Homework Solutions for Chem 422

Chapter 26

1. a) Elution is the process of washing substances through a chromatographic column with the mobile phase.

   b) The mobile phase in chromatography is the one that moves over or through an immobilized phase in a column or on the surface of a plate.

   c) The stationary phase in a chromatographic column is a solid or liquid that is fixed in place.

   d) The distribution constant (K) in chromatography is the ratio of the concentration of the analyte in the stationary phase to its concentration in the mobile phase when the two phases are in equilibrium.

   e) The retention time (t_R) for an analyte is the time between its injection onto a column and the appearance of its peak as it elutes from the column.

   f) The retention factor (k) is the ratio of the amount of analyte in the stationary phase to the amount in the mobile phase. It is generally calculated by $k' = (t_R - t_M)/t_M = t_R'/t_M$.

   g) The selectivity factor (α) of a column for two analytes (A eluting before B) is given by $\alpha = K_B/K_A = k'(B)/k'(A) = t_R'(B)/t_R'(A)$.

   h) The plate height (H) of a chromatographic column is defined by the relationship $H = \sigma^2/L$, where σ is the standard deviation of the concentration distribution for the analyte in its elution band (in units of length) and L is the length of the column packing.

   i) Longitudinal diffusion is a source of band broadening in a column in which an analyte diffuses from the concentration center of a band to the more dilute regions on either side.

   j) Eddy diffusion is a source of band broadening in a column in which analyte particles travel through the column by pathways that differ in length, and hence time.

   k) The resolution (R_s) of a column for two analytes (A eluting before B) is given by $R_s = [t_R(B) - t_R(A)]/[(W_A + W_B)/2]$, where W is the baseline width of a chromatographic peak in the same units as the analyte retention time.

   l) The eluent in chromatography is the fresh mobile phase that carries the sample through the column.

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3. The variables that lead to increased zone broadening include:

    1) large particle diameters for column packing

    2) large column diameters

    3) high temperatures (for gas chromatography)

    4) thick layers of liquid stationary phases

    5) very high or very low flow rates

    6) high viscosity mobile phase (for liquid chromatography)

    7) slow introduction of sample onto column

6. Variables that affect the selectivity factor (α) include:

    1) composition of the mobile phase (for liquid chromatography)

    2) column temperature (for gas chromatography)

    3) composition of the stationary phase

7. In gas chromatography, the retention factor is varied by changing the column temperature during the run (temperature programming). In liquid chromatography, the retention factor is varied by changing the composition of the mobile phase during the run (gradient elution).

8. The number of plates in a column for a given analyte can be determined by measuring the retention time (t_R) and the width of a peak at its base (W) or its half height ($W_{½}$). The number of plates is then given by:

$$N = 16\left(\frac{t_R}{W}\right)^2 = 5.54\left(\frac{t_R}{W½}\right)^2$$

9. Decreasing the peak widths will increase resolution as will increasing the peak separation.

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10. There is a minimum in a plot of plate height versus flow rate because band broadening due to longitudinal diffusion effects decreases with increasing flow rate while broadening due to mobile-phase and stationary-phase mass-transfer effects increases with increasing flow rate. Since longitudinal diffusion is much less a factor in liquid chromatography, the minimum plate height is found at a much lower flow rate than for gas chromatography.

11. Gradient elution is a method used in liquid chromatography in which the composition of the mobile phase is changed continuously or in steps in order to improve separations.

12. The variables that improve band separation include:

    1) increased column length

    2) variations in mobile phase composition, including changes in pH (for liquid chromatography)

    3) stationary phases that produce significantly different partition coefficients

    4) use of a stationary phase that selectively complexes certain analytes

    5) choice of optimum temperature

13. Slow sample introduction leads to band broadening.

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14. a) Calculate the number of plates using the equation given in the answer to problem 8 above.

Species	N
A	$16(5.4/0.41)^2 = 2775$
B	$16(13.3/1.07)^2 = 2472$
C	$16(14.1/1.16)^2 = 2364$
D	$16(21.6/1.72)^2 = 2523$
	$\Sigma N = 10{,}134$

b) Average N = 10,134/4 = 2534 = 2.5×10^3 plates

$$s = \sqrt{\frac{\Sigma(x_i - \bar{x})^2}{N-1}} = 174 = 0.2 \times 10^3$$

c) H = 24.7 cm/2534 plates = 9.7×10^{-3} cm/plate

15. a) Calculate the retention factor using the equation $k' = (t_R - t_M)/t_M$.

$k_A' = (5.4 - 3.1)/3.1 = 0.74$

$k_B' = (13.3 - 3.1)/3.1 = 3.3$

$k_C' = (14.1 - 3.1)/3.1 = 3.5$

$k_D' = (21.6 - 3.1)/3.1 = 6.0$

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16. a) Calculate the resolution by the equation $R_s = [t_R(C) - t_R(B)]/[(W_B + W_C)/2]$.

$R_s = (14.1 - 13.3)/[(1.07 + 1.16)/2] = 0.72$

b) Calculate the selectivity factor by the equation $\alpha = t_R'(C)/t_R'(B)$.

$\alpha = (14.1 - 3.1)/(13.3 - 3.1) = 1.08$

18. a) Calculate the number of plates using the equation given in the answer to problem 8 above.

Component	N
methylcyclohexane	$16(10.0/0.76)^2 = 2770$
methylcyclohexene	$16(10.9/0.82)^2 = 2827$
toluene	$16(13.4/1.06)^2 = 2557$
	$\Sigma N = 8154$

Average N = 8154/3 = 2718 = 2.7×10^3 plates