

Balancing Reaction Equations

Oxidation State

Reduction-oxidation Reactions

OCN 623 – Chemical Oceanography

- Balanced chemical **reactions** are the **math** of chemistry they show the **relationship** between the reactants and the products
- We will later use **thermodynamics** 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 carbon dioxide system

Outline

- Types of reactions and equations
- Net ionic equations
- Electron-transfer reactions
- Common oxidation states of elements
- Determining oxidation number of elements & compounds
- Reduction-oxidation reactions

References

- Snoeyink, V.L., and D. Jenkins (1980) *Water Chemistry*. John Wiley & Sons, New York.
- Stumm, W., and J.J. Morgan (1996) *Aquatic Chemistry, 3rd Ed.* John Wiley & Sons, New York.

Summary of Types of Reactions and Equations

Table 8.1 Summary of Types of Reactions and Equations

Reactants	Reaction Type	Products	Reference
Element + element Element + compound Compound + compound	Combination	One compound	Equation 8.8
One compound	Decomposition	Element + element Element + compound Compound + compound	Equation 8.9
O ₂ * + compound of C, H, and O	Complete oxidation or burning	CO ₂ * + H ₂ O*	Equation 8.10
Element + ionic compound or acid ***	Oxidation–Reduction†	Element + ionic compound	Equation 8.11
Two ionic compounds	Precipitation§	Two ionic compounds	Equation 8.12
Acid + base	Neutralization§	Ionic compound (salt) + H ₂ O	Equation 8.13

*The reactant oxygen and the products carbon dioxide and water are usually not mentioned in the description of a reaction of this kind.

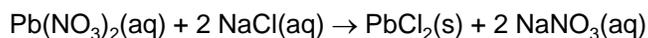
†There are several kinds of oxidation–reduction reactions. The one described in this chapter occurs in water solution. Its equation is called a single replacement equation.

§Precipitation and neutralization reactions are usually described by a double replacement equation.

Net Ionic Equations

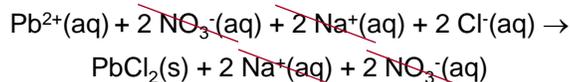
An example:

If a solution of lead nitrate is added to a solution of sodium chloride, lead chloride precipitates:



(This is a *conventional equation*)

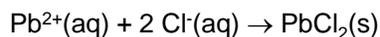
To better describe the reaction, the formulas of the dissolved substances are replaced with the actual species in solution:



(This is an *ionic equation*)

We can then eliminate the “spectators”.

The result is a *net ionic equation*, which tells exactly what chemical change took place, and nothing else:

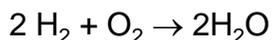


Steps in writing a balanced net ionic equation:

- Write the conventional equation, including designations of state [(g), (l), (s), (aq)]. Balance the equation.
- Write the ionic equation by replacing each *dissolved substance* (aq) with the species in solution. Never change states in this step. Be sure the equation is balanced for both atoms and charge.
- Write the net ionic equation by removing the spectators. Reduce coefficients to lowest terms. Be sure the equation is balanced for both atoms and charge.

Electron-transfer Reactions

Example: H₂ combining with O₂ to form water:



An electron is transferred from H to O:

the H₂ is oxidized and the O₂ is reduced

We use the **oxidation number (oxidation state)** to keep track of electron shifts in chemical reactions:

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

Reduction: Gain of electrons by an element
....oxidation number **decreases**

Common Oxidation States of Elements

IA		IIA		GROUPS										VIIA		VIIIA																																											
1 H +1		3 Li +1	4 Be +2	13 Al +3	14 Si +4	15 P +3 +5	16 S +2 +4 +6	17 Cl +1 +3 +5 +7	18 Ar	19 K +1	20 Ca +2	21 Sc +3	22 Ti +2 +3 +4	23 V +2 +3 +4 +5	24 Cr +2 +3 +4 +6	25 Mn +2 +3 +4 +6 +7	26 Fe +2 +3	27 Co +2 +3	28 Ni +2	29 Cu +1 +2	30 Zn +2	31 Ga +3	32 Ge +2 +4	33 As +3 +5	34 Se +2 +4 +6	35 Br +1 +3 +5	36 Kr +2 +4	55 Cs +1	56 Ba +2	57 La +3	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	72 Hf +4	73 Ta +5	74 W +4 +6	75 Re +4 +6 +7	76 Os +3 +4 +6	77 Ir +3 +4	78 Pt +2 +4	79 Au +1 +3	80 Hg +1 +2	81 Tl +1 +3	82 Pb +2 +4	83 Bi +3	84 Po	85 At	86 Rn

Figure 20.1 Oxidation states of the elements. The most common or stable states are shown in heavy type.

Determining Oxidation Number of Elements & Compounds

- Uncombined or free elements** (not ionized) have an oxidation number of **0**.
E.g., all of the atoms in these molecules: H_2 , Na, S_8 , O_2 , P_4 .
- Monatomic ions** (i.e., charged species which contain only one atom) have an oxidation number is **equal to the charge on the ion**.
E.g., Na and K only form ions with charges of +1; thus, their oxidation numbers are +1 in all compounds (see Fig. 20.1).
- The oxidation number of **oxygen** is **generally -2**.
Exceptions: case #1, and oxygen atoms directly bonded to O or F.

4. The oxidation number of **hydrogen is generally +1**.

Exceptions: case #1, and hydrogen atoms combined with elements such as Na or Ca (*hydrides*).

5. **Oxidation numbers of elements in a molecule must add up to the charge of the molecule.**

E.g., The sum of the oxidation numbers must be 0 for neutral molecules.

For H₂O:

H: oxid number is +1

O : oxid number is -2

Net charge = 2(+1) + 1(-2) = 0

6. **Fractional oxidation numbers are possible.**

E.g., in Na₂S₄O₆ (*sodium tetrathionate*), S has an oxidation number of +10/4:

O: 6(-2) = -12

Na: 2(+1) = 2

Sum of O + Na = -10, which must be balanced by S:

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

7. **The oxidation number is designated by an Arabic number below the atom, or a Roman or Arabic number after the atom (in parentheses)**

Oxidation states for important N, S and C compounds:

Nitrogen Compounds		Sulfur Compounds		Carbon Compounds	
Substance	Oxidation States	Substance	Oxidation States	Substance	Oxidation States
NH ₄ ⁺	N = -III, H = +I	H ₂ S	S = -II, H = +I	HCO ₃ ⁻	C = +IV
N ₂	N = 0	S ₈ (s)	S = 0	HCOOH	C = +II
NO ₂ ⁻	N = +III, O = -II	SO ₃ ²⁻	S = +IV, O = -II	C ₆ H ₁₂ O ₆	C = 0
NO ₃ ⁻	N = +V, O = -II	SO ₄ ²⁻	S = +VI, O = -II	CH ₃ OH	C = -II
HCN	N = -III, C = +II, H = +I	S ₂ O ₃ ²⁻	S = +II, O = -II	CH ₄	C = -IV
SCN ⁻	S = -I, C = +III, N = -III	S ₄ O ₆ ²⁻	S = +2.5, O = -II	C ₆ H ₅ COOH	C = -2/7
		S ₂ O ₈ ²⁻	S = +V, O = -II		

A More Complete Set of Rules

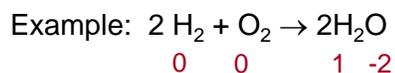
RULES FOR ASSIGNING OXIDATION NUMBERS

1. The sum of all the oxidation numbers of the atoms in an electrically neutral chemical substance must be zero. In H₂S, for example, each H atom has an oxidation number of +1, and the oxidation number of the S atom is -2. The sum is 2(+1) + (-2) = 0.
2. In polyatomic ions, the sum of oxidation numbers must equal the charge on the ion. For example, in NH₄⁺, each H atom has an oxidation number of +1, and the oxidation number of the N atom is -3, making the total 4(+1) + (-3) = +1, which is the charge on the ion. In SO₄²⁻, each O atom has an oxidation number of -2 (see Rule 5). The sum of oxidation numbers for the ion must be -2, which is the charge on the ion. Since the sum of the oxidation numbers of the four O atoms is -8, the oxidation number of the S atom must be +6.
3. The oxidation number of an atom in a monatomic ion is its charge. In Na⁺, sodium has an oxidation number of +1. In S²⁻, sulfur has an oxidation number of -2.
4. The oxidation number of an atom in a single-element neutral substance is 0. Thus, the oxidation number of every sulfur atom in S₂, S₈, and S₈ is 0; the oxidation number of chlorine in Cl₂ is 0; the oxidation number of oxygen in O₂ or O₃ is 0. Every element has at least one form in which its oxidation state is 0.
5. Some elements have the same oxidation number in all or nearly all of their compounds. When F combines with other elements, its oxidation number is always -1. The halogens Cl, Br, and I have the oxidation number -1 except when they combine with oxygen or a halogen of lower atomic number. Oxygen usually has the oxidation number -2, except when it combines with F or with itself in such compounds as the peroxides or superoxides. Hydrogen always has the oxidation number +1 when combined with nonmetals and -1 when combined with metals. A metal in group IA of the periodic table always has an oxidation number of +1. A metal in group IIA always has an oxidation number of +2.
6. Metals almost always have positive oxidation numbers.
7. A bond between identical atoms in a molecule makes no contribution to the oxidation number of that atom because the electron pair of the bond is divided equally. In hydrogen peroxide, H₂O₂, for example, the two O atoms are bonded to one another. We can calculate the oxidation number of O by determining the contribution of the two H atoms, each of which has an oxidation number of +1. Since the sum of the oxidation numbers of the H atoms is +2 and the molecule is neutral, the sum of the oxidation numbers of the two O atoms is -2, giving each an oxidation number of -1.

Reduction-Oxidation Reactions

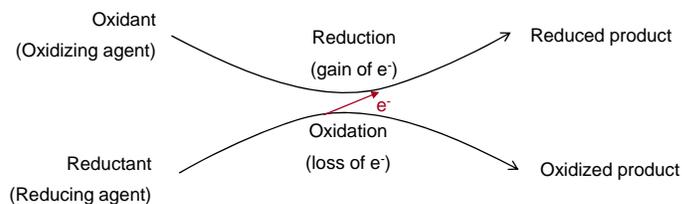
Oxidation is a chemical process in which an atom shows an *increase* in oxidation number

Reduction is a chemical process in which an atom shows an *decrease* in oxidation number



- The hydrogen changes oxidation number from 0 to +1 (is oxidized)
- The oxygen changes oxidation number from 0 to -2 (is reduced)

In General....



*** *Because there are no free electrons in nature, every oxidation is accompanied by a reduction, and vice versa* ***

An Example – The Oxidation of Zinc

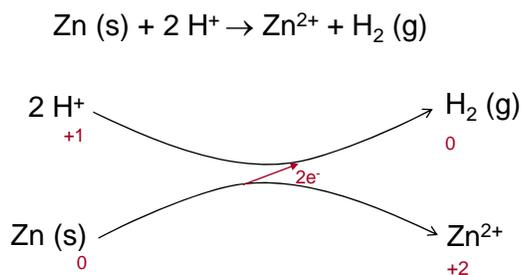


FIG. 2.3 Terms Used in Describing Oxidation-Reduction

Term	Change in oxidation number	Change in electrons
Oxidation	Increase	Loss of electrons
Reduction	Decrease	Gain of electrons
Oxidant → Oxidizing agent	Decrease	Accepts electrons
Reductant → Reducing agent	Increase	Donates electrons
Substance oxidized	Increase	Loses electrons
Substance reduced	Decrease	Gains electrons

Table 18.1 Relative Strengths of Oxidizing and Reducing Agents

	Oxidizing Agent	→	Reducing Agent	
↑	$F_2(g) + 2e^-$	→	$2 F^-$	↑
	$Cl_2(g) + 2e^-$	→	$2 Cl^-$	
	$\frac{1}{2} O_2(g) + 2 H^+ + 2e^-$	→	H_2O	
	$Br_2(l) + 2e^-$	→	$2 Br^-$	
	$NO_3^- + 4 H^+ + 3e^-$	→	$NO(g) + 2 H_2O$	
	$Ag^+ + e^-$	→	$Ag(s)$	
	$Fe^{3+} + e^-$	→	Fe^{2+}	
	$I_2(s) + 2e^-$	→	$2 I^-$	
	$Cu^{2+} + 2e^-$	→	$Cu(s)$	
	$2 H^+ + 2e^-$	→	$H_2(g)$	
	$Ni^{2+} + 2e^-$	→	$Ni(s)$	
	$Co^{2+} + 2e^-$	→	$Co(s)$	
	$Cd^{2+} + 2e^-$	→	$Cd(s)$	
	$Fe^{2+} + 2e^-$	→	$Fe(s)$	
	$Zn^{2+} + 2e^-$	→	$Zn(s)$	
	$Al^{3+} + 3e^-$	→	$Al(s)$	
	$Na^+ + e^-$	→	$Na(s)$	
	$Ca^{2+} + 2e^-$	→	$Ca(s)$	
↓	$Li^+ + e^-$	→	$Li(s)$	↓

Note: Strengths not necessarily related to # of electrons transferred

Procedure for balancing redox reactions in aqueous solutions:

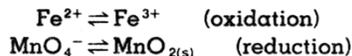
1. Identify the principal reactants and products, that is, species other than H^+ , OH^- , and H_2O , in the oxidation half-reaction and the reduction half-reaction and write each half-reaction in crude form.
2. Then to obtain balanced half-reactions, balance the atoms other than hydrogen and oxygen by multiplying the reactants or products by appropriate integers.
3. Balance the oxygen using H_2O .
4. Balance the hydrogen with H^+ .
5. Balance the charge with electrons.
6. Multiply each half-reaction by an appropriate integer so that both contain the same number of electrons.
7. Add the two balanced half-reactions.
8. Steps 1 to 7 will sometimes produce an equation that has H^+ as a reactant or a product. If it is known that the reaction takes place in alkaline solution, add the reaction for dissociation of water to the balanced equation to eliminate H^+ and form H_2O .

Example 7-1

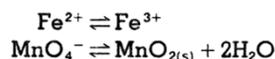
Balance the reaction in which ferrous iron (Fe^{2+}) is oxidized to ferric iron (Fe^{3+}) by permanganate (MnO_4^-), which itself is reduced to manganese dioxide ($\text{MnO}_{2(s)}$). The reaction takes place in alkaline solution.

Solution

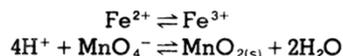
1. The reactants and products are



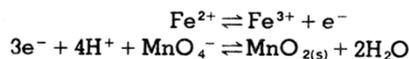
2. The atoms other than H and O are already balanced.
3. Balance the oxygen with water.



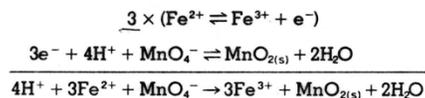
4. Balance the hydrogen with H^+ .



5. Balance the charge with electrons, e^- .

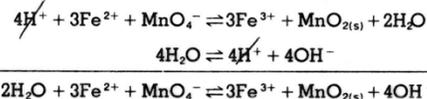


6. Multiply the Fe half-reaction by 3, then add the two half-reactions, thus eliminating electrons



The equation is now balanced. In some instances it may be desirable to modify it to take into account other reactions and to make it more useful, as shown in steps (7) and (8).

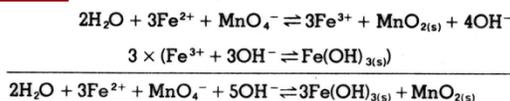
7. The reaction takes place in alkaline solution. Add the water dissociation equation to eliminate H^+ as a reactant,



Q: How do we know that this happens?

A: Gibbs free energy calculation (next lecture)

8. Further, we know that in alkaline solution, Fe^{3+} and OH^- will combine to form $\text{Fe}(\text{OH})_{3(s)}$. Adding this reaction, we obtain the final equation.



This last step would not have been necessary if in step (1) we had taken $\text{Fe}(\text{OH})_{3(s)}$ as the product rather than Fe^{3+} .

Here are two more examples of redox reactions:

1. Oxidation of Mn^{2+} to MnO_4^- by PbO_2
2. Oxidation of $\text{S}_2\text{O}_3^{2-}$ to $\text{S}_4\text{O}_6^{2-}$ by O_2

Homework:

Balance each of these two reactions using the eight steps we discussed.
Assume that the reactions take place in alkaline solution.

Due: Thursday, Jan. 17