Topic 8.9: Henderson-Hasselbalch Equation

Revision Notes · AP Chemistry

UNIT 8 · ACIDS AND BASES

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The Name for the Ratio Relation

Topics 8.4, 8.7 and 8.8 all worked with one relation between pH, pKa and the ratio of the two members: the Henderson-Hasselbalch equation.

$pH = pKa + \log([A^-] \div [HA])$

It is the Ka expression in disguise. For

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

$Ka = [H_3O^+][A^-] \div [HA]$

Taking the negative logarithm of both sides separates the terms into pKa, pH and the log of the ratio. The same step run backwards gives $[H_3O^+] = Ka \times [HA] \div [A^-]$.

What the symbols demand. $[A^-]$ and $[HA]$ are the members' equilibrium concentrations, base form over acid form, and the pKa is the acid member's.

Reading the Ratio

Ratio 1: pH = pKa. log(1) = 0, so equal members put the pH exactly on pKa. An equal-member pH that is not pKa means something upstream is wrong.

Each factor of ten is one unit. Ratio 10 puts pH one unit above pKa; ratio 0.10, one unit below; ratio 100, two units above. Doubling the base member, or halving the acid member, multiplies the ratio by 2 and adds log(2) = 0.30; halving the ratio subtracts 0.30.

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Percent in each form. The base form's share of the pair is ratio ÷ (1 + ratio): 50% at pH = pKa, 91% one unit above, 99% two units above. Mirrored below: 91% acid form one unit down, 99.9% three units down.

Worked Examples

Example 1: A direct substitution, checked exactly. A buffer holds 0.20 mol L^{-1} CH_3COOH and 0.10 mol L^{-1} CH_3COO^-, pKa = 4.74. pH = 4.74 + log(0.10 ÷ 0.20) = 4.74 − 0.30 = 4.44. The exact solve returns $[H_3O^+]$ = 3.6 × 10^{-5} mol L^{-1} and pH 4.44, because the shift is a tiny fraction of the smaller stock.

Example 2: The base pair, by both routes. A buffer holds 0.10 mol L^{-1} NH_3 and 0.050 mol L^{-1} NH_4^+, pKb of NH_3 = 4.74. By the base form: pOH = 4.74 + log(0.050 ÷ 0.10) = 4.44, so pH = 14.00 − 4.44 = 9.56. By the acid form, pKa of NH_4^+ = 9.26: pH = 9.26 + log(0.10 ÷ 0.050) = 9.56. The exact solve agrees.

Example 3: Reading percent and concentration off a pH. A buffer pair has pKa = 7.20 and reads pH 7.50. The ratio is $10^{(7.50-7.20)}$ = $10^{0.30}$ = 2.0, so the base form outnumbers the acid form two to one. With [HA] = 0.10 mol L^{-1}, $[A^-]$ = 0.20 mol L^{-1}, and the base form is 2 ÷ 3 = 67% of the pair.

Example 4: An ammonia buffer under acid attack, by both routes. One litre holds 0.20 mol of NH_3 and 0.20 mol of NH_4^+, so pH = pKa = 9.26. Add 0.040 mol of HCl, converting NH_3 into NH_4^+ and leaving 0.16 mol of NH_3 and 0.24 mol of NH_4^+. By the acid form, pH = 9.26 + log(0.16 ÷ 0.24) = 9.26 − 0.18 = 9.08. By the base form, pOH = 4.74 + log(0.24 ÷ 0.16) = 4.92, so pH = 14.00 − 4.92 = 9.08.

Running It Backwards: From Target pH to Recipe

Turned around, the equation designs buffers.

ratio = $10^{(pH-pKa)}$

Target pH 3.50 with HF / F^-, pKa = 3.17, needs ratio $10^{(3.50-3.17)}$ = $10^{0.33}$ = 2.14, so every 0.10 mol of HF stands beside 0.21 mol of F^-. Back-check: 3.17 + log(2.14) = 3.50.

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Amounts, not just the ratio. A ratio fixes proportions only: split a chosen total between the members, or convert the ratio into volumes of stock solutions.

The Base Form: pOH = pKb + log([BH^+] ÷ [B])

For a weak base B with its conjugate acid BH^+, the parallel equation is pOH = pKb + log([BH^+] ÷ [B]).

The conjugate acid stands on top. It feels backwards until the source is visible:

$K_b = [BH^+][OH^-] \div [B]$

Its negative logarithm puts BH^+ over B, the same way the Ka expression puts A^- over HA.

One pair, two constants. pKa of BH^+ + pKb of B = 14.00 at 25 °C, so either form follows from one given constant: pKb 4.74 for NH_3 and pKa 9.26 for NH_4^+ are one fact read two ways.

After an Addition: Recount First, Substitute Second

The equation reads the members as they stand after an addition, so finish the stoichiometry first. One litre holds 0.25 mol of HF and 0.25 mol of F^-, at pH = pKa = 3.17. Add 0.050 mol of HCl. Its H_3O^+ converts F^- into HF:

$F^- + H_3O^+ \rightarrow HF + H_2O$

leaving 0.30 mol of HF and 0.20 mol of F^-. Only now substitute: pH = 3.17 + log(0.20 ÷ 0.30) = 2.99. The exact solve returns 3.00; the 0.01 gap is the shift the equation sets aside.

Where the Equation Stops Working

Fed with equilibrium concentrations, the equation is exact. The approximation enters when stocks stand in for equilibrium concentrations: the assumption is that ionization moves too little of each member to change them.

Very dilute buffers. At 1.0×10^{-4} mol L^{-1} of each acetate member, the equation reads ratio 1 and reports pH = pKa = 4.74. The exact solve returns 4.86: [H_3O^+] there reaches 1.4×10^{-5} mol L^{-1}, and water's own ions can no longer be ignored.

Extreme ratios. With 0.10 mol L^{-1} CH_3COOH and only 0.0010 mol L^{-1} CH_3COO^-, the equation reports 4.74 + log(0.010) = 2.74; the exact solve returns 3.03. The acid's own ionization adds about 9×10^{-4} mol L^{-1} of CH_3COO^-, nearly doubling the scarce member to 0.0019 mol L^{-1}.

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No pair, no equation. A lone weak acid, a lone conjugate base salt, and any strong acid mixture have no standing pair. The first two belong to Topic 8.3's ICE tables and Topic 8.5's equivalence points.

The trust test. Compare the smaller stock with the shift, roughly $[H_3O^+]$ or $[OH^-]$ itself. At a percent or less of that stock, the two agree; at a sizable fraction, solve exactly and report that value.

Polyprotic Pairs: The pKa of the Step in Hand

A diprotic acid offers two pairs, each answering to its own pKa: H_2A / HA^- to pKa1 through

$H_2A + H_2O \rightleftharpoons H_3O^+ + HA^-$

and HA^- / A^{2-} to pKa2. Equal members give pH = pKa of that step: with $[H_2A] = [HA^-]$, the pH is pKa1, and the second step's ratio $[A^{2-}] \div [HA^-]$ there is $10^{(pH-pKa2)}$, tiny when the pKa values are well separated.

Traps That Cost Marks in Topic 8.9

Inverting the ratio. It is base form over acid form. Feed 0.20 over 0.10 instead of 0.10 over 0.20 into Example 1 and out comes 5.04 in place of 4.44.

Feeding in Ka instead of pKa. The equation is built from logarithms; a Ka of 1.8×10^{-5} must arrive as pKa 4.74.

Forgetting the recount. After an addition, substitute the new stocks, never the original ones.

In the base form, putting B on top. BH^+ is the numerator; B there flips the log term's sign.

Reading pH = pKa + 2 as ratio 2. The 2 is a logarithm: the ratio is $10^2 = 100$, and the pair is 99% in base form.

Trusting it at any dilution. With stocks around 10^{-4} mol L^{-1} that number can sit tenths of a unit from the exact solve.

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Key Relationships to Remember

- pH = pKa + log([A^-] ÷ [HA]), the Ka expression rearranged; equivalently [H_3O^+] = Ka × [HA] ÷ [A^-]
- Ratio 1 gives pH = pKa; a factor of 10 in the ratio moves pH by 1 unit, a factor of 2 by 0.30
- Ratio required for a target pH: [A^-] ÷ [HA] = $10^{(pH-pKa)}$; fraction in base form = ratio ÷ (1 + ratio)
- Base form: pOH = pKb + log([BH^+] ÷ [B]); pKa of BH^+ + pKb of B = 14.00 at 25 °C
- After any addition of strong acid or base: recount both members in moles first, then substitute
- Stocks stand in for equilibrium concentrations; the equation is reliable only while the shift is negligible beside both stocks
- A diprotic pair uses the pKa of its own step: H_2A / HA^- answers to pKa1, HA^- / A^{2-} to pKa2

Continue Revising

Topic 8.9 Quiz: Henderson-Hasselbalch Equation

Topic 8.9 Worksheet

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