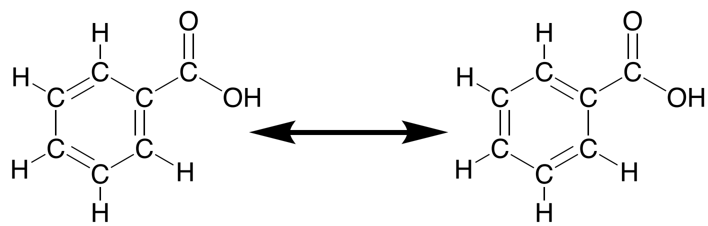
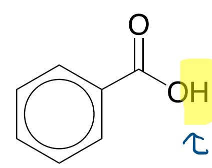
Separations in organic synthesis

A. Next year many of you will take organic chemistry, together with its lab. You'll take advantage of acid-base chemistry to help you purify molecules. One of the first labs in CHEM 2203 (Organic Chemistry I Lab) has students separating benzoic acid from a neutral compound (9-fluorenone, which rather surprisingly does <u>not</u> contain fluorine!) by using acid-base chemistry.

Benzoic acid (C_6H_5COOH) has many uses, from the practical (as a food preservative) to the pretty (as the "snow" in a snow globe). Benzoic acid is fully represented by the resonance structures:



but organic chemists will use the following shorthand:



acidic hydrogen

The pK_a for benzoic acid is 4.20 at 25 °C.

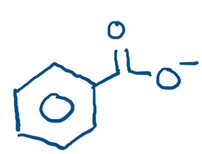
First, give the value of K_a for benzoic acid, write the chemical equation that corresponds to that equilibrium constant, and formulate the equilibrium expression quantitated by the K_a.

$$K_a = 10^{-4.20} = 6.3 \times 10^{-5}$$

$$C_6H_5COOH\,(aq) + H_2O\,(l) \rightleftarrows C_6H_5COO^-\,(aq) + H_3O^+\,(aq)$$

$$K_a = \frac{[C_6H_5COO^-][H_3O^+]}{[C_6H_5COOH]}$$

B. Sketch the conjugate base of benzoic acid. You can start with the shorthand form at right above. Why do you think, of the six H atoms in benzoic acid, the organic chemists only bother drawing that one?



The organic chemists draw that hydrogen because that's the acidic one.

C. If you made 1.00 L of a 0.200 M solution of benzoic acid in water at 25 °C, what would be the concentrations of (still un-ionized) benzoic acid, its ionized conjugate base, H_3O^+, and OH^-? What would be the pH of the solution? Be sure to show all your work.

$$C_6H_5COOH(aq) + H_2O(l) \rightleftarrows C_6H_5COO^-(aq) + H_3O^+(aq)$$

	C_6H_5COOH	H_2O	$C_6H_5COO^-$	H_3O^+
I	0.200	—	0	0
C	$-x$	—	$+x$	$+x$
E	$0.200-x$ ≈ 0.200	—	$+x$	$+x$

x is small because K is small

$$K_a = \frac{[C_6H_5COO^-][H_3O^+]}{[C_6H_5COOH]} = \frac{(x)(x)}{0.200-x} \approx \frac{(x)(x)}{0.200} = 6.3 \times 10^{-5}$$

$$x^2 = 1.26 \times 10^{-5}$$

$$x = [H_3O^+] = 3.55 \times 10^{-3}\ M$$

[benzoic acid] = $[C_6H_5COOH] \approx 0.200\ M$ (actually $0.200 - (3.55 \times 10^{-3}\ M) = 0.196\ M$)

ionized conjugate base = $[C_6H_5COO^-] = 3.55 \times 10^{-3}\ M$

$[H_3O^+] = 3.55 \times 10^{-3}\ M$

$[H_3O^+] \cdot [OH^-] = 1.00 \times 10^{-14}$

so $[OH^-] = \frac{1.00 \times 10^{-14}}{[H_3O^+]} = \frac{1.00 \times 10^{-14}}{3.55 \times 10^{-3}\ M} = 2.82 \times 10^{-12}\ M$

$pH = -\log[H_3O^+] = 2.45$

D. If you add 0.050 moles of NaOH to the solution from part (C), what would be the resulting concentrations of benzoic acid and its conjugate base? What would be the solution pH? Be sure to show all your work.

$NaOH \rightarrow Na^+(aq) + OH^-(aq)$ (strong acid: full dissociation)

0.050 moles

$C_6H_5COOH(aq) + OH^-(aq) \rightarrow C_6H_5COO^-(aq) + H_2O(l)$

start 0.200 moles | 0 moles

end 0.200 − 0.050 = 0.150 moles | 0 + 0.050 = 0.050 moles

$$[C_6H_5COOH] = \frac{0.200 - 0.050 \text{ moles}}{1L} = \frac{0.150 \text{ moles}}{1L} = 0.150M$$

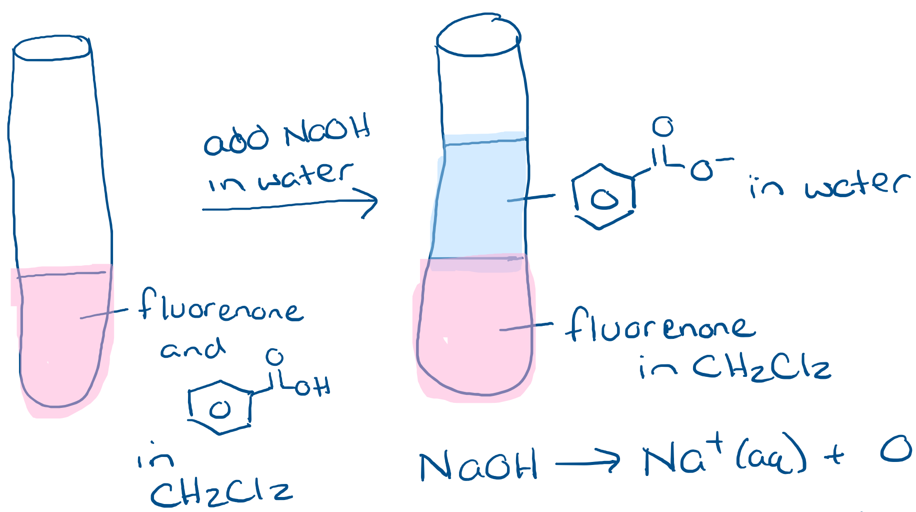
$$[C_6H_5COO^-] = \frac{0 + 0.050 \text{ moles}}{1L} = \frac{0.050 \text{ moles}}{1L} = 0.050M$$

$$pH = pKa + \log\frac{[base]}{[acid]} = 4.20 + \log\frac{0.050M}{0.150M}$$

$$= 4.20 + (-0.477)$$

$$= \boxed{3.72}$$

E. In the CHEM 2203 lab, students separate a mixture of (neutral and essentially non-polar) 9-fluorenone and benzoic acid. The mixture starts out in the solvent methylene chloride (CH_2Cl_2: it's a little bit polar but not nearly as polar as water). In this lab students add excess NaOH in water to the mixture. The water isn't miscible with the CH_2Cl_2 solvent, so it makes two layers. Explain using drawings <u>and</u> chemical reactions how adding NaOH in water helps to separate 9-fluorenone and benzoic acid.



$NaOH \rightarrow Na^+(aq) + OH^-(aq)$

$C_6H_5COOH(aq) + OH^-(aq) \rightarrow C_6H_5COO^-(aq) + H_2O(l)$

$C_6H_5COO^-$ (is more soluble in the water than in CH_2Cl_2