Balancing Reaction Equations
Oxidation State
Reduction-oxidation Reactions

OCN 623 – Chemical Oceanography

Chemistry is the glue that holds together all the other fields of oceanography

Chemistry interacts directly with each of the other fields

Chemical distributions in the ocean secretly record and integrate the biological, physical and geological processes

There are 118 chemical elements many with multiple oxidation states and isotopes—lots of tracers to investigate the world

Balanced chemical reactions are the math of chemistry

They show the relationship between the reactants and the products

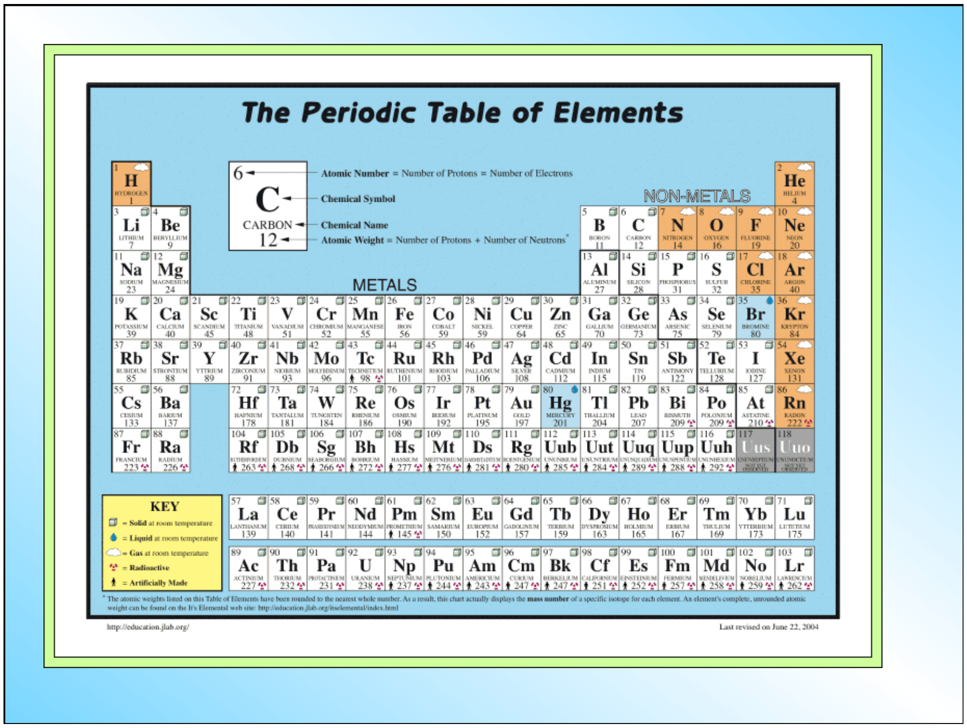
We will use thermodynamics later on to calculate the feasibility of reactions and to understand how equilibrium is established

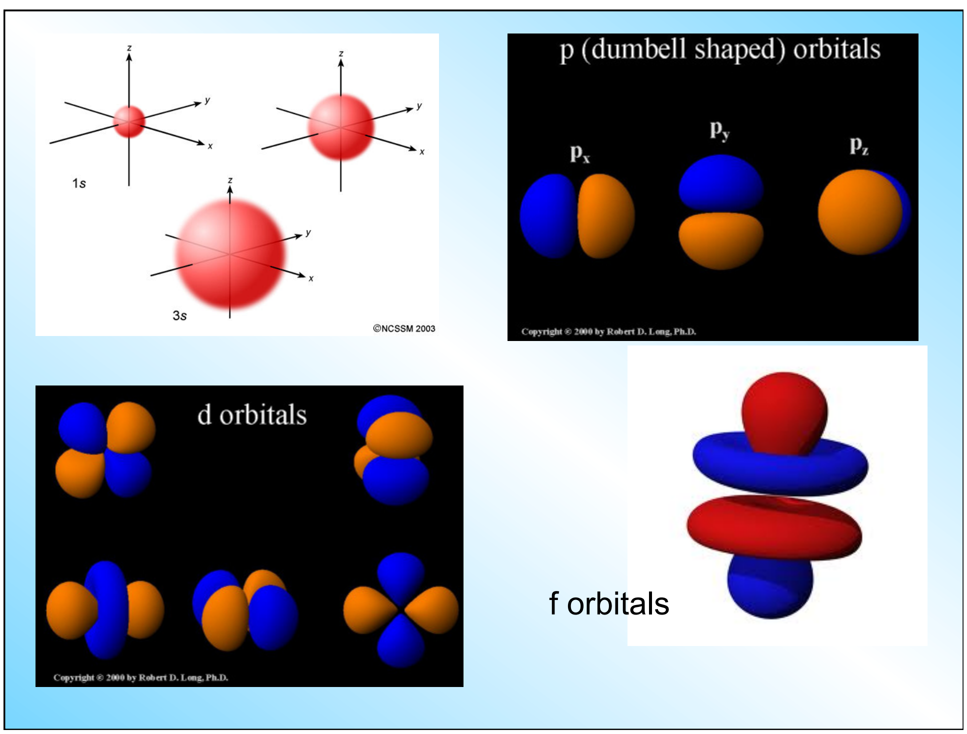
The concept of equilibrium allows us to understand chemical processes such as ionic speciation, oxidation state distributions gas solubility, the carbonate system ……

Elements are electrically neutral, the number of protons in the nucleus exactly balances the number of electrons that fill the shells

Element	Electron Configuration
Hydrogen	$1s^1$
Helium	$1s^2$
Lithium	$1s^2 2s^1$
Beryllium	$1s^2 2s^2$
Boron	$1s^2 2s^2 2p^1$
Carbon	$1s^2 2s^2 2p^2$
Nitrogen	$1s^2 2s^2 2p^3$
Oxygen	$1s^2 2s^2 2p^4$
Fluorine	$1s^2 2s^2 2p^5$
Neon	$1s^2 2s^2 2p^6$
Sodium	$1s^2 2s^2 2p^6 3s^1$
Magnesium	$1s^2 2s^2 2p^6 3s^2$
Aluminium	$1s^2 2s^2 2p^6 3s^2 3p^1$
Silicon	$1s^2 2s^2 2p^6 3s^2 3p^2$
Phosphorus	$1s^2 2s^2 2p^6 3s^2 3p^3$
Sulfur	$1s^2 2s^2 2p^6 3s^2 3p^4$
Chlorine	$1s^2 2s^2 2p^6 3s^2 3p^5$
Argon	$1s^2 2s^2 2p^6 3s^2 3p^6$

Shells are filled in order with each additional electron occupying the lowest energy shell available


The Periodic Table of Elements
Atomic Number = Number of Protons = Number of Electrons
Chemical Symbol
Chemical Name
Atomic Weight = Number of Protons + Number of Neutrons*
NON-METALS
METALS
KEY
= Solid at room temperature
= Liquid at room temperature
= Gas at room temperature
= Radioactive
= Artificially Made
http://education.jlab.org/
Last revised on June 22, 2004


1s
3s
©NCSSM 2003
p (dumbell shaped) orbitals
p_x
p_y
p_z
Copyright © 2000 by Robert D. Long, Ph.D.
d orbitals
Copyright © 2000 by Robert D. Long, Ph.D.
f orbitals

A. Oxidation state or number

Oxidation: Loss of electrons from an element.
Oxidation number increases

Reduction: Gain of electrons by an element.
Oxidation number decreases

If we want to determine whether reaction is oxidation or reduction

Need to know oxidation number of the element and how it changes

Rules for determining oxidation number of an element

1. Oxidation state of an element in its elementary state = 0

   e.g. Cl_2, Na, P,….etc.

2. Oxidation state of an element in a monatomic (only one atom) ion is equal to the charge on the ion

   e.g. Na^{+}= +1; Cl^{-} = -1; Fe^{3+} = +3

3. Oxidation state of certain elements is the same in all, or almost all of their compounds

e.g. Group 1A elements: Li, Na, K, Rb, Cs =+1

Group 2A elements: Be, Mg, Ca, Sr, Ba, Ra = +2

Group VII b elements: F, Cl, Br, I, At = -1 in binary compounds

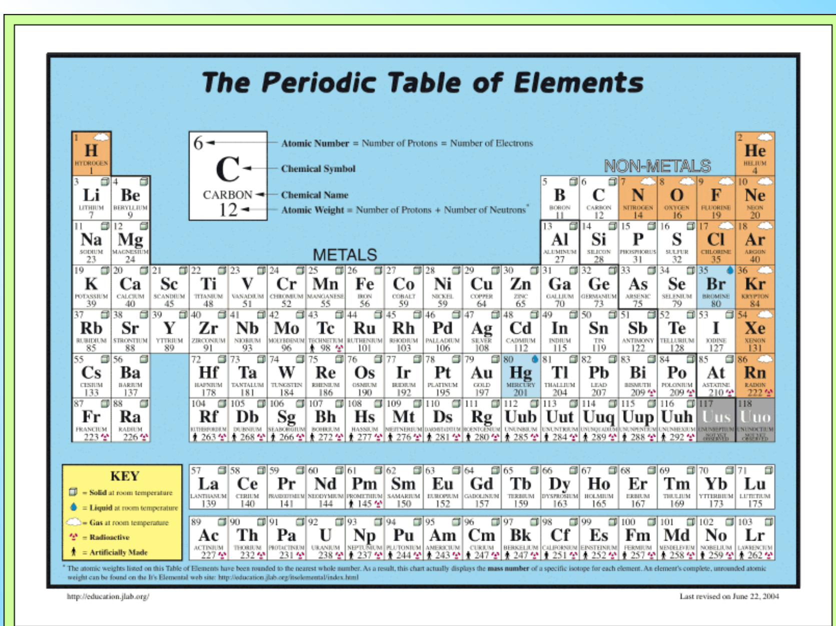
Oxygen is almost always -2 (Except: when bonded to O or F)

H is almost always +1; Except with a metal, e.g. NaH, CaH_2 is -1

4. The sum of the oxidation states in a neutral species is = 0; In a charged ion it is equal to the charge on the ion

e.g. Na_2Se: Na = +1x2 = 2, thus Se = -2

MnO_4^- : O= -2x4 = -8, thus Mn =8-1 = 7



5. Fractional oxidation numbers are possible. *E.g.*, in $Na_2S_4O_6$ (*sodium tetrathionate*), S has an oxidation number of +10/4:

O: 6(-2) = -12

Na: 2(+1) = 2

Residual = -10, which must be balanced by S:

S: 4(+10/4) = +10

6. The oxidation number is designated by:

- Arabic number below the atom, or
- Roman numeral or Arabic number after the atom (in parentheses)

What is the oxidation state of the elements in KNO_3?

K= ?; O= ?; N=?

$K_2Cr_2O_7$? K= ?; O= ?, Cr= ?

Oxidation is an increase in oxidation state
e.g. Cl^- to Cl_2 is -1 to 0

Reduction is a decrease in oxidation state
SO_4^{2-} to H_2S is a reduction S VI to S -II

Recognising oxidation/reduction
$KMnO_4$ to MnO_2 oxidation or reduction?

B. Balancing oxidation-reduction reactions

Conventionally always put the oxidised species on the left, the reduced species on the right

e.g. $MnO_4^-{}_{(aq)} + Cl^-{}_{(aq)} = Mn^{2+}{}_{(aq)} + Cl_{2(g)}$

1. Separate the reaction into a reduction and oxidation part

$MnO_4^-{}_{(aq)} = Mn^{2+}{}_{(aq)}$ reduction

$Cl^-{}_{(aq)} = Cl_{2(g)}$ oxidation

2. Balance each 1/2 reaction with respect to mass then with respect to charge. Use e^-, H^+, H_2O or OH^-

$2Cl^-{}_{(aq)} = Cl_{2\,(g)}$ mass

$2Cl^-{}_{(aq)} = Cl_{2\,(g)} + 2e^-$ mass + charge **A**

$MnO_4^-{}_{(aq)} = Mn^{2+}{}_{(aq)} + 4H_2O$ (mass oxygen)

$MnO_4^-{}_{(aq)} + 8H^+ = Mn^{2+}{}_{(aq)} + 4H_2O$ (mass oxygen+ hydrogen)

$MnO_4^-{}_{(aq)} + 8H^+ + 5e^- = Mn^{2+}{}_{(aq)} + 4H_2O$ (mass + charge) **B**

3. Combine half reactions so electron gain equals loss

5*A = 10 e^-; 2*B = 10 e^- i.e. 5*A +2*B

$10\,Cl^-{}_{(aq)} + 2MnO_4^- + 16H^+ = 5Cl_{2(g)} + 2Mn^{2+}{}_{(aq)} + 8H_2O$

4. Check for atom and charge balance

C. Oxidation of organic matter

$CH_2O + SO_4^{2-} + H_2O = CO_2 + H_2S$

0 IV ox state of C

How did we get the oxidation state of the C in CH_2O?

Separate into oxidation and reduction half reactions

$SO_4^{2-} + 8e^- + 10\ H^+ = H_2S + 4H_2O$ **A**
$CH_2O + H_2O = CO_2 + 4H^+ + 4\ e^-$ **B**

Combine so electrons balance:
A + B*2

$2\ CH_2O + SO_4^{2-} + 2\ H_2O + 10H^+ = H_2S + 4\ H_2O + 2\ CO_2 + 8\ H^+$

Simplify by subtracting 8 H^+ and 2 H_2O from each side.

$2\ CH_2O + SO_4^{2-} + 2H^+ = H_2S + 2\ H_2O + 2\ CO_2$

This reaction is the oxidation of organic matter through the reduction of sulphate, you will see this reaction later in reducing sediments.

D. An example in basic solution:

$I^- + MnO_4^- = I_2 + MnO_2$

Oxidation: $2I^- = I_2 + 2e^-$ **A**
Reduction: $MnO_4^- + 4H^+ + 3e^- = MnO_2 + 2H_2O$

remove H^+ by adding OH^- to each side * 4 ($4H^+ + 4OH^- = 4\ H_2O$)

$MnO_4^- + 4\ H_2O + +3e^- = MnO_2 + 2H_2O + 4OH^-$
simplify: $MnO_4^- + 2\ H_2O + 3e^- = MnO_2 + 4OH^-$ **B**

combine so electrons balance: A * 3 + B * 2

$6I^- + 2MnO_4^- + 4H_2O = 3I_2 + 2MnO_2 + 8OH^-$

E. A weathering reaction.

$Fe_2SiO_4 + O_2 = Fe_2O_3 + FeSiO_3$
II III II ox state of Fe i.e. Fe is oxidised
Iron Olivine = Haemetite + Ferrosilite (Fe pyroxene)
Separate and balance for mass and charge

$O_2 + 4\ e^- = 2O^{2-}$ reduction **A**
$2Fe_2SiO_4 + H_2O = Fe_2O_3 + 2e^- + 2FeSiO_3 + 2H^+$ oxidation **B**
Note have added H_2O on LH side
Combine eqns balancing e^- A+ 2*B
$4Fe_2SiO_4 + 2H_2O + O_2 + 4\ e^- = 2Fe_2O_3 + 4e^- + 4FeSiO_3 + 4H^+ + 2O^{2-}$
cancel $4e^-$ on each side then cancel as $2H_2O = 4H^+ + 2O^{2-}$

$4Fe_2SiO_4 + O_2 = 2Fe_2O_3 + 4FeSiO_3$

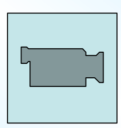
Removal of oxygen by oxidation of reduced iron compounds

Example where the same compound is being oxidised and reduced:

$Cl_2 + H_2O = HOCl + H^+ + Cl^-$
$Cl_2 + 2e^- = 2Cl^-$ (reduction of Cl)
$Cl_2 + 2H_2O = 2\ HOCl + 2H^+ + 2e^-$ (oxidation of Cl)
$2Cl_2 + 2H_2O = 2\ HOCl + 2H^+ + 2\ Cl^-$

This may have been what happened to Cl_2 released from the degassing of the early Earth.

The Periodic table



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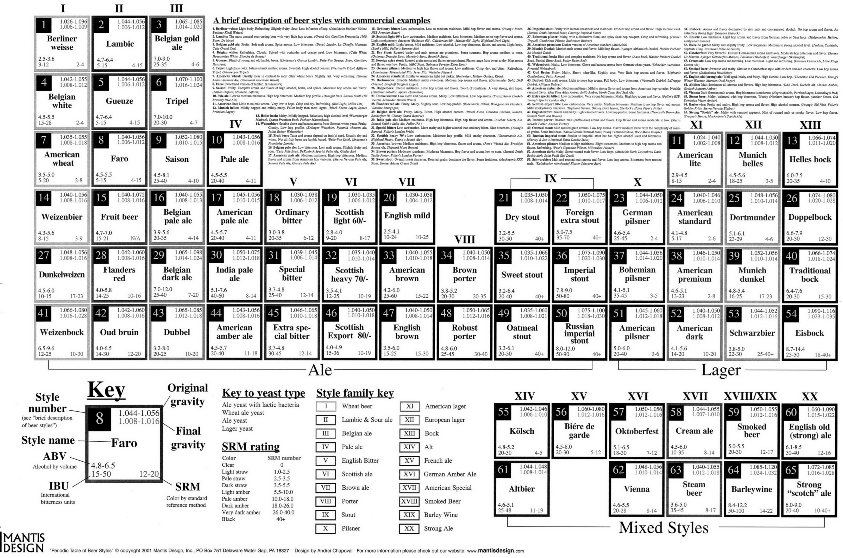
Periodic Table of Beer Styles



Rejected elements of the periodic table