Homework 10

27-1 In gas-liquid chromatography, the stationary phase is a liquid that is immobilized on a solid. Retention of sample constituents involves equilibria between a gaseous and a liquid phase. In gas-solid chromatography, the stationary phase is a solid surface that retains analytes by physical adsorption. Here separations involve adsorption equilibria.

27-5 A concentration-sensitive detector responds to the concentration of the analyte in the mobile phase, whereas a mass-sensitive responds to the number of analyte molecules or ions that come in contact with the detector. Peak areas for a concentration-sensitive detector increase as the flow rate decreases because the analyte is in contact with the detector for a longer period. Peak areas for a mass-sensitive detector are not greatly affected by flow rate. Using CS for concentration sensitive and MS for mass sensitive, we find for each of the detectors listed (a) CS, (b) MS, (c) MS, (d) CS, (e) MS, (f) MS/

27-28 Gas-solid chromatography is used primarily for separating low-molecular-weight gaseous species, such as carbon dioxide, carbon monoxide, and oxides of nitrogen.

27-29 Gas-solid chromatography has limited application because active or polar compounds are retained more or less permanently on the packings. In addition severe tailing is often observed owing to the nonlinear character of the physical adsorption process.

28-1 (a) Substances that are somewhat volatile and are thermally stable.
(b) Molecular species that are nonvolatile or thermally unstable.
(c) Most low to moderate molecular weight organic compounds that are nonvolatile or thermally unstable.
(d) Substances that are ionic.
(e) High-molecular-weight compounds that are soluble in nonpolar solvents.
(f) High-molecular-weight hydrophilic compounds.
(g) Low-molecular-weight nonpolar gases.
(h) Nonpolar low to moderate molecular weight organic compounds and particularly isomeric organic species.
(j) Small organic and inorganic ions.

28-2 Three methods for improving resolution include:
(1) adjustment of k_A' and k_B' by employing a multicomponent mobile phase and varying the ratio of the components to find an optimal mixture;
(2) variation in the chemical composition of the solvent system in such a way as to make α larger;
(3) employing a different packing in which α is greater.

28-22 For a normal-phase packing, Equation 28-3 (page 832) applies. That is,

$$\frac{k_2'}{k_1'} = 10^{(P_1' - P_2')/2} \qquad (1)$$

where P_1' and P_2' are the polarity indexes of chloroform and cyclohexane, respectively.

(a) $k_1' = (29.1 - 1.05)/1.05 = \underline{\underline{26.7}}$

(b) $P_{AB}' = 0.50 \times 4.1 + 0.50 \times 0.1 = 2.10$

Substituting into (1) gives

$$\frac{10}{26.7} = 10^{(2.1 - P_2')/2}$$

Taking the log of both sides of this equation gives

$$\log \frac{10}{26.7} = -0.427 = (2.1 - P_2')/2$$

$$P_2' = 2 \times 0.427 + 2.1 = 2.95$$

Substituting P_2' for P_{AB}',

$2.95 = \phi_A \times 4.1 + \phi_B \times 0.1$ and $\phi_A + \phi_B = 1.00$

We can get $\phi_A = 0.712$, $\phi_B = 0.288$

Thus the mixture should be 71% $CHCl_3$ and 29% n-hexane.