

Getting to the Henderson-Hasselbalch equation

H-H gives a way to go back and forth between pH & pKa showing you how a buffer can decide where the pH will stay!

acid water



conjugate

base

hydronium ion



Take water
as constant



we often simplify to (H^+)

[] means

"concentration of"

p tells you to take
negative $\log_{10}$
aka $\log_{10}(1/\text{thing})$

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

K_a = equilibrium constant
(ionization constant aka acid
dissociation constant)

$$\text{p}K_a = -\log_{10}(K_a)$$

The more acidic the solution,
the higher the $[\text{H}^+]$ and thus
the lower the pH

$$\text{pH} = \text{p}K_a + \log_{10}\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

The stronger the acid,
the bigger the K_a and
thus the smaller the $\text{p}K_a$

Using the Henderson-Hasselbalch equation

p: take negative $\log_{10}$ of thing (aka $\log_{10}(1/\text{thing})$)

H: hydronium ion (H_3O^+)/
proton (H^+) concentration

K_a: acid dissociation constant

$$\text{pH} = \text{pK}_a + \log_{10} \left(\frac{[\text{A}^-]}{[\text{HA}]} \right)$$

conjugate base: A^-
deprotonated form
conjugate acid: HA
protonated form

★ Molar Ratio A^- is easiest
to find directly from HH

⚠ Don't confuse Molar *Ratio* and Molar *Fraction*!

Molar Ratio (MR) A^- :
parts A^- per 1 part HA $\left(\frac{[\text{A}^-]}{[\text{HA}]} \right)$

Molar Fraction (MF) A^- :
parts A^- per total parts ($\text{A}^- + \text{HA}$) $\left(\frac{[\text{A}^-]}{[\text{A}^-] + [\text{HA}]} \right)$

By rearranging H-H:

$$\left(\frac{[\text{A}^-]}{[\text{HA}]} \right) = 10^{(\text{pH} - \text{pK}_a)}$$

$$\text{Molar Ratio (MR) } \text{A}^- = 10^{(\text{pH} - \text{pK}_a)}$$

$$\text{fraction } \text{A}^- = \frac{\text{MR}}{1 + \text{MR}}$$

aka

$$\text{fraction } \text{A}^- = \frac{10^{(\text{pH} - \text{pK}_a)}}{1 + 10^{(\text{pH} - \text{pK}_a)}}$$

To convert to a **percentage A^-** : molar fraction $\text{A}^- \times 100 \%$

To convert to a **concentration A^-** : molar fraction $\text{A}^- \times \text{total concentration } ([\text{HA}] + [\text{A}^-])$ (any units)

- My typical strategy**
- 1) Find molar ratio A^- (since it's easiest to find directly from H-H)
 - 2) Use that value to find fraction A^- or HA
 - 3) Convert to %, concentration, etc. as needed



Don't confuse Molar *Ratio* and Molar *Fraction*!

Molar Ratio (MR) A⁻:
parts A⁻ **per 1 part HA** $\left(\frac{[A^-]}{[HA]} \right)$

Molar Fraction (MF) A⁻:
parts A⁻ per total parts (A⁻ + HA) $\left(\frac{[A^-]}{[A^-] + [HA]} \right)$



By rearranging H-H:

Molar Ratio A⁻ is
easiest to find
directly from H-H

$$\left(\frac{[A^-]}{[HA]} \right) = 10^{(pH - pK_a)}$$

aka

$$MR A^- = 10^{(pH - pK_a)}$$

fraction A⁻ = $\frac{10^{(pH - pK_a)}}{1 + 10^{(pH - pK_a)}}$

aka

$$\text{fraction } A^- = \frac{MR A^-}{1 + MR A^-}$$

To convert to a **percentage A⁻**: molar fraction A⁻ x 100 %

To convert to a **concentration A⁻**: molar fraction A⁻ x total concentration ([HA] + [A⁻]) (any units)

For example ...

If you have 2 molecules of conjugate base (A⁻) per 2 molecules of conjugate acid (HA), the molar ratio is 2/2. This can be simplified to 1/1 (1 molecule A⁻ per 1 molecule HA) = 1. (But remember, it's really 1/1!)

But, only 2/(2+2) = 2/4 = 1/2 of the molecules are the conjugate base!

So, in this case, Molar Ratio (MR) A⁻ = 1 and Molar Fraction (MF) A⁻ = 1/(1+1) = 1/2 = 0.5

The +1 on the bottom is because the MR tells us the number of one per 1 of the other

We could convert this to a percentage by multiplying by 100%: 1/2 x 100% = 50%

And if we knew the total concentration of acid + base we could multiply it by 0.5 to get the concentration of A⁻. For example, if the total concentration was 500 mM, the concentration of A⁻ would be 500 mM x 0.5 = 250 mM.

H-H in terms of the conjugate base (A^-) (deprotonated form)

My typical strategy

- 1) Find molar ratio A^- (since it's easiest to find directly from H-H)
- 2) Use that value to find fraction A^- or HA
- 3) Convert to %, concentration, etc. as needed



Molar Ratio A^- is easiest to find directly from H-H

Molar Ratio

Parts of one **per 1**
part of the other

Molar Ratio (MR) A^- :
parts A^- **per 1 part HA** $\left(\frac{[A^-]}{[HA]} \right)$ $MR A^- = 10^{(pH - pK_a)}$

Molar Fraction

Parts of one per
total parts

Molar Fraction (MF) A^- :
parts A^- per total parts
($A^- + HA$) $\left(\frac{[A^-]}{[A^-] + [HA]} \right)$ fraction $A^- = \frac{10^{(pH - pK_a)}}{1 + 10^{(pH - pK_a)}}$

aka

$$\text{fraction } A^- = \frac{MR}{1 + MR}$$

or $\frac{1}{\text{fraction HA}}$

Concentration

concentration $A^- = \text{fraction } A^- \times \text{total concentration } ([HA] + [A^-])$

or: concentration $A^- = \text{total concentration} - [HA]$

Percentage

To convert to a percentage A^- : molar fraction $A^- \times 100 \%$

H-H in terms of the conjugate acid (HA) (protonated form)

My typical strategy

- 1) Find molar ratio A^- (since it's easiest to find directly from H-H)
- 2) Use that value to find fraction A^- or HA
- 3) Convert to %, concentration, etc. as needed

Molar Ratio

Parts of one **per 1**
part of the other

Molar Ratio (MR) HA: $\left(\frac{[HA]}{[A^-]} \right)$
parts HA **per 1 part** A^-

$$MR_{HA} = \frac{1}{10^{(pH - pK_a)}}$$

Molar Fraction

Parts of one per
total parts

Molar Fraction (MF) HA: $\left(\frac{[HA]}{[A^-] + [HA]} \right)$
parts HA per total parts
($A^- + HA$)

$$\text{fraction HA} = \frac{1}{1 + 10^{(pH - pK_a)}}$$

aka

$$\text{fraction HA} = \frac{1}{1 + MR}$$

$$\text{or } \frac{1}{\text{fraction } A^-}$$

Concentration

concentration HA = fraction HA x total concentration ($[HA] + [A^-]$)

or: concentration HA = total concentration - $[A^-]$

Percentage

To convert to a percentage HA: molar fraction HA x 100 %