P3. The Adventures of Hodja Nasreddin

Equipment

Item	Quantity	Label
Part A		
pH meter with stand and probe stored in 3 M KCl	1	
Volumetric pipette, 50 mL	1	
Glass rod	1	
Part B		
Thermometer	1	
Funnel for filtration	1	
Cotton wool	1	
Glass beaker, 200 mL	2	
Measuring cylinder, 50 mL	1	
Plastic Pasteur pipette, 3 mL	2	
Plastic cup, 250 mL	20	

Chemicals

Name	State	Concentration	Quantity	Placed in	Label
Part A					
Solution **X3**	aq	To be determined	200 mL	Plastic bottle, 250 mL	**X3**
Solution **X4**	aq	To be determined	200 mL	Plastic bottle, 250 mL	**X4**
Solution **X5**	aq	To be determined	200 mL	Plastic bottle, 250 mL	**X5**
Solution **X6**	aq	To be determined	200 mL	Plastic bottle, 250 mL	**X6**
Part B					
Solution **Y1**	aq	-	3 mL	Eppendorf tube, 4 mL	**Y1**
Sliced red cabbage	s	-	15 g	Glass bottle, 100 mL	**RC**
Hydrochloric acid	aq	0.0100 M	100 mL	Plastic bottle, 250 mL	**HCl 0.01 M**

15 % of total										
Question	3.1	3.2	3.3	3.4	3.5	3.6	3.7	3.8	3.9	**Total**
Points	2	0	50	12	1	9	2	10	1	**87**

Part A

The chemist Nasreddin prepared solutions of **different acids** with the same pH value. To do this, he took:

- a strong monoprotic acid HA,

- a weak monoprotic acid HB,

- a diprotic acid H_2C.

He obtained six solutions (**X1–X6**), all with **the same pH value** when rounded to the nearest integer. These six solutions included three solutions of individual acids and three pairwise mixtures, which contained individual acids in a 1 : 1 molar ratio (not necessarily in order given below).

HA	HB	H_2C	HA + HB (1 : 1)	HA + H_2C (1 : 1)	HB + H_2C (1 : 1)

In this part, you need to **perform titrations** of solutions **X3–X6** with a pH meter. Unfortunately, on the way to IChO 2026, Nasreddin lost solutions **X1** and **X2**, but he promises to help in determining their composition.

1. Using a volumetric pipette, **transfer** 50.0 mL of **X3** into a **plastic cup**.
2. **Measure** the pH of **X3** using the pH meter.

Q3.1 **Tick** the pH value of **X3** to the nearest integer. 2 pt

SOLUTION:

pH = 1	pH = 2	pH = 3	pH = 4	pH = 5	pH = 6	pH = 7	pH = 8	pH = 9	pH = 10
☐	☐	☒	☐	☐	☐	☐	☐	☐	☐

3. Using the pH meter, **titrate** 50.0 mL of **X3** with 0.0100 M NaOH solution by adding **0.5 mL portions** of NaOH solution and measuring the pH of the resulting solution until it reaches ~10. **Do not use** the stirring plate in this experiment.
4. **Record** the pH values. When a more accurate measurement is required, **wait** until the displayed pH value is stable for at least 5 seconds.
5. **Repeat** steps 1, 3 and 4 for **X4–X6**.

Q3.2	**Record** your results for the titration of solutions **X3–X6**. You **may sketch** the titration curves on the provided grids, but they will not be graded.	0 pt

Q3.3 **Determine** the ranges of NaOH volume (in mL) that correspond to the equivalence points during the titrations of **X3–X6**. **Tick** the appropriate boxes based on your results from **Q3.2**. 50 pt

For example, if the equivalence point lies in the range $4.0 < V \leq 4.5$, you **must tick** the box as shown below:

V_{NaOH}	3.5	☐	4.0	☑	4.5	☐	5.0

SOLUTION:

For **X3**: $V_{\mathrm{NaOH,1}}$ = Box or Box+1, $V_{\mathrm{NaOH,2}}$ = Box'
For **X4**: V_{NaOH} = Box
For **X5**: V_{NaOH} = Box
For **X6**: $V_{\mathrm{NaOH,1}}$= Box, $V_{\mathrm{NaOH,2}}$ = Box' or Box'+1
For **X3** (Jump 1):
Box or Box+1: 7.5 pt
Box-1 or Box+2: 3 pt
For **X3** (Jump 2):
Box': 7.5 pt
Box'-1 or Box'+1: 5 pt
Box'-2 or Box'+2: 2.5 pt
Each extra choice: –3 pt
Overall mark cannot be negative.

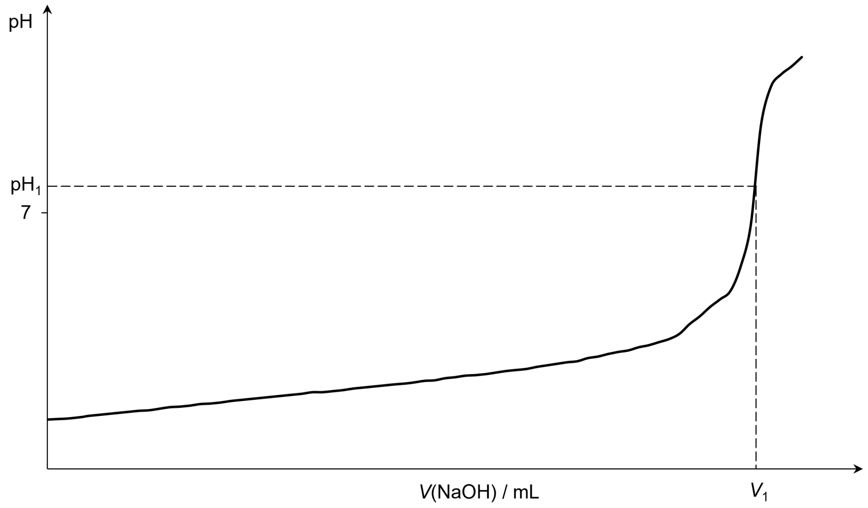
For **X4**:
Box: 10 pt
Box-1 or Box+1: 4 pt
Each extra choice: –4 pt
Overall mark cannot be negative.

For **X5**:
Box: 10 pt
Box-1 or Box+1: 4 pt
Each extra choice: –4 pt
Overall mark cannot be negative.

For **X6** (Jump 1):
Box or Box+1: 7.5 pt
Box-1 or Box+2: 3 pt
For **X6** (Jump 2):
Box': 7.5 pt
Box'-1 or Box'+1: 3 pt
Each extra choice: –3 pt
Overall mark cannot be negative.

Q3.3 is not graded based on **Q3.2**. Only the answer specified in **Q3.3** is graded. If **Q3.3** is not answered, the pH jumps are identified according to data in **Q3.2** and graded with a 50% penalty.

Nasreddin provides the following titration curve of 50.0 mL **X1** with 0.0100 M NaOH solution, where $V_1 = 34.75\,\mathrm{mL}$:



He also notes that for solution **X2**, the ratio between the total V(NaOH) to reach the second equivalence point relative to V(NaOH) to reach the first equivalence point is approximately 3 : 2.

Q3.4 **Determine** the composition of **X1–X6**. **Tick** the appropriate boxes. 12 pt

SOLUTION:

	HA	HB	H_2C	HA + HB (1:1)	HA + H_2C (1:1)	HB + H_2C (1:1)
X1	☐	☒	☐	☐	☐	☐
X2	☐	☐	☐	☐	☒	☐
X3	☐	☐	☒	☐	☐	☐
X4	☐	☐	☐	☒	☐	☐
X5	☒	☐	☐	☐	☐	☐
X6	☐	☐	☐	☐	☐	☒

Each correct answer: 2 pt.
For extra tick: 0 pt for both chosen acid(s) and mixture(s).

SOLUTION (explanation):

The strong acid HA must have a concentration of ca. 1 mM to have a pH of 3. Its titration would result in a curve with a single pH jump and the volume of NaOH at the equivalence point of ca. $\frac{1 \cdot 10^{-3} \cdot 50}{0.01} = 5$ mL. This is observed in the titration of **X5** with the titre of MV±0.25 mL.

Next, it is best to analyse **X3** and **X6**, which exhibit two pH jumps. In the case of **X3**, the volume of NaOH to reach the first equivalence point is almost the same as the volume of NaOH to further reach the second equivalence point. This is only possible for either H_2C with two pK_a values that are rather different from each other, or for the 1:1 mixture of HA and HB, when the acids get titrated separately, meaning that pK_a for HB is relatively high, so HB is very weak. With the titre of MV±0.25 mL NaOH to reach the first equivalence point, the solution **X3** would either contain x mM H_2C or x/2 mM HA + x/2 mM HB. However, it would be impossible to reach pH 3 with these concentrations of HA and HB if HB is a very weak acid. Therefore **X3** is H_2C, which seems to be a rather strong acid in the first step but weak in the second step.

In the case of **X6**, we observe that the volume of NaOH to reach the first equivalence point is approximately two times larger than the volume of NaOH to further reach the second equivalence point. For 1:1 mixtures of given acids, it is only possible for HA + H_2C or for HB + H_2C. Knowing that H_2C shows two distinct pH jumps when titrated, the first jump for **X6** is due to the neutralisation of either HA and H_2C (first proton) or HB and H_2C (first proton). With the titre of MV±0.25 mL NaOH to reach the first equivalence point, the solution **X6** would then contain y mM HA/HB and y mM H_2C. However, as the pH of the initial solution is 3, it cannot contain y mM of strong acid HA with the same amount of a rather strong acid H_2C. Therefore, we can conclude that **X6** is 1:1 HB+H_2C, while **X2** must be 1:1 HA+H_2C, as there are no other curves left with two pH jumps and 2:1 titre ratio.

X1 and **X4** exhibit single pH jumps, and the only acids left are HB and the 1:1 mixture of HA+HB. The much larger titre of 34.75 mL for **X1** than MV±0.25 mL for **X4** indicates that **X1** is the solution of a weak acid HB. This is due to a higher concentration of a weak acid alone, rather than its mixture with the strong acid HA, which will be needed to create a solution with pH 3. Therefore. **X1** is HB, and **X4** is 1:1 HA+HB.

Q3.5 **Give** the pH of the resulting solution after mixing equal volumes of **X1–X6**. 1 pt

SOLUTION:

After mixing of equal volumes of **X3–X6** (or **X1–X6** in general), firstly, the concentration of H^+ doesn't change, because the moles of H^+ and the volume of solution increase by the same amount. Secondly, in the following equilibria, the ratios of acid and conjugate base don't change because they depend only on $[H^+]$:

$$K_a(HB) = \frac{[H^+][B^-]}{[HB]} \Longrightarrow \frac{[B^-]}{[HB]} = \frac{K_a(HB)}{[H^+]}$$

$$K_{a1}(H_2C) = \frac{[H^+][HC^-]}{[H_2C]} \Rightarrow \frac{[HC^-]}{[H_2C]} = \frac{K_{a1}(H_2C)}{[H^+]}$$

$$K_{a2}(H_2C) = \frac{[H^+][C^{2-}]}{[HC^-]} \Rightarrow \frac{[C^{2-}]}{[HC^-]} = \frac{K_{a2}(H_2C)}{[H^+]}$$

Thus, pH remains unchanged. Students can mix equal volumes of available solutions (**X3–X6**) and measure the pH of the resulting solution.

pH = 3

1 pt for the correct answer. The answer must be consistent with **Q3.1** or **Q3.2**.

Part B

Nasreddin also prepared universal indicators **Y1** and **Y2** for acid−base titration. To prepare **Y2**, he made an extract from red cabbage.

Prepare a fresh solution of **Y2** from red cabbage as follows:

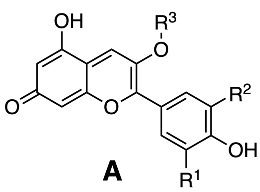
1. **Transfer** all the sliced red cabbage into the 200 mL glass beaker with 60 mL of water.
2. **Place** the beaker on the hotplate and **heat** it at 70–95°C for 20 min.
3. **Filter** the extract through the funnel with cotton wool and **collect** the **Y2** solution in the clean 200 mL glass beaker.
4. **Determine** the order of colour transitions of **Y2** as pH changes using the available solutions and equipment. Using 100 μL of **Y2** per 1 mL of analyte provides the most reliable results.

Q3.6 **Arrange** the colours of **Y2** in order of increasing pH using the colour abbreviations listed below. 9 pt

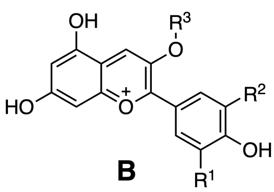
Red/pink	Yellow	Green	Blue	Violet
R	Y	G	B	V

SOLUTION:
To identify the colour changes of **Y2**, the student can add this indicator into **X3–X6** during titration with the pH meter and determine the colour of this indicator at different pH values. The best solutions are **X3** and **X6**, because they contain a polyprotic acid H_2C and form more stable pH regions. Another option is making solutions with different pH by dilution of solutions of HCl and NaOH.
Correct order: R < V < B < G < Y
R in the first position: 1 pt, R in the second position: 0.5 pt
R < V (only when next to each other): 2 pt
V < B (only when next to each other): 2 pt
B < G (only when next to each other): 2 pt
G in the fourth position: 1 pt, G in the fifth position: 0.5 pt
Y in the fifth position: 1 pt
Reverse order (Y < G < B < V < R): 3 pt

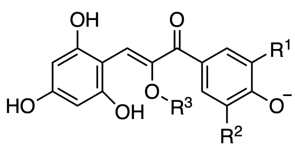
The extract of red cabbage contains anthocyanins responsible for such a wide range of colours. Below are the structures of anthocyanins at different pH:



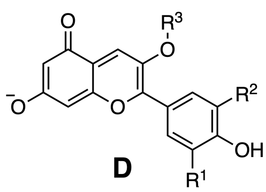
A



B



C



D

Q3.7 **Arrange A–D** according to which structures are most dominant as the pH is changed from low to high. 2 pt

SOLUTION:

The molecular formulae are:

A	B	C	D
$[C_{15}H_7O_5R^1R^2R^3]$	$[C_{15}H_8O_5R^1R^2R^3]^+$	$[C_{15}H_8O_6R^1R^2R^3]^-$	$[C_{15}H_6O_5R^1R^2R^3]^-$

If the formulae are compared:
B is the protonated form of **A** in an acidic medium.
A is a neutral molecule.
D is the form of **A**, which lost 1 acidic proton in a basic medium.
C is the form of **D**, to which one water molecule has added in a more basic medium. The opening of the ring is slower than protonation/deprotonation reactions, which is consistent with the much slower colour change from green to yellow at higher pH compared to other colour changes.

$\boxed{B} < \boxed{A} < \boxed{D} < \boxed{C}$

Fully correct answer (**B** < **A** < **D** < **C**): 2 pt
Correct order of charges, but **D** and **C** swapped (**B** < **A** < **C** < **D**): 1 pt

To prepare **Y1**, Nasreddin mixed two individual indicators from the table:

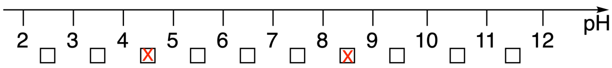
#	Indicator	pH range of colour changes
1	Bromophenol blue (**BPB**)	yellow < 3.0 – 4.6 < blue
2	Congo red (**CR**)	blue < 3.0 – 5.2 < red
3	Bromocresol green (**BG**)	yellow < 3.8 – 5.4 < blue
4	Methyl red (**MR**)	red < 4.4 – 6.2 < yellow
5	Chlorophenol red (**CPR**)	yellow < 5.2 – 6.8 < purple
6	Bromothymol blue (**BTB**)	yellow < 6.0 – 7.6 < blue
7	Phenol red (**PR**)	yellow < 6.8 – 8.2 < pink
8	Thymol blue (**TB**)	yellow < 8.0 – 9.6 < blue
9	Phenolphthalein (**PP**)	colourless < 8.2 – 10.0 < pink
10	Alizarin yellow R (**AYR**)	yellow < 10.1 – 12.0 < red

Determine the pH ranges of the colour changes of **Y1** using the pH meter and available solutions. Using 5 μL of **Y1** per 1 mL of analyte provides the most reliable results.

Q3.8 **Tick** the appropriate boxes for the pH ranges of the colour changes of **Y1**. 10 pt

SOLUTION:

One can use the same method as in **Q3.6** for determining the order of the colour changes of **Y1**.



Choice of 4–5 and/or 5–6 for the first transition: 5 pt.
Choice of 8–9 and/or 9–10 for the second transition: 5 pt.
Extra choice: –5 pt.
Overall score cannot be negative.

Q3.9 **Determine** the composition of **Y1**. **Tick** the appropriate boxes. 1 pt

SOLUTION:

The observed colours: pH 2 to 4 – red, pH 5 – orange (mix of red and yellow), pH 6 to 9 – yellow, pH 10 to 12 – green (mix of yellow and blue). This corresponds to methyl red (**MR**) and thymol blue (**TB**).
Bromothymol blue (**BTB**) can also be accepted instead of **TB** if pH of the second transition was indicated in **Q3.8** as 6–7 and/or 7–8.
Each correct answer: 0.5 pt
Ticking more than two boxes: 0 pt.