

How to Solve Word Problems in Chemistry

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We see that the conversion factor used here is the inverse of the one used in Example 1. In each case, we used the one we needed to convert from the unit that we *had* to the one that we *wanted*. □

We can use more than one factor to do conversions that are a little more complicated.

EXAMPLE 3 Change 1.660 hours to seconds.

Solution We know that there are exactly 60 minutes in an hour, and exactly 60 seconds in each minute:

$$1.660 \text{ hours} \left(\frac{60 \text{ minutes}}{1 \text{ hour}} \right) = 99.60 \text{ minutes}$$

$$99.60 \text{ minutes} \left(\frac{60 \text{ seconds}}{1 \text{ minute}} \right) = 5976 \text{ seconds}$$

Alternatively, we can do both operations without solving for the intermediate answer in minutes:

$$1.660 \text{ hours} \left(\frac{60 \text{ minutes}}{1 \text{ hour}} \right) \left(\frac{60 \text{ seconds}}{1 \text{ minute}} \right) = 5976 \text{ seconds}$$

Since we know that there are 3600 seconds in an hour, we do not need two factors, but there will be many problems in chemistry later in this book in which more than one factor is needed, so it is well that we learned how to handle more than one factor here. □

Working dimensional analysis problems with familiar problems will enable us to use the methods with the less familiar problems still to come. We can't make the mistake of not learning the method here because we don't need it yet.

We can use percentages as factors in working with dimensional analysis. For example if an elementary school class is 40% girls and 60% boys, we can tell how many children are in a class with 48 boys:

$$48 \text{ boys} \left(\frac{100 \text{ children}}{60 \text{ boys}} \right) = 80 \text{ children}$$

In chemistry, if a compound of elements A and B is 25% by mass element A, there is (25 g A)/(100 g total) by definition. But also, there is (75 g B)/(100 g total) and also there is (25 g A)/(75 g B).

Table 1-1 Order of Precedence**Highest**

Parentheses

Exponentiation or unary minus

Multiplication or division

Addition or subtraction

Lowest

precedence than do addition or subtraction. The orders of precedence are presented in Table 1-1.

Operations of equal precedence are done from left to right except for exponentiation and unary minus, which are done from right to left. (Unary minus is a minus sign that denotes a negative number rather than a subtraction.)

EXAMPLE 6 Calculate each answer on the calculator:

(a) $2 + 3 \times 4 - 5$

(b) ab/cd , where $a = 6$, $b = 3$, $c = 2$, and $d = 4$

(c) 2^{x^2} with $x = 3$

(d) -3^2

(e) $(-3)^2$

Solution

(a) The answer displayed is 9, corresponding to $2 + 12 - 5$. (The multiplication is done first.)

(b) The answer displayed is 2.25, corresponding to $\frac{18}{8}$. If the answer displayed was 36, the 9 in the display was *multiplied* by the 4. Because the calculator has a different precedence rule for division and multiplication than we follow in the algebraic expression ab/cd , where both multiplications are done first, we must divide the 18 by 2 and then *divide* that answer by 4. Alternatively, we may place parentheses around the (2×4) .

$$\boxed{6} \boxed{\times} \boxed{3} \boxed{\div} \boxed{2} \boxed{\div} \boxed{4} \boxed{=}$$

or $\boxed{6} \boxed{\times} \boxed{3} \boxed{\div} \boxed{(} \boxed{2} \boxed{\times} \boxed{4} \boxed{)} \boxed{=}$

(c) 512. This answer is equivalent to 2^9 rather than 8^2 since exponentiation is done right to left.

(d) -9 . The squaring is done on the 3, not on -3 , because exponentiation and unary minus are done right to left.

Thus they will be charging 75% of their regular rate:

$$\frac{16 \text{ dollars (regular)}}{100 \text{ dollars of loan}} \left(\frac{75 \text{ dollars (special)}}{100 \text{ dollars (regular)}} \right) = \frac{12 \text{ dollars (special)}}{100 \text{ dollars of loan}} = 12\%$$

5. (a) -7 (b) 0.75 (c) 75
(d) -6.0 (The subtraction left only two significant digits.)
(e) 0.668 [Not too different from answer (b) because the values were not too different.]
(f) 80.1 [Not too different from answer (c) because the values were not too different.]
6. (a) -3.80×10^{15} (Watch the minus sign and the significant digits.)
(b) 0.116 (c) 4.57×10^{-14} (Note that -14 is larger than -15.)
(d) 1.60×10^{-19} (We never touched the multiply key!)
7. (a) 100.0 (b) 4.470 (c) 7.389 (d) 10.292
8. Each model calculator is different, so read the instruction booklet if the instructions here are not applicable.
(a) 0.377 (Use the $1/x$ key.)
(b) 55.2 (Use the Δ key or another method on a more powerful calculator.)
(c) 5.00 (Use the 2^{nd} F and LOG keys.)
(d) 1.2×10^3 (Use the 2^{nd} F and LOG keys; use only two significant digits, since the 3 shows the magnitude of this number.)
9. Each model calculator is different, so the results may be slightly different from these.
(a) -0.586700236 (b) -3.586700236 (c) -9.586700236
(d) -13.58670024

The only difference among the numbers given are the powers of 10. The only difference in the logarithms are the integer portions [except for a round-off in part (d)]. The *characteristic* (integer portion) of the logarithm shows only the magnitude of the original number, and the first three digits of the *mantissa* (the decimal fractional part) are the significant digits (reflecting the three significant digits in the numbers given). We should report the values
(a) -0.587 (b) -3.587 (c) -9.587 (d) -13.587

Measurement

2.1 Metric System Calculations

The **metric system** along with its newer counterpart, the **SI (system internationale)** system of measurement, was designed to make our measurements and our calculations as easy as possible. Once we have learned it, it is much easier to use than the English system, as we will see later. It is possible to learn more than 90% of the metric system needed in a beginning chemistry course using only the seven terms and their abbreviations in Table 2-1. The units will be introduced in the three following subsections. The prefixes will also be introduced there, but will be intensively used in the metric conversion subsection. Please note carefully the abbreviations, and use the proper one for each term. Note that the abbreviations for meter and for milli- are both the same—m. It is easy to tell the difference because milli- is a prefix, so an m before another letter means milli-. If the m is not before another letter, it means meter. Please note that of the abbreviations in Table 2-1, only the L for liter is capitalized. We must use the proper capitalization from the start or we will mix ourselves up. For example, capital M stands for another quantity (molarity) or another prefix (mega-).

Length or Distance

The unit of length or distance in the metric system is the **meter**. The meter was originally defined as 1 ten-millionth of the distance from the north pole to the equator through Paris, France. That is a rather difficult measurement to make, so later the meter was defined as the distance between two scratches in a special bar kept in a vault in Sevre, France. There is an even later definition, but we will be satisfied that it is the distance between those two

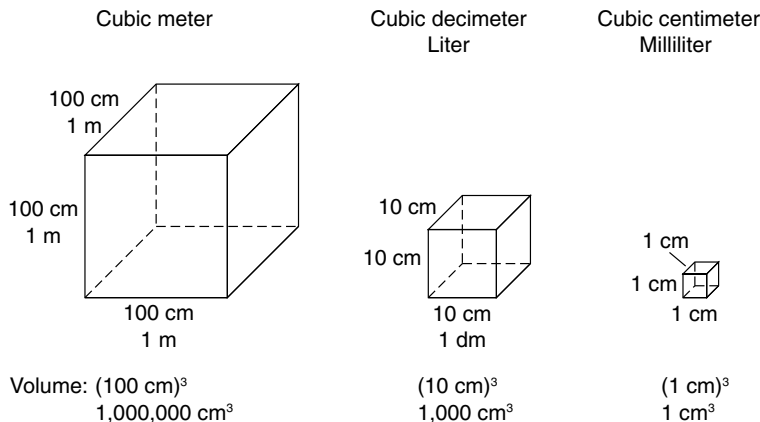


Fig. 2-2 Relationships of SI and Metric Units of Volume. (Not drawn to scale.)

(b) $1.49 \text{ m} \left(\frac{1 \text{ cm}}{0.01 \text{ m}} \right) = 149 \text{ cm}$ (substitute 0.01 for the c)

(c) $1.49 \text{ m} \left(\frac{1 \text{ mm}}{0.001 \text{ m}} \right) = 1490 \text{ mm}$ (substitute 0.001 for the first m) $\square$

EXAMPLE 3 Convert 2.50 m^3 to cubic centimeters.

Solution

$$2.50 \text{ m}^3 \left(\frac{1,000,000 \text{ cm}^3}{1 \text{ m}^3} \right) = 2,500,000 \text{ cm}^3 = 2.50 \times 10^6 \text{ cm}^3$$

Note that 1 cubic meter is equal to 1 million cubic centimeters! (See Fig. 2-2.) $\square$

EXAMPLE 4 Convert 2.50 m^3 to liters.

Solution We know that 1 cubic meter is equal to 1000 cubic decimeters (Fig. 2-2) and that it is also 1000 L.

$$2.50 \text{ m}^3 \left(\frac{1000 \text{ L}}{1 \text{ m}^3} \right) = 2500 \text{ L} \quad \square$$

Units in Scientific Calculations

When arithmetic operations are done with measurements, sometimes the units must be adjusted. (1) In addition or subtraction problems, the units of the measurements must be the same. For example, to add 2.00 m and 10.0 cm, we must change one of the values to the units of the other: $200\text{ cm} + 10.0\text{ cm}$, is one possibility. (2) In multiplication or division of lengths, the square of lengths, and/or the cube of lengths, the length units must be the same. For example, to divide 2 cm^3 by a length, the length must be in centimeters. To multiply 2.00 m and 10.0 cm, again we should change one to the units of the other: $200\text{ cm} \times 10.0\text{ cm}$, is one possibility. (3) Otherwise, in multiplication or division, the units do not have to be the same. To divide 40.0 g by 23.0 cm^3 , we do not have to change any units because grams is not a unit of length.

2.2 Significant Digits

No measurement can be made perfectly. Every measuring instrument has a limit as to how precisely it can be read. For example, we would never try to measure the length of our shadow with an automobile odometer (mileage indicator). Scientists attempt to read every instrument to one tenth the smallest scale division. Thus a meter stick with 1000 division marks (that is, 100 centimeters, with each centimeter divided into 10 parts) can be estimated to 0.1 mm. When a scientist reports the results of the measurement, the scientist uses as many digits as necessary to indicate how precisely the measurement was made. The scientist might report 0.0531 m to report a length. We have to recognize which of these digits record the precision of the measurement, which are present *only to specify the magnitude of the answer*, and which do both. If the digit helps report the precision, it is called a **significant digit** or a **significant figure**. The word *significant* in this sense does not mean *important*; it means *having to do with precision*! Every digit serves to report either the magnitude or the precision of the measurement, or both. If the digit reports the magnitude only, it is nonsignificant.

Significant Digits in Reported Values

First we must learn to recognize which digits in a properly reported number are significant. They include all nonzero digits. Zeros are determined to be significant or not according to the following rules:

1. All zeros to the right of all other digits *and* to the right of the decimal point are significant. For example, in 1.200 cm, the zeros are significant.

(d) We merely drop the last 3, leaving us three significant digits. Do not confuse the number of significant digits with the number of decimal place digits. (e) We drop the 48, since the 4 is less than 5. We do *not* drop one digit at a time. We do not round the 4 to 5 by dropping the last digit and then change the 6 to 7 by dropping that 5. The 48 is less than 50, so we do not round up the last remaining digit. □

Sometimes it is necessary to *add* digits to obtain the proper number of significant digits in our answer.

EXAMPLE 9 Divide 7.86 cm^2 by 3.93 cm .

Solution The answer on our calculator is 2 (cm), but the answer must contain three significant digits, so we add two zeros to the calculator's result to get 2.00 cm . □

The question is often asked "How many significant digits should we use?" The answer is that we determine how many by using the measurements given in the problem. For example, if the products in a multiplication all have four significant digits, then we use four in the final answer. If a quantitative problem has no numeric data in its statement, and a percent composition problem (Section 4.3), then we use at least three significant digits in its solution so that rounding errors don't give incorrect results.

2.3 Scientific Notation

Scientists refer to numbers from literally astronomical to almost infinitesimal. In order to do so conveniently, we use **scientific notation**, also known as **standard exponential notation**. Scientific notation is a form of a number with a decimal coefficient times a power of 10. The following number is in scientific notation, with its parts identified:

$$\begin{array}{ccc}
 \text{base} & & \text{exponent} \\
 & \swarrow & \searrow \\
 1.246 \times 10^3 & & \\
 \swarrow & & \searrow \\
 \text{coefficient} & & \text{exponential part}
 \end{array}$$

A number in scientific notation has a coefficient that is 1 or more but less than 10, and it has an integral exponent, which may be positive, zero, or negative.

EXAMPLE 10 Which one(s) of the following numbers are in scientific notation?

12. How many significant digits are present in the Kelvin scale equivalent of 0°C ?
13. What is the sum, to the proper number of significant digits, of $1.83 \times 10^{11} \text{ m}$ and $6.74 \times 10^9 \text{ m}$?
14. What is the sum, to the proper number of significant digits, of $1.83 \times 10^{11} \text{ cm}$ and $6.74 \times 10^9 \text{ m}$?
15. Calculate the density of a rectangular solid that is 40.0 cm by 10.0 cm by 5.00 cm and has a mass of 4.50 kg .
16. Which has a greater density, a sample of oxygen gas at 2.00 g/dm^3 or a sample of water at 1.00 g/cm^3 ? Explain.
17. A rectangular drinking trough for animals is 2.10 m long, 43.1 cm wide, and 21.7 cm deep. A $2.60 \times 10^5 \text{ g}$ sample of liquid with density 1.73 kg/dm^3 is placed in it. (a) To find the depth of the liquid, what should we do to the measurements with regard to their units? (b) How can we calculate the volume of the trough? (c) What can we calculate from the density and the mass of liquid? (d) Do we expect the volumes of the trough and the liquid to be the same? (e) How can we calculate the height of the liquid from its volume, length, and width?
18. If light travels $3.00 \times 10^8 \text{ m/s}$, what distance can light travel in 1.00 year?
19. If light travels $3.00 \times 10^8 \text{ m/s}$ and it takes light about 500 s to get from the sun to the earth, how far away is the sun?
20. It takes light about 4 years to get from the nearest big star to the earth and light travels $3.00 \times 10^8 \text{ m/s}$. How far away is the star?
21. A rectangular drinking trough for animals is 2.10 m long, 43.1 cm wide, and 21.7 cm deep. A $2.60 \times 10^5 \text{ g}$ sample of liquid with density 1.73 kg/dm^3 is placed in it. (a) Convert the length to centimeters and the density to grams per cubic centimeter. (b) Calculate the volume of the trough. (c) Calculate the volume of the liquid. (d) Are the volumes of the trough and the liquid the same? (e) Calculate the height of the liquid.
22. Calculate the volume of 2.50 kg of mercury (density 13.6 g/mL).
23. Calculate the mass of 1.75 L of iron (density 7.86 g/mL).
24. A sample of a pure substance has a mass of 329 g and a volume of 41.9 mL . Use a table of densities to determine the identity of the substance.
25. Convert 35°C to the Kelvin scale.
26. Convert 422 K to Celsius.
27. Convert the density 5.94 kg/m^3 (a) to g/cm^3 . (b) to kg/dm^3 .
28. Under certain conditions, air has a density of about 1.3 kg/m^3 .

The **weighted average** of several sets of items is the average with regard to the number in each set. For example, if the Jones family has triplet boys, each weighing 90 pounds, and one girl, who weighs 50 pounds, the average of one boy and the girl is 70 pounds, but the weighted average of all the children is 80 pounds:

90 pounds

90 pounds or $3(90 \text{ pounds}) + 50 \text{ pounds} = 320 \text{ pounds}$

90 pounds

50 pounds

320 pounds

Weighted average = $(320 \text{ pounds}) / (4 \text{ children}) = 80 \text{ pounds}$

The atomic mass of each element can be determined in two different ways: (1) as was done historically, by comparing the naturally occurring mixture versus a standard (now ^{12}C), or (2) as presently done with the modern *mass spectrometer*, by measuring the mass of each isotope and the percentage abundance of each.

EXAMPLE 1 (a) The atoms of a certain element have a mass 2.026 times the mass of an equal number of ^{12}C atoms. What is the atomic mass of the element? (b) Which element is it? (c) What is the best way to make sure that we get equal numbers of atoms of two elements to compare their masses?

Solution

(a) The mass of the average atom is 2.026 times that of a ^{12}C atom:

$$2.026(12.00 \text{ amu}) = 24.31 \text{ amu}$$

(b) Magnesium (see the periodic table).

(c) The best way to get equal numbers of atoms is to make a compound of the two elements that has them in a 1:1 ratio. □

EXAMPLE 2 Naturally occurring magnesium consists 78.70% of ^{24}Mg , with atoms of mass 23.98504 amu, 10.13% of ^{25}Mg , with atoms of mass 24.98584 amu, and 11.17% ^{26}Mg , with atoms of mass 25.98259 amu. Calculate the atomic mass of magnesium.

4.3 Percent Composition

The subscripts in the formula of a compound give the mole ratio of atoms of the elements in the compound. For example, H_2SO_4 has a mole ratio of 2 mol of hydrogen atoms to 1 mol of sulfur atoms to 4 mol of oxygen atoms. The percent composition refers to the mass ratio of the elements converted to percentage. To get the percent composition, take an arbitrary quantity of the compound (1.00 mol is easiest), convert each number of moles of the elements to grams with the molar masses of the atoms, then calculate the percentage by dividing the mass of each element by the total mass in the given quantity of compound (in this case, 1.00 mol).

EXAMPLE 10 Calculate the percent composition of NH_4NO_3 , another fertilizer.

Solution The masses are calculated as shown above:

$$2 \text{ mol N} \left(\frac{14.01 \text{ g N}}{1 \text{ mol N}} \right) = 28.02 \text{ g N}$$

$$4 \text{ mol H} \left(\frac{1.008 \text{ g H}}{1 \text{ mol H}} \right) = 4.032 \text{ g H}$$

$$3 \text{ mol O} \left(\frac{16.00 \text{ g O}}{1 \text{ mol O}} \right) = 48.00 \text{ g O}$$

$$\text{Total} = 80.05 \text{ g}$$

(Note that we use 16.00 g/mol of oxygen atoms; this problem has nothing to do with oxygen molecules, O_2 .)

The percentage of each element is the mass of the element divided by the total mass, times 100% to convert to percent:

$$\frac{4.032 \text{ g H}}{80.05 \text{ g}} \times 100.0\% = 5.037\% \text{ H}$$

$$\frac{28.02 \text{ g N}}{80.05 \text{ g}} \times 100.0\% = 35.00\% \text{ N}$$

$$\frac{48.00 \text{ g O}}{80.05 \text{ g}} \times 100.0\% = 59.95\% \text{ O}$$

$$\text{Total} = 99.99\%$$

We should always check our answer to see that it is reasonable! A total between 99.5% and 100.5% is reasonable. □

4.4 Empirical Formulas

Empirical formula problems should be done with at least three significant digits in each value. If fewer significant digits are used, rounding errors may yield an incorrect formula.

We have learned how to convert a formula to percent composition; we will now do the opposite—convert a percent composition to the empirical formula. The **empirical formula** of a compound is its simplest formula, having the smallest possible set of integral subscripts. Thus CH_2 is an empirical formula, but C_2H_4 is not, because its subscripts can both be divided by 2. The empirical formula tells the mole ratio of the atoms of each element to those of every other element in the compound. If we start with a set of masses for the elements in the compound, we can change them to moles as shown in Section 4.2. We then have to make that set of moles into an integer set of moles, and use those integers as subscripts in our formula.

EXAMPLE 11 Calculate the empirical formula of glucose, a simple sugar, if a certain sample contains 393.4 g of carbon, 66.07 g of hydrogen, and 524.2 g of oxygen.

Solution We first change each of the masses to moles:

$$393.4 \text{ g C} \left(\frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) = 32.76 \text{ mol C}$$

$$66.07 \text{ g H} \left(\frac{1 \text{ mol H}}{1.008 \text{ g H}} \right) = 65.55 \text{ mol H}$$

$$524.2 \text{ g O} \left(\frac{1 \text{ mol O}}{16.00 \text{ g O}} \right) = 32.76 \text{ mol O}$$

We now have a mole ratio of these elements, but it is not an integer ratio. The easiest way to get an integer ratio is to divide all of these moles by the magnitude of the smallest:

$$\frac{32.76 \text{ mol C}}{32.76} = 1.000 \text{ mol C} \qquad \frac{32.76 \text{ mol O}}{32.76} = 1.000 \text{ mol O}$$

$$\frac{65.55 \text{ mol H}}{32.76} = 2.001 \text{ mol H}$$

9. Calculate the number of moles of ethylene glycol, $\text{C}_2\text{H}_6\text{O}_2$, used as antifreeze in cars, that are in 47.7 g of $\text{C}_2\text{H}_6\text{O}_2$.
10. Calculate the mass in grams of 5.00×10^{20} H_2O molecules.
11. Calculate the number of moles of hydrogen atoms in 17.4 g of $(\text{NH}_4)_2\text{SO}_4$.
12. Calculate the percent composition of borax, $\text{Na}_2\text{B}_2\text{O}_7$, used in commercial laundry processes.
13. Calculate the empirical formula of "hypo," used in photographic development, consisting of 29.1% Na, 40.5% S, and 30.4% O.
14. Calculate the percent composition of rubbing alcohol, $\text{C}_3\text{H}_8\text{O}$.
15. Calculate the molecular formula of a compound with molar mass 104 g/mol composed of 92.3% carbon and 7.7% hydrogen.
16. Consider the formula of hydrazinium nitrate, $\text{N}_2\text{H}_6(\text{NO}_3)_2$.
(a) Calculate its molar mass. (b) Calculate the number of moles of the compound in 17.4 g of it. (c) Calculate the number of moles of nitrogen atoms in that quantity of compound. (d) Calculate the number of individual nitrogen atoms in that quantity.
17. Calculate the number of individual nitrogen atoms in 171 g of ammonium azide, NH_4N_3 .

Solutions to Supplementary Problems

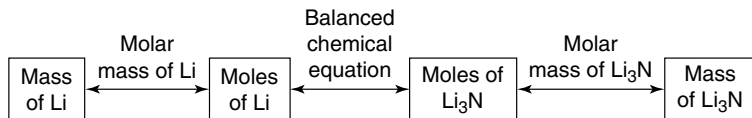
1. Note. The 12.01 amu is the atomic mass—the weighted average of all the isotopes of carbon (the same reasoning tells us that no American family has 2.3 children.)
2. (a) $2.05(12.01 \text{ amu}) = 27.0 \text{ amu}$
(b) $2.42(27.0 \text{ amu}) = 65.3 \text{ amu}$
3.
$$\frac{(60.4\%)(68.9257 \text{ amu}) + (39.6\%)(70.9249 \text{ amu})}{100\%} = 69.7 \text{ amu}$$
4. Let x = the percentage of the 78.9183 amu isotope, then $(100 - x)$ = the percentage of the other isotope.

$$\frac{x(78.9183 \text{ amu}) + (100 - x)(80.9163 \text{ amu})}{100} = 79.909 \text{ amu}$$

$$\begin{aligned} 78.9183x + 8091.63 - 80.9163x &= 7990.9 \\ -1.998x &= -100.7 \\ x &= 50.40\% \\ \text{and } (100 - x) &= 49.60\% \end{aligned}$$

5. (a) $2(14.0 \text{ amu}) + 9(1.0 \text{ amu}) + 3(1.0 \text{ amu}) + 4(16.0 \text{ amu})$
 $= 132.0 \text{ amu}$ (b) 46.0 amu (c) $4(31.0 \text{ amu}) = 124 \text{ amu}$

We can diagram the overall process as we did in Chapter 4.



5.3 Other Conversions

Any quantity that can be converted to moles of reactant or product may be presented in the statement of a problem. Examples are number of formula units of reactant or product, or number of moles of an element in one of the reactants or products, as well as data on solutions or gases that will be presented later (in Chapters 6 and 7). In any case, merely convert the quantity given to moles, use the balanced chemical equation as presented in Section 5.1 to determine the number of moles of reactant or product that was asked about, and finish the problem as required.

EXAMPLE 3 Calculate the mass of oxygen gas produced by the thermal decomposition of 9.97×10^{23} formula units of KClO_3 . KCl is the other product.

Solution



$$9.97 \times 10^{23} \text{ formula units } \text{KClO}_3 \times$$

$$\left(\frac{1 \text{ mol } \text{KClO}_3}{6.02 \times 10^{23} \text{ formula units of } \text{KClO}_3} \right) = 0.0166 \text{ mol } \text{KClO}_3$$

Next, find the number of moles of oxygen, the substance that was asked about:

$$0.0166 \text{ mol } \text{KClO}_3 \left(\frac{3 \text{ mol } \text{O}_2}{2 \text{ mol } \text{KClO}_3} \right) = 0.0249 \text{ mol } \text{O}_2$$

Finally, find the mass of oxygen:

$$0.0249 \text{ mol } \text{O}_2 \left(\frac{32.0 \text{ g } \text{O}_2}{1 \text{ mol } \text{O}_2} \right) = 0.797 \text{ g } \text{O}_2$$

8. (a) Calculate the number of moles of a solid unknown acid, HA, that is present if 17.40 mL of 3.00 M NaOH is required to neutralize it. (b) Calculate the molar mass of the acid if 4.17 g of the acid was used in part (a).
9. Calculate the molarity, molality, and mole fraction of a solution of 0.0150 mol of NaCl in 50.0 g of water if the solution has a density of 1.02 g/mL.
10. Calculate the mole fraction of each component in a solution of 50.0 g CH₃OH and 75.0 g of H₂O.
11. A 0.100 M solution of NaOH is treated with a 0.100 M solution of HNO₃. At the equivalence point (where the reaction is just completed), what is the concentration of the NaNO₃ produced?
12. Calculate the molar mass of an acid, H₂A, if 6.66 g of the acid required 22.22 mL of 3.000 M NaOH to completely neutralize it.
13. A solution was 2.40 m and contained 245 g of solvent. Calculate the molality of the solution after dilution with 125 g more of solvent.
14. Calculate the molality of an alcohol in aqueous solution if the mole fraction of the alcohol is 0.150.
15. Calculate the molar mass of an unknown base, B, with molecules that each react with two hydrochloric acid ions. 7.99 g of the base is neutralized by 41.44 mL of 3.00 M HCl.



16. Calculate the molality of an aqueous solution 2.24 M in sucrose, C₁₂H₂₂O₁₁. Assume that the density of the solution is 2.05 g/mL.)

Solutions to Supplementary Problems

1. $\frac{80.0 \text{ mmol}}{250 \text{ mL}} = 0.320 \text{ M}$
2. $\frac{1.71 \text{ mol}}{0.500 \text{ L}} = 3.42 \text{ M}$ (Watch the units!)
3. $4.22 \text{ mol} \left(\frac{1 \text{ L}}{2.00 \text{ mol}} \right) = 2.11 \text{ L}$
4. $50.00 \text{ mL} \left(\frac{1.500 \text{ mmol}}{1 \text{ mL}} \right) \left(\frac{0.001 \text{ mol}}{1 \text{ mmol}} \right) = 0.07500 \text{ mol}$
5. The number of moles of solute in the initial solution is calculated first:

$$1.70 \text{ L} \left(\frac{2.06 \text{ mol}}{1 \text{ L}} \right) = 3.50 \text{ mol}$$

do with molarity (Section 6.1). Thus measurement at STP of the volume of a sample of gas enables calculation of the number of moles of gas in the sample, and vice versa.

EXAMPLE 5 (a) Calculate the volume occupied by 0.750 mol of O_2 at STP. (b) Calculate the number of moles of N_2 that occupies 7.00 L at STP.

Solution

$$(a) 0.750 \text{ mol} \left(\frac{22.4 \text{ L (at STP)}}{1.00 \text{ mol}} \right) = 16.8 \text{ L}$$

$$(b) 7.00 \text{ L} \left(\frac{1 \text{ mol}}{22.4 \text{ L (at STP)}} \right) = 0.313 \text{ mol} \quad \square$$

If the sample of gas is not at STP, we can use the combined gas law to calculate what its volume would be at STP, then convert that volume to number of moles. Similarly, if the number of moles are given, we can use the molar volume to calculate the volume at STP and then convert that with the combined gas law to any temperature and pressure required. (See Fig. 7-1.)

EXAMPLE 6 Calculate the number of moles of O_2 that occupies 17.2 L at 25°C and 755 torr.

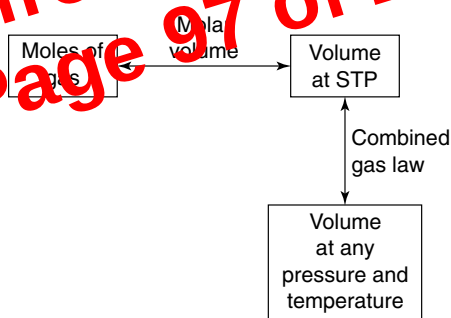


Fig. 7-1 Two Step Mole-Volume Problem. To convert moles of a gas to a volume at any temperature and pressure, first convert the moles to volume at STP with the molar volume (first arrow), then convert the volume to the required volume at the given conditions with the combined gas law. If given the P - V - T data, use the combined gas law first, then the molar volume. Where do we start? Where the complete data are given. Work toward the answer required.

$$P_2 V_2 = n_2 R T_2:$$

$$\frac{P_1}{P_{\text{total}}} = \frac{n_1}{n_{\text{total}}}$$

□

EXAMPLE 14 Calculate the oxygen pressure in a mixture of 0.500 mol of oxygen and 0.750 mol of nitrogen with a total pressure of 40.0 kPa.

Solution

$$\begin{aligned}\frac{P_{\text{oxygen}}}{P_{\text{total}}} &= \frac{n_{\text{oxygen}}}{n_{\text{total}}} \\ \frac{P_{\text{oxygen}}}{40.0 \text{ kPa}} &= \frac{0.500 \text{ mol}}{1.250 \text{ mol}} \\ P_{\text{oxygen}} &= 16.0 \text{ kPa}\end{aligned}$$

□

When a gas is collected over water, some of the water evaporates and its vapor forms a mixture with the other gas. Evaporation continues until the rate of evaporation of the liquid water equals the rate at which the water vapor condenses, and a state of **physical equilibrium** is achieved.

A mixture of a normal gas and water vapor behaves just like any other gas mixture *as long as no more water can evaporate and no water vapor can condense*. But when the gas mixture is in equilibrium with liquid water, any attempt to reduce the pressure of the water vapor will result in more liquid water evaporating. Any attempt at increasing the water vapor pressure by reducing the volume, for example) will result in water vapor condensing. Thus the vapor pressure of water in equilibrium with liquid water is a constant at any given temperature. Tables of water vapor pressure at various temperatures are given in texts and typically the water vapor pressure at a specified temperature is given on exams.

EXAMPLE 15 (a) A mixture of oxygen and water vapor at a total pressure of 107 kPa is in equilibrium with liquid water at 25°C, at which temperature the water vapor pressure is 3.2 kPa. Calculate the pressure of the oxygen. (b) Oxygen is collected over water at 25°C under a barometric pressure of 107 kPa. ($P_{\text{H}_2\text{O}} = 3.2 \text{ kPa}$) Calculate the pressure of the oxygen.

Solution

(a) The pressure of the oxygen is the total pressure minus the water vapor pressure:

$$P_{\text{oxygen}} = 107 \text{ kPa} - 3.2 \text{ kPa} = 104 \text{ kPa}$$

Solution

$$\frac{r_{\text{hydrogen}}}{r_{\text{oxygen}}} = \sqrt{\frac{MM_{\text{oxygen}}}{MM_{\text{hydrogen}}}} = \sqrt{\frac{32.0 \text{ g/mol}}{2.02 \text{ g/mol}}} = \sqrt{15.8} = 3.98$$

$$r_{\text{hydrogen}} = 3.98(r_{\text{oxygen}})$$

Hydrogen effuses about four times as fast as oxygen under the same conditions of temperature and pressure. $\square$

EXAMPLE 18 In a certain experiment, argon effuses from a porous cup at 4.00 mmol/minute. How fast would chlorine effuse under the same conditions?

Solution

$$\frac{r_{\text{chlorine}}}{r_{\text{argon}}} = \sqrt{\frac{MM_{\text{argon}}}{MM_{\text{chlorine}}}} = \sqrt{\frac{39.9 \text{ g/mol}}{70.9 \text{ g/mol}}} = 0.750$$

$$r_{\text{chlorine}} = (0.750)(4.00 \text{ mmol/minute}) = 3.00 \text{ mmol/minute}$$

Hints:

1. Once again, it is important to remember that hydrogen, nitrogen, oxygen, fluorine, and chlorine, when uncombined with other elements, are gases that exist as diatomic molecules.
2. For ease of solution, let the unknown rate appear in the numerator.
3. The proportion is inverse; if the rate of a given gas appears in the numerator, its molar mass is in the denominator, and vice versa. $\square$

The *time* it takes for a gas to diffuse a certain distance is inversely proportional to its *rate* of diffusion. (The faster something moves, the less time it takes to reach its destination.) If a Graham's law problem asks for a time, the problem may be solved in terms of rates, and that information used to get the final answer.

EXAMPLE 19 If escaping ammonia gas can be smelled across a room in 5.00 minutes, how long would it take to smell chlorine gas under identical conditions?

Solution The rate ratio is calculated as usual:

$$\frac{r_{\text{ammonia}}}{r_{\text{chlorine}}} = \sqrt{\frac{MM_{\text{chlorine}}}{MM_{\text{ammonia}}}} = \sqrt{\frac{70.9 \text{ g/mol}}{17.0 \text{ g/mol}}} = 2.04$$

Because the ammonia diffuses 2.04 times as fast, the chlorine will take 2.04 times as long to get there:

$$\text{Time} = (2.04) (5.00 \text{ minutes}) = 10.2 \text{ minutes}$$

Note that the heavier gas (chlorine) takes longer to arrive (because it diffuses more slowly). $\square$

7.6 Kinetic Molecular Theory Calculations

One of the postulates of the **kinetic molecular theory (KMT)** states that the average kinetic energy of the molecules of a gas is directly proportional to the *absolute* temperature.

$$\overline{\text{KE}} = 3RT/2N$$

where R is expressed in joules per mole per kelvin ($1 \text{ J} = 1 \text{ L}\cdot\text{kPa}$). T is absolute temperature and N is Avogadro's number. A line (called a *bar*) over a variable designates the quantity as an average. Thus $\overline{\text{KE}}$ means the average kinetic energy.

If two samples of gas are at the same temperature, the average kinetic energies of their molecules are equal. That does not mean that the average velocities of their molecules are equal, however. If the gases are not the same, their molecules have different molecular masses. Because the kinetic energy is equal to half the mass times the square of the velocity, their velocities must be different.

$$\overline{\text{KE}} = \frac{1}{2}m\overline{v^2}$$

Since $\overline{\text{KE}}$ for the two gases is the same, but m is different, $\overline{v^2}$ must also be different. Thus the lighter gas molecules must travel faster on average. (This is the basis for Graham's law.)

EXAMPLE 20 Samples of hydrogen and nitrogen are at the same temperature. (a) Compare the average kinetic energies of their molecules. (b) Compare qualitatively the average velocities of their molecules.

Solution

- (a) Since the temperatures are the same, the average kinetic energies are the same.
- (b) Since the mass of each hydrogen molecule is less than that of each nitrogen molecule, the average velocity of hydrogen molecules must be greater than that of nitrogen molecules. $\square$

- (a) V_2 is $0.790 \text{ L} - 0.200 \text{ L} = 0.590 \text{ L}$. P_2 is given by the combined gas law:

$$P_2 = \frac{P_1 V_1 T_2}{V_2 T_1} = \frac{(255 \text{ kPa})(0.790 \text{ L})(348 \text{ K})}{(0.590 \text{ L})(298 \text{ K})} = 399 \text{ kPa}$$

- (b) V_2 is again $0.790 \text{ L} - 0.200 \text{ L} = 0.590 \text{ L}$. P_2 is again 399 kPa .

- (c) V_2 is 0.200 L . P_2 is again given by the combined gas law:

$$P_2 = \frac{P_1 V_1 T_2}{V_2 T_1} = \frac{(255 \text{ kPa})(0.790 \text{ L})(348 \text{ K})}{(0.200 \text{ L})(298 \text{ K})} = 1180 \text{ kPa}$$

5. $n = 0.444 \text{ mol}$ $V = 666 \text{ mL} = 0.666 \text{ L}$
 $T = -8^\circ\text{C} + 273^\circ = 265 \text{ K}$

$$P = \frac{nRT}{V} = \frac{(0.444 \text{ mol})(8.31 \text{ L}\cdot\text{kPa}/\text{mol}\cdot\text{K})(265 \text{ K})}{(0.666 \text{ L})} = 1170 \text{ kPa}$$

6. (a) The number of moles of hydrogen is given by

$$n = \frac{PV}{RT} = \frac{[(785/760) \text{ atm}](6.00 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(298 \text{ K})} = 0.253 \text{ mol}$$

According to the balanced chemical equation, the number of moles of oxygen is half that, 0.127 mol . The volume of oxygen is

$$V = \frac{nRT}{P} = \frac{(0.127 \text{ mol})(0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(298 \text{ K})}{[(785/760) \text{ atm}]} = 3.01 \text{ L}$$

- (b) The number of moles of hydrogen is given by

$$n = \frac{PV}{RT} = \frac{[(805/760) \text{ atm}](6.00 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(326 \text{ K})} = 0.237 \text{ mol}$$

According to the balanced chemical equation, the number of moles of oxygen is half that, 0.119 mol . The volume of oxygen is

$$V = \frac{nRT}{P} = \frac{(0.119 \text{ mol})(0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(326 \text{ K})}{(805/760) \text{ atm}} = 3.01 \text{ L}$$

Note that it is the *change in temperature* that is included in this equation. □

EXAMPLE 3 Calculate the quantity of heat required to raise the temperature of 2.00 g of water from 21.00°C to 25.00°C.

Solution The change in temperature is 4.00°C, so this example is the same as the prior one. □

EXAMPLE 4 Calculate the quantity of heat required to change the temperature of 2.00 g of water from 25.00°C to 21.00°C.

Solution This time, the change in temperature is 21.00°C – 25.00°C = –4.00°C, so the quantity of heat is

$$q = mc\Delta t = (2.00 \text{ g})(4.184 \text{ J/g}\cdot^{\circ}\text{C})(-4.00^{\circ}\text{C}) = -33.5 \text{ J}$$

The minus sign means that heat must be *removed* from the water. □

EXAMPLE 5 (a) Calculate the temperature change when 55.7 J of heat is added to 12.0 g of water at 22.0°C. (b) what is the final temperature?

Solution

(a) $q = mc\Delta t \Rightarrow (12.0 \text{ g})(4.184 \text{ J/g}\cdot^{\circ}\text{C})(\Delta t) = 55.7 \text{ J}$
 $\Delta t = 1.11^{\circ}\text{C}$

(b) The final temperature is 1.11°C higher than the initial temperature, or

$$t_f = 22.0^{\circ}\text{C} + 1.11^{\circ}\text{C} = 23.1^{\circ}\text{C}$$

Note the difference between the *change in temperature* and the *final temperature*! □

To what temperature would the water in Example 5 be warmed if 55.7 J of electrical energy or 55.7 J of energy from a chemical reaction had been added? It doesn't matter to the water what form of energy has been used; just the quantity of energy is important. (See Supplementary Problems 13, 21, and 22.)

EXAMPLE 6 What mass of water is heated 2.30°C when 87.4 J of heat is added to it?

the phase change takes place at constant temperature, there is no $^{\circ}\text{C}$ as part of the unit and there is no Δt term in the equation to calculate the associated heat.

EXAMPLE 11 Calculate the heat required to melt 14.7 g of ice at 0°C .

Solution The problem is given in grams and the value from Table 8-2 is in moles, so a conversion factor is used:

$$14.7 \text{ g} \left(\frac{1 \text{ mol}}{18.0 \text{ g}} \right) \left(\frac{6.00 \text{ kJ}}{1 \text{ mol}} \right) = 4.90 \text{ kJ} \quad \square$$

EXAMPLE 12 If it takes 439 J of heat to warm 14.7 g of ice to 0°C , how much heat would it take to warm the ice to the freezing point and then melt it? (See prior example.)

Solution The total heat required is the heat for the warming process plus the heat of fusion. As usual, watch out for the units and the significant digits!

$$4.90 \text{ kJ} + 439 \text{ J} = 4.90 \text{ kJ} + 0.439 \text{ kJ} = 5.34 \text{ kJ} \quad \square$$

The last example indicates that to calculate the total heat required to heat a sample and to change its phase requires a separate calculation for each. For example, to calculate the heat required to change liquid water at 80°C to water vapor at 110°C , we have to calculate the heat required to warm the liquid to 100°C , the heat required to vaporize the water at 100°C , and the heat required to warm the vapor. Then we add the three terms to get the total heat for the process.

EXAMPLE 13 Calculate the heat required to change 45.0 g of liquid water at 80.0°C to water vapor at 110.0°C . Use the data of Tables 8-1 and 8-2.

Solution To calculate the heat used to warm the liquid water to 100°C takes a specific heat calculation:

$$q = mc\Delta t = (45.0 \text{ g})(4.184 \text{ J/g} \cdot ^{\circ}\text{C})(20.0^{\circ}\text{C}) = 3770 \text{ J}$$

To calculate the heat used to vaporize the water takes a heat of vaporization calculation:

$$45.0 \text{ g} \left(\frac{1 \text{ mol}}{18.0 \text{ g}} \right) \left(\frac{40.6 \text{ kJ}}{1 \text{ mol}} \right) = 102 \text{ kJ}$$

formation of water is -286 kJ/mol and that there are two moles present in the equation. Also note that when a sum is subtracted, it is equivalent to *subtracting each member* in the sum:

$$(a + b) - (c + d) = a + b - c - d \quad \square$$

If a different quantity from the number of moles in the equation is specified in the problem, calculate the value using the number of moles in the equation, then compute the value for the quantity specified in the problem.

EXAMPLE 16 Calculate the enthalpy change for the reaction of 23.7 g of CH_4 with oxygen to yield carbon dioxide and water.

Solution The number of kilojoules is calculated for 1 mol , just as was done in Example 15. Then ΔH is calculated for the 23.7 g specified in the problem:

$$\Delta H = 23.7 \text{ g CH}_4 \left(\frac{1 \text{ mol CH}_4}{16.0 \text{ g CH}_4} \right) \left(\frac{-891 \text{ kJ}}{1 \text{ mol CH}_4} \right) = -21.2 \text{ kJ}$$

from the
prior problem

$\square$

EXAMPLE 17 Calculate the enthalpy change for the reaction of CH_4 with oxygen to yield carbon dioxide and 75.9 g of water.

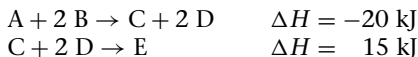
Solution Again the result of Example 15 is used:

$$75.9 \text{ g H}_2\text{O} \left(\frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} \right) \left(\frac{-891 \text{ kJ}}{2 \text{ mol H}_2\text{O}} \right) = -1880 \text{ kJ}$$

Note that the -891 kJ enthalpy change of Example 15 is associated with 2 mol of water in the balanced chemical equation! $\square$

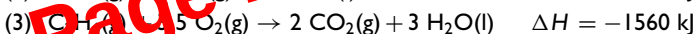
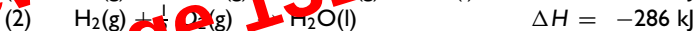
Hess's Law

If enthalpy of formation data are not available but other types of enthalpy data are, and if we can combine the chemical equations for the available reactions to give the desired reaction, we can combine the enthalpy changes in the same way. This is a statement of **Hess's law**. For example, consider the general reactions



We can add these equations and add their associated enthalpy

10. Write an equation to represent each of the following: (a) formation of PCl_3 . (b) fusion of ice. (c) combustion of CH_4 . (d) sublimation of $\text{CO}_2(\text{s})$ (dry ice).
11. Calculate the enthalpy change for the reaction of one mole of C_2H_6 with oxygen to yield carbon dioxide and water.
12. Calculate the quantity of heat required to raise 100.0 g of water from 273.15 K to 293.15 K.
13. A chemical reaction raised the temperature of 200.0 g of a solution ($c = 4.17 \text{ J/g} \cdot ^\circ\text{C}$) by 1.43°C . (a) Calculate the quantity of heat added to the solution. (b) Calculate the quantity of heat released by the chemical reaction.
14. What mass of water rises 10.3°C in temperature when 1.24 kJ of heat is added to it?
15. Calculate the enthalpy change for the reaction of barium oxide with carbon dioxide to yield barium carbonate.
16. Calculate the enthalpy change for the reaction of 175 g of barium oxide with carbon dioxide to yield barium carbonate.
17. Calculate the enthalpy of combustion of carbon monoxide from the enthalpies of formation of carbon monoxide and carbon dioxide.
18. Calculate the enthalpy of the following reaction given the enthalpies of combustion in equations 1 to 3 below:



19. Calculate the enthalpy change for the reaction of C_2H_6 with 46.9 g of oxygen to yield carbon dioxide and water.
20. Calculate the final temperature of the water if 100.0 g of water at 20.0°C and 100.0 g of water at 68.0°C are mixed.
21. The enthalpy of neutralization of a strong acid with a strong base is -55.2 kJ/mol of water formed. If 100.0 mL of 1.00 M NaOH and 100.0 mL of 1.00 M HCl, both at 25.0°C , are mixed, assume that the heat capacity of the resulting solution is $4.18 \text{ J/g} \cdot ^\circ\text{C}$ and that the density of that solution is 1.02 g/mL . (a) Write a balanced chemical equation for the reaction. (b) Determine the number of moles of water that will be formed. (c) Determine the quantity of heat that the reaction will release. (d) How much heat is absorbed by the resulting solution? (e) Calculate the mass of the solution. (f) Calculate the change in temperature of the solution. (g) Calculate the final temperature of the solution.

9. To calculate the value of q for cooling the liquid water to the freezing point takes a specific heat calculation:

$$q = mc\Delta t = (35.0 \text{ g})(4.184 \text{ J/g}\cdot^{\circ}\text{C})(-22.0^{\circ}\text{C}) = -3220 \text{ J}$$

To calculate value of q to freeze the water takes a heat of solidification calculation:

$$35.0 \text{ g} \left(\frac{1 \text{ mol}}{18.0 \text{ g}} \right) \left(\frac{-6.00 \text{ kJ}}{1 \text{ mol}} \right) = -11.7 \text{ kJ}$$

To calculate the value of q for cooling the ice takes a specific heat calculation:

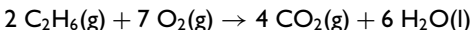
$$q = mc\Delta t = (35.0 \text{ g})(2.089 \text{ J/g}\cdot^{\circ}\text{C})(-10.0^{\circ}\text{C}) = -731 \text{ J}$$

The total heat required is $q = -3.22 \text{ kJ} + (-11.7 \text{ kJ}) + (-0.731 \text{ kJ}) = -15.7 \text{ kJ}$

10. (a) $\text{P(s)} + \frac{3}{2} \text{Cl}_2(\text{g}) \rightarrow \text{PCl}_3(\text{l})$
 (b) $\text{H}_2\text{O(s)} \rightarrow \text{H}_2\text{O(l)}$
 (c) $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O(l)}$
 (d) $\text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g})$
 11. $\text{C}_2\text{H}_6(\text{g}) + \frac{7}{2} \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g}) + 3 \text{H}_2\text{O(l)}$

$$\begin{aligned} \Delta H &= \Delta H_f(\text{products}) - \Delta H_f(\text{reactants}) \\ &= 2\Delta H_f(\text{CO}_2) + 3\Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{C}_2\text{H}_6) - \frac{7}{2}\Delta H_f(\text{O}_2) \\ &= 2(-393 \text{ kJ}) + 3(-286 \text{ kJ}) - (-83.7 \text{ kJ}) - \frac{7}{2}(0 \text{ kJ}) = -1560 \text{ kJ} \end{aligned}$$

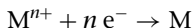
Alternatively,



$$\begin{aligned} \Delta H &= \Delta H_f(\text{products}) - \Delta H_f(\text{reactants}) \\ &= 4\Delta H_f(\text{CO}_2) + 6\Delta H_f(\text{H}_2\text{O}) - 2\Delta H_f(\text{C}_2\text{H}_6) - 7\Delta H_f(\text{O}_2) \\ &= 4(-393 \text{ kJ}) + 6(-286 \text{ kJ}) - 2(-83.7 \text{ kJ}) - 7(0 \text{ kJ}) = -3120 \text{ kJ} \end{aligned}$$

This ΔH is for two moles of C_2H_6 , so we divide this value by 2 to get the value per mole, -1560 kJ . Either method gives the same result.

in the compound. Thus, for a reaction



(1) the more electricity that passed, the greater was the mass of metal produced. (2) the greater the atomic mass of M, the greater was the mass of metal produced. (3) the higher the value of n , the lower was the mass of metal produced.

These generalities are known as Faraday's laws. Fortunately, we do not have to worry about learning Faraday's laws in order to solve problems involving electrolysis cell reactions. All that we need to be able to do is to write net ionic equations for the reactions and remember the values for the constants listed above. As usual, we use dimensional analysis, starting with the quantity given.

EXAMPLE 1 Calculate the mass of copper metal produced from CuSO_4 solution by passage of a 3.00-A current for 7250 seconds.

Solution

$$7250 \text{ s} \left(\frac{3.00 \text{ C}}{1 \text{ s}} \right) \left(\frac{1 \text{ mol } e^{-}}{96,500 \text{ C}} \right) \left(\frac{1 \text{ mol Cu}}{2 \text{ mol } e^{-}} \right) \left(\frac{63.5 \text{ g Cu}}{1 \text{ mol Cu}} \right) = 7.16 \text{ g Cu}$$

from the definition from the equation atomic mass

EXAMPLE 2 Calculate the time required to deposit 7.00 g of silver from a solution of AgNO_3 with a current of 4.00 A.

Solution

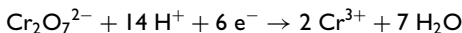
$$7.00 \text{ g Ag} \left(\frac{1 \text{ mol Ag}}{108 \text{ g Ag}} \right) \left(\frac{1 \text{ mol } e^{-}}{1 \text{ mol Ag}} \right) \left(\frac{96,500 \text{ C}}{1 \text{ mol } e^{-}} \right) \left(\frac{1 \text{ s}}{4.00 \text{ C}} \right) = 1560 \text{ s} \quad (26.1 \text{ minutes})$$

If two quantities are given and the current is to be calculated, we convert the quantities given to coulombs and seconds and divide them to get the answer.

EXAMPLE 3 Calculate the current required to deposit 40.0 g of gold from AuCl_3 solution in 7.00 hours.

passes through the other.) If 10.0 g of copper is deposited from CuSO_4 in the first, what mass of silver is deposited from silver nitrate from the second?

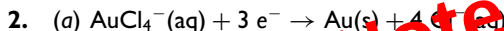
- Calculate the time required to reduce 17.0 g of Sn^{2+} to tin metal with a current of 4.45 A.
- A 1% change in concentration of which of the species in the following half-reaction will make the greatest change in potential?



Solutions to Supplementary Problems

$$1. \quad 3.55 \text{ hours} \left(\frac{3600 \text{ s}}{1 \text{ hour}} \right) \left(\frac{2.75 \text{ C}}{1 \text{ s}} \right) \left(\frac{1 \text{ mol e}^-}{96,500 \text{ C}} \right) \left(\frac{1 \text{ mol Cu}}{2 \text{ mol e}^-} \right) \times$$

$$\left(\frac{63.5 \text{ g Cu}}{1 \text{ mol Cu}} \right) = 11.6 \text{ g Cu}$$

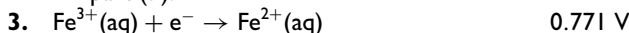


$$145 \text{ g Au} \left(\frac{1 \text{ mol Au}}{197 \text{ g Au}} \right) \left(\frac{3 \text{ mol e}^-}{1 \text{ mol Au}} \right) \left(\frac{96,500 \text{ C}}{1 \text{ mol e}^-} \right) = 213,000 \text{ C}$$

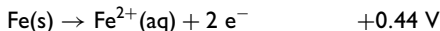
$$225.0 \text{ minutes} \left(\frac{60 \text{ s}}{1 \text{ min}} \right) = 13,500 \text{ s}$$

$$\frac{213,000 \text{ C}}{13,500 \text{ s}} = 15.8 \text{ A}$$

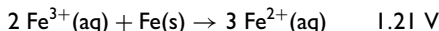
(b) Since 3 hours is 180 minutes, 3 hours and 45.0 minutes is 225.0 minutes, so this problem is exactly the same as that in part (a).



Reversing the second of these equations yields



Multiplying the first equation by 2 to get two moles of electrons in each equation, without changing its potential, then adding this equation to the second yields:



Since the potential is positive, the reaction goes spontaneously as written; iron(II) is produced.

- (a) $\text{C}_2\text{H}_3\text{O}_2^-(\text{aq}) + \text{H}^+(\text{aq}) \rightleftharpoons \text{HC}_2\text{H}_3\text{O}_2(\text{aq})$
 (b) $\text{NaC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{HCl}(\text{aq}) \rightleftharpoons \text{HC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{NaCl}(\text{aq})$
5. Which of the following reactions proceeds more than 50% to completion?
- (a) $\text{HC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{C}_2\text{H}_3\text{O}_2^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
 $\text{HC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{C}_2\text{H}_3\text{O}_2^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$
 (b) $\text{C}_2\text{H}_3\text{O}_2^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{OH}^-(\text{aq})$
 $\text{C}_2\text{H}_3\text{O}_2^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \rightleftharpoons \text{HC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$

Answers to Leading Questions

1. The value of this K is $1/(2.5 \times 10^{-13}) = 4.0 \times 10^{12}$.
2. Whenever water is involved in a reaction but is not the solvent for the reaction. For example, when the reaction is a gas-phase reaction or a reaction in another solvent, the concentration of water is included.
3. Calculation using the value of K . (Remember, we calculated values of K before we used x .)
4. (a) The ions react to form 6.7% of un-ionized acid, leaving 1.3% in the ionic form. It doesn't make any difference which way we write the equation, so if we add reactants or products, the system shifts until the same equilibrium mixture is established. (b) The net ionic equation for this reaction is that given in part (a), so the answer is the same.
5. (a) The first equation represents an equilibrium reaction of a weak acid, that proceeds to the right only a tiny percentage. The second equation represents a reaction of an acid and a base that proceeds almost to completion.
- (b) The first equation represents an equilibrium reaction of the conjugate of a weak acid with water that proceeds to the right only a tiny percentage. (The reverse reaction of an acid with a strong base proceeds almost to completion.) The second equation proceeds extensively, since its reverse is the ionization of a weak acid in water, which we know proceeds only slightly.

Supplementary Problems

1. From the value of the equilibrium constant for



$$K = \frac{[C]}{[A][B]^2} = \frac{(0.100)}{(1.10)(1.50)^2} = 0.0404$$

Compare this solution to that of Example 5, and notice the great difference made by the fact that D is a solid and therefore its concentration is not included in the equilibrium constant expression.

$$4. (a) K = \frac{[C]^2}{[A][B]^2} = \frac{(3.22)^2}{(0.220)(0.456)^2} = 227$$

(b)	A	+ 2 B	⇌ 2 C
Initial concentrations (M)	0.220	0.456	3.22
Change due to reaction (M)	+0.10	+0.20	-0.20
Equilibrium concentrations (M)	0.32	0.66	3.02

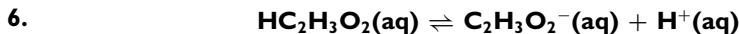
$$K = \frac{[C]^2}{[A][B]^2} = \frac{(3.02)^2}{(0.32)(0.66)^2} = 65$$

(c) Since the rise in temperature caused the equilibrium to shift left (the K is smaller, so the concentration of product is smaller), it is an exothermic reaction.



Initial concentrations (M)	0.100	0.0000	0.0000
Change due to reaction (M)	4.2×10^{-3}	4.2×10^{-3}	4.2×10^{-3}
Equilibrium concentrations (M)	0.096	4.2×10^{-3}	4.2×10^{-3}

$$K_a = \frac{[\text{CHO}_2^-][\text{H}^+]}{[\text{HCHO}_2]} = \frac{(4.2 \times 10^{-3})^2}{0.096} = 1.8 \times 10^{-4}$$



Initial concentrations (M)	0.250	0.150	0.000
Change due to reaction (M)	x	x	x
Equilibrium concentrations (M)	$0.250 - x$	$0.150 + x$	x

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} = \frac{(1.9 \times 10^{-4})^2}{(0.100)} = 3.6 \times 10^{-7}$$

15. $[\text{H}^+] = 6.0 \times 10^{-6}$

	$\text{HA(aq)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{A}^-(\text{aq})$		
Initial			
concentration (M)	0.100	0.000	0.150
Change due to reaction (M)	6.0×10^{-6}	6.0×10^{-6}	6.0×10^{-6}
Equilibrium			
concentration (M)	0.100	6.0×10^{-6}	0.150

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(6.0 \times 10^{-6})(0.150)}{(0.100)} = 9.0 \times 10^{-6}$$

16. The H^+ from the ionization of HCl (a strong acid) represses the ionization of the acetic acid, so the concentration of H^+ is 0.150 M, entirely from the HCl.

	$\text{HC}_2\text{H}_3\text{O}_2(\text{aq}) \rightleftharpoons \text{C}_2\text{H}_3\text{O}_2^-(\text{aq}) + \text{H}^+(\text{aq})$		
Initial			
concentration (M)	0.100	0.000	0.150
Change due to reaction (M)	x	x	x
Equilibrium			
concentration (M)	$0.100 - x$	x	$0.150 + x$

Neglecting x when added to or subtracted from larger values yields

$$K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{(0.150)[\text{C}_2\text{H}_3\text{O}_2^-]}{(0.100)} = 1.8 \times 10^{-5}$$

$$[\text{C}_2\text{H}_3\text{O}_2^-] = 1.2 \times 10^{-5}$$

In 0.100 M acetic acid alone, the acetate ion concentration (equal to the hydrogen ion concentration) is 1.3×10^{-3} M. The hydrogen ion from the strong acid has lowered it to 1.2×10^{-5} M, as predicted by LeChatelier's principle. The presence of any *stronger* acid will repress the ionization of any weaker acid in the same solution.

17. (a) This is not a limiting quantities problem because the two do not react. (b) NH_4^+ and Cl^- . (c) H^+ and OH^- , as in every aqueous solution. (d) $\text{H}_2\text{O(l)} + \text{NH}_3(\text{aq}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$ (e) The

its standard state has a finite (nonzero) entropy, unlike its enthalpy of formation (Chapter 8). $\square$

12.2 Gibbs Free Energy Change

The **free energy change**, ΔG , is equal to the enthalpy change minus the product of the absolute temperature times the entropy change. Its value enables us to predict in which direction an equation will proceed, or if the system is at equilibrium. It is defined as

$$\Delta G = \Delta H - T\Delta S$$

We will use this equation extensively.

EXAMPLE 2 Calculate the free energy change for a reaction at 25°C in which the enthalpy change is 24.4 kJ and the entropy change is 35.1 J/K.

Solution

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= 24.4 \text{ kJ} - (298 \text{ K})(0.0351 \text{ kJ/K}) = 13.9 \text{ kJ}\end{aligned}$$

Note that it was necessary to convert joules to kilojoules (or vice versa) and also that the kelvins in the second term canceled. $\square$

The free energy of a substance, like its enthalpy, is a relative quantity. Similarly, the **standard free energy of formation**, ΔG_f° , of a substance is the free energy change of the reaction of the elements in their standard states to produce the substance in its standard state, quite analogous to the enthalpy of formation. Also analogous is the fact that the free energy of formation of an *element* in its standard state is zero by definition. Standard free energy changes of selected substances are presented in Table 12-2. The equation given above for ΔG , with all quantities in their standard states, becomes:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

We must be very careful to use the degree sign where and only where it is supposed to be used; that sign on the thermodynamic functions means that all substances are in their standard states (Chapter 8). Any equation that is true for ΔG in general is also true for ΔG° (under the special conditions of unit activities for all reactants and products). The reverse is *not* true.

to the molarity ratio *at equilibrium*! If ΔG° is positive, $\ln K$ is negative, and K is less than 1.

EXAMPLE 8 Calculate the value of the equilibrium constant for a reaction with ΔG° equal to 255 J at 25°C. Comment on the magnitude of the constant.

Solution

$$\Delta G^\circ = -RT \ln K = 255 \text{ J} = -(8.31 \text{ J/K})(298 \text{ K}) \ln K$$

$$\ln K = -0.103$$

$$K = 0.902$$

The positive value of ΔG° means that the equilibrium constant has a value less than 1 since it suggests that the equation would spontaneously shift left from its concentrations at unit activity (all 1).

12.4 Relationship of ΔG to Potential

We have seen that a negative value of ΔG means that a reaction may proceed spontaneously in the direction of the equation as written and, in Chapter 9, that an electrochemical reaction will proceed as written if the potential is positive. We may wonder if there is any connection between free energy change and potential, and indeed there is:

$$\Delta G = -\epsilon nF$$

where ϵ is the potential, n is the number of moles of electrons, and F is the Faraday constant, 96,500 C/mol e^- . The minus sign is easy to remember, since the potential is positive and the free energy change is negative for spontaneous reactions.

EXAMPLE 9 Calculate the free energy change for a two-electron reaction in which the potential is -5.00 V .

Solution

$$\begin{aligned}\Delta G &= -\epsilon nF = -(-5.00 \text{ V})(2 \text{ mol } e^-)(96,500 \text{ C/mol } e^-) \\ &= 965,000 \text{ J} = 965 \text{ kJ}\end{aligned}$$

Note that 1 C times 1 V equals 1 J (and that the answer has been converted to kilojoules for significant digit purposes). A negative

$$\begin{aligned}
 \Delta G^\circ &= \Delta G_f^\circ(\text{products}) - \Delta G_f^\circ(\text{reactants}) \\
 &= \Delta G_f^\circ(\text{CO}_2) + 2\Delta G_f^\circ(\text{H}_2\text{O}) - \Delta G_f^\circ(\text{CH}_4) - 2\Delta G_f^\circ(\text{O}_2) \\
 &= (-394.4 \text{ kJ}) + 2 \text{ mol}(-237.13 \text{ kJ/mol}) - (-50.8 \text{ kJ}) - \\
 &\quad 2 \text{ mol}(0 \text{ kJ/mol}) = -817.9 \text{ kJ}
 \end{aligned}$$

For 2.65 g of CH₄:

$$2.65 \text{ g CH}_4 \left(\frac{1 \text{ mol CH}_4}{16.0 \text{ g CH}_4} \right) \left(\frac{-817.9 \text{ kJ}}{1 \text{ mol CH}_4} \right) = -135 \text{ kJ}$$

6. Because ΔH and ΔS do not change much with temperature, we can use their 25°C values at 125°C:

$$\begin{aligned}
 \Delta G &= \Delta H - T\Delta S = 4.22 \text{ kJ} - (398 \text{ K})(-6.10 \text{ J/K}) \\
 &= 4.22 \text{ kJ} + 2.43 \text{ kJ} = 6.65 \text{ kJ}
 \end{aligned}$$

7. $\Delta G = \Delta G^\circ + RT \ln Q$

$$\begin{aligned}
 &= \Delta G^\circ + (8.31 \text{ J/K})(298 \text{ K}) \ln \frac{[\text{C}]}{[\text{A}]^2[\text{B}]} \\
 &= (-877 \text{ J}) + (8.31 \text{ J/K})(298 \text{ K}) \ln \frac{(0.34 \text{ M})}{(0.50)^2(1.75)} = -3580 \text{ J}
 \end{aligned}$$

- 8.

$$\begin{aligned}
 \Delta G &= -\epsilon n F \\
 -12,700 \text{ J} &= -(0)(\text{mol e}^-)(96,500 \text{ C/mol e}^-) \\
 \epsilon &= 0.131 \text{ V}
 \end{aligned}$$

Note: ϵ divided by 1 C equals 1 V.

9. For the reaction to be nonspontaneous, ΔG must be zero (or positive).

$$\begin{aligned}
 \Delta G &= 0 = \Delta G^\circ + RT \ln Q \\
 0 &= -1000 \text{ J} + (8.31 \text{ J/K})(298 \text{ K}) \ln Q \\
 \ln Q &= 0.404 \\
 Q &= 1.50
 \end{aligned}$$

10. For the reaction to be nonspontaneous, ΔG must be zero (or positive).

$$\begin{aligned}
 \Delta G &= \Delta H - T\Delta S \\
 0 &= (-5010 \text{ J}) - T(-10.0 \text{ J/K}) \\
 T &= 501 \text{ K}
 \end{aligned}$$

$$\Delta G^\circ = -RT \ln K$$

$$\ln K = -\frac{(-817,900 \text{ J})}{(8.31 \text{ J/K})(298 \text{ K})} = 330$$

$$\log K = (\ln K)/(\ln 10) = 330/(2.303) = 143$$

$$K = 10^{143}$$

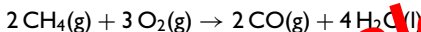
This huge value of K corresponds to the very large magnitude of ΔG° .

16. $\Delta G^\circ = -RT \ln K = -\epsilon^\circ n F$

$$\ln K = \frac{\epsilon^\circ n F}{RT} = \frac{(-0.00100 \text{ V})(2)(96,500 \text{ C})}{(8.31 \text{ J/K})(298 \text{ K})} = -0.0779$$

$$K = 0.925$$

17. (a) For 2 mol of $\text{CH}_4(\text{g})$:



$$\Delta G^\circ = \Delta G_f^\circ(\text{products}) - \Delta G_f^\circ(\text{reactants})$$

$$= 2\Delta G_f^\circ(\text{CO}) + 4\Delta G_f^\circ(\text{H}_2\text{O}) - 2\Delta G_f^\circ(\text{CH}_4) - 3\Delta G_f^\circ(\text{O}_2)$$

$$= 2(-137.2 \text{ kJ}) + 4(-237.13 \text{ kJ}) - 2(-50.8 \text{ kJ}) - 3(0 \text{ kJ})$$

$$= -1,121.3 \text{ kJ}$$

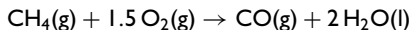
$$\Delta G^\circ = -RT \ln K$$

$$\ln K = \frac{1,121,300 \text{ J}}{(8.31 \text{ J/K})(298 \text{ K})} = 453$$

$$\log K = (\ln K)/(\ln 10) = 453/2.303 = 197$$

$$K = 10^{197}$$

(b) For 1 mol of $\text{CH}_4(\text{g})$:



$$\Delta G^\circ = \Delta G_f^\circ(\text{products}) - \Delta G_f^\circ(\text{reactants})$$

$$= \Delta G_f^\circ(\text{CO}) + 2\Delta G_f^\circ(\text{H}_2\text{O}) - \Delta G_f^\circ(\text{CH}_4) + 1.5\Delta G_f^\circ(\text{O}_2)$$

$$= (-137.2 \text{ kJ}) + 2(-237.13 \text{ kJ}) - (-50.8 \text{ kJ}) - 1.5(0 \text{ kJ})$$

$$= -560.7 \text{ kJ}$$

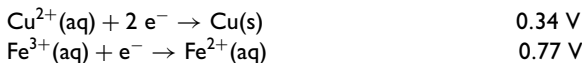
Note that the increase in pressure of 100.0% did *not* decrease the volume 100.0%.

$$26. \quad q = 0 = m_{\text{water}} c_{\text{water}} \Delta t_{\text{water}} + m_{\text{metal}} c_{\text{metal}} \Delta t_{\text{metal}}$$

$$0 = (242 \text{ g})(4.184 \text{ J/g}^\circ\text{C})(t - 14.5^\circ\text{C}) + (43.9 \text{ g})(0.451 \text{ J/g}^\circ\text{C})(t - 59.3^\circ\text{C})$$

$$t = 15.4^\circ\text{C}$$

27. The two reduction half-cells are



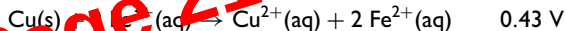
We reverse the equation with the lower potential, and change the sign of the potential:



We multiply the other equation by 2 to get equal numbers of electrons, without changing the potential:



All that is left to do is to add these equations, and add the corresponding potentials:



$$28. \quad 1.50 \text{ L} \left(\frac{1000 \text{ mL}}{1 \text{ L}} \right) \left(\frac{13.6 \text{ g}}{1 \text{ mL}} \right) \left(\frac{1 \text{ mol Hg}}{200.6 \text{ g}} \right) \left(\frac{6.02 \times 10^{23} \text{ atoms}}{1 \text{ mol}} \right) = 6.12 \times 10^{25} \text{ atoms}$$

29. The total heat involved is the sum of the heats of three steps:

$$q = mc\Delta t = (51.7 \text{ g})(4.184 \text{ J/g}^\circ\text{C})(-50.3^\circ\text{C}) = -10.9 \text{ kJ}$$

$$51.7 \text{ g} \left(\frac{-335 \text{ J}}{1 \text{ g}} \right) = -17.3 \text{ kJ}$$

$$q = mc\Delta t = (51.7 \text{ g})(2.089 \text{ J/g}^\circ\text{C})(-5.4^\circ\text{C}) = -0.58 \text{ kJ}$$

The total heat required is

$$(-10.9 \text{ kJ}) + (-17.3 \text{ kJ}) + (-0.58 \text{ kJ}) = -28.8 \text{ kJ}$$

$$30. \quad \Delta G^\circ = -RT \ln K$$

$$= -(8.31 \text{ J/K})(298 \text{ K}) \ln(4.44) = -3.69 \times 10^3 \text{ J} = -3.69 \text{ kJ}$$

Ideal gas law. $PV = nRT$.

Indicator (acid-base). A compound that is one color in acid solution and a different color in base solution, used to signal the end point of an acid-base titration.

Joule. The SI unit of energy.

Kelvin. The unit of the absolute (Kelvin) temperature scale.

Kinetic molecular theory. The theory that explains the behavior of gases (and other phases) in terms of the properties of their molecules.

KMT. Kinetic molecular theory.

Law of combining volumes. The ratio of the volumes of gases in a given chemical reaction, all measured at the same temperature and pressure, are in the ratio of the coefficients of the balanced chemical equation.

Law of conservation of mass. In any chemical reaction (or physical change), mass cannot be created or destroyed.

Law of definite proportions. Each (pure) compound is composed of the same percentage by mass of its elements. For example, every sample of pure water is 88.8% oxygen and 11.2% hydrogen by mass.

Law of multiple proportions. For two or more compounds consisting of the same elements, for a given mass of one of the elements the masses of the other element(s) are in a small, integral ratio.

Le Chatelier's principle. If a stress is applied to a system at equilibrium, the equilibrium will tend to shift in an effort to reduce the stress.

Limiting quantity. The quantity of one reactant in a chemical reaction that is not sufficient to react with all the other reactant(s) present.

Liter. The unit of volume in the (older) metric system.

Meter. The basic unit of length in the metric system.

Metric system. The system of units used by scientists in which multiples or subdivisions of units are powers of 10 times the unit, and all such multiples or subdivisions are designated by the same prefix no matter what unit is involved.

Millimole. One-thousandth of a mole.

Molal. The unit of molality.

Molality. The number of moles of solute per kilogram of solvent in a solution.

Molar. The unit of molarity.

Molar mass. The formula mass of any substance, expressed in grams per mole.

cubic meter as the unit of volume rather than the liter, and pascals used for pressure.)

Significant digit. A digit in a properly reported value that indicates the precision with which a measurement was made.

Significant figure. Significant digit.

Specific heat. The heat required to raise one gram of a substance 1°C .

Standard. The defined quantity against which all other quantities are compared. For example, the *standard* of mass (in SI as well as legally in the United States) is the kilogram, whereas the gram is the *unit* of mass.

Standard absolute entropy. The entropy of a substance compared to its entropy when crystalline and at 0 K.

Standard enthalpy of formation. The enthalpy change in a process of forming a substance in its standard state from its elements in their standard states.

Standard exponential notation. Scientific notation.

Standard free energy of formation. Free energy of formation when each substance is at unit activity.

Standard half-cell. A half-cell in which each substance is at unit activity.

Standard reduction potential. The reduction potential of a half-cell in which each substance is at unit activity.

Standard state. A state in which each substance is at unit activity.

Standard temperature and pressure. 0°C and 1 atm pressure.

Stoichiometry. The study of the quantitative relationships among substances in a chemical reaction.

STP. Standard temperature and pressure.

Sublimation. The passage of a substance from the solid state directly to the gaseous state.

System internationale. SI—the modern version of the metric system.

Titration. The technique in which a measured volume of one solution is treated with a measured volume of another, in which the known molarity of one solution allows the calculation of the molarity of the other.

Unit activity. Pure solids and liquid, 1 M solute, and/or gas at 1 atm pressure.

Vaporization. Passage of a liquid into the gas phase.

Vapor-pressure lowering. The reduction of the vapor pressure of a solution (compared to the pure solvent) due to the presence of the solute.

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