

Carnegie Mellon University
Department of Civil and Environmental Engineering

**12-725: Fate, Transport, and Physicochemical Processes of Organic Contaminants
in Aquatic Systems and their Measurement in Environmental Samples**

Problem Set #3 Spring 2020

1. Explain in your own words the terms subcooled liquid and superheated liquid. How is the vapor pressure of a subcooled liquid and solid of a given compound related to each other?

A subcooled liquid is a liquid that is cooled to a temperature below its melting temperature but not allowed to crystallize. A superheated liquid is a liquid that has been heated above its boiling point, but not allowed to vaporize.

They are related to each other by ΔS_{fus} . Equation 8-21

$$\ln\left(\frac{P_{is}^*}{P_{il}^*}\right) = \frac{-\Delta_{fus}S_i(T_m)}{R} \left[\frac{T_m}{T} - 1 \right]$$

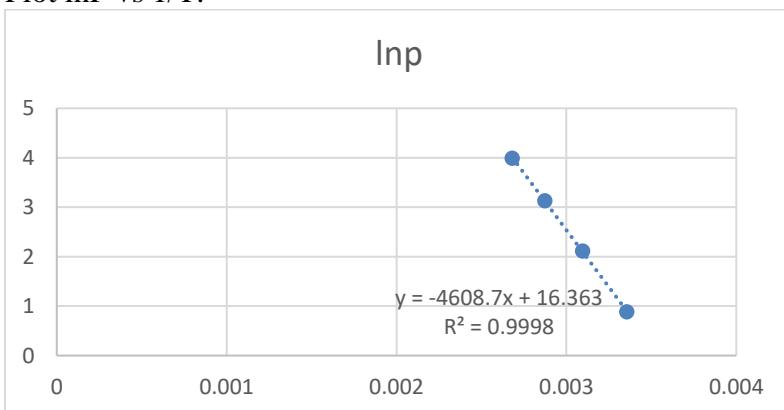
2. P8.2 and P8.4 in EOC

P8.2

a. Solve by experimental data:

$$\ln P = \frac{\Delta H_f}{R} \frac{1}{T} + C$$

Plot $\ln P$ vs $1/T$:



According to the plot, $y = -4608.7x + 16.363$

$$\text{Thus, } \ln P(20^\circ\text{C}) = -4608.7 \times \frac{1}{293} + 16.363 = 0.6336$$

$P = 1884 \text{ Pa}$

$$\text{Concentration: } C_{air} = \frac{P}{RT} = \frac{1884}{8.314 \times 293} = 0.773 \text{ mol/m}^3$$

$$\text{mol of PCE in air: } n = C \times V = 0.773 \times 50 = 38.7 \text{ mol}$$

$$\text{Density of PCE} = 1.62 \text{ g/cm}^3$$

Total amount of PCE in air:

$$n_{total} = \frac{10 \times 1.62 \times 1000}{165.83} = 97.7 \text{ mol} > 38.7 \text{ mol}$$

The maximum PCE concentration is 0.773 mol/m^3 in air in the room. 38.7 mol of PCE evaporated to the air.

Solve by predicted numbers:

$$\log P_{il}^* = -0.89L_i - 0.44S_i^2 - 5.43A_iB_i + 6.51$$

According to Table 7.3: Li=3.58, Si=0.44, Ai=Bi=0

$$\log P_{il}^* = 3.24$$

$$P_{il}^*(298K) = 1.74 \text{ kPa}$$

$$\Delta_{vap}H_i = -8.79\log P_{il} + 70 = 41.5 \text{ KJ/mol}$$

Thus,

$$\ln \frac{P_{il}(T2)}{P_{il}(T1)} = -\frac{41500}{8.314} \times \left(\frac{1}{T2} - \frac{1}{T1}\right)$$

$$\ln \frac{P_{il}(20^\circ C)}{P_{il}(25^\circ C)} = -0.29 \rightarrow \frac{P_{il}(20^\circ C)}{P_{il}(25^\circ C)} = 0.75$$

Therefore, $P_{il}(20^\circ C) = 0.75 \times 1.74 = 1.3 \text{ kPa}$

$$\text{Concentration of PCE in air: } C = \frac{1300}{8.314 \times 293} = 0.53 \text{ mol/m}^3$$

Total amount of PCE in air: $n = C \times V = 0.53 \times 50 = 26.5 \text{ mol} > 97.7 \text{ mol}$

The maximum concentration of PCE in air is 0.53 mol/m^3 . Total amount of PCE in air is 26.5 mol .

b. Solve by experimental data:

$$\text{At T=80°C, } \ln P = -4608.7 \times \frac{1}{273+80} + 16.363 = 3.31 \rightarrow P = 27.4 \text{ kPa}$$

$$n_{air} = C \times V = \frac{27.4 \times 1000 \times 15}{8.314 \times (273 + 80)} = 140 \text{ mol} > 97.7 \text{ mol}$$

$$\text{Thus, } C_{max} = \frac{n}{V} = \frac{97.7}{15} = 6.51 \text{ mol/m}^3$$

The maximum concentration in sauna is 6.51 mol/m^3 .

Solve by predicted numbers:

$$\ln \frac{P_{il}(T2)}{P_{il}(T1)} = -\frac{41500}{8.314} \times \left(\frac{1}{T2} - \frac{1}{T1}\right)$$

$$\ln \frac{P_{il}(80^\circ C)}{P_{il}(25^\circ C)} = 2.61 \rightarrow \frac{P_{il}(20^\circ C)}{P_{il}(25^\circ C)} = 13.6$$

Thus, $P_{il}(80^\circ C) = 13.6 \times 1.74 = 23.7 \text{ kPa}$

$$\text{Total PCE in air: } n = \frac{23.7 \times 1000 \times 15}{8.314 \times (273 + 80)} = 121 \text{ mol} > 97.7 \text{ mol}$$

$$\text{Thus, } C_{max} = \frac{n}{V} = \frac{97.7}{15} = 6.51 \text{ mol/m}^3$$

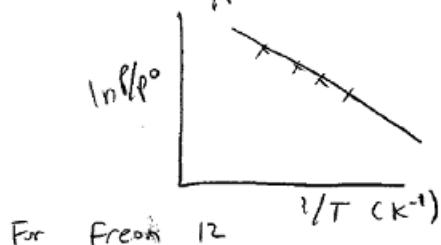
The maximum concentration in sauna is 6.51 mol/m³.

Comment: Comparing the results from experimental data and predicted data, the maximum concentration of PCE and total amount of PCE in air are similar to each other. This is because of the predicted numbers were also based on regression of large number of experimental results. All parameters used in eq-8-19 also accounted for the intermolecular forces including molar volume, VdW interactions, polar interactions, etc, which also make the predictions more precise.

P8.4

- i. To determine the normal boiling point of a compound one must find T @ which $P \sim 1 \text{ atm}$ or 101.3 kPa

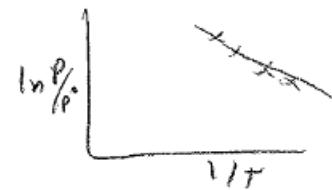
plot $\ln P/P^0$ vs. $1/T$



$$y = -2439.9x + 14.654$$

(from Excel)

$$\ln(101.3) = 4.618$$



$$y = -2751.7x + 15.753$$

Find x @ which $y = 4.618$

$$T_b^{-1} = \frac{4.618 - 14.654}{-2439.9}$$

$$= 4.11 \times 10^{-3}$$

i) $T_b = 243.1 \text{ K}$
 $= -30^\circ\text{C}$

$$T_b^{-1} = \frac{4.618 - 15.753}{-2751.7}$$

$$= 4.0466$$

$$T_b = 247.1 \text{ K}$$
 $= -26^\circ\text{C}$

- b) Find T where both have same VP

$$-2439.9x + 14.654 = -2751.7x + 15.753$$

$$311.8x = 1.099$$

$$x = 3.52 \times 10^{-3}$$

$$T = 283 \text{ K} = 10.6^\circ\text{C}$$

c) The slope of each line yields a value for $\Delta H_{\text{vap}}/R$

$$\text{recall: } \ln P_L^\circ = -\frac{\Delta H_{\text{vap}}}{T} + 13$$

$$\text{where } A = \Delta H_{\text{vap}}/R$$

for Freon 12

$$-\frac{\Delta H_{\text{vap}}}{R} = -2439.9$$

$$\begin{aligned}\Delta H_{\text{vap}} &= (2439.9) \left(8.314 \frac{\text{J}}{\text{mol K}}\right) \\ &= 20.3 \text{ kJ/mol}\end{aligned}$$

for HCF 134-a

$$-\frac{\Delta H_{\text{vap}}}{R} = -2751.7$$

$$\begin{aligned}\Delta H_{\text{vap}} &= (2751.7) \left(8.314 \frac{\text{K}}{\text{mol}}\right) \\ &= 22.9 \text{ kJ/mol}\end{aligned}$$

For ΔS_{vap} , we use the following equation: $\Delta S_{\text{vap}} = (\Delta H_{\text{vap}} - \Delta G_{\text{vap}})/T$

For Freon 12:

$$\text{At } 283\text{K } \Delta H_{\text{vap}}^\circ = 20.3 \text{ kJ/mol}$$

$$\Delta G_{\text{vap}}^\circ = -RT\ln P_{iL}^* = -14.2 \text{ kJ/mol}$$

$$\Delta S_{\text{vap}}^\circ = 121.9 \text{ J/mol/K}$$

For HCF 134-a

$$\Delta H_{\text{vap}}^\circ = 22.9 \text{ kJ/mol}$$

$\Delta G_{\text{vap}}^\circ = -RT\ln P_{iL}^* = -14.2 \text{ kJ/mol}$ (at 283K, the vapor pressure of those two compounds are equal)

$$\Delta S_{\text{vap}}^\circ = 131.1 \text{ J/mol/K}$$

d) @ 30°C

$$\ln P_{12}^{\circ} = -2439.9 \left(\frac{1}{(273.15 + 30)} \right) + 74.654$$

$$P_{12}^{\circ} = 739 \text{ kPa}$$

$$P_{1324}^{\circ} = 793 \text{ kPa}$$

@ 50°C

$$P_{12}^{\circ} = 1216$$

$$P_{1324}^{\circ} = 1391$$

There is not a considerable difference between the two compounds @ 30°C.

3. Explain why a poly-parameter linear free energy approach can be used to estimate the vapor pressure of organic compounds? Do you expect this to give a better or worse estimate of the vapor pressure compared to the other estimation methods that were discussed in class?

A poly-parameter LFER can be used to estimate VP of organic compounds because the terms in the relationship account for all of the intermolecular forces affecting the vapor pressure, e.g. molar volume, VdW interactions, polar interactions, etc.

In principle, it should provide better estimates than the other relationships because it accounts for MORE of the interactions between molecules. In practice, it can be difficult to find all of the inputs required for a compound.

4. State in your own words the meaning of $G_{i,w}^E$. What thermodynamic values determine the physical meaning of $G_{i,w}^E$? Provide a physical explanation for these thermodynamic values.

$G_{i,w}^E$ is the partial molar free excess of dissolution into water. It captures all of the *non-ideal* interactions affecting the dissolution process, mostly its interaction with water. It is comprised of an enthalpic component (ΔH) and an entropic component (ΔS). The enthalpic component related to the energy of interaction (intermolecular forces) between the molecule and water. The entropic part represents the change in the "randomness" of the molecule, i.e. the number of independent ways that it can be in space in water vs. in a pure liquid (or solid) of itself.

5. Table 9.2 in your textbook lists the enthalpic and entropic contributions to the excess free energy of dissolution in water (pure liquid to water). Explain the trends observed for $H_{i,w}^E$ and $G_{i,w}^E$ for the following compounds in the table for benzene, 1,3,5-trichlorobenzene, hexane, and 1-hexanol.

For hexane and hexanol, H^E_{iw} is quite similar (0 for hexane and -5 for hexanol). They have similar size, thus similar cavity formation energy cost. Hexane requires less energy to break the interactions in pure liquid phase compared to hexanol (which requires the break of H bond), but it also gains less energy upon interactions with water compared to hexanol. The negative value (-5) for hexanol indicated that it gains a small amount of energy in water relative to itself. This is likely due to more water-OH-R interactions compared to the R-OH—HO-R interactions in hexanol. However, overall the energy cost ($G^E_{i,w}$) are similar between the two compounds that are both liquids at 25°C and almost the same size/symmetry, so S^E_{iw} is also similar for both compounds.

For hexane and benzene, the $H^E_{i,w}$ is similar. Their size are similar, thus similar energy cost for cavity formation. Hexane requires less energy to break interactions in pure liquid as hexane can only form London dispersive force while benzene forms dipole-dipole interactions in pure liquid. However, when interacting with water, hexane as an apolar compound can only form dipole-induced dipole interaction while benzene can form dipole-dipole interactions, which allows benzene to gain slightly more energy. Therefore the H^E_{iw} are quite similar. Also, the two compounds that are both liquids at 25°C so S^E_{iw} is also similar for both compounds, giving similar $G^E_{i,w}$.

Comparing benzene with 1,3,5-trichlorobenzene, the $H^E_{i,w}$ and $G^E_{i,w}$ for 1,3,5-trichlorobenzene are significantly higher than benzene. Firstly, the halogens atoms have a large volume, making 1,3,5-trichlorobenzene larger than benzene. The energy for cavity formation in water is higher. Also, with larger size and surface area, the van der waals force between 1,3,5-trichlorobenzene molecules are also higher than benzene in pure liquid. When dissolved in water, both compounds can only form Van der Walls with water, similar energy gain. Thus, $H^E_{i,w}$ is higher for 1,3,5-trichlorobenzene than benzene. Since the TS^E_{iw} for both compounds are similar, and $H^E_{i,w}$ is higher for 1,3,5-trichlorobenzene, $G^E_{i,w}$ for 1,3,5-trichlorobenzene is higher than benzene.

- Derive the expressions relating a compounds aqueous activity coefficient to its aqueous solubility for a compound that is a a) liquid, b) solid, and c) gas at the temperature of interest.

$$\mu_{iL} = \mu_{iL}^* + RT \ln \gamma_{iL} x_{iL}$$

$$\mu_{iw} = \mu_{iw}^* + RT \ln \gamma_{iw} x_{iw}$$

When the chemical potential is equal in both phases:

$$\ln \frac{x_{iw}^{sat}}{x_{iL}} = \frac{RT \ln \gamma_{iL} - RT \ln \gamma_{iw}^{sat}}{RT}$$

Since $\gamma_{iL}=1$ and $x_{iL}=1$ we get the result that the solubility is the inverse of the activity coefficient for a liquid of subcooled liquid.

$$x_w^{sat} = \frac{1}{\gamma_w^{sat}} \quad (\text{Liquids or subcooled liquids or superheated gases})$$

For solids:

$$\mu_{is} = \mu_{iL}^* + RT \ln \gamma_{is} x_{is}$$

$$\begin{aligned}\mu_{iw} &= \mu_{iL}^* + RT \ln \gamma_{iw} x_{iw} \\ \mu_{iw} - \mu_{is} &= \mu_{iw} - (\mu_{iL}^* + \Delta_{fus} G_i)\end{aligned}$$

But

$$\Delta_{fus} G_i = RT \ln \frac{P_{iL}^o}{P_{is}^o}$$

Plugging in the $\Delta_{fus} G_i$ into the equation yields at equilibrium:

$$0 = RT \ln \gamma_{iw} x_{iw} - (RT \ln \gamma_{iL} x_{iL} - RT \ln \frac{P_{iL}^o}{P_{is}^o})$$

Rearranging is previously yields:

$$x_w^{sat} = \frac{1}{\gamma_w^{sat}} \cdot \frac{P_{(s)}^o}{P_{(L)}^o} \quad (\text{Solids})$$

For gasses:

$$\mu_{ig} = \mu_{iL}^* + RT \ln \gamma_{ig} x_{ig}$$

$$\mu_{iw} = \mu_{iL}^* + RT \ln \gamma_{iw} x_{iw}$$

$$\mu_{iw} - \mu_{ig} = \mu_{iw} - (\mu_{iL}^* + \Delta_{vap} G_i)$$

But

$$\Delta_{vap} G_i = -RT \ln \frac{P_{iL}^o}{1atm}$$

Plugging in similarly as for solids we get the equation for the solubility of a gas.

$$x_w^{sat} = \frac{1}{\gamma_w^{sat}} \cdot \frac{1atm}{P_{(L)}^o} \quad (\text{Gases})$$

7. P9.3 in EOC

- a) The solubility of anthracene in toluene is limited at 20 °C because anthracene is a solid at ambient temperature. So despite being miscible in toluene, it stills needs to melt.

b) one can estimate the solubility of anthracene in toluene using eqn 5-10 in your text.

$$x_{i,w}^{sat} = \frac{1}{\gamma_{i,w}^{sat}} \exp\left(\frac{-\Delta G_{fus}}{RT}\right)$$

$$x_{i,w}^{sat} = \frac{1}{\gamma_{i,w}^{sat}} \left(\frac{P_{is}}{P_{iL}} \right)$$

$\tau=0$

$\sigma=4$

$T_m=490.5\text{K}$

$T=293$

$$\ln \frac{P_{is}^*}{P_{iL}^*} = -(6.80 + 1.1\tau - 2.3 \log \sigma) \left[\frac{T_m}{T} - 1 \right]$$

$$P_{is}^*/P_{iL}^* = \exp\left(-(6.8 - 2.3 \log 4) \left(\frac{490.5}{293} - 1 \right)\right) = 0.026$$

So, assuming $\gamma_{i,tol}=1$

$$x_{iw}^{sat} = 0.026 = \frac{n_{ant}}{n_{ant} + n_{tol}}$$

$$n_{tol} = 250\text{cm}^3 \frac{0.87\text{g}}{\text{cm}^3} \frac{1\text{mol}}{93\text{g}} = 2.34\text{mol}$$

$$n_{ant} = 0.062\text{mol} = 11\text{g}$$

c) the anthracene concentration is 0.25M in toluene

8. P9.9 in EOC

No submitted in this week's homework. It has been postponed to HK#4.