Appendix

Appendix 1: Normality

Normality expresses concentration in terms of the equivalents of one chemical species reacting stoichio-metrically with another chemical species. Note that this definition makes an equivalent, and thus normality, a function of the chemical reaction. Although a solution of H_2SO_4 has a single molarity, its normality depends on its reaction.

We define the number of equivalents, n, using a reaction unit, which is the part of a chemical species participating in the chemical reaction. In a precipitation reaction, for example, the reaction unit is the charge of the cation or anion participating in the reaction; thus, for the reaction

$$Pb^{2+}(aq) + 2I^-(aq) \rightleftharpoons PbI_2(s)$$
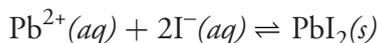
$n=2$ for $Pb^{2+}(aq)$ and $n=1$ for $2I^-(aq)$. In an acid–base reaction, the reaction unit is the number of H^+ ions that an acid donates or that a base accepts. For the reaction between sulfuric acid and ammonia

$$H_2SO_4(aq) + 2NH_3(aq) \rightleftharpoons 2NH_4^+(aq) + SO_4^{2-}(aq)$$
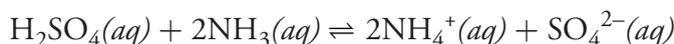
$n=2$ for $H_2SO_4(aq)$ because sulfuric acid donates two protons, and $n=1$ for $NH_3(aq)$ because each ammonia accepts one proton. For a complexation reaction, the reaction unit is the number of electron pairs that the metal accepts or that the ligand donates. In the reaction between Ag^+ and NH_3

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$$
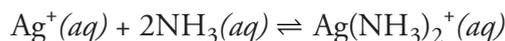
$n=2$ for $Ag^+(aq)$ because the silver ion accepts two pairs of electrons, and $n=1$ for NH_3 because each ammonia has one pair of electrons to donate. Finally, in an oxidation–reduction reaction the reaction unit is the number of electrons released by the reducing agent or accepted by the oxidizing agent; thus, for the reaction

$$2Fe^{3+}(aq) + Sn^{2+}(aq) \rightleftharpoons Sn^{4+}(aq) + 2Fe^{2+}(aq)$$
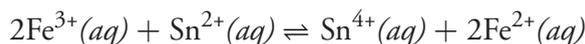
$n=1$ for $Fe^{3+}(aq)$ and $n=2$ for $Sn^{2+}(aq)$. Clearly, determining the number of equivalents for a chemical species requires an understanding of how it reacts.

Normality is the number of equivalent weights, EW, per unit volume. An equivalent weight is the ratio of a chemical species' formula weight, FW, to the number of its equivalents, n.

$$EW = \frac{FW}{n}$$

The following simple relationship exists between normality, N, and molarity, M.

$$N = n \times M$$

Appendix 2: Propagation of Uncertainty

In Chapter 4 we considered the basic mathematical details of a propagation of uncertainty, limiting our treatment to the propagation of measurement error. This treatment is incomplete because it omits other sources of uncertainty that influence the overall uncertainty in our results. Consider, for example, Practice Exercise 4.2, in which we determined the uncertainty in a standard solution of Cu^{2+} prepared by dissolving a known mass of Cu wire with HNO_3, diluting to volume in a 500-mL volumetric flask, and then diluting a 1-mL portion of this stock solution to volume in a 250-mL volumetric flask. To calculate the overall uncertainty we included the uncertainty in the sample's mass and the uncertainty of the volumetric glassware. We did not consider other sources of uncertainty, including the purity of the Cu wire, the effect of temperature on the volumetric glassware, and the repeatability of our measurements. In this appendix we take a more detailed look at the propagation of uncertainty, using the standardization of NaOH as an example.

Standardizing a Solution of NaOH[1]

Because solid NaOH is an impure material, we cannot directly prepare a stock solution by weighing a sample of NaOH and diluting to volume. Instead, we determine the solution's concentration through a process called a standardization.[2] A fairly typical procedure is to use the NaOH solution to titrate a carefully weighed sample of previously dried potassium hydrogen phthalate, $C_8H_5O_4K$, which we will write here, in shorthand notation, as KHP. For example, after preparing a nominally 0.1 M solution of NaOH, we place an accurately weighed 0.4-g sample of dried KHP in the reaction vessel of an automated titrator and dissolve it in approximately 50 mL of water (the exact amount of water is not important). The automated titrator adds the NaOH to the KHP solution and records the pH as a function of the volume of NaOH. The resulting titration curve provides us with the volume of NaOH needed to reach the titration's endpoint.[3]

   The end point of the titration is the volume of NaOH corresponding to a stoichiometric reaction between NaOH and KHP.

$$NaOH + C_8H_5O_4K \rightarrow C_8H_4O_4^- + K^+ + Na^+ + H_2O(l)$$

Knowing the mass of KHP and the volume of NaOH needed to reach the endpoint, we use the following equation to calculate the molarity of the NaOH solution.

$$C_{NaOH} = \frac{1000 \times m_{KHP} \times P_{KHP}}{M_{KHP} \times V_{NaOH}}$$

where C_{NaOH} is the concentration of NaOH (in mol KHP/L), m_{KHP} is the mass of KHP taken (in g), P_{KHP} is the purity of the KHP (where $P_{KHP} = 1$ means that the KHP is pure and has no impurities), M_{KHP} is the molar mass of KHP (in g KHP/mol KHP), and V_{NaOH} is the volume of NaOH (in mL). The factor of 1000 simply converts the volume in mL to L.

Identifying and Analyzing Sources of Uncertainty

Although it seems straightforward, identifying sources of uncertainty requires care as it easy to overlook important sources of uncertainty. One approach is to use a cause-and-effect diagram, also known as an Ishikawa

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1   This example is adapted from Ellison, S. L. R.; Rosslein, M.; Williams, A. EURACHEM/CITAC Guide: Quantifying Uncertainty in Analytical Measurement, 2nd Edition, 2000 (available at http://www.measurementuncertainty.org/).

2   See Chapter 5 for further details about standardizations.

3   For further details about titrations, see Chapter 9.
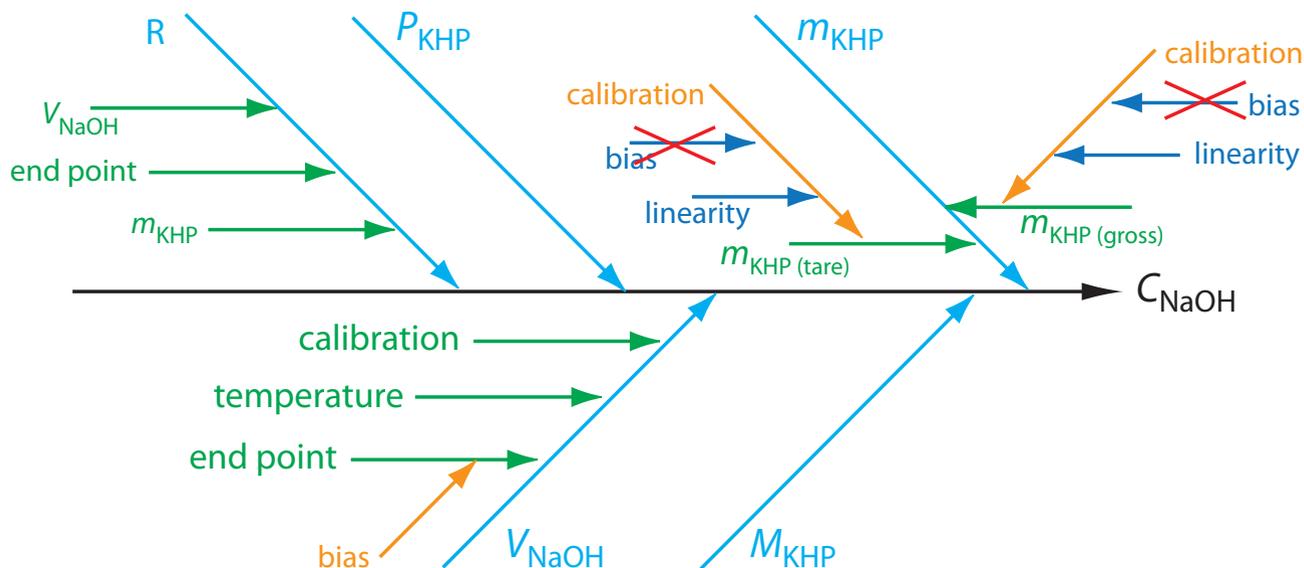
Figure A2.1 Cause-and-effect diagram for the standardization of NaOH by titration against KHP. The trunk, shown in black, represents the the concentration of NaOH. The remaining arrows represent the sources of uncertainty that affect C_{NaOH}. Light blue arrows, for example, represent the primary sources of uncertainty affecting C_{NaOH}, and green arrows represent secondary sources of uncertainty that affect the primary sources of uncertainty. See the text for additional details.

diagram—named for its inventor, Kaoru Ishikawa—or a fish bone diagram. To construct a cause-and-effect diagram, we first draw an arrow pointing to the desired result; this is the diagram's trunk. We then add five main branch lines to the trunk, one for each of the four parameters that determine the concentration of NaOH and one for the method's repeatability. Next we add additional branches to the main branch for each of these five factors, continuing until we account for all potential sources of uncertainty. Figure A2.1 shows the complete cause-and-effect diagram for this analysis.

Before we continue, let's take a closer look at Figure A2.1 to be sure we understand each branch of the diagram. To determine the mass of KHP we make two measurements: taring the balance and weighing the gross sample. Each measurement of mass is subject to a calibration uncertainty. When we calibrate a balance, we are essentially creating a calibration curve of the balance's signal as a function of mass. Any calibration curve is subject to a systematic uncertainty in the y-intercept (bias) and an uncertainty in the slope (linearity). We can ignore the calibration bias because it contributes equally to both $m_{KHP(gross)}$ and $m_{KHP(tare)}$, and because we determine the mass of KHP by difference.

$$m_{KHP} = m_{KHP(gross)} - m_{KHP(tare)}$$

The volume of NaOH at the end point has three sources of uncertainty. First, an automated titrator uses a piston to deliver the NaOH to the reaction vessel, which means the volume of NaOH is subject to an uncertainty in the piston's calibration. Second, because a solution's volume varies with temperature, there is an additional source of uncertainty due to any fluctuation in the ambient temperature during the analysis. Finally, there is a bias in the titration's end point if the NaOH reacts with any species other than the KHP.

Repeatability, R, is a measure of how consistently we can repeat the analysis. Each instrument we use—the balance and the automatic titrator—contributes to this uncertainty. In addition, our ability to consistently

detect the end point also contributes to repeatability. Finally, there are no additional factors that affect the uncertainty of the KHP's purity or molar mass.

Estimating the Standard Deviation for Measurements

To complete a propagation of uncertainty we must express each measurement's uncertainty in the same way, usually as a standard deviation. Measuring the standard deviation for each measurement requires time and may not be practical. Fortunately, most manufacture provides a tolerance range for glassware and instruments. A 100-mL volumetric glassware, for example, has a tolerance of ± 0.1 mL at a temperature of $20\,^{\circ}$C. We can convert a tolerance range to a standard deviation using one of the following three approaches.

Assume a Uniform Distribution. Figure A2.2a shows a uniform distribution between the limits of $\pm x$, in which each result between the limits is equally likely. A uniform distribution is the choice when the manufacturer provides a tolerance range without specifying a level of confidence and when there is no reason to believe that results near the center of the range are more likely than results at the ends of the range. For a uniform distribution the estimated standard deviation, s, is

$$s = \frac{x}{\sqrt{3}}$$

This is the most conservative estimate of uncertainty as it gives the largest estimate for the standard deviation.

Assume a Triangular Distribution. Figure A2.2b shows a triangular distribution between the limits of $\pm x$, in which the most likely result is at the center of the distribution, decreasing linearly toward each limit. A triangular distribution is the choice when the manufacturer provides a tolerance range without specifying a level of confidence and when there is a good reason to believe that results near the center of the range are more likely than results at the ends of the range. For a uniform distribution the estimated standard deviation, s, is

$$s = \frac{x}{\sqrt{6}}$$

This is a less conservative estimate of uncertainty as, for any value of x, the standard deviation is smaller than that for a uniform distribution.

Assume a Normal Distribution. Figure A2.3c shows a normal distribution that extends, as it must, beyond the limits of $\pm x$, and which is centered at the mid-point between $-x$ and x. A normal distribution is the choice when we know the confidence interval for the range. For a normal distribution the estimated standard deviation, s, is

$$s = \frac{x}{z}$$

where z is 1.96 for a 95% confidence interval and 3.00 for a 99.7% confidence interval.
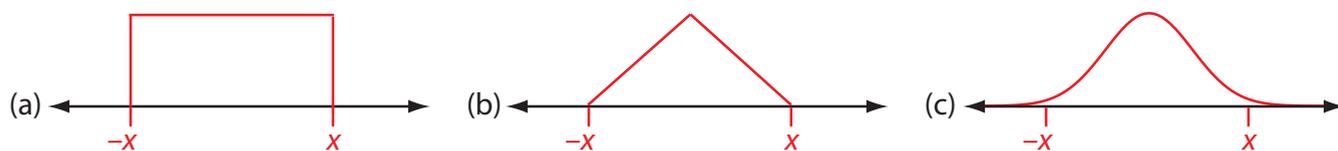
Figure A2.2 Three possible distributions for estimating the standard deviation from a range: (a) a uniform distribution; (b) a triangular distribution; and (c) a normal distribution.

Completing the Propagation of Uncertainty

Now we are ready to return to our example and determine the uncertainty for the standardization of NaOH. First we establish the uncertainty for each of the five primary sources—the mass of KHP, the volume of NaOH at the end point, the purity of the KHP, the molar mass for KHP, and the titration's repeatability. Having established these, we can combine them to arrive at the final uncertainty.

Uncertainty in the Mass of KHP. After drying the KHP, we store it in a sealed container to prevent it from readsorbing moisture. To find the mass of KHP we first weigh the container, obtaining a value of 60.5450 g, and then weigh the container after removing a portion of KHP, obtaining a value of 60.1562 g. The mass of KHP, therefore, is 0.3888 g, or 388.8 mg.

To find the uncertainty in this mass we examine the balance's calibration certificate, which indicates that its tolerance for linearity is ± 0.15 mg. We will assume a uniform distribution because there is no reason to believe that any result within this range is more likely than any other result. Our estimate of the uncertainty for any single measurement of mass, $u(m)$, is

$$u(m) = \frac{0.15 \text{ mg}}{\sqrt{3}} = 0.09 \text{ mg}$$

Because we determine the mass of KHP by subtracting the container's final mass from its initial mass, the uncertainty of the mass of KHP $u(m_{KHP})$, is given by the following propagation of uncertainty.

$$u(m_{KHP}) = \sqrt{(0.09 \text{ mg})^2 + (0.09 \text{ mg})^2} = 0.13 \text{ mg}$$

Uncertainty in the Volume of NaOH. After placing the sample of KHP in the automatic titrator's reaction vessel and dissolving with water, we complete the titration and find that it takes 18.64 mL of NaOH to reach the end point. To find the uncertainty in this volume we need to consider, as shown in Figure A2.1, three sources of uncertainty: the automatic titrator's calibration, the ambient temperature, and any bias in determining the end point.

To find the uncertainty resulting from the titrator's calibration we examine the instrument's certificate, which indicates a range of ± 0.03 mL for a 20-mL piston. Because we expect that an effective manufacturing process is more likely to produce a piston that operates near the center of this range than at the extremes, we will assume a triangular distribution. Our estimate of the uncertainty due to the calibration, $u(V_{cal})$ is

$$u(V_{cal}) = \frac{0.03 \text{ mL}}{\sqrt{6}} = 0.012 \text{ mL}$$

To determine the uncertainty due to the lack of temperature control, we draw on our prior work in the lab, which has established a temperature variation of $\pm 3\,°C$ with a confidence level of 95%. To find the uncertainty, we convert the temperature range to a range of volumes using water's coefficient of expansion

$$\left(2.1 \times 10^{-4}\,°C^{-1}\right) \times \left(\pm 3\,°C\right) \times 18.64 \text{ mL} = \pm 0.012 \text{ mL}$$

and then estimate the uncertainty due to temperature, $u(V_{temp})$ as

$$u(V_{temp}) = \frac{0.012 \text{ mL}}{1.96} = 0.006 \text{ mL}$$

Titrations using NaOH are subject to a bias due to the adsorption of CO_2, which can react with OH^-, as shown here.

$$CO_2(aq) + 2OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l)$$
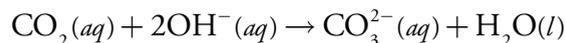
If CO_2 is present, the volume of NaOH at the end point includes both the NaOH reacting with the KHP and the NaOH reacting with CO_2. Rather than trying to estimate this bias, it is easier to bathe the reaction vessel in a stream of argon, which excludes CO_2 from the titrator's reaction vessel.

Adding together the uncertainties for the piston's calibration and the lab's temperature fluctuation gives the uncertainty in the volume of NaOH, $u(V_{NaOH})$ as

$$u(V_{NaOH}) = \sqrt{(0.012 \text{ mL})^2 + (0.006 \text{ mL})^2} = 0.013 \text{ mL}$$

Uncertainty in the Purity of KHP. According to the manufacturer, the purity of KHP is 100% ± 0.05%, or 1.0 ± 0.0005. Assuming a rectangular distribution, we report the uncertainty, $u(P_{KHP})$ as

$$u(P_{KHP}) = \frac{0.0005}{\sqrt{3}} = 0.00029$$

Uncertainty in the Molar Mass of KHP. The molar mass of $C_8H_5O_4K$ is 204.2212 g/mol, based on the following atomic weights: 12.0107 for carbon, 1.00794 for hydrogen, 15.9994 for oxygen, and 39.0983 for potassium. Each of these atomic weights has an quoted uncertainty that we can convert to a standard uncertainty assuming a rectangular distribution, as shown here (the details of the calculations are left to you).

element	quoted uncertainty	standard uncertainty
carbon	±0.0008	±0.00046
hydrogen	±0.00007	±0.000040
oxygen	±0.0003	±0.00017
potassium	±0.0001	±0.000058

Adding together the uncertainties gives the uncertainty in the molar mass, $u(M_{KHP})$, as

$$u(M_{KHP}) = \sqrt{8 \times (0.00046)^2 + 5 \times (0.000040)^2 + 4 \times (0.00017)^2 + (0.000058)} = 0.0038 \text{ g/mol}$$

Uncertainty in the Titration's Repeatability. To estimate the uncertainty due to repeatability we complete five titrations, obtaining results for the concentration of NaOH of 0.1021 M, 0.1022 M, 0.1022 M, 0.1021 M, and 0.1021 M. The relative standard deviation, s_r, for these titrations is

$$s_r = \frac{5.477 \times 10^{-5}}{0.1021} = 0.0005$$

If we treat the ideal repeatability as 1.0, then the uncertainty due to repeatability, $u(R)$, is equal to the relative standard deviation, or, in this case, 0.0005.

Combining the Uncertainties. Table A2.1 summarizes the five primary sources of uncertainty. As described earlier, we calculate the concentration of NaOH we use the following equation, which is slightly modified to include a term for the titration's repeatability, which, as described above, has a value of 1.0.

Table A2.1   Values and Uncertainties for the Standardization of NaOH

	source	value, x	uncertainty, $u(x)$
m_{KHP}	mass of KHP	0.3888 g	0.00013 g
V_{NaOH}	volume of NaOH at end point	18.64 mL	0.013 mL
P_{KHP}	purity of KHP	1.0	0.00029
M_{KHP}	molar mass of KHP	204.2212 g/mol	0.0038 g/mol
R	repeatability	1.0	0.0005

$$C_{NaOH} = \frac{1000 \times m_{KHP} \times P_{KHP}}{M_{KHP} \times V_{NaOH}} \times R$$

Using the values from Table A2.1, we find that the concentration of NaOH is

$$C_{NaOH} = \frac{1000 \times 0.3888 \times 1.0}{204.2212 \times 18.64} \times 1.0 = 0.1021 \, M$$

Because the calculation of C_{NaOH} includes only multiplication and division, the uncertainty in the concentration, $u(C_{NaOH})$ is given by the following propagation of uncertainty.

$$\frac{u(C_{NaOH})}{C_{NaOH}} = \frac{u(C_{NaOH})}{0.1021 \, M} = \sqrt{\frac{(0.00013)^2}{(0.3888)^2} + \frac{(0.00029)^2}{(1.0)^2} + \frac{(0.0038)^2}{(204.2212)^2} + \frac{(0.013)^2}{(18.64)^2} + \frac{(0.0005)^2}{(1.0)^2}}$$

Solving for $u(C_{NaOH})$ gives its value as ± 0.00010 M, which is the final uncertainty for the analysis.

Evaluating the Sources of Uncertainty

Figure A2.3 shows the relative uncertainty in the concentration of NaOH and the relative uncertainties for each of the five contributions to the total uncertainty. Of the contributions, the most important is the volume of NaOH, and it is here to which we should focus our attention if we wish to improve the overall uncertainty for the standardization.
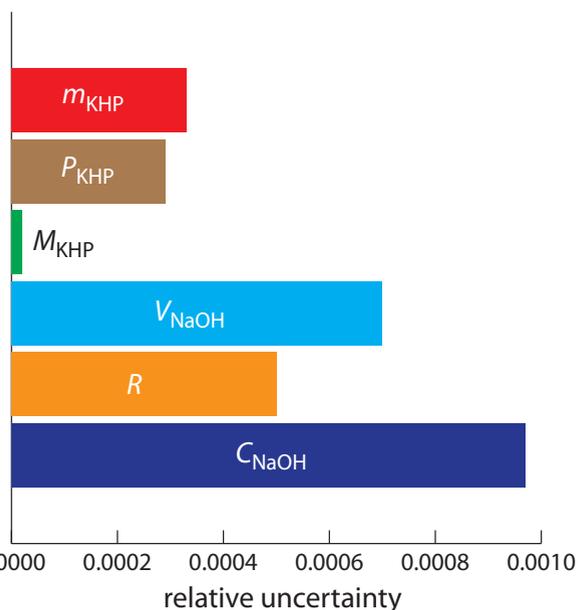
Figure A2.3 Bar graph showing the relative uncertainty in C_{NaOH}, and the relative uncertainty in each of the main factors affecting the overall uncertainty.

Appendix 3: Single-Sided Normal Distribution

The table in this appendix gives the proportion, P, of the area under a normal distribution curve that lies to the right of a deviation, z

$$z = \frac{X - \mu}{\sigma}$$

where X is the value for which the deviation is being defined, μ is the distribution's mean value and σ is the distribution's standard deviation. For example, the proportion of the area under a normal distribution to the right of a deviation of 0.04 is 0.4840 (see entry in red in the table), or 48.40% of the total area (see the area shaded blue in the figure to the right). The proportion of the area to the left of the deviation is $1 - P$. For a deviation of 0.04, this is 1–0.4840, or 51.60%.

When the deviation is negative—that is, when X is smaller than μ—the value of z is negative. In this case, the values in the table give the area to the left of z. For example, if z is –0.04, then 48.40% of the area lies to the left of the deviation (see area shaded green in the figure shown below on the left).

To use the single-sided normal distribution table, sketch the normal distribution curve for your problem and shade the area corresponding to your answer (for example, see the figure shown above on the right, which
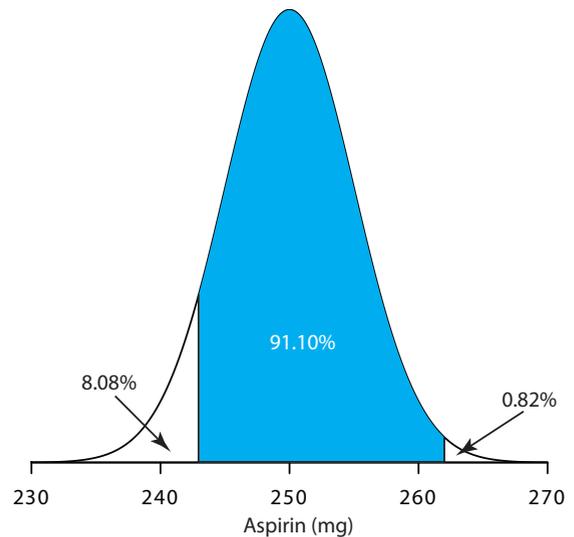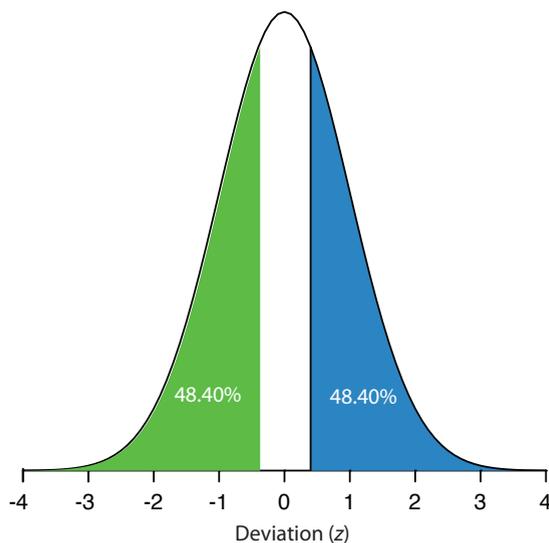
is for Example 4.11). This divides the normal distribution curve into three regions: the area corresponding to your answer (shown in blue), the area to the right of this, and the area to the left of this. Calculate the values of z for the limits of the area corresponding to your answer. Use the table to find the areas to the right and to the left of these deviations. Subtract these values from 100% and, voilà, you have your answer.

z	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.0	0.5000	0.4960	0.4920	0.4880	0.4840	0.4801	0.4761	0.4721	0.4681	0.4641
0.1	0.4602	0.4562	0.4522	0.4483	0.4443	0.4404	0.4365	0.4325	0.4286	0.4247
0.2	0.4207	0.4168	0.4129	0.4090	0.4502	0.4013	0.3974	0.3396	0.3897	0.3859
0.3	0.3821	0.3783	0.3745	0.3707	0.3669	0.3632	0.3594	0.3557	0.3520	0.3483
0.4	0.3446	0.3409	0.3372	0.3336	0.3300	0.3264	0.3228	0.3192	0.3156	0.3121
0.5	0.3085	0.3050	0.3015	0.2981	0.2946	0.2912	0.2877	0.2843	0.2810	0.2776
0.6	0.2743	0.2709	0.2676	0.2643	0.2611	0.2578	0.2546	0.2514	0.2483	0.2451
0.7	0.2420	0.2389	0.2358	0.2327	0.2296	0.2266	0.2236	0.2206	0.2177	0.2148
0.8	0.2119	0.2090	0.2061	0.2033	0.2005	0.1977	0.1949	0.1922	0.1894	0.1867
0.9	0.1841	0.1814	0.1788	0.1762	0.1736	0.1711	0.1685	0.1660	0.1635	0.1611
1.0	0.1587	0.1562	0.1539	0.1515	0.1492	0.1469	0.1446	0.1423	0.1401	0.1379
1.1	0.1357	0.1335	0.1314	0.1292	0.1271	0.1251	0.1230	0.1210	0.1190	0.1170
1.2	0.1151	0.1131	0.1112	0.1093	0.1075	0.1056	0.1038	0.1020	0.1003	0.0985
1.3	0.0968	0.0951	0.0934	0.0918	0.0901	0.0885	0.0869	0.0853	0.0838	0.0823
1.4	0.0808	0.0793	0.0778	0.0764	0.0749	0.0735	0.0721	0.0708	0.0694	0.0681
1.5	0.0668	0.0655	0.0643	0.0630	0.0618	0.0606	0.0594	0.0582	0.0571	0.0559
1.6	0.0548	0.0537	0.0526	0.0516	0.0505	0.0495	0.0485	0.0475	0.0465	0.0455
1.7	0.0466	0.0436	0.0427	0.0418	0.0409	0.0401	0.0392	0.0384	0.0375	0.0367
1.8	0.0359	0.0351	0.0344	0.0336	0.0329	0.0322	0.0314	0.0307	0.0301	0.0294
1.9	0.0287	0.0281	0.0274	0.0268	0.0262	0.0256	0.0250	0.0244	0.0239	0.0233
2.0	0.0228	0.0222	0.0217	0.0212	0.0207	0.0202	0.0197	0.0192	0.0188	0.0183
2.1	0.0179	0.0174	0.0170	0.0166	0.0162	0.0158	0.0154	0.0150	0.0146	0.0143
2.2	0.0139	0.0136	0.0132	0.0129	0.0125	0.0122	0.0119	0.0116	0.0113	0.0110
2.3	0.0107	0.0104	0.0102		0.00964		0.00914		0.00866	
2.4	0.00820		0.00776		0.00734		0.00695		0.00657	
2.5	0.00621		0.00587		0.00554		0.00523		0.00494	
2.6	0.00466		0.00440		0.00415		0.00391		0.00368	
2.7	0.00347		0.00326		0.00307		0.00289		0.00272	
2.8	0.00256		0.00240		0.00226		0.00212		0.00199	
2.9	0.00187		0.00175		0.00164		0.00154		0.00144	
3.0	0.00135									
3.1	0.000968									
3.2	0.000687									
3.3	0.000483									
3.4	0.000337									
3.5	0.000233									
3.6	0.000159									
3.7	0.000108									
3.8	0.0000723									
3.9	0.0000481									
4.0	0.0000317									

Appendix 4: Critical Values for *t*-Test

Assuming you have calculated t_{exp}, there are two approaches to interpreting a *t*-test. In the first approach you choose a value of α for rejecting the null hypothesis and read the value of $t(\alpha, v)$ from the table shown below. If $t_{exp} > t(\alpha, v)$, you reject the null hypothesis and accept the alternative hypothesis. In the second approach, you find the row in the table below corresponding to your degrees of freedom and move across the row to find (or estimate) the α corresponding to $t_{exp} = t(\alpha, v)$; this establishes largest value of α for which you can retain the null hypothesis. Finding, for example, that α is 0.10 means that you would retain the null hypothesis at the 90% confidence level, but reject it at the 89% confidence level. The examples in this textbook use the first approach.

Values of *t* for...				
...a confidence interval of:	90%	95%	98%	99%
...an α value of:	0.10	0.05	0.02	0.01
Degrees of Freedom				
1	6.314	12.706	31.821	63.657
2	2.920	4.303	6.965	9.925
3	2.353	3.182	4.541	5.841
4	2.132	2.776	3.747	4.604
5	2.015	2.571	3.365	4.032
6	1.943	2.447	3.143	3.707
7	1.895	2.365	2.998	3.499
8	1.860	2.306	2.896	3.255
9	1.833	2.262	2.821	3.250
10	1.812	2.228	2.764	3.169
12	1.782	2.179	2.681	3.055
14	1.761	2.145	2.624	2.977
16	1.746	2.120	2.583	2.921
18	1.734	2.101	2.552	2.878
20	1.725	2.086	2.528	2.845
30	1.697	2.042	2.457	2.750
50	1.676	2.009	2.311	2.678
∞	1.645	1.960	2.326	2.576

The values in this table are for a two-tailed *t*-test. For a one-tail *t*-test, divide the α values by 2. For example, the last column has an α value of 0.005 and a confidence interval of 99.5% when conducting a one-tailed *t*-test.

Appendix 5: Critical Values for the F-Test

The following tables provide values for $F(0.05, \nu_{num}, \nu_{denom})$ for one-tailed and for two-tailed F-tests. To use these tables, decide whether the situation calls for a one-tailed or a two-tailed analysis and calculate F_{exp}

$$F_{exp} = \frac{s_A^2}{s_B^2}$$

where s_A^2 is greater than s_B^2. Compare F_{exp} to $F(0.05, \nu_{num}, \nu_{denom})$ and reject the null hypothesis if $F_{exp} > F(0.05, \nu_{num}, \nu_{denom})$. You may replace s with σ if you know the population's standard deviation.

$F(0.05, \nu_{num}, \nu_{denom})$ for a One-Tailed F-Test

$\nu_{num} \Rightarrow$ $\Downarrow \nu_{denom}$	1	2	3	4	5	6	7	8	9	10	15	20	∞
1	161.4	199.5	215.7	224.6	230.2	234.0	236.8	238.9	240.5	241.9	245.9	248.0	254.3
2	18.51	19.00	19.16	19.25	19.30	19.33	19.35	19.37	19.38	19.40	19.43	19.45	19.50
3	10.13	9.552	9.277	9.117	9.013	8.941	8.887	8.845	8.812	8.786	8.703	8.660	8.526
4	7.709	6.994	6.591	6.388	6.256	6.163	6.094	6.041	5.999	5.964	5.858	5.803	5.628
5	6.608	5.786	5.409	5.192	5.050	4.950	4.876	4.818	4.722	4.753	4.619	4.558	4.365
6	5.591	5.143	4.757	4.534	4.387	4.284	4.207	4.147	4.099	4.060	3.938	3.874	3.669
7	5.591	4.737	4.347	4.120	3.972	3.866	3.787	3.726	3.677	3.637	3.511	3.445	3.230
8	5.318	4.459	4.066	3.838	3.687	3.581	3.500	3.438	3.388	3.347	3.218	3.150	2.928
9	5.117	4.256	3.863	3.633	3.482	3.374	3.293	3.230	3.179	3.137	3.006	2.936	2.707
10	4.965	4.103	3.708	3.478	3.326	3.217	3.135	3.072	3.020	2.978	2.845	2.774	2.538
11	4.844	3.982	3.587	3.257	3.204	3.095	3.012	2.948	2.896	2.854	2.719	2.646	2.404
12	4.747	3.885	3.490	3.259	3.106	2.996	2.913	2.849	2.796	2.753	2.617	2.544	2.296
13	4.667	3.806	3.411	3.179	3.025	2.915	2.832	2.767	2.714	2.671	2.533	2.459	2.206
14	4.600	3.739	3.344	3.112	2.958	2.848	2.764	2.699	2.646	2.602	2.463	2.388	2.131
15	4.534	3.682	3.287	3.056	2.901	2.790	2.707	2.641	2.588	2.544	2.403	2.328	2.066
16	4.494	3.634	3.239	3.007	2.852	2.741	2.657	2.591	2.538	2.494	2.352	2.276	2.010
17	4.451	3.592	3.197	2.965	2.810	2.699	2.614	2.548	2.494	2.450	2.308	2.230	1.960
18	4.414	3.555	3.160	2.928	2.773	2.661	2.577	2.510	2.456	2.412	2.269	2.191	1.917
19	4.381	3.552	3.127	2.895	2.740	2.628	2.544	2.477	2.423	2.378	2.234	2.155	1.878
20	4,351	3.493	3.098	2.866	2.711	2.599	2.514	2.447	2.393	2.348	2.203	2.124	1.843
∞	3.842	2.996	2.605	2.372	2.214	2.099	2.010	1.938	1.880	1.831	1.666	1.570	1.000

$F(0.05, \nu_{num}, \nu_{denom})$ for a Two-Tailed F-Test

$\nu_{num} \Rightarrow$ $\Downarrow \nu_{denom}$	1	2	3	4	5	6	7	8	9	10	15	20	∞
1	647.8	799.5	864.2	899.6	921.8	937.1	948.2	956.7	963.3	968.6	984.9	993.1	1018
2	38.51	39.00	39.17	39.25	39.30	39.33	39.36	39.37	39.39	39.40	39.43	39.45	39.50
3	17.44	16.04	15.44	15.10	14.88	14.73	14.62	14.54	14.47	14.42	14.25	14.17	13.90
4	12.22	10.65	9.979	9.605	9.364	9.197	9.074	8.980	8.905	8.444	8.657	8.560	8.257
5	10.01	8.434	7.764	7.388	7.146	6.978	6.853	6.757	6.681	6.619	6.428	6.329	6.015
6	8.813	7.260	6.599	6.227	5.988	5.820	5.695	5.600	5.523	5.461	5.269	5.168	4.894
7	8.073	6.542	5.890	5.523	5.285	5.119	4.995	4.899	4.823	4.761	4.568	4.467	4.142
8	7.571	6.059	5.416	5.053	4.817	4.652	4.529	4.433	4.357	4.259	4.101	3.999	3.670
9	7.209	5.715	5.078	4.718	4.484	4.320	4.197	4.102	4.026	3.964	3.769	3.667	3.333
10	6.937	5.456	4.826	4.468	4.236	4.072	3.950	3.855	3.779	3.717	3.522	3.419	3.080
11	6.724	5.256	4.630	4.275	4.044	3.881	3.759	3.644	3.588	3.526	3.330	3.226	2.883
12	6.544	5.096	4.474	4.121	3.891	3.728	3.607	3.512	3.436	3.374	3.177	3.073	2.725
13	6.414	4.965	4.347	3.996	3.767	3.604	3.483	3.388	3.312	3.250	3.053	2.948	2.596
14	6.298	4.857	4.242	3.892	3.663	3.501	3.380	3.285	3.209	3.147	2.949	2.844	2.487
15	6.200	4.765	4.153	3.804	3.576	3.415	3.293	3.199	3.123	3.060	2.862	2.756	2.395
16	6.115	4.687	4.077	3.729	3.502	3.341	3.219	3.125	3.049	2.986	2.788	2.681	2.316
17	6.042	4.619	4.011	3.665	3.438	3.277	3.156	3.061	2.985	2.922	2.723	2.616	2.247
18	5.978	4.560	3.954	3.608	3.382	3.221	3.100	3.005	2.929	2.866	2.667	2.559	2.187
19	5.922	4.508	3.903	3.559	3.333	3.172	3.051	2.956	2.880	2.817	2.617	2.509	2.133
20	5.871	4.461	3.859	3.515	3.289	3.128	3.007	2.913	2.837	2.774	2.573	2.464	2.085
∞	5.024	3.689	3.116	2.786	2.567	2.408	2.288	2.192	2.114	2.048	1.833	1.708	1.000

Appendix 6: Critical Values for Dixon's Q-Test

The following table provides critical values for $Q(\alpha, n)$, where α is the probability of incorrectly rejecting the suspected outlier and n is the number of samples in the data set. There are several versions of Dixon's Q-Test, each of which calculates a value for Q_{ij} where i is the number of suspected outliers on one end of the data set and j is the number of suspected outliers on the opposite end of the data set. The values given here are for Q_{10}, where

$$Q_{exp} = Q_{10} = \frac{|\text{outlier's value} - \text{nearest value}|}{\text{largest value} - \text{smallest value}}$$

The suspected outlier is rejected if Q_{exp} is greater than $Q(\alpha, n)$. For additional information consult Rorabacher, D. B. "Statistical Treatment for Rejection of Deviant Values: Critical Values of Dixon's 'Q' Parameter and Related Subrange Ratios at the 95% confidence Level," *Anal. Chem.* **1991**, *63*, 139–146.

Critical Values for the Q-Test of a Single Outlier (Q_{10})

$\alpha \Rightarrow$ $\Downarrow n$	0.1	0.05	0.04	0.02	0.01
3	0.941	0.970	0.976	0.988	0.994
4	0.765	0.829	0.846	0.889	0.926
5	0.642	0.710	0.729	0.780	0.821
6	0.560	0.625	0.644	0.698	0.740
7	0.507	0.568	0.586	0.637	0.680
8	0.468	0.526	0.543	0.590	0.634
9	0.437	0.493	0.510	0.555	0.598
10	0.412	0.466	0.483	0.527	0.568

Appendix 7: Critical Values for Grubb's Test

The following table provides critical values for $G(\alpha, n)$, where α is the probability of incorrectly rejecting the suspected outlier and n is the number of samples in the data set. There are several versions of Grubb's Test, each of which calculates a value for G_{ij} where i is the number of suspected outliers on one end of the data set and j is the number of suspected outliers on the opposite end of the data set. The values given here are for G_{10}, where

$$G_{exp} = G_{10} = \frac{\left|X_{out} - \bar{X}\right|}{s}$$

The suspected outlier is rejected if G_{exp} is greater than $G(\alpha, n)$.

$G(\alpha, n)$ for Grubb's Test of a Single Outlier		
$\alpha \Rightarrow$ $\Downarrow n$	0.05	0.01
3	1.155	1.155
4	1.481	1.496
5	1.715	1.764
6	1.887	1.973
7	2.202	2.139
8	2.126	2.274
9	2.215	2.387
10	2.290	2.482
11	2.355	2.564
12	2.412	2.636
13	2.462	2.699
14	2.507	2.755
15	2.549	2.755

Appendix 8: Recommended Primary Standards

All compounds should be of the highest available purity. Metals should be cleaned with dilute acid to remove any surface impurities and rinsed with distilled water. Unless otherwise indicated, compounds should be dried to a constant weight at 110 °C. Most of these compounds are soluble in dilute acid (1:1 HCl or 1:1 HNO_3), with gentle heating if necessary; some of the compounds are water soluble.

Element	Compound	FW (g/mol)	Comments
aluminum	Al metal	26.982	
antimony	Sb metal	121.760	
	$KSbOC_4H_4O_6$	324.92	prepared by drying $KSbC_4H_4O_6 \cdot 1/2H_2O$ at 110 °C and storing in a desiccator
arsenic	As metal	74.922	
	As_2O_3	197.84	toxic
barium	$BaCO_3$	197.84	dry at 200 °C for 4 h
bismuth	Bi metal	208.98	
boron	H_3BO_3	61.83	do not dry
bromine	KBr	119.01	
cadmium	Cd metal	112.411	
	CdO	128.40	
calcium	$CaCO_3$	100.09	
cerium	Ce metal	140.116	
	$(NH_4)_2Ce(NO_3)_4$	548.23	
cesium	Cs_2CO_3	325.82	
	Cs_2SO_4	361.87	
chlorine	NaCl	58.44	
chromium	Cr metal	51.996	
	$K_2Cr_2O_7$	294.19	
cobalt	Co metal	58.933	
copper	Cu metal	63.546	
	CuO	79.54	
fluorine	NaF	41.99	do not store solutions in glass containers
iodine	KI	166.00	
	KIO_3	214.00	
iron	Fe metal	55.845	
lead	Pb metal	207.2	
lithium	Li_2CO_3	73.89	
magnesium	Mg metal	24.305	
manganese	Mn metal	54.938	

Element	Compound	FW (g/mol)	Comments
mercury	Hg metal	200.59	
molybdenum	Mo metal	95.94	
nickel	Ni metal	58.693	
phosphorous	KH_2PO_4	136.09	
	P_2O_5	141.94	
potassium	KCl	74.56	
	K_2CO_3	138.21	
	$K_2Cr_2O_7$	294.19	
	$KHC_8H_4O_2$	204.23	
silicon	Si metal	28.085	
	SiO_2	60.08	
silver	Ag metal	107.868	
	$AgNO_3$	169.87	
sodium	NaCl	58.44	
	Na_2CO_3	106.00	
	Na_2C2O_4	134.00	
strontium	$SrCO_3$	147.63	
sulfur	elemental S	32.066	
	K_2SO_4	174.27	
	Na_2SO_4	142.04	
tin	Sn metal	118.710	
titanium	Ti metal	47.867	
tungsten	W metal	183.84	
uranium	U metal	238.029	
	U_3O_8	842.09	
vanadium	V metal	50.942	
zinc	Zn metal	81.37	

Sources: (a) Smith, B. W.; Parsons, M. L. *J. Chem. Educ.* **1973**, *50*, 679–681; (b) Moody, J. R.; Greenburg, P. R.; Pratt, K. W.; Rains, T. C. *Anal. Chem.* **1988**, *60*, 1203A–1218A.

Appendix 9: Correcting Mass for the Buoyancy of Air

Calibrating a balance does not eliminate all sources of determinate error in the signal. Because of the buoyancy of air, an object always weighs less in air than it does in a vacuum. If there is a difference between the object's density and the density of the weights used to calibrate the balance, then we can make a correction for buoyancy.[1] An object's true weight in vacuo, W_v, is related to its weight in air, W_a, by the equation

$$W_v = W_a \times \left[1 + \left(\frac{1}{D_o} - \frac{1}{D_w} \right) \times 0.0012 \right]$$ A9.1

where D_o is the object's density, D_w is the density of the calibration weight, and 0.0012 is the density of air under normal laboratory conditions (all densities are in units of g/cm^3). The greater the difference between D_o and D_w the more serious the error in the object's measured weight.

The buoyancy correction for a solid is small, and frequently ignored. It may be significant, however, for low density liquids and gases. This is particularly important when calibrating glassware. For example, we can calibrate a volumetric pipet by carefully filling the pipet with water to its calibration mark, dispensing the water into a tared beaker, and determining the water's mass. After correcting for the buoyancy of air, we use the water's density to calculate the volume dispensed by the pipet.

Example

A 10-mL volumetric pipet was calibrated following the procedure just outlined, using a balance calibrated with brass weights having a density of $8.40 \ g/cm^3$. At $25\,^\circ C$ the pipet dispensed 9.9736 g of water. What is the actual volume dispensed by the pipet and what is the determinate error in this volume if we ignore the buoyancy correction? At $25\,^\circ C$ the density of water is $0.99705 \ g/cm^3$.

SOLUTION

Using equation A9.1 the water's true weight is

$$W_v = 9.9736 \ \text{g} \times \left[1 + \left(\frac{1}{0.99705} - \frac{1}{8.40} \right) \times 0.0012 \right] = 9.9842 \ \text{g}$$

and the actual volume of water dispensed by the pipet is

$$\frac{9.9842 \ \text{g}}{0.99705 \ \text{g/cm}^3} = 10.014 \ \text{cm}^3 = 10.014 \ \text{mL}$$

If we ignore the buoyancy correction, then we report the pipet's volume as

$$\frac{9.9736 \ \text{g}}{0.99705 \ \text{g/cm}^3} = 10.003 \ \text{cm}^3 = 10.003 \ \text{mL}$$

introducing a negative determinate error of -0.11%.

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1   Battino, R.; Williamson, A. G. *J. Chem. Educ.* **1984**, *61*, 51–52.

PROBLEMS

The following problems will help you in considering the effect of buoyancy on the measurement of mass.

1. In calibrating a 10-mL pipet a measured volume of water was transferred to a tared flask and weighed, yielding a mass of 9.9814 grams. (a) Calculate, with and without correcting for buoyancy, the volume of water delivered by the pipet. Assume that the density of water is 0.99707 g/cm3 and that the density of the weights is 8.40 g/cm3. (b) What are the absolute and relative errors introduced by failing to account for the effect of buoyancy? Is this a significant source of determinate error for the calibration of a pipet? Explain.

2. Repeat the questions in problem 1 for the case where a mass of 0.2500 g is measured for a solid that has a density of 2.50 g/cm3.

3. Is the failure to correct for buoyancy a constant or proportional source of determinate error?

4. What is the minimum density of a substance necessary to keep the buoyancy correction to less than 0.01% when using brass calibration weights with a density of 8.40 g/cm3?

Appendix 10: Solubility Products

The following table provides pK_{sp} and K_{sp} values for selected compounds, organized by the anion. All values are from Martell, A. E.; Smith, R. M. *Critical Stability Constants*, Vol. 4. Plenum Press: New York, 1976. Unless otherwise stated, values are for 25 °C and zero ionic strength.

Bromide (Br⁻)	pK_{sp}	K_{sp}
CuBr	8.3	$5.\times10^{-9}$
AgBr	12.30	5.0×10^{-13}
Hg_2Br_2	22.25	5.6×10^{-13}
$HgBr_2$ ($\mu=0.5$ M)	18.9	1.3×10^{-19}
$PbBr_2$ ($\mu=4.0$ M)	5.68	2.1×10^{-6}

Carbonate (CO_3^{2-})	pK_{sp}	K_{sp}
$MgCO_3$	7.46	3.5×10^{-8}
$CaCO_3$ (calcite)	8.35	4.5×10^{-9}
$CaCO_3$ (aragonite)	8.22	6.0×10^{-9}
$SrCO_3$	9.03	9.3×10^{-10}
$BaCO_3$	8.30	5.0×10^{-9}
$MnCO_3$	9.30	5.0×10^{-10}
$FeCO_3$	10.68	2.1×10^{-11}
$CoCO_3$	9.98	1.0×10^{-10}
$NiCO_3$	6.87	1.3×10^{-7}
Ag_2CO_3	11.09	8.1×10^{-12}
Hg_2CO_3	16.05	8.9×10^{-17}
$ZnCO_3$	10.00	1.0×10^{-10}
$CdCO_3$	13.74	1.8×10^{-14}
$PbCO_3$	13.13	7.4×10^{-14}

Chloride (Cl⁻)	pK_{sp}	K_{sp}
CuCl	6.73	1.9×10^{-7}
AgCl	9.74	1.8×10^{-10}
Hg_2Cl_2	17.91	1.2×10^{-18}
$PbCl_2$	4.78	2.0×10^{-19}

Chromate (CrO_4^{2-})	pK_{sp}	K_{sp}
$BaCrO_4$	9.67	2.1×10^{-10}
$CuCrO_4$	5.44	3.6×10^{-6}
Ag_2CrO_4	11.92	1.2×10^{-12}
Hg_2CrO_4	8.70	2.0×10^{-9}

Cyanide (CN^-)	pK_{sp}	K_{sp}
$AgCN$	15.66	2.2×10^{-16}
$Zn(CN)_2$ ($\mu = 3.0$ M)	15.5	$3. \times 10^{-16}$
$Hg_2(CN)_2$	39.3	$5. \times 10^{-40}$

Ferrocyanide [$Fe(CN)_6^{4-}$]	pK_{sp}	K_{sp}
$Zn_2[Fe(CN)_6]$	15.68	2.1×10^{-16}
$Cd_2[Fe(CN)_6]$	17.38	4.2×10^{-18}
$Pb_2[Fe(CN)_6]$	18.02	9.5×10^{-19}

Fluoride (F^-)	pK_{sp}	K_{sp}
MgF_2	8.18	6.6×10^{-9}
CaF_2	10.41	3.9×10^{-11}
SrF_2	8.54	2.9×10^{-9}
BaF_2	5.76	1.7×10^{-6}
PbF_2	7.44	3.6×10^{-8}

Hydroxide (OH^-)	pK_{sp}	K_{sp}
$Mg(OH)_2$	11.15	7.1×10^{-12}
$Ca(OH)_2$	5.19	6.5×10^{-6}
$Ba(OH)_2 \cdot 8H_2O$	3.6	$3. \times 10^{-4}$
$La(OH)_3$	20.7	$2. \times 10^{-21}$
$Mn(OH)_2$	12.8	1.6×10^{-13}
$Fe(OH)_2$	15.1	$8. \times 10^{-16}$
$Co(OH)_2$	14.9	1.3×10^{-15}
$Ni(OH)_2$	15.2	$6. \times 10^{-16}$
$Cu(OH)_2$	19.32	4.8×10^{-20}
$Fe(OH)_3$	38.8	1.6×10^{-39}

	pKsp	Ksp
$Co(OH)_3$ ($T = 19\,^{\circ}C$)	44.5	$3.\times10^{-45}$
Ag_2O ($+ H_2O \rightleftharpoons 2Ag^+ + 2OH^-$)	15.42	3.8×10^{-16}
Cu_2O ($+ H_2O \rightleftharpoons 2Cu^+ + 2OH^-$)	29.4	$4.\times10^{-30}$
$Zn(OH)_2$ (amorphous)	15.52	3.0×10^{-16}
$Cd(OH)_2$ (β)	14.35	4.5×10^{-15}
HgO (red) ($+ H_2O \rightleftharpoons Hg^{2+} + 2OH^-$)	25.44	3.6×10^{-26}
SnO ($+ H_2O \rightleftharpoons Sn^{2+} + 2OH^-$)	26.2	$6.\times10^{-27}$
PbO (yellow) ($+ H_2O \rightleftharpoons Pb^{2+} + 2OH^-$)	15.1	$8.\times10^{-16}$
$Al(OH)_3$ (α)	33.5	$3.\times10^{-34}$

Iodate (IO_3^-)	pKsp	Ksp
$Ca(IO_3)_2$	6.15	7.1×10^{-7}
$Ba(IO_3)_2$	8.81	1.5×10^{-9}
$AgIO_3$	7.51	3.1×10^{-8}
$Hg_2(IO_3)_2$	17.89	1.3×10^{-18}
$Zn(IO_3)_2$	5.41	3.9×10^{-6}
$Cd(IO_3)_2$	7.64	2.3×10^{-8}
$Pb(IO_3)_2$	12.61	2.5×10^{-13}

Iodide (I^-)	pKsp	Ksp
AgI	16.08	8.3×10^{-17}
Hg_2I_2	28.33	4.7×10^{-29}
HgI_2 ($\mu = 0.5$ M)	27.95	1.1×10^{-28}
PbI_2	8.10	7.9×10^{-9}

Oxalate ($C_2O_4^{2-}$)	pKsp	Ksp
CaC_2O_4 ($\mu = 0.1$ M, $T = 20\,^{\circ}C$)	7.9	1.3×10^{-8}
BaC_2O_4 ($\mu = 0.1$ M, $T = 20\,^{\circ}C$)	6.0	$1.\times10^{-6}$
SrC_2O_4 ($\mu = 0.1$ M, $T = 20\,^{\circ}C$)	6.4	$4.\times10^{-7}$

Phosphate (PO_4^{3-})	pKsp	Ksp
$Fe_3(PO_4)_2 \cdot 8H_2O$	36.0	$1.\times10^{-36}$
$Zn_3(PO_4)_2 \cdot 4H_2O$	35.3	$5.\times10^{-36}$
Ag_3PO_4	17.55	2.8×10^{-18}

Pb$_3$(PO$_4$)$_2$ ($T=38\,^{\circ}$C)	43.55	3.0×10^{-44}

Sulfate (SO$_4{}^{2-}$)	pK_{sp}	K_{sp}
CaSO$_4$	4.62	2.4×10^{-5}
SrSO$_4$	6.50	3.2×10^{-7}
BaSO$_4$	9.96	1.1×10^{-10}
Ag$_2$SO$_4$	4.83	1.5×10^{-5}
Hg$_2$SO$_4$	6.13	7.4×10^{-7}
PbSO$_4$	7.79	1.6×10^{-8}

Sulfide (S^{2-})	pK_{sp}	K_{sp}
MnS (green)	13.5	$3.\times10^{-14}$
FeS	18.1	$8.\times10^{-19}$
CoS (β)	25.6	$3.\times10^{-26}$
NiS (γ)	26.6	$3.\times10^{-27}$
CuS	36.1	$8.\times10^{-37}$
Cu$_2$S	48.5	$3.\times10^{-49}$
Ag$_2$S	50.1	$8.\times10^{-51}$
ZnS (α)	24.7	$2.\times10^{-25}$
CdS	27.0	$1.\times10^{-27}$
Hg$_2$S (red)	53.3	$5.\times10^{-54}$
PbS	27.5	$3.\times10^{-28}$

Thiocyanate (SCN$^-$)	pK_{sp}	K_{sp}
CuSCN ($\mu=5.0$ M)	13.40	4.0×10^{-14}
AgSCN	11.97	1.1×10^{-12}
Hg$_2$(SCN)$_2$	19.52	3.0×10^{-20}
Hg(SCN)$_2$ ($\mu=1.0$ M)	19.56	2.8×10^{-20}

Appendix 11: Acid Dissociation Constants

The following table provides pK_a and K_a values for selected weak acids. All values are from Martell, A. E.; Smith, R. M. *Critical Stability Constants*, Vols. 1–4. Plenum Press: New York, 1976. Unless otherwise stated, values are for 25 °C and zero ionic strength. Those values in brackets are considered less reliable.

Weak acids are arranged alphabetically by the names of the neutral compounds from which they are derived. In some cases—such as acetic acid—the compound is the weak acid. In other cases—such as for the ammonium ion—the neutral compound is the conjugate base. Chemical formulas or structural formulas are shown for the fully protonated weak acid. Successive acid dissociation constants are provided for polyprotic weak acids; where there is ambiguity, the specific acidic proton is identified.

To find the K_b value for a conjugate weak base, recall that

$$K_a \times K_b = K_w$$

for a conjugate weak acid, HA, and its conjugate weak base, A^-.

Compound	Conjugate Acid	pK_a	K_a
acetic acid	CH_3COOH	4.757	1.75×10^{-5}
adipic acid		4.42 5.42	3.8×10^{-5} 3.8×10^{-6}
alanine	$^+H_3N\text{—}CH\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}OH$, CH_3	2.348 (COOH) 9.867 (NH_3)	4.49×10^{-3} 1.36×10^{-10}
aminobenzene	$\text{—}NH_3^+$	4.601	2.51×10^{-5}
4-aminobenzene sulfonic acid	$^-O_3S\text{—}$$\text{—}NH_3^+$	3.232	5.86×10^{-4}
2-aminobenozic acid	COOH, NH_3^+	2.08 (COOH) 4.96 (NH_3)	8.3×10^{-3} 1.1×10^{-5}
2-aminophenol ($T = 20$ °C)	OH, NH_3^+	4.78 (NH_3) 9.97 (OH)	1.7×10^{-5} 1.05×10^{-10}
ammonia	NH_4^+	9.244	5.70×10^{-10}

Compound	Conjugate Acid	pK_a	K_a
arginine		1.823 (COOH) 8.991 (NH_3) [12.48] (NH_2)	1.50×10^{-2} 1.02×10^{-9} $[3.3 \times 10^{-13}]$
arsenic acid	H_3AsO_4	2.24 6.96 11.50	5.8×10^{-3} 1.1×10^{-7} 3.2×10^{-12}
asparagine ($\mu = 0.1$ M)		2.14 (COOH) 8.72 (NH_3)	7.2×10^{-3} 1.9×10^{-9}
asparatic acid		1.990 (α-COOH) 3.900 (β-COOH) 10.002 (NH_3)	1.02×10^{-2} 1.26×10^{-4} 9.95×10^{-11}
benzoic acid		4.202	6.28×10^{-5}
benzylamine		9.35	4.5×10^{-10}
boric acid ($pK_{a2}, pK_{a3}: T = 20\,°C$)	H_3BO_3	9.236 [12.74] [13.80]	5.81×10^{-10} $[1.82 \times 10^{-13}]$ $[1.58 \times 10^{-14}]$
carbonic acid	H_2CO_3	6.352 10.329	4.45×10^{-7} 4.69×10^{-11}
catechol		9.40 12.8	4.0×10^{-10} 1.6×10^{-13}
chloroacetic acid	$ClCH_2COOH$	2.865	1.36×10^{-3}
chromic acid ($pK_{a1}: T = 20\,°C$)	H_2CrO_4	-0.2 6.51	1.6 3.1×10^{-7}

Compound	Conjugate Acid	pK_a	K_a
citric acid		3.128 (COOH) 4.761 (COOH) 6.396 (COOH)	7.45×10^{-4} 1.73×10^{-5} 4.02×10^{-7}
cupferrron ($\mu = 0.1$ M)		4.16	6.9×10^{-5}
cysteine		[1.71] (COOH) 8.36 (SH) 10.77 (NH_3)	$[1.9 \times 10^{-2}]$ 4.4×10^{-9} 1.7×10^{-11}
dichloracetic acid	$Cl_2CHCOOH$	1.30	5.0×10^{-2}
diethylamine	$(CH_3CH_2)_2NH_2^+$	10.933	1.17×10^{-11}
dimethylamine	$(CH_3)_2NH_2^+$	10.774	1.68×10^{-11}
dimethylglyoxime		10.66 12.0	2.2×10^{-11} $1. \times 10^{-12}$
ethylamine	$CH_3CH_2NH_3^+$	10.636	2.31×10^{-11}
ethylenediamine	$^+H_3NCH_2CH_2NH_3^+$	6.848 9.928	1.42×10^{-7} 1.18×10^{-10}
ethylenediaminetetraacetic acid (EDTA) ($\mu = 0.1$ M)		0.0 (COOH) 1.5 (COOH) 2.0 (COOH) 2.66 (COOH) 6.16 (NH) 10.24 (NH)	1.0 3.2×10^{-2} 1.0×10^{-2} 2.2×10^{-3} 6.9×10^{-7} 5.8×10^{-11}
formic acid	HCOOH	3.745	1.80×10^{-4}
fumaric acid		3.053 4.494	8.85×10^{-4} 3.21×10^{-5}
glutamic acid		2.33 (α-COOH) 4.42 (λ-COOH) 9.95 (NH_3)	5.9×10^{-3} 3.8×10^{-5} 1.12×10^{-10}

Compound	Conjugate Acid	pK_a	K_a
glutamine ($\mu = 0.1$ M)	$^+H_3N-CH-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-OH$ $\|$ CH_2 $\|$ CH_2 $\|$ $C=O$ $\|$ NH_2	2.17 (COOH) 9.01 (NH$_3$)	6.8×10^{-3} 9.8×10^{-10}
glycine $^+H_3NCH_2COOH$	$^+H_3N-CH-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-OH$ $\|$ H	2.350 (COOH) 9.778 (NH$_3$)	4.47×10^{-3} 1.67×10^{-10}
glycolic acid	$HOOCH_2COOH$	3.831 (COOH)	1.48×10^{-4}
histidine ($\mu = 0.1$ M)	$^+H_3N-CH-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-OH$ $\|$ CH_2 $\|$ (imidazole ring, $^+HN\cdots NH$)	1.7 (COOH) 6.02 (NH) 9.08 (NH$_3$)	$2. \times 10^{-2}$ 9.5×10^{-7} 8.3×10^{-10}
hydrogen cyanide	HCN	9.21	6.2×10^{-10}
hydrogen fluoride	HF	3.17	6.8×10^{-4}
hydrogen peroxide	H_2O_2	11.65	2.2×10^{-12}
hydrogen sulfide	H_2S	7.02 13.9	9.5×10^{-8} 1.3×10^{-14}
hydrogen thiocyanate	HSCN	0.9	1.3×10^{-1}
8-hydroxyquinoline	(quinoline ring with $\overset{+}{N}H$ and OH)	4.91 (NH) 9.81 (OH)	1.2×10^{-5} 1.6×10^{-10}
hydroxylamine	$HONH_3^+$	5.96	1.1×10^{-6}
hypobromous acid	HOBr	8.63	2.3×10^{-9}
hypochlorous acid	HOCl	7.53	3.0×10^{-8}
hypoiodous acid	HOI	10.64	2.3×10^{-11}
iodic acid	HIO_3	0.77	1.7×10^{-1}
isoleucine	$^+H_3N-CH-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-OH$ $\|$ $CH-CH_3$ $\|$ CH_2 $\|$ CH_3	2.319 (COOH) 9.754 (NH$_3$)	4.80×10^{-3} 1.76×10^{-10}

Compound	Conjugate Acid	pK_a	K_a
leucine		2.329 (COOH) 9.747 (NH$_3$)	4.69×10^{-3} 1.79×10^{-10}
lysine ($\mu = 0.1$ M)		2.04 (COOH) 9.08 (α-NH$_3$) 10.69 (ε-NH$_3$)	9.1×10^{-3} 8.3×10^{-10} 2.0×10^{-11}
maleic acid		1.910 6.332	9.1×10^{-3} 9.1×10^{-3}
malic acid		3.459 (COOH) 5.097 (COOH)	9.1×10^{-3} 9.1×10^{-3}
malonic acid	HOOCCH$_2$COOH	2.847 5.696	9.1×10^{-3} 9.1×10^{-3}
methionine ($\mu = 0.1$ M)		2.20 (COOH) 9.05 (NH$_3$)	9.1×10^{-3} 9.1×10^{-3}
methylamine	CH$_3$NH$_3^+$	10.64	9.1×10^{-3}
2-methylanaline		4.447	9.1×10^{-3}
4-methylanaline		5.084	9.1×10^{-3}
2-methylphenol		10.28	9.1×10^{-3}
4-methylphenol		10.26	9.1×10^{-3}

Compound	Conjugate Acid	pK_a	K_a
nitrilotriacetic acid ($T=20\,°C$) ($pK_{a1}:\mu=0.1$ m)	(structure: COOH, NH$^+$, HOOC, COOH)	1.1 (COOH) 1.650 (COOH) 2.940 (COOH) 10.334 (NH$_3$)	9.1×10^{-3} 9.1×10^{-3} 9.1×10^{-3} 9.1×10^{-3}
2-nitrobenzoic acid	(structure: COOH, NO$_2$)	2.179	9.1×10^{-3}
3-nitrobenzoic acid	(structure: COOH, NO$_2$)	3.449	9.1×10^{-3}
4-nitrobenzoic acid	(structure: O$_2$N—C$_6$H$_4$—COOH)	3.442	3.61×10^{-4}
2-nitrophenol	(structure: OH, NO$_2$)	7.21	6.2×10^{-8}
3-nitrophenol	(structure: OH, NO$_2$)	8.39	4.1×10^{-9}
4-nitrophenol	(structure: O$_2$N—C$_6$H$_4$—OH)	7.15	7.1×10^{-8}
nitrous acid	HNO_2	3.15	7.1×10^{-4}
oxalic acid	$H_2C_2O_4$	1.252 4.266	5.60×10^{-2} 5.42×10^{-5}
1,10-phenanthroline	(structure: NH$^+$, N)	4.86	1.38×10^{-5}
phenol	(structure: C$_6$H$_5$—OH)	9.98	1.05×10^{-10}

Compound	Conjugate Acid	pK_a	K_a
phenylalanine		2.20 (COOH) 9.31 (NH_3)	6.3×10^{-3} 4.9×10^{-10}
phosphoric acid	H_3PO_4	2.148 7.199 12.35	7.11×10^{-3} 6.32×10^{-8} 4.5×10^{-13}
phthalic acid		2.950 5.408	1.12×10^{-3} 3.91×10^{-6}
piperdine		11.123	7.53×10^{-12}
proline		1.952 (COOH) 10.640 (NH)	1.12×10^{-2} 2.29×10^{-11}
propanoic acid	CH_3CH_2COOH	4.874	1.34×10^{-5}
propylamine	$CH_3CH_2CH_2NH_3^+$	10.566	2.72×10^{-11}
pryidine		5.229	5.90×10^{-6}
resorcinol		9.30 11.06	5.0×10^{-10} 8.7×10^{-12}
salicylic acid		2.97 (COOH) 13.74 (OH)	1.1×10^{-3} 1.8×10^{-14}
serine		2.187 (COOH) 9.209 (NH_3)	6.50×10^{-3} 6.18×10^{-10}
succinic acid		4.207 5.636	6.21×10^{-5} 2.31×10^{-6}
sulfuric acid	H_2SO_4	strong 1.99	— 1.0×10^{-2}

Compound	Conjugate Acid	pK_a	K_a
sulfurous acid	H_2SO_3	1.91 7.18	1.2×10^{-2} 6.6×10^{-8}
D-tartaric acid		3.036 (COOH) 4.366 (COOH)	9.20×10^{-4} 4.31×10^{-5}
threonine		2.088 (COOH) 9.100 (NH$_3$)	8.17×10^{-3} 7.94×10^{-10}
thiosulfuric acid	$H_2S_2O_3$	0.6 1.6	$3.\times10^{-1}$ $3.\times10^{-2}$
trichloroacetic acid ($\mu=0.1$ M)	Cl_3CCOOH	0.66	2.2×10^{-1}
triethanolamine	$(HOCH_2CH_2)_3NH^+$	7.762	1.73×10^{-8}
triethylamine	$(CH_3CH_2)_3NH^+$	10.715	1.93×10^{-11}
trimethylamine	$(CH_3)_3NH^+$	9.800	1.58×10^{-10}
tris(hydroxymethyl)amino meth-ane (TRIS or THAM)	$(HOCH_2)_3CNH_3^+$	8.075	8.41×10^{-9}
tryptophan ($\mu=0.1$ M)		2.35 (COOH) 9.33 (NH$_3$)	4.5×10^{-3} 4.7×10^{-10}
tryosine (pK_{a1}: $\mu=0.1$ M)		2.17 (COOH) 9.19 (NH$_3$) 10.47 (OH)	6.8×10^{-3} 6.5×10^{-10} 3.4×10^{-11}
valine		2.286 (COOH) 9.718 (NH$_3$)	5.18×10^{-3} 1.91×10^{-10}

Appendix 12: Formation Constants

The following table provides K_i and β_i values for selected metal–ligand complexes, arranged by the ligand. All values are from Martell, A. E.; Smith, R. M. *Critical Stability Constants*, Vols. 1–4. Plenum Press: New York, 1976. Unless otherwise stated, values are for 25 °C and zero ionic strength. Those values in brackets are considered less reliable.

Acetate CH_3COO^-	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log K_5$	$\log K_6$
Mg^{2+}	1.27					
Ca^{2+}	1.18					
Ba^{2+}	1.07					
Mn^{2+}	1.40					
Fe^{2+}	1.40					
Co^{2+}	1.46					
Ni^{2+}	1.43					
Cu^{2+}	2.22	1.41				
Ag^{2+}	0.73	−0.09				
Zn^{2+}	1.57					
Cd^{2+}	1.93	1.22	−0.89			
Pb^{2+}	2.68	1.40				

Ammonia NH_3	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log K_5$	$\log K_6$
Ag^+	3.31	3.91				
Co^{2+} ($T=20$ °C)	1.99	1.51	0.93	0.64	0.06	−0.73
Ni^{2+}	2.72	2.17	1.66	1.12	0.67	−0.03
Cu^{2+}	4.04	3.43	2.80	1.48		
Zn^{2+}	2.21	2.29	2.36	2.03		
Cd^{2+}	2.55	2.01	1.34	0.84		

Chloride Cl^-	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log K_5$	$\log K_6$
Cu^{2+}	0.40					
Fe^{3+}	1.48	0.65				
Ag^+ ($\mu=5.0$ M)	3.70	1.92	0.78	−0.3		
Zn^{2+}	0.43	0.18	−0.11	−0.3		
Cd^{2+}	1.98	1.62	−0.2	−0.7		
Pb^{2+}	1.59	0.21	−0.1	−0.3		

Cyanide CN^-	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log K_5$	$\log K_6$
Fe^{2+}						35.4 (β_6)
Fe^{3+}						43.6 (β_6)
Ag^+		20.48 β_2	0.92			
Zn^{2+}		11.07 β_2	4.98	3.57		
Cd^{2+}	6.01	5.11	4.53	2.27		
Hg^{2+}	17.00	15.75	3.56	2.66		
Ni^{2+}				30.22 (β_4)		

Ethylenediamine $H_2N\diagdown\diagup NH_2$	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log K_5$	$\log K_6$
Ni^{2+}	7.38	6.18	4.11			
Cu^{2+}	10.48	9.07				
Ag^+ ($T=20\,°C$, $\mu=0.1$ M)	4.700	3.00				
Zn^{2+}	5.66	4.98	3.25			
Cd^{2+}	5.41	4.50	2.78			

EDTA	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log K_5$	$\log K_6$
Mg^{2+} ($T=20\,°C$, $\mu=0.1$ M)	8.79					
Ca^{2+} ($T=20\,°C$, $\mu=0.1$ M)	10.69					
Ba^{2+} ($T=20\,°C$, $\mu=0.1$ M)	7.86					
Bi^{3+} ($T=20\,°C$, $\mu=0.1$ M)	27.8					
$Co^{2+}+$ ($T=20\,°C$, $\mu=0.1$ M)	16.31					
Ni^{2+} ($T=20\,°C$, $\mu=0.1$ M)	18.62					
Cu^{2+} ($T=20\,°C$, $\mu=0.1$ M)	18.80					
Cr^{3+} ($T=20\,°C$, $\mu=0.1$ M)	[23.4]					
Fe^{3+} ($T=20\,°C$, $\mu=0.1$ M)	25.1					
Ag^+ ($T=20\,°C$, $\mu=0.1$ M)	7.32					
Zn^{2+} ($T=20\,°C$, $\mu=0.1$ M)	16.50					
Cd^{2+} ($T=20\,°C$, $\mu=0.1$ M)	16.46					
Hg^{2+} ($T=20\,°C$, $\mu=0.1$ M)	21.7					
Pb^{2+} ($T=20\,°C$, $\mu=0.1$ M)	18.04					

Al^{3+} ($T = 20\,°C$, $\mu = 0.1$ M)   16.3

Fluoride F$^-$	log K_1	log K_2	log K_3	log K_4	log K_5	log K_6
Al^{3+} ($\mu = 0.5$ M)	6.11	5.01	3.88	3.0	1.4	0.4

Hydroxide OH$^-$	log K_1	log K_2	log K_3	log K_4	log K_5	log K_6
Al^{3+}	9.01	[9.69]	[8.3]	6.0		
Co^{2+}	4.3	4.1	1.3	0.5		
Fe^{2+}	4.5	[2.9]	2.6	−0.4		
Fe^{3+}	11.81	10.5	12.1			
Ni^{2+}	4.1	3.9	3.			
Pb^{2+}	6.3	4.6	3.0			
Zn^{2+}	5.0	[6.1]	2.5	[1.2]		

Iodide I$^-$	log K_1	log K_2	log K_3	log K_4	log K_5	log K_6
Ag$^+$ ($T = 18\,°C$)	6.58	[5.12]	[1.4]			
Cd^{2+}	2.28	1.64	1.08	1.0		
Pb^{2+}	1.92	1.28	0.7	0.6		

Nitriloacetate (structure shown)	log K_1	log K_2	log K_3	log K_4	log K_5	log K_6
Mg^{2+} ($T = 20\,°C$, $\mu = 0.1$ M)	5.41					
Ca^{2+} ($T = 20\,°C$, $\mu = 0.1$ M)	6.41					
Ba^{2+} ($T = 20\,°C$, $\mu = 0.1$ M)	4.82					
Mn^{2+} ($T = 20\,°C$, $\mu = 0.1$ M)	7.44					
Fe^{2+} ($T = 20\,°C$, $\mu = 0.1$ M)	8.33					
Co^{2+} ($T = 20\,°C$, $\mu = 0.1$ M)	10.38					
Ni^{2+} ($T = 20\,°C$, $\mu = 0.1$ M)	11.53					
Cu^{2+} ($T = 20\,°C$, $\mu = 0.1$ M)	12.96					
Fe^{3+} ($T = 20\,°C$, $\mu = 0.1$ M)	15.9					
Zn^{2+} ($T = 20\,°C$, $\mu = 0.1$ M)	10.67					

Cd^{2+} ($T=20\,^\circ$C, $\mu=0.1$ M)	9.83					
Pb^{2+} ($T=20\,^\circ$C, $\mu=0.1$ M)	11.39					

Oxalate $C_2O_4^{2-}$	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log K_5$	$\log K_6$
Ca^{2+} ($\mu=1$ M)	1.66	1.03				
Fe^{2+} ($\mu=1$ M)	3.05	2.10				
Co^{2+}	4.72	2.28				
Ni^{2+}	5.16					
Cu^{2+}	6.23	4.04				
Fe^{3+} ($\mu=0.5$ M)	7.53	6.11	4.85			
Zn^{2+}	4.87	2.78				

1,10-Phenanthroline						

	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log K_5$	$\log K_6$
Fe^{2+}			20.7 (β_3)			
Mn^{2+} ($\mu=0.1$ M)	4.0	3.3	3.0			
Co^{2+} ($\mu=0.1$ M)	7.08	6.64	6.08			
Ni^{2+}	8.6	8.1	7.6			
Fe^{3+}			13.8 (β_3)			
Ag^+ ($\mu=0.1$ M)	5.02	7.04				
Zn^{2+}	6.2	[5.9]	[5.2]			

Thiosulfate $S_2O_3^{2-}$	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log K_5$	$\log K_6$
Ag^+ ($T=20\,^\circ$C)	8.82	4.85	0.53			

Thiocyanate SCN^-	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log K_5$	$\log K_6$
Mn^{2+}	1.23					
Fe^{2+}	1.31					
Co^{2+}	1.72					
Ni^{2+}	1.76					
Cu^{2+}	2.33					
Fe^{3+}	3.02					

Ag^+	4.8	3.43	1.27	0.2
Zn^{2+}	1.33	0.58	0.09	−0.4
Cd^{2+}	1.89	0.89	0.02	−0.5
Hg^{2+}		17.26 (β_2)	2.71	1.83

Appendix 13: Standard Reduction Potentials

The following table provides E^o and $E^{o\prime}$ values for selected reduction reactions. Values are from the following sources: Bard, A. J.; Parsons, B.; Jordon, J., eds. *Standard Potentials in Aqueous Solutions*, Dekker: New York, 1985; Milazzo, G.; Caroli, S.; Sharma, V. K. *Tables of Standard Electrode Potentials*, Wiley: London, 1978; Swift, E. H.; Butler, E. A. *Quantitative Measurements and Chemical Equilibria*, Freeman: New York, 1972.

Solids, gases, and liquids are identified; all other species are aqueous. Reduction reactions in acidic solution are written using H^+ in place of H_3O^+. You may rewrite a reaction by replacing H^+ with H_3O^+ and adding to the opposite side of the reaction one molecule of H_2O per H^+; thus

$$H_3AsO_4 + 2H^+ + 2e^- \rightleftharpoons HAsO_2 + 2H_2O$$

becomes

$$H_3AsO_4 + 2H_3O^+ + 2e^- \rightleftharpoons HAsO_2 + 4H_2O$$

Conditions for formal potentials ($E^{o\prime}$) are listed next to the potential.

Aluminum	E^o (V)	$E^{o\prime}$(V)
$Al^{3+} + 3e^- \rightleftharpoons Al(s)$	−1.676	
$Al(OH)_4^- + 3e^- \rightleftharpoons Al(s) + 4OH^-$	−2.310	
$AlF_6^{3-} + 3e^- \rightleftharpoons Al(s) + 6F^-$	−2.07	

Antimony	E^o (V)	$E^{o\prime}$(V)
$Sb + 3H^+ + 3e^- \rightleftharpoons SbH_3(g)$	−0.510	
$Sb_2O_5(s) + 6H^+ + 4e^- \rightleftharpoons 2SbO^+ + 3H_2O(l)$	0.605	
$SbO^+ + 2H^+ + 3e^- \rightleftharpoons Sb(s) + H_2O(l)$	0.212	

Arsenic	E^o (V)	$E^{o\prime}$(V)
$As + 3H^+ + 3e^- \rightleftharpoons AsH_3(g)$	−0.225	
$H_3AsO_4 + 2H^+ + 2e^- \rightleftharpoons HAsO_2 + 2H_2O(l)$	0.560	
$HAsO_2 + 3H^+ + 3e^- \rightleftharpoons As(s) + 2H_2O(l)$	0.240	

Barium	E^o (V)	$E^{o\prime}$(V)
$Ba^{2+} + 2e^- \rightleftharpoons Ba(s)$	−2.92	
$BaO(s) + 2H^+ + 2e^- \rightleftharpoons Ba(s) + H_2O(l)$	2.365	

Beryllium	$E°$ (V)	$E°'$(V)
$Be^{2+} + 2e^- \rightleftharpoons Be(s)$	−1.99	

Bismuth	$E°$ (V)	$E°'$(V)
$Bi^{3+} + 3e^- \rightleftharpoons Bi(s)$	0.317	
$BiCl_4^- + 3e^- \rightleftharpoons Bi(s) + 4Cl^-$	0.199	

Boron	$E°$ (V)	$E°'$(V)
$B(OH)_3 + 3H^+ + 3e^- \rightleftharpoons B(s) + 3H_2O(l)$	−0.890	
$B(OH)_4^- + 3e^- \rightleftharpoons B(s) + 4OH^-$	−1.811	

Bromine	$E°$ (V)	$E°'$(V)
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	1.087	
$HOBr + H^+ + 2e^- \rightleftharpoons Br^- + H_2O(l)$	1.341	
$HOBr + H^+ + e^- \rightleftharpoons \frac{1}{2}Br^- + H_2O(l)$	1.604	
$BrO^- + H_2O(l) + 2e^- \rightleftharpoons Br^- + 2OH^-$		0.76 in 1 M NaOH
$BrO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}Br_2(l) + 3H_2O$	1.5	
$BrO_3^- + 6H^+ + 6e^- \rightleftharpoons Br^- + 3H_2O$	1.478	

Cadmium	$E°$ (V)	$E°'$(V)
$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$	−0.4030	
$Cd(CN)_4^{2-} + 2e^- \rightleftharpoons Cd(s) + 4CN^-$	−0.943	
$Cd(NH_3)_4^{2+} + 2e^- \rightleftharpoons Cd(s) + 4NH_3$	−0.622	

Calcium	$E°$ (V)	$E°'$(V)
$Ca^{2+} + 2e^- \rightleftharpoons Ca(s)$	−2.84	

Carbon	$E°$ (V)	$E°'$(V)
$CO_2(g) + 2H^+ + 2e^- \rightleftharpoons CO(g) + H_2O(l)$	−0.106	
$CO_2(g) + 2H^+ + 2e^- \rightleftharpoons HCO_2H$	−0.20	
$2CO_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2C_2O_4$	−0.481	
$HCHO + 2H^+ + 2e^- \rightleftharpoons CH_3OH$	0.2323	

Cerium	$E°$ (V)	$E°'$(V)
$Ce^{3+} + 3e^- \rightleftharpoons Ce(s)$	−2.336	
$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$	1.72	1.70 in 1 M $HClO_4$ 1.44 in 1 M H_2SO_4 1.61 in 1 M HNO_3 1.28 in 1 M HCl

Chlorine	$E°$ (V)	$E°'$(V)
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-$	1.396	
$ClO^- + H_2O(l) + e^- \rightleftharpoons \frac{1}{2}Cl_2(g) + 2OH^-$		0.421 in 1 M NaOH
$ClO^- + H_2O(l) + 2e^- \rightleftharpoons Cl^- + 2OH^-$		0.890 in 1 M NaOH
$HClO_2 + 2H^+ + 2e^- \rightleftharpoons HOCl + H_2O$	1.64	
$ClO_3^- + 2H^+ + e^- \rightleftharpoons ClO_2(g) + H_2O$	1.175	
$ClO_3^- + 3H^+ + 2e^- \rightleftharpoons HClO_2 + H_2O$	1.181	
$ClO_4^- + 2H^+ + 2e^- \rightleftharpoons ClO_3^- + H_2O$	1.201	

Chromium	$E°$ (V)	$E°'$(V)
$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$	−0.424	
$Cr^{2+} + 2e^- \rightleftharpoons Cr(s)$	−0.90	
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O(l)$	1.36	
$CrO_4^{2-} + 4H_2O(l) + 3e^- \rightleftharpoons 2Cr(OH)_4^- + 4OH^-$		−0.13 in 1 M NaOH

Cobalt	$E°$ (V)	$E°'$(V)
$Co^{2+} + 2e^- \rightleftharpoons Co(s)$	−0.277	
$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	1.92	
$Co(NH_3)_6^{3+} + e^- \rightleftharpoons Co(NH_3)_6^{2+}$	0.1	
$Co(OH)_3(s) + e^- \rightleftharpoons Co(OH)_2(s) + OH^-$	0.17	
$Co(OH)_2(s) + 2e^- \rightleftharpoons Co(s) + 2OH^-$	−0.746	

Copper	$E°$ (V)	$E°'$(V)
$Cu^+ + e^- \rightleftharpoons Cu(s)$	0.520	
$Cu^{2+} + e^- \rightleftharpoons Cu^+$	0.159	
$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$	0.3419	
$Cu^{2+} + I^- + e^- \rightleftharpoons CuI(s)$	0.86	
$Cu^{2+} + Cl^- + e^- \rightleftharpoons CuCl(s)$	0.559	

Fluorine	$E°$ (V)	$E°'$(V)
$F_2(g) + 2H^+ + 2e^- \rightleftharpoons 2HF$	3.053	
$F_2(g) + +2e^- \rightleftharpoons 2F^-$	2.87	

Gallium	$E°$ (V)	$E°'$(V)
$Ga^{3+} + 3e^- \rightleftharpoons Ga(s)$		

Gold	$E°$ (V)	$E°'$(V)
$Au^+ + e^- \rightleftharpoons Au(s)$	1.83	
$Au^{3+} + 2e^- \rightleftharpoons Au^+$	1.36	
$Au^{3+} + 3e^- \rightleftharpoons Au(s)$	1.52	
$AuCl_4^- + 3e^- \rightleftharpoons Au(s) + 4Cl^-$	1.002	

Hydrogen	$E°$ (V)	$E°'$(V)
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	0.00000	
$H_2O + e^- \rightleftharpoons \frac{1}{2}H_2(g) + OH^-$	−0.828	

Iodine	$E°$ (V)	$E°'$(V)
$I_2(s) + 2e^- \rightleftharpoons 2I^-$	0.5355	
$I_3^- + 2e^- \rightleftharpoons 3I^-$	0.536	
$HIO + H^+ + 2e^- \rightleftharpoons I^- + H_2O(l)$	0.985	
$IO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}I_2(s) + 3H_2O(l)$	1.195	
$IO_3^- + 3H_2O(l) + 6e^- \rightleftharpoons I^- + 6OH^-$	0.257	

Iron	$E°$ (V)	$E°'$(V)
$Fe^{2+} + 2e^- \rightleftharpoons Fe(s)$	−0.44	
$Fe^{3+} + 3e^- \rightleftharpoons Fe(s)$	−0.037	
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	0.771	0.70 in 1 M HCl 0.767 in 1 M HClO$_4$ 0.746 in 1 M HNO$_3$ 0.68 in 1 M H$_2$SO$_4$ 0.44 in 0.3 M H$_3$PO$_4$
$Fe(CN)_6^{3-} + e^- \rightleftharpoons Fe(CN)_6^{4-}$	0.356	
$Fe(phen)_6^{3+} + e^- \rightleftharpoons Fe(phen)_6^{2+}$	1.147	

Lanthanum	$E°$ (V)	$E°'$(V)
$La^{3+} + 3e^- \rightleftharpoons La(s)$	−2.38	

Lead	$E°$ (V)	$E°'$(V)
$Pb^{2+} + 2e^- \rightleftharpoons Pb(s)$	−0.126	
$PbO_2(s) + 4OH^- + 2e^- \rightleftharpoons Pb^{2+} + 2H_2O(l)$	1.46	
$PbO_2(s) + 4SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$	1.690	
$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}$	−0.356	

Lithium	$E°$ (V)	$E°'$(V)
$Li^+ + e^- \rightleftharpoons Li(s)$	−3.040	

Magnesium	$E°$ (V)	$E°'$(V)
$Mg^{2+} + 2e^- \rightleftharpoons Mg(s)$	−2.356	
$Mg(OH)_2(s) + 2e^- \rightleftharpoons Mg(s) + 2OH^-$	−2.687	

Manganese	$E°$ (V)	$E°'$(V)
$Mn^{2+} + 2e^- \rightleftharpoons Mn(s)$	−1.17	
$Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$	1.5	
$MnO_2(s) + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O(l)$	1.23	
$MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_2(s) + 2H_2O(l)$	1.70	
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O(l)$	1.51	
$MnO_4^- + 2H_2O(l) + 3e^- \rightleftharpoons MnO_2(s) + 4OH^-$	0.60	

Mercury	$E°$ (V)	$E°'$(V)
$Hg^{2+} + 2e^- \rightleftharpoons Hg(l)$	0.8535	
$2Hg^{2+} + 2e^- \rightleftharpoons Hg_2^{2+}$	0.911	
$Hg_2^{2+} + 2e^- \rightleftharpoons 2Hg(l)$	0.7960	
$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$	0.2682	
$HgO(s) + 2H^+ + 2e^- \rightleftharpoons Hg(l) + H_2O(l)$	0.926	
$Hg_2Br_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Br^-$	1.392	
$Hg_2I_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2I^-$	−0.0405	

Molybdenum	$E°$ (V)	$E°'$(V)
$Mo^{3+} + 3e^- \rightleftharpoons Mo(s)$	–0.2	
$MoO_2(s) + 4H^+ + 4e^- \rightleftharpoons Mo(s) + 2H_2O(l)$	–0.152	
$MoO_4^{2-} + 4H_2O(l) + 6e^- \rightleftharpoons Mo(s) + 8OH^-$	–0.913	

Nickel	$E°$ (V)	$E°'$(V)
$Ni^{2+} + 2e^- \rightleftharpoons Ni(s)$	–0.257	
$Ni(OH)_2 + 2e^- \rightleftharpoons Ni(s) + 2OH^-$	–0.72	
$Ni(NH_3)_6^{2+} + 2e^- \rightleftharpoons Ni(s) + 6NH_3$	–0.49	

Nitrogen	$E°$ (V)	$E°'$(V)
$N_2(g) + 5H^+ + 4e^- \rightleftharpoons N_2H_5^+$	–0.23	
$N_2O(g) + 2H^+ + 2e^- \rightleftharpoons N_2(g) + H_2O(l)$	1.77	
$2NO(g) + 2H^+ + 2e^- \rightleftharpoons N_2O(g) + H_2O(l)$	1.59	
$HNO_2 + H^+ + e^- \rightleftharpoons NO(g) + H_2O(l)$	0.996	
$2HNO_2 + 4H^+ + 4e^- \rightleftharpoons N_2O(g) + 3H_2O(l)$	1.297	
$NO_3^- + 3H^+ + 2e^- \rightleftharpoons HNO_2 + H_2O(l)$	0.94	

Oxygen	$E°$ (V)	$E°'$(V)
$O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	0.695	
$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O(l)$	1.229	
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O(l)$	1.763	
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-$	0.401	
$O_3(g) + 2H^+ + 2e^- \rightleftharpoons O_2(g) + H_2O(l)$	2.07	

Phosphorous	$E°$ (V)	$E°'$(V)
$P(s, \text{white}) + 3H^+ + 3e^- \rightleftharpoons PH_3(g)$		
$H_3PO_3 + 2H^+ + 2e^- \rightleftharpoons H_3PO_2 + H_2O(l)$		
$H_3PO_4 + 2H^+ + 2e^- \rightleftharpoons H_3PO_3 + H_2O(l)$		

Platinum	$E°$ (V)	$E°'$(V)
$Pt^{2+} + 2e^- \rightleftharpoons Pt(s)$		
$PtCl_4^{2-} + 2e^- \rightleftharpoons Pt(s) + 4Cl^-$		

Potassium	$E°$ (V)	$E°'$(V)
$K^+ + e^- \rightleftharpoons K(s)$		

Ruthenium	$E°$ (V)	$E°'$(V)
$Ru^{3+} + e^- \rightleftharpoons Ru^{2+}$	0.249	
$RuO_2(s) + 4H^+ + 4e^- \rightleftharpoons Ru(s) + 2H_2O(l)$	0.68	
$Ru(NH_3)_6^{3+} + e^- \rightleftharpoons Ru(s) + Ru(NH_3)_6^{2+}$	0.10	
$Ru(CN)_6^{3-} + e^- \rightleftharpoons Ru(s) + Ru(CN)_6^{4-}$	0.86	

Selenium	$E°$ (V)	$E°'$(V)
$Se(s) + 2e^- \rightleftharpoons Se^{2-}$		−0.67 in 1 M NaOH
$Se(s) + 2H^+ + 2e^- \rightleftharpoons H_2Se(g)$	−0.115	
$H_2SeO_3 + 4H^+ + 4e^- \rightleftharpoons Se(s) + 3H_2O(l)$	0.74	
$SeO_4^{3-} + 4H^+ + e^- \rightleftharpoons H_2SeO_3 + H_2O(l)$	1.151	

Silicon	$E°$ (V)	$E°'$(V)
$SiF_6^{2-} + 4e^- \rightleftharpoons Si(s) + 6F^-$	−1.37	
$SiO_2(s) + 4H^+ + 4e^- \rightleftharpoons Si(s) + 2H_2O(l)$	−0.909	
$SiO_2(s) + 8H^+ + 8e^- \rightleftharpoons SiH_4(g) + 2H_2O(l)$	−0.516	

Silver	$E°$ (V)	$E°'$(V)
$Ag^+ + e^- \rightleftharpoons Ag(s)$	0.7996	
$AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^-$	0.071	
$Ag_2C_2O_4(s) + 2e^- \rightleftharpoons 2Ag(s) + C_2O_4^{2-}$	0.47	
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$	0.2223	
$AgI(s) + e^- \rightleftharpoons Ag(s) + I^-$	−0.152	
$Ag_2S(s) + 2e^- \rightleftharpoons 2Ag(s) + S^{2-}$	−0.71	
$Ag(NH_3)_2^+ + e^- \rightleftharpoons Ag(s) + 2NH_3$	−0.373	

Sodium	$E°$ (V)	$E°'$(V)
$Na^+ + e^- \rightleftharpoons Na(s)$	−2.713	

Strontium	$E°$ (V)	$E°'$(V)
$Sr^{2+} + 2e^- \rightleftharpoons Sr(s)$	−2.89	

Sulfur	$E°$ (V)	$E°'$(V)
$S(s) + 2e^- \rightleftharpoons S^{2-}$	−0.407	
$S(s) + 2H^+ + 2e^- \rightleftharpoons H_2S$	0.144	
$S_2O_6^{2-} + 4H^+ + 2e^- \rightleftharpoons 2H_2SO_3$	0.569	
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	1.96	
$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-}$	0.080	
$2SO_3^{2-} + 2H_2O(l) + 2e^- \rightleftharpoons S_2O_4^{2-} + 4OH^-$	−1.13	
$2SO_3^{2-} + 3H_2O(l) + 4e^- \rightleftharpoons S_2O_3^{2-} + 6OH^-$		−0.576 in 1 M NaOH
$2SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons S_2O_6^{2-} + 2H_2O(l)$	−0.25	
$SO_4^{2-} + H_2O(l) + 2e^- \rightleftharpoons SO_3^{2-} + 2OH^-$	−0.936	
$SO_4^{2-} + 4H^+ + +2e^- \rightleftharpoons H_2SO_3^{2-} + H_2O(l)$	0.172	

Thallium	$E°$ (V)	$E°'$(V)
$Tl^{3+} + 2e^- \rightleftharpoons Tl^+$		1.25 in 1 M HClO$_4$ 0.77 in 1 M HCl
$Tl^{3+} + 3e^- \rightleftharpoons Tl(s)$	0.742	

Tin	$E°$ (V)	$E°'$(V)
$Sn^{2+} + 2e^- \rightleftharpoons Sn(s)$		−0.19 in 1 M HCl
$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	0.154	0.139 in 1 M HCl

Titanium	$E°$ (V)	$E°'$(V)
$Ti^{2+} + 2e^- \rightleftharpoons Ti(s)$	−0.163	
$Ti^{3+} + e^- \rightleftharpoons Ti^{2+}$	−0.37	

Tungsten	$E°$ (V)	$E°'$(V)
$WO_2(s) + 4H^+ + 4e^- \rightleftharpoons W(s) + 2H_2O(l)$	−0.119	
$WO_3(s) + 6H^+ + 6e^- \rightleftharpoons W(s) + 3H_2O(l)$	−0.090	

Uranium	$E°$ (V)	$E°'$(V)
$U^{3+} + 3e^- \rightleftharpoons U(s)$	−1.66	
$U^{4+} + e^- \rightleftharpoons U^{3+}$	−0.52	
$UO_2^+ + 4H^+ + e^- \rightleftharpoons U^{4+} + 2H_2O(l)$	0.27	
$UO_2^{2+} + e^- \rightleftharpoons UO_2^+$	0.16	
$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O(l)$	0.327	

Vanadium	$E°$ (V)	$E°'$(V)
$V^{2+} + 2e^- \rightleftharpoons V(s)$	−1.13	
$V^{3+} + e^- \rightleftharpoons V^{2+}$	−0.255	
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O(l)$	0.337	
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O(l)$	1.000	

Zinc	$E°$ (V)	$E°'$(V)
$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$	−0.7618	
$Zn(OH)_4^{2-} + 2e^- \rightleftharpoons Zn(s) + 4OH^-$	−1.285	
$Zn(NH_3)_4^{2+} + 2e^- \rightleftharpoons Zn(s) + 4NH_3$	−1.04	
$Zn(CN)_4^{2-} + 2e^- \rightleftharpoons Zn(s) + 4CN$	−1.34	

Appendix 14: Random Number Table

The following table provides a list of random numbers in which the digits 0 through 9 appear with approximately equal frequency. Numbers are arranged in groups of five to make the table easier to view. This arrangement is arbitrary, and you can treat the table as a sequence of random individual digits (1, 2, 1, 3, 7, 4…going down the first column of digits on the left side of the table), as a sequence of three digit numbers (111, 212, 104, 367, 739… using the first three columns of digits on the left side of the table), or in any other similar manner.

Let's use the table to pick 10 random numbers between 1 and 50. To do so, we choose a random starting point, perhaps by dropping a pencil onto the table. For this exercise, we will assume that the starting point is the fifth row of the third column, or 12032. Because the numbers must be between 1 and 50, we will use the last two digits, ignoring all two-digit numbers less than 01 or greater than 50, and rejecting any duplicates. Proceeding down the third column, and moving to the top of the fourth column when necessary, gives the following 10 random numbers: 32, 01, 05, 16, 15, 38, 24, 10, 26, 14.

These random numbers (1000 total digits) are a small subset of values from the publication *Million Random Digits* (Rand Corporation, 2001) and used with permission. Information about the publication, and a link to a text file containing the million random digits is available at http://www.rand.org/pubs/monograph_reports/MR1418/.

11164	36318	75061	37674	26320	75100	10431	20418	19228	91792
21215	91791	76831	58678	87054	31687	93205	43685	19732	08468
10438	44482	66558	37649	08882	90870	12462	41810	01806	02977
36792	26236	33266	66583	60881	97395	20461	36742	02852	50564
73944	04773	12032	51414	82384	38370	00249	80709	72605	67497
49563	12872	14063	93104	78483	72717	68714	18048	25005	04151
64208	48237	41701	73117	33242	42314	83049	21933	92813	04763
51486	72875	38605	29341	80749	80151	33835	52602	79147	08868
99756	26360	64516	17971	48478	09610	04638	17141	09227	10606
71325	55217	13015	72907	00431	45117	33827	92873	02953	85474
65285	97198	12138	53010	95601	15838	16805	61004	43516	17020
17264	57327	38224	29301	31381	38109	34976	65692	98566	29550
95639	99754	31199	92558	68368	04985	51092	37780	40261	14479
61555	76404	86210	11808	12841	45147	97438	60022	12645	62000
78137	98768	04689	87130	79225	08153	84967	64539	79493	74917
62490	99215	84987	28759	19177	14733	24550	28067	68894	38490
24216	63444	21283	07044	92729	37284	13211	37485	10415	36457
16975	95428	33226	55903	31605	43817	22250	03918	46999	98501
59138	39542	71168	57609	91510	77904	74244	50940	31553	62562
29478	59652	50414	31966	87912	87514	12944	49862	96566	48825

Appendix 15: Polarographic Half-Wave Potentials

The following table provides $E_{1/2}$ values for selected reduction reactions. Values are from Dean, J. A. *Analytical Chemistry Handbook*, McGraw-Hill: New York, 1995.

Element	$E_{1/2}$ (volts vs. SCE)	Matrix
$Al^{3+} + 3e^- \rightleftharpoons Al(s)$	-0.5	0.2 M acetate (pH 4.5–4.7)
$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$	-0.60	0.1 M KCl 0.05 M H_2SO_4 1 M HNO_3
$Cr^{3+} + 3e^- \rightleftharpoons Cr(s)$	-0.35 (+3 → +2) -1.70 (+2 → 0)	1 M NH_4Cl plus 1 M NH_3 1 M NH_4^+/NH_3 buffer (ph 8–9)
$Co^{3+} + 3e^- \rightleftharpoons Co(s)$	-0.5 (+3 → +2) -1.3 (+2 → 0)	1 M NH_4Cl plus 1 M NH_3
$Co^{2+} + 2e^- \rightleftharpoons Co(s)$	-1.03	1 M KSCN
$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$	0.04 -0.22	0.1 M KSCN 0.1 M NH_4ClO_4 1 M Na_2SO_4 0.5 M potassium citrate (pH 7.5)
$Fe^{3+} + 3e^- \rightleftharpoons Fe(s)$	-0.17 (+3 → +2) -1.52 (+2 → 0)	0.5 M sodium tartrate (pH 5.8)
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	-0.27	0.2 M $Na_2C_2O_4$ (pH < 7.9)
$Pb^{2+} + 2e^- \rightleftharpoons Pb(s)$	-0.405 -0.435	1 M HNO_3 1 M KCl
$Mn^{2+} + 2e^- \rightleftharpoons Mn(s)$	-1.65	1 M NH_4Cl plus 1 M NH_3
$Ni^{2+} + 2e^- \rightleftharpoons Ni(s)$	-0.70 -1.09	1 M KSCN 1 M NH_4Cl plus 1 M NH_3
$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$	-0.995 -1.33	0.1 M KCl 1 M NH_4Cl plus 1 M NH_3

Appendix 16: Countercurrent Separations

In 1949, Lyman Craig introduced an improved method for separating analytes with similar distribution ratios.[1] The technique, which is known as a countercurrent liquid–liquid extraction, is outlined in Figure A16.1 and discussed in detail below. In contrast to a sequential liquid–liquid extraction, in which we repeatedly extract the sample containing the analyte, a countercurrent extraction uses a serial extraction of both the sample and the extracting phases. Although countercurrent separations are no longer common—chromatographic separations are far more efficient in terms of resolution, time, and ease of use—the theory behind a countercurrent extraction remains useful as an introduction to the theory of chromatographic separations.

To track the progress of a countercurrent liquid-liquid extraction we need to adopt a labeling convention. As shown in Figure A16.1, in each step of a countercurrent extraction we first complete the extraction and then transfer the upper phase to a new tube containing a portion of the fresh lower phase. Steps are labeled sequentially beginning with zero. Extractions take place in a series of tubes that also are labeled sequentially, starting with zero. The upper and lower phases in each tube are identified by a letter and number, with the letters U and L representing, respectively, the upper phase and the lower phase, and the number indicating the step in the countercurrent extraction in which the phase was first introduced. For example, U_0 is the upper phase introduced at step 0 (during the first extraction), and L_2 is the lower phase introduced at step 2 (during the third extraction). Finally, the partitioning of analyte in any extraction tube results in a fraction p remaining in the upper phase, and a fraction q remaining in the lower phase. Values of q are calculated using equation A16.1, which is identical to equation 7.26 in Chapter 7.

$$(q_{aq})_1 = \frac{(\text{moles aq})_1}{(\text{moles aq})_0} = \frac{V_{aq}}{DV_{org} + V_{aq}} \qquad \text{A16.1}$$

The fraction p, of course is equal to $1 - q$. Typically V_{aq} and V_{org} are equal in a countercurrent extraction, although this is not a requirement.

Let's assume that the analyte we wish to isolate is present in an aqueous phase of 1 M HCl, and that the organic phase is benzene. Because benzene has the smaller density, it is the upper phase, and 1 M HCl is the lower phase. To begin the countercurrent extraction we place the aqueous sample containing the analyte in tube 0 along with an equal volume of benzene. As shown in Figure A16.1a, before the extraction all the analyte is present in phase L_0. When the extraction is complete, as shown in Figure A16.1b, a fraction p of the analyte is present in phase U_0, and a fraction q is in phase L_0. This completes step 0 of the countercurrent extraction. If we stop here, there is no difference between a simple liquid–liquid extraction and a countercurrent extraction.

After completing step 0, we remove phase U_0 and add a fresh portion of benzene, U_1, to tube 0 (see Figure A16.1c). This, too, is identical to a simple liquid-liquid extraction. Here is where the power of the countercurrent extraction begins—instead of setting aside the phase U_0, we place it in tube 1 along with a portion of analyte-free aqueous 1 M HCl as phase L_1 (see Figure A16.1c). Tube 0 now contains a fraction q of the analyte, and tube 1 contains a fraction p of the analyte. Completing the extraction in tube 0 results in a fraction p of its contents remaining in the upper phase, and a fraction q remaining in the lower phase. Thus, phases U_1 and L_0 now contain, respectively, fractions pq and q^2 of the original amount of analyte. Following the same logic, it is easy to show that the phases U_0 and L_1 in tube 1 contain, respectively, fractions p^2 and pq of analyte. This completes step 1 of the extraction (see Figure A16.1d). As shown in the remainder of Figure A16.1, the countercurrent extraction continues with this cycle of phase transfers and extractions.

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1   Craig, L. C. *J. Biol. Chem.* **1944**, *155*, 519–534.

Figure A16.1 Scheme for a countercurrent extraction: (a) The sample containing the analyte begins in L_0 and is extracted with a fresh portion of the upper, or mobile phase; (b) The extraction takes place, transferring a fraction p of analyte to the upper phase and leaving a fraction q of analyte in the lower, or stationary phase; (c) When the extraction is complete, the upper phase is transferred to the next tube, which contains a fresh portion of the sample's solvent, and a fresh portion of the upper phase is added to tube 0. In (d) through (g), the process continues, with the addition of two more tubes.

$n\downarrow$ $r\rightarrow$	0	1	2	3
Table A16.1		**Fraction of Analyte Remaining in Tube r After Extraction Step n for a Countercurrent Extraction**		
0	1	—	—	—
1	q	p	—	—
2	q^2	$2pq$	p^2	—
3	q^3	$3pq^2$	$3p^2q$	p^3

In a countercurrent liquid–liquid extraction, the lower phase in each tube remains in place, and the upper phase moves from tube 0 to successively higher numbered tubes. We recognize this difference in the movement of the two phases by referring to the lower phase as a stationary phase and the upper phase as a mobile phase. With each transfer some of the analyte in tube r moves to tube $r + 1$, while a portion of the analyte in tube $r - 1$ moves to tube r. Analyte introduced at tube 0 moves with the mobile phase, but at a rate that is slower than the mobile phase because, at each step, a portion of the analyte transfers into the stationary phase. An analyte that preferentially extracts into the stationary phase spends proportionally less time in the mobile phase and moves at a slower rate. As the number of steps increases, analytes with different values of q eventually separate into completely different sets of extraction tubes.

We can judge the effectiveness of a countercurrent extraction using a histogram showing the fraction of analyte present in each tube. To determine the total amount of analyte in an extraction tube we add together the fraction of analyte present in the tube's upper and lower phases following each transfer. For example, at the beginning of step 3 (see Figure A16.1g) the upper and lower phases of tube 1 contain fractions pq^2 and $2pq^2$ of the analyte, respectively; thus, the total fraction of analyte in the tube is $3pq^2$. Table A16.1 summarizes this for the steps outlined in Figure A16.1. A typical histogram, calculated assuming distribution ratios of 5.0 for analyte A and 0.5 for analyte B, is shown in Figure A16.2. Although four steps is not enough to separate the

Figure A16.2 Progress of a countercurrent extraction for the separation of analytes A and B showing the fraction of anlayte in each tube after (a) step 0, (b) step 1, (c) step 2, and (d) step 3. The distribution ratio, D, is 5.0 for analyte A and 0.5 for analyte B. The volumes of the two phases are identical.

analytes in this instance, it is clear that if we extend the countercurrent extraction to additional tubes, we will eventually separate the analytes.

Figure A16.1 and Table A16.1 show how an analyte's distribution changes during the first four steps of a countercurrent extraction. Now we consider how we can generalize these results to calculate the amount of analyte in any tube, at any step during the extraction. You may recognize the pattern of entries in Table A16.1 as following the binomial distribution

$$f(r,n) = \frac{n!}{(n-r)!r!} p^r q^{n-r} \qquad \text{A16.2}$$

where $f(r, n)$ is the fraction of analyte present in tube r at step n of the countercurrent extraction, with the upper phase containing a fraction $p \times f(r, n)$ of analyte and the lower phase containing a fraction $q \times f(r, n)$ of the analyte.

Example A16.1

The countercurrent extraction shown in Figure A16.2 is carried out through step 30. Calculate the fraction of analytes A and B in tubes 5, 10, 15, 20, 25, and 30.

SOLUTION

To calculate the fraction, q, for each analyte in the lower phase we use equation A6.1. Because the volumes of the lower and upper phases are equal, we get

$$q_A = \frac{1}{D_A + 1} = \frac{1}{5 + 1} = 0.167 \qquad q_B = \frac{1}{D_B + 1} = \frac{1}{4 + 1} = 0.200$$

Because we know that $p + q = 1$, we also know that p_A is 0.833 and that p_B is 0.333. For analyte A, the fraction in tubes 5, 10, 15, 20, 25, and 30 after the 30th step are

$$f(5,30) = \frac{30!}{(30-5)!5!}(0.833)^5(0.167)^{30-5} = 2.1 \times 10^{-15} \approx 0$$

$$f(10,30) = \frac{30!}{(30-10)!10!}(0.833)^{10}(0.167)^{30-10} = 1.4 \times 10^{-9} \approx 0$$

$$f(15,30) = \frac{30!}{(30-15)!15!}(0.833)^{15}(0.167)^{30-15} = 2.2 \times 10^{-5} \approx 0$$

$$f(20,30) = \frac{30!}{(30-20)!20!}(0.833)^{20}(0.167)^{30-20} = 0.013$$

$$f(25,30) = \frac{30!}{(30-25)!25!}(0.833)^{25}(0.167)^{30-25} = 0.192$$

$$f(30,30) = \frac{30!}{(30-30)!30!}(0.833)^{30}(0.167)^{30-30} = 0.004$$

Figure A16.3 Progress of a countercurrent extraction for the separation of analyte A and B showing the fraction of analyte in each tube after 30 steips. The distribution ratio, D, is 5.0 for analyte A and 0.5 for analyte B. The volumes of the two phases are identical. See Example A16.1 for further details.

The fraction of analyte B in tubes 5, 10, 15, 20, 25, and 30 is calculated in the same way, yielding respective values of 0.023, 0.153, 0.025, 0, 0, and 0. Figure A16.3, which provides the complete histogram for the distribution of analytes A and B, shows that 30 steps is sufficient to separate the two analytes.

Constructing a histogram using equation A16.2 is tedious, particularly when the number of steps is large. Because the fraction of analyte in most tubes is approximately zero, we can simplify the histogram's construction by solving equation A16.2 only for those tubes containing an amount of analyte exceeding a threshold value. For a binomial distribution, we can use the mean and standard deviation to determine which tubes contain a significant fraction of analyte. The properties of a binomial distribution were covered in Chapter 4, with the mean, μ, and the standard deviation, s, given as

$$\mu = np$$

$$\sigma = \sqrt{np(1-p)} = \sqrt{npq}$$

Furthermore, if both np and nq are greater than 5, the binomial distribution is closely approximated by the normal distribution and we can use the properties of a normal distribution to determine the location of the analyte and its recovery.[2]

Example A16.2

Two analytes, A and B, with distribution ratios of 9 and 4, respectively, are separated using a countercurrent extraction in which the volumes of the upper and lower phases are equal. After 100 steps determine the 99% confidence interval for the location of each analyte.

2   Mark, H.; Workman, J. *Spectroscopy* **1990**, *5(3)*, 55–56.

SOLUTION

The fraction, q, of each analyte remaining in the lower phase is calculated using underlined equation A16.1. Because the volumes of the lower and upper phases are equal, we find that

$$q_A = \frac{1}{D_A + 1} = \frac{1}{9 + 1} = 0.10$$

$$q_B = \frac{1}{D_B + 1} = \frac{1}{4 + 1} = 0.20$$

Because we know that $p + q = 1$, we also know that p_A is 0.90 and p_B is 0.80. After 100 steps, the mean and the standard deviation for the distribution of analytes A and B are

$$\mu_A = np_A = (100)(0.90) = 90 \text{ and } \sigma_A = \sqrt{np_A q_A} = \sqrt{(100)(0.90)(0.10)} = 3$$

$$\mu_B = np_B = (100)(0.80) = 80 \text{ and } \sigma_B = \sqrt{np_B q_B} = \sqrt{(100)(0.80)(0.20)} = 4$$

Given that np_A, np_B, nq_A, and nq_B are all greater than 5, we can assume that the distribution of analytes follows a normal distribution and that the confidence interval for the tubes containing each analyte is

$$r = \mu \pm z\sigma$$

where r is the tube's number and the value of z is determined by the desired significance level. For a 99% confidence interval the value of z is 2.58 (Appendix 4); thus,

$$r_A = 90 \pm (2.58)(3) = 90 \pm 8$$

$$r_B = 80 \pm (2.58)(4) = 80 \pm 10$$

Because the two confidence intervals overlap, a complete separation of the two analytes is not possible using a 100 step countercurrent extraction. The complete distribution of the analytes is shown in Figure A16.4.

Figure A16.4 Progress of the countercurrent extraction in Example A16.2 after 100 steps. Although analyte A moves more quickly than analyte B, the similarity of their distribution ratios, and thus the similarity in their values of q, means the separation of analytes A and B is not yet complete.

Example A16.3

For the countercurrent extraction in Example A16.2, calculate the recovery and separation factor for analyte A if the contents of tubes 85–99 are pooled together.

SOLUTION

From Example A16.2 we know that after 100 steps of the countercurrent extraction, analyte A is normally distributed about tube 90 with a standard deviation of 3. To determine the fraction of analyte A in tubes 85–99, we use the single-sided normal distribution in Appendix 3 to determine the fraction of analyte in tubes 0–84, and in tube 100. The fraction of analyte A in tube 100 is determined by calculating the deviation z

$$z = \frac{r - \mu}{\sigma} = \frac{99 - 90}{3} = 3$$

and using the table in Appendix 3 to determine the corresponding fraction. For $z = 3$ this corresponds to 0.135% of analyte A. To determine the fraction of analyte A in tubes 0–84 we again calculate the deviation

$$z = \frac{r - \mu}{\sigma} = \frac{85 - 90}{3} = -1.67$$

From Appendix 3 we find that 4.75% of analyte A is present in tubes 0–84. Analyte A's recovery, therefore, is

$$100\% - 4.75\% - 0.135\% \approx 95\%$$

To calculate the separation factor we determine the recovery of analyte B in tubes 85–99 using the same general approach as for analyte A, finding that approximately 89.4% of analyte B remains in tubes 0–84 and that essentially no analyte B is in tube 100. The recover for B, therefore, is

$$100\% - 89.4\% - 0\% \approx 10.6\%$$

and the separation factor is

$$S_{B,A} = \frac{R_A}{R_B} = \frac{10.6}{95} = 0.112$$

Appendix 17: Review of Chemical Kinetics

A reaction's equilibrium position defines the extent to which the reaction can occur. For example, we expect a reaction with a large equilibrium constant, such as the dissociation of HCl in water

$$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

to proceed nearly to completion. A large equilibrium constant, however, does not guarantee that a reaction will reach its equilibrium position. Many reactions with large equilibrium constants, such as the reduction of MnO_4^- by H_2O

$$4MnO_4^-(aq) + 2H_2O(l) \rightleftharpoons 4MnO_2(s) + 3O_2(g) + 4OH^-(aq)$$

do not occur to an appreciable extent. The study of the rate at which a chemical reaction approaches its equilibrium position is called kinetics.

A17.1 Chemical Reaction Rates

A study of a reaction's kinetics begins with the measurement of its reaction rate. Consider, for example, the general reaction shown below, involving the aqueous solutes A, B, C, and D, with stoichiometries of a, b, c, and d.

$$aA + bB \rightleftharpoons cC + dD \qquad\qquad \text{A17.1}$$

The rate, or velocity, at which this reaction approaches its equilibrium position is determined by following the change in concentration of one reactant or one product as a function of time. For example, if we monitor the concentration of reactant A, we express the rate as

$$R = -\frac{d[A]}{dt} \qquad\qquad \text{A17.2}$$

where R is the measured rate expressed as a change in concentration of A as a function of time. Because a reactant's concentration decreases with time, we include a negative sign so that the rate has a positive value.

We also can determine the rate by following the change in concentration of a product as a function of time, which we express as

$$R' = -\frac{d[C]}{dt} \qquad\qquad \text{A17.3}$$

Rates determined by monitoring different species do not necessarily have the same value. The rate R in equation A17.2 and the rate R' in equation A17.3 have the same value only if the stoichiometric coefficients of A and C in reaction A17.1 are identical. In general, the relationship between the rates R and R' is

$$R = \frac{a}{c} \times R'$$

A17.2 The Rate Law

A rate law describes how a reaction's rate is affected by the concentration of each species in the reaction mixture. The rate law for reaction A17.1 takes the general form of

$$R = k[A]^{\alpha}[B]^{\beta}[C]^{\gamma}[D]^{\delta}[E]^{\varepsilon}\ldots \tag{A17.4}$$

where k is the rate constant, and α, β, γ, δ, and ε are the reaction orders of the reaction for each species present in the reaction.

There are several important points about the rate law in equation A17.4. First, a reaction's rate may depend on the concentrations of both reactants and products, as well as the concentration of a species that does not appear in the reaction's overall stoichiometry. Species E in equation A17.4, for example, may be a catalyst that does not appear in the reaction's overall stoichiometry, but which increases the reaction's rate. Second, the reaction order for a given species is not necessarily the same as its stoichiometry in the chemical reaction. Reaction orders may be positive, negative, or zero, and may take integer or non-integer values. Finally, the reaction's overall reaction order is the sum of the individual reaction orders for each species. Thus, the overall reaction order for equation A17.4 is $\alpha + \beta + \gamma + \delta + \varepsilon$.

A17.3 Kinetic Analysis of Selected Reactions

In this section we review the application of kinetics to several simple chemical reactions, focusing on how we can use the integrated form of the rate law to determine reaction orders. In addition, we consider how we can determine the rate law for a more complex system.

FIRST-ORDER REACTIONS

The simplest case we can treat is a first-order reaction in which the reaction's rate depends on the concentration of only one species. The best example of a first-order reaction is an irreversible thermal decomposition of a single reactant, which we represent as

$$A \rightarrow Products \tag{A17.5}$$

with a rate law of

$$R = -\frac{d[A]}{dt} = k[A] \tag{A17.6}$$

The simplest way to demonstrate that a reaction is first-order in A, is to double the concentration of A and note the effect on the reaction's rate. If the observed rate doubles, then the reaction must be first-order in A. Alternatively, we can derive a relationship between the concentration of A and time by rearranging equation A17.6 and integrating.

$$\frac{d[A]}{[A]} = -k\,dt$$

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -k\int_0^t dt \tag{A17.7}$$

Evaluating the integrals in equation A17.7 and rearranging

$$\ln\frac{[A]_t}{[A]_0} = -kt \tag{A17.8}$$

$$\ln[A]_t = -kt + \ln[A]_0 \tag{A17.9}$$

shows that for a first-order reaction, a plot of $\ln[A]_t$ versus time is linear with a slope of $-k$ and a y-intercept of $\ln[A]_0$. Equation A17.8 and equation A17.9 are known as integrated forms of the rate law.

Reaction A17.5 is not the only possible form of a first-order reaction. For example, the reaction

$$A + B \rightarrow \text{Products} \tag{A17.10}$$

will follow first-order kinetics if the reaction is first-order in A and if the concentration of B does not affect the reaction's rate. This may happen if the reaction's mechanism involves at least two steps. Imagine that in the first step, A slowly converts to an intermediate species, C, which rapidly reacts with the remaining reactant, B, in one or more steps, to form the products.

$$A \rightarrow B \quad \text{(slow)}$$

$$B + C \rightarrow \text{Products} \quad \text{(fast)}$$

Because a reaction's rate depends only on those species in the slowest step—usually called the rate-determining step—and any preceding steps, species B will not appear in the rate law.

SECOND-ORDER REACTIONS

The simplest reaction demonstrating second-order behavior is

$$2A \rightarrow \text{Products}$$

for which the rate law is

$$R = -\frac{d[A]}{dt} = k[A]^2$$

Proceeding as we did earlier for a first-order reaction, we can easily derive the integrated form of the rate law.

$$\frac{d[A]}{[A]^2} = -k\,dt$$

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = -k \int_0^t dt$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

For a second-order reaction, therefore, a plot of $[A]_t^{-1}$ versus t is linear with a slope of k and a y-intercept of $[A]_0^{-1}$. Alternatively, we can show that a reaction is second-order in A by observing the effect on the rate when we change the concentration of A. In this case, doubling the concentration of A produces a four-fold increase in the reaction's rate.

Example A17.1

The following data were obtained during a kinetic study of the hydration of p-methoxyphenylacetylene by measuring the relative amounts of reactants and products by NMR.[1]

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1   Kaufman, D,; Sterner, C.; Masek, B.; Svenningsen, R.; Samuelson, G. *J. Chem. Educ.* **1982**, *59*, 885–886.

time (min)	% p-methyoxyphenylacetylene
67	85.9
161	70.0
241	57.6
381	40.7
479	32.4
545	27.7
604	24

Determine whether this reaction is first-order or second-order in *p*-methoxyphenylacetylene.

SOLUTION

To determine the reaction's order we plot ln(%pmethoxyphenylacetylene) versus time for a first-order reaction, and (%p-methoxyphenylacetylene)$^{-1}$ versus time for a second-order reaction (see Figure A17.1). Because a straight-line for the first-order plot fits the data nicely, we conclude that the reaction is first-order in *p*-methoxyphenylacetylene. Note that when we plot the data using the equation for a second-order reaction, the data show curvature that does not fit the straight-line model.

PSEUDO-ORDER REACTIONS AND THE METHOD OF INITIAL RATES

Unfortunately, most reactions of importance in analytical chemistry do not follow the simple first-order or second-order rate laws discussed above. We are more likely to encounter the second-order rate law given in equation A17.11 than that in equation A17.10.

$$R = k[A][B] \qquad\qquad A17.11$$

Figure A17.1 Integrated rate law plots for the data in Example A17.1 assuming (a) first-order kinetics and (b) second-order kinetics.

Demonstrating that a reaction obeys the rate law in equation A17.11 is complicated by the lack of a simple integrated form of the rate law. Often we can simplify the kinetics by carrying out the analysis under conditions where the concentrations of all species but one are so large that their concentrations remain effectively constant during the reaction. For example, if the concentration of B is selected such that $[B] \gg [A]$, then equation A17.11 simplifies to

$$R = k'[A]$$

where the rate constant k' is equal to $k[B]$. Under these conditions, the reaction appears to follow first-order kinetics in A and, for this reason we identify the reaction as pseudo-first-order in A. We can verify the reaction order for A using either the integrated rate law or by observing the effect on the reaction's rate of changing the concentration of A. To find the reaction order for B, we repeat the process under conditions where $[A] \gg [B]$.

A variation on the use of pseudo-ordered reactions is the initial rate method. In this approach we run a series of experiments in which we change one at a time the concentration of those species expected to affect the reaction's rate and measure the resulting initial rate. Comparing the reaction's initial rate for two experiments in which only the concentration of one species is different allows us to determine the reaction order for that species. The application of this method is outlined in the following example.

Example A17.2

The following data was collected during a kinetic study of the iodation of acetone by measuring the concentration of unreacted I_2 in solution.[2]

experiment number	$[C_3H_6O]$ (M)	$[H_3O^+]$ (M)	$[I_2]$ (M)	Rate (M s^{-1})
1	1.33	0.0404	6.65×10^{-3}	1.78×10^{-6}
2	1.33	0.0809	6.65×10^{-3}	3.89×10^{-6}
3	1.33	0.162	6.65×10^{-3}	8.11×10^{-6}
4	1.33	0.323	6.65×10^{-3}	1.66×10^{-5}
5	0.167	0.323	6.65×10^{-3}	1.64×10^{-6}
6	0.333	0.323	6.65×10^{-3}	3.76×10^{-6}
7	0.667	0.323	6.65×10^{-3}	7.55×10^{-6}
8	0.333	0.323	3.32×10^{-3}	3.57×10^{-6}

SOLUTION

The order of the rate law with respect to the three reactants is determined by comparing the rates of two experiments in which there is a change in concentration for only one of the reactants. For example, in experiment 2 the $[H_3O^+]$ and the rate are approximately twice as large as in experiment 1, indicating that the reaction is first-order in $[H_3O^+]$. Working in the same manner, experiments 6 and 7 show that the reaction is also first order with respect to $[C_3H_6O]$, and experiments 6 and 8 show that the rate of the reaction is independent of the $[I_2]$. Thus, the rate law is

$$R = k[C_3H_6O][H_3O^+]$$

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2   Birk, J. P.; Walters, D. L. *J. Chem. Educ.* **1992**, *69*, 585–587.

To determine the value of the rate constant, we substitute the rate, the $[C_3H_6O]$, and the $[H_3O^+]$ for each experiment into the rate law and solve for k. Using the data from experiment 1, for example, gives a rate constant of 3.31×10^{-5} M^{-1} sec^{-1}. The average rate constant for the eight experiments is 3.49×10^{-5} M^{-1} sec^{-1}.