Oxidation numbers and Balancing by Half-reactions

Oxidation numbers and half reactions are tools used by chemists to better understand reduction-oxidation reactions. These are reactions that involve transfer of electrons from atoms of one element to atoms of another elements (or, sometimes, between atoms of the same element in different compounds).

Learning Objectives

- To understand what is meant by oxidation numbers and better understand why some reactions are classified as reduction-oxidation (redox) reactions.
- To understand why many redox reactions consume or produce water and/or $H^+(aq)$ or $OH^-(aq)$

Success Criteria

- Be able to assign oxidation numbers to any element in any substance, given the formula.
- Be able to balance half-reactions, and use them to balance complete redox reactions..

Resources

ACS *Chemistry*, sections 6.9-6.10.

Vocabulary and New Concepts

Oxidation #, oxidation, reduction, oxidizing agent (oxidant), reducing agent (reductant), half-reaction.

Focus Information (a.k.a. the "Model")

Acid-base reactions (as described by Bronsted and Lowry) involve transfer of one or more protons (H^+ ions) from an acid (= proton donor) to a base (= proton acceptor). Lewis describes acid-base reactions in terms of donation of electron pairs, but it is important to note that what Lewis describes as "donation" is more aptly described as "sharing" (the Lewis base does not totally relinquish the lone pair it donates to form the new bond in the Lewis acid adduct).

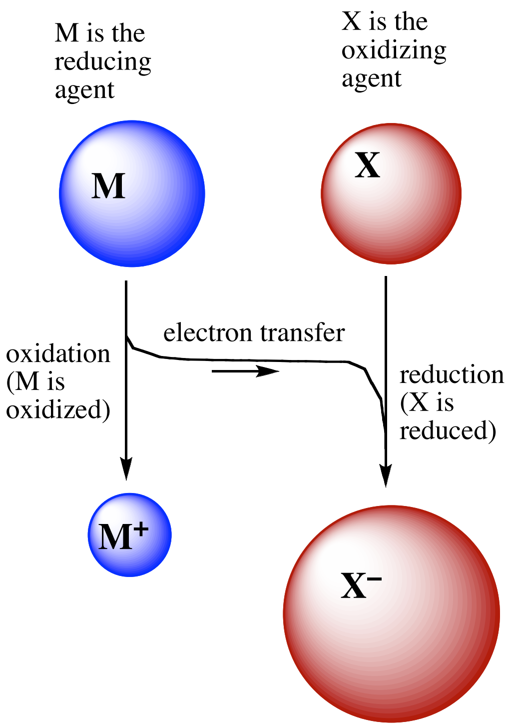
Reduction-oxidation (a.k.a. "redox") reactions involve transfer of one or more electrons from a reductant (= **reduc**ing **a**ge**nt** = electron donor) to an oxidant (= **oxid**izing **a**ge**nt**). In contrast to Lewis acid-base reactions, the transfer of electrons is complete, and does not need to involve pairs of electrons.

Reduction-oxidation reactions are often more complex than acid-base reactions because after electron transfer, the products can undergo Bronsted or Lewis acid-base reactions, or precipitation reactions.

Understanding redox reactions is helped by a bookkeeping trick called "oxidation numbers" which assign electrons (and virtual charges) to each atom of each compound. This allows us to say which atoms are oxidized and which are reduced in a redox reaction, which in turn allows us to identify the compound that is the oxidant and the compound that is the reductant.

Assigning Oxidation Numbers (cf. ACS Chemistry*, Table 6.5, p. 407)*

Simple oxidation numbers rules are given below.



Rules for Assigning Oxidation Numbers

Oxidation # of …		**EXAMPLES**
atom in an element	= zero	O_2, S_8, Ar, Fe
monoatomic ion	= charge	K^+, Ba^{2+}, Cl^-
fluorine in a compound	= -1	BF_3, SF_6
oxygen in a compound *(unless oxygen is bound to fluorine or another oxygen)*	= -2	Fe_2O_3, CO, CO_2
hydrogen in covalent compounds with non-metals	= +1	CH_4, $C_6H_{12}O_6$
hydrogen in ionic compounds with metals (metal hydrides)	= -1	NaH, CaH_2

Additional rules (no exceptions:)

- Oxdn. # ≤ group # (groups 1-11)
- Oxdn # ≤ group #-10 (groups 12-18)
- Oxdn. # ≥ group # - 18
- Sum of oxidation numbers = zero for neutral molecule
- Sum of oxidation numbers = charge on ion

Exercises

1. Assign oxidation numbers to each element in these substances. The rules given above, and your textbook, are resources, but you will have to make some judgment calls in a few cases. Be able to explain these difficult choices to the other members of your group and then to the class.

$NaPF_6$	K_2TiO_3	Li_2O	$(NH_4)I_3$	$CoCl_2$•6 H_2O
O_2	HClO	$Na_2[O_2]$	Hf	OF_2
O_3 (ozone)	$Ti(SeO_3)_2$	CsO_2	CaH_2	$MnCl_3$
Fe_2O_3	Na_2PtCl_6	$K_2Sn(OH)_6$	$LiAlH_4$	$Pb(IO_4)_2$

Rules for Balancing Half-reactions (net ionic equations, acidic or basic solutions)

Illustrated for reduction of sodium dichromate ($Na_2Cr_2O_7$) to chromium(III) in acidic solution. All ions may be safely assumed to be in aqueous solution, and $H_3O^+(aq)$ is written as H^+ (analogous to the shorthand that $Cr(H_2O)_6^{3+}(aq)$ is written as Cr^{3+}).

1) Start by writing unbalanced equation from known info.	$Na_2Cr_2O_7 \rightarrow Cr^{3+}$
2) Assume that soluble ionic species will dissolve, and	$2\ Na^+ + Cr_2O_7^{2-} \rightarrow Cr^{3+}$
ignore spectator ions *(in example: Na^+ is spectator ion)*	$Cr_2O_7^{2-} \rightarrow Cr^{3+}$
3) Assign oxdn. #'s to element that is oxidized or reduced *(ex.: Cr)*	+6 +3
4) Balance redox-active element (and any other element except H&O)	$Cr_2O_7^{2-} \rightarrow 2\ Cr^{3+}$
5) Add electrons to appropriate side of equation to account for oxidation # change *(ex.: 2 Cr atoms each reduced by 3 e^-)*	$Cr_2O_7^{2-} + 6\ e^- \rightarrow 2\ Cr^{3+}$
6) Balance charge by adding H^+ (acidic) or OH^- (basic)	total charge -8 → +6
(ex: add 14 H^+ to left side to fix charge imbalance)	$Cr_2O_7^{2-} + 6\ e^- + 14\ H^+ \rightarrow 2\ Cr^{3+}$
7) Add waters to balance oxygen	$Cr_2O_7^{2-} + 6\ e^- + 14\ H^+ \rightarrow 2\ Cr^{3+} + 7\ H_2O$

Additional Exercises

2. Write balanced *half*-reactions as *net ionic equations* for each of these processes, and identify it as an oxidation or a reduction.

H_2SO_3 (sulfurous acid) to HSO_4^- (hydrogen sulfate) in acidic aqueous solution

MnO_4^- to Mn^{2+} in acidic aqueous solution

Oxalic acid ($H_2C_2O_4$) to carbon dioxide in acidic aqueous solution

O_2 to water in acidic aqueous solution

Iron metal to solid ferric oxide in basic aqueous solution

Sodium sulfite to sodium sulfate in basic aqueous solution

Sodium chromate (Na_2CrO_4) to chromium(III) oxide (Cr_2O_3) in basic aqueous solution

Putting Half-reactions together for balanced Redox reactions

Balancing redox reactions is helped by thinking of a redox reaction as the sum of two "half-reactions". To obtain balance, the reduction half-reaction must produce the same number of electrons as are consumed in the oxidation half reaction.

- If the half-reactions as written don't have the same number of electrons, multiply the coefficients of one or both half-reactions by a small integer so that the number of electrons becomes the same.
- Then add the half-reactions together, and cancel out the electrons. You may also be able to cancel out H_2O, H^+ or OH^- (none of these should appear on both sides of the equation).

Additional Exercises

3. Pair up any two half reactions in acidic solution (from previous page) to create a *balanced* reduction-oxidation reaction equation.

4. Pair up two half reactions in basic solution (from above) to create a *balanced* reduction-oxidation reaction equation.

5. If time permits, create an additional balanced reduction-oxidation reaction equation. If you haven't already done so, include an example where there are different numbers of electrons in the starting oxidation and reduction half-reactions.

More Information – Common Oxidation Numbers

The following is a table of **common oxidation numbers**. (The zero oxidation number is found in all pure elements, and is omitted from the table). Similar tables may be found in most General Chemistry textbooks, although there is no consensus among chemists for which oxidation numbers are "common".

H -1, +1																	He
Li +1	Be +2											B +3	C -4 to +4	N -3, +3, 5	O -2	F -1	Ne
Na +1	Mg +2											Al +3	Si +4	P -3, +3, 5	S -2, +4, 6	Cl -1, +1, 7	Ar
K +1	Ca +2	Sc +3	Ti +2, 4	V +2, 4, 5	Cr +2, 3, 6	Mn +2, 4, 7	Fe +2, 3	Co +2, 3	Ni +2	Cu +1, 2	Zn +2	Ga +3	Ge -4, +4	As -3, +3, 5	Se -2, +4, 6	Br -1, +1, 5	Kr
Rb +1	Sr +2	Y +3	Zr +4	Nb +4, 5	Mo +3, 4, 6	Tc +4, 7	Ru +2, 3, 4	Rh +1, 3	Pd +2	Ag +1	Cd +2	In +1, 3	Sn +2, 4	Sb +3, 5	Te -2, +4, 6	I -1, +1,5,7	Xe
Cs +1	Ba +2	La +3	Hf +4	Ta +5	W +4, 5, 6	Re +3,4,6,7	Os +4, 8	Ir +3, 4	Pt +2, 4	Au +1, 3	Hg +1, 2	Tl +1, 3	Pb +2, 4	Bi +3	Po	At	Rn
Fr +1	Ra +2	Ac +3	Rf	Db	Sg	Bh	Hs	Mt	Ds	Uuu	Uub		Uuq				
			Ce +3, 4	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	
			Th +4	Pa	U +3, 4, 6	Np +3, 4, 5	Pu +3, 4, 6	Am +3, 4	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Questions for Discussion

1. Which ions in this table have only a single common oxidation number? How is this common oxidation number related to the group number?

2. Including the elements with multiple common oxidation numbers, what generalizations can you make about the oxidation numbers based on the position in the periodic table?

3. You **will** encounter oxidation states not in this table (so don't rely on it in working problems). Can you identify an example (or several) of a compound or ion with an oxidation number not found in this table?