University of Canterbury

Term Test I, 2008

Wednesday, 30 April 4.10 – 5:10 pm

Prescription Number(s):	CHEM 224
Paper Title:	Analytical and Environmental Chemistry

Time Allowed:	60 MINUTES + reading time
Number of pages:	FIVE

Answer **ALL** questions

Graph paper is supplied.

Total marks = 60.
You should allocate about
1 minute per mark.

The following equations might be useful.

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

$$V_R = V_0(1 + k') = V_0 + K_D V_S \qquad k' = \frac{t_R - t_0}{t_0} = K_D V_S / V_M \qquad R_s = \frac{2(t_{R_2} - t_{R_1})}{(t_{W_2} + t_{W_1})}$$

1. (4 marks)

What do each of the terms N, α, t_R, H, μ, t_0, R_S, V_R, t_W, K_D, V_0 and k' stand for?

2. (7 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?

(e) What happens in reverse-phase chromatography if the polarity of the mobile phase is increased – will k' increase or decrease?

(f) What happens in normal-phase chromatography if the polarity of the mobile phase is increased – will k' increase or decrease?

(g) When separating a mixture by reversed-phase chromatography using 50% methanol/50% water, the value of k' was too low (~2). Should you use a higher or a lower concentration of methanol to correct this problem? Explain your answer.

(h) When separating a mixture by normal-phase chromatography using 50% hexane/50% ether, the value of k' was too low (~2). Should you use a higher or a lower concentration of ether to correct this problem? Explain your answer.

3. (14 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 in qualitative (general) terms why *H* is smaller when:

- smaller particles of uniform size
- lower mobile phase velocities
- less viscous mobile phases
- thinner films

are used in the chromatographic process. The diagram on the following page might be useful.

(c) Sketch the general shape of a typical van Deemter plot (*H vs* μ) for:

(i) gas/liquid chromatography; and

(ii) liquid/solid chromatography.

Why do the curves differ in general shape?

4. (10 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.

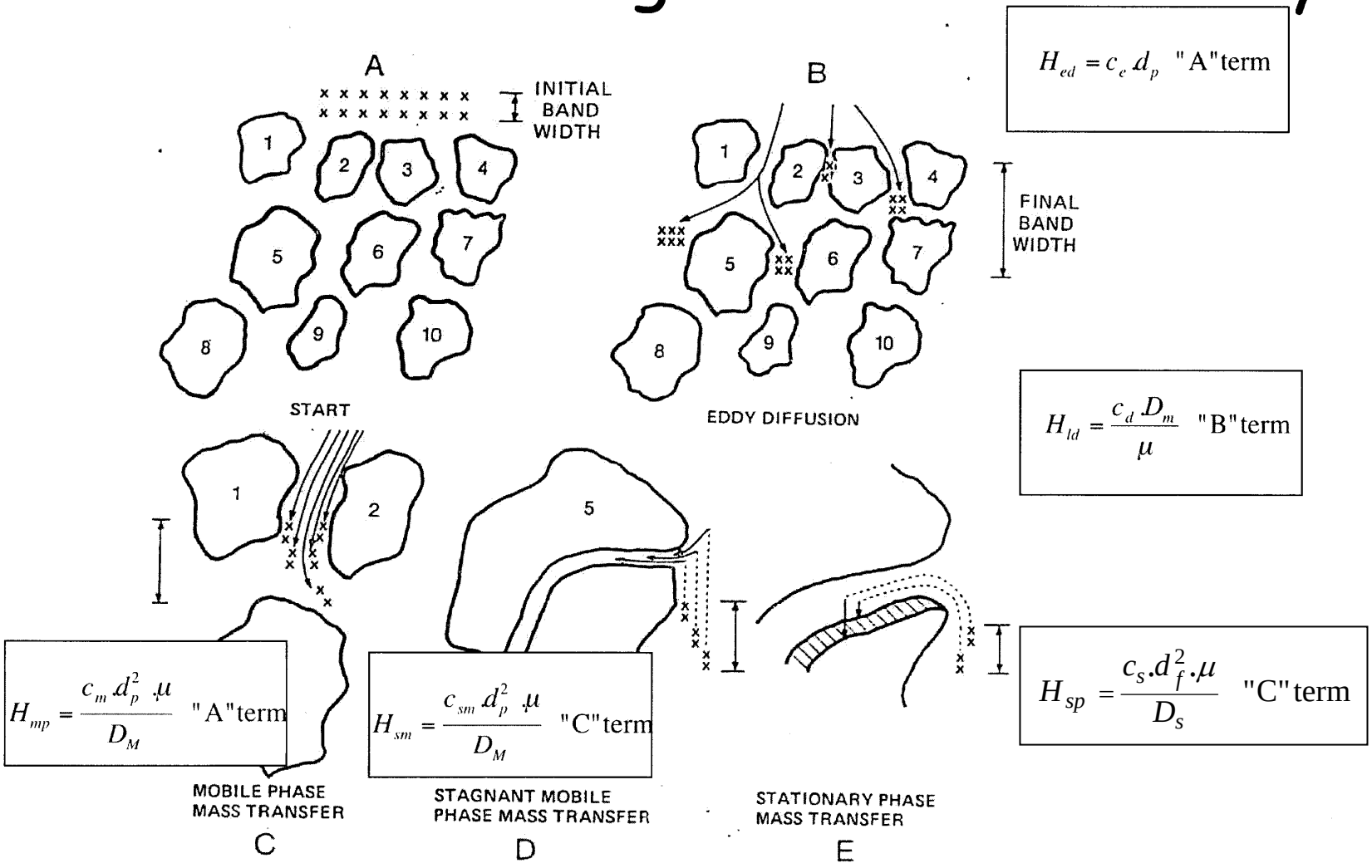
(b) The separation of two closely related compounds of molecular weight 600 Da, which are insoluble in hydrocarbon solvents, but freely soluble in polar solvents such as methanol.

(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*.

Factors Affecting Column Efficiency



$$H_{ed} = c_e \, d_p \quad \text{"A"term}$$

$$H_{ld} = \frac{c_d \, D_m}{\mu} \quad \text{"B"term}$$

$$H_{mp} = \frac{c_m \, d_p^2 \, \mu}{D_M} \quad \text{"A"term}$$

$$H_{sm} = \frac{c_{sm} \, d_p^2 \, \mu}{D_M} \quad \text{"C"term}$$

$$H_{sp} = \frac{c_s . d_f^2 . \mu}{D_s} \quad \text{"C"term}$$

5. (20 marks)

(a) Compound X was repeatedly analysed on the same 10-m gas/liquid chromatography column using nitrogen as carrier gas. Each time a different flow velocity (μ) was used. The results are tabulated below: .

Sample	Flow velocity (μ) cm/sec	Retention time (sec)	Peak width at half height (sec)
1	7	625	7.9
2	10	438	5.2
3	15	292	3.2
4	25	175	1.8
5	40	110	1.2
6	60	73	0.8
7	80	61	0.7

(i) Prepare a van Deemter plot (*H vs* μ) using the graph paper supplied.

(ii) What value is H_{opt} and what is μ_{opt}?

(b) What is the minimum length of column required for complete resolution of X from a related compound Y ($\alpha = 1.12$)?

(c) If helium was used as the carrier gas, would your van Deemter plot look different? Explain.

6. (5 marks)

What is the minimum number of theoretical plates required if the extrapolated base widths of two symmetrical peaks eluting off a chromatography column at 100 s and 103 s do not overlap?

END OF PAPER