

pH of natural waters

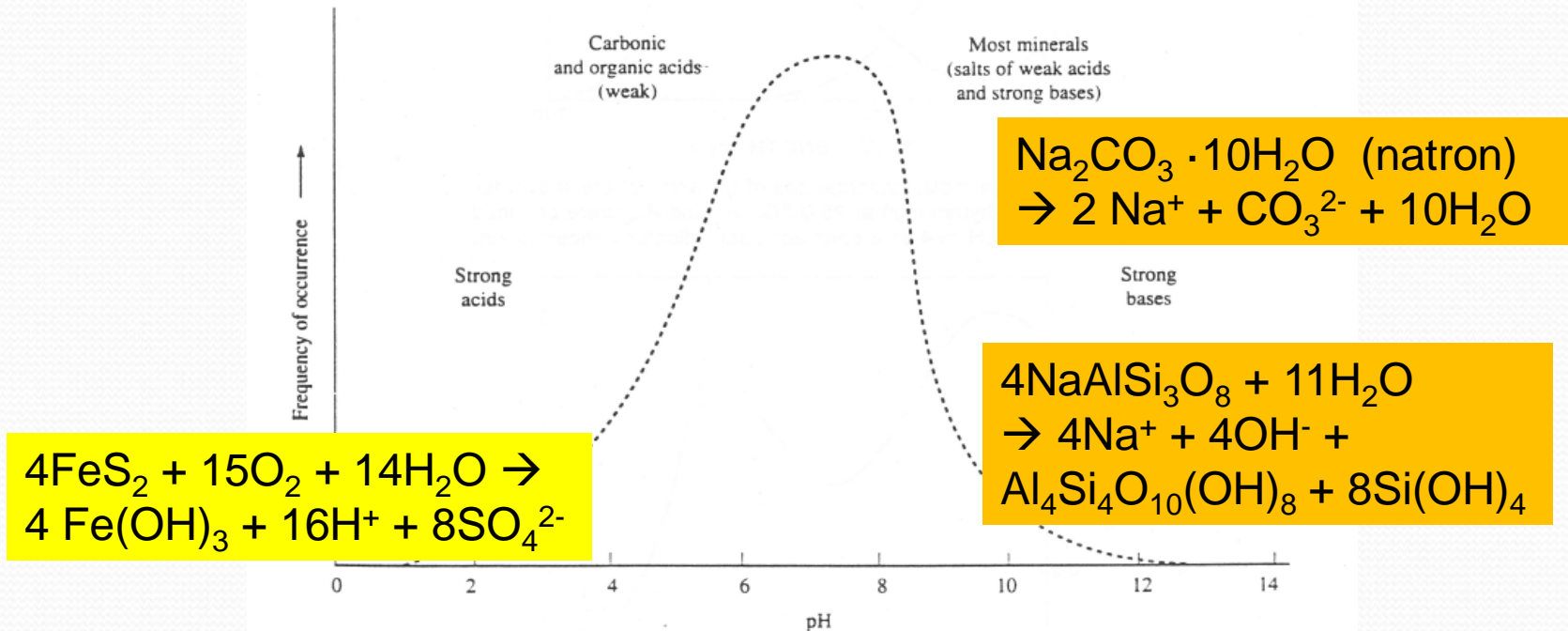


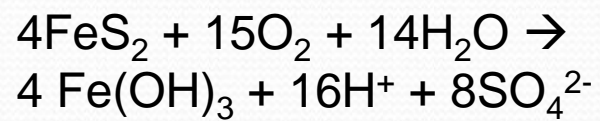
Figure 5.4 Schematic plot showing the frequency of occurrence of pH values and the major controls on natural-water pH's.

In natural solutions having pH values between 4.5 and 7, the acids are weak and usually include carbonic acid and smaller amounts of organic acids. These are generally water-dominated systems. Solutions with either very low or very high pH's are generally rock-dominated systems.

Kawah Ijen, Indonesia

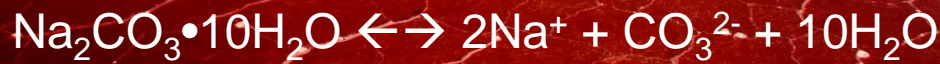


Richmond Mine, Iron Mountain, California



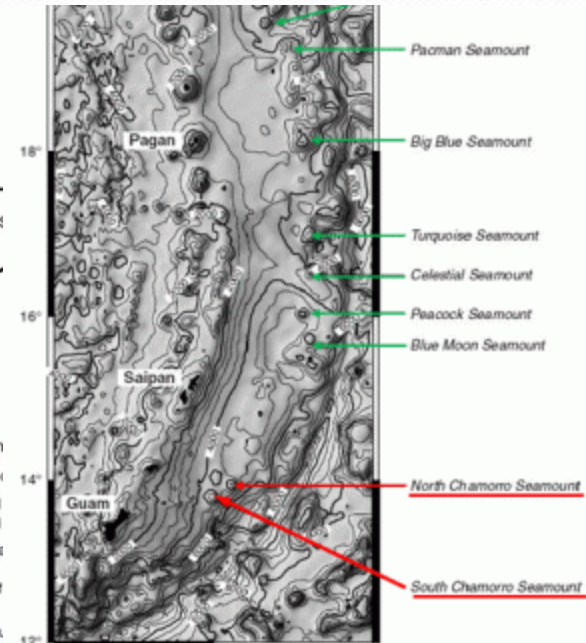
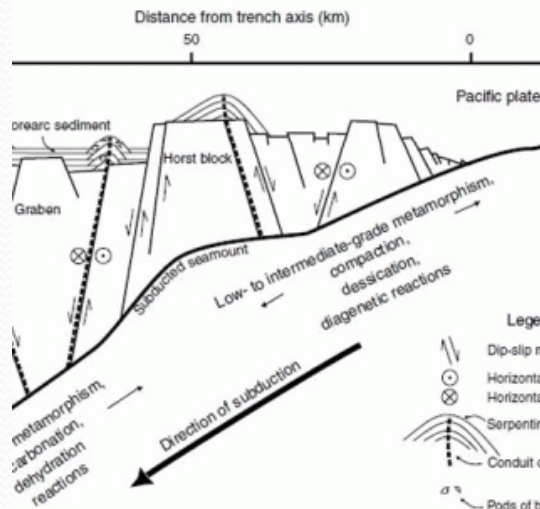
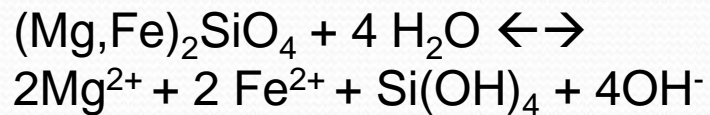


Lake Natron, Tanzania

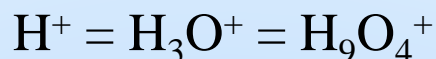


Paul & Paveena McKenzie via Getty Images

Porewater rising through
serpentinite mud volcanoes
on the Mariana forearc



pH measurements and pH scales



Soren Sorensen (1909) proposed an electrochemical procedure for the determination of the hydrogen ion concentration which he dubbed the “hydrogen ion exponent”:

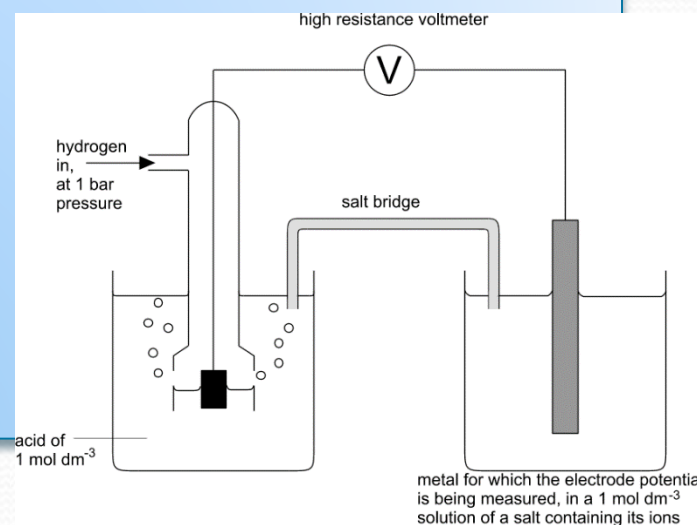
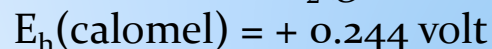
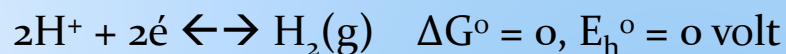
$$p_s\text{H} = -\log [\text{H}^+]$$

where $[\text{H}^+] = \alpha [\text{HCl}]$ and α is the degree of ionization of HCl in NaCl-HCl solutions

The electrochemical potential (EMF) between solutions of various H^+ concentrations was measured with a set of electrodes.



By definition, the potential at the Pt: H_2 (g: 1 atm, 1 N HCl) electrode is null:



pH measurements

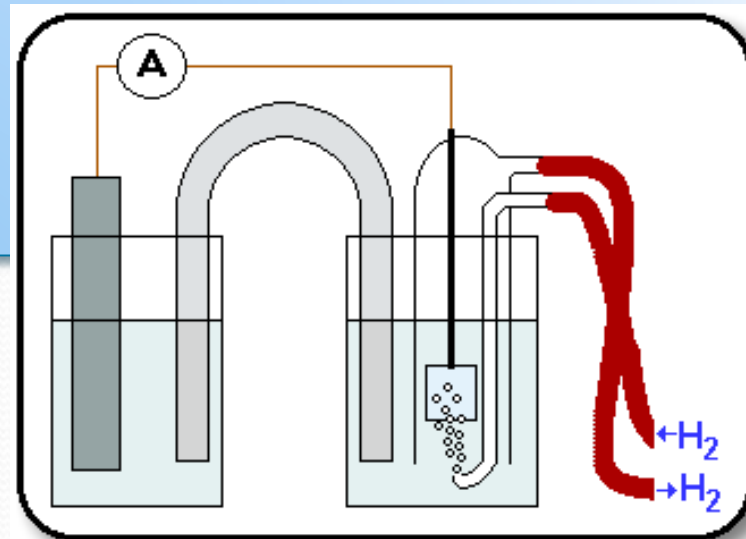
As modern formulations of thermodynamic concepts and theories of electrolyte solutions were developed, it was shown that the electromotive force (EMF) of a galvanic cell is related directly to the activity rather than concentrations of the redox couple involved in the reaction.

Hence, in 1924, Sorensen and Linderstrom-Lang proposed a new acidity unit:

$$p_a(\text{H}^+) = -\log a(\text{H}^+)$$

Eventually, it was recognized that the activity of a single ion plays no real part in the EMF of a galvanic cell ...

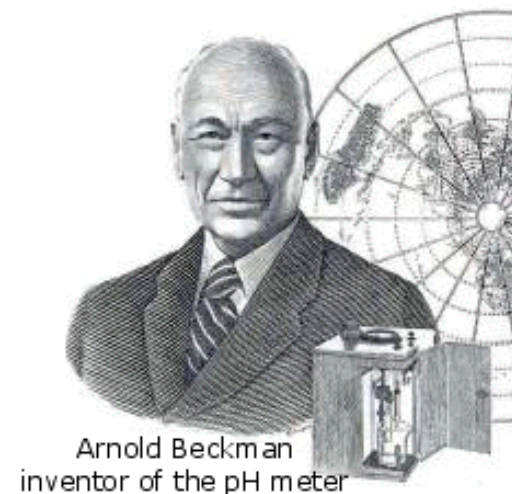
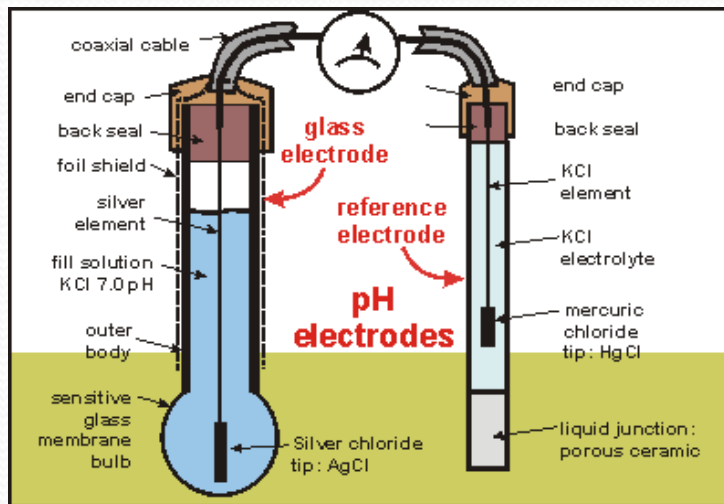
Nevertheless, there remained a need to have a reproducible pH scale based on a convenient method to characterize acid-base reactions.



Operational definition of pH

Reference electrode | Concentrated KCl sol'n || Test solution | electrode reversible to hydrogen ion

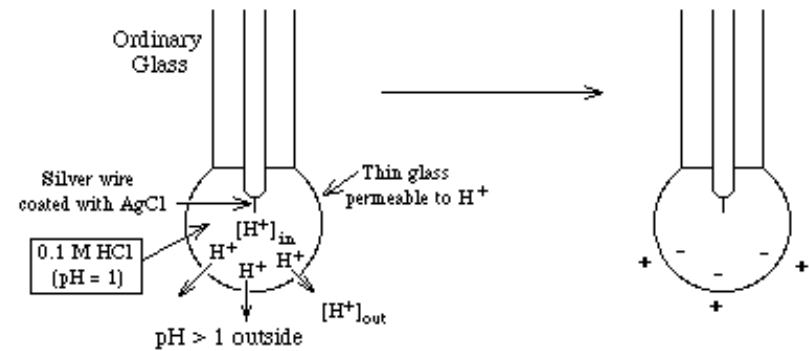
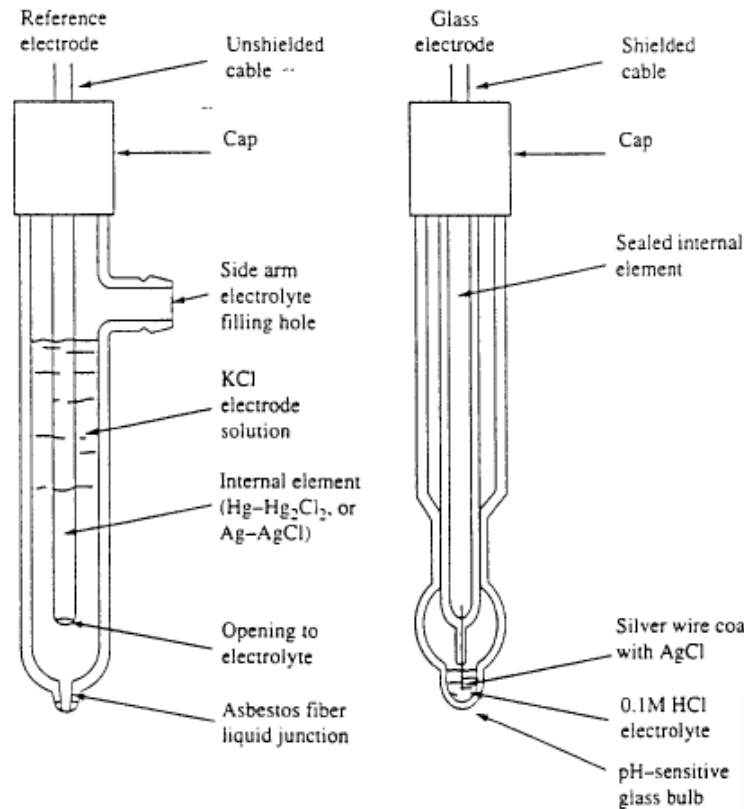
Reference electrode: H^+/H_2 , Hg_2Cl_2/Hg or $AgCl/Ag$
Hydrogen ion reversible electrode: H^+/H_2 , glass electrode



Arnold Beckman
inventor of the pH meter

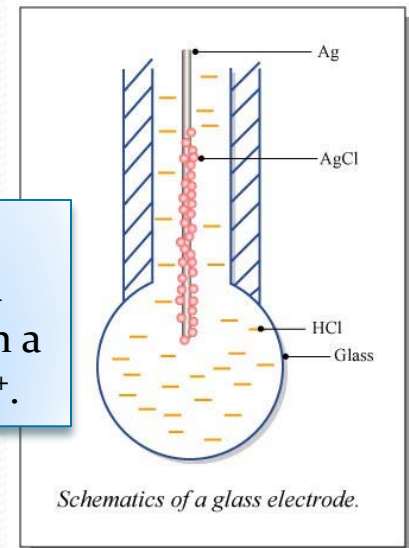
The use of the pH scale became widespread in 1935 when Arnold Beckman developed and sold a simple, portable pH meter.

Typical commercial reference & glass electrodes

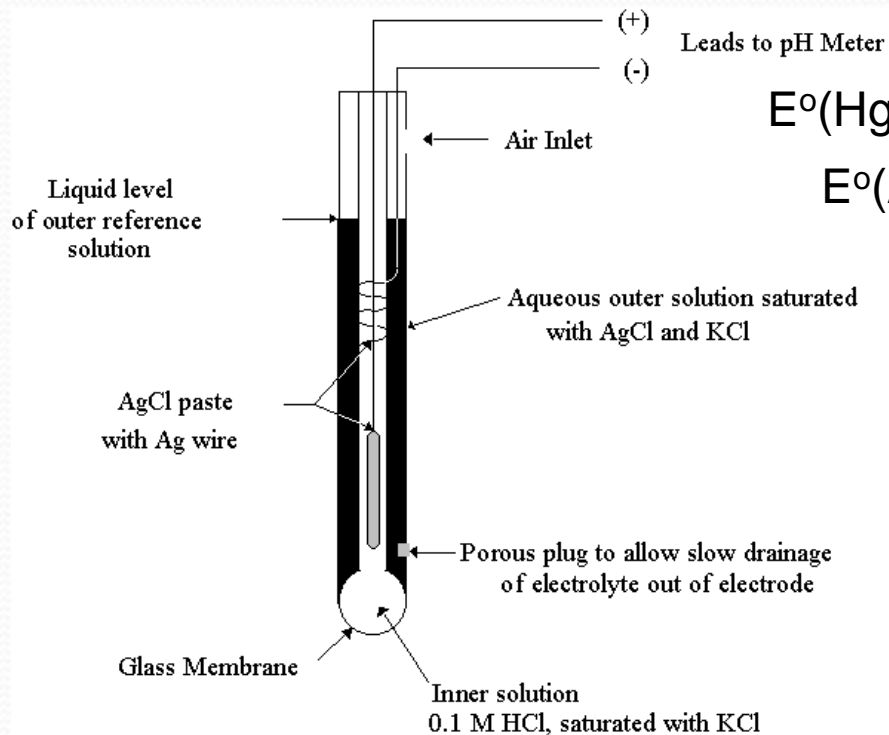


The potential of the reference electrode is set by the redox potential of the redox couple under standard state.

The glass electrode membrane works as a cation exchanger with a high specificity for H⁺.



Combination pH glass electrode

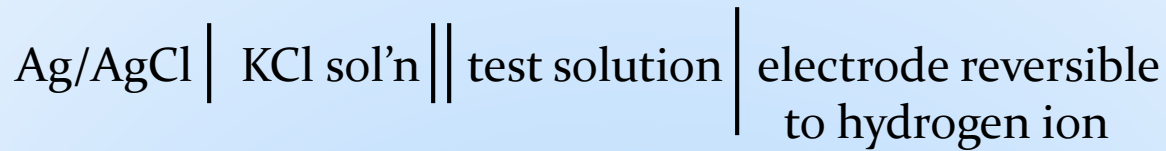


$$E^{\circ}(\text{Hg}^{+}/\text{Hg}^{\circ}, \text{sat KCl}) = +0.2444 \text{ V vs SHE}$$

$$E^{\circ}(\text{Ag}^{+}/\text{Ag}^{\circ}, \text{sat KCl}) = +0.230 \text{ V vs SHE}$$

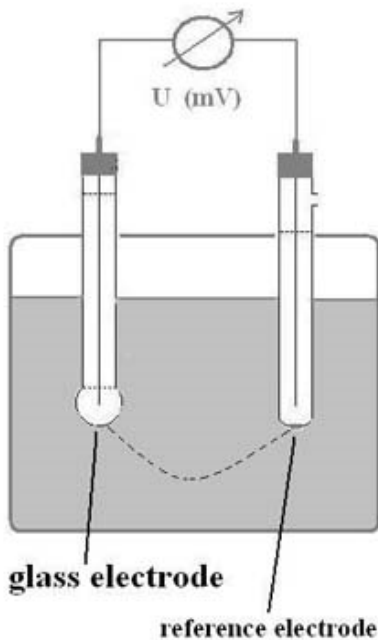
Conventional and operational definitions of pH

The use of a glass electrode and salt bridge adds to the problem.



$$E = E^\circ + RT/F \ln (H^+) (Cl^-) + E_j$$

where E_j is the liquid junction potential between the two half-cells.



This potential is generated by the difference in composition between the solutions on both sides of the salt bridge.

$$E = \{E^\circ + RT/F \ln (Cl^-) + E_j\} + RT/F \ln (H^+) = E^{\circ'} + RT/F \ln (H^+) \\ = \text{conventional definition where the value of } E^{\circ'} \text{ and } (H^+) \\ \text{depend on the value assigned to each other.}$$

In the operational definition, pH of a solution X is related to the pH assigned to a standard (S):

$$\text{pH}(X) = \text{pH}(S) + [E_X - E_S / (RT \ln 10 / F)]$$

NIST-traceable buffer solutions (infinite dilution convention)

Table 2.2.3.2. – pH of reference buffer solutions at various temperatures

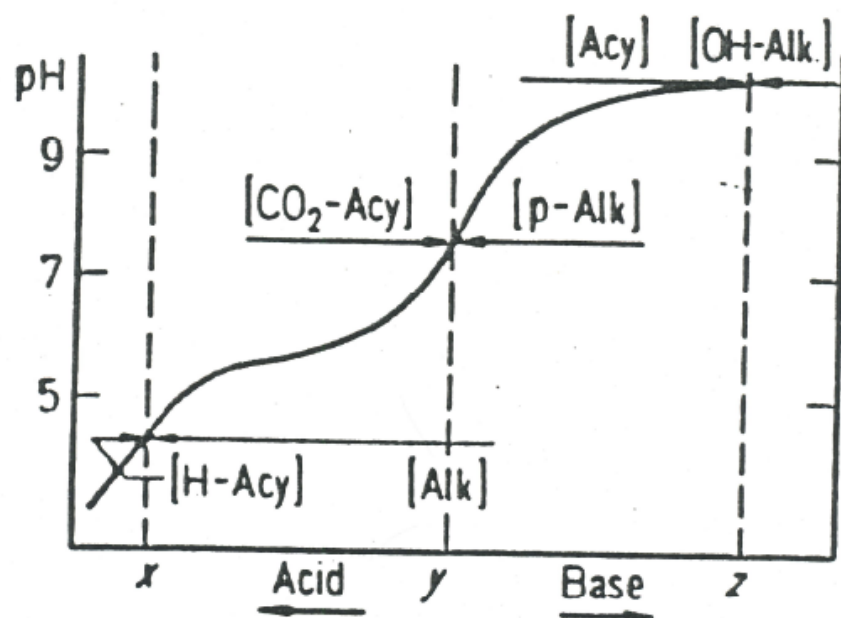
Temperature (°C)	Potassium tetraoxalate 0.05 M	Potassium hydrogen tartrate saturated at 25 °C	Potassium dihydrogen citrate 0.05 M	Potassium hydrogen phthalate 0.05 M	Potassium dihydrogen phosphate 0.025 M + disodium hydrogen phosphate 0.025 M	Potassium dihydrogen phosphate 0.0087 M + disodium hydrogen phosphate 0.0303 M	Disodium tetraborate 0.01 M	Sodium carbonate 0.025 M + sodium bicarbonate 0.025 M	Calcium hydroxide, saturated at 25 °C
	$C_4H_3KO_8 \cdot 2H_2O$	$C_4H_5KO_6$	$C_6H_7KO_7$	$C_8H_5KO_4$	$KH_2PO_4 + Na_2HPO_4$	$KH_2PO_4 + Na_2HPO_4$	$Na_2B_4O_7 \cdot 10H_2O$	$Na_2CO_3 + NaHCO_3$	$Ca(OH)_2$
15	1.67		3.80	4.00	6.90	7.45	9.28	10.12	12.81
20	1.68		3.79	4.00	6.88	7.43	9.23	10.06	12.63
25	1.68	3.56	3.78	4.01	6.87	7.41	9.18	10.01	12.45
30	1.68	3.55	3.77	4.02	6.85	7.40	9.14	9.97	12.29
35	1.69	3.55	3.76	4.02	6.84	7.39	9.10	9.93	12.13
$\frac{\Delta pH^{(1)}}{\Delta t}$	+ 0.001	- 0.0014	- 0.0022	+ 0.0012	- 0.0028	- 0.0028	- 0.0082	- 0.0096	- 0.034

(1) pH variation per degree Celsius.



Alkalinity/acidity/neutralizing capacity

There are different ways to define these capacity factors, but all definitions essentially relate to the proton condition at a given reference state.



Term	End Point	Definition
I. Acid-Neutralizing Capacity (ANC)		
Caustic alkalinity	$f = 2$	$[\text{OH}^- - \text{Alk}] = [\text{OH}^-] - [\text{HCO}_3^-] - 2[\text{H}_2\text{CO}_3^*] - [\text{H}^+]$ (1)
p-Alkalinity	$f = 1$	$[\text{p-Alk}] = [\text{OH}^-] + [\text{CO}_3^{2-}] - [\text{H}_2\text{CO}_3^*] - [\text{H}^+]$ (2)
Alkalinity	$f = 0$	$[\text{Alk}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$ (3)
II. Base-Neutralizing Capacity (BNC)		
Mineral acidity	$f = 0$	$[\text{H-Acy}] = [\text{H}^+] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] - [\text{OH}^-]$ (4)
CO ₂ -acidity	$f = 1$	$[\text{CO}_2\text{-Acy}] = [\text{H}_2\text{CO}_3^*] + [\text{H}^+] - [\text{CO}_3^{2-}] - [\text{OH}^-]$ (5)
Acidity	$f = 2$	$[\text{Acy}] = 2[\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{H}^+] - [\text{OH}^-]$ (6)
III. Combinations		
	$f = 2 - g$	(7) $[\text{Alk}] + [\text{CO}_2\text{-Acy}] = C_T$ (11)
		(8) $[\text{Alk}] + [\text{H-Acy}] = 0$ (12)
		(9) $[\text{Acy}] + [\text{OH-Alk}] = 0$ (13)
		(10) $[\text{p-Alk}] + [\text{CO}_2\text{-Acy}] = 0$ (14)

The concept of alkalinity

The concept of alkalinity is derived from the fundamental principle that solutions are electrically neutral (no net charge). In other words, the number of positive charges carried by cations is equal to the total number of charges carried by anions:

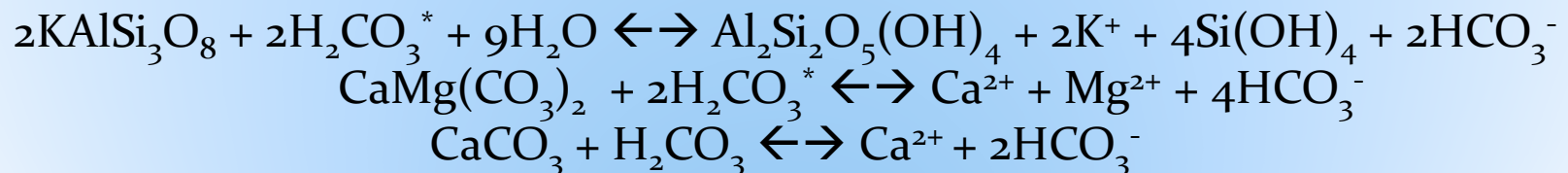
$$\sum Z_i [i] = 0$$

where $[i]$ is the concentration of i and Z is the charge of the i^{th} ion.

For the simple $\text{CO}_2\text{-H}_2\text{O}$ system, the charge balance equation is:

$$\begin{aligned} [\text{H}^+] &= [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{OH}^-] \\ [\text{Alk}] = C_B &= [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \end{aligned}$$

In most natural waters, the acid-base system is dominated by the carbonate alkalinity. This alkalinity is mostly derived from the weathering of silicate and carbonate minerals by carbonic acid.



Alkalinity/acidity/neutralizing capacity

In a more complex aqueous systems one may have to include other bases if they are present in relatively significant concentrations:

$$[\text{Alk}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{NH}_3] + [\text{HS}^-] + 2[\text{S}^{2-}] + [\text{H}_3\text{SiO}_4^-] + 2[\text{H}_2\text{SiO}_4^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{Org}^-] + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] - [\text{H}_3\text{PO}_4] + [\text{OH}^-] - [\text{H}^+]$$

The reference state remains H_2CO_3^* , so that species such as H_2PO_4^- are not titrated into H_3PO_4 since it is a stronger acid than H_2CO_3^* .

If a natural water contains more protons than that given by the zero proton condition (or the H_2CO_3^* equivalence point – contains acids stronger than H_2CO_3^*), then this water contains H-acidity (H-Acy) or mineral acidity.

$$[\text{H-Acy}] = [\text{H}^+] - ([\text{OH}^-] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}]) = - [\text{Alk}]$$

[H-Acy] can be determined by an alkalimetric titration (i.e., with a strong base such as NaOH) of the acid solution to the H_2CO_3^* end-point. This corresponds to the acid content of the solution beyond that which is contributed by acids stronger than H_2CO_3^* .

Alkalinity/acidity/neutralizing capacity

There are a number of other conceptual definitions of the acid-neutralizing and the base-neutralizing capacities of aquatic systems. The various definitions algebraically express the proton excess or proton deficiency of the system with respect to a given reference level (generally H_2CO_3^* , HCO_3^- , or CO_3^{2-}).

For example, the acidity of a water sample is given by:

$$[\text{Acy}] = 2[\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{H}^+] - [\text{OH}^-] = C_A$$

where $[\text{Acy}]$ is given in equivalents per liter. In this case, the reference state is CO_3^{2-} instead of H_2CO_3^* .

For an acid-mine drainage system, the total acidity might be given by:

$$[\text{Acy}] = [\text{H}^+] + [\text{HSO}_4^-] + 2[\text{Fe}^{2+}] + 3[\text{Fe}^{3+}] + 2[\text{FeOH}^{2+}] + 3[\text{Al}^{3+}] + 2[\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] - [\text{OH}^-]$$

The reference state remains the same, CO_3^{2-} . In this case we have simply summed up those species present in solution which can donate protons before HCO_3^- is converted to CO_3^{2-} .

Alkalinity/acidity/neutralizing capacity

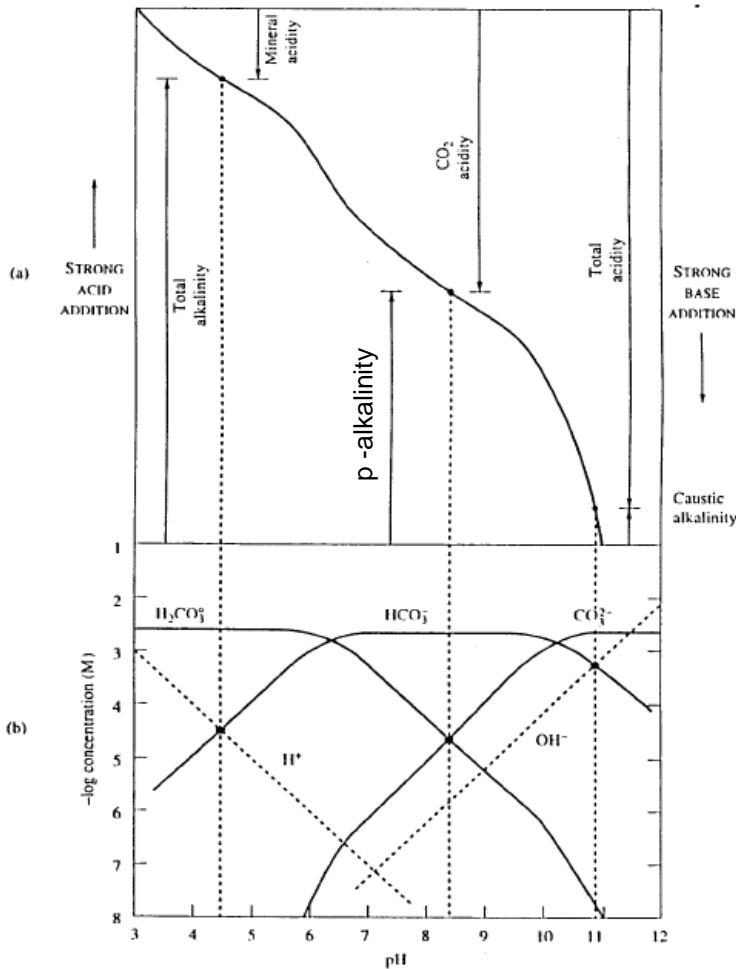


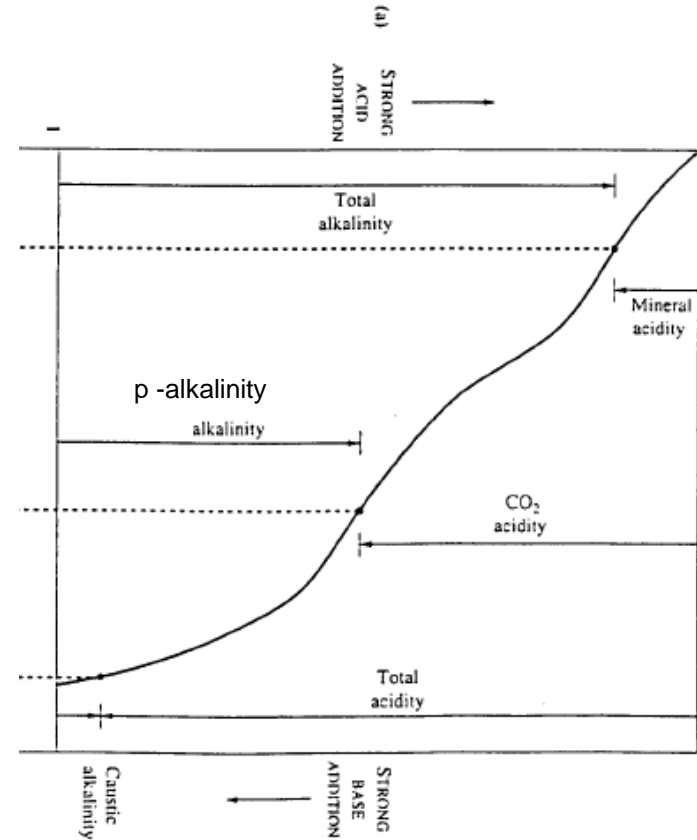
Figure 5.6 The carbonate distribution diagram of a solution with constant $C_T = 2.5 \times 10^{-3} \text{ M}$ showing (a) the strong acid titration curve for the same solution from pH 12 to 3 and strong base titration curve between pH 3 and 12. Dashed straight lines in (b) indicate concentrations of H^+ and OH^- , which are independent of C_T . Modified after V. L. Snoeyink and D. Jenkins, *Water Chemistry*. Copyright © 1980 by John Wiley & Sons, Inc. Used by permission of John Wiley & Sons, Inc.

The pH values at the respective equivalence points for the acidity and alkalinity titrations (~4.3 and 10.3) represent approximate thresholds beyond which most life processes in natural waters are seriously impaired.

They represent convenient measures for estimating the maximum capacity of a natural water to neutralize acidic or caustic wastes without extreme disturbance of biological activity.

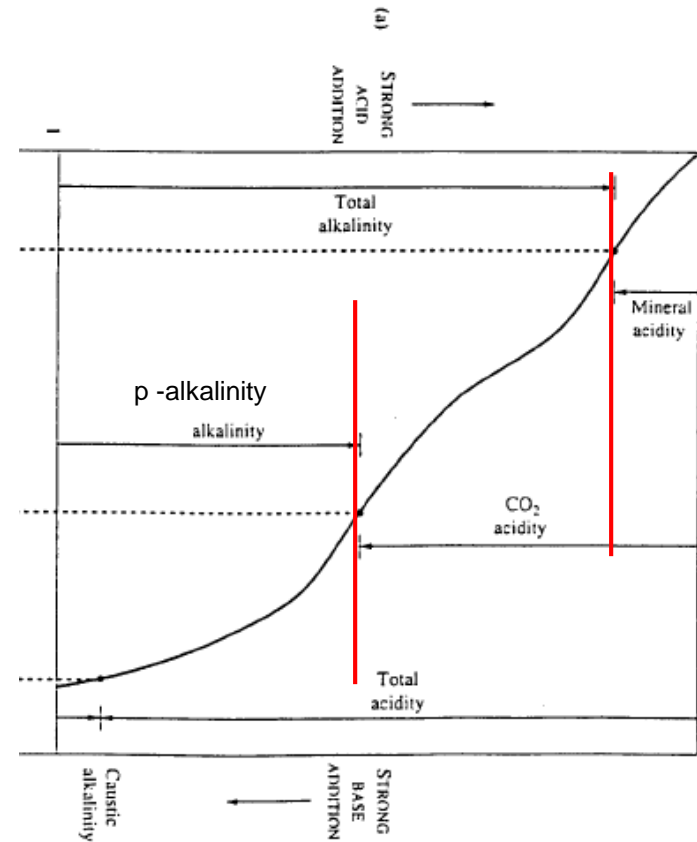
Alkalinity/acidity/neutralizing capacity

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<i>p</i> -Alkalinity	$f = 1$	$[\text{p-Alk}] = [\text{OH}^-] + [\text{CO}_3^{2-}] - [\text{H}_2\text{CO}_3^*] - [\text{H}^+]$ (2)
Alkalinity	$f = 0$	$[\text{Alk}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$ (3)
II. Base-Neutralizing Capacity (BNC)		
Mineral acidity	$f = 0$	$[\text{H-Acy}] = [\text{H}^+] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] - [\text{OH}^-]$ (4)
CO_2 -acidity	$f = 1$	$[\text{CO}_2\text{-Acy}] = [\text{H}_2\text{CO}_3^*] + [\text{H}^+] - [\text{CO}_3^{2-}] - [\text{OH}^-]$ (5)
Acidity	$f = 2$	$[\text{Acy}] = 2[\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{H}^+] - [\text{OH}^-]$ (6)
III. Combinations		
$f = 2 - g$	(7)	$[\text{Alk}] + [\text{CO}_2\text{-Acy}] = C_T$ (11)
$[\text{Alk}] + [\text{H-Acy}] = 0$	(8)	$[\text{Alk}] + [\text{Acy}] = 2C_T$ (12)
$[\text{Acy}] + [\text{OH-Alk}] = 0$	(9)	$[\text{Alk}] - [\text{p-Alk}] = C_T$ (13)
$[\text{p-Alk}] + [\text{CO}_2\text{-Acy}] = 0$	(10)	$[\text{CO}_2\text{-Acy}] - [\text{H-Acy}] = C_T$ (14)



Alkalinity/acidity/neutralizing capacity

Term	End Point	Definition
<i>I. Acid-Neutralizing Capacity (ANC)</i>		
Caustic alkalinity	$f = 2$	$[\text{OH}^- - \text{Alk}] = [\text{OH}^-] - [\text{HCO}_3^-] - 2[\text{H}_2\text{CO}_3^*] - [\text{H}^+] \quad (1)$
<i>p</i> -Alkalinity	$f = 1$	$[\text{p-Alk}] = [\text{OH}^-] + [\text{CO}_3^{2-}] - [\text{H}_2\text{CO}_3^*] - [\text{H}^+] \quad (2)$
Alkalinity	$f = 0$	$[\text{Alk}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \quad (3)$
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Acidity	$f = 2$	$[\text{Acy}] = 2[\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{H}^+] - [\text{OH}^-] \quad (6)$
<i>III. Combinations</i>		
$f = 2 - g$	(7)	$[\text{Alk}] + [\text{CO}_2\text{-Acy}] = C_T \quad (11)$
$[\text{Alk}] + [\text{H-Acy}] = 0$	(8)	$[\text{Alk}] + [\text{Acy}] = 2C_T \quad (12)$
$[\text{Acy}] + [\text{OH-Alk}] = 0$	(9)	$[\text{Alk}] - [\text{p-Alk}] = C_T \quad (13)$
$[\text{p-Alk}] + [\text{CO}_2\text{-Acy}] = 0$	(10)	$[\text{CO}_2\text{-Acy}] - [\text{H-Acy}] = C_T \quad (14)$



Alkalinity/acidity/neutralizing capacity

Unlike the individual concentrations of the pH-sensitive species (e.g., H_2CO_3^* , HCO_3^- , $\text{B}(\text{OH})_4^-$, etc.) and pH, ANC and BNC are conservative properties of the system that are pressure and temperature independent.

$$[\text{Alk}] = (V_a[\text{Alk}]_a + V_b[\text{Alk}]_b)/(V_a + V_b)$$

The same is true of C_T , if the system is **closed** to the atmosphere:

$$C_T = \Sigma\text{CO}_2 = (V_a C_{T-a} + V_b C_{T-b})/(V_a + V_b)$$

Whereas the addition or removal of CO_2 , or more rigorously H_2CO_3^* will affect C_T , it does not change the alkalinity of a solution.

$$[\text{Alk}] = C_B = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

Alkalinity/acidity/neutralizing capacity

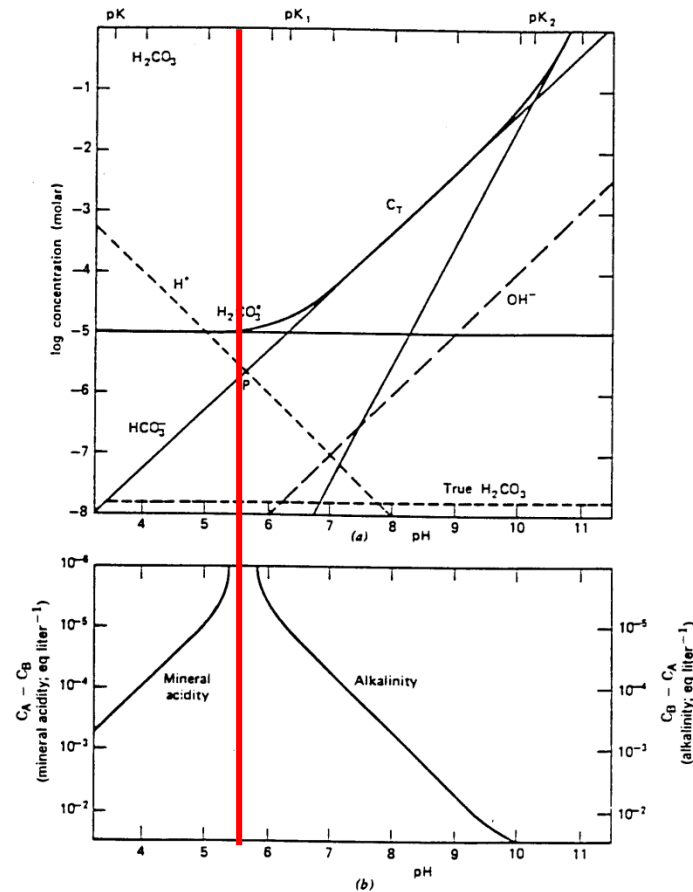
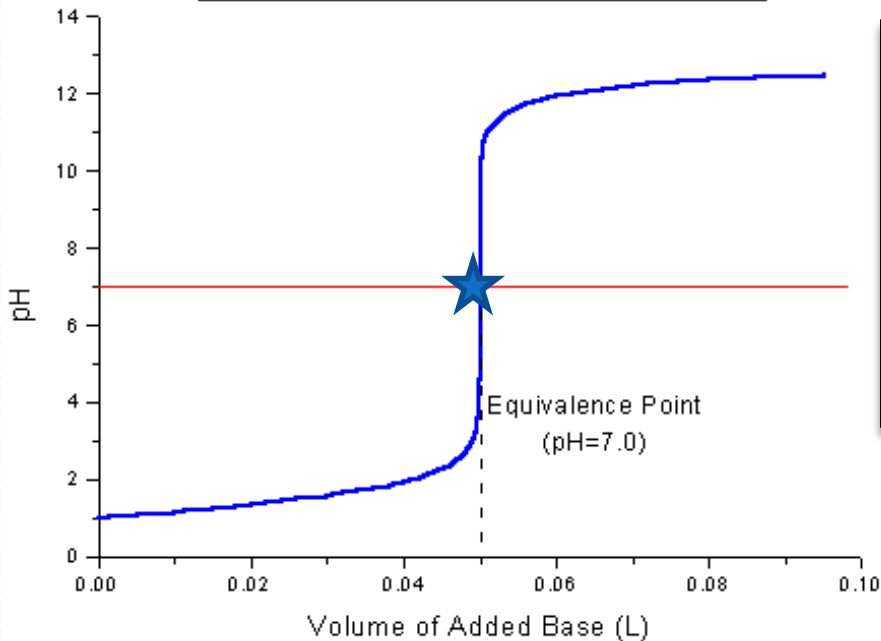


Figure 4.9. Aqueous carbonate species in equilibrium with $p_{CO_2} = 10^{-3.5}$ atm (see Figure 4.5). At pH values different from that of a pure CO_2 solution, the solution contains either alkalinity (Alk) or mineral acidity (H-Acy).

Acid-base titration

(strong acid titrated by a strong base)

0.05L of 0.1M HCl Titrated with 0.1M NaOH



At $V = 0$, $[\text{H}^+] = [\text{Cl}^-] + [\text{OH}^-]$ and
 $\Sigma \text{Cl} = [\text{Cl}^-] + [\text{HCl}^\circ] = C_A$

At $V \neq 0$, $[\text{Na}^+] + [\text{H}^+] = [\text{Cl}^-] + [\text{OH}^-]$
 $\rightarrow C_B = [\text{Na}^+] = [\text{Cl}^-] + [\text{OH}^-] - [\text{H}^+]$

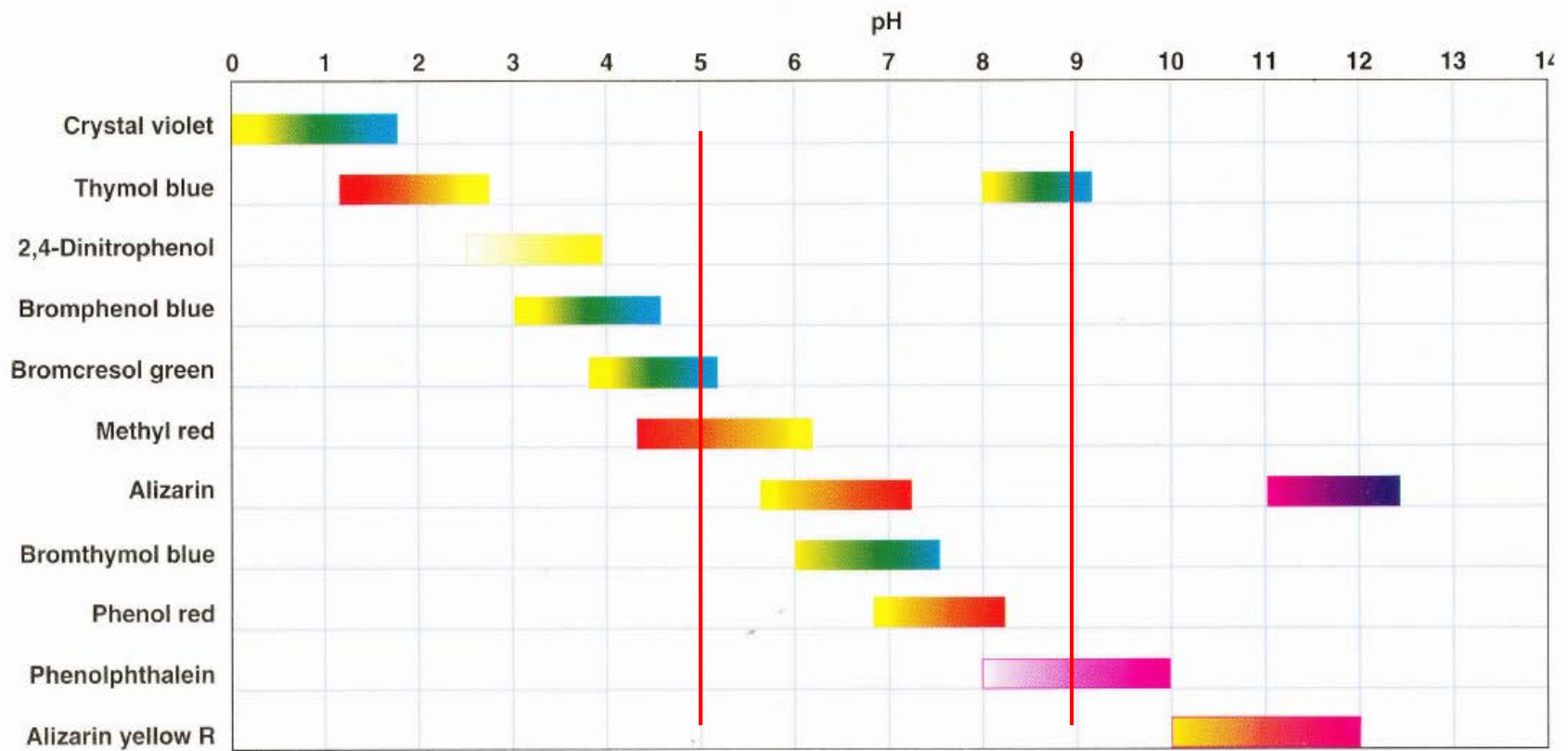
$[\text{H}^+] = \text{acid in solution} = C_A - C_B = (V_{\text{init}} [\text{Cl}^-]_{\text{init}} - V_{\text{tit}} [\text{Na}^+]_{\text{tit}}) / (V_{\text{init}} + V_{\text{tit}})$

At the equivalence point, $C_A = C_B = (V_{\text{init}} [\text{Cl}^-]_{\text{init}}) = (V_{\text{tit}} [\text{Na}^+]_{\text{tit}})$

or $[\text{OH}^-] = [\text{H}^+] \rightarrow \text{pH} = 7$

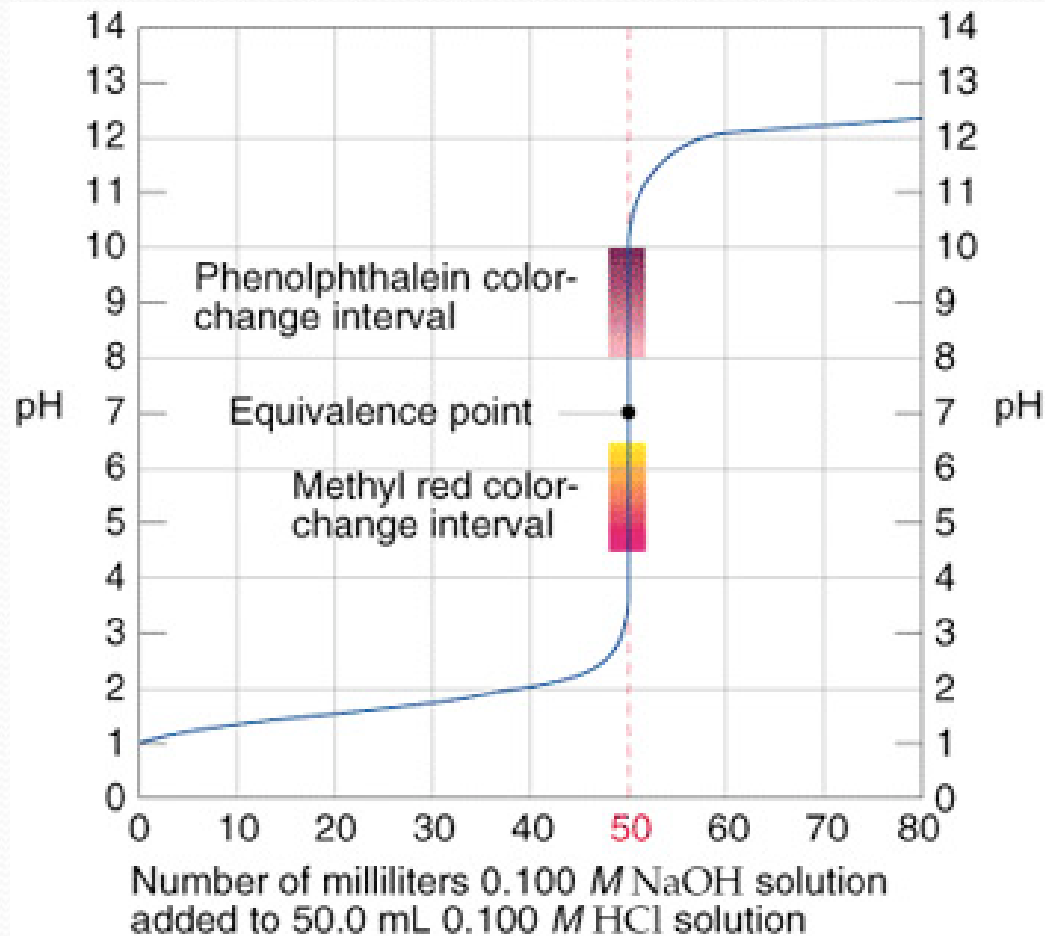
Beyond the equivalence point, $[\text{OH}^-] = \text{excess OH}^- = C_B - C_A$
 $= (V_{\text{tit}} [\text{Na}^+]_{\text{tit}} + V_{\text{init}} [\text{Cl}^-]_{\text{init}}) / V_{\text{tot}}$

Choice of color indicators



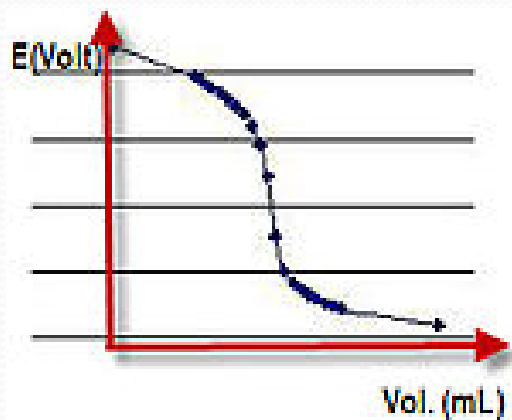
Acid-base titration

(strong acid titrated by a strong base)

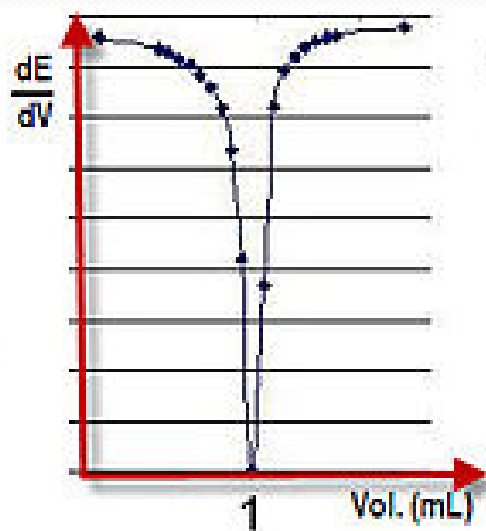


Acid-base titration

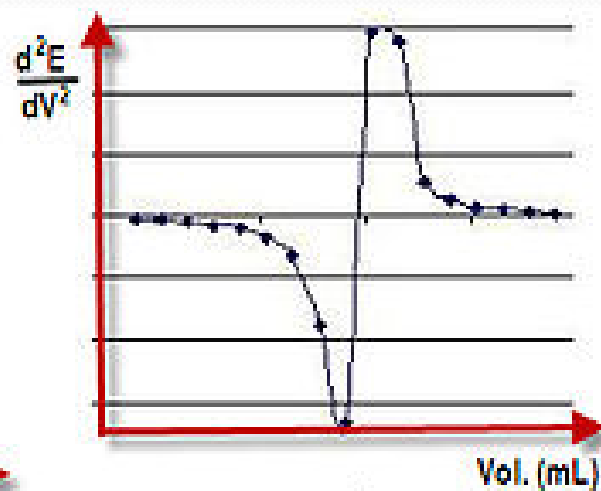
(strong acid titrated by a strong base)



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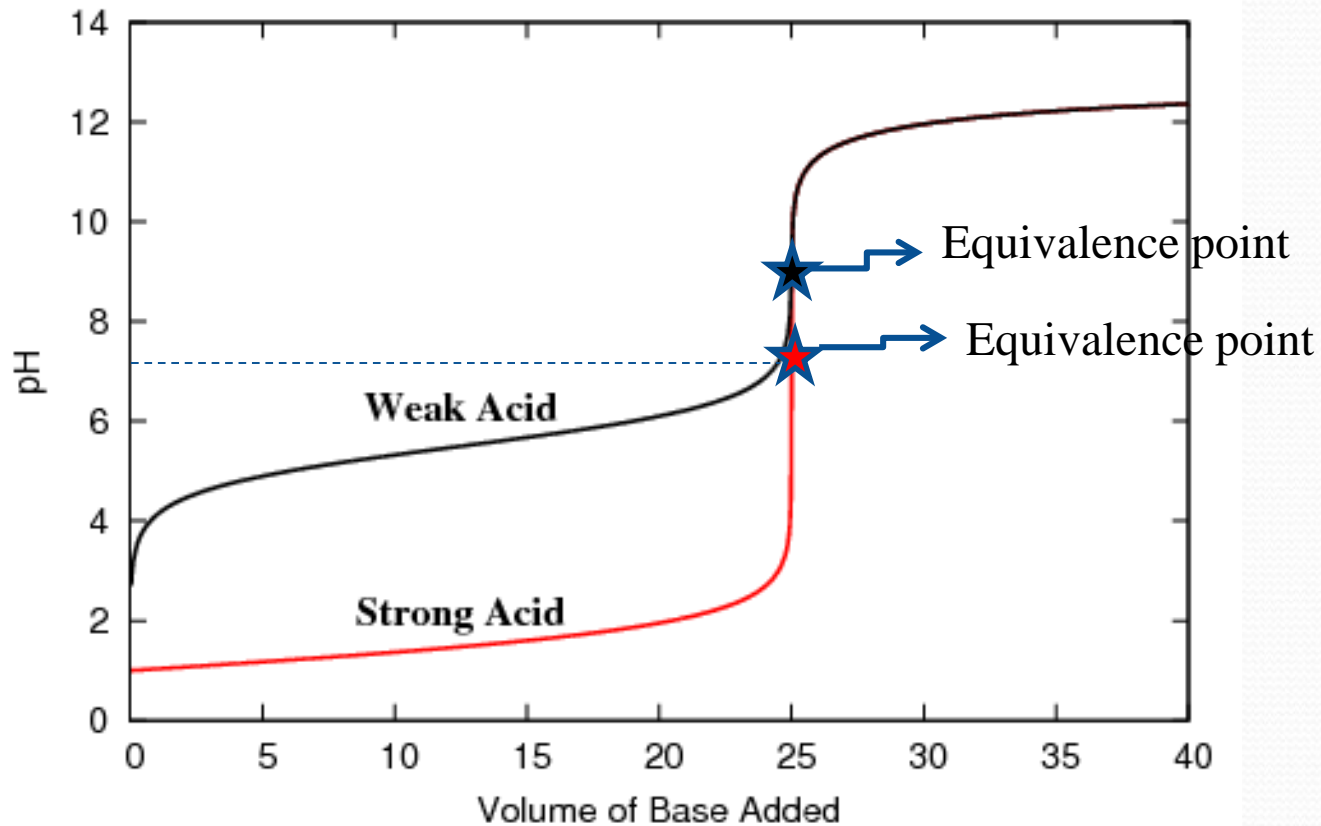
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Acid-base titration

Titration Curves



Acid-base titration

(weak acid titrated by a strong base)

Assuming that we are titrating 40 mL of a 0.1M HA with 0.1M NaOH



Reactions	Mass action	Equilibrium constants
$\text{HA} \leftrightarrow \text{H}^+ + \text{A}^-$	$K_a = [\text{H}^+][\text{A}^-]/[\text{HA}]$	$10^{-4.75}$
$\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-$	$K_w = [\text{H}^+][\text{OH}^-]$	10^{-14}

Charge balance: $[\text{H}^+] + [\text{Na}^+] = [\text{A}^-] + [\text{OH}^-]$

Mass balance: $\Sigma[\text{A}] = [\text{HA}]_0 = [\text{HA}] + [\text{A}^-]$

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

$C_A = \Sigma[\text{A}] = [\text{HA}]_0 = [\text{HA}] + [\text{A}^-]$

At any point along the titration curve:

$$[\text{H}^+] = [\text{A}^-] + [\text{OH}^-] - [\text{Na}^+] = \frac{[\text{HA}]_0}{1 + ([\text{H}^+]/K_a)} + \frac{K_w}{[\text{H}^+]} - [\text{Na}^+]$$

Acid-base titration

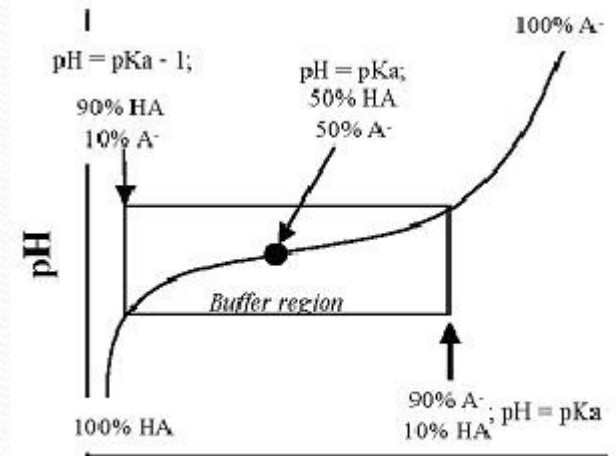
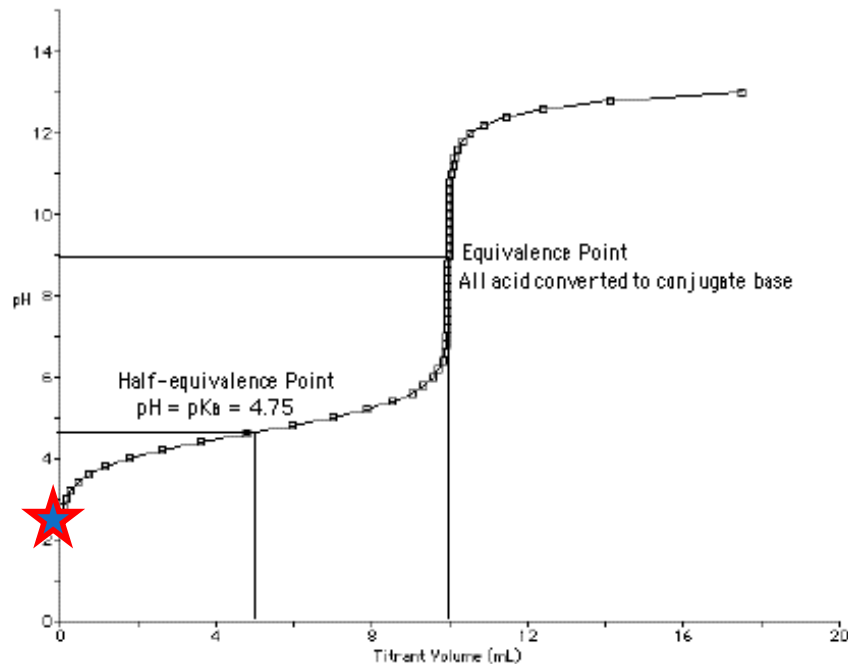
(weak acid titrated by a strong base)

At $v = 0$, $[H^+] = (K_a [HA]_0)^{0.5}$

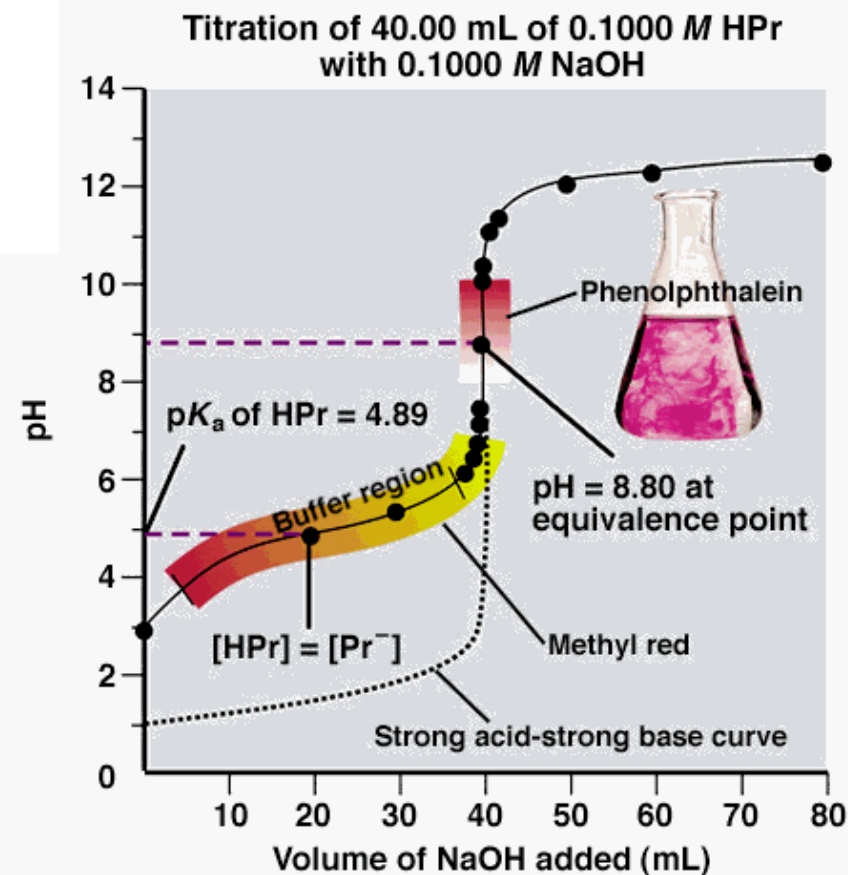
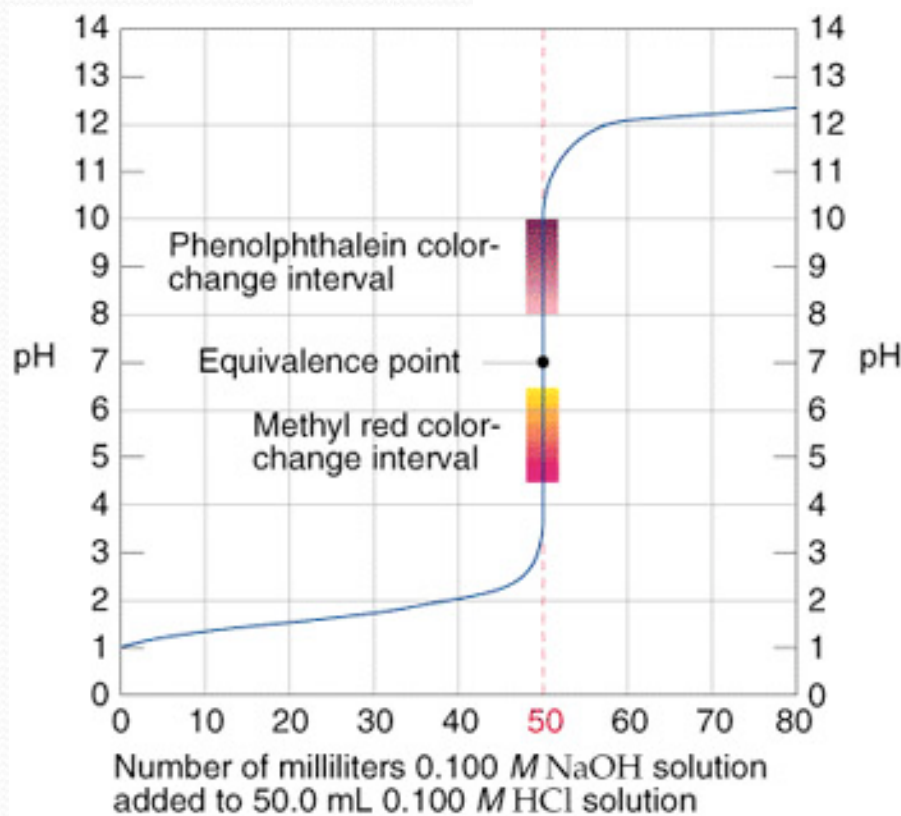
mid-way to the equivalence point, $[HA] = [A^-]$, $pH = pK_a$

at the equivalence point, $C_A = C_B$, $[H^+] = K_w / (K_b [A^-])^{0.5}$

beyond the equivalence point, $[OH^-] = C_B - C_A = \text{excess } OH^- / \text{total volume}$

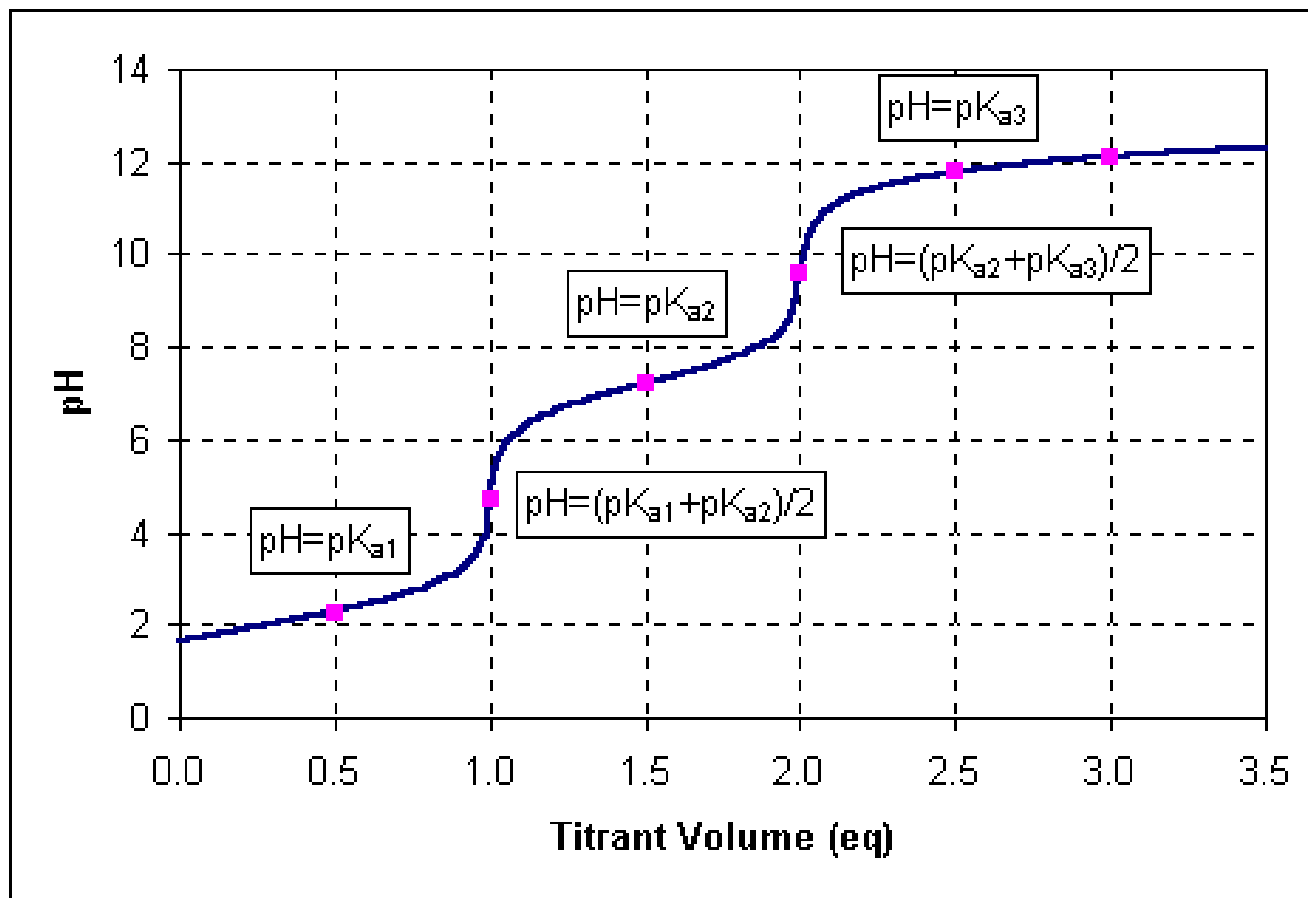


Acid-base titration

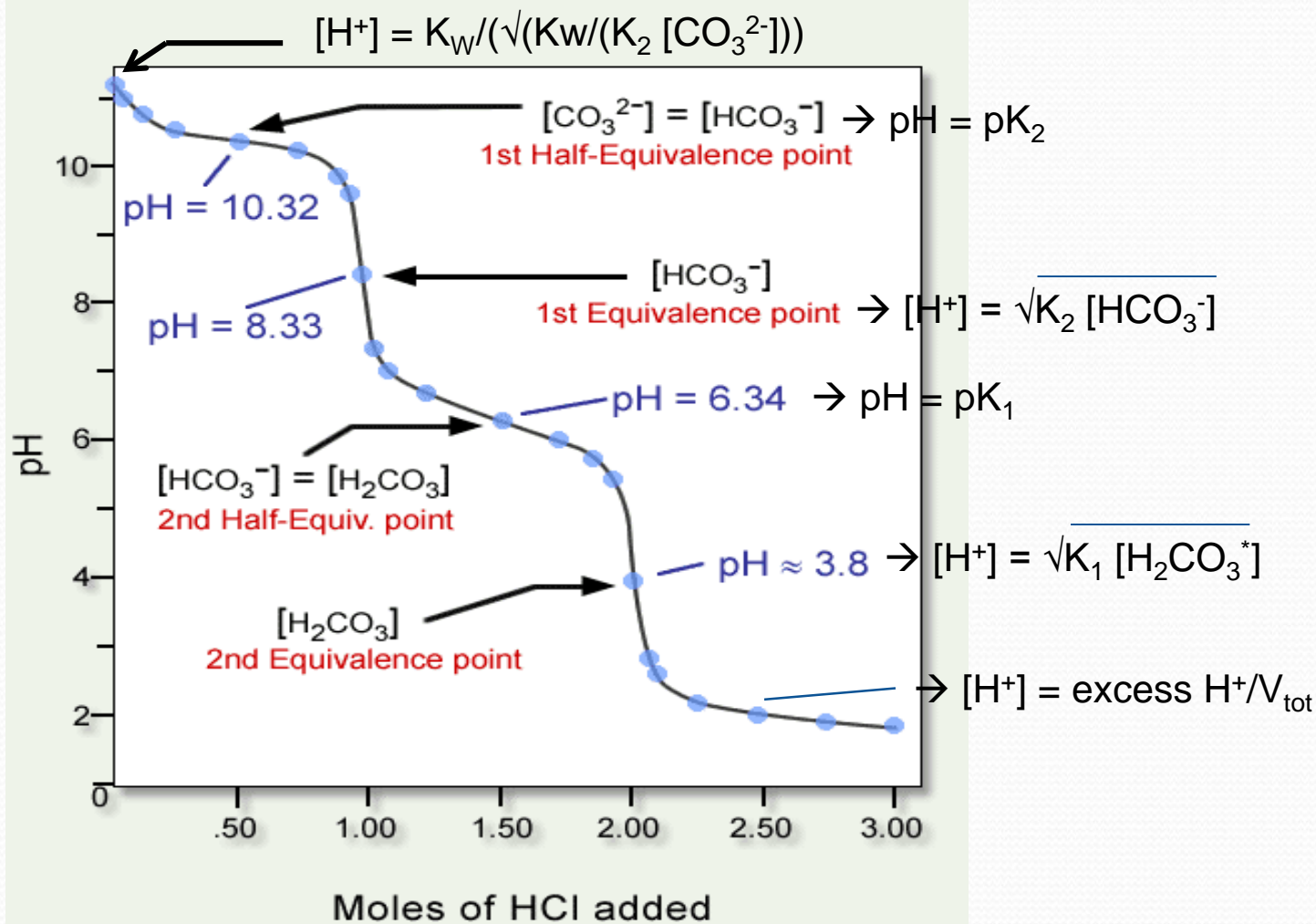


Acid-base titration

(polyprotic acid titrated by a strong base)



Titration of Na_2CO_3 with HCl



Buffer capacity

pH is an intensity factor, not to be confused with the capacity of a solution to give or accept a proton (acidity, alkalinity), also to be distinguished from the buffer capacity of the solution.

The buffer capacity of a solution is a measure of its ability to resist changes of pH upon the addition of a strong acid or base. In natural waters, pH buffering is mostly due to the interaction of weak acids and bases and their salts with water. The buffer capacity is defined as:

$$\beta = dC_B/dpH = -dC_A/dpH$$

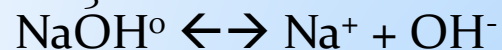
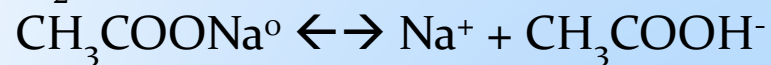
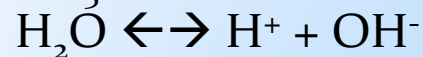
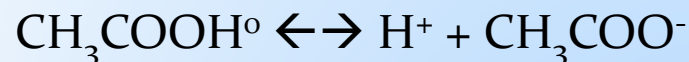
where dC_A (or dC_B) is an infinitesimal addition of strong acid (or base) and dpH is the corresponding change in pH. β is simply the inverse slope of the alkalinity or acidity titration curve and is always reported as a positive value.

Buffer systems

To withstand the addition of strong acid or strong base without changing its pH, a buffer solution must contain an acidic component that can neutralize added OH^- ion and a basic component that can neutralize added $[\text{H}_3\text{O}^+]$. They cannot be just any acid and base, however, because they must be present in the same solution without neutralizing each other.

In the presence of a conjugate acid-base pair, pH changes only slightly upon the addition of a strong acid or base.

Reactions



Mass Action Equations

$$K_a = 1.85 \times 10^{-5} \quad \text{or} \quad \text{p}K_a = 4.75$$

$$K_w = 10^{-14} \quad \text{or} \quad \text{p}K_w = 14$$

$$\text{p}K_{(3)} = -0.1$$

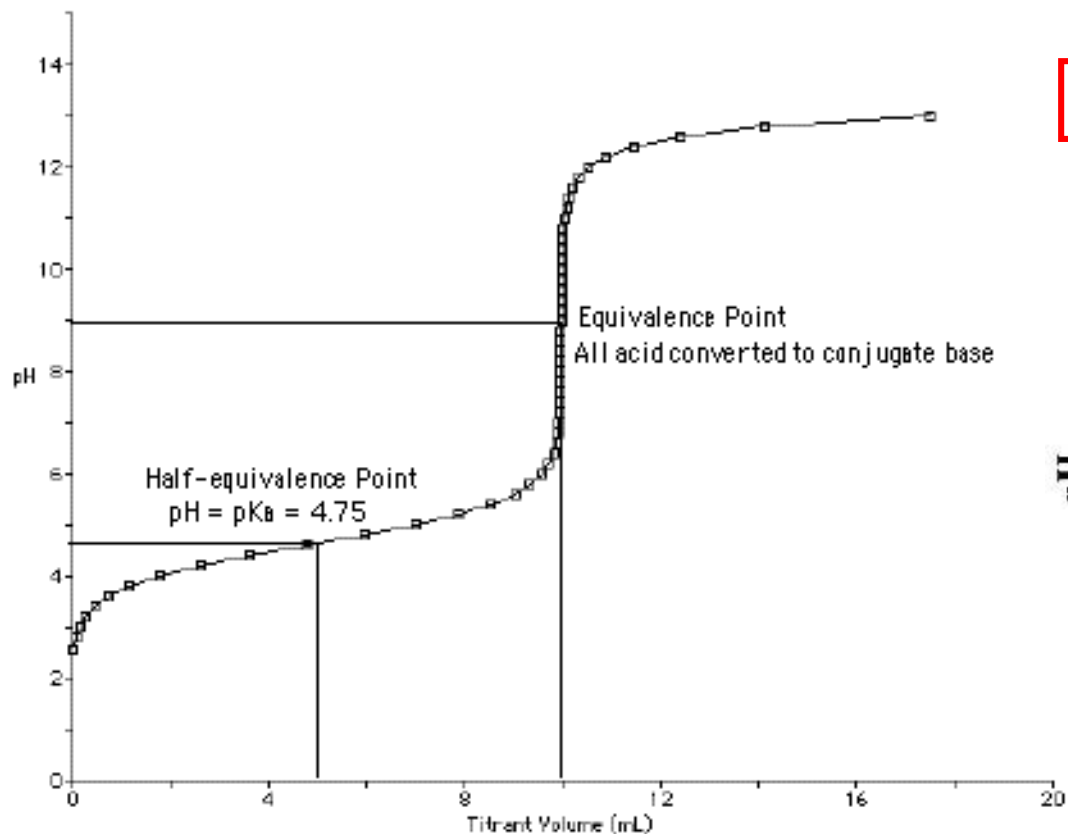
$$\text{p}K_{(4)} = -0.2$$

For our purposes we can ignore $[\text{NaAc}^\circ]$ and $[\text{NaOH}^\circ]$ since they are almost completely dissociated.

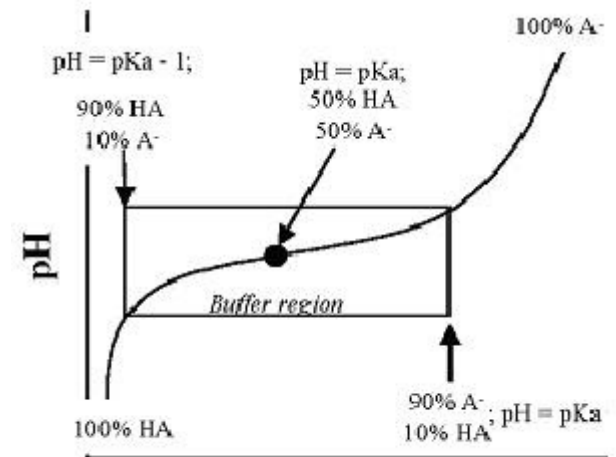
Solving for $[\text{H}_3\text{O}^+]$, we obtain: $[\text{H}_3\text{O}^+] = K_a \times [\text{CH}_3\text{COOH}] / [\text{CH}_3\text{COO}^-]$
or $\text{pH} = \text{p}K_a + \log [\text{CH}_3\text{COO}^-] / [\text{CH}_3\text{COOH}]$

The buffer is therefore most effective when the components of the conjugate pair have similar concentrations.

Buffer systems



$$\text{pH} = \text{pK}_a + \log \left(\frac{[\text{A}^-]}{[\text{HA}]} \right)$$



Buffer capacity of pure water

To calculate the buffer capacity of pure water we will assume that it is being titrated with NaOH.

Charge balance equation: $[\text{Na}^+] + [\text{H}^+] = [\text{OH}^-]$

Mass balance for the added base $C_B = [\text{Na}^+] = [\text{OH}^-] - [\text{H}^+]$

Substituting in terms of $[\text{H}^+]$:

$$C_B = K_W/[\text{H}^+] - [\text{H}^+]$$
$$dC_B = \{-K_W/[\text{H}^+]^2 - 1\} d[\text{H}^+]$$

Since $\text{pH} = -\log [\text{H}^+] = -\ln [\text{H}^+]/2.303$,

$$d[\text{H}^+] = \text{dpH} (-2.303[\text{H}^+])$$

Substituting for $d[\text{H}^+]$, we obtain:

$$dC_B/\text{dpH} = \beta(\text{H}_2\text{O}) = 2.303 \{K_W/[\text{H}^+] + [\text{H}^+]\} = 2.303 \{[\text{OH}^-] + [\text{H}^+]\}$$

Buffer capacity of pure water

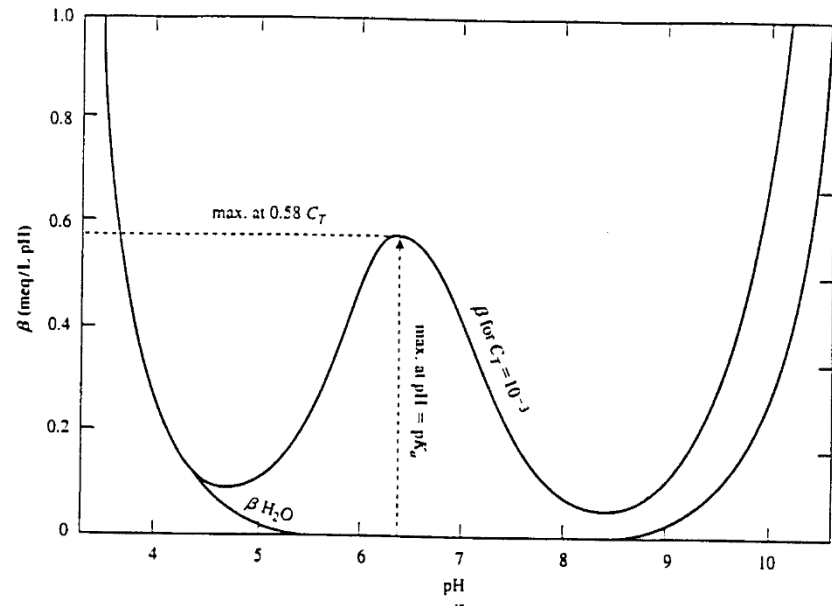
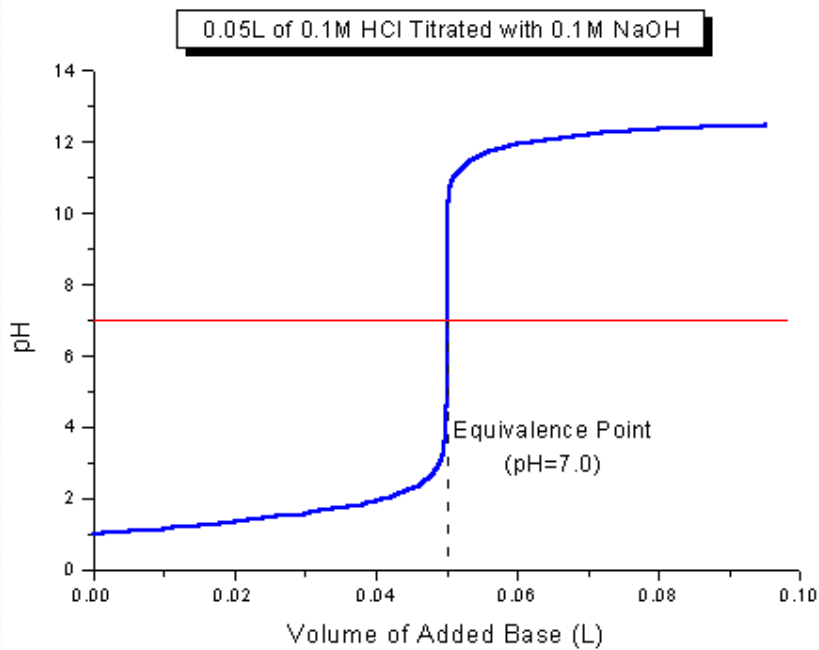


Figure 5.10 A linear plot of the buffer capacity of carbonic acid species as a function of pH for $C_T = 10^{-3.0}$ M showing that the maximum buffer capacity equals $0.58 C_T$, and occurs at $pH = pK_1(H_2CO_3^*) = 6.35$. The lower curve is the buffer capacity of water, β_{H_2O} .

β is simply the inverse slope of the alkalinity or acidity titration curve and is always reported as a positive value.

Buffer capacity of a weak acid



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

Charge balance: $[\text{Na}^+] + [\text{H}^+] = [\text{A}^-] + [\text{OH}^-]$, or $C_B = [\text{Na}^+] = [\text{A}^-] + [\text{OH}^-] - [\text{H}^+]$

Mass balance: $C_A = \Sigma[\text{A}] = [\text{HA}] + [\text{A}^-]$

Substituting $[\text{A}^-] = K_a C_A / (K_a + [\text{H}^+])$ into $C_B = K_a C_A / (K_a + [\text{H}^+]) + K_W / [\text{H}^+] - [\text{H}^+]$

Differentiating, we find: $-dC_B/d[\text{H}^+] = \{K_a C_A / (K_a + [\text{H}^+])^2 + K_W / [\text{H}^+]^2 + 1\}$

Substituting $d[\text{H}^+] = -2.303[\text{H}^+] \text{d pH}$, we obtain:

$$dC_B/d\text{pH} = \beta = 2.303 \{[\text{H}^+] + K_W / [\text{H}^+] + K_a C_A [\text{H}^+] / (K_a + [\text{H}^+])^2\}$$

The first two terms in the bracket are the buffer capacity of water, and the third is the buffer capacity due to the weak acid. For intermediate pH's, the water terms become negligible and β reduces to:

$$\beta = 2.303 K_a C_A \{[\text{H}^+] / (K_a + [\text{H}^+])^2\}$$

As you would expect from the slope of the titration curve, the maximum buffer capacity for a weak acid occurs at a $\text{pH} = \text{p}K_a$

Buffer capacity of pure water

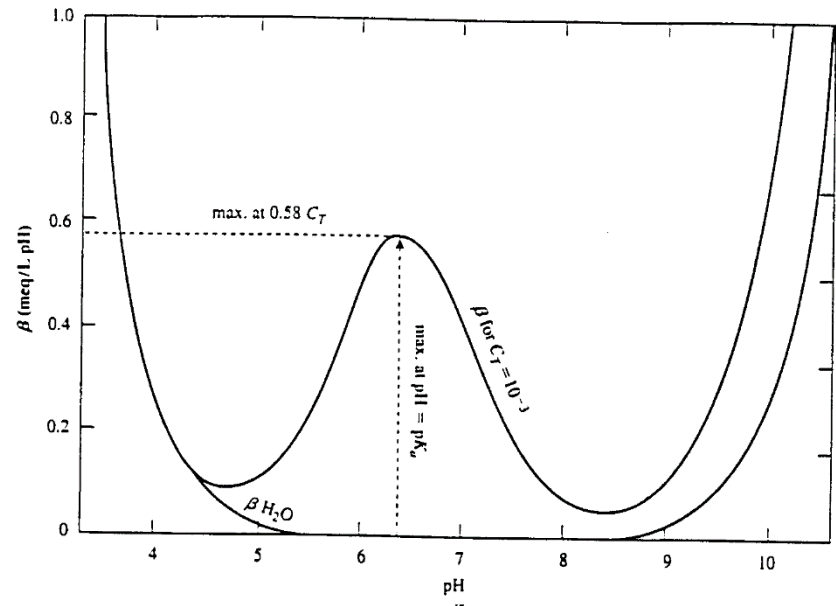
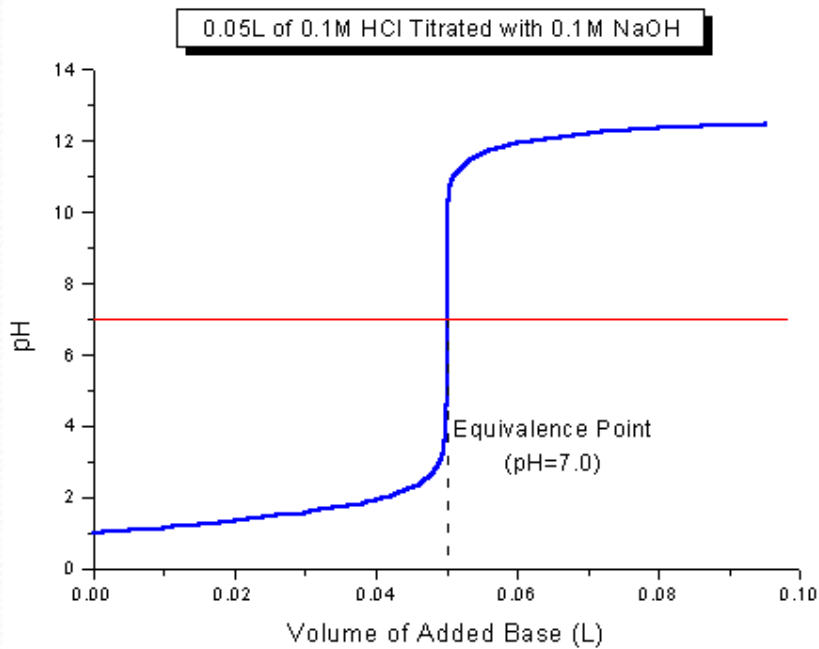


Figure 5.10 A linear plot of the buffer capacity of carbonic acid species as a function of pH for $C_T = 10^{-3.0}$ M showing that the maximum buffer capacity equals $0.58 C_T$, and occurs at $\text{pH} = \text{pK}_1(\text{H}_2\text{CO}_3^*) = 6.35$. The lower curve is the buffer capacity of water, β_{H_2O} .

β is simply the inverse slope of the alkalinity or acidity titration curve and is always reported as a positive value.

Buffer capacity of a polyprotic acid

For a polyprotic acid (e.g., H_4B), the buffer capacity or index is the sum of the contributions from each successive acid species, or in general terms:

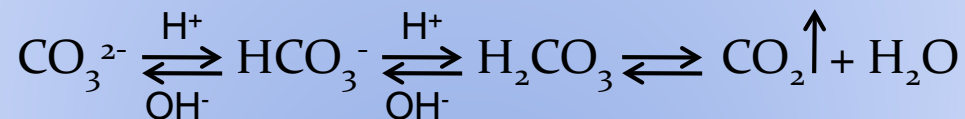
$$\beta = \beta(H_2O) + \beta(H_3B^-) + \beta(H_2B^{2-}) + \beta(HB^{3-}) + \beta(B^{4-})$$
$$= 2.303 \{ [H^+] + K_W/[H^+] + K_1 C_A [H^+] / (K_1 + [H^+])^2 + K_2 C_A [H^+] / (K_2 + [H^+])^2 + \dots \}$$

where C_A is the total concentration of acid species and K_1 and K_2 are the first and second stepwise dissociation constants of the acids.

$$\beta = dC_B/dpH = -dC_A/dpH \approx 2.303 \sum \lambda_i^2 [X_i]$$

Where λ is the neutralizing capacity of species i and $[X]$ is the concentration of compounds capable of neutralizing a proton or OH^- .

The pH of most natural waters is buffered by the carbonate system:



Buffer capacity of natural waters

If a parcel of water to which the acid was added is in contact with the atmosphere, the excess CO_2 produced by the sequential protonation of CO_3^{2-} and HCO_3^- will be able to escape to the atmosphere further reducing the increase in pH.

$$\beta = 2.303 ([\text{HCO}_3^-] + 4[\text{CO}_3^{2-}] + [\text{H}^+] + [\text{OH}^-])$$

If the parcel of water is isolated from the atmosphere and cannot rid itself of the generated CO_2 , its buffering mechanisms is diminished.

$$\beta = 2.303 ([\text{H}_2\text{CO}_3^*] + [\text{CO}_3^{2-}] + [\text{H}^+] + [\text{OH}^-])$$

Consequently, at $\text{pH} \approx 8$, the buffer capacity of the carbonate system in equilibrium with a gas phase is roughly 100 times greater than that of an isolated aqueous phase.

On the other hand, the buffer capacity of the system would be greatly increased by the presence of solid CaCO_3 , since acid added to the system would readily react with the solid:



in which case, if the system is open to the atmosphere:

$$\beta = 2.303 (4[\text{Ca}^{2+}] + [\text{HCO}_3^-] + 4[\text{CO}_3^{2-}] + [\text{H}^+] + [\text{OH}^-])$$

Buffer capacity provided by the carbonic acid system in aqueous solutions

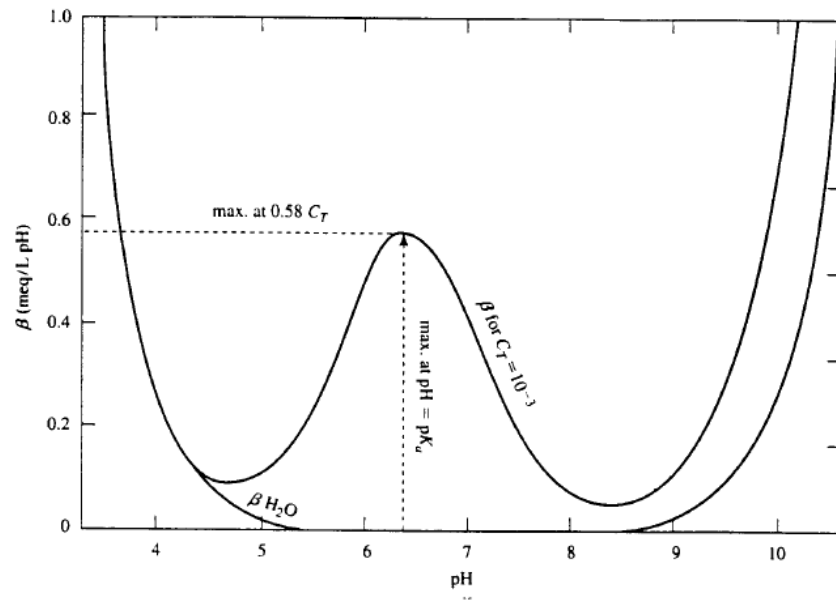


Figure 5.10 A linear plot of the buffer capacity of carbonic acid species as a function of pH for $C_T = 10^{-3.0}$ M showing that the maximum buffer capacity equals $0.58 C_T$, and occurs at $\text{pH} = \text{p}K_1(\text{H}_2\text{CO}_3^*) = 6.35$. The lower curve is the buffer capacity of water, $\beta_{\text{H}_2\text{O}}$.

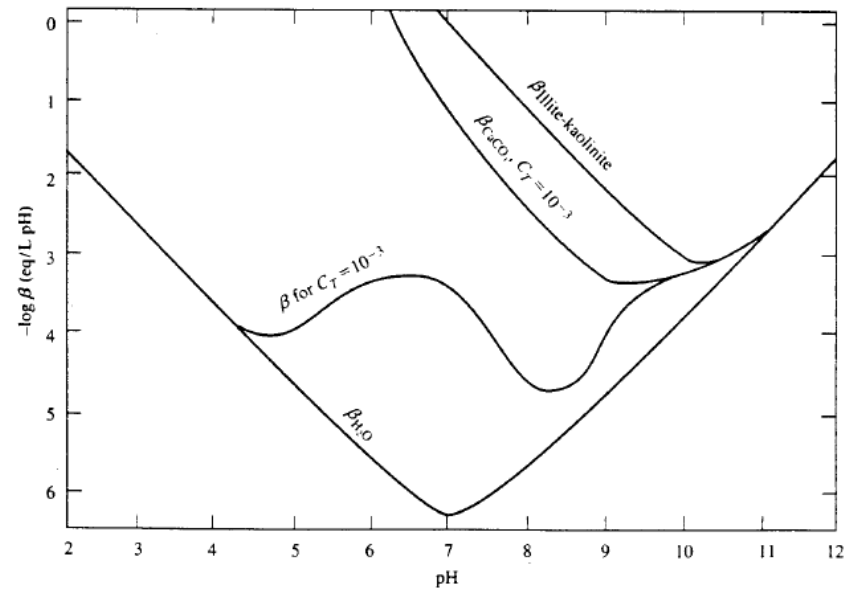
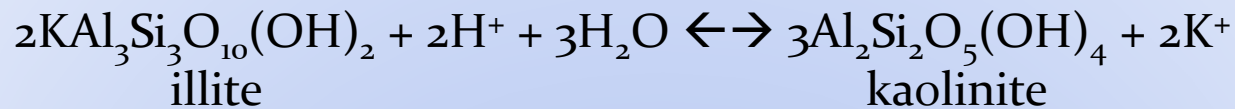


Figure 5.11 A log plot of the buffer capacity due to carbonic acid species for $C_T = 10^{-3.0}$ M (see Fig. 5.10); at saturation with respect to calcite for $C_T = 10^{-3.0}$ M; and for equilibrium between the clays illite and kaolinite. The lower curve is $\beta_{\text{H}_2\text{O}}$.

Buffer capacity of natural waters

On longer time scales, it has been proposed that the pH of natural waters should be regulated by reactions with clay minerals, such as between kaolinite and illite or muscovite. This reaction can be written as:



for which the mass action law gives: $K_{\text{eq}} = [\text{K}^+]/[\text{H}^+] = 10^{6.5}$

If we were to titrate a clay suspension with HCl, the charge balance equation could be written as:

$$[\text{H}^+] + [\text{K}^+] = [\text{OH}^-] + [\text{Cl}^-]$$

or $C_A = [\text{Cl}^-] = [\text{K}^+] + [\text{H}^+] - [\text{OH}^-] = 10^{6.5}[\text{H}^+] + [\text{H}^+] - 10^{-14}/[\text{H}^+]$

Taking the derivative,

$$dC_A/d[\text{H}^+] = (1 + 10^{6.5} + 10^{-14}/[\text{H}^+]^2)$$

$$\beta = -dC_A/d\text{pH} = 2.303 [\text{H}^+] dC_A/d[\text{H}^+] = 2.303 ([\text{H}^+] + K_W/[\text{H}^+] + 10^{6.5} [\text{H}^+])$$