Solutions to Exercises

Note: There may be more than one correct path to a correct answer.

Chapter 1. Problem Solving

1. If your answer doesn't agree with the published answer, possibilities include a) your answer may be incorrect, b) the published answer may be incorrect, c) both may be incorrect, d) both may be correct (i.e. there may be more than one correct answer), e) typographical error (answer out of place).

2. Terminology: chemistry is a noun (object), but could refer to an object of study or practice, etc. As an object of study, chemistry could refer to what is expected to be known by a novice, all that is known, all that may be known, etc; as a practice, chemistry could refer to practical applications, theoretical principles, processes where substances change called chemical reactions, etc. The word reasonable might connote logic, understanding, ethical practice, demand, etc.

    One might logically conclude that the subject of chemistry should be understandable, or that the field of chemistry should be non-productive (if it is reasonable to assume that chemistry is harmful to the environment, say), etc.

    This example is not meant to be totally trivial. Communication involves common understanding of terminology, construction (syntax) and meaning (semantics). For example, the word "add" may mean different things depending on the context; e.g. calculators (add two integers), travel agents (add the mileage, add a flight, total the cost). Clear definitions and logical thinking are essential to science.

3. There seems to be an implicit assumption that Alice wants to go somewhere. If she doesn't specify any destination, the Cat may give an arbitrary route. If she specifies an ambiguous destination, the Cat may specify multiple routes. If she specifies an non-existent destination, the Cat may specify a non-existent routes.

4.

$$123_{10} \times 456_{10} = 1111011_2 \times 111001000_2 = 1101101100011000_2 = 56088_{10}$$

Multiplication of the first number times the second in binary involves summing the result of repeatedly multiplying the rightmost digit of the first number by the second number, followed with shifting the first number one place to the right (dividing by 2) and adding a 0 to the right end of the second number (multiplying by 2), until no non-zero digits remain in the first number.

5. Given some process exists for doing arithmetic accurately (pencil and paper, calculator, supercomputer, etc), the initial amount in the checking account, and a (an assumed complete, accurate) list of debits (including withdrawals) and credits (including deposits) to the account, to the initial amount subtract the amount of each debit and add the amount of each credit.

More precisely:

1. Record the initial amount.

2. While there are entries in the list of debits and credits:

   If the entry in the list is a credit,

   Add the amount of the entry to the current total.

   If the entry in the list is a debit,

   Subtract the amount of the entry from the current total.

Note that this algorithm requires the existence of some additional sub-algorithms. The recording process in the above procedure could be made with pencil and paper, entering the number into a calculator or computer keyboard, etc. Addition and subtraction may be done by hand using the rules of arithmetic, using the arithmetic operations available in the calculator or computer, etc.

6. It is fairly easy to see by exploring the possibilities that the only response to a first move on a corner that preserves a draw is an answer to the center. Thus a first move to a corner is a good choice if the opponent is inexperienced, and a response to a first move to a corner should always be a response to the center. Exploration of other possibilities generates a fairly complicated set of sequences (called the *game tree*). (This would lead to a provable algorithm, not merely a plausible heuristic.) One general heuristic in game

theory is the *minimax* strategy, which maximizes gain and minimizes loss. Applied to tick-tack-toe, it might lead to the strategy that maximizes the number of rows controlled while minimizing the number of rows controlled by the opponent.

7. First get accepted to college, then register, then satisfy the prerequisites to the chemistry course, then enroll for chemistry, buy the books, attend class, take notes, study, practice, take exams.

   Actually getting accepted to college involves nested algorithms: graduate from high school (graduate from middle school(...)); earn some money (get a job (get a social security number,...)). What else is nested?

Chapter 2. Unit Conversions

1.
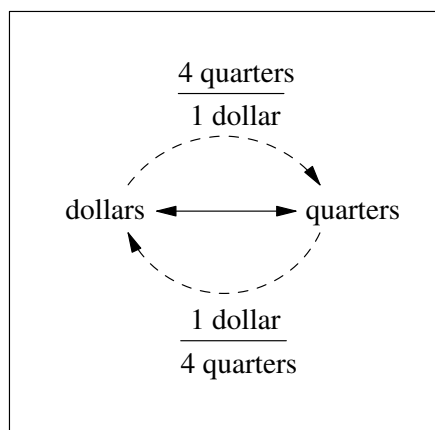
Fig. S.1 The Dollars to Quarters Conversion Map

2.

$$3 \text{ eggs} \times (\frac{1 \text{ dozen eggs}}{12 \text{ eggs}}) \times (\frac{80 \text{ cents}}{1 \text{ dozen eggs}}) = 20 \text{ cents}$$

Of course if this really is your neighbor, you shouldn't charge anything for the eggs.

3.   Begin by defining the number of days in a year (say Gregorian - 365, except 366 for years that are divisible by 4 but not by 100 but by 400), hours in a day (24), minutes in an hour (60), seconds in a minute (60). One possible algorithm begins by converting the given years into days and adds them to the given days, converts the total days into hours and adds them to the given hours, converts the total hours into minutes and adds them to the given minutes, and converts the total minutes into seconds. Note that the algorithm is repetitive on different input.

4.   The problem may be broken into two parts, the first of which computes the number of seconds in one year, and the second of which uses that result to compute a distance given a velocity and a time (v = d/t).

$$1 \text{ year} = 365 \text{ days}(\frac{24 \text{ hr}}{1 \text{ day}})(\frac{60 \text{ min}}{1 \text{ hr}})(\frac{60 \text{ sec}}{1 \text{ min}}) + 6 \text{ hr}(\frac{50 \text{ min}}{1 \text{ hr}})(\frac{60 \text{ sec}}{1 \text{ min}}) + 9 \text{ min}(\frac{60 \text{ sec}}{1 \text{ min}}) + 9.55 \text{sec}$$

$$1 \text{ year} = 31558149.55 \text{ sec}$$

$$1 \text{ year}(\frac{31558149.55 \text{ sec}}{1 \text{ year}})(\frac{2.99792458 \text{ x } 10^8 \text{ m}}{1 \text{ sec}})(\frac{.9144 \text{ yd}}{1 \text{ m}})(\frac{3 \text{ ft}}{1 \text{ yd}})(\frac{1 \text{ mi}}{5280 \text{ ft}}) = 4.91536511 \text{ x } 10^{12} \text{ mi}$$

The answer has been rounded off to the least accurate factor, 9 significant figures for the experimentally measured velocity of light (the remaining factors are definitions with infinite precision).

5.
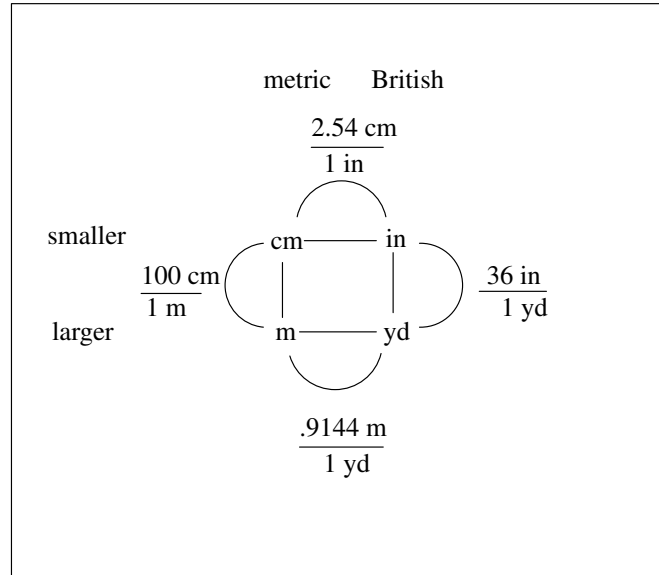
Fig. S.2 A Length Conversion Conversion Map

6. First move the conversion factor between lb and kg down to make room for a second pair of units below those of Fig. 2.5, tonnes on the left below kg and tons on the right below lb. Then add the corresponding conversion factors to the left and right of the added units, respectively.

7. First convert the U.S. money into pennies (5 per nickel, 10 per dime, 25 per quarter, 100 per dollar, etc), then convert the total pennies, X, into pence.

$$\text{X cents} \times (\frac{1 \ \$}{100 \ \text{cents}}) \times (\frac{1.75 \ \text{pound}}{1 \ \$}) \times (\frac{100 \ \text{pence}}{1 \ \text{pound}})$$

Last, convert the pence into larger British denominations by working from larger to smaller denominations and dividing. The integer quotient is the number of each denomination. The remainder is then divided by the next smaller denomination to determine the

amount of that denomination. E.g. 543 pence is 543/100 = 5 pound + 43 pence. 43 pence/25 = 1 25p + 18 pence. 18/10 = 1p + 8 pence. Total = 5 pounds, 1 25p, 1p and 8 pence.

8. The process is essentially the same as that of the previous exercise. Only the numbers are different.

9.
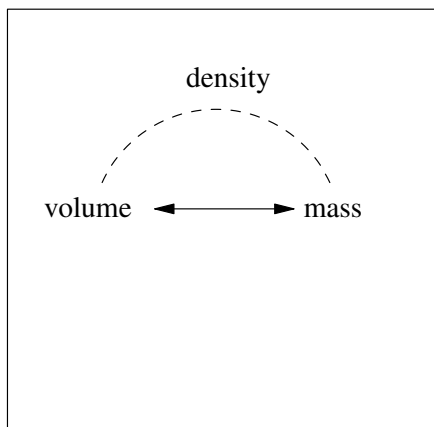
Fig. S.3 The Density Conversion Map

10.

$$(\frac{1 \text{ mi}}{4 \text{ min}}) \times (\frac{60 \text{ min}}{1 \text{ hr}}) = 15 \text{ mi/hr}$$

Chapter 3. Mathematical Tools

1. 5050 (as Gauss showed in grade school).
2. 10! = 3628800, as any good scientifi c calculator shows.

3.

$$\exp(1) = \sum_{n=0}^{n=\infty} \frac{1}{n!}$$

Since $14! = 1.1 \times 10^{-11}$, terms beyond the 14th will contribute nothing to the tenth decimal place (even their sum won't). Calculating the sum backwards so nothing is lost (calculator factorial, 1/x and memory functions are useful here), $e = 2.7182818284(59045...)$.

4. The two given points go straight into the formula for slope:

$$\text{Slope} = \frac{y_2 - y_1}{x_2 - x_1} = \frac{0 - 1}{1 - 0} = -1.$$

5. The equation $y = x^2$ is an upward-pointing parabola symmetric about the y axis with minimum at the origin. The slope of a curve at an extremum (minimum or maximum) is zero, so the slope = 0 at the origin. At $x = 1$, the value of $y = x^2 = 1$, and the slope at the point (1,1) is 2. (This may be confirmed using a table of derivatives from calculus, such as Table 3.1, where it is seen that $y' = 2x = 2$ when $x = 1$.)

6. There is a tendency to confuse 4 *divided by* ½ with 4 *by* ½, which means 4 *times* ½. Let a stand for the answer. Then $a = \frac{4}{½}$. Applying the algebraic equivalence of equation operations, multiply both sides by ½ to get ½a = 4, then multiply both sides by 2 to get $a = 2 \times 4 = 8$.

7. Linear regression analysis gives -2949 for the slope of the best straight line passing through the data. (Multiplication by $-R = -8.3145$ and division by 1000 to convert Joules to kilojoules gives 24.5 kJ/mol, which may be compared with the average value calculated in Example 14.1 of 24.4 kJ/mol.)

Fig. 14.4 shows confirms that a straight line is an acceptable fitting function for this data.

8. The secant numerical method should converge to the same final value, 22.29597 liters, independent of the starting conditions, provided they are near the same root.

9. Here is the record of a *Maple* session:

```
# Example 11.2
>
# DEFINE A SYSTEM OF LINEAR EQUATIONS
> C:=a=d;
```

$$C := a = d$$

```
> H:=6*a+2*c=4*d+2*g;
```

$$H := 6\ a + 2\ c = 4\ d + 2\ g$$

```
> O:=a+7*b+4*c=2*d+12*e+4*f+g;
```

$$O := a + 7\ b + 4\ c = 2\ d + 12\ e + 4\ f + g$$

```
> Cr:=2*b=2*e;
```

$$Cr := 2\ b = 2\ e$$

```
> S:=c=3*e+f;
```

$$S := c = 3\ e + f$$

```
> charge:=-2*b=-2*f;
```

$$charge := -\ 2\ b = -\ 2\ f$$

```
> arbitrary:=a=1;
```

$$arbitrary := a = 1$$

```
>
# SOLVE THE SYSTEM
> solve({C,H,O,Cr,S,charge,arbitrary},{a,b,c,d,e,f,g});
```

$$\{a = 1,\ d = 1,\ f = 2/3,\ g = 11/3,\ c = 8/3,\ e = 2/3,\ b = 2/3\}$$

```
>
# EXIT
> quit;
```

Chapter 4. Models

1. Genotype, as the name suggests, refers to genetic makeup of organisms, the information passed on from generation to generation. Phenotype is more nebulous but essentially refers to the properties and behavior of the organism. While genes may determine certain fixed physical characteristics, other quanities such as behavior can be determined by how things are arranged and exposure to the external environment. Thus one model for behavior considers the interplay between genetic and external influences (behavoirists tend to weight experience over genes).

   Because biological organisms are so complex, it is not easy to define the state of a biological system. Parameters include eye color, maximum potential height, propensity for molecular disease, and certainly genetic makeup. Age, height, weight, mood are variables. The Human Genome Project is a plan to determine the human genotype at the DNA level. IQ and creativity distinguish individuals and may be assumed to remain constant, but this is not a settled question.

2. The law of supply and demand is an inverse proportionality model - the less the supply, the greater the demand. John Keynes, inventor of Keynsian Economic theory, developed an networked model of large system (macro) economies with the production of goods as a measure of economic health. Mathematically, it is a linear flow system with several variables and parameters.

3. Taking the limit of p(t) as t becomes large, the exponential term goes to zero and p = 1. Since p = P/L, P = L. The maximum size is not determined by the parameters a or k, but L, which is why that symbol is used (Limiting).

4. Here is the record of a *Maple* session:

```
# Verhulst Equation
>
> dsolve(diff(p(t),t) = k*p*(1 - p), p(t), explicit);


                                    1
                    p(t)  =  -  --------------------
                                - 1 - exp(- k t) _C1
```

```
> simplify(");
```

$$p(t) = \frac{1}{1 + \exp(-\ k\ t)\ \_C1}$$

```
> quit;
```

5. If k = 0, all p_n = 0 for n > 0.

    For k = 1, P_n converges very slowly to 0: 0.1000000000, 0.0900000000, 0.0819000000, 0.0751923900,   0.0695384945,   0.0647028923,   0.0605164280,   0.0568541899, 0.0536217910, 0.0507464946, ... 0.

    For k = 2, P_n converges to 0.5: 0.1000000000, 0.1800000000, 0.2952000000, 0.4161139200,   0.4859262512,   0.4996038592,   0.4999996861,   0.5000000000, 0.5000000000, 0.5000000000, ...

    For k = 3, P_n slowly converges to 0.666...: 0.1000000000, 0.2700000000, 0.5913000000,   0.7249929300,   0.5981345444,   0.7211088336,   0.6033326511, 0.7179670897, 0.6074710435, 0.7153499244, ... 0.666...

    For k = 4, P_n is random (chaotic): 0.1000000000, 0.3600000000, 0.9216000000, 0.2890137600,   0.8219392261,   0.5854205387,   0.9708133262,   0.1133392473, 0.4019738493, 0.9615634951, ...

6. Since the wave function depends on time (t) the same way it depends on space (x), we expect a plot of f(x,t) at a given point in space to show the same sinusoidal behavior in time that it shows for space. A three dimensional plot of f(x,t) is a spiral with sinusoidal projections on the A/t and A/x planes.

Chapter 5. Mechanics

1. Speed is velocity without regard to direction. A sprinter's speed isn't constant, but most of his sprint is a nearly constant speed. The definition of velocity can be used to calculate the average speed of his run. Converting the units gives

$$\text{average speed} = \frac{\Delta d}{\Delta t} = \left(\frac{100\ \text{m}}{9.85\ \text{s}}\right) \times \left(\frac{100\ \text{cm}}{1\ \text{m}}\right) \times \left(\frac{1\ \text{in}}{2.54\ \text{cm}}\right) \times \left(\frac{1\ \text{ft}}{12\ \text{in}}\right) \times \left(\frac{1\ \text{mi}}{5280\ \text{ft}}\right) \times \left(\frac{60\ \text{s}}{1\ \text{min}}\right) \times \left(\frac{60\ \text{min}}{1\ \text{hr}}\right) = 22.71\ \frac{\text{mi}}{\text{hr}}$$

2. Equating the two expressions for average speed,

$$\text{average speed} = \frac{\Delta d}{\Delta t} = \frac{v_i + v_f}{2}$$

Since $v_i = 0$,

$$v_f = 2\frac{\Delta d}{\Delta t} = 2(\frac{1/4 \text{ mi}}{8 \text{ s}}) \times (\frac{3600 \text{ s}}{1 \text{ hr}}) = 225 \text{ mi/hr}$$

3. From the definition,

$$KE \equiv \frac{mv^2}{2} = 1/2(150 \text{ lb})(\frac{0.4536 \text{ kg}}{1 \text{ lb}})[(\frac{25 \text{ mi}}{1 \text{ hr}})(\frac{1609.344 \text{ m}}{1 \text{ mi}})(\frac{1 \text{ hr}}{3600 \text{ s}})]^2(\frac{1 \text{ kJ}}{10^3 \text{ J}}) = 4.25 \text{ kJ}$$

Given that the kinetic energy is equivalent to a change in potential energy, from Newton's gravitational laws,

$$KE = \Delta PE = mg\Delta h$$

$$h = \frac{KE}{mg\Delta} = \frac{4249 \text{ J}}{150 \text{ lb}(\frac{.4536 \text{ kg}}{1 \text{ lb}})(\frac{9.80665 \text{ m}}{s^2})} = 6.37 \text{ m}$$

So how fast is a diver off a 10 m board going when they hit the water?

4. According to Hooke's Law of oscillating (vibrating) springs the restoring force is proportional to the displacement, r:

$$PE_{vibration} = -\int fdr = -\int -krdr = \frac{kr^2}{2}$$

This has a mathematical form similar to that of kinetic energy, but with a different set of variables.

5. Since energy is conserved, the gain in kinetic energy on the descent is equal to the loss in stored potential energy. By Eqns. 5.7 and 5.10,

$$\Delta KE = \frac{mv^2}{2} = \Delta PE = mg\Delta h$$

Thus

$$v = \sqrt{2g\Delta h} = \sqrt{2 \times 9.80665 \text{ m/s}^2 \times 2\text{m}} = 4.4 \text{ m/s}$$

or nearly 10 mi/hr. Anyone who has ever been kicked by a swinging child can attest to the large kinetic energy they have at the bottom of their swing.

6. Since swinging higher increases the potential energy in the gravitational field, there must be an input of energy. This comes through the mechanical work of swinging limbs and pulling on the ropes. Looking further, the mechanical work is produced by bio-chemical reactions in the body which release energy through the muscles. The source of the biochemical energy is sugar molecules from plants in food. The plants synthesize the energetic sugar molecules using light energy from the sun. So ultimately, the sun pumps the swing!

Chapter 6. Chemical Elements

1. Tc stands for technetium (Greek for artificial), the first element to be produced artifi-cially by bombardment (in 1937). No stable isotopes are known, although it has been observed in the spectra of certain stars.

2. The Atomic Mol Map Algorithm points the way (from atoms to g). Two routes are pos-sible.

$$10 \text{ atoms Au} \times \left(\frac{196.9665 \text{ amu Au}}{1 \text{ atom Au}}\right) \times \left(\frac{1 \text{ g}}{6.0221367 \times 10^{23} \text{ amu}}\right) = 3.270708 \times 10^{-21} \text{ g Au}$$

3. The Atomic Mol Map Algorithm again points the way (from mos to amu). Note this is the other diagonal route that takes two conversions, and again, two routes are possible.

$$10 \text{ mol Au} \times \left(\frac{6.0221367 \times 10^{23} \text{ atoms}}{1 \text{ mol}}\right) \times \left(\frac{196.9665 \text{ amu Au}}{1 \text{ atom Au}}\right) = 1.186141 \times 10^{27} \text{ amu Au}$$

4. There are $\dfrac{n!}{m!(n-m)!}$ ways of choosing n things out of m, so there are $\dfrac{4!}{2!(4-2)!} = \dfrac{(4)(3)(2)}{(2)(2)} = 12$ ways of choosing 2 corners things out of 4 in the Atomic Mol Map. There are then 24 possible conversion processes in the map.

Chapter 7. Atomic Structure

1. Percentage is $100(\frac{\text{part}}{\text{whole}})$. An abundance ratio of 3.1271 to 1 implies a percentage distribution of $\frac{3.1271}{3.1271 + 1} = .7577$ for the isotope of mass 34.969, and $\frac{1}{3.1271 + 1} = .2423$ for the isotope of mass 36.967. Eq. 7.1 gives

$$\text{average AM} = 0.7577 \text{x} 34.969 + 0.2423 \text{x} 36.967 = 35.453$$

2. From the periodic table, the atomic number of hydrogen is 1. From Eq. 7.4, the number of electrons $= Z - q = 1 - 1 = 0$. Thus ionic hydrogen atoms are bare protons with no electrons. (Since no other element can exist as a bare nucleus in chemical environments, this explains some of the unique chemical properties of hydrogen ions.)

3. Sodium is an element with atomic number 11. Therefore it has 11 protons and 10 electrons.

4. In Section 7.4 it states ultraviolet light has wavelengths less than 400 nm (actually down to 1 nm). Eq. 7.5 gives the relationship between photon energy and wavelength:

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

Since energies are inversely proportional to wavelength, the minimum UV energy occurs at 400 nm:

$$\Delta E_{UV} \geq \frac{(6.6256 \text{ x } 10^{-34} \text{ J s})(2.99792458 \text{ x } 10^{8} \frac{m}{s})}{400 \text{ nm}} \times (\frac{10^{9}\text{nm}}{1 \text{ m}}) = 5.0 \text{ x } 10^{-21} \text{ J}$$

5. From Eq. (7.6) with $Z = 1$, and $n = 1$

$$v_n = \frac{2\pi Z e^2}{nh} = \frac{2\pi(1.518919 \times 10^{-14} \text{ (Jm)}^{1/2})^2}{6.626176 \times 10^{-34} \text{ Js}} = 2.187691756 \times 10^6 \text{ m/s}$$

6. $4s\uparrow$.

7. The electronic configuration of neutral lead is given in Example 8.6. Since outer shell electrons are removed most easily, and within a shell higher subshell is more easily removed, the lead ion has lost the 6p electrons. The configuration of Pb^{2+} is

$[Xe]6s^25d^{10}4f^{14}$.
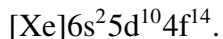
8. S^{2-}, Cl^-, Ar, K^+ and Ca^{2+} all have the same number of electrons (*isoelectronic*), 18. However the number of protons increases from 16 to 20, producing an increasing nuclear charge on the electrons drawing them closer. Thus the size is expected to decrease in regular fashion. Experimental values in the order shown are 184 pm, 181 pm, 94 pm, 133 pm, 99 pm. The value for neutral Ar is obtained from different experiments than those for ions.

Chapter 8. The Periodic Table

1. Using Mendeleev's heuristic of neighbor averaging, the estimated atomic masses of Ga and As, Si and Sn, Al and Sb, and P and In, are respectively, (69.72+74.92)/2 = 72.32, (28.09+188.7)/2 = 73.4, (26.98+121.8) = 74.4 and (30.97+114.8)/2 = 72.9. The observed atomic mass of Ge = 72.59. For some elements the horizontal average is much closer to the measured value than the averages in other directions.

2. Using Mendeleev's heuristic of neighbor averaging, the horizontal average density of Ge is (6.10+5.73)/2 = 5.91 g/mL and the vertical average is (2.33+7.37)/2 = 4.85 g/mL. The average of the averages is 5.38 g/mL. The measured value is 5.32 g/mL.

3. C, Si, Ge, Sn and Pb all have a np^2 outer shell configuration.

4. Check to see if the valence formula given in the text can be used. Arsenic has the symbol As and is found in family number five of the periodic table, one of the representative families. Since five is greater than four, the valence formula to use is 8 − n, where n is the family number. Thus the valence of arsenic is 8 − 5 = 3.

5. From the Periodic Trend Heuristic, elemental silicon is expected to have two solid forms similar to carbon. One of these is crystalline like diamond, but more brittle.

6. From the Periodic Trend Heuristic, compounds in similar families should have similar properties. Therefore the compound between selenium and hydrogen should be toxic as is the compound between sulfur and hydrogen. The tellurium-hydrogen compound is also toxic, but the oxygen-hydrogen compound, water, is essential to life.

6. Sodium is to the left of magnesium, which is, in turn, to the left of aluminum on the same row of the periodic table. According to the Periodic Trend Heuristic, atomic size decreases in the order given, as does mass, both contributing to an increases in density. Observed densities are $D_{Na} = 0.97$ g/cm^3, $D_{Mg} = 1.74$ g/cm^3, $D_{Al} = 2.70$ g/cm^3. The

trend does not continue across the row as the elements become non-metallic beyond aluminum.

8. According to the Periodic Trend Heuristic, electron affinity should increase with decreasing size, that is up a column and across a row. Thus lithium should have the largest electron affinity of the alkali metals, and fluorine of the halogens, and the halogens as a group should have larger electron affinities than the alkali metals. Observed values (in kJ/mol) of electron affinity are Fr = −44 (est.), CS = −45, Rb = −47, K = −48, Na = −53, Li = −60, (H = −72), and At = −270 (est.), I = −295, Br = −323, Cl = −348, F = −322.

Chapter 9. Chemical Formulas

1. Using the Algorithm for Calculating Molecular Masses from Chemical Formulas,

$$\text{molecular mass} = 3 \times \text{AM}_{\text{Mg}} + 2 \times \text{AM}_{\text{P}} + 8 \times \text{AM}_{\text{O}} = 262.858$$

2. From the Empirical Formula Algorithm, 100 amu of compound contains 65.191 amu Br and 34.809 amu O. The number of atoms of each element is 65.191/79.904 = 0.81587 and 34.809/15.9994 = 2.1756. Dividing both atom numbers by the smallest gives a ratio of O/Br = 2.6666 = 2 + 2/3 = 8/3. The empirical formula is therefore Br_3O_8.

3. The molecular mass of Br_3O_8 is 367.71. Dividing this value into the molecular mass of 1104 according to the Molecular Formula Algorithm gives the value 2.9996, very close to 3. Thus the molecular formula is Br_9O_{24}.

4. Following the Molecular Mol Map,

$$3 \text{ g } H_2O \times \left(\frac{1 \text{ mol } H_2O}{18 \text{ g}}\right) = 0.167 \text{ mol } H_2O$$

$$3 \text{ molecules } H_2O \times \left(\frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ moleucles}}\right) = 4.98 \times 10^{-24} \text{ mol } H_2O$$

5. There are 6 ways to connect the four corners of the Molecular Mol Map, so there must be 12 paths from a given corner to another, and therefore 12 different types of questions that can be addressed.

6. From Fig. 9.2 a path can be constructed connecting V (volume) to molecule, passing through g and amu (or through g and mol). A possible solution is similar to that of

Example 9.5 with one additional conversion using the density.

$$1 \text{ CC water} \times \left(\frac{1 \text{ g}}{1 \text{ CC}}\right) \times \left(\frac{6.02 \text{x} 10^{23} \text{ amu}}{1 \text{ g}}\right) \times \left(\frac{1 \text{ molecule water}}{18 \text{ amu water}}\right) = 3.3 \text{ x} 10^{22} \text{ molecules water}$$

Chapter 10. Nomenclature

1. Deriving a formula from a name should be the inverse of deriving a name from a formula, so the algorithm should essentially be an inverted version of the Organic Compound Nomenclature Algorithm.

2. Sodium nitride is Na_3N, while sodium nitrite is $NaNO_2$. Thus they differ in the number of sodium, nitrogen and oxygen atoms. (They have quite different chemical properties as well.)

Chapter 11. Chemical Equations

1. Single displacement: $A + BC = AC + B$, or $A + BC = AB + C$. Double displacement: $AB + CD = AD + CB$. (Note that more positive groups are written before more negative groups.)

2. Decomposition connotes breaking down, comming apart, decaying. In chemistry, it refers to reactions of the form $AB = A + B$.

3. Not only are molecules destroyed and created in chemical reactions, but the number of molecules is not even conserved. What is conserved is atoms. Charge reflects the number of electrons and protons and is conserved as well. Energy is conserved in the system and surroundings, but not in the reaction itself.

4. Following the Algebraic Algorithm for Balancing Chemical Reactions:

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

   $$aHNO_2 = bHNO_3 + cNO + dH_2O$$
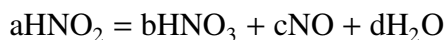
   2. There are n = 4 molecules and n-1 = 3 elements (H, N and O), indicating a single chemical reaction.

   3. Equating the number of atoms of the element on both sides of the equation:

$$\begin{aligned} \text{H:} \quad & a = b + 2d \\ \text{N:} \quad & a = b + c \\ \text{O:} \quad & 2a = 3b + c + d \end{aligned}$$

4. Arbitrarily set one of the unknowns to unity:

$$a = 1$$

5. One solution route eliminates b between the first two equations to obtain a relation between d and c. Substituting values for b and d in terms of c in the third equation yields the solution for c. Back substitution yields solutions for b and d.

6. Clearing fractions, the balanced chemical equation is:

$$6\,HNO_2 = 2\,HNO_3 + 4\,NO + 2\,H_2O$$
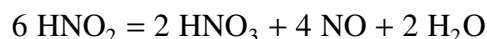
Reducing to simplest integers according to convention, the final balanced chemical equation is:

$$3\,HNO_2 = HNO_3 + 2\,NO + H_2O$$
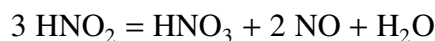
7. The final balanced equation has 3 atoms of H, 3 of N and 6 of O on each side.

5. The question is, how many ways can 8 objects (the vertices representing amounts of matter) be made into pairs (conversion origin and destinations)? The first member of the pairs can be chosen in 8 ways. Having chosen one member (which is eliminated from the choices), there remains 7 members to choose for the second pair. Since the choices are independent, there are $8 \times 7 = 56$ possible pairs, or types of conversion problems based on the mol map. (And this is only for each pair of participants in a chemical reaction.) If the origin and destination could be switched for each pair to produce another problem, there would be twice as many possible types, but the symmetry of interchanging what A and B represent forbids this.

The Extended Mol Maps have $12 \times 11 = 132$ possible pairs.

6. Following the Stoichiometric Mol Map Algorithm:

   1. The balanced chemical equation is:

$$2\,H_2 + O_2 = 2\,H_2O$$
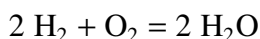
2. We need to get to mol_{H_2O} (mol_B) from g_{H_2} (g_A).

3. A short indirect path which connects mol_{H_2} with g_{H_2O} passes through mol_{H_2}.

4. The conversion factors needed are the molar mass of dihydrogen (2) and the "conversion" between mols of dihydrogen and mols of water. The latter is derived from the balanced chemical equation; in this case, it is (2 mol H_2/2 mol H_2O).

5. Starting with 1 g H_2,

$$1 \text{ g } H_2 \times \left(\frac{1 \text{ mol } H_2}{2 \text{ g } H_2}\right) \times \left(\frac{2 \text{ mol } H_2O}{2 \text{ mol } H_2}\right) = 1/2 \text{ mol } H_2O$$
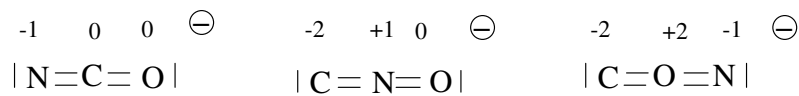
7. Two stoichiometric calculations are needed in limiting reagent problems. One of the calculations was done in the last problem. To that result we add a similar calculation starting with one gram of dioxygen and excess dihydrogen, to obtain 1/16 mol water as product. Since 1/16 is less than 1/2, the reaction will stop when the limiting reagent dioxygen is used up, producing a maximum of 1/16 mol water.

8. Add legs to the Stoichiometric Mol Map connecting to grams on the map, with the appropriate conversions factors, such as lbs to g, etc.

9. Using the Expanded Stoichiometric Mol Map, the origin is V_A, where A stands for Br_2(l), and the destination is $V(gas)_B$, where B stands for Cl_2(g). Either the Ideal Gas Law equation can be used directly to compute the volume of gas at the temperature and pressure given, or the Change of State Ideal Gas Law Algorithm can be used to compute the change in volume from that at STP (22.414 L) to the temperature and pressure given. We will use the latter as it produces one line of calculations.

$$5 \text{ mL } Br_2(l)\left(\frac{3.12 \text{ g } Br_2(l)}{1 \text{ mL } Br_2(l)}\right)\left(\frac{1 \text{ mol } Br_2}{159.808 \text{ g } Br_2}\right)\left(\frac{3 \text{ mol } Cl_2}{1 \text{ mol } Br_2}\right)\left(\frac{22.414 \text{ L}}{1 \text{ mol } Cl_2}\right)_{STP}\left(\frac{760 \text{ torr}}{650 \text{ torr}}\right)\left(\frac{323.15 \text{ K}}{273.15 \text{ K}}\right)$$
$$= 3.03 \text{ L } Cl_2$$

10. The object is to use the Extended Stoichiometric Mol Map for solutions. In solution titration problems, the requested amount may be concentration of an unknown solution of given volume, or volume of known concentration.

Chapter 12. Chemical Bonding

1. The Lewis structures and formal charges for the three possible arrangements of the atoms of the cyanate ion are

$$\overset{-1}{|\underline{N}} = \overset{0}{C} = \overset{0}{\underline{O}}| \; \ominus \qquad \overset{-2}{|\underline{C}} = \overset{+1}{N} = \overset{0}{\underline{O}}| \; \ominus \qquad \overset{-2}{|\underline{C}} = \overset{+2}{O} = \overset{-1}{\underline{N}}| \; \ominus$$

The arrangement NCO has the lowest formal charges and is preferred. Note it is closest to carbon dioxide.

2. Using the Basic Bonding Heuristic, first classify the elements. Sodium is a metal and nitrogen and oxygen are close non-metals elements. Thus the nitrogen to oxygen bonds are covalent making the covalent polyatomic nitrate ion. Sodium bonds to the non-metal part through ionic bonds. Sodium nitrate is analogous to sodium chloride in bonding, and is expected to be a solid salt as well (which it is).

3. There are four mass peaks from singly-ionized HCl:

	^{35}Cl	^{37}Cl
^{1}H	36	38
^{2}H	37	39

The atomic fragments have four different masses for the two isotopes of each element, but only three differ from those of the parent; ^{37}Cl has the same mass as $^{2}H^{35}Cl$. Therefore there are seven distinct peaks in the mass spectrum of hydrogen chloride, corresponding to masses 1, 2, 35, 36, 37, 38 and 39.

4. Two three-bond triangular structures containing one double bond are possible. The one with the double bond between the nitrogen atoms has zero formal charges, and is to be preferred to the two-bonded structures of Example 12.5.

5. The Basic Bonding Heuristic shows that chlorine oxides should be isolated covalent molecules, so we turn our attention to Lewis structures and their consequences. By the

Lewis Structure Algorithm, Cl_2O has 20 valence electrons with the chlorine atoms surrounding the oxygen atom. Each atom has an octet of electrons if there are single Cl-O bonds. ClO_2, on the other hand has 19 valence electrons, an odd number, with the oxygen atoms surrounding the chlorine atom. There is no hope of assigning octets to each atom if there is an odd number of electrons, but two of the atoms can have octets of electrons if there are single Cl-O bonds. The odd electron suggests that ClO_2 is more reactive than Cl_2O, in agreement with experimental facts.

6. The Lewis structure for phosphorus acid with three OH groups bound to P satisfies the octet rule and has zero formal charges. A Lewis structure with P bonded to two OH groups and one O atom and one H atom can be drawn which also satisfies the octet rule but has non-zero formal charges on P and the lone O atom. The experimental evidence (x-ray analysis showing the arrangement of the atoms) supports the exceptional structure. The formula for phosphorus acid should be written $HOPO(OH)_2$. It's a much stronger acid than its family analogue arsenious acid, $As(OH)_3$ (which is not exceptional), and is comparable in strength to other acids having lone O atoms such as sulfurous acid $OS(OH)_3$. This exception illustrates the inaccurate nature of oversimplified models.

7. The Lewis structures of Cl_2O and ClO_2 are described in the the previous solution. In each case there is a central atom surrounded by two other atoms. There is either $3\frac{1}{2}$ or 4 pairs of electrons on the central atom. According to the VSEPR Molecular Geometry Heuristic, these pairs form 4 groups of electrons in both molecules, suggesting a geometry determined by four groups of electrons directed from the central atom to the corners of a tetrahedron (triangular-based, triangular-faced pyramid). Since there are other atoms at only two corners of the tetrahedron, the geometry of the three nuclei is bent for both molecules. Since chlorine has a larger shell quantum number it is larger than oxygen (r_{Cl} = 99 pm, r_O = 73 pm), which is reflected in an longer observed bond length (1.70 pm for OCl_2, 1.49 pm for ClO_2). If size were the determining factor, one would expect the bond angle in OCl_2 to be larger than that of ClO_2, but the opposite is observed (110.8 degrees for OCl_2, 118.5 degrees for ClO_2), presumably due to the lone electron.

8. O_2^{2+}, O_2^{+}, O_2^{0}, O_2^{-} and O_2^{2-} have $6 \times 2 - 2 = 10$, $6 \times 2 - 1 = 11$, $6 \times 2 = 12$, O_2^{-} and $6 \times 2 + 2 = 14$ valence electrons, respectively, and $16 - 2 = 14$, $16 - 1 = 15$, $16 - 0 = 16$, $16 + 1 = 17$, $16 + 2 = 18$ and total electrons, respectively. Lewis formulas

can be constructed with a single O-O bond and octets on both atoms for O_2^{2-}, but the odd electron O_2^- will be unsymmetrical with one odd electron on one of the atoms, suggesting resonance.

A valence bond description would count 4 σ bonds on each atom of the Lewis formulas (one of which contains only one electron in the case of O_2^-). The Valence Bond Description Algorithm therefore indicates sp^3 hybridization on each oxygen atom for each molecule.

The Molecular Orbital Aufbau Algorithm adds electrons to the antibonding $2p\pi^*$ MO orbital of neutral O_2, with a decrease in bond order, suggesting a weakening of the bond with increasing negative charge (as more electrons are attached). Bond order decreases regularly through the series. The observed bond lengths of O_2^{2+}, O_2^+, O_2^0, O_2^- and O_2^{2-} are 104, 112, 121, 133 and 149 pm, respectively. The observed bond energies of are (unknown), 653, 503, 393, and 140 kJ/mol, respectively.
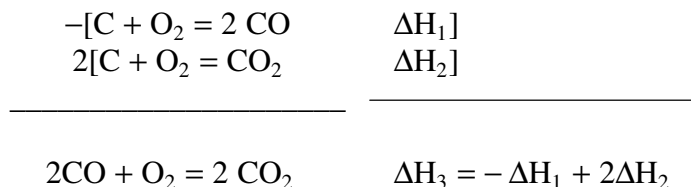
Superoxide (O_2^-) and peroxide (O_2^{2-}) compounds of the active metals are known, but they are usually less stable than the regular oxides. For example, sodium oxide sublimes at 1275 °C, sodium peroxide decomposes as 460 °C, and sodium superoxide is not stable enough to measure.

9. Since HF is isoelectronic with B_2, it should have a similar electron configuration (see Table 8.1). The bond order is one signifying a single bond, which is consistent with a Lewis structure following the duet/octet rule. HF has a bond energy of 565 kJ, which is unusually high, similar to H_2, and is polar, unlike B_2.

10. According to the Lewis Heuristic, H_2O has two OH single bonds and H_2O_2 has two OH single bonds plus one OO single bond. Thus hydrogen peroxide has 146 more kJ/mol relative to its atoms than does water (the value of BE(O-O)). However hydrogen peroxide has an additional oxygen atom, so a fair comparison should include an oxygen atom with the water so that both molecules are measured relative to the same atoms. Since oxygen exists as a diatomic molecule with a double bond, 498/2 = 249 kJ/mol should be added to the bond energy of water. Thus water plus oxygen is more stable (relative to 2 H and 2 O atoms) than hydrogen peroxide by 249 − 146 = 103 kJ/mol. (An equivalent result can be obtained by comparing the energies of the left and right sides of the balanced chemical equation $H_2O + 1/2 O_2 = H_2O_2$.) This is why hydrogen peroxide makes a good rocket fuel.

Solutions to Exercises

11. Halogen-halogen bond strengths are expected to decrease with increasing atom size. This is confirmed by the data of Table 8.2, with the notable exceptionally low bond strength of difluorine (greed doesn't pay in this case). Note that qualitatively, hydrogen trends can be included with those of the halogens.

12. Average NH bond strength = $\dfrac{449 + 384 + 339}{3}$ kJ/mol = 391 kJ/mol.

Chapter 13. Thermodynamics

1. The usual definition of the universe is everything that exists. It this is the case, then it must be an isolated system, for which the total energy is a constant. If the definition of the universe is everything that is *known* to exist, then there could be other universes, with which this universe could exchange energy.

2. A super ball is manufactured to store energy in chemical bonds. As it bounces, the energy is slowly released giving it the appearence of having a ''super'' (more than ordinary) amount of energy. Note that if it really had unlimited energy it would eventually bounce into space.

3. Combining the two steps to obtain the desired reaction according the Hess Law Algorithm,

$$-[C + O_2 = 2\ CO \qquad \Delta H_1]$$
$$2[C + O_2 = CO_2 \qquad \Delta H_2]$$
$$\overline{\qquad\qquad\qquad\qquad} \quad \overline{\qquad\qquad\qquad\qquad}$$
$$2CO + O_2 = 2\ CO_2 \qquad \Delta H_3 = -\Delta H_1 + 2\Delta H_2$$

4. The balanced equation for hydrocarbon combustion is

$$C_nH_{2n+2} + \frac{3n+1}{2} O_2 = nCO_2 + (n+1)H_2O$$
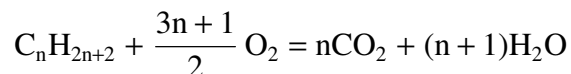
Therefore, from the Reaction Heats from Formation Heats Algorithm, Eq. (13.8),

$$\Delta H_{comb}(C_nH_{2n+2}) = n\Delta H_f(CO_2) + (n+1)\Delta H_f(H_2O) - \Delta H_f(C_nH_{2n+2}) = nc + (n+1)w - h$$

5. The balanced reaction is:

$$CH_4 + 2\ O_2 = CO_2 + 2\ H_2O$$
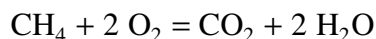
Using the Reaction Heats from Bond Energies Algorithm,

$$\Delta E_{rxn} = [4BE(C-H) + 2BE(O=O)] - 2[BE(C=O)] - 4[BE(O-H)]$$

$$= [4(414) + 2(498)] - 2[(799)] - 4[(467)] = -814kJ$$

The experimental value is −802 kJ

6. Since there is little energy (or heat) of mixing (zero for ideal gases), and mixing involves an increase in disorder, or entropy, $\Delta S > 0$, and $\Delta G = -T\Delta S < 0$, so mixing is an *entropy driven* process.

7. If no work is performed, then $\Delta S = \Delta E/T = q/T$ and

$$\Delta S_{total} = \Delta S_{water} + \Delta S_{surroundings} = \frac{q_{water}}{T_{water}} + \frac{q_{surroundings}}{T_{surroundings}}$$

No heat flows into the water unless the surrounding temperature is higher than that of the water; $T_{surroundings} < T_{water}$. Then since the amount of heat gained by the water equals that lost by the surroundings,

$$\Delta S = \frac{q}{T_{water}} - \frac{q}{T_{surroundings}} = q(\frac{T_{surroundings} - T_{water}}{T_{water}T_{surroundings}}) > 0$$

8. The entropy of the gas *decreases*, in harmony with Eq. (13.20) and the fact that the gas is becoming less disordered. Of course, the entropy of the surroundings must *increase* to cause the compression of the gas, and it must increase more than that of the gas decreases by the Second Law.

9. Use the formula for variation in pressure with altitude:

$$p = p_0 e^{-mgh/kT}$$

$$p = 1 \text{ atm } e^{-\frac{(29 \text{ g/mol})(9.81 \text{ m/s}^2)(29028 \text{ ft})(0.3048 \text{ m/ft})(1 \text{ kg/10}^3 \text{ g})}{(1.38\times10^{-23} \text{ J/molecule}-K)(230 \text{ K})(1 \text{ kgm}^2/s^2/1 \text{ J})(6.02\times10^{23} \text{ molecule/mol})}}$$

$$p = 0.268 \text{ atm}$$

About three-fourths of the atmosphere is below that height.

9. From Eq. (13.14) (watch the units):

$$T_{boiling} = \frac{\Delta E_{vaporization}}{\Delta S_{vaporization}} = \frac{44,000 \text{ J/mol}}{119 \text{ J/mol} - K} = 370 \text{ K}$$

or 97 °C.

11. Sugar hydrogen bonds with itself and with water, so the enthalpy change on disolving is not very large. Mixing with water increases the entropy of the solution over that of the crystal because the system becomes more disorganized. Dissolution is entropy driven and solubility increases somewhat with increasing temperature. (Consider how many sugar cubes will dissolve in hot water compared with cold.)

12. Methyl alcohol, CH_3CHOH, is polar and hydrogen bonded. It is therefore very similar to water, and dissolves extensively. Thermodynamically, the heat of solution measures the difference between the bonding of the unmixed liquids and that of the mixed solution. The major contributor to the intermolecular attractions is hydrogen bonding and there is not much difference between the bonding in the unmixed and mixed cases. Therefore, one expects the heat of solution to be small. (Experimentally it is about −7 kJ/mol.) The entropy of solution is expected to be positive as one goes from a unmixed to mixed state. $\Delta G_{solution}$ is thus negative and solution is favorable.

13. There is only one way for sum 2 (Cat's eyes) can occur (1+1), two ways for the sum 3 to occur (1+2 and 2+1), three for the sum 4 (1+3, 2+2, 3+1), four for the sum 5 (1+4, 2+3, 3+2, 4+1), five for the sum 6 (1+5, 2+4, 3+3, 4+2, 5+1), six for the sum 7, or craps (1+6, 2+5, 3+4, 4+3, 5+2, 6+1), five for the sum 8 (2+6, 3+5, 4+4, 5+3, 6+2), four for the sum 9 (3+6, 4+5, 5+4, 6+3), three for the sum 10 (4+6, 5+5, 6+4), two for the sum 11 (5+6, 5+6), and one for the sum 12 (boxcars) (6+6). There are thus 36 total possible outcomes (which is the product of 6 and 6 since the dice are independent), and the distribution of probabilities is:

outcome:	1	2	3	4	5	6	7	8	9	10	11	12
probability:	1/36	2/36	3/36	4/36	5/36	6/36	5/36	4/36	3/36	2/36	1/36	

14. The 20 yes/no questions selects one out of a maximum of $2^{20} = 1,048,576$ possibilities. The formula for information with equal weighting gives $I = lg(N) = lg(2^{20}) = 20$ bits of information acquired.

   Note that less information would be obtained if the questions were not carefully chosen to be discriminating, with a limit of only one bit of information if all the questions were the same (or effectively the same). Redundant questioning does not ordinarily increase knowledge.

15. a) Since the solid is more organized than the liquid and the gas is more disorganized, $S_{solid} < S_{liquid} < S_{gas}$. b) Since S is proportional to the natural logarithm of mass (according to Table 1.31), for $mass_2 > mass_1$, $S_{mass_2} > S_{mass_1}$. c) Due to their rotation and vibration, polyatomic molecules have more possible arrangements than monatomics and therefore greater entropy.

16. From Table 13.2 we find for N_2 $\Theta_{t=3} = 1.089 \times 10^{-15}$ cm^2 K, $\Theta_{r=2} = 2.88$ K, $\Theta_{v=1} = 3374$ K (300 K is not high enough to excite vibrational states in the molecule), $\sigma = 2$ (two equivalent orientations in space), $\omega_e = 1$ (no electronic degeneracy in the ground state), $\Theta_{electronic} = 1.13 \times 10^5$ K (300 K is not high enough to excite electronic states in the molecule). Applying the formulas in Table 13.1, and noting that $V = l^3 = 22,414 \times \dfrac{300}{273}$ cm^3 (the molar volume of an ideal gas at 300 K), the contributions are

$$S = S_{translation} + S_{rotation} + S_{vibration} = 150.4 + 41.2 + 0.0 = 191.6 \text{ J/mol} - \text{K}$$

which compares very favorably with the experimental value of 192.0 J/mol-K.

Chapter 14. Intermolecular Bonding

1. $\text{K.E.} = \dfrac{3}{2}kT = \dfrac{3}{2}(8.3145 \dfrac{\text{J}}{\text{mol} - \text{K}})(10,000 \text{ K}) = 124.7$ kJ. (This is temperature comparable to the surface of the sun and energy enough to break chemical bonds.)

2. DNA is a huge molecule with much covalent bonding and large dispersion forces. Since DNA exists in the nuclei of cells, it must be highly folded similar to a covalent network molecule. According to the State of Matter Heuristic, DNA could be exist in a solid state at room temperature. Pure DNA is, in fact, crystalline at room temperature.

3. Eight sigma bonds in diamond means that each carbon atom is covalently bound to four neighbors, that are, in turn, bound to four more neighbors each, resulting in a three-dimensional network. According to the State of Matter Heuristic, diamond should should exist as a solid at room temperature. A diamond is a macroscopic single molecule. (Who said they never saw a molecule?)

4. The molar heat of vaporization requires breaking one mole of intermolecular bonds. The energy to do so comes from kinetic energy. Equating the kinetic energy from the equipartition theorem to the heat of vaporization gives the rule:

$$\Delta H_{vaporization} = KE = \frac{s}{2}kT_b$$

where s is at least 3 (for translational motion).

5. Fluorine belongs to the halogen family containing chlorine, bromine and iodine, the states of which are gas, liquid and solid, respectively, at room temperature (as discussed in the section on Classes of Intermolecular Bonds). All members are diatomic, non-polar covalent molecules. Fluorine has the fewest number of electrons of the halogens and should have the smallest dispersion attractions. Therefore it is a gas at room temperature.

6. Assuming I_2 vibrates freely, the value of s in the solid is 2x3a = 2x3x2 = 12, and C = 12R/2 = 12(8.314)/2 = 58.2 J/mol-K, and for translating, rotating and vibrating diatomic gas molecules, s = 3 + 2 + 2x1 = 7, C = 7R/2 = 7(8.314)/2 = 29.1 J/mol-K. These values compare favorably with the experimental C_s = 54.4 J/mol-K and C_g = 28.6 J/mol-K.

Chapter 15. Gases

1. This problem doesn't state that the gas is ideal, what the room temperature is, or what the pressure is, so it is not possible to identify and solve an equation of state for the volume. (See the Gas Law Decision Table.)

2. Assuming no gas escapes ($n_f = n_i$), $\dfrac{T_f}{T_i} = (\dfrac{P_f}{P_i})(\dfrac{V_f}{V_i}) = (\dfrac{1}{2})(\dfrac{1}{1}) = \frac{1}{2}$

3. Assume the pressure cooker starts out at room temperature (25°C) and pressure (1 atm) and is heated at constant volume to boiling of water (100°C). The entries in the table in the Ideal Gas Algorithm have the same volume and mols, but different pressures and temperatures: P_i = 1 atm, P_f = ? atm, T_i = 298 K, T_f = 373 K. Thus

$$P_f = (\frac{373}{298})P_i = 1.5\ P_i$$

Thus $\Delta p \approx 1/4$ atm.

4. From the Ideal Gas Law at constant pressure, $V_i = n_i\dfrac{RT}{P}$, $V_T = n_T\dfrac{RT}{P}$, so $\dfrac{V_i}{V_T} = \dfrac{n_i}{n_T} = X_i$, and $\sum X_i = 1 \Rightarrow \sum V_i = V_T$.

5. At constant temperature, from the Kinetic-Molecular Theory, the kinetic energy is constant as well for any molecule, such as i, j, etc:

$$K.\,E. = kT = 1/2 \; m_i v_i{}^2 = 1/2 \; m_j v_j{}^2$$

Rearranging and solving for the velocity ratio,

$$\frac{v_i}{v_j} = \sqrt{\frac{m_j}{m_i}},$$

which says that the velocity is inversely proportional to the square root of the mass.

6. Following Example 15.6 and using the b value from the van der Waals Parameters table:

$$b_{Cl_2} = 0.05622 \; \frac{L}{mol} \; (\frac{1 \; mol}{6.022 \; x \; 10^{23} molecules}) \; x \; (\frac{10^3 \; mL}{1 \; L}) \; x \; (\frac{10^{10} \; pm}{1 \; cm})^3$$

$$= 9.334 \; x \; 10^7 \; \frac{pm^3}{molecule} = \frac{4}{3} \pi d^3$$

$$d_{Cl_2} = 281 \; pm$$

$$r_{Cl} = 281/2 \; pm = 141 \; pm$$

(Diatomic chlorine is not strictly spherical as assumed here.)

Chapter 16. Solids

1. The Si/O radius ratio is $41/140 = 0.29$. According to the Crystal Structure Algorithm, oxygen ions are close packed with silicon ions in tetrahedral holes.

2. Assume FCC close packing. Then the length of the edge of the face centered cube is $\frac{4r}{\sqrt{2}}$, since the touching atoms lie on the face of the diagonal of the cube (1 radius in each corner and a diameter in the middle of the face). Solving Eq. (16.3) for the edge length, a, equating it to $\frac{4r}{\sqrt{2}}$ and solving for r gives

$$r_{Ar} = \frac{(\frac{AM \; x \; atoms/cell}{D \; x \; N_A})^{1/3}}{4\sqrt{2}}$$

$$= \frac{(\frac{39.948 \; g/mol \; x \; 4 \; atoms/cell}{1.65 \; g/cm^3 \; x \; 6.022 \times 10^{23} \; atoms/mol})^{1/3}}{4\sqrt{2}} = 0.964 \times 10^{-8} cm = 96.4 \; pm$$

This may be compared with the van der Waals radius of Example 15.6. Solids are expected to be more tightly packed than gases, but atoms are not classical spheres and the "size" of an atom reflects its range of influence.

3. From Eq. (16.5)

$$\tilde{LE}(LiF) = \Delta\tilde{E}_{sublimation}(Li) + \tilde{BE}(F_2)/2 + \tilde{IP}(Li) + \tilde{EA}(F) - \Delta\tilde{E}_f(LiF)$$

$$\tilde{LE}(LiF) = 158 + 159/2 + 520 - 333 + 614 = 1038 \text{ kJ/mol}$$

The answer is in Table 8.1.

4. Assume a Mie potential energy function with Coulombic attraction (n = 1), and ion separation equal to the sum of the ionic radii, 68 + 133 = 201 pm. Following the example calculation for NaCl:

$$LE = \frac{1.518919 \times 10^{-14} \text{ (Jm)}^{1/2^2}(1.747558)(\frac{1}{m} - 1)}{201 \text{ pm}} (\frac{10^{12} \text{ pm}}{1 \text{ m}})(\frac{6.022 \times 10^{23} \text{ molecules}}{1 \text{ mol}})(\frac{1 \text{ kJ}}{10^3 \text{ J}})$$

$$LE = 1107 \text{ kJ/mol}$$

Note this is just the result for NaCl with a different ion separation: 689 kJ/mol ($\frac{282}{201}$).

Chapter 17. Solutions

1. According to Avogadro's Law, the volume of an ideal gas is proportional to the number of mols (a special case of the Ideal Gas Law.) Thus the volume fraction and the mole fraction must be the same.

2. As in the last problem, the mole fraction is equal to the volume fraction. Further, the mole fraction is $1/2$, so $n_a = n_b$.

$$\%_{mass} = 100 \frac{m_a}{m_a + m_b}$$

$$= 100 \frac{n_a AM_a}{n_a AM_a + n_b AM_a}$$

$$= 100 \frac{AM_a}{AM_a + AM_b}$$

Therefore,

$$\%_{Ar} = 100 \text{ x } \frac{40}{40 + 131} = 23\%$$

$$\%_{Xe} = 100 \text{ x } \frac{131}{40 + 131} = 77\%$$

Chapter 18. Chemical Kinetics

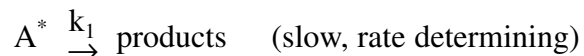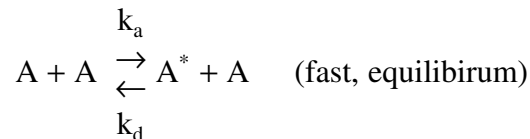1. From the data of Example 18.5, construct values of 1/T and ln(k):

Experiment	T (K)	1/T	k (min^{-1})	ln(k)
1	273	0.003663	0.0000472	-9.961
2	298	0.003356	0.00203	-6.200
3	338	0.002959	0.292	-1.231

The Algorithm for Determining the Slope of a Curve can be applied to the data. For the numerical method of selecting pairs of points, the results are essentially the same as in the example, with an average of 102.9 kJ/mol for the activation energy. The best least squares line through the plot of ln(k) *vs* 1/T gives 103.2 kJ/mol for the activation energy.

2. The problem is how to account for an observed first order reaction in terms of collisions, which obviously require at least two participating molecules. One possibility is to assume that binary collisions are insufficient to break bonds. Thus a rapid equilibrium could be set up between colliding molecules having enough energy to break a bond, but not localized in the bond. Molecular vibrations would allow the collisional energy to redistribute among the bonds until it collected into the weakest bond, at which time the molecule would disintegrate. Such behavior is observed for "unimolecular" decompositions of large molecules, where vibrational energy can occasionally collect in the critical bond. The observed rate order is unity because the energy rearrangement is independent of collisions, and depends only on the total concentration of molecules.

In 1922 F. A. Lindemann (later Lord Cherwell) proposed a three-step mechanism to account for first-order reactions. The first two steps are rapid reversible "activation" and "deactivation" binary collision processes (which may be assumed to reach equilibrium and follow the Law of Mass Action). The rate limiting step involves the slower (than collision) rearrangement of internal energy of the activated species A* into the

critical bond to be broken.

$$A + A \overset{k_a}{\underset{k_d}{\rightleftarrows}} A^* + A \quad \text{(fast, equilibirum)}$$

$$A^* \overset{k_1}{\rightarrow} \text{products} \quad \text{(slow, rate determining)}$$

$$\text{rate} = k_1[A^*] = \frac{k_1 k_a}{k_d}[A]$$

3.

$$k = \frac{r}{C^3} = \frac{-\dfrac{\Delta C}{\Delta t}}{C^3} = C^{-4}\, t^{-1}$$

Chapter 19. Chemical Equilibria

1. Following the Mass Action Equilibrium Algorithm,

	HCN	:	HNC
Initial:	1		0
Change:	−x		+x
Final:	1−x		x

Solving $\dfrac{x}{1-x} = 4$ for x gives x = [HNC] = 4/5M.

2. In H-S-H, the second proton draws charge toward it, weaking the H-S bond. In $H-S^-$, the electron cloud is more free to shift into the H-S bond, strengthening it. The stronger acid is the one with the weaker H-S bond, H-S-H.

3. Using the Lewis Algorithm, dihydrogen appears in two places (0.00 V and −0.83 V) and dioxygen in three (+1.23 V, +0.68 V, +0.40 V). The balanced fuel cell reaction is:

$$2\ H_2 + O_2 = 2\ H_2O$$
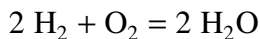
There are actually two pairs of half reactions which give this total reaction, both with the same value of E_{cell}^0 with $n_e = 4$:

$$4E_{cell}^0 = 4(+1.23) - 4 \times 0.0 = 4(+0.40) - 4(-0.83) = 4(+1.23)\ V$$

So $E_{cell}^0 = +1.23$ V. Experimentally the observed potential is about 0.9 V due to the "overvoltage" of O_2. Presumably paramagnetic dioxygen sticks to the electrode due to it unpaired electrons.

4. For the reaction $2H_2O_2 = 2H_2O + O_2$ the Lewis Table gives, E_{cell} = +1.763 - 1.229 = 0.534 V. Therefore the reaction lies to the product side and hydrogen peroxide is unstable. However, the decomposition is not instantaneous. Hydrogen peroxide is commonly stored in dark bottles and an inhibitor added to increase shelf life. The decomposition is catalyzed by blood, and the release of oxygen oxidizes material, including bacteria. For this reason hydrogen peroxide is used as an antiseptic.