pH vs pK_a: Which form dominates?

Given the generic weak acid reaction: $HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$

more acidic

pH < pK_a [HA] > [A⁻]

Added acid: ↑ $[H_3O^+]$ = ↑ [products]; according to Le Chatelier, reaction will shift left to favor reactants, thus the HA form predominates: $\frac{HA}{A^-} > 1$

pH = pK_a [HA] = [A⁻]

Ideal buffer ratio, HA = A⁻ thus neither form predominates: $\frac{HA}{A^-} = 1$

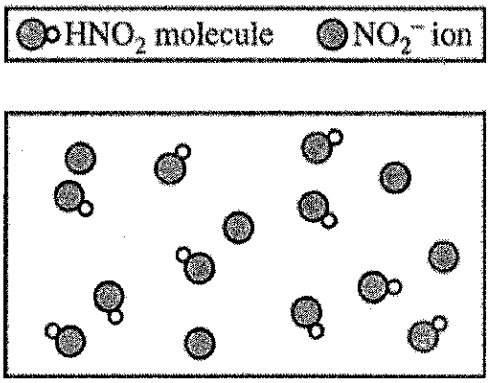
pH > pK_a more basic [A⁻] > [HA]

Added base: ↑ $[OH^-]$ = ↓ $[H_3O^+]$ = ↓ [products]; according to Le Chatelier, reaction will shift right to favor products, thus the A⁻ form predominates: $\frac{HA}{A^-} < 1$

*This is why, during a titration, you want to choose an indicator with a $pK_a \approx pH$ at equivalence point (if the indicator is a weak acid). An indicator works because the acid form of the indicator, HA, is a different color than the conjugate base form, A^-.

Let's Practice!

1. A buffer is made using HNO_2 as one of the ingredients. ($K_a = 4.0 \times 10^{-4}$, pKa = 3.40). A particulate representation of a small portion of the buffer is shown below. (Cations and water molecules are not shown.) Is the pH of the buffer represented in the diagram greater than, less than, or equal to 3.40? Justify your answer.



$HNO_2 = 10$

$NO_2^- = 5$

Less than!

$$pH = pK_a + \log\frac{[NO_2^-]}{[HNO_2]} = 3.40 + \log\left(\frac{5}{10}\right) = 3.10$$

$\Rightarrow pH < 3.40$

OR

↳ If $[HNO_2] = [NO_2^-]$, pH = pK_a and the pH of Sol'n would be 3.40. Since $[HNO_2] > [NO_2^-]$ in the diagram, the Sol'n has a pH < 3.40.