3

Stoichiometry

This chapter is concerned with stoichiometry. As with all the chapters in Part II, there are several sections: overview, several specific technical topics, illustrative open-ended problems, and open-ended problems. The purpose of the first section is to introduce the reader to the subject of stoichiometry. As one might suppose, a comprehensive treatment is not provided although several sections addressing additional specific technical topics are included. The next section contains three open-ended problems; the authors' solution (there may be other solutions) is also provided. The last section contains 44 problems; *no* solutions are provided here.

3.1   Overview

This overview section is concerned with stoichiometry. As one might suppose, it was not possible to address all topics directly or indirectly related to stoichiometry. However, additional details may be obtained from either the references provided at the end of this Overview and/or at the end of the chapter.

Note: Readers already familiar with the details associated with this subject may choose to bypass this Overview.

In order to better understand the design as well as the operation and performance of equipment in the chemical industry, it is necessary for chemical engineers (as well as applied scientists) to understand the fundamentals and principles underlying stoichiometry. How can one predict what products will be emitted from effluent streams? At what temperature must a unit be operated to ensure the desired performance? How much energy in the form of heat is given off? Is it economically feasible to recover this heat? Is the design appropriate? The answers to these questions are rooted not only in stoichiometry but also in the various theories of chemistry, physics, and applied economics.

The remaining topics covered in this section include:

1. The Conservation Law
2. The Conservation Laws for Mass, Energy and Momentum
3. Stoichiometry

Note: the bulk of the material in this chapter has been drawn from the original work of Reynolds [1].

3.2   The Conservation Law

Mass, energy and momentum are all conserved. As such, each quantity obeys the general conservation law below, as applied within a system.

$$
\begin{Bmatrix} quantity \\ into \\ system \end{Bmatrix} - \begin{Bmatrix} quantity \\ out\ of \\ system \end{Bmatrix} + \begin{Bmatrix} quantity \\ generated \\ in\ system \end{Bmatrix} = \begin{Bmatrix} quantity \\ accumulated \\ in\ system \end{Bmatrix} \quad (3.1)
$$

Equation (3.1) may also be written on a *time* basis:

$$
\begin{Bmatrix} rate\ of \\ quantity \\ into \\ system \end{Bmatrix} - \begin{Bmatrix} rate\ of \\ quantity \\ out\ of \\ system \end{Bmatrix} + \begin{Bmatrix} rate\ of \\ quantity \\ generated \\ in\ system \end{Bmatrix} = \begin{Bmatrix} rate\ of \\ quantity \\ accumulated \\ in\ system \end{Bmatrix} \quad (3.2)
$$

The conservation law may be applied by the practitioner at the *macroscopic, microscopic*, or *molecular* level. One can best illustrate the differences in these methods with an example. Consider a system in which a fluid is flowing through a cylindrical tube (see Figure 3.1). One can define the system as the fluid contained within the tube between points 1 and 2 at any time.

If one is interested in determining changes occurring at the inlet and outlet of the system, the conservation law is applied on a macroscopic level to the entire system. The resultant equation describes the *overall* changes occurring *to* the system without regard for internal variations *within* the system. This approach is usually applied by the practicing chemical engineer.

The microscopic approach is employed when detailed information concerning the behavior *within* the system is required, and this is often requested of and by the chemical engineer or scientist. The conservation law is then applied to a *differential* element within the system which is large compared to an individual molecule, but small compared to the entire system. The resultant equation is then expanded, via integration, to describe the behavior of the entire system. This is defined by some as the *transport phenomena* approach [2,3].

The molecular approach involves the application of the conservation law to individual molecules. This leads to a study of statistical and quantum mechanics—both of which are beyond the scope of this text. In any case, the description of individual molecules at the molecular level is of little value to the practicing chemical engineer. However, the statistical averaging of molecular quantities in either a differential or finite element within a system leads to a more meaningful description of the behavior of the system.

The macroscopic approach is primarily adopted and applied in this text, and little to no further reference to microscopic or molecular analyses will be made. This chapter's aim, then, is to express the laws of conservation for mass, energy, and momentum in algebraic or finite difference form.

Figure 3.1 Conservation law application.

3.3   Conservation of Mass, Energy, and Momentum [1]

The *conservation law* for mass can be applied to any process, equipment, or system. The general form of this law is given by Equations (3.3) and (3.4).

$$
\left\{ \begin{array}{c} mass \\ in \end{array} \right\} - \left\{ \begin{array}{c} mass \\ out \end{array} \right\} + \left\{ \begin{array}{c} mass \\ generated \end{array} \right\} = \left\{ \begin{array}{c} mass \\ accumulated \end{array} \right\}
$$

$$
I \quad - \quad O \quad + \quad G \quad = \quad A
$$

(3.3)

or on a time rate basis by

$$
\left\{ \begin{array}{c} rate\ of \\ mass \\ in \end{array} \right\} - \left\{ \begin{array}{c} rate\ of \\ mass \\ out \end{array} \right\} + \left\{ \begin{array}{c} rate\ of \\ mass \\ generated \end{array} \right\} = \left\{ \begin{array}{c} rate\ of \\ mass \\ accumulated \end{array} \right\}
$$

$$
I \quad - \quad O \quad + \quad G \quad = \quad A
$$

(3.4)

The *law of conservation of mass* states that mass can neither be created nor destroyed. Nuclear reactions, in which interchanges between mass and energy are known to occur, provide a notable exception to this law. Even in chemical reactions, a certain amount of mass-energy interchange takes place. However, in normal chemical engineering applications, nuclear reactions do not occur and the mass-energy exchange in chemical reactions is so minuscule that it is not worth taking into account.

The *law of conservation of energy*, which like the law of conservation of mass, applies for all processes that do not involve nuclear reactions, states that energy can neither be created nor destroyed. As a result, the energy level of the system can change only when energy crosses the system boundary, i.e.,

$$
\Delta \left(\text{Energy level of system} \right) = \text{Energy crossing boundary} \quad (3.5)
$$

(Note: The symbol "Δ" means "change in".) Energy crossing the boundary can be classified in one of two different ways: *heat*, Q, or *work*, W. *Heat* is energy moving between the system and the surroundings by virtue of a temperature driving force and heat flows from high temperature to low temperature. The entire system is not necessarily at the same temperature; neither are the surroundings. If a portion of the system is at a higher temperature than a portion of the surroundings and as a result, energy is transferred from the system to the surroundings, that energy is classified as heat. If part of the system is at a higher temperature than another part of the system and energy is transferred

between the two parts, that energy is *not* classified as heat because it is *not* crossing the boundary. Work is also energy moving between the system and surroundings, but the driving force here is something other than temperature difference, e.g., a mechanical force, a pressure difference, gravity, a voltage difference, a magnetic field, etc. Note that the definition of work is a *force acting through a distance*. All of the examples of driving forces just cited can be shown to provide a force capable of acting through a distance [4].

The energy level of a system has three contributions: kinetic energy, potential energy, and internal energy. Any body in motion possesses kinetic energy. If the system is moving as a *whole*, its kinetic energy, E_k, is proportional to the mass of the system and the square of the velocity of its center of gravity. The phrase "as a whole" indicates that motion inside the system relative to the system's center of gravity does not contribute to the E_k term, but rather to the internal energy term. The terms *external kinetic energy* and *internal kinetic energy* are sometimes used here. An example would be a moving railroad tank car carrying propane gas. (The propane gas is the system.) The center of gravity of the propane gas is moving at the velocity of the train, and this constitutes the system's external kinetic energy. The gas molecules are also moving in random directions relative to the center of gravity and this constitutes the system's internal energy due to motion inside the system, i.e., internal kinetic energy. The potential energy, E_p, involves any energy the system as a whole possesses by virtue of its position (more precisely, the position of its center of gravity) in some force field, e.g., gravity, centrifugal, electrical, etc., that provides the system with the potential for accomplishing work. Again, the phase "as a whole" is used to differentiate between *external* potential energy, E_p, and *internal* potential energy. *Internal potential energy refers* to potential energy due to force fields inside the system. For example, the electrostatic force fields (bonding) between atoms and molecules provide these particles with the potential for work. The *internal energy*, U, is the sum of all internal kinetic and internal potential energy contributions [4].

The *law of conservation of energy*, which is also called the *first law of thermodynamics*, may now be written as

$$\Delta(U + E_k + E_p) = Q + W \qquad (3.6)$$

or equivalently as

$$\Delta U + \Delta E_k + \Delta E_p = Q + W \qquad (3.7)$$

It is important to note the sign convention for Q and W adapted for the above equation. Since any term is always defined as the final minus the

initial state, both the heat and work terms must be positive when they cause the system to gain energy, i.e., when they represent energy flowing from the surroundings to the system. Conversely, when the heat and work terms cause the system to lose energy, i.e., when energy flows from the system to the surroundings, they are negative in sign. This sign convention is not universal and the reader must take care to check what sign convention is being used by a particular author when referring to the literature. For example, work is often defined in some texts as positive when the system does work on the surroundings [4,5].

The conservation law for momentum is treated in Chapter 5.

3.4   Stoichiometry [1]

When chemicals react, they do so according to a strict proportion. When oxygen and hydrogen combine to form water, the ratio of the amount of oxygen to the amount of hydrogen consumed is always 7.94 by mass and 0.500 by moles. The term *stoichiometry* refers to this phenomenon, which is sometimes called the *chemical law of combining weights*. The reaction equation for the combining of hydrogen and oxygen is

$$2H_2 + O_2 = 2H_2O \tag{3.8}$$

In chemical reactions, atoms are neither generated nor consumed, merely rearranged with different bonding partners. The manipulation of the coefficients of a reaction equation so that the number of atoms each element on the left of the equation is equal to that on the right is referred to as *balancing* the equation. Once the equation is balanced, the whole number molar ratio that must exist between any two components of the reaction can be determined simply by observation; these are known as *stoichiometric ratios*. There are three such ratios (not counting the reciprocals) in the above reaction. These are:

2 mol H_2 consumed/mol O_2 consumed
1 mol H_2O generated/mol H_2 consumed
2 mol H_2O generated/mol O_2 consumed

The unit mole represents either the *gmol* or the *lbmol*. Using molecular weights, these stoichiometric ratios (which are molar ratios) may easily be converted to mass ratios. For example, the first ratio above may be

converted to a mass ratio by using the molecular weights of H_2 (2.016) and O_2 (31.999) as follows:

(2 gmol H_2 consumed)(2.016 g/gmol) = 4.032 g H_2 consumed
(1 gmol O_2 consumed)(31.999 g/gmol) = 31.999 g H_2 consumed

The mass ratio between the hydrogen and oxygen consumed is therefore

4.032/31.999 = 0.126 g H_2 consumed/g O_2 consumed

These molar and mass ratios are used in material balances to determine the amounts or flow rates of components involved in chemical reactions.

Multiplying a balanced reaction equation through by a constant does nothing to alter its meaning. The reaction used as an example above is often written

$$H_2 + \frac{1}{2}O_2 = H_2O \qquad (3.9)$$
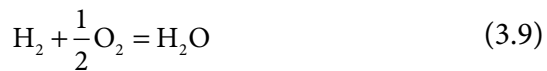
In effect, the stoichiometric coefficients of Equation (3.8) have been multiplied by 0.5. There are times, however, when care must be exercised because the solution to the problem depends on the manner or form the reaction is written. This is the case with chemical equilibrium problems and problems involving thermochemical reaction equations. These are addressed in the next chapter.

There are three different types of material balances that may be written when a chemical reaction is involved: the *molecular balance*, the *atomic balance*, and the *"extent of reaction" balance*. It is a matter of convenience which of the three types is used. Each is briefly discussed below.

The molecular balance is the same as that described earlier. Assuming a steady-state continuous reaction, the accumulation term, a, is zero for all components involved in the reaction, the balance equation (3.3) becomes

$$I + G = O + C \qquad (3.10)$$

where C = consumption

If a total material balance is performed, the above form of the balance equation must be used if the amounts or flow rates are expressed in terms of moles, e.g., lbmol or gmol/h, since the total number of moles can change

during a chemical reaction. If, however, the amounts or flow rates are given in terms of mass, e.g., kg or lb/h, the G and C terms may be dropped since mass cannot be gained or lost in a chemical reaction. Thus,

$$I = O \qquad (3.11)$$

In general, however, when a chemical reaction is involved, it is usually more convenient to express amounts and flow rates using moles rather than mass.

A material balance that is not based on the chemicals (or molecules), but rather on the atoms that make up the molecules, is referred to as an atomic balance. Since atoms are neither created nor destroyed in a chemical reaction, the G and C terms equal zero and the balance once again becomes

$$I = O \qquad (3.11)$$

As an example, consider once again the combination of hydrogen and oxygen to form water

$$2H_2 + O_2 = 2H_2O \qquad (3.8)$$

As the reaction progresses, O_2 and H_2 molecules (or moles) are consumed while H_2O molecules (or moles) are generated. On the other hand, the number of oxygen atoms (or moles of oxygen atoms) and the number of hydrogen atoms (or moles of hydrogen atoms) do not change. Care must also be taken to distinguish between molecular oxygen and *atomic* oxygen. If, in the above reaction, one starts out with 1000 lbmol of O_2 (oxygen molecules), one is also starting out with 2000 lbmol of O (oxygen atoms).

A detailed an expanded treatment of stoichiometry is available in the following two references:

1. D. Green and R. Perry, *Perry's Chemical Engineers' Handbook,* 8th edition, McGraw-Hill, New York City, NY, 2008 [5].
2. L. Theodore, *Chemical Engineering: The Essential Reference*, McGraw-Hill, New York City, NY, 2014 [6].

3.5   Illustrative Open-Ended Problems

This and the last Section provide open-ended problems. However, solutions *are* provided for the three problems in this Section in order for the reader to hopefully obtain a better understanding of these problems, which differ from the traditional problems/illustrative examples. The first problem is relatively straightforward while the third (and last problem) is somewhat more difficult and/or complex. Note that solutions are not provided for the 44 open-ended problems in the next Section.

Problem 1: There are four methods that can be used to characterize an emission source. These include the use of:

1.   emission factors;
2.   mass balance considerations;
3.   engineering calculations, and;
4.   direct emission measurements.

Describe each of these approaches and indicate what conditions one may be utilized over the other.

Solution: One approach to describing four methods for source characterization is provided below, by highlighting the strengths and weaknesses of each.

1. *Emission factors* are emission rates that have been compiled by EPA and/or other regulatory agencies based on data generated from a given source that are normalized to some unit of production or rate of chemical use, i.e., mass of formaldehyde released from a vehicle or vehicle-driven mile or the mass of butadiene released/gal of product transferred, etc. These factors are compiled for an industry and/or a process on a product-specific basis so that emission rates from similar operations can be estimated without having to repeat direct measurements or detailed calculations for a given emission source. Emission factors are very useful in developing screening-level estimates of emission rates from a large number of sources where time and/or money are limited. They do suffer from significant inaccuracies, however, if the factor utilized is obtained from a process not closely related to the one for which emission rates are being predicted.

2. *Mass balance considerations* involve the evaluation of a chemical process or system as a whole in terms of the mass of reactants added to the

system and the mass of products generated on a constituent by constituent basis. This tracking of constituent mass is termed the aforementioned mass balance approach, and because one knows that mass cannot be created nor destroyed, the mass of any species added to the system that cannot be accounted for in the product must either have been retained within the system or released from the system as a liquid, solid, or gaseous stream. This method requires that the mass flow rate of all influent and effluent streams can be quantified accurately, and that the chemical reactions taking place within the system, if any, are understood.

3. Engineering calculations involve the prediction of emission rates from chemical processes and product storage, transport, treatment, or disposal systems based on fundamental science and engineering principles. These calculations generally involve the use of chemical property data (solubility, vapor pressure, viscosity, density, diffusivity, etc.), the physical system (volume, depth, surface area, etc.) and operating conditions (flow rate, mixing rate, temperature, etc.) to estimate specific releases from a given process.

4. *Direct emission measurements* involve the direct determination of emission rates from specific sources. These measurements provide input to emission factors and engineering calculation approaches. The direct measurement approach is the only true way to generate accurate emission rates for a given source operating under a given set of conditions.

Problem 2: Develop an equation describing the adiabatic flame temperature of a hydrocarbon as a function of its net heating value and the excess air employed in the (combustion) process.

Comment: Refer to Theodore, et al [7] and Santoleri, et al [8] for details.

Solution: Some reasonable assumptions can be made to simplify the rigorous approach for calculations involving the adiabatic flame temperature. When compared to the rigorous approach, a simpler (and in many instances, a more informative) set of equations results that are valid for purposes of engineering calculation. One such approach is detailed below [8].

1. The sensible enthalpy change associated with the cooling step can in many instances be neglected compared to the net heating value (combustions step) of the combined waste-fuel mixture. For this condition,

$$\Delta H_{st} = \Delta H_e = \Delta H_w = \Delta H_f = 0 \qquad (3.12)$$

2. Although the products of combustion include many components, the major or primary components are nitrogen, carbon dioxide, and water (vapor). The average heat capacities of these components over the temperature range 60–2000°F (the latter being a typically incinerator operating temperature) are 0.27, 0.27, and 0.52 Btu/lb•°F, respectively. The arithmetic average of these three components is 0.35. However, since this product stream consists primarily of nitrogen, the average heat capacity of the combined mixture (not including the excess air) may be assigned a value of approximately 0.3 Btu/lb•°F.

3. The average heat capacity of the (excess) air is ≈0.27 Btu/lb•°F over the temperature range 60-2000°F. This value may be rounded to 0.30.

$$\Delta H_e = m_e (0.3)(T - T_0) \tag{3.13}$$

where m_e = mass of excess air per unit mass of waste-fuel mixture (lb/lb mixture)

4. There is no heat loss under truly adiabatic conditions.

5. Since most of the heating value data are available at 60°F, the reference or standard temperature should be arbitrarily set to this condition, i.e., 60°F, and NHVs should be obtained at approximately this temperature.

6. Perhaps the key assumption in this development is that associated with the stoichiometric air requirements for the combined waste-fuel mixture. Interestingly, the stoichiometric air requirement, v_{se} (ft³ air/lb mixture), divided by the NHV for many hydrocarbons is approximately 0.01 ft³ air/Btu (or 100 Btu/ft³air). Using the density of air at 60°F, this ratio can be converted to approximately 750 lb air/10⁶ Btu or 7.5×10^{-4} lb air/Btu. Thus, for this condition the stoichiometric air requirement (m_{st}) is given by:

$$m_{st} = 7.5 \times 10^{-4} \ NHV \tag{3.14}$$

7. Applying the six assumptions listed above results in the following equation for the adiabatic flame temperature, T, in terms of the excess air, EA, and the net heating value, NHV.

$$T = 60 + \frac{\text{NHV}}{(0.3)\left[1 + (1 + \text{EA})(7.5 \times 10^{-4})(\text{NHV})\right]} \qquad (3.15)$$

Note: The units of T and *NHV* are °F and Btu/lb, respectively; *EA* is a dimensionless fraction.

Santoleri, et al [8] provides additional details. This topic is also revisited in Part III, Chapter 25—Thermodynamics Term Projects.

Problem 3: The heat-generating unit in a coal-fired power plant may be simply described as a continuous-flow reactor, into which fuel (mass flow rate F) and air (mass flow rate A) are fed, and from which effluents ("flue gas", mass flow rate E) are discharged.

1. Draw a flow diagram representing this process. Show all flows into and out of the unit. Write a mass balance equation for this process.
2. Suppose the fuel contains a mass fraction y of incombustible component C (for example, ash). Assume that all of the ash is carried out of the reactor with the flue gas (note that in reality, a fraction of the ash generated will remain within the heat-generating unit as bottom ash and must be removed periodically). Write a mass balance equation for component C. What is the mass fraction (z) of C in the exit stream E? Quantitatively discuss the effect of increasing the combustion air flow upon z?
3. Suppose a fraction x of the flue gas is recycled to the inlet of the "reactor". (This is commonly done to help suppress the formation of pollutants, primarily NO_x). Redraw the flow diagram, including the recycle stream (R). Write a mass balance equation for the overall process, and a mass balance equation around the reactor only. Quantitatively discuss how these equations are different from that in [1].
4. An air pollution control device is added to the exhaust stream. It is able to remove x% of the incombustible pollutant C by scrubbing with water. Let S be the mass flow rate of scrubbed material in the water stream. Add this air pollution control unit to the flow diagram, and include all process

streams into and out of the unit. Express S in terms of F, A, and E for various % values of x.

Solution

1. The mass balance is simply F+A=E as indicated in the simple flow diagram in Figure 3.2
2. Since C is not combustible, $C_{in} = C_{out}$, so a component mass balance on C gives

$$yF +(0) A = xE \qquad (3.16)$$

Using $E = F + A$, yields $yF = z(F + A)$, and $z = y (F/(F + A))$.Therefore, increasing the flow rate A decreases the mass fraction of C in the exhaust (a dilution effect). (This is the reason that *effluent* concentrations are often given at a specified excess air concentrations).

3. The new flow diagram can be drawn as indicated below in Figure 3.3. The overall mass balance is unchanged at:

$$F+A=E \text{ (unchanged)} \qquad (3.17)$$

The mass balance around the reactor becomes:

$$F + A + xE = (1 + x) E \qquad (3.18)$$

$$F + A = E \text{ (also unchanged)} \qquad (3.19)$$

Note that one must specify the recycle amount (x) or some other information regarding concentrations to determine the recycle rate since it cannot be determined from these equations alone.
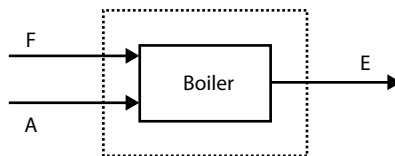
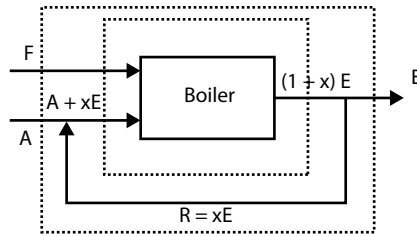

Figure 3.2 Boiler flow diagram.
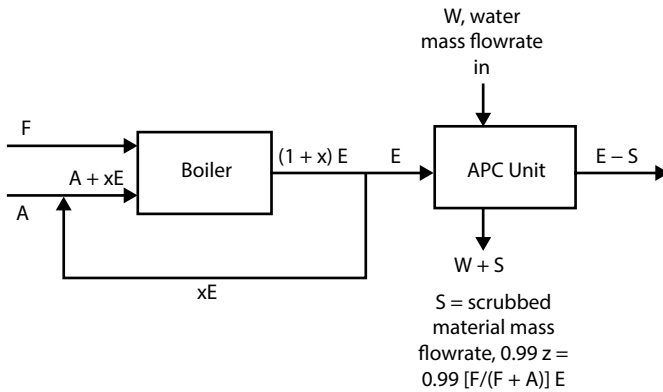
Figure 3.3 Revised boiler flow diagram.

Figure 3.4 Boiler flow diagram with air pollution control unit.

4. The final revised flow diagram with the air pollution control unit takes the form provided in Figure 3.4.

3.6   Open-Ended Problems

This last Section of the chapter contains open-ended problems as they relate to stoichiometry. No detailed and/or specific solution is provided; that task is left to the reader, noting that each problem has either a unique solution or a number of solutions or (in some cases) no solution at all. These are characteristics of open-ended problems described earlier.

There are comments associated with some, but not all, of the problems. The comments are included to assist the reader while attempting to solve the problems. However, it is recommended that the solution to each problem should initially be attempted without the assistance of the comments.

There are 44 open-ended problems in this Section. As stated above, if difficulty is encountered in solving any particular problem, the reader should next refer to the comment, if any is provided with the problem.

The reader should also note that the more difficult problems are generally located at or near the end of the Section.

1. Select a refereed, published article on stoichiometry from the literature and provide a review.
2. Provide some normal everyday domestic applications involving the general topic of stoichiometry.
3. Develop an original problem in stoichiometry that would be suitable as an illustrative example in a book.
4. Prepare a list of the various books which have been written on stoichiometry. Select the three best and justify your answer. Also select the three weakest books and justify your answer.
5. Provide a layman's definition of stoichiometry.
6. Provide a technical definition of stoichiometry.
7. The relationship between the mass of reactants and products involved in a chemical reaction can be derived from a consideration of the equation for the reaction in question and the molecular weights of the materials involved. Should this type of analysis be performed on a mass, mole, or molecular (atomic) basis? Explain your response.
8. Interview a practicing chemical engineer and request his description of the chemical engineering profession and what a chemical engineer does.
9. List the various sources of information available in literature for the chemical engineer.
10. Search the internet (or library) and report on the careers of at least three major players in the chemical engineering field.
11. Develop another method of scientific notation of numbers. Comment: Should a log scale be considered?
12. Develop another set of notations that can be employed in chemical engineering.
13. Develop an equation that relates the atomic number of an element with its atomic weight. Comment: A table of (international) atomic weights is obviously required.
14. List the various systems of units employed by chemical engineers. Also, develop another system of units.
15. Develop another set of units for pressure.
16. There are presently four temperature scales that the practicing engineer employs. Develop another temperature scale that one might consider using in certain applications.

Comment: Carefully review the °C, °F, K, and °R tempera-
ture scales and the relationship between each of the scales.
In addition, should consideration be given to basing the
new scale on the melting and/or boiling point of a particu-
lar element or compound?

17. List the quantities that are conserved. How many conserva-
tion laws are there?

18. The composition of a gas, liquid, or solid mixture can be
expressed in many ways. List and describe at least three of
them.

19. Describe the concept of a "basis" in stoichiometric calcula-
tions to a layman.

20. Select common examples from everyday life that can be
describe as *purge*, *bypass*, and *recycle*.

21. Obtain the density or specific gravity of a solid from several
sources in the literature. Explain the variation of values.
Comment: Review the various definitions of density for
solids.

22. Generate a series of equations that could be used to
describe the vapor pressure of water as a function of
temperature.

23. Many years ago, one of the authors as part of a consulting job
was asked to convert the Mollier Chart into equation form.
You have been assigned that task.
Comment: This will require regressing Mollier Chart infor-
mation data. Some probability and statistics background is
required.

24. Provide a layman's definition of the *wet-bulb* temperature
and *dry-bulb* temperature. Also describe the difference
between the two.

25. Convert a standard humidity chart into equation form.
Include as many properties as possible in the correlation.

26. Describe what, if any, advantages are derived from basing
humidity data on a mole basis.

27. Prepare another type of humidity chart that one could
potentially obtain a copyright on.

28. Describe how to best evaluate the constants in an equation of
state.

29. Develop another real or ideal gas law.
Comment: Carefully review all the laws that have been
developed previously.

30. Describe the Buckingham π approach to dimensional analysis. Include a procedure to follow in employing this method of analysis.
31. List all possible terms that are required for an energy balance on a chemical reactor. Also list the quantitative information required in an energy analysis of the system.
32. All forms of energy must be included in an energy balance. Describe the various forms of energy, including those that are not easily recognized in everyday life. Be sure to consider all forms of energy.
33. It is difficult to distinguish between energy and mass at the atomic and subatomic levels. Discuss this relationship and its relevance to Einstein's energy equation.
34. There are various equations (linear, parabolic, etc.) in the literature that describe heat capacity variations with temperature. Discuss the advantages and disadvantages of the various forms of these describing equations.
35. Select several chemicals from the literature that provide heat capacity variation with temperature. Develop equations of your choice that describe the temperature variation.
36. Describe what, if any, advantages are derived from basing enthalpy of reaction data on a mole basis.
37. Generate a list of sources of thermodynamic data. The sources should provide information on heat capacity, enthalpy, entropy, internal energy, enthalpy of reaction, free energy of reaction, etc.
    Comment: The list could be enormous.
38. A gaseous mixture of 5% methane in air is contained in a heavy-walled steel vessel at 1 atm and 80°F. A voltage was accidentally applied to the vessel resulting in a spark, causing the methane-air mixture to explode.
    - Assuming that the vessel remains intact, calculate the resulting pressure in the vessel if the gases equilibrate at 1,200°F.
    - Repeat the calculations for various mixtures of methane in air.
39. An auditorium has a volume of 100,000 ft^3. The CO_2 concentration in air before a meeting is 0.04 percent. One hour after the meeting room is in session, the CO_2 concentration is 0.14 per cent. The room is ventilated by 50,000 ft^3/min of

fresh air (0.04 percent CO_2). What is the CO_2 concentration 6 hours after the session has ended? How would the presence of an adsorbent in the auditorium affect the results?

40. There is wide scatter between bond dissociation energies of various molecules, particularly hydrocarbons. For example, the bond dissociation energy of H_2 (H-H) and N_2 (N-N) are 104 and 171 kcal/gmol (at 25°C), respectively, while it is 102 kcal/gmol for CH_4 (CH_3-H). Attempt to correlate these dissociation energies at 25°C with the molecules.
    Comment: Bond dissociation energies for a host of molecules are required.

41. The approximate composition of air is provided in Table 3.1. Attempt to correlate the above composition data with atomic weight.

42. Attempt to improve on Raoult's equation by developing a generalized equation (or equations) that can be employed to describe *non-ideal* vapor-liquid equilibrium.

43. Describe Einstein's equation pertaining to the relationship between mass and energy in an essay (1000 words).

44. Refer to the previous problem. Discuss if Einstein's equation would still apply on the surface of the moon… or another planet.

Table 3.1 Air Concentration

Gas	Percent by Volume
Nitrogen	78
Oxygen	21
Argon	0.94
Carbon dioxide	3.1×10^{-2}
Neon	1.5×10^{-3}
Helium	5.0×10^{-3}
Krypton	1.0×10^{-4}
Xenon	9.0×10^{-6}

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