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Topic 8.7: pH and pKa

Revision Notes · AP Chemistry

UNIT 8 · ACIDS AND BASES

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One Definition Behind Four Scales

pH, pOH, pKa and pKb are the same move applied four times.

$pX = -\log X$

So $pH = -\log [H_3O^+]$, $pOH = -\log [OH^-]$, $pKa = -\log Ka$ and $pKb = -\log Kb$.

Why take a logarithm at all? Ka values run from about 10^{7} down to 10^{-10} and below, so the pKa scale compresses that range into numbers comparable at a glance.

pKa belongs to the acid, not the solution. Diluting acetic acid changes the solution's pH, but its pKa stays 4.74, fixed by the acid and the temperature, while pH moves with concentration.

Converting Between a Constant and Its p-Value

The two directions are exact inverses, and running one backwards is the built-in check on the other.

$pKa = -\log Ka$ and $Ka = 10^{-pKa}$

From Ka to pKa. HCN has $Ka = 4.9 \times 10^{-10}$, so $pKa = -\log(4.9 \times 10^{-10}) = 9.31$. An acid with $Ka = 1.0 \times 10^{-5}$ lands exactly on pKa = 5.00.

From pKa to Ka. HF has pKa = 3.17, so $Ka = 10^{-3.17} = 6.8 \times 10^{-4}$.

One unit means a factor of ten. A pKa gap of 1 is a Ka factor of 10; a gap of 2 is 100, and 3 is 1,000.

$\text{ratio} = 10^{(\text{pKa gap})}$

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Reading Strength Off the pKa Scale

Lower pKa means larger Ka and a stronger acid, so the scale runs backwards: HF (pKa 3.17) > CH_3COOH (pKa 4.74) > HCN (pKa 9.31).

CH_3COOH and HCN differ by 9.31 − 4.74 = 4.57 units, so their Ka values differ by $10^{4.57} \approx 3.7 \times 10^4$, and HF sits 1.57 units below CH_3COOH, a factor of about 37.

Strong acids fall off the bottom of the scale. HCl has Ka ≈ 10^7, so pKa ≈ −7. A negative pKa is not an error: it is what −log returns whenever Ka exceeds 1, and it marks a strong acid.

The Conjugate Sum: pKa + pKb = 14.00

For any conjugate pair, Ka × Kb = Kw. Taking −log of both sides turns the product into a sum.

pKa + pKb = pKw = 14.00 at 25 °C

From it, HCN (pKa 9.31) gives CN^- pKb = 14.00 − 9.31 = 4.69, and NH_3 (pKb 4.74) gives NH_4^+ pKa = 9.26.

Two conditions. The pair must be genuinely conjugate, differing by exactly one proton, and 14.00 is a 25 °C value, because Kw changes with temperature.

pH + pOH = 14.00: The Same Kw in Disguise

Because $[H_3O^+] \times [OH^-] = Kw$, the same algebra gives pH + pOH = 14.00 at 25 °C.

A solution with pH 4.32 has pOH = 9.68 and $[OH^-] = 10^{-9.68} = 2.1 \times 10^{-10}$ M.

Where the pH Sits Against pKa

For the ionization

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

comparing the solution's pH with the acid's pKa tells you which form dominates, with no equilibrium calculation at all:

pH = pKa + log([A^-] ÷ [HA])

pH = pKa: the two forms are equal. [HA] = [A^-] and the acid is 50% ionized. This is the half-equivalence point, which is why that point measures pKa.

pH below pKa: HA dominates; pH above pKa: A^- dominates.

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The ratio is $[A^-] \div [HA] = 10^{(pH - pKa)}$: at pKa + 1 the ratio is 10 and the acid is about 91% ionized; at pKa + 2 it is 100 and about 99% ionized; one unit below pKa, about 9% is ionized; two units below, about 1%.

Polyprotic Acids: One pKa for Each Proton

A diprotic acid carries two pKa values, one per step: H_2CO_3 has pKa1 = 6.37 and pKa2 = 10.33.

$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$

$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$

The second is the larger, because that proton must leave an anion.

The dominating form is bracketed by its neighbouring pKa values: at pH 8.0, between 6.37 and 10.33, HCO_3^- dominates; below 6.37, H_2CO_3 dominates; above 10.33, CO_3^{2-} takes over.

At the first equivalence point the amphiprotic middle form dominates, with pH ≈ the average of the two pKa values: for pKa1 = 2.0 and pKa2 = 7.0, pH ≈ (2.0 + 7.0) ÷ 2 = 4.5.

Significant Figures on a Log Scale

For a logarithm, the significant figures of the concentration become the decimal places of the p-value: 0.050 M earns pH 3.65. The digits before the decimal point only locate the power of ten, so 3.6505 overstates the precision, and the same rule governs pKa.

Worked Examples

Example 1: One chain of conversions for HCN. From $K_a = 4.9 \times 10^{-10}$, $pK_a = -\log(4.9 \times 10^{-10}) = 9.31$. The conjugate base CN^- has $pK_b = 14.00 - 9.31 = 4.69$, so $K_b = 10^{-4.69} = 2.0 \times 10^{-5}$. Check: $K_w \div K_a = 1.0 \times 10^{-14} \div 4.9 \times 10^{-10} = 2.0 \times 10^{-5}$.

Example 2: PH from pKa for a weak acid solution. A 0.050 M solution of an acid with pKa = 6.00. Convert first: $K_a = 10^{-6.00} = 1.0 \times 10^{-6}$. Then $[H_3O^+] \approx \sqrt{(K_a \times 0.050)} = \sqrt{(5.0 \times 10^{-8})} = 2.24 \times 10^{-4}$ M, so pH = 3.65. The shortcut is licensed because 2.24×10^{-4} is only 0.45% of 0.050; the exact quadratic returns the same 3.65.

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Example 3: The conjugate base of HF. HF has pKa = 3.17, so its conjugate base F^- has pKb = 14.00 − 3.17 = 10.83. Then Kb = $10^{-10.83}$ = 1.5×10^{-11}. Check: Kw ÷ Ka = $1.0 \times 10^{-14} \div 6.8 \times 10^{-4} = 1.5 \times 10^{-11}$, agreeing exactly.

Example 4: PH of a 0.050 M acid from its pKa. An acid has pKa = 5.00 and a 0.050 M solution is prepared. Convert first: Ka = $10^{-5.00} = 1.0 \times 10^{-5}$. Then $[H_3O^+] \approx \sqrt{(Ka \times 0.050)} = \sqrt{(5.0 \times 10^{-7})} = 7.07 \times 10^{-4}$ M, so pH = 3.15. The shortcut is licensed because 7.07×10^{-4} is only 1.4% of 0.050; the exact quadratic returns the same 3.15.

Traps That Cost Marks in Topic 8.7

"The larger pKa is the stronger acid." Backwards: the minus sign in −log inverts the order, so pKa 2.0 beats pKa 9.31 by an enormous margin.

"A pKa difference of 2 means the Ka values differ by 2." It means a factor of 10^2 = 100. pKa gaps are exponents, not multipliers.

"pKa and pH are the same thing." pKa is a constant of the acid; pH belongs to a solution and moves with concentration. They coincide only when [HA] = $[A^-]$.

"pKa + pKb = 14 works for any acid and any base." Only for a conjugate pair, and only at 25 °C. Pairing the pKa of HF (3.17) with the pKb of CN^- (4.69) gives 7.86, which means nothing.

"pKa must be positive." Strong acids have Ka > 1 and negative pKa values; HCl sits at about −7. A negative result is information, not a mistake.

"At pH = pKa + 1 the acid is fully ionized." The ratio $[A^-] \div [HA]$ is 10, so about 91% is ionized and 9% is still HA.

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Key Relationships to Remember

- pX = −log X, and every conversion inverts exactly: $K_a = 10^{-pK_a}$ and $[H_3O^+] = 10^{-pH}$
- Lower pKa means larger Ka and a stronger acid; a pKa gap of n units is a Ka ratio of 10^n
- Strong acids have Ka > 1 and negative pKa (HCl ≈ −7); weak acids have positive pKa, mostly 3 to 10
- Ka × Kb = Kw for a conjugate pair, so pKa + pKb = 14.00 at 25 °C; the same Kw gives pH + pOH = 14.00
- At pH = pKa, $[HA] = [A^-]$ and the acid is 50% ionized; in general $[A^-] \div [HA] = 10^{(pH-pK_a)}$
- One pH unit either side of pKa gives about 91% or 9% ionized; two units gives about 99% or 1%
- Polyprotic acids carry one pKa per proton, rising at each step; the dominating form is bracketed by its neighbouring pKa values, and a first equivalence point sits near (pKa1 + pKa2) ÷ 2
- Decimal places in a pH or pKa equal the significant figures in the concentration or constant it came from

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Topic 8.7 Worksheet

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