Chapter 11. Chemical Equations

11.1. Chemical Equation Concepts

Under the right circumstances substances change into new substances. Such changes are called **chemical transformations**, or **reactions**. The original substances are called **reac-tants**, the substances resulting from the change are called **products**. Chemical reactions reveal the basic properties of substances that form the heart of chemistry.

Until about the time of Dalton, investigators really didn't understand the reason some substances seem to disappear and others appear in their place; the chemical disappearing act was *magical*.¹ Early chemists did systematize chemical reactions into categories involving similar substances or similar behaviors. Reactions are still commonly classified qualitatively according to the type and/or number of participants. *Precipitations* and *distillations* describe the production of insoluble and gaseous products, respectively. Reactions involving the element hydrogen as a reactant are called *hydrogenations*, those consuming oxygen *oxidations*, chlorine *chlorinations*, etc. *Single* and *double displacement (metathesis) reactions* exchange one or two components between reactants. Neutralizations of *Acid-base* and *oxidation/reduction* reactions are systematized in terms of the transfer of common species (protons and electrons, respectively). Chapter 19 elaborates further on these latter two classes of reactions.

Only when scientists like Lavoisier measured the masses of otherwise invisible participating gases in chemical reactions could an universal law of conservation of matter be observed, and the stage set for a quantitative atomic reaction theory.² Substances differ because they have different element compositions. Element analyses of reactants and

¹ None other than the founder of modern physics himself, Sir Isaac Newton is fondly remembered for his alchemical excursions into the secret arts which demolished a chimney at Cambridge University.

² Through "pneumatic" (gas) experiments, Lavoisier discovered the principle component of the atmosphere, nitrogen (which he named *azote*, without life), elucidated the role of *oxygen* (acid former) in combustion, respiration and oxidation, and dethroned the last remaining Greek element, water, by passing it through a heated gun barrel to decompose it into its elements.

products of chemical reactions showed that elements are neither destroyed nor created when substances are. These observations, coupled with the conservation of mass observed for reactions, led John Dalton to surmise that *atoms are not destroyed nor created during chemical reactions, but rearranged from reactant to product molecules*. That is, according to Dalton, *chemical reactions consist of rearrangements of the atoms in molecules*. The insight of the atomic nature of chemical reactions by John in one stroke 1) rationalized the law of conservation of matter discovered by Lavoisier, 2) explained the previously discovered laws of "definite", or fixed composition of matter, 3) led to the discovery of multiple proportions (integer ratios) of certain substances which combine in more than one ratio (such as CO and CO_2), and 4) provided a quantitative heuristic for analyzing chemical transformations in terms of relative atomic masses.

The atomic concept led to chemical models and formula notation to represent molecules, and paved the way to analyze and predict amounts involved in reactions quantitatively. In the next two sections we will explore the consequences of the atomic interpretation of the law of conservation of matter and see how it determines the numbers and amounts of participating molecules in reactions.

11.2. Balanced Chemical Equations

A **balanced chemical equation** is a mathematical statement of equality with reactants on the *left* and products on the *right* (by convention), represented by chemical formulas³ for the variables, and numerical *prefixes*, or **stoichiometric coefficients** for the parameters. The values of the coefficients are strictly determined by the **law of conservation of atoms** (i.e. that atoms are neither created nor destroyed in chemical transformations). An example is $H_2 + Cl_2 = 2HCl$, which represents one molecule of dihydrogen reacting with one molecule of dichlorine to produce two molecules of hydrogen chloride product. The balancing coefficients (numbers of molecules) are 1 and 1 on the left (stoichiometric coefficients of unity are dropped by convention), and 2 on the right. *The number of atoms of each element is the same on both sides of a "balanced equation"* (2 each in this example), which conserves mass. Note in this example there are also equal numbers of *molecules* on both sides of the equation (2). But this need not always be the case, and in general, *the number of molecules on both sides of a balanced chemical equation are NOT necessarily equal*. Consider S + O₂ = SO₂; here is an "equation" for which one plus one equals one, not two! This point is worth remembering when thinking of chemical reactions as "equations".

³ Chemical formulas consist of Roman letters representing the atoms of the various elements comprising the molecule, subscripted with integers signifying the numbers of atoms of each element in each molecule. Ele-

Although the implications may not fully be appreciated at first, it is important to keep in mind that all observable chemical processes may be described by balanced chemical reactions. Ironically, because of their fundamental nature, balanced chemical reactions are often left out of the statements of problems, and simply assumed, and unfortunately often overlooked by students as aids in trying to find solutions. A useful tip to remember is that *when chemical reactions are being considered, the effort it takes to identify reactants and products and balance the equation may be returned in organizing thinking and discovering solution processes.*

Although the number of molecules on each side of a chemical equation do not have to be equal, it is no accident that the term "equation" and the equality symbol (=) are used to represent the chemical conversion symbolically. The equality symbol connotes to the chemist two equivalencies. Explicitly it represent the equal numbers of atoms on reactant and product sides (balanced chemical reaction). Implicitly it represents equalities between various *pairs* of molecules taking part in the reaction from which useful conversion factors can be derived. We will treat these implications in turn.

We first turn our attention to the balancing process. There are several algorithms chemists use to balance chemical reactions. The first usually encountered is the *inspection* method for balancing chemical reactions, where atoms are counted and balancing coefficients are guessed. While it may work adequately well for reactions involving simple chemical formulas, it is not very systematic. In fact, it is a trial and error process, involving guessing and iterating until the numbers of atoms of each element on both sides of the equation are equal. As such it is not even a very powerful heuristic.

There are other, more sophisticated methods for more complicated specialized chemical reactions, but they are also based on "inspection" heuristics for the most part. We will instead present a systematic algorithm which works for all possible chemical equations, yet is simple enough to teach even to a relatively dumb programmable calculator. Because it is based on linear algebra, it will be referred to as *The Algebraic Algorithm for Balancing Chemical Equations*. Recalling the equality between reactants and products resulting from rearranging atoms but neither creating nor destroying them, one is led to the idea of focusing

ment symbols constitute the chemical alphabet; words are the formulas and sentences are statements in the form of balanced chemical equations; reaction mechanisms (discussed in the chapter on Chemical Kinetics) may be thought of as chemical paragraphs.

on equating atoms, not molecules on both sides of the reaction.

Of course one must consider that the atoms are bound together in molecules in certain fi xed proportions, as denoted by subscripts in chemical formulas. Molecular formulas cannot be changed without changing the substances they represent. What are free to change are the *numbers* of molecules participating in a reaction, the prefixes, or *balancing (stoichiometric) coefficients*. Treating the balancing coefficients of the participating molecules of the chemical equation as unknowns, mass is conserved by equating the number of atoms of each element on both sides of the reaction. If charged molecules are involved (ions), charge (electrons) must be conserved as well by equating the total charge on both sides of the reaction. This yields *a system of linear equations* which may be solved for the coefficients of the reaction integers by multiplying the equation through by the a common divisor. This does not upset the balance of atoms and brings the equation into standard form. *By convention balanced chemical equations have the lowest possible set of integer coefficients consistent with conservation of matter (atoms)*.

Since balanced chemical equations represent only relative numbers of molecules (or ratios), and not absolute numbers, only n-1 equations will be generated for n molecules (including charge as well as atoms), which is mathematically consistent with ratio solutions to linear systems. That is, all the coeffi cients can be determined but one, which remains arbitrary. If the n reacting molecules have less than n-1 participating elements the system is *underdetermined*, which indicates two or more *simultaneous* chemical reactions are occurring.

There are a number of methods for solving systems of linear equations, including the Linear Equation System Solving Algorithm of Section 3.8, but because the system has few terms (is sparse), we recommend an inspection method in this case (manipulating the equations using the algebraic equivalency operations) to solve the system. For mathematical convenience, we will add an arbitrary n-th equation. We can arbitrarily set one of the unknowns to some convenient value, say, unity without affecting the fi nal results (ratios). It doesn't matter much which unknown is chosen (except that a particular choice may be easier for pencil-and-paper solutions).

The Algebraic Algorithm for Balancing Chemical Equations

Purpose: To determine the minimal set of integer molecular formula coefficients which conserves atoms in a chemical equation.

Procedure:

- 1. Write the reaction using n different symbols (letters) to represent the unknown balancing coefficients.
- 2. Identify the n-1 elements involved in the reaction. If charged molecules (ions) are involved, count charge (imbalance between numbers of protons and electrons) as an additional "element".
- 3. For each *element*, construct a linear algebraic equation that equates the number of atoms of the element on both sides of the reaction:
 - a. For each molecule in the chemical equation in which the element appears, *multiply* the *subscript on the element* by the unknown *coeffi cient of the molecule*.
 - b. For each element, *sum* (add up) the products of subscripts and coefficients for the molecules on the left and right sides of the equation and *equate* the sums.
- 4. Choose one of the unknowns and set it equal to some convenient value.
- 5. Solve the resulting n linear equations for the n unknowns.
- 6. If common factors exist among the coefficients, divide each coefficient by them to reduce the coefficients to the minimal set of integers. If fractional coefficients result, clear the balanced equation of fractions by multiplying each coefficient by the least common multiple of the denominators.
- 7. Check the final answer by counting atoms of each element (and charge) on each side.

A simple example will illustrate the method.

Example 11.1 Consider the reaction of the formation of water from its elements.

1. The unbalanced reaction, written in terms of the algorithm is:

$$aH_2 + bO_2 = cH_2O$$

- 2. There are n = 3 molecules (H₂, O₂, and H₂O) and n-1 = 2 elements (H and O), indicating a single chemical reaction (and not a sum of independent equations).
- An equation for the each element is produced by equating the number of atoms of the element on both sides of the equation. In this example, each element occurs in only one molecule on each side of the chemical equation, so no summations are needed.

H:
$$2a = 2c$$

O: $2b = c$

4. Arbitrarily set one of the unknowns to unity:

5. Solve the system of n linear algebraic equations. At this point, there are several mathematical procedures which may be applied to solve simultaneous linear equations. We choose inspection, substitution and elimination operations.

Given a = 1, the H equation yields c = a = 1. The O equation then yields $b = \frac{1}{2} c = \frac{1}{2}$. The balanced chemical equation is:

$$1 \text{ H}_2 + 1/2 \text{ O}_2 = 1 \text{ H}_2\text{O}$$

6. Since the balanced equation involves fractions, they will be eliminated to conform to the convention. To clear fractions, multiply the chemical equation through by 2:

$$2 H_2 + O_2 = 2 H_2O$$

(Coeffi cients of unity are dropped by convention.)

We may observe that if b instead of a had been set to unity in step 4, integers would have resulted in the solution. This is easy to see ahead of time here, but it may not be so obvious which variable should be set to unity in more complicated reactions. 7. The final balanced equation has 4 atoms of H on each side, and 2 of oxygen on each side, so matter (atoms) is conserved.

Reactions which have elements distributed over reactant or product molecules require summing product terms for the elements. Here is an example, which involves this and several other complicating features as well to illustrate how they are treated.

Example 11.2 Balance the reaction below, which represents a *net ionic* equation from which the non-participating ("spectator") ions have been canceled.

1. Unbalanced reaction with unknowns:

a
$$CH_3CH_2OH + b Cr_2O_7^{2-} + c H_2SO_4 = d CH_3CO_2H + e Cr_2(SO_4)_3 + f SO_4^{2-} + g H_2O_4$$

Comment: molecules involving carbon are *organic* substances, whose formulas are often written in an expanded fashion to indicate their bonding structure.

- 2. Seven unknowns and six "elements" (C, H, O, Cr, S and charge).
- 3. Conservation of atoms (and charge):

C:	(1+1)a = (1+1)d
H:	(3+2+1)a+2c = (3+1)d+2g
O:	a + 7b + 4c = 2d + (3)(4)e + 4f + g
Cr:	2b = 2e
S:	c = 3e + f
charge:	$(-2)\mathbf{b} = (-2)\mathbf{f}$

Comment: All occurrences of elements which are distributed in a molecule (like C and H in CH_3CH_2OH) or occur in groups as part of a molecule (like the O in $Cr_2(SO_4)_3$) must be counted to conserve atoms in the reaction.

4. Setting one of the variables to unity:

a = 1

Comment: Which variable to choose is a toss-up. Some advantage in solving the system by elimination might be gained by choosing the unknown which occurs the most places (a, b, c, d, e, and f each occur in three places), or in simplifying one of the more complicated equations (like the one for O).

- 5. Rewriting the equations, given a = 1, and reducing:
 - C: d = 1H: 3 + c = 2d + gO: 1 + 7b + 4c = 2d + 12e + 4f + gCr: b = eS: c = 3e + fcharge: b = f

The sparseness of the equations suggests inspection instead of The Linear Equation System Solver Algorithm. Substituting d = 1, and using the Cr and charge equations to replace e and f by b:

H:
$$1 + c = g$$

O: $4c = 1 + 9b + g$
S: $c = 4b$

Using the first and last equations to eliminate c and g in terms of b:

O: 16b = 1 + 9b + (1 + 4b)

Therefore b = e = f = 2/3; c = 4b = 8/3, and g = c + 1 = 11/3. The balanced equation is: CH₃CH₂OH + 2/3 Cr₂O₇²⁻ + 8/3 H₂SO₄ = CH₃CO₂H + 2/3 Cr₂(SO₄)₃ + 2/3 SO₄²⁻ + 11/3 H₂O

Comment: Here is where a programmable calculator could come in handy.

6. Clearing fractions:

 $3 \text{ CH}_{3}\text{CH}_{2}\text{OH} + 2 \text{ Cr}_{2}\text{O}_{7}^{2-} + 8 \text{ H}_{2}\text{SO}_{4} = 3 \text{ CH}_{3}\text{CO}_{2}\text{H} + 2 \text{ Cr}_{2}(\text{SO}_{4})_{3} + 2 \text{ SO}_{4}^{2-} + 11 \text{ H}_{2}\text{O}_{4} = 3 \text{ CH}_{3}\text{CO}_{2}\text{H} + 2 \text{ Cr}_{2}(\text{SO}_{4})_{3} + 2 \text{ SO}_{4}^{2-} + 11 \text{ H}_{2}\text{O}_{4} = 3 \text{ CH}_{3}\text{CO}_{2}\text{H} + 2 \text{ Cr}_{2}(\text{SO}_{4})_{3} + 2 \text{ SO}_{4}^{2-} + 11 \text{ H}_{2}\text{O}_{4} = 3 \text{ CH}_{3}\text{CO}_{2}\text{H} + 2 \text{ Cr}_{2}(\text{SO}_{4})_{3} + 2 \text{ SO}_{4}^{2-} + 11 \text{ H}_{2}\text{O}_{4} = 3 \text{ CH}_{3}\text{CO}_{2}\text{H} + 2 \text{ Cr}_{2}(\text{SO}_{4})_{3} + 2 \text{ SO}_{4}^{2-} + 11 \text{ H}_{2}\text{O}_{4} = 3 \text{ CH}_{3}\text{CO}_{2}\text{H} + 2 \text{ Cr}_{2}(\text{SO}_{4})_{3} + 2 \text{ SO}_{4}^{2-} + 11 \text{ H}_{2}\text{O}_{4} = 3 \text{ CH}_{3}\text{CO}_{2}\text{H} + 2 \text{ Cr}_{2}(\text{SO}_{4})_{3} + 2 \text{ SO}_{4}^{2-} + 11 \text{ H}_{2}\text{O}_{4} = 3 \text{ CH}_{3}\text{CO}_{2}\text{H} + 2 \text{ Cr}_{2}(\text{SO}_{4})_{3} + 2 \text{ SO}_{4}^{2-} + 11 \text{ H}_{2}\text{O}_{4} = 3 \text{ CH}_{3}\text{CO}_{2}\text{H} + 2 \text{ Cr}_{2}(\text{SO}_{4})_{3} + 2 \text{ SO}_{4}^{2-} + 11 \text{ H}_{2}\text{O}_{4} = 3 \text{ CH}_{3}\text{CO}_{2}\text{H} + 2 \text{ Cr}_{2}(\text{SO}_{4})_{3} + 2 \text{ SO}_{4}^{2-} + 11 \text{ H}_{2}\text{O}_{4} = 3 \text{ CH}_{3}\text{CO}_{2}\text{H} + 2 \text{ Cr}_{2}(\text{SO}_{4})_{3} + 2 \text{ SO}_{4}^{2-} + 11 \text{ H}_{2}\text{O}_{4} = 3 \text{ CH}_{3}\text{CO}_{2}\text{H} + 2 \text{ Cr}_{2}(\text{SO}_{4})_{3} + 2 \text{ SO}_{4}^{2-} + 11 \text{ H}_{2}\text{O}_{4} = 3 \text{ CH}_{3}\text{CO}_{2}\text{H} + 2 \text{ C}_{3}\text{CO}_{4} = 3 \text{ CH}_{3}\text{CO}_{4} = 3 \text{ CH}_{3}\text{CH}_{4} = 3 \text{ CH}_{3}\text{CO}_{4} = 3 \text{ CH}_{3} = 3$

7. Checking the Atom balance:

C:	$3 \times 2 = 3 \times 2 = 6$
H:	$3 \times (3 + 2 + 1) + 8 \times 2 = 3 \times (3 + 1) + 11 \times 2 = 34$
Cr:	$2 \times 2 = 2 \times 2 = 4$
O:	$3 \times 1 + 2 \times 7 + 8 \times 4 = 3 \times 2 + 2 \times 4 \times 3 + 2 \times 4 + 11 \times 1 = 49$
charge:	$3 \times 0 + 2 \times (-2) + 8 \times 0 = 3 \times 0 + 2 \times 0 + 2 \times (-2) + 11 \times 0 = -4$

This last example illustrates the trade-off between methods. Inspection can get snarly, but so can solving simultaneous equations. It is also only fair to point out that simple mistakes in solving simultaneous equations are very hard to find. It is always advisable to make a check of the final result. If atoms are not balanced, it may be better to start over fresh instead of trying to locate an error. Of course computers are very suited to solving such systems; see Section 3.11 for an example of solving systems of linear equations.

11.3. Chemical Stoichiometry

The word **stoichiometry** derives from the Greek *stoicheion* + *metron*, meaning *element measurements*. It is applied to chemistry to mean *predicting* the amounts of matter involved in chemical reactions. The underlying notion on which stoichiometric calculations are based is the law of conservation of atoms during their rearrangement to form product molecules from reactants in chemical reactions, the insight first stated by John Dalton, the author of chemical stoichiometry.

We will present a tool which helps analyze a variety of potential stoichiometric problems and aid in their solution, called the **Stoichiometry Mol Map**.

Given a balanced chemical equation, several questions can be asked regarding the amounts of matter involved. In fact, since amounts of matter may be measured in different units, such as grams, amu, mols or molecules, there are several possible questions for each pair of molecules in the equation. With all this variety, a systematic approach would have advantages. In the macroscopic world of the laboratory we measure amounts of matter in terms of convenient units, like grams. In the microscopic world of molecules, amounts of matter are measured in terms of number, number of atoms in a molecule, number of molecules in a reaction, etc. We have seen in the Molecular Mol Map of Section 7.6 that the connection between mass and number is molar or molecular mass. The Molecular Mol Map, then, guides us through the process of making the connection between the way we measure a given amount of matter and the way nature measures amount of matter. However, the Molecular Mol Map is restricted to only one substance, and chemical reactions involve more than one substance. The connection between substances, as we have seen, is the balanced chemical reaction. A complete discussion of the stoichiometry of chemical reactions requires possible consideration of both amount conversions and substance conversions. This suggests linking mol maps for different substances together through the substance connection, the balanced chemical reaction. Usually only two substances in the reaction are considered at a time. In this way we are led to consider adding another dimension to the Molecular Mol Map which shows substance conversion along a new axis. The new conversion factors, based on the balanced chemical equation, "convert" one substance into another.⁴ The **Stoichiometry Mol Map** contains all the possible starting points and destinations for the various ways of expressing amounts of two substances, and shows the possible travel routes connecting any pair of starting and ending points.



Fig. 11.1 The Stoichiometry Mol Map

⁴ Conversion connotes chemical conversion of reactants into products, but "conversion" factor mol ratios are constructed for *pairs* of participating molecules in the reaction, including pairs of reactants or pairs of products.

The accompanying algorithm is similar to that of the Molecular Mol Map.

The Stoichiometry Mol Map Algorithm

Purpose: To determine amounts of substances involved in chemical reactions. Procedure:

- 1. If not given, write the balanced chemical reaction.
- 2. Identify from the statement of the problem the (given) starting and (requested) ending points on the Stoichiometry Mol Map.
- 3. Determine a path on the map which leads from the starting point to the ending point.
- 4. Identify the conversion factors connecting the points along the path.
- 5. Apply the conversion factors on the edges of the Stoichiometry Mol Map path to the given (starting point) quantity to obtain the requested (ending point) quantity.

A few examples will illustrate the use of the Stoichiometry Mol Map. The most common stoichiometric calculation predicts the number of grams of a product from the number of grams of a reactant.

Example 11.3 Calculate the number grams of water which are produced from one gram of dihydrogen reacting with excess dioxygen.⁵

1. The balanced chemical equation is:

$$2 H_2 + O_2 = 2 H_2O$$

2. We need to get to $g_{H_2O}(g_B)$ from $g_{H_2}(g_A)$.

⁵ "Excess" means the dioxygen doesn't limit the amount of water produced.

- 3. On the Stoichiometry Mol Map, it is not possible to go directly from g_A to g_B , unless specific conversion factors connecting grams to grams are given (highly unlikely, since they are specific to the particular participating molecules). An indirect path which connects g_{H_2} with g_{H_2O} passes through mol_{H_2} and mol_{H_2O} .⁶
- 4. The conversion factors needed are the molar masses of dihydrogen (2) and water (18), and the "conversion" between mols of dihydrogen and mols of dioxygen. The latter is derived from the balanced chemical equation; in this case, it is $(2 \text{ mol } \text{H}_2/2 \text{ mol } \text{H}_2\text{O})$.
- 5. Starting with 1 g H_2 ,

$$1 \text{ g } \text{H}_2 \times (\frac{1 \text{ mol } \text{H}_2}{2 \text{ g } \text{H}_2}) \times (\frac{2 \text{ mol } \text{H}_2 \text{O}}{2 \text{ mol } \text{H}_2}) \times (\frac{18 \text{ g } \text{H}_2 \text{O}}{1 \text{ mol } \text{H}_2 \text{O}}) = 9 \text{ g } \text{H}_2 \text{O}$$

Example 11.4 Conversely, we could calculate the number of grams of water which are produced from one gram of dioxygen reacting with excess dihydrogen. Because this example is so similar to the last one, we will let the reader fill in the steps of the algorithm, and just give the final result. Starting with 1 g O_2 ,

$$1 \text{ g } O_2 \times (\frac{1 \text{ mol } O_2}{32 \text{ g } O_2}) \times (\frac{2 \text{ mol } H_2 O}{1 \text{ mol } O_2}) \times (\frac{18 \text{ g } H_2 O}{1 \text{ mol } H_2 O}) = 1.125 \text{ g } H_2 O$$

Example 11.5 Now let us calculate the number of grams of water which are produced from *one gram* of dihydrogen reacting with *one gam* of dioxygen.

This question is similar to those of the previous two examples, and should be related to them somehow. In fact, it is a synthesis of the last two examples. Consider the results of the calculations; when there is excess dioxygen, 9 g of water are produced; when there is excess dihydrogen, only 1.125 g of water are produced. It should be clear that reacting one gram of dihydrogen with one gram of dioxygen can not produce any more than 1.125 g of product. In situations like these where arbitrary amounts of reactants are combined, one of them usually limits the amount of product, called the **limiting reagent** (dioxygen in this example). Limiting reagent problems always require some form of two separate stoichiometry calculations. Perhaps you can think of another way

⁶ Several alternate routes are possible. Can you identify them?

to solve this problem, and convince yourself it is equivalent to the way given here, in that the same number of calculations are required.

The starting and ending points of the Stoichiometry Mol Map do not have to be of the same type, as the following example illustrates.

Example 11.6 Calculate the number of *molecules* of water that are produced from one gram of dihydrogen reacting with excess dioxygen.

1. The balanced chemical equation is:

$$2 H_2 + O_2 = 2 H_2O$$

- 2. We need to get to molecule_{H₂O} (molecule_B) from g_{H_2} (g_A).
- 3. Several alternate routes are possible, none of which is direct. The choice is a matter of taste. We will choose the indirect path which connects g_{H_2} with molecule_{H₂O} passing through mol_A and molecule_A to molecule_B (molecule_{H₂O}).
- 4. The conversion factors needed, in order along the path, are the molar mass of dihydrogen (2), Avogadro's number, and the "conversion" between molecules of dihydrogen and molecules of dioxygen. The latter is derived from the balanced chemical equation; it is (2 molecules H_2)/(2 molecules H_2 O).
- 5. Starting with 1 g H_2 ,

$$1 \text{ g } \text{H}_2 \times (\frac{1 \text{ mol } \text{H}_2}{2 \text{ g } \text{H}_2}) \times (\frac{6.02 \text{ x } 10^{23} \text{ molecules } \text{H}_2}{1 \text{ mol } \text{H}_2}) \times (\frac{2 \text{ molecules } \text{H}_2\text{O}}{2 \text{ molecules } \text{H}_2}) = 3.0 \text{ x } 10^{23} \text{ molecules } \text{H}_2\text{O}$$

11.4. Volume Stoichiometry

Mass is not the only measure of amount (mols) of matter. The volume of pure (unmixed) matter is proportional to the mass through the density. The amount of a gas compound participating in a chemical reaction can be expressed several ways, including mass (g), number (mol), concentration at given pressure and temperature (M), density at given temperature and pressure (g/L), volume at given pressure and temperature (V), and pressure at given volume and temperature (p). Either the Equation of State Ideal Gas Law or the Change of State Gas Law can be applied to the gaseous components of chemical reactions (but not to the liquid or solid components) (Chapter 15). A common application of gas laws to chemical

reactions uses the molar gas volume (22.413837 L/mol) as a conversion factor to convert between mols of gas reactant or product and volume at STP (1 atm, 273.15 K). Stoichiometric calculations of chemical reactions can be extended to include volume calculations involving gases. The Volume Stoichiometry Algorithm of Fig. 11.2 shows this extension. Note that the map includes *Gay-Lussac's Law of Simple Reacting Proportions* for volume ratios of reacting gases under the same temperature and pressure (dotted line).

The Stoichiometry Mol Map may be extended to solutions in a way similar to gases, since concentration is a conversion factor (Chapter 17). In the Solution Stoichiometry Mol Map of Fig. 11.3 we add mass percentage and molarity concentration conversion factors to the basic Stoichiometry Mol Map.



Fig. 11.2 The Volume Stoichiometry Mol Map



Fig. 11.3 The Solution Stoichiometry Mol Map

The algorithm which implements the Gas and Solution Stoichiometry Mol Maps simply adds the appropriate conversions to get to the Stoichiometry Mol Map Algorithm.

The Extended Stoichiometry Algorithm

Purpose: To determine the amounts of substances in chemical reactions involving gases, solutions and volumes of pure substances.

Procedure:

- 1. Write the balanced chemical reaction indicating the given substance (A) and the requested substance (B).
- 2. If the amount of the given substance (A) is measured by
 - a) volume of pure substance, convert the volume to mass using the density of A.
 - b) volume of gas, convert the volume to mols using the ideal gas law.
 - c) volume of solution, convert the volume to mols using the concentration of the solution.
- 3. Use the Stoichiometry Mol Map to convert between substances A and B.
- 4. If the amount of substance (B) is requested in
 - a) volume of pure substance, convert the mols of B to mass of B using the density of B.
 - b) volume of gas, convert the mols of B to volume of B using the ideal gas law.
 - c) volume of solution, convert the mols of B to solution volume using the concentration of the solution.

To illustrate the generality of stoichiometry, we show examples that extend stoichiometry to gases and solutions.

Example 11.7

How many liters of oxygen gas at STP are needed to react with 1 g dihydrogen gas to produce water?

1. Balanced chemical equation. A is H_2 , B is O_2 .

$$2 H_2 + O_2 = 2 H_2O$$

- 2. Here the amount of A (dihydrogen gas) is measured in mass, so we proceed directly to the conversions of the Stoichiometry Mol Map.
- 3. From the Stoichiometry Mol Map, grams of dihydrogen may be converted to mols of dioxygen:

1 g H₂ ×
$$(\frac{1 \mod H_2}{2 g H_2})$$
 × $(\frac{1 \mod O_2}{2 \mod H_2})$ = 1/4 mol O₂

4. The result is requested in volume of gas. Using molar volume of a gas at STP as a conversion factor (Gas Stoichiometry Mol Map):

$$1/4 \text{ mol } O_2 \times (\frac{22.414 \text{ L}}{1 \text{ mol}}) = 5.60 \text{ L} O_2$$

Note that in this problem, the last conversion could have been combined with those in step 3.

Example 11.8

How many liters of dioxygen gas at STP are needed to react with 10 mL of a 2 M solution of dihydrogen to produce water?

1. Balanced chemical equation. A is H_2 , B is O_2 .

$$2 H_2 + O_2 = 2 H_2O$$

2. Here the amount of A (dihydrogen) is measured in molarity, so a conversion between solution volume and mols is needed (Solution Stoichiometry Mol Map).

10 mL solution × $(\frac{1 \text{ L solution}}{1000 \text{ mL solution}})$ × $(\frac{2 \text{ mol } H_2}{1 \text{ L solution}})$ = 0.020 mol H₂

3. From the Stoichiometry Mol Map, mols of dihydrogen may be converted to mols of dioxygen:

0.020 mol H₂ ×
$$(\frac{1 \text{ mol } O_2}{2 \text{ mol } H_2}) = 0.010 \text{ mol } O_2$$

4. Using molar volume of a gas at STP as a conversion factor (Volume Stoichiometry Mol Map):

0.010 mol O₂ ×
$$(\frac{22.414 \text{ L}}{1 \text{ mol}}) = 0.22 \text{ L O}_2$$

With practice, the separate conversions would be combined into one step:

$$10 \text{ mL soln} \times (\frac{1 \text{ L soln}}{1000 \text{ mL soln}}) \times (\frac{2 \text{ mol } \text{H}_2}{1 \text{ L soln}}) \times (\frac{1 \text{ mol } \text{O}_2}{2 \text{ mol } \text{H}_2}) \times (\frac{22.414 \text{ L}}{1 \text{ mol}}) = 0.22 \text{ L O}_2$$

Summary

Chemical reactions are the most complicated process in chemistry. Models and theories reduce the complexity to manageable concepts and equations.

The fundamental chemical statement is the balanced chemical equation. Dalton knew it, and he knew how central it was to the atomic theory in mass relationships. With it he could account for the Law of Conservation of Matter, the Law of Constant Combining Ratios, and he could determine the *relative* masses of the invisible atoms. He used it to *derive* the Law of Multiple Proportions for reactions which produce a number of possible products, and showed that the data had lain in the literature unrecognized for half a century.

Chemical reactions take place through collisions which disrupt chemical bonds and rearrange atoms to make new molecules. Conservation of atoms allows analysis and prediction through the laws of stoichiometry summarized in The Stoichiometry Mol Map. The Stoichiometry Mol Map organizes in simple graphical form a host of calculations involving amounts of matter in reactions expressed in a variety of ways. *All stoichiometric problems are based on the Stoichiometry Mol Map and balanced chemical equations*. The Molecular Mol Map, embedded in Stoichiometry Mol Map, is used for converting mass and number measures of amount of matter when there is no conversion of the matter itself (chemical reactions). The Stoichiometry Mol Map is, in turn, embedded in a broader class of situations where the amount of matter is expressed less directly, such as of volume of solution, volume of gas, volume of pure substance.

It may be worth emphasizing, that no problem using the Stoichiometry Mol Map requires more than three conversion factors to get from a given corner to any other, not counting any extended conversions.

CHEMICAL EQUATIONS EXERCISES

- 1. What are the general forms of single and double displacement reactions, expressed using capital letters for chemical symbols?
- 2. What would be the opposite of a decomposition reaction?
- 3. What is conserved in chemical reactions?
- 4. Balance the chemical reaction for the thermal decomposition of nitrous acid.

$$HNO_2 = HNO_3 + NO + H_2O$$

- 5. How many possible kinds of questions can be asked, based on the Stoichiometry Mol Maps?
- 6. How many mols of water can be produced from reacting one gram of dihydrogen with excess dioxygen?
- 7. How many mols of water can be produced from reacting one gram of dihydrogen with *one gram* of dioxygen?
- 8. How should the Stoichiometry Mol Map be extended to deal with problems involving lbs, or some other measure of mass?
- 9. How many liters of Cl_2 at 50 °C and 650 torr are released when 5 mL of liquid Br_2 are added to suffi cient FeCl₃ solution? The balanced reaction is

$$3Br_2(l) + 2FeCl_3(aq) = 3Cl_2(g) + 2FeBr_3(aq)$$

10. How may the Stoichiometry Mol Map be applied to titration problems?

CHEMICAL EQUATIONS EXERCISE HINTS

- 1. Zinc metal is known to displace copper ion out of solution.
- 2. The word decomposition can have several meanings.
- 3. Possible quantities that may be conserved include mass, energy, heat, molecules, charge, etc.
- 4. When you get tired of trying to balance it by inspection, try the algebraic method.
- 5. Consider the possible pairs of vertices.

- 6. Check the Stoichiometry Mol Map.
- 7. This is a *limiting reagent* problem. Apply the Stoichiometry Mol Map twice.
- 8. Notice how the Stoichiometry Mol Map was extended for gases and solutions. What is the conversion factor if the data is in lbs, and where does it apply?
- 9. According to the CRC Handbook, the density of $Br_2(l)$ is 3.12 g/mL.
- 10. Titration refers to adding one reactant to another up to the stoichiometric amount (no limiting or excess reagent), usually in solution.