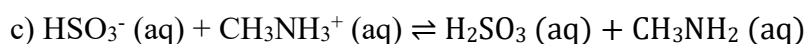
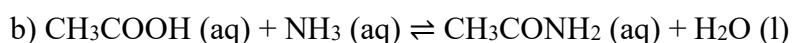
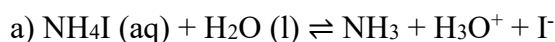


**Preliminary remark when approaching acid-base chemistry problems in CH-100:**

At the level of units, please be reminded that  $1 \text{ M} = 1 \text{ mol/L}$  and that we accept that exact expression of the equilibrium constant should be written using **activities**, as opposed to **concentrations**. We make the approximation that the numerical values of concentrations expressed in mol/L are equal to the activities in a dilute system. Thus, each concentration should be divided by  $c_0 = 1 \text{ mol/L}$  to obtain a dimensionless activity value for each reagent, which can then be used to calculate the equilibrium constant. Since this does not change the numerical result of acid–base calculations, we will ignore this formal aspect in the exercise solutions.

---

**Exercise 1.** Which of the following can be classified as reactions of Brønsted-Lowry acid and bases? For those that can be classified so, identify which reactant is the acid and which one is the base by Brønsted-Lowry definition. *Hint: It may help to write the net ionic equations following dissolution in water.*



**Solution:**

a) First, write the net ionic species:

- $\text{NH}_4\text{I}(\text{aq}) \rightarrow \text{NH}_4^+ + \text{I}^-$
- If we exclude  $\text{I}^-$  ions, reaction becomes:  $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$

Classification: YES, this is a Brønsted–Lowry acid–base reaction.

Identify acid/base:

- $\text{NH}_4^+$  donates a proton  $\rightarrow$  Brønsted–Lowry acid
- $\text{H}_2\text{O}$  accepts a proton  $\rightarrow$  Brønsted–Lowry base

b) Given the identity of some components one can assume that this is acid/base reaction:

$\text{CH}_3\text{COOH}$  = acetic acid

$\text{NH}_3$  = weak base

However, the products is:  $\text{CH}_3\text{CONH}_2$  (acetamide) +  $\text{H}_2\text{O}$

This is not the result of a simple proton transfer, but a different chemical reaction.

Classification: NOT a Brønsted–Lowry acid–base reaction.

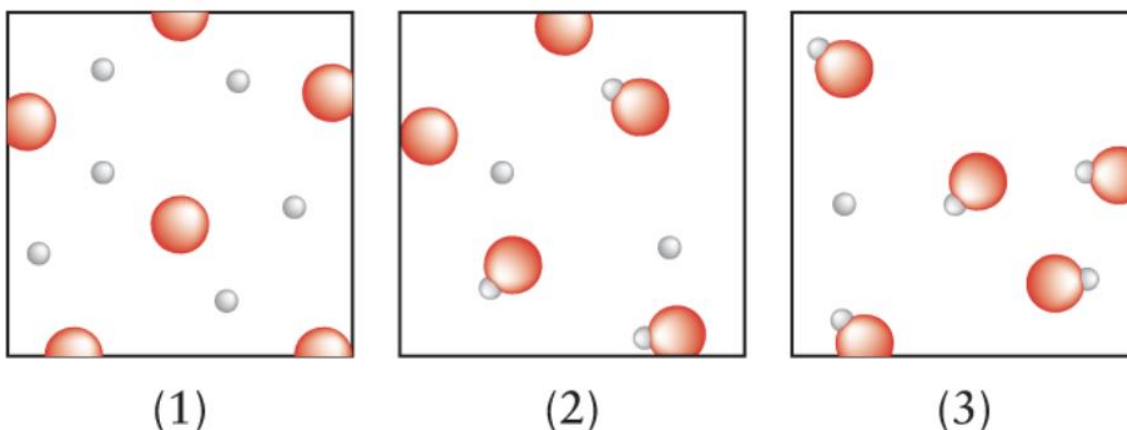
c) This reaction involves an exchange of protons.

Classification: YES, this is a Brønsted–Lowry acid–base reaction.

Identify acid/base:

- $\text{CH}_3\text{NH}_3^+ \rightarrow \text{CH}_3\text{NH}_2$  (loses  $\text{H}^+$ )  $\rightarrow$  Brønsted–Lowry acid
- $\text{HSO}_3^- \rightarrow \text{H}_2\text{SO}_3$  (gains  $\text{H}^+$ )  $\rightarrow$  Brønsted–Lowry base

**Exercise 2.** The images shown represent the solutes in the solutions of three acids (water molecules are not shown, hydrogen atoms and hydronium ions are represented by small gray spheres and conjugate bases are represented by large red spheres).



- a) Which acid is strong acid?
- b) Which acid has the strongest conjugate base?
- c) Which acid has the highest  $pK_a$

**Solution:**

- a) Solution 1 features the strong acid as evidenced by the absence of any acid molecules (= linked gray and orange spheres). Hydrogens are completely dissociated.
- b) Solution 3 features the acid with the strongest conjugate base. The stronger the conjugate base  $\rightarrow$  the more it pushes the equilibrium towards the production of acid molecules (= linked gray and orange spheres).
- c) Solution 3 has the highest  $pK_a$  value corresponding to the lowest  $pK_b$  for the conjugate base.  
 The higher the  $pK_a \rightarrow$  the weaker the acid.  
 The lower the  $pK_b \rightarrow$  the stronger the base (conjugate)

**Exercise 3.** In the table below you will find several examples of weak acids and bases with their  $K$  constants under aqueous conditions at  $25^\circ\text{C}$ . For each example, there are fields corresponding to the acid or base form as well as its conjugate base or acid, respectively.

Substance	Type	$K_a$	$K_b$	$pK_a$	$pK_b$
HA <sub>(1)</sub>	Weak acid	$3.2 \times 10^{-6}$			
HA <sub>(2)</sub>	Weak acid			4.75	
B <sub>(1)</sub>	Weak base		$1.8 \times 10^{-5}$		
B <sub>(2)</sub>	Weak base				5.10

- a) For each substance, determine any missing  $K_a/K_b$  or  $pK_a/pK_b$  values.
- b) Which acid is stronger among HA<sub>(1)</sub> and HA<sub>(2)</sub>. Explain your rationale.
- c) Which base is stronger among B<sub>(1)</sub> and B<sub>(2)</sub>. Explain your rationale.

**Solution:**

a) The solution involves using:

- Relationship between K to the corresponding pK:  $pK = -\log_{10}(K)$
- Relationship between  $K_a$  and  $K_b$  as well as  $pK_a$  and  $pK_b$  for conjugate pairs:

$$K_a \times K_b = 10^{-14}$$

$$pK_a + pK_b = 14$$

Substance	Type	$K_a$	$K_b$	$pK_a$	$pK_b$
HA <sub>(1)</sub>	Weak acid	$3.2 \times 10^{-6}$	$3.13 \times 10^{-9}$	<b>5.495</b>	<b>8.505</b>
HA <sub>(2)</sub>	Weak acid	$1.78 \times 10^{-5}$	$5.62 \times 10^{-10}$	<b>4.75</b>	<b>9.25</b>
B <sub>(1)</sub>	Weak base	$5.57 \times 10^{-10}$	$1.8 \times 10^{-5}$	<b>9.255</b>	<b>4.745</b>
B <sub>(2)</sub>	Weak base	$1.26 \times 10^{-9}$	$7.94 \times 10^{-6}$	<b>8.90</b>	<b>5.10</b>

b) Acids are compared based on their  $K_a$  or  $pK_a$  values

higher  $K_a$  → stronger acid

lower  $pK_a$  → stronger acid

Therefore HA<sub>(2)</sub> is stronger than HA<sub>(1)</sub>.

c) Bases are compared based on their  $K_b$  or  $pK_b$  values

higher  $K_b$  → stronger base

lower  $pK_b$  → stronger base

Therefore B<sub>(1)</sub> is stronger than B<sub>(2)</sub>.

**Exercise 4.** Determine how the pH of pure water at 25 °C changes when sodium hydroxide (NaOH), a strong base, is dissolved to produce a final concentration:

a)  $2 \cdot 10^{-2}$  mol/L

b)  $2 \cdot 10^{-8}$  mol/L

$K_w$  of water at 25 °C is  $1 \cdot 10^{-14}$ .

**Solution**

a) NaOH is a strong base and that means that the entire amount of  $OH^-$  ions will be released into the solution upon dissolving. Given that the total amount of base ( $2 \cdot 10^{-2}$  mol/L) is much higher than the equilibrium concentrations of  $H_3O^+$  and  $OH^-$  at room temperature ( $1 \cdot 10^{-7}$  mol/L), the contribution of water to the equilibrium  $OH^-$  amount can be ignored.

Therefore, we can just use the pOH and pH equations as shown below:

$$[OH^-] = 2.0 \times 10^{-2} \text{ M}$$

$$pOH = -\log(2.0 \times 10^{-2}) = 1.699$$

$$pH = 14.00 - 1.699 \approx 12.30$$

b) At acid or base concentrations that approach the equilibrium concentrations of  $H_3O^+$  and  $OH^-$  at room temperature ( $1 \cdot 10^{-7}$  mol/L), the contribution of these species in solution cannot be ignored. In this case

we have  $2 \cdot 10^{-8}$  mol/L which is actually below the concentration of  $\text{OH}^-$  in pure water. So we should not just take this concentration as the total  $\text{OH}^-$ , but rather treat this challenge similar to how we did the calculations for weak acids and bases (in this case  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  from water representing the weak acid-base pair).

The initial concentrations just after mixing (before re-equilibration) are:

$$\begin{aligned} - [\text{H}_3\text{O}^+] &= 1 \cdot 10^{-7} \text{ mol/L} \\ - [\text{OH}^-] &= 1 \cdot 10^{-7} + 2 \cdot 10^{-8} \text{ mol/L} = 1.2 \cdot 10^{-7} \text{ mol/L} \end{aligned}$$

Let's setup the table as we did in class with just 2 reagents in this case:

	$\text{H}_3\text{O}^+$	$\text{OH}^-$
<b>Initial</b>	$1 \cdot 10^{-7}$	$1 \cdot 10^{-7} + 2 \cdot 10^{-8}$
<b>Change</b>	-x	-x
<b>Equilibrium</b>	$1 \cdot 10^{-7} - x$	$1.2 \cdot 10^{-7} - x$

Part of the  $\text{H}_3\text{O}^+$  will react with  $\text{OH}^-$ , producing x mol/L of water molecules. Hence, the equilibrium concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  will be changed by x.

The equilibrium concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  are connected by Kw:

$$\begin{aligned} [\text{H}_3\text{O}^+]_{\text{eq}} \cdot [\text{OH}^-]_{\text{eq}} &= K_w \\ (1 \cdot 10^{-7} - x) \cdot (1.2 \cdot 10^{-7} - x) &= 1 \cdot 10^{-14} \\ x^2 - 2.2 \cdot 10^{-7} \cdot x + 0.2 \cdot 10^{-14} &= 0 \end{aligned}$$

The solutions of quadratic equation are:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Where: a = 1; b =  $2.2 \cdot 10^{-7}$ ; c =  $0.2 \cdot 10^{-14}$

This equation produces 2 solutions for x:

$$\begin{aligned} x_1 &= 2.1 \cdot 10^{-7} \rightarrow \text{This would make the } [\text{H}_3\text{O}^+]_{\text{eq}} \text{ and } [\text{OH}^-]_{\text{eq}} \text{ value negative. NOT VALID!} \\ x_2 &= 9.5 \cdot 10^{-9} \rightarrow \text{This would make the } [\text{H}_3\text{O}^+]_{\text{eq}} \text{ and } [\text{OH}^-]_{\text{eq}} \text{ value positive. VALID!} \end{aligned}$$

So we take the  $x_2$  as the valid solution of this equation and return to our table above:

	$\text{H}_3\text{O}^+$	$\text{OH}^-$
<b>Initial</b>	$1 \cdot 10^{-7}$	$1 \cdot 10^{-7} + 2 \cdot 10^{-8}$
<b>Change</b>	$-9.5 \cdot 10^{-9}$	$-9.5 \cdot 10^{-9}$
<b>Equilibrium</b>	$1 \cdot 10^{-7} - 9.5 \cdot 10^{-9}$	$1.2 \cdot 10^{-7} - 9.5 \cdot 10^{-9}$
<b>Equilibrium =</b>	$9.05 \cdot 10^{-8}$	$1.105 \cdot 10^{-7}$

We can use  $[\text{H}_3\text{O}^+]_{\text{eq}}$  concentration to calculate the resulting pH:

$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+]_{\text{eq}} \approx 7.043$$

**Exercise 5.** In the table below you will find several examples of Brønsted acids and bases:

	Conj. Pair 1	Conj. Pair 2	Conj. Pair 3	Conj. Pair 4
<b>Acidic form</b>	HCO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>		
<b>Basic form</b>			HSO <sub>3</sub> <sup>-</sup>	HS <sup>-</sup>
<b>K<sub>a</sub> at 25°C</b>	4,7 · 10 <sup>-11</sup>		1,6 · 10 <sup>-2</sup>	
<b>pK<sub>a</sub> at 25°C</b>		9.25		7.00

a) Please complete the missing fields in the table.

b) For each conjugate pair, determine if the predominant form (= present at higher concentration) will be acidic or basic at:

pH=3

pH=7

pH=11

### Solution

a)

	Conj. Pair 1	Conj. Pair 2	Conj. Pair 3	Conj. Pair 4
<b>Acidic form</b>	HCO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	H <sub>2</sub> SO <sub>3</sub>	H <sub>2</sub> S
<b>Basic form</b>	CO <sub>3</sub> <sup>2-</sup>	NH <sub>3</sub>	HSO <sub>3</sub> <sup>-</sup>	HS <sup>-</sup>
<b>K<sub>a</sub> at 25°C</b>	4.7 · 10 <sup>-11</sup>	5.6 · 10 <sup>-10</sup>	1.6 · 10 <sup>-2</sup>	1.0 · 10 <sup>-7</sup>
<b>pK<sub>a</sub> at 25°C</b>	10.33	9.25	1.80	7.00

b)

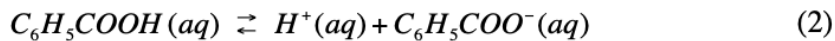
	Conj. Pair 1	Conj. Pair 2	Conj. Pair 3	Conj. Pair 4
<b>pH = 3</b>	HCO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	HSO <sub>3</sub> <sup>-</sup>	H <sub>2</sub> S
<b>pH = 7</b>	HCO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	HSO <sub>3</sub> <sup>-</sup>	H <sub>2</sub> S and HS <sup>-</sup>
<b>pH = 11</b>	CO <sub>3</sub> <sup>2-</sup>	NH <sub>3</sub>	HSO <sub>3</sub> <sup>-</sup>	HS <sup>-</sup>

If pH < pK<sub>a</sub> → The acidic form is more prevalent  
 If pH = pK<sub>a</sub> → Both forms will be at equal concentration  
 If pH > pK<sub>a</sub> → The basic form is more prevalent

**Exercise 6.** 0.02 M benzoic acid (C<sub>6</sub>H<sub>5</sub>COOH) was dissolved in water and the resulting solution has a pH of 2.96. Calculate the pK<sub>a</sub> of this acid.

### Solution:

The overall equations for the two equilibria that occur in solution are:



Benzoic acid is largely responsible for the generation of  $H^+$  in solution, because it is at a significantly higher concentration than  $H_2O$ . This assumption is true until the concentration drops below  $<10^{-6}$  mol/L, at which point the contribution of water should be added to the calculations.

First, we can setup the table to describe the initial and final concentrations of each species:

	$C_6H_5COOH$	$H^+$	$C_6H_5COO^-$
<b>Initial</b>	0.02	0	0
<b>Change</b>	$-x$	$+x$	$+x$
<b>Equilibrium</b>	$0.02 - x$	$x$	$x$

Considering the data from the text, and the above equilibrium equations we get:

$$pH = 2,96 \quad \Rightarrow \quad [H^+] = 10^{-pH} = 10^{-2,96} = 1,1 \cdot 10^{-3} M$$

$$[C_6H_5COO^-] = [H^+] = 1,1 \cdot 10^{-3} M$$

Now it remains to determine  $[C_6H_5COOH]$ . The concentration of this species must decrease since the acid dissociates. If we apply this to our table we get:

	$C_6H_5COOH$	$H^+$	$C_6H_5COO^-$
<b>Initial</b>	0.02	0	0
<b>Change</b>	$-1,1 \cdot 10^{-3}$	$1,1 \cdot 10^{-3}$	$1,1 \cdot 10^{-3}$
<b>Equilibrium</b>	$1,89 \cdot 10^{-2}$	$1,1 \cdot 10^{-3}$	$1,1 \cdot 10^{-3}$

At this point you can calculate the  $K_a$  and  $pK_a$  values directly:

$$K_a = \frac{[C_6H_5COO^-][H^+]}{[C_6H_5COOH]} = \frac{(1,1 \cdot 10^{-3})^2}{1,89 \cdot 10^{-2}} = 6,4 \cdot 10^{-5}$$

$$pK_a = -\log K_a = 4,19$$

You could have also used the HH equation (solved for  $pK_a$ ).

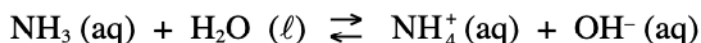
### Exercise 7.

a) Ammonia ( $NH_3$ ) was dissolved in 1L of water to the final concentration of 0.1 mol/L. Considering that the  $pK_a(NH_4^+) = 9.25$ , calculate the resulting pH of the solution.

b) If 1L of pure water was added to this solution while maintain the same temperature, what would be the effect on pH.

**Solution:**

To resolve this problem we have to consider the  $\text{NH}_3/\text{NH}_4^+$  conjugate pair in aqueous solution.



Where  $\text{NH}_3$  is the base, while  $\text{NH}_4^+$  is a conjugate acid. Given that the  $\text{NH}_3$  was used to make this solution it is appropriate to use  $K_b$  to characterize the equilibrium above (although the solution can also be reached using  $K_a$  of  $\text{NH}_4^+$ ). From the relationship between conjugate pairs we can get:

$$\text{p}K_b = 14 - \text{p}K_a = 4.75$$

$$\text{p}K_b = -\log K_b \quad \bullet \quad K_b = 10^{-4.75} = 1,78 \cdot 10^{-5}$$

Now let's see what the equilibrium concentrations of all non- $\text{H}_2\text{O}$  components will be. We can setup a table as shown below:

	$\text{NH}_3$	$\text{OH}^-$	$\text{NH}_4^+$
<b>Initial</b>	0.1	0	0
<b>Change</b>	$-x$	$+x$	$+x$
<b>Equilibrium</b>	$0.1 - x$	$x$	$x$

Here we use the equation for  $K_b$ , based on the conjugate equilibrium reaction shown above and the estimated equilibrium concentrations from the table:

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{0,1 - x} = 1,78 \cdot 10^{-5}$$

The exact solution will require dealing with the quadratic equation, but we can also use the assumption that  $[\text{NH}_3]_{\text{initial}} \gg x$ , which is true for weak acids and bases. This simplifies the solution to:

$$x = (K_b \cdot [\text{NH}_3]_{\text{initial}})^{1/2} = 1.33 \cdot 10^{-3} \quad \text{-->} \quad [\text{OH}^-] = 1.33 \cdot 10^{-3} \text{ mol/L}$$

From here, we can calculate the pOH and pH values as:

$$\text{pOH} = -\log [\text{OH}^-] = 2.88$$

$$\text{pH} = 14 - \text{pOH} = 11.12$$

b) We can follow the same principle as in (a). Upon addition of water, the equilibrium concentrations of all reagents will change but they will still be connected by the same  $K_b$ . What is important to note is that the new equilibrium concentrations will not simply be  $\frac{1}{2}$  of the previous ones.

To solve this problem, we must calculate the effect of dilution on the concentration of all reagents. This can be done by using the previous equilibrium values (calculated in (a) for 1L) and adjusting for the dilution effect in a table, but this would make the calculations a bit complicated. A simpler way of solving this is to realize that it is in fact an equilibrium and therefore it does not matter whether the additional 1L of water was added at the beginning or later. The  $\text{NH}_3/\text{NH}_4^+$  components would reach the same equilibrium concentrations either way.

So basically we can redo the same calculations as in (a), but we just have to consider that now we have 2L of water instead of 1L. That means that the new “starting” concentration of  $\text{NH}_3$  is:

$$[\text{NH}_3]_{\text{diluted}} \cdot V_{\text{diluted}} = [\text{NH}_3]_{\text{initial}} \cdot V_{\text{initial}}$$

$$[\text{NH}_3]_{\text{diluted}} = [\text{NH}_3]_{\text{initial}} \cdot V_{\text{initial}} / V_{\text{diluted}} = 0.05 \text{ mol/L}$$

If we setup the same table and the same equation as show in (a), we will get:

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{0,05 - x} = 1,78 \cdot 10^{-5}$$

Solving for x with the same approximation as in (a) we get:

$$x = (K_b \cdot [\text{NH}_3]_{\text{initial}})^{1/2} = 9.43 \cdot 10^{-4} \quad \text{-->} \quad [\text{OH}^-] = 9.43 \cdot 10^{-4} \text{ mol/L}$$

From here, we can calculate the pOH and pH values as:

$$\begin{aligned} \text{pOH} &= -\log [\text{OH}^-] = 3.03 \\ \text{pH} &= 14 - \text{pOH} = 10.97 \end{aligned}$$

The solution is less basic (lower pH, higher pOH) compared to more concentrated solution above.

**Exercise 8.** Consider 100 mL of an aqueous solution containing  $\text{CH}_3\text{COO}^-\text{Na}^+$  at the concentration of 0.2 mol/L. Assume that the salt has completely dissolved into ions in water.

- What is the pH of the resulting solution?
- Determine the pH of the solution after the addition of 0.1 g of sodium hydroxide (NaOH). Assume negligible effect on the total volume of the solution.
- What will be the change in pH following the addition of 1 L of pure water ( $\text{H}_2\text{O}$ ) to the solution resulting from b).

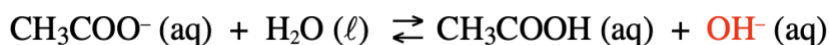
$\text{pK}_a(\text{CH}_3\text{COOH}) = 4.75$   
 $\text{MW}(\text{NaOH}) = 40 \text{ g/mol}$ .

### Solution

Assuming the full ionization of  $\text{CH}_3\text{COONa}$  the following species are generated:



As discussed in class the resulting metallic ions (e.g.,  $\text{Na}^+$ ) do not display any significant basic or acidic properties and  $\text{Na}^+$  will therefore not contribute to the pH equilibrium. The only buffering effect will come from the anion of  $\text{CH}_3\text{COO}^-$ , similar to the example in class:



In this case the  $\text{CH}_3\text{COO}^-$  ion will serve as a base ( $K_b$ ) while  $\text{CH}_3\text{COOH}$  will serve as a conjugate acid ( $K_a$ ). Given that the equilibrium above, the easiest approach is to first calculate the  $K_b$  for  $\text{CH}_3\text{COO}^-$ :

$$\text{p}K_a + \text{p}K_b = 14$$

$$\text{p}K_b = 14 - 4,75 = 9,25 \quad \Rightarrow \quad K_b = 5,62 \cdot 10^{-10}$$

Now let's see what the equilibrium concentrations of all non- $\text{H}_2\text{O}$  components from the reaction described above will be. We can setup a table as shown below:

	$\text{CH}_3\text{COO}^-$	$\text{OH}^-$	$\text{CH}_3\text{COOH}$
<b>Initial</b>	0.2	0	0
<b>Change</b>	$-x$	$+x$	$+x$
<b>Equilibrium</b>	$0.2 - x$	$x$	$x$

Considering the equation for  $K_b$ :

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

We can apply the numbers and get:

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{x^2}{0,2 - x} = 5,62 \cdot 10^{-10}$$

The exact solution will require dealing with the quadratic equation, but we can also use the assumption that  $[\text{CH}_3\text{COO}^-]_{\text{initial}} \gg x$ , which is true for weak acids and bases. This simplifies the solution to:

$$x = (K_b \cdot [\text{CH}_3\text{COO}^-]_{\text{initial}})^{1/2} = 1,06 \cdot 10^{-5} \quad \rightarrow \quad [\text{OH}^-] = 1,06 \cdot 10^{-5} \text{ mol/L}$$

From here, we can calculate the pOH and pH values as:

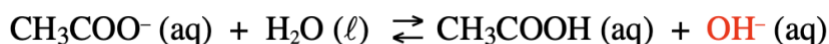
$$\text{pOH} = -\log [\text{OH}^-] = 4,97$$

$$\text{pH} = 14 - \text{pOH} = 9,03$$

b) NaOH is a strong base which completely dissociates in water solutions, thereby releasing an equivalent concentration of  $\text{OH}^-$  ions as the starting concentration of the NaOH. However, in this case it is added as a solid with negligible effects on total volume. So first we must calculate the concentration of solubilized NaOH ( $=\text{OH}^-$ ), considering the 100 ml (= 0.1 L) volume:

$$c_{\text{OH}^-} = \frac{0,1 \text{ g}}{40 \text{ g mol}^{-1} \cdot 0,1} = 2,5 \cdot 10^{-2} \text{ mol L}^{-1}$$

We have the same acid-base reaction equilibrium as above:



The concentration of  $\text{OH}^-$  has increased compared to start of the experiment thereby altering the previous equilibrium. However, similar to the exercise before, the easiest way to solve this problem is to realize that due to the nature of equilibrium state in similar acid-base reactions, the time of addition of different chemical components does not influence the end-result. At a given temperature, the equilibrium will be defined by the corresponding  $K_b$  and  $K_a$  values and the concentrations of different reagents will adjust accordingly.

So we can assume the same starting concentration for  $\text{CH}_3\text{COO}^-$  as at the beginning of the experiment and just add the new 0.025 mol/L for  $\text{OH}^-$ . The concentration table looks like:

	$\text{CH}_3\text{COO}^-$	$\text{OH}^-$	$\text{CH}_3\text{COOH}$
<b>Initial</b>	0.2	0.025	0
<b>Change</b>	-x	+x	+x
<b>Equilibrium</b>	$0.2 - x$	$0.025 + x$	x

So if we apply these numbers into the equation for  $K_b$  (assuming  $[\text{CH}_3\text{COO}^-] \gg x$ ) we get,

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{(0,025 + x)x}{0,2 - x} \approx \frac{0,025x}{0,2} = 5,62 \cdot 10^{-10}$$

Solving for x:

$$x = 4.5 \cdot 10^{-9} \quad \rightarrow \quad [\text{OH}^-] = 0.025 \text{ mol/L} + 4.5 \cdot 10^{-9} \text{ mol/L} \approx 0.025 \text{ mol/L}$$

From here, we can calculate the pOH and pH values as:

$$\begin{aligned} \text{pOH} &= -\log [\text{OH}^-] = 1.6 \\ \text{pH} &= 14 - \text{pOH} = 12.4 \end{aligned}$$

Following the addition of 0.1g of NaOH into the 100 mL solution of  $\text{CH}_3\text{COONa}$ , the pH changed from 9.03 to 12.4. Interestingly, the contribution of  $\text{OH}^-$  ions produced by the  $\text{CH}_3\text{COO}^-/\text{CH}_3\text{COOH}$  equilibrium was very low compared to NaOH.

c) Upon addition of water, the equilibrium concentrations of all reagents will change but they will still be connected by the same  $K_b$ . What is important to note is that the new equilibrium concentrations will not simply be 1/11 of the previous ones. So we have to setup the table assuming the new volume of 1.1 L and the same absolute amounts of reagents as in (b).

For all reagents we can recalculate the “starting” concentrations as:

$$[c]_{\text{diluted}} \cdot V_{\text{diluted}} = [c]_{\text{initial}} \cdot V_{\text{initial}}$$

Which results in:

	CH <sub>3</sub> COO <sup>-</sup>	OH <sup>-</sup>	CH <sub>3</sub> COOH
<b>Initial</b>	0.018	0.0023	0
<b>Change</b>	-x	+x	+x
<b>Equilibrium</b>	0.018 - x	0.0023 + x	x

Then we apply these values into the same Kb equation as above:

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{(0,0023 + x)x}{0,018 - x} \approx \frac{0,0023 \cdot x}{0,018} = 5,62 \cdot 10^{-10}$$

Solving for x:

$$x = 4.4 \cdot 10^{-9} \quad \rightarrow \quad [\text{OH}^-] = 0.0023 \text{ mol/L} + 4.4 \cdot 10^{-9} \text{ mol/L} \approx 0.0023 \text{ mol/L}$$

From here, we can calculate the pOH and pH values as:

$$\begin{aligned} \text{pOH} &= -\log [\text{OH}^-] = 2.64 \\ \text{pH} &= 14 - \text{pOH} = 11.36 \end{aligned}$$

**Exercise 9.** You are working with a buffer solution based on the acid-base conjugate pair (HA, A<sup>-</sup>) with **pKa = 4.76**. You apply some amount of strong base to adjust the pH of solution, and you experimentally measure that it is now at **pH = 6.0**. Determine the ratio between the base and acid forms of this buffer (assume T=25°C and standard aqueous conditions).

**Solution**

This is purely asking you to use the Henderson–Hasselbalch equation to determine the [A<sup>-</sup>]/[HA] ratio in the buffering agent:

$$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{A}^-]}{[\text{HA}]} \right)$$

If we solve for [A<sup>-</sup>]/[HA]:

$$\frac{[\text{A}^-]}{[\text{HA}]} = 10^{\text{pH} - \text{p}K_a}$$

Which gives:

$$\frac{[\text{A}^-]}{[\text{HA}]} = 10^{1.24}$$

So, the ratio of  $[\text{A}^-]/[\text{HA}] = 17.38$