Lecture 7 & 8

7.1 Oxidation-Reduction (Redox) Reactions

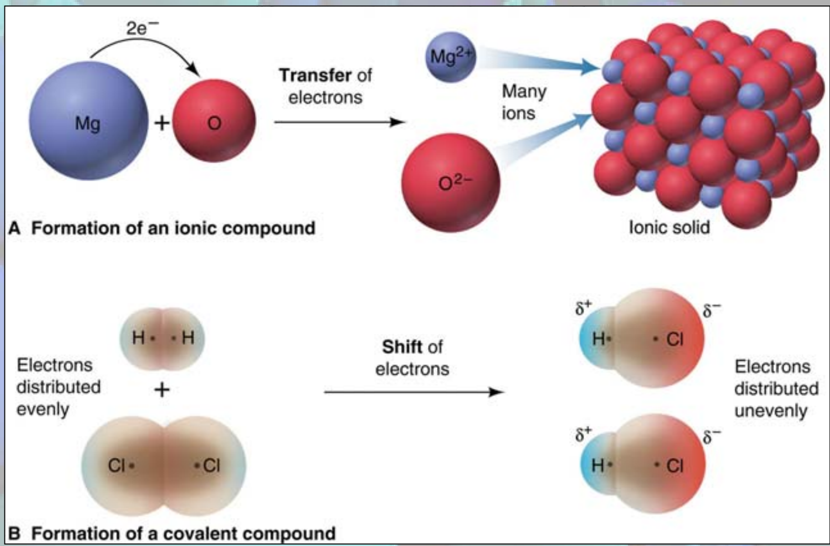
8.1 Introduction to Coordination Chemistry

Back to the first lecture ……

Initial step of this reaction: $BaO_2 + Mg \longrightarrow BaO + MgO$

$$2Mg\ (s) + O_2\ (g) \longrightarrow 2MgO\ (s)$$

The redox process in compound formation



Oxidation-Reduction Reactions

(electron transfer reactions)

$2Mg\ (s) + O_2\ (g) \longrightarrow 2MgO\ (s)$

OIL RIG

$2Mg \longrightarrow 2Mg^{2+} + 4e^-$ ***Oxidation*** half-reaction (lose e^-)

$O_2 + 4e^- \longrightarrow 2O^{2-}$ ***Reduction*** half-reaction (gain e^-)

$2Mg + O_2 + \cancel{4e^-} \longrightarrow 2Mg^{2+} + 2O^{2-} + \cancel{4e^-}$

$2Mg + O_2 \longrightarrow 2MgO$

Oxidation number (O.N.)

The charge the atom would have in a molecule (or an ionic compound) if electrons were completely transferred.

1. Free elements (uncombined state) have an oxidation number of zero.

   Na, Be, K, Pb, H_2, O_2, P_4, S_8 = 0

2. In monatomic ions, the oxidation number is equal to the charge on the ion.

   Li^+, Li = +1; Fe^{3+}, Fe = +3; O^{2-}, O = –2

3. The oxidation number of oxygen is **usually** –2. In H_2O_2 and O_2^{2-} it is –1.

Rules for Assigning an Oxidation Number (O.N.)

General rules

1. For an atom in its elemental form (Na, O_2, Cl_2, etc.): O.N. = 0
2. For a monoatomic ion: O.N. = ion charge
3. The sum of O.N. values for the atoms in a compound equals zero. The sum of O.N. values for the atoms in a polyatomic ion equals the ion's charge.

Rules for specific atoms or periodic table groups

1. For Group 1A(1):	O.N. = +1 in all compounds
2. For Group 2A(2):	O.N. = +2 in all compounds
3. For hydrogen:	O.N. = +1 in combination with nonmetals
4. For fluorine:	O.N. = -1 in combination with metals and boron
5. For oxygen:	O.N. = -1 in peroxides O.N. = -2 in all other compounds(except with F)
6. For Group 7A(17):	O.N. = -1 in combination with metals, nonmetals (except O), and other halogens lower in the group

4. The oxidation number of hydrogen is +1 *except* when it is bonded to metals in binary compounds. In these cases, its oxidation number is –1. e.g. NaH

5. Group IA metals are +1, IIA metals are +2 and fluorine is always –1.

6. The sum of the oxidation numbers of all the atoms in a molecule or ion is equal to the charge on the molecule or ion.

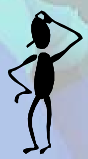
Oxidation numbers of all the elements in HCO_3^- ?

HCO_3^-

O = -2 H = +1

3x(-2) + 1 + ? = -1

C = +4



Oxidation numbers of all the elements in the following ?

IF_7

F = -1

7x(-1) + ? = 0

I = +7

$NaIO_3$

Na = +1 O = -2

3x(-2) + 1 + ? = 0

I = +5

$K_2Cr_2O_7$

O = -2 K = +1

7x(-2) + 2x(+1) + 2x(?) = 0

Cr = +6

Oxidation Numbers

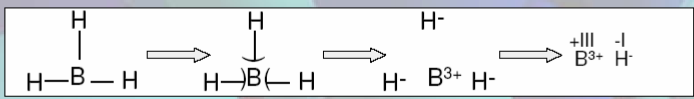
……….. in salts = ionic charge

Examples: $\overset{+I}{Na^{+}}\ \overset{-I}{Cl^{-}}$ $\quad \overset{+I}{Li^{+}}\ \overset{-I}{F^{-}}$ $\quad \overset{+I}{K^{+}}\ \overset{-I}{H^{-}}$ $\quad \overset{+II}{Mg^{2+}}\ \overset{-II}{O^{2-}}$ $\quad \overset{+II}{Fe^{2+}}\ \overset{+III}{Fe^{3+}}\ \overset{-II}{O^{2-}}$

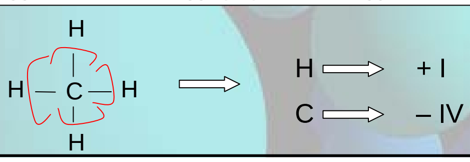
Procedure to determine O.N. in covalent molecules

Move bonding electrons to the electron negative partner and count the fictive charge:

borane:



Methane:



Sample Problem **Determining the Oxidation Number of an Element**

PROBLEM: Determine the oxidation number (O.N.) of each element in these compounds:

(a) zinc chloride **(b)** sulfur trioxide **(c)** nitric acid

PLAN: The O.N.s of the ions in a polyatomic ion add up to the charge of the ion and the O.N.s of the ions in the compound add up to zero.

SOLUTION:

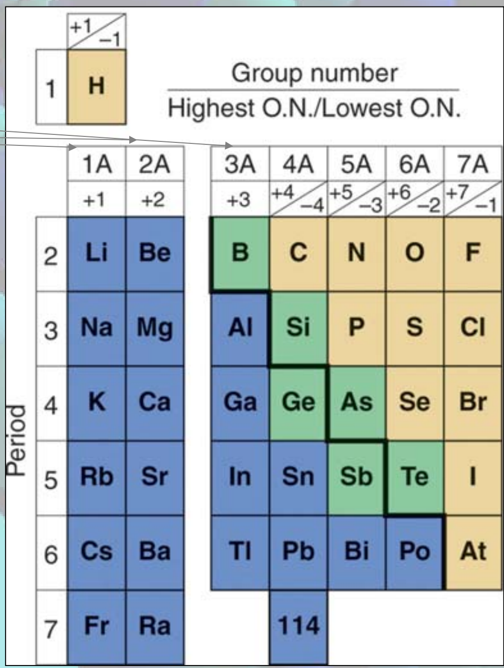
(a) $ZnCl_2$. The O.N. for zinc is +2 and that for chloride is -1.

(b) SO_3. Each oxygen is an oxide with an O.N. of -2. Therefore the O.N. of sulfur must be +6.

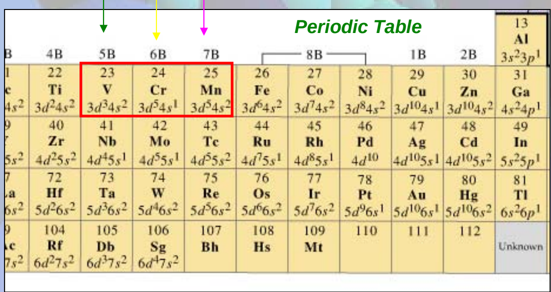
(c) HNO_3. H has an O.N. of +1 and each oxygen is -2. Therefore the N must have an O.N. of +5.

Elements: N.O. = 0

Highest and lowest oxidation numbers of reactive main-group elements



Oxidation Numbers



Max. Oxidation number:

V ….. max. **+V**

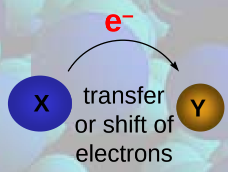
Cr ….. max. **+VI**

Mn …. max. **+VII**

CrO_4^{2-} $Cr_2O_7^{2-}$ $(NH_4)VO_3$

MnO_4^{2-}

A summary of terminology for oxidation-reduction (redox) reactions



X loses electron(s)	Y gains electron(s)
X is oxidized	Y is reduced
X is the reducing agent	Y is the oxidizing agent
X increases its oxidation number	Y decreases its oxidation number

Spontaneous Redox Reactions

……… Zn rod in $CuSO_4$ solution

Observation: Elemental copper deposits on the Zn rod

$$Zn\ (s) + CuSO_4\ (aq) \longrightarrow ZnSO_4\ (aq) + Cu\ (s)$$

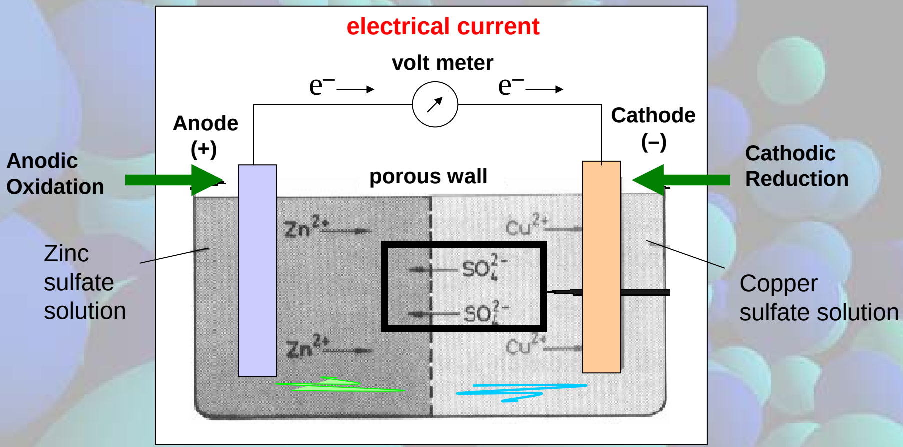
→ Tip: The "nobler" metal likes to get reduced, wants to be in the elemental form. The un-noble metal gets oxidized.

Cu^{2+} is reduced $\quad Cu^{2+} + 2e^- \longrightarrow Cu$

Zn is oxidized $\quad Zn \longrightarrow Zn^{2+} + 2e^-$

Cu^{2+} is the ***oxidizing agent*** $\quad$ Zn is the ***reducing agent***

Redox – Reaction and electrical conductivity



Cell 1 **Cell 2**

$Zn \longrightarrow Zn^{2+} + 2e^{-}$ $Cu^{2+} + 2e^{-} \longrightarrow Cu$

Copper wire reacts with silver nitrate to form silver metal.
What is the oxidizing agent in the reaction?

$$Cu\ (s) + 2AgNO_3\ (aq) \longrightarrow Cu(NO_3)_2\ (aq) + 2Ag\ (s)$$

"silver nobler than copper"

Half-Equations:

$Cu \longrightarrow Cu^{2+} + 2e^{-}$

$Ag^{+} + 1e^{-} \longrightarrow Ag$ Ag^{+} is reduced Ag^{+} is the oxidizing agent

Sample Problem **Recognizing Oxidizing and Reducing Agents**

$$\overset{+2\,-2}{PbO(s)} + \overset{+2\,-2}{CO(g)} \longrightarrow \overset{0}{Pb(s)} + \overset{+4\,-2}{CO_2(g)}$$

(b) $PbO(s) + CO(g) \longrightarrow Pb(s) + CO_2(g)$

The O.N. of C increases; it is oxidized; it is the reducing agent.

The O.N. of Pb decreases; it is reduced; it is the oxidizing agent.

$$\overset{0}{2H_2(g)} + \overset{0}{O_2(g)} \longrightarrow \overset{+1\,-2}{2H_2O(g)}$$

(c) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$

The O.N. of H increases; it is oxidized; it is the reducing agent.

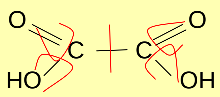
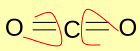
The O.N. of O decreases; it is reduced; it is the oxidizing agent.

Balancing Redox Equations

Oxalic acid $H_2C_2O_4$ is oxidised by the permanganate ion MnO_4^- in acidic solution. During the reaction Mn^{2+} and CO_2 is formed.

$MnO_4^-(aq) + H_2C_2O_4(aq) \dashrightarrow Mn^{2+}(aq) + CO_2(g)$

Calculate the oxidation numbers:

MnO_4^-	$Mn + 4(-2) = -1$	$\Rightarrow Mn = +7$
$H_2C_2O_4$		$\Rightarrow C = +3$
CO_2	$C + 2(-2) = 0$ 	$\Rightarrow C = +4$

Balancing Redox Equations – Half Equations

$\overset{+7}{MnO_4^-}(aq) \dashrightarrow \overset{+2}{Mn^{2+}}(aq)$ Reduction

$\overset{+3}{H_2C_2O_4}(aq) \dashrightarrow \overset{+4}{2CO_2}(g)$ Oxidation

1st step: Identify the oxidation and the reduction and balance then the total oxidation numbers with electrons (Red: electrons on the left side, Ox: electrons on the right side)

Reduction: $\overset{+7}{MnO_4^-} + 5e^- \dashrightarrow \overset{+2}{Mn^{2+}}$

Oxidation: $\overset{2(+3)}{H_2C_2O_4} \dashrightarrow \overset{2(+4)}{2CO_2} + 2e^-$

2nd step: Here the reaction is performed under acidic condition. So balance the charge of the half equations with protons. (If a reaction occurs under basic conditions OH- ions are used to balance the equation).

Reduction: $\overset{+7}{MnO_4^-} + 5e^- + 8H^+ \dashrightarrow \overset{+2}{Mn^{2+}}$

charge: -6 *charge: +2*

Oxidation: $\overset{2(+3)}{H_2C_2O_4} \dashrightarrow \overset{+4}{2CO_2} + 2e^- + 2H^+$

charge: –2

3rd step: Balance with water, so that you obtain "proper" half equations.

Reduction: $MnO_4^- + 5e^- + 8H^+ \dashrightarrow Mn^{2+} + 4\,H_2O$

Oxidation: $H_2C_2O_4 \dashrightarrow 2\,CO_2 + 2e^- + 2H^+$

4th step: Multiply the equations to have the same number of electrons on each side. Simplify and add the equations.

Reduction: $MnO_4^- + 5e^- + 8H^+ \longrightarrow Mn^{2+} + 4\,H_2O$ | x 2

Oxidation: $H_2C_2O_4 \longrightarrow 2CO_2 + 2e^- + 2H^+$ | x 5

6

Reduction: $2MnO_4^- + 10e^- + 16H^+ \longrightarrow 2\,Mn^{2+} + 8\,H_2O$

Oxidation: $5H_2C_2O_4 \longrightarrow 10CO_2 + 10e^- + 10H^+$

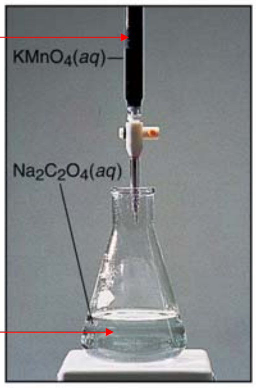
Redox: $2\,MnO_4^- + 5H_2C_2O_4 + 6H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

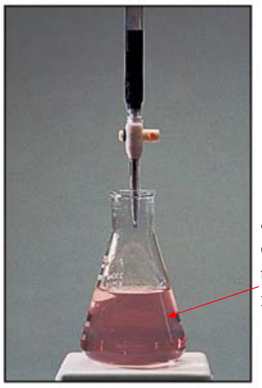
Remember: in alkaline solutions you have to balance with OH^-.

A redox titration

known concentration

unknown concentration





all the oxalic acid used for the reduction

Net ionic equation:

$$\overset{+7}{2MnO_4^-(aq)} + \overset{+3}{5C_2O_4^{2-}(aq)} + 16H^+(aq) \longrightarrow \overset{+2}{2Mn^{2+}(aq)} + \overset{+4}{10CO_2(g)} + 8H_2O(l)$$

Sample Problem **Balancing Redox Equations by the Oxidation Number Method**

PROBLEM: Use the oxidation number method to balance the following equations:

(a) $Cu(s) + HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + NO_2(g) + H_2O(l)$

SOLUTION:

Oxidation numbers: Cu: 0; HNO_3: +1, +5, 3(-2); $Cu(NO_3)_2$: +2, +5, -2; NO_2: +4, -2; H_2O: +1, -2

(a) $Cu(s) + HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + NO_2(g) + H_2O(l)$

O.N. of Cu increases because it loses $2e^-$; it is oxidized and is the reducing agent.
O.N. of N decreases because it gains $1e^-$; it is reduced and is the oxidizing agent.

loses $2e^-$ balance other ions

$Cu(s) + HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + NO_2(g) + H_2O(l)$

gains $1e^-$ x2 to balance e^-

balance unchanged polyatomic ions

Sample Problem **Balancing Redox Equations by the Oxidation Number Method**

continued

Oxidation: $Cu^0 \rightarrow Cu^{2+} + 2e^-$
Reduction: $\overset{+5}{HNO_3} + 1e^- \rightarrow \overset{+4}{NO_2}$

Oxidation: $Cu^0 \rightarrow Cu^{2+} + 2e^-$
Reduction: $HNO_3 + 1e^- + H^+ \rightarrow NO_2$

Oxidation: $Cu^0 \rightarrow Cu^{2+} + 2e^-$
Reduction: $HNO_3 + 1e^- + H^+ \rightarrow NO_2 + H_2O$ **x2**

Oxidation: $Cu^0 \rightarrow Cu^{2+} + \cancel{2}e^-$
Reduction: $2HNO_3 + \cancel{2}e^- + 2H^+ \rightarrow 2NO_2 + 2H_2O$

$Cu^0 + 2HNO_3 + \cancel{2}e^- + 2H^+ \rightarrow Cu^{2+} + 2NO_2 + 2H_2O$
(H^+ → **HNO_3**)

$Cu(s) + 4HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$

Exercise

Permanganate ions react with bromine ions in **basic** solution to form MnO_2 and BrO_3^-. Write the balanced equation for the reaction.

O.N.	
Br^-	Br = -1
BrO_3^-	Br = +5

O.N.	
MnO_4^-	Mn = +7
MnO_2	Mn = +4

Half reactions

MnO_4^- $+3e^-$ ⟶ MnO_2 **Reduction**

Br^- ⟶ BrO_3^- $+6e^-$ **Oxidation**

Balance the equations and add the two half reaction together.

continued

Reduction: $MnO_4^- + 3e^- \longrightarrow MnO_2$ **Charge: –4 ⟶ 0**

Oxidation: $Br^- \longrightarrow BrO_3^- + 6e^-$ **Charge: –1 ⟶ –7**

Reduction: $MnO_4^- + 3e^- \longrightarrow MnO_2 + 4OH^-$

Oxidation: $Br^- + 6OH^- \longrightarrow BrO_3^- + 6e^-$

Reduction: $MnO_4^- + 3e^- + 2H_2O \longrightarrow MnO_2 + 4OH^-$

Oxidation: $Br^- + 6OH^- \longrightarrow BrO_3^- + 6e^- + 3H_2O$

continued

Reduction: $MnO_4^- + 3e^- + 2H_2O \longrightarrow MnO_2 + 4OH^-$ | x2

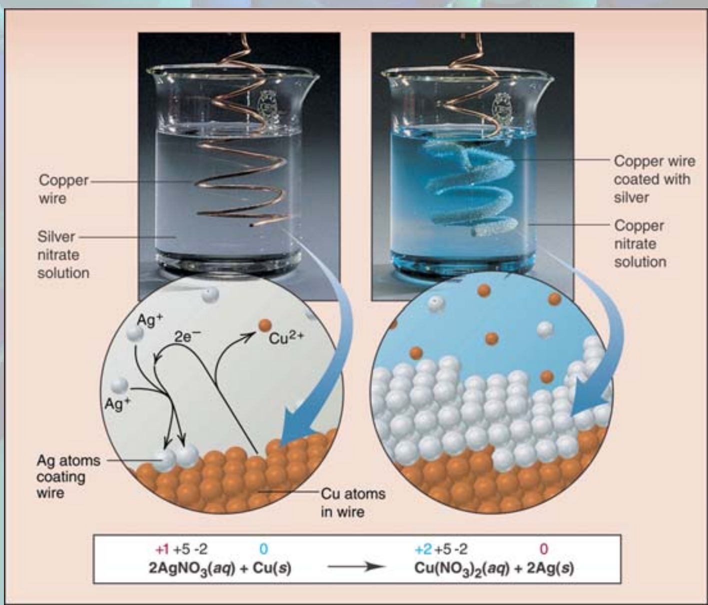
Oxidation: $Br^- + 6OH^- \longrightarrow BrO_3^- + 6e^- + 3H_2O$

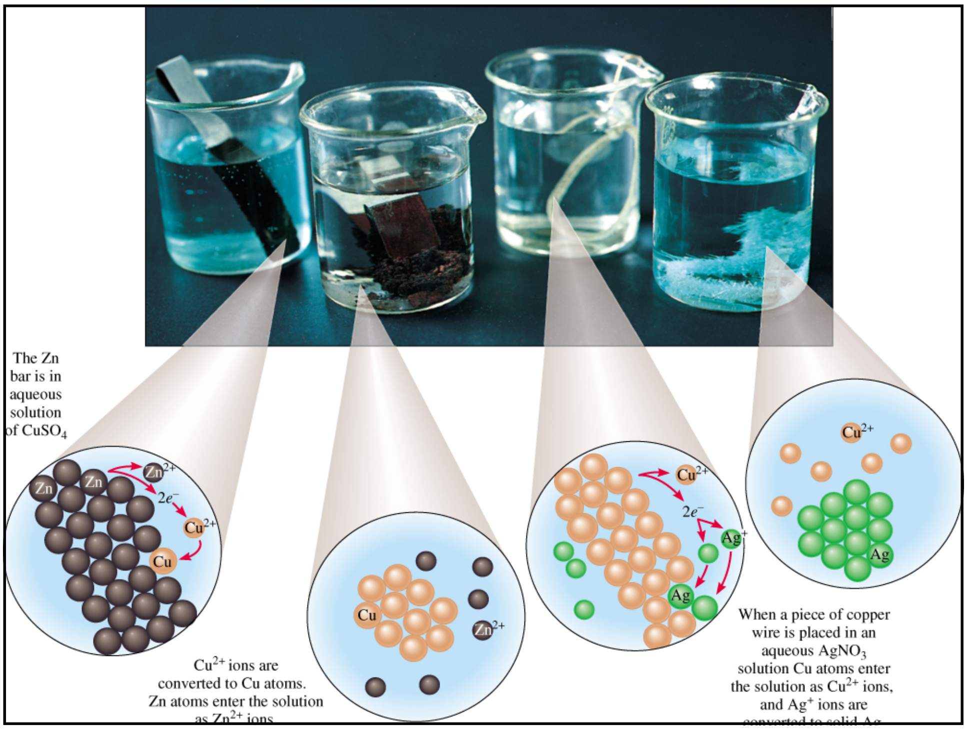
Reduction: $2MnO_4^- + \cancel{6e^-} + \cancel{4}H_2O \longrightarrow 2MnO_2 + \cancel{8}OH^-$ (2)

Oxidation: $Br^- + \cancel{6OH^-} \longrightarrow BrO_3^- + \cancel{6e^-} + 3\cancel{H_2O}$

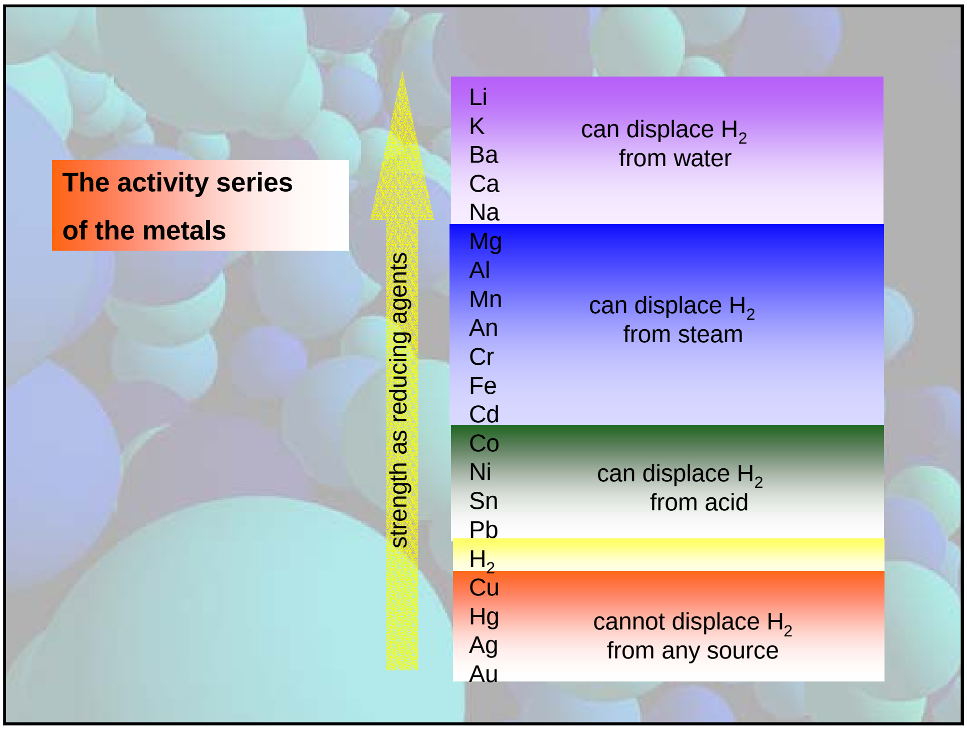
$$2MnO_4^-(aq) + Br^-(aq) + H_2O(l) \longrightarrow 2MnO_2(s) + BrO_3^-(aq) + 2OH^-(aq)$$

Displacing one metal with another





The Zn bar is in aqueous solution of $CuSO_4$
Zn
Zn^{2+}
$2e^-$
Cu^{2+}
Cu
Cu^{2+} ions are converted to Cu atoms. Zn atoms enter the solution as Zn^{2+} ions.
Ag
Ag^+
When a piece of copper wire is placed in an aqueous $AgNO_3$ solution Cu atoms enter the solution as Cu^{2+} ions, and Ag^+ ions are

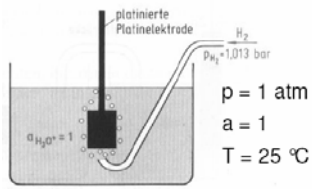


The activity series of the metals
strength as reducing agents
Li
K
Ba
Ca
Na
can displace H_2 from water
Mg
Al
Mn
An
Cr
Fe
Cd
can displace H_2 from steam
Co
Ni
Sn
Pb
can displace H_2 from acid
H_2
Cu
Hg
Ag
Au
cannot displace H_2 from any source

The activity series of the metals

$c(Cu^{2+}) = c(Zn^{2+})$

$\Delta E = E(Cu/Cu^{2+}) - E(Zn/Zn^{2+}) = E^0(Cu/Cu^{2+}) - E^0(Zn/Zn^{2+})$
$= +0{,}34 - (-0{,}76) = 1{,}10\ [V]$



p = 1 atm
a = 1
T = 25 °C

$H_2 + 2H_2O \rightleftharpoons 2H_3O^+ + 2e^-$

Reduced Form	=	oxidized form	+ ze–	Standard Reduction Potential E° (V)
Li	$\rightleftharpoons$	Li^+	$+ e^-$	−3,04
K	$\rightleftharpoons$	K^+	$+ e^-$	−2,92
Ba	$\rightleftharpoons$	Ba^{2+}	$+2e^-$	−2,90
Ca	$\rightleftharpoons$	Ca^{2+}	$+2e^-$	−2,87
Na	$\rightleftharpoons$	Na^+	$+ e^-$	−2,71
Mg	$\rightleftharpoons$	Mg^{2+}	$+2e^-$	−2,36
Al	$\rightleftharpoons$	Al^{3+}	$+3e^-$	−1,68
Mn	$\rightleftharpoons$	Mn^{2+}	$+2e^-$	−1,19
Zn	$\rightleftharpoons$	Zn^{2+}	$+2e^-$	−0,76
Cr	$\rightleftharpoons$	Cr^{3+}	$+3e^-$	−0,74
S^{2-}	$\rightleftharpoons$	S	$+2e^-$	−0,48
Fe	$\rightleftharpoons$	Fe^{2+}	$+2e^-$	−0,41
Cd	$\rightleftharpoons$	Cd^{2+}	$+2e^-$	−0,40
Co	$\rightleftharpoons$	Co^{2+}	$+2e^-$	−0,28
Sn	$\rightleftharpoons$	Sn^{2+}	$+2e^-$	−0,14
Pb	$\rightleftharpoons$	Pb^{2+}	$+2e^-$	−0,13
Fe	$\rightleftharpoons$	Fe^{3+}	$+3e^-$	−0,036
$H_2 + 2H_2O$	$\rightleftharpoons$	$2H_3O^+$	$+2e^-$	0
Sn^{2+}	$\rightleftharpoons$	Sn^{4+}	$+2e^-$	+0,15
Cu^+	$\rightleftharpoons$	Cu^{2+}	$+ e^-$	+0,15
$SO_2 + 6H_2O$	$\rightleftharpoons$	$SO_4^{2-} + 4H_3O^+$	$+2e^-$	+0,17
Cu	$\rightleftharpoons$	Cu^{2+}	$+2e^-$	+0,34
Cu	$\rightleftharpoons$	Cu^+	$+ e^-$	+0,52
$2I^-$	$\rightleftharpoons$	I_2	$+2e^-$	+0,54
$H_2O_2 + 2H_2O$	$\rightleftharpoons$	$O_2 + 2H_3O^+$	$+2e^-$	+0,68
Fe^{2+}	$\rightleftharpoons$	Fe^{3+}	$+ e^-$	+0,77
Ag	$\rightleftharpoons$	Ag^+	$+ e^-$	+0,80
Hg	$\rightleftharpoons$	Hg^{2+}	$+2e^-$	+0,85

"less noble" metals

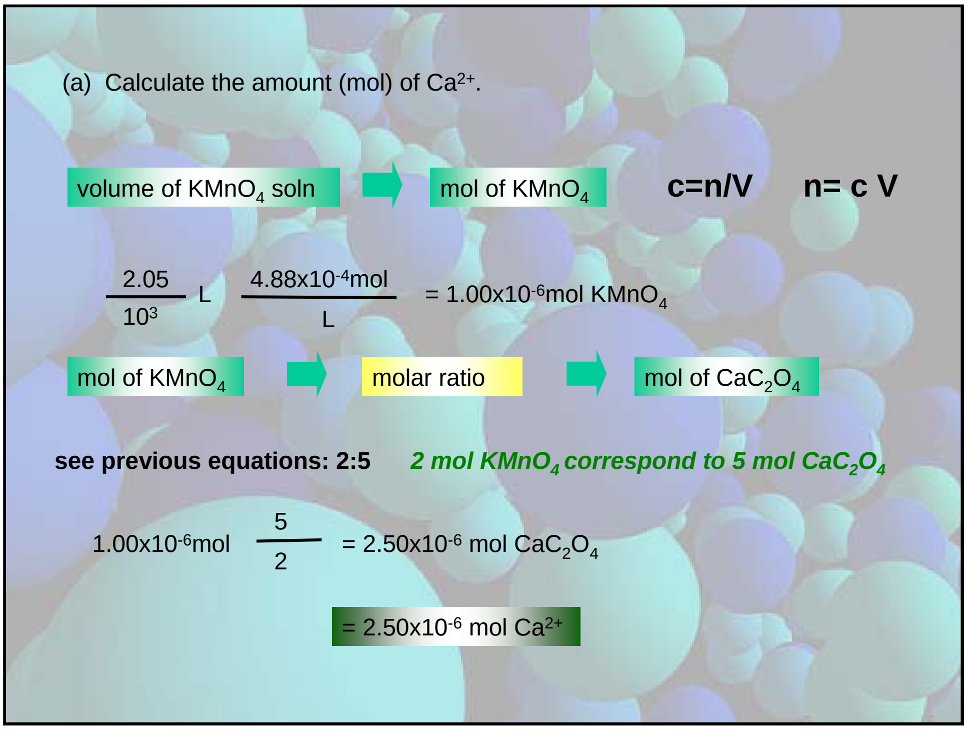
noble metals, non-metals and their compounds

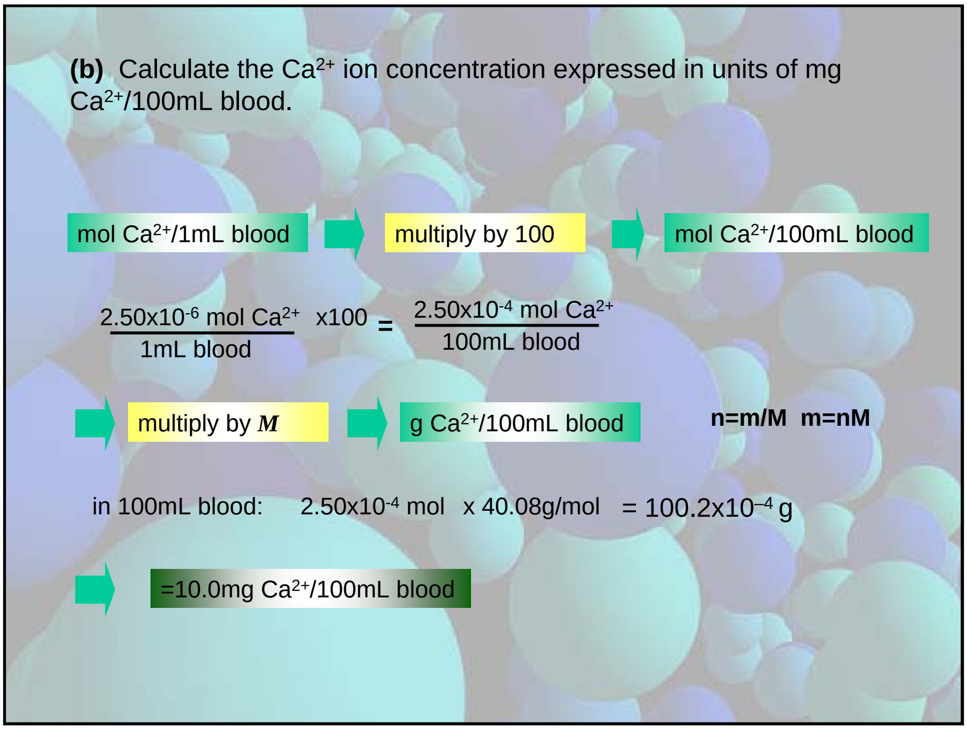
Sample Problem **Finding an Unknown Concentration by a Redox Titration**

PROBLEM: Calcium ions (Ca^{2+}) are required for blood to clot and for many other cell processes. An abnormal Ca^{2+} concentration is indicative of disease. To measure the Ca^{2+} concentration, 1.00mL of human blood was treated with $Na_2C_2O_4$ solution. The resulting CaC_2O_4 precipitate was filtered and dissolved in dilute H_2SO_4. This solution required 2.05mL of 4.88×10^{-4}M $KMnO_4$ to reach the end point. The unbalanced equation is:

$$KMnO_4(aq) + CaC_2O_4(s) + H_2SO_4(aq) \longrightarrow MnSO_4(aq) + K_2SO_4(aq) + CaSO_4(s) + CO_2(g) + H_2O(l)$$

(a) Calculate the amount (mol) of Ca^{2+}.
(b) Calculate the Ca^{2+} ion concentration expressed in units of mg Ca^{2+}/100mL blood.


(a) Calculate the amount (mol) of Ca^{2+}.
volume of $KMnO_4$ soln
mol of $KMnO_4$
c=n/V
n= c V
$\frac{2.05}{10^3}$ L $\frac{4.88x10^{-4}mol}{L}$ = $1.00x10^{-6}$mol $KMnO_4$
mol of $KMnO_4$
molar ratio
mol of CaC_2O_4
see previous equations: 2:5
2 mol $KMnO_4$ correspond to 5 mol CaC_2O_4
$1.00x10^{-6}$mol $\frac{5}{2}$ = $2.50x10^{-6}$ mol CaC_2O_4
= $2.50x10^{-6}$ mol Ca^{2+}


(b) Calculate the Ca^{2+} ion concentration expressed in units of mg Ca^{2+}/100mL blood.
mol Ca^{2+}/1mL blood
multiply by 100
mol Ca^{2+}/100mL blood
$\frac{2.50x10^{-6} \text{ mol } Ca^{2+}}{1mL \text{ blood}}$ x100 = $\frac{2.50x10^{-4} \text{ mol } Ca^{2+}}{100mL \text{ blood}}$
multiply by *M*
g Ca^{2+}/100mL blood
n=m/M m=nM
in 100mL blood: $2.50x10^{-4}$ mol x 40.08g/mol = $100.2x10^{-4}$ g
=10.0mg Ca^{2+}/100mL blood