

University of Canterbury

Mid Year Examination and Test Period 2006

Prescription Number(s):	ENCH 241
Paper Title:	Engineering Chemistry 2

Time Allowed: **THREE HOURS**

Number of pages: **FOURTEEN**

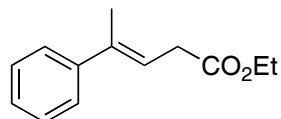
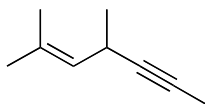
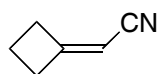
Answer **ALL** questions

Total marks: 180

TURN OVER

1. (12 marks)

For each of the following **three** structures:



- Assign the hybridization of each carbon;
- Assign the geometry of the bonds around each carbon;
- Identify a stereogenic centre and draw it in its R configuration. Explain your answer.

2. (12 marks)

- Draw the all-*anti* conformation of *n*-hexane and explain why this is the thermodynamically preferred conformation;
- Draw Newman projections for all eclipsed and staggered conformations of *n*-hexane generated on rotation about the C3-C4 bond. Indicate with reasons the relative stabilities of each.

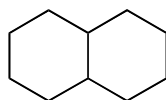
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3. (12 marks)

Discuss ways in which enantiomers can be distinguished and separated. Illustrate your answer with examples.

4. (12 marks)

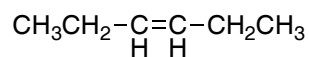
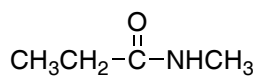
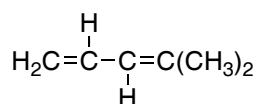
- (a) Draw chair conformations for the two diastereoisomers of decalin.
- (b) Is ring inversion (flipping) possible in each case? Draw any ring inverted conformations and refer to any inversion of axial and equatorial groups in your answer.



Decalin

5. (12 marks)

The following molecules exist as *cis* and *trans* isomers.



- (a) In each case, draw both isomers
- (b) Giving reasons, rank the three molecules above in terms of the ease with which their isomeric forms interconvert.

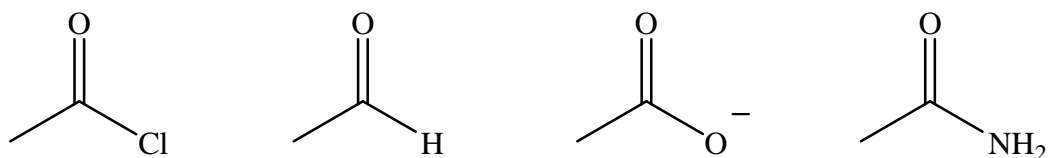
Acidity (pK_a) data that might be useful for questions 6 to 10:

Acid	pK_a	Acid	pK_a
HCl	-7	CH ₃ CH ₂ OH	16.0
H ₃ O ⁺	-1.7	CH ₃ CHO	17
CH ₃ COOH	4.75	CH ₃ COCH ₃	19
CH ₃ COCH ₂ COCH ₃	9	CH ₃ COSCoA	21.0
HCN	9.2	CH ₃ COOCH ₂ CH ₃	25.0
H ₄ N ⁺	9.3	HC≡CH	25
CH ₃ CH ₂ SH	10.3	CH ₃ CONH ₂	30
H ₂ O	15.7	H ₃ N	35
		CH ₃ CH ₃	60

6. (15 marks)

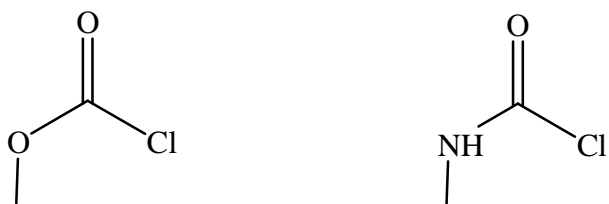
Resonance structures are drawn for compounds that cannot be adequately described by a single Lewis structure.

(a) draw out resonance structures for each of the following compounds:



(b) Place the compounds in order of decreasing reactivity towards nucleophiles. Give reasons for the order you have selected.

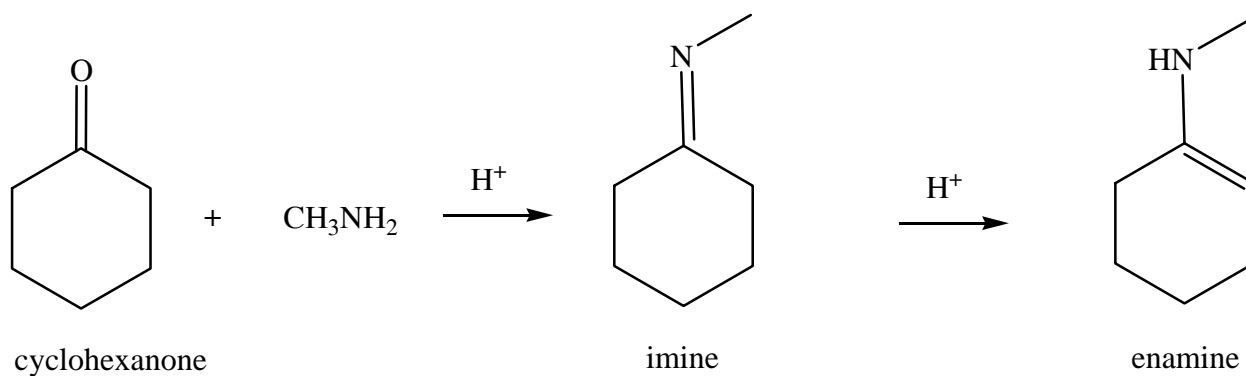
(c) Which of the following two compounds would you expect to react faster with a nucleophile? Explain your answer.



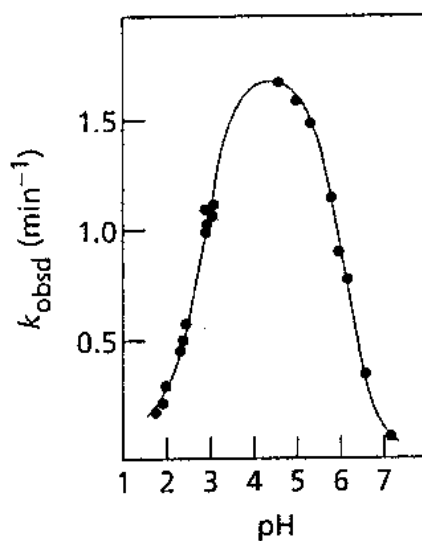
TURN OVER

7. (12 marks)

- (a) Using curly arrows to show the mechanism, draw out the steps involved in the reaction of cyclohexanone with methylamine in the presence of a trace of H^+ to form an imine.



- (b) The pH-rate profile diagram for this reaction is shown below.

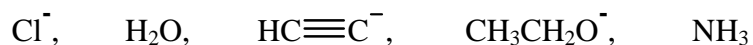


- (i) Why is the rate dependent on the pH?
- (ii) Why is the maximum rate observed at pH 4.5?
- (c) Using curly arrows show how the imine can be converted into the enamine.

8. (12 marks)

Answer **EITHER**:

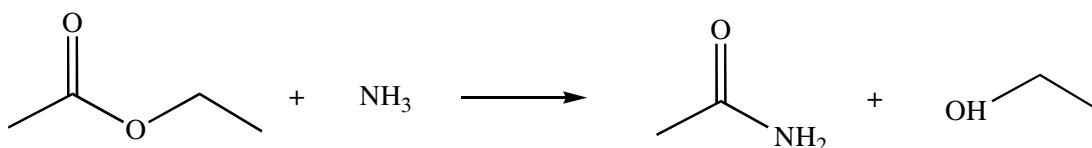
- (a) Place each of the following in order of **decreasing** nucleophilicity and explain your choice of order.



- (b) Place each of the following in order of **decreasing** leaving group ability and explain your choice of order.

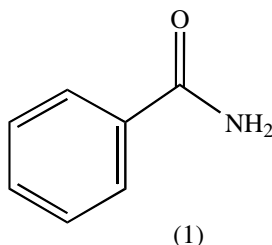


- (c) Explain why the following reaction proceeds as shown.



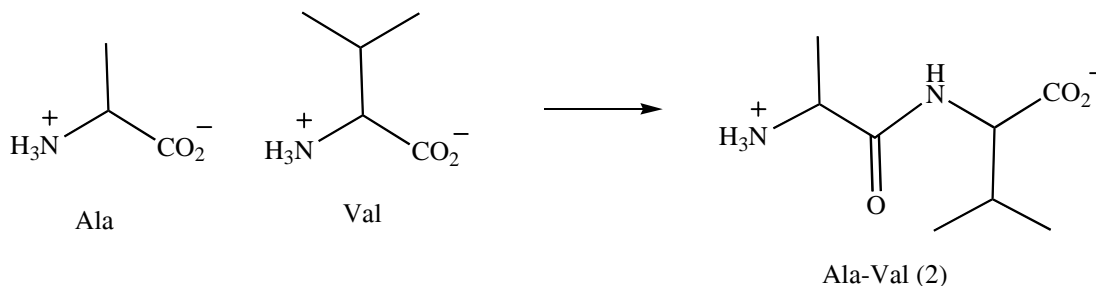
OR:

- (a) For a laboratory or industrial setting, suggest **TWO** methods that could be used for making benzamide (1).



TURN OVER

- (b) What approach, or approaches, would nature take to making the dipeptide Ala-Val (2) from the amino acids Ala and Val?

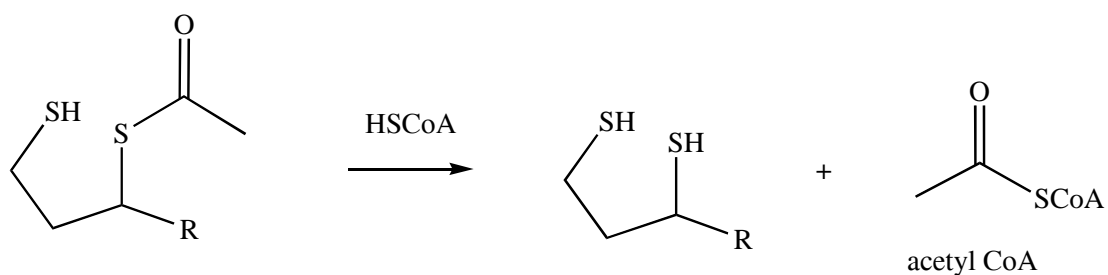


9. (12 marks)

Answer **EITHER**:

Thiol esters such as acetyl CoA play key roles in many metabolic cycles.

- (a) Explain why:
- (i) acetyl CoA is more reactive towards nucleophilic substitution; and
 - (ii) the α -methylene hydrogens of acetyl CoA are more acidic than those of ethyl acetate.
- (b) The final step in acetyl CoA production is shown below. Using curly arrows, describe a mechanism for this reaction.

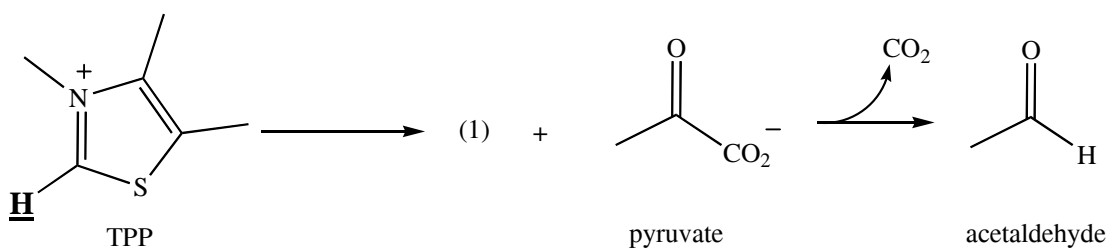


OR:

(a) What reaction is mediated by each of the following coenzymes in association with the appropriate apoenzyme (ie the holoenzyme):

- (i) pyridoxal phosphate;
- (ii) lipoic acid;
- (iii) nicotinamide;
- (iv) biocytin.

(b) Thiamine diphosphate (TPP) is a coenzyme that mediates the oxidative decarboxylation of α -keto acids. The “business” part of TPP is shown below.

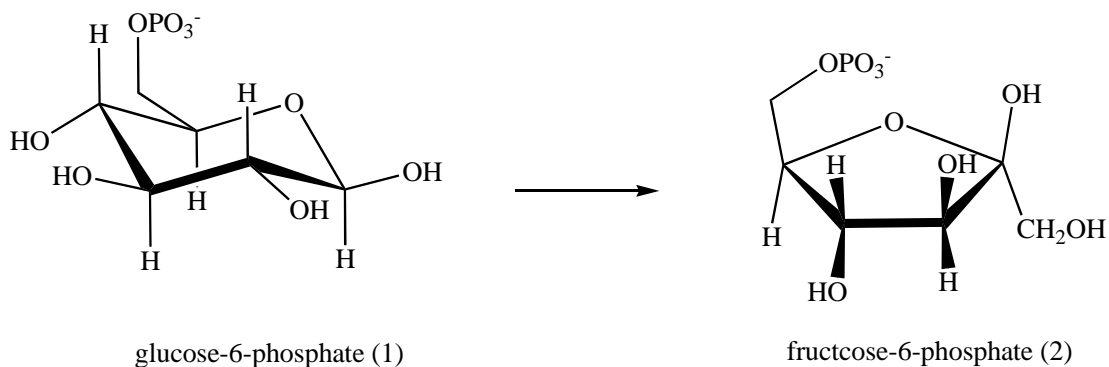


- (i) The highlighted hydrogen is acidic ($\text{p}K_a = 18$). Explain why.
 - (ii) If that acidic hydrogen is removed, (1) is formed. What is the structure of (1) and what is the name of this class of compound?
- (c) (1) is the reactive form of TPP. Using curly arrows show how (1) reacts with pyruvate and how the intermediate formed is then converted through to acetaldehyde.

TURN OVER

10. (9 marks)

In the glycolysis pathway glucose-6-phosphate (1) is converted into fructose-6-phosphate (2).



- (a) The trivial names for (1) and (2) are glucose-6-phosphate and fructose-6-phosphate. Suggest more formal names that correctly describe each structure. *[Note: the optical rotations of both glucose-6-phosphate (1) and fructose-6-phosphate (2) are positive]*
- (b) Using curly arrows suggest a mechanism for this isomerisation.

[Hint: Consider using the open chain form of the sugars in your mechanism.]

11. (20 marks)

(a) (i) **Derive the Langmuir** adsorption isotherm in the form

$$\theta = \frac{V}{V_{\text{mon}}} = \frac{KP}{1 + KP}$$

using a simple model of adsorption. State clearly any assumptions that are made, and the nature of any parameters you introduce.

(V is the volume of gas adsorbed on a surface; V_{mon} is the volume corresponding to monolayer coverage; P is the pressure of gas in contact with the surface.)

(ii) The **BET** isotherm may be expressed as

$$\frac{V}{V_{\text{mon}}} = \frac{cz}{(1 - z)\{1 - (1 - c)z\}}$$

Briefly outline the **additional** assumptions that are made in the derivation of this expression i.e. how is the Langmuir model extended? ($z = P/P^*$ where P^* is the vapour pressure of a macroscopic layer of liquid (liquefied gas) on the surface; c is a constant.)

Note: No derivation is required in this part.

(b) The adsorption of carbon monoxide (CO) on to a solid surface is known to follow the **Langmuir** isotherm. A series of measurements is made of the volumes of CO gas being adsorbed on a particular solid sample using a gas burette. All gas volume measurements are corrected to equivalent volumes in mm^3 at 20°C and 101.3 kPa . The solid sample adsorbs 195 mm^3 when the pressure of CO in contact with the solid is 100 kPa . The effective surface area of the solid sample is 2.24 m^2 and one CO molecule occupies an area of $1.71 \times 10^{-19} \text{ m}^2$ when adsorbed. **Calculate** the values of V_{mon} and K in the Langmuir isotherm for this sample (see part (a) above.)

[**Data:** $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$; $0^\circ\text{C} = 273 \text{ K}$; $N_{\text{Av}} = 6.022 \times 10^{23} \text{ (molecules) mol}^{-1}$]

TURN OVER

The following equations might be useful for questions 12 to 15:

$$N = 16 \left(\frac{t_R}{t_W} \right)^2 = \frac{L}{H} \quad R = \frac{\sqrt{N}}{4} \left(\frac{\alpha - 1}{\alpha} \right) \frac{k_2'}{(k_2' + 1)} \quad \alpha = \frac{k_2'}{k_1'} \quad t_R = t_0(1 + k')$$

$$V_R = V_0(1 + k') = V_0 + K_D V_S \quad k' = \frac{t_R - t_0}{t_0} = K_D V_S / V_M \quad R = \frac{2(t_{R2} - t_{R1})}{(t_{W2} + t_{W1})}$$

12. (7 marks)

The compounds ferritin (molecular mass 450 000) and transferrin (molecular mass 80 000) were separated by gel exclusion chromatography on Bio-Gel P-300. The column had a length of 37 cm and a 1.5-cm diameter. Eluate fractions of 0.65 mL were collected. The peak maxima came at fraction 22 for ferritin and fraction 32 for transferrin.

- What are the values of V_0 and V_S ?
- What is K_D for transferrin?

13. (5 marks)

In gas-liquid chromatography what steps could be taken to improve the resolution between two closely spaced peaks ($R_S < 1.5$)?

14. (20 marks)

Compounds A and B had retention times of 16.4 and 17.63 min, respectively, on a 30 cm HPLC column packed with 10 micron particles. t_0 for the column was 1.30 min. The peak widths (at base) for A and B were 1.11 and 1.21, respectively.

Calculate the:

- (a) k' for A and B;
- (b) column resolution;
- (c) average number of plates for the column;
- (d) plate height;
- (e) length of column required to achieve a resolution, R_S , of 1.5;
- (f) time taken for B to elute on the longer column;
- (g) plate height required for a resolution, R_S , of 1.5 on the original 30 cm column in the original time of 17.63 min.

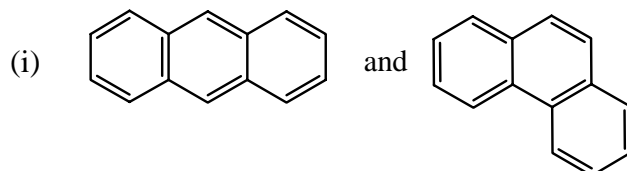
15. (8 marks)

Answer **EITHER**:

- (a) Describe the ideal characteristics of a glc detector.
- (b) Describe the principle upon which each of the following glc detectors is based:
- (i) thermal conductivity;
 - (ii) electron capture;
 - (iii) flame ionization.
- (c) Select **ONE** of the detectors above and list its principle advantages and disadvantages.

OR:

- (a) What classes, or types of compounds are best analysed by each of the following types of chromatography?
- (i) gas-liquid;
 - (ii) gel-permeation;
 - (iii) liquid-absorption;
 - (iv) reversed-phase partition.
- (b) Suggest, with brief reasons, what type of chromatography you think would be most suitable for separating each of the following:



- (ii) $\text{CH}_3\text{CH}_2\text{OH}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
- (iii) Ba^{2+} and Sr^{+2}
- (iv) $\text{C}_4\text{H}_9\text{COOH}$ and $\text{C}_5\text{H}_{11}\text{COOH}$

END OF PAPER