Chapter 19.   Chemical Equilibria

19.1. Dynamic Equilibrium

Two fundamental questions to address for any chemical reaction are *where is the reaction going* and *how fast is it getting there*? Chemical reactions go to a state of **equilibrium**, where there is no further detectable change in amounts of the participants in the reaction. As we shall see, although the amounts of substances participating in a reaction follow the laws of stoichiometry, it is not necessary, and indeed is usually *not* the case, that the maximum amount of product will be produced, even if there is no limiting reagent. Where reactions are going is the subject of the present chapter. How fast reactants get to products is the subject of chemical kinetics (Chapter 18).

The notion of equilibrium connotes *stasis*, lack of motion, lack of change. On the macroscopic scale this means that ordinary measuring apparatus can no longer detect any change, if one occurred at all. The quantities of interest which change as a chemical reaction approaches equilibrium are the amounts of substances, usually measured in terms of grams or mols for gases, liquids or solids, and concentrations for solutions. Concentration is usually measured in molarity for for liquid solutions and partial pressures for gaseous solutions.

The fundamental notion of chemical equilibrium is that *all chemical reactions are reversible, to some extent*. This means that after a reaction has had time to equilibrate, there will always be some remaining reactants as well as products produced. To be sure, the *amounts* of reactants or products left may so small that the reaction will be observed to "go to completion", or perhaps to not "go" at all, but in many reactions of practical interest, significant amounts of both products and reactants remain after a very long time.

The equations which govern chemical equilibria are relatively simple, involving concentrations to powers and exponential functions of temperature. These functional forms are similar to those found in the study of kinetics and suggest an association between equilibrium and kinetics. This association is called *microscopic reversibility*, which says that although there may not be any observed changes occurring on the macroscopic scale, on the *microscopic* (molecular) scale, much is happening indeed.

Consider a jar containing water. If left open, the water eventually evaporates. It takes some time to evaporate (at ordinary temperatures) because liquid molecules must surmount the bonding barrier at the surface of the liquid before they can vaporize. Now consider what appears to happen when a lid is placed on the jar. If evacuated above the liquid initially, some liquid vaporizes as evidenced by a careful measurement of the height of the surface. Eventually, the surface ceases to descend, signaling the onset of an equilibrium state. However, if the molecules were visible, we would find that at the surface molecules are leaving and returning at rapid rates. The reason the surface level doesn't change is due to the fact that *the rate of condensation has become equal to the rate of evaporation*. This state of apparent macroscopic calm with microscopic frenzy is referred to as **dynamic equilibrium**[1]

Dynamic equilibrium forms a bridge between equilibrium and kinetics. For a general reversible reaction,

$$aA + bB + \cdots = pP + qQ + \ldots, \tag{19.1}$$
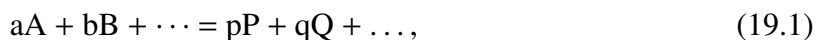
When the backward and forward rates become equal, the concentrations reach steady (constant) state values. From the kinetic rate law, Eq. (8.12).[2]

$$r_{backward} = r_{forward}$$

$$k_{backward} \prod_{i}^{P}(C_e)_i^{n_i} = k_{forward} \prod_{i}^{R}(C_e)_i^{n_i}$$

$$K \equiv \frac{k_{forward}}{k_{backward}} = \prod_{i}^{P}(C_e)_i^{n_i} - \prod_{i}^{R}(C_e)_i^{n_i}$$

---

[1] One way to demonstrate dynamic equilibrium directly is to inject some liquid *tritiated* water (water containing the hydrogen isotope of mass three). Since tritium is radioactive, its presence may be detected with a radioactive sensitive counter. No matter which phase is tritiated, very soon, radioactivity is detected in both phases, changing in intensity until it becomes equal in abundance (fraction) in both phases.

[2] Although derived for a one-step process, the result is valid for a multi-step process as shown below.

$$K = \prod_{i}^{\times P/R} (C_e)_i^{n_i} = \frac{[P]_e^p [Q]_e^q \cdots}{[A]_e^a [B]_e^b \cdots} \qquad (19.2)$$

where square brackets are an alternative notation denoting concentrations which prove convenient when additional subscripts are used to express concentration conditions. This equation is called the **law of mass action**. The *units* of K depend on the units chosen for concentration. By convention molarities are used for solutions and atmospheres for gases, which are proportional to molarity for ideal gases:

$$p = \left(\frac{n}{V}\right)RT = MRT$$

Pure liquids and solids are not dissolved in anything and have no concentration. However their densities have the dimensions of concentration. Since densities are constant, their values may be combined with the other constants in the equation, effectively (but not actually) rendering their concentrations equal to unity. The convention is that K includes any such constants. Subscripts on K are used to provide additional information, such as units (K_C for molarity, K_p for pressure), class of reaction (K_i for ionization, K_{sp} for solubility product), etc. In practice, the units on K (which can be mixed and of fractional power) are usually not included with the numerical value, and are inferred from the reaction, which should always be given (including phases) to avoid any ambiguity in K.

Unlike the general rate law equation, *in the mass action equation the powers of concentrations are always identical to the stoichiometric coefficients in the balanced chemical equation*. This suggests that equilibrium is independent of reaction mechanism, which follows qualitatively from the idea that products must return to reactants over the same path as reactants pursued to products. This argument is made plausible by considering what could happen if alternate paths could be used to communicate between reactants and products. In such a case it would be possible to tap the cycle to generate energy without doing any work, thereby producing a perpetual motion machine, violating the laws of thermodynamics.

Note that, according to the definition of K, doubling a reaction generates a corresponding K that is *squared*, and in general *multiplying a reaction by a factor n raises the corresponding K to the nth power*.

$$R \rightarrow nR => K \rightarrow K^n \qquad (19.3)$$
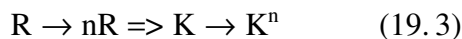
As a special case, *reversing* a reaction (multiplying the reaction equation by minus one) causes K to be *inverted* (1/K).

K is a positive number which indicates what the ratio of products to reactants is at equilibrium. It is a proportionality constant between reactant concentrations and product concentrations; roughly $C_P = KC_R$. When $K < 1$, then the product of the reactant concentrations (raised to powers) is less than the product of the product concentrations (raised to powers), and the reaction is said to "lie to the left", or "favor reactants". Conversely, when $K > 1$, the opposite situation exists, and the reaction is said to "lie to the right", or "favor products". K = 1 indicates comparable amounts of reactants and products at equilibrium. The following table summarizes the general situation.

Table 19.1. Magnitude of the Equilibrium Constant

K	P/R	Situation
$K < 1$	$P < R$	Reactants dominate (lies left)
$K = 1$	$P = R$	Reactants $\approx$ Products (balanced)
$K > 1$	$P > R$	Products dominate (lies right)

The temperature dependence of the equilibrium constant can also be derived from the temperature dependencies of forward and backward rate coefficients:

$$K(T) = \frac{k(T)_{forward}}{k(T)_{backward}} = \frac{A\,e^{-\frac{E_a^{forward}}{RT}}}{A\,e^{-\frac{E_a^{backward}}{RT}}} = e^{-\left(\frac{E_a^{forward} - E_a^{backward}}{RT}\right)} \qquad (19.4)$$

Note that $E_{forward} - E_{backward} = \Delta E_{reaction}$.

19.2. General Mass Action

Equilibrium is a special case of a more general situation with arbitrary amounts of reactants and products. A more general derivation requires a more general theory, and we turn to thermodynamics to derive expressions for the general situation. The natural thermodynamic

quantity for chemical reactions is the Gibbs free energy, ΔG. Expressing ΔG in terms of ΔH by Eq. (13.27), and ΔH in terms of ΔE by Eq. (13.25) (using the product rule of differentiation), we have for a process taking place at a given temperature,

$$\Delta G = \Delta H - T\Delta S = \Delta E + P\Delta V + V\Delta P - T\Delta S \tag{19.5}$$

From Eq. (13.1) $\Delta E = q + w$. Expressing the heat for a process taking place at constant temperature as $q = T\Delta S$ from Eq. (13.13) (see Eq. (13.14)), and the work at constant pressure as $w = -P\Delta V$, leaves

$$\Delta G = V\Delta P \tag{19.6}$$

From the ideal gas law, Eq. (15.7), $PV = (\frac{n}{V})RT = CRT$, where C represents concentration (molarity or pressure, which is proportional to molarity). Taking the limit of small changes in Eq. (19.6), and noting that at constant temperature $dP = RTdC$ and $V = n/C$ from the definition of molarity, we have (cf. Table 3.1)

$$dG = \frac{n}{C} RT\, dC = nRT\, \frac{dC}{C} = nRT\, d\ln(C) \tag{19.7}$$

Integrating (cf. Table 3.1)

$$G - G^0 = nRT\, \ln(C) - nRT\, \ln(C^0) = nRT\, \ln(\frac{C}{C^0}) \tag{19.8}$$

The reference state is called the *standard state* and refers to unit concentrations ($C^0 = 1$), leaving

$$G = G^0 + nRT\, \ln(C) \equiv G^0 + RT\, \ln(C^n) \tag{19.9}$$

Now consider a chemical reaction.

$$\Delta G_{rxn} = G_{products} - G_{reactants} \tag{19.10}$$

There is a relationship like Eq. (19.9) for each component, leading to an expression for the total difference in free energy between products and reactants:

$$\Delta G_{rxn} = \Delta G_{rxn}^0 + RT\, \ln \prod^{+P, -R} C_i{}^{n_i} \equiv \Delta G_{rxn}^0 + RT\, \ln(Q) \tag{19.11}$$

where Q, called the **reaction quotient**, is the quotient of products of product and reactant concentrations raised to powers equal to the stoichiometric coefficients in the balanced

chemical equation:

$$Q \equiv \prod_i^{\times P / R} C_i^{n_i} = \frac{[P]^p [Q]^q \cdots}{[A]^a [B]^b \cdots} \qquad (19.12)$$

Applying the thermodynamic condition for equilibrium, $\Delta G_{rxn} = 0$, to Eq. (19.11) leads to

$$\Delta G_{rxn}^0 = - RT \ln \prod^{+P, -R} (C_e)_i^{n_i} \qquad (19.13)$$

Identifying the product on the right as the equilibrium constant in Eq. (19.2) gives

$$\Delta G_{rxn}^0 = - RT \ln(K) \qquad (19.14a)$$

$$K(T) = e^{-\frac{\Delta G_{rxn}^0}{RT}} \qquad (19.14b)$$

R is the molar gas constant in energy units, 8.31441 J/mol-K. This fundamental relationship links thermodynamics to equilibrium. Given the equilibrium constant for a reaction (from experiment), the free energy of reaction can be calculated from Eq (19.4a). Conversely given the free energy of reaction (from thermodynamic tables), the equilibrium constant can be calculated from Eq (19.4b).

Example 19.1 Estimate the vapor pressure of water at 25 °C.

Vapor pressure is due to equilibrium between liquid and gas: $H_2O(\text{liquid}) = H_2O(\text{gas})$, for which the equilibrium constant equals the vapor pressure: $K_p = p_{H_2O}$. (Recall that concentrations for gaseous reactants are expressed in atmospheres, and that pure liquids do not enter the mass action expression.)

The free energy of vaporization can be obtained from tables of formation free energies. $\Delta G_{vaporization} = \Delta G_f(\text{gas}) - \Delta G_f(\text{liquid})$. At standard temperature (25 °C), the values combine to $\Delta G_{vaporization} = -228.6 \text{ kJ} - (-237.2 \text{ kJ}) = 8.6 \text{ kJ}$.

The van't Hoff equation (when rearranged to solve for K) is

$$K_p(25°C) = p_{H_2O} = \exp(-\frac{\Delta G^0_{vap}}{RT}) = \exp(-\frac{8,600}{8.31441 \times 298.15}) = 0.0311 \text{ atm } (\frac{760 \text{ torr}}{1 \text{ atm}}) = 23.6 \text{ torr.}$$

Note that ΔG is converted to Joules to be compatible with R and that 25 °C is converted to Kelvin. The vapor pressure of 23.6 torr compares very well with the experimental value of 23.76 torr.

Combining Eq. (19.11) and (19.14) leads to a general relationship:

$$\Delta G_{rxn} = RT \ln \frac{Q}{K} \qquad (19.15)$$

We will refer to this connection between thermodynamics and reaction equilibrium as the **generalized law of mass action, or van't Hoff equation**. Note that $Q = 1$ recovers Eq. (19.14) and $Q = K$ recovers the equilibirum condition $\Delta G = 0$.

If an arbitrary mixture of reactants and/or products is allowed to react, Q indicates how the reaction will proceed. If Q is less than K, product concentrations are too low for equilibrium and/or reactant concentrations are too high, so the reaction builds up products at the expense of reactants (the reaction (19.1) proceeds to the right). The opposite holds for $Q > K$. Unlike the Arrhenius equation for kinetics where the activation energy is (for all practical purposes) always positive, leading to a universal increase in rate coefficient with increasing temperature, ΔG_{rxn} will be positive for endothermic reactions but negative for exothermic reactions, with the result that the equilibrium constant will increase with increasing temperature for endothermic reactions, but *decrease* with increasing temperature for exothermic reactions (Eq. (19.14)). The equilibrium constant increases (reaction shifts right) with increasing temperature for endothermic reactions, and decreases (reaction shifts left) with increasing temperature for exothermic reactions. This is one manifestation of **Le Chatelier's Principle**, which says essentially, *equilibria shift to offset stress*.[3] Applied to the concentration relationship of the law of mass action, Le Chatelier's Principle says that perturbing an equilibrium system by adding or removing a reactant or product will cause a shift in the equilibrium which tends to remove or replace it, respectively. The shift is not absolute in the sense that the added substance is completely removed or the removed substance is completely replaced, however. Reactants and products will all adjust simultaneously until the ratio of products and reactants again equals the value of the equilibrium constant, according to the mass action law,

———————————

[3] This fundamental principle, borrowed from chemistry, has been applied ubiquitously to many areas, from psychology (people like to remain "status quo"), to economics (law of "supply and demand").

Eq. (19.3). The following table summarizes the general situation.

Table 19.2. Reaction quotient *vs* Equilibrium Constant

Q/K	ΔG	Situation
Q < K	ΔG < 0	P ← R (goes left)
Q = K	ΔG = 0	P = R (equilibrium)
Q > K	ΔG > 0	P → R (goes right)

19.3. Mass Action Calculations

The law of mass action and the van't Hoff equation constitute the fundamental relations of equilibrium. *Equilibrium applications involve solving the mass action or van't Hoff equation for one unknown.* This suggests that values for all the variables but one must be provided in equilibrium calculations. In the case of concentrations, values may not be given explicitly, but may be inferred from the balanced chemical equation. Stoichiometric ratios effectively provide additional equations to reduce the number of unknowns. Although the algebra can become subtle, the fact remains that one equation can be solved for only one unknown. The *key to solving equilibrium problems is to reduce the problem to one equation in one unknown.*

The "law" of mass action, Eq. (19.2), is an equation involving three types of quantities, concentrations ([A], [B], etc), powers of concentration (a, b, etc) and equilibrium constant (K). For a given reaction, the stoichiometric factors a, b, etc are known. Although K is a parameter (constant for a given reaction), rather than a variable like concentration, there are times when the value of K may be sought. For example, the value of the parameter K must be determined experimentally from equilibrium experiments before it can be used in predicting other experimental conditions. Thus mass action problems fall into two categories: concentration(s) unknown, given the balanced reaction and K, or K unknown, given the balanced reaction and concentrations. *The balanced chemical equation provides stoichiometric relations between the concentrations which may used to effectively reduce the number of unknowns to unity.* The Mass Action Table introduced in the algorithm below helps organize the stoichiometry. This perspective leads to an algorithm for solving problems based on the mass action law. Some facility with algebra may be required to cast equilibrium concentrations in terms of one variable, and to solve the (polynomial) mass action equation.[4]

------

[4] Introductory chemistry problems are usually restricted to linear and quadratic equations, easily solved by humans. Higher-order equations that appear are reduced to lower degree through approximations. Computers

The Mass Action Equilibrium Algorithm

Purpose: To apply the law of mass action, Eq. (19.2) to equilibrium calculations.

Procedure:

1. Write down the balanced chemical reaction for the process being considered:
    $aA + bB + \cdots = pP + qQ + \cdots$

2. Identify the givens and unknowns from the input. If some of the concentrations are not known, construct a **mass action table** to organize stoichiometric ratios in terms of a common variable, x (values are in mols or concentrations, consistent with initial values before reaction takes place, x is the change from the Initial state to the Final state, and Final refers to equilibrium):

	aA	+	bB	+ ...	=	pP	+	qQ	+ ...
Initial:	a_0		b_0	...		p_0		q_0	...
Change:	$-ax$		$-bx$	...		$+px$		$+qx$	...
Final:	$a_0 - ax$		$b_0 - bx$	...		$p_0 + px$		$q_0 + qx$	...

3. Solve the mass action equation for the appropriate unknown variable K, concentration ([ ]), or x: $K = \dfrac{[P]^p[Q]^q \cdots}{[A]^a[B]^b \cdots}$ or $K = \dfrac{[p_0 + px]^p[q_0 + qx]^q \cdots}{[a_0 - ax]^a[b_0 - bx]^b \cdots}$.

4. Convert any requested concentrations expressed as functions of x to final concentrations from the entries in the mass action table.

Example 19.2 Find the value of K for the reaction between dihydrogen and diiodine, given the experimental observation that introduction of H_2 at an initial concentration of 5.30 M and I_2 at an initial concentration of 7.94 M into a flask results in an observed equilibrium concentration of HI of 9.49 M, all values at 717.7 K.

---

can solve equations of any degree approximately, using numerical algorithms. See Section 3.6 on Solving General Equations for One Variable.

1. The chemical equation must be identified, or K cannot be defined. Since reactants are dihydrogen and diiodine, and the product concentration of hydrogen iodide is given, it may be assumed no other products are formed. The balanced reaction and associated mass action equation, then, are:

$$H_2 + I_2 = 2\,HI$$

$$K = \frac{C_{HI}}{C_{H_2}C_{I_2}} \equiv \frac{[HI]^2}{[H_2][I_2]}$$
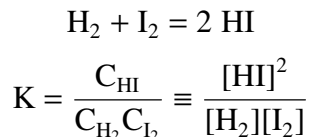
2. The givens are initial concentrations of H_2 and I_2 and the equilibrium concentration of HI. Unknowns are the equilibrium concentrations of H_2 and I_2 and the value of K. Since the equilibrium concentrations for H_2 and I_2 are not explicitly given, they must be deduced from the balanced chemical equation. The mass action table is:

	H_2	+	I_2	$\rightleftharpoons$	2HI
Initial:	5.30		7.94		0
Change:	−x		−x		+2x
Final:	5.30−x		7.94−x		2x = 9.49

Note that the variable x is written as an unknown related to the given final concentration of HI: $x = 9.49/2 = 4.745$. The equilibrium concentrations of H_2 and I_2 can now be readily obtained from the expressions for their final concentrations:

$$[H_2]_f = 5.30 - 4.745 = 0.555\ M$$

$$[I_2]_f = 7.94 - 4.745 = 3.195\ M$$

The mass action equation can now be solved for K:

$$K = \frac{(9.49)^2}{(0.555)(3.195)} = 50.8$$

Example 19.3 Find the values of the concentrations of all species at equilibrium if H_2 and I_2 are introduced into a flask with initial concentrations of 5.30 M and 7.94 M, respectively. The value of the equilibrium constant is 50.8 at 717.7 K. (This is the inverse problem of the previous example.)

1. The chemical equation may be inferred to be the same as that of the previous example:
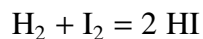
$$H_2 + I_2 = 2\,HI$$

$$K = \frac{[HI]^2}{[H_2][I_2]}$$

2. Since none of the equilibrium concentrations are given, construct the mass action table:

	H$_2$	+	I$_2$	$\Longrightarrow$	2HI
Initial:	5.30		7.94		0
Change:	−x		−x		+2x
Final:	5.30−x		7.94−x		2x

3. In this case the variable x is unknown, and must be found from the mass action equation:

$$K = \frac{(2x)^2}{(5.30-x)(7.94-x)} = 50.8$$

Expanding and collecting terms in x gives:

$$0.921x^2 - 13.24x + 42.08 = 0$$

The Quadratic Equation Solving Algorithm from Section 3.5 may be employed to solve for x = 4.745. The equilibrium concentrations of H$_2$ and I$_2$ can now be readily obtained:

$$H_2 = 5.30 - 4.745 = 0.56\ M$$

$$I_2 = 7.94 - 4.745 = 3.20\ M$$

$$HI_2 = 2 \times 4.745 = 9.49\ M$$

It would prove instructive to solve the quadratic equation from the last example using the iteration method of section 3.8. It is more tedious than applying the quadratic formula, but becomes essential when higher degree polynomials result from the Mass Action Equilibrium Algorithm.

Before leaving the general subject of equilibria it is worthwhile observing that in many industrial processes reactions are not permitted to reach equilibrium. This can be achieved by removing products or continually recycling reactants. In such *flow* processes, it is possible to drive reactions asymptotically to completion using Le Chatelier's principle.

19.4. Solubility Equilibria

Slightly soluble salts have equilibria constants called *solubility product constants*, K_{sp}. Solubility is measured by the amount which dissolves so if dissociation occurs, stoichiometric ratios must be considered. For a typical salt comprised of a metal (M) and nonmetal (N) part,

$$M_m N_n = mM^{n+} + nN^{m-}$$

If s represents the mols of $M_m N_n$ dissolved, then there are ms mols of M^{n+} and ns mols of N^{m-} produced. The general expression for the solubility product is

$$K_{sp} = C_{M^{n+}}^m \, C_{N^{m-}}^n = (ms)^m (ns)^n = m^m n^n s^{m+n} \tag{19.16}$$

Example 19.4 What is the molar solubility of Bi_2S_3 in water if $K_{sp} = 1.6 \times 10^{-72}$?

In this case m = 2 and n = 3 so $K_{sp} = 2^2 3^3 s^5 = 108 s^5$ and $s = (\dfrac{K_{sp}}{108})^{1/5} = 1.7 \times 10^{-15}$ M.

19.5. Acid Base Equilibria

Alchemists divided substances into three general categories, depending on certain properties of their aqueous solutions. **Acidic solutions** taste sour (L. *aciditus*) and turn litmus fungus red. **Basic solutions** taste bitter (L. *low*) and turn litmus fungus blue. **Salt solutions** are neither acidic nor basic and may result from **neutralization** reactions between acidic solutions and basic solutions, or directly from dissolving salts into water. Acids and bases are further classified as *strong or weak*. For practical purposes *the common strong acids are nitric, sulfuric, hydrochloric, hydrobromic and hydroiodic; other common acids may be assumed to be weak; the only common strong bases contain hydroxide ion*. A more refined, quantitative measure of acid and base strength is based on equilibrium concepts.

The notion of chemical substances as compounds of elementary matter led to the idea that acids and bases have something common to their class which distinguishes their

categories. Lavoisier, who was fascinated with the role of oxygen in combustion, corrosion and respiration, believed that oxygen was a common component in all acids. This is not inconsistent with modern observation for several acids (HNO_3, H_3PO_4, etc.), but inconsistent for others, including common hydrochloric ("muriatic") acid, formed by dissolving hydrogen chloride gas into water.

An improved explanation of acidic and basic behavior, given by Arrhenius near the end of the Nineteenth Century, assumed that acids produce hydrogen ions in water, and bases produce hydroxide ions; Neutralization was described as ''acid plus base gives salt plus water''. Arrhenius' concept of acids and bases could account for much of the behavior of acids and bases, but unfortunately could not explain, for example, why ammonia gas dissolved in water produces a basic solution.

An more general notion of acids and bases was published independently by Bronsted and Lowry around 1923. This concept adopted Arrhenius' notion of acids, but expanded the base concept to include any substance which accepts protons. Neutralization, according to Bronsted and Lowery, involves the *transfer* of a proton from an acid to a base, producing in the products another acid and base, said to be ''conjugate'' to the reactant base and acid, respectively. Bronsted linked acids and bases in **conjugate pairs**, which are related by the acceptance or release of a proton. Neutralization in the Bronsted sense states that an acid reacts with a base to produce a new acid and new base through the transfer of a proton. A significant insight of the Bronsted approach is the recognition of the role of the solvent, water, which can act as either an acid (proton donor), *or* a base (proton acceptor). Such ability to play the dual role of reacting as an acid or a base is called **amphoterism**.

A useful heuristic envisions acid/base reactions as occurring in two steps, one with the acid producing the proton and the other with the base accepting a proton. Such component steps are called ''half reactions''. A complete acid/base reaction results from combining two half reactions in such a way that protons are conserved (transferred without loss or gain). Subtracting two half reactions ensures this requirement.

A listing of half reactions, called a *Bronsted Table*, summarizes a multitude of possible acid/base combinations (n entries can be combined into $n(n-1) \approx n^2$ pairs). *Total reactions are always constructed by subtracting two half reactions (to cancel protons).*[5] Similar to the

———————

[5] Note that, just like arithmetic and algebra, *subtracting* two chemical half reactions is equivalent to *reversing* one half reaction and *adding* it to the other.

way a periodic of element properties can be used to deduce the properties of many combinations of elements, a table of half reactions can be used to derive information regarding a large number of total reactions obtained by combining two half reactions.

In the Bronsted Table given below, acids are on the left with their conjugate bases on the right, with the general reaction given at the head. The notation HB^q denotes a Bronsted acid with a general charge q, capable of dissociating to a proton and its conjugate base with one less charge, B^{q-1}. The value of q can be positive, negative or zero, as illustrated by the entries in the table, with the common case of negative values resulting from ionization of neutral acids (q = 0). Acids are listed according to decreasing *strength* (value of K_a), with their conjugate bases increasing in strength. The values of K_a give a quantitative measure of acid strength, but qualitative trends can be deduced from a consideration of bond strengths. A useful heuristic is that *the strength of hydro acids of the form HB, increases with decreasing strength of the H-B bond*. The relative strengths of H-B bonds can be deduced from the *charge density* (charge/size ratio) on the B atom. *The larger the charge density on B, the stronger the H-B bond, and the weaker the acid*. This can be illustrated with the hydrohalide acids, HBr, HCl, and HF. According to The Periodic Trend Algorithm of Section 8.4, fluorine is smaller than chlorine, which is in turn smaller than bromine. Thus charge density increases with decreasing size in the order Br, Cl, F, and HB bond strength increases and acid strength decreases in the same order. Actual bond strengths are given in Example 12.13: HBr(378 kJ/mol), HCl(477 kJ/mol), HF(590 kJ/mol). Oxyacids, of the form HOB, have a proton bound to oxygen, which is in turn bound to B. In this case, the proton responds to the charge density on B indirectly, and *the strength of oxy acids of the form HOB, increases with decreasing strength of the H-O bond, caused by increasing strength of the B-O bond*. Therefore, increasing the charge density on B strengthens the B-O bond, and drawing the electron cloud into the bond *weakens* the O-H bond. Thus *the larger the charge density on B, the stronger the O-B bond, the weaker the O-H bond, and the stronger the acid*. Thus, going across the second row of the periodic table the charge on the element (oxidation number) increases while the size decreases.

Table 19.3. Properties of Hydroxy Compounds of the Second Row of the Periodic Table

Compound	Name	Oxidation Number	pK_a	Classification
NaOH	sodium hydroxide	+1(Na)	14	strong base
$Mg(OH)_2$	magnesium hydroxide	+2(Mg)	insoluble	strong base
$Al(OH)_3$	aluminum hydroxide	+3(Al)	11.2	amphoteric
$OSi(OH)_2$	silicic acid	+4(Si)	9.6	very weak acid
$OP(OH)_3$	sulfurous acid	+5(P)	2.1	weak acid
$O_2S(OH)_2$	sulfuric acid	+6(S)	−2	strong acid
O_3ClOH	perchloric acid	+7(Cl)	−7.3	very strong acid

This trend is further is illustrated by the oxyhalo acids, such as $HClO$, $HClO_2$, $HClO_3$, and $HClO_4$. In this case the charge density increases with the formal charge on Cl (values are +1, +3, +5, +7 in the order listed). Acid strength increases in the same order, as seen in the Bronsted Table.
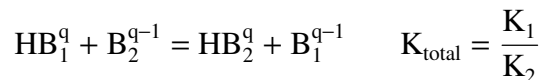
Table 19.4 The Bronsted Table

Name	$HB^{q+1} = H^+ + B^q$	$K_a(25°C)$	pK_a
Hydrobromic	$HBr = H^+ + Br^-$	$\approx 10^{+9}$	-9
Hydrochloric	$HCl = H^+ + Cl^-$	$3 \times 10^{+8}$	-8.5
Perchloric	$HClO_4 = H^+ + ClO_4^-$	$2 \times 10^{+7}$	-7.3
Permanganic	$HMnO_4 = H^+ + MnO_4^-$	$\approx 10^{+8}$	-8
Chloric	$HClO_3 = H^+ + ClO_3^-$	$5 \times 10^{+2}$	-2.7
Sulfuric (1)	$H_2SO_4 = H^+ + HSO_4^-$	$1 \times 10^{+2}$	-2
Nitric	$HNO_3 = H^+ + NO_3^-$	$2 \times 10^{+1}$	-1.3
Hydronium (1)	$H_3O^+ = H^+ + H_2O$	$1.00 = 10^0$	0.00
Trichloroacetic	$CCl_3COOH = H^+ + CCl_3COO^-$	2×10^{-1}	0.70
Oxalic (1)	$HOOCCOOH = H^+ + HOOCCOO^-$	5.90×10^{-2}	1.23
Dichloroacetic	$CHCl_2COOH = H^+ + CHCl_2COO^-$	3.32×10^{-2}	1.48
Sulfurous (1)	$H_2SO_3 = H^+ + HSO_3^-$	1.54×10^{-2}	1.81
Sulfuric (2)	$HSO_4^- = H^+ + SO_4^{2-}$	1.20×10^{-2}	1.92
Chlorous	$HClO_2 = H^+ + ClO_2^-$	1×10^{-2}	2.0
Phosphoric (1)	$H_3PO_4 = H^+ + H_2PO_4^-$	7.52×10^{-3}	2.12
Glycinium ion (1)	$CH_2(NH_3)COOH^+ = H^+ + CH_2(NH_2)COOH$	4.46×10^{-3}	2.35
Hydrotelluric (1)	$H_2Te = H^+ + HTe^-$	2.3×10^{-3}	2.64
Bromoacetic	$CH_2BrCOOH = H^+ + CH_2BrCOO^-$	2.05×10^{-3}	2.69
Chloroacetic	$CH_2ClCOOH = H^+ + CH_2ClCOO^-$	1.40×10^{-3}	2.85
Nitrous	$HNO_2 = H^+ + NO_2^-$	4.6×10^{-4}	3.34
Hydrofluoric	$HF = H^+ + F^-$	3.53×10^{-4}	3.45
Formic	$HCOOH = H^+ + HCOO^-$	1.77×10^{-4}	3.75
Hydroselenic (1)	$H_2Se = H^+ + HSe^-$	1.7×10^{-4}	3.77
Benzoic	$C_6H_5COOH = H^+ + C_6H_5COO^-$	6.46×10^{-5}	4.19
Oxalic (2)	$HOOCCOO^- = H^+ + {}^-OOCCOO^-$	6.4×10^{-5}	4.19
Acetic	$CH_3COOH = H^+ + CH_3COO^-$	1.76×10^{-5}	4.75
Aluminum ion hydrate (1)	$Al(H_2O)_n^{3+} = H^+ + Al(OH)(H_2O)_{n-1}^{2+}$	1.5×10^{-5}	4.82
Propionic	$CH_3CH_2COOH = H^+ + CH_3CH_2COO^-$	1.34×10^{-5}	4.87
Hydrotelluric (2)	$HTe^- = H^+ + Te^{2-}$	1×10^{-5}	5.0
Carbonic (1)	$CO_2 + H_2O = H^+ + HCO_3^-$	4.3×10^{-7}	6.37
Sulfurous (2)	$HSO_3^- = H^+ + SO_3^{2-}$	1.02×10^{-7}	6.91
Hydrosulfuric (1)	$H_2S = H^+ + HS^-$	9.1×10^{-8}	7.04
Phosphoric (2)	$H_2PO_4^- = H^+ + HPO_4^{2-}$	6.23×10^{-8}	7.21
Hypochlorous	$HOCl = H^+ + OCl^-$	2.95×10^{-8}	7.53
Hypobromous	$HOBr = H^+ + OBr^-$	2×10^{-9}	8.7
Ammonium ion (1)	$NH_4^+ = H^+ + NH_3$	5.62×10^{-10}	9.25

Hydrocyanic	$HCN = H^+ + CN^-$	4.93×10^{-10}	9.31
Glycine (2)	$CH_2(NH_2)COOH = H^+ + CH_2(NH_2)COO^-$ $.67 \times 10^{-10}$		9.78
Hydroselenic (2)	$HSe^- = H^+ + Se^{2-}$	1×10^{-10}	10.0
Carbonic (2)	$HCO_3^- = H^+ + CO_3^{2-}$	5.61×10^{-11}	10.25
Hypoiodous	$HOI = H^+ + OI^-$	2.3×10^{-11}	10.6
Methylammine ion	$CH_3NH_3^+ = H^+ + CH_3NH_2$	2.20×10^{-11}	10.66
Hydrogen peroxide	$H_2O_2 = H^+ + HO_2^-$	2.4×10^{-12}	11.62
Hydrosulfuric (2)	$HS^- = H^+ + S^{2-}$	1.1×10^{-12}	11.96
Phosphoric (3)	$HPO_4^{2-} = H^+ + PO_4^{3-}$	2.2×10^{-13}	12.67
Water (2)	$H_2O = H^+ + OH^-$	$K_w = 1.00 \times 10^{-14}$	14.00
Sodium ion hydrate	$Na(H_2O)^+ = H^+ + NaOH$	$\approx 10^{-20}$	20
Ammonia (2)	$NH_3 = H^+ + NH_2^-$	$\approx 10^{-30}$	30
Hydroxide (3)	$OH^- = H^+ + O^{2-}$	$\approx 10^{-36}$	36
Hydrogen	$H_2 = H^+ + H^-$	$\approx 10^{-38}$	38

In addition to showing qualitative trends in acid/base strength, Bronsted Tables may display quantitative information about acid/base reactions in the form of equilibrium constants, K, which measure the extent of completion of a reaction; the larger the K, the more products formed. The Bronsted Table given above also lists (redundantly) a logarithmic function of extent of reaction, $pK_a = -\log_{10} K_a$; the *smaller* K_a is, the *larger* pK_a is. When two reactions are combined into a net reaction by subtraction, the equilibrium constant corresponding to the net reaction is the *quotient* of the equilibrium constants for the two half reactions, with numerator and denominator equal to the equilibrium constants of the added and subtracted half reactions, respectively.

Typical Bronsted acid/base exercises determine the underlying half reactions for a given complete reaction. How can we develop a procedure to do this (given the total, find the parts)? Half reactions in the Bronsted Table are subtracted to conserve protons. Thus, given a Bronsted Table, the appropriate pair can be identified from the given reactants and products.

$$HB_1^q = H^+ + B_1^{q-1} \qquad K_1$$
$$- [\ HB_2^q = H^+ + B_2^{q-1}\ ] \qquad (K_2)^{-1}$$

_____

$$HB_1^q + B_2^{q-1} = HB_2^q + B_1^{q-1} \qquad K_{total} = \frac{K_1}{K_2}$$
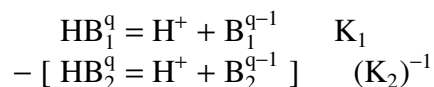
Recall from Section 2 that reversing the second reaction inverts its K.
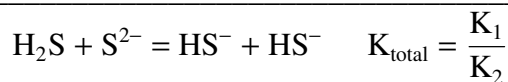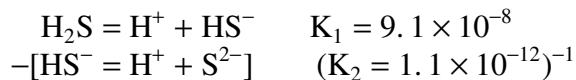

Bronsted Table Algorithm

Purpose: To identify acid/base half reactions from a given total reaction.

Procedure:

1. Scan the Bronsted Table for the reactants and products of the given reaction.
2. From the possible matches, identify two entries which have conjugate pairs in the given reaction.
3. Reverse one entry half reaction and add to the other in such a way that the resulting reactants and products agree with those of the given reaction.
4. If a net equilibrium constant is requested, divide the equilibrium constant for the reversed half reaction into that of the added half reaction.

**Example 19.5** What is the value of the equilibrium constant for the reaction $H_2S + S^{2-} = 2HS^-$?

1. H_2S appears only one place in the Bronsted Table, under the hydrosulfuric (1) entry, as does S^{2-}, under the hydrosulfuric (2) entry (the numbers refer to first and second ionizations processes).
2. In both cases, HS^- is the conjugate species.
3.

$$
\begin{array}{ll}
H_2S = H^+ + HS^- & K_1 = 9.1 \times 10^{-8} \\
-[HS^- = H^+ + S^{2-}] & (K_2 = 1.1 \times 10^{-12})^{-1}
\end{array}
$$

$$
\overline{\phantom{H_2S + S^{2-} = HS^- + HS^- \qquad K_{total} = \frac{K_1}{K_2}}}
$$

$$H_2S + S^{2-} = HS^- + HS^- \qquad K_{total} = \frac{K_1}{K_2}$$

4. $K_{total} = \dfrac{K_1}{K_2} = 8.27 \times 10^{+4}$

Example 19.6 Discuss the reaction of ammonia with water.

NH_3 appears twice in the Bronsted Table, once as a acid (left side) and once as a base (right side). As water also appears as an acid and a base, two possible reactions between ammonia and water are possible:

$$NH_3 + H_2O = NH_2^- + H_3O^+$$

$$NH_3 + H_2O = NH_4^+ + OH^-$$
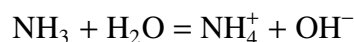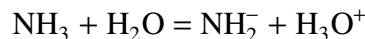
The equilibrium constants for the respective reactions are $\dfrac{10^{-30}}{10^0} = 10^{-30}$ and $\dfrac{10^{-14}}{5.62 \times 10^{-10}} = 1.78 \times 10^{-5}$. Both reactions lie to the reactants side at equilibrium, but the second dominates over the first by twenty-five oders of magnitude and lies suffi-ciently to the products side to produce a basic solution. Thus the first reaction is negligi-ble and ammonia is a base in water.

Note that the ionization of a base in water that is conjugate to an acid has a ionization constant complementary to that of water. The second ammonia ionization above illustrates this general result. to the analog of Eq. (19.24) using Eq. (19.19) and $K_w = K_a K_b$

$$\boxed{K_a K_b = K_w \qquad (19.17)}$$

The quantitative measure of the acidity or basisity of an aqueous solution is the concen-tration of hydrogen ion (or hydrated hydrogen ion, called hydronium ion H_3O^+), or equiv-alently its negative logarithm:

$$pH \equiv -\log_{10}(C_{H^+}) \qquad (19.18a)$$

$$C_{H^+} = 10^{-pH} \qquad (19.18b)$$

$$pOH \equiv -\log_{10}(C_{OH^-}) \qquad (19.18c)$$

$$C_{OH^-} = 10^{-pOH} \qquad (19.18d)$$

From the Bronsted Table Algorithm the meaning of strong acids and bases becomes apparent. Consider the acids above hydronium (i.e. with K > 1). Since hydronium has an equilibrium constant value of unity, combining the half reaction for hydronium with any acid above it will produce a reaction where the acid is converted to hydronium with a total equilibrium constant equal to than that of hydronium, a value greater than unity: $\frac{K_1}{1} = K_1$. Equilibrium constant values greater than unity indicate greater concentrations of products than reactants, and the equilibrium is said to "lie to the right". The strongest acids lie far to the right, indicating (nearly) complete conversion to hydronium, or, equivalently, complete ionization to hydrogen ion. A similar argument holds for the bases below hydroxide as an base. In fact, *in aqueous solution the strongest acid that can exist is hydronium and the strongest base is hydroxide*. Stronger acids and bases than these are essentially totally converted to them, a process referred to as **leveling**. *Weak acids and bases lie between hydronium and hydroxide in the Bronsted Table* (the two boxed entries in the table). Note that the first ionization of diprotic acids is significantly greater than the second ionization. For example, sulfuric acid is a strong acid, but hydrogen sulfate ("bisulfate") ion is a weak acid.

The Mass Action Equilibrium Algorithm can be applied to weak acids and bases to solve for equilibrium constants from pH values, or *vice versa*.

Example 19.7 Calculate the pH of pure water.

The acid base reaction in pure water is

$$H_2O + H_2O = H_3O^+ + OH^-$$
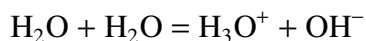
for which the equilibrium constant from the Bronsted Table is $K_w = 1.00 \times 10^{-14}$. Since $K = C_{H_3O^+}C_{OH^-}$ and and $C_{H_3O^+} = C_{OH^-}$, $K_w = C_{H_3O^+}^2$ and $C_{H_3O^+} = \sqrt{K_w} = 1.0 \times 10^{-7}$. Therefore the pH of water is $-\log(1.0 \times 10^{-7}) = 7$.

Note the general realtionship between hydrogen and hydroxide concentrations:

$$C_{H^+} C_{OH^-} = 1 \times 10^{-14} \qquad (19.19a)$$

$$pH + pOH = 14 \qquad (19.19b)$$

Example 19.8 Calculate the value of the equilibrium constant for the ionization of formic acid from the observed pH = 2.38 for a 0.10 M solution.

The Mass Action Equilibrium Algorithm gives the path to an answer.

1. Neutral acids are substances of the form HB which dissociate in aqueous solution into ions (ionize), one of which is hydrogen ion:

$$HB = H^+ + B^-$$

2. From Eq. (19.18b)

$$C_{H^+} = 10^{-pH} = 10^{-2.38} = 4.17 \times 10^{-3.}$$

Since the equilibrium concentrations of the remaining species (HB and B^-) are not given, we construct a mass action table:

	HB	$\rightleftharpoons$	H^+	+	B^-
Initial	0.10		0		0
Change	−x		+x		+x
Final	0.10−x		+x = 4.17×10^{-3}		+x

3. Solving the mass action equation for K gives:

$$K = \frac{(x)(x)}{(0.10 - x)} = \frac{(4.17 \times 10^{-3})^2}{(0.10 - 4.17 \times 10^{-3})} = 1.81 \times 10^{-4}$$

19.6. Acid Base Titrations

Titrations consist of addition of one reactant to another until equivalent amounts of each are mixed. Acid/base titrations add acids to bases or vice versa. We will discuss the common case of aqueous solutions of strong base added to acids. *Titration curves* show the pH as a function of titrant added to the other solution. As seen in Fig. 19.1, as the acid strength decreases, the region of changing pH near equivalence narrows and it becomes increasingly more diffi cult to detect the end point of the titration.
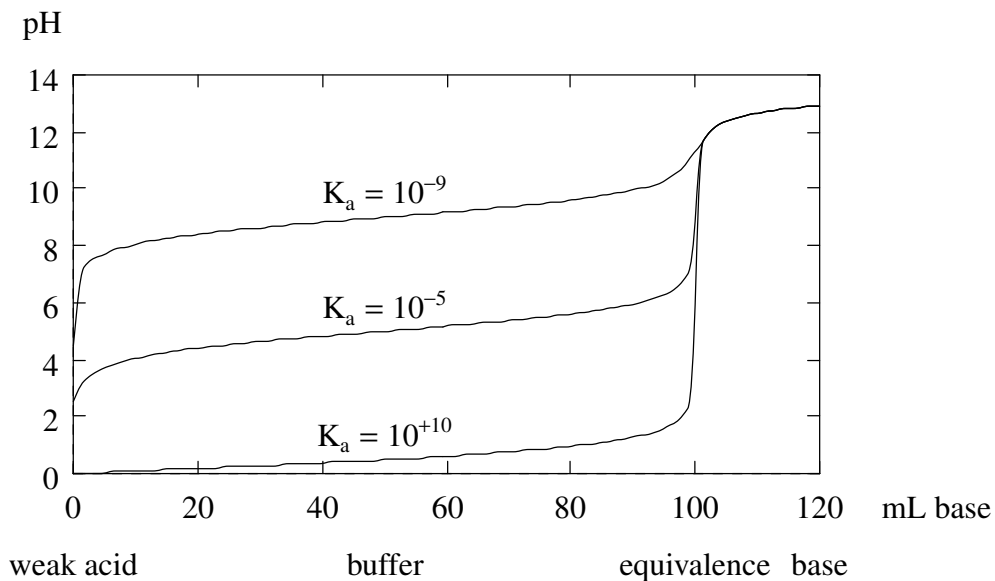
pH

Fig. 19.1 Titration of 100 mL 0.1 M Acid with 0.1 M Base

The key to determining the pH along the course of a titration is to let the reaction fi rst go conceptually to *completion* and then let it "relax" to *equilibrium*.

Example 19.9 Calculate the pH of a 0.10 M acetic acid solution which has been titrated 1/4 the way to neutralization. For acetic acid, $K_i = 1.8 \times 10^{-5}$

The Mass Action Equilibrium Algorithm again gives the path to an answer. We will first work out the case for when the titration is a general fraction f of the way to completion.

1. Acid equilibria was introduced in the previous example:

$$HB = H^+ + B^-$$

Titration involves neutralization by reaction of acids with bases. Simple strong bases ionize to produce hydroxide ion, OH^-, which reacts with the acid, represented by HB:
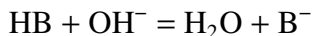
$$HB + OH^- = H_2O + B^-$$

2. pH is defined as $pH = -bg[H^+]$, suggesting solving for $[H^+]$ at equilibrium. However, before equilibrium is achieved, the neutralization reaction occurs. This suggests a modified mass action table.[6]

	HB	+	OH^-	$\rightleftharpoons$	H_2O	+	B^-
Initial	$a_0 = 0.10$		0		-		0
After reaction	$(1-f)a_0$		0		-		fa_0
Change	$-x$		$+x$		-		$+x$
At equilibrium	$(1-f)a_0 - x$		x		-		$fa_0 + x$

3. The mass action equation is:

$$K = \frac{[H^+](fa_0 + x)}{[(1-f)a_0 - x]}$$

Solving for $[H]^+$,

$$[H^+] = K\frac{[(1-f)a_0 - x]}{(fa_0 + x)} \approx K\frac{((1-f)a_0)}{(fa_0)} = K(\frac{1}{f} - 1)$$

The approximation comes from recognizing that the shift in equilibrium after reaction (x) is small compared to the concentrations produced by the neutralization.

_____

[6] No entry is given for the concentration of liquid water. Its density of 1 g/mL corresponds to 55.5 M.

For the case f = 1/4,

$$[H^+] = 3 \ K = 5.4 \times 10^{-5}$$

Finally, the pH can be calculated from its definition:

$$pH = -\log[H^+] = -\log[5.4 \times 10^{-5}] = 4.27$$

Here is some typical *Maple* input used to generate titration curves like Fig. 19.1.

```
# Monoprotic weak acid/strong base titration

Ka:=Float(1.76,-5);                     # Weak acid ionization equilibrium constant
Va:=100;                                # Initial mL weak acid
Ma:=1;                                  # Weak acid molarity
Mb:=1;                                  # Strong base molarity

MH:= proc(Vb) # Hydrogen ion molarity (MH) as a function of mL base added (Vb)
    option operator;
        V:=Va+Vb;                       # Total volume of solution
        Ca:=(Va*Ma-Vb*Mb)/V;            # Concentration of acid after reaction
        Cb:=Mb*Vb/V;                    # Concentration of conjugate base
        solve(Ka=MH*(Cb+MH)/(Ca-MH),MH) # Solve mass action equation for MH
    end:

interface(plotdevice=postscript, plotoutput='T.ps');  # Specify an available plotting devic

pH_vals:= [[Vb,evalf(-log10(MH(Vb)[1]))] $ Vb=0..99]: # Compute a 100 point titration curve
plot(pH_vals, '+mL base'=0..100, pH=0..14, title='Acid/Base Titration Curve');

quit;                                   # Finish executing maple
```

The general aqueous calculation process can be shortened by performing the algebra and making approximations (which need to be checked when used). In aqueous solution there are always multiple equilibria, as the solvent participates as well as any solutes. We will consider the case of an acid or base dissolved in water. We will ignore the roll of water in the equilibria as the formulas are unchanged when the pure solvent concentration is unity. For notational simplicity, we will show charges in reactions, but delete them in algebraic equations. Also we will let letters stand for concentrations. The two basic equilibria are the dissociation of water and the solute:

$$HOH = H^+ + OH^- \qquad K_w = (H)(OH) \qquad (19.20)$$

$$HB^q = H^+ + B^{q-1} \qquad K_a = \frac{(H)(B)}{(HB)} \qquad (19.21)$$
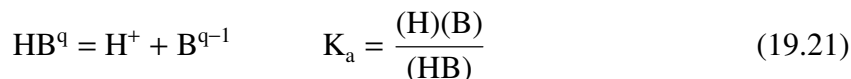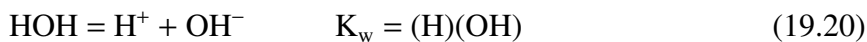
These are two equations in four unknowns, H, OH, HB and B. Two additional equations are obtained from conservation of mass. B is distributed between HB and B and equal to the original total concentration of HB and B.

$$C_a + C_b = HB + B \qquad (19.22)$$

Conservation of H atoms recognizes water and the acid as sources.[7] Since $H - OH$ represents the H in solution in excess of that contributed by water,

$$C_a = HB + H - OH \qquad (19.23)$$

Adding Eqns. (19.22) and (19.23) solves for B:

$$B = H + C_b - \frac{K_w}{H}$$

Using this equation and Eq. (19.21) to eliminate B and HB in Eq. (19.22) leads to

$$C_a + C_b = (\frac{K_a + H}{K_a})(H + C_b - \frac{K_w}{H}) \qquad (19.24)$$

This equation describes all the situations of a single species in water, strong acid, weak acid,

---

[7] An alternaive (but not independent) equation conserves total charge to maintain solution neutrality.

$$H - OH + qHB + (q - 1)B = 0$$

strong base, weak base and buffer (weak acid/weak base conjugate pair). However it is a cubic equation with no simple analytic solution. Solutions can be obtained numerically, or approximate analytic formulas can be obtained for the various cases. We will develop the approximate formulas.

For the case $C_b = 0$ (acid solutions), Eq. (19.24) becomes

$$C_a = (\frac{K_a + H}{K_a})(H - \frac{K_w}{H})$$
(19.25)

When $K_a \gg H$ (strong acid), $H \gg \dfrac{K_w}{H}$ as well, and Eq. (19.25) becomes

$$H_{SA} \approx C_a$$
(19.26)

as expected for total ionization of a strong acid. When $K_a \ll H$ (weak acid), Eq. (19.25) becomes

$$K_a C_a \approx H - \frac{K_w}{H}$$

which is a quadratic. Solving,

$$H_{WA} \approx \sqrt{K_a C_a + K_w}$$
(19.27)

For the case $C_a = 0$ (base solutions), Eq. (19.24) may be transformed to a base analog of Eq. (19.25) using Eq. (19.17) and Eq. (19.20):

$$C_b = (\frac{K_b + OH}{K_b})(OH - \frac{K_w}{OH})$$
(19.28)

Thus the same approximate equations apply for bases as acids:

$$H_{SB} \approx C_a$$
(19.29)

$$OH_{WB} \approx \sqrt{K_b C_b + K_w}$$
(19.30)

For the case $C_a \neq 0$, $C_b \neq 0$ the solution is a buffer, consisting of a weak acid/weak base conjugate pair in solution. In order for the buffer to be effective, $C_b \gg H$, $\dfrac{K_w}{H}$ and Eq. (19.24) becomes

$$C_a + C_b = (\frac{K_a + H}{K_a})(C_b)$$

or

$$H_{buffer} \approx \frac{C_a}{C_b} K_a \qquad (19.24)$$

Note the result is the same for weak acid plus salt (weak base) buffers as well as weak base plus salt (weak acid) buffers. Also note the weak acid and weak base formulas apply to hydrolysis of salts of weak acids and bases as well, which are themselves weak conjugate bases and acids, respectively.

A summary of the formulas relevant to aqueous acid base equilibria follows:

Acid/Base Equilibria Formulas

$$pH \equiv -\log[H^+] = 14 - pOH \qquad pK \equiv -\log K$$

$$K_a \equiv \frac{[H^+][B^{q-1}]}{[HB^q]} \qquad K_b \equiv \frac{[HB^q][OH^-]}{[B^{q-1}]} \qquad K_a K_b = K_w \equiv [H^+][OH^-]$$

General case: $\quad C_a + C_b = (\dfrac{K_a + C_{H^+}}{K_a})(C_{H^+} + C_b - \dfrac{K_w}{C_{H^+}})$

Strong acid case ($C_b = 0$, large K_a): $\qquad \boxed{[H^+]_{SA} \approx C_a}$

Weak acid case ($C_b = 0$, small K_a): $\qquad \boxed{[H^+]_{WA} \approx \sqrt{K_a C_a + K_w}}$

Strong base case ($C_a = 0$, large K_b): $\qquad \boxed{[OH^-]_{SB} \approx C_b}$

Weak base case ($C_a = 0$, small K_b): $\qquad \boxed{[OH^-]_{WB} \approx \sqrt{K_b C_b + K_w}}$

Buffer case ($C_a, C_b \neq 0$, small K_a): $\qquad \boxed{[H^+]_{buffer} \approx \dfrac{C_a}{C_b} K_a}$

Example 19.10 Calculate the pH of a 0.10 M acetic acid solution which has been titrated 1/4 the way to neutralization, using approximation formulas.

The situation is partial neutralization of weak acid with strong base, so the solution is a buffer. From the Category table we see that x represents the proton concentration, C_a the concentration of remaining acid and C_s the concentration of conjugate base. Using the

modified mass action table of the previous example and the buffer approximation formula,

$$[\text{H}^+] \approx \frac{(1.8 \times 10^{-5})(3(0.10)/4)}{0.10/4} = 5.4 \times 10^{-5}$$

and the pH = 4.27 just as before.

It is worth noting that during acid/base titrations pH $\approx$ pK_a + log(C_b/C_a), which means that when $C_b = C_a$, that is, half way to the equivalence point (for unity stoichiometric ratio), pH = pK_a. This provides a method for determining the value of pK_a: Titrate to the equivalence point noting the pH, then read the pH half-way to equivalence.

19.7. Oxidation Reduction Equilibria

The concept of acids and bases was greatly expanded by G. N. Lewis, who published his ideas about the same time as Bronsted and Lowery. Lewis reasoned that since all chemical reactions involve rearrangements of chemical bonds, and that chemical bonds are the result of electronic structure in molecules, acid/base reactions should be understandable in terms of the rearrangements of electrons. In a sense, Lewis shifted the focus from the proton (which is usually hidden beneath filled subshell core electrons) to its opposite, the electron. *Lewis acids are electron acceptors and Lewis bases are electron donors.* The range of acids with this notion is extended to non-aqueous solutions and pure substances in the solid, liquid and gaseous states. Although the Lewis perspective is broader than that of the Bronsted perspective, the Bronsted concept is still popular for the common cases of aqueous solutions.

Example 19.11 The classic strong acid, strong base reaction is between hydrochloric acid and sodium hydroxide to produce sodium chloride and water ("acid plus base gives salt plus water"). However, gaseous hydrogen chloride can react with solid sodium oxide to produce the same products (Write out the reaction). It is difficult to describe the reaction in Bronsted half-reaction terms. More striking, sulfur trioxide is the anhydride of sulfuric acid (i.e. yields sulfuric acid when added to water), as is calcium oxide the anhydride of calcium hydroxide. However the essential reaction taking place in aqueous solution can occur without any water being involved:

$$\text{SO}_3(\text{g}) + \text{CaO}(\text{s}) = \text{CaSO}_4(\text{s})$$
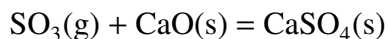
In a sense, Lewis theory goes beyond acid/base reactions to include all rearrangements of electrons, but one class of reactions is particularly appropriate to Lewis acids and bases, namely oxidations and reductions. **Oxidation** generalizes simple reaction with oxygen to include any reaction for which electrons are lost (and oxidation number therefore increases). **Reduction** can be thought of as the opposite of oxidation, namely reaction involving the gain of electrons (and reduction in oxidation number). The generalization of the idea that oxygen oxidizes substances through strong electronegativity (electron greed), is that *oxidation is caused by reaction with an oxidizing agent, and reduction by reaction with a reducing agent*.

Since matter (including electrons) must be conserved in chemical reactions, *oxidation is always accompanied by reduction in chemical reactions, and oxidation/reduction reactions involve the transfer of electrons*. Thus one can say a substance that is oxidized by an oxidizing agent itself acts as a reducing agent to the oxidizing agent. The coupling of oxidation and reduction, sometimes called *redox*, together with the understanding of the transference of electrons suggests decomposing redox reactions into pairs of oxidation or reduction half-reactions, as with aqueous acid/base reactions. A table of such half reactions is appropriately called a *Lewis Table*, also called a *standard reduction table*. It is arbitrary whether redox half reactions are written as reductions or oxidations: we will choose to write them all as reductions (corresponding oxidation half reactions are reversed reductions). Pairs of reduction or oxidation half reactions may be combined to eliminate the transferred electrons by subtraction, just as they were combined to eliminate the transferred protons in acid/base reactions. One important difference between a Lewis Table and a Bronsted Table is that redox half reactions can involve the loss or gain of several electrons, whereas aqueous acid/base involve the loss or gain of single protons. A second difference is that the measure of oxidation or reduction strength is made through *electropotential*, or *electromotive force (EMF)*, measured in *volts*, instead of through equilibrium constant. Actually, there is a relationship between EMF and K, somewhat similar to that between pK and K:

$$E^0 = \frac{RT}{n_e F} \ln(K) \qquad (19.31)$$

where E^0 is the *cell potential*, R is the molar gas constant (8.3145 J/mol-K in energy units), T is temperature in Kelvin, n_e is the number of mols of electrons transferred (number of

equivalents), and F is the charge of one mol of electrons, called the Faraday[8], with value 9.648456×10^4 J/mol − V. The superscript 0 on E denotes the standard state of 25 °C and concentrations of solutions and pressures of gases of unity. In the Lewis Table below, oxidation strength increases and reduction strength decreases with increasing positive reduction potential, E^0,

_____

[8] Michael Faraday (1791-1867), discoverer of several chemicals including benzene, electrical induction, electric polarization of light, inventor of the electric motor and generator. Faraday did not have facility with mathematics, but his insights and experiments were developed into the unified theory of electricity and magnetism by his colleague Clerk Maxwell. Faraday's popular Christmas Lectures, published as *The Chemical History of a Candle* are still recommended reading for their accuracy, clarity and beauty. He experimented with conduction of electricity through gas plasmas in tubes that were the precursors to radio, cathode ray and television tubes, and mass spectrometers. Although Faraday interpreted his solution electrolysis experiments in terms of a fundamental particle of charge and identified chemical affinity with electrical force, he was not attracted to Dalton's atomic theory. Considered by many to be one of the great experimental geniuses of all time, he appears to have suffered from mercury poisoning (from electrical conduction experiments), which left him in a debilitated mental state for much of his life. He declined elections to the presidency of the Royal Society of London and knighthood, but did accept a retirement apartment at Hampton Court from Queen Victoria.

Table 19.5 The Lewis Table

Reduction	E^0 (Volts)
$F_2(g) + 2e^- = 2F^-(aq)$	+2.866
$Co^{3+}(g) + e^- = Co^{2+}(aq)$	+1.842
$H_2O_2(aq) + 2H^+(aq) + 2e^- = 2H_2O$	+1.763
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- = PbSO_4$	+1.691
$Ce^{4+}(g) + e^- = Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- = Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- = Au(aq)$	+1.498
$Cl_2(g) + 2e^- = 2Cl^-(aq)$	+1.358
$MnO_2(s) + 4H^+(aq) + 2e^- = Mn^{2+}(aq) + 2H_2O$	+1.229
$O_2(g) + 4H^+(aq) + 4e^- = 2H_2O$	+1.229
$Br_2(l) + 2e^- = 2Br^-(aq)$	+1.066
$NO_3^-(aq) + 4H^+(aq) + 3e^- = NO(g) + 2H_2O$	+0.964
$Ag^+(aq) + e^- = Ag(s)$	+0.800
$Fe^{3+}(aq) + e^- = Fe^{2+}(aq)$	+0.771
$O_2(g) + 2H^+(aq) + 2e^- = H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O + 3e^- = MnO_2(s) + 4OH^-(aq)$	+0.595
$I_2(s) + 2e^- = 2I^-(aq)$	+0.536
$O_2(g) + 2H_2O + 4e^- = 4OH^-(aq)$	+0.401
$Cu^{2+}(aq) + 2e^- = Cu(s)$	+0.342
$AgCl(s) + e^- = Ag(s) + Cl^-(aq)$	+0.222
$Cu^{2+}(aq) + e^- = Cu^+(aq)$	+0.153
$AgBr(s) + e^- = Ag(s) + Br^-(aq)$	+0.095
$2H^+(aq) + 2e^- = H_2(g)$	0.000
$Pb^{2+}(aq) + 2e^- = Pb(s)$	−0.126
$Sn^{2+}(aq) + 2e^- = Sn(s)$	−0.137
$AgI(s) + e^- = Ag(s) + I^-(aq)$	−0.151
$Co^{2+}(g) + 2e^- = Co(aq)$	−0.277
$NAD^+(aq) + H^+(aq) + 2e^- = NADH$	−0.320
$PbSO_4(s) + 2e^- = Pb(s) + SO_4^{2-}(aq)$	−0.359
$Fe^{2+}(aq) + 2e^- = Fe(s)$ / $Zn^{2+}(aq) + 2e^- = Zn(s)$	−0.447 / −0.762
$2H_2O + 2e^- = H_2(g) + 2OH^-(aq)$	−0.828

$Mn^{2+}(aq) + 2e^- = Mn(s)$	−1.128
$Al^{3+}(aq) + 3e^- = Al(s)$	−1.662
$Mg^{2+}(aq) + 2e^- = Mg(s)$	−2.357
$Na^+(aq) + e^- = Na(s)$	−2.714
$Ca^{2+}(aq) + 2e^- = Ca(s)$	−2.868
$Sr^{2+}(aq) + 2e^- = Sr(s)$	−2.888
$Ba^{2+}(aq) + 2e^- = Ba(s)$	−2.906
$K^+(aq) + e^- = K(s)$	−2.936
$Li^+(aq) + e^- = Li(s)$	−3.040

Note the correlations of EMF for elements with the Periodic Trend Algorithm of Section 6.5. The halogens, alkali metals and alkaline earths are ordered roughly the same as in the periodic table with the most electron greedy elements at the top of the Lewis Table and the most generous at the bottom.

In the case of oxidation/reduction reactions, electrical energy may be captured by physically separating the half reactions into *half cells* and connecting them with electrical and chemical conductors (solutions containing mobile ions). The EMF is called the *cell potential*, measured in volts, and is computed as the difference between two half-cell potentials in the Lewis Table. This is seen by applying Eq. (19.31) to two half reactions:

$$n_{e_{cell}}E_{cell} = n_{e_{red}}E_{red} - n_{e_{ox}}E_{ox} \qquad (19.32)$$

where the subscripts refer to the half cells in which reduction and oxidation take place. The values to use in Eq. (19.32) are for standard conditions are listed in Lewis Tables. In the usual case of transfer of electrons, $n_{e_{cell}} = n_{e_{red}} = n_{e_{ox}}$ and n_e can be ignored. Note how division of the equilibrium constants resulting from differencing half reactions in the Bronsted Table becomes subtraction of half cell potentials in the Lewis Table. This is a consequence of the logarithmic relationship between E and K. The negative sign on E_{ox} comes from reversing the half reaction in a reduction table, corresponding to inverting K. The Bronsted Table Algorithm has a corresponding Lewis Table Algorithm:

Lewis Table Algorithm

Purpose: To identify oxidation/reduction half reactions from a given total reaction.

Procedure:

1. Scan the Lewis Table for the reactants and products of the given reaction.
2. From the possible matches, select two entries which have conjugate pairs in the given reaction.
3. Subtract one entry half reaction from the other in such a way that the resulting reactants and products agree with those of the given reaction.
4. If a net EMF is requested, subtract the EMF for the subtracted half reaction from that of the added half reaction.

Example 19.12 Identify the Lewis half reactions and calculate the EMF for the reaction $2Li(s) + F_2(g) = 2LiF$.

1. The reactants are found at the top and bottom of the Lewis Table.
2. There are no other reactions involving fluorine and lithium.
3. The fluorine reaction needs to be added and the lithium reduction subtracted (reversed) to agree with the given reaction.
4. According to Eq. (19.32), $n_e = 2$ and the standard cell EMF is

$$2E^0_{cell} = 2E_{F_2} - 2E_{Li^+} = 2(+2.87) - 2(-3.05) \text{ V} = 2(5.92) \text{ V}$$

$$E^0_{cell} = 5.92 \text{ V}$$

This reaction, which involves the most electronegative and positive elements, has understandably one of the largest possible cell potentials. How are EMF cells used to produce larger voltages? Individual cells are connected in a series of cells, called *batteries*, for which the voltages are additive according to the laws of electricity.

Example 19.13

The Lewis Table shows that zinc should dissolve in acids to produce dihydrogen: $Zn + 2H^+ = Zn^{2+} + H_2$, $2E_{cell} = 2(0.000) - 2(-0.828) \text{ V}$, or $E_{cell} = +0.828 \text{ V}$ and $\Delta G = -n_e FE$ is negative causing the products to dominate over reactants at equilibrium.

If Zn dissolves in acids, why doesn't it dissolve in water, which always has a little acid in it? According to the Nernst Equation, the potential would be less in neutral water, where the concentration of H^+ is 10^{-7}, than in 1 M acid by

$-\dfrac{0.05916}{2}\log\dfrac{p_{H_2}}{C_{H^+}} = -0.209$ V at room temperature for the same P_{H_2}. The cell poten-
tial is still positive (0.828 - 0.209 = 0.619 V), indicating the reaction should proceed.
However, thermodynamics is not the total story. The rate of reaction is dependent on
concentrations and, if proportional to hydrogen ion concentration, would proceed 10^{-7}
times slower than in 1 M acid. Thus what would react in 10 s in 1 M acid would require
10^7 s to react in neutral water, or about 3 *years*.

Example 19.14 Entries in the Lewis Table can be used to explain corrosion protection.
Metals above dioxygen do not react with dioxygen because the resulting cell potential
would be negative (corresponding to an equilibrium constant less than unity), while
those below dioxygen can react with dioxygen to form oxides. Thus, gold plating is one
corrosion protection stratagem ($E^0_{Au/O_2} = -0.27$ V). Some metals, like silver,
chromium, aluminum and tin are protected from further oxidation through formation of
thin but impenetrable oxidized coats by reacting with atmospheric gases. "Tin" cans
used to store foods are actually tin-coated iron; when the tin coating is breached, the tin
reacts with the iron with positive cell potential ($E^0_{Sn^{2+}/Fe} = +0.30$ V), and rusting is
accelerated. Zinc, on the other hand, is below iron, so if iron were oxidized it would, in
turn, preferentially oxidize the zinc ($E^0_{Fe^{2+}/Zn} = +0.32$ V). Coating iron with zinc is
called *galvanizing* the iron, and metals above iron, such as zinc and magnesium are used
to form "sacrificial" couples with iron.

Identifying the free energy as the available work in an electrochemical cell,
$\Delta G = -n_e FE$, leads from Eq. (19.14) to the relationship between cell potential and equilib-
rium constant, Eq. (19.31). The more general Eq. (19.15) leads to a more general relation-
ship for cell potential under arbitrary concentrations, called the *Nernst* equation:

$$E = E^0 - \frac{RT}{n_e F}\ln(Q) \qquad (19.33)$$

A convenient form for calculations at 25°C is

$$E = E^0 - \frac{0.05912}{n_e}\log(Q)$$

Note at equilibrium $Q = K$; thus E goes to zero and the cell becomes "dead".

Example 19.15 *Concentration cells* derive from a curious result of the Nernst equation
applied to electrochemical cells having the same half reaction in each half cell, but at

different concentrations. In this case, $E_{cell}^0 = E_{red}^0 - E_{ox}^0 = 0$, and

$$E = -\frac{RT}{n_eF} \ln(Q) = -\frac{RT}{n_eF} \ln(\frac{C_{dilute}}{C_{concentrated}}) \geq 0$$

At 25 °C each ten-fold difference in concentration between half cells generates $+0.0591/n_e$ V, where n_e is the number of electrons in the half-reaction.

Summary

Chemical equilibrium is static on a macroscopic scale, but dynamic on a molecular scale. The fundamental law of equilibrium is an equation which relates the concentrations of reactants and products to a parameter, called the equilibrium constant.

Two special categories of chemical reactions, acid/base and electrochemical exchange protons and electrons, respectively. The exchange property allows quantitative tabulation of numerous possible reactions in terms of a relatively small number of half reactions.

CHEMICAL EQUILIBRIA EXERCISES

1. If K for the HCN = HNC rearrangement is 4, what is the concentration of HNC at equilibrium after one molar HCN is introduced into an empty flask?
2. Compare the acid strengths of H_2S and HS^-.
3. What is the maximum voltage a hydrogen fuel cell could produce?
4. Is an aqueous hydrogen peroxide solution stable?

CHEMICAL EQUILIBRIA EXERCISE HINTS

1. This is a particularly simple mass action equilibrium problem for the reaction of the form A = B.
2. H_2S and HS^- are both hydro acids.
3. A oxygen/hydrogen fuel cell has the same reaction as the combustion of gaseous hydrogen.
4. Consider the reaction: $2H_2O_2 = 2H_2O + O_2$.