

Chapter 3

Prototypical Reactions

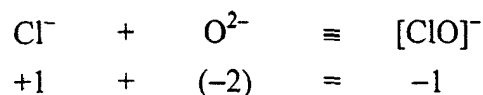
Chapter 3, with a first look at reactions and reactivity, completes the overview of classical chemistry begun in the first two chapters. Going beyond a static picture of structure alone—of atoms and molecules as building blocks—we begin to consider the possibility of change. We begin to consider the means by which the building blocks can be rearranged.

Still at the Lewis level, this thumbnail sketch of chemical change prefigures the more detailed development that runs through the second half of PoC: from the drive to equilibrium (Section 3-1 and Chapters 12 through 14) ... to the interactions of acid and base (Section 3-2 and Chapter 16) ... to oxidation and reduction (Section 3-3 and Chapter 17) ... to dissolution and precipitation (Section 3-4 and Chapter 15) ... to radical reactions (Section 3-5 and Example 18-12) ... to kinetics and catalysis (Section 3-6 and Chapter 18). The unifying theme throughout is the tendency of nature to smooth away differences of all kinds—an end fulfilled, in so many reactions, by the bringing together of the “haves” and “have-nots” of the electronic microworld.

The opening exercises deal with the determination of oxidation numbers, an essential first step in the understanding of redox reactions (Section 3-3, Chapter 17).

1. The rules specifically applicable to these oxyanions are: (1) Oxygen always takes an oxidation number of -2 , except in peroxides, superoxides, and oxygen-fluorine bonds. (2) The net charge on an ion must equal the algebraic sum of the oxidation numbers attributed to its component atoms. See pages 90–92 and R3.2–R3.3 of *PoC*, as well as Examples 3-1, 3-2, and 3-3 (beginning on page R3.6).

(a) One oxygen atom (oxidation number = -2) plus one chlorine atom (oxidation number = $+1$) together account for the -1 charge of the hypochlorite ion, ClO^- . Taking this view, we thus ascribe a fictitious ionic character to an otherwise covalent structure:

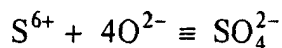
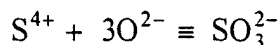


(b) There are two oxygen atoms in the chlorite ion, each with oxidation number equal to -2 . Chlorine therefore must have an oxidation number of $+3$ to produce a net charge of -1 in ClO_2^- .

(c) Three oxygen atoms [$3 \times (-2) = -6$] plus one chlorine atom (oxidation number = $+5$) yield an overall charge of -1 in ClO_3^- , the chlorate ion.

(d) The four oxygens in the perchlorate ion, ClO_4^- , contribute an aggregate oxidation number of -8 , leaving chlorine with the value $+7$.

2. Use the same procedure as in the preceding exercise: (1) Assign an oxidation number of -2 to each oxygen. (2) Recognize that the oxidation numbers must all add together to yield the actual net charge. Determine the oxidation number of sulfur accordingly, as if the bonding were ionic rather than covalent:



3. The applicable rules are: (1) Oxygen is assigned an oxidation number of -2 in all compounds, except when bonded either to another oxygen (as in a peroxide or superoxide) or to fluorine. (2) The sum of the oxidation numbers from all of the atoms in a neutral molecule is equal to zero.

(a) Two nitrogen atoms, each with an average oxidation number of $+1$, are balanced by a single oxygen atom (-2) to produce the neutral molecule N_2O .

QUESTION: Why say an *average* oxidation number?

ANSWER: The qualifier “average” reminds us that our concept of oxidation state is a blunt instrument, a handy device that lets us apportion charges in a very rough way. Even if we know nothing about a molecule’s Lewis structure, we still can say—again, we can *roughly* say—which of two sites is more likely to attract electrons. And by assigning these fictitious partial charges, we can make all kinds of useful predictions. We can recognize differences among related compounds such as N_2O , NO , NO_2 , and so forth. We can identify a redox process. We can venture guesses about chemical reactivity.

The predictions come at a price, though: the assumption that all atoms of a given type behave in exactly the same way in all environments. There are two nitrogen atoms in N_2O , for example, and our rules force upon both of them the same oxidation state. Is it reasonable to do so? Maybe yes, maybe no. Without some information about the structure, we cannot be sure.

For an alternative view (one that does treat each atom as a distinct site), we have the notion of *formal charge*. See Exercises 7 and 8.

(b) An assignment of -2 to oxygen and $+2$ to nitrogen guarantees electrical neutrality for the molecule NO .

(c) Each of the two oxygen atoms in NO_2 contributes an oxidation number of -2 . The single nitrogen atom then takes on the value $+4$ to counterbalance the combined -4 from the oxygens.

(d) The nitrogen atom in NO_3 exists as $+6$, in opposition to the combined value of -6 from the three oxygens (-2 for each).

(e) Two nitrogen atoms (average oxidation number = $+3$) plus three oxygen atoms (each -2) produce the neutral compound N_2O_3 :

$$2 \times (+3) + 3 \times (-2) = 0$$

(f) In N_2O_4 , the four oxygens [$4 \times (-2) = -8$] are matched by two nitrogens in $+4$ oxidation states [$2 \times (+4) = +8$].

(g) There are two nitrogens (each $+5$) and five oxygens (each -2) in N_2O_5 .

4. Here the applicable rules are: (1) Any atom in its elemental state is assigned an oxidation number of 0. (2) Oxygen is assigned an oxidation number of -2 everywhere except in peroxides, superoxides, and oxygen-fluorine bonds. (3) Hydrogen is assigned an oxidation number of $+1$ in all compounds except metal hydrides (such as NaH , where it is -1) and elemental hydrogen (where it is 0). (4) The sum of the oxidation numbers from all of the atoms in a neutral molecule is zero.

(a) P_4 , white phosphorus, is an elemental form of phosphorus. The oxidation state of P in P_4 is 0.

(b) Each of the four phosphorus atoms in P_4O_6 exists in a $+3$ oxidation state. The positive contribution from phosphorus ($+12$) is balanced by the negative contribution from oxygen [$6 \times (-2) = -12$] in the electrically neutral compound.

(c) Chlorine exists as $+7$ and oxygen exists as -2 in Cl_2O_7 .

(d) HNO_2 : hydrogen, +1; nitrogen, +3; oxygen, -2.

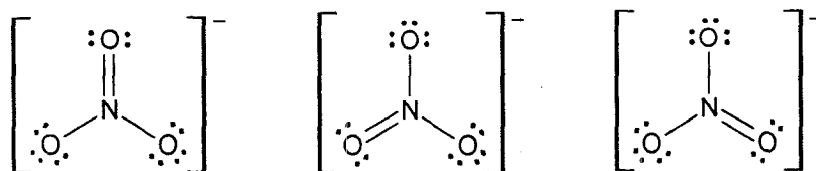
(e) HNO_3 : hydrogen, +1; nitrogen, +5; oxygen, -2.

5. Each of the four oxygen atoms in PO_4^{3-} exists in the oxidation state -2, thus contributing a combined value of -8 to the phosphate ion. The central phosphorus atom is then assigned an oxidation state of +5, consistent with an overall ionic charge of -3. In the phosphite ion (PO_3^{3-}), with one fewer oxygen atom present, the oxidation state of phosphorus falls to +3.

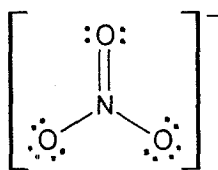
6. In both CO_3^{2-} and CO , the carbon atom is bonded to a species with higher electronegativity: oxygen. The polar bonds are skewed so that more electrons reside near the oxygen. In C_3H_8 , however, the electrons are biased toward the carbons, which are more electronegative than hydrogen.

7. Formal charge is compared with oxidation state in Example 3-3 of *Review and Guide to Problems*, beginning on page R3.8 of *PoC*.

(a) There are 24 valence electrons in NO_3^- (five from the nitrogen, six from each of three oxygens, and one more for the negative charge). The following three Lewis structures, in which each atom has an octet, are therefore all equivalent:



To compute formal charge, note that elemental nitrogen is normally surrounded by five valence electrons and elemental oxygen by six. We then compare the valence in the structure



with the valence in the isolated atoms, dividing equally the shared electrons in each bond. Thus the nitrogen is assigned four electrons (*half* of the eight electrons in the four bonds), whereas the two singly bonded oxygens are assigned seven apiece: six nonbonding electrons (in the three lone pairs) plus one bonding electron (*half* of the bonding pair). The doubly bonded oxygen, finally, is allocated six electrons: four nonbonding electrons (two lone pairs) plus two bonding electrons (*half* of the double bond).

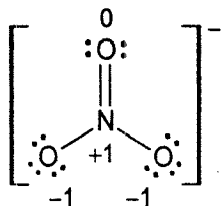
Electron totals and corresponding formal charges are summarized in the table that follows:

	VALENCE ELECTRONS	- NONBONDING ELECTRONS	$-\frac{1}{2} \times$ BONDING ELECTRONS	= FORMAL CHARGE
N	5	0	$\frac{1}{2} \times 8$	+1
-O	6	6	$\frac{1}{2} \times 2$	-1
=O	6	4	$\frac{1}{2} \times 4$	0

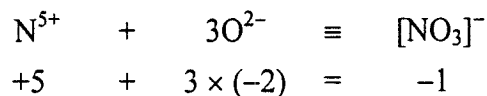
The sum of the four formal charges (from N, -O, -O, and =O),

$$1 - 1 - 1 + 0 = -1$$

equals the net charge on the ion, as it must:

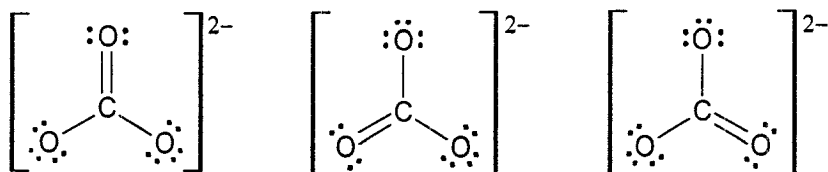


The oxidation numbers, considerably different, are -2 for each oxygen (fixed by convention) and $+5$ for nitrogen (chosen to yield a net ionic charge of -1):

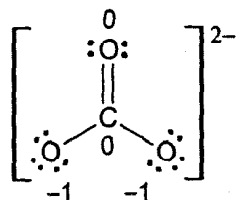


See Exercises 1 through 5 for additional practice in establishing oxidation numbers.

(b) The calculation for CO_3^{2-} , an ion isoelectronic with NO_3^- , is similar. Again, 24 electrons (four from carbon, six from each of three oxygens, plus two extra for the charge) are distributed over three equally valid Lewis structures:



Each atom has an octet, and the formal charges



are then calculated as follows:

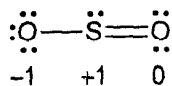
	VALENCE ELECTRONS	- NONBONDING ELECTRONS	$-\frac{1}{2} \times$ BONDING ELECTRONS	= FORMAL CHARGE
C	4	0	$\frac{1}{2} \times 8$	0
-O	6	6	$\frac{1}{2} \times 2$	-1
=O	6	4	$\frac{1}{2} \times 4$	0

The oxidation numbers are -2 for each oxygen and +4 for carbon.

(c) Two equivalent Lewis structures provide octets for each of the three atoms in SO_2 :



The 18 valence electrons (six from sulfur plus six from each of the two oxygens) produce formal charges

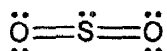


of +1 (for sulfur), -1 (for singly bonded oxygen), and 0 (for doubly bonded oxygen):

	VALENCE ELECTRONS	- NONBONDING ELECTRONS	$-\frac{1}{2} \times$ BONDING ELECTRONS	= FORMAL CHARGE
S	6	2	$\frac{1}{2} \times 6$	+1
-O	6	6	$\frac{1}{2} \times 2$	-1
=O	6	4	$\frac{1}{2} \times 4$	0

The oxidation numbers are -2 for each oxygen and +4 for sulfur.

A third Lewis structure, supported by experimental evidence, places 10 electrons around the sulfur atom



and yields zero formal charge at each position:

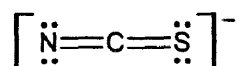
	VALENCE ELECTRONS	- NONBONDING ELECTRONS	$-\frac{1}{2} \times$ BONDING ELECTRONS	= FORMAL CHARGE
S	6	2	$\frac{1}{2} \times 8$	0
O	6	4	$\frac{1}{2} \times 4$	0

Sulfur, a third-row element, can expand its valence beyond an octet.

Formal charge (Example 3-3) also provides a way to judge the "quality" of a valid, but perhaps implausible, Lewis structure. See the next exercise.

8. There are 16 valence electrons to distribute in each structure (four from carbon, five from nitrogen, six from sulfur, and one extra for the negative charge).

Consider first the form



The nitrogen site, with four unshared electrons and four shared electrons, is assigned a total of six electrons in the molecular ion,

$$4 \text{ (nonbonding)} + \frac{1}{2} \times 4 \text{ (bonding)} = 6$$

one more than in an uncombined atom. The formal charge on N is thus -1:

$$\begin{aligned} \text{Formal charge} &= \text{valence} - \text{nonbonding} - \frac{1}{2} \times \text{bonding} \\ &= 5 - 4 - \frac{1}{2} \times 4 = -1 \end{aligned}$$

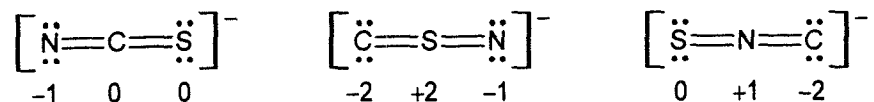
Carbon, by contrast, is fully surrounded by eight bonding electrons, leaving it formally neutral:

$$\begin{aligned} \text{Formal charge} &= \text{valence} - \text{nonbonding} - \frac{1}{2} \times \text{bonding} \\ &= 4 - 0 - \frac{1}{2} \times 8 = 0 \end{aligned}$$

Sulfur, assigned four bonding electrons and four nonbonding electrons, is formally neutral as well:

$$\begin{aligned} \text{Formal charge} &= \text{valence} - \text{nonbonding} - \frac{1}{2} \times \text{bonding} \\ &= 6 - 4 - \frac{1}{2} \times 4 = 0 \end{aligned}$$

Formal charges for all three structures are obtained in the same way,



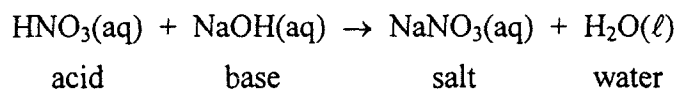
from which we conclude that the most plausible arrangement is $[\text{N}=\text{C}=\text{S}]^-$. Formal charges are smallest in this form, and the nitrogen atom—the most electronegative of the three—bears the negative charge.

Acid–base reactions (Section 3-2 and pages R3.4–R3.5) and redox reactions (Section 3-3 and pages R3.2–R3.4) are taken up in the next group of exercises. See also Example 3-5.

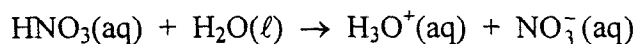
9. An Arrhenius acid increases the concentration of the hydronium ion, H_3O^+ , in aqueous solution. An Arrhenius base increases the concentration of the hydroxide ion, OH^- . Brought together, acid and base combine to form H_2O and a neutralized salt.

See Exercise 11 and the text references therein for a review of the Arrhenius model as well as the Brønsted-Lowry and Lewis models.

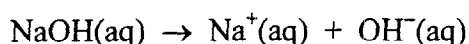
(a) Nitric acid and sodium hydroxide react in aqueous solution (aq), producing sodium nitrate (a soluble salt) and liquid water (ℓ):



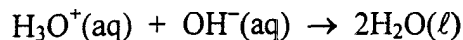
Note that HNO_3 , a strong Arrhenius acid, dissociates completely in water to yield the solvated ions H_3O^+ and NO_3^- ,



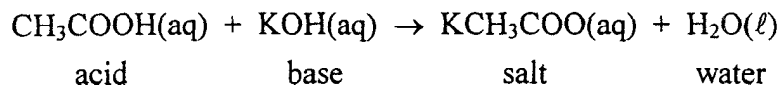
whereas NaOH , a strong Arrhenius base, dissociates completely into Na^+ and OH^- :



Since $\text{NaNO}_3(\text{aq})$ exists as the dissolved ions $\text{Na}^+(\text{aq})$ and $\text{NO}_3^-(\text{aq})$, we may equivalently represent the neutralization by a net ionic equation of the type treated in part (c):

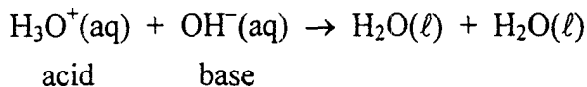


(b) Acetic acid (CH_3COOH) is a weak acid, incompletely dissociated in solution. Potassium hydroxide (KOH) is a strong base. They react to produce the soluble salt potassium acetate (KCH_3COO) plus water:



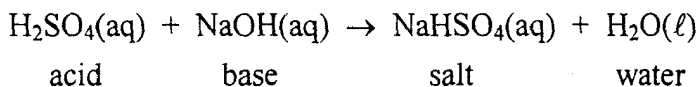
Potassium hydroxide exists as the solvated ions $\text{K}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$. Potassium acetate exists as the solvated ions $\text{K}^+(\text{aq})$ and $\text{CH}_3\text{COO}^-(\text{aq})$.

(c) Here we have a generic acid–base reaction between a hydronium ion and a hydroxide ion, already encountered in part (a):



H_3O^+ , acting as a Brønsted-Lowry acid, transfers a proton to the Brønsted-Lowry base OH^- . Two molecules of water are generated by the neutralization.

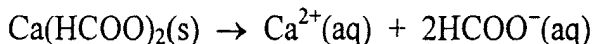
(d) Observing that the salt NaHSO_4 is produced, we see at once that the base in question must be NaOH :



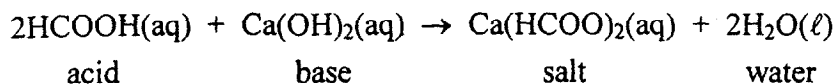
H_2SO_4 , a strong acid, loses one H^+ to become HSO_4^- in aqueous solution. Sodium hydroxide and sodium hydrogen sulfate exist as the dissolved ions $\text{Na}^+(\text{aq})$, $\text{OH}^-(\text{aq})$, and $\text{HSO}_4^-(\text{aq})$. Hydronium and hydroxide ions combine to form water.

10. More acid–base reactions.

(a) Since the salt $\text{Ca}(\text{HCOO})_2$ (calcium formate) dissociates as

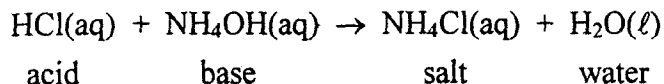


we know that the acid reacting with $\text{Ca}(\text{OH})_2$ must be HCOOH (formic acid):



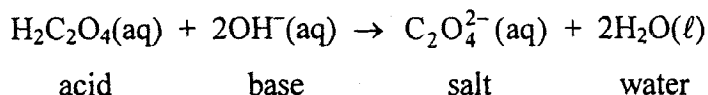
Formic acid is a weak acid; calcium hydroxide is a strong base.

(b) Here we have hydrochloric acid reacting with ammonium hydroxide, a neutralization of a strong acid by a strong base:



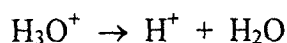
The neutralization product is ammonium chloride, a soluble salt that exists as the solvated ions $\text{NH}_4^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$. Both acid and base are completely dissociated in solution.

(c) The neutralization of oxalic acid (a weak acid) by the hydroxide ion:

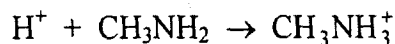


Reacting with OH^- , the diprotic acid $\text{H}_2\text{C}_2\text{O}_4$ loses two H^+ ions. We insert 2OH^- as a reactant and one additional H_2O as a product to balance both charge and mass.

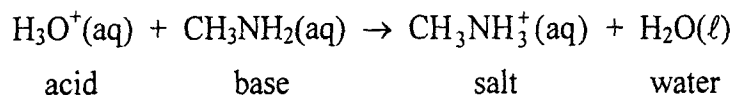
(d) Observing that the reactant H_3O^+ loses a proton to become the product H_2O ,



we surmise that the dissociated proton has been transferred to the base CH_3NH_2 :



The complete, balanced equation follows directly:



11. Recall our three views of acids and bases: the Lewis model, the Brønsted-Lowry model, and the Arrhenius model.

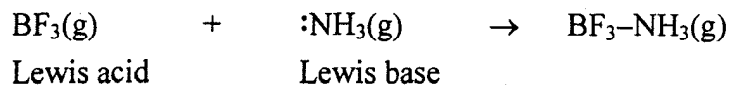
In the Lewis conception, an acid–base interaction means the coordination of a pair of electrons between a donor (the base) and an acceptor (the acid) to form a neutralized “salt” complex. We recognize a Lewis acid as a species deficient in electrons, a species like

H^+ , a hydrogen atom stripped down to its single-proton nucleus;

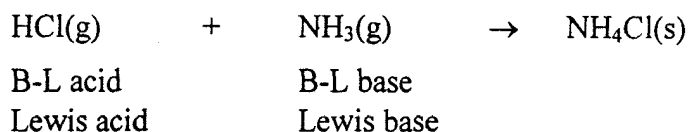
or Fe^{3+} , a metal ion that has lost some of its electrons and thus (maybe) can get them back;

or BF_3 , a molecule that contains an atom two electrons short of an octet and thus (maybe) can bond to a fourth group offering a lone pair.

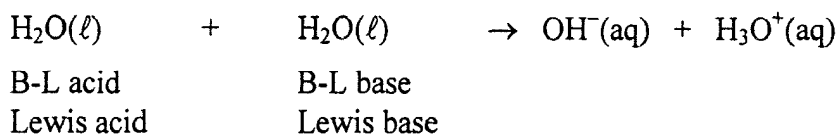
A Lewis base, a complementary partner, then emerges as a structure *rich* in electrons, a structure that can remedy the deficiency of the acid—a structure with accessible electron pairs, like the chloride ion, Cl^- ... or the H_2O molecule... or the ammonia molecule, NH_3 :



In the Brønsted-Lowry picture, it is not a pair of electrons but rather a single proton (H^+) that serves as the medium of exchange. A Brønsted-Lowry acid *gives* the proton; a Brønsted-Lowry base takes it. HCl acts as a Brønsted-Lowry acid by transferring H^+ (itself a *Lewis acid*) to a proton-receptive Brønsted-Lowry base such as NH_3 (which, similarly, is also a *Lewis base*):



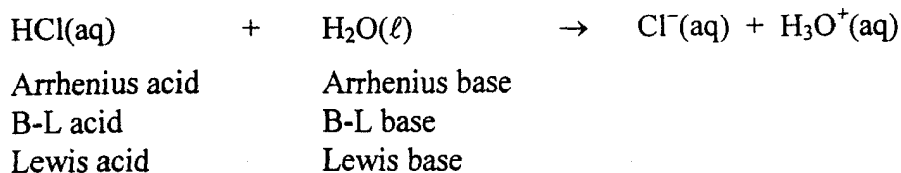
Water, especially versatile, acts as both a Brønsted-Lowry acid and a Brønsted-Lowry base when H^+ passes from one H_2O molecule to another:



The transfer results in the formation of hydronium and hydroxide ions, H_3O^+ and OH^- .

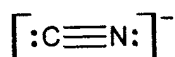
Finally, in the Arrhenius conception it is specifically the presence of H_3O^+ and OH^- that announces the interaction of acid and base. Defined exclusively for aqueous solution, an Arrhenius acid causes the concentration of H_3O^+ to increase. An Arrhenius base, complementary to the acid, increases instead the concentration of OH^- .

For example, the aqueous dissociation of HCl into H_3O^+ and Cl^- enables us to classify hydrochloric acid more finely as an *Arrhenius* acid—not just a Lewis acid, not just a Brønsted-Lowry acid, but an Arrhenius acid as well. Dissolved in water, HCl produces hydronium ions:

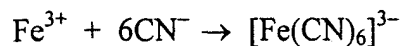


For more information, see *PoC* pages 79–86 and various portions of *Review and Guide to Problems*. For a comprehensive treatment, see all of Chapter 16.

(a) The transition-metal ion Fe^{3+} comes into existence when an iron atom loses a portion of its valence electron density. The resulting species is a Lewis acid, an electron-deficient site that can accept a pair of electrons from a Lewis base—a Lewis base, perhaps, like the cyanide ion with its two lone pairs:



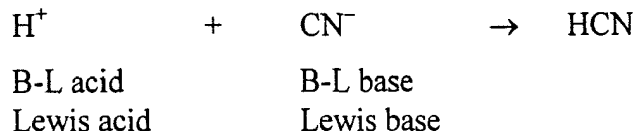
The base gives a pair, and the acid takes a pair. A *coordinate covalent* (or *dative*) bond is the result:



We call the product a *coordination complex*, a class of compound described briefly on page 81 of *PoC*. Chapter 19 is devoted entirely to the subject of coordination complexes formed by transition metals and Lewis bases.

Note that Fe^{3+} is a Lewis acid and only a Lewis acid. Lacking a proton to give, it cannot be a Brønsted-Lowry acid. Unable to increase the concentration of H_3O^+ in water, it cannot be an Arrhenius acid.

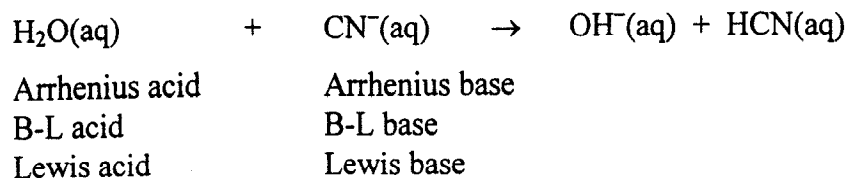
The cyanide ion, by contrast, functions also as a Brønsted-Lowry base. Accepting a proton from a Brønsted-Lowry acid, CN^- becomes HCN:



And when that proton comes from H_2O to create OH^- ,

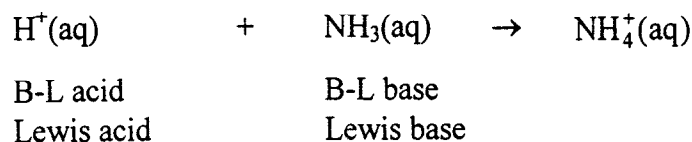


the hydrolytic (“water breaking-down”) cyanide ion fits the definition of an Arrhenius base as well:

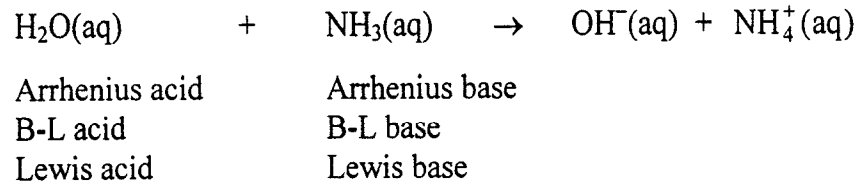


(b) The interaction between octet-deficient BF_3 (a Lewis acid) and NH_3 (a Lewis base, carrying a lone pair on nitrogen) is discussed on pages 63–65 and page 80 of *PoC*, as well as on page 65 above.

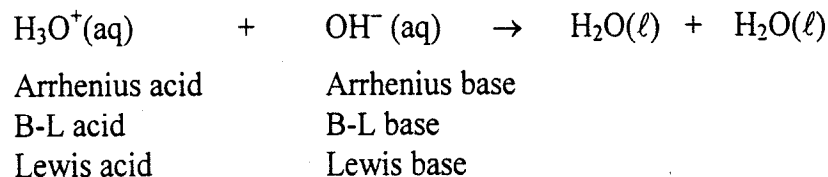
BF_3 acts only as a Lewis base, whereas NH_3 can serve as both a Brønsted-Lowry base



and an Arrhenius base:



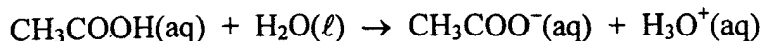
(c) H_3O^+ and OH^- , respectively, are acids and bases in every sense. They give and take electron pairs (Lewis); they give and take H^+ (Brønsted-Lowry); and they are literally Arrhenius’s special hydronium and hydroxide ions:



(d) The aluminum ion, Al^{3+} , is a Lewis acid and nothing more. It can accept a pair of electrons—say from OH^- in the compound $\text{Al}(\text{OH})_3$ —but it lacks the capacity either to donate a proton or to produce hydronium ions.

The hydroxide ion, OH^- , is a base according to all three models. It offers accessible lone pairs (Lewis). It accepts a proton to form H_2O (Brønsted-Lowry). It is hydroxide itself, an Arrhenius base by definition.

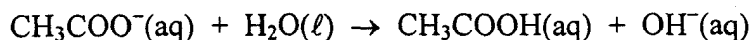
(e) CH_3COOH (a Brønsted-Lowry acid) loses a hydrogen ion to become CH_3COO^- (a Brønsted-Lowry base). In aqueous solution, moreover, the two partners serve as our exemplary Arrhenius acid and conjugate base, to be described at length in Chapter 16:



Acetic acid and the acetate ion interact as Lewis acids and bases as well.

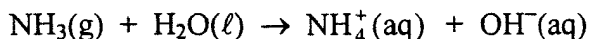
12. In each of these acid–base reactions, we identify the missing species and balance the equation by inspection.

(a) A water molecule transfers a proton to the acetate ion, CH_3COO^- , thereby producing acetic acid (CH_3COOH) and hydroxide ion. CH_3COO^- acts as a base, and H_2O acts as an acid:



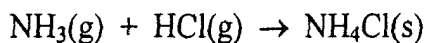
The reaction demonstrates a typical *hydrolysis* (“water breaking-down”) process undergone by a weak base. See Sections 16-3 through 16-5 and related material in Chapter 16 *Review and Guide to Problems*.

(b) Dissolution of ammonia in water produces the ammonium and hydroxide ions:



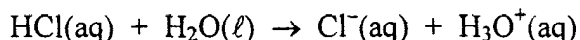
NH_3 functions as a weak base, accepting a proton from H_2O (à la Brønsted-Lowry) and simultaneously donating its lone pair of electrons to the incoming H^+ (à la Lewis). Since the reaction yields OH^- ions in aqueous solution, it fits into the Arrhenius category as well.

(c) Reacting with HCl in the gas phase, ammonia serves as a Lewis and Brønsted-Lowry base—but not as an Arrhenius base. A solid product, ammonium chloride, falls out:



In the absence of liquid water, no solvated OH^- ions are produced.

A point of nomenclature: When HCl reacts outside of aqueous solution (as here), the compound is typically called *hydrogen chloride*. But when the same molecule, HCl , behaves as an Arrhenius acid,

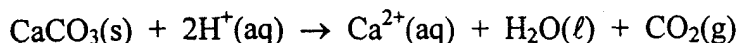


we call it *hydrochloric acid*. See pages A14–A15 in *PoC* (Appendix A).

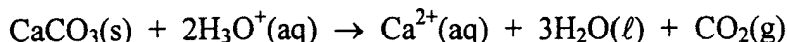
(d) Calcium carbonate dissolves poorly in water, but readily in acidic solution. The missing product is carbon dioxide, CO_2 , a gas at room temperature:



Expressed as a net ionic equation, the reaction simplifies to a form



in which $\text{H}^+(\text{aq})$ is shorthand for the hydronium ion, $\text{H}_3\text{O}^+(\text{aq})$. More explicitly, we might write



13. A change in oxidation number signals a *redox* reaction, a partial shift of electrons from giver to taker.

The *giver* of electrons undergoes *oxidation*. Losing electrons, it becomes more positive. Its oxidation number goes up—from, say, -1 to 0 or from 0 to $+1$.

The *taker* of electrons undergoes *reduction*. Gaining electrons, it becomes more negative. Its oxidation number goes down (is reduced) in an algebraic sense—from, say, $+1$ to 0 or from 0 to -1 .

The giver, by forcing its electrons on the taker, is the agent that brings about a reduction of something else. Undergoing oxidation itself, this electron-giving *reducing agent* (or *reductant* or *reducer*, both synonyms) sponsors the reduction of its partner.

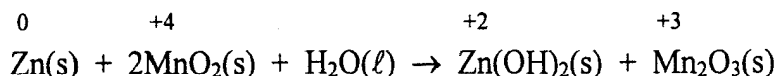
The taker, by extracting electrons from the giver, is the agent that brings about the oxidation of something else. Undergoing reduction itself, this electron-taking *oxidizing agent* (or *oxidant* or *oxidizer*, both synonyms) sponsors an oxidation of its partner.

Let the symmetry of the language describing oxidation and reduction be a guide. They are complementary processes, one dependent on the other, forever paired—just like the reactions of acid and base.

(a) Calculate the oxidation numbers, recalling that oxygen atoms are assigned values of -2 and hydrogen atoms are assigned values of $+1$ in most environments. Recall further that (1) the oxidation number of any atom in a pure element is zero; and (2) the sum of the component oxidation numbers for any intact species, neutral or ionic, is equal to the net charge of that species.

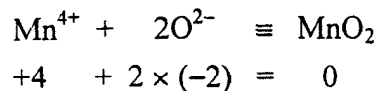
For example, we note that oxygen (value = -2) and hydrogen (value = $+1$) combine to produce a net oxidation state of -1 for OH^- . Then, finding two hydroxide ions paired with zinc in $\text{Zn}(\text{OH})_2$, we determine that zinc exists in the compound as Zn^{2+} . And so on, for each participant in the reaction.

Next, with oxidation numbers determined, we look for changes between reactants and products:

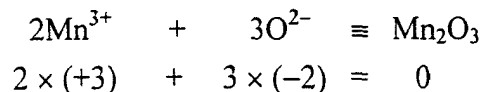


Observe: Zinc goes from an oxidation number of 0 in its elemental form (solid Zn) to a higher value, +2, when it becomes Zn^{2+} in $Zn(OH)_2$. Zn loses electrons. It undergoes *oxidation*. It causes something else to undergo reduction. Zn is the *reducing agent*.

And what does metallic zinc reduce here? It reduces manganese. It reduces Mn from an oxidation number of +4 in MnO_2 ,



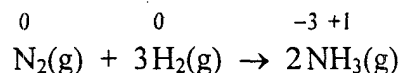
to an oxidation number of +3 in Mn_2O_3 :



The reactant MnO_2 gains electrons. It undergoes *reduction*. It causes Zn to undergo oxidation. MnO_2 is the *oxidizing agent*.

No other atom suffers a change in oxidation number. Oxygen remains at -2, and hydrogen remains at -1.

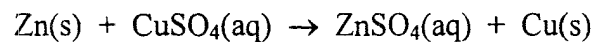
(b) Recognize immediately that N_2 and H_2 are elemental forms of nitrogen and hydrogen, existing in the zero oxidation state:



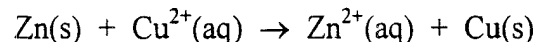
Hydrogen, which goes from 0 in H_2 to +1 in NH_3 , is itself oxidized. H_2 is the reducing agent.

Nitrogen, which goes from 0 in N_2 to -3 in NH_3 , is itself reduced. N_2 is the oxidizing agent.

(c) Knowing that the sulfate ion, SO_4^{2-} , carries a charge of -2, we recognize that both copper and zinc exist as +2 in the compounds $CuSO_4$ and $ZnSO_4$, respectively. Proceeding from there, we ignore the spectator sulfate ions and write the overall reaction



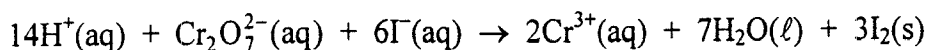
in net ionic form:



The reducing agent, Zn^0 , is oxidized to Zn^{2+} . The oxidizing agent, Cu^{2+} , is reduced to Cu^0 .

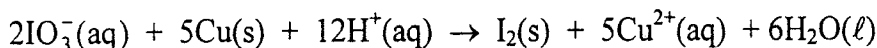
This redox reaction of copper and zinc will power our prototype electrochemical cell in Chapter 17.

(d) The iodine atom in Γ^- , the reducing agent, is oxidized from an initial value of -1 in its iodide form to a final value of 0 in elemental I_2 . The Cr^{6+} species in the dichromate ion ($Cr_2O_7^{2-}$), the oxidizing agent, gains electrons and is reduced to Cr^{3+} :



14. More of the same.

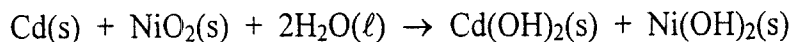
(a) The reaction is between elemental copper and the iodate ion, IO_3^- :



Oxidizing agent: IO_3^- (iodine reduced from $+5$ in IO_3^- to 0 in I_2)

Reducing agent: Cu (oxidized to Cu^{2+})

(b) The reaction that powers the nickel-cadmium battery:



Oxidizing agent: NiO_2 [nickel reduced from $+4$ in NiO_2 to $+2$ in $Ni(OH)_2$]

Reducing agent: Cd [oxidized to Cd^{2+} in $Cd(OH)_2$]

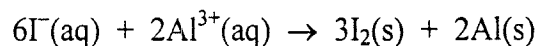
(c) The reaction that powers the lead storage battery used in automobiles:



Oxidizing agent: PbO_2 (lead reduced from Pb^{4+} in PbO_2 to Pb^{2+} in $PbSO_4$)

Reducing agent: Pb (oxidized to Pb^{2+} in $PbSO_4$)

(d) The reduction of the aluminum ion to pure metal, brought about by the iodide ion:

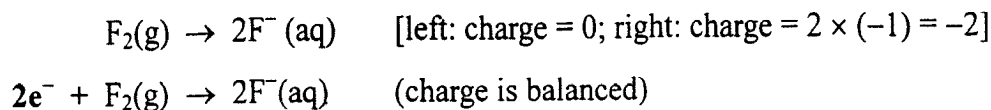


Oxidizing agent: Al^{3+} (reduced to Al)

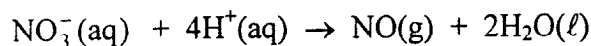
Reducing agent: Γ^- (oxidized to I_2)

15. Add electrons to either side of the equation, as needed, to ensure that the total charge remains constant from beginning to end.

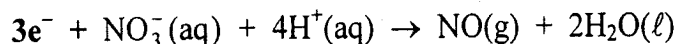
(a) Fluorine gas is reduced to the fluoride ion. F_2 gains two electrons per molecule reduced:



(b) The original equation shows a net charge of +3 on the left and 0 on the right:

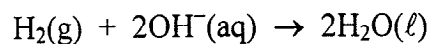


To balance, add three electrons on the left:



Nitrogen is reduced from +5 in NO_3^- to +2 in NO. It gains electrons.

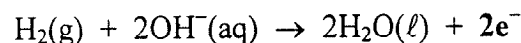
(c) We have an oxidation of molecular hydrogen in basic solution, during which the oxidation number of H goes from 0 in H_2 to +1 in H_2O . The unbalanced equation



shows zero charge on the right but -2 on the left:

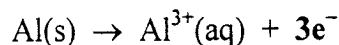
$$2OH^- \equiv 2 \times (-1) = -2$$

To conserve charge, we need to add a compensating two electrons on the right:



H_2 is oxidized. It loses electrons.

(d) The reaction in question is the oxidation of aluminum metal to the triply positive aluminum ion. Three electrons are required on the right:



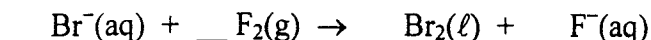
Redox equations more complicated than those found in the next exercise are considered later, in Chapter 17. For a systematic method of balancing such equations in acidic or basic solution, see Section 17-8 and Examples 17-1 and 17-2 (beginning on page R17.6 of PoC). Corresponding exercises are provided on pages R17.22 and R17.23.

16. Balance the atoms separately for each half-reaction (oxidation, reduction) and then balance the charge, taking the following steps: (1) Add electrons, as needed, to the

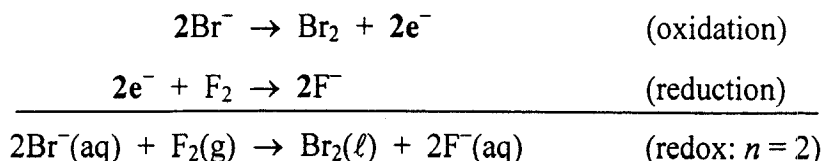
appropriate sides of the reduction and oxidation equations. (2) If necessary, multiply the separate half-reactions by numerical factors to guarantee that the number of electrons lost is equal to the number of electrons gained.

For a demonstration, see Example 3-4 in *PoC* (beginning on page R3.10).

(a) Decompose the overall redox equation

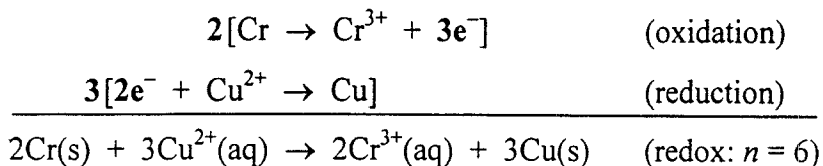


into individual oxidation and reduction half-reactions:



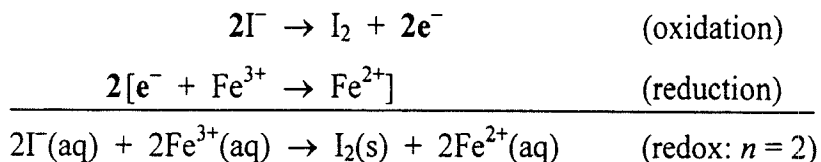
Two moles of electrons are transferred.

(b) Multiply the oxidation half-reaction by 2 and the reduction half-reaction by 3:



Six moles of electrons are transferred.

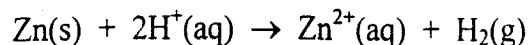
(c) Multiply the reduction half-reaction by 2 and add it to the oxidation half-reaction:



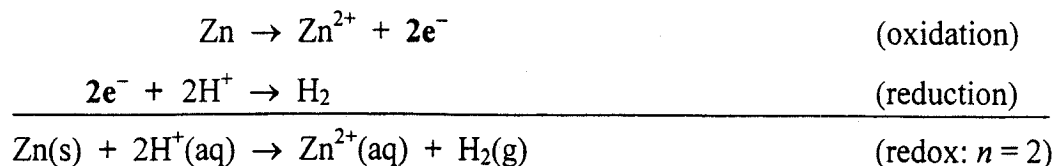
Two moles of electrons are transferred.

17. First, follow the example of Exercise 13 and identify the oxidizing and reducing agents. Second, write the oxidation and reduction reactions as separate equations, taking care to balance the charge in each of these two *half-reactions* (see Example 3-4 in *PoC* and also Exercise 16). Third, if necessary, multiply the half-reactions by numerical factors to ensure that charge is conserved in the coupled redox process. The number of electrons lost must be equal to the number of electrons gained. Fourth, add the two half-reactions and recover the correct overall equation.

(a) Inspecting the full equation,

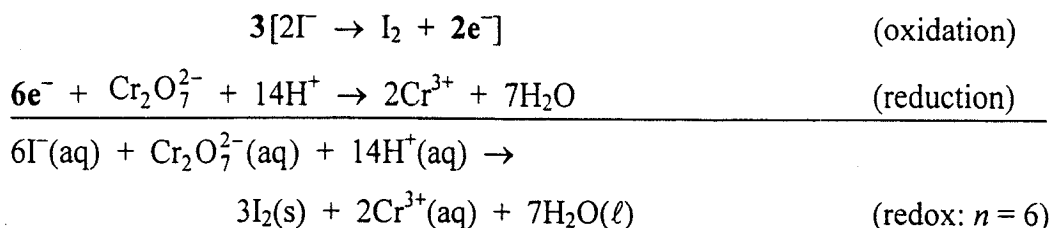


we see right away that metallic zinc is oxidized while H^+ is reduced:

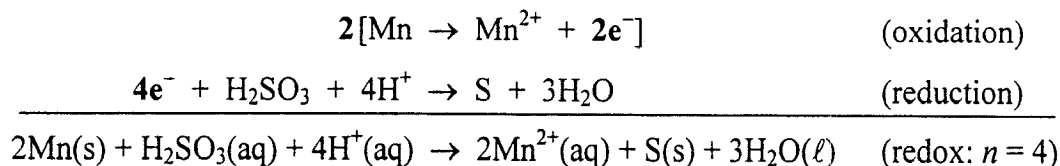


The electrons show up only in the individual oxidation and reduction equations, not the equation for the process overall. Two moles of electrons ($n = 2$) enter on the left; two moles of electrons exit on the right. Nothing is lost and nothing is gained. Charge is conserved.

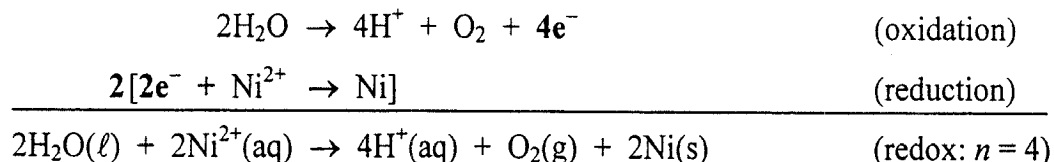
(b) Six moles of electrons are transferred:



(c) Four moles of electrons are transferred:



(d) Four moles of electrons are transferred:

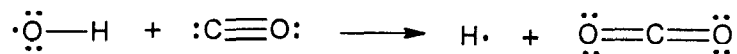


Free radicals (Section 3-5 and Example 3-5) are covered briefly in the next three exercises.

18. To identify a radical, determine from the Lewis structure whether the species contains one or more unpaired valence electrons—as will be true for any system with an odd number of electrons.

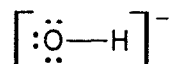
For a review of how to count electrons and draw Lewis structures, see Section 2-4, Examples 2-4 and 2-5, and Exercises 11, 12, and 32 through 40 in Chapter 2.

(a) The radicals are OH (a group with one unpaired electron) and H (a free atom, with just a single electron):



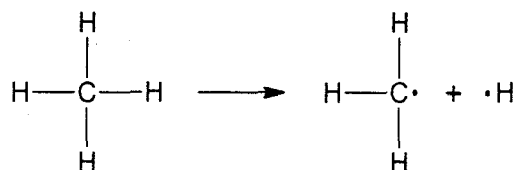
Neither carbon monoxide (CO) nor carbon dioxide (CO₂) is a radical. The electrons in each molecule are grouped in pairs.

Note that the OH radical, an electrically neutral species, is not to be confused with the hydroxide ion, OH⁻. The additional valence electron in OH⁻ (the eighth) creates a third lone pair on the oxygen site:

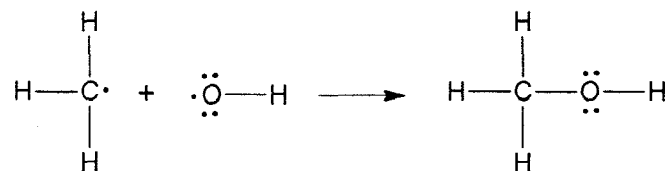


Hydroxide is not a radical.

(b) We know from part (a) that OH is a radical. So, too, is CH₃, which forms when a molecule of CH₄ loses one H and its associated electron:



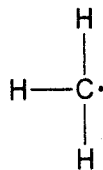
The radicals CH₃ and OH can combine to form a molecule (methanol, CH₃OH) in which all of the electrons are paired:



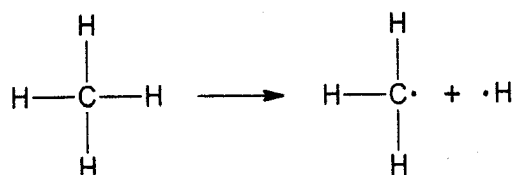
(c) A free atom of bromine, with seven valence electrons, is a radical. Six of the electrons are distributed in three pairs, leaving one electron by itself:



Similarly, in the methyl radical (CH_3) there are three bonding pairs and one unpaired electron around the carbon:

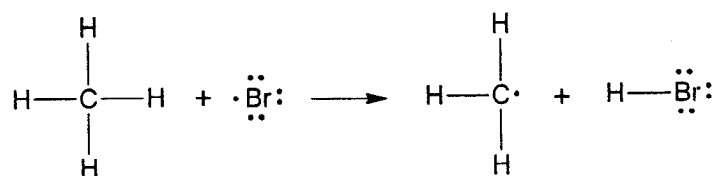


Note, in particular, how removal of a hydrogen atom (nucleus plus electron) from a molecule of methane (CH_4) produces a methyl radical:

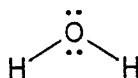


The eight valence electrons in CH_4 are otherwise paired into four single bonds, leaving no electrons unpaired. Methane is not a radical.

Thus a bromine radical extracts a hydrogen radical from CH_4 to yield a new radical (CH_3) and a paired-up molecule (HBr):



(d) We already know (see parts a and c) that OH and Br are radicals, whereas HBr is not. Neither is water,



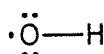
a closed-shell molecule in which two bonding pairs and two lone pairs surround the central oxygen.

19. The radicals identified in the preceding exercise are H , OH , CH_3 , and Br . What follows is a slightly more detailed accounting of the four Lewis structures.

First, hydrogen. A hydrogen atom has just one electron, unpaired by necessity:

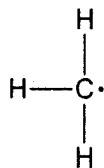


Second, the hydroxyl radical receives one valence electron from hydrogen and six from oxygen, making a total of seven:



With one bonding pair and two lone pairs on the oxygen site, a single (radical) electron remains unpaired.

Next, the methyl radical has seven valence electrons (four from carbon and one from each of three hydrogens). Six of the electrons occupy three bonding pairs, and the seventh remains free:



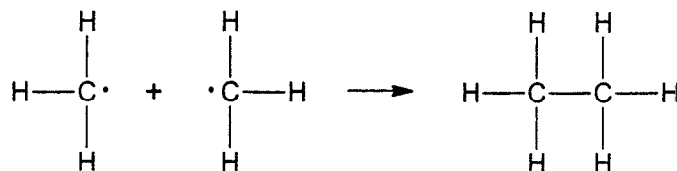
The bromine atom, finally, has seven valence electrons, with one unpaired:



The remaining six electrons are grouped into three lone pairs.

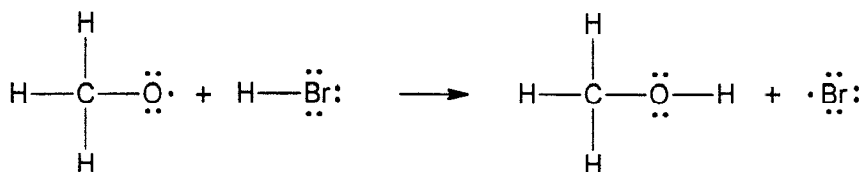
20. More radical reactions.

(a) Two methyl radicals, each with one unpaired electron, combine to produce a molecule with no unpaired electrons—ethane (C_2H_6):



The odd electrons come together to produce a single bond.

(b) Here the methoxy radical (CH_3O) extracts a hydrogen atom from HBr , producing the closed-shell molecule methanol (CH_3OH) and a bromine radical (Br):



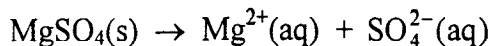
Both CH_3O and Br contain one unpaired electron apiece.

Solutes and solvents, mostly, round out the exercises for this chapter. See Section 3-4 and Examples 3-5 through 3-7 in PoC.

21. Some additional practice in recognizing the presence of ions in solution—similar in spirit to Exercises 16 and 17 of Chapter 2. The polyatomic sulfate, hydroxide, acetate, ammonium, and carbonate ions are highlighted.

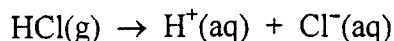
For an extensive list of anions and cations, see Table A-1 in Appendix A of *PoC* (beginning on page A11).

(a) The ionic solid MgSO_4 is a 1:1 compound of magnesium and sulfate ions, each doubly charged:

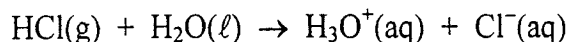


Recall that magnesium is a member of Group II, the alkaline earth metals. In combination, an atom of magnesium typically loses its two valence electrons to become the cation Mg^{2+} .

(b) Hydrogen chloride (hydrochloric acid) dissociates into hydrogen and chloride ions:

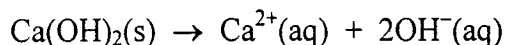


More explicitly, we may write the process as



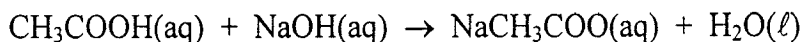
to equate the solvated hydrogen cation, $\text{H}^+(\text{aq})$, with the hydronium ion: $\text{H}_3\text{O}^+(\text{aq})$.

(c) One mole of calcium hydroxide dissociates into one mole of calcium ions and two moles of hydroxide ions:

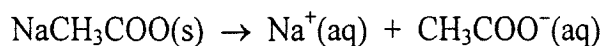


Like magnesium, calcium belongs to Group II. It loses its two valence electrons to produce a doubly positive cation.

(d) Sodium acetate is the neutralization product of acetic acid (CH_3COOH) and sodium hydroxide (NaOH):



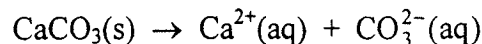
It dissociates, accordingly, into sodium cations and acetate anions:



(e) NH_4OH , an Arrhenius base, releases ammonium and hydroxide ions in aqueous solution:



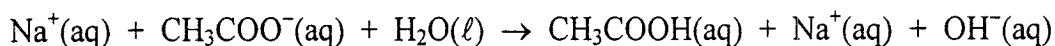
(f) Here we have the Ca^{2+} ion paired with the carbonate ion, CO_3^{2-} , a doubly negative molecular anion:



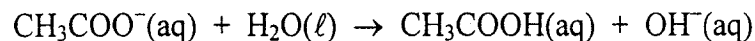
22. Strong electrolytes dissociate effectively 100% into their ionic constituents. Examples include strong acids (such as HCl), strong bases (such as NaOH), and soluble salts (such as NaCH_3COO).

Weak electrolytes, by contrast, dissociate only partially. Examples include weak acids (CH_3COOH), weak bases (NH_3), and insoluble salts (PbSO_4).

(a) NaCH_3COO and NaOH , both strong electrolytes, dissociate completely into ions:

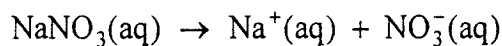
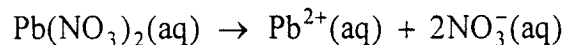
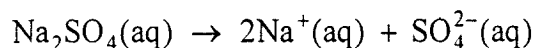


The lone sodium ion on each side is therefore only a *spectator* to the reaction, which we then reduce to its more concise, net ionic form:



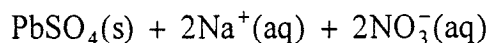
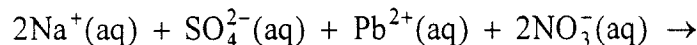
$\text{Na}^+(\text{aq})$, omitted from the net ionic equation, remains unchanged throughout the process.

(b) A look at Table C-17 in Appendix C of *PoC* (page A94) confirms that nitrate salts are soluble in water, as is sodium sulfate:

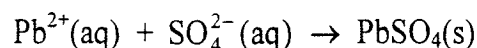


Lead sulfate, indicated in the problem as a solid, is insoluble.

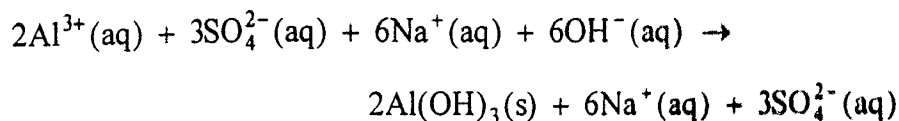
Showing all solvated species explicitly,



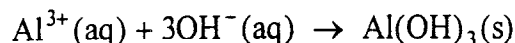
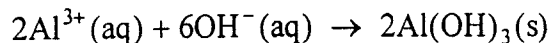
we recognize and eliminate the spectator sodium and nitrate ions:



(c) All participants except $\text{Al}(\text{OH})_3$ are dissociated into ions:

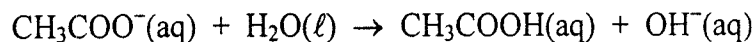


Removing the spectator sodium and sulfate ions, we obtain the net ionic equation reduced to lowest terms:



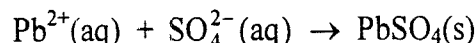
23. We look more closely at the reactions introduced in the previous exercise, simplified now to their net ionic equations.

(a) An acetate anion, acting as a base, takes a proton from a water molecule (which acts reciprocally as a partner acid). The unionized form of acetic acid (CH_3COOH) is regenerated, along with hydroxide ion:



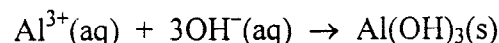
The process is an acid–base reaction in all three senses—specifically a basic *hydrolysis* reaction, to be explored in depth in Chapter 16.

(b) Solvated Pb^{2+} and SO_4^{2-} ions are produced by dissolution of $\text{Pb}(\text{NO}_3)_2$ and Na_2SO_4 , respectively. They then precipitate from solution to yield the insoluble salt PbSO_4 :



It is a dissolution–precipitation reaction—or, generously interpreted, a coming-together reminiscent of Lewis’s acid–base interaction.

(c) Another dissolution and precipitation:

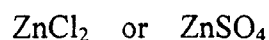


The product is an insoluble solid, aluminum hydroxide.

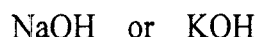
The final group of exercises focuses on a single chemical problem (the precipitation of zinc hydroxide) as a way to build skill in calculations involving molarity. See, in particular, Example 3-7 (pages R3.15–R3.16 of PoC) as well as related material in Chapter 9 (Section 9-2 and Example 9-2).

Another expression of concentration, mole fraction, also appears in Section 9-2 and finds application in Dalton's law (Chapter 10) and Raoult's law (Chapter 11). Molality is introduced in Chapter 11 (page 418) in the context of freezing-point depression and vapor-pressure elevation.

24. We need something that yields $\text{Zn}^{2+}(\text{aq})$ and something else that yields $\text{OH}^{-}(\text{aq})$. Choosing from the list provided, we can mix either

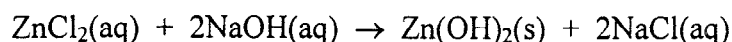


with

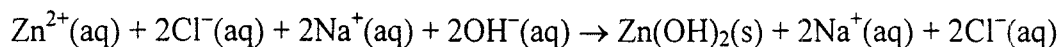


to produce $\text{Zn}(\text{OH})_2$. See the next exercise for the continuation of the story.

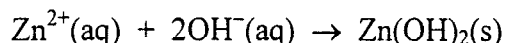
25. Take, for example, the precipitation reaction



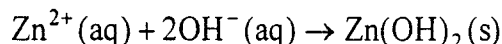
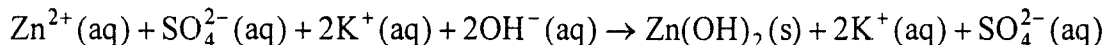
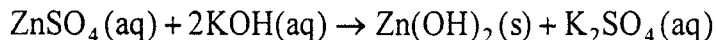
and simplify the resulting ionic equation



to its net form:



Note that the net ionic equation remains the same, independent of our choice of starting materials. As a demonstration, repeat the procedure for a mixture of ZnSO_4 and KOH :



26. Convert grams into moles and milliliters into liters to obtain the proper units of molarity (moles per liter):

$$\frac{5.00 \text{ g ZnCl}_2}{200.0 \text{ mL}} \times \frac{1 \text{ mol ZnCl}_2}{136.30 \text{ g ZnCl}_2} \times \frac{1000 \text{ mL}}{\text{L}} = \frac{0.183 \text{ mol ZnCl}_2}{\text{L}} = 0.183 \text{ M}$$

The result is limited to three significant figures by the value 5.00 g.

27. Broadly applicable, the unit-factor method facilitates conversion from one set of units into another.

(a) Observe, first, that the product of molarity (mol L^{-1}) and volume (L) is expressed in moles:

Molarity \times volume = amount

$$\frac{\text{mol}}{\text{L}} \times \text{L} = \text{mol}$$

With that, we convert the amount contained in 500.0 mL of solution from moles into grams:

$$\begin{array}{c} \text{MOLARITY} \quad \times \quad \text{VOLUME} \\ \frac{0.3750 \text{ mol ZnCl}_2}{\text{L}} \times \left(500.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \right) \times \frac{136.30 \text{ g ZnCl}_2}{\text{mol ZnCl}_2} = 25.56 \text{ g ZnCl}_2 \end{array}$$

(b) Each mole of ZnCl_2 yields one mole of Zn^{2+} ions upon dissolution:

$$\begin{aligned} \left(\frac{0.3750 \text{ mol ZnCl}_2}{\text{L}} \times 0.5000 \text{ L} \right) \times \frac{1 \text{ mol Zn}^{2+}}{\text{mol ZnCl}_2} \times \frac{6.022 \times 10^{23} \text{ Zn}^{2+} \text{ ions}}{\text{mol Zn}^{2+}} \\ = 1.129 \times 10^{23} \text{ Zn}^{2+} \text{ ions} \end{aligned}$$

Recall from Chapter 2 that Avogadro's number,

$$N_0 = \frac{6.022 \times 10^{23} \text{ particles}}{\text{mol}}$$

serves as a universal conversion factor between particles and moles.

(c) A mole of ZnCl_2 releases *two* moles of Cl^- ions when dissolved:

$$\begin{aligned} \left(\frac{0.3750 \text{ mol ZnCl}_2}{\text{L}} \times 0.5000 \text{ L} \right) \times \frac{2 \text{ mol Cl}^-}{\text{mol ZnCl}_2} \times \frac{6.022 \times 10^{23} \text{ Cl}^- \text{ ions}}{\text{mol Cl}^-} \\ = 2.258 \times 10^{23} \text{ Cl}^- \text{ ions} \end{aligned}$$

28. Consider the definition of concentration:

$$\text{Concentration} = \frac{\text{amount of material}}{\text{volume}}$$

If the amount of dissolved material is kept constant, then the concentration will respond inversely to any change in volume. A decrease in volume will *increase* the concentration, whereas an increase in volume will decrease it.

If we double the volume, we halve the concentration. To dilute 100 mL of a 1.00 M solution to a final concentration of 0.500 M, we must add sufficient water to yield a total volume of 200 mL:

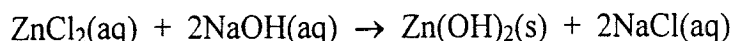
$$\text{New concentration} = \frac{\text{initial amount}}{\text{final volume}} = \frac{1.00 \text{ mol L}^{-1} \times 0.100 \text{ L}}{0.200 \text{ L}} = \frac{0.100 \text{ mol}}{0.200 \text{ L}} = 0.500 \text{ M}$$

When the volume quadruples, the concentration falls by a factor of 4. To dilute our initial 100 mL to a final value of 0.250 M, we must increase the total volume to 400 mL.

Similarly, a tenfold increase in volume brings about a tenfold reduction in concentration. Diluted to a new total volume of 1000 mL, an initially 100-mL sample of *any* 1.00 M solution will arrive at a final concentration of 0.100 M.

Take note: *any* solution. The identity of the solute is irrelevant; it plays no role in the dilution equation. We derive the same final volumes whether the solution contains ZnCl₂ or C₆H₁₂O₆ or anything else.

29. Starting with a balanced equation,



we calculate the initial amount of each reactant involved in the precipitation:

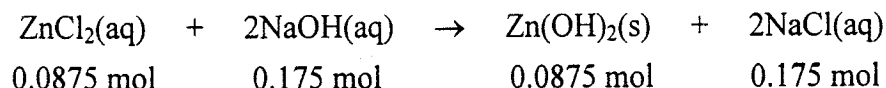
$$\frac{0.600 \text{ mol ZnCl}_2}{\text{L}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times 300.0 \text{ mL} = 0.180 \text{ mol ZnCl}_2$$

$$\frac{0.250 \text{ mol NaOH}}{\text{L}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times 700.0 \text{ mL} = 0.175 \text{ mol NaOH}$$

Doing so, we see that zinc chloride is present in excess. NaOH, the limiting reactant, combines in 1:2 stoichiometry with ZnCl₂ and disappears completely over the course of reaction. Only 0.0875 mol ZnCl₂ (less than the quantity available) is needed to consume the full amount of NaOH (0.175 mol):

$$0.175 \text{ mol NaOH} \times \frac{1 \text{ mol ZnCl}_2}{2 \text{ mol NaOH}} = 0.0875 \text{ mol ZnCl}_2$$

The reaction then goes as



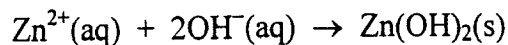
(a) The mass of solid precipitate is 8.70 g:

$$0.0875 \text{ mol Zn(OH)}_2 \times \frac{99.40 \text{ g Zn(OH)}_2}{\text{mol Zn(OH)}_2} = 8.70 \text{ g Zn(OH)}_2$$

(b) Na^+ and Cl^- spectator ions stay dissolved throughout, together with the excess Zn^{2+} ions already noted:

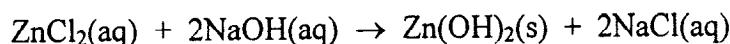
$$\begin{array}{r} 0.180 \text{ mol Zn}^{2+} \text{ initially present} \\ - 0.0875 \text{ mol Zn}^{2+} \text{ precipitated} \\ \hline 0.093 \text{ mol Zn}^{2+} \text{ excess} \end{array}$$

The net ionic equation is



(c) Effectively, the limiting reactant is OH^- (the active ion in NaOH).

30. From the stoichiometry of the reaction,



we determine the required amount and volume of NaOH:

$$\begin{aligned} 5.00 \text{ g Zn(OH)}_2 \times \frac{1 \text{ mol Zn(OH)}_2}{99.40 \text{ g Zn(OH)}_2} \times \frac{2 \text{ mol NaOH}}{\text{mol Zn(OH)}_2} \\ = 0.1006 \text{ mol NaOH} \times \frac{1 \text{ L NaOH}}{0.250 \text{ mol NaOH}} \\ = 0.402 \text{ L NaOH} \quad (3 \text{ sig fig}) \end{aligned}$$

To realize the stated yield, however, there must be at least 0.0503 mol ZnCl_2 on hand:

$$0.1006 \text{ mol NaOH} \times \frac{1 \text{ mol ZnCl}_2}{2 \text{ mol NaOH}} = 0.0503 \text{ mol ZnCl}_2$$

And indeed there is:

$$\frac{0.600 \text{ mol ZnCl}_2}{\text{L}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times 300.0 \text{ mL} = 0.180 \text{ mol ZnCl}_2$$

(a) The required volume of 0.250 M NaOH is 402 mL, calculated above.

(b) A total of 0.0503 mol ZnCl_2 reacts with 0.1006 mol NaOH , producing 0.0503 mol Zn(OH)_2 . The amount of Zn^{2+} remaining in solution is 0.130 mol:

$$\begin{array}{r} 0.180 \text{ mol Zn}^{2+} \text{ initially present} \\ - 0.0503 \text{ mol Zn}^{2+} \text{ precipitated} \\ \hline 0.130 \text{ mol Zn}^{2+} \text{ excess} \end{array}$$