

1.

Subcooled Liquid

The term subcooling refers to a liquid existing at a temperature below its normal boiling point. It tells us something about the molecular interactions of the compound in its pure liquid form at a temperature where the compound is actually a solid.

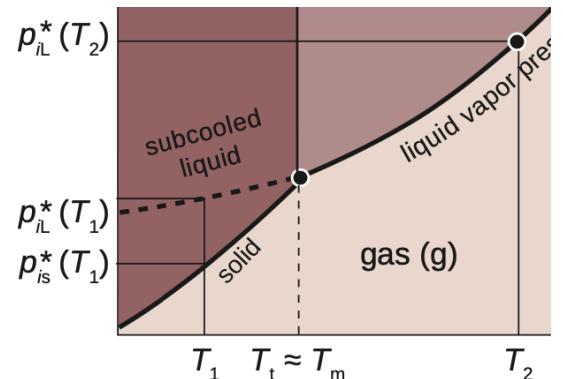
Superheated Liquid

Superheated is a liquid when it has been heated above its boiling point, but by increasing pressure, it is still in the liquid state and the system have both a liquid phase and a gas phase, and the liquid phase is referred to as a “Superheated”.

From Fig 8.2

The vapor pressure of a subcooled liquid should be always greater than the one of the solid, on the other hand, the eq 8-23 also illustrate this point. Because $p_{iL}^*(T_2) > p_{iL}^*(T_1)$

$$\frac{p_{is}^*}{p_{iL}^*} = e^{-(6.80+1.1\tau-2.3\log\sigma)[\frac{T_m}{T}-1]} < 1 \text{ then } p_{is}^* < p_{iL}^*$$



2. (1)

You teach Environmental Organic Chemistry, and for a demonstration of partitioning processes of organic compounds, you bring a glass bottle containing 10 L of the com- mon solvent, tetrachloroethene (PCE), into your classroom. After closing the door, you stumble, and you drop the bottle. The bottle breaks, and the solvent spills onto the floor. Soon, you can smell the solvent vapor in the air. (The odor threshold of PCE is between 8 and 30 mg m⁻³). Answer the following questions:

- (a) What is the maximum PCE concentration that you can expect in the air in the room ($T = 20^\circ\text{C}$)? How much of the solvent has evaporated if you assume that the air volume is 50 m³? (Neglect any adsorption of PCE on the walls and furniture.)
- (b) If the same accident happened in your sauna (volume 15 m³, $T = 80^\circ\text{C}$), what maximum PCE concentration would you and your friends be exposed to there?

In an old *CRC Handbook of Chemistry and Physics* (Lide, 1995), you find the follow- ing vapor pressure data for PCE:

| | | | | |
|--------------------------------|------|------|------|------|
| $T (\text{ }^\circ\text{C})$. | 25 | 50 | 75 | 100 |
| $p^*_i (\text{kPa})$. | 2.42 | 8.27 | 22.9 | 54.2 |

Use both the experimental data as well as Eq. 8-19 and 8-14 to solve this problem. Compare the predicted with the experimental data. Any comments?

1.

| T | p_i^* (Pa) | Inp_i^* | $\Delta_{vap}H_i(298K)$ |
|-----|--------------|-----------|-------------------------|
| 298 | 2420 | 7.79 | 37.79 |
| 323 | 8270 | 9.02 | |
| 348 | 22900 | 10.39 | |
| 373 | 54200 | 10.90 | |

$$Inp^* = -\frac{A}{T} + B$$

Using the experimental data, can we calculate the slope and intercept the linear.

$$\text{where } A = \frac{\Delta H_{vap}}{R} \text{ and } B = 16.4$$

Then $\Delta_{vap}H_i(298K) = 37.79 \text{ Kj/mol}$

$$\frac{p^*(293K)}{p^*(298K)} = e^{-\frac{\Delta H_{vap}(298K)}{R}[\frac{T_2 - T_1}{T_1 T_2}]} = 0.768$$

$$p^*(293K) = 0.768 \times 24.2 = 1.86 \text{ kPa}$$

Then

The concentration of PCE in its pure phase liquid:

$$\text{Using the ideal gas law } p = cRT \text{ thus } C_{air} = \frac{p^*(293K)}{293K \times 8.314} = 0.76 \text{ mol/m}^3 = 126.52 \text{ g/m}^3$$

$$m_{air} = C_{air} \times V = 6.33 \text{ kg}$$

Using Eq 8-14 and Eq 8-19

$$p^*(298K) = 10^{-0.89L_i - 0.44S_i^2 - 5.43A_iB_i + 6.51} = 10^{0.24} \text{ kPa}$$

$$\Delta_{vap}H_i = -8.79 \times \log p_{iL}^* + 70 = 40.26 \text{ kJ/mol}$$

$$\frac{p^*(293K)}{p^*(298K)} = e^{-\frac{\Delta H_{vap}(298K)}{R}[\frac{T_2 - T_1}{T_1 T_2}]} = 0.751$$

$$p^*(293K) = 0.751 \times 10^{0.24} = 1.3 KPa$$

Then

The concentration of PCE in its pure phase liquid:

$$\text{Using the ideal gas law } p = cRT \text{ thus } C_{air} = \frac{p^*(293K)}{293K \times 8.314} = 0.533 \text{ mol/m}^3 = 88.50 \text{ g/m}^3$$

$$m_{air} = C_{air} \times V = 4.42 \text{ kg}$$

(b) T = 353K and V = 15m³ and using experimental data:

$$\frac{p^*(353K)}{p^*(298K)} = e^{-\frac{\Delta H_{vap}(298K)}{R}[\frac{T_2 - T_1}{T_1 T_2}]} = 14.49$$

$$p^*(353K) = 26.93 KPa$$

Then

The concentration of PCE in its pure phase liquid:

$$\text{Using the ideal gas law } p = cRT \text{ thus } C_{air} = \frac{p^*(353K)}{293K \times 8.314} = 9.17 \text{ mol/m}^3 = 1521.9 \text{ g/m}^3$$

$$m_{air} = C_{air} \times V = 22.83 \text{ kg}$$

Using Eq 8-14 and Eq 8-19

$$p^*(298K) = 10^{-0.89L_i - 0.44S_i^2 - 5.43A_iB_i + 6.51} = 10^{0.24} KPa$$

$$\Delta_{vap}H_i = -8.79 \times \log p_{iL}^* + 70 = 40.26 KJ/mol$$

$$\frac{p^*(353K)}{p^*(298K)} = e^{-\frac{\Delta H_{vap}(298K)}{R}[\frac{T_2 - T_1}{T_1 T_2}]} = 17.25$$

$$p^*(353K) = 29.99 KPa$$

Then

The concentration of PCE in its pure phase liquid:

$$\text{Using the ideal gas law } p = cRT \text{ thus } C_{air} = \frac{p^*(353K)}{293K \times 8.314} = 10.22 \text{ mol/m}^3 = 1694.5 \text{ g/m}^3$$

$$m_{air} = C_{air} \times V = 25.41 \text{ kg}$$

Comment: Using experience to calculate ΔH_{vap} is smaller than the one from Eq 8-14 and Eq 8-19, thus, the vapor pressures at different temperature will be different and the one from experience data should be greater.

3.

Hydrofluorocarbon 134a (1,1,1,2-tetrafluoroethane, F_3C-CH_2F) is used as a replacement for Freon 12 (see Problem 8.3) for refrigeration applications. Why is such a replacement necessary and what is the advantage of HFC-134a from an environmental protection point of view?

Some vapor pressure data for Freon 12 is given in Problem 8.3. The vapor pressure data of HFC-134a has been determined very carefully and is as follows:

| | | | | | | |
|--------------------------------|-------|-------|-------|-------|-------|-------|
| $T (\text{ }^\circ\text{C})$. | -40.0 | -30.0 | -20.0 | -10.0 | 0 | +10.0 |
| p_i^* (kPa) | 51.6 | 84.7 | 132.9 | 200.7 | 292.9 | 414.8 |

- (a) Determine the normal boiling points (in ${}^\circ\text{C}$) of these compounds from the data provided.
- (b) At what temperature (in ${}^\circ\text{C}$) will they have an equal vapor pressure?
- (c) Compare the enthalpies ($\Delta_{\text{vap}}H_i$) and entropies ($\Delta_{\text{vap}}S_i$) of vaporization of the two compounds at ambient temperatures. Can you rationalize any differences you observe between the two compounds?
- (d) Automobile air conditioners commonly operate at temperatures between 30 and 50 ${}^\circ\text{C}$. Are the vapor pressures of the two compounds significantly (i.e., greater than 10%) different in this temperature region?

| T of HFC-134a | Pi of HFC-134a | T of Freon 12 | Pi of Freon 12 |
|---------------|----------------|---------------|----------------|
| -40 | 51.6 | -25 | 123 |
| -30 | 84.7 | 0 | 308 |
| -20 | 132.9 | 25 | 651 |
| -10 | 200.7 | 50 | 1216 |
| 0 | 292.9 | 75 | 2076 |

| | | | |
|---|-------|---|-----|
| 10 | 414.8 | NaN | NaN |
| $\Delta H_{vap} = 22.53 \text{ kJ/mol}$ | | $\Delta H_{vap} = 19.99 \text{ kJ/mol}$ | |
| A = -2748 | | A = -2743.7 | |
| B = 15.7 | | B = 14.6 | |

$$In p^* = -\frac{A}{T_b} + B \text{ When the temperature at the boiling point, the } p = 101.315 \text{ KPa}$$

Then T_b of HFC is 247.0K which is between -30C to -20C, the result is valid.

On the other hand

$$In p^* = -\frac{A}{T_b} + B \text{ When the temperature at the boiling point, the } p = 101.315 \text{ KPa}$$

Then T_b of Freon 12 is 243K which is below -25C , the result is valid.

$$(2) -\frac{A_{HFC}}{T} + B_{HFC} = -\frac{A_{Freon}}{T} + B_{Freon} \text{ where } T = 3.9 \text{ K}$$

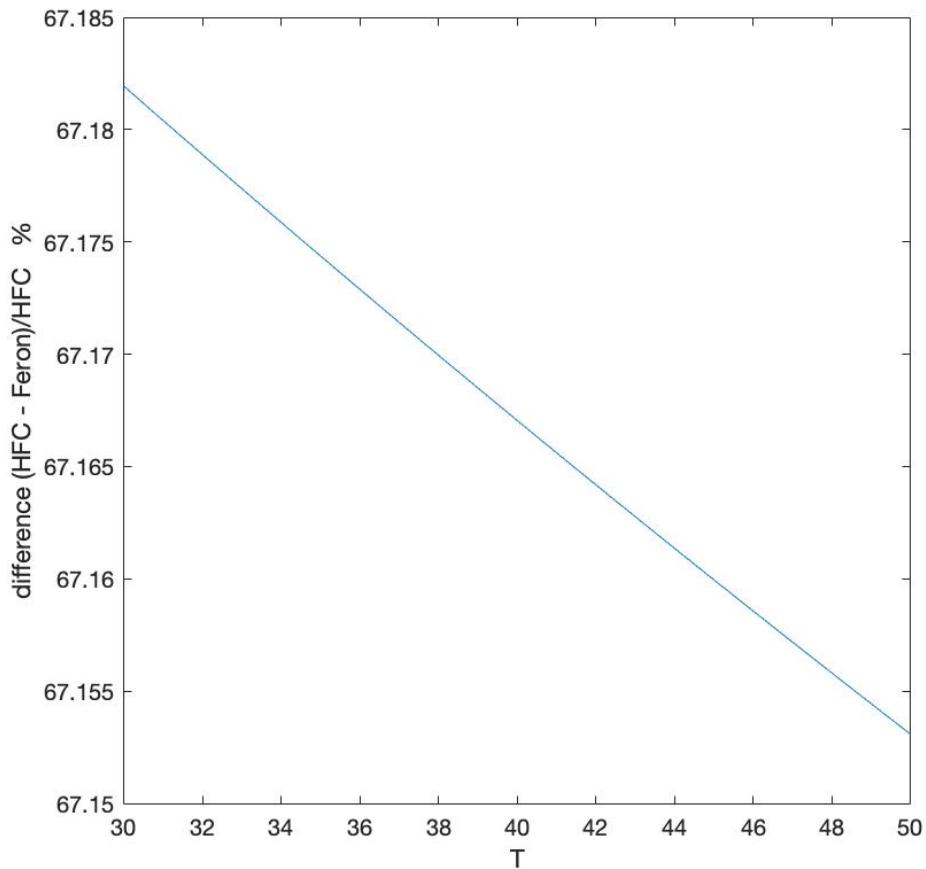
The vapor pressure of these two compounds is the same at this temperature

$$(3) \text{When at he boiling point, using the equation } \Delta_{vap} S_i = \frac{\Delta_{vap} H}{T_b}$$

The $\Delta_{vap} S_i = 91.2 \text{ J/mol}$ in HFC-134a on the other hand, The $\Delta_{vap} S_i = 82.3 \text{ J/mol}$ in the Freon 12.

(4) Yes, HFC 134a is about 67.16% greater than Freon 12 from 30C to 50C

3. The goal of this approach is to capture the structural variety of organic compounds and bulk phase characteristics affecting intermolecular interactions in one single equation. On the other hand, The basic concept is to express $\Delta_{12} G_i$ in Eq 7-3 or 7-4 by a linear combination of free energy terms



explicitly describing cavity formation as well as vdW and H-bonding interactions between the solute and solvent molecules.

In my opinion, this method is better than other estimate methods, because it takes account for the structure difference and intermolecular force, such as vdW and H-bonds.

4.

$$G_{i,w}^E = RTIn\gamma_{i,w}^E = H_{i,w}^E - TS_{i,w}^E$$

1 where H^E and S^E are the (partial molar) excess enthalpy and excess entropy, respectively. of the compound i in phase water.

Where $G_{i,w}^E$ is the excess free energy of the compound in saturated aqueous solution for the case when one chooses the pure liquid ($X_{iL} = 1$) as the reference stat.

The R constant, temperature a, and activity coefficient of the compound as thermodynamic values to determine the physical meaning of $G_{i,w}^E$

5.

| Compound | $H_{i,w}^E$ | $G_{i,w}^E$ |
|------------------------|-------------|-------------|
| Benzene | 2 | 17 |
| 1,3,5-trichlorobenzene | 16 | 34 |
| 1-hexanol | -5 | 17 |
| Hexane | 0 | 32 |

$H_{i,w}^E$: For some of the smaller compounds (e.g., hexane, 1-hexanol in Table 9.2), the enthalpy that has to be “spent” to isolate the molecules from their pure liquid is about equal to the enthalpy gained when inserting the compound in water; the excess enthalpy is close to zero. For larger compounds such as the 1,3,5-trichlorobenzene, the excess enthalpy becomes larger, but the entropy term is still an important factor in determining the “dislike” of the compound for the aqueous phase. This entropic effect explains what is often referred to as “hydrophobicity.”

$G_{i,w}^E$: 1-hexanol has the lowest $G_{i,w}^E$ value due to H-bonding, the entropy of bipolar compounds in their pure liquid is lower as compared to the entropy of the structurally related apolar or monopolar compounds, thus leading to a comparably smaller loss in entropy when they transfer into water.

6. For liquid, at any instant in time during our experiment, we can express the chemical potentials of the organic compound, i , in each of the two phases

$$\begin{aligned}\mu_{iL} &= \mu_{iL}^* + RT \ln \gamma_{iL} x_{iL} \\ \mu_{iw} &= \mu_{iL}^* + RT \ln \gamma_{iw} x_{iw}\end{aligned}$$

Then

$$\mu_{iw} - \mu_{iL} = RT \ln \gamma_{iw} x_{iw} - RT \ln \gamma_{iL} x_{iL}$$

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

Then where $G_{i,w}^E$ is the excess free energy of the compound in saturated aqueous solution for the case when one chooses the pure liquid ($x_{iL} = 1$) as the reference state

$$C_{iw}^{\text{sat}}(L) = \frac{1}{\bar{V}_w \gamma_{iw}^{\text{sat}}} \quad \text{for organic liquids}$$

where V_w is the molar volume of water.

For solid: As discussed in Chapter 8, the free energy cost involved in the solid-to-liquid conversion is referred to as the free energy of fusion, $\Delta_{fus}G_{i,w}$, which can be derived from vapor pressure data

$$\Delta_{fus}G_i = RT \ln \frac{p_{iL}^*}{p_{is}^*}$$

In analogy to Eq. 9-2, we can now express the difference in chemical potential as:

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

in molar units:

$$C_{iw}^{\text{sat}}(s) = \frac{1}{\bar{V}_w \gamma_{iw}^{\text{sat}}} e^{-\Delta_{fus}G_i/RT}$$

For gas: As discussed in Chapter 4, the partial pressure of a compound in the gas phase (ideal gas) at equilibrium above a liquid solution is identical to the fugacity of the compound in the solution

$$p_i = \gamma_{iw}x_{iw}p_{iL}^*$$

So express the mole fraction solubility of a gaseous organic substance as a function of the partial pressure p_i :

$$x_{iw}^{p_i} = \frac{1}{\gamma_{iw}^{p_i}} \cdot \frac{p_i}{p_{iL}^*}$$

7.

I assume 22.6g anthracene perfectly dissolve into toluene and just reach saturation.

Then

$$S = \frac{m_{anthracene}}{m_{toluene}} = \frac{22.6g}{V_{toluene} \times \rho_{toluene}} = \frac{22.6}{0.25 * 0.87} = 103.9g/kg$$

Using the anthracene solubility in toluene is from 9.2g/kg (16.5C) to 129.4g/kg(100C),

Then I assume the solubility at 20C should be 15 g/kg

Which is way smaller than the S calculated above. As the result, 22.6g anthracene will be super saturates in this condition.

$$C_{disslove} = \frac{(15 * 0.25 * 0.87)}{178.23} / 250mL = 0.073mol/L$$

$$m_{undissolved} = m_{anthracene} - s_{actual} \times m_{toluene} = 22.6 - (15 * 0.25 * 0.87) = 19.34g$$

If we want to reach 0.5M requirement, we should increase the environment temperature which allows the solubility to reach 103.9 g/kg. Or change the solvent.