Chemistry 201

General Rules
Balancing Chemical Equations

NC State University

Chemical equations

We have considered stoichiometry in detail. In this section we consider the foundation for writing chemical reactions. While balancing the coefficients in order obtain the correct stoichiometry is important there are several *important* aspects that we must also consider to complete the task of writing meaningful chemical equations. First, we need to consider the phase of materials. Second, we need to consider the conservation of mass and charge. Third, we need to consider the independence of various processes.

Including phase information

The phase of a component in a chemical reaction is included using parentheses with the label (s),(ℓ), or (g) for solid, liquid and gas, respectively. Another important label is (aq), which is used to denote that a substance is in an aqueous solution. Often we must consider the temperature in order to write the correct symbols. The default temperature is 298 K. Thermodynamic values are tabulated at 298 K and unless otherwise specified you may assume that a reaction takes place at 298 K.

Mass balance

Mass balance is the statement that matter must be conserved throughout the chemical reaction. It is mass balance that gives us the justification for the approach of writing “atom equations” in our procedure for balancing chemical equations. The numbers of atoms of each type must be conserved in the reactants and products. This simply rule gives us the constraints we need to write balanced chemical reactions for an independent net reaction. We do need to be careful to consider the fact that sometimes the chemical reactions that we write not independent, but rather are linear combinations of chemical reactions.

Charge balance

We have not yet encountered charge in this course. However, just as there is a mass balance criterion, we must have charge balance as well. This constraint will be used when we consider electrochemical reactions since they are tabulated as half cell reactions with a certain number of electrons involved. The goal of the balancing in the case of half cell reactions will be to eliminate the electrons by finding the least common denominator between donor and acceptor reactions. This procedure will guarantee charge neutrality.

Independent net reactions

A final concern is that the reactions we write should be linearly independent. However, there are a number of cases in chemistry where the reactions in common use are not linearly independent. This means that there is more than one way to balance the reaction. This can be awkward for the instructor and can lead to loss of points by the student (for no good reason) since there is more than one “correct” answer. We need to be aware that this can happen.

Example: carbon dioxide

In this section we consider an approach to the determination of the number of independent reactions. We can write down a number of reactions that involve the species,

$$H^+(aq), CO_3{}^{2-}(aq), HCO_3{}^-(aq), H_2O(\ell), CO_2(aq), CO_2(g)$$

In our considerations of the processes we consider the process of carbon dioxide in the atmosphere in equilibrium with aqueous carbon dioxide, given by Henry's law. We will bring this aspect into the problem once we have determined the number of independent or net processes.

Example: carbon dioxide

Aqueous CO_2 is included as a species since we do not observe the formation of $H_2CO_3(aq)$, but rather we CO_2 reacts with water in two separate acid-base equilibria,

$$H_2O + CO_2 \rightarrow HCO_3{}^{-} + H^{+}$$
$$HCO_3{}^{-} \rightarrow CO_3{}^{2-} + H^{+}$$

From the above list of chemical species present in the system at equilibrium, we construct a table that consists of a species-atom matrix as shown below.

	H^+	CO_3^{2-}	H_2O	$CO_2(aq)$	$CO_2(g)$	HCO_3^-
H	1	0	2	0	0	1
C	0	1	0	1	1	1
O	0	3	1	2	2	3

Row reduction of the element species matrix

Each entry in the matrix corresponds to the elemental composition of each species. The original organization is arbitrary, but in the end you will want to have a diagonal unit matrix (row reduction).

The row reduction process can be described as follows:

1. Any row can be multiplied by any number (positive, negative, integral, a fraction)
2. Any row can be added to any other (before or after multiplication - so if you multiply by -1 this means you can add or subtract any row from any other.)
3. You can repeat these operations as many times as you wish.
4. You can interchange any two rows (the species heading the row moves with the row).

Matrix in echelon form

This matrix is in echelon form. Note that the species have changed in the left hand column.

	H^+	CO_3^{2-}	H_2O	$CO_2(aq)$	$CO_2(g)$	HCO_3^-
H	1	0	0	2	2	1
C	0	1	0	1	1	1
O	0	0	1	-1	-1	0

In the original species-by-element matrix each column is a vector in a space in which the elements are basis vectors. Row reduction changes the basis vectors to species in the system at equilibrium i.e. each column expresses the species labeling the column as a combination of species in the system. This means that each non-trivial column is a net reaction. The process of row reduction assures that the column vectors are independent.

Matrix in echelon form

This matrix is in echelon form. Note that the species have changed in the left hand column.

	H^+	CO_3^{2-}	H_2O	$CO_2(aq)$	$CO_2(g)$	HCO_3^-
H	1	0	0	2	2	1
C	0	1	0	1	1	1
O	0	0	1	-1	-1	0

We make the identification of the species with the element in the diagonal part.

	H^+	CO_3^{2-}	H_2O	$CO_2(aq)$	$CO_2(g)$	HCO_3^-
H^+	1	0	0	2	2	1
CO_3^{2-}	0	1	0	1	1	1
H_2O	0	0	1	-1	-1	0

Independent reactions

The process of row reduction assures that the column vectors are independent.

$$CO_2(aq) = 2H^+(aq) + CO_3^{2-}(aq) - H_2O(\ell)$$
$$CO_2(g) = 2H^+(aq) + CO_3^{2-}(aq) - H_2O(\ell)$$
$$HCO_3^-(aq) = 2H^+(aq) + CO_3^{2-}(aq)$$

These chemical reactions are a complete set of independent net reactions. As such they provide a basis for a complete consideration of the equilibrium state. They may be added and subtracted with the cancellation of species to obtain alternative sets of independent net reactions, but each set will contain exactly three net reactions and will provide a basis for the same consideration of the equilibrium state.

Linear combinations also independent

The following are linear combinations from the set found by row-reduction:

$$CO_2(aq) = CO_2(g)$$
$$CO_2(aq) + H_2O(\ell) = H^+(aq) + HCO_3^-(aq)$$
$$HCO_3^-(aq) = H^+(aq) + CO_3^{2-}(aq)$$