1. (4 pts) State Henry’s Law, as it applies to the equilibrium of a substance between air (vapor phase) and aqueous solution (liquid phase). Over what approximate range of aqueous concentration (expressed in mole fraction and in mol/L) do you expect Henry’s Law to apply to non-dissociating organic compounds? Explain your answer in terms of the activity coefficient and its concentration dependence.

2. (6 pts) Henry’s constants are expressed in a variety of different units. Often the most useful way of expressing Henry’s constant is in the form of a dimensionless ratio of mass concentrations:

\[ H_\infty = \frac{\text{g/L in gas phase}}{\text{g/L in liquid solution}} \]

a. (3 pts) In your course reader, look up the values of vapor pressure and aqueous solubility for carbon tetrachloride (CCl₄, also called tetrachloromethane) at 25 °C. Use these to calculate the value of \( H_\infty \) for carbon tetrachloride at 25 °C.

b. (3 pts) Then, estimate the value of \( H_\infty \) for CCl₄ at 10 °C and 35 °C using the temperature dependence given in the Reader.

3. (7 pts) Methyl-ethyl ketone (MEK, formula CH₃-CO-C₂H₅) is a widely used industrial solvent. It is also called 2-butanone. If you look up the chemical properties in Section 4B of your course reader, you will find the following properties for 25 °C:

\[ \log_{10}(P^{sat}) = 4.09, \text{ for } P^{sat} \text{ measured in Pa} \]

\[ \log_{10}(H_\infty) = -2.60 \]

a. (3 pts) From these data, estimate the aqueous solubility in units mol/L, assuming that Henry’s Law is valid over the entire solubility range of MEK.

b. (4 pts) State whether you expect Henry’s Law to be valid over this entire range. Explain why or why not. If you think Henry’s Law is not valid over the range, does it affect your estimate of \( C^{SL} \)? If so, do you think the actual value should be higher or lower than what you reported in part (a)?
4. (15 pts)
   a. (3 pts) Calculate the distribution coefficient, $K_d$, that pertains to the partitioning of CCl$_4$ between water and solids, given that $K_{ow} = 440$ and the organic carbon content of the solid phase is $f_{OC} = 0.2$. Use the Karickhoff relationship given in class. Be sure to specify the units of $K_d$.
   b. (3 pts) Suppose that the density of the solid phase is $\rho_s = 1.1$ g/cm$^3$. Calculate the ratio of concentrations of CCl$_4$ in the solid and solution phases, $K_p$ -- use units of (g CCl$_4$ per m$^3$ solid)/(g CCl$_4$ per m$^3$ aqueous solution).
   c. (3 pts) Suppose you had a column of water with some suspended particulate matter. The particulate matter has density $\rho_s = 1.1$ g/cm$^3$, as in part (b), above, and occupies 0.01% of the total volume of the system. Calculate the equilibrium distribution of CCl$_4$ mass between solid and solution phases, i.e., what fraction of the CCl$_4$ mass is in each phase? Hint: what is the relationship between mass ratio, volume ratio, and concentration ratio?
   d. (3 pts) Now suppose that you had a sediment. The sediment contains both a solid phase (i.e., the solid grains) and a water phase (which fills the pores in between the solid grains). The solid phase occupies 60% of the total volume; or, in other words, the porosity of the sediment is 40%. The particulate matter has density $\rho_s = 1.1$ g/cm$^3$, as in part (b), above. Calculate the equilibrium distribution of CCl$_4$ mass between the solid and solution phases, i.e., what fraction of the CCl$_4$ mass is in each phase?
   e. (3 pts) Discuss your answers to b, c, and d in terms of the differences between the concentration ratios and the mass distribution ratios.

5. (9 pts) Methanol, CH$_3$OH, is completely miscible in water. Henry’s constant expressed as a dimensionless ratio of mole fractions is $H_{xy} = 0.30$ [moles in vapor/moles of air] / [moles in solution/moles of water]
   a. (3 pts) If the vapor pressure of pure liquid methanol is 0.191 atm at 298 K, calculate the value of the activity coefficient in aqueous solution at 1 atm. Over what approximate range of concentration do you expect your estimate to be valid?
   b. (3 pts) Judging by the value calculated in part (a), do you consider methanol to be hydrophilic or hydrophobic? Explain.
   c. (3 pts) Using the above, estimate a numerical value for the octanol-water partition coefficient (concentration basis) for methanol. Explain your reasoning and justify any assumptions.

6. (9 pts) A closed bottle contains 10 mL air and 90 mL water at 25 °C. Suspended in the water is 36 mg of particulate (i.e. solid) matter having a specific gravity of 1.00 and an organic carbon fraction of 0.10. The bottle contains 10 mg of tetrachloroethene (CCl$_2$=CCl$_2$), also known as perchloroethylene (PCE), which has the following properties at 25 °C:
   \[
   MW = 165.8; \ P^m = 2500 \text{ Pa}; \ C_{SL} = 0.14 \text{ g/L}; \ K_{ow} = 7.6 \times 10^2
   \]
   Assuming the system is at equilibrium, calculate the mass of PCE in each of the three phases (air, aqueous solution, and suspended solids). Ignore degradation or other loss mechanisms. Hint: use a mass balance.