

What happens when acids and bases are mixed together?

strong base into weak acid:

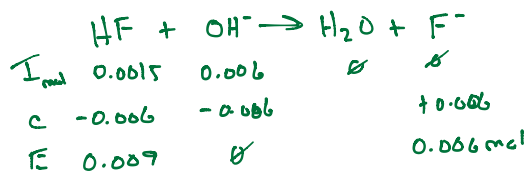
- To predict pH changes:

- ① stoichiometry problem
- ② equilibrium problem

Example: 150 mL of 10 mM HF ($pK_a = 3.25$)
 - determine the pH if 6 mL of 1M NaOH is added to it.

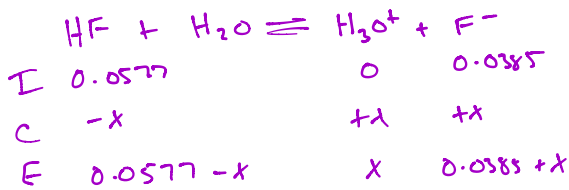
$$\text{mol HF} = 0.15 \text{ L} \left(\frac{0.01 \text{ mol}}{\text{L}} \right)$$

$$\text{mol OH}^- = 0.006 \text{ L} \left(\frac{1 \text{ mol}}{\text{L}} \right)$$



- so when the stoichiometry problem is done, 0.009 mol HF

Now equilibrium problem:



$$\frac{0.009 \text{ mol}}{0.15 + 0.006 \text{ L}} = 0.0577 \text{ M } = [\text{HF}]$$

$$\frac{0.006 \text{ mol}}{0.156 \text{ L}} = 0.0385 \text{ M } = [\text{F}^-]$$

$$K_a = 10^{-3.25} = 5.62 \times 10^{-4} = \frac{x(0.0385 + x)}{0.0577 - x}$$

$$3.245 \times 10^{-5} - 5.62 \times 10^{-5} x = 0.0385x + x^2$$

$$x^2 + 0.039062x - 3.24 \times 10^{-5} = 0$$

$$x = \frac{-0.039 - \sqrt{(0.039)^2 - 4(-3.24 \times 10^{-5})}}{2} = 8.137 \times 10^{-4} = [\text{H}_3\text{O}^+]$$

pH = 3.089

There is an easier way to do the equilibrium problem:

Here is a derivation that you may want to be familiar with:



$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

HA + A⁻
are general terms
for an acid
& conjugate base

Keep grouped take the log of both sides

$$\log K_a = \log H_3O^+ + \log \frac{[A^-]}{[HA]}$$

$$-\log K_a \quad -\log H_3O^+$$

$$-\log [H_3O^+] = -\log K_a + \log \frac{[A^-]}{[HA]}$$

Henderson Hasselbalch
Equation

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

try using this equation in place of the equilibrium step above:

$$0.0577 \text{ M } [HF]$$

$$0.0385 \text{ M } F^-$$

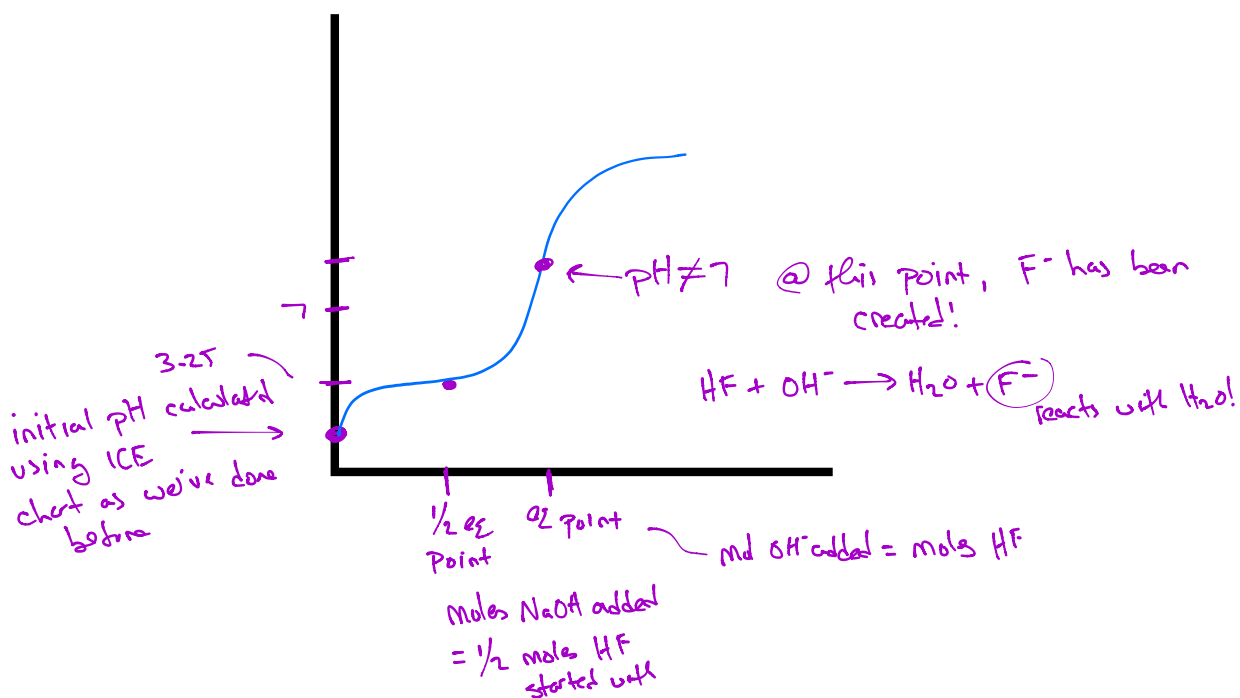
these are [A⁻]
+ [HA]
in the H-H equation

$$pH = 3.25 + \log \frac{0.0385}{0.0577}$$

$$pH = 3.25 + -0.1757$$

$$pH = 3.07$$

- the only difference is in rounding of the eq. prob.



This Henderson-Hasselbalch equation describes **BUFFERED** solutions.

Buffer: solution containing a weak acid AND its conjugate base

The buffer range is ± 1 pH unit of the pK_a !

↳ these are incredibly important in chemistry + biology because they are able to resist large changes in pH if H_3O^+ or OH^- is added.

Imagine a situation where you have 100 mL of 50 mM HF + 50 mM KF present =

- ① What is the pH of this solution?
- ② What is the pH if 5 mL of 100 mM HCl is added?
 - What species are present?
 - What Major species?
- ③ What is the pH + major species once 50 mL ^{100 mM} HCl is added?
- ④ pH + major species once 50 mL of 100 mM NaOH is added?

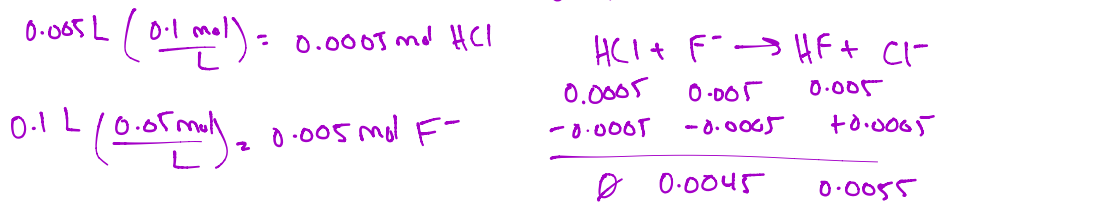
① pK_a of HF is 3.25 $pH = 3.25 + \log \frac{0.5}{0.5} = 3.25$

$A^- = 50 \text{ mM } F^-$
 $HA = 50 \text{ mM HF}$

When $[HA] = [A^-]$ $pH = pK_a$
 This is the 1/2 eq. point!

Species present: HF, F^- , K^+

② 5 mL 100 mM HCl added → stoichiometry problem!



$[HF] = \frac{0.0055}{0.105} = 0.0524 \text{ M}$

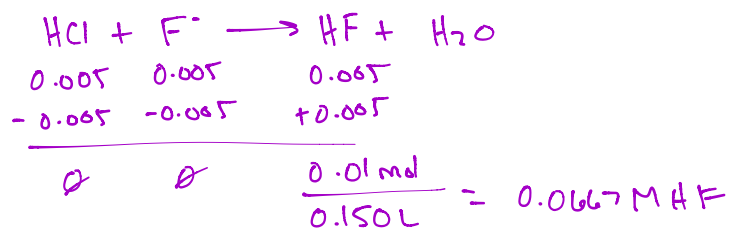
↑
new volume

$[F^-] = \frac{0.0045}{0.105} = 0.0429$

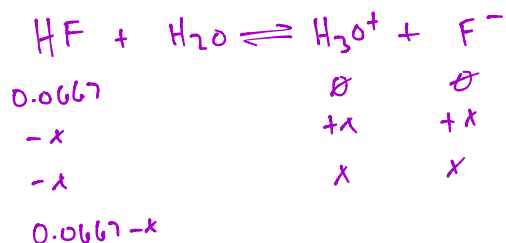
$pH = 3.25 + \log \frac{0.0429}{0.0524} = 3.16$

major species:
 K^+ , Cl^- , HF, F^-

③ 50 mL 100 mM HCl added. $0.05 \text{ L} \left(\frac{0.1 \text{ mol}}{\text{L}} \right) = 0.005 \text{ mol HCl}$



Now equilibrium!

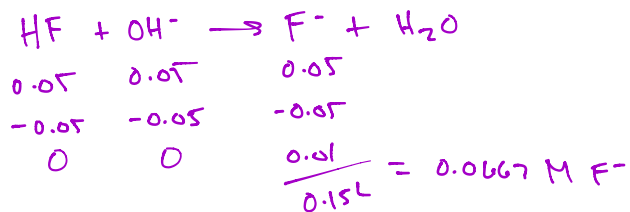


$$5.62 \times 10^{-4} = \frac{x^2}{0.0667-x} \rightarrow \text{quadratic: } x = 5.85 \times 10^{-3} = [\text{H}_3\text{O}^+]$$

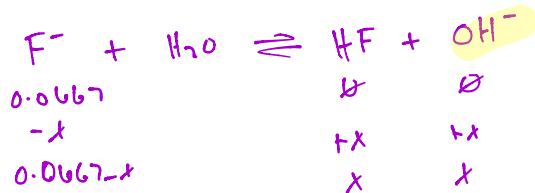
$\text{pH} = 2.23$

- What's important to recognize about this point is that the solution is no longer buffered! Adding more HCl makes the pH change significantly

④ adding 50 mL of 100 mM NaOH. This is the same situation as above: moles OH^- added = mol HF (acidic form of buffer)



Now equilibrium!



- need K_b ! $\text{p}K_b = 14 - 3.25$

$$\text{p}K_b = 10.75$$

$$K_b = 1.78 \times 10^{-11}$$

$$1.78 \times 10^{-11} = \frac{x^2}{0.0667-x}$$

$$\text{quadratic: } x = 1.09 \times 10^{-6} = [\text{OH}^-]$$

$$\text{pOH} = 5.96$$

$$\text{pH} = 14 - \text{pOH}$$

$$\text{pH} = 8.04$$

Major species: Na^+ , OH^- , F^- , H^+

Describe how to make a ^{100 mL} solution buffered at pH 5.20 from 1 M acetic acid and 1 M sodium acetate. The pK_a of acetic acid is 4.75. The total concentration of HA + A⁻ should be 100 mM.

① Determine ratio of A⁻: HA

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$5.20 = 4.75 + \log \frac{[\text{A}^-]}{[\text{HA}]} \quad \frac{[\text{A}^-]}{[\text{HA}]} = 2.81$$

② Note that A⁻ + HA = 100 mM

$$[\text{A}^-] = 2.81 [\text{HA}]$$

$$2.81 [\text{HA}] + [\text{HA}] = 100 \text{ mM}$$

$$3.81 [\text{HA}] = 100 \text{ mM}$$

$$[\text{HA}] = 26.46 \text{ mM}$$

$$[\text{A}^-] = 100 - 26.46 = 73.75 \text{ mM}$$

③ calculate volume of each stock solution:

$$(0.02646 \text{ M}) 100 \text{ mL} = 1.00 \text{ M } V$$

$$V = 2.646 \text{ mL HAe}$$

$$(0.07375 \text{ M}) (100 \text{ mL}) = 1.00 \text{ M } (V)$$

$$V = 7.375 \text{ mL Ac}^-$$

Take 2.646 mL of the stock acetic acid solution and 7.375 mL of the sodium acetate. Mix the together and dilute to 100 mL with H₂O (90 mL)