APPENDIX A: SCIENTIFIC NOTATION

Special notations are useful for expressing the precisions of very large and very small quantities. The diameter of a helium atom, for instance, is 0.000 000 000 24 metres, and the average distance from the Earth to its moon is 384 000 000 metres. Writing numbers with this many zeros is cumbersome, and it is easy to make a mistake. To shorten the writing of small and large numbers, scientists commonly use **scientific notation**.

Scientific notation is based on the fact that any number can be expressed as a number between 1 and 10 multiplied or divided by 10 an appropriate number of times. For example, 384 000 000 metres can be written as follows:

$$(3.84)(10)(10)(10)(10)(10)(10)(10)(10) = 3.84 \times 10^8 \text{ metres}$$

Similarly, 0.000 000 000 24 metres is written as follows:

$$2.4/((10)(10)(10)(10)(10)(10)(10)(10)(10)(10)) = 2.4 \times 10^{-10} \text{ metres}$$

The numeral "8" in 10^8 and the numeral "–10" in 10^{-10} are examples of **exponents** or **powers.** The scientific notation, 3.84×10^8 m, contains an exponent (or power of ten) of 8.

Converting to Scientific Notation

When a number is *divided* by 10, the decimal point moves one place to the *left*; when a number is *multiplied* by 10, the decimal point moves one place to the *right*:

$$\frac{384}{10} = 38.4 \qquad \textit{and} \qquad (0.0024)(10) = 0.024$$

Multiplying *or* dividing a number by 10 changes its value, but multiplying *and* dividing a number by 10 leaves its value unchanged. Thus, to convert a number larger than 10 to scientific notation, first divide by 10 the number of times that gives a number between 1 and 10, then multiply by 10 that same number of times. Here, for example, is the conversion of the number of seconds in a day into scientific notation:

$$\frac{86{,}400 \text{ s/day}}{(10)(10)(10)(10)} \times (10)(10)(10)(10) = 8.6400 \times 10^4 \text{ s/day}$$

8.6400 ↓ 10^4

The four divisions by 10 move the decimal point four places to the left, and the four multiplications by 10 are written as 10^4.

A number larger than 10 can be quickly converted into scientific notation by moving the decimal point to the left enough places to give a number between 1 and 10, and multiplying by 10 raised to the positive power that equals the number of places moved. For example, the number 96 485 can be expressed as 9.6485 multiplied by 10^4:

$$96\ 485 = 9.6485 \times 10^4$$

To convert a number smaller than 1 into scientific notation, first multiply by 10 as many times as needed to give a number between 1 and 10, and then divide by 10 that same number of times. Here, for example, is the conversion into scientific notation of the fraction of a day represented by one second:

$$0.000\ 011\ 574 \text{ day/s} \; (10)(10)(10)(10)(10) \times \frac{1}{(10)(10)(10)(10)(10)} = 1.1574 \times 10^{-5} \text{ day/s}$$

1.1574 ↓ 10^{-5}

To convert a number smaller than 10 into scientific notation, move the decimal point to the right enough places to give a number between 1 and 10 and multiply by 10 raised to the negative power equal to the number of places moved.

With practice, these conversions can be carried out quite quickly. The key is to count the number of places the decimal point must be moved and write the exponent accordingly. Here are some additional examples:

$$10\ 00\ 000 \text{ mm/km} = 1.000\ 000 \times 10^6 \text{ mm/km}$$

$$299\ 792\ 458 \text{ m/s} = 2.997\ 924\ 58 \times 10^8 \text{ m/s}$$

$$0.08314 \text{ L bar mol}^{-1}\text{K}^{-1} = 8.314 \times 10^{-2} \text{ L bar mol}^{-1}\text{K}^{-1}$$

Working with Powers of Ten

Chemistry students must be able to add, subtract, multiply, and divide numbers that are expressed in scientific notation. This is easily accomplished on a calculator by entering the numbers using power-of-ten notation, but it is also useful to understand how these operations are carried out. Multiplication and division are handled in one fashion, but addition and subtraction are handled in another fashion.

To *multiply* two numbers expressed in scientific notation, multiply the values and *add* the exponents:

$$(2.450 \times 10^2)(1.680 \times 10^3) = (2.450)(1.680) \times 10^{(2+3)} = 4.116 \times 10^5$$

Retain signs when adding exponents:

$$(2.450 \times 10^2)(1.680 \times 10^{-3}) = (2.450)(1.680) \times 10^{(2-3)} = 4.116 \times 10^{-1}$$

To *divide* numbers expressed in power-of-ten notation, divide the values and *subtract* the exponent of the divisor from that of the number divided:

$$\frac{2.450 \times 10^2}{1.680 \times 10^3} = \frac{2.450}{1.680} \times 10^{(2-3)} = 1.458 \times 10^{-1}$$

As with multiplication, retain signs when subtracting exponents:

$$\frac{2.450\times10^{2}}{1.680\times10^{-3}} = \frac{2.450}{1.680}\times10^{(2-(-3))}$$
$$= 1.458\times10^{5}$$

Addition and subtraction require a different approach. Consider, for example, the addition of these two numbers:

$$(2.450\times10^{2}) + (1.680\times10^{3}) = ?$$

Using standard notation, this addition is as follows:

$$\begin{array}{r} 1680 \\ +\ 245.0 \\ \hline 1925 \end{array}$$

To obtain this result in scientific notation, express both numbers using the *same* power of ten, most conveniently the largest such power, and then do the addition:

$$2.450\times10^{2} = 0.2450\times10^{3}$$
$$(0.2450\times10^{3}) + (1.680\times10^{3}) = 1.925\times10^{3}$$

To add or subtract numbers expressed in power-of-ten notation, first express all numbers using the *same power of ten*. Then add or subtract the values and retain the same power of ten. Calculators automatically take care of these power-of-ten manipulations.

Subtraction may give a result that is smaller than 1. When this happens, the convention is to change the exponent to make the numerical value between 1 and 10. Here, for example, is the difference between the atomic radii of oxygen atoms and fluorine atoms:

O atom	F atom	Difference
$(1.40\times10^{-10}\,\text{m})$	$-(1.35\times10^{-10}\,\text{m})$	$= 0.05\times10^{-10}\,\text{m}$
		Proper notation
		$= 5\times10^{-12}\,\text{m}$

To express this result using a number between 1 and 10, we moved the decimal point two places to the right and increased the negative power of ten by 2.

This last example helps to show how the use of scientific notation simplifies the operations with the very small and very large numbers encountered in chemistry. Carried out in standard notation, this subtraction requires a whole lot of zeros:

$$\begin{array}{r} 0.000\ 000\ 000\ 140\ \text{m} \\ -0.000\ 000\ 000\ 135\ \text{m} \\ \hline 0.000\ 000\ 000\ 005\ \text{m} \end{array}$$

APPENDIX B: QUANTITATIVE OBSERVATIONS

Chemists usually want to know not only *what* is happening but also to what extent (*how much*). Quantitative measurements have three equally important parts: *numerical value*, appropriate *units*, and *precision*. Any experimentally measured quantity *always includes all these parts*. Numerical value refers to the numbers. Units are what allow us to scale a numerical value appropriately. For example, 20 *kilometres* is a very different length than 20 *centimetres*. Precision requires further description.

Precision and Significant Figures

The precision of a quantitative value is the degree of certainty with which it is known. For example, "about 20 km" is a less precise statement than "21.5 km." The basic rule for precision is that the number of digits in the numerical value expresses the precision of the measurement.

As an example of this rule, consider measuring the length of a table. After a quick measurement, you might estimate, "This table is 1.8 metres long." You have expressed the length as a two-digit number, meaning that you know the table to be longer than 1.7 metres but shorter than 1.9 metres. A more careful measurement with a tape measure might yield a result containing four digits, 1.826 metres. This means that the table is longer than 1.825 metres but shorter than 1.827 metres.

The number of digits in a numerical result is called its number of **significant figures.** Unless otherwise stated, the measurement is precise to within one unit in the last significant figure. Thus, a result reported as 1.826 metres has four significant figures. Unless additional information is given, the last digit (6) is uncertain by one unit: the length is 1.826 ± 0.001 metres. That is, the length falls somewhere between 1.825 metres and 1.827 metres.

When quantities are expressed in scientific notation, extra zeros always indicate extra precision. For instance, 3.840×10^{8} metres means "not less than 3.839×10^{8}, nor more than 3.841×10^{8} metres." On the other hand, 3.84×10^{8} metres means "not less than 3.83×10^{8}, nor more than 3.85×10^{8} metres."

The precision of a measurement depends on the quality of the measuring device used to obtain the measurement. Whereas very sensitive instruments yield measurements of high precision, less sensitive instruments yield results of lower precision. An electronic balance can determine the mass of 24 pennies to the nearest 0.0001 g, giving a measurement with six significant figures: 63.5465 g. A pan balance, on the other hand, can determine this same mass only to the

nearest 0.01 g, giving a measurement with four significant figures: 63.55 g.

When a quantity fluctuates in value, the precision in its measurement is also limited by these fluctuations. For example, the distance between the Earth and its moon fluctuates with time, because the moon's orbit is elliptical rather than perfectly circular. The average distance is 3.844×10^5 km, but the actual distance varies between 3.564×10^5 km and 4.067×10^5 km. Thus, the instantaneous distance between the Earth and its moon varies by 5.03×10^4 km in the course of a month.

Relative and Absolute Precision

The degree of precision in a given experimental value can be expressed either as an **absolute** precision or as a **relative** precision. Absolute precision is the numerical uncertainty in the experimental value, and relative precision is the absolute precision divided by the experimental value. Absolute precisions have units, but relative precisions are always dimensionless ratios. Each of these ways of looking at precision has useful applications.

To illustrate these concepts, return to the example of table length. If we measure a table to be 1.826 metres long, the absolute precision of the measurement is 0.001 metres. The relative precision is the absolute precision divided by the length, (0.001 m)/(1.826 m), or 5×10^{-4}. This relative precision can be expressed as 1/1826, or 5×10^{-4}, or 0.05%, or 5 parts per 10 000. Each of these expressions is a ratio of two values that have the same units, so each ratio is dimensionless. Notice that because the absolute precision contains only one significant figure, this relative precision also contains only one significant figure.

When measurements are added or subtracted to compute a result, the *absolute* precision is more useful. When measurements are multiplied or divided to compute a result, the *relative* precision is more useful. As illustrations, return to the table example and consider the area and perimeter of the table top. Suppose that measurements show its width to be 3.20×10^{-1} metres. The absolute precision of this measurement is 0.001 metres. The relative precision of the width measurement is the appropriate ratio: (0.001 m)/(3.20×10^{-1} m), which is 1/320, or 3×10^{-3}.

Now combine these measurements to determine the perimeter P and the area A. Perimeter is $P = 2L + 2W = 2(1.826\text{ m}) + 2(3.20 \times 10^{-1}\text{ m}) = 4.292$ m, and area is $A = (L)(W) = (1.826\text{ m})(3.20 \times 10^{-1}\text{ m}) = 5.84 \times 10^{-1}\text{ m}^2$. How precisely is each of these computed values known? We find the precision of a computed result from the precisions of individual measurements by considering the largest possible variation in each individual measurement.

First, consider the table's perimeter. According to the precision of the measurements, the length might be as large as 1.827 m or as small as 1.825 m. The width might be as large as 0.321 m or as small as 0.319 m. Thus, the perimeter could be as large as 2(1.827) + 2(0.321) = 4.296 m, and it might be as small as 2(1.825) + 2(0.319) = 4.288 m. The precision in the perimeter is ± 0.004 m. This is the *sum of the absolute precisions* of the individual values: 0.001 + 0.001 + 0.001 + 0.001 = 0.004.

Applying the same logic to the area reveals that it might be as large as $1.827 \times 0.321 = 5.86 \times 10^{-1}\text{ m}^2$ or as small as $1.825 \times 0.319 = 5.82 \times 10^{-1}\text{ m}^2$. The area is $5.84 \times 10^{-1} \pm 0.025 \times 10^{-1}\text{ m}^2$, giving an imprecision of $(0.025 \times 10^{-1})/(5.84 \times 10^{-1}) = 4 \times 10^{-3}$. This is the *sum of the relative precisions* of length (5×10^{-4}) and width (3×10^{-3}).

Rules for Determining Precision

The precision of a composite result can always be determined by the type of analysis described above, but this procedure is tedious. Fortunately, the outcome is always the same. For *addition and subtraction*, the *absolute* precision of the result is the sum of the *absolute* precisions of the individual values. For *multiplication and division*, the *relative* precision of the result is the sum of the *relative* precisions of the individual values.

Another example illustrates the application of these rules. To determine the density of a liquid, a student filled a 25 mL graduated cylinder until it contained 25.0 mL of liquid. The mass of the full cylinder was 47.5764 g. The student removed liquid until the cylinder contained 20.0 mL of liquid, whereupon its mass was 43.0464 g. Table B-1 on the next page summarizes the measurements, computations, and precisions involved in this example.

The absolute precision of each *measured quantity* is found directly from the measurement. The absolute precision of the mass of the cylinder is the precision of the balance, 0.0001 g. Each relative precision is the absolute precision divided by the measured value; thus, the relative precision of the mass of the cylinder is 1/475 000. The precision of each *computed quantity* is determined by adding the precisions of quantities used in the calculation. The values in bold face are found directly. The volume transferred (5.0 mL) is obtained by *subtracting* two volumes, so its *absolute* precision is the sum of the *absolute* precisions of the volumes (0.1 + 0.1 = 0.2 mL). Similar reasoning applies to the mass transferred. The density (0.9060 g/mL) is obtained by *dividing* mass by volume, so its *relative* precision is the sum of the *relative* precisions of transferred mass and transferred volume (1/25 + 1/20 000 = 1/25). Once the relative precision of the density has been calculated, it can be used to compute the absolute precision of the density: (1/25)(0.9060 g/mL) = ± 0.04 g/mL.

Rounding Off

In the above example, the density might be as large as 0.94 g/mL or as small as 0.87 g/mL. It would be incorrect to write it as 0.9060 g/mL, because the use of four significant figures implies that the value is known to 0.0001 g/mL. All nonsignificant figures must be eliminated, a process that is called

TABLE B-1 Measured and Derived Quantities and Precisions

Quantity	Value	Absolute Precision	Relative Precision
Measured Quantities			
Initial cylinder volume	25.0 mL	0.1 mL	1/250
Initial cylinder mass	47.5764 g	0.0001 g	1/475 000
Final cylinder volume	20.0 mL	0.1 mL	1/200
Final cylinder mass	43.0464 g	0.0001 g	1/430 000
Computed Quantities			
Volume transferred	5.0 mL	**0.2 mL**	2/50 = 1/25
Mass transferred	4.5300 g	**0.0002 g**	1/20 000
Liquid density	0.9060 g/mL	0.04 g/mL	1/25

rounding off. Because the uncertainty in the density is in the *second* decimal place, this result is rounded off to two decimals: 0.91 g/mL. This still overstates the precision, because 0.91 g/mL implies a precision of 0.01 g/mL, but this result is actually known only to 0.04 g/mL. However, rounding off one more place to give 0.9 g/mL would imply an uncertainty of 0.1 g/mL, which is larger than the actual uncertainty. The convention is to round off until dropping one more digit would result in an uncertainty larger than the actual uncertainty.

When the digit following the last significant digit is 5 or greater, the remaining digit is increased by 1 unit. For example, 0.9060 becomes 0.91. If the digit following the last significant digit is less than 5, the remaining digit remains unchanged. For example, 0.9045 rounded to two significant figures is 0.90.

Shortcuts to Precision

You can spend much effort figuring out the appropriate number of significant figures in a result. Every time a scientist makes a measurement, precision and significant figures are a concern, but chemists are usually more interested in what experiments reveal than they are in significant figures. Precision may be extremely important, for example when determining the level of a particular carcinogen in a sample of ground water. Because the amount of carcinogen may be critical to human health, the precision of this measurement would have to be carefully stated. Precision is not so important to a chemist whose goal is to prepare new compounds. The chemist wishes to achieve a high yield but is not concerned about whether a yield is 90% or 90.05%.

The following simple guidelines are sufficient to determine the appropriate number of significant figures in General Chemistry.

To determine the number of significant figures in an individual measurement, count the number of digits, from left to right, beginning with the first one that is non-zero.

305	3 significant figures
1.00	3 significant figures
0.020	2 significant figures

When adding or subtracting, set the number of *decimal places* in the answer equal to the number of *decimal places* in the number with the fewest places. The number of significant figures is irrelevant:

	0.12	2 decimal places
	1.6	**1 decimal place**
	11.490	3 decimal places
Sum:	13.2	**1 decimal place**

When multiplying or dividing, set the number of *significant figures* in the answer equal to that of the quantity with the fewest *significant figures*. The number of decimal places is irrelevant:

	1.365	×	2.63	×	0.33	= 1.2
Significant figures:	4		3		2	2

The last example is one where the simplified procedure gives a different result than the more elaborate one. One number (0.33) has a relative precision of 1/33, so the result, 1.1847, could be rounded to 1.18 (1 part in 118) rather than to 1.2 (1 part in 12). If the importance of the result is its quantitative value, 1.18 would be the more appropriate number to report; if its importance is in its qualitative significance, report 1.2. (But don't spend a lot of time worrying about it: either way of reporting is legitimate! What is not legitimate is to report this result as 1.1847.)

Calculators do not necessarily give results with the correct number of significant figures. They automatically drop trailing zeros even when they are significant (try multiplying or adding 3.00 and 5.00 on your calculator) and they carry extra decimal places even when they are insignificant (try dividing 5.00 by 3.00 on your calculator). Never believe the number of significant figures on your calculator!

APPENDIX C: IONIZATION ENERGIES AND ELECTRON AFFINITIES OF THE FIRST 36 ELEMENTS

Z	Symbol	*EA*	IE_1	IE_2	IE_3	$n^\dagger$
1	H	–72.8	1312	—	—	
2	He	>0*	2372	5250	—	1
3	Li	–59.7	520.2	7298	11815	
4	Be	>0	899.4	1757	14848	
5	B	–26.8	800.6	2427	3660	
6	C	–121.9	1086	2353	4620	
7	N	>0	1402	2856	4578	
8	O	–141.1	1314	3388	5300	
9	F	–328.0	1681	3374	6050	2
10	Ne	>0	2081	3952	6122	
11	Na	–52.9	495.6	4562	6912	
12	Mg	>0	737.7	1451	7733	
13	Al	–42.7	577.6	1817	2745	
14	Si	–133.6	786.4	1577	3232	
15	P	–72.0	1012	1908	2912	
16	S	–200.4	999.6	2251	3357	3
17	Cl	–348.8	1251	2297	3822	
18	Ar	>0	1520	2666	3931	
19	K	–48.4	418.8	3051	4420	
20	Ca	–2.4	589.8	1145	4912	
21	Sc	–18.2	633	1235	2389	
22	Ti	–7.7	658	1310	2653	
23	V	–50.8	650	1414	2828	
24	Cr	–64.4	652.8	1591	2987	
25	Mn	>0	717.4	1509	3248	
26	Fe	–14.6	763	1561	2957	
27	Co	–63.9	758	1646	3232	
28	Ni	–111.6	736.7	1753	3396	4
29	Cu	–119.2	745.4	1958	3554	
30	Zn	>0	906.4	1733	3833	
31	Ga	–28.9	578.8	1979	2963	
32	Ge	–119	762.1	1537	3302	
33	As	–78	947	1798	2736	
34	Se	–195.0	940.9	2045	2974	
35	Br	–324.6	1140	2103	3500	
36	Kr	>0	1351	2350	3565	

All values are in kJ/mol.

*A value >0 means that the anion is unstable, so its electron affinity cannot be experimentally determined.

† *n* is the principal quantum number of the electron whose ionization energy is listed.

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APPENDIX D: STANDARD THERMODYNAMIC FUNCTIONS

$T = 298.15$ K; $p = 1.000$ bar; Aqueous species at 1.000 M

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol K)
Aluminum			
Al(*s*)	0	0	28.3
$AlCl_3$(*s*)	–704.2	–628.8	109.3
Al_2O_3(*s*)	–1675.7	–1582.3	50.9
Antimony			
Sb(*s*)	0	0	45.7
Sb_4O_6(*s*)	–1417.1	–1253.0	246.0
Argon			
Ar(*g*)	0	0	154.843
Arsenic			
As(*s*)	0	0	35.1
As_2O_5(*s*)	–924.9	–782.3	105.4
$AsCl_3$(*l*)	–305.0	–259.4	216.3
Barium			
Ba(*s*)	0	0	62.5
BaO(*s*)	–548.0	–520.3	72.1
$BaCO_3$(*s*)	–1213.0	–1134.4	112.1
$BaCl_2$(*s*)	–855.0	–806.7	123.7
$BaSO_4$(*s*)	–1473.2	–1362.2	132.2
Beryllium			
Be(*s*)	0	0	9.5
$Be(OH)_2$(*s*)	–902.5	–815.0	51.9
Boron			
B(*s*)	0	0	5.9
B_2O_3(*s*)	–1273.5	–1194.3	54.0
H_3BO_3(*s*)	–1094.3	–968.9	90.0
BCl_3(*g*)	–403.8	–388.7	290.1
Bromine			
Br(*g*)	111.9	82.4	175.0
Br_2(*l*)	0	0	152.2
Br_2(*g*)	30.9	3.1	245.5
Br^-(*aq*)	–121.4	–104.0	82.4
BrO^-(*aq*)	–94.1	–33.4	42
HBr(*g*)	–36.3	–53.4	198.7
Cadmium			
Cd(*s*)	0	0	51.8
CdO(*s*)	–258.4	–228.7	54.8
$CdCl_2$(*s*)	–391.5	–343.9	115.3

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol K)
Calcium			
Ca(*s*)	0	0	41.6
Ca^{2+}(*aq*)	–543.0	–553.6	–56.2
CaO(*s*)	–634.9	–603.3	38.1
$Ca(OH)_2$(*s*)	–985.2	–897.5	83.4
$CaCO_3$(*s*)	–1207.6	–1129.1	91.7
$CaCl_2$(*s*)	–795.4	–748.8	108.4
CaF_2(*s*)	–1228	–1176	68.5
CaH_2(*s*)	–185.1	–142.5	41.4
CaS(*s*)	–482.4	–477.4	56.5
$CaSO_4$(*s*)	–1434.5	–1322.0	106.5
Carbon			
C(*s, graphite*)	0	0	5.7
C(*s, diamond*)	1.9	2.9	2.4
CH_4(*g*)	–74.6	–50.5	186.3
C_2H_2(*g*)	227.4	209.9	200.9
C_2H_4(*g*)	52.4	68.4	219.3
C_2H_6(*g*)	–84.0	–32.0	229.2
C_3H_6(*g*)	20.0	74.62	226.9
C_3H_8(*g*)	–103.8	–23.4	270.3
C_6H_6(*l*)	49.1	124.5	173.4
CO(*g*)	–110.5	–137.2	197.7
CO_2(*g*)	–393.5	–394.4	213.8
HCN(*g*)	135.1	124.7	201.8
CS_2(*l*)	89.0	64.6	151.3
CCl_4(*l*)	–128.2	–65.21	216.40
$CHCl_3$(*l*)	–134.1	–73.7	201.7
CH_3CHO(*g*)	–166.2	–127.6	263.8
CH_3CO_2H(*l*)	–484.3	–389.9	159.8
CH_3OH(*l*)	–239.2	–166.6	126.8
CH_3CH_2OH(*l*)	–277.6	–174.8	160.7
CH_3CN(*l*)	40.6	86.5	149.6
Chlorine			
Cl(*g*)	121.3	105.3	165.2
Cl_2(*g*)	0	0	223.1
Cl^-(*aq*)	–167.1	–131.0	56.5
HCl(*g*)	–92.3	–95.3	186.9
ClO^-(*aq*)	–107.1	–36.8	42

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol K)
Chlorine (cont.)			
$ClO_2^-(aq)$	–67	17	101
$ClO_3^-(aq)$	–104	–3	162
$ClO_4^-(aq)$	–128.1	–8.52	184.0
$ClO(g)$	101.8	98.1	226.6
$ClO_2(g)$	102.5	120.5	256.8
Chromium			
$Cr(s)$	0	0	23.8
$Cr_2O_3(s)$	–1139.7	–1058.1	81.2
$CrCl_3(s)$	–556.5	–486.1	123.0
Cobalt			
$Co(s)$	0	0	30.0
$CoO(s)$	–237.9	–214.2	53.0
$CoCl_2(s)$	–312.5	–269.8	109.2
Copper			
$Cu(s)$	0	0	33.2
$CuO(s)$	–157.3	–129.7	42.6
$CuS(s)$	–53.1	–53.6	66.5
$CuCl_2(s)$	–220.1	–175.7	108.1
$CuCl(s)$	–137.2	–119.9	86.2
$CuBr(s)$	–104.6	–100.8	96.1
$CuI(s)$	–67.8	–69.5	96.7
$CuSO_4(s)$	–771.4	–662.2	109.2
Fluorine			
$F(g)$	79.4	62.3	158.8
$F_2(g)$	0	0	202.8
$F^-(aq)$	–335.4	–278.79	–13.8
$HF(g)$	–273.3	–275.4	173.8
Germanium			
$Ge(s)$	0	0	31.1
$GeCl_4(g)$	–495.8	–457.3	347.7
$GeO_2(s)$	–580.0	–521.4	39.7
Gold			
$Au(s)$	0	0	47.4
Helium			
$He(g)$	0	0	126.153
Hydrogen			
$H_2(g)$	0	0	130.680
$H_2O(l)$	–285.83	–237.1	69.95
$H_2O(g)$	–241.83	–228.72	188.835
$H_2O_2(l)$	–187.8	–120.4	109.6
$H^+(aq)$	0	0	0
$H_3O^+(aq)$	–285.83	–237.1	69.95
Iodine			
$I_2(s)$	0	0	116.1
$I_2(g)$	62.4	19.3	260.7
$I^-(aq)$	–56.78	–51.57	106.5
$HI(g)$	26.5	1.7	206.6
Iron			
$Fe(s)$	0	0	27.3
$Fe_2O_3(s)$	–824.2	–742.2	87.4
$FeO(s)$	–272.0	–251.4	60.8
$Fe_3O_4(s)$	–1118.4	–1015.4	146.4
$Fe(OH)_3(s)$	–823.0	–696.5	106.7
$FeCl_2(s)$	–341.8	–302.3	118.0
$FeCl_3(s)$	–399.5	–334.0	142.3
$FeSO_4(s)$	–928.4	–820.8	107.5
$FeS(s)$	–100.0	–100.4	60.3
$FeS_2(s)$	–178.2	–166.9	52.9
Krypton			
$Kr(g)$	0	0	164.085
Lead			
$Pb(s)$	0	0	64.8
$PbCl_2(s)$	–359.4	–314.1	136.0
$PbO(s)$	–217.3	–187.9	68.7
$PbO_2(s)$	–277.4	–217.3	68.6
$PbS(s)$	–100.4	–98.7	91.2
Lithium			
$Li(s)$	0	0	29.1
$Li^+(aq)$	–278.47	–293.31	12.2
$Li_2O(s)$	–597.9	–561.2	37.6
$LiOH(s)$	–484.9	–439.0	42.8
$LiCl(s)$	–408.6	–384.4	59.3
Magnesium			
$Mg(s)$	0	0	32.67
$Mg^{2+}(aq)$	–467.0	–454.8	–137
$MgO(s)$	–601.6	–569.3	27.0
$Mg(OH)_2(s)$	–924.5	–833.5	63.2
$MgCl_2(s)$	–641.3	–591.8	89.6
$MgF_2(s)$	–1124.2	–1071.1	57.2
$MgCO_3(s)$	–1095.8	–1012.1	65.7
$MgSO_4(s)$	–1284.9	–1170.6	91.6
Manganese			
$Mn(s)$	0	0	32.0
$MnO(s)$	–385.2	–362.9	59.7
$MnO_2(s)$	–520.0	–465.1	53.1
$MnCl_2(s)$	–481.3	–440.5	118.2
$MnCO_3(s)$	–894.1	–816.7	85.8
$MnSO_4(s)$	–1065.25	–957.36	112.1

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol K)
Mercury			
Hg(*l*)	0	0	75.9
Hg(*g*)	61.4	31.8	175.0
HgO(*s*)	–90.8	–58.5	70.3
$HgCl_2$(*s*)	–224.3	–178.6	146.0
Hg_2Cl_2(*s*)	–265.4	–210.7	191.6
HgS(*s*)	–58.2	–50.6	82.4
Neon			
Ne(*g*)	0	0	146.328
Nickel			
Ni(*s*)	0	0	29.9
NiO(*s*)	–239.7	–211.7	37.99
$NiCl_2$(*s*)	–305.3	–259.0	97.7
Nitrogen			
N_2(*g*)	0	0	191.61
NH_3(*g*)	–45.9	–16.4	192.8
NH_3(*aq*)	–80.29	–26.50	111.3
NH_4^+(*aq*)	–133.3	–79.31	111.2
N_2H_4(*l*)	50.6	149.3	121.2
NO(*g*)	91.3	87.6	210.8
NO_2(*g*)	33.2	51.3	240.1
N_2O(*g*)	81.6	103.7	220.0
N_2O_4(*g*)	11.1	99.8	304.4
N_2O_5(*g*)	13.3	117.1	355.7
NH_4Cl(*s*)	–314.4	–202.9	94.6
NH_4NO_3(*s*)	–365.6	–183.9	151.1
$(NH_2)_2CO$(*s*)	–333.1	–198	105
HNO_3(*g*)	–133.9	–73.5	266.9
Oxygen			
O_2(*g*)	0	0	205.152
O_3(*g*)	142.7	163.2	238.9
OH^-(*aq*)	–230.0	–157.244	–10.9
Phosphorus			
P(*s*, *white*)	0	0	41.1
P(*s*, *red*)	–17.6	–12.1	22.8
P_4(*g*)	58.9	24.4	280.0
PH_3(*g*)	5.4	13.4	210.2
P_4O_{10}(*s*)	–2984.0	–2697.7	228.86
H_3PO_4	–1271.7	–1123.6	150.8
PCl_5(*g*)	–374.9	–305.0	364.6
PCl_3(*g*)	–287.0	–267.8	311.8
Potassium			
K(*s*)	0	0	64.7
K^+(*aq*)	–252.1	–283.27	101.2
KO_2(*s*)	–284.9	–239.4	116.7
KOH(*s*)	–424.6	–378.9	78.9
KCl(*s*)	–436.5	–408.5	82.6
$KClO_3$(*s*)	–397.7	–296.3	143.1
Potassium (cont.)			
KI(*s*)	–327.9	–324.9	106.3
Selenium			
Se(*s*)	0	0	42.4
H_2Se(*g*)	29.7	15.9	219.0
Silicon			
Si(*s*)	0	0	18.8
SiH_4(*g*)	34.3	56.9	204.6
SiO_2(*s*)	–910.7	–856.3	41.5
$SiCl_4$(*l*)	–687.0	–619.8	239.7
SiC(*s*)	–65.3	–62.8	16.6
Silver			
Ag(*s*)	0	0	42.6
Ag^+(*aq*)	105.8	77.107	73.4
Ag_2O(*s*)	–31.1	–11.2	121.3
AgCl(*s*)	–127.0	–109.8	96.3
AgBr(*s*)	–100.4	–96.9	107.1
$AgNO_3$(*s*)	–124.4	–33.4	140.9
Sodium			
Na(*s*)	0	0	51.3
Na^+(*aq*)	–240.3	–261.905	58.5
Na_2O(*s*)	–414.2	–375.5	75.1
NaOH(*s*)	–425.6	–379.5	64.5
NaF(*s*)	–576.6	–546.3	51.1
NaCl(*s*)	–411.2	–384.1	72.1
NaBr(*s*)	–361.1	–349.0	86.8
NaI(*s*)	–287.8	–286.1	98.5
Na_2CO_3(*s*)	–1130.7	–1044.4	135.0
Strontium			
Sr(*s*)	0	0	55.0
SrO(*s*)	–592.0	–561.9	54.4
$SrCl_2$(*s*)	–828.9	–781.1	114.9
Sulphur			
S_8(*s*)	0	0	31.80
S_8(*g*)	102.30	49.63	430.23
H_2S(*g*)	–20.6	–33.4	205.8
SO_2(*g*)	–296.8	–300.1	248.2
SO_3(*g*)	–395.7	–371.1	256.8
H_2SO_4(*l*)	–814	–690.0	156.9
SO_4^{2-}(*aq*)	–909.3	–774.53	18.5
SF_6(*g*)	–1220.5	–1116.5	291.5
Tellurium			
Te(*s*)	0	0	49.7
TeO_2(*s*)	–322.6	–270.3	79.5
Tin			
Sn(*s*, *white*)	0	0	51.2
Sn(*s*, *gray*)	–2.1	0.13	44.1
SnO(*s*)	–280.7	–251.9	57.2

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol K)
Tin (cont.)			
$SnO_2(s)$	–577.6	–515.8	49.0
$SnCl_4(s)$	–511.3	–440.1	258.6
Titanium			
$Ti(s)$	0	0	30.7
$TiCl_4(l)$	–804.2	–737.2	252.3
$TiCl_4(g)$	–763.2	–726.3	353.2
$TiO_2(s)$	–944.0	–888.8	50.6
Uranium			
$U(s)$	0	0	50.2
$UO_2(s)$	–1085.0	–1031.8	77.0
Uranium (cont.)			
$UF_6(g)$	–2147.4	–2063.7	377.9
Xenon			
$Xe(g)$	0	0	169.685
$XeF_4(s)$	–261.5	–138	316
Zinc			
$Zn(s)$	0	0	41.63
$ZnO(s)$	–350.5	–320.5	43.7
$ZnCl_2(s)$	–415.1	–369.4	111.5
$ZnS(s)$	–206.0	–201.3	57.7

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APPENDIX E: EQUILIBRIUM CONSTANTS

K_b VALUES

Name	Formula	pK_b	K_b
Ammonia	NH_3	4.75	1.8×10^{-5}
Aniline	$C_6H_5NH_2$	9.13	7.4×10^{-10}
Diethylamine	$(C_2H_5)_2NH$	3.16	6.9×10^{-4}
Dimethylamine	$(CH_3)_2NH$	3.27	5.4×10^{-4}
Ethylamine	$C_2H_5NH_2$	3.35	4.5×10^{-4}
Ethylenediamine	$(CH_2NH_2)_2$	4.08	8.3×10^{-5}
Hydrazine	H_2NNH_2	5.89	1.3×10^{-6}
Hydroxylamine	$HONH_2$	8.06	8.7×10^{-9}
Methylamine	CH_3NH_2	3.34	4.6×10^{-4}
Pyridine	C_5H_5N	8.77	1.7×10^{-9}
Triethylamine	$(C_2H_5)_3N$	3.25	5.6×10^{-4}
Trimethylamine	$(CH_3)_3N$	4.19	6.5×10^{-5}
Urea	H_2NCONH_2	13.82	1.5×10^{-14}

K_a VALUES

Name	Formula	pK_a	K_a
Oxoacids			
Arsenic	H_3AsO_4	2.26	5.5×10^{-3}
Boric	H_3BO_3	9.27	5.4×10^{-10}
Carbonic	H_2CO_3	6.35	4.5×10^{-7}
K_{a2}	HCO_3^-	10.33	4.7×10^{-11}
Chlorous	$HClO_2$	1.94	1.1×10^{-2}
Chromic	H_2CrO_4	0.74	1.8×10^{-1}

K_a VALUES (cont.)

Name	Formula	pK_a	K_a
Oxoacids (cont.)			
K_{a2}	$HCrO_4^-$	6.49	3.2×10^{-7}
Hypobromous	HBrO	8.55	2.8×10^{-9}
Hypochlorous	HClO	7.40	4.0×10^{-8}
Hypoiodous	HIO	10.5	3.2×10^{-11}
Iodic	HIO_3	0.78	1.7×10^{-1}
Nitrous	HNO_2	3.25	5.6×10^{-4}
Paraperiodic	H_5IO_6	1.55	2.8×10^{-2}
Periodic	HIO_4	1.64	7.3×10^{-2}
Phosphoric	H_3PO_4	2.16	6.9×10^{-3}
K_{a2}	$H_2PO_4^-$	7.21	6.2×10^{-8}
K_{a3}	HPO_4^{2-}	12.32	4.8×10^{-13}
Phosphorous	H_3PO_3	1.3	5.0×10^{-2}
K_{a2}	$H_2PO_3^-$	6.70	2.0×10^{-7}
Sulphuric	H_2SO_4	strong	
K_{a2}	HSO_4^-	1.99	1.0×10^{-2}
Sulphurous	H_2SO_3	1.85	1.4×10^{-2}
K_{a2}	HSO_3^-	7.20	6.3×10^{-8}
Carboxylic acids			
Acetic	CH_3CO_2H	4.75	1.8×10^{-5}
Benzoic	$C_6H_5CO_2H$	4.20	6.3×10^{-5}
Chloroacetic	$ClCH_2CO_2H$	2.87	1.4×10^{-3}
Formic	HCO_2H	3.75	1.8×10^{-4}

K_a VALUES (cont.)

Name	*Formula*	pK_a	K_a
Carboxylic acids (cont.)			
Oxalic	$(CO_2H)_2$	1.25	5.6×10^{-2}
K_{a2}	$HO_2CCO_2^-$	3.81	1.5×10^{-4}
Propanoic	$C_2H_5CO_2H$	4.87	1.3×10^{-5}
Trichloroacetic	Cl_3CCO_2H	0.66	2.2×10^{-1}
Other acids			
Cyanic	HCNO	3.46	3.5×10^{-4}
Hydrazoic	HN_3	4.6	2.5×10^{-5}
Hydrocyanic	HCN	9.21	6.2×10^{-10}
Hydrofluoric	HF	3.20	6.3×10^{-4}
Hydrogen peroxide	H_2O_2	11.62	2.4×10^{-12}
Hydrogen sulphide	H_2S	7.05	8.9×10^{-8}
K_{a2}	HS^-	19	1×10^{-19}
Phenol	C_6H_5OH	9.99	1.0×10^{-10}

K_{sp} VALUES, SALTS AT 25 °C

Formula	pK_{sp}	K_{sp}
Bromides		
AgBr	12.27	5.35×10^{-13}
CuBr	8.20	6.3×10^{-9}
Carbonates		
Ag_2CO_3	11.07	8.46×10^{-12}
$BaCO_3$	8.59	2.6×10^{-9}
$CaCO_3$	8.47	3.36×10^{-9}
$CdCO_3$	12.00	1.0×10^{-12}
$CoCO_3$	12.85	1.4×10^{-13}
$CuCO_3$	9.85	1.4×10^{-10}
$FeCO_3$	10.51	3.1×10^{-11}
$MgCO_3$	5.17	6.8×10^{-6}
$MnCO_3$	10.66	2.2×10^{-11}
$NiCO_3$	6.84	1.4×10^{-7}
$PbCO_3$	13.13	7.4×10^{-14}
$SrCO_3$	9.25	5.6×10^{-10}
$ZnCO_3$	9.82	1.5×10^{-10}
Chlorides		
AgCl	9.74	1.8×10^{-10}
CuCl	6.76	1.7×10^{-7}
$PbCl_2$	4.77	1.7×10^{-5}
Fluorides		
BaF_2	6.74	1.8×10^{-7}
CaF_2	10.46	3.45×10^{-11}
PbF_2	7.48	3.3×10^{-8}
Hydroxides		
$Al(OH)_3$	32.34	4.6×10^{-33}
$Ba(OH)_2$	3.59	2.55×10^{-4}
$Ca(OH)_2$	5.30	5.0×10^{-6}
$Cd(OH)_2$	14.14	7.2×10^{-15}
$Co(OH)_2$	14.23	5.9×10^{-15}
$Co(OH)_3$	43.8	1.6×10^{-44}
$Cu(OH)_2$	14.96	1.1×10^{-15}
$Fe(OH)_2$	16.32	4.8×10^{-17}
$Fe(OH)_3$	38.55	2.8×10^{-39}
$Mg(OH)_2$	11.25	5.6×10^{-12}
$Ni(OH)_2$	15.26	5.5×10^{-16}
$Pb(OH)_2$	19.85	1.4×10^{-20}
$Sn(OH)_2$	26.26	5.5×10^{-27}
$Zn(OH)_2$	16.52	3×10^{-17}
Phosphates		
$Ba_3(PO_4)_2$	22.47	3.4×10^{-23}
$Ca_3(PO_4)_2$	32.70	2.0×10^{-33}
Sulphates		
Ag_2SO_4	4.92	1.2×10^{-5}
$BaSO_4$	9.96	1.1×10^{-10}
$CaSO_4$	4.31	4.9×10^{-5}
$PbSO_4$	7.60	2.5×10^{-8}
Sulphides		
Ag_2S	49.20	6.3×10^{-50}
CoS	20.40	4.0×10^{-21}
Cu_2S	47.60	2.5×10^{-48}
CuS	25.20	6.3×10^{-26}
FeS	18.80	1.6×10^{-19}
Hg_2S	47.00	1.0×10^{-47}
HgS	52.40	4.0×10^{-53}
MnS	13.34	4.6×10^{-14}
NiS	20.97	1.1×10^{-21}
PbS	28.05	8.9×10^{-29}
SnS	27.49	3.2×10^{-28}
ZnS	24.53	3.0×10^{-25}

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APPENDIX F: STANDARD REDUCTION POTENTIALS, E°

$T = 298.15$ K, and $p = 1.00$ bar.
Listed alphabetically by element; all values are in volts.

All ionic species are aqueous. H_2O is liquid.
All other neutrals are solids unless otherwise specified.

Aluminum	
$Al^{3+} + 3\ e^- \rightarrow Al$	−1.662
$Al(OH)_3 + 3\ e^- \rightarrow Al + 3\ OH^-$	−2.31
Arsenic	
$HAsO_2(aq) + 3\ H_3O^+ + 3\ e^- \rightarrow As + 5\ H_2O$	+0.248
Barium	
$Ba^{2+} + 2\ e^- \rightarrow Ba$	−2.912
$Ba(OH)_2 + 2\ e^- \rightarrow Ba + 2\ OH^-$	−2.99
Boron	
$H_3BO_3(aq) + 3\ H_3O^+ + 3\ e^- \rightarrow B + 6\ H_2O$	−0.8698
Bromine	
$Br_2(aq) + 2\ e^- \rightarrow 2\ Br^-$	+1.0873
$Br_2(l) + 2\ e^- \rightarrow 2\ Br^-$	+1.066
$HBrO(aq) + H_3O^+ + 2\ e^- \rightarrow Br^- + 2\ H_2O$	+1.331
$BrO_3^- + 6\ H_3O^+ + 5\ e^- \rightarrow Br_2(l) + 3\ H_2O$	+1.423
Cadmium	
$Cd^{2+} + 2\ e^- \rightarrow Cd$	−0.403
$Cd(OH)_2 + 2\ e^- \rightarrow Cd + 2\ OH^-$	−0.809
Calcium	
$Ca^{2+} + 2\ e^- \rightarrow Ca$	−2.868
$Ca(OH)_2 + 2\ e^- \rightarrow Ca + 2\ OH^-$	−3.02
Carbon	
$CO_2(g) + 2\ H_3O^+ + 2\ e^- \rightarrow HCO_2H + 2\ H_2O$	−0.199
$2\ CO_2(g) + 2\ H_3O^+ + 2\ e^- \rightarrow H_2C_2O_4 + 2\ H_2O$	−0.49
$CNO^- + H_2O + 2\ e^- \rightarrow CN^- + 2\ OH^-$	−0.970
p-Benzoquinone $+ H_3O^+ + 2\ e^- \rightarrow$ Hydroquinone $+ H_2O$	+0.6992
Cesium	
$Cs^+ + e^- \rightarrow Cs$	−3.026
Chlorine	
$Cl_2(g) + 2\ e^- \rightarrow 2\ Cl^-$	+1.35827
$2\ HClO(aq) + 2\ H_3O^+ + 2\ e^- \rightarrow Cl_2(g) + 2\ H_2O$	+1.611
$ClO^- + H_2O + 2\ e^- \rightarrow Cl^- + 2\ OH^-$	+0.81
$ClO_3^- + 6\ H_3O^+ + 6\ e^- \rightarrow Cl^- + 9\ H_2O$	+1.451
$ClO_4^- + 2\ H_3O^+ + 2\ e^- \rightarrow ClO_3^- + 3\ H_2O$	+1.189
$2\ ClO_4^- + 16\ H_3O^+ + 14\ e^- \rightarrow Cl_2(g) + 24\ H_2O$	+1.39
$ClO_4^- + 6\ H_3O^+ + 6\ e^- \rightarrow ClO^- + 9\ H_2O$	+1.36
$ClO_4^- + 8\ H_3O^+ + 8\ e^- \rightarrow Cl^- + 12\ H_2O$	+1.389
Chromium	
$Cr^{3+} + 3\ e^- \rightarrow Cr$	−0.744
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.407
$Cr^{2+} + 2\ e^- \rightarrow Cr$	−0.913
$Cr_2O_7^{2-} + 14\ H_3O^+ + 6\ e^- \rightarrow 2\ Cr^{3+} + 21\ H_2O$	+1.36
$Cr(OH)_3 + 3\ e^- \rightarrow Cr + 3\ OH^-$	−1.48
Cobalt	
$Co^{3+} + e^- \rightarrow Co^{2+}$	+1.92
$Co^{2+} + 2\ e^- \rightarrow Co$	−0.28
$[Co(NH_3)_6]^{3+} + e^- \rightarrow [Co(NH_3)_6]^{2+}$	−0.108
Copper	
$Cu^{2+} + 2\ e^- \rightarrow Cu$	+0.3419
$Cu^{2+} + e^- \rightarrow Cu^+$	+0.153
$Cu^+ + e^- \rightarrow Cu$	+0.521
$Cu(OH)_2 + 2\ e^- \rightarrow Cu + 2\ OH^-$	−0.222
Fluorine	
$F_2(g) + 2\ e^- \rightarrow 2\ F^-$	+2.866
Gold	
$Au^{3+} + 3\ e^- \rightarrow Au$	+1.498
$Au(CN)_2^- + e^- \rightarrow Au + 2\ CN^-$	−0.60
Hydrogen	
$2\ H_3O^+ + 2\ e^- \rightarrow H_2(g) + 2\ H_2O$	0 (by definition)
$2\ H_2O + 2\ e^- \rightarrow H_2(g) + 2\ OH^-$	−0.828
$H_2O_2(aq) + 2\ H_3O^+ + 2\ e^- \rightarrow 2\ H_2O$	+1.776
Iodine	
$I_2 + 2\ e^- \rightarrow 2\ I^-$	+0.5355
$I_3^- + 2\ e^- \rightarrow 3\ I^-$	+0.536
$2\ IO_3^- + 12\ H_3O^+ + 10\ e^- \rightarrow I_2 + 18\ H_2O$	+1.195
$H_5IO_6 + H_3O^+ + 2\ e^- \rightarrow IO_3^- + 4\ H_2O$	+1.601
Iron	
$Fe^{3+} + 3\ e^- \rightarrow Fe$	−0.037
$Fe^{2+} + 2\ e^- \rightarrow Fe$	−0.447
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.771
$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$	+0.358
Lead	
$Pb^{2+} + 2\ e^- \rightarrow Pb$	−0.1262
$PbO_2 + HSO_4^-(aq) + 3\ H_3O^+(aq) + 2\ e^- \rightarrow PbSO_4(s) + 5\ H_2O(l)$	+1.6913
$PbO_2 + 4\ H_3O^+ + 2\ e^- \rightarrow Pb^{2+} + 6\ H_2O$	+1.455
$PbSO_4 + H_3O^+ + 2\ e^- \rightarrow Pb + HSO_4^- + H_2O$	−0.3588
Lithium	
$Li^+ + e^- \rightarrow Li$	−3.0401
Magnesium	
$Mg^{2+} + 2\ e^- \rightarrow Mg$	−2.37
$Mg(OH)_2 + 2\ e^- \rightarrow Mg + 2\ OH^-$	−2.69
Manganese	
$Mn^{2+} + 2\ e^- \rightarrow Mn$	−1.185
$MnO_4^- + 4\ H_3O^+ + 3\ e^- \rightarrow MnO_2 + 6\ H_2O$	+1.679
$MnO_4^- + 2\ H_2O + 3\ e^- \rightarrow MnO_2 + 4\ OH^-$	+0.595
$MnO_4^- + 8\ H_3O^+ + 5\ e^- \rightarrow Mn^{2+} + 12\ H_2O$	+1.507
$MnO_2 + 4\ H_3O^+ + 2\ e^- \rightarrow Mn^{2+} + 6\ H_2O$	+1.224
Mercury	
$Hg^{2+} + 2\ e^- \rightarrow Hg(l)$	+0.851
$Hg_2Cl_2 + 2\ e^- \rightarrow 2\ Hg(l) + 2\ Cl^-$	+0.26808
$2\ Hg^{2+} + 2\ e^- \rightarrow Hg_2^{2+}$	+0.920
$Hg_2^{2+} + 2\ e^- \rightarrow 2\ Hg(l)$	+0.7973

Nickel	
$Ni^{2+} + 2\ e^- \rightarrow Ni$	–0.257
$Ni(OH)_2 + 2\ e^- \rightarrow Ni + 2\ OH^-$	–0.72
$NiO_2 + 4\ H_3O^+ + 2\ e^- \rightarrow Ni^{2+} + 6\ H_2O$	+1.678
Nitrogen	
$N_2(g) + 8\ H_3O^+ + 6\ e^- \rightarrow 2\ NH_4^+ + 8\ H_2O$	+0.092
$NO_2(g) + 2\ H_3O^+ + 2\ e^- \rightarrow NO(g) + 3\ H_2O$	+1.03
$N_2O(g) + 2\ H_3O^+ + 2\ e^- \rightarrow N_2(g) + 3\ H_2O(l)$	+1.766
$NO_3^- + 4\ H_3O^+ + 3\ e^- \rightarrow NO(g) + 6\ H_2O$	+0.957
$2\ NO(g) + 2\ H_3O^+ + 2\ e^- \rightarrow N_2O(g) + 3\ H_2O$	+1.591
$NO_2^-(g) + H_2O + 3\ e^- \rightarrow NO(g) + 2\ OH^-$	–0.46
$NO_3^- + 2\ H_2O + 3\ e^- \rightarrow NO(g) + 4\ OH^-$	+0.109
Oxygen	
$O_2(g) + 2\ H_3O^+ + 2\ e^- \rightarrow H_2O_2(l) + 2\ H_2O$	+0.695
$O_2(g) + 2\ H_2O + 2\ e^- \rightarrow H_2O_2(l) + 2\ OH^-$	–0.146
$O_2(g) + 4\ H_3O^+ + 4\ e^- \rightarrow 6\ H_2O$	+1.229
$O_2(g) + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$	+0.401
$O_3(g) + 2\ H_3O^+ + 2\ e^- \rightarrow O_2(g) + 3\ H_2O$	+2.076
Platinum	
$Pt^{2+} + 2\ e^- \rightarrow Pt$	+1.18
Potassium	
$K^+ + e^- \rightarrow K$	–2.931
Selenium	
$SeO_3^{2-} + 3\ H_2O + 4\ e^- \rightarrow Se + 6\ OH^-$	–0.366
Silver	
$Ag^+ + e^- \rightarrow Ag$	+0.7996
$AgCl + e^- \rightarrow Ag + Cl^-$	+0.22233
$AgBr + e^- \rightarrow Ag + Br^-$	+0.07133
$AgI + e^- \rightarrow Ag + I^-$	–0.15224
Sodium	
$Na^+ + e^- \rightarrow Na$	–2.71
Sulphur	
$S + 2\ H_3O^+ + 2\ e^- \rightarrow H_2S + 2\ H_2O$	+0.14
$S_4O_6^{2-} + 2\ e^- \rightarrow 2\ S_2O_3^{2-}$	+0.08
Tin	
$Sn^{2+} + 2\ e^- \rightarrow Sn$	–0.137
$Sn^{4+} + 2\ e^- \rightarrow Sn^{2+}$	+0.151
Titanium	
$Ti^{2+} + 2\ e^- \rightarrow Ti$	–1.630
$Ti^{3+} + e^- \rightarrow Ti^{2+}$	–0.85
$TiO_2 + 4\ H_3O^+ + 2\ e^- \rightarrow Ti^{2+} + 6\ H_2O$	–0.502
Zinc	
$Zn^{2+} + 2\ e^- \rightarrow Zn$	–0.7618
$[Zn(NH_3)_4]^{2+} + 2\ e^- \rightarrow Zn + 4\ NH_3(aq)$	–1.04

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APPENDIX G: COMMON POLYATOMIC IONS

Ion	*Chemical Formula*	*Ion*	*Chemical Formula*
Acetate	CH_3COO^-	Hypochlorite	ClO^-
Ammonium	NH_4^+	Hydronium	H_3O+
Benzoate	$C_6H_5COO^-$	Hydroxide	OH^-
Bicarbonate	HCO_3^-	Nitrate	NO_3^-
Bisulphate	HSO_4^-	Nitrite	NO_2^-
Bisulphite	HSO_3^-	Oxalate	$C_2O_4^{2-}$
Carbonate	CO_3^{2-}	Perchlorate	ClO_4^-
Chlorate	ClO_3^-	Permanganate	MnO_4^-
Chlorite	ClO_2^-	Phosphate	PO_4^{3-}
Chromate	CrO_4^{2-}	Sulphate	SO_4^{2-}
Cyanide	CN^-	Sulphite	SO_3^{2-}
Cyanate	CNO^-	Thiosulphate	$S_2O_3^{2-}$
Dichromate	$Cr_2O_7^{2-}$	Thiocyanate	CNS^-
Formate	$HCOO^-$		

SOLUTIONS TO ODD-NUMBERED PROBLEMS

Chapter 1

1.1 (a) H; (b) He; (c) Hf; (d) N; (e) Ne; (f) Nb

1.3 (a) arsenic; (b) argon; (c) aluminum; (d) americium; (e) silver; (f) gold; (g) astatine; (h) actinium

1.5 (a) Br_2; (b) HCl; (c) C_2H_5I; (d) C_3H_6O

1.7 (a) CCl_4; (b) H_2O_2; (c) P_4O_{10}; (d) Fe_2S_3

1.9 (a) 1.00000×10^5; (b) 1.0×10^4; (c) 4.00×10^{-4}; (d) 3×10^{-4}; (e) 2.753×10^2

1.11 (a) 4.32×10^2 kg; (b) 6.24×10^{-10} s; (c) 1.024×10^{-9} kg; (d) 9.300×10^7 m; (e) 8.64×10^4 s; (f) 1.08×10^{-3} m

1.13 7.10×10^{-3} kg

1.15 9.98×10^2 kg/m^3

1.17 Silver cube

1.19 11.7 mL

1.21 39.948 g/mol

1.23 (a) 0.141 mol; (b) 5.45×10^{-6} mol; (c) 1.67×10^{-4} mol; (d) 5.41×10^4 mol

1.25 (a) 3.92×10^{20} atoms; (b) 1.14×10^{20} atoms; (c) 3.87×10^{19} atoms; (d) 1.48×10^{19} atoms

1.27 (a) 153.81 g/mol; (b) 110.27 g/mol; (c) 48.00 g/mol; (d) 86.84 g/mol; (e) 144.64 g/mol; (f) 169.88 g/mol

1.29 (a) $C_9H_{11}NO_3$; 181.19 g/mol; (b) $C_{11}H_{12}N_2O_2$, 204.23 g/mol; (c) $C_5H_9NO_4$, 147.13 g/mol; (d) $C_6H_{14}N_2O_2$, 146.19 g/mol

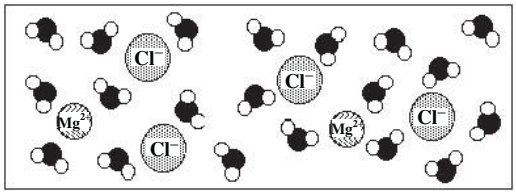
1.31 (a) 2.20×10^{20} molecules; (b) 2.57×10^{19} molecules; (c) 7.66×10^{19} molecules; (d) 1.00×10^{19} molecules

1.33 (a) 9.99×10^{-18} g; (b) 7.6×10^{-13} g; (c) 1.484×10^{-21} g

1.35 2.6×10^{-6} mol; 1.6×10^{18} molecules; No. of H atoms = 4.8×10^{19} atoms; 8.0×10^{-5} mg

1.37 (a) $M_{Mg^{2+}} = 0.328$ M; $M_{Cl^-} = 0.655$ M;

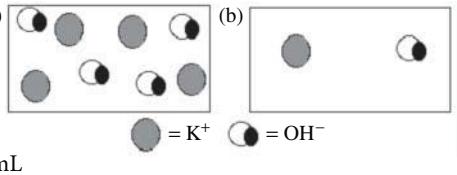
(b)



1.39 (a) $[K^+] = [OH^-] = 0.308$ M;

(b) $[K^+] = [OH^-] = 0.077$ M;

(c) (a) (b)



1.41 5.17 mL

1.43 (a) $[CO_3^{2-}] = 0.175$ M; $[Na^+] = 0.350$ M;

(b) $[NH_4^+] = [Cl^-] = 0.033$ M;

(c) $[SO_4^{2-}] = 1.84 \times 10^{-3}$ M; $[K^+] = 3.69 \times 10^{-3}$ M

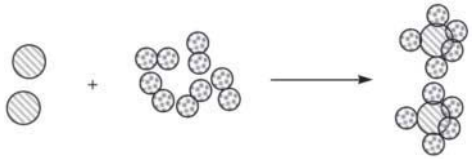
1.45 (a) $NH_4NO_3 \longrightarrow N_2O + 2\ H_2O$

(b) $P_4O_{10} + 6\ H_2O \longrightarrow 4\ H_3O_4$

(c) $2\ HIO_3 \longrightarrow I_2O_5 + H_2O$

(d) $2\ As + 5\ Cl_2 \longrightarrow 2\ AsCl_5$

1.47



1.49 (a) $2\ H_2 + CO \longrightarrow CH_3OH$

(b) $CaO + 3\ C \longrightarrow CO + CaC_2$

(c) $2\ C_2H_4 + O_2 + 4\ HCl \longrightarrow 2\ C_2H_4Cl_2 + 2\ H_2O$

1.51

1.53 (a) $3\ Ca(OH)_2 + 2\ H_3PO_4 \longrightarrow 6\ H_2O + Ca_3(PO_4)_2$

(b) $Na_2O_2 + 2\ H_2O \longrightarrow 2\ NaOH + H_2O_2$

(c) $BF_3 + 3\ H_2O \longrightarrow 3\ HF + H_3BO_3$

(d) $2\ NH_3 + 3\ CuO \longrightarrow 3\ Cu + N_2 + 3\ H_2O$

1.55 (a) 34.7 g CO; (b) 3.21 g C; (c) 2.85 g O_2

1.57 1.77×10^3 g

1.59 511 g

1.61 45.5 kg HF; 138 kg CCl_2F_2; 83.0 kg HCl

1.63 68.6%

1.65 28 kg

1.67 76.3%; 258 kg CCl_4; 67.2 kg HF

1.69 lettuce; 66

1.71 91.3 kg

1.73 (a) Limiting reactant = CO, 1.14 metric ton; (b) Limiting reactant = CaO, 0.499 metric ton CO and 1.14 metric ton CaC_2; (c) Limiting reactant = HCl, 1.36 metric ton $C_2H_4Cl_2$ and 0.247 metric ton H_2O

1.75 8.60 g; 1.71 g O_2

Chapter 2

2.1 A pinhole in the top of the tube would let air leak into the space until the internal pressure matched the external, atmospheric pressure. The barometer would then indicate zero pressure.

2.3 When air is pumped into a flat tire, the tire expands and resists compression. Both these observations are the result of the pressure exerted by the gas molecules making up air.

2.5 (a) 6.07×10^4 Pa, 0.607 bar; (b) 2.48×10^5 Pa, 2.48 bar; (c) 61 Pa, 6.1×10^{-4} bar; (d) 1.35×10^2 Pa, 1.35×10^{-3} bar

2.7 4.04 mol; 100 L

2.9 (a) $p_i/T_i = p_f/T_f$; (b) $V = nRT/p$; (c) $p_iV_i = p_fV_f$

2.11 0.221 L

2.13 (a) equation is valid; (b), (c), and (d) not valid

2.15 7.8×10^{-7} atm

2.17 $p(N_2) = 593.4$ Torr; $p(O_2) = 159.2$ Torr; $p(Ar) = 7.10$ Torr; and $p(CO_2) = 2.47 \times 10^{-1}$ Torr

2.19 (a) He; (b) He; (c) 0.67

2.21 $p(CH_4) = 2.05$ bar; $p(C_2H_6) = 0.28$ bar; and $p(C_3H_8) = 9.5 \times 10^{-3}$ bar

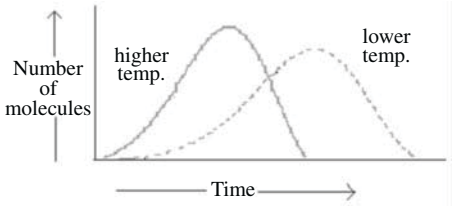
2.23 3.94 L

2.25 0.443 bar

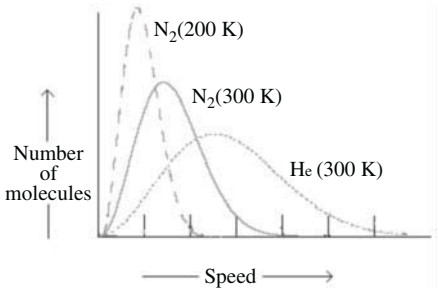
2.27 2.27×10^5 g

2.29 2.9×10^4 g

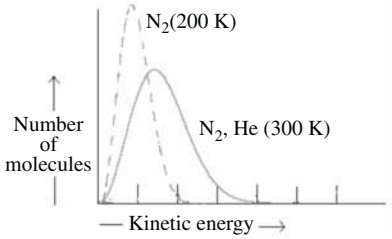
2.31



2.33



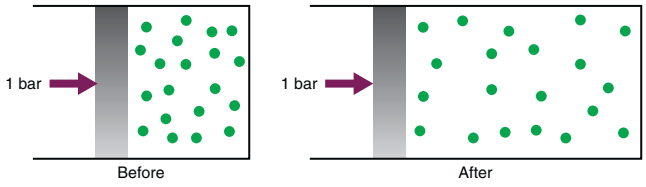
2.35



2.37 (a) 1.93×10^3 m/s, 11.2 kJ/mol; (b) 394 m/s, 3.74 kJ/mol; (c) 319 m/s, 11.2 kJ/mol

2.39 (a) At very high pressure, molecules are very close together, so their volumes are significant compared with the volume of their container; the first condition is not met and the gas is not ideal. (b) At very low temperature, molecules move very slowly, so the forces between molecules, even though small, are sufficient to influence molecular motion; the second condition is not met and the gas is not ideal.

2.41 (a) 1 bar, generated by gas molecules colliding with the face of the piston; (b) increase in average molecular speed causes an increase in pressure, so the piston will move outward, leading to a lower frequency of collisions with the wall, reducing the pressure until the internal pressure is once again 1 bar.



2.43 As a gas cools, its molecules move more slowly, so they impart smaller impulses on the walls of their container. This reduces the internal pressure, so the balloon collapses until the increase in gas density inside the balloon brings the internal pressure back up to 1.000 bar.

2.45 121 g/mol; CF_2Cl_2

2.47 5.89 g/L

2.49 226 m/s

2.51 CH_4 diffuses faster, because it has the smaller M.

2.53 0.98; 0.97; easier to separate as a monoxide

2.55 0.826 bar; 0.826 bar; the two values are similar because the pressure is low enough that the molecules are far apart and intermolecular forces are small. Also, the temperature is high enough that the kinetic energy of the molecules is high enough to overcome what intermolecular forces do exist.

2.57 87.8 bar; this value is higher because the intermolecular forces in hydrogen are smaller and because hydrogen is a much smaller molecule than fluorine.

2.59 112.8 bar

2.61 +0.0049

2.63 20.8 °C

2.65 6.8×10^2 L

Chapter 3

3.1 (a) On the tree, an apple possesses some gravitational potential energy. As an apple falls, that potential energy is converted into kinetic energy of motion. (b) When an apple hits the ground, the impact transfers energy to molecules in the earth and in the apple. As a result, there is a slight increase in temperature; the kinetic energy of the apple has been converted into thermal energy.

3.3 9.43×10^{-20} J

3.5 -7.22×10^{-19} J

3.7 (a) Radiant energy is consumed and thermal energy is produced. (b) Chemical potential energy is consumed and kinetic energy is produced. (c) Chemical potential energy is consumed and thermal energy is produced.

3.9 2.12×10^2 m/s

3.11 (a) 17.8 °C; (b) 30.6 °C; (c) 33.8 °C; and (d) 22.2 °C

3.13 water: 8.29×10^5 J; kettle: 4.37×10^4 J

3.15 23.6 °C

3.17 131 kJ

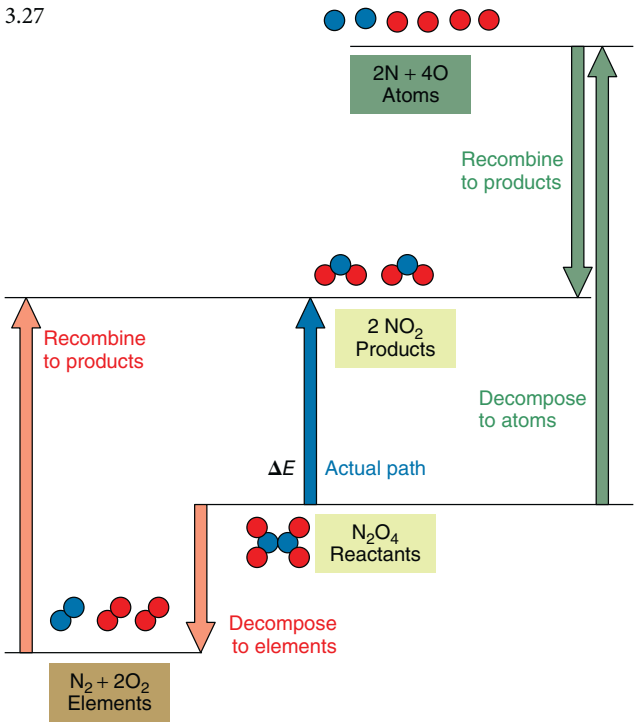
3.19 14 km

3.21 (a) $2\ C_7H_6O_2 + 15\ O_2 \longrightarrow 14\ CO_2 + 6\ H_2O$; (b) -3.221×10^3 kJ/mol; and (c) -4.295×10^2 kJ/mol

3.23 Moving down the column, the bond energy decreases. We predict that the H—Se bond has an energy between H—S and H—Te, and the H—Po bond is weaker than H—Te.

3.25 165 kJ

3.27



3.29 H_2O, −475 kJ; NH_3, −90 kJ; and $CH_4 + H_2O$, −205 kJ

3.31 -1.4×10^3 J

3.33 14.4 kJ/°C

3.35 34.46 kJ; -4.96×10^3 kJ/mol

3.37 -2.5×10^2 J

3.39 (a) −1411.1 kJ; (b) 91.8 kJ; (c) −1597.0 kJ; and (d) −21.2 kJ

3.41 (a) −1406.1 kJ; (b) 86.8 kJ; (c) −1597.0 kJ; and (d) −21.2 kJ

3.43 (a) $3\ K(s) + P(s) + 2\ O_2(g) \longrightarrow K_3PO_4(s)$

(b) $2\ C(graphite) + 2\ H_2(g) + O_2(g) \longrightarrow CH_3CO_2H(l)$

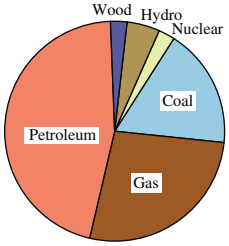
(c) $3\ C(graphite) + \frac{9}{2}\ H_2(g) + \frac{1}{2}\ N_2(g) \longrightarrow (CH_3)_3N(g)$

(d) $2\ Al(s) + \frac{3}{2}\ O_2(g) \longrightarrow Al_2O_3(s)$

3.45 (a) −1166.2 kJ; and (b) −1531.4 kJ

3.47 1×10^{16} J

3.49 Total is 7.89×10^{19} kJ

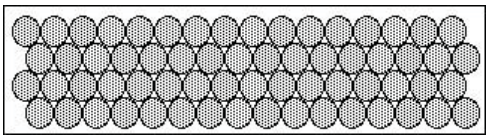


Chapter 4

4.1 (a) $V_{Ag} = 1.706 \times 10^{-29}$ m^3/atom, $V_{Pb} = 3.034 \times 10^{-29}$ m^3/atom; (b) $d_{Ag} = 2.57 \times 10^{-10}$ m, $d_{Pb} = 3.12 \times 10^{-10}$ m; and (c) thickness$_{Ag} = 1.7 \times 10^{-3}$ m, thickness$_{Pb} = 2.0 \times 10^{-3}$ m

4.3 Gas pressure results from transfer of momentum between atoms and container walls, indicating that atoms have momentum and mass; mass spectrometers sort atomic and molecular ions according to their masses; all matter are made up of atoms and have mass.

4.5



4.7 (a) 6.92×10^{16} Hz; (b) 1.28×10^{18} Hz; (c) 4.08×10^8 Hz; and (d) 6.56×10^{13} Hz

4.9 (a) 6.29×10^{-2} m; (b) 1.04×10^6 cm; (c) 5.0×10^9 mm; and (d) 1.04×10^8 μm

4.11 (a) 4.049×10^{-19} J/photon, 2.438×10^2 kJ/mol; (b) 7.79×10^{-18} J/photon, 4.69×10^3 kJ/mol; and (c) 1.6855×10^{-23} J/photon, 1.0150×10^{-2} kJ/mol

4.13 1.7×10^{16} photons

4.15 (a) 1.61×10^{-7} m, 1.86×10^{15} Hz; and (b) 5.60×10^{-7} m, 5.35×10^{14} Hz

4.17 (a) 2.31×10^{-7} m; (b) 3.4×10^{-19} J; and (c) 5.8×10^{-7} m

4.19

4.21 (a) 1 to 1000 m; (b) yellow; and (c) radar region

4.23 745 kJ/mol

4.25 $\lambda_{8-1} = 92.57$ nm, $\lambda_{9-1} = 92.26$ nm; both are in the ultraviolet region

4.27 Under normal conditions, absorptions occur between the lowest state and any higher-energy state. Emission originates from any higher state, to any lower state.

4.29 5.4857990×10^{-4} g/mol

4.31 (a) 1.45 nm; (b) 6.38 nm; and (c) 4.41 μm

4.33 (a) 1.71×10^{-20} J; (b) 1.11×10^{-38} J; and (c) 3.08×10^{-33} J

4.35

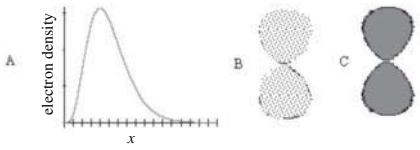
n	6	6	6	6	6	6
l	1	1	1	1	1	1
m_l	+1	+1	0	0	−1	−1
m_s	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$

4.37 $l = 0$, $m_l = 0$; $l = 1$, $m_l = 1$, 0, or −1; and $l = 2$, $m_l = +2$, +1, 0, −1, or −2; in all cases, $m_s = +\frac{1}{2}$ or $-\frac{1}{2}$

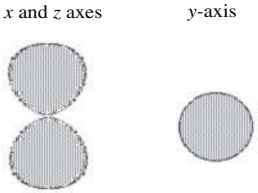
4.39 (a) non-existent: m_s must be $+\frac{1}{2}$ or $-\frac{1}{2}$; (b) actual; (c) non-existent: l must be less than n; and (d) actual

4.41 3, 2, 2, $+\frac{1}{2}$

4.43



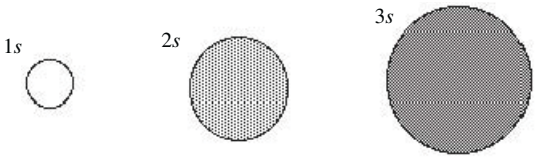
4.45



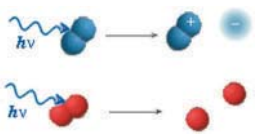
4.47 (a) 2p, $n = 2$, $l = 1$; (b) and (c) 3d, $n = 3$, $l = 2$

4.49 Electron density plots fail to show whether or not an orbital has spherical symmetry, and they do not directly show electron densities.

4.51



4.53



4.55 $E = 352$ kJ/mol; $E_{kinetic} = 2.10 \times 10^{-19}$ J

4.57 (a) O_2, N_2, and O_3 (thermosphere); and (b) O_3 (stratosphere)

4.59 (a) ~50 km; (b) upper stratosphere; and (c) formation of ozone

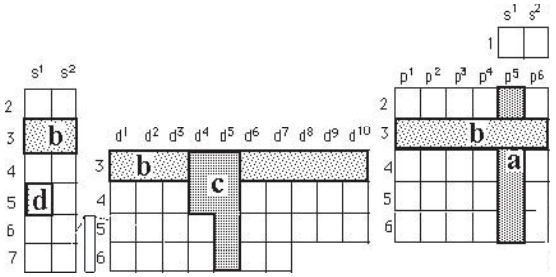
Chapter 5

5.1 (a) He 1s, lower value of n; (b) Kr 5s, lower value of l; and (c) He^+ 2s, less screened by 1s electrons

5.3 H atom, no screening effect, so orbital energy depends only on n and Z, and all $n = 3$ orbitals have identical energy. He atom, the second electron screens the first, and the amount of screening decreases as l increases.

5.5 (a) IE of the He 2p orbital is not much larger than that of the H 2p orbital. (b) IE of the He^+ 2p orbital is four times larger than that of the H 2p orbital.

5.7



5.9 Atomic number = 114; valence orbital = 7*p*

5.11 Row 7, Column 17 (directly below astatine)

5.13 O, 6 valence electrons; V, 5; Rb, 1; Sn, 4; Cd, 2

5.15 (a) Be, 4 electrons, $1s^2\ 2s^2$

n	2	2
l	0	0
m_l	0	0
m_s	$+\frac{1}{2}$	$-\frac{1}{2}$

(b) O, 8, $1s^1\ 2s^2\ 2p^4$;

n	2	2	2	2	2	2
l	0	0	1	1	1	1
m_l	0	0	1	0	−1	1
m_s	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$

(c) Ne, 10 electrons, $1s^1\ 2s^2\ 2p^6$; first six valence electrons the same as for O; remaining two:

n	2	2
l	1	1
m_l	0	−1
m_s	$-\frac{1}{2}$	$-\frac{1}{2}$

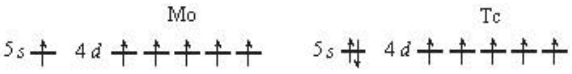
(d) P, 15 electrons, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$

n	3	3	3	3	3
l	0	0	1	1	1
m_l	0	0	−1	1	0
m_s	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$

5.17

5.19 (a) Pauli-forbidden; (b) Pauli-forbidden; (c) excited-state configuration; (d) excited-state configuration; (e) ground-state configuration; (f) non-existent orbital; and (g) non-existent orbital

5.21



5.23 C: [He] $2s^2\ 2p^2$; Cr: [Ar] $4s^1\ 3d^5$; Sb: [Kr] $5s^2\ 4d^{10}\ 5p^3$; Br: [Ar] $4s^2\ 3d^{10}\ 4p^5$

5.25 Seven: $1s^1\ 2s^2\ 2p^4$; $2s^2\ 2p^5$; $1s^1\ 2s^1\ 2p^5$; $1s^2\ 2s^1\ 2p^4$; $1s^2\ 2p^5$; $2s^1\ 2p^6$; $1s^1\ 2p^6$

5.27 Ar > Cl > K > Cs

5.29 Column 1 (Cs). The trends in the ionization energies and electron affinity suggest this.

5.31 N, electron adds to an already occupied orbital; electron–electron repulsion makes this an unfavourable process. Mg, electron adds to the next higher orbital, which is significantly higher in energy. Zn, electron adds to the next higher orbital, which is significantly higher in energy.

5.33 $Y^{3+} < Sr^{2+} < Rb^{+} < Br^{-} < Se^{2-} < As^{3-}$

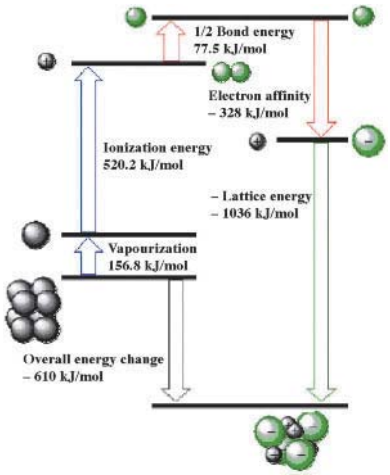
5.35 Stable anion: Cl; stable cations: Ca, Cu, Cs, Cr

5.37 −270 kJ/mol

5.39 (a) $Ba^{3+}\ O^{3-}$; (b) $Ba^{+}\ O^{-}$; (c) $Ba^{2+}\ O^{2-}$. The gain in lattice energy more than offsets the additional energy required to form the ions, but the energy required to remove the third electron from Ba is prohibitive.

5.41 −610 kJ/mol

5.43



5.45 The decrease from Rb_2O to Cs_2O will be about the same as from K_2O to Rb_2O, 75 kJ/mol. The predicted value is 2163 − 75 = 2088 kJ/mol.

5.47 Metal: Po; non-metal: O, S, Se; metalloid: Te

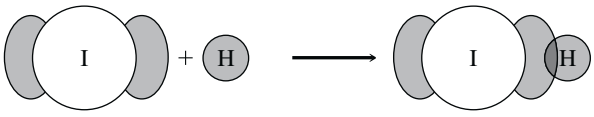
5.49 Metal: Ca, Cu, Cs, Cr; non-metal: C, Cl

5.51 Al, Ga, Sn, Bi

Chapter 6

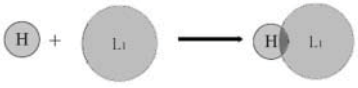
6.1 (a) O: $1s^2\ 2s^2\ 2p^4$, six $n = 2$ electrons;
(b) P: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$, five $n = 3$ electrons;
(c) B: $1s^2\ 2s^2\ 2p^1$, three $n = 2$ electrons; and
(d) Br: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^5$, seven $n = 4$ electrons

6.3 One valence 5*p* orbital of the iodine atom overlaps with the 1*s* orbital of the hydrogen atom to form a bond:



6.5 (a) Al, group 13, 3 valence electrons; (b) As, group 15, 5 valence electrons; (c) F, group 17, 7 valence electrons; and (d) Sn, group 14, 4 valence electrons.

6.7 The 2*s* orbital of a lithium atom can overlap with the 1*s* orbital of a hydrogen atom to produce an orbital with high electron density between the nuclei:



6.9 (a) N (3.0) will attract electrons more than C (2.5);
(b) S (2.5) will attract electrons more than H (2.1);

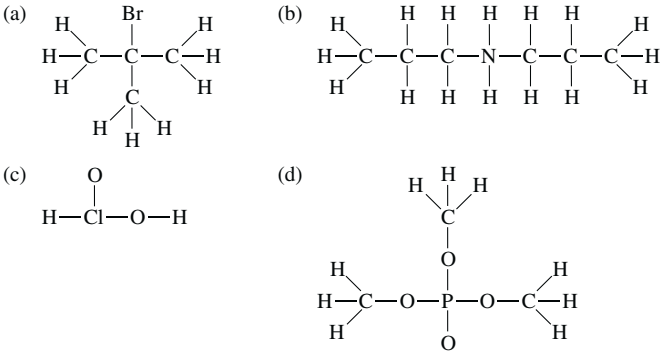
(c) I (2.5) will attract electrons more than Zn (1.6); and (d) S (2.5) will attract electrons more than As (2.0).

6.11 (a) δ^+ Si—O δ^-; (b) δ^- N—C δ^+; (c) δ^+ Cl—F δ^-; and (d) δ^- Br—C δ^+.

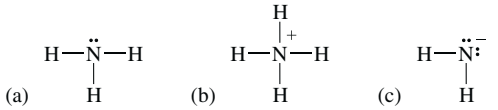
6.13 $PH_3 < H_2S < NH_3 < H_2O$

6.15 (a) 32; (b) 90; (c) 24; and (d) 32

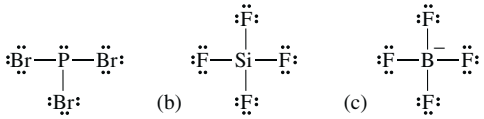
6.17



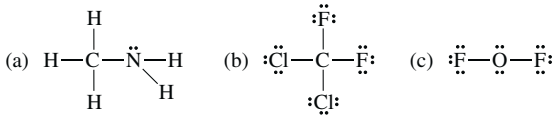
6.19



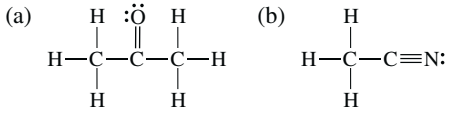
6.21

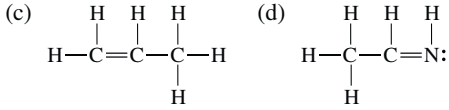


6.23

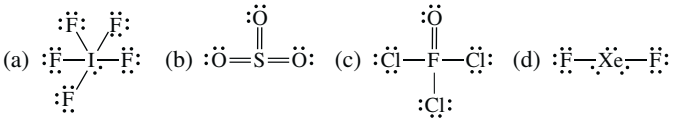


6.25

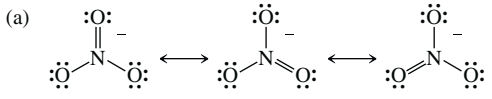


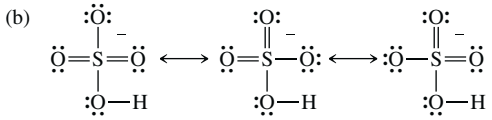


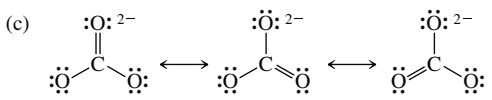
6.27

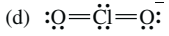


6.29

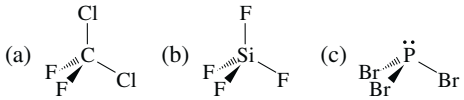




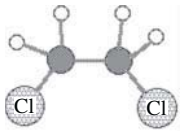




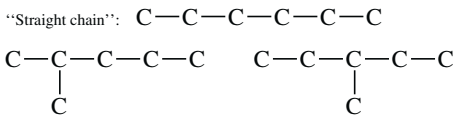
6.31 (a) tetrahedral; (b) tetrahedral; and (c) trigonal pyramidal



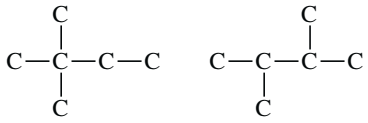
6.33



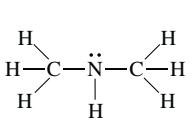
6.35

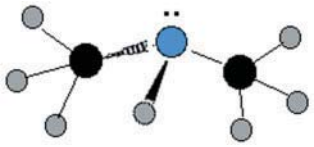


Putting the branched carbon in Position 4 gives the same isomer as putting it in Position 2

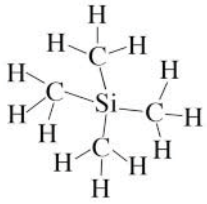


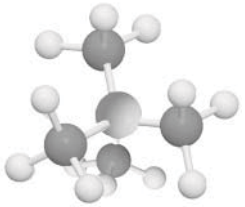
6.37 Shape about the N atom is trigonal pyramidal; shape about C atoms is tetrahedral





6.39

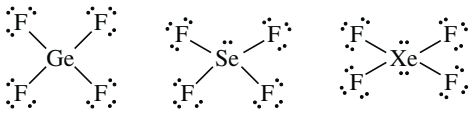




Hybridization = sp^3; geometry = tetrahedral

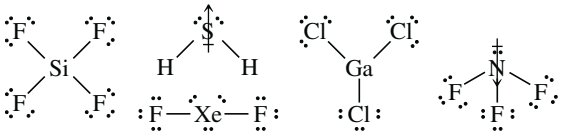
6.41 (a) T-shaped; (b) seesaw; (c) trigonal planar; and (d) square pyramidal

6.43 GeF_4, tetrahedron, sp^3; SeF_4, seesaw, dsp^3; XeF_4, square plane, d^2sp^3



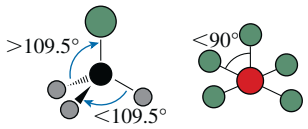
6.45 (a) bent, 120°; (b) trigonal bipyramidal, 90° and 120°; (c) seesaw, 90° and 120°; and (d) square planar, 90°

6.47 H_2S and NF_3 have dipole moments.



6.49 CO_2 has no lone pairs on the inner C atom, giving SN = 2, linear shape, and bond polarities that cancel. SO_2 has a lone pair on the inner S atom, bent shape, and polar bonds whose moments do not cancel.

6.51 (a) ideal; (b) and (c) deviate



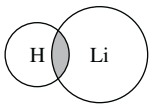
6.53 H—N < C≡N < N≡N < N—N < Cl—N

6.55 C—C < H—N < C=C < C=O < N≡N

Chapter 7

7.1 The bond forms by overlap of two 4*p* orbitals.

7.3 The bond in LiH forms by overlap of the hydrogen 1*s* orbital and the lithium 2*s* orbital.



7.5 Each bond results from overlap between a 5*p* orbital from Sb and a 2*p* orbital from F. There are three identical bonds that point at near-right angles to one another.

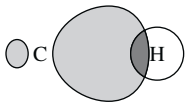
7.7 (a) sp^3; (b) sp^3; (c) sp^2; and (d) sp^3d^2

7.9 (a) sp^3; (b) sp; and (c) sp^3d^2

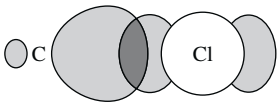
7.11 (a) sp^3; (b) sp^3d; (c) sp^2; and (d) sp

7.13 (a) sp^2; (b) sp^3d; (c) sp^3d^2; and (d) sp^3

7.15 C has SN = 4, is tetrahedral, and uses sp^3 hybrids to form three C—Cl bonds and one C—H bond. Cl uses a 3*p* orbital for bond formation and has lone pairs in the 3*s* and two other 3*p* orbitals. H atom uses its 1s orbital to form the C—H bond.

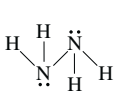


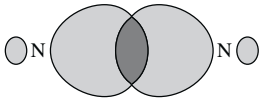
C—H bond



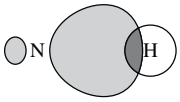
C—Cl bond

7.17 4 sp^3 (N)–1*s* (H) σ bonds, 1 sp^3 (N)–sp^3 (N) σ bond, 2 lone pairs in sp^3 hybrids



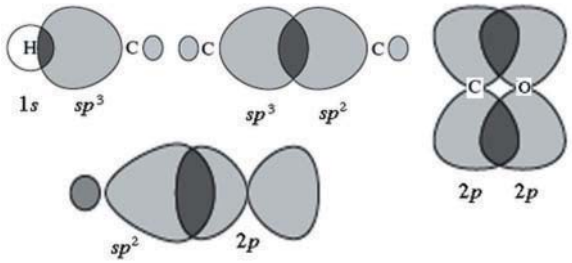


N—N bond

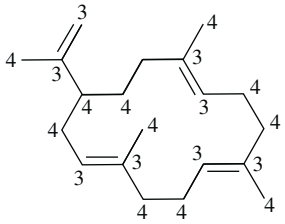


N—H bond

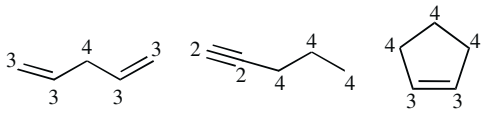
7.19 Acetone has three inner C atoms. Two have only single bonds (one C—C and three C—H); these have SN = 4. The atom bonded to O has one π bond and SN = 3.



7.21 Some of the inner atoms have all single bonds, SN = 4, sp^3 hybridization, and tetrahedral geometry; others have one double bond, SN = 3, sp^2 hybridization, and trigonal planar geometry. The SN values for the 20 carbon atoms are shown in the line structure at right.

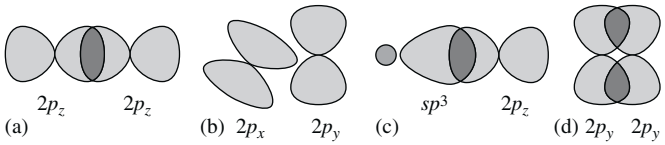


7.23



1,4-Pentadiene 1-Pentyne Cyclopentene

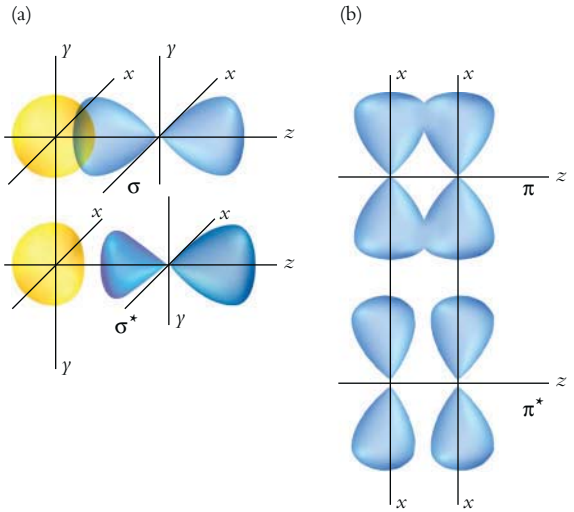
7.25 (a) σ bond; (b) no bond; (c) σ bond; and (d) π bond



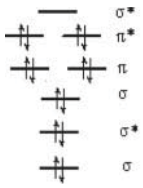
7.27 From weakest to strongest bond, the order is H_2^{2-}, H_2^-, H_2

7.29 (a) CO; (b) N_2; (c) CN^-

7.31



7.33 There are eight bonding electrons and six antibonding electrons, for a net of two bonding electrons and a single bond for this ionic species.



7.35 C atom has *sp* hybrids that overlap with 3*p* orbitals from the S atoms to form two σ bonds. There are two delocalized π systems at right angles to each other, each made up of a 2*p* orbital on the C atoms overlapping side-by-side with a 3*p* orbital on each S atom. As in CO_2, eight electrons occupy the delocalized π orbitals.

7.37 Isoelectronic with CO_2; Lewis structure is

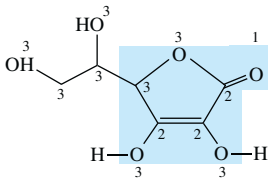
$$:\ddot{N}\equiv C\equiv\ddot{N}:^{2-}$$

C atom has SN = 2, *sp* hybridization, and linear geometry. There are two sets of three-centre delocalized π orbitals.

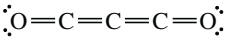
7.39 N bonded to H is bent, sp^2 hybridized, angle between 109–120°; outer N is not hybridized, middle N atom is linear, *sp* hybridized.

7.41 Xanthin has a delocalized π system in which all 26 double-bonded C atoms contribute.

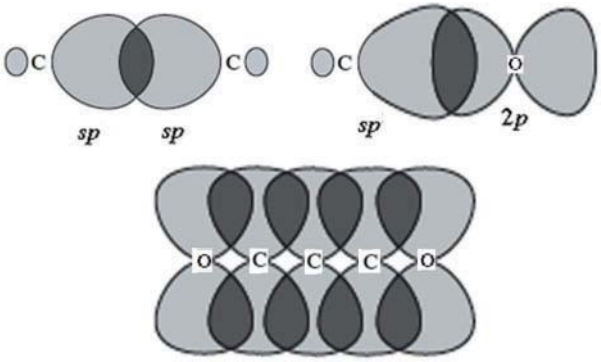
7.43 (a) Hybridization is as shown on the line drawing ($3 = sp^3$, $2 = sp^2$). (b, c) 2 π bonds, on adjacent atoms, four electrons in the extended π system; and (d) eight atoms screened in blue



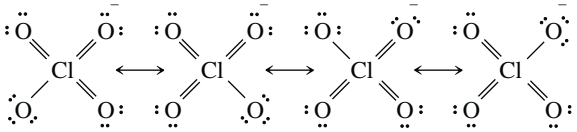
7.45 Lewis structure:



Linear, σ bond network can be described using *sp* hybrids; two sets of delocalized π orbitals, each extending over all five atoms:



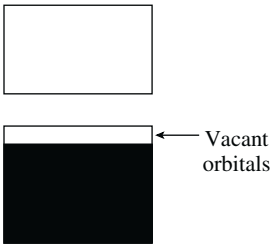
7.47 Tetrahedral geometry, sp^3 hybrids on Cl overlap with 2*p* orbitals from O; π system extends over all five atoms, incorporating *d* orbitals from the inner Cl atom; three bonding π orbitals occupied by six electrons.



7.49 (a) undoped; (b) *n*-type; and (c) undoped

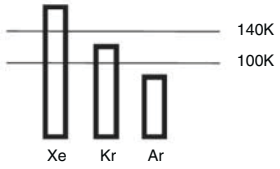
7.51 Each K atom contributes one valence electron to the valence (bonding) band of the solid, each Fe atom contributes eight electrons. Thus, iron has much greater bonding, making it harder and giving it a higher melting point than potassium.

7.53 *p*-type semiconductor



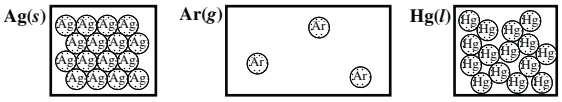
Chapter 8

8.1



8.3 (a) less significant; (b) more significant; and (c) less significant

8.5

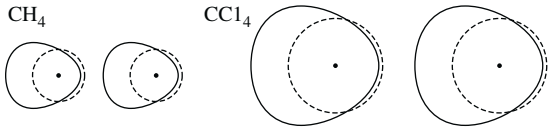


8.7 –8.9%

8.9 21.8 bar; –24% deviation from ideal gas behaviour

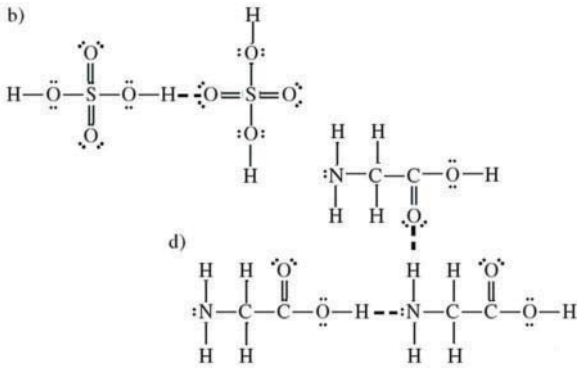
8.11 CH_4 (hardest to liquefy) < CF_4 < CCl_4 (easiest to liquefy)

8.13

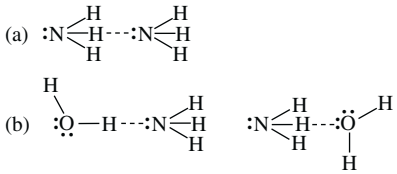


8.15 Propane (lowest bp) < *n*-pentane < ethanol (highest bp)

8.17 (a) and (c) no hydrogen bonding; (b) and (d) hydrogen bonding



8.19



8.21 Pentane (C_5) < gasoline (C_8) < fuel oil (C_{12})

8.23 Water will be concave because of the dipole-dipole interactions between it and the Al_2O_3. Mercury will be convex because its metallic bonds are so different from the dipoles in Al_2O_3.

8.25 Paper towels contain cellulose, which forms many hydrogen bonds with water. There are no strong intermolecular interactions between an oil and the fibres of paper towels.

8.27 (a) benzene, no dipole moment; (b) hexane, no H-bonding; and (c) heptane, smaller dispersion forces

8.29 Sn: metallic solid; S_8: molecular solid; Se: network solid; SiO_2: network solid; Na_2SO_4: ionic solid

8.31 (a) The bonding in metals comes from extended networks of delocalized electrons, whereas the bonding in network solids includes many individual covalent bonds. (b) Metals conduct electricity, are malleable and ductile, and are shiny in appearance. Network solids are non-conductors or semiconductors, are brittle, and often have dull appearances.

8.33 (a) molecular solid; (b) ionic solid; (c) metallic solid; (d) network solid; and (e) molecular solid

8.35 6.11×10^{-22} g

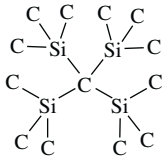
8.37 8.90 g/cm^3

8.39 144 pm

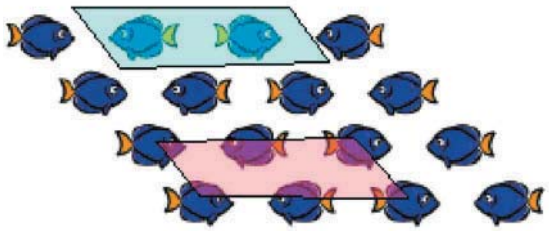
8.41 The density of a solid depends not only on the nature of the elements it contains but also on the tightness of bonding. Graphite has a more open bonding pattern than diamond.

8.43 $CaTiO_3$

8.45



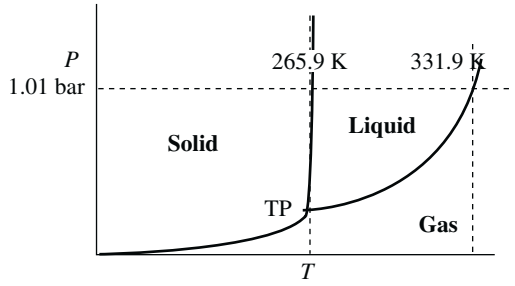
8.47



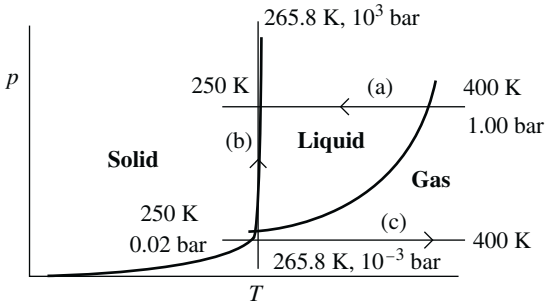
8.49 8

8.51 (a) methane, smaller dispersion forces; (b) ethanol, hydrogen bonding; and (c) argon, higher polarizability

8.53



8.55 (a) Gas cools, liquefies at 331.9 K, and solidifies at 265.9 K. (b) Compressing the gas causes it to liquefy at about $p = 6 \times 10^{-2}$ bar and solidify at about 0.5 bar. (c) Solid sublimes to the vapour at about 265 K.



8.57 980. J

Chapter 9

9.1 (a) solvent, liquid water; primary solute, carbon dioxide (normally a gas); (b) solvent, liquid water; primary solute, ethanol (normally a liquid); (c) solvent, gaseous N_2; primary solutes, O_2 (normally a gas) and water (normally a liquid)

9.3 $X_{methanol} = 0.0747$, $X_{water} = 0.925$

9.5 $b = 1.88 \times 10^{-1}$ mol/kg; $X = 1.08 \times 10^{-2}$; % = 2.14%

9.7 $X_{hydrogen\ peroxide} = 0.18$, $X_{water} = 0.82$; $M = 9.8$ M; $b = 13$ mol/kg

9.9 $X_{ammonia} = 0.042$; $X_{water} = 0.958$; Mass fraction ammonia = 0.0399; $b = 2.44$ mol/kg

9.11 (a) 120. g; (b) 6.50 mol/kg

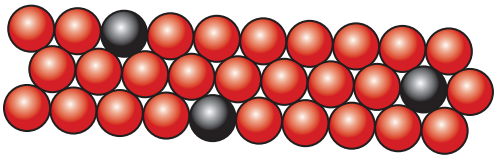
9.13 The hydrocarbon molecules in salad dressing have dispersion-type intermolecular forces but low polarity and no hydrogen-bonding capability. A solution of acetic acid in water has high polarity and a large hydrogen-bonding capability. Hydrogen bonds would have to be broken for the two liquids to mix, making mixing energetically unfavourable.

9.15 Ionic salts and polar organic materials such as alcohols

9.17 H_2O has strong hydrogen bonding, and so does CH_3OH, so this pair is miscible; C_8H_{18} and CCl_4 both have only dispersion forces, so this pair is miscible.

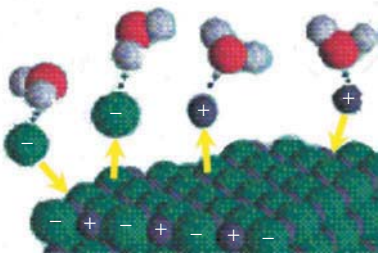
9.19 CCl_4 is most like I_2; NaCl is a salt, so it only dissolves in water; Au, a metal, requires another metal, Hg; and paraffin, a hydrocarbon, is best matched by *n*-octane, another hydrocarbon.

9.21



9.23 Methane does not form H-bonds, so life is unlikely.

9.25



9.27 Energy must be supplied to the molecules that escape.

9.29 48%

9.31 $K_H = 59.53$ M/bar; $p = 4.2$ kPa

9.33 $p_{total} = 5.87$ kPa

9.35 $X_{ethanol} = 0.363$

9.37 $p_{vap,\ solution} = (0.964)(1.01\ bar) = 0.974$ bar

9.39 $T_f = -0.438$ °C

9.41 $T_b = 100.121$ °C

9.43 0.20 M sucrose (lowest) < 0.20 M NaCl < 0.40 M sucrose < 0.25 M $MgCl_2$ (highest)

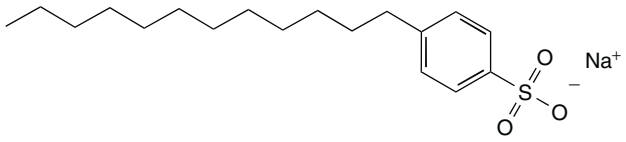
9.45 (a) $M = 180$ g/mol; (b) $C_6H_{12}O_6$

9.47 8.00 bar

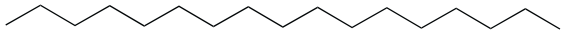
9.49 Similarities: colloidal suspensions, similar compositions; difference: milk is a suspension of solids (fats) in water, whereas whipped cream is a suspension of a gas (air) in a solid (coagulated fat) that also contains liquid.

9.51 Best surfactant: Sodium alkylbenzenesulphonate; worst surfactant: octadecane

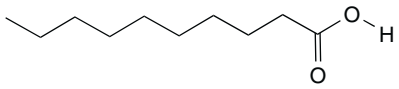
(a)



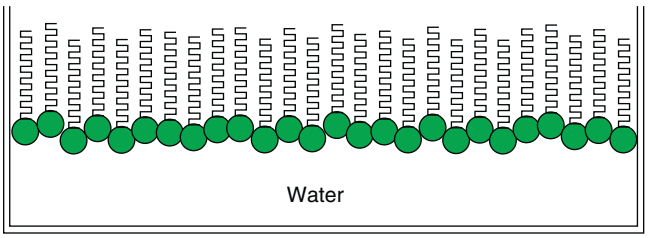
(b)



(c)

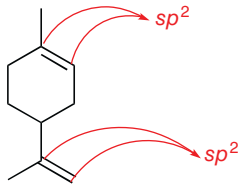


9.53



Chapter 10

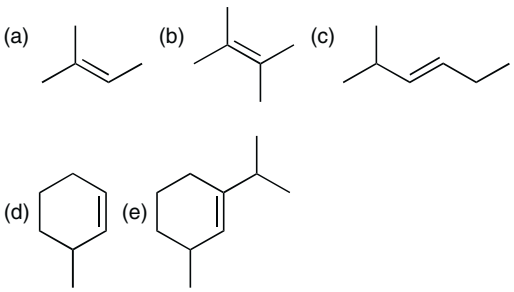
10.1



All other carbon atoms sp^3

10.3 (a) 2-methylpentane; (b) 2,3-dimethylbutane; (c) 2-methylpentane; (d) 2,4-dimethylpentane; (e) 3-methylpentane

10.5



10.7 (a) *sp* hybridization, (b) sp^3 hybridization, (c) sp^2 hybridization

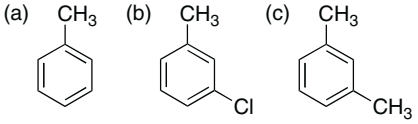
10.9 2,2-dimethylbutane

10.11 2,3-dimethylpentane

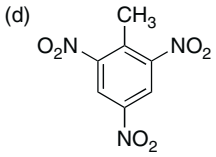
10.13 (a) 2: 1,1-dimethylcyclopropane and 1,2-dimethylcyclopropane, (b) 3: 1,1-dimethylcyclobutane, 1,2-dimethylcyclobutane, and 1,3-dimethylcyclobutane

10.15 (a) *o*-bromonitrobenzene, (b) *p*-dicyclohexylbenzene, (c) *m*-dinitrobenzene

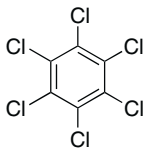
10.17



(d)



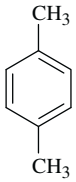
(e)



10.19 Benzene is a planar molecule where all three "double" bonds are conjugated such that the π electrons of these double bonds are delocalized around the ring. Two resonance structures can be drawn for benzene. Any situation in which resonance structures can be drawn for a molecule increases the stability of the molecule over similar structures for which no resonance is possible.

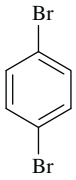
10.21 Three (1,2,3-, 1,2,4- and 1,3,5-trichlorobenzene)

10.23



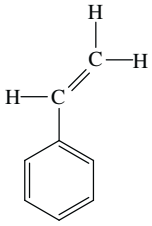
para-Methyltoluene (*p*-methyltoluene)

10.25

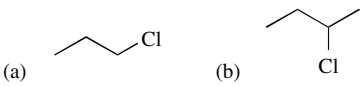


para disubstitution

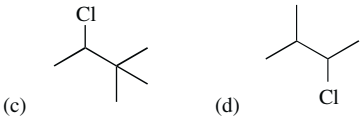
10.27



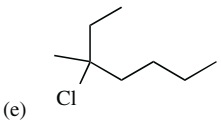
10.29



Primary 1° Secondary 2°

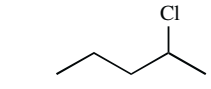


Secondary 2° Secondary 2°

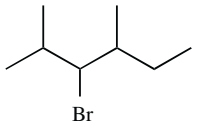


Tertiary 3°

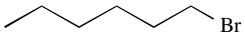
10.31



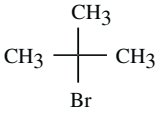
2-Chloropentane

(b) 

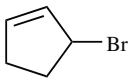
3-Bromo-2,4-dimethylhexane

(c) 

1-Bromohexane (or *n*-hexyl bromide also acceptable)

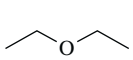
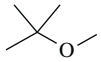
(d) 

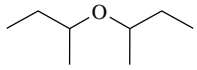
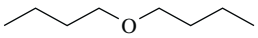
tert-Butyl bromide

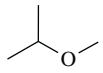
(e) 

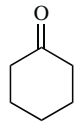
3-Bromocyclopentene

10.33 (a) 2-Butanol, (b) Cyclohexylmethanol, (c) Cyclohexanol, (d) 1-Methylcyclohexanol, (e) 2,2-Dimethyl-3-pentanol

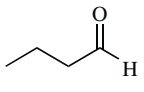
10.35 (a)  (b) 

(c)  (d) 

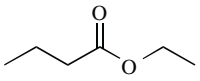
(e) 

10.37 (a) 

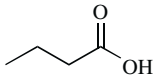
Ketone

(b) 

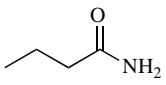
Aldehyde

(c) 

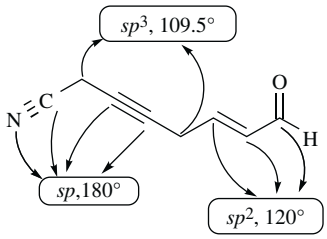
Ester

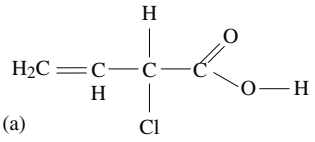
(d) 

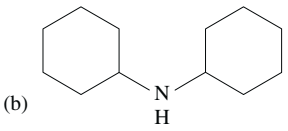
Carboxylic acid

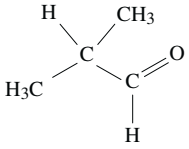
(e) 

Amide

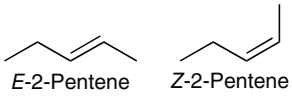
10.39 

10.41 (a) 

(b) 

(c) 

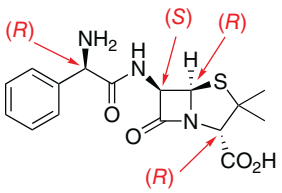
10.43 (a) No *E*/*Z* isomerization; (b) No *E*/*Z* isomerization

(c) 

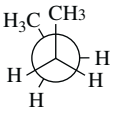
E-2-Pentene *Z*-2-Pentene

(d) No *E*/*Z* isomerization; (e) No *E*/*Z* isomerization

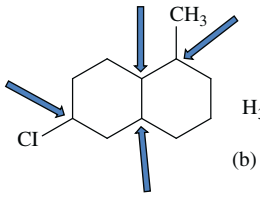
10.45 (a) achiral, (b) achiral, (c) chiral, (d) chiral, (e) chiral

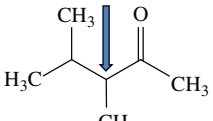
10.47 

Amoxicillin

10.49 

10.51 (a) 4; (b) 1

(a) 

(b) 

10.53 This is (*R*)-carvone. No, only the double bond in the ring could be labelled as *Z*. The other double bond has two hydrogens on one end, and so *cis*/*trans* and *E*/*Z* notations would be meaningless here.

10.55 1-(*R*), 2-(*S*). They are enantiomers (i.e., non-superimposable mirror images).

10.57 (a) *S*; (b) not chiral; (c) *S*

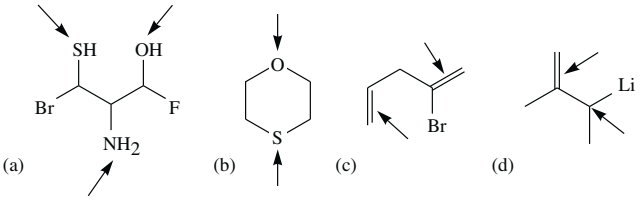
Chapter 11

11.1 (a) Elimination; (b) addition; (c) substitution; (d) substitution

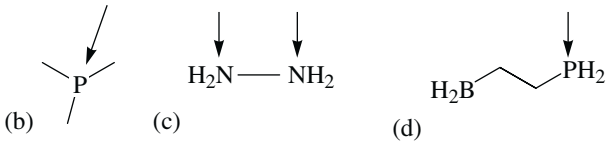
11.3 (a) Addition; (b) addition; (c) none, this is a rearrangement, not an addition, elimination, or substitution. To confirm this, count all the atoms in the starting material and the product. You will find that nothing is added, eliminated, or substituted; (d) substitution.

11.5 (a) Addition; (b) addition; (c) addition

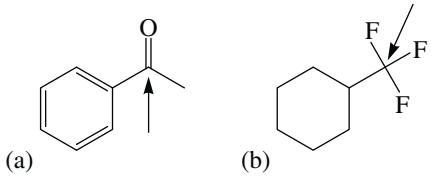
11.7 The nucleophilic centres are indicated by arrows:

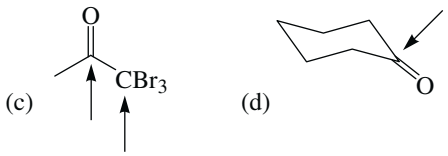


11.9 Molecule (a) is not nucleophilic at all. It is actually an electrophile called a Lewis acid. The nucleophilic centres are indicated by arrows:

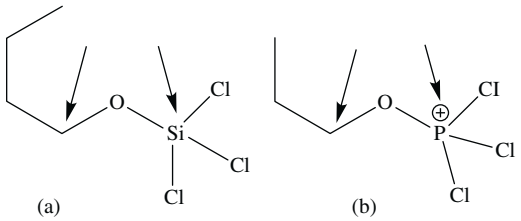


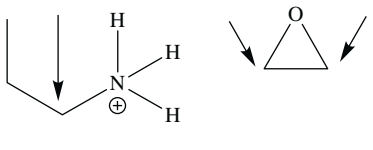
11.11 Electrophilic centres are indicated by arrows:





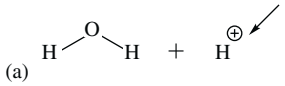
11.13 Electrophilic centres are indicated by arrows:

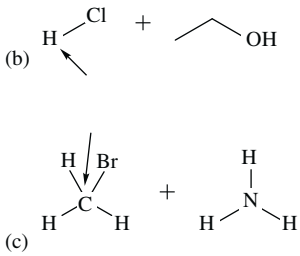


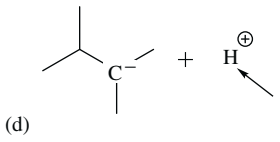


Note: Look at (b) and (c) and note the difference in the positions of P and N in the periodic table. P can accept a pair of electrons to expand its octet, whereas N cannot. Although N can accept the pair of electrons from the C—N bond in (c), it cannot accept a pair of electrons from an external nucleophile, and thus, in a strict sense, the N in molecule (c) is an electrophilic centre.

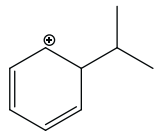
11.15 The electrophilic centre of the electrophile is shown by an arrow:





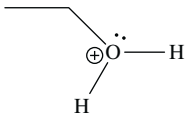


11.17 (a) A pair of π electrons from the benzene structure move to the positive carbon of the carbocation to form a new bond to a carbon at one end of the "double" bond. Within the ring, the carbon at the other end has a positive charge:



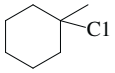
(b) A pair of π electrons from the double bond move to the positive proton to form a bond from one end of the alkene, and the carbon at the other end of the double bond has a positive charge:

(c) A lone pair of electrons on the oxygen atom of the water molecule move to the positive centre of the carbocation, forming a bond between oxygen and the carbon atom. As the oxygen has increased its normally allowable number of bonds to other atoms beyond two, it is positively charged:

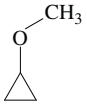


11.19 (a) Electrons move from the negative bromide ion to the positive carbocation centre to form a bond:

(b) Electrons move from the negative chloride ion to the positive carbocation centre to form a bond:



(c) Electrons move from the negative oxygen to the positive carbocation centre to form a bond:



11.21 (a) The nucleophile is the alkoxide, the substrate is the alkyl bromide, the product is the ether, and the leaving group is bromide.

(b) The nucleophile is the thiolate (the sulphur equivalent of an alkoxide), the substrate is the alkyl bromide, the product is the thiolether (the sulphur equivalent of an ether), and the leaving group is bromide.

(c) The nucleophile is the carbanion, the substrate is the alkyl bromide, the product is the alkane (heptane), and the leaving group is bromide.

11.23 (a) The nucleophile is azide ion (the N_3^- ion), the substrate is the alkyl iodide, the product is the alkyl azide (RN_3), and the leaving group is the iodide ion.

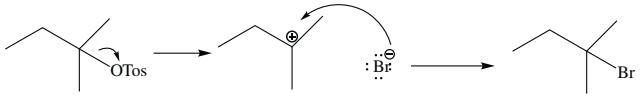
(b) Both the nucleophile and the substrate are present on the same molecule here; the nucleophile is the alkoxide (-O- end) of the molecule, the substrate is the entire alkoxy bromide molecule, the product is called a pyran (a six-membered ring with an oxygen), and the leaving group is the bromide ion. Note that these types of reactions where substrate, nucleophile, and leaving group are present in the same molecule are common for a type of reaction called a cyclization, where the product is a cyclic system.

(c) The nucleophile is hydride ion (H^- ion), the substrate is the ketone (acetone), the product is the alkoxide, and there is no leaving group in this example. The reason for this is that the nucleophile attacked at a multiply bonded centre, and the "leaving group" in this case was a pair of electrons from the π bond of the C=O bond moving to the electronegative oxygen of the ketone. This is a common type of reaction and occurs at carbonyl carbons quite frequently with various nucleophiles.

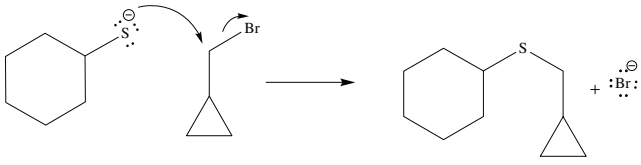
11.25 Good leaving groups are conjugate bases of strong acids (like Cl^- and Br^-); i.e., weak bases. Poor leaving groups are conjugate bases of weak acids (like OH^-); i.e., strong bases.

(a) Br^- = good leaving group
(b) $CH_3—O^-$ = poor leaving group
(c) NH_2^- = poor leaving group
(d) Cl^- = good leaving group
(e) CH_3COO^- (acetate anion) = good leaving group

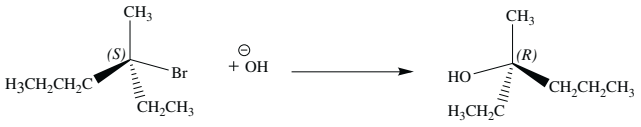
11.27 (a)



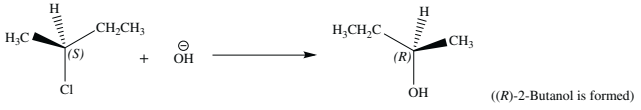
(b)



11.29 (a)

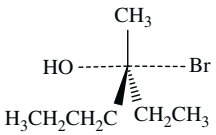


(b)

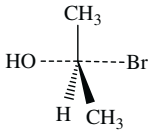


((*R*)-2-Butanol is formed)

11.31 (a)

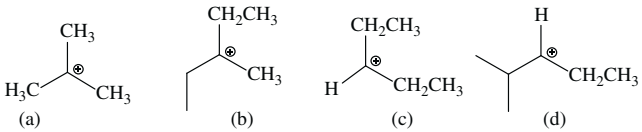


(b)

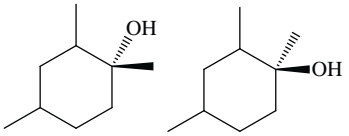


Molecule (b) will be faster as it is less sterically hindered.

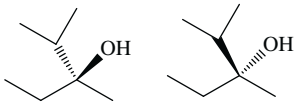
11.33



11.35 (a)



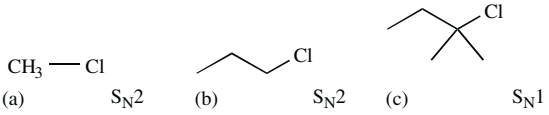
(b)

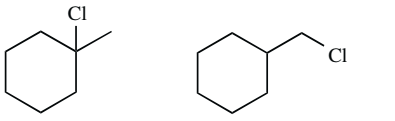


11.37 (a) The ethoxide ion is the nucleophile. The primary alkyl bromide is the substrate. The substitution results in an ether, and the leaving group is the bromide ion. Since the substrate is a primary alkyl halide, the mechanism would be S_N2.

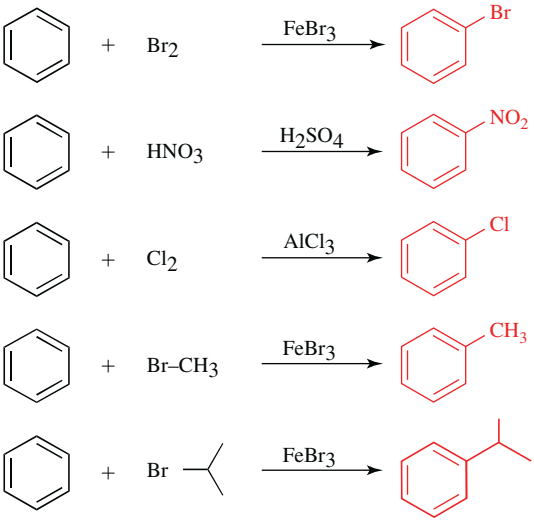
(b) The EtO^- ion is the nucleophile. The tertiary alkyl iodide is the substrate. The substitution results in an ether (R-O-R'), and the leaving group is the iodide ion. Since the substrate is a tertiary alkyl halide, the mechanism would be S_N1.

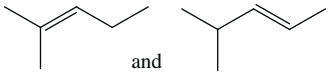
11.39



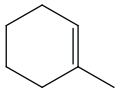
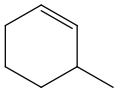


11.41

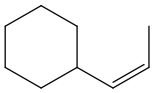
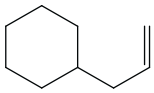


11.43 (a)  and

The structure on the left is the more highly substituted alkene and will therefore be the major product.

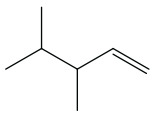
(b)  and 

The structure on the left is the more highly substituted alkene and will therefore be the major product.

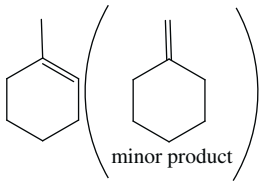
(c)  and 

The structure on the left is the more highly substituted alkene and will therefore be the major product.

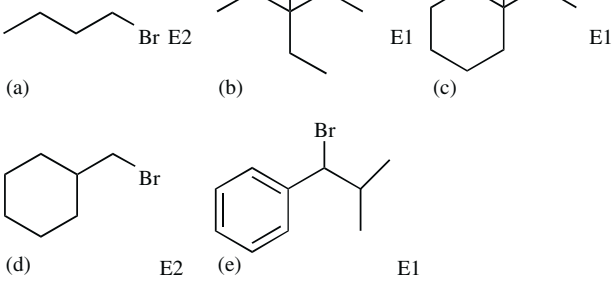
11.45 (a) The mechanism will be E2, as the alkyl halide is a primary alkyl halide. The product will be



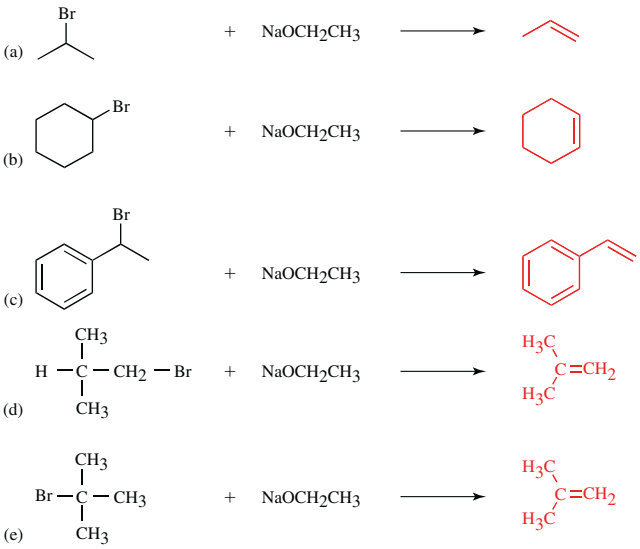
(b) The mechanism will be E1, as the alkyl halide is a tertiary alkyl halide. Two products could be formed:

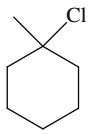


11.47



11.49

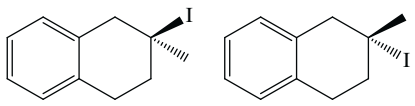


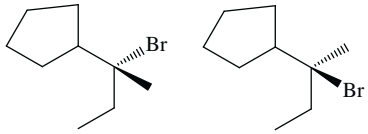
11.51 (a) 

1-Chloro-1-methylcyclohexane

(b) 

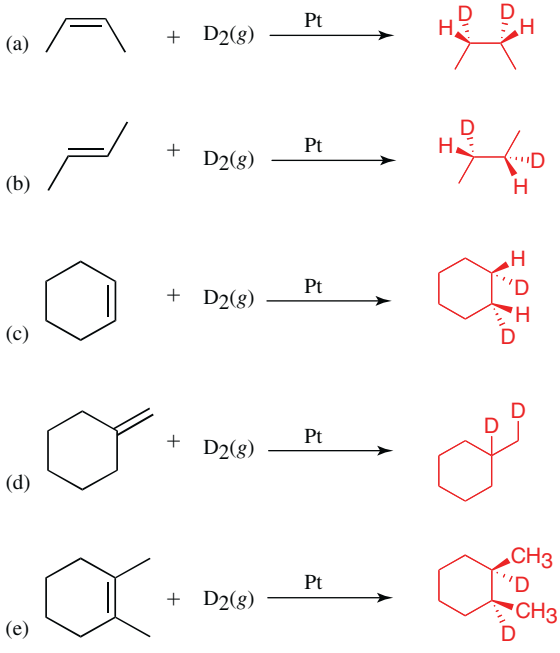
2-Chloro-2-methylpropane (tertiary butyl chloride)

11.53 (a) 

.(b) 

11.55 Heterogeneous refers to the fact that the catalyst is a different phase of matter (solid Pt in this case) than the reagent (gaseous H_2 in this case) (and also usually a liquid solution of alkene). The role of the catalyst is to lower the energy required for the reaction to proceed, without taking part in the overall reaction. In hydrogenation, the Pt metal serves to activate the $H_2(g)$ by "stretching" the H—H bond.

11.57



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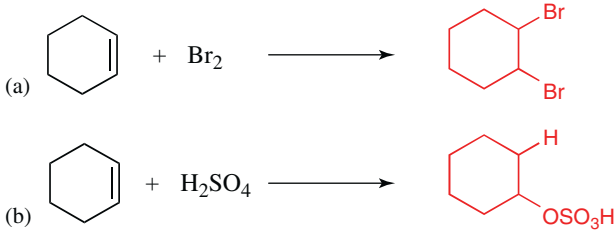

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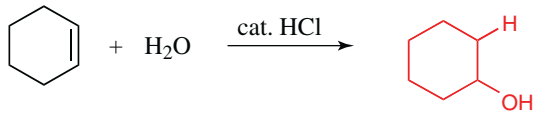
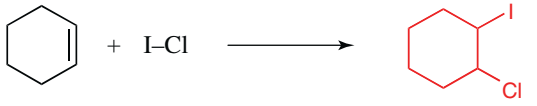
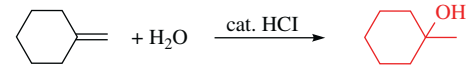
(d) 

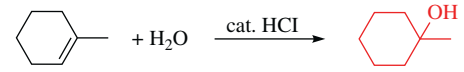
(e) 

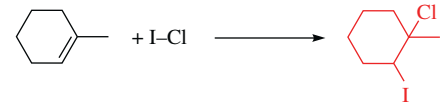
11.61

(a) 

(b) 

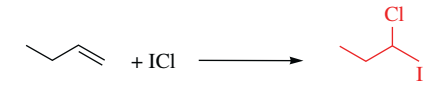
(c) 

(d) 

(e) 

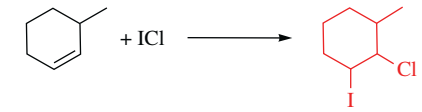
11.63 Products (a), (c), and (d) are chiral.

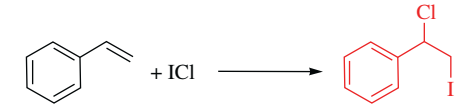
11.65

(a) 

(b) 

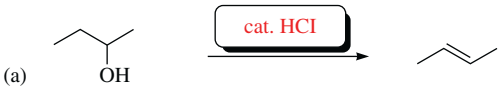
(c) 

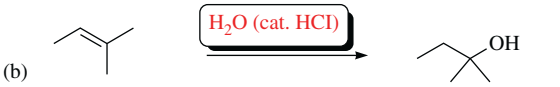
(d) 

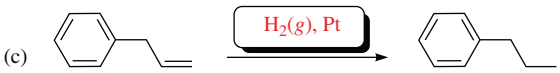
(e) 

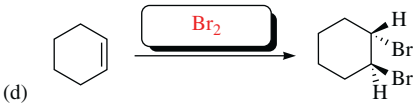
11.67 All of the products in 11.65 are chiral.

11.69

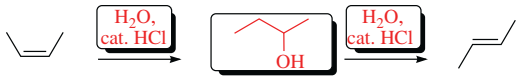
(a) 

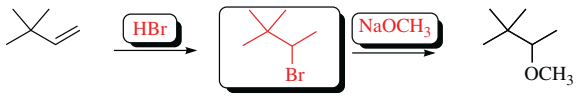
(b) 

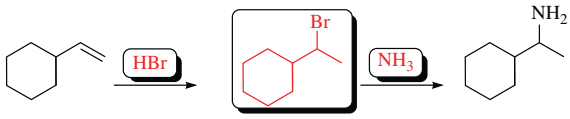
(c) 

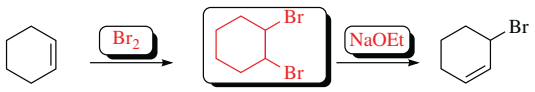
(d) 

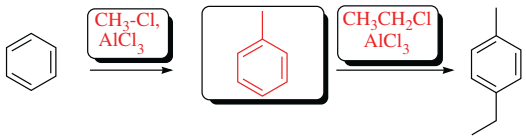
11.71

(a) 

(b) 

(c) 

(d) 

(e) 

Chapter 12

12.1 (a) A sand castle is organized in a particular way. Waves disperse the sand. (b) Mixing liquids disperses their molecules. (c) Sticks in a bundle are aligned in one direction. When dropped, the sticks lose their alignment and become more dispersed. (d) Water molecules in the gas phase are more dispersed than those in the liquid phase.

12.3 Initially the ink is concentrated in a droplet, but the molecules gradually become dispersed throughout the liquid.

12.5 (a) The air molecules in a tire are relatively constrained. A puncture allows gas molecules to escape from the tire and become more dispersed. (b) The fragrant molecules in a perfume bottle are relatively constrained. When

the bottle is open, molecules escape from the confined volume and become more dispersed.

12.7 (a) Energy dispersal requires that heat flows from high to low temperature, never in the opposite direction. (b) Matter dispersal requires that the spontaneous direction is toward greater dispersal, and a "sand castle" represents constrained matter.

12.9 72

12.11 (a) 16.8 J/K; (b) −15.3 J/K; and (c) 1.5 J/K

12.13 (a) $\Delta S_{sys} > 0$, $\Delta S_{surr} < 0$; (b) $\Delta S_{sys} > 0$, $\Delta S_{surr} < 0$; and (c) $\Delta S_{sys} > 0$, $\Delta S_{surr} < 0$. $\Delta S_{total} > 0$ always.

12.15 −94.0 J/K; $\Delta S_{surr} > 94.0$ J/K

12.17 (a) 16 J/mol K; (b) 9.3 J/mol K; (c) 48.8 J/mol K; and (d) 1.00×10^2 J/mol K

12.19 (a) $MgCl_2$, because it produces more moles of ions per mole of substance; (b) HgS, because it has a higher molar mass; and (c) $Br_2(l)$, because it is a liquid

12.21 Ozone has three atoms per molecule, whereas O_2 and H_2 have only two. H_2 has lower molar mass than O_2.

12.23 He: $S° = 126.153$ J/mol K; H_2: $S° = 65.340$ J/mol K; CH_4: $S° = 37.26$ J/mol K; C_3H_6: $S° = 25.21$ J/mol K. Entropy per mole of atoms decreases as the number of atoms in a molecule increase, because tying together atoms into a molecule increases the amount of order among those atoms.

12.25 (a) 416 J/K; (b) 1.7×10^2 J/K; and (c) 9.0×10^1 J/K

12.27 (a) −198.1 J/K; (b) −137.7 J/K; (c) 12.3 J/K; and (d) −267.3 J/K

12.29 (a) reduction in number of moles of gaseous substances; (b) reduction in number of moles of gaseous substances; (c) all reagents are relatively constrained solid substances; and (d) reduction in number of moles of gaseous substances

12.31 (a) positive; (b) negative; and (c) negative

12.33 (a) $\Delta G_{system} < 0$ for any spontaneous process at constant T and p; (b) the free energy of a system decreases in any process at constant T and p; and (c) $\Delta G = \Delta H - T\Delta S$ at constant T

12.35 (a) −32.8 kJ; (b) 326.4 kJ; (c) −206.1 kJ; and (d) −1331.4 kJ

12.37 (12.27b) 311.3 kJ; and (12.27c) −204.3 kJ

12.39 (a) −46.2 kJ; and (b) 319.7 kJ

12.41 $\Delta H°_{reaction} = -559.6$ kJ; $\Delta S°_{reaction} = -574.9$ J/K; $\Delta G°_{reaction} = -388.2$ kJ

12.43 (a) no temperature; and (b) zero concentration of products

12.45 5.2×10^{-5} bar

12.47 119 °C

12.49 44.3 kJ/mol; this value is higher than that at the boiling point because at the boiling point, the water molecules have more kinetic energy, and therefore need less additional energy to escape into the gas phase.

12.51 The first "reaction" would be child 1 starting on the ground and rising into the air. The second "reaction" would be child 2 starting in the air and falling to the ground. In this case, child 2 would undergo the spontaneous reaction. The motion of child 1 would be non-spontaneous. The common intermediate is the seesaw board, which acts as a lever transferring energy from one child to the other.

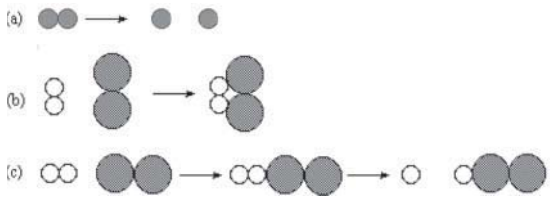
12.53 $ATP + C_6H_{12}O_6$ (fructose) + $C_6H_{12}O_6$ (glucose) $\longrightarrow$ $ADP + C_{12}H_{22}O_{11} + H_3PO_4$; $\Delta G° = -7.6$ kJ

Chapter 13

13.1 (a) pouring the coffee from the urn into the cup; (b) entering the items on the cash register (if the market has a good laser scanner, paying and receiving change may be rate-determining); and (c) preparing for the jump and passing through the door

13.3 (a) $I_2 \longrightarrow I + I$; (b) $H_2 + I_2 \longrightarrow H_2I_2$; and (c) $H_2 + I_2 \longrightarrow H + HI_2$

13.5



13.7 (a) $I_2 \longrightarrow I + I$
$I + H_2 \longrightarrow HI + H$
$H + I \longrightarrow HI$

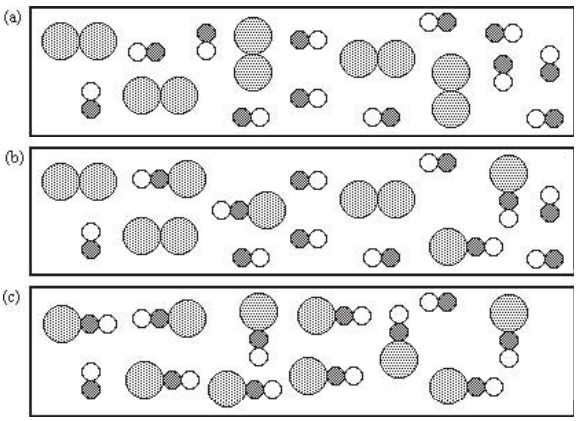
(b) $H_2 + I_2 \longrightarrow H_2I_2$
$H_2I_2 \longrightarrow HI + HI$

(c) $H_2 + I_2 \longrightarrow H + HI_2$
$H + HI_2 \longrightarrow HI + HI$

13.9 (a) $\text{Rate} = -\dfrac{\Delta[Cl_2]}{\Delta t}$

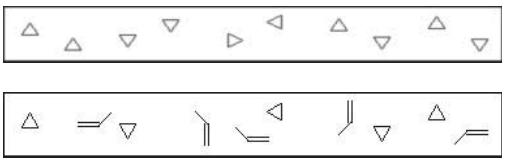
(b) $-\dfrac{\Delta[Cl_2]}{\Delta t} = \dfrac{1}{2}\dfrac{\Delta[NOCl]}{\Delta t}$; and (c) 94 M/s

13.11



13.13 (a) 2.2×10^{-3} mol/min; and (b) 1.1×10^{-2} mol

13.15



13.17 (a) 6.0×10^6; (b) 1.0×10^{-9}; and (c) in first-order reactions, the fraction reacting is independent of concentration.

13.19 (a) Rate = k[C][AB]; (b) units = (conc.)$^{-1}$ (time)$^{-1}$; and (c) $C + AB \longrightarrow BC + A$
$A + AB \longrightarrow B + A_2$
$B + C \longrightarrow BC$
Net: $2\,C + 2\,AB \longrightarrow 2\,BC + A_2$

13.21 (a) Rate = $k[C]^2[AB]$; (b) units = $(\text{conc.})^{-2}\,(\text{time})^{-1}$; and (c) $2C + AB \longrightarrow BC + AC$

$AC + AB \longrightarrow BC + A_2$

Net: $2\,C + 2\,AB \longrightarrow 2\,BC + A_2$

13.23 Slower by a factor of 0.56 because the product $[O_3][NO]$ is smaller by this factor

13.25 (a) This reaction is first-order; (b) $k = 6.14 \times 10^{-4}\ s^{-1}$; (c) 0.936 bar; and (d) 2.62×10^3 s

13.27 (a) 2.4 min; and (b) 3.2×10^{-4} M

13.29 (a) 12.0 h; and (b) 0.0324 M

13.31 Do two experiments; in each $[H_2O]_0 > 100\,[N_2O_5]_0$ but with two different values for $[H_2O]_0$. Plot $\ln\left(\frac{[N_2O_5]_0}{[N_2O_5]}\right)$ and $\frac{1}{[N_2O_5]} - \frac{1}{[N_2O_5]_0}$ vs. t to determine order with respect to N_2O_5, and use the ratio of slope values and H_2O concentrations to determine order with respect to H_2O. After determining the reaction order, rate constant can be determined from the slope of the linear plot (as described in Example 13-7 in the text).

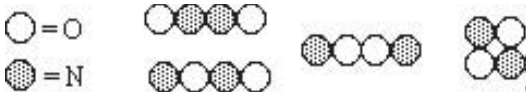
13.33 Rate = $k[S_2O_8^{2-}][\,I^-]$; $k = 2.3\ M^{-1}\ min^{-1}$

13.35 Rate = $k_2\left(\frac{k_1}{k_{-1}}\right)\frac{[C][AB]^2}{[BC]}$

13.37 (a) $O_3 + O \longrightarrow 2\,O_2$; (b) Rate = $k_2\frac{k_1}{k_{-1}}[O_3][O_2]$;

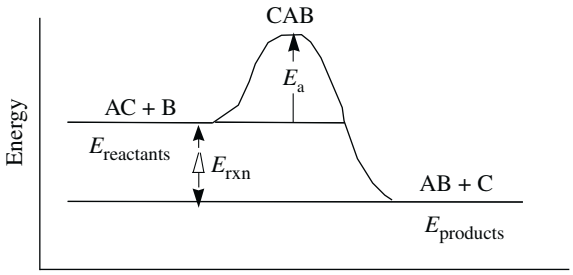
and (c) it is improbable to have two simultaneous fragmentations of O_5.

13.39 (a) Rate = $k_2\left(\frac{k_1}{k_{-1}}\right)[NO^2][O_2]$; (b) yes; and (c) the intermediate with an N—N bond is the most likely.

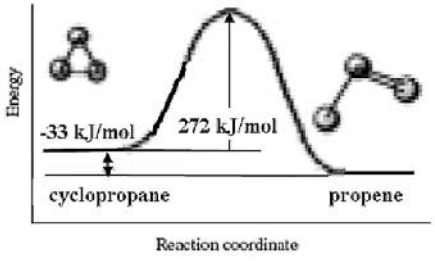


13.41 When $E_a = 0$, k is independent of temperature. This happens when a reaction can occur without first breaking any chemical bonds.

13.43 Activated complex:

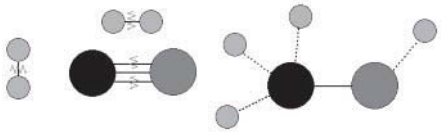


13.45



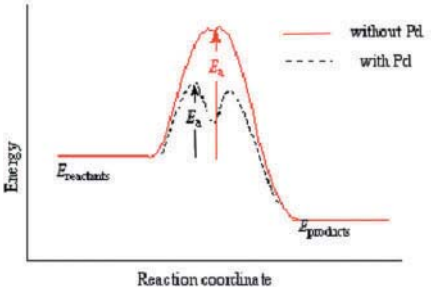
13.47 13 kJ/mol

13.49 Bond breakage (wavy lines): Bond formation (dotted lines):

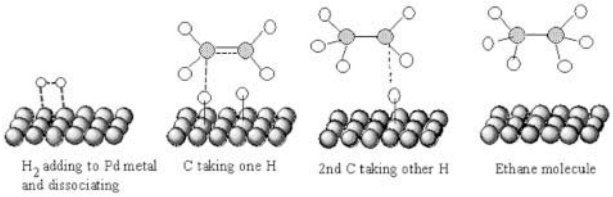


Hydrogen gas could adsorb on the catalyst's surface as H atoms, which will then react readily with CO molecules.

13.51 (a)

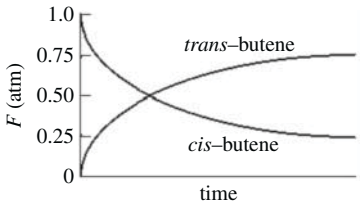


(b) catalyst: Pd metal; intermediate: H atoms on the Pd metal surface; and (c)



Chapter 14

14.1

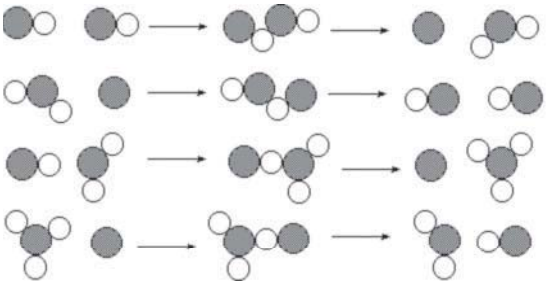


14.3 (a) $Cl^-(aq) + ClO_2^-(aq) \xrightarrow{k_{-1}} ClO^-(aq) + ClO^-(aq)$

$Cl^-(aq) + ClO_3^-(aq) \xrightarrow{k_{-2}} ClO^-(aq) + ClO_2(aq)$

(b) $K_{eq} = \frac{[ClO_3^-]_{eq}[Cl^-]_{eq}^2}{[ClO^-]_{eq}^3}$; and (c) $K_{eq} = \frac{k_1 k_2}{k_{-1}k_{-2}}$

14.5 Your molecular pictures of elementary reactions should show the reactants, the products, and (if applicable) the intermediate collision complex:



14.7 To test the reversibility of a reaction, set up a system containing the products and observe whether or not

reactants form. Here, a solution containing Cl^- and ClO_3^- ions should react to form some ClO^- ions.

14.9 (a) $K_{eq} = \dfrac{(p_{IF_5})^2_{eq}}{(p_{F_2})^5_{eq}}$; (b) $K_{eq} = \dfrac{1}{(p_{O_2})^5_{eq}}$;

(c) $K_{eq} = (p_{CO})^2_{eq}$; (d) $K_{eq} = \dfrac{1}{(p_{CO})_{eq}(p_{H_2})^2_{eq}}$; and

(e) $K_{eq} = \dfrac{[H_3O^+]^2_{eq}[PO_4^{3-}]_{eq}}{[H_3PO_4]_{eq}}$

14.11 (a) $2\ IF_5(g) \rightleftharpoons I_2(s) + 5\ F_2(g)$, $K_{eq} = \dfrac{(p_{F_2})^5_{eq}}{(p_{IF_5})^2_{eq}}$;

(b) $P_4O_{10}(s) \rightleftharpoons P_4(s) + 5\ O_2(g)$, $K_{eq} = (p_{O_2})^5_{eq}$;

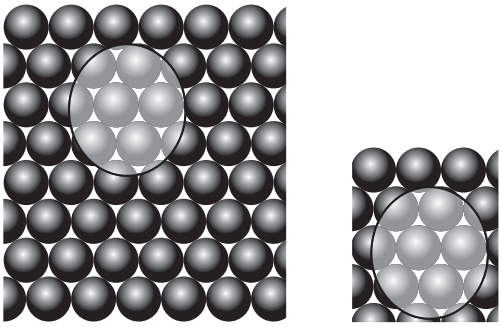
(c) $BaO(s) + 2\ CO(g) \rightleftharpoons BaCO_3(s)$, $K_{eq} = \dfrac{1}{(p_{CO})^2_{eq}}$;

(d) $CH_3OH(l) \rightleftharpoons CO(g) + 2\ H_2(g)$, $K_{eq} = (p_{CO_2})_{eq}(p_{H_2})^2_{eq}$; and

(e) $PO_4^{3-}(aq) + 3\ H_3O^+(aq) \rightleftharpoons H_3PO_4(aq) + 3\ H_2O(l)$, $K_{eq} = \dfrac{[H_3PO_4]_{eq}}{[H_3O^+]^3_{eq}[PO_4^{3-}]_{eq}}$

14.13 (a) $p = 1$ bar for F_2 and IF_5, $X = 1$ for I_2;
(b) $p = 1$ bar for O_2, $X = 1$ for P_4 and P_4O_{10};
(c) $p = 1$ bar for CO, $X = 1$ for others;
(d) $p = 1$ bar for CO and H_2, $X = 1$ for CH_3OH; and
(e) $c = 1$ M for H_3PO_4, H_3O^+, and PO_4^{3-}, $X = 1$ for H_2O

14.15 Your views should be like those in Figure 13-4, showing two different-sized samples with equal-sized portions of each highlighted to show that equal volumes contain equal numbers of atoms:



14.17 9.9×10^6

14.19 (a) 3.3×10^3; (b) 1×10^{90}; (c) 3×10^{-60}; and (d) 2.9×10^{39}

14.21 2×10^{109}; 3×10^{-75}

14.23 1.8×10^3; 9.2×10^{18}

14.25 (a), (b), and (d), adding CO causes the reaction to go to the right, forming products; (c), adding CO causes the reaction to proceed to the left, forming reactants.

14.27 (a) no effect; (b) more solid will dissolve; (c) some solid will precipitate; and (d) no effect

14.29 This reaction can be driven to the left by removing SO_2, removing Cl_2, adding SO_2Cl_2, or increasing the temperature.

14.31 0.92

14.33 1.3×10^{-5}

14.35 $(p_{H_2})_{eq} = (p_{Br_2})_{eq} = 2.5 \times 10^{-2}$ bar; $(p_{HBr})_{eq} = 10.0$ bar

14.37 $(p_{CO_2})_{eq} = 1.4$ bar and $(p_{CO})_{eq} = 3.6$ bar

14.39 (a) H_2O and CH_3CO_2H; (b) H_2O, NH_4^+, and Cl^-; (c) H_2O, K^+, and Cl^-; (d) H_2O, Na^+, and $CH_3CO_2^-$; and (e) H_2O, Na^+, and OH^-

14.41 (a) $CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$; (b) $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$; (c) no equilibria other than the water equilibrium; (d) $CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)$; and (e) no equilibria other than the water equilibrium

14.43 (a) $(CH_3)_2CO$ (acetone) and H_2O; (b) H_2O, K^+, and Br^-; (c) H_2O, Li^+, and OH^-; and (d) H_2O, H_3O^+, and HSO_4^-

14.45 (a) $K_{eq} = \dfrac{[ClO_2^-][H_3O^+]}{HClO_2} = K_a$;

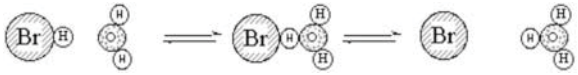
(b) $K_{eq} = \dfrac{1}{[Fe^{3+}][OH^-]^3} = \dfrac{1}{K_{sp}}$; and

(c) $K_{eq} = \dfrac{[HCN]}{[CN^-][H_3O^+]} = \dfrac{1}{K_a}$

14.47 (a) Na^+; (b) Cl^- and K^+; and (c) K^+ and NO_3^-

Chapter 15

15.1



15.3 $[H_3O^+] = 1.25 \times 10^{-3}$ M; $[OH^-] = 8.00 \times 10^{-12}$ M

15.5 $[H_3O^+] = [Cl^-] = 0.121$ M; $[OH^-] = 8.26 \times 10^{-14}$ M

15.7 $[H_3O^+] = 4.12 \times 10^{-2}$ M; $[OH^-] = 2.43 \times 10^{-13}$ M

15.9 (a) −0.60; (b) 5.426; (c) 2.32; and (d) 3.593

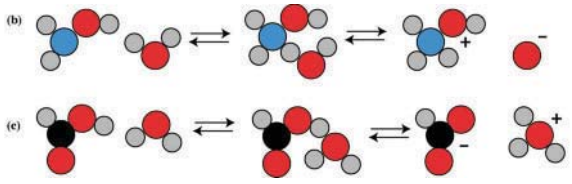
15.11 (a) 14.60; (b) 8.574; (c) 11.68; and (d) 10.407

15.13 (a) 0.22 M; (b) 1.4×10^{-8} M; (c) 2.1×10^{-4} M; and (d) 4.7×10^{-15} M

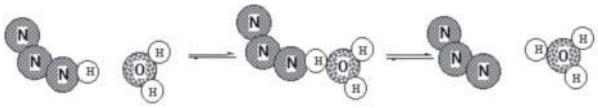
15.15 (a) 4.6×10^{-14} M; (b) 7.1×10^{-7} M; (c) 4.8×10^{-11} M; and (d) 2.1 M

15.17 (a) 9.70; (b) 10.04; and (c) 1.80

15.19

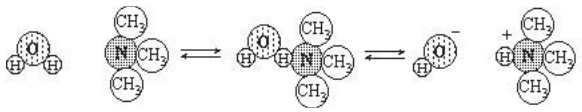


15.21 (a) major species: HN_3 and H_2O, minor species: N_3^-, H_3O^+, and OH^-; (b) $[H_3O^+] = [N_3^-] = 6.1 \times 10^{-3}$ M and $[HN_3] = 1.50$ M; (c) 2.21; and (d)



15.23 0.41 %

15.25 (a) major species: $N(CH_3)_3$ and H_2O, minor species: $HN(CH_3)_3^+$, OH^-, and H_3O^+; (b) $[OH^-] = [HN(CH_3)_3^+] = 4.8 \times 10^{-3}$ M, $[N(CH_3)_3] = 0.345$ M; (c) 11.68; and (d)

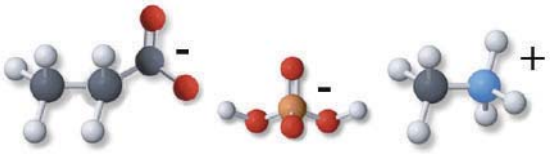


15.27 0.49 %

15.29 (a) weak base; (b) weak acid; (c) weak acid; and (d) strong base

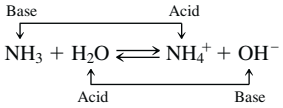
15.31

Propanoic acid	Phosphoric acid	Methylamine
(acid)	(acid)	(base)

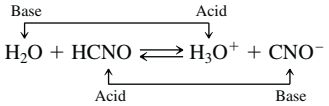


15.33 C_5H_5N conjugate acid is $C_5H_5NH^+$; $HONH_2$ conjugate acid is $HONH_3^+$; HCO_2H conjugate base is HCO_2^-.

15.35 (a)



(b)



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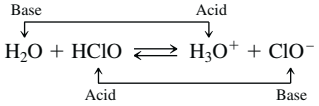

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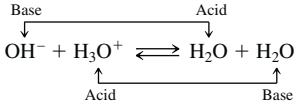


15.37 (a) major species are Na^+, SO_3^{2-}, and H_2O; (b) $H_2O + SO_3^{2-} \rightleftharpoons HSO_3^- + OH^-$; and (c) 10.43

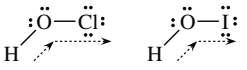
15.39 (a) major species are NH_4^+, NO_3^-, and H_2O; (b) $H_2O + NH_4^+ \rightleftharpoons NH_3 + H_3O^+$; and (c) 5.63

15.41 (a) basic, $H_2O + HS^- \rightleftharpoons OH^- + H_2S$;
(b) basic, $H_2O + OI^-(aq) \rightleftharpoons OH^- + HOI(aq)$;
(c) neutral, $H_2O(l) + H_2O(l) \rightleftharpoons OH^-(aq) + H_3O^+(aq)$; and
(d) acidic, $H_2O(l) + HC_5H_5N^+(aq) \rightleftharpoons H_3O^+(aq) + C_5H_5N(aq)$

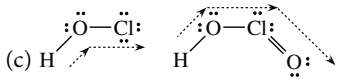
15.43 $NaI < NaF < NaC_6H_5CO_2 < Na_3PO_4 < NaOH$

15.45 (a) H_2SO_4 (anions are poorer proton donors than neutrals); (b) HClO (Cl is more electronegative); and (c) $HClO_2$ (more O atoms)

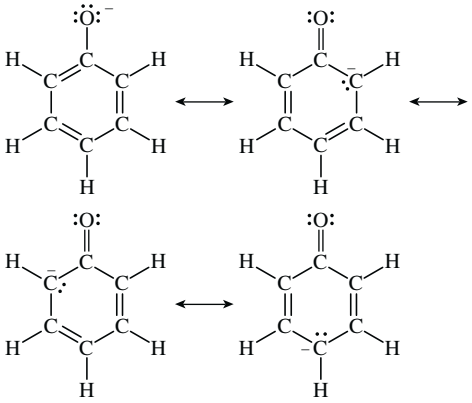
15.47 (b)



(c)



15.49



Charge in the phenolate anion is distributed around the ring, stabilizing the anion.

15.51 $[Na^+] = [C_2H_3O_2^-] = 0.250$ M; $[OH^-] = 1.2 \times 10^{-5}$ M; $[H_3O^+] = 8.3 \times 10^{-10}$ M

15.53 $[H_3O^+] = [HCO_3^-] = 8.4 \times 10^{-5}$ M; $[CO_3^{2-}] = 4.7 \times 10^{-11}$ M; $[OH^-] = 1.2 \times 10^{-10}$ M

15.55 $[Na^+] = 0.11$ M; $[OH^-] = [HCO_3^-] = 3.2 \times 10^{-3}$ M; $[CO_3^{2-}] = 0.052$ M; $[H_2CO_3] = 2.2 \times 10^{-8}$ M; $[H_3O^+] = 3.1 \times 10^{-12}$ M

Chapter 16

16.1 (a) no buffer properties; (b) buffer, 9.25; (c) no buffer properties; and (d) buffer, 9.25

16.3 8.88

16.5 1.4×10^{-3} mol

16.7 $H_3O^+(aq) + CO_3^{2-}(aq) \rightleftharpoons H_2O(l) + HCO^{3-}(aq)$; $OH^-(aq) + HCO_3^-(aq) \rightleftharpoons H_2O(l) + CO_3^{2-}(aq)$

16.9 (a) buffer containing HCO_3^- and CO_3^{2-}; (b) and (c) no buffer; and (d) buffer containing HCO_3^- and CO_3^{2-}

16.11 For pH = 3.50, the HCO_2H/HCO_2^- system should be used. Sodium formate could be used along with HCl solution. For pH = 12.60, the HPO_4^{2-}/PO_4^{3-} system should be used. Potassium phosphate could be used along with HCl solution.

16.13 37 g

16.15 55 mL

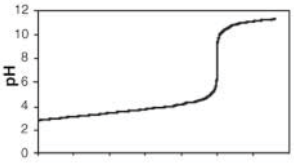
16.17 55.7 g sodium carbonate, 0.789 L HCl solution

16.19 1.5 g, still a buffer because not all of the base will have been destroyed

16.21 (a) $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$, pH < 7; (b) $H_2O(l) + H_2O(l) \rightleftharpoons OH^-(aq) + H_3O^+(aq)$; pH = 7; and (c) $CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons CH_3CO_2^-(aq) + H_3O^+(aq)$, pH < 7

16.23 (a) 2.8; (b) 7.8; and (c) 3.5

16.25 Phenol red



16.27 8.80; thymol blue

16.29 (a) 4.05; (b) 7.21; (c) 9.76; (d) 12.32; and (e) 12.62

16.31 (a) $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$,
$K_{sp} = [Ag^+]_{eq}\,[Cl^-]_{eq}$
(b) $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4{}^{2-}(aq)$,
$K_{sp} = [Ba^{2+}]_{eq}\,[SO_4{}^{2-}]_{eq}$
(c) $Fe(OH)_2(s) \rightleftharpoons Fe^{2+}(aq) + 2\ OH^-(aq)$,
$K_{sp} = [Fe^{2+}]_{eq}\,[OH^-]_{eq}{}^2$
(d) $Ca_3(PO_4)_2(s) \rightleftharpoons 3\ Ca^{2+}(aq) + 2\ PO_4{}^{3-}(aq)$,
$K_{sp} = [Ca^{2+}]_{eq}{}^3[PO_4{}^{3-}]_{eq}{}^2$

16.33 (a) 9.1×10^{-4} g; (b) 1.2×10^{-3} g; (c) 9.8×10^{-5} g; and (d) 1.6×10^{-5} g

16.35 2.3×10^{-9}

16.37 0.53 g

16.39 1.6×10^3

16.41 0.125 M

16.43 (a) $[Fe(CN)_6]^{3-}$; (b) $[Zn(NH_3)_4]^{2+}$; and (c) $[V(en)_3]^{3+}$

16.45 $[Zn^{2+}] = 4.9 \times 10^{-9}$ M; $[Zn(NH_3)_4{}^{2+}] = 5.4 \times 10^{-3}$ M; $[NH_3] = 0.228$ M

16.47 $[Cl^-] = 0.14$ M; $[Pb^{2+}] = 8.5 \times 10^{-15}$ M; $[Na^+] = 0.17$ M; $[PbCl_4{}^{2-}] = 0.0075$ M

16.49 $Mn^{2+} + en \rightleftharpoons [Mn(en)]^{2+}$

$[Mn(en)]^{2+} + en \rightleftharpoons [Mn(en)_2]^{2+}$

$[Mn(en)_2]^{2+} + en \rightleftharpoons [Mn(en)_3]^{2+}$

16.51 7.5 g

Chapter 17

17.1 (a) O is −2, H is +1, and Fe is +3; (b) F is −1, N is +3; (c) O is −2, H is +1, C is −2; (d) K^+ is +1, O is −2, and C is +4; (e) in $NH_4{}^+$, H is +1 and N is −3; in $NO_3{}^-$, O is −2 and N is +5; (f) Cl is −1, Ti is +4; (g) Pb is +2; in sulphate, O is −2, S is +6; and (h) P is 0

17.3 (a) not redox; (b) redox; (c) not redox; (d) redox; and (e) redox

17.5 (a) +5; (b) −1; (c) +7; (d) 0; (e) +3; and (f) +1

17.7 (a) $Na \longrightarrow Na^+ + e^-$ and $2\ H_2O + 2\ e^- \longrightarrow H_2 + 2\ OH^-$; (b) $Au + 4\ Cl^- \longrightarrow [AuCl_4]^- + 3\ e^-$ and $NO_3{}^- + 4\ H_3O^+ + 3\ e^- \longrightarrow NO + 6\ H_2O$; (c) $MnO_4{}^- + 8\ H_3O^+ + 5\ e^- \longrightarrow Mn^{2+} + 12\ H_2O$ and $C_2O_4{}^{2-} \longrightarrow 2\ CO_2 + 2\ e^-$; and (d) $C + 3\ H_2O \longrightarrow CO + 2\ H_3O^+ + 2e^-$ and $2\ H_3O^+ + 2\ e^- \longrightarrow H_2 + 2\ H_2O$

17.9 (a) $Cu^+ + 3\ H_2O \longrightarrow CuO + 2\ H_3O^+ + e^-$
(b) $S + 2\ H_3O^+ + 2\ e^- \longrightarrow H_2S + 2\ H_2O$
(c) $AgCl + e^- \longrightarrow Ag + Cl^-$;
(d) $I^- + 6\ OH^- \longrightarrow IO_3{}^- + 3\ H_2O + 6\ e^-$
(e) $IO_3{}^- + 2\ H_2O + 4\ e^- \longrightarrow IO^- + 4\ OH^-$
(f) $H_2CO + 5\ H_2O \longrightarrow CO_2 + 4\ H_3O^+ + 4\ e^-$

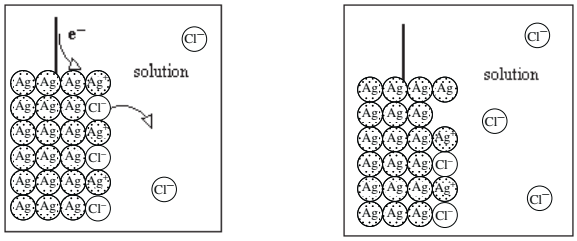
17.11 (a) $2\ Cu^+ + 4\ H_2O + S \longrightarrow 2\ CuO + 2\ H_3O^+ + H_2S$
(b) $3\ Ag_2O + I^- \longrightarrow 6\ Ag + IO_3{}^-$
(c) $2\ I^- + IO_3{}^- \longrightarrow 3\ IO^-$
(d) $2\ S + H_2CO + H_2O \longrightarrow 2\ H_2S + CO_2$

17.13 (a) Cl^-; (b) $MnO_4{}^-$; (c) $MnO_4{}^-$; (d) Cl^-; (e) $MnO_4{}^-$; and (f) Cl^-

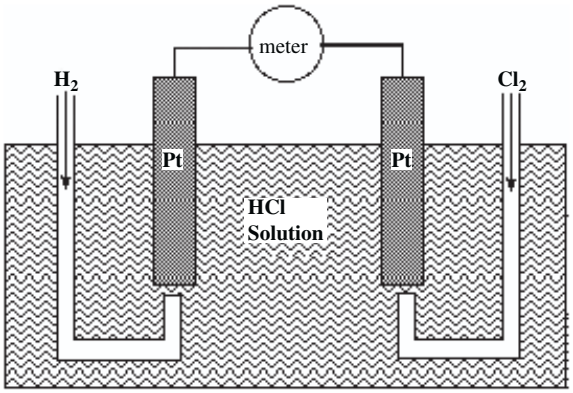
17.15 (a) $3\ CN^- + 2\ MnO_4{}^- + H_2O \longrightarrow 3\ CNO^- + 2\ MnO_2 + 2\ OH^-$; (b) $4\ As + 3\ O_2 + 2\ H_2O \longrightarrow 4\ HAsO_2$; (c) $Br^- + 2\ MnO_4{}^- + H_2O \longrightarrow BrO_3{}^- + 2\ MnO_2 + 2\ OH^-$; (d) $3\ NO_2 + 3\ H_2O \longrightarrow 2\ NO_3{}^- + NO + 2\ H_3O^+$; (e) $ClO_4{}^- + 6\ Cl^- + 6\ H_3O^+ \longrightarrow ClO^- + 9\ H_2O + 3\ Cl_2$; and (f) $AlH_4{}^- + 4\ H_2CO + 4\ H_2O \longrightarrow Al^{3+} + 4\ CH_3OH + 4\ OH^-$

17.17 (a), (b), (c), and (d) spontaneous

17.19



17.21



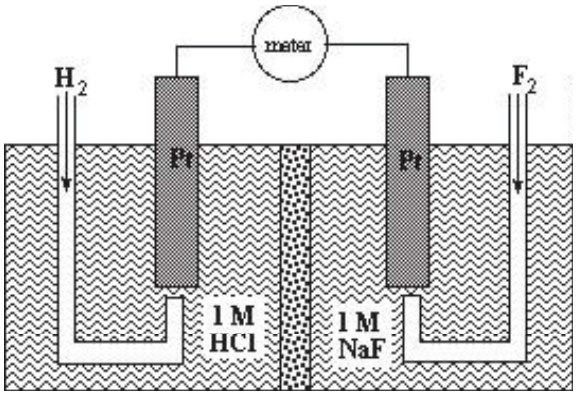
17.23 The silver–silver chloride electrode (17.19) is active, whereas the platinum electrodes (17.21) are passive.

17.25 The shorthand notation is always written as anode to cathode (left to right).
(a) $Ag(s) \mid Ag^+(aq) \parallel Fe^{2+}(aq) \mid Fe(s)$
(b) $Pt(s) \mid H_2O_2(aq), H_3O^+(aq) \mid O_2(g) \parallel NO_3{}^-(aq), H_3O^+(aq) \mid NO(g) \mid Pt(s)$
(c) $Pt(s) \mid H_2(g) \mid H_3O^+(aq) \parallel Cl_2(g) \mid Cl^-(aq) \mid Pt(s)$

17.27 (a) 1.565 V; (b) 0.981 V; and (e) 0.002 V

17.29 $8\ NO + 3\ H_2O \longrightarrow 3\ N_2O + 2\ NO_3{}^- + 2\ H_3O^+$; $E^\circ_{cell} = 0.634$ V

17.31 Set up a standard hydrogen electrode on one side and a Pt electrode immersed in 1 M solution of NaF with F_2 bubbling over the electrode. The H_2/H_3O^+ electrode will be the anode.



17.33 Ba, Ca, Cs, Li, Mg, K, and Na. All these metals lie in the *s* block of the periodic table and easily lose 1 or 2 electrons.

17.35 (a) −906.0 kJ; (b) -1.14×10^3 kJ; and (e) −1 kJ

17.37 $E = 1.35$ V

17.39 $m_{Pb} = 9.5 \times 10^{-2}$ g; $m_{PbO_2} = 0.11$ g

17.41 1.35×10^3 s

17.43 1.98 g

17.45 0.039 V

17.47 (a) 0.137 V; (b) 0.0187 V; (c) −0.159 V

17.49 $Q = \dfrac{1}{[H_3O^+]^2[HSO_4^-]^2}$; as the battery operates, these concentrations decrease, Q and ln Q increase, and the potential of the battery decreases with use.

17.51 Zn oxidizes more easily and will preferentially corrode, protecting the steel propeller.

17.53 Lead storage batteries are heavy. For space flights, weight is a more important consideration than rechargeability, so lead batteries are not suitable.

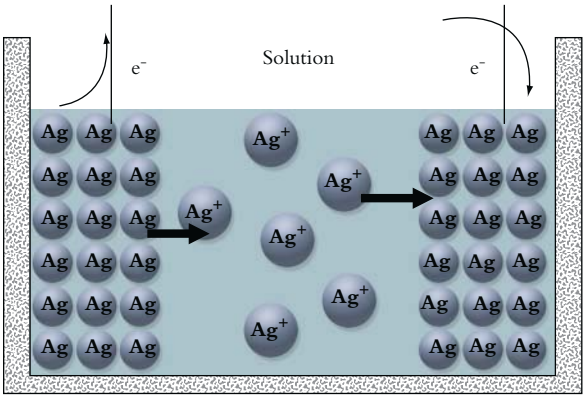
17.55 19.9 g

17.57 The oxidation reaction is $Cu \longrightarrow Cu^{2+} + 2\ e^-$. The reduction of H_3O^+ occurs: $2\ H_3O^+ + 2\ e^- \longrightarrow 2\ H_2O + H_2$ ($E^\circ = 0$ V)

17.59 (a) Attach the negative wire to the Cd electrode; $Cd(s) + 2\ OH^-(aq) \rightleftharpoons Cd(OH)_2(s) + 2e^-$; (b) 4.56 h

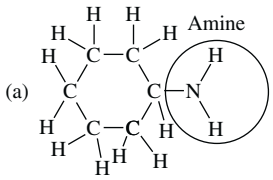
17.61 1.89×10^3 C; 2.10 A

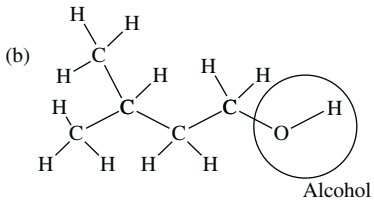
17.63

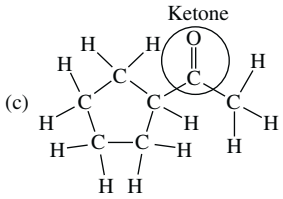


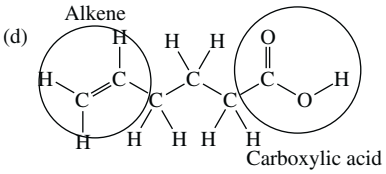
Chapter 18

18.1

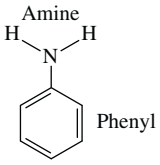
(a) 

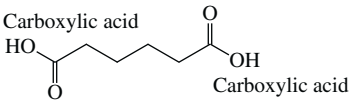
(b) 

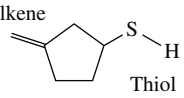
(c) 

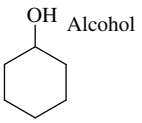
(d) 

18.3

(a) 

(b) 

(c) 

(d) 

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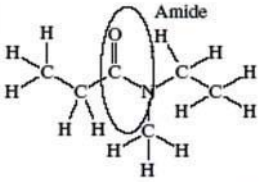
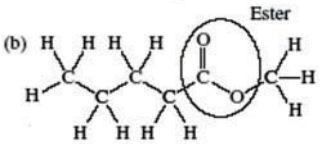
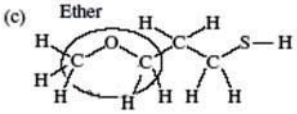
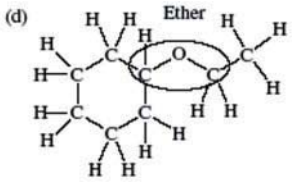
(a) 

(b) 

(c) 

(d) 

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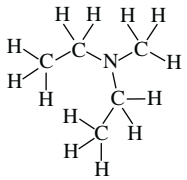
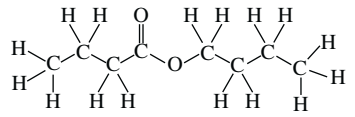
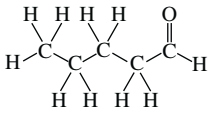
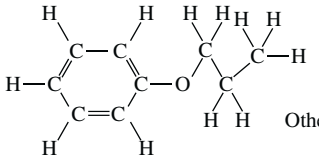
(a) 

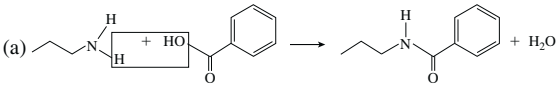
Other isomers are also possible.

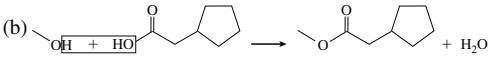
(b)  Other isomers are also possible.

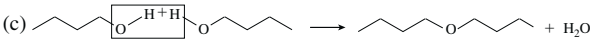
(c)  Others are also possible.

(d)  Others are also possible.

18.9

(a) 

(b) 

(c) 

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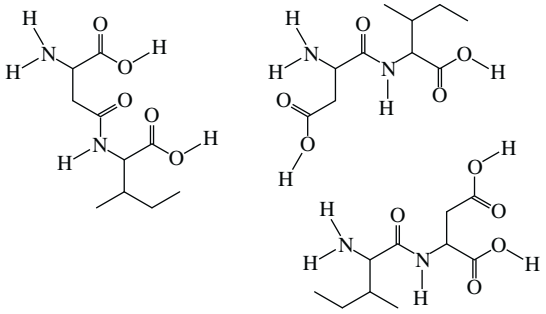
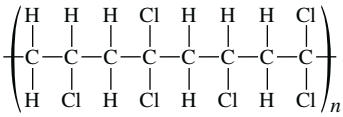
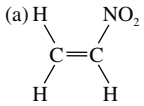
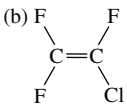
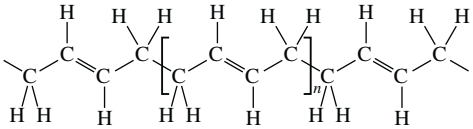


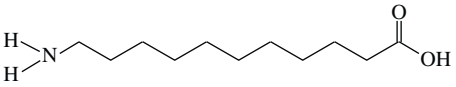
18.13 

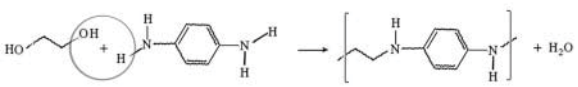
18.15 (a) 

(b) 

18.17 

Polybutadiene contains double bonds, whereas polyethylene does not.

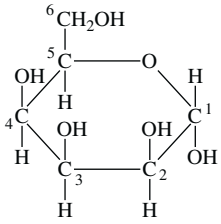
18.19 

18.21 

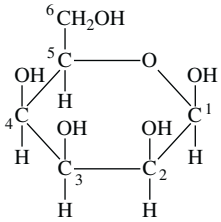
18.23 Automobile tire

18.25 (a) elastomers; (b) fibres; and (c) plastics

18.27 Dioctylphthalate reduces the amount of cross-linking and adds a fluid component to the polymer, so the polymer becomes more flexible.

18.29 

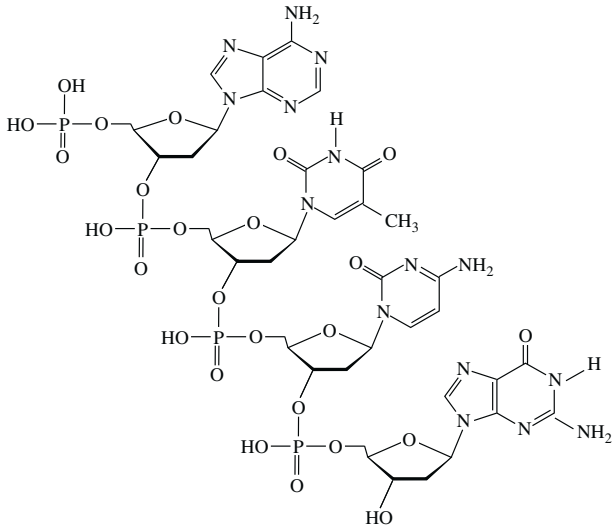
α-Talose

18.31 

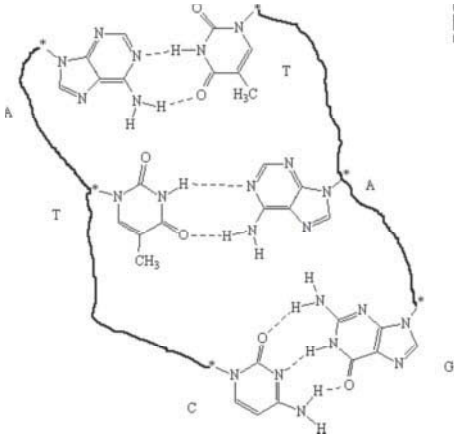
β-Talose

18.33 Polymers of α-glucose (e.g., glycogen) coil on themselves; polymers of β-glucose (e.g., cellulose) form planar sheets.

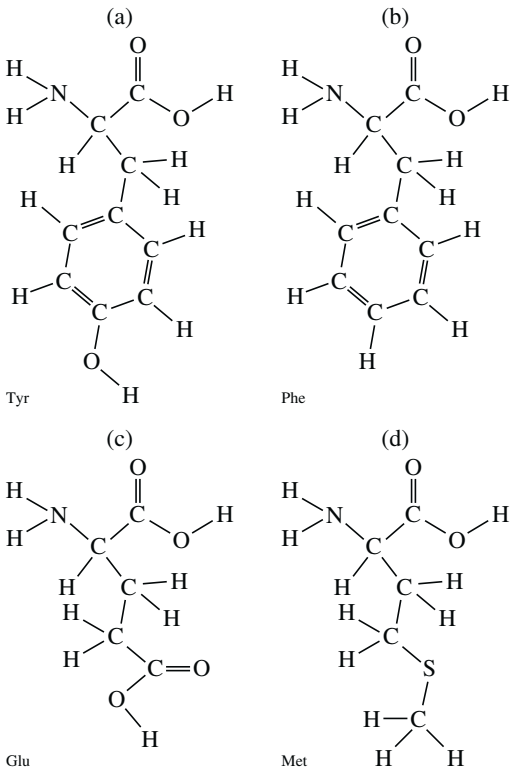
18.35 T-T-A-C-G-T-G-A-C

18.37 

18.39 The complementary sequence is T-A-G.



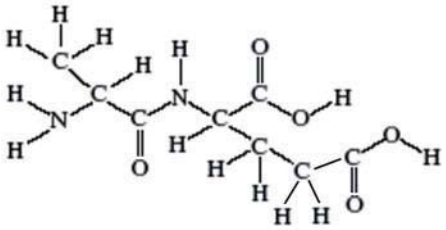
18.41



18.43 Hydrophilic side chains: Tyr and Glu; hydrophobic side chains: Met and Phe

18.45 (a) Glycine, hydrophobic side chain; (b) serine, hydrophilic; and (c) cysteine, hydrophilic

18.47 Six combinations: Met-Ala, Ala-Met, Ala-Glu, Glu-Ala, Met-Glu, and Glu-Met. Only Ala-Glu is shown here:



Chapter 19

19.1 (a) Mn is +2; (b) Mo is +5; (c) V is +5; (d) Au is +3; and (e) Fe is +3

19.3 (a) chromium, Cr; (b) cadmium, Cd; and (c) copper, Cu

19.5 (a) $3d^5$; (b) $5d^6$; (c) $3d^8$; and (d) $4d^4$

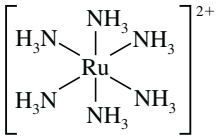
19.7 (a) Pd; (b) Au; and (c) Co

19.9 (a) Ru has oxidation state +2, d^6
(b) Cr has oxidation state +3, d^3
(c) Pd has oxidation state +2, d^8
(d) Ir has oxidation state +3, d^6
(e) Ni has oxidation state 0, s^2d^8

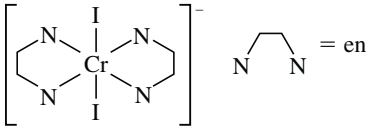
19.11 (a) hexaammineruthenium(II) chloride;
(b) *trans*-(ethylenediamine)diiodochromium(III) iodide
(c) *cis*-dichlorobis(trimethylphosphine)palladium(II)
(d) *fac*-triamminetrichloroiridium(III)
(e) tetracarbonylnickel(0)

19.13

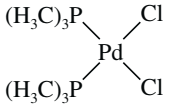
(a) Six NH_3 in an octahedron around the central Ru:



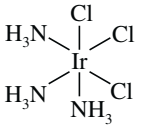
(b) Two I at opposite ends of one axis, two en in a square plane around the central Cr:



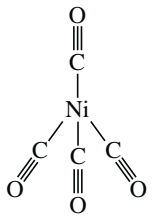
(c) Square planar arrangement about Pd, with two Cl adjacent each other:



(d) Octahedral arrangement around Ir, with three Cl in a triangular face:

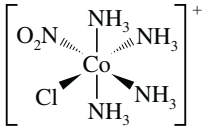


(e) Tetrahedral arrangement of C≡O about a central Ni:

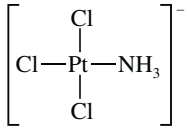


19.15 (a) *cis*-$[Co(NH_3)_4ClNO_2]^+$; (b) $[PtNH_3Cl_3]^-$; (c) *trans*-$[Cu(en)_2(H_2O)_2]^{2+}$; and (d) $[FeCl_4]^-$

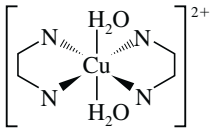
19.17 (a)



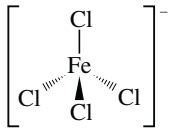
(b)



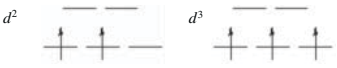
(c)



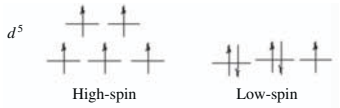
(d)



19.19 (a) and (b)



(c) and (d)

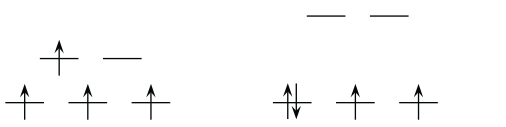


19.21 (a) diamagnetic; (b) paramagnetic with four unpaired electrons; (c) paramagnetic with two unpaired electrons; and (d) diamagnetic

19.23 The colours of transition-metal complexes are generally determined by *d*–*d* transitions, but Zr^{4+} has no valence electron that can undergo a transition that would absorb visible light.

19.25 (a) 6; (b) +3, $3d^5$; (c) octahedral; (d) paramagnetic; and (e) one

19.27

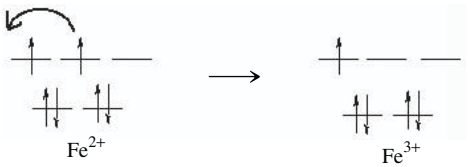


Small splitting (H_2O) Large splitting (CN^-)

19.29 257 kJ/mol, orange

19.31 Haemoglobin has four subunits, whereas myoglobin has just one. As a consequence, haemoglobin has a more complex cooperative chemical behaviour than myoglobin.

19.33 Remove 1 electron



Fe^{2+} Fe^{3+}

19.35 (a) $CuFeS_2 + 2\ O_2 \longrightarrow CuO + FeO + 2\ SO_2$
(b) $Si + O_2 + CaO \longrightarrow CaSiO_3$
(c) $TiCl_4 + 4\ Na \longrightarrow 4\ NaCl + Ti$

19.37 1.06×10^6 g; 2.05×10^5 L

19.39 183.3 kJ; 63.3 kJ

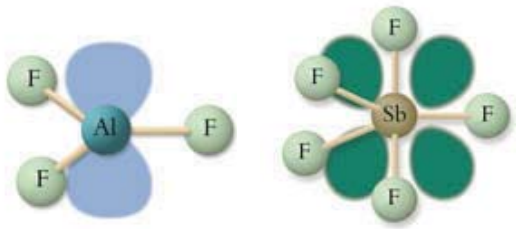
19.41 The coinage metals are copper, silver, and gold. They are used for money, electrical wire, and decorative objects such as jewelry.

19.43 Titanium is used as an engineering metal because of its relatively low density, high bond strength, resistance to corrosion, and ability to withstand high temperatures, all of which make it a favoured structural material.

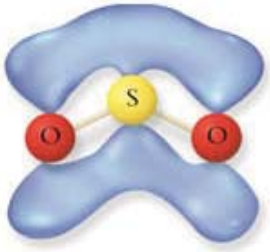
Chapter 20

20.1 (a) Lewis acid is Ni, Lewis base is CO; (b) Lewis acid is $SbCl_3$, Lewis base is Cl^-; (c) Lewis acid is $AlBr_3$, Lewis base is $(CH_3)_3P$; and (d) Lewis acid is BF_3, Lewis base is ClF_3.

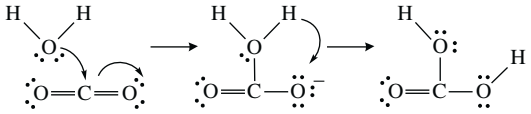
20.3 (a) acceptor: 3*p* orbital; (b) acceptor: 3*d* orbital



(c) acceptor: delocalized π orbital



20.5 In the first step, an electron pair from the O atom of H_2O displaces a π bond in Lewis acid–base adduct formation. Then a proton from H_2O migrates to a C—O oxygen atom:



Adduct formation Proton transfer

20.7 Fe^{3+} (high charge) < V^{3+} (lowest *Z*, high charge) < Fe^{2+} < Pb^{2+} (large *n*)

20.9 (a) hardest is BF_3, then BCl_3, and $AlCl_3$ is softest; (b) the hardest acid is Al^{3+} (row 3), then Tl^{3+} (row 6), and Tl^+ (low charge) is softest; and (c) polarizability increases with *n*, so hardest is $AlCl_3$, then $AlBr_3$, and AlI_3 is softest.

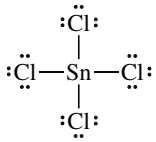
20.11 When an electronegative O atom bonds to a less negative S atom, it withdraws electron density from S, decreasing the polarizability about S and increasing the hardness of the base.

20.13 (a) metathesis occurs, giving $AlCl_3$ and NaI; (b) no reaction occurs; (c) metathesis occurs, giving H_2O and CaS; (d) metathesis occurs, giving $(CH_3)_3P$ and LiCl; and (e) no reaction occur.

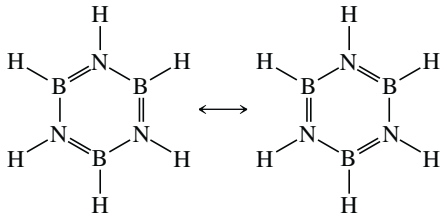
20.15 Al_2Cl_6 contains two "bridging" chlorine atoms. Standard procedures would predict tetrahedral geometry about all inner atoms, but the Al—Cl—Al bond angles of 91° indicate that Cl uses *p* orbitals. Each Al atom can be described as using sp^3 hybrids to form four σ bonds to four different Cl atoms. In Lewis acid–base terms, the bridged molecule forms from two $AlCl_3$ units linking together in double-adduct formation between the Al Lewis-acid atoms and two Cl Lewis-base atoms.

20.17 Thallium lies below indium and gallium, so its properties should be similar to those metals: valence of 3, soft Lewis acid. Like its neighbour Pb, it is toxic.

20.19 $SnCl_4$ can function as a Lewis acid because Sn has empty *d* orbitals from which it can accept electrons to form more bonds:



20.21 Lewis structure:

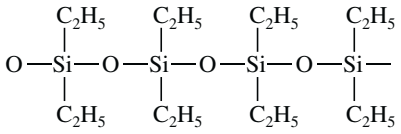


The B and N atoms have bonding and geometry that can be described using sp^2 hybrid orbitals, resulting in three σ bonds around each ring atom. In addition, there is a delocalized π bonding network encompassing all six ring atoms and containing six electrons.

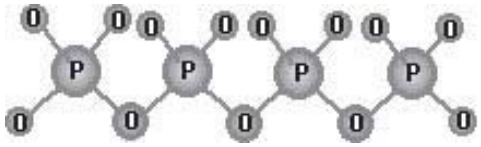
20.23 Si has a larger band gap.

20.25 $2\ C_2H_5Cl + Si(Cu) \longrightarrow (C_2H_5)_2SiCl_2 + Cu$
$(C_2H_5)_2SiCl_2 + 2\ H_2O \longrightarrow (C_2H_5)_2Si(OH)_2 + 2\ HCl$

Condensation will eliminate water to give the polymer:



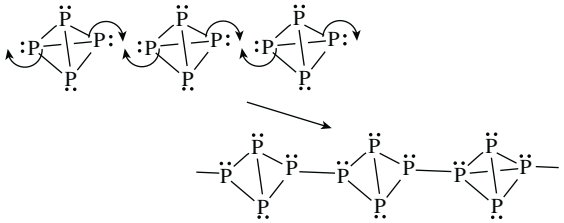
20.27 $P_4O_{13}^{6-}$:



20.29 Brønsted-Lowry acid–base reaction:

$$Ca_5(PO_4)_3F(s) + 5\ H_2SO_4(aq) \longrightarrow 3\ H_3PO_4(aq) + 5\ CaSO_4(s) + HF(aq)$$

20.31

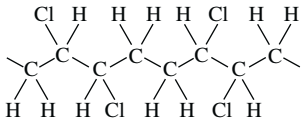


20.33 There are two industrial reactions in Section 20.6 in which sulphuric acid acts as a Brønsted acid:

$$CaF_2(s) + H_2SO_4(l) \longrightarrow 2\ HF(g) + CaSO_4(s)$$

$$FeTiO_3(s) + 2\ H_2SO_4(aq) + 5\ H_2O(l) \xrightarrow{150-180^\circ C} TiOSO_4(aq) + FeSO_4 \bullet 7H_2O(s)$$

20.35



20.37 $TiO_2(s) + C(s) + 2\ Cl_2(g) \longrightarrow TiCl_4(l) + CO_2(g)$

C is oxidized from 0 to +4 and is the reducing agent; Cl is reduced from −1 to 0 and is the oxidizing agent.

Chapter 21

21.1

Part:	(a)	(b)	(c)
Z	10	82	40
A	20	205	90
N	10	123	50

21.3 ^{53}Mn: unstable, too few neutrons; ^{54}Mn: unstable, odd–odd; ^{55}Mn: stable; and ^{56}Mn: unstable, too many neutrons and odd–odd

21.5 $\Delta E = 8.99 \times 10^{16}$ kJ

21.7 $\Delta E = -1.079 \times 10^{11}$ kJ/mol;
ΔE (per nucleon) $= -8.11 \times 10^{8}$ kJ/mol nucleon

21.9 The repulsive barrier is greater for $^4He + {}^4He \longrightarrow {}^8Be$ than for $^1H + {}^6Li \longrightarrow {}^7Be$; ^{8}Be is more stable.

21.11

Description	Symbol	Name
(a) high-energy photon	γ	gamma ray
(b) mass number 4	α	alpha particle
(c) positive particle with m_e	β^+	positron

21.13 (a) $^{125}_{52}$Te; (b) $^{123}_{51}$Sb ; and (c) $^{127}_{53}$I

21.15 ^{53}Mn, β^+ or EC; ^{54}Mn, β, β^+ or EC; ^{55}Mn is stable; ^{56}Mn, β

21.17 $t_{1/2} = 1.2$ years

21.19 $^{232}_{90}Th \longrightarrow \alpha + {}^{228}_{88}Ra \longrightarrow \beta + {}^{228}_{89}Ac \longrightarrow \beta + {}^{228}_{90}Th \longrightarrow \alpha + {}^{224}_{88}Ra$

$^{224}_{88}Ra \longrightarrow \alpha + {}^{220}_{86}Rn \longrightarrow \alpha + {}^{216}_{84}Po \longrightarrow \beta + {}^{216}_{85}At \longrightarrow \alpha + {}^{212}_{83}Bi$

$^{212}_{83}Bi \longrightarrow \beta + {}^{212}_{84}Po \longrightarrow \alpha + {}^{208}_{82}Pb$

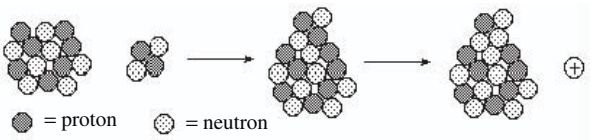
21.21 (a) $^{12}_{6}C + {}^{1}_{0}n \longrightarrow ({}^{13m}_{6}C) \longrightarrow {}^{12}_{5}B + {}^{1}_{1}P$

(b) $^{16}_{8}O + {}^{4}_{2}\alpha \longrightarrow ({}^{20m}_{10}Ne) \longrightarrow {}^{20}_{10}Ne + \gamma$

(c) $^{247}_{96}Cm + {}^{11}_{5}B \longrightarrow ({}^{258m}_{101}Md) \longrightarrow {}^{255}_{101}Md + 3\,{}^{1}_{0}n$

21.23 The reaction in this problem is

$$^{14}_{7}N + \alpha \longrightarrow (^{18}_{9}F) \longrightarrow {}^{18}_{8}O + \beta^+$$



21.25 Cs, Ba, La, Ce

21.27 $\Delta E = -1.648 \times 10^{10}$ kJ/mol, somewhat less than Section Exercise 21.4.1 result

21.29 The core of a nuclear reactor generates radiation that converts any material in its vicinity into radioactive substances. Thus, the heat exchanger in immediate contact with the core becomes radioactive and must be separated from the turbine that generates electricity. The primary heat exchanger transfers energy to a secondary heat exchanger, which does not become radioactive and can safely drive the turbine.

21.31 $\Delta E_{total} = -2.4 \times 10^9$ kJ

21.33 $\upsilon = 5.3 \times 10^6$ m/s

21.35 Your description should include the extremely high energies required to initiate fusion and the difficulties in containing the fusion components at the temperature required for nuclei to have these high energies.

21.37

Stage	Temperature	Composition
H-burning	4×10^7 K	C, N, H, He, e^-
He-burning	10^8 K	He, Be, C, and O
C-burning	10^9 K	All nuclides from $Z = 6$ (c) up to $Z = 26$ (Fe)

21.39 Your description should include the fact that elements beyond $Z = 26$ are less stable than Fe, so they cannot be generated by fusion of lighter elements.

21.41 $E = 4.4 \times 10^{-4}$ J

21.43 3.41×10^4 β/s

21.45 Exposure to radiation results first in damage to those cells that reproduce most quickly, including the white blood cells that are responsible for fighting infection and the mucous membrane lining of the intestinal tract. Thus the early symptoms of radiation exposure include reduced resistance to infection and nausea due to disruption of the digestive tract.

21.47 3.5×10^9 years

21.49 Add a radioactive iron isotope to the manufacturer's iron waste stream before treatment, and monitor the iron content of the river downstream. If radioactivity appears in the river water, the source is the manufacturer; if not, the iron in the river comes from some other source.

21.51 Run the hydrolysis in water that is enriched with a radioactive isotope of oxygen. Isolate the two products and analyze them for radioactivity. Whichever product shows radioactivity is the one whose added oxygen atom comes from water.