Begin your response to **QUESTION 1** on this page.

CHEMISTRY

SECTION II

Time—1 hour and 45 minutes

7 Questions

YOU MAY USE YOUR CALCULATOR FOR THIS SECTION.

Directions: Questions 1–3 are long free-response questions that require about 23 minutes each to answer and are worth 10 points each. Questions 4–7 are short free-response questions that require about 9 minutes each to answer and are worth 4 points each.

For each question, show your work for each part in the space provided after that part. Examples and equations may be included in your responses where appropriate. For calculations, clearly show the method used and the steps involved in arriving at your answers. You must show your work to receive credit for your answer. Pay attention to significant figures.

1. A student reacts 0.300 g of methyl salicylate ($C_8H_8O_3$) with a stoichiometric amount of a strong base. This product is then acidified to produce salicylic acid crystals ($HC_7H_5O_3$).

(a) For every 1 mole of $C_8H_8O_3$ (molar mass 152.15 g/mol) reactant used, 1 mole of salicylic acid crystals ($HC_7H_5O_3$, molar mass 138.12 g/mol) is produced. Calculate the maximum mass, in grams, of $HC_7H_5O_3$ that could be produced in this reaction.

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As part of the experimental procedure to purify the $HC_7H_5O_3$ crystals after the reaction is complete, the crystals are filtered from the reaction mixture, rinsed with distilled water, and dried. Some physical properties of $HC_7H_5O_3$ are given in the following table.

Properties of Salicylic Acid ($HC_7H_5O_3$)	
Melting point	159°C
Solubility in H_2O at 25°C	2.2 g/L
Specific heat capacity	1.17 J/(g·°C)
Heat of fusion	27.1 kJ/mol

(b) The student's experiment results in an 87% yield of dry $HC_7H_5O_3$. The student suggests that some of the $HC_7H_5O_3$ crystals dissolved in the distilled water during the rinsing step. Is the student's claim consistent with the calculated percent yield value? Justify your answer.

(c) Given the physical properties in the table, calculate the quantity of heat that must be absorbed to increase the temperature of a 0.105 g sample of dry $HC_7H_5O_3$ (molar mass 138.12 g / mol) crystals from 25°C to the melting point of 159°C and melt the crystals completely.

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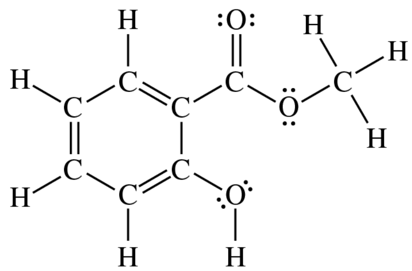
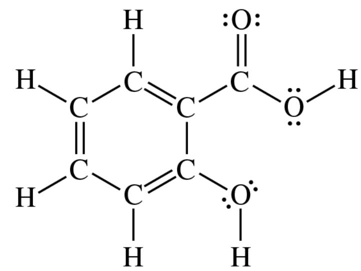
The structures and melting points for methyl salicylate and salicylic acid are shown.



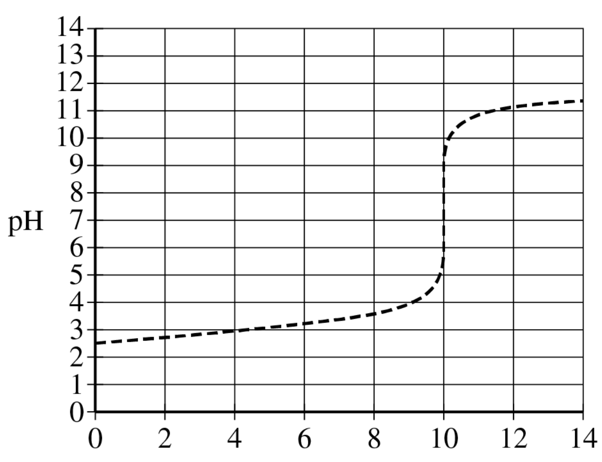
Methyl Salicylate
Melting Point: –9°C



Salicylic Acid
Melting Point: 159°C

(d) The same three types of intermolecular forces (London dispersion forces, dipole-dipole interactions, and hydrogen bonding) exist among molecules of each substance. Explain why the melting point of salicylic acid is higher than that of methyl salicylate.

The student titrates 20.0 mL of 0.0100 M $HC_7H_5O_3(aq)$ with 0.0200 M NaOH, using a probe to monitor the pH of the solution. The data are plotted producing the following titration curve.



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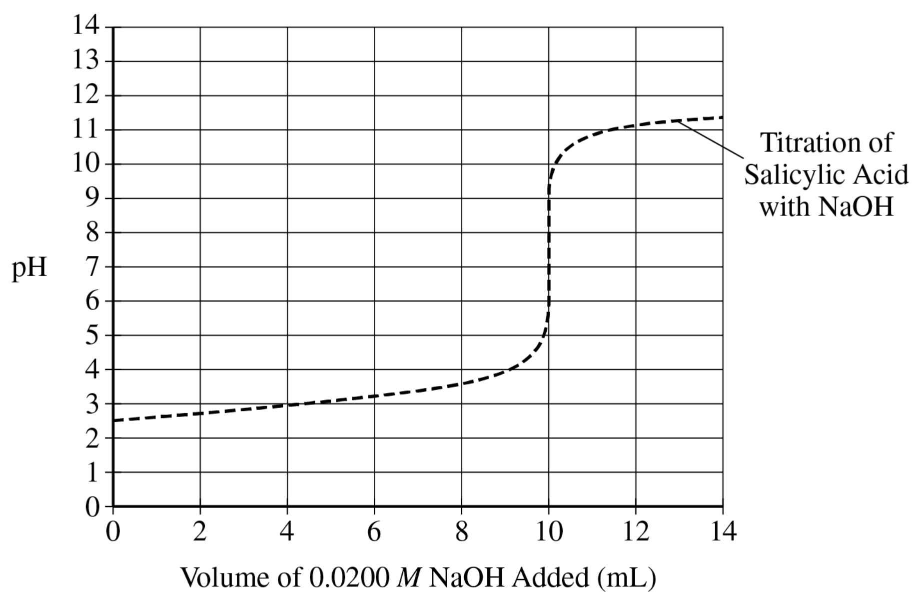
Continue your response to **QUESTION 1** on this page.

(e) Using the information in the graph, estimate the pK_a of $HC_7H_5O_3$. ______________

(f) When the pH of the titration mixture is 4.00, is there a higher concentration of the weak acid, $HC_7H_5O_3$, or its conjugate base, $C_7H_5O_3^-$, in the flask? Justify your answer.

(g) The student researches benzoic acid ($HC_7H_5O_2$) and finds that it has similar properties to salicylic acid ($HC_7H_5O_3$). The K_a for benzoic acid is 6.3×10^{-5}. Calculate the value of pK_a for benzoic acid.

(h) The student performs a second titration, this time titrating 20.0 mL of a 0.0100 M benzoic acid solution with 0.0200 M NaOH. Sketch the curve that would result from this titration of benzoic acid on the following graph, which already shows the original curve from the titration of 20.0 mL of 0.0100 M salicylic acid. The initial pH of the benzoic acid solution is 3.11.



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Question 1: Long Answer — 10 points

(a) For the correct calculated value: **1 point**

$$0.300 \text{ g } C_8H_8O_3 \times \frac{1 \text{ mol } C_8H_8O_3}{152.15 \text{ g}} \times \frac{1 \text{ mol } HC_7H_5O_3}{1 \text{ mol } C_8H_8O_3} \times \frac{138.12 \text{ g}}{1 \text{ mol } HC_7H_5O_3} = 0.272 \text{ g } HC_7H_5O_3$$

(b) For the correct answer and a valid justification: **1 point**

Yes (consistent). Because the acid is soluble in water, some crystals may dissolve during rinsing, causing the mass of the collected precipitate to be lower than expected. This would lead to a percent yield less than 100%.

(c) For the correct calculated value of either q: **1 point**

Accept one of the following:

- $q_{heat} = mc\Delta T = (0.105 \text{ g})(1.17 \text{ J/(g} \cdot {^\circ}\text{C}))(159^\circ\text{C} - 25^\circ\text{C}) = 16.5 \text{ J}$
- $q_{melt} = 0.105 \text{ g} \times \dfrac{1 \text{ mol}}{138.12 \text{ g}} \times \dfrac{27{,}100 \text{ J}}{1 \text{ mol}} = 20.6 \text{ J}$

For the correct calculated value of the other q and the total heat: **1 point**

$q_{total} = q_{heat} + q_{melt} = 16.5 \text{ J} + 20.6 \text{ J} = 37.1 \text{ J}$

Total for part (c) 2 points

(d) For a correct explanation: **1 point**

Molecules of salicylic acid have more hydrogen bonding sites than molecules of methyl salicylate have, which leads to stronger intermolecular forces and a higher melting point for salicylic acid.

(e) For the correct answer: **1 point**

The pK_a *is approximately 3.*

(f) For the correct answer and a valid justification, consistent with part (e): **1 point**

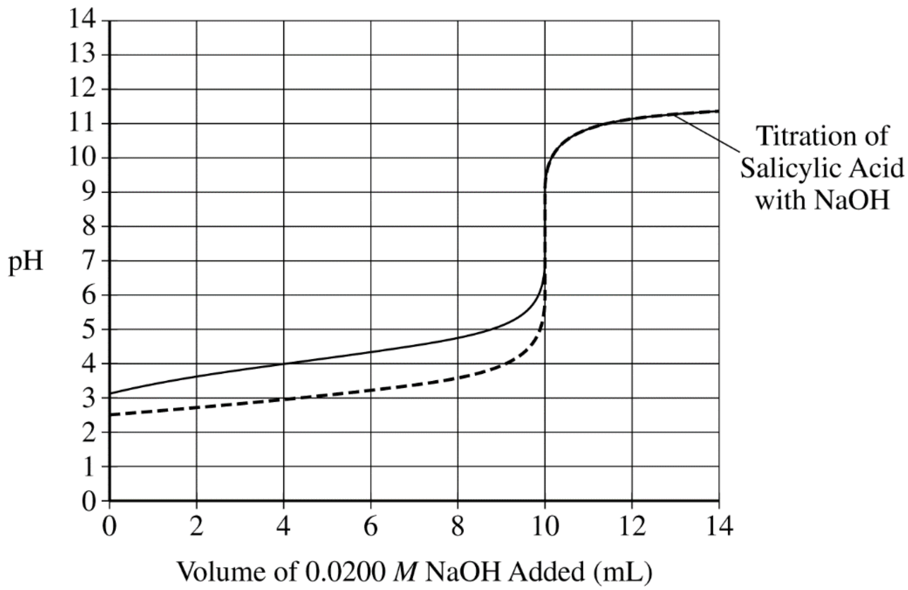
Accept one of the following:

- *The conjugate base,* $C_7H_5O_3^-$. *When* $pH = 4$, *the titration is beyond the half-equivalence point, where* $[HC_7H_5O_3] = [C_7H_5O_3^-]$. *Thus,* $[C_7H_5O_3^-]$ *must be greater than* $[HC_7H_5O_3]$.
- *The conjugate base,* $C_7H_5O_3^-$. *Because the* pH *of the solution is greater than the* pK_a *of the acid, the majority of the molecules will be deprotonated.*

(g) For the correct calculated value: **1 point**

$pK_a = -\log(6.3 \times 10^{-5}) = 4.20$

(h)	For a curve that shows a correct starting and half-equivalence point, consistent with part (g):	**1 point**
	The curve starts at pH $\approx$ 3.11 *and passes through the* pK_a *calculated in part (g) at* 5 *mL*. *See example response below.*	
	For a curve that shows the correct equivalence point:	**1 point**
	The curve inflects vertically at 10 *mL showing the same volume of base needed to reach the equivalence point.*	



Total for part (h) **2 points**

Total for question 1 **10 points**