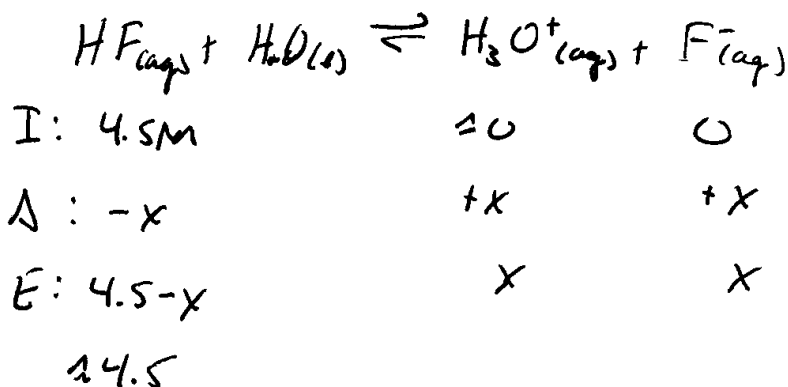


# CH302H HW8 Key

①

1. a)  $[HF] = \frac{0.45 \text{ moles}}{0.10 \text{ L}} = 4.5 \text{ M}$

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = 6.6 \times 10^{-4}$$



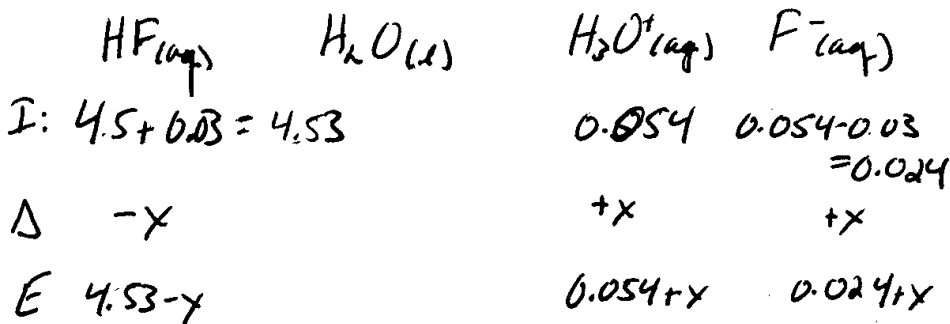
$$K_a = \frac{x^2}{4.5}$$

$$x = (4.5 K_a)^{1/2} = ((4.5)(6.6 \times 10^{-4}))^{1/2} = 0.054$$

$$[H_3O^+] = [F^-] = 0.054 \text{ M}; [HF] = 4.5 \text{ M}$$
$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{(1 \times 10^{-14})}{0.054} = 1.9 \times 10^{-13} \text{ M}$$

b) HCl has  $K_a = \text{large}$ , so this acid completely dissociates. There are many ways we could analyze this, but let's assume that 100% of those protons are picked up by  $F^-$  to make HF, which then dissociates to  $H_3O^+ + F^-$ .  $K_a(HF)$  does not change.

new ICE table:



Here the assumption that  $x \ll 4.53$  is probably still ok, but we cannot assume that  $x \ll 0.054$  or  $0.024$ . We are going to have to solve the quadratic.  $\rightarrow$

1/b) continued

(1.3)

$$K_a = \frac{(0.054+x)(0.024+x)}{4.53} = 6.6 \times 10^{-4}$$

$$0.0030 = 6.0013 + 0.078x + x^2$$

$$x^2 + 0.078x + -0.0017 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.078 \pm \sqrt{(0.078)^2 - 4(1)(-0.0017)}}{2(1)}$$

$$x = \frac{-0.078 \pm 0.114}{2} = \underline{0.0531}, -0.0669$$

↑  
this root doesn't make sense for this problem

$$\begin{aligned} [HF] &= 4.53 \\ [H_3O^+] &= 0.054 + 0.0531 = 0.11 \text{ M} \\ [F^-] &= 0.024 + 0.0531 = 0.077 \text{ M} \\ [OH^-] &= \frac{(1.0 \times 10^{-14})}{0.11} = 9.1 \times 10^{-14} \\ [Cl^-] &= 0.03 \text{ M} \end{aligned}$$

(c) the original soln. had ~~pH~~ pH = 1.3. After adding HCl, pH = 0.96. It's not a great buffer, but it's better than nothing.

2. Need buffer w/ pH = 8.2. From table 15.2, the two closest possibilities are HClO ( $K_a = 3.0 \times 10^{-8}$ ,  $pK_a = 7.53$ ) or

HCN ( $K_a = 6.17 \times 10^{-10}$ ,  $pK_a = 9.21$ ). Let's pick the closer one to start w/.

$$pH = pK_a - \log \frac{[HClO]}{[ClO^-]} ; \log \frac{[HClO]}{[ClO^-]} = pK_a - pH = 7.53 - 8.2 = -0.67$$

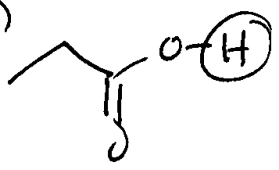
$$\frac{[HClO]}{[ClO^-]} = 0.21$$

We need more of the conjugate base than the conjugate acid, which makes sense based on our pH needs compared to  $pK_a$  options

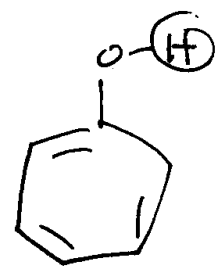
- We also need both of these species in relatively large excess, say

$$\underline{[HClO] = 0.10 M, [ClO^-] = 0.48 M}$$

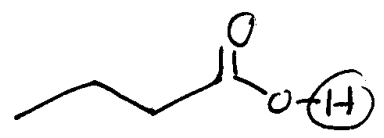
3. a)



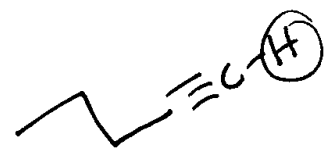
ethanoic acid



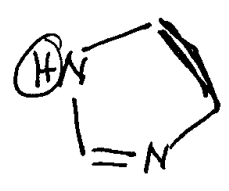
phenol



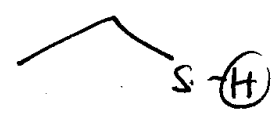
propanoic acid



pentyne



imidazole

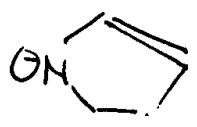


ethane thiol

\*NB: In most of these structures, the most acidic H atom is explicitly written in the structural shorthand. This is just coincidence, because we do not explicitly write out H atoms bonded to C. You always must include all H atoms when figuring out these problems

b) let's do the easiest 1st:

- pentyne <sup>deprotonation</sup> places a  $\ominus$  charge on a carbon = bad
- ethane thiol deprotonation places a  $\ominus$  charge on a S. This will not be as happy a molecule as a  $\ominus$  on a N or C.
- Both phenol + imidazole deprotonation place a  $\ominus$  charge on an electronegative atom. At first glance it might look like [O-]c1ccccc1 is more stable; however,

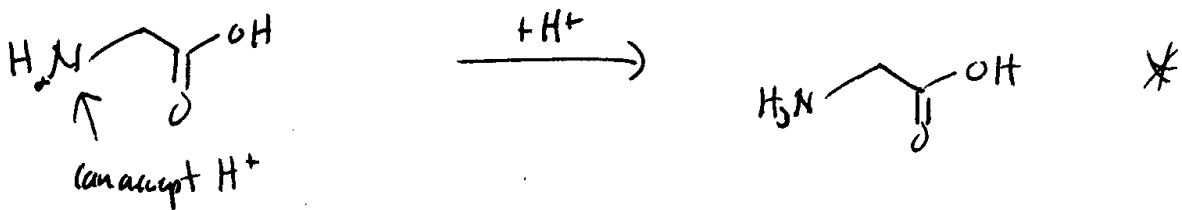
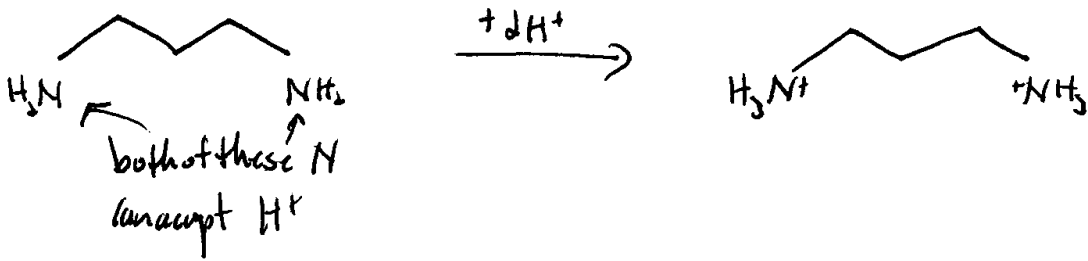
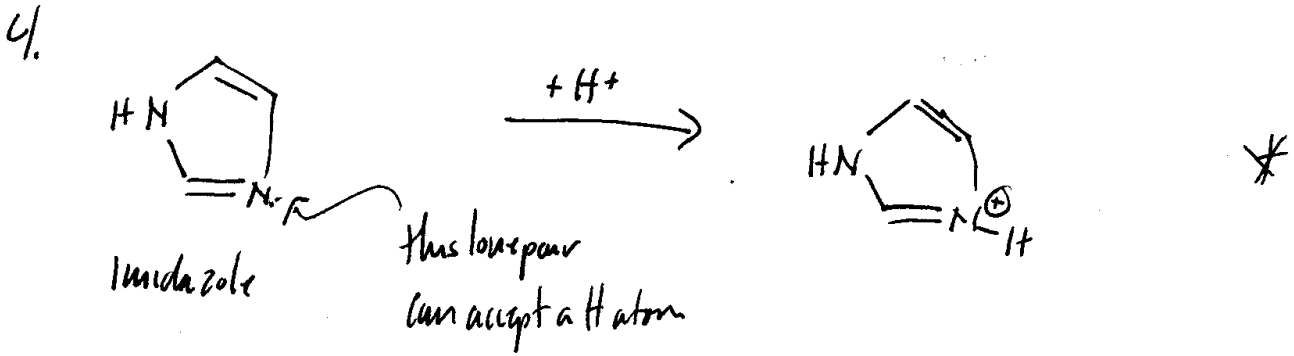


can share this  $\ominus$  charge w/ 1 more N atom, so this is actually the better candidate here  $\rightarrow$

3b) cont. - the two acids are the most happy when deprotonated, but which is better? We don't really have additional information to judge, so call them  $\approx$  same

In order of increasing pKa (i.e. decreasing Ka or acid strength)

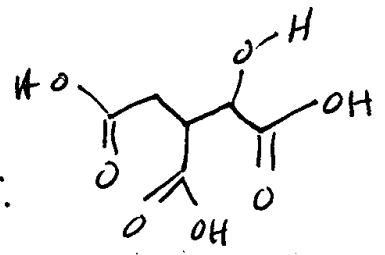
ethanoic acid & propanoic acid < imidazole < phenol < ethanol < pentane



\* - these molecules are amphoteric - can act as both an acid + a base

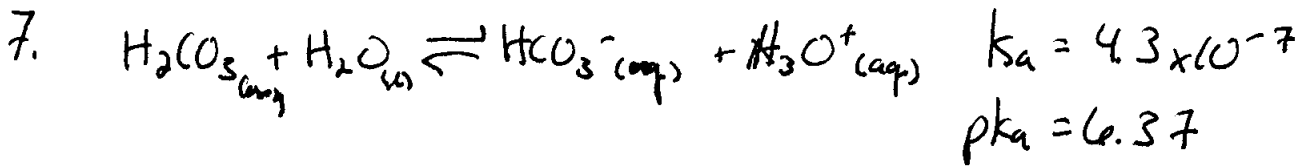
5. This is actually a very real-world problem. A solution of high conc. NaOH is great for titrations, but is very hard to make to a needed degree of accuracy because it is so hygroscopic. The solution to your problem is make a solution of NaOH to as close as 0.5 M as possible, then measure its exact concentration by titrating w/ a solution of strong acid such as HCl(aq).

6. Lemon contains citric acid:



which has 4 titratable protons:

these can neutralize the basic N atom of the foul-smelling amines.



Let's look at both endpoints:

$$pH = 7.35$$

$$pH = pK_a - \log \frac{[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]}$$

$$\log \frac{[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]} = pK_a - pH = 6.37 - 7.35 = -0.98$$

$$\frac{[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]} = 0.10 \quad \text{So } 10 \times \text{HCO}_3^- \text{ needed}$$


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$$pH = 7.45$$

$$\log \frac{[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]} = 6.37 - 7.45 = -1.08$$

$$\frac{[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]} = 0.083 \quad \text{So slightly more than } 10 \times \text{HCO}_3^- \text{ needed}$$


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