

Subject of electrochemistry:

- dissociation (solutions of electrolytes, melts of salts)
- conductivity
- phenomena at interfaces s/l (electrolysis, galvanic cells)

Conductors:

- electrons (or holes) are moving:
metals, graphite, graphene, semiconductors
- ions are moving (or jumping):
solutions of electrolytes , molten salts, ionic liquids
- both electrons and ions are moving:
plasma

strong electrolyte: (almost) completely ionizes (dissociates)

no uncharged molecules in the solution

H_2SO_4 , KOH , $\text{Ca}(\text{OH})_2$, NaCl , BaSO_4 , ...

not necessarily to max. degree:



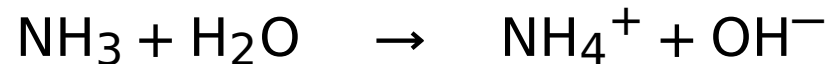
weak electrolyte: contains neutral (not dissociated) molecules

organic acids and bases, NH_3 , H_2O , ...

standard states: solvent (water): \bullet ; in dilute \odot $a_{\text{water}} = 1$

ions: $[c]$ ($a_i = \gamma_i c_i / c^{\text{st}}$)

dissociation constant = equilibrium constant of the dissociation reaction



pH

log = log₁₀, p = -log

$$\text{pH} = -\log a_{\text{H}^+} \stackrel{\gamma_{\text{H}^+}=1}{=} -\log \frac{c_{\text{H}^+}}{c^{\text{st}}} = -\log \frac{c_{\text{H}^+}}{\text{mol dm}^{-3}} \stackrel{?}{=} -\log[\text{H}^+] \stackrel{?}{=} -\log\{\text{H}^+\}$$

Dissociation of water:



Ionic product (autoionization constant) of water K_w :

$$K_w = \frac{a_{\text{H}^+} a_{\text{OH}^-}}{a_{\text{H}_2\text{O}}} \approx \frac{c_{\text{H}^+} c_{\text{OH}^-}}{(c^{\text{st}})^2} \equiv [\text{H}^+][\text{OH}^-] \doteq 1.00 \times 10^{-14} \text{ (25 }^\circ\text{C)}$$

Equivalently (at 25 °C):

$$\text{pH} + \text{pOH} = \text{p}K_w = 14 \quad \text{more accurate } 13.997$$

● depends on temperature: $\text{p}K_w(100^\circ\text{C}) = 12.29$

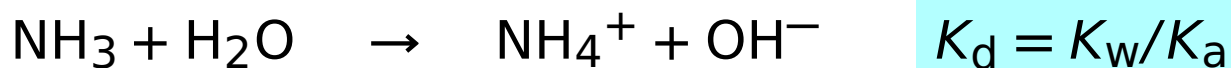
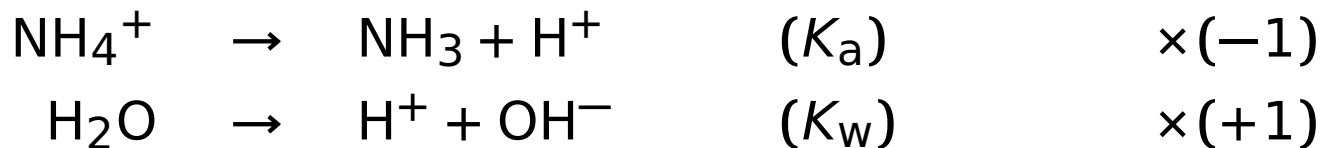
● heavy water: $\text{p}K_w(25^\circ\text{C}) = 14.87$
(isotopic effect: D is more strongly bound)

Acidity constant (ionization constant) K_a is common in tables = equilibrium constant of deprotonisation, often given as pK_a

● acids: dissociation constant of the acid



● bases: dissociation constant of the conjugated acid



Example. Acidity constant of ammonium is $pK_a = 9.25$ (at 25°C). Calculate the dissociation constant of ammonium hydroxide (water solution of NH_3).

1.78×10^{-5}

Example. Calculate pH of aqueous HCl of concentration 0.01 mol dm^{-3} .
100 % dissociation to the 1st degree:

$$c_{\text{H}^+} = c_{\text{HCl}} \Rightarrow \text{pH} = -\log a_{\text{H}^+} \approx -\log c_{\text{H}^+} = 2$$

Example. Calculate pH of aqueous H_2SO_4 of concentration $0.001 \text{ mol dm}^{-3}$.
It dissociates completely to the 1st degree, partially to the 2nd degree, but since here $c \ll K_2 = 1.3 \times 10^{-2}$, we can assume also 100 % dissociation.

$$c_{\text{H}^+} = 2c_{\text{H}_2\text{SO}_4} \Rightarrow \text{pH} = -\log a_{\text{H}^+} \approx -\log(2c_{\text{H}^+}) = 2.7$$

more accurate 2.75 (partial dissociation + Debye-Hückel)

Example. Calculate pH of aqueous NaOH of concentration 0.01 mol dm^{-3} at 25°C .
 $c_{\text{OH}^-} = 0.01 \text{ mol dm}^{-3}$, $c_{\text{H}^+} = 10^{-14}/0.01 = 10^{-12} \text{ mol dm}^{-3}$, $\text{pH} = 12$

Example. Calculate pH of 0.001 M aqueous $\text{Ca}(\text{OH})_2$ at 25°C .

$$c_{\text{OH}^-} = 0.002 \text{ mol dm}^{-3}, \text{pOH} = 2.7, \text{pH} = 14 - 2.7 = 11.3$$



Determine pH of a weak acid from known concentration.

(analytic) concentration: c_0

acidity constant: K_a

Assumptions:

● $c_{\text{OH}^-} \ll c_{\text{H}^+}$

● $\gamma_i = 1$ (approximation of infinite dilution)

	compound	0	eq.
Balance:	HA	c_0	$c_0 - x$
	A^-	0	x
	H^+	0	x

Equation:
$$\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{x^2}{c_0 - x} = K_a$$

Correctly $\frac{x^2}{(c_0 - x)c^{\text{st}}} = K_a$. We will neglect c^{st} (concentrations should be inserted in mol dm^{-3}).

Equation:
$$\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{x^2}{c_0 - x} = K_a$$

Solution:

$$c_{\text{H}^+} = x = \sqrt{\left(\frac{K_a}{2}\right)^2 + K_a c_0} - \frac{K_a}{2} \stackrel{c_0 \gg K_a}{\approx} \sqrt{K_a c_0}$$

Summary of approximations:

- the acid is stronger than water ($K_a \gg K_w$)
- concentration c_0 is high enough ($c_0 \gg K_a$), then most of the acid is not ionized
- c_0 is not too high so that we can use the infinite dilution approximations ($\gamma_i = 1$)

Alternate form:

$$\text{pH} = \frac{1}{2} (\text{p}K_a + \text{p}c_A)$$

Degree of dissociation:

$$\alpha \approx \sqrt{\frac{K_a}{c_0}}$$



How much of deprotonated form can we find in a solution of given pH?

compound	0	eq.
HA	c_0	$c_0 - x$
A^-	0	x
H^+	c_{H^+}	c_{H^+}

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

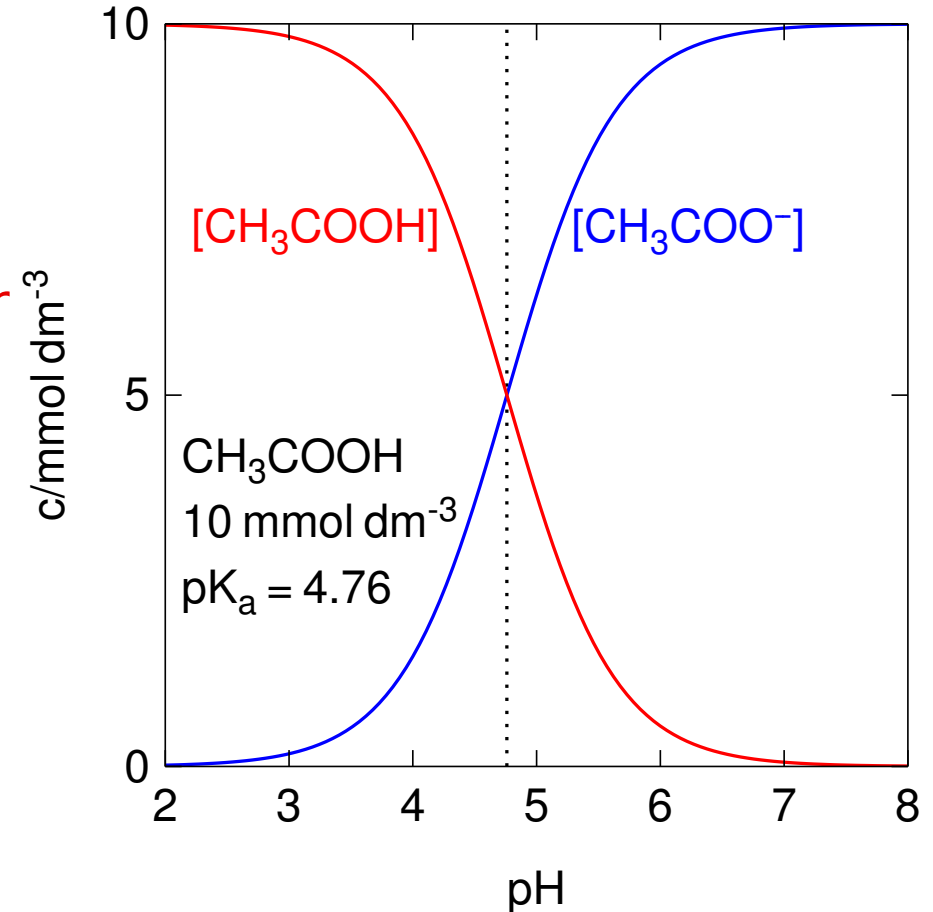
← maintained by buffer

$$x = c_{\text{A}^-} = \frac{c_0 K_a}{c_{\text{H}^+} + K_a}$$

Degree of dissociation:

$$\alpha = \frac{1}{c_{\text{H}^+}/K_a + 1}$$

● We have assumed the infinite dilution approximations



$$\alpha = \frac{1}{2} \text{ for } \text{pH} = \text{p}K_a$$

Calculate pH of rainwater at 25 °C and 1 bar.

9/28
col04

● Henry constant of dissolution of CO₂: $K_h = 0.033 \text{ mol dm}^{-3} \text{ bar}^{-1}$

● Acidity constant of CO₂: $pK_{a1} = 6.37$. This is total for reactions



● CO₂ in the air (2019/2 Mauna Loa): $y = 411 \text{ ppm}$ (18th century: $y = 280 \text{ ppm}$)

● CO₃²⁻ can be neglected ($pK_{a2} = 10.32$)

● OH⁻ can be neglected

$$\begin{aligned} c_{\text{CO}_2} &= K_h y_{\text{CO}_2} p = 0.033 \text{ mol dm}^{-3} \text{ bar}^{-1} \times 0.000411 \times 1 \text{ bar} \\ &= 1.36 \times 10^{-5} \text{ mol dm}^{-3} \end{aligned}$$

Balance: $c_{\text{H}^+} = c_{\text{HCO}_3^-}$ (**Not** $c_{\text{CO}_2} \stackrel{?}{=} c_{\text{CO}_{2.0}} - c_{\text{H}^+}$ because CO₂ is given by equilibrium, not initial concentration.)

Equation:

$$\frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} = K_{a1} \quad \swarrow \frac{-\log 1.36 \times 10^{-5}}$$

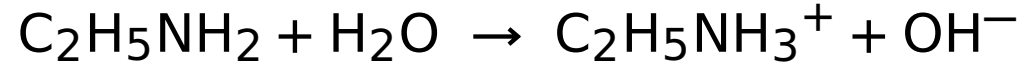
$$[\text{H}^+] = \sqrt{K_{a1}[\text{CO}_2]}, \quad \text{pH} = \frac{1}{2}(pK_{a1} + p[\text{CO}_2]) = \frac{1}{2}(6.37 + 4.87) = 5.62$$

the real pH is usually lower (HNO₃, H₂SO₄)

(18th cent.: pH = 5.70)

pH of a weak base

Example. Calculate pH of aqueous solution of ethylamine of concentration $c_0 = 0.01 \text{ mol dm}^{-3}$ at 25°C . The acidity constant of ethylammonium is $K_a = 1.6 \times 10^{-11}$.



Dissociation constant of ethylamine: $K_d = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{1.6 \times 10^{-11}} = 0.000625$

Assumptions: $[\text{H}^+] \ll [\text{OH}^-]$, $\gamma = 1$. And in the same way as for weak acids:

	compound	0	eq.
Balance:	$\text{C}_2\text{H}_5\text{NH}_2$	c_0	$c_0 - x$
	$\text{C}_2\text{H}_5\text{NH}_3^+$	0	x
	OH^-	0	x

Equil.: $\frac{[\text{C}_2\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_2\text{H}_5\text{NH}_2]} = \frac{x^2}{c_0 - x} = K_d$

$$x = [\text{OH}^-] = \sqrt{\left(\frac{K_d}{2}\right)^2 + K_d c_0} - \frac{K_d}{2} \stackrel{c_0 \gg K_d}{\approx} \sqrt{K_d c_0}$$

or:

$$\text{pH} = \frac{1}{2}(\text{p}K_a + \text{p}K_w - \text{p}c_0)$$

Dissociation of water has to be taken into account.



“Explicit” balance

compound	0	eq.
HA	c_0	$c_0 - x$
A^-	0	x
H^+	0	$x + y$
OH^-	0	y

Equations

$$\frac{(x + y)x}{c_0 - x} = K_a$$

$$(x + y)y = K_w$$

● 2 equations, 2 unknowns: x, y

“Implicit” balance

compound	balance
A	$[\text{A}^-] + [\text{HA}] = c_0$
charge	$[\text{H}^+] - ([\text{A}^-] + [\text{OH}^-]) = 0$

Equations

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

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

● 4 equations, 4 unknowns:
 $[\text{H}^+], [\text{HA}], [\text{A}^-], [\text{OH}^-]$

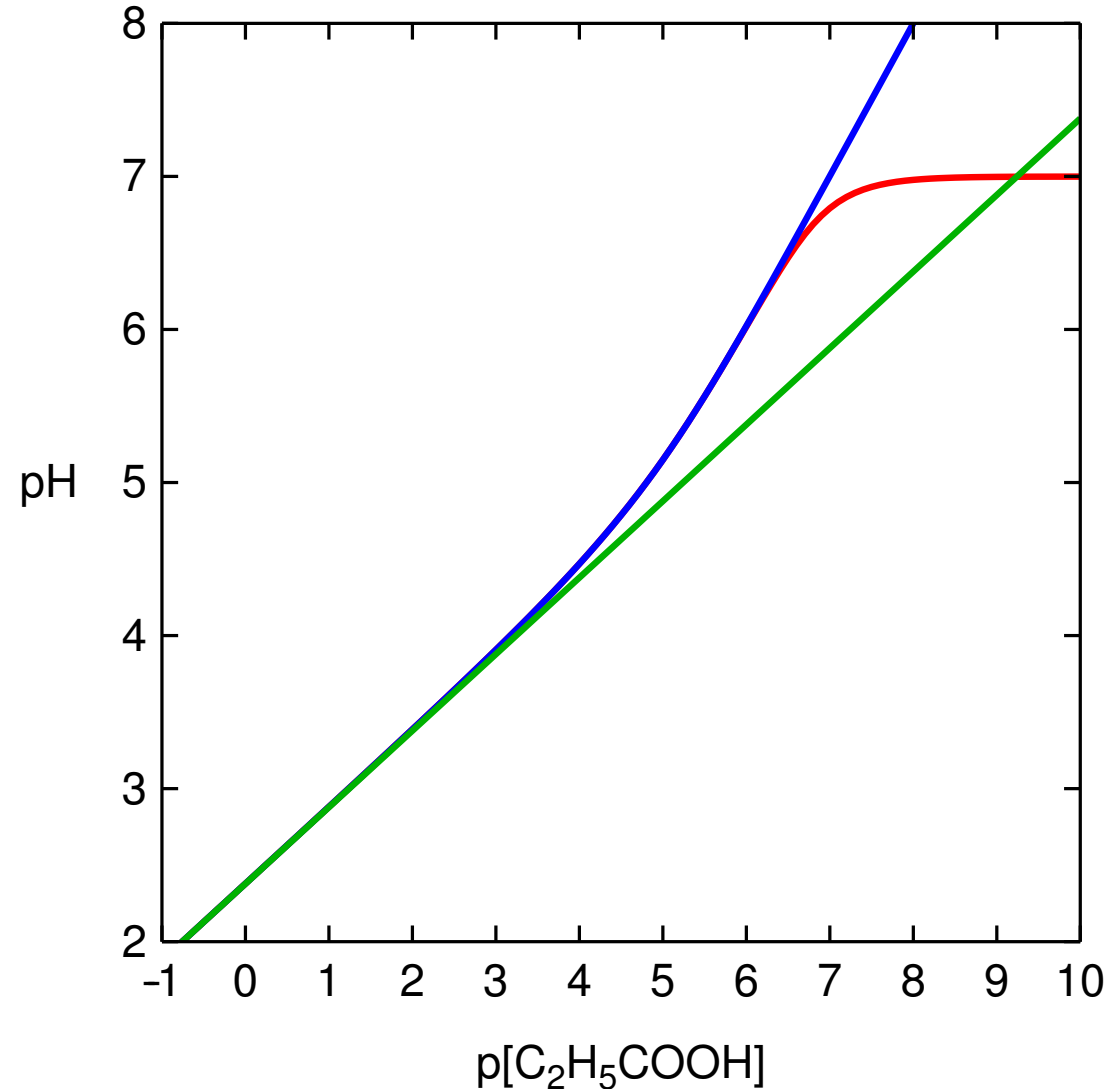
CH_3COOH , $\text{p}K_a = 4.76$

— “exact”

$$[H^+] = \sqrt{\left(\frac{K_a}{2}\right)^2 + K_a C_0} - \frac{K_a}{2}$$

— $[H^+] = \sqrt{K_a C_0}$
(approximate formula)

In a realistic region of concentrations the simplified formula is sufficient



Simultaneous equilibria: ion speciation

Aminoacids, ionization degree according to pH. E.g., HIS, LYS:



H^+ easily detaches from AH_3^{2+} , hardly from AH
 $\Rightarrow K_{a1} > K_{a2} > K_{a3}$ or $\text{p}K_{a1} < \text{p}K_{a2} < \text{p}K_{a3}$.

Balance:

$$[\text{A}^-] + [\text{AH}] + [\text{AH}_2^+] + [\text{AH}_3^{2+}] = c_0$$

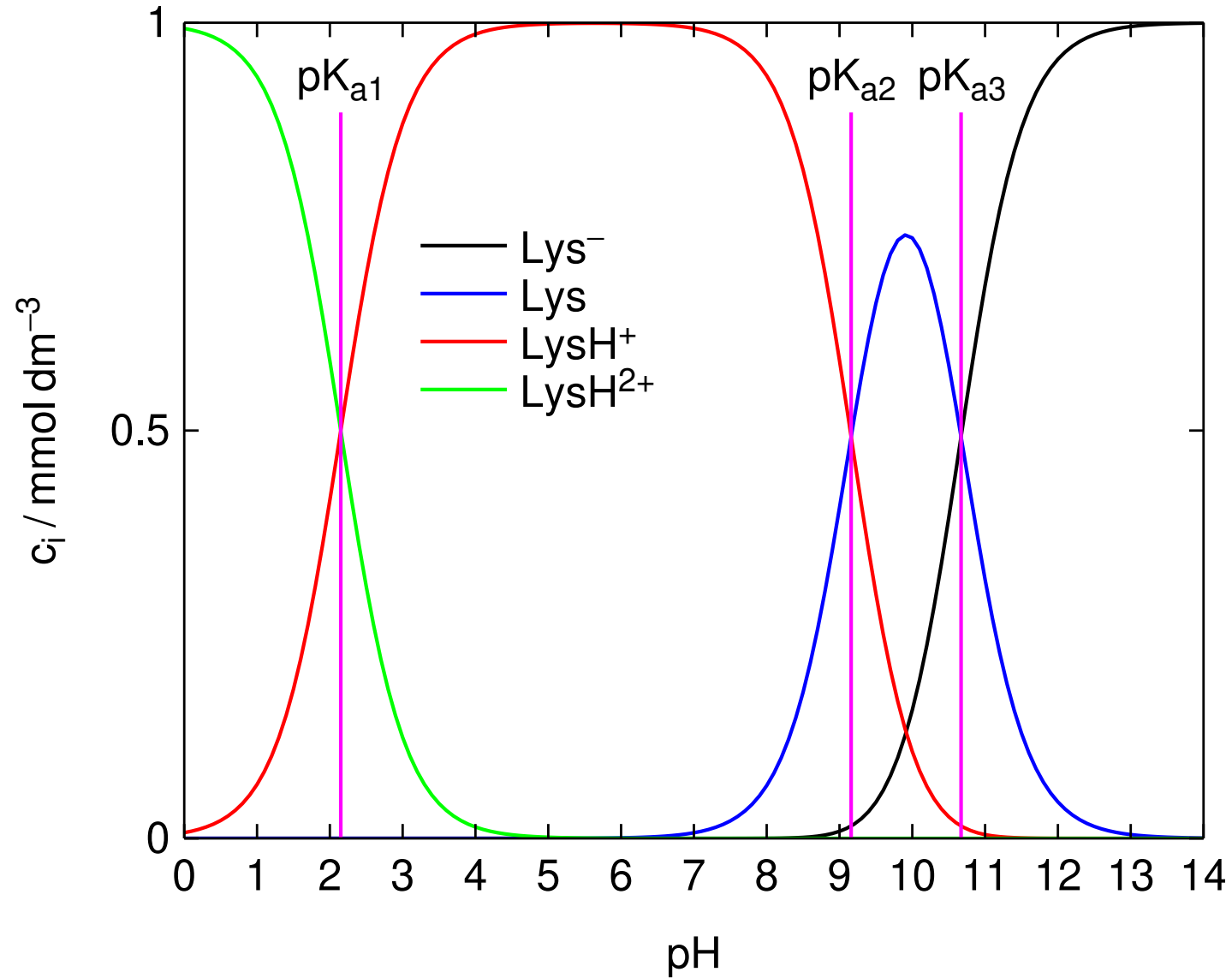
Equation:

$$\frac{[\text{AH}_2^+][\text{H}^+]}{[\text{AH}_3^{2+}]} = K_{a1}$$

$$\frac{[\text{AH}][\text{H}^+]}{[\text{AH}_2^+]} = K_{a2}$$

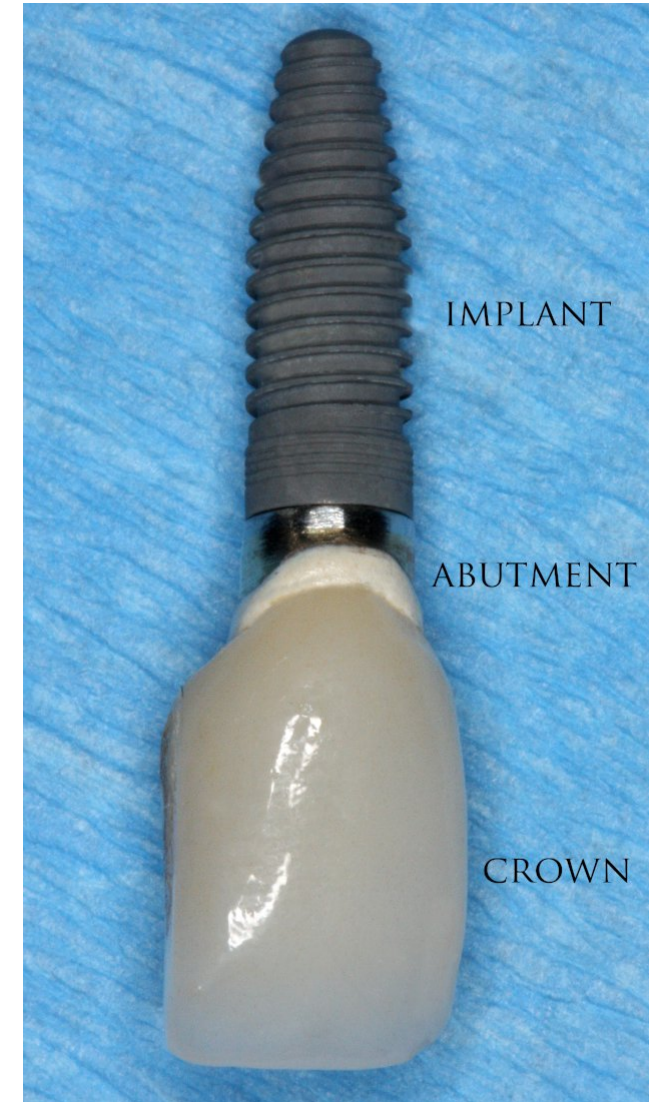
$$\frac{[\text{A}^-][\text{H}^+]}{[\text{AH}]} = K_{a3}$$

$\text{NH}_2\text{-(CH}_2\text{)}_4\text{-CH(NH}_2\text{)-COOH}$, $\text{pK}_{\text{a}1} = 2.15$, $\text{pK}_{\text{a}2} = 9.16$, $\text{pK}_{\text{a}3} = 10.67$



Titanium dental implants are treated (e.g.) in a phosphoric acid solution. Calculate the needed concentration (in pure water) for $\text{pH} = 3.42$. Data: $\text{p}K_{a1} = 2.18$, $\text{p}K_{a2} = 7.198$, $\text{p}K_{a3} = 12.319$.

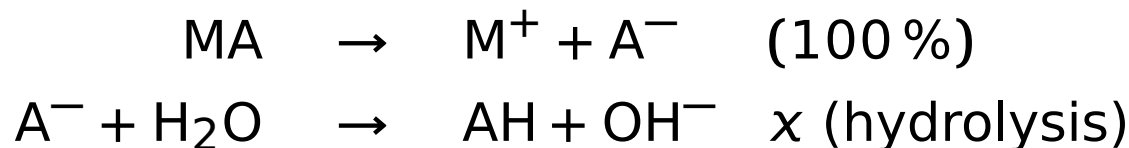
0.40 mmol/L ($\text{H}_3\text{PO}_4 + \text{H}_2\text{PO}_4^-$)
0.38 mmol/L (H_3PO_4 neglected)



credit: Wikipedia

Salt of weak acid + strong base

E.g., M=Na, A=CH₃COO.



compound	0	eq.	conditions
M ⁺	c ₀	c ₀	
A ⁻	c ₀	c ₀ - x	
OH ⁻	0	x	
HA	0	x	
H ⁺	0	K _w /x	for [OH ⁻] ≫ [H ⁺]

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \approx \frac{\frac{K_w}{x}(c_0 - x)}{x}$$

Solution:

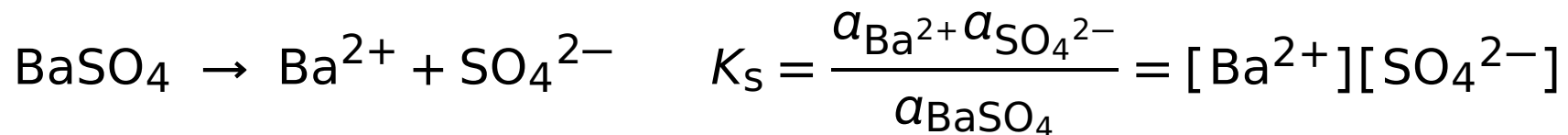
$$x = \sqrt{\frac{c_0 K_w}{K_a} + \left(\frac{K_w}{2K_a}\right)^2} - \frac{K_w}{2K_a} \approx \sqrt{\frac{c_0 K_w}{K_a}} \Rightarrow \text{pH} \approx \frac{1}{2}(\text{p}K_w + \text{p}K_a - \text{p}c_0)$$

where the last approximation holds for $c_0 \gg \frac{K_w}{K_a}$ & $x \gg \sqrt{K_w}$, i.e., $c_0 \gg K_a$

Solubility product = equilibrium constant of dissociation.

● activities of salts (s) are $a_{\text{salt}} = 1$

● $\gamma_i = 1$ assumed for ions



Example. How much Mg(OH)_2 (in mg) dissolves in 1 L of pure water?

Data: $K_s = 2.6 \times 10^{-11}$, $M(\text{Mg(OH)}_2) = 58.3 \text{ g mol}^{-1}$

Balance: $[\text{OH}^-] = 2[\text{Mg}^{2+}] = 2c$

Equation: $K_s = [\text{Mg}^{2+}][\text{OH}^-]^2 = c(2c)^2 = 4c^3$

Solution: $c = [\text{Mg(OH)}_2] = (K_s/4)^{1/3} = 0.0001866 \text{ mol dm}^{-3}$,

$$c_w = cM_{\text{Mg(OH)}_2} = 11 \text{ mg dm}^{-3}$$

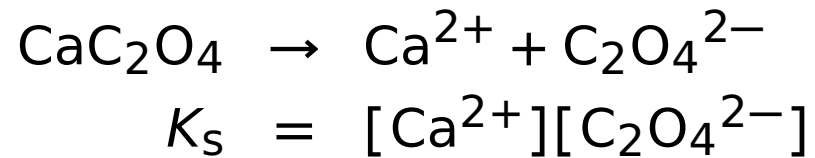
Often problems with hydrolysis, complexation, ...

Calcium oxalate: $K_s(\text{CaC}_2\text{O}_4) = 3.9 \times 10^{-9}$.

a) how much dissolves in pure water?

b) how much dissolves in blood?

$$([\text{Ca}^{2+}] = 2.4 \text{ mmol dm}^{-3})$$



Solution:

$$\begin{aligned}\text{a) } [\text{C}_2\text{O}_4^{2-}] &= [\text{Ca}^{2+}] = \sqrt{K_s} \\ &\doteq 62 \mu\text{mol dm}^{-3}\end{aligned}$$

hydrolysis of $\text{C}_2\text{O}_4^{2-}$ unimportant (62.49 vs. 62.45 $\mu\text{mol dm}^{-3}$)

$$\text{b) } [\text{C}_2\text{O}_4^{2-}] = K_s/[\text{Ca}^{2+}] \doteq 1.6 \mu\text{mol dm}^{-3}$$

● Solubility decreases in a presence of one of the ions (CaCl_2 , $\text{Na}_2\text{C}_2\text{O}_4$)

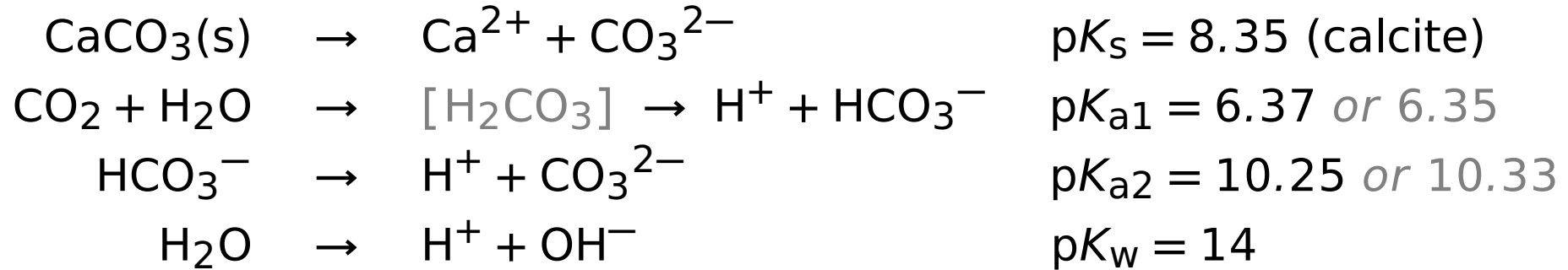
● But: upon adding $\text{H}_2\text{C}_2\text{O}_4$ the solubility slightly increases because $\text{C}_2\text{O}_4^{2-}$ is protonated at lower pH

● Other ions (e.g., NaCl) slightly increase solubility (more later . . .)



oxalis

Karsts, seawater, ...



Henry constant of CO_2 in water : $K_h = 0.033 \text{ mol dm}^{-3} \text{ bar}^{-1}$

Partial pressure of p_{CO_2} is known (atmosphere)

Balance

- CO_2 given by p_{CO_2}
 \Rightarrow no balance of H_xCO_3
- $\text{CaCO}_3(\text{s})$ is in surplus \Rightarrow no balance of Ca
- charge balance:

$$2[\text{Ca}^{2+}] + [\text{H}^+] - 2[\text{CO}_3^{2-}] - [\text{HCO}_3^-] - [\text{OH}^-] = 0$$



Case study: system $\text{CaCO}_3(\text{s},\text{aq}) + \text{CO}_2(\text{g},\text{aq})$

Equation:

$$[\text{CO}_2] = y_{\text{CO}_2} p K_h \quad (\text{given})$$

$$[\text{Ca}^{2+}][\text{CO}_3^{2-}] = K_s \quad (1)$$

$$\frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} = K_{a1} \quad (2)$$

$$\frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = K_{a2} \quad (3)$$

$$[\text{H}^+][\text{OH}^-] = K_w \quad (4)$$

+ charge balance:

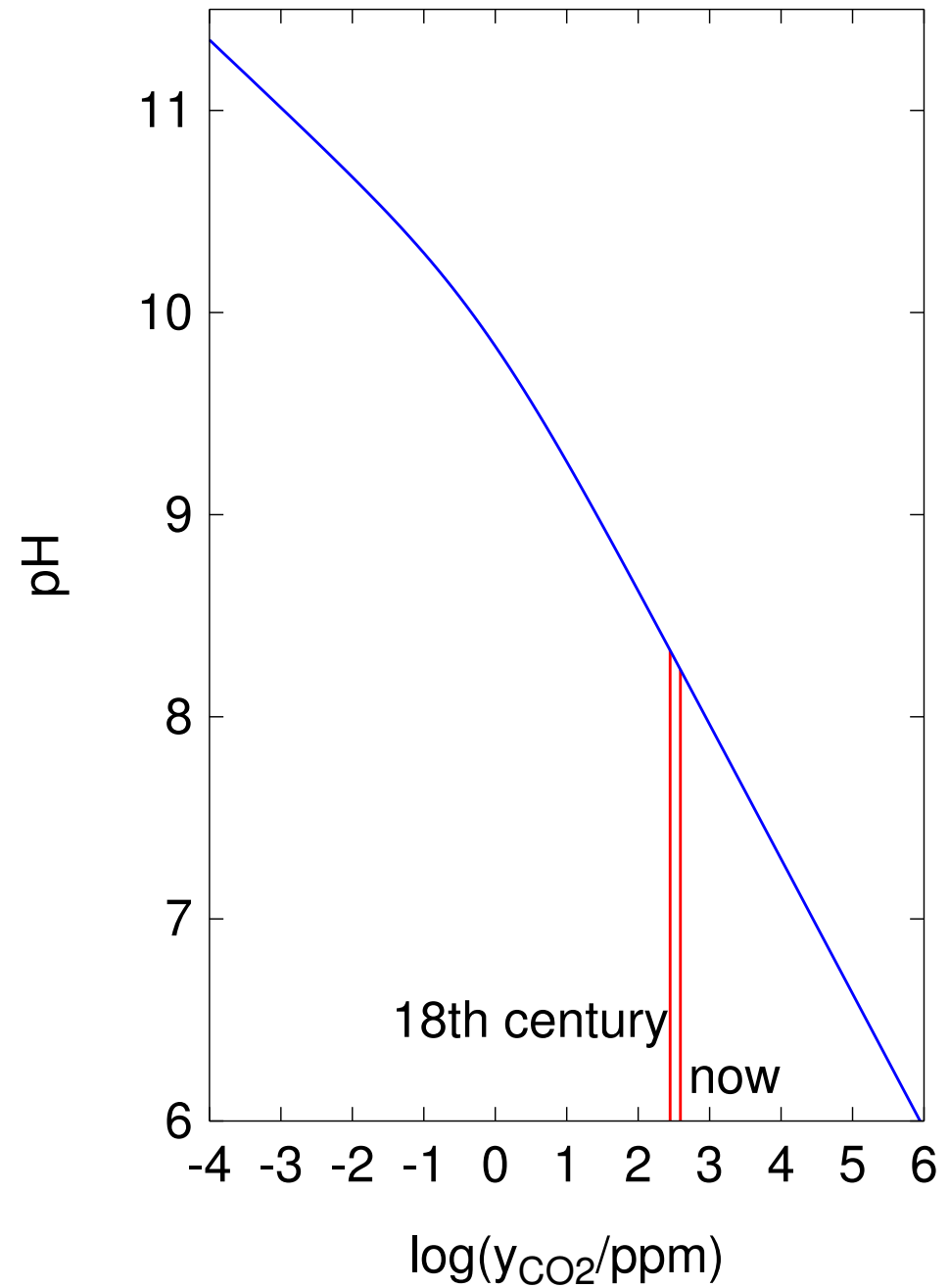
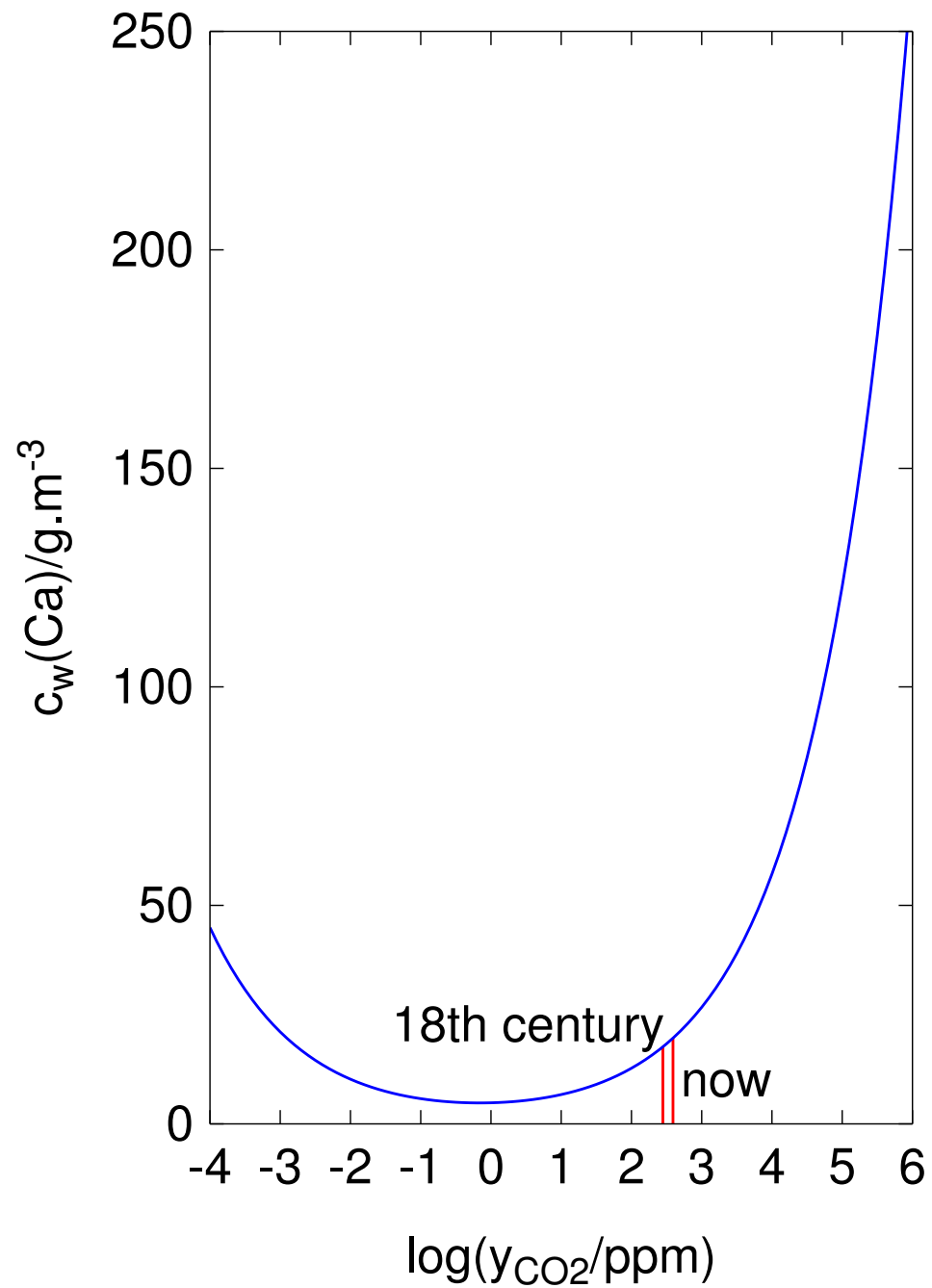
$$2[\text{Ca}^{2+}] + [\text{H}^+] - 2[\text{CO}_3^{2-}] - [\text{HCO}_3^-] - [\text{OH}^-] = 0 \quad (5)$$

⇒ 5 equations, 5 unknowns:

$[\text{Ca}^{2+}]$, $[\text{CO}_3^{2-}]$, $[\text{H}^+]$, $[\text{HCO}_3^-]$, $[\text{OH}^-]$.

- Solubility of limestone in rainwater
(recalculated to Ca^{2+})
19.7 mg dm^{-3} 2015 (400 ppm CO_2), pH=8.23
17.6 mg dm^{-3} before industrial revolution (280 ppm CO_2), pH=8.33
- For comparison:
4.8 mg dm^{-3} in pure water (no CO_2 , pH=9.9)
2.7 mg dm^{-3} hydrolysis neglected ($c^{\text{st}}\sqrt{K_s}$, pH=7)
- Contents of Ca^{2+} and pH (more ions present...):
Blood: 100 mg dm^{-3} , pH = 7.35–7.45
Sea: 400 mg dm^{-3} , pH = 7.5–8.4

Case study: system $\text{CaCO}_3(\text{s, aq}) + \text{CO}_2(\text{g, aq})$

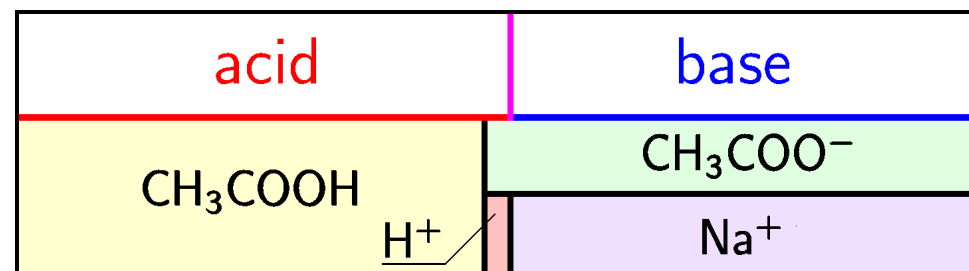


Buffer = solution able to keep pH (almost) constant if acid or base is added.

Typical example: solution of a weak acid HA ($[HA] = c_{\text{acid}}$) + its salt MA (of strong base, $[MA] = [M^+] = c_{\text{base}}$), e.g., CH_3COOH + CH_3COONa

acid
base

compound	0	eq.
M^+	c_{base}	c_{base}
A^-	c_{base}	$c_{\text{base}} + x$
H^+	0	x
HA	c_{acid}	$c_{\text{acid}} - x$



$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{x(c_{\text{base}} + x)}{c_{\text{acid}} - x}$$

Approximate solution:

$$x = K_a \frac{c_{\text{acid}} - x}{c_{\text{base}} + x} \approx K_a \frac{c_{\text{acid}}}{c_{\text{base}}}$$

$$[H^+] = K_a \frac{c_{\text{acid}}}{c_{\text{base}}}$$

$$\text{pH} = \text{p}K_a + \log_{10} \frac{c_{\text{base}}}{c_{\text{acid}}}$$

$$[H^+] = K_a \frac{c_{\text{acid}}}{c_{\text{base}}} \quad \text{pH} = \text{p}K_a + \log_{10} \frac{c_{\text{base}}}{c_{\text{acid}}}$$

Assumptions and generalization:

- $[OH^-], [H^+] \ll c_{\text{acid}}, c_{\text{base}}; c_{\text{acid}} \overset{\text{roughly}}{\approx} c_{\text{base}}, c_{\text{acid}}, c_{\text{base}} \gg K_a; \gamma_i = 1$
- Holds true also for a mixture of a weak base B ($B + H_2O \rightarrow BH^+ + OH^-$) and its salt BHX (of strong acid), $c_{\text{acid}} = [BHX] = [X^-], c_{\text{base}} = [B]$
- Maximum buffer capacity for $c_{\text{acid}} = c_{\text{base}}$ (see below)

Buffer capacity

Let us add a small amount dc of a strong base MOH \Rightarrow dc of HA is neutralized to MA (=“base”).

Add strong acid = remove strong base

$$\begin{aligned}c_{\text{acid}} &\rightarrow c_{\text{acid}} - dc \\c_{\text{base}} &\rightarrow c_{\text{base}} + dc\end{aligned}$$

$$\text{Buffer capacity} = \beta = \frac{dc}{d(\text{pH})} = -\ln 10 [\text{H}^+] \frac{dc}{d[\text{H}^+]}$$

the amount of a strong base needed to increase pH by 1

The same assumptions as Henderson–Hasselbalch:

$$[\text{H}^+](c) = K_a \frac{c_{\text{acid}}}{c_{\text{base}}}$$

$$[\text{H}^+](c + dc) = K_a \frac{c_{\text{acid}} - dc}{c_{\text{base}} + dc} = K_a \frac{c_{\text{acid}}}{c_{\text{base}}} \left[1 - dc \left(\frac{1}{c_{\text{acid}}} + \frac{1}{c_{\text{base}}} \right) \right]$$

$$\frac{d[\text{H}^+]}{dc} = -K_a \frac{c_{\text{acid}}}{c_{\text{base}}} \left(\frac{1}{c_{\text{acid}}} + \frac{1}{c_{\text{base}}} \right) = -\frac{c_{\text{acid}} + c_{\text{base}}}{c_{\text{acid}}c_{\text{base}}} [\text{H}^+]$$

$$\beta = \ln 10 \frac{c_{\text{acid}}c_{\text{base}}}{c_{\text{acid}} + c_{\text{base}}}$$

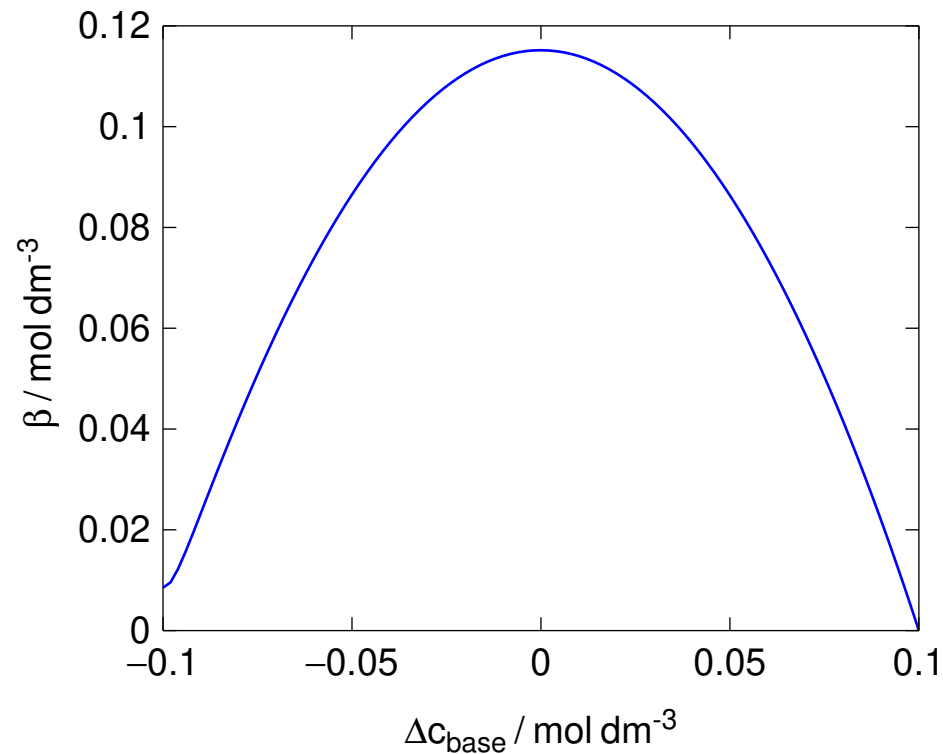
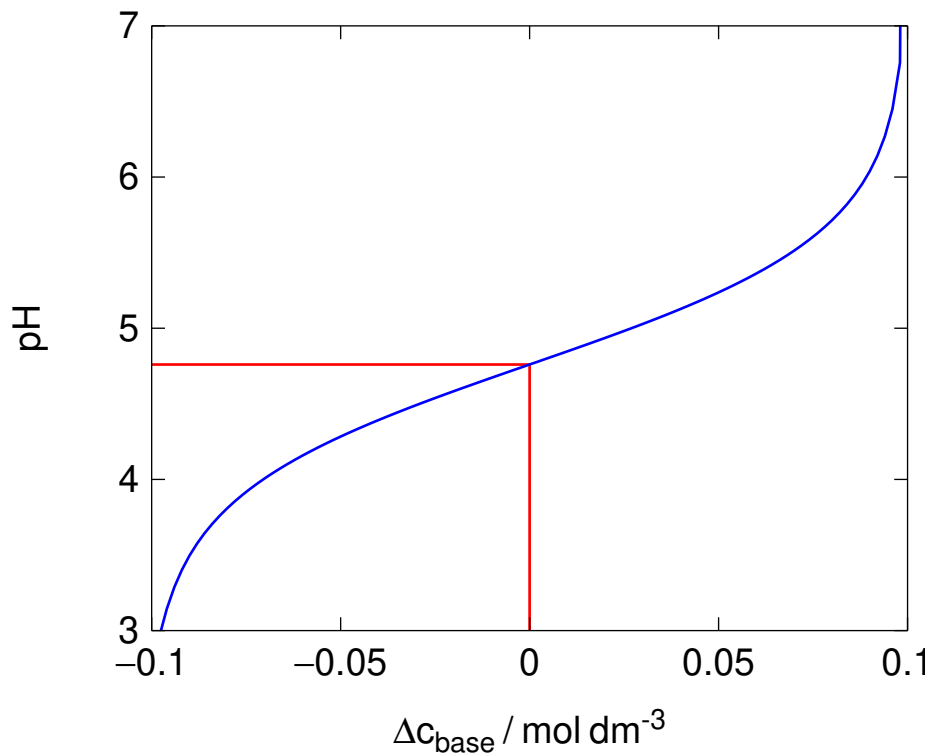
$$\ln 10 \doteq 2.3026$$

$$\beta = \ln 10 \frac{c_{\text{acid}}c_{\text{base}}}{c_{\text{acid}} + c_{\text{base}}}$$

Given A ($c_{A,\text{total}} = c_{\text{acid}} + c_{\text{base}}$), β reaches maximum at $c_{\text{acid}} = c_{\text{base}}$

Maximum buffer capacity is reached for an equimolar mixture

Example: acetate buffer, $c_{\text{acid}} = c_{\text{base}} = 0.1 \text{ mol dm}^{-3}$, $\text{pH} = \text{p}K_{\text{a}} = 4.76$



graphs: exact solution with $\gamma = 1$

Main part of the blood buffer system

● Henry constant of CO₂ in water at body temperature:
 $K_h = 0.025 \text{ mol dm}^{-3} \text{ bar}^{-1}$

● Acidity constant of CO₂ at body temperature: $pK_{a1} = 6.1$ for



● Contents of hydrogen carbonates (mostly NaHCO₃):
 $[\text{HCO}_3^-] = 24 \text{ mmol dm}^{-3} = c_{\text{base}}$

● pH = 7.35 to 7.45

$$[\text{H}^+] = K_{a1} \frac{c_{\text{acid}}}{c_{\text{base}}}$$

$$c_{\text{acid}} = \frac{[\text{H}^+]c_{\text{base}}}{K_{a1}}, \quad p_{\text{CO}_2} = \frac{c_{\text{acid}}}{K_h} = \frac{[\text{H}^+]c_{\text{base}}}{K_{a1}K_h}$$

⇒ $p_{\text{CO}_2} = 5.4$ to 4.3 kPa (~ 5 vol.% in alveolar air)

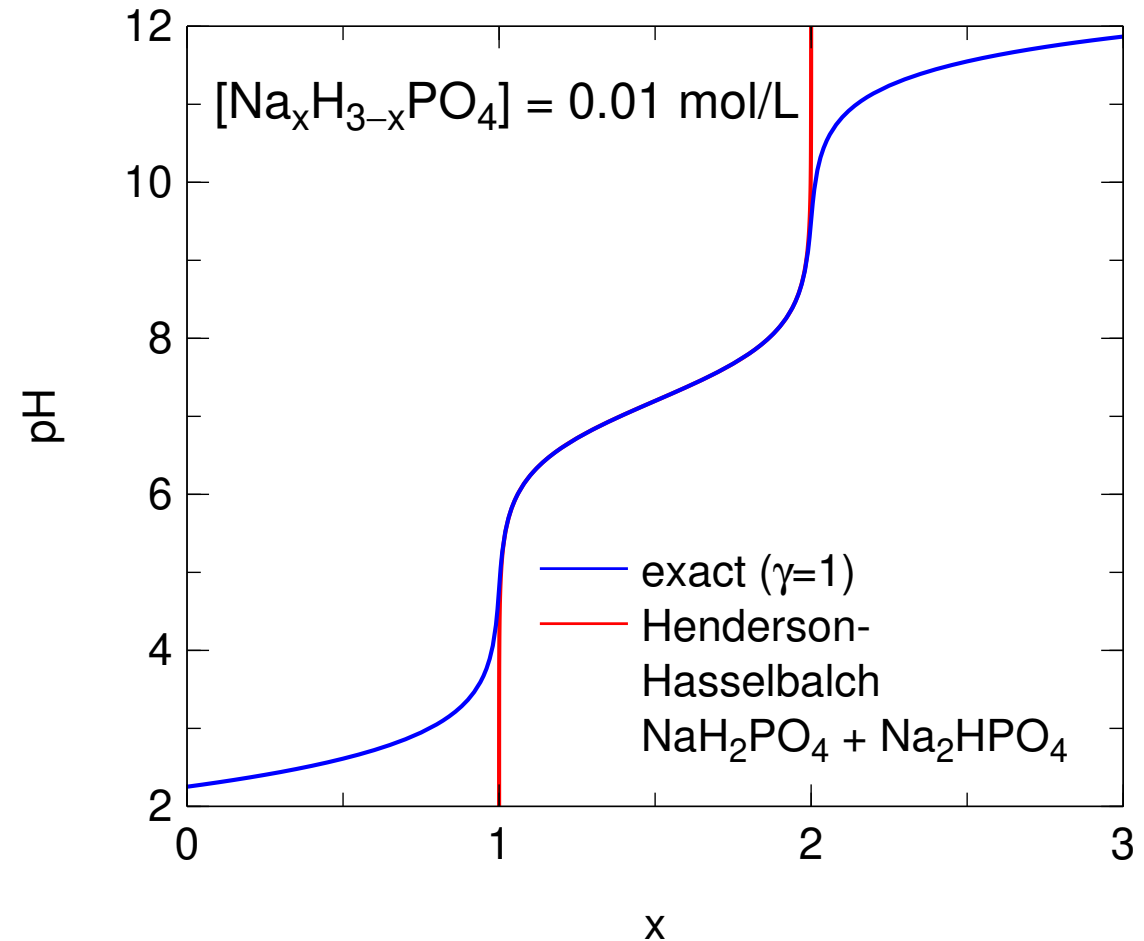
Outside range ⇒ respiratory acidosis/alkalosis

H_3PO_4 :

$$pK_{a1} = 2.148$$

$$pK_{a2} = 7.198$$

$$pK_{a3} = 12.319$$



isotonic, $\text{pH}=7.4$: NaCl , KCl , Na_2HPO_4 (base), KH_2PO_4 (acid)

(Phosphate buffered saline)

NB: The deviation caused by nonideality is not negligible in concentrated solutions.

The experimental pH is by about 0.5 less than calculated. E.g., the maximum capacity is for $\text{pH} = 6.8$, not 7.2.