Acid-Base & Buffers

Escalating Difficulty Handout

Honors Chemistry $\longrightarrow$ AP Chemistry $\longrightarrow$ USNCO / IChO

18 Problems • 3 Tiers • Full Solutions • Cited Sources

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Handout Roadmap

Tier	Topics	Problems	Source Level
HONORS	Strong acid/base pH, conjugate pairs, pH scale	1–5	OpenStax, Regents
AP CHEM	ICE tables, K_a, Henderson-Hasselbalch, buffers, titrations, diprotic	6–15	AP FRQ, ACS-style
USNCO/IChO	Open/closed buffer systems, triprotic amino acids, true vs. apparent K_a	16–18	IChO Prep, USNCO

TIER 1 • Honors Chemistry • 5 Problems

Strong acid/base $\Rightarrow$ ionizes 100%. No equilibrium needed. Just read off $[H_3O^+]$ or $[OH^-]$ directly from concentration $\times$ stoichiometry.

HONORS Problem 1 — Strong Acid & Base pH

Source: OpenStax Chemistry 2e, Ch. 14, Exercise 18 (CC BY 4.0).

Calculate the pH and pOH of each solution at 25 °C (complete ionization):

(a) 0.200 M HCl

(b) 0.0143 M NaOH

(c) 3.0 M HNO_3

(d) 0.0031 M $Ca(OH)_2$

★ Solution

(a) HCl is a strong acid: $[H_3O^+] = 0.200\,\text{M}$.

$$\text{pH} = -\log(0.200) = 0.699, \quad \text{pOH} = 14.000 - 0.699 = 13.301$$

(b) NaOH is a strong base: $[OH^-] = 0.0143\,\text{M}$.

$$\text{pOH} = -\log(0.0143) = 1.845, \quad \text{pH} = 14.000 - 1.845 = 12.155$$

(c) $[H_3O^+] = 3.0\,\text{M}$.

$$\text{pH} = -\log(3.0) = -0.477, \quad \text{pOH} = 14.477$$

(d) $Ca(OH)_2$ yields $2\,OH^-$ per formula unit: $[OH^-] = 2 \times 0.0031 = 0.0062\,\text{M}$.

$$\text{pOH} = -\log(0.0062) = 2.21, \quad \text{pH} = 14.00 - 2.21 = 11.79$$

◇ Pro Tip

Yes, pH can be negative! Whenever $[H_3O^+] > 1\,\text{M}$, $\text{pH} < 0$. The pH scale is *not* bounded by 0 or 14.

HONORS Problem 2 — Conjugate Acid-Base Pair ID

Source: OpenStax Chemistry 2e, Ch. 14, Exercise 7 (CC BY 4.0).

For each species, identify its conjugate acid and conjugate base:

(a) OH^-
(b) H_2O
(c) HCO_3^-
(d) NH_3
(e) HSO_4^-
(f) H_2O_2
(g) HS^-
(h) $H_5N_2^+$

★ Solution

Add H^+ → conjugate acid. Remove H^+ → conjugate base.

Species	Conj. Acid ($+H^+$)	Conj. Base ($-H^+$)
(a) OH^-	H_2O	O^{2-}
(b) H_2O	H_3O^+	OH^-
(c) HCO_3^-	H_2CO_3	CO_3^{2-}
(d) NH_3	NH_4^+	NH_2^-
(e) HSO_4^-	H_2SO_4	SO_4^{2-}
(f) H_2O_2	$H_3O_2^+$	HO_2^-
(g) HS^-	H_2S	S^{2-}
(h) $H_5N_2^+$	$H_6N_2^{2+}$	H_4N_2

HCO_3^- and HSO_4^- are **amphiprotic**—they can donate or accept a proton. This shows up constantly on AP exams!

HONORS Problem 3 — NOT a Conjugate Pair

Source: Minnesota State, Prof. Jasperse, Gen. Chem. II Practice (Chem 210), Q6.

Which is **not** a conjugate acid–base pair?

(a) NH_3 and NH_4^+
(b) H_3O^+ and OH^-
(c) $H_2PO_4^-$ and HPO_4^{2-}
(d) HS^- and H_2S
(e) NH_3 and NH_2^-

★ **Solution**

A conjugate pair must differ by **exactly one** H^+.

$$H_3O^+ \longrightarrow H_2O \longrightarrow OH^- \quad \Leftarrow \text{ that's two protons apart.}$$

$\therefore$ **Answer: (b).** The correct pairs are H_3O^+/H_2O and H_2O/OH^-.

HONORS Problem 4 — pH + pOH = 14

Source: Minnesota State, Prof. Jasperse, Gen. Chem. II Practice (Chem 210), Q23.

A solution with pH = 9.50 has a pOH of: (a) 9.50 (b) 0.50 (c) 4.50 (d) 23.5 (e) 19.0

★ **Solution**

At 25 °C: $pH + pOH = 14.00$.

$$pOH = 14.00 - 9.50 = 4.50 \qquad \textbf{Answer: (c)}$$

Since $pH > 7$, the solution is basic.

HONORS Problem 5 — Logarithmic Scale Ratio

Source: New York State Regents Chemistry, June 2022, Q49.

Solution A has pH = 2.0 and Solution B has pH = 4.0. How many times greater is $[H_3O^+]$ in A than in B?

(1) 10 (2) 2 (3) 100 (4) 4

★ **Solution**

Each pH unit $= 10\times$ change in $[H_3O^+]$.

$$\frac{[H_3O^+]_A}{[H_3O^+]_B} = \frac{10^{-2}}{10^{-4}} = 10^{4-2} = 10^2 = 100$$

Answer: (3).

Quick rule: $\Delta\text{pH} = n$ means a 10^n-fold difference in $[H_3O^+]$.

TIER 2 • AP Chemistry • 10 Problems

◇ Pro Tip

The Big Three tools for Tier 2:

1. **ICE table** — set up equilibrium, solve for x, check 5% approximation.
2. **Henderson-Hasselbalch:** $\text{pH} = \text{p}K_\text{a} + \log\dfrac{[\text{base}]}{[\text{acid}]}$
3. **Stoichiometry first, then equilibrium** — for titration/mixing problems.

AP CHEM Problem 6 — Weak Acid $[H_3O^+]$ from K_a

Source: Minnesota State, Jasperse, Chem 210 Practice (ACS Gen. Chem. style).

What is the hydronium ion concentration of a 0.010 M solution of acetic acid? $K_a = 1.8 \times 10^{-5}$.

(a) 1.8×10^{-3} (b) 1.8×10^{-5} (c) 1.0×10^{-2} (d) 1.8×10^{-7} (e) 4.2×10^{-4}

★ Solution

$$\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$$

$$K_a = \frac{x^2}{0.010 - x} \approx \frac{x^2}{0.010} = 1.8 \times 10^{-5}$$

$$x^2 = 1.8 \times 10^{-7} \implies x = \sqrt{1.8 \times 10^{-7}} = 4.2 \times 10^{-4}\ \text{M}$$

Check: $\dfrac{4.2 \times 10^{-4}}{0.010} = 4.2\% < 5\%$ ✓ **Answer: (e)**

See "K_a and an initial concentration"? ⇒ Set up $K_a = x^2/C_0$, solve, check 5%.

AP CHEM Problem 7 — Calculating K_a from pH

Source: 2014 AP Chemistry Exam, FRQ #2(b). College Board.

Propanoic acid $\text{CH}_3\text{CH}_2\text{COOH}$ has a 0.20 M solution with pH = 2.79 at 25 °C. Determine K_a.

★ Solution

$$[\text{H}_3\text{O}^+] = 10^{-2.79} = 1.62 \times 10^{-3}\ \text{M}$$

At equilibrium: $[\text{CH}_3\text{CH}_2\text{COO}^-] = [\text{H}_3\text{O}^+] = 1.62 \times 10^{-3}\ \text{M}$

$[CH_3CH_2COOH] = 0.20 - 0.00162 = 0.198\,\text{M}$

$$K_a = \frac{(1.62 \times 10^{-3})^2}{0.198} = \frac{2.63 \times 10^{-6}}{0.198} = 1.3 \times 10^{-5}$$

This matches the literature value for propanoic acid.

AP CHEM Problem 8 — ICE Table for Weak Acid pH

Source: 2021 AP Chemistry Exam, FRQ #1(b). College Board.

Calculate the pH of a 0.25 M solution of methanoic acid (HCOOH). $K_a = 1.8 \times 10^{-4}$.

★ **Solution**

ICE table:

	HCOOH	H_3O^+	$HCOO^-$
I	0.25	≈ 0	0
C	$-x$	$+x$	$+x$
E	$0.25 - x$	x	x

$$K_a = \frac{x^2}{0.25 - x} \approx \frac{x^2}{0.25} = 1.8 \times 10^{-4}$$

$$x = \sqrt{0.25 \times 1.8 \times 10^{-4}} = \sqrt{4.50 \times 10^{-5}} = 6.71 \times 10^{-3}\ \text{M}$$

Check: $6.71 \times 10^{-3}/0.25 = 2.7\% < 5\%$ ✓

$$\text{pH} = -\log(6.71 \times 10^{-3}) = 2.17$$

AP CHEM Problem 9 — Buffer pH via Henderson-Hasselbalch

Source: Texas A&M, Gen. Chem. FYP Sample Questions, Ch. 19.

What is the pH of a solution of 0.20 M NH_3 and 0.15 M NH_4Cl?
$K_b(NH_3) = 1.8 \times 10^{-5}$ (a) 2.15 (b) 4.62 (c) 8.26 (d) 9.38 (e) 8.89

★ **Solution**

This is a **basic buffer**: weak base + its conjugate acid.
$\text{p}K_\text{b} = -\log(1.8 \times 10^{-5}) = 4.74$ $\quad \text{p}K_\text{a}(NH_4^+) = 14.00 - 4.74 = 9.26$
Henderson-Hasselbalch:

$$\text{pH} = \text{p}K_\text{a} + \log\frac{[\text{base}]}{[\text{acid}]} = 9.26 + \log\frac{0.20}{0.15} = 9.26 + 0.125 = 9.38$$

Answer: (d)

◇ **Pro Tip**

For base buffers, **always** convert to pK_a of the conjugate acid. Then H-H works the same way every time.

AP CHEM Problem 10 — Buffer + Strong Base Addition

Source: Texas A&M, Gen. Chem. FYP Sample Questions, Ch. 19.

1.00 mol NH_3 and 1.00 mol NH_4Cl are mixed in 1.00 L of water. To 500 mL of this solution, 30.0 mL of 1.00 M NaOH is added. Find the pH.
$K_b(NH_3) = 1.8 \times 10^{-5}$ (a) 8.96 (b) 9.83 (c) 9.31 (d) 9.11 (e) 9.57

★ **Solution**

Step 1: In 500 mL of stock: $n_{NH_3} = 0.500$ mol, $n_{NH_4^+} = 0.500$ mol.
Step 2: NaOH added: $0.0300\text{ L} \times 1.00\text{ M} = 0.0300$ mol OH^-.
Step 3: Reaction $NH_4^+ + OH^- \longrightarrow NH_3 + H_2O$:
$n_{NH_3} = 0.500 + 0.030 = 0.530$ mol, $n_{NH_4^+} = 0.500 - 0.030 = 0.470$ mol
Step 4: Henderson-Hasselbalch (mole ratio = concentration ratio in same volume):

$$\text{pH} = 9.26 + \log\frac{0.530}{0.470} = 9.26 + 0.052 = 9.31$$

Answer: (c). The pH shifted only 0.05 units—that's the power of a buffer!

AP CHEM Problem 11 — Buffer Preparation to Target pH

Source: Texas A&M, Gen. Chem. FYP Sample Questions, Ch. 19.

How many grams of NaF must be added to 2.00 L of 0.100 M HF to give pH = 4.00?
$K_a(HF) = 7.2 \times 10^{-4}$; $M(NaF) = 42.0$ g/mol.
(a) 300 g (b) 36 g (c) 0.84 g (d) 6.9 g (e) 60 g

★ **Solution**

$pK_a = -\log(7.2 \times 10^{-4}) = 3.14$
H-H: $4.00 = 3.14 + \log\dfrac{[F^-]}{0.100}$

$$\log\frac{[F^-]}{0.100} = 0.86 \implies [F^-] = 0.100 \times 10^{0.86} = 0.724\text{ M}$$

$$n_{NaF} = 0.724 \times 2.00 = 1.45\text{ mol} \implies m = 1.45 \times 42.0 = 60.9 \approx 60\text{ g}$$

Answer: (e).

"Prepare a buffer at pH = X" ⇒ H-H backward: solve for the required [base]/[acid] ratio, then convert to moles/grams.

AP CHEM Problem 12 — Titration Buffer Region pH

Source: Texas A&M, Gen. Chem. FYP Sample Questions, Ch. 19.

300 mL of 0.10 M HF is mixed with 200 mL of 0.10 M KOH. Calculate the pH.
$K_a(\text{HF}) = 7.2 \times 10^{-4}$ (a) 2.82 (b) 2.96 (c) 3.32 (d) 3.44 (e) 3.53

★ Solution

Stoichiometry first:
$n_{\text{HF}} = 0.030\,\text{mol}$, $n_{\text{OH}^-} = 0.020\,\text{mol}$ (KOH is limiting)
$\text{HF} + \text{OH}^- \longrightarrow \text{F}^- + \text{H}_2\text{O}$
After reaction: $n_{\text{HF}} = 0.010\,\text{mol}$, $n_{\text{F}^-} = 0.020\,\text{mol}$.
Total volume $= 0.500\,\text{L}$: $[\text{HF}] = 0.020\,\text{M}$, $[\text{F}^-] = 0.040\,\text{M}$.

$$\text{pH} = 3.14 + \log\frac{0.040}{0.020} = 3.14 + \log(2) = 3.14 + 0.301 = 3.44$$

Answer: (d).

◇ Pro Tip

For any mixing/titration problem: (1) do stoichiometry in moles; (2) find new concentrations; (3) apply H-H or equilibrium.

AP CHEM Problem 13 — AP FRQ: Buffer Design with HNO_2

Source: 2017 AP Chemistry Exam, FRQ #3, parts (c)–(e). College Board.

Nitrous acid HNO_2 has $K_a = 4.0 \times 10^{-4}$, $\text{p}K_\text{a} = 3.40$.

(i) Explain why adding 0.100 M NaOH to 0.100 M HNO_2 can form a buffer. Write the net ionic equation.

(ii) What volume of 0.100 M NaOH should be added to 100. mL of 0.100 M HNO_2 to make a buffer at pH = 3.40?

(iii) A second student makes a buffer with 0.100 mol $NaNO_2$ in 100 mL of 1.00 M HNO_2. Which buffer has greater capacity?

(iv) A particulate diagram shows 10 HNO_2 molecules and 5 NO_2^- ions. Is the pH >, <, or = 3.40?

★ Solution

(i) The NaOH partially neutralizes HNO_2, leaving a mixture of weak acid and its conjugate base:

$$\text{HNO}_2(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{NO}_2^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$$

A buffer requires both a weak acid and its conjugate base—this reaction creates exactly that.

(ii) For $\text{pH} = \text{p}K_\text{a} = 3.40$, we need $[\text{NO}_2^-] = [\text{HNO}_2]$ (equal moles).
Initial: $n_{\text{HNO}_2} = 0.100 \times 0.100 = 0.0100\,\text{mol}$. Convert exactly half:
$n_{\text{NaOH}} = 0.0100/2 = 0.00500\,\text{mol} \implies V = 0.00500/0.100 = \mathbf{50.0}\,\text{mL}$.

(iii) The second buffer has $\sim 0.1\,\text{mol}$ of each component vs. $\sim 0.005\,\text{mol}$ each. **The second buffer has far greater capacity.** More moles = more acid/base can be absorbed before pH shifts significantly.

(iv) Ratio: $[HNO_2]/[NO_2^-] = 10/5 = 2$, so acid dominates:

$$\text{pH} = 3.40 + \log(5/10) = 3.40 - 0.30 = 3.10$$

$\therefore$ pH is **less than** 3.40.

AP CHEM Problem 14 — Equimolar Buffer & Dilution Effect

Source: 2023 AP Chemistry Exam, FRQ #4. College Board.

A student prepares a buffer using 25.00 mL of 0.100 M CH_3NH_2 ($K_b = 4.4 \times 10^{-4}$) and an equimolar mass of CH_3NH_3Cl.

(a) Calculate the mass of CH_3NH_3Cl containing 0.00250 mol.

(b) A second buffer uses half the concentrations (0.050 M base, half the salt). Is its pH greater than, less than, or equal to the first buffer?

★ Solution

(a) $M(CH_3NH_3Cl)$: C(12.01) + 3H(3.024) + N(14.01) + 3H(3.024) + Cl(35.45) = 67.52 g/mol

$$m = 0.00250 \times 67.52 = 0.169 \text{ g}$$

(b) Equal. Halving both concentrations preserves the ratio [base]/[acid] = 1. By H-H:

$$\text{pH} = \text{p}K_\text{a} + \log(1) = \text{p}K_\text{a} + 0 = 14.00 - 3.36 = 10.64$$

Dilution of a buffer does **NOT** change its pH (as long as the ratio is preserved). It *does* decrease buffer capacity.

AP CHEM Problem 15 — Diprotic Acid: pK_{a2} and Buffer Ratio

Source: 2024 AP Chemistry Exam, FRQ #2(f)–(g). College Board.

Maleic acid is diprotic: $K_{a1} = 1.5 \times 10^{-2}$, $K_{a2} = 8.5 \times 10^{-7}$.

(a) Calculate pK_{a2}.

(b) A buffer at pH = 7.00 uses $C_4H_2O_4^{2-}$ and $HC_4H_2O_4^-$. Find $[C_4H_2O_4^{2-}]/[HC_4H_2O_4^-]$.

★ Solution

(a) $\text{p}K_{a2} = -\log(8.5 \times 10^{-7}) = 7 - \log(8.5) = 7 - 0.929 = 6.07$

(b) Henderson-Hasselbalch with the second dissociation:

$$7.00 = 6.07 + \log\left(\frac{[\mathrm{C_4H_2O_4}^{2-}]}{[\mathrm{HC_4H_2O_4}^{-}]}\right)$$

$$\log(\text{ratio}) = 0.93 \implies \text{ratio} = 10^{0.93} = 8.5$$

The conjugate base must be $8.5\times$ the concentration of the hydrogen maleate ion—pH is nearly a full unit above $\mathrm{p}K_{\mathrm{a}2}$.

TIER 3 • USNCO / IChO • 3 Problems

◇ Pro Tip

These problems require you to go **beyond** Henderson-Hasselbalch. You'll need to integrate Henry's law with buffer chemistry, handle triprotic amino acid speciation, and distinguish between apparent and true equilibrium constants.

USNCO/IChO Problem 16 — Blood Bicarbonate: Open vs. Closed Systems

Source: 50th IChO (Bratislava/Prague, 2018), Preparatory Problems, Problem 9.

The daily production of metabolic acids in the body is about 60 mmol, released into 6 dm^3 of blood. The blood bicarbonate buffer starts at pH = 7.4 with $p(CO_2) = 5.3$ kPa at 37 °C.
Data: $pK_a(37\,°C) = 6.1$; Henry's constant $H_{cp} = 2.3 \times 10^{-4}$ mol m^{-3} Pa^{-1}.

(a) Calculate pH after the acid load in a **closed system** (no CO_2 escape).

(b) Calculate pH in an **open system** ($p(CO_2)$ maintained by breathing). Does it stay in range 7.35–7.45?

★ Solution

Preliminary — initial concentrations:
$[CO_2(aq)] = H_{cp} \times p(CO_2) = 2.3 \times 10^{-4} \times 5300 = 1.22$ mM
From H-H: $7.4 = 6.1 + \log\left(\dfrac{[HCO_3^-]}{1.22}\right) \implies [HCO_3^-] = 1.22 \times 10^{1.3} = 24.3$ mM.
Acid load per liter = 60/6 = 10.0 mM. Buffering: $HCO_3^- + H^+ \longrightarrow CO_2(aq) + H_2O$.

(a) Closed system (CO_2 accumulates):
$[HCO_3^-]_{new} = 24.3 - 10.0 = 14.3$ mM, $[CO_2]_{new} = 1.22 + 10.0 = 11.22$ mM.

$$\text{pH} = 6.1 + \log\frac{14.3}{11.22} = 6.1 + 0.105 = \mathbf{6.21}$$

This is **dangerously acidotic**—incompatible with life!

(b) Open system (lungs maintain $p(CO_2)$ constant):
$[HCO_3^-]_{new} = 14.3$ mM, $[CO_2] = 1.22$ mM (unchanged).

$$\text{pH} = 6.1 + \log\frac{14.3}{1.22} = 6.1 + 1.069 = \mathbf{7.17}$$

This is below the normal range of 7.35–7.45. The bicarbonate buffer alone cannot fully compensate; phosphate buffers, hemoglobin, proteins, and renal compensation are all needed.

The key insight: In an open system, the denominator ($[CO_2]$) stays fixed while only the numerator ($[HCO_3^-]$) drops. In a closed system, the denominator increases simultaneously, creating a devastating **double-effect** on the log ratio. This is why respiratory CO_2 removal is critical.

USNCO/IChO Problem 17 — Triprotic Amino Acid: Lysine Equilibria

Source: 49th IChO (Thailand, 2017), Preparatory Problems, Task 10.

Lysine has three ionizable groups: $pK_{a1} = 2.16$ (carboxyl), $pK_{a2} = 9.06$ (α-ammonium), $pK_{a3} = 10.54$ (side-chain ammonium). The fully protonated form is H_3Lys^{2+}.

(a) Starting with $100\,cm^3$ of $0.100\,mol\,dm^{-3}$ H_3Lys^{2+}, find the volume of $0.500\,M$ KOH to reach pH = 9.50.

(b) Find the pH when $5.00\,g$ of the zwitterion HLys ($M = 146.19\,g/mol$) dissolves in $100.0\,cm^3$ of water.

★ Solution

(a) $n_{H_3Lys^{2+}} = 0.100 \times 0.100 = 0.0100\,mol$.

Species ladder: $H_3Lys^{2+} \xrightarrow{pK_{a1}} H_2Lys^{+} \xrightarrow{pK_{a2}} HLys \xrightarrow{pK_{a3}} Lys^{-}$
pH = 9.50 lies between $pK_{a2} = 9.06$ and $pK_{a3} = 10.54$, so the buffer pair is H_2Lys^{+}/HLys. The first proton (carboxyl) is fully removed. We're partially through removing the second (α-NH_3^{+}).

KOH needed:

- Fully deprotonate carboxyl ($pK_{a1} = 2.16$): $0.0100\,mol$
- Partially deprotonate α-NH_3^{+}: fraction f

$$9.50 = 9.06 + \log\frac{f}{1-f} \implies \frac{f}{1-f} = 10^{0.44} = 2.754 \implies f = \frac{2.754}{3.754} = 0.7337$$

Additional KOH: $0.7337 \times 0.0100 = 0.007337\,mol$.
Total: $0.0100 + 0.007337 = 0.01734\,mol$.

$$V = \frac{0.01734}{0.500} = 0.03467\ L = \mathbf{34.7}\ mL$$

(b) $n_{HLys} = 5.00/146.19 = 0.0342\,mol$, $C = 0.342\,M$.
HLys is an amphoteric zwitterion sitting between pK_{a2} and pK_{a3}:

$$pH = \frac{pK_{a2} + pK_{a3}}{2} = \frac{9.06 + 10.54}{2} = \mathbf{9.80}$$

This approximation holds since $C \gg K_{a2}$ and $C \gg K_{a3}$.

For any amphiprotic species, $pH \approx \frac{pK_{a\,above} + pK_{a\,below}}{2}$. This is the **isoelectric point** for amino acids.

USNCO/IChO Problem 18 — True vs. Apparent K_a of Carbonic Acid

Source: USNCO National Exam, Part II (~2000). ACS/USNCO archives.

The dissociation constants for H_2CO_3: $K_{a1} = 4.2 \times 10^{-7}$, $K_{a2} = 4.7 \times 10^{-11}$.

(a) Write balanced equations for each dissociation.

(b) Which carbonate buffer pair is best for blood plasma (pH = 7.40)?

(c) The "true" K_{a1} (using actual $[H_2CO_3]$ rather than total dissolved CO_2) is 2×10^{-4}. What percentage of dissolved CO_2 exists as H_2CO_3?

★ **Solution**

(a)

$$K_{a1}: \quad H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$
$$K_{a2}: \quad HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$$

(b) $pK_{a1} = -\log(4.2 \times 10^{-7}) = 6.38, \quad pK_{a2} = -\log(4.7 \times 10^{-11}) = 10.33.$
Blood pH $= 7.40$ is closest to pK_{a1}, so the best pair is $\mathbf{H_2CO_3}$ **(dissolved** $\mathbf{CO_2}$**)** / $\mathbf{HCO_3^-}$.

(c) The "apparent" K_{a1} lumps all dissolved CO_2 into the denominator, while the "true" K_{a1} uses only the small fraction that is actually H_2CO_3:

$$K_{a1}^{\text{app}} = \frac{[H^+][HCO_3^-]}{[CO_2]_{\text{total}}}, \qquad K_{a1}^{\text{true}} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]_{\text{actual}}}$$

Taking the ratio:

$$\frac{K_{a1}^{\text{app}}}{K_{a1}^{\text{true}}} = \frac{[H_2CO_3]_{\text{actual}}}{[CO_2]_{\text{total}}} = \frac{4.2 \times 10^{-7}}{2 \times 10^{-4}} = 2.1 \times 10^{-3} = \mathbf{0.21}\%$$

Only $\sim 0.2\%$ of dissolved CO_2 is actually H_2CO_3. The vast majority ($\sim 99.8\%$) remains as $CO_2(aq)$.

True H_2CO_3 is a **moderately strong** acid ($K_a \approx 2 \times 10^{-4}$, comparable to HNO_2!). The "weak acid" reputation comes from the apparent K_a, which is artificially depressed by dividing by all the unreacted CO_2.

Quick-Reference: Core Formulas

Concept	Equation
Strong acid/base pH	$\mathrm{pH} = -\log[\mathrm{H_3O^+}]; \quad \mathrm{pH} + \mathrm{pOH} = 14.00$ at $25\,^\circ\mathrm{C}$
Weak acid equil.	$K_a = \dfrac{x^2}{C_0 - x} \approx \dfrac{x^2}{C_0}$ (if $x < 5\%$ of C_0)
Henderson-Hasselbalch	$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log \dfrac{[\text{conjugate base}]}{[\text{weak acid}]}$
Amphiprotic species	$\mathrm{pH} \approx \dfrac{\mathrm{p}K_{\mathrm{a\,below}} + \mathrm{p}K_{\mathrm{a\,above}}}{2}$
Henry's law ($\mathbf{CO_2}$)	$[\mathrm{CO_2(aq)}] = H_{cp} \times p(\mathrm{CO_2})$
Buffer capacity	$\uparrow$ moles of buffer components $\Rightarrow \uparrow$ capacity (pH unchanged)
$K_b \leftrightarrow K_a$	$K_a \cdot K_b = K_w = 1.0 \times 10^{-14}; \quad \mathrm{p}K_\mathrm{a} + \mathrm{p}K_\mathrm{b} = 14.00$

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