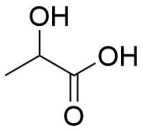
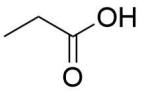
Q5 This question is about cheese

Former Prime Minister Liz Truss once said that "We import two thirds of our cheese. That is a disgrace."

When we started writing this paper in summer 2022, we thought a question on cheese would be timely, given that the 2023 International Chemistry Olympiad is being held in Switzerland (a country with many famous cheeses) and that Liz Truss would be the Prime Minister at the time of Round 1.

While there are many differences in the process of cheese manufacture, the conversion of lactose to lactic acid during fermentation is a key chemical process wherever the cheese is from.

lactic acid   propanoic acid

(a) Lactic acid has an acid dissociation constant, $K_a = 1.38 \times 10^{-4}$.

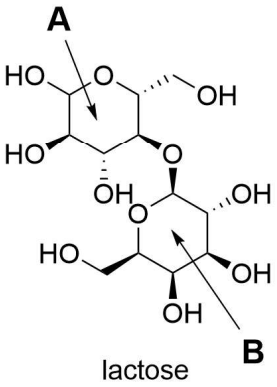
(i) Draw the conjugate base of lactic acid.

(ii) Calculate the pK_a of lactic acid.

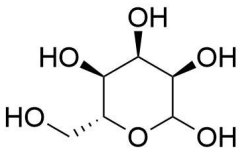
Lactic acid is more acidic than propanoic acid. This is due to a hydrogen bond which stabilises its conjugate base.

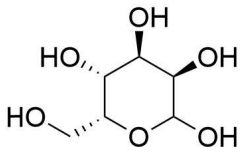
(b) Draw out the structure of the conjugate base of lactic acid showing this hydrogen bond.

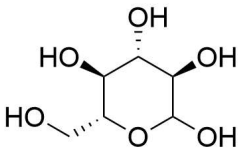
Lactose, the starting sugar in milk, is a disaccharide with formula $C_{12}H_{22}O_{11}$. In the first step of the conversion to lactic acid, lactose is converted into two monosaccharides.

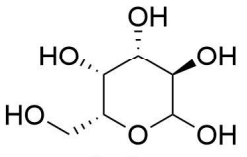


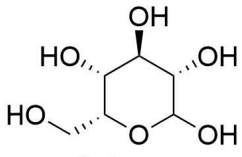
lactose

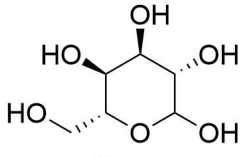

allose

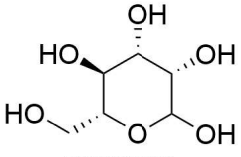

gulose

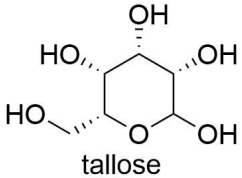

glucose


galactose


iodose


altrose


mannose


tallose

(c) **(i)** How would you classify the reaction of lactose to form the two monosaccharides. Tick the correct answer(s) in the answer booklet.

Oxidation Reduction Condensation Hydrolysis Isomerisation Elimination

(ii) Write the names of monosaccharide sugars (A and B) that make up lactose.

The conversion of lactose to lactic acid is accomplished by bacteria in a complex biochemical process, however lactic acid is often the sole product.

(d) Write an equation for the conversion of lactose to lactic acid.

Many varities of Swiss cheese, such as Emmental, are famous for the holes or 'eyes' that appear in the cheese. To produce the holes another species of bacteria, *Propionibacterium freudenreichii* is important. This bacterium carries out the reaction of lactic acid to propanoic acid, ethanoic acid, carbon dioxide and water. The production of carbon dioxide causes the bubbles to appear.

(e) Write an equation for the production of carbon dioxide carried out by this bacterium. In the net reaction, lactic acid is the sole reagent, and ethanoic acid and carbon dioxide are produced in equal amounts.

Assume during fermentation at 21 °C, a spherical bubble of diameter 1.5 cm appears in the cheese.

(f) **(i)** Calculate the volume of this bubble in m^3.

(ii) Assuming the bubble is pure CO_2 at atmospheric pressure, p_{atm} = 101 325 Pa, calculate the mass of lactic acid which was fermented by the bacteria to produce this bubble. For the calculation assume that CO_2 obeys the ideal gas law,

$$pV = nRT$$

Note: the state symbol for cheese is (ch).

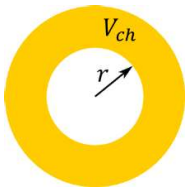
Carbon dioxide dissolved in cheese can exist in two forms: dissolved gaseous carbon dioxide, $CO_{2(ch)}$, or dissolved hydrogen carbonate, $HCO_3^-{}_{(ch)}$.

$$CO_{2(ch)} + H_2O \rightleftharpoons HCO_3^-{}_{(ch)} + H^+{}_{(ch)}, \quad K = \frac{[H^+_{(ch)}][HCO^-_{3(ch)}]}{[CO_{2(ch)}]} = 4.47 \times 10^{-7} \text{ mol dm}^{-3},$$

At the end of the fermentation, $[CO_{2(ch)}] + [HCO_3^-{}_{(ch)}] = 3.70 \times 10^{-2}$ mol dm^{-3}, and pH = 5.20

(g) Calculate the equilibrium concentration of carbon dioxide dissolved in cheese, $[CO_{2(ch)}]$.

We now examine how CO_2 bubbles ("eyes") of a certain size are formed in the early stages of fermentation. Suppose a bubble of radius r is in contact with a fixed volume of cheese V_{ch} at temperature T. The pressure of CO_2 inside the bubble, p_b, is related to the concentration of dissolved CO_2 by Henry's law,



$$[CO_{2(ch)}] = k_H\, p_b$$

(h) In the table in the answer booklet, tick which expression gives the molar amounts of $CO_{2(g)}$, $CO_{2(ch)}$ and $HCO_3^-{}_{(ch)}$, in terms of p_b, r, k_H, V_{ch}, T, pH, and relevant constants.

$\boldsymbol{k_H V_{ch} p_b}$	$\boldsymbol{\frac{4\pi r^3 p_b}{3RT}}$	$\boldsymbol{\frac{4\pi r^3 p_b}{3RT} K \cdot 10^{pH}}$	$\boldsymbol{K \cdot 10^{pH} k_H V_{ch} p_b}$	$\boldsymbol{\frac{V_{ch} p_b}{3RT}}$	$\boldsymbol{K \cdot 10^{-pH} k_H V_{ch} p_b}$

The sum of molar amounts in part **(h)** is a constant, labelled η, and the pressure inside the bubble is modelled by the equation

$$p_b = p_{atm} + \frac{\gamma}{r}$$

where γ is a constant.

(i) Substituting this expression for p_b, express the sum of molar amounts as

$$(a + br^3)\left(p_{atm} + \frac{\gamma}{r}\right) = \eta$$

giving a and b in terms of k_H, V_{ch}, K, T, pH, and relevant constants.

This equation gives the bubble size, r, but is too complicated to solve by hand. Instead, we use the smallness of $\boldsymbol{\frac{\gamma}{r}}$ compared to p_{atm} to approximate it with the simpler equation

$$r = \left(\frac{d}{b}\right)^{\frac{1}{3}}\left(1 - \frac{\gamma\eta}{3p_{atm}^2 d}\cdot\frac{1}{r}\right) \quad \text{, where } d = \frac{\eta}{p_{atm}} - a$$

At this stage of the fermentation:

$a = 1.70 \times 10^{-9}$ mol Pa^{-1}
$b = 1.75 \times 10^{-3}$ mol Pa^{-1} m^{-3}
$\eta = 2.35 \times 10^{-4}$ mol
$\gamma = 9.28$ Pa m

(j) Calculate the two possible values of r that satisfy the simplified equation and state which is the correct physical solution consistent with $\boldsymbol{\frac{\gamma}{r}}$ being small compared to p_{atm}.