

∴ NONE of these reactions involves OXIDATION

2. Vapour pressure is temperature dependent. $\uparrow T, \uparrow P$

$$\ln(P_2/P_1) = -\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

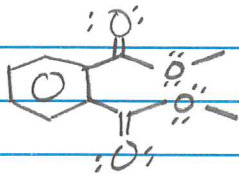
$$\ln(P_2/16,600 \text{ Pa}) = -\frac{107,300 \text{ J/mol}}{8,314 \text{ J/mol K}} \left(\frac{1}{268.2 \text{ K}} - \frac{1}{298.2 \text{ K}} \right)$$

$$= -4.8411$$

$$\therefore P_2/16,600 \text{ Pa} = e^{-4.8121} = 7.898 \times 10^{-3}$$

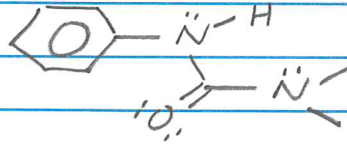
$$\text{and } P_2 = 131 \text{ Pa}$$

3.



H-bond acceptor

Liquid at R.T.



H-bond donor & acceptor

Solid at R.T.

$$C_w^{sat}(L) = \frac{1}{V_w \gamma_w^{sat}}$$

$$\therefore \gamma_w^{sat} = \frac{1}{(0.0180 \frac{L}{mol})(10^{-1.66} \frac{mol}{L})}$$

$$= 2.54 \times 10^3$$

more hydrophobic

∴ larger aqueous activity co-efficient

$$C_w^{sat}(s) = C_w^{sat}(L) \frac{P_{cs}^0}{P_{cl}^0}$$

$$\therefore C_w^{sat}(L) = C_w^{sat}(s) \frac{P_{cl}^0}{P_{cs}^0}$$

$$= \frac{10^{-1.63} M}{e^{-6.8 \left(\frac{408.2}{298} - 1 \right)}}$$

$$= \frac{2.344 \times 10^{-2} M}{8.089 \times 10^{-2}}$$

$$= 0.2898 \frac{mol}{L}$$

$$\therefore \gamma_w^{sat} = \frac{1}{(0.0180 \frac{L}{mol})(0.2898 \frac{mol}{L})}$$

$$= 192$$

INTUITION confirmed!

(whew)

more hydrophilic
∴ smaller aqueous activity co-efficient

$$\ln \frac{P_{cs}^0}{P_{cl}^0} = -6.8 \left(\frac{T_m}{T} - 1 \right)$$

$$\therefore \frac{P_{cs}^0}{P_{cl}^0} = e^{-6.8 \left(\frac{T_m}{T} - 1 \right)}$$

used here →

$$(4.) \quad a) \quad \log K_{ow} = -0.87 \log C_w^{sat} + 0.68$$

$$\log C_w^{sat} = -0.053 V_m + 3.2$$

$$\therefore \log K_{ow} = -0.87 (-0.053 V_m + 3.2) + 0.68$$

$$\log K_{ow} = 0.0461 V_m - 2.784 + 0.68$$

$$V_m \approx \frac{MW}{\rho} = \frac{142 \text{ g/mol}}{1.0 \text{ g/cm}^3} = 142 \text{ cm}^3/\text{mol}$$

$$\begin{aligned} \therefore \log K_{ow} &= 0.0461 (142) - 2.104 \\ &= 6.55 - 2.104 \\ &= 4.45 \end{aligned}$$

(see also fig. 1)

b) LFER's involving one parameter rely on similar inter-molecular interactions between solute and solvent systems. This requirement is generally only observed for a series of molecules that bear identical functional groups

5. Considering three phase system of air, water and octanol we can write

$$f_{air} = \frac{C_{air} \cdot V_{air}}{C_{air} V_{air} + C_{water} V_{water} + C_{octanol} V_{octanol}}$$

$$K_{aw} = \frac{C_{air}}{C_{water}} \quad \& \quad K_{ow} = \frac{C_{octanol}}{C_{water}}$$

$$\therefore C_{water} = \frac{C_{air}}{K_{aw}}$$

$$\therefore C_{octanol} = K_{ow} \cdot C_{water}$$

Substituting into f_{air} expression yields,

$$f_{air} = \frac{C_{air} \cdot V_{air}}{C_{air} V_{air} + \frac{C_{air}}{K_{aw}} \cdot V_{water} + K_{ow} C_{water} V_{octanol}}$$

$$= \frac{\cancel{C_{air}} V_{air}}{\cancel{C_{air}} V_{air} + \frac{\cancel{C_{air}}}{K_{aw}} \cdot V_{water} + K_{ow} \frac{\cancel{C_{air}}}{K_{aw}} \cdot V_{octanol}}$$

$$= \frac{V_{air}}{V_{air} + \frac{V_{water}}{K_{aw}} + \frac{K_{ow}}{K_{aw}} \cdot V_{octanol}}$$

or

$$\frac{K_{aw} V_{air}}{K_{aw} V_{air} + V_{water} + K_{ow} V_{octanol}}$$

Q. E. D.

(6)

a) multi-parameter LFER for K_w

$$\ln K_w = -\ln P^{\circ}(L) + s \left[V^{2/3} \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right) \right] + a(\alpha) + b(\beta) + v(\bar{V}) + C$$

vapour pressure of sub-cooled liquid ($P^{\circ}(L)$) - reports strength of intermolecular forces in solute that need to be overcome to separate solute molecules

vdW dispersion energy term $\left[V^{2/3} \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right) \right]$ related to polarizability of solute and reports energy of solute being solvated by water

α is a hydrogen bond donating energy term related to specific functional groups ($-OH, -NH_2$) that form 'H-bonds' to water

β is a hydrogen bond accepting energy term related to specific functional groups with lone pair electrons that form 'H-bonds' to water

\bar{V} is a molar volume term which relates to the energy costs of creating a 'hole' in between water molecules to accommodate solute

b) pre-requisites for using MPLC to predict K_{ow}

- constant chromatographic conditions (i.e. solvent, temperature, flow rate etc)

- structurally related series of compounds with known K_{ow} to establish LFER

- use of relative retention times (i.e. capacity factor)

c) thermodynamic property from K_{aw} w temp.

The temperature dependence of K_{aw} will be related to the enthalpy change (std. state) for the air-water partitioning process.

A plot of $\ln K_{aw}$ vs inverse temperature will yield straight line with slope = $-\frac{\Delta H_{aw}}{R}$

d) air-octanol partitioning varies widely for apolar
(See solution to Q7 on PS2)

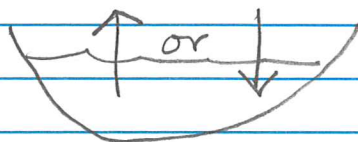
e) salt added before liq.-liq. extraction

Adding salt to an aqueous sample will reduce the water solubility of an organic solute (i.e. increase f_w^{sat}). This increases the partitioning into an organic solvent which pre-concentrates the solute and improves analytical recovery and sensitivity.

f) quantitative estimation methods

- predict intrinsic properties prior to synthesizing new compds.
- faster, cheaper, more ethical than live animal testing
- does not require pure authentic compds
- safer when dealing with highly toxic compds

7.



is pond source or sink
with respect to air

Calculate K_{aw} and compare to Q_{aw}

$$K_{aw} = \frac{K_H}{RT}$$

$$\text{and } K_H \cong \frac{p^0}{C_w^{\text{sat}}}$$

$$\therefore K_H \cong \frac{10^{-2.57} \text{ atm}}{10^{-2.04} \text{ M}} @ 25^\circ\text{C}$$

$$= \frac{2.69 \times 10^{-3} \text{ atm}}{9.12 \times 10^{-3} \text{ M}}$$

$$= 0.295 \text{ atm M}^{-1}$$

$$\therefore K_{aw} = \frac{0.295 \text{ atm M}^{-1}}{\left(\frac{0.08206 \text{ L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right) (298\text{K})}$$

$$= 0.0121$$

$$Q_{aw} = \frac{C_{\text{air}}}{C_{\text{water}}}$$

$$= \frac{200 \mu\text{g m}^{-3}}{1 \text{ mg L}^{-1}}$$

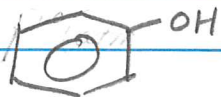
$$= \frac{0.200 \text{ mg m}^{-3}}{1 \times 10^3 \text{ mg m}^{-3}}$$

$$= 2.00 \times 10^{-4}$$

Since $Q_{aw} \ll K_{aw}$, net flux is from
pond to atmosphere.
& pond is a source.

Additional environmental data includes temperature
and salinity of pond water.

8.



Solid
at R.T.

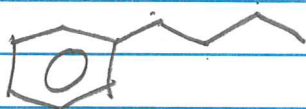
bipolar
most water soluble and low
vapour pressure due to
hydrogen bonding with water
and between solute molecules

$$P^0 = 2.6 \times 10^{-4}$$

\therefore

$$C_w^{\text{sat}} = 6.3 \times 10^{-1} \text{ M}$$

$$P^0 = 2.6 \times 10^{-4} \text{ atm}$$



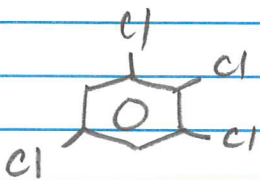
Liquid at
R.T.

apolar

lowest melting point
 \therefore highest vapour pressure
and low water solubility

$$\therefore P^0 = 1.4 \times 10^{-3} \text{ atm}$$

$$C_w^{\text{sat}} = 1.0 \times 10^{-4} \text{ M}$$

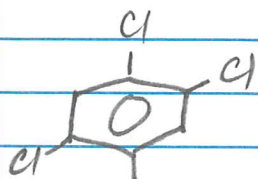


Solid at R.T.
 $T_m = 55^\circ\text{C}$

apolar or slightly monopolar
large molar volume due to Cl's
low vapour pressure and water
solubility, but higher than
1,2,4,5-tetrachloro benzene due
due lower melting point

$$\therefore P^0 = 1.9 \times 10^{-4} \text{ atm}$$

$$C_w^{\text{sat}} = 1.6 \times 10^{-5} \text{ M}$$



solid at R.T.
 $T_m = 140^\circ\text{C}$

apolar (symmetry)

lowest vapour pressure and water
solubility

$$\therefore P^0 = 3.0 \times 10^{-5}, C_w^{\text{sat}} = 2.5 \times 10^{-6} \text{ M}$$

b) tendency to bio-accumulate $\propto \log K_{ow}$

$$\text{and } K_{ow} \propto \frac{1}{C_w^{sat}}$$

\therefore phenol least likely to bio-accumulate

c) global distribution is generally associated with higher K_{aw}

$$K_{aw} \approx P^o / C_w^{sat}$$

11.8	1,2,3,5-tetrachloro benzene
14	n-butyl benzene
4×10^{-4}	phenol
12	1,2,4,5-tetrachloro benzene

\therefore n-butyl benzene most likely to be globally transported