University of Canterbury

Term Test I, 2009

Prescription Number(s):	ENCH 241
Paper Title:	Analytical and Physical Chemistry

Time Allowed:	90 MINUTES
Number of pages:	SIX

Answer **ALL** questions

Graph paper is supplied.

Total marks = 80.
You should allocate about
1 minute per mark.

The following equations might be useful.

$$N = 16\left(\frac{t_R}{t_W}\right)^2 = \frac{L}{H} \qquad R_s = \frac{\sqrt{N}}{4}\frac{(\alpha - 1)}{\alpha}\left(\frac{k_2}{k_2+1}\right) \qquad \alpha = \frac{k_2}{k_1} \qquad t_R = t_M(1 + k)$$

$$V_R = V_M(1 + k) = V_M + K_D V_S \qquad k = \frac{t_R - t_M}{t_M} = K_D V_S / V_M \qquad R_s = \frac{2(t_{R_2} - t_{R_1})}{(t_{W_2} + t_{W_1})}$$

$$v = \pi r^2 h \qquad V_S = V_t - V_M$$

$$\textit{Langmuir Isotherm: } \theta_A = \frac{K^A_{equ} \cdot P_A}{1 + K^A_{equ} \cdot P_A}; \textit{ BET Isotherm: } \frac{V}{V_{mon}} = \frac{cz}{(1 - z)\{1 - (1 - c)z\}} \text{ where } z = \frac{P}{P^*}$$

1. (16 marks)

You are given a 25 cm HPLC column packed with solid support particles of 10 micrometre diameter and are asked to analyse a mixture of two compounds, A and B. At a column velocity of 0.25 cm/sec the column has a plate count, *N*, of 2,500 and it takes 25 minutes for the second compound B to elute. ·

(a) What is the value of *H* on this column?

(b) What is the value of k_B?

(c) If $\alpha = 1.1$, what is the value of k_A?

(d) With what peak width, t_w, does compound B elute?

(e) What is the retention time, t_R, of compound A?

(f) What is the resolution, R_s, between A and B?

(g) To fully separate A from B, how many theoretical plates, *N,* would be required?

2. (4 marks)

(a) In reverse-phase chromatography, which class of compound elutes first – polar or non-polar?

(b) In normal-phase chromatography, which class of compound elutes first – polar or non-polar?

(c) In reverse-phase chromatography, is the stationary phase polar or non-polar?]

(d) In normal-phase chromatography is the stationary phase polar or non-polar?

3. (8 marks)

Suggest a suitable chromatographic procedure for each of the following scenarios. In each case **justify** your choice of the method selected.

(a) The separation of a water-soluble ionic toxin, molecular weight 825 Da from higher-molecular-weight ionic peptides and lower-molecular-weight neutral compounds.

(b) The separation of two closely related compounds of molecular weight 600 Da, which are insoluble in hydrocarbon solvents, but freely soluble in polar solvents such as methanol.

(c) "Seagull Petroleum" is selling cheap petrol (a mixture of volatile hydrocarbons). It is suspected that this petrol contains too much benzene (carcinogenic) and not enough toluene. How could you confirm this?

(d) The separation and quantitation of a mixture of polycyclic aromatic hydrocarbons (PAHs)* from a sampling of Christchurch air during winter.

* *e.g. benzene, naphthalene anthracene , benzpyrene etc*.

4. (12 marks)

Answer THREE of the following

(a) What is the purpose of a suppressor column in ion-exchange chromatography? How does it work?

(b) Explain how affinity chromatography works. As part of your answer, outline the classes of compounds that can be separated using affinity chromatography.

(c) Explain how to prepare a calibration curve for quantitative analysis.

(d) Explain how the retention factor, k, can be manipulated to improve separation in gas chromatography. As part of your answer provide the range of ideal k values and explain why a value of $k > 10$ is undesirable.

5. (6 marks)

Answer EITHER (a) OR (b).

(a) The two types of detectors commonly used for GC analyses of samples from oil spills are flame ionisation detector (FID) and mass spectrometer (MS). Briefly explain how these two detectors work and outline the advantages of using an MS detector compared to an FID detector.

OR

(b) Explain the purpose of derivatising compounds for both gas chromatography and liquid chromatography. Provide ONE example of a derivatisation reaction used to prepare samples for gas chromatography. Explain whether in quantitative analysis you would need to derivatise both your samples and your standards.

6. (4 marks)

(a) Give ONE example of a method used to extract organic compounds from solid samples.

(b) Give ONE example of a method used to extract organic compounds from aqueous samples.

(c) Explain why an internal standard is often used for quantitative analyses of organic compounds.

7. (4 marks)

Blue Dextran (MW 750,000) was eluted from a gel permeation column (2-cm dia × 40 cm length) of Sephadex G-50 (fractionation range MW 1,500 to 30,000) in a volume of 34.6 mL.

(a) At what retention volume would haemoglobin (MW 64,000) be expected?

(b) What would be the retention volume of a molecule with $K_D = 0.75$?

8. (6 marks)

The van Deemter equation describes the phenomenon of band broadening in chromatographic processes.

$$H = A + B/\mu + C\mu$$

(a) What do the parameters A, B and C stand for?

(b) Explain why minimising the value of H is important.

9. (20 marks) Answer EITHER Part A OR Part B.

Part A. Answer ALL questions (I-IV) below:

(I) Give a definition of a catalyst AND provide an appropriate graphical illustration of the role of a catalyst in enabling the reaction to proceed.

(II) Name three major advantages of heterogeneous catalysts over homogeneous catalysts.

(III) Name two major disadvantages of heterogeneous catalysts.

(IV) Explain what the following properties of a catalyst refer to:

regioselectivity;

stereoselectivity;

enantioselectivity;

stereospecificity.

Discuss why improvements in control over different types of selectivity are important for the development of better catalysts.

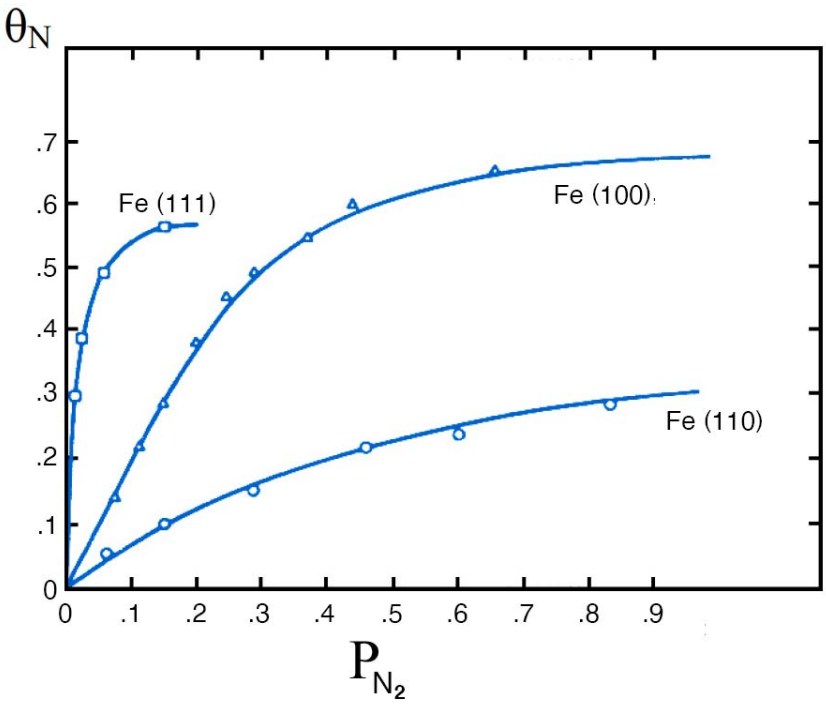
Part B. Answer ALL questions (I-IV) below:

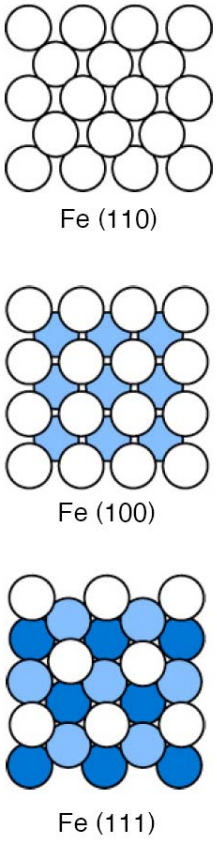
(I) Discuss the roles of physisorption and chemisorption in heterogeneous catalysis and provide an appropriate sketch of an energy plot as part of your answer.

(II) The Langmuir isotherm is a powerful, yet simple model for adsorption processes. State the assumptions used in the derivation of the Langmuir isotherm.

(III) In which range of θ_A (or V_{ad}/V_∞) is it difficult to judge if the adsorption process is better described by the Langmuir or the BET isotherm?

(IV) Assume that the adsorption process illustrated by the Figure below is described by the Langmuir isotherm. Identify which parameter of the Langmuir isotherm equation could be used to explain the observed differences in adsorption of nitrogen on to Fe (111), Fe (100) and Fe (110) surfaces? Rationalise your answer in the light of the general principles of chemisorption (refer to Figure below for help).





END OF PAPER