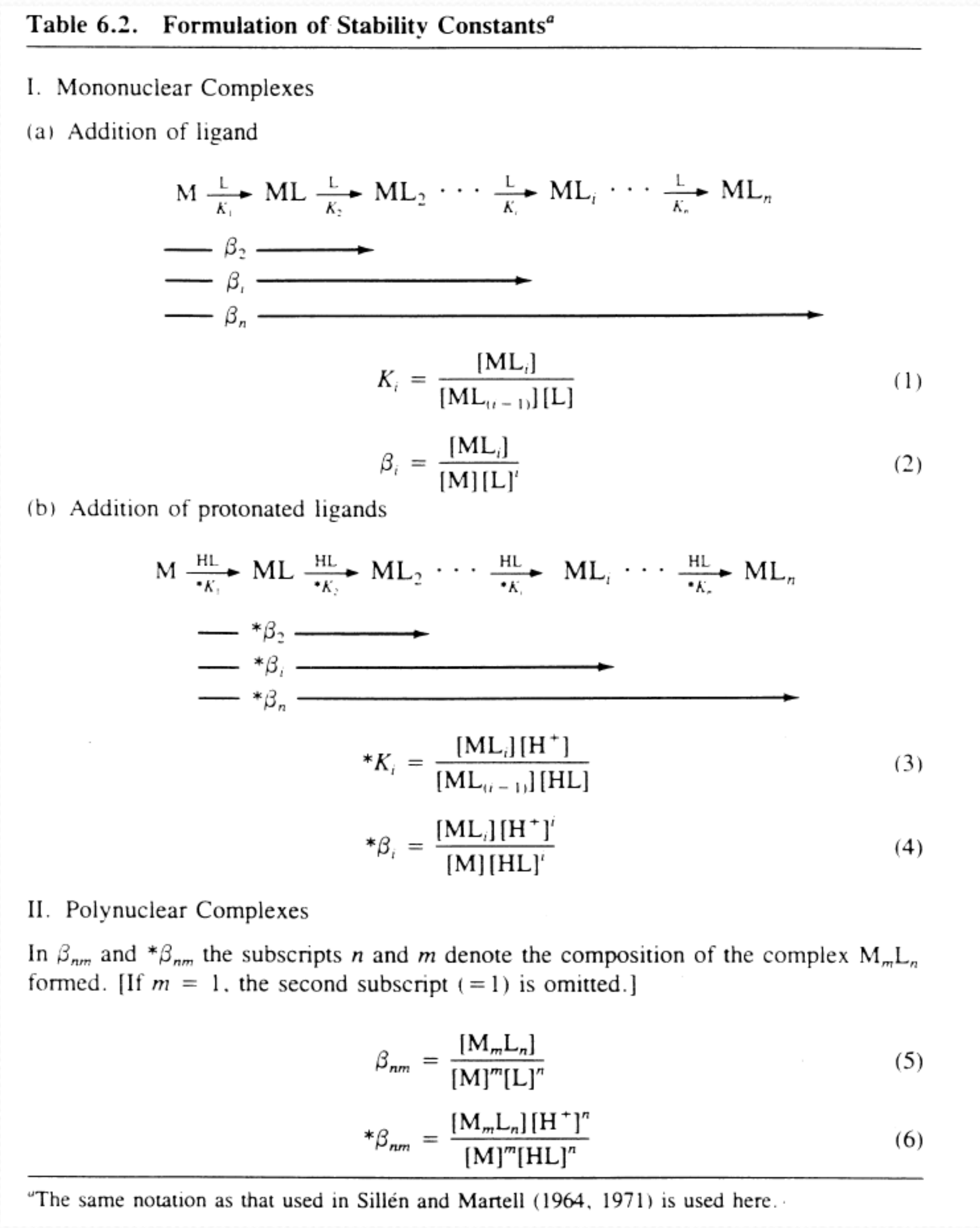


Table 6.2. Formulation of Stability Constants[a]

I. Mononuclear Complexes

(a) Addition of ligand

$$M \xrightarrow[K_1]{L} ML \xrightarrow[K_2]{L} ML_2 \cdots \xrightarrow[K_i]{L} ML_i \cdots \xrightarrow[K_n]{L} ML_n$$

$$\text{——}\ \beta_2 \longrightarrow$$

$$\text{——}\ \beta_i \longrightarrow$$

$$\text{——}\ \beta_n \longrightarrow$$

$$K_i = \frac{[ML_i]}{[ML_{(i-1)}][L]} \qquad (1)$$

$$\beta_i = \frac{[ML_i]}{[M][L]^i} \qquad (2)$$

(b) Addition of protonated ligands

$$M \xrightarrow[*K_1]{HL} ML \xrightarrow[*K_2]{HL} ML_2 \cdots \xrightarrow[*K_i]{HL} ML_i \cdots \xrightarrow[*K_n]{HL} ML_n$$

$$\text{——}\ {}^*\beta_2 \longrightarrow$$

$$\text{——}\ {}^*\beta_i \longrightarrow$$

$$\text{——}\ {}^*\beta_n \longrightarrow$$

$$*K_i = \frac{[ML_i][H^+]}{[ML_{(i-1)}][HL]} \qquad (3)$$

$$*\beta_i = \frac{[ML_i][H^+]^i}{[M][HL]^i} \qquad (4)$$

II. Polynuclear Complexes

In β_{nm} and $*\beta_{nm}$ the subscripts n and m denote the composition of the complex M_mL_n formed. [If $m = 1$, the second subscript $(=1)$ is omitted.]

$$\beta_{nm} = \frac{[M_mL_n]}{[M]^m[L]^n} \qquad (5)$$

$$*\beta_{nm} = \frac{[M_mL_n][H^+]^n}{[M]^m[HL]^n} \qquad (6)$$

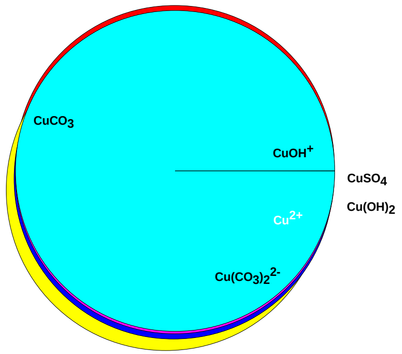
---

[a] The same notation as that used in Sillén and Martell (1964, 1971) is used here.

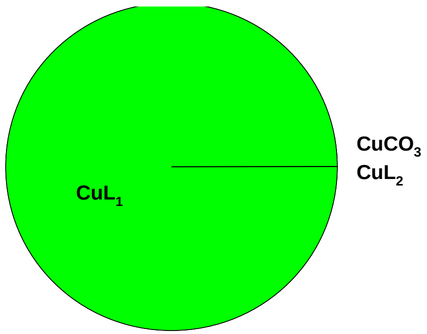
Associated electrolytes

(speciation of Cu(+II) in seawater)

Inorganic speciation of Cu^{2+}



Organic speciation of Cu^{2+}



$Cu^{2+} + L_1 = CuL_1 \quad K_1 = 10^{12}$

$Cu^{2+} + L_2 = CuL_2 \quad K_2 = 10^9$

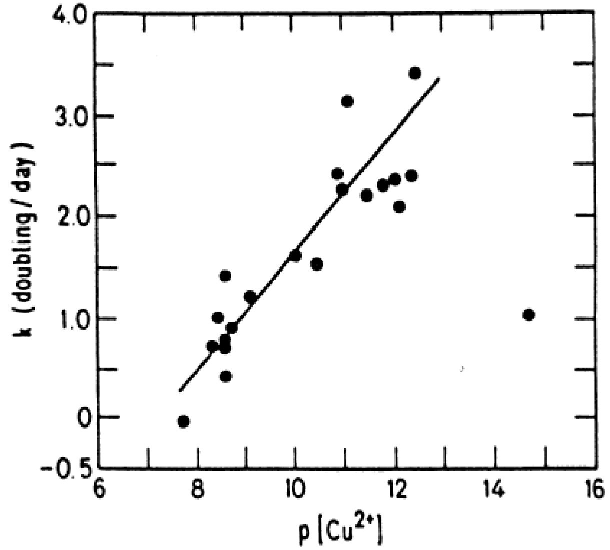
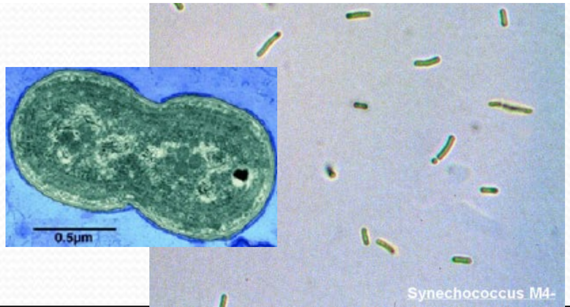


Figure 6.20 Effect of "free" Cu·aq^{2+} on growth of algae (*Chaetoceros socialis*) in seawater. The seawater contained pCu buffers made by appropriate additions of Cu(II) and of various chelators. pCu (= − log [Cu^{2+}]) was calculated from the concentrations of total Cu(II) and complex formers present and from pH. (From Jackson and Morgan [63].)



Associated electrolytes

(speciation of Cd(II) with chloride)

As temperature increases, the dielectric constant of water decreases so that an ion-pair (outer-sphere complex) may develop into an inner-sphere complex.

Reactions	K_i		ß$_i$
$Cd^{2+} + Cl^- \leftrightarrow CdCl^+$	21	$Cd^{2+} + Cl^- \leftrightarrow CdCl^+$	21
$CdCl^- + Cl^- \leftrightarrow CdCl_2^o$	7.9	$Cd^{2+} + 2Cl^- \leftrightarrow CdCl_2^o$	$K_1K_2 = 166$
$CdCl_2^o + Cl^- \leftrightarrow CdCl_3^-$	1.23	$Cd^{2+} + 3Cl^- \leftrightarrow CdCl_3^-$	$K_1K_2K_3 = 204$
$CdCl_3^- + Cl^- \leftrightarrow CdCl_4^{2-}$	0.35	$Cd^{2+} + 4Cl^- \leftrightarrow CdCl_4^{2-}$	$K_1K_2K_3K_4 = 71.5$

$$\Sigma Cd = C = [Cd^{2+}] + [CdCl^+] + [CdCl_2^o] + [CdCl_3^-] + [CdCl_4^{2-}]$$

substituting the cumulative constants we obtain:

$$\Sigma Cd = C = [Cd^{2+}]\ (\ 1 + \text{ß}_1[Cl^-] + \text{ß}_2[Cl^-]^2 + \text{ß}_3[Cl^-]^3 + \text{ß}_4[Cl^-]^4) = [Cd^{2+}]\ (\ 1 + \Sigma\ \text{ß}_n[Cl^-]^n)$$

Associated electrolytes

(speciation of Cd(II) with chloride)

The fraction of free cadmium, as well as all the other species, can be expressed as a fraction of the total Cd concentration in terms of the cumulative (or overall) constants and the chloride concentration.

$$\Sigma Cd = C = [Cd^{2+}] + [CdCl^{+}] + [CdCl_2^{o}] + [CdCl_3^{-}] + [CdCl_4^{2-}]$$

$$= [Cd^{2+}]\ (1 + ß_1[Cl^-] + ß_2[Cl^-]^2 + ß_3[Cl^-]^3 + ß_4[Cl^-]^4) = [Cd^{2+}]\ (1 + \Sigma\ ß_n[Cl^-]^n)$$

$$\alpha_o = [Cd^{2+}]/C = 1/(1 + ß_1[Cl^-] + ß_2[Cl^-]^2 + ß_3[Cl^-]^3 + ß_4[Cl^-]^4)$$

$\alpha_1 = [CdCl^{+}]/C = ß_1[Cl^-]\ \alpha_o$,
$\alpha_2 = [CdCl_2^{o}]/C = ß_2[Cl^-]^2\ \alpha_o$,
$\alpha_3 = [CdCl_3^{-}]/C = ß_3[Cl^-]^3\ \alpha_o$, and
$\alpha_4 = [CdCl_4^{2-}]/C = ß_4[Cl^-]^4\ \alpha_o$

Associated electrolytes

(speciation as a function of [Cl$^-$])

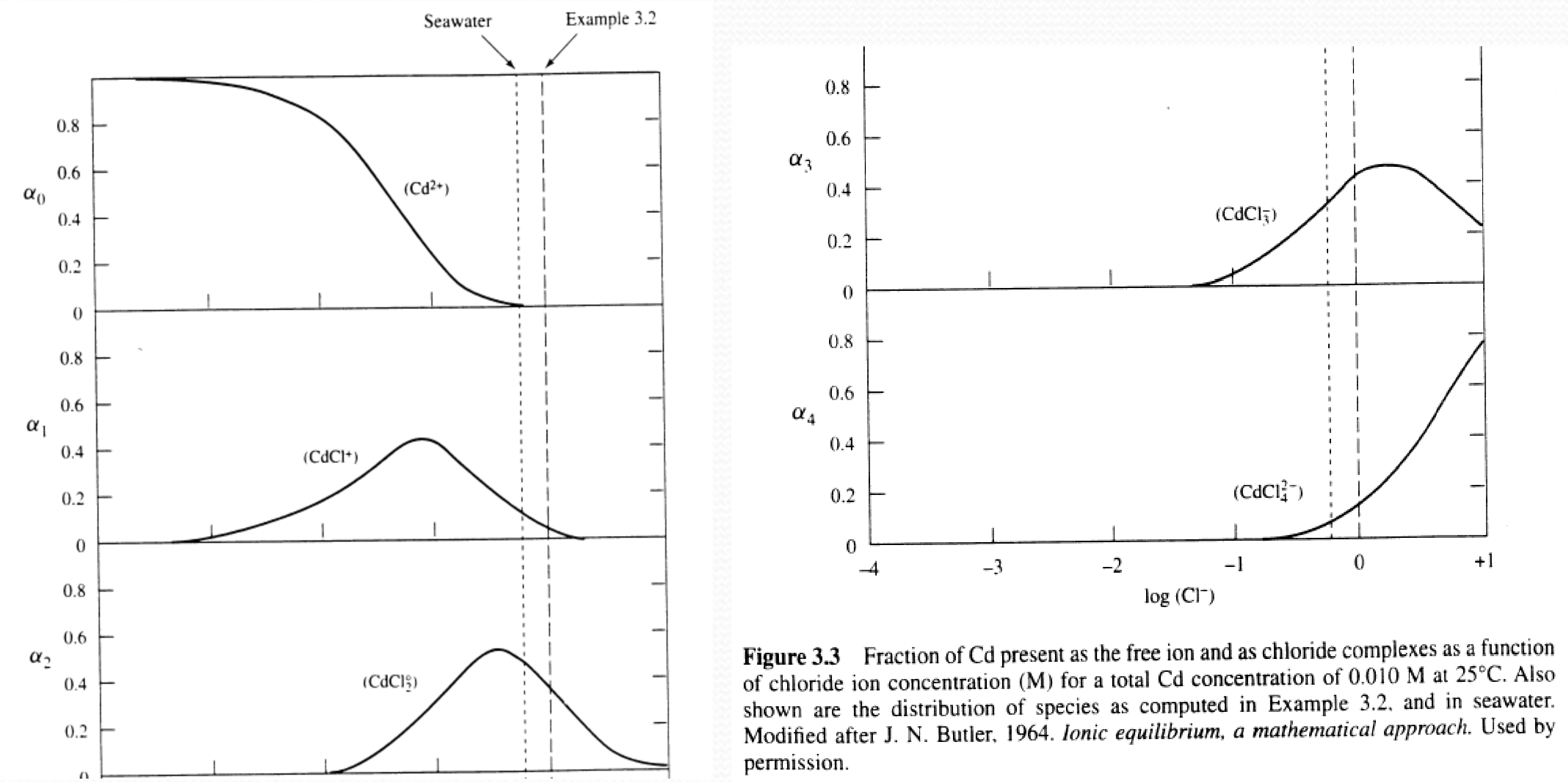


Figure 3.3 Fraction of Cd present as the free ion and as chloride complexes as a function of chloride ion concentration (M) for a total Cd concentration of 0.010 M at 25°C. Also shown are the distribution of species as computed in Example 3.2, and in seawater. Modified after J. N. Butler, 1964. *Ionic equilibrium, a mathematical approach.* Used by permission.

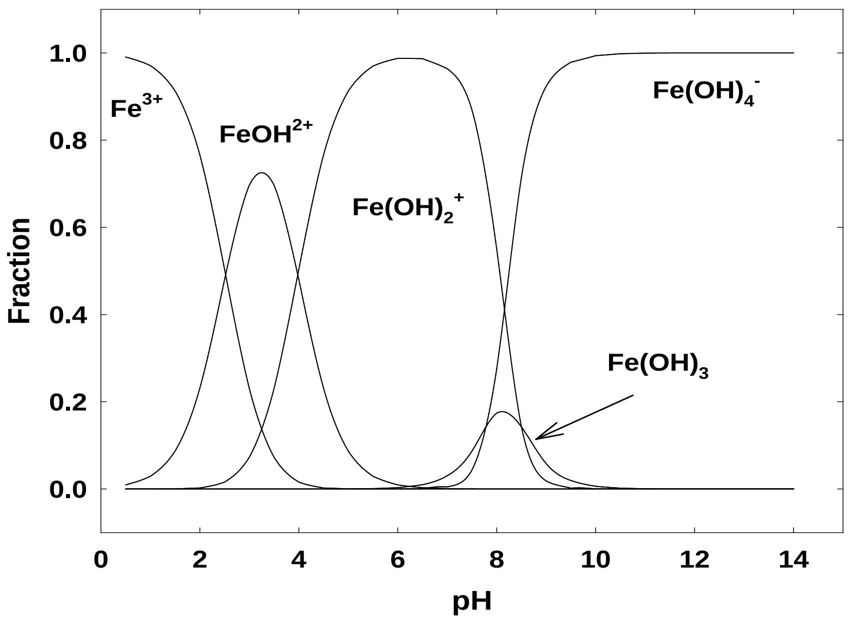
As the dielectric constant of water decreases, its ability to hold charges in solution decreases and neutral complexes become favoured.

Metal complexation

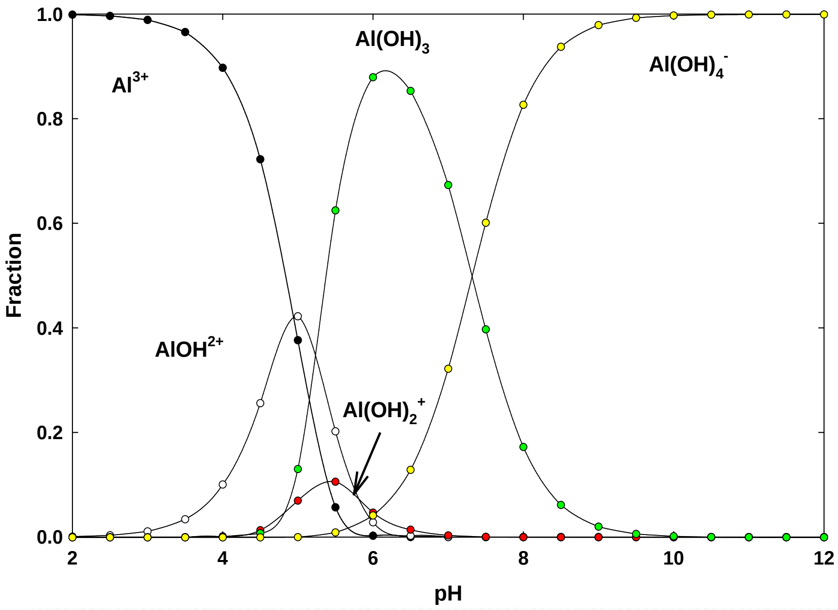
(speciation as a function of pH)

1) Complexes generally increase the solubility of metals that are buffered by the presence of a sparingly soluble mineral.

Speciation of Fe(III) in NaCl



Speciation of Al(III) in NaCl



Metal complexation

(speciation as a function of pH)

1) Complexes generally increase the solubility of metals which are buffered by the presence of a sparingly soluble mineral.

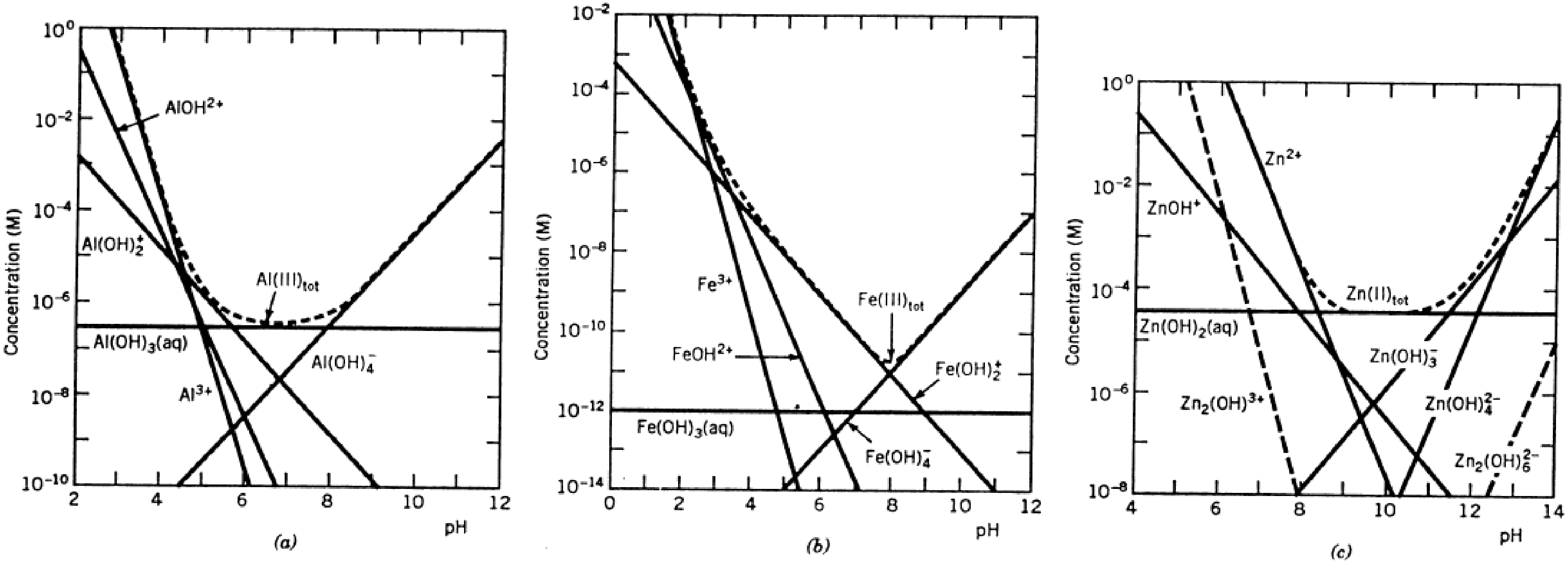


Figure 6.8. Effect of hydrolysis on solubility of (hydr)oxides: (a) solubility of α-$Al(OH)_3(s)$ (gibbsite), (b) solubility of amorphous $FeOOH(s)$, and (c) solubility of amorphous $Zn(OH)_2(s)$. Data from Baes and Mesmer (1976). Multinuclear species are omitted.

Metal complexation

2) The *properties of complexes rather than those of the free ions determine the mobility of elements in solution.*

For example, the group V and VI elements form strong oxyanions: AsO_4^{3-}, PO_4^{3-}, SO_4^{2-}. The mobilities and environmental properties of these elements are therefore chiefly determined by those of their complexes.

3) The nature of the complex can greatly modify (increase or decrease) the adsorptive properties of an element.

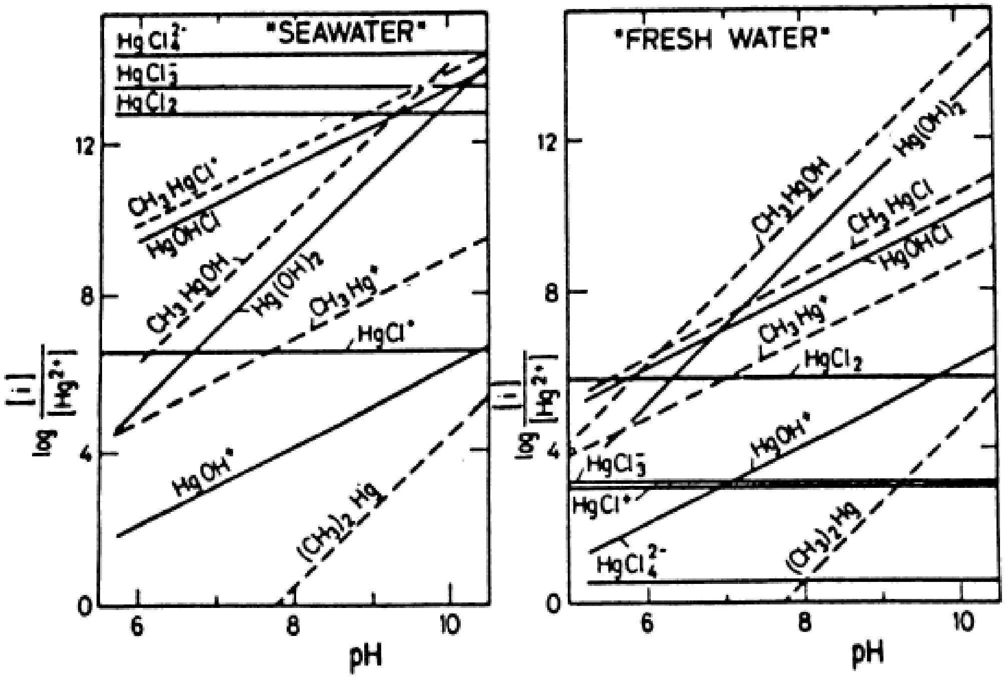
For example, AsO_4^{3-} (arsenate - As(V)) will adsorb more strongly than AsO_3^{3-} (arsenite – As(III)) to iron oxides, whereas it is the opposite for selenate (SeO_4^{2-} -Se(VI)) and selenite (SeO_3^{2-} -Se(IV)).

Other studies have shown that the scavenging efficiency of metal oxides for Hg(II) decreases as the [Cl^-] increases in solution. The $Hg(OH)_2^o$ complex predominates over a wide range of pH in low [Cl^-] natural waters

Metal complexation

4) The nature of the complexes will determine the toxicity and bioavailability of metals in natural waters.

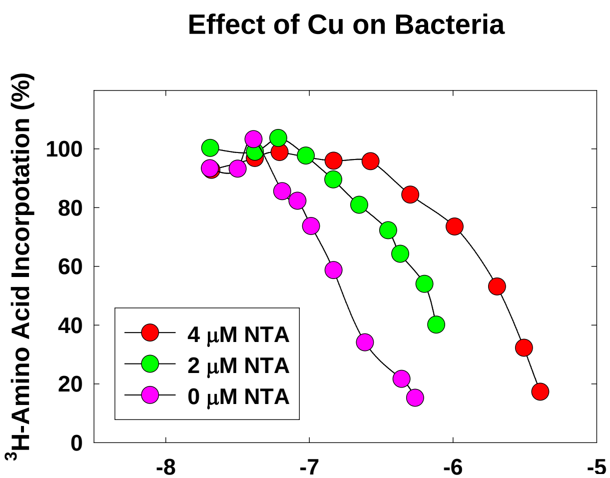
Methyl-mercury, CH_3Hg^+, is the most toxic mercury compound found in natural aquatic systems and is readily accumulated through the food chain.

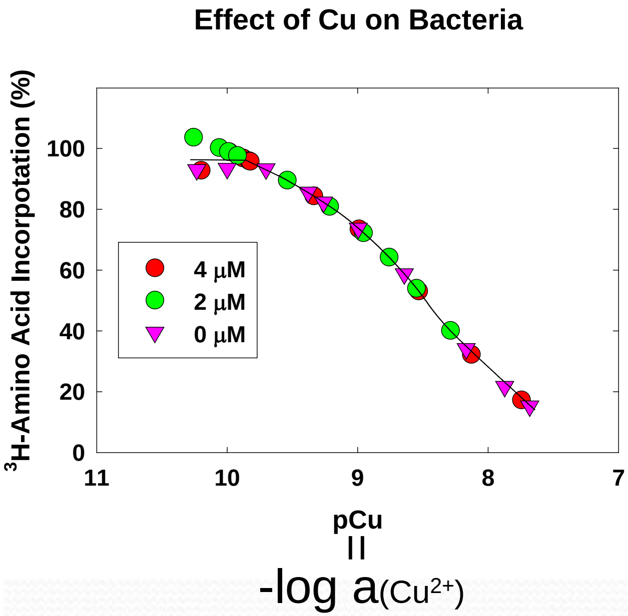


Metal toxicity/bioavailability

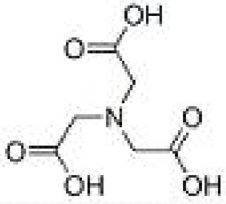
(FIAM model)

4) The nature of the complexes will determine the toxicity and bioavailability of metals in natural waters.


Effect of Cu on Bacteria


Effect of Cu on Bacteria

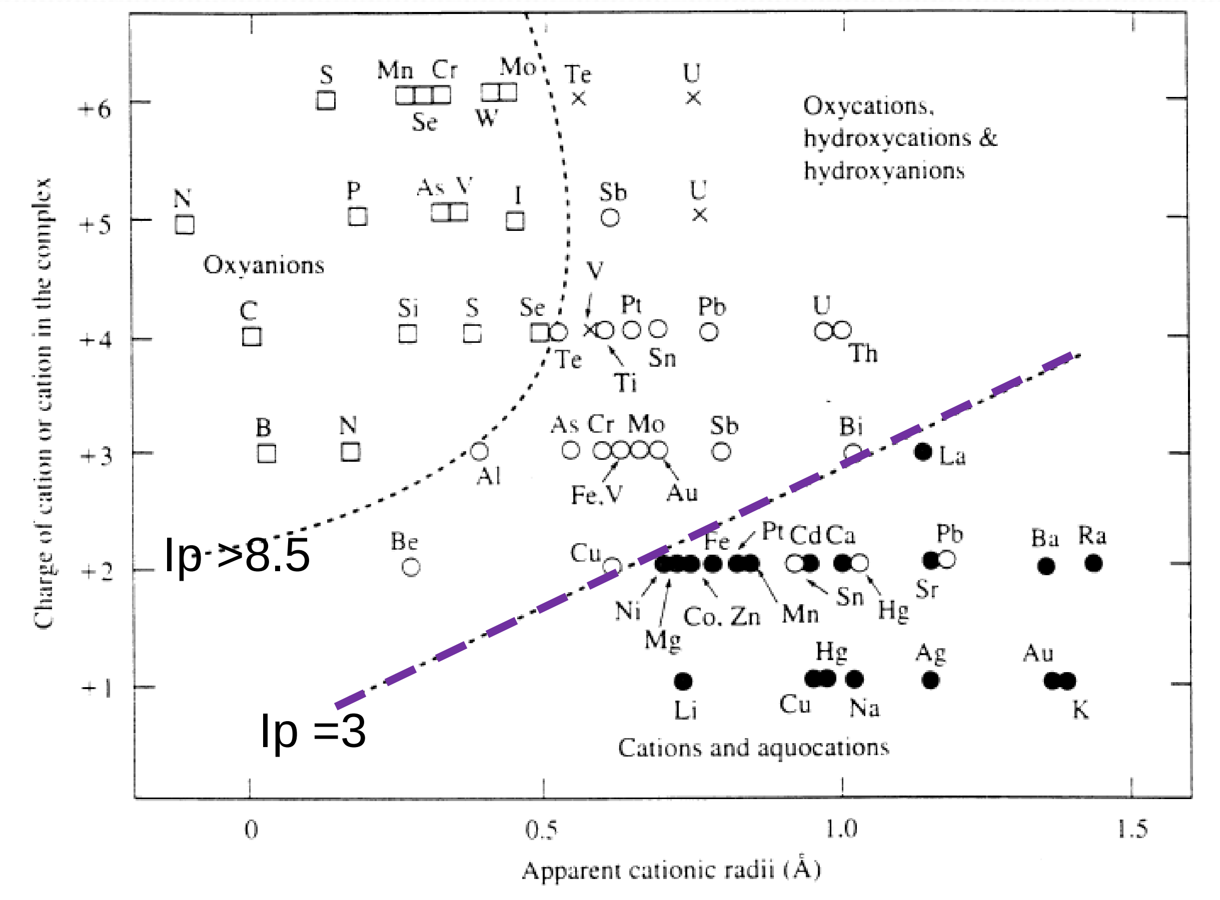
NTA – nitrilotriacetic acid



The nature of the complex and its charge will determine whether or not it can be transported through cell walls and interfere with internal biochemical processes.

Speciation in water

The number of water molecules surrounding a cation (coordination number of the cation with respect to H_2O) is a measure of the cation's surface-charge density (proportional to Z/r = Ip, the ionic potential in a solid).



● Cations and aquocations

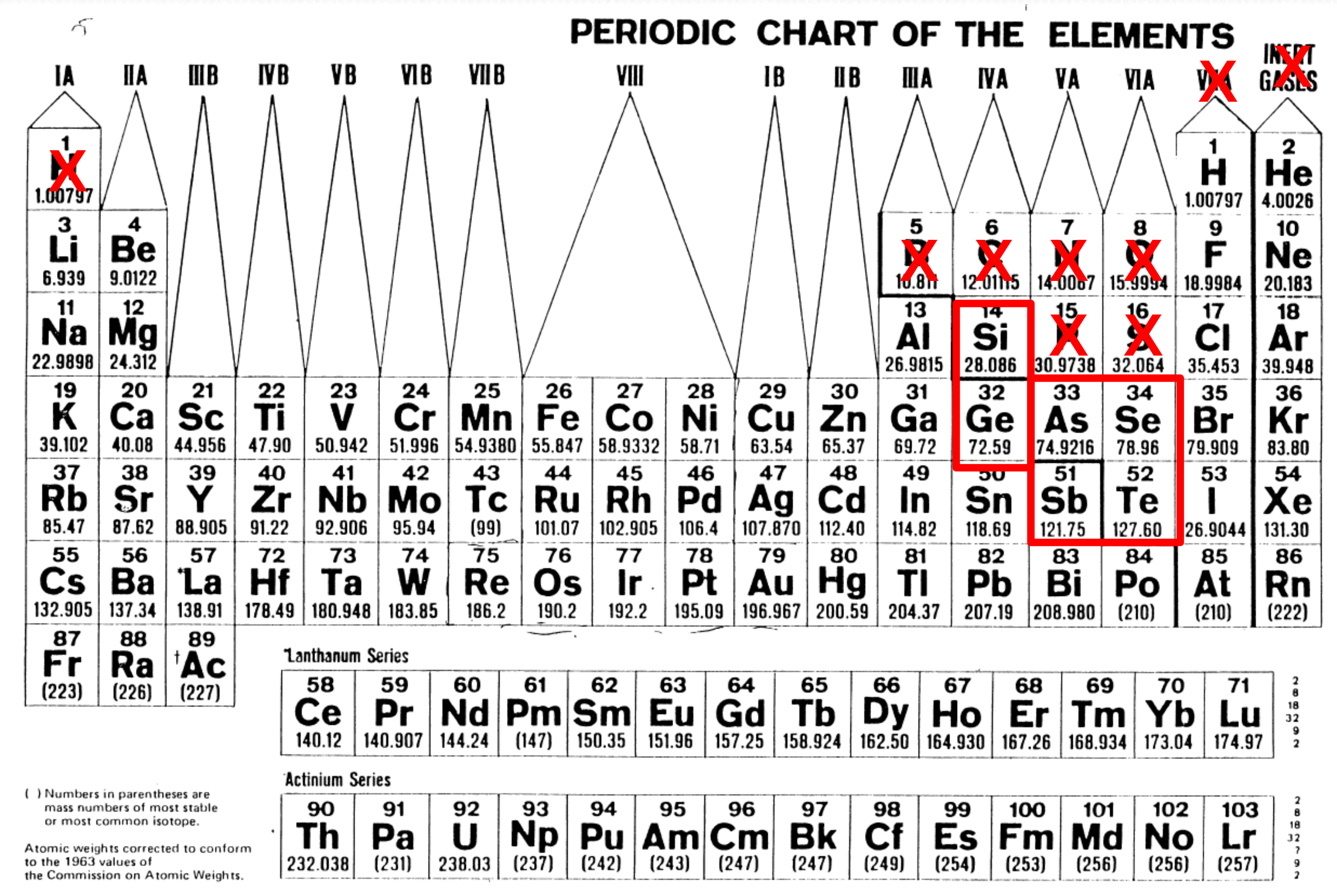
○ Hydroxycations and hydroxyanions

x oxycations

☐ oxyanions

● Cs; Ip = 0.6

Metal (and metalloid) classification



PERIODIC CHART OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	INERT GASES
1 H 1.00797																1 H 1.00797	2 He 4.0026
3 Li 6.939	4 Be 9.0122											5 B 10.811	6 C 12.01115	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183
11 Na 22.9898	12 Mg 24.312											13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.9044	54 Xe 131.30
55 Cs 132.905	56 Ba 137.34	57 *La 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 †Ac (227)															

*Lanthanum Series

58	59	60	61	62	63	64	65	66	67	68	69	70	71	
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	2 8 18 32 9 2
140.12	140.907	144.24	(147)	150.35	151.96	157.25	158.924	162.50	164.930	167.26	168.934	173.04	174.97	

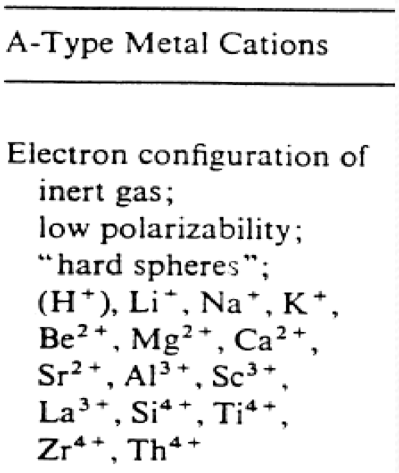
†Actinium Series

90	91	92	93	94	95	96	97	98	99	100	101	102	103	
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	2 8 18 32 7 9 2
232.038	(231)	238.03	(237)	(242)	(243)	(247)	(247)	(249)	(254)	(253)	(256)	(256)	(257)	

( ) Numbers in parentheses are mass numbers of most stable or most common isotope.

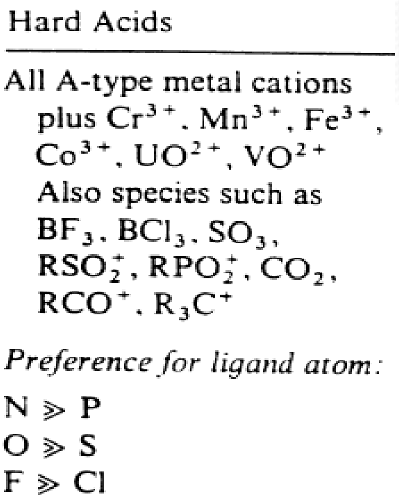
Atomic weights corrected to conform to the 1963 values of the Commission on Atomic Weights.

Metal classification



A-Type Metal Cations
Electron configuration of inert gas; low polarizability; "hard spheres"; (H$^+$), Li$^+$, Na$^+$, K$^+$, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Al^{3+}, Sc^{3+}, La^{3+}, Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}

Pearsons' classification



Hard Acids
All A-type metal cations plus Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, UO^{2+}, VO^{2+} Also species such as BF$_3$, BCl$_3$, SO$_3$, RSO$_2^+$, RPO$_2^+$, CO$_2$, RCO$^+$, R$_3$C$^+$

Preference for ligand atom:

N ≫ P

O ≫ S

F ≫ Cl

These d° cations are ions with high spherical symmetry and electron clouds which are not easily deformed or polarizable by electric fields of other ions. They form few complexes, mostly complexes with strong ionic character, such as with fluoride ions and ligands where oxygen is the donor atom. They basically are complexes that form between elements with the large differences in electronegativity.

Electronegativity is defined as the ability of an atom in a molecule to attract an electron to itself, a Lewis acid. When ΔEN =0, the bonding is purely covalent, until ΔEN reaches 1.7 covalency predominates. Larger ΔEN values indicate chiefly electrostatic or ionic bonding between the cation and ligand,

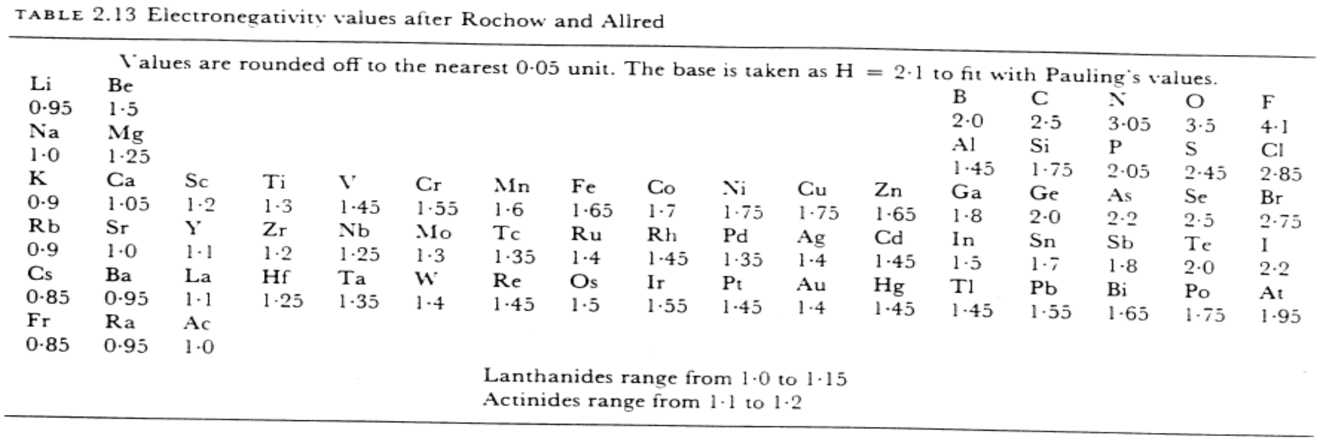


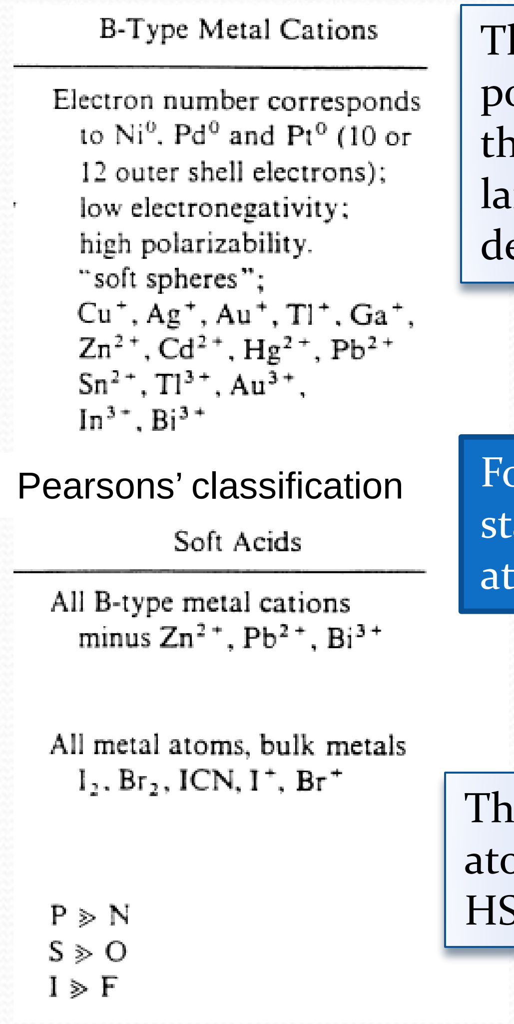
TABLE 2.13 Electronegativity values after Rochow and Allred

Values are rounded off to the nearest 0·05 unit. The base is taken as H = 2·1 to fit with Pauling's values.

Li	Be											B	C	N	O	F
0·95	1·5											2·0	2·5	3·05	3·5	4·1
Na	Mg											Al	Si	P	S	Cl
1·0	1·25											1·45	1·75	2·05	2·45	2·85
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
0·9	1·05	1·2	1·3	1·45	1·55	1·6	1·65	1·7	1·75	1·75	1·65	1·8	2·0	2·2	2·5	2·75
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
0·9	1·0	1·1	1·2	1·25	1·3	1·35	1·4	1·45	1·35	1·4	1·45	1·5	1·7	1·8	2·0	2·2
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
0·85	0·95	1·1	1·25	1·35	1·4	1·45	1·5	1·55	1·45	1·4	1·45	1·45	1·55	1·65	1·75	1·95
Fr	Ra	Ac														
0·85	0·95	1·0														

Lanthanides range from 1·0 to 1·15
Actinides range from 1·1 to 1·2

Metal classification



B-Type Metal Cations

Electron number corresponds to Ni^0. Pd^0 and Pt^0 (10 or 12 outer shell electrons);
low electronegativity;
high polarizability.
"soft spheres";
Cu^+, Ag^+, Au^+, Tl^+, Ga^+, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Sn^{2+}, Tl^{3+}, Au^{3+}, In^{3+}, Bi^{3+}

Pearsons' classification

Soft Acids

All B-type metal cations minus Zn^{2+}, Pb^{2+}, Bi^{3+}

All metal atoms, bulk metals
I_2, Br_2, ICN, I^+, Br^+

$P \gg N$
$S \gg O$
$I \gg F$

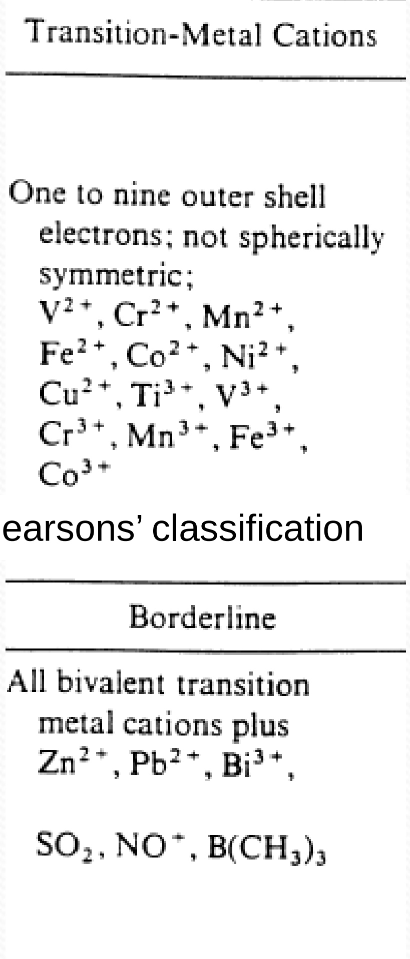
These metal ions have electron sheets that are easily distorted or polarizable. They tend to share their electrons with large anions. Unlike their d° counterparts, they form strong complexes because they form largely covalent bonded complexes and the stability of these complexes decreases with increasing ΔEN.

For example, the halide complexes increase in stability with decreasing EN (or increasing atomic weight or ionic size) of the ligand.

Complex	log K°
AgF^o	-0.3
$AgCl^o$	3.0
$AgBr^o$	4.3
AgI^o	8.1

They coordinate preferentially with bases containing I, S or N as donor atoms. They form insoluble sulfides and soluble complexes with S^{2-} and HS^- with stabilities increasing: $S^{2-} > SH^- > OH^- > F^-$.

Metal classification



Transition-Metal Cations
One to nine outer shell electrons; not spherically symmetric; V^{2+}, Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ti^{3+}, V^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}

Borderline
All bivalent transition metal cations plus Zn^{2+}, Pb^{2+}, Bi^{3+}, SO_2, NO^+, $B(CH_3)_3$

Pearsons’ classification

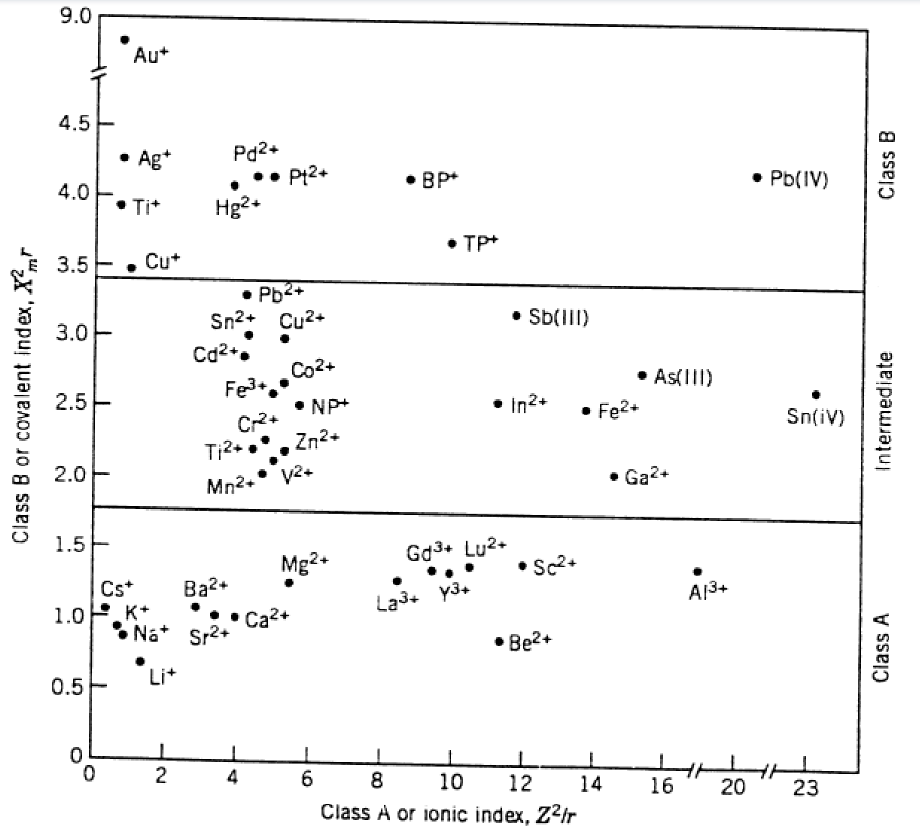
Although the transition metals (C-type) can be subdivided into different classes according to the order of the affinity for a series of ligands, in general, for almost every ligand, the stability of their complexes increases in the so-called "Irving-Williams" order.

$Mn^{2+}(d^5s^2) < Fe^{2+}(d^6s^2) < Co^{2+}(d^7s^2) < Ni^{2+}(d^8s^2) < Cu^{2+}(d^{10}s^1) > Zn^{2+}(d^{10}s^2)$

With the exception of Cu^{2+}, this corresponds to the order of increasing Ip. This order reflects the enhancement of the stability of complexes resulting from the electronic interaction between the cation and ligand, more specifically the degenerescence of the d orbitals and the distribution of the electrons between various energy levels → LFSE

Metal classification

A separation between A, B, and C-type metals and metalloids can be visualized by plotting an index of the B-character of the cations (i.e., their tendency to form covalent bonds = X^2r where X is the electronegativity) as a function of the ionic potential ($Ip = Z^2/r$), a measure of a metal ion’s propensity to form ionic bonds.



Interactions between metallic cations and ligands

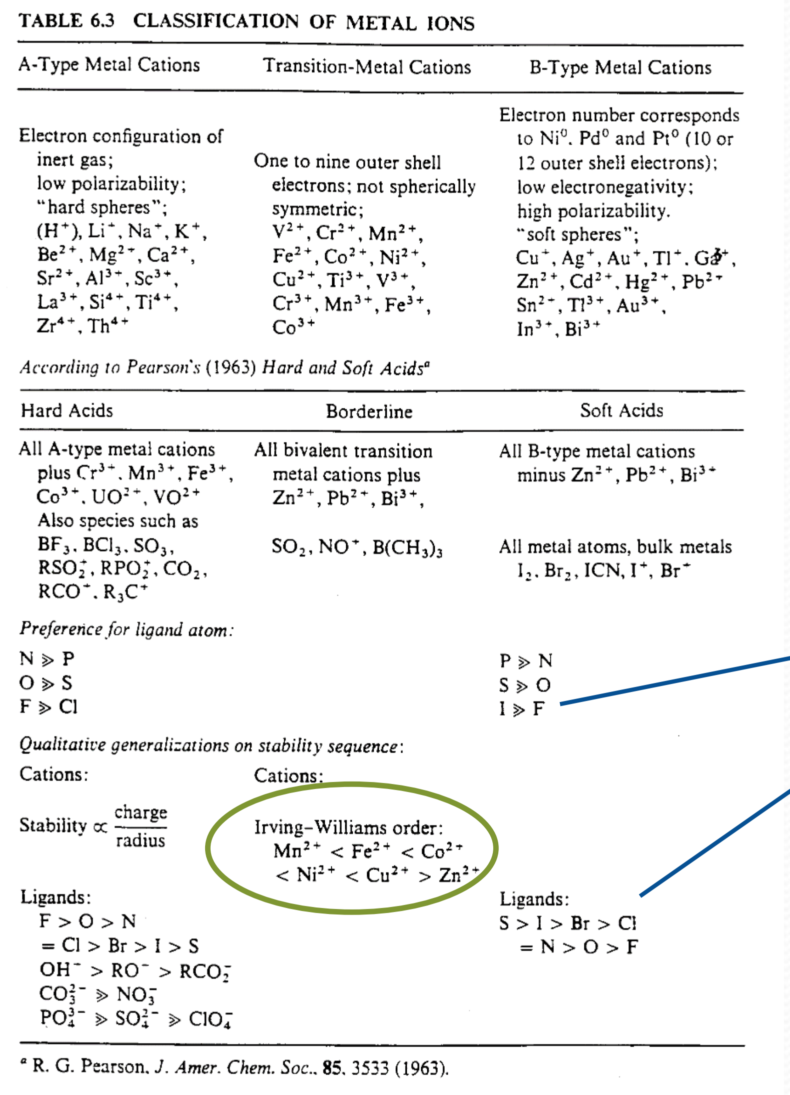


TABLE 6.3 CLASSIFICATION OF METAL IONS

A-Type Metal Cations	Transition-Metal Cations	B-Type Metal Cations
Electron configuration of inert gas; low polarizability; "hard spheres"; (H^+), Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Al^{3+}, Sc^{3+}, La^{3+}, Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}	One to nine outer shell electrons; not spherically symmetric; V^{2+}, Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ti^{3+}, V^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}	Electron number corresponds to Ni^0, Pd^0 and Pt^0 (10 or 12 outer shell electrons); low electronegativity; high polarizability. "soft spheres"; Cu^+, Ag^+, Au^+, Tl^+, Ga^{3+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+} Sn^{2+}, Tl^{3+}, Au^{3+}, In^{3+}, Bi^{3+}

According to Pearson's (1963) *Hard and Soft Acids*[a]

Hard Acids	Borderline	Soft Acids
All A-type metal cations plus Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, UO^{2+}, VO^{2+} Also species such as BF_3, BCl_3, SO_3, RSO_2^+, RPO_2^+, CO_2, RCO^+, R_3C^+	All bivalent transition metal cations plus Zn^{2+}, Pb^{2+}, Bi^{3+}, SO_2, NO^+, $B(CH_3)_3$	All B-type metal cations minus Zn^{2+}, Pb^{2+}, Bi^{3+} All metal atoms, bulk metals I_2, Br_2, ICN, I^+, Br^+
Preference for ligand atom:		
$N \gg P$ $O \gg S$ $F \gg Cl$		$P \gg N$ $S \gg O$ $I \gg F$
Qualitative generalizations on stability sequence:		
Cations: Stability $\propto \frac{\text{charge}}{\text{radius}}$	Cations: Irving–Williams order: $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$	
Ligands: $F > O > N = Cl > Br > I > S$ $OH^- > RO^- > RCO_2^-$ $CO_3^{2-} \gg NO_3^-$ $PO_4^{3-} \gg SO_4^{2-} \gg ClO_4^-$		Ligands: $S > I > Br > Cl = N > O > F$

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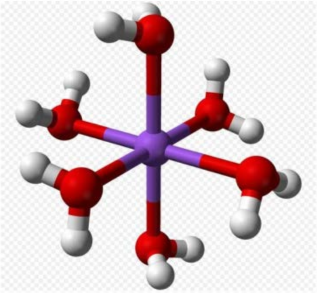
[a] R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).



Complex	log K°
AgF°	-0.3
AgCl°	3.0
AgBr°	4.3
AgI°	8.1

Interaction with organic ligands

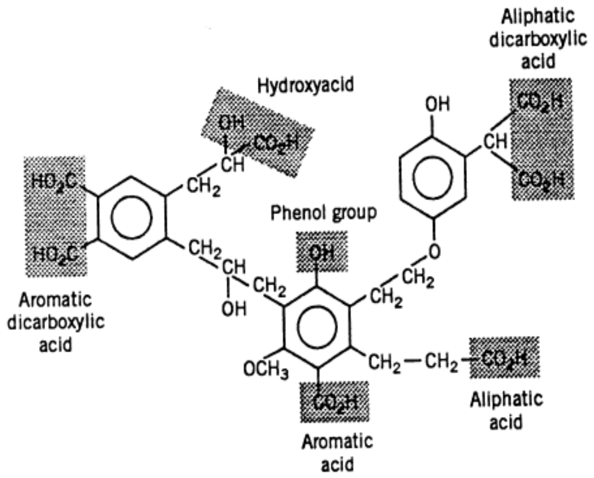


Figure 3.12. Exemplification of different possible —OH and —COOH groups in a hypothetical humic acid polymer. (From Thurman, 1985.)

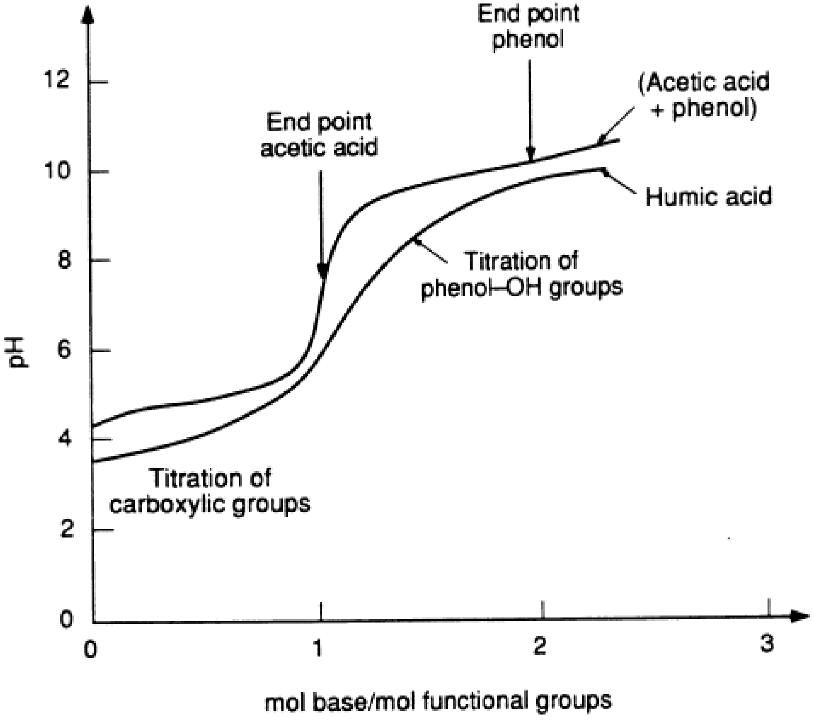
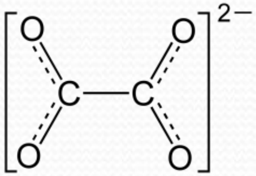
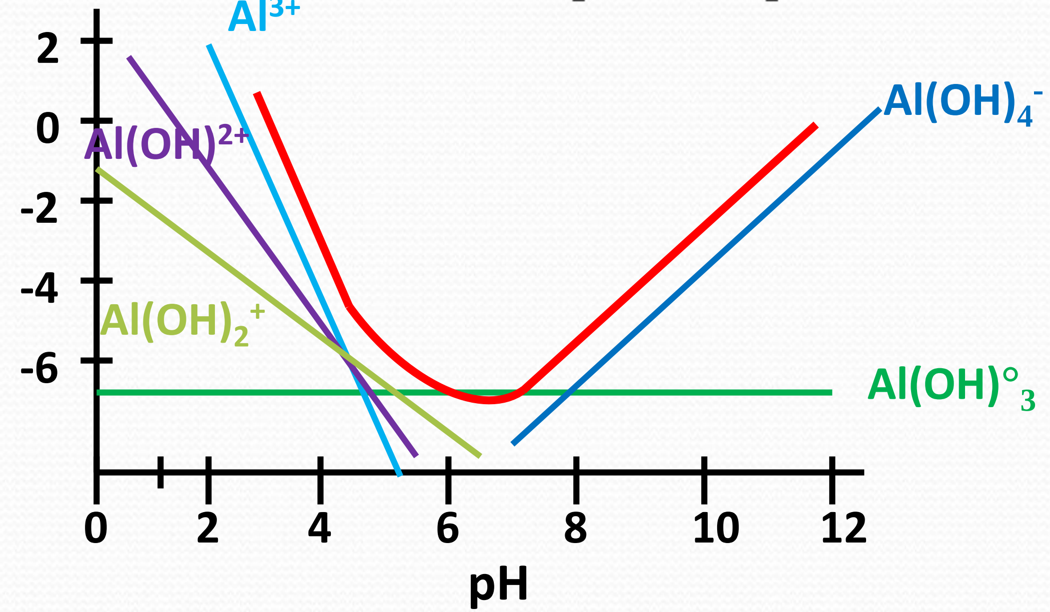


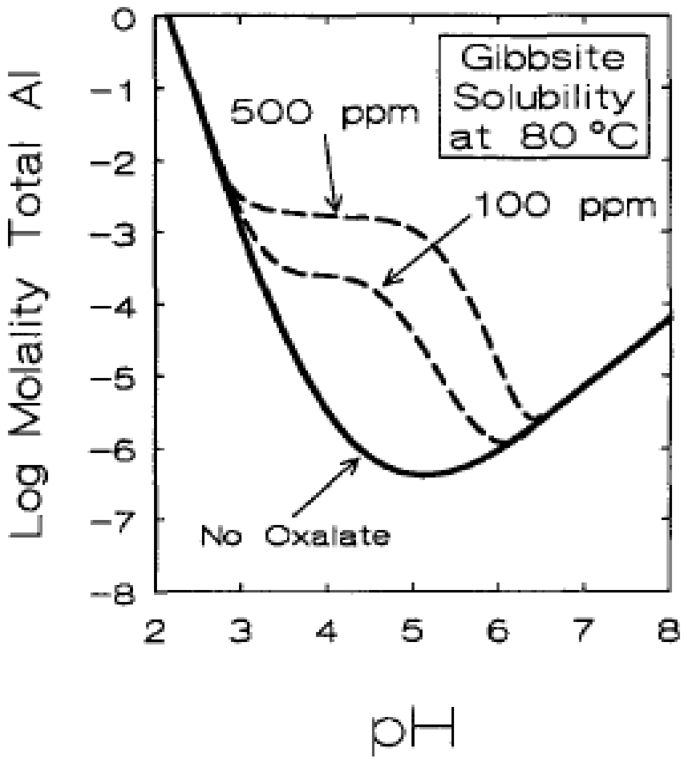
Figure 3.13. Comparison of alkalimetric titration of an equimolar (10^{-4} M) acetic acid (pK_a = 4.8) and phenol (pK_a = 10) with titration of humic acid containing $\sim 10^{-4}$ mol carboxylic groups.

Gibbsite solubility in the presence of oxalate

From: Fein (1991: Geology 19, 1037-1040)







$$\Sigma[Al] = [Al^{3+}] + [AlOH^{2+}] + [Al(OH)_2^{+}] + [Al(OH)_3^{\circ}] + [Al(OH)_4^{-}] + [Al(Ox)_3^{3-}]$$

Interaction with organic ligands

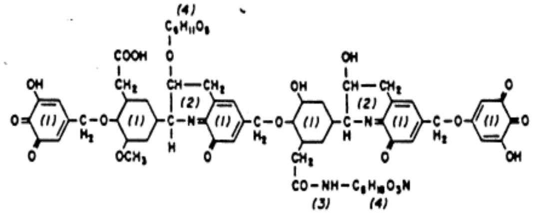


Fig. 3.6. The structure of the humic acid molecule (according to Dragunov, 1948). (1) Aromatic ring of the di- and trihydroxyphenol type, part of which has the double linkage of a quinone groupings; (2) Nitrogen in cyclic forms; (3) Nitrogen of peripheral chains; (4) Carbohydrate residues. (From Kononova, 1966.)

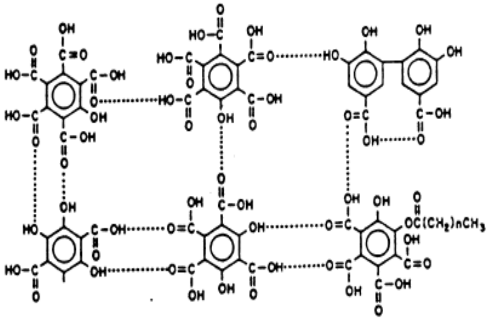


Fig. 3.7. Partial chemical structure of fulvic acid. (From Schnitzer, 1978.)

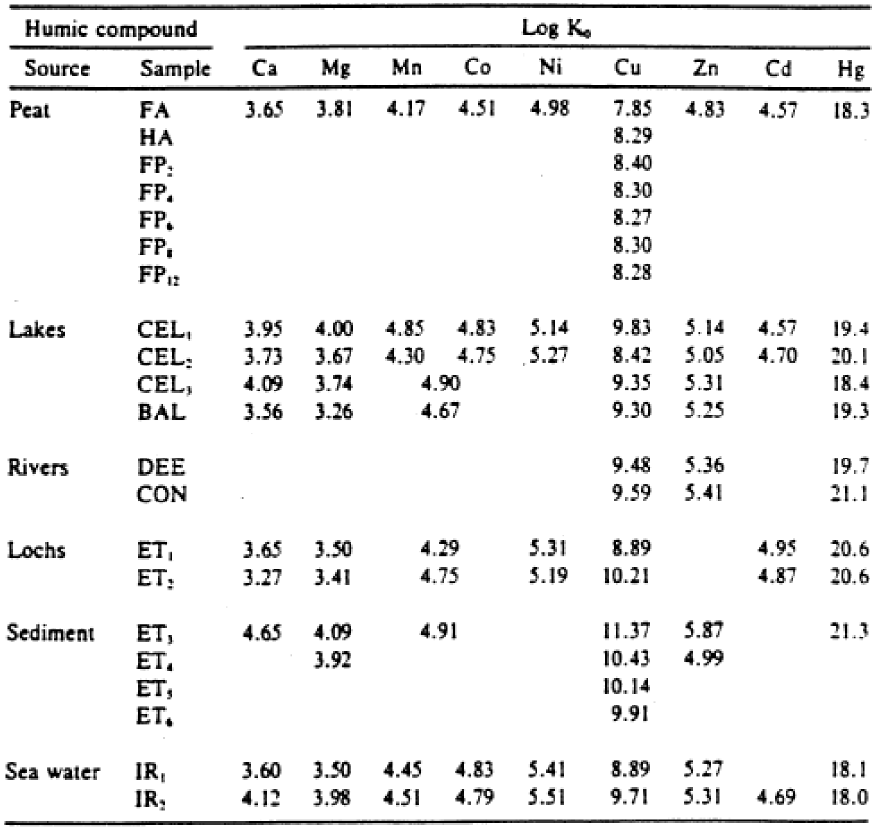
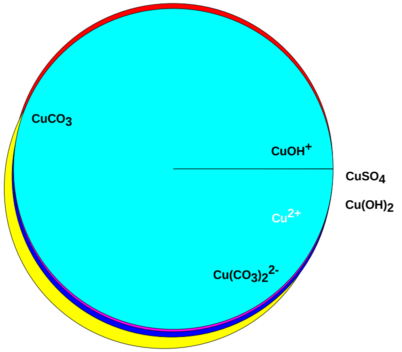


Table 4.10. Tabulation of overall stability constants (as log K_o) for humic compounds with Ca, Mg, Mn, Co, Ni, Cu, Zn, Cd, and Hg at pH 8.0 I = 0.02, derived by gel complexometry (after Mantoura et al., 1978, with permission from Estuarine and Coastal Marine Science, vol. 6. Copyright by Academic Press Inc. (London) Ltd.).

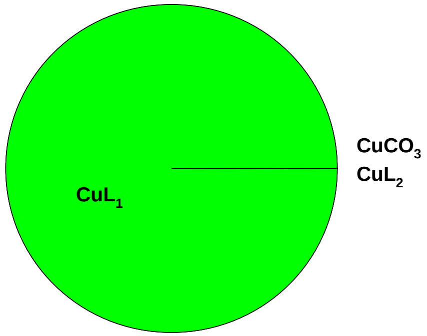
Humic compound		Log K_o								
Source	Sample	Ca	Mg	Mn	Co	Ni	Cu	Zn	Cd	Hg
Peat	FA	3.65	3.81	4.17	4.51	4.98	7.85	4.83	4.57	18.3
	HA						8.29			
	FP$_2$						8.40			
	FP$_4$						8.30			
	FP$_6$						8.27			
	FP$_8$						8.30			
	FP$_{12}$						8.28			
Lakes	CEL$_1$	3.95	4.00	4.85	4.83	5.14	9.83	5.14	4.57	19.4
	CEL$_2$	3.73	3.67	4.30	4.75	5.27	8.42	5.05	4.70	20.1
	CEL$_3$	4.09	3.74	4.90			9.35	5.31		18.4
	BAL	3.56	3.26	4.67			9.30	5.25		19.3
Rivers	DEE						9.48	5.36		19.7
	CON						9.59	5.41		21.1
Lochs	ET$_1$	3.65	3.50	4.29		5.31	8.89		4.95	20.6
	ET$_2$	3.27	3.41	4.75		5.19	10.21		4.87	20.6
Sediment	ET$_3$	4.65	4.09	4.91			11.37	5.87		21.3
	ET$_4$		3.92				10.43	4.99		
	ET$_5$						10.14			
	ET$_6$						9.91			
Sea water	IR$_1$	3.60	3.50	4.45	4.83	5.41	8.89	5.27		18.1
	IR$_2$	4.12	3.98	4.51	4.79	5.51	9.71	5.31	4.69	18.0

Interaction with organic ligands

Inorganic speciation of Cu^{2+}



Organic speciation of Cu^{2+}



$Cu^{2+} + L_1 = CuL_1 \quad K_1 = 10^{12}$

$Cu^{2+} + L_2 = CuL_2 \quad K_2 = 10^9$

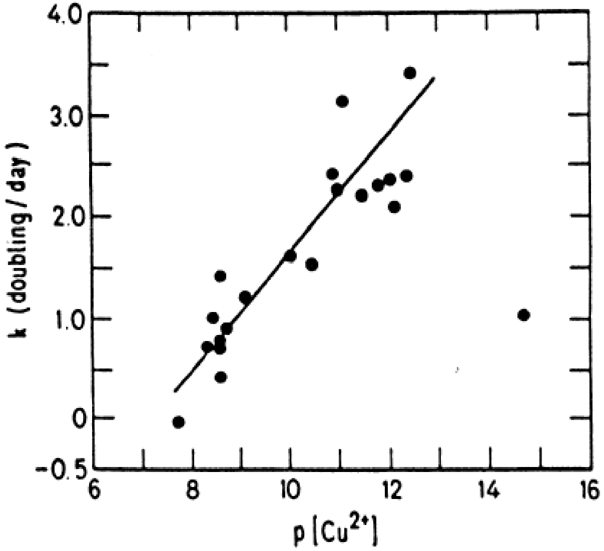


Figure 6.20 Effect of "free" $Cu \cdot aq^{2+}$ on growth of algae (*Chaetoceros socialis*) in seawater. The seawater contained pCu buffers made by appropriate additions of Cu(II) and of various chelators. pCu ($= -\log [Cu^{2+}]$) was calculated from the concentrations of total Cu(II) and complex formers present and from pH. (From Jackson and Morgan [63].)

Interaction with organic ligands

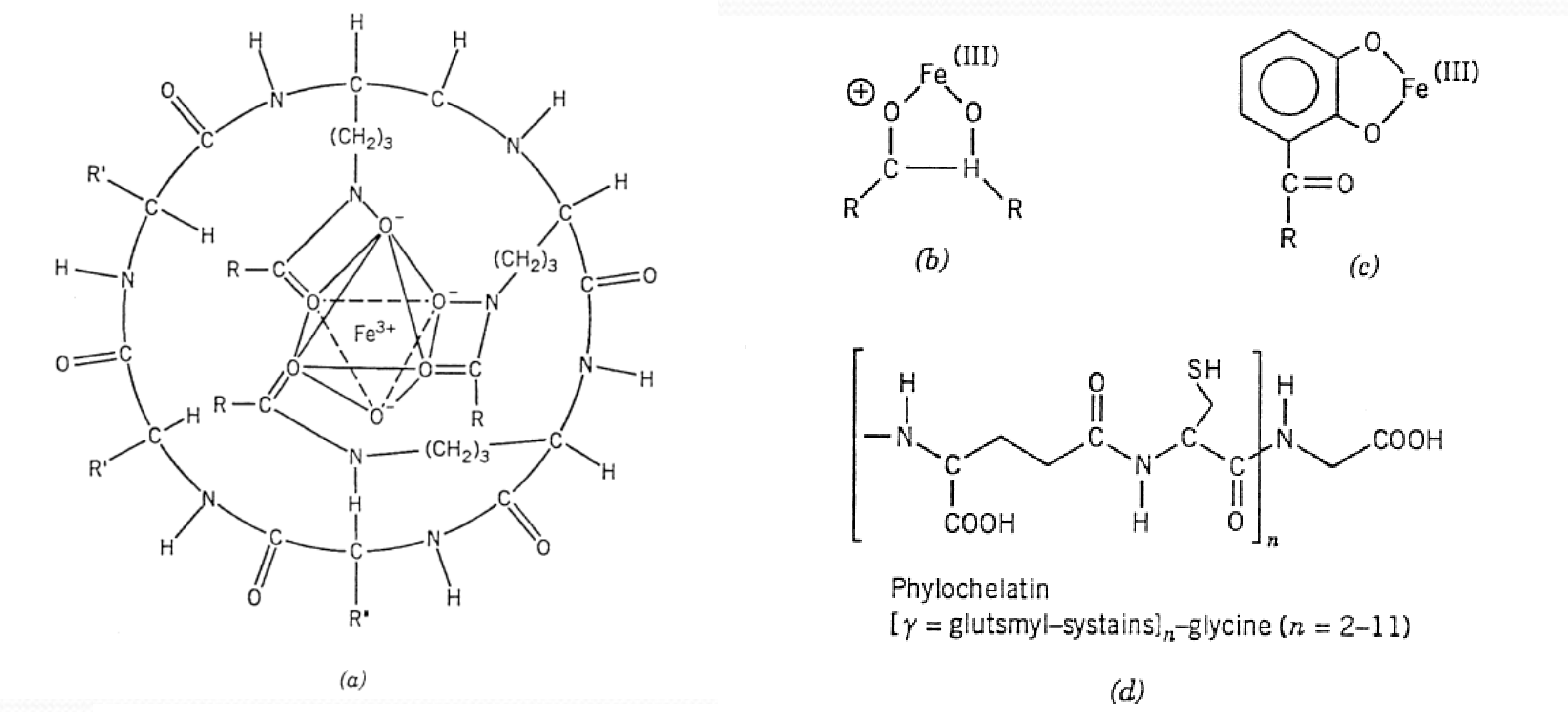


Figure 6.18. Macrocyclic complex formers. (a) Structure of a ferrichrome (desferri-ferrichrome), one of the strongest complex formers presently known for Fe(III). The iron-binding center is an octahedral arrangement of six oxygen donor atoms of trihydroxamate. Such naturally occurring ferrichromes play an important role in the biosynthetic pathways involving iron. Complexing functionalities of some biogenic ligands: (b) hydroxamate siderophores, (c) catechol siderophores, and (d) phytochelatines. For detailed structures see Neilands (1981).