Acid-base equilibria of the aquatic environment

A Chem1 Reference Text

Stephen K. Lower
Simon Fraser University
`lower@sfu.ca`

Natural waters contain a wide variety of solutes that act together to determine the pH, which typically ranges from 6 to 9. Some of the major processes that affect the acid-base balance of natural systems are:

- Contact with atmospheric carbon dioxide

- Input of acidic gases from volcanic and industrial emissions

- Contact with minerals, rocks, and clays

- Presence of buffer systems such as carbonate, phosphate, silicate, and borate

- Presence of acidic anions, such as $Fe(H_2O)_6^{3+}$

- Input and removal of CO_2 through respiration and photosynthesis

- Other biological processes, such as oxidation $(O_2 + H^+ + e^- \longrightarrow H_2O)$, nitrification, denitrification, and sulfate reduction.

In this chapter and also in the next one which deals specifically with the carbonate system, we will consider acid-base equilibria as they apply to natural waters. We will assume that you are already familiar with such fundamentals as the Arrhenius and Brønsted concepts of acids and bases and the pH scale. You should also have some familiarity with the concepts of free energy and activity. The treatment of equilibrium calculations will likely extend somewhat beyond what you encountered in your General Chemistry course, and considerable emphasis will be placed on graphical methods of estimating equilibrium concentrations of various species.

1 Proton donor-acceptor equilibria

1.1 Acid-base strengths

The tendency of an acid or a base to donate or accept a proton cannot be measured for individual species separately; the best we can do is compare two donor-acceptor systems. One of these is commonly the *solvent*, normally water. Thus the proton exchange

$$HA + H_2O \longrightarrow H_3O^+ + A^- \qquad\qquad K_1 \qquad\qquad (1)$$

acid		pK_a	base	pK_b
$HClO_4$	perchloric acid	~ -7	ClO_4^-	~ 21
HCl	hydrogen chloride	~ -3	Cl^-	~ 17
H_2SO_4	sulfuric acid	~ -3	HSO_4^-	~ 17
HNO_3	nitric acid	-1	NO_3^-	15
H_3O^+	hydronium ion	0	H_2O	14
H_2SO_3	sulfurous acid	1.8	HSO_3^-	12.2
HSO_4^-	bisulfate	1.9	SO_4^{2-}	12.1
H_3PO_4	phosphoric acid	2.1	$H_2PO_4^-$	11.9
$[Fe(H_2O)_6]^{3+}$	aquo ferric ion	2.2	$[Fe(H_2O)_5OH]^{2+}$	11.8
HF	hydrofluoric acid	3.2	F^-	10.8
CH_3COOH	acetic acid	4.7	CH_3COO^-	9.3
$[Al(H_2O)_6]^{3+}$	aquo aluminum ion	4.9	$[Al(H_2O)_5OH]^{2+}$	9.1
$H_2CO_3{}^*$	total dissolved CO_2	6.3	HCO_3^-	7.7
H_2S	hydrogen sulfide	7.1	HS^-	6.9
$H_2PO_4^-$	dihydrogen phosphate	7.2	$H_2PO_4^{2-}$	6.8
HSO_3^-	bisulfite ion	7.2	SO_3^{2-}	6.8
$HOCl$	hypochlorous acid	8.0	OCl^-	6.0
HCN	hydrogen cyanide	9.2	CN^-	4.8
H_3BO_4	boric acid	9.3	$B(OH)_4^-$	4.7
NH_4^+	ammonium ion	9.3	NH_3	4.7
$Si(OH)_4$	o-silicic acid	9.5	$SiO(OH)_3^-$	4.5
HCO_3^-	bicarbonate	10.3	CO_3^{2-}	3.7
$SiO(OH)_3^-$	silicate	12.6	$SiO_2(OH)_2^{2-}$	1.4
HS^-	bisulfide	~ 14	S^{2-}	~ 0
H_2O	water	14	OH^-	0
NH_3	ammonia	~ 23	NH_2^-	~ -9
OH^-	hydroxide ion	~ 24	O^{2-}	~ -10

Table 1: pK values of acids and bases in aqueous solutions at $25\,°C$

is the sum of the reactions

$$HA \longrightarrow H^+ + A^- \qquad\qquad K_2 \tag{2}$$

$$H_2O + H^+ \longrightarrow H_3O^+ \qquad\qquad K_3 = 1 \tag{3}$$

The unity value of K_3 stems from the defined value of $\Delta G° = 0$ for this reaction, and assumes that the activity of the H_2O is unity. Combining these equilibrium constants, we have

$$K_2 = K_1 = K_2 K_3 = K_a \frac{\{H^+\}\{A^-\}}{\{HA\}} \tag{4}$$

and

$$pK_a = -\log K_a, \qquad\qquad K_a = 10^{-pK_a} \tag{5}$$

Formally, equilibrium constants for reactions in ionic solutions are defined in terms of activities, in which the reference state is a hypothetical one in which individual ion activities are unity but there are

no ion-ion interactions in the solution of the ion in pure water.

$$K = \frac{\{H^+\}\{A^-\}}{\{HA\}\{H_2O\}} \tag{6}$$

There has been considerable debate about the K_a values of water and of the hydronium ion. The conventional value of 10^{-14} shown for H_2O in Table 1 is very commonly used, but it does not reflect the observed relative acid strength of H_2O when it is compared with other very weak acids. When such comparisons are carried out in media in which H_2O and the other acid are present in comparable concentrations, water behaves as a much weaker acid with $K_a \approx 10^{-16}$.

To understand the discrepancy, we must recall that acids are usually treated as *solutes*, so we must consider a proton-donor H_2O molecule in this context. Although the fraction of H_2O molecules that will lose a proton is extremely small (hence the designation of those that do so as solute molecules), virtually *any* H_2O molecule is capable of accepting the proton, so these would most realistically be regarded as *solvent* molecules.

The equation that defines the acid strength of water is

$$H_2O_{(solute)} + H_2O_{(solvent)} \longrightarrow H_3O^+ + OH^-$$

whose equilibrium constant is

$$K = \frac{(\{H^+\}/1)(\{A^-\}/1)}{(\{H_2O\}/1)(\{H_2O\}} /55.5) \tag{7}$$

in which the standard states are shown explicitly. Do you see the problem? The standard state of a *solute* is normally taken as unit molality, so we don't usually show it (or even think about it!) in most equilibrium expressions for substances in solution. For a solute, however, the standard state is the pure liquid, which for water corresponds to a molality of 55.5.

The value of $K_a = 10^{-14}$ for water refers to the reaction $H_2O \longrightarrow H^+ + OH^-$ in which H_2O is treated only as the solvent. Using Eq 7, the corresponding K_a has the value $10^{14} \div 55.5 = 1.8 \times 10^{-16}$, which is close to the observed acid strength noted above[1].

What difference does all this make? In the context of Table 1 or Fig. 2, the exact pK_a of water is of little significance since no other species having similar pK_as are shown. On the other hand, if one were considering the acid-base reaction between glycerol ($pK_a = 14.2$) and water, the prediction of equilibrium concentrations (and in this case, the direction of the net reaction) would depend on which value of the water pK_a is used.

Instead of using pure water as the reference state, an alternative convention is to use a solution of some arbitrary constant ionic strength in which the species of interest is "infinitely dilute". In practice, this means a concentration of less than about one-tenth of the total ionic concentration. This convention, which is widely used in chemical oceanography, incorporates the equilibrium quotient into the equilibrium constant:

$$^cK = \frac{[H^+][A^-]}{[HA]} \tag{8}$$

A third alternative is to use a "mixed acidity constant" in which the hydrogen ion concentration is expressed on the activity scale (which corresponds to the values obtained by experimental pH measurements) but the acid and base amounts are expressed in concentrations.

$$K' = \frac{\{H^+\}[A^-]}{HA} \tag{9}$$

The value of K' can be estimated from the Güntelberg approximation for single-ion activities:

$$pK' = pK + \frac{0.5(z_{acid}^2 - z_{base}^2)\sqrt{I}}{1 + \sqrt{I}} \tag{10}$$

in which I is the ionic strength, and z_{acid} and z_{base} are the ionic charges of the acid and base species.

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[1]For a more complete discussion and further references, see Campbell M. and Waite B., "The K_a values of water and the hydronium ion for comparison with other acids", *J. Chem. Education* 1990: 67(5) 386-388.
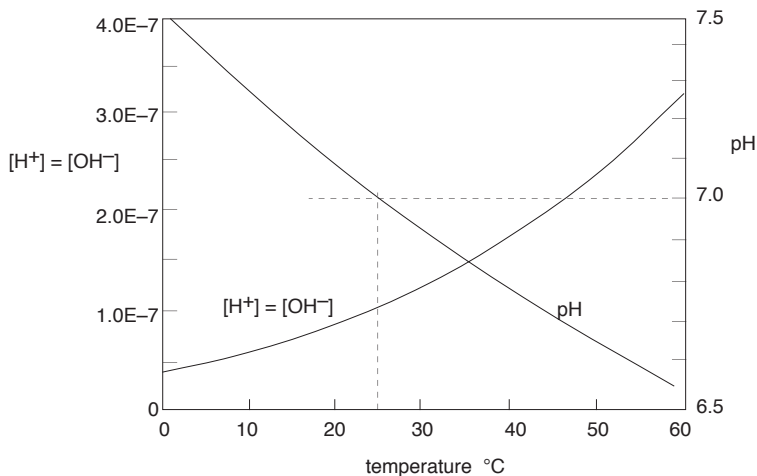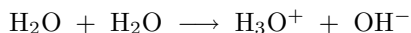
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Figure 1: Dependence of $[H^+]$ and pH of pure water on temperature.

## 1.2 The ion product of water

For the autoprotolysis of water

$$H_2O \; + \; H_2O \; \longrightarrow \; H_3O^+ \; + \; OH^-$$

$$K_w = \{H_3O^+\}\{OH^-\} \approx [H^+][OH^-] \tag{11}$$

The value of K_w is affected by temperature (it undergoes a 100-fold increase between $0\,°C$ and $60\,°C$), pressure (it is about doubled at 1000 atm) and ionic strength. In pure water at $25\,°C$ $K_w = 1.008 \times 10^{-14}$; in seawater it is 6.3×10^{-13}.

Recall that a *neutral* solution is one in which $\{H^+\} = \{OH^-\}$. This means that the pH of a neutral solution is not necessarily 7.0; it varies with temperature, pressure, and ionic strength. For pure water at 1 atm, the pH is 6.998 at $25\,°C$ and it is 7.47 at $0\,°C$.

The ion product K_w is also the "$K_a K_b$ product" for a conjugate acid-base system. Using the ammonia system as an example, the base constant K_b corresponds to

$$NH_3 \; + \; H_2O \; \longrightarrow \; NH_4^+ \; + \; OH^-$$
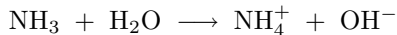
and

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} \tag{12}$$

For the conjugate acid NH_4^+

$$K_a = \frac{[H^+][NH_3]}{[NH_4^+]} \tag{13}$$

From these two relations, it is obvious that

$$K_w = K_a K_b \tag{14}$$

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1.3   the pH scale

The pH as we commonly use it nowadays indicates the *availability* of protons in the solution; that is, the ability of the solution to supply protons to a base such as H_2O. This is the same as the hydrogen ion *concentration* $[H^+]$ only in rather dilute solutions; at ionic concentrations (whether of H^+ or other ions) greater than about $0.01\,M$, electrostatic interactions between the ions cause the relation between the pH (as measured by direct independent means) and $[H^+]$ to break down. Thus we would *not* expect the pH of a $0.100\,M$ solution of HCl to be exactly 1.00.

Potentiometric devices such as the pH meter respond most closely to what is believed to be the hydrogen ion *activity*:

$$pH = -\log\{H^+\} \tag{15}$$

There is, however, no single definition of pH. Sørensen's original 1909 definition was in terms of $[H^+]$, which approximates $\{H^+\}$ in very dilute solutions. The IUPAC definition is an operational one, based on a measured cell potential involving a standard buffer solution. The (U.S.) National Bureau of Standards has also established pH values for pure standard solutions such as potassium hydrogen tartrate.

2   pH and the proton free energy

An acid, being a proton donor, can only *act* as an acid if there is a suitable base present to accept the proton. What do we mean by "suitable" in this context? Simply that a base, in order to accept a proton, must provide a lower-free energy resting place for the proton than does the acid. Thus you can view an acid-base reaction as the "fall" of the proton from a higher free energy to a lower free energy.

2.1   Proton sources and sinks

Viewed in this way, an acid is a proton *source*, a base is a proton *sink*. The tendency for a proton to move from source to sink depends on how far the proton can fall in energy, and this in turn depends on the energy difference between the source and the sink. This is entirely analogous to measuring the tendency of water to flow down from a high elevation to a lower one; this tendency (and also the amount of energy that can be extracted in the form of electrical work if the water flows through a power station at the bottom of the dam) will be directly proportional to the difference in elevation (difference in potential energy) between the source (top of the dam) and the sink (bottom of the dam).

Look carefully at Figure 2. In the center columns of the diagram, you see a list of acids and their conjugate bases. These acid-base pairs are plotted on an energy scale which is shown at the left side of the diagram. This scale measures the free energy released when one mole of protons is transferred from a given acid to H_2O. Thus if one mole of HCl is added to water, it dissociates completely and heat is released as the protons fall from the source (HCl) to the lower free energy that they possess in the H_3O^+ ions that are formed when the protons combine with H_2O.

Any acid shown on the left side of the vertical line running down the center of the diagram can donate protons to any base (on the right side of the line) that appears below it. The greater the vertical separation, the greater will be the fall in free energy of the proton, and the more complete will be the proton transfer at equilibrium.

Notice the H_3O^+-H_2O pair shown at zero kJ on the free energy scale. This zero value of free energy corresponds to the proton transfer process

$$H_3O^+ \ + \ H_2O \ \longrightarrow \ H_2O \ + \ H_3O^+$$
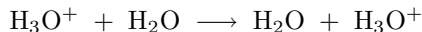
which is really no reaction at all, hence the zero fall in free energy of the proton. Since the proton is equally likely to attach itself to either of two identical H_2O molecules, the equilibrium constant is unity.
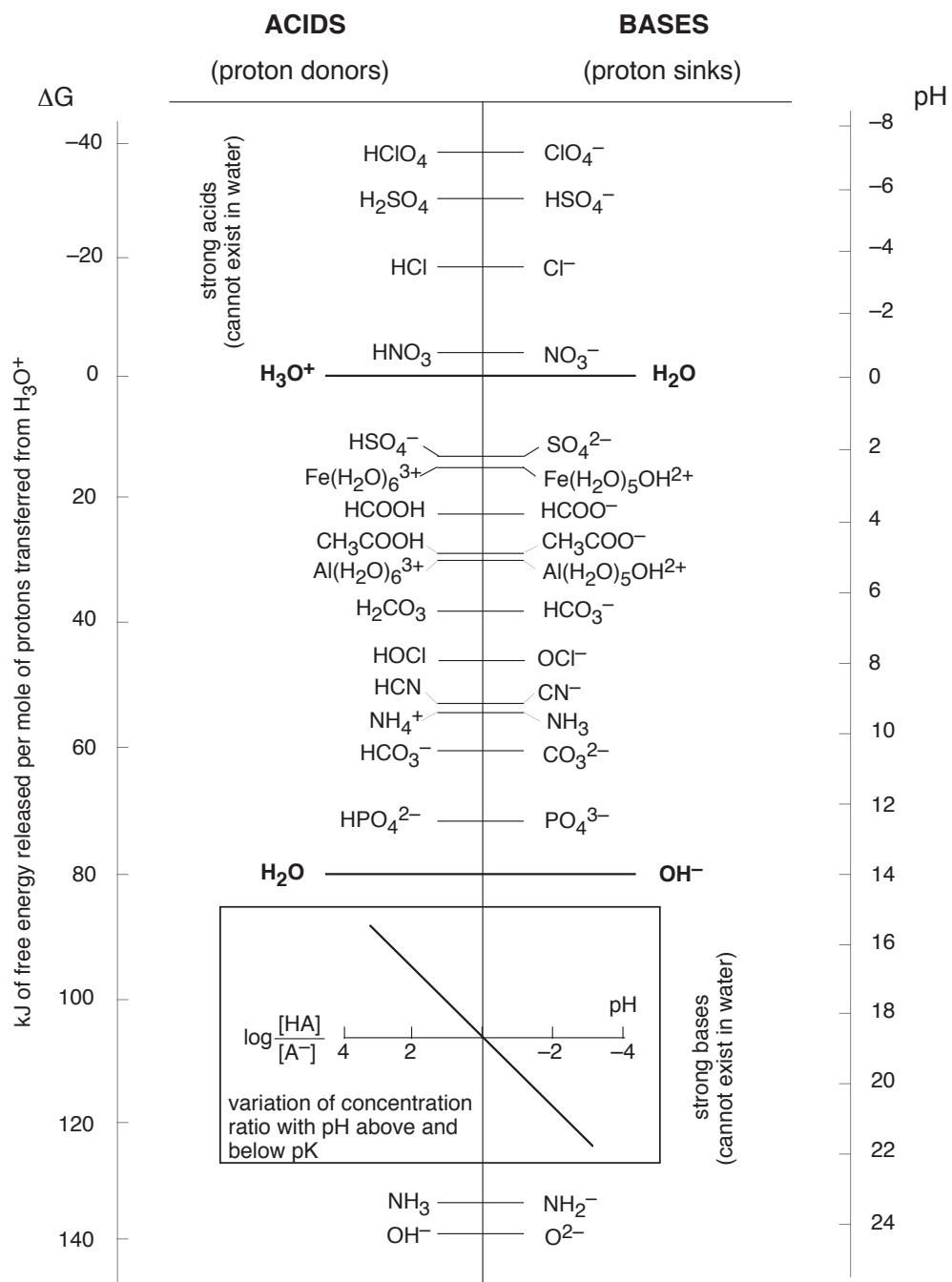
Figure 2: Free energy diagram for acids and bases in aqueous solution.

Now look at the acid/base pairs shown at the top of the table, above the H_3O^+-H_2O line. All of these acids can act as proton sources to sinks (bases) that appear below them. Since H_2O is a suitable sink for these acids, all such acids will lose protons to H_2O in aqueous solutions. These are therefore all *strong* acids that are 100% dissociated in aqueous solution; this total dissociation reflects the very large equilibrium constants that are associated with any reaction that undergoes a fall in free energy of more than a few kilojoules per mole.

2.2 Leveling effect

Because H_2O serves as a proton sink to any acid in which the proton free energy level is greater than zero, the strong acids such as HCl and H_2SO_4 cannot "exist" (as acids) in aqueous solution; they exist as their conjugate bases instead, and the only proton donor present will be H_3O^+. This is the basis of the *leveling effect*, which states that *the strongest acid that can exist in aqueous solution is* H_3O^+.

Now consider a weak acid, such as HCN at about 40 kJ/mol on the scale. This positive free energy means that in order for a mole of HCN to dissociate (transfer its proton to H_2O), the proton must *gain* 40 kJ of free energy per mole. In the absence of a source of energy, the reaction will simply not go; HCN is dissociated only to a minute extent in water.

2.3 Dissociation of weak acids

Why is HCN dissociated at all? The molecules in solution are continually being struck and bounced around by the thermal motions of neighboring molecules. Every once in a while, a series of fortuitous collisions will provide enough kinetic energy to a HCN molecule to knock off the proton, effectively boosting it to the level required to attach itself to water. This process is called *thermal excitation* , and its probability falls off very rapidly as the distance (in kJ/mol) that the proton must rise increases. The protons on a "stronger" weak acid such as HSO_4^- or CH_3COOH will be thermally excited to the H_3O^+ level much more frequently than will the protons on HCN or HCO_3^-, hence the difference in the dissociation constants of these acids.

2.4 Titration

Although a weak acid such as HCN will not react with water to a significant extent, you are well aware that such an acid can still be titrated with strong base to yield a solution of NaCN at the equivalence point. To understand this process, find the H_2O-OH^- pair at about 80 kJ/mol on the free energy scale. Because the OH^- ion can act as a proton sink to just about every acid shown on the diagram, the addition of strong base in the form of NaOH solution allows the protons at any acid above this level to fall to the OH^- level according to the reaction

$$H^+ + OH^- \longrightarrow H_2O$$
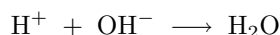
Titration, in other words, consists simply in introducing a low free energy sink that can drain off the protons from the acids initially present, converting them all into their conjugate base forms.

2.5 Strong bases

There are two other aspects of the H_2O-H_3O^+ pair that have great chemical significance. First, its location at 80 kJ/mol tells us that for a H_2O molecule to transfer its proton to another H_2O molecule (which then becomes a H_3O^+ ion whose relative free energy is zero), a whopping 80 kJ/mol of free energy must be supplied by thermal excitation. This is so improbable that only one out of about 10 million H_2O

molecules will have its proton kicked upstairs at a given time; this corresponds to the small value of the ion product of water, about 10^{-14}.

The other aspect of the H_2O-OH^- pair is that its location defines the hydroxide ion as the strongest base that can exist in water. On our diagram only two stronger bases (lower proton free energy sinks) are shown: the amide ion NH_2^-, and the oxide ion O^{2-}. What happens if you add a soluble oxide such as Na_2O to water? Since O^{2-} is a proton sink to H_2O, it will react with the solvent, leaving OH^- as the strongest base present:

$$Na_2O \ + \ H_2O \ \longrightarrow \ 2OH^- \ + \ Na^+$$

This again is the leveling effect; all bases stronger than OH^- appear equally strong in water, simply because they are all converted to OH^-.

2.6   Proton free energy and pH

On the right side of Figure 2 is a pH scale. At the pH value corresponding to a given acid-base pair, the acid and base forms will be present at equal concentrations. For example, if you dissolve some solid sodium sulfate in pure water and then adjust the pH to 2.0, about half of the SO_4^{-2} will be converted into HSO_4^-. Similarly, a solution of Na_2CO_3 in water will not contain a very large fraction of CO_3^{2-} unless the pH is kept above 10.

The pH is a measure of the free energy per mole of protons. This can be seen by writing

$$\text{pH} = \text{p}K_a + \log\frac{[\text{A}^-]}{[HA]} = \frac{\Delta G^\circ}{2.3\,RT} + \log\frac{[\text{A}^-]}{[HA]} \tag{16}$$

and since

$$\Delta G = \Delta G^\circ + RT \ln Q$$
$$\frac{\Delta G}{2.3\,RT} = \frac{\Delta G^\circ}{2.3\,RT} + \log\frac{[\text{A}^-]}{[HA]} \tag{17}$$

It is for this reason that we can show both pH and free energy scales in Fig. 2.

You already know that the free energy of a substance increases with its concentration, so it makes sense that at lower pH values (greater H^+ concentration) the proton free energy in the solution will be higher. This provides another view of the effect of pH on the relative concentrations of the conjugate pairs of various acid-base systems in a solution; the pH effectively sets the average free energy of protons available in the solution. As the value of this latter quantity increases, higher proton-vacant levels will be converted into their protonated forms, and there will be more thermal excitation of these protons to H_2O, resulting in more H_3O^+ ions.

Suppose we have a mixture of many different weak acid-base systems, such as exists in most biological fluids or natural waters, including the ocean. The available protons will fall to the lowest free energy levels possible, first filling the lowest-energy sink, then the next, and so on until there are no more proton-vacant bases below the highest proton-filled (acid) level. Some of the highest protonated species will donate protons to H_2O through thermal excitation, giving rise to a concentration of H_3O^+ that will depend on the concentrations of the various species. The equilibrium pH of the solution is a measure of this H_3O^+ concentration, but this in turn reflects the relative free energy of protons required to keep the highest protonated species in its acid form; it is in this sense that pH is a direct measure of proton free energy.

In order to predict the actual pH of any given solution, we must of course know something about the nominal concentrations (C_a) of the various acid-base species, since this will strongly affect the distribution of protons. Thus if one proton-vacant level is present at twice the concentration of another, it will cause twice as many acid species from a higher level to become deprotonated. In spite of this limitation, the proton free energy diagram provides a clear picture of the relationships between the various acid and base species in a complex solution.

3 Quantitative treatment of acid-base equilibria

3.1 Strong acids and bases

An acid or base is said to be "strong" if it is completely ionized in aqueous solution. Hydrochloric acid is a common example of a strong acid. When HCl gas is dissolved in water, the resulting solution contains the ions H_3O^+, OH^-, and Cl^-.

In order to specify the concentrations of these three species, we need three independent relations between them. (Mathematically, this means that we must write three equations which are then solved simultaneously). These relations are obtained by observing that certain conditions must always be true in any solution of HCl. These are:

1. The *dissociation equilibrium of water* must always be satisfied:

$$[H_3O^+][OH^-] = K_w \tag{18}$$

2. For any acid-base system, one can write a *material balance* equation that relates the concentrations of the various dissociation products of the substance to its "nominal concentration", which we designate here as C_a. For a solution of HCl, this equation would be

$$[HCl] + [Cl^-] = C_a$$

but since HCl is a strong acid, we can neglect the first term and write the trivial mass balance equation

$$[Cl^-] = C_a \tag{19}$$

3. In any ionic solution, the sum of the positive and negative electric charges must be zero; in other words, all solutions are electrically neutral. This is known as the *electroneutrality principle*.

$$[H_3O^+] = [OH^-] + [Cl^-] \tag{20}$$

The next step is to combine these three equations into a single expression that relates the hydronium ion concentration to C_a. This is best done by starting with an equation that relates several quantities, such as Eq 20, and substituting the terms that we want to eliminate. Thus we can get rid of the $[Cl^-]$ term by substituting Eq 19 into Eq 20:

$$[H_3O^+] = [OH^-] + C_a \tag{21}$$

A $[OH^-]$-term can always be eliminated by use of Eq 18:

$$[H_3O^+] = C_a + \frac{K_w}{[H_3O^+]} \tag{22}$$

This equation tells us that the hydronium ion concentration will be the same as the nominal concentration of a strong acid as long as the solution is not very dilute. As the acid concentration falls below about $10^{-6}\,M$, however, the second term predominates; $[H_3O^+]$approaches $\sqrt{K_w}$, or $10^{-7}\,M$. The hydronium ion concentration can of course never fall below this value; no amount of dilution can make the solution alkaline!

Notice that Eq 22 is a quadratic equation; in regular polynomial form it would be

$$[H_3O^+]^2 - C_a[H_3O^+] - K_w = 0 \tag{23}$$

3.2 The strong ion difference

Suppose that we mix a solution of NaOH with a solution of HCl; this would happen during a titration, for example. In this case, we have a fourth variable, the Na^+ concentration. This alters the charge balance equation:

$$[Na^+] - [Cl^-] + [H_3O^+] - [OH^-] = 0 \tag{24}$$

Combining this with Eq 18 we obtain

$$[H_3O^+]^2 + ([Na^+] - [Cl^-])[H_3O^+]K_w = 0 \tag{25}$$

This can be solved for $[H_3O^+]$ by means of the quadratic formula, yielding

$$[H_3O^+] = \left(K_w + \frac{[Na^+] - [Cl^-]}{4}\right)^{\frac{1}{2}} - \frac{[Na^+] - [Cl^-]}{2} \tag{26}$$

Notice that the hydronium ion concentration depends on the *difference* between the concentrations of the cation and the anion. This difference term is known as the *strong ion difference*, abbreviated SID:

$$[SID] = [Na^+] - [Cl^-] \tag{27}$$

Thus Eq 26 becomes

$$[H^+] = \sqrt{K_w + [SID]/2} - [SID]/2 \tag{28}$$

What is a "strong" ion? It is one whose concentration is always the same as the nominal concentration of the acid, base or salt that it comes from. Thus the anions of strong acids and the cations of most metals are strong ions. The ions H_3O^+ and OH^- are *not* strong ions; their concentrations are only the same as those of their parent acid or base if the acid or base is totally dissociated in solution, and the solution is not too dilute. Other examples of "weak" ions are acetate, bicarbonate, etc.

In general, then,

$$[SID] = \sum[\text{strong cations}] - \sum[\text{strong anions}] \tag{29}$$

The SID is a very useful concept, because it allows us to write a simple equation that is completely general. For example, Eq 29 can be applied to a complex mixture made from HCl, $MgSO_4$, NH_4OH and NaOH:

$$[SID] = [Na^+] + [K^+] + [Mg^{2+}] - [Cl^-] - [SO_4^{2+}] \tag{30}$$

There are three particulary important points about the SID that you should understand:

1. Since it is a concentration *difference*, [SID] can be positive or negative; its sign tells us whether the solution is acidic or alkaline:

$$
\begin{array}{lll}
[SID] < 0 & [H_3O^+] > [OH^-] & \text{(acidic solution)} \\
[SID] = 0 & [H_3O^+] = [OH^-] = \sqrt{K_w} & \text{(neutral solution)} \\
[SID] > 0 & [H_3O^+] < [OH^-] & \text{(alkaline solution)}
\end{array}
$$

2. When an acid is titrated with a base, we are in effect simply increasing the [SID] (from its initial negative value) by adding a strong cation.

3. Although [SID] can be positive or negative, the sum of the moles of charge from *all* the ions (strong and weak ones together) must always be zero. This means that when $[SID] \neq 0$, the difference must be compensated for by *"weak"* ions.

The SID is also known as the *alkalinity or the* acid-neutralizing capacity; the higher the [SID] (i.e., the greater the concentration of base such as NaOH or Na_2CO_3), the more moles/litre of strong acid required to reduce the pH to a given reference level. This reference level is not necessarily, or even usually, 7.0; for natural waters, a level of about 4.5 is employed, since this corresponds to the pH of pure water in equilibrium with atmospheric CO_2. Since virtually all natural waters contain dissolved strong cations such as Na^+, Ca^{2+} etc., all such waters possess some degree of alkalinity, even if they are acidic on the pH scale.

3.3   Weak monoprotic acids

Most acids are weak; there are hundreds of thousands of them, whereas there are no more than a few dozen strong acids.

We can treat weak acid solutions in exactly the same general way as we did for strong acids. The only difference is that we must now include the equilibrium expression for the acid. We will start with the simple case of the pure acid in water, and then go from there to the more general one in which strong cations are present.

In this exposition, we will refer to "hydrogen ions" and $[H^+]$ for brevity, and will assume that the acid HA dissociates into H^+ and its conjugate base A^-.

3.4   Pure acid in water

In addition to the species H^+, OH^-, and A^- which we had in the strong-acid case, we now have the undissociated acid HA; four variables, four equation.

1. *equilibria.* We now have two equilibrium relations:

$$[H^+][OH^-] = K_w \tag{31}$$

$$\frac{[H^+][A^-]}{[HA]} = K_a \tag{32}$$

2. *mass balance.* The mass balance relation expresses the nominal concentration of the acid in terms of its two conjugate forms:

$$C_a = [HA] + [A^-] \tag{33}$$

3. *electroneutrality.*

$$[H^+] = [A^-] + OH^- \tag{34}$$

We can use Eq 33 to get an expression for [HA], and this can be solved for $[A^-]$; these are substituted into Eq 32 to yield

$$K_a = \frac{[H^+]([H^+] - [OH^-])}{C_a - ([H^+] - [OH^-])} \tag{35}$$

Getting rid of $[OH^-]$, solving for $[H^+]$, we obtain a cubic equation:

$$[H^+]^3 + K_a[H^+]^2 - (K_w + C_aK_a)[H^+]) - K_wK_a = 0 \tag{36}$$

For most practical applications, we can make approximations that eliminate the need to solve a cubic equation.

1. Unless the acid is extremely weak or the solution is very dilute, the concentration of OH$^-$ can be neglected in comparison to that of [H$^+$]. If we assume that [OH$^-$] $\ll$ [H$^+$], then Eq 35 can be simplified to

$$K_a = \frac{[\text{H}^+]^2}{C_a - [\text{H}^+]} \tag{37}$$

which is a quadratic equation:

$$[\text{H}^+]^2 + K_a[\text{H}^+] - K_a C_a = 0 \tag{38}$$

2. If the acid is fairly concentrated (usually more than 10^{-3} M), a further simplification can frequently be achieved by making the assumption that [H$^+$] $\ll$ C_a. This is justified when most of the acid remains in its un-ionized form [HA], so that relatively little H$^+$ is produced. In this event, Eq 37 reduces to

$$K_a = \frac{[\text{H}^+]^2}{C_a} \tag{39}$$

or

$$[\text{H}^+] \approx (K_a C_a)^{\frac{1}{2}} \tag{40}$$

3.5 Calculations on mixtures of acids

Many practical problems relating to environmental and physiological chemistry involve solutions containing more than one acid. Several methods have been published for calculating the hydrogen ion concentration in solutions containing an arbitrary number of acids and bases[2]. These generally involve iterative calculations carried out by a computer.

In this section, we will restrict ourselves to a much simpler case of two acids, with a view toward showing the general method of approaching such problems by starting with charge- and mass-balance equations and making simplifying assumptions when justified.

In general, the hydrogen ions produced by the stronger acid will tend to suppress dissociation of the weaker one, and both will tend to suppress the dissociation of water, thus reducing the sources of H$^+$ that must be dealt with.

Consider a mixture of two weak acids HX and HY; their respective nominal concentrations and equilibrium constants are denoted by C_x, C_y, K_x and K_y. Starting with the charge balance expression

$$[\text{H}^+] = [\text{X}^-] + [\text{Y}^-] + [\text{OH}^-]$$

We use the equilibrium constants to replace the conjugate base concentrations with expressions of the form

$$[\text{X}^-] = K_x \frac{[\text{HX}]}{[\text{H}^+]}$$

to yield

$$[\text{H}^+] = \frac{[\text{HX}]}{K_x} + \frac{[\text{HY}]}{K_y} + K_w$$

Multiplying both sides by [H$^+$] allows us to eliminate [OH$^-$]:

$$[\text{H}^+]^2 = K_x[\text{HX}] + K_y[\text{HY}]$$

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[2]See, for example, *J. Chem. Education* 67(6) 501-503 (1990) and 67(12) 1036-1037 (1990).

If neither acid is very strong nor very dilute, we can replace equilibrium concentrations with nominal concentrations:

$$[H^+] \approx \sqrt{C_x K_x + C_y K_y + K_w}$$

For a solution containing 0.10 M acetic acid (K_a= 1.75E-5) and 0.20 M phenol (K_a= 1.00E-10) this yields a reasonable answer. But if 0.001 M chloracetic acid (K_a= .0014) is used in place of phenol, the above expression becomes

$$[H^+] = \sqrt{1.40\text{E-6} + 1.75\text{E-8} + 10^{-14}} = 0.00118 \, M$$

which exceeds the concentration of the stronger acid; because the acetic acid makes a negligible contribution to $[H^+]$ here, the simple approximation given above is clearly invalid.

We now use the mass balance expression for the stronger acid

$$[HX] + [X^-] = C_x$$

to solve for $[X^-]$ which is combined with the expression for K_x to yield

$$[X^-] = C_x - \frac{[H^+][X^-]}{K_x}$$

Solving this for $[X^-]$ gives

$$[X^-] = \frac{C_x K_x}{K_x + [H^+]}$$

The approximation for the weaker acetic acid (HY) is still valid, so we retain it in the substituted electronegativity expression:

$$[H^+] = \frac{C_x K_x}{K_x + [H^+]} + \frac{C_y K_y}{[H^+]}$$

which is a cubic equation that can be solved by approximation.

3.6   Mixture of an acid and its conjugate base

If we add some sodium hydroxide to a solution of an acid, then an equivalent amount of the acid will be converted into its base form, resulting in a "partly neutralized" solution in which both the acid and its conjugate base are present in significant amounts. Solutions of this kind are far more common than those of a pure acid or a pure base, and it is very important that you have a thorough understanding of them.

For example, suppose that we have a solution containing 0.010 mole of acetic acid. To this we add 0.002 mole of sodium hydroxide, which consumes this same amount of acid and produces 0.002 mole of acetate ion. If the volume of the final solution is 100 ml, then the nominal acid and base concentrations are

$$C_a = \frac{.010 - .002 \text{ mol}}{.100 \text{ L}} = .080 \, M \qquad \text{and} \qquad C_b = \frac{.002}{.100} = .020 \, M$$

Note that this solution would be indistinguishable from one prepared by combining $C_a = .080$ mole of acetic acid with $C_b = 0.020$ mole of sodium acetate and adjusting the volume to 100 ml.

The equilibrium expressions for such a solution are just the ones for the pure-acid case: Eq 31 and Eq 32 . The mass balance for the acid now contains the additional term C_b; note that in the preceding example, this sum will have the value 0.100 M:

$$[HA] + [A^-] = C_a + C_b \tag{41}$$

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There is a new mass balance equation for the cation, but it is trivial:

$$[\text{Na}^+] = C_b \tag{42}$$

The charge balance equation must also include $[\text{Na}^+]$:

$$[\text{Na}^+] + [\text{H}^+] = [\text{OH}^-] + [\text{A}^-] \tag{43}$$

Substituting Eq 42 into the above expression yields an equation for $[\text{A}^-]$:

$$[\text{A}^-] = C_b + [\text{H}^+] - [\text{OH}^-] \tag{44}$$

Inserting this into Eq 41 and solving for $[\text{HA}]$,

$$[\text{HA}] = C_a - ([\text{H}^+] - [\text{OH}^-]) \tag{45}$$

Finally we substitute these last two expressions into the equilibrium constant Eq 32 :

$$[\text{H}^+] = K_a \frac{C_a - [\text{H}^+] + [\text{OH}^-]}{C_b + [\text{H}^+] - [\text{OH}^-]} \tag{46}$$

which is cubic in $[\text{H}^+]$ when $K_w/[\text{OH}^-]$ is replaced by $[\text{H}^+]$:

$$[\text{H}^+]^3 + (C_b + 1)[\text{H}^+]^2 - (K_w + C_a K_a)[\text{H}^+] - K_w = 0 \tag{47}$$

In almost all practical cases it is possible to make simplifying assumptions. Thus if the solution is known to be acidic or alkaline, then the $[\text{OH}^-]$ or $[\text{H}^+]$ terms in Eq 46 can be neglected. In acidic solutions, for example, Eq 46 becomes

$$\boxed{[\text{H}^+] \approx K_a \frac{C_a - [\text{H}^+]}{C_b + [\text{H}^+]}} \tag{48}$$

If the concentrations C_a and C_b are sufficiently large, it may be possible to neglect the $[\text{H}^+]$ terms entirely, leading to the commonly-seen expression

$$\boxed{[\text{H}^+] \approx K_a \frac{C_a}{C_b}} \tag{49}$$

This latter relation is an extremely important one which you must know; it is sometimes referred to as the *Henderson-Hasselbalch equation.*

Pitfalls of the Henderson-Hasselbalch equation   The above equation will be found in virtually all textbooks and is widely used in practical calculations. What most books do not tell you is that Eq 49 is no more than an "approximation of an approximation" which can give incorrect and misleading results when applied to situations in which the simplifying assumptions are not valid. Unless you know what you are doing, your starting point should normally be Eq 48 for solutions that are expected to be acidic, or an analogous relation which can easily be derived for alkaline solutions.

Problem Example 1
Calculate the pH of a solution prepared by adding 0.10 mole of NaOH to a solution containing 0.20 mole/litre of iodic acid, HIO_3, $K_a = 0.2$.

Figure 3: Buffering action as a function of buffer concentration
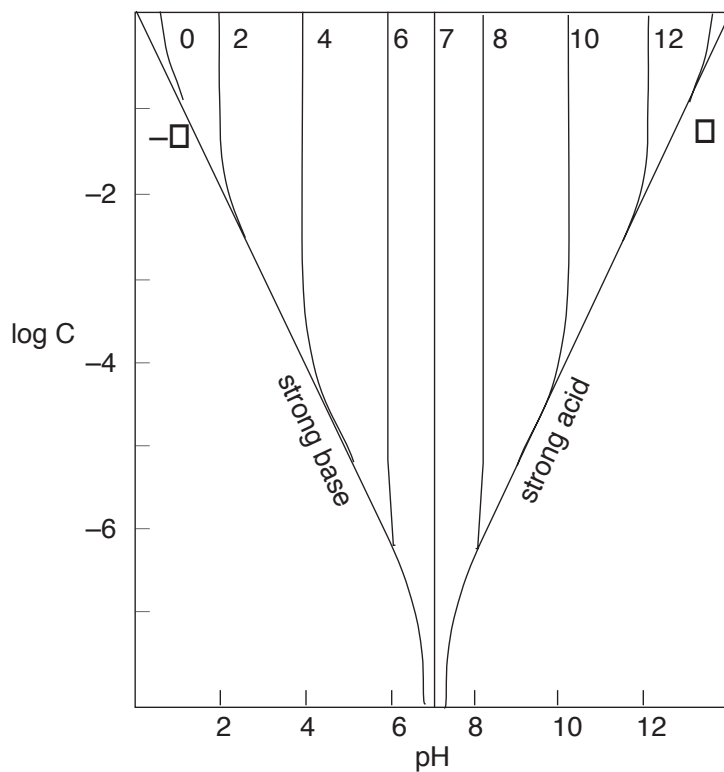
How dilute can a solution with $[A^-] = C_b$ be and still exhibit useful buffering action? As you can see from these plots, the answer depends very much on the pK_a of the particular acid-base system. (The pK_a values are indicated near the top of the figure.) The lines marked $\pm\infty$ correspond to the limiting cases of a strong acid and a non-acid. The vertical part of each plot corresponds to the concentration range in which the approximation Eq 49 is valid.

Solution: Eq 49 predicts a hydrogen ion concentration of

$$[H^+] = K_a \frac{C_a}{C_b} = 0.2 \frac{0.10}{0.10} = 0.2$$

or a pH of 0.70, but this is wrong. The problem is that HIO_3 is a rather "strong" weak acid, so the value of $[H^+]$ will be comparable in magnitude to those of C_a and C_b in Eq 48. Placing this equation in standard polynomial form yields

$$[H^+]^2 + (C_a + K_a)[H^+] - K_a C_a = 0 \tag{50}$$

Solving this for $[H^+]$ using the values in the problem gives a hydrogen ion concentration of $0.056\ M$ and a pH of 1.2; notice that these results are quite different from what Eq 49 would predict.

Be careful about confusing the two relations

$$[H^+] = K_a \frac{[HA]}{[A^-]} \qquad \text{and} \qquad [H^+] \approx K_a \frac{C_a}{C_b}$$

The one on the left is simply a re-writing of the equilibrium constant expression, and is therefore *always true*. Of course, without knowing the actual equilibrium values of $[HA]$ and $[A^-]$, this relation is of little direct use in pH calculations. The equation on the right is *never true*, but will yield good results if the acid is sufficiently weak in relation to its concentration to keep the $[H^+]$ from being too high. Otherwise, the high $[H^+]$ will convert a significant fraction of the A^- into the acid form HA, so that the ratio $[HA]/[A^-]$ will differ from C_a/C_b in the above two equations. Consumption of H^+ by the base will also raise the pH above the value predicted by Eq 49 as we saw in the preceding problem example.

Finally, notice that Eq 49 can give absurd values of hydrogen ion concentration if one of C_a or C_b is extremely small.

3.7   General case of a weak acid/base system, using [SID]

By using the strong ion difference defined in Eq 29 , we can obtain a single set of relations which will be valid for both of the cases which we have just treated. This is especially useful for following the titration of a weak acid with a strong base; as was pointed out previously, such a titration corresponds to raising the [SID] from the negative value it has in the pure acid to zero, its value at the equivalence point. If the acid is being titrated with sodium hydroxide, then $[SID] = [Na^+]$.

The four equations required to specify the values of $[A^-]$, $[OH^-]$, $[HA]$ and $[A^-]$ are the same as in the pure-acid case, except that the [SID] term is added to the charge balance:

$$\begin{aligned}
\text{water dissociation :} \qquad & [H^+][OH^-] = K_w \\
\text{acid dissociation :} \qquad & \frac{[H^+][A^-]}{[HA]} = K_a \\
\text{mass balance :} \qquad & [HA] + [A^-] = C_a \\
\text{charge balance :} \qquad & [SID] + [H^+] - [A^-] - [OH^-] = 0
\end{aligned}$$

Eliminating $[OH^-]$ and $[A^-]$ by appropriate substitution, the last equation can be written as

$$[SID] + [H^+] - \frac{K_w}{[H^+]} - K_a \frac{C_a}{K_a + [H^+]} = 0 \tag{51}$$

Clearing fractions and rewriting in polynomial form, this becomes

$$[\text{H}^+]^3 + [\text{H}^+]^2(K_a + [\text{SID}]) + [\text{H}^+]\{K_a([\text{SID}] - C_a) - K_w\} - K_a K_w = 0 \tag{52}$$

In a moderately concentrated solution of a weak acid which has been partially neutralized, [SID] is positive and large compared to $[\text{H}^+]$ and $[\text{OH}^-]$. If the latter two terms are dropped from the charge balance expression, the electroneutrality condition becomes $[\text{A}^-] \approx [\text{SID}]$. Using this approximation, together with $[\text{HA}] \approx C_a$ we can develop the expression corresponding to Eq 49:

$$[\text{H}^+] = \frac{K_a[\text{HA}]}{[\text{A}^-]} \approx \frac{C_a}{[\text{SID}]}K_a \tag{53}$$

3.8   Example calculations involving conjugate species

Problem Example 2

Calculate the pH of a solution containing 0.0100 mole of ammonium chloride and 0.0200 mole of ammonia in 100 ml of solution.

Solution: The equilibrium here is

$$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$$
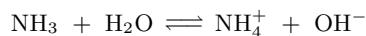
For NH_4^+, $K_a = 10^{-9.3}$ and thus $K_b = 10^{-(14-(-9.3))} = 10^{-4.7}$:

$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 10^{-4.7}$$

The nominal concentrations of the acid and conjugate base are respectively $C_a = 0.100\,M$ and $C_b = 0.200\,M$. The mass balance expressions are

$$[\text{NH}_4^+] + [\text{NH}_3] = C_a + C_b = 0.30 \qquad \text{and} \qquad [\text{Cl}^-] = C_a$$

and the charge balance is given by

$$[\text{Cl}^-] + [\text{OH}^-] = [\text{H}^+] + [\text{NH}_4^+] \approx [\text{NH}_4^+]$$

in which the approximation shown above is justified by our knowledge that the solution will be weakly alkaline. The equilibrium concentrations of the conjugate species are then

$$[\text{NH}_4^+] = 0.100 + [\text{OH}^-] \qquad \text{and} \qquad [\text{NH}_3] = 0.200 - [\text{OH}^-]$$

Because C_a and C_b are large compared to $[\text{OH}^-]$ (the solution is not expected to be strongly alkaline), the $[\text{OH}^-]$ terms in the above expressions can be dropped and the equilibrium expression becomes

$$\frac{(0.100)[\text{OH}^-]}{0.200} = 2.0\text{E–}5$$

from which we find $[\text{OH}^-] = 4.0\text{E–}5$, pOH = 4.4 and <u>pH = 9.6</u>.

Problem Example 3

What will be the change in the pH if 10 ml of $0.100\,M$ HCl is added to 100 ml of the above solution?
Solution: We can continue using the approximations for the concentrations of the conjugate species that we developed in the preceding example. Addition of the strong acid (1.0 mmol) converts this amount of NH_3 into NH_4^+ and also increases the total volume of the solution. The values of C_b and C_a are now

$$C_b = [\text{NH}_3] = \frac{(20\text{ mmol} - 1\text{ mmol})}{110\text{ ml}} = 0.173\,M$$

and

$$C_a = [NH_4^+] = \frac{(10 \text{ mmol} + 1 \text{ mmol})}{110 \text{ ml}} = 0.100 \, M$$

Substituting these into the equilibrium constant expression yields

$$[OH^-] = \frac{[NH_3]}{[NH_4^+]} K_b = 1.73 \times 2.0 \times 10^{-5} = 3.46\text{E--}5$$

The new pOH is 4.5, so addition of the acid has changed the pH to 9.5, a decrease of only 0.1 pH unit.

Problem Example 4

Calculate the pH of a 0.01 M solution of ammonium chloride in pure water.
Solution: From the charge balance expression

$$[NH_4^+] + [H^+] = [OH^-] + [Cl^-]$$

we can drop the $[OH^-]$ term since we know that the solution will be weakly acidic. Using this approximation and the mass balance on the conjugate species, we have

$$[NH_4^+] = 0.01 - [H^+] \qquad \text{and} \qquad [NH_3] = [H^+]$$

Substituting these into the K_a expression for $[NH_4^+]$, we obtain

$$[H^+] = \frac{[NH_4^+]}{[NH_3]} K_a = \frac{0.01 - [H^+]}{[H^+]} \times 5.0 \times 10^{-10}$$

Can we drop the $[H^+]$ term in the numerator? Doing so yields

$$[H^+] = \sqrt{0.01 \times 5 \times 10^{-10}} = 2.2\text{E--}6$$

Because this value is small compared to 0.01, this approximation is acceptable and the pH is 5.6.

A salt of a weak acid gives an alkaline solution, while that of a weak base yields an acidic solution. What happens if we dissolve a salt of a weak acid *and* a weak base in water?

Problem Example 5

Estimate the pH of a 0.0100 M solution of ammonium formate in water. Formic acid, HCOOH, is the simplest organic acid and has $K_a = 10^{-3.7} = 1.76\text{E--}4$. For NH_4^+, $K_a = 10^{-9.3}$.
Solution: Three equilibria are possible here; the reaction of the ammonium and formate ions with water, and their reaction with each other:

$$\begin{array}{llll}
NH_4^+ + H_2O & \rightleftharpoons & NH_3 + H_3O^+ & K_1 = 10^{-9.3} \\
HCOO^- + H_2O & \rightleftharpoons & HCOOH + OH^- & K_2 = \frac{10^{-14}}{10^{-3.7}} = 10^{-10.3} \\
NH_4^+ + HCOO^- & \rightleftharpoons & NH_3 + HCOOH & K_3
\end{array}$$
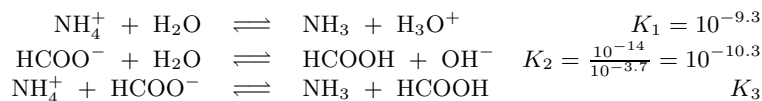
Inspection reveals that the last equation is the sum of the first two, plus the reaction

$$H^+ + OH^- \longrightarrow 2\,H_2O \qquad K_4 = 1/K_w$$
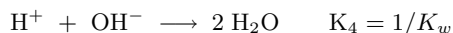
The value of K_3 is therefore

$$K_3 = \frac{10^{-9.3} \times 10^{-10.3}}{K_w} = 10^{-5.6}$$

A rigorous treatment of this system would require that we solve these equations simultaneously with the charge balance and the two mass balance equations. However, because K_3 is several orders

of magnitude greater than K_1 or K_2, we can greatly simplify things by neglecting the other equilibria and considering only the reaction between the ammonium and formate ions. Notice that the products of this reaction will tend to suppress the extent of the first two equilibria, reducing their importance even more than the relative values of the equilibrium constants would indicate.

From the stoichiometry of ammonium formate we can write can write

$$[\text{NH}_4^+] = [\text{HCOO}^-] \qquad \text{and} \qquad [\text{NH}_3] = [\text{HCOOH}]$$

Then

$$K_3 = \frac{[\text{NH}_3][\text{HCOOH}]}{[\text{NH}_4^+][\text{HCOO}^-]} = \frac{[\text{HCOOH}]^2}{[\text{HCOO}^-]^2} = \frac{K_w}{K_a K_b}$$

in which K_b is the base constant of ammonia, $K_w/10^{-9.3}$.

From the formic acid dissociation equilibrium we have

$$\frac{[\text{HCOOH}]}{[\text{HCOO}^-]} = \frac{[\text{H}^+]}{K_a}$$

Rewriting the expression for K_3,

$$K_3 = \frac{[\text{HCOOH}]^2}{[\text{HCOO}^-]^2} = \frac{[\text{H}^+]^2}{K_a{}^2} = \frac{K_w}{K_a K_b}$$

Which yields

$$[\text{H}^+] = \sqrt{\frac{K_w K_a}{K_b}} = 10^{-6.5}$$

___

What is interesting about this last example is that *the pH of the solution is apparently independent of the concentration* of the salt. If $K_a = K_b$ then this is *always* true and the solution will be neutral (neglecting activity effects in solutions of high ionic strength). Otherwise, it is only an approximation that remains valid as long as the salt concentration is substantially larger than the magnitude of either equilibrium constant. Clearly, the pH of any solution must approach that of pure water as the solution becomes more dilute.

3.9 Diprotic acids

A diprotic acid such as H_2SO_4 can donate its protons in two steps, yielding first a monoprotonated species HSO_4^- and then the completely deprotonated form SO_4^{2-}. Since there are five unknowns (the concentrations of the acid, of the two conjugate bases and of H_3O^+ and OH^-), we need five equations to define the relations between these quantities. These are

- *Equilibria:*

$$[\text{H}^+][\text{OH}^-] = \text{K}_\text{w} \tag{54}$$

$$\frac{[\text{H}^+][\text{HA}^-]}{[\text{H}_2\text{A}]} = K_{a1} \tag{55}$$

$$\frac{[\text{H}^+][\text{A}^{2-}]}{[\text{HA}^-]} = K_{a2} \tag{56}$$

- *Charge balance:*

$$[\text{H}_3\text{O}^+] = [\text{HA}] + 2[\text{A}^{2-}] \tag{57}$$

- *Material balance:* When we start with C_a moles per litre of the acid H_2A, the concentrations of those species containing the species A must add up to the amount initially present.

$$C_a = [H_2A] + [HA^-] + [A^{2-}] \tag{58}$$

The full equation is

$$K_2 = \frac{[H^+]\left([H^+] - [OH^-] - \frac{2K_2([H^+]-[OH^-])}{[H^+]+2K_2}\right)}{C_a - \left([H^+] - [OH^-] - \frac{2K_2([H^+]-[OH^-])}{[H^+]+2K_2}\right)} \tag{59}$$

which can be expressed as the quartic polynomial

$$[H^+]^4 + [H^+]^3([A^-] + K_1) = [H^+]^2(K_1K_2 - K_w) - [H^+][K_1([A^-]K_2 + K_w)] - K_1K_2K_w = 0 \tag{60}$$

There are very few, if any practical situations in which this exact relation needs to be used. If the solution is at all acidic then $[OH^-]$ is negligible compared to $[H^+]$ and the first equation reduces to

$$K_1 = \frac{[H^+]\left([H^+] - \frac{2K_2[H^+]}{[H^+]+2K_2}\right)}{C_a - \left([H^+] - \frac{K_2[H^+]}{[H^+]+2K_2}\right)} \tag{61}$$

For many polyprotic acids the second acid constant K_2 is small. If the solution is sufficiently acidic so that $K_2 \ll [H^+]$, then the preceding expression can be greatly simplified:

$$K_1 = \frac{[H^+]^2}{C_a - [H^+]} \tag{62}$$

This is the usual starting point for most practical calculations. Finally, if the solution is sufficiently concentrated (and K_a is sufficiently small) so that $[H^+] \ll C_a$, we can obtain

$$[H^+] = (K_aC_a)^{\frac{1}{2}} \tag{63}$$

Notice that the K_2 term does not appear in these last two equations; this suggests that the pH of a weak polyprotic acid is largely determined by the first ionization step. One rationale for this is that the H_3O^+ produced by the first ionization step will, according to Le Châtelier's principle, tend to repress the ionization of the second step.

4 Mixtures of conjugate acids and bases

4.1 Buffer solutions

A solution in which both the acid and base forms of a conjugate pair are present in significant concentrations corresponds to a partially-neutralized acid or base in which [SID] is positive and large compared to $[H^+]$, $[A^-]$ and $[OH^-]$. These are the same conditions that to the approximation Eq 53 which, when rewritten in logarithmic form, is known as the *Henderson-Hasselbalch equation*

$$pH = pK_a + \log\frac{[SID]}{[A^-]} = pK_a + \log\frac{C_b}{[A^-]} \tag{64}$$

The tendency of added strong acid or base to change the pH of a solution is seen to depend on the relative magnitudes of the two terms on the right. This tendency is given by the slope of the titration curve:

$$\beta = \frac{dC_b}{d\text{pH}} = -\frac{d[\text{A}^-]}{d\text{pH}} \tag{65}$$

The quantity β is known as the *buffer intensity* or buffer index. An exact expression for β can be obtained
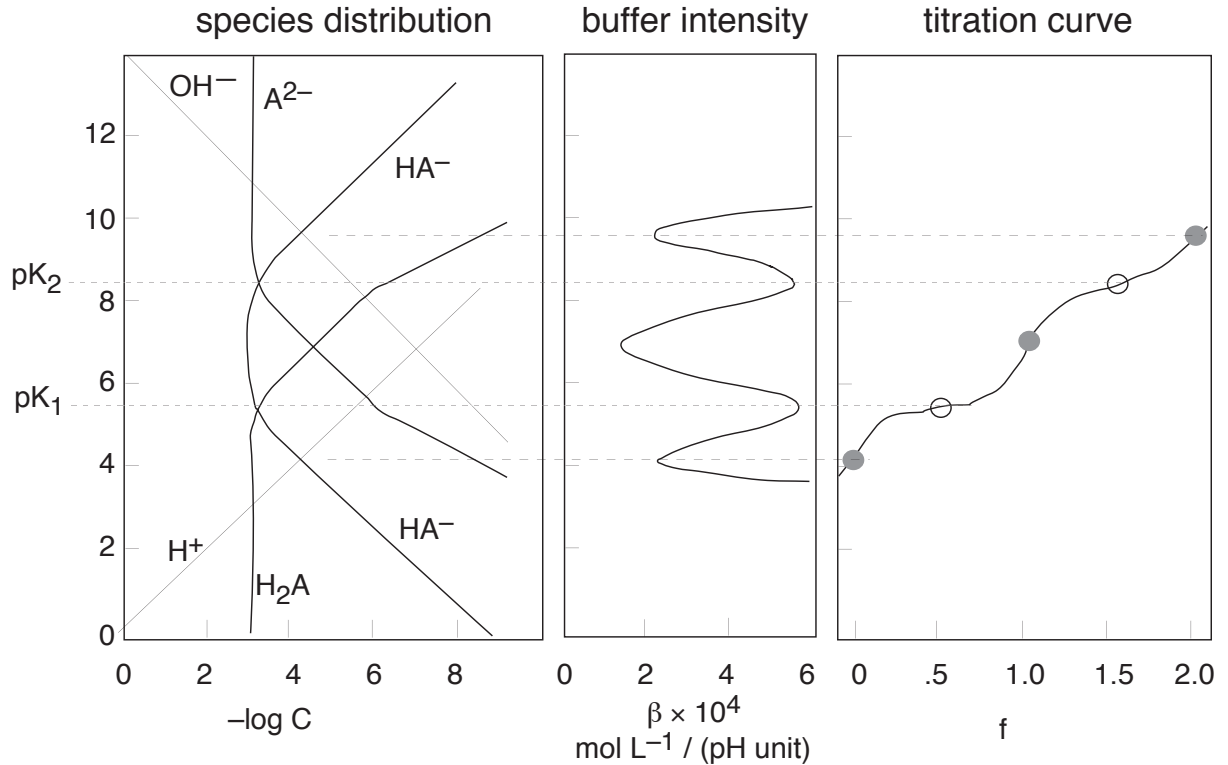
Figure 4: Buffer intensity and titration curve for a diprotic acid

by differentiating the equation for $[\text{H}^+]$:

$$\beta = \frac{[\text{H}^+]^2 + K_a[\text{H}^+]}{3[\text{H}^+]^2 + 2[\text{H}^+](K_a + [\text{SID}]) + K_a([\text{SID}] - [\text{A}^-]) - K_w} \tag{66}$$

A *buffer solution* is one whose pH tends to be insensitive to the amount of strong acid or strong base added, and which therefore has a large buffer intensity. In pure water, β is very small: 4.6×10^{-7} mol/l.

Under optimum buffering conditions when $[\text{SID}] \approx C_a/2$,

$$\beta = 2.5 + \frac{C_a}{4K_a} - \frac{K_w}{2K_a{}^2} \tag{67}$$

or, approximately,

$$\beta \approx \frac{C_a}{4K_a} \tag{68}$$

A common misconception is that only *weak*-acid/base systems can act as buffer solutions. The set of plots shown in Fig. 5 demonstrate that this is not correct; even a solution having $[\text{SID}] = 0$ can act as a buffer, *but only at very high or low pH values.* Within this effective range, a solution containing no weak acid at all is even a better buffer, since changes in $[\text{H}^+]$ are almost completely compensated for by water autoprotolysis. In a weak-acid solution, A^- ions (as well as OH^- ions) are available to maintain charge balance, so the fraction of negative ions that are capable of neutralizing any added H^+ is smaller.

The real effect of a conventional buffer system is to set the pH range of buffering from its strong-acid value of $[\text{H}^+] \approx K_w/[\text{SID}]$ to a value closer to neutrality. Within this range, buffering is most effective at higher $[\text{A}^-]$ and when $[\text{HA}] = [\text{A}^-]$.

4.2 Titrations

The titration of an aqueous solution of an acid HA consists in measuring the volume of strong base MOH required to reach the *equivalence point* at which $[\text{M}^+] = [\text{A}^-]$. If HA is a strong acid, the equivalence point corresponds to $[\text{SID}] = 0$; for a weak acid, $[\text{SID}] = [\text{M}^+]$.

If the solution being titrated contains C equivalents/l of acid, the equivalent fraction of base added is given by

$$f = \frac{[\text{M}^+]}{C} = \frac{[\text{SID}]}{C} \tag{69}$$

The *titration curve* is a plot of pH as a function of the titration fraction f. At the beginning of the titration, $f = 0$ for a solution of a strong acid. At $f = 0.5$, $\text{pH} = \text{p}K_a$; at the equivalence point, $f = 1$ and the pH is that of a solution of the pure salt MA. For polyprotic acids, $f = 2$ at the second equivalence point, etc.

If V_b litres of base is required to titrate V_a litres of a monoprotic acid to the equivalance point, the titration curve is defined by the exact equation

$$[\text{H}^+]^3 + [\text{H}^+]^2 \left(\frac{V_b C_b}{V_a + V_b} + K_a \right) + [\text{H}^+] \left(\frac{K_a C_b V_b - K_a [\text{A}^-] V_a}{V_a + V_b} \right) - K_w K_a = 0 \tag{70}$$

The weaker the acid, the less well-defined is the rise in pH near the equivalence point (Fig. 6). This can be regarded as an effect of buffering, which is always most effective near the $\text{p}K_a$ of the acid.

4.3 Ionization fractions

It is important to be able to express the relative amounts of a conjugate acid-base system present in the protonated and deprotonated forms. The simple ratio $[\text{HA}]/[\text{A}^-]$ (or its inverse) is often used, but this suffers from the disadvantage of being indeterminate when the concentration in the denominator is zero. For many purposes it is more convenient to use the *ionization fractions*

$$\alpha_0 \equiv \alpha_{\text{HA}} = \frac{[\text{HA}]}{[\text{HA}] + [\text{A}^-]}; \qquad\qquad \alpha_1 \equiv \alpha_{\text{A}^-} = \frac{[\text{A}^-]}{[\text{HA}] + [\text{A}^-]} \tag{71}$$

The fraction α_1 is also known as the *degree of dissociation* of the acid. By making appropriate substitutions using the relation

$$[\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]} \tag{72}$$

. we can express the ionization fractions as a function of the pH:

$$\alpha_0 \equiv \alpha_{\text{HA}} = \frac{[\text{H}^+]}{K_a + [\text{H}^+]}; \qquad\qquad \alpha_1 \equiv \alpha_{\text{A}^-} = \frac{K_a}{K_a + [\text{H}^+]} \tag{73}$$
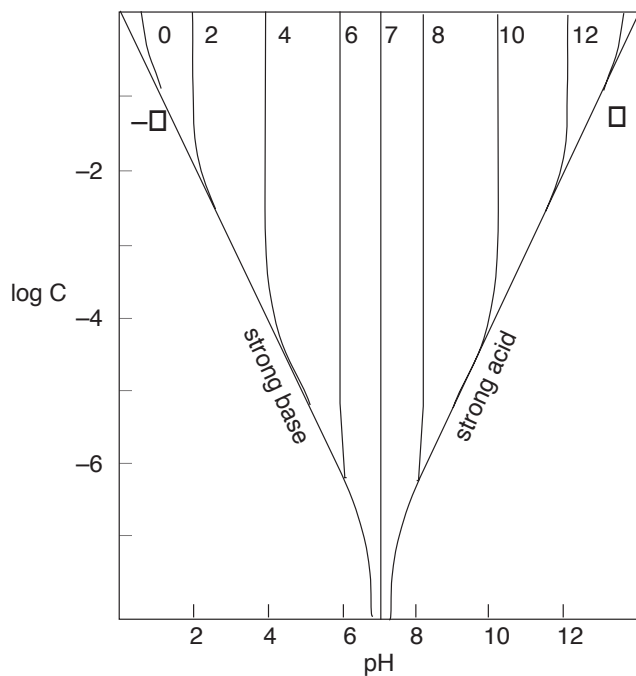
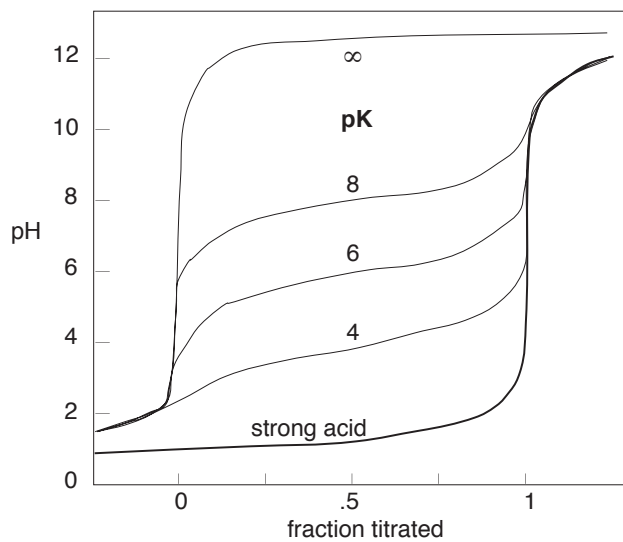Figure 5: Buffering in strong- and weak-acid solutions

Figure 6: Titration curves of acids and bases of various strengths

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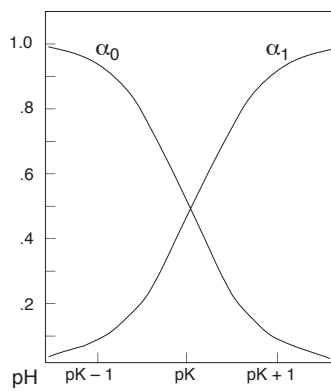Figure 7: Titration curve for a polyprotic acid, H_3PO_4

Figure 8: Equilibrium fraction diagram for a monoprotic acid.

In the plot of these two functions shown in Fig. 8, notice the crossing point where $[\text{HA}] = [\text{A}^-]$ when $[\text{H}^+] = K_a$. This corresponds to unit value of the quotient in Eq 72.

For a polyprotic system, $\sum_i \alpha_i = 1$. For a diprotic acid,

$$[\text{H}_2\text{A}] = [\text{A}^-]\alpha_0, \qquad\qquad [\text{HA}^-] = C_a\alpha_1, \qquad\qquad [\text{A}^{2-}] = C_a\alpha_2 \tag{74}$$

also,

$$\alpha_0 = \frac{[\text{H}^+]}{K_1}\alpha_1, \qquad\qquad \alpha_1 = \frac{[\text{H}^+]}{K_2}\alpha_2 \tag{75}$$

During the course of a titration, the electroneutrality condition requires that

$$C_b = C_a\alpha_1 + [\text{OH}^-] - [\text{H}^+] = C_a\alpha_1 + [\text{OH}^-] + [\text{H}^+] \tag{76}$$

and thus

$$f = \alpha_1 + \frac{[\text{OH}^-] - [\text{H}^+]}{C_a} \tag{77}$$

In exact calculations it is necessary to correct for dilution of the acid by the water introduced with the base:

$$C = C_\circ \frac{V_\circ}{V_\circ + V} \tag{78}$$

in which the subscripted terms refer to the initial acid solution.

5   Logarithmic concentration diagrams

By treating the pH as a master variable that uniquely determines the concentrations of all species involved in a given equilibrium system, it is possible to develop graphical presentations that are easy to construct and highly informative.

Look at Fig. 9 and note the two diagonal lines labeled $[\text{H}^+]$ and [oh-]. These are simply the definitions of pH and pOH and their placements should be apparent. The other two lines, representing the concentrations of the acid and base forms as functions of the pH, are constructed by making approximations appropriate to the various pH ranges.

- Where $\text{pH} = \text{p}K_a$, $[\text{HA}] = [\text{A}^-] = C_a/2$; this defines the point labeled **2** whose y-coordinate is at $\log C_a - \log 2$, which falls 0.3 unit below $\log C_a$.

- When $\text{pH} \ll \text{p}K_a$, the mixture consists essentially of a solution of HAc in water. The proton balance for such a solution is

$$[\text{H}_3\text{O}^+] = [\text{A}^-] + [\text{OH}^-] \approx [\text{A}^-] \tag{79}$$

  Within this pH region, the slope of the [A]-vs-pH curve is easily shown to be unity:

$$[\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]}$$

  solving for $[\text{A}^-]$ and using C_a in place of [HA], we have

$$[\text{A}^-] \approx \frac{C_a K_a}{[\text{H}^+]} \qquad \text{or} \qquad \log[\text{A}^-] \approx \log C_a - \text{p}K_a + \text{pH}$$

  which is then differentiated:

$$\frac{d(\log[\text{A}^-])}{d\text{pH}} = 1 \tag{80}$$

  This slope together with point **1** define the line representing $[\text{A}^-]$ in the left part of the diagram.
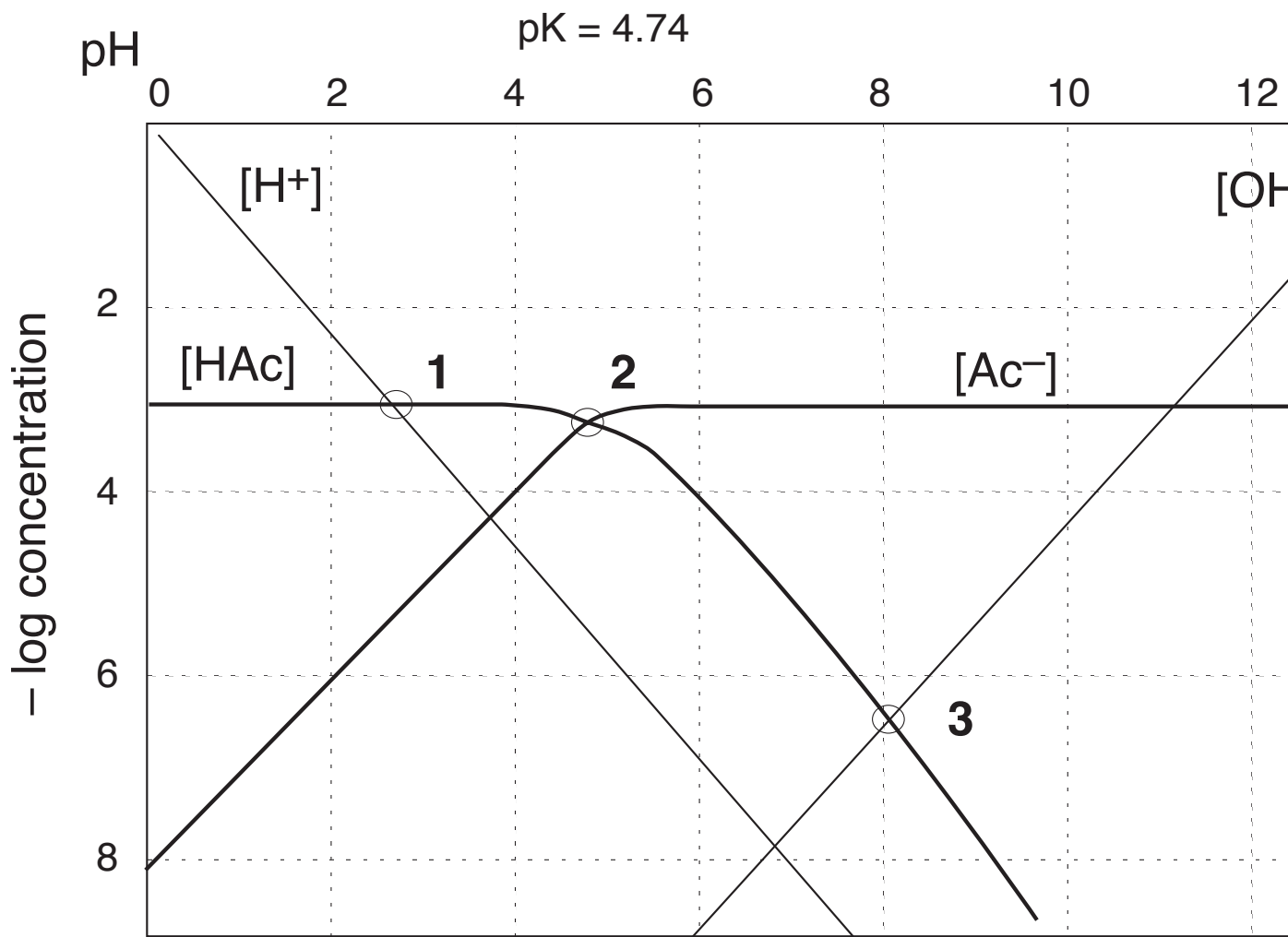
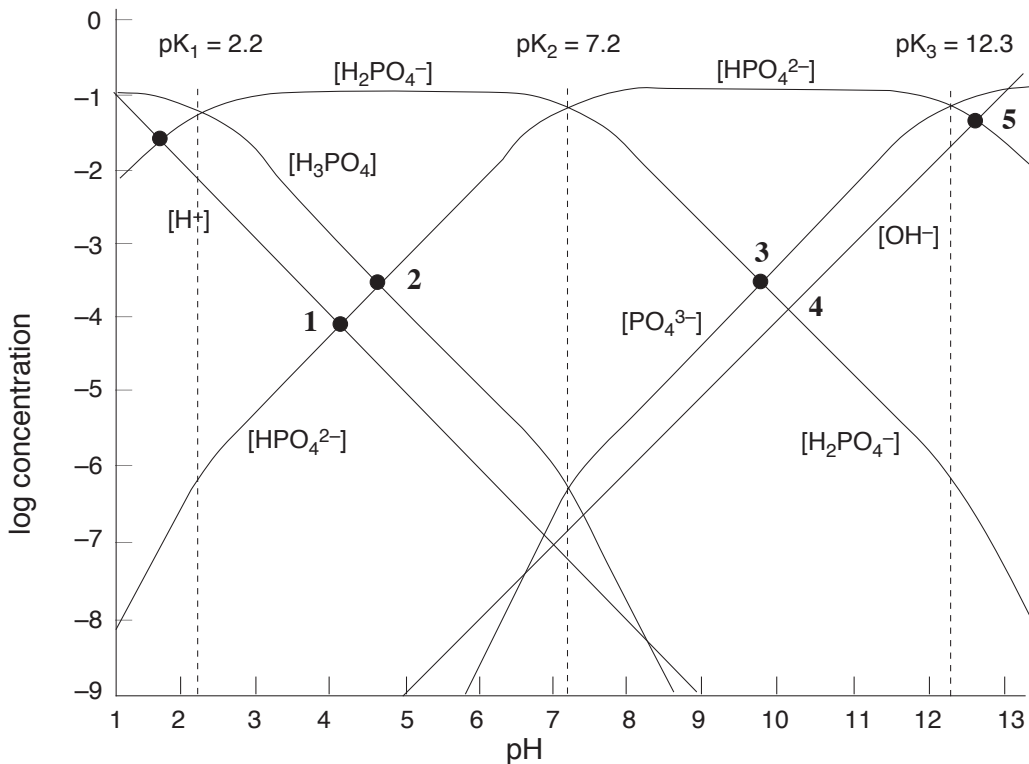Figure 9: Log-C vs pH diagram for a $10^{-3}\,M$ acetic acid solution.

Figure 10: Log-C diagram for the phosphoric acid system

- In alkaline solutions where $\text{pH} \gg \text{p}K_a$,

$$[\text{HA}] \approx \frac{[\text{A}^-][\text{H}^+]}{K_a}, \qquad\qquad \log[\text{HA}] = \log C_a - \text{pH} + K_a$$

which gives a slope of -1:

$$\frac{d[\text{HA}]}{d\text{pH}} = -1 \tag{81}$$

The proton condition for a solution consisting mostly of the base form is

$$[HA] + [\text{H}^+] = [\text{OH}^-] \qquad \text{or} \qquad [\text{HA}] \approx [\text{OH}^-] \tag{82}$$

which defines point **3** in Fig. 9.

Logarithmic concentration diagrams afford a quick means of estimating the equilibrium composition of acid-base systems without resorting to computation. For this purpose, we add the lines corresponding to $[\text{H}^+]$ and $[\text{OH}^-]$. The slopes of these lines will be ± 1, and the lines for [HA] and [A$^-$] will be parallel to them.

5.1 Polyprotic acids

Whereas pH calculations for solutions of polyprotic acids become quite complex, the log-C plots for such systems simply contain a few more lines but are no more difficult to construct that those for monoprotic

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acids. Fig. **??** shows a plot for the triprotic acid H_3PO_4. There are three pK_a's, each corresponding to a crossing point of the lines depicting the concentrations of a pair of conjugate species.

One new feature is that at each pK_a, the slope the line representing any species that is one pK_a removed from that particular equilibrium changes from ± 1 to ± 2. This means that the species in question rapidly becomes insignificant as the pH continues to change in one direction. If C_a is not extremely small, one can obtain reasonably good estimates of pH of solutions of any single ampholyte by considering only the appropriate section of the diagram.

6 Acid- and base neutralizing capacity

As a measure of the average proton free energy per proton, the pH expresses only the *intensity* aspect of acidity; as such, pH is not conserved when the temperature, density, or ionic strength of a solution is changed, or when the concentration is altered.

The corresponding *capacity* factor would be conserved under the above changes, and represents the number of equivalents per litre of strong acid or base required to bring the system to some arbitrary proton level– usually to the pH corresponding to a given equivalence point.

One such capacity factor is [SID], also known as [ANC], acid-neutralizing capacity, or *alkalinity*. Conceptually, [ANC] represents the difference in concentrations of species containing protons in excess of the reference level, and the concentrations of species possessing empty proton levels.

For a solution of pure HA in water, the HA itself and H_2O define the proton reference level; species such as H_2A^+ and H_3O^+ represent proton-excess levels, and A^- and OH^- are proton-deficient levels:

$$[ANC] \equiv [SID] = [A^-] + [OH^-] - [H^+] = C_a\alpha_1 + [OH^-] - [H^+] \tag{83}$$

[ANC] expresses the net deficiency of protons with respect to the reference level, i.e., the number of equivalents per litre of protons that must be added to fill all the empty levels up to HA.

The concept of alkalinity becomes most useful in more complicated systems (such as carbonate) and in solutions containing more than one acid-base system.

Another view of [ANC] is that it is the integration of the buffer intensity over a given pH range:

$$[ANC] = \int_{f_m}^{f_n} \beta d(\text{pH}) \tag{84}$$

Although [ANC] can assume negative values, it is customary to use another quantity, [BNC] in this region. Base-neutralizing capacity is also known as the *acidity*. [BNC] measures the quantity of protons that must be removed (by reaction with strong base) in order to empty all proton levels down to and including HA, thus restoring the system to A^- and H_3O^+.

$$[BNC] = [HA] + [H^+] - [OH^-] = [A^-]\alpha_0 + [H^+] - [OH^-] \tag{85}$$

Problem Example 6 ───────────────────────────

Find the [ANC] of a solution of

1. 0.01 M HCl: $[A^-]\alpha_1 + [OH^-] - [H^+] = (.01)(1) - .01 = \underline{0.0\,M}$

2. .01 M NaOH: $(.01)(0) + .01 - 0 = \underline{.01\,M}$

3. .01 M acetic acid at pH $= pK_a = 4.7$; $(.01)(.5) - 2 \times 10^{-5} \approx \underline{.005}$ eq/L

Problem Example 7

Find the [ANC] and [BNC] of a solution of acetic acid ($pK_a = 4.7$, $K_a = 1.8 \times 10^{-5}$, that has been adjusted to a pH of 6.0 by addition of NaOH.

$$\alpha_0 = \frac{[\text{H}^+]}{K_a + [\text{H}^+]} = \frac{10^{-6}}{(18+1) \times 10^{-6}} = \frac{1}{19} = .053$$

$$\alpha_1 = 1 - .053 = .947$$

$$[\text{ANC}] = (.01)(.947) - 10^{-6} = \underline{.00957 \text{ eq/l}}$$

$$[\text{BNC}] \approx (.01)(.053) = \underline{.00053 \text{ eq/l}}$$
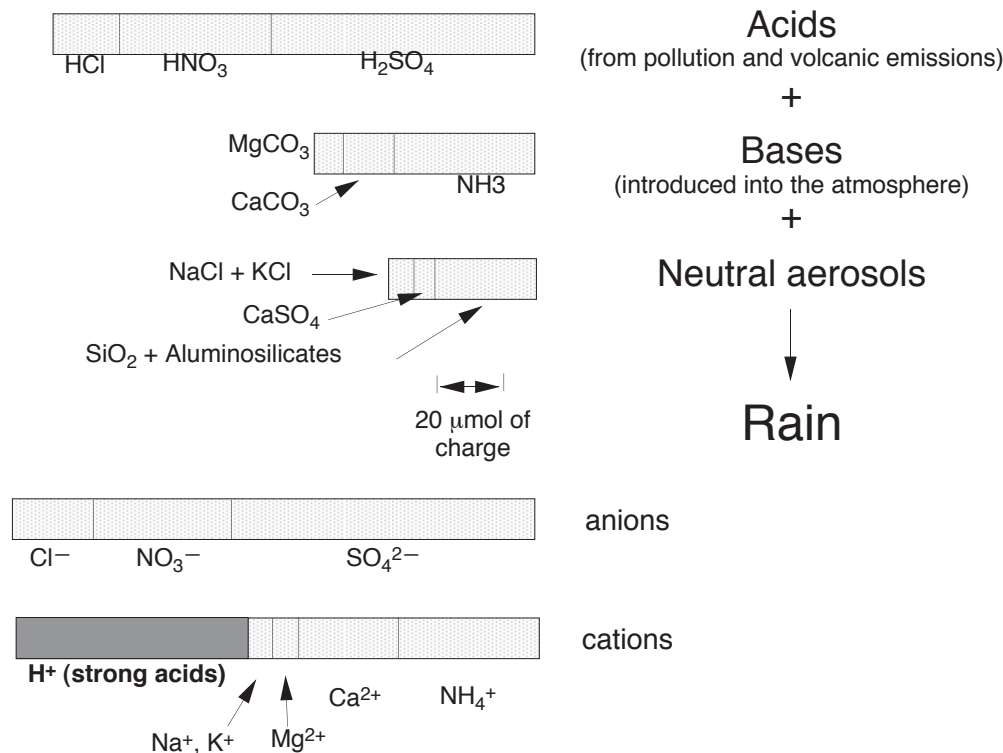
Figure 11: Origin of acid rain

7   Acid rain

As will be explained in the next section on the carbonate system, *all* rain is "acidic" in the sense that exposure of water to atmospheric carbon dioxide results in the formation of carbonic acid H_2CO_3 which will eventually reduce the pH to 5.7.

The term *acid rain* is therefore taken to mean rain whose pH is controlled by substances other than CO_2 and which can lower the pH into the range of 3-4. The major culprits are sulfuric, nitric, and hydrochloric acids. Most of the H_2SO_4 comes from the photooxidation of SO_2 released from the burning of fossil fuels and from industrial operations such as smelting.

As shown in Fig. **??**, the atmosphere receives both acidic and basic substances from natural sources (volcanic emissions, salt spray, windblown dust and microbial metabolism) as well as from pollution. These react in a kind of gigantic acid-base titration to give a solution in which hydrogen ions must predominate in order to maintain charge balance.

November 6, 1994

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