① Show that the mole fraction of CCl_4 is 0.18

Suppose we have 1.0 L of solvent mixture

$1.0 \text{ L solvent} \times \dfrac{1520 \text{ g solvent}}{\text{L solvent}} \times \dfrac{1 \text{ mole solvent}}{138 \text{ g solvent}} = 11.01 \text{ mol solvent}$

Mass fraction = 0.20 $\Rightarrow$ $1.0 \text{ L solvent} \times \dfrac{1520 \text{ g solvent}}{1 \text{ L solvent}} \times \dfrac{0.20 \text{ g } CCl_4}{1.0 \text{ g solvent}} = 304 \text{ g } CCl_4$

$304 \text{ g } CCl_4 \times \dfrac{1 \text{ mole } CCl_4}{153.8 \text{ g } CCl_4} = 1.9766 \text{ mol } CCl_4$

mole fraction $= \dfrac{1.9766 \text{ mol } CCl_4}{11.01 \text{ mol solvent}} = 0.1795 \approx \underline{0.18} \checkmark$

② Estimate conc. of CCl_4 in the aqueous phase

$C_i^{water} = X_i^{solvent} \times C^{SL}$ and we know $X_i^{solvent} = 0.18$

$C^{SL} = 10^{-2.20} \dfrac{mol}{L}$ from table $\Rightarrow$ $C^{SL} = 0.0063 \dfrac{mol}{L}$

$0.00631 \dfrac{mol}{L} \times \dfrac{153.8 \text{ g}}{mol} \times \dfrac{1000 \text{ mg}}{1 \text{ g}} = C^{SL} = 970.4 \text{ mg}/L$

$\therefore C_i^{water} = (0.18)(970.4 \text{ mg}/L) = \underline{174 \text{ mg}/L}$ to three sig. digits...
OK if you said 170, 175, 180

Now convert that to mole fraction

Assume it's dilute enough that the pond water is mostly water.

Thus

$X_i^{water} = 174 \dfrac{mg \, CCl_4}{L \, water} \times \dfrac{1 \text{ g } CCl_4}{1000 \text{ mg}} \times \dfrac{1 \text{ mol } CCl_4}{153.8 \text{ g } CCl_4} \times \dfrac{1 \text{ L water}}{998 \text{ g water}} \times \dfrac{18.01 \text{ g}}{1 \text{ mole water}}$

$\underline{X_i^{water} = 2.0 \times 10^{-5}}$ ... dilute enough that Henry's Law would be valid

③ Estimate/calculate concentration of CCl_4 in sediment

At equilibrium, $q_i^{sed} = K_d \, C_i^{water}$

$K_d = f_{oc} \cdot K_{oc}$

$\log_{10} K_{oc} = 0.88 \log_{10} (K_{ow}) - 0.27$ and $\log_{10}(K_{ow})$ is given

So: $\log_{10} K_{oc} = (0.88)(2.73) - 0.27 = 2.1324$

$$K_{oc} = 10^{2.1324} \frac{L \, water}{kg \, organic \, carbon} = 135.6 \frac{L \, water}{kg \, organic \, carbon}$$

$$K_d = \left(0.10 \frac{kg \, organic \, carbon}{kg \, sediment}\right)\left(135.6 \frac{L \, water}{kg \, org. \, c}\right) = 13.56 \frac{L \, water}{kg \, sediment}$$

$$q_i^{sediment} = \left(174 \frac{mg \, CCl_4}{L \, water}\right)\left(13.56 \frac{L \, water}{kg \, sediment}\right) = \underline{\underline{2360 \frac{mg \, CCl_4}{kg \, sed.}}}$$

④ Are air and water at equilibrium if $C_i^{air} = 17 \, ^{mg}/L$?

Need H_{cc}. Given $\log_{10}(H_{pc}) = 1.38 \Rightarrow H_{pc} = 23.99 \frac{L \cdot atm}{mol}$

$$H_{cc} = \frac{H_{pc}}{RT} = \frac{23.99 \, L \cdot atm/mol}{\left(0.08206 \frac{L \cdot atm}{mol \cdot K}\right)(298.15 \, K)} = \underline{\underline{0.98}}$$

$C_i^{water} = 174 \, ^{mg}/L \qquad C_i^{air} = 17 \, ^{mg}/L \qquad H_{cc} = 0.98$

Notice $C_i^{water} \gg \dfrac{C_i^{air}}{H_{cc}}$ or $C_i^{air} \ll H_{cc} \, C_i^{water}$

Thus <u>the system is not at equilibrium</u>

CCl_4 <u>will move from the water to the air</u> because there is "too much" CCl_4 in the water and "not enough" CCl_4 in the air... or fugacity of CCl_4 in the water exceeds fugacity in the air!

⑤ Estimate/calculate K_L

We know $\dfrac{1}{K_L} = \dfrac{1}{k_L} + \dfrac{1}{k_G H_{cc}}$

For CCl_4, we notice H_{cc} is pretty high --- $H_{cc} = 0.98$

Thus we see $k_G H_{cc} \gg k_L$ even if k_G is "only" $20 * k_L$

The gas-side resistance is negligible

$\dfrac{1}{K_L} \approx \dfrac{1}{k_L}$ $\Rightarrow$ $K_L \approx k_L$ $\Rightarrow$ $\underline{\underline{K_L \approx 1.1 \times 10^{-5} \ ^m/s}}$

⑤ Alternate method -- the "long way" --- not recommended, but fine ---

Suppose $k_G = 20 * k_L$ $\Rightarrow$ $k_G = 2.2 \times 10^{-4} \ ^m/s$ ... lower limit

$\dfrac{1}{K_L} = \dfrac{1}{1.1\times10^{-5} \ ^m/s} + \dfrac{1}{(0.98)(2.2\times10^{-4} \ ^m/s)} = 95547.3 \ \dfrac{s}{m}$

$K_L = 1.0466 \times 10^{-5} \approx 1.0 \times 10^{-5} \ ^m/s$

And if $k_G = 100 * k_L$ $\Rightarrow$ $k_G = 1.1 \times 10^{-3} \ ^m/s$ ... upper limit

$\dfrac{1}{K_L} = \dfrac{1}{(1.1\times10^{-5} \ ^m/s)} + \dfrac{1}{(0.98)(1.1\times10^{-3} \ ^m/s)} = 91836.7 \ \dfrac{s}{m}$

$K_L = 1.0889 \times 10^{-5} \approx 1.1 \times 10^{-5} \ ^m/s$

So we see $K_L \approx 1.05\times10^{-5} \ \dfrac{m}{s} - 1.09 \times 10^{-5} \ \dfrac{m}{s}$

$\underline{\underline{K_L \approx 1.07 \times 10^{-5} \ \dfrac{m}{s}}}$ to reasonable error

⑥ Rate of CCl_4 mass transfer?

From problem ⑤ we know CCl_4 is exiting the pond, going to air.
How fast?

$$J = K_L \left[C_i^{water} - \frac{C_i^{air}}{H_{cc}} \right]$$

$$J = \left(1.1 \times 10^{-5} \ \frac{m}{s} \right) \left[174 \ \frac{g}{m^3} - \frac{17 \ g/m^3}{0.98} \right] = 0.00172 \ \frac{g}{m^2 \cdot s}$$

$$J \cdot A = \left(40,000 \ m^2 \right) \left(0.00172 \ \frac{g}{m^2 \cdot s} \right) = 68.9 \ \frac{g}{s} \cdot \frac{86,400 \ s}{d}$$

Exiting the pond at $\underline{6 \times 10^6 \ g/d} = 6000 \ kg/d$

Hmmm. That is probably not realistic. At that rate, all of it would be gone in under a day. Probably means the estimate of k_L was too large.

... also, probably we would not have $C_i^{water} = 174 \ mg/L$, that is too high, so we are over-estimating the flux. But OK for here.

⑦ Derive formula from question 2

If the water and the solvent mixture are at equilibrium,

$$\hat{f}_i^{water} = \hat{f}_i^{solvent} \qquad \text{where here } i \text{ denotes } CCl_4$$

$$x_i^{water} \, \gamma_i^{water} \, P^v = x_i^{solvent} \, \gamma_i^{solvent} \, P^v$$

Notice P^v cancels out $\Rightarrow$ $x_i^{water} \, \gamma_i^{water} = x_i^{solvent} \, \gamma_i^{solvent}$

Assume solvent mixture is ideal $\Rightarrow \gamma_i^{solvent} = 1$

Also $\gamma_i^{water} = \dfrac{1}{x_i^{SL}}$

$\therefore \quad x_i^{water} \cdot \dfrac{1}{x_i^{SL}} = x_i^{solvent}$

$$\underline{x_i^{water} = x_i^{solvent} \, x_i^{SL}}$$

But then we can just convert aqueous mole fractions to aqueous concentrations

$$\underline{\underline{C_i^{water} = x_i^{solvent} \, C_i^{SL}}} \qquad \text{... which is what we had in problem ②}$$

⑧ Which phase has greater mass of CCl_4 ?

Water: $\left(2.5 \times 10^5 \, m^3\right)\left(174 \frac{g}{m^3}\right) = 4.35 \times 10^7 \, g \; CCl_4$ in water

Sediment: $\left(1000 \, m^3 \text{ sediment}\right)\left(1500 \frac{kg \text{ sediment}}{m^3 \text{ sediment}}\right)\left(2360 \frac{mg}{kg}\right)\left(\frac{1 \, g}{1000 \, mg}\right)$

$$= 3.54 \times 10^6 \, g \; CCl_4 \text{ in sediment}$$

There is about 12 times more CCl_4 in the water than in the sediment.

Why?

-- principally because the volume of the water $(2.5 \times 10^5 \, m^3)$ is much larger than the volume of the sediment $(1000 \, m^3)$, by a factor of 250.

This volume difference is partially overcome by the fact that CCl_4 somewhat prefers organic phases to aqueous phases -- $K_{ow} = 537$ and $K_d \approx 14 \frac{L \text{ water}}{kg \text{ sediment}}$. But the mild preference for organic phases is not enough to overcome the huge volume difference between water and sediment. Hence, most of the CCl_4 mass resides in the water, not in the sediment.

$$K_p = 13.56 \frac{L \text{ water}}{kg \text{ sediment}} * \frac{1500 \, kg \text{ sediment}}{1 \, m^3 \text{ sediment}} * \frac{1 \, m^3}{1000 \, L} = 20.3 \frac{L \text{ water}}{L \text{ sediment}}$$

That's kind of like H_{cc} -- a dimensionless partitioning coefficient.

$$\frac{M_i^{sed}}{M_i^{water}} = \left(\frac{V^{sed}}{V^{water}}\right) k_p = \left(\frac{1000 \, m^3}{2.5 \times 10^5 \, m^3}\right)(20.34) = 0.08$$

The mass of CCl_4 in the sediment is about 8% of that in the water.