Acids and bases. pH computations.

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A (Brønsted-) acid is a species, which donates a proton (H^+) to another species:

$$HA + B \rightleftharpoons A^- + HB \qquad (1)$$
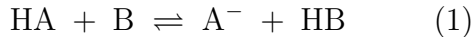
The proton acceptor is called a base. Thus in general

$$Acid_1 + Base_2 \rightleftharpoons Base_1 + Acid_2 \qquad (2)$$

When HA looses a proton, the generated species (here A^-) is called the corresponding (or conjugate) base to HA.

Usually the solvent is water, and an acid may react with water according to

$$HA + H_2O \rightleftharpoons A^- + H_3O^+ \qquad (3)$$
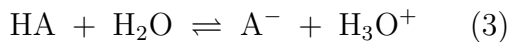
The corresponding equilibrium constant

$$K_a = \frac{[H_3O^+][A^-]}{[HA]x_{H_2O}} \simeq \frac{[H_3O^+][A^-]}{[HA]} \qquad (4)$$

is called the ionization constant of the acid.

For the auto-ionization of water

$$H_2O + H_2O \rightleftharpoons OH^- + H_3O^+ \qquad (5)$$

we have the equilibrium constant

$$K_w \simeq [H_3O^+][OH^-] \qquad (6)$$

where we have omitted the possible deviation from one of x_{H_2O}. K_w has the value $1.0\,10^{-14}M^2$ at 25º C.

For the base A^- we also have the equilibrium

$$A^- + H_2O \rightleftharpoons HA + OH^- \qquad (7)$$

with the equilibrium constant

$$K_b \simeq \frac{[HA][OH^-]}{[A^-]} \qquad (8)$$

K_b is the ionization constant for the base. Note that the reaction (7) is *not* the reverse of (3) and thus K_b is not the reciprocal of K_a. Rather we get

$$
\begin{aligned}
K_a K_b &= \frac{[H_3O^+][A^-]}{[HA]}\frac{[HA][OH^-]}{[A^-]} \\
&= [H_3O^+][OH^-] = K_w \qquad (9)
\end{aligned}
$$

(Concentration-) pH is defined as $pH = -\log[H_3O^+]$.
With similar notations, we get

$$
\begin{aligned}
pH + pOH &= pK_w = 14.0 \qquad (10) \\
pK_a + pK_b &= pK_w = 14.0 \qquad (11)
\end{aligned}
$$

Some acids are practically completely dissociated in water, and are known as strong acids. Examples are HCl, HNO_3 and $HClO_4$. If such an acid is dissolved in water with the nominal concentration C, the actual concentration of the acid is very small, and $pH = -\log[H_3O^+] \simeq -\log C$. Thus a very diluted solution of hydrochloric acid with $C = 1.0\,10^{-3}M$ has pH = 3.0. Correspondingly, a 0.1 M solution of sodium hydroxide has pOH = 1.0, and thus a pH = 14.0 - 1.0 = 13.0.

If solutions of HCl and NaOH are mixed, H_3O^+ and OH^- react to water, and a surplus of one of the ions thus defines the pH: 20.0 mL of 0.200 M HCl and 15.0 mL 0.100 M NaOH yields (approximately) 35.0 mL solution. There is $20.0 \times 0.200 = 4.00$mmol of HCl and 1.50 mmol of NaOH initially, but after reaction only 4.00 - 1.5 = 2.50 mmol H_3O^+ left. The result is thus a solution of a strong acid for which pH is easily estimated: $pH = -\log(2.50/35.0) = 1.15$.

If the acid does not dissociate completely, it is called a weak acid. This happens, when $K_a \ll 1$.
Analogously, a weak base has $K_b \ll 1$.

pH in weak acid

If a nominal concentration of HA is given as C, HA dissociates and leaves an actual concentration C-x

$$HA \ + \ H_2O \ \rightleftharpoons \ A^- \ + \ H_3O^+$$

(I)   C   -   -
(II)   C-x   x   x
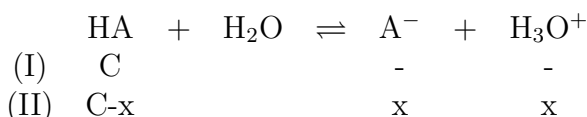
Here we have neglegted the contribution from the auto-ionization of water to $[H_3O^+]$. We get

$$K_a = \frac{x^2}{C-x} \qquad (12)$$

which may be solved for x, in terms of C and K_a. Quite often x $\ll$ C and x may then be neglected in the denominator, with the approximate result

$$x = \sqrt{K_a C} \qquad (13)$$

which may be rewritten

$$pH = \frac{pK_a + pC}{2} \qquad (14)$$

 Thus for a 0.1 M solution of acetic acid HAc ($pK_a = 4.75$) we get pH = (4.75 + 1.0)/2 = 2.88.

We check this result:
x = $10^{-2.88} = 1.33 \ 10^{-3} \ll$ C and thus our approximation is validated. For the degree α of dissociation we get $\alpha = x/C = 0.0133$ and thus only about one per cent of the weak acid is dissociated.

pH in weak base

The corresponding base to acetic acid is the acetate ion Ac^-. For the reaction with water, we have

$$Ac^- \ + \ H_2O \ \rightleftharpoons \ HAc \ + \ OH^-$$

(I)   C   -   -
(II)   C-x   x   x
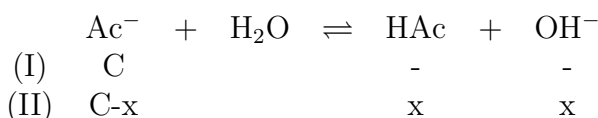
We get

$$K_b = \frac{x^2}{C-x} \simeq \frac{x^2}{C} \qquad (15)$$

with x = $[OH^-]$ and thus

$$x = \sqrt{K_b C} \qquad (16)$$

As above this may be rewritten

$$pOH = \frac{pK_b + pC}{2} \qquad (17)$$
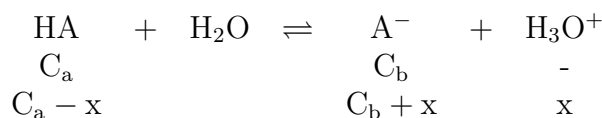
For a 0.1 M solution of sodium acetate, we thus have

$$pOH = \frac{14.0 - 4.75 + 1.0}{2} = 5.125 \quad (18)$$

and again x $\ll$ C.
For pH we get 14.0 - 5.125 = 8.88.

pH in a buffer (weak acid plus corresponding weak base)

If both HAc and its corresponding base Ac^- are added, we get

$$HA \ + \ H_2O \ \rightleftharpoons \ A^- \ + \ H_3O^+$$

     C_a C_b -
     $C_a - x$ $C_b + x$ x

and inserted in K_a this yields

$$K_a = \frac{(C_b + x)x}{C_a - x} \simeq x\frac{C_b}{C_a} \qquad (19)$$

where we assume that x = $[H_3O^+]$ is much smaller than both C_a and C_b. We thus get

$$x = K_a C_a / C_b \qquad (20)$$
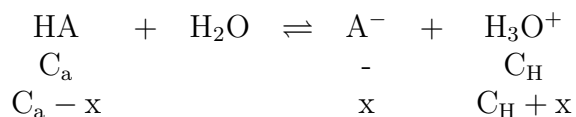
which may be rewritten

$$pH = pK_a + \log\frac{C_b}{C_a} \qquad (21)$$

 which is known as the buffer equation. For a solution which has nominal concentrations C(HAc) = 0.100 M and C(Ac^-) = 0.200 M we get

$$pH = 4.75 + \log\frac{0.200}{0.100} = 5.05 \qquad (22)$$

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Thus $x \ll C_a < C_b$ is fulfilled.

pH in weak acid plus strong acid

If we mix HCl with HAc, we get

	HA	+	H$_2$O	$\rightleftharpoons$	A$^-$	+	H$_3$O$^+$
	C$_a$				-		C$_H$
	C$_a$ $-$ x				x		C$_H$ + x

and inserted in K_a this yields

$$K_a = \frac{x(C_H + x)}{C_a - x} \simeq \frac{xC_H}{C_a} \qquad (23)$$

Note that $[H_3O^+] = C_H + x$ now. We may estimate x as

$$x = K_a C_a / C_H \qquad (24)$$

As an example consider $C_a = 0.100$ M and $C(HCl) \equiv C_H = 0.01$ M. We get
$x = 10^{-4.75} \times 0.1/0.01 = 1.8 \ 10^{-4} \ll C_H$ and thus

$$pH = -\log(C_H + x) \simeq -\log C_H \qquad (25)$$

which evaluates to 2.00. Thus when a strong acid is present together with a weak acid, we may neglect the contribution from the weak acid.

By the same reasoning, we may neglect the contribution from a weak base in the presence of a strong base, like OH$^-$.

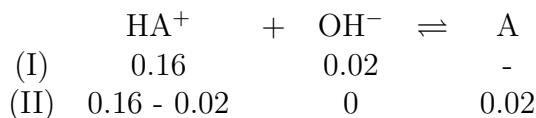## pH in weak acid plus strong base

Consider a mixture of 8.0 mL 0.200 M ammoniumchloride NH$_4^+$, Cl$^-$ and 2.00 mL of 0.100 M NaOH. We have
$C(NH_4^+) = 1.60/10.0 = 0.16$ M and
$C(OH^-) = 0.2/10.0 = 0.020$ M.
NH$_4^+$ is a weak acid (HA$^+$) with p$K_a = 9.25$. Its corresponding base is ammonia NH$_3$. We thus get

	HA$^+$	+	OH$^-$	$\rightleftharpoons$	A
(I)	0.16		0.02		-
(II)	0.16 - 0.02		0		0.02

The result is thus a solution, which mainly consists of a weak acid and its corresponding weak base, that is, a buffer. We thus get

$$
\begin{aligned}
pH &= pK_a + \log \frac{n_{OH^-}}{n_{HA^+} - n_{OH^-}} \\
&= 9.25 + \log(2/14) = 8.40 \quad (26)
\end{aligned}
$$

Here we have tacitly used the rule 'The strongest acid reacts with the strongest base, until one is depleted'. Initially there are two acids, NH$_4^+$ and H$_2$O, of which the (weak) acid NH$_4^+$ is the strongest. Similarly, OH$^-$ is a stronger base than water. We thus let NH$_4^+$ and OH$^-$ react until one is depleted. The content of the solution is then examined, and we observe that it is composed of a mixture, for which we can fairly easily estimate pH.

Also the strong base was present in an amount less than that of the weak acid. If OH$^-$ had been in excess, we had been left with a mixture of a weak base (NH$_3$) and the excess of OH$^-$. Again, this is a situation we have already treated: we neglegt the weak base and calculate pOH for the OH$^-$ excess.

The case with a weak base, say acetate ion, plus a strong acid, say HCl, is treated analogously. If the strong acid is depleted, a buffer results. If the weak base is depleted, we calculate pH from the excess HCl.

pH in polyprotes

An acid like H$_2$CO$_3$ is a weak acid with respect to donoring a proton to water. The result is the corresponding base, HCO$_3^-$, which in turn, however, may also donate a proton to water, and thus react as an acid as well. The two corresponding ionization constants are known as K_{a1} and K_{a2} respectively. In general, for a diprote acid H$_2$A we have

$$K_{a1} = \frac{[H_3O^+][HA^-]}{[H_2A]} \qquad (27)$$

$$K_{a2} = \frac{[H_3O^+][A^{2-}]}{[HA^-]} \qquad (28)$$

For a solution of H$_2$A with nominal concentration C_a it is usually a sufficiently good approximation to treat the acid, as if only the first dissociation takes place, and thus ignore the second. For H$_2$CO$_3$ p$K_1 = 6.37$ and p$K_2 = 10.70$. For $C_a = 0.100$M we get

$$pH = \frac{pK_{a1} + pC}{2} = \frac{6.37 + 1.00}{2} = 3.69 \qquad (29)$$

To see that this is close to the required result, we may estimate, how much the second

dissociation contributes. Let x $= 10^{-3.69}$. For the second step we have

$$\text{HA}^- \;+\; \text{H}_2\text{O} \;\rightleftharpoons\; \text{A}^{2-} \;+\; \text{H}_3\text{O}^+$$

x				x
x − y			y	x + y
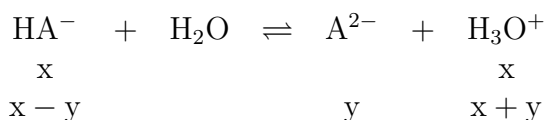
Our assumption is that $y \ll x$. From K_{a2} we obtain

$$K_{a2} \simeq \frac{y(x+y)}{x-y} \qquad (30)$$

or $y = K_{a2} = 10^{-10.7}$ which is indeed much less than x.

Analogously, a weak diprote base (like A^{2-} above) may also be treated as a monoprot for the estimation of pOH. Thus for a 0.100 M solution of sodium carbonate, Na_2CO_3, the ion CO_3^{2-} is a weak base with $\text{p}K_b = 14.0 - \text{p}K_{a2} = 14.0 - 10.7 = 3.3$.

pH in ampholytes

Whereas H_2CO_3 may be treated as a monoprote acid, and Na_2CO_3 as a monoprote base, the hydrogencarbonate ion HCO_3^- is both an acid (forming CO_3^{2-}) and the corresponding base (to H_2CO_3). Such species are known as amphiprotes or ampholytes.

Consider a solution of NaHCO_3 in water. If we use the principle above and let the strongest acid react with the strongest base, we have: HCO_3^- is the strongest acid present, and HCO_3^- is the strongest base as well. We thus get
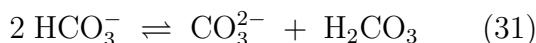
$$2\,\text{HCO}_3^- \;\rightleftharpoons\; \text{CO}_3^{2-} \;+\; \text{H}_2\text{CO}_3 \qquad (31)$$

From this it is seen that $[\text{CO}_3^{2-}] \simeq [\text{H}_2\text{CO}_3]$ in the solution. Now consider the product

$$K_{a1}K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^-]}\frac{[\text{H}_3\text{O}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$
$$\simeq [\text{H}_3\text{O}^+]^2 \qquad (32)$$

and thus we have the approximation

$$\boxed{\text{pH} = \frac{\text{p}K_{a1} + \text{p}K_{a2}}{2} \qquad (33)}$$

The two pK values, which appear in this formula are the pK, in which the ampholyte is the corresponding base (pK_{a1} here) and the ampholytes own acid ionization constant. H_3PO_4 is a triprote, and the species H_2PO_4^- and HPO_4^{2-} are both ampholytes. For a solution of Na_2HPO_4 we thus get $\text{pH} = (\text{p}K_{a2} + \text{p}K_{a3})/2$.

pH in weak polyprotes plus strong acid

A mixture of 50.0 mL 0.200 M Na_2HPO_4 and 30.0 mL 0.100 M HCl contains 10 mmol Na_2HPO_4 and 3 mmol HCl. We let the strongest acid react with the strongest base, and thus H^+ reacts with HPO_4^{2-}. The ampholyte is in excess, and we end up with a solution containing 3.0 mmol H_2PO_4^- and 7.0 mmol HPO_4^{2-}. This is a buffer, for which we compute $\text{pH} = \text{p}K_{a2} + \log(7.0/3.0)$.

Had we used equimolar amounts, say 10 mmol of each, HPO_4^{2-} had been converted to 10.0 mmol of H_2PO_4^-. The result is a solution of an ampholyte, with $\text{pH} = (\text{p}K_{a1} + \text{p}K_{a2})/2$.

If we had used 60.0 mL 0.200 M HCl instead, we now start with 12.0 mmol HCl. 10 of these are used to convert HPO_4^{2-} to 10.0 mmol H_2PO_4^-. The 2.0 mmol HCl excess then reacts further with the strongest base present, which is now H_2PO_4^- and the end result is 8 mmol H_2PO_4^- and 2.0 mmol H_3PO_4, which is again a buffer, this time with $\text{pH} = \text{p}K_{a1} + \log(8.0/2.0)$.

The reaction of weak polyprotes with strong base like NaOH is treated analogously.

Titration curves

If we have a solution of a weak acid, and slowly add a strong base like NaOH, we shall see that pH increases rapidly, when equimolar amounts of the weak acid and strong base are approached. This may be used for volumetric analysis. If the concentration of the weak acid is initially unknown, the amount of NaOH may be recorded, where this pH shift occurs. The original acid content is then equal to the added base content at the equivalence point.

To construct typical titration curves, we may start with a weak acid like HAc with

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$pK_a = 4.75$ and known concentration $C = 0.0100$ M, say. A 20.00 mL solution thus contains 0.200 mmol HAc initially. The NaOH solution with accurate concentration 0.1000 M is contained in a burette, a long narrow cylinder flask graduated to display the volume used. We will construct the curve displaying pH as a function of mL base added, see Fig.(1).

Initial point. 0 mL base added.
As HAc is a weak acid, pH in the initial solution may be estimated using the standard formula Eq.(14).

Points before the equivalence point.
To reach the equivalence point, we need 0.200 mmol base, that is 2.000 mL. We will call this n_o mL. If we add a fraction α of this amount, we end up with a buffer. The ratio $C_b/C_a = (\alpha n_o/V)/((n_o - \alpha n_o)/V)$ and thus

$$pH = pK_a + \log \frac{\alpha}{1.0 - \alpha} \qquad (34)$$

independent of the volume in the titration flask. Note especially that for $\alpha = 0.5$ we get $pH = pK_a$. At this point the change in pH per mL base is the smallest, and the titration curve thus is close to horizontal.

Equivalence point.
For $\alpha = 1.0$ all the HAc is converted to the corresponding base Ac⁻, and the pH in the solution may thus be estimated from Eq.(17). We now have $C_b = n_o/V \simeq n_o/(V_a + V_{NaOH})$. Note that pH generally is not equal to 7.0 at the equivalence point. From the displayed curve, we see that the buffering capability of the solution is gone now, and pH increases substantially at the equivalence point. Thus the curve is near-vertical here.

Points past the equivalence point.
For $\alpha > 1.0$, we have used n_o mmol to convert HAc to Ac⁻, and the excess of strong base is then $(\alpha - 1)n_o$ mmol. F. ex. if we add 2.500 mL NaOH, the excess is $0.500 \times 0.1000 = 0.0500$ mmol and the volume is 22.5 mL. Thus $[OH^-] = 0.0500/22.5$ from which pOH is calculated. Asymptotically, pH approaches the pH of NaOH in the burette, which is 14.0 -1.0 = 13.0 here.
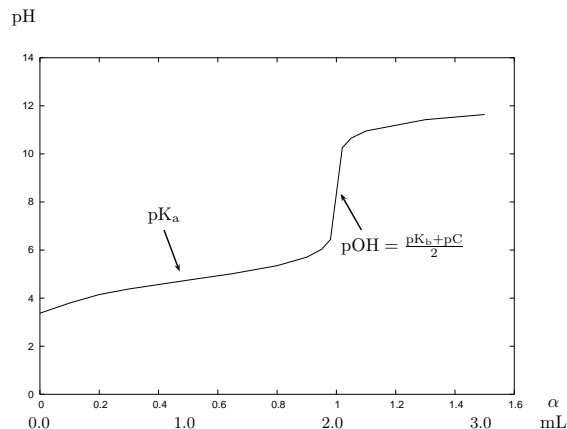

Figure 1: Titration curve for monoprote weak acid

Titration curves for polyprotes.

This may be illustrated with the titration of a weak diprote acid H₂A. The calculations follow the scheme for a monoprote acid initially, notably at $\alpha = 0.5$ we get $pH = pK_{a1}$. But at the 1. equivalence point, the corresponding base is now the species HA⁻, which is an ampholyte, and Eq.(17) is thus replaced by Eq.(33).

If we add more NaOH, the first n_o mmol, corresponding to $\alpha = 1.0$, are now used to convert H₂A to HA⁻, but a new buffer arises for $1.0 < \alpha < 2.0$ based on pK_{a2}. Notably, for $\alpha = 1.5$ we get $pH = pK_{a2}$. At the second equivalence point, $\alpha = 2.0$, we have a solution of the weak base A²⁻ with $pK_b = 14.0 - pK_{a2}$. For $\alpha > 2.0$ we are left with an excess of the strong base, as before.
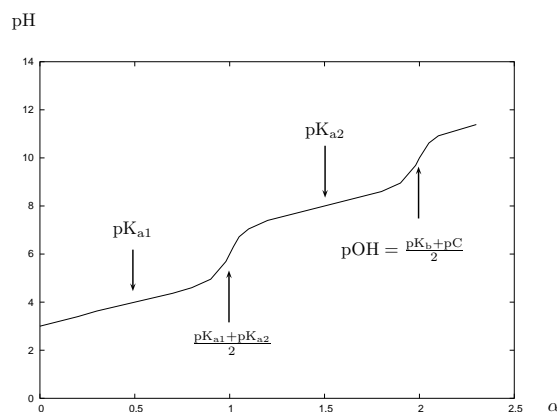

Figure 2: Titration curve for diprote weak acid with $pK_{a1} = 4.0$ and $pK_{a2} = 8.0$.

The curve is thus approximately flat around $\alpha = 0.5$ and $\alpha = 1.5$, but rises sharply at the two equivalence points, with $\alpha = 1.0$ and $\alpha = 2.0$, see Fig.(2). However, if some of the pK's are close together, there is too little space to manifest the vertical character at the equivalence point in between. The curve thus appears to go from one near-horizontal buffer zone into another such flat zone, without a pronounced vertical part. The same may occur, if some of the pK's are close to either 0 or 14.

Indicators

pH may be measured in an electrochemical cell, and this will be discussed in the text on electrochemistry. It is thus possible to follow the pH change and record the fast pH changes automatically.

It is possible also to determine the pH change visually. Some weak acids, and/or their bases, are very strongly colored. A small insignificant amount of such a substance to the solution under investigation will not change pH appreciably. If the small total concentration present is $C = [s] + [b]$, we may rewrite the expression for the indicators ionization constant in terms of the fraction $\alpha = [s]/C$.

$$K_{\mathrm{I}} = \frac{[\mathrm{H_3O^+}][\mathrm{b}]}{[\mathrm{s}]} = \frac{[\mathrm{H_3O^+}](1 - \alpha)}{\alpha} \quad (35)$$

and thus

$$\mathrm{pH} = \mathrm{p}K_{\mathrm{I}} + \log \frac{(1 - \alpha)}{\alpha} \quad (36)$$

This is superficially like the buffer equation, but the latter only holds for pH near $\mathrm{p}K_{\mathrm{a}}$ of the buffer system, whereas Eq.(36) is valid for all pH, since it is simply a logarithmic version of the expression for the ionization constant, in terms of the *actual* fractions of the acid or base. Here, one of these fractions may be very small.

If α is displayed from Eq.(36) as a function of pH, α is close to one on the acidic side of $\mathrm{p}K_{\mathrm{I}}$, whereas α drops to near zero on the basic side of $\mathrm{p}K_{\mathrm{I}}$. See Fig.(3).

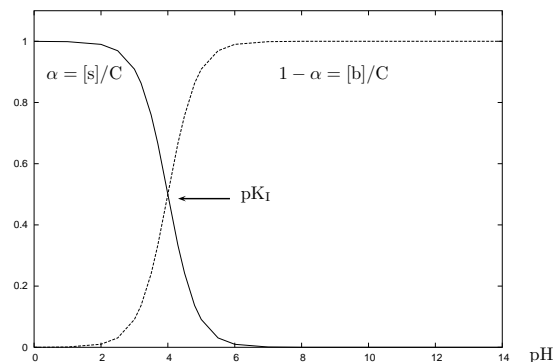Suppose now that s is deep blue, whereas b is deep yellow. If pH is close to $\mathrm{p}K_{\mathrm{I}}$,

Figure 3: Bjerrum diagram for a weak monoprote acid. The fraction of acid $\alpha = [s]/C$ as a function of pH is shown. The corresponding base fraction is $1 - \alpha$. At $\mathrm{pH} = \mathrm{p}K_{\mathrm{a}}$ both fractions are equal to 1/2. An indicator I may shift color, when pH changes past $\mathrm{p}K_{\mathrm{I}} \equiv \mathrm{p}K_{\mathrm{a}}$.

the system appears green. However, if a drop of this indicator system is added to a system under titration, initially the solution may be on the acidic side of $\mathrm{p}K_{\mathrm{I}}$ and thus blue. When pH changes past $\mathrm{p}K_{\mathrm{I}}$, the color changes to yellow. If an indicator has been chosen with $\mathrm{p}K_{\mathrm{I}}$ close to the pH of the equivalence point, and pH changes rapidly here, one drop of NaOH may be sufficient for the indicator to switch color substantially. This then reveals that the equivalence point was passed, and the burette reading may be recorded.

PC programs

The approximation formulas above are not always satisfactory. For accurate work, it is possible to write up a balance equation, which involves all species of relevance to the problem. Usually this results in a polynomial equation of quite high order (a fifth order polynomial, say). It is, however, an easy task to let the computer search iteratively for pH values, which satisfy this equation.

While such a procedure may yield values in better agreement with experimentally recorded pH values, qualitative features may be studied on the basis of the simplified formulas discussed above.

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