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Topic 8.10: Buffer Capacity

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UNIT 8 · ACIDS AND BASES

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Capacity Is a Count of Moles

The definition. Buffer capacity is the amount of strong acid or strong base a buffer can absorb before its pH changes significantly. In this topic the end is concrete: the point where one member of the pair is used up and the pH starts to swing.

Two questions, two different answers. The ratio of the members sets the pH. The amounts of the members set the capacity. Topics 8.4 to 8.9 lived on the ratio; this topic lives on the amounts.

Each direction has its own cap. Added H_3O^+ is consumed by the base member:

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

so the moles of A^- in the flask cap the acid the buffer can take. Added OH^- is consumed by the acid member:

$HA + OH^- \rightarrow A^- + H_2O$

so the moles of HA cap the base. Capacity is two numbers, not one.

More Material, More Capacity

Concentration scales it directly. Add the same 0.020 mol of NaOH to two acetate buffers, each 1.0 L at pH = pKa. The 0.50 ÷ 0.50 mol L^{-1} buffer rises by 0.03 pH units, to 4.78. The 0.050 ÷ 0.050 mol L^{-1} buffer rises by 0.37, to 5.11. Same ratio, same pH, same attack: ten times the material absorbs the attack with a tenth of the disturbance, roughly.

Volume scales it the same way. Capacity counts moles, and moles are concentration × volume. Two litres of a 0.10 ÷ 0.10 buffer hold 0.20 mol of each member, the stock of 1.0 L of a 0.20 ÷ 0.20

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buffer, and absorb as much attack. A concentration quoted without a volume says nothing about capacity.

Dilution splits the two properties. Dilute a buffer and the ratio survives, so the pH survives with it; the moles per litre do not. A tenfold dilution leaves the pH reading untouched and cuts the attack each litre can absorb to a tenth.

The Ratio Sets the Balance, Not the Size

Equal members balance the two caps. At pH = pKa the stocks are equal, so the caps are equal: the buffer is as strong against base as against acid. For a fixed total of material, the smaller of the two caps is also as large as it can be.

Move one unit and one direction thins out. Hold the total fixed at 0.22 mol in 1.0 L. Split 1:1, the caps are 0.11 mol each way. At ratio 10, which is pH = pKa + 1, the split is 0.20 mol of A^- against 0.020 mol of HA: a fat cap against acid and a thin one against base. At ratio 100, pH = pKa + 2, the HA stock is 0.0022 mol: the first 0.0022 mol of added base ends the buffer in that direction, while 0.218 mol of acid could still be absorbed the other way.

Direction before size. A buffer one unit above pKa is the better shield against acid and the worse one against base. Ask which attack is coming first.

Worked Examples

Example 1: One buffer, three sizes of attack. One litre holds 0.20 mol of CH_3COOH and 0.20 mol of CH_3COO^-, pKa = 4.74, starting at pH 4.74. Add 0.020 mol of HCl: the recount leaves 0.22 mol of CH_3COOH and 0.18 mol of CH_3COO^-, and pH = 4.74 + log(0.18 ÷ 0.22) = 4.66; the exact solve returns 4.66. The falls steepen: the pH does not drop a full unit until 0.164 mol of HCl has been added, and the acid cap itself is the whole A^- stock, 0.20 mol. At exactly 0.20 mol the pair is gone, the solution is 0.40 mol L^{-1} CH_3COOH alone, and the exact solve gives pH 2.57. One more 0.010 mol of HCl has nothing left to convert and stands as strong acid, taking the pH to 1.97.

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Example 2: An ammonia buffer, strong one way. One litre holds 0.30 mol of NH_3 and 0.10 mol of NH_4^+, with pKa of NH_4^+ = 9.26, so pH = 9.26 + log(0.30 ÷ 0.10) = 9.73. The caps are unequal: added HCl spends NH_3, of which there is 0.30 mol; added NaOH spends NH_4^+, of which there is only 0.10 mol. Adding 0.050 mol of HCl leaves 0.25 mol of NH_3 and 0.15 mol of NH_4^+, pH 9.48, a move of 0.26. Adding the same 0.050 mol of NaOH leaves 0.35 mol of NH_3 and 0.050 mol of NH_4^+, pH 10.10, a move of 0.37, and it has burned through half of the entire base-direction stock doing it.

Example 3: Sizing a buffer to a specification. A 1.0 L acetate buffer at pH = pKa must absorb 0.040 mol of NaOH with a pH rise of no more than 0.15 units. With equal members of n mol each, the rise is log((n + 0.040) ÷ (n − 0.040)), so the specification needs (n + 0.040) ÷ (n − 0.040) ≤ $10^{0.15}$ = 1.41, giving n ≥ 0.234 mol of each member. A design with 0.25 mol of each checks out: the rise is log(0.29 ÷ 0.21) = 0.14, inside the 0.15 allowed.

Example 4: The same moles, two flasks. A 500 mL acetate buffer at 0.30 mol L^{-1} of each member holds 0.15 mol of each, exactly the stock of 1.0 L at 0.15 mol L^{-1} of each. Add 0.050 mol of HCl to either: the recount leaves 0.20 mol of CH_3COOH and 0.10 mol of CH_3COO^-, and pH = 4.74 + log(0.10 ÷ 0.20) = 4.44 in both. Concentration and volume trade against each other; only the moles count.

Judging and Designing: Work in Moles

Convert everything to moles first. Concentrations mislead across volumes and ratios mislead across totals. The comparison that settles capacity is member moles against the moles of the expected attack, direction by direction.

Design runs the same arithmetic backwards. Choose the pair by pKa, set the ratio for the target pH, then size the stocks so that the expected load still leaves both members standing with the pH inside its allowed move. Holding 0.050 mol of added base inside a rise of 0.20 units, starting from equal members, takes at least 0.221 mol of each member; 0.25 mol of each does it with room to spare.

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Traps That Cost Marks in Topic 8.10

"Same pH, same capacity." Two buffers can share a pH and differ a hundredfold in what they absorb. The pH reads the ratio; capacity reads the moles.

"Capacity is a property of the pair." The same acetate pair has a different capacity at every concentration, volume and ratio. Capacity belongs to the actual flask: this much of each member, in this volume.

"The buffer breaks at a pH, not at a mole count." Exhaustion is stoichiometric. It arrives when the addition has consumed the defending member, whatever the pH then reads. Compute the cap in moles first.

"pH = pKa + 2 still buffers, just higher." At ratio 100 the minor member is about 1% of the pair. In its direction the buffer is a label, not a defence.

"One capacity number covers both directions." With unequal members the caps differ, and quoting the larger one flatters the buffer. State the direction, or state both numbers.

"Diluted buffer, same protection." Dilution preserves the pH and divides the capacity.

Key Relationships to Remember

- Buffer capacity: the moles of strong acid or base a buffer absorbs before a member is exhausted and the pH swings, or before a stated pH move is used up
- Added acid is capped by the moles of A^-; added base is capped by the moles of HA
- Capacity scales with the absolute amount of each member, concentration × volume, never with the ratio
- At pH = pKa the two caps are equal, and the smaller cap is at its largest for a fixed total of material
- One unit from pKa the scarcer member is about 9% of the pair; two units away, about 1%, and capacity in that direction falls with it
- After any addition: recount both members in moles, confirm both still stand, then recompute the pH from the new ratio
- Dilution leaves the ratio and the pH unchanged and divides the capacity per litre by the dilution factor

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