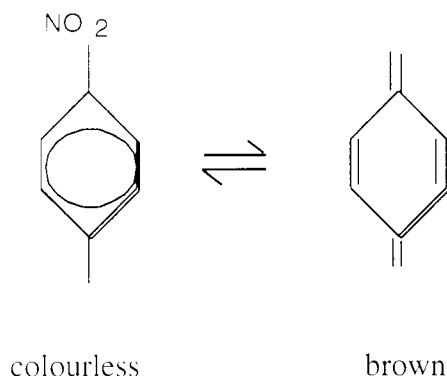


1. The compound para nitrophenol,  $C_6H_4(NO_2)OH$  behaves as an acid base indicator. In aqueous solution it exists in the following equilibrium.



Explain how this system can act as an indicator. Give the colour of the indicator in acid and basic solutions.

2. A technician read the following information on a bottle of concentrated ammonia:

Density =  $0.88 \text{ g cm}^{-3}$   
Approximate pH = 10

- (a) Why is concentrated ammonia solution **not** suitable as a primary standard?  
(b) The table below shows the pKa values for acid-alkali indicators.

INDICATOR	pKa
bromocresol green	4.7
bromothyl blue	7.0
phenolphthalein	9.3

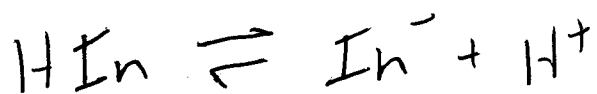
Choose the indicator most suitable for use in the titration of hydrochloric acid against ammonia solution.

3. Most indicators are weak acids of formula HIn. Information on some indicators is shown below.

Indicator	Ka	Colour change ( low pH --> high pH)
Methyl yellow	$5.1 \times 10^{-4}$	red --> yellow
Bromothyl blue	$1.0 \times 10^{-7}$	yellow --> blue
Thymol blue	$1.3 \times 10^{-9}$	yellow --> blue

- (a) At what pH would the colour change be expected to occur for each of the indicators?  
(b) A pupil is carrying out a titration of ethanoic acid and sodium hydroxide. Which indicator is most suitable? Explain your answer.

1. Since  $C_6H_4(NO_2)OH$  is a weak acid the following equilibrium will be set up



This means that the concentration of the ionised and unionised form of the molecule will be affected by the  $H^+$  conc. The precise relationship is given by the equation below

$$\frac{[In^-]}{[HIn]} = \frac{K_{in}}{[H^+]} \quad \text{where } K_{in} \text{ is the dissociation constant of the acid indicator} \quad \text{--- (1)}$$

If the ionised form ( $A^-$ ) has a different colour from the unionised form ( $HA$ ) then the colour observed will depend on which form has the higher concentration which will be determined by the ~~above~~  $H^+$  ion concentration. The indicator will change colour when  $pH = pK_{in} \pm 1$ . This is because at the change in colour  $\frac{[A^-]}{[HA]} = 1$  so equation (1) becomes

$$\frac{K_{in}}{[H^+]} = 1 \quad \& \quad [H^+] = K_{in} \quad \text{and taking the}$$

- log of both side we get

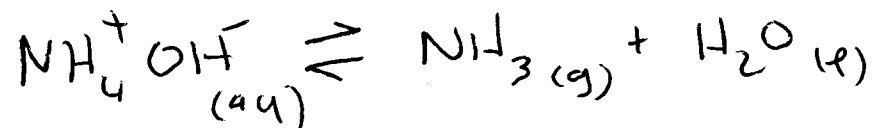
$$-\log [H^+] = -\log K_{in}$$

$$pH = pK_{in}$$

(b) In acid conditions the unionised form will dominate i.e.  $C_6H_4(NO_2)OH$  therefore colour will be colourless

In basic conditions the ionised form will dominate therefore colour will be brown

2. (a) Ammonia solution is not suitable as a primary standard as it is not stable. Its concentration will decrease in a short period of time due to the reaction below



(b)

bromocresol green would be suitable. This is because the end point of the reaction will be at a pH less than 7 due to the fact the salt formed when a weak base is neutralised by a strong acid like HCl will be acidic. The <sup>pH of the</sup> colour change for an indicator is given by the formula below

$$\text{pH} = \text{pK}_{in} \pm 1$$

so the colour change for bromocresol green would occur at  $\text{pH } 4.7 \pm 1$  i.e. acid conditions.

3

(a)  $\text{pK}_{in} = -\log K_{in}$

So for

methyl yellow  $\text{pK}_{in} = -\log(5.1 \times 10^{-4}) = 3.29$

and Bromothylol blue  $\text{pK}_{in} = -\log(1.0 \times 10^{-7}) = 7$

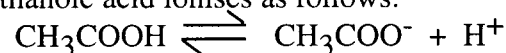
and Thymol blue  $\text{pK}_{in} = -\log(1.3 \times 10^{-9}) = 8.89$

Since colour change occurs at  $\text{pH} = \text{pK}_a \pm 1$  colour change for methyl yellow will be <sup>at pH</sup> 3.29, for Bromothylol 7 and for thymol blue it will be 8.89.

(b) Thymol blue would be the most suitable indicator because end point will be above pH 7 due to salt formed being alkaline.

1. (a) Calculate the pH of a solution of ethanoic acid of concentration  $0.01 \text{ mol l}^{-1}$ .  
 (b) A mixture of ethanoic acid and sodium ethanoate solution constitutes a buffer solution. Show how this buffer solution is able to resist a change in pH when small quantities of the following are added:
  - (i) hydrochloric acid.
  - (ii) sodium hydroxide solution.
 (Use of equations may be helpful).  
 (c) A buffer solution was prepared from equal volumes of  $0.25 \text{ mol l}^{-1}$  ethanoic acid and  $0.15 \text{ mol l}^{-1}$  sodium ethanoate. Calculate the pH of the buffer solution.

2. Aqueous ethanoic acid ionises as follows:



$$\Delta H = 0 \text{ kJ mol}^{-1}$$

$$K_a = 1.8 \times 10^{-5}$$

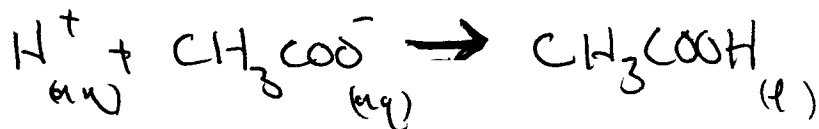
- (a) Explain what will happen to  $K_a$  if the temperature is raised.
  - (b) A little hydrochloric acid is added to the ethanoic acid solution.
    - (i) What will be the effect on the  $K_a$ ? Explain your reasoning.
    - (ii) What will be the effect on the concentration of ethanoate ions in the solution. Explain your answer.
3. Benzoic acid ( $\text{C}_6\text{H}_5\text{COOH}$ ) is a weak monobasic acid ( $K_a = 6.4 \times 10^{-5}$ )
    - (a) Calculate the hydrogen ion concentration in  $0.02 \text{ mol l}^{-1}$  benzoic acid.
    - (b) What is the pH of  $0.02 \text{ mol l}^{-1}$  benzoic acid?
    - (c) What is the pH of a solution containing 7.2g of sodium benzoate in 1 litre of  $0.02 \text{ mol l}^{-1}$  benzoic acid?

## Ex 2.12

1 (a) 
$$\text{pH} = \frac{1}{2} \text{p}K_a - \frac{1}{2} \log C$$
$$= \frac{1}{2} \times 4.77 - \frac{1}{2} \log(0.01)$$
$$= 2.385 - \frac{1}{2} \times (-2)$$
$$= \underline{3.38}$$

$K_a(\text{CH}_3\text{COOH}) = 1.7 \times 10^{-5}$   
 $\text{p}K_a = -\log(1.7 \times 10^{-5})$   
 $= \underline{4.77}$

(b) (i) When  $\text{H}^+$  ions are added the weak acid equilibrium is affected. The equilibrium will shift to reduce the effect of the increase in  $\text{H}^+$  concentration. This will occur by the ethanoate ions joining with the  $\text{H}^+$  ions added to form ethanoic acid molecules



(ii) When hydroxide ions are added they react with  $\text{H}^+$  ion making water. This decrease the concentration of the  $\text{H}^+$  ions which will affect the weak acid equilibrium. The equilibrium will shift to reduce the decrease in  $\text{H}^+$  ions. It will do this by ethanoic acid molecules ionising to make more  $\text{H}^+$  ions

(c) 
$$\text{CH}_3\text{COOH}_{(l)} \rightarrow \text{CH}_3\text{COO}^-_{(aq)} + \text{H}^+_{(aq)}$$
$$\text{pH} = \text{p}K_a - \log \frac{[\text{acid}]}{[\text{Salt}]}$$
$$= 4.77 - \log \frac{0.25}{0.15} = 4.77 - \log 1.66$$
$$= 4.77 - 0.22$$
$$= \underline{4.55}$$

2. (a) No effect as  $\Delta H = 0$

(b) (i) No effect, add HCl to increase concentration of  $H^+$  ions but  $K_a$  is independent of changes in concentration. The equilibrium will shift to reduce concentration of  $H^+$  ions but when equilibrium is re-established and the new concentrations of reactants and products are used to calculate  $K_a$ , the same value is obtained.

(ii) The concentration of ethanoate ions will decrease. This is because when the hydrochloric acid is added the concentration of  $H^+$  ion increases. This affects the weak acid equilibrium which will shift to reduce the  $H^+$  ion concentration. It will do this by ethanoate ions joining with  $H^+$  ion to form ethanoic acid molecules.

$$3(a) \quad K_a = \frac{[H^+]^2}{c}$$

$$[H^+] = \sqrt{K_a \times c} = \sqrt{6.4 \times 10^{-5} \times 0.02}$$

$$= 0.00113 \text{ mol/l}$$

$$(b) \quad pH = -\log [H^+] = -\log (0.00113)$$

$$= \underline{2.95}$$

$$(c) \quad pH = pK_a - \log \frac{[\text{acid}]}{[\text{Salt}]}$$

$$= 4.19 - \log \frac{0.02}{0.05}$$

$$= 4.1 - (0.4)$$

$$= \underline{4}$$

$$pK_a = -\log K_a = -\log (6.4 \times 10^{-5})$$

$$= \underline{4.19}$$

$$[C_6H_8COO] = \frac{\text{mol}}{\text{vol}} = \frac{0.059}{1}$$

$$= 0.059 \text{ mol/l}$$

$$\text{moles } C_6H_8COO = \frac{7.2}{144} = 0.05$$