Chapter 8
Vapor Pressure

Solutions

Problem 8.1* ***Basic Vapor Pressure Calculations***

(a) Prepare the data to be expressed as in the linear relationship Eq. 8.7. Note that at 45.0 and 74.6°C, TeMB is a solid. Hence, group the data according to the aggregate state of the compound.

Perform least squares fits of ln p_i^* versus 1 / T (see Figure below). The results are:

$$\text{Solid compound:}\quad \ln p_{is}^*(\text{mm Hg}) = -\frac{8609\text{K}}{T} + 27.1 \qquad (1)$$

$$\text{Liquid compound:}\quad \ln p_{i\text{L}}^*(\text{mm Hg}) = -\frac{5676\text{K}}{T} + 18.7 \qquad (2)$$

If you would have converted mm Hg to bar (1 mm Hg = 0.01333 bar), the intercepts of Eqs. 1 and 2 would be 20.5 and 12.1, respectively.

Insert T = 293.2 K (20°C) into Eq. 1, calculate p_{is}^*:

$$p_{is}^*\ (20°\text{C}) = 0.10\ \text{mm Hg} = 0.000133\ \text{bar} = 13.3\ \text{Pa}$$

Insert T = 423.2 K (150°C) into Eq. 2, calculate $p_{i\text{L}}^*$:

$$p_{i\text{L}}^*\ (150°\text{C}) = 198\ \text{mm Hg} = 0.264\ \text{bar} = 26400\ \text{Pa}$$

Hence, the vapor pressure of TeMB is more than three orders of magnitude greater at 150°C than at 20°C, illustrating the strong temperature dependence of this compound property.

(b) Insert T = 293.2 K into Eq. 2 to estimate the vapor pressure of subcooled TeMB at 20°C:

$$p_{i\text{L}}^*\ (20°\text{C}) = 0.52\ \text{mm Hg} = 0.00069\ \text{bar} = 69\ \text{Pa}$$

Hence, at 20°C, $p_{i\text{L}}^*$ is about five times larger than p_{is}^*. Remember, however, that you have extrapolated this value over quite a large temperature range. Use Eq. 8-9 to calculate $\Delta_{\text{fus}}G_i$:

$$\Delta_{\text{fus}}G_i\ (20^\circ C) = RT\ln\frac{p_{i\text{L}}^*}{p_{is}^*} = (2.44\ \text{kJ mol}^{-1})\ln\frac{(0.00069)}{(0.000133)} = 4.0\ \text{kJ mol}^{-1}$$

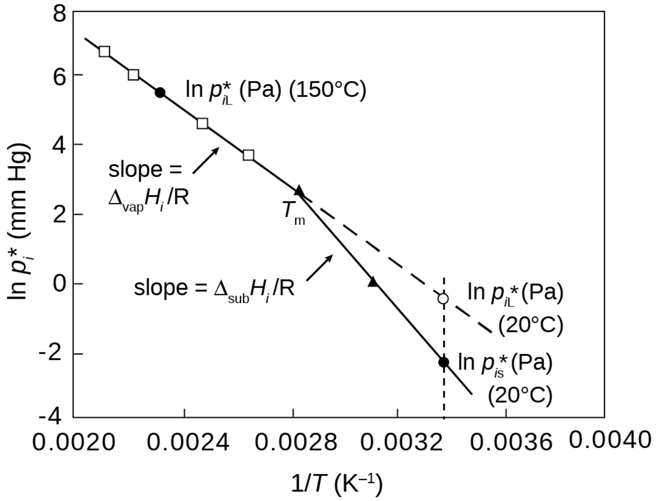
Estimate $\Delta_{\text{fus}}H_i$ from the average $\Delta_{\text{vap}}H_i$ and $\Delta_{\text{sub}}H_i$ that you can derive from the slopes of the regression lines Eqs. 1 and 2 (see also Eqs. 8-10 and 8-11):

$$\Delta_{\text{fus}}H_i = \Delta_{\text{sub}}H_i - \Delta_{12}H_i = \text{R}\cdot\text{slope 1} - \text{R}\cdot\text{slope 2} = 24.4\ \text{kJ mol}^{-1}\ ,$$

and since $\Delta_{\text{fus}}S_i = (\Delta_{\text{fus}}H_i - \Delta_{\text{fus}}G_i) / T$, you get

$$\Delta_{\text{fus}}S_i = 69.6 \text{ J mol}^{-1}\text{K}^{-1}$$

Note again that in these calculations, all $\Delta_{12}H_i$ values have been assumed to be constant over the temperature range considered. Therefore, all changes in $\Delta_{\text{fus}}G_i$ (which is zero at T_m) are attributed to a change in $\Delta_{\text{fus}}S_i$ with changing temperature. This is, of course, not exactly correct.



Temperature dependence of the vapor pressure of TeMB: Plot of ln p_i^* versus 1/T.

Problem 8.2 ***A Solvent Spill in Your Class Room***

In the temperature range considered, PCE is a liquid. Hence, all four data points can be used to establish the vapor pressure-temperature equation. In Appendix C (Wiley website) you find the molecular weight (165.83 g mol^{-1}), the density at 20°C (1.62 g cm^{-3}), and the Abraham parameters (V_i=0.84, L_i=3.58, S_i=0.44, A_i=0, B_i=0) of PCE. At 20°C 10 L of PCE correspond, therefore, to 16.2 kg or 97.69 moles.

(a) The linear regression of the four data points (ln p_i^* vs. 1/T) yields:

$$\ln\ p_i^*(\text{kPa}) = -4609\ (1/T) + 16.36$$

Insertion of T = 293K gives a p_i^* value at 20°C of 1.88 kPa or a maximum PCE concentration (p_i^*/RT) = (0.0188bar/24.35 L bar mol^{-1}) = 0.77 mmol L^{-1} or 128 g m^{-3}. This is more than 4 orders of magnitude above the odor threshold. The total amount of PCE evaporated in the 50 m^3 is then about 6.4 kg (4 L) or about 40% of the PCE that was originally in the bottle.

Using Eq. 8-19 yields a vapor pressure of about 1.7 kPa at 25°C. With Eq. 8-14, one may use this estimated vapor pressure to estimate PCE's enthalpy of vaporization to be 42 kJ mol^{-1}. With this enthalpy and the vapor pressure at 298K, Eq. 8-7 can be used to calculate the vapor pressure at 293K as 1.3 kPa. This estimate corresponds quite well with the value extrapolated from the experimental data (much less than a factor of 2).

(b) At 80°C all PCE has evaporated yielding a maximum concentration of 16.2 kg /15 m^3 = 1.08 kg m^{-3} which is about 5 orders of magnitude above the odor threshold!

Problem 8.3 ***How Much Freon is Left in the Old Pressure Bottle Left at a Dump Site?***

At 0°C the minimum pressure required to have liquid Freon 12 in the bottle is more than 300 kPa or 3 bar, hence at 10°C the pressure would have to be higher. Therefore you can assume that there is no liquid Freon 12 present in the bottle, and you can estimate the amount present:

$C_{i\mathrm{bottle}} = p_i/RT = 2.7\ \mathrm{bar}/(23.54\ \mathrm{bar\ L\ mol^{-1}}) = 0.115\ \mathrm{mol\ L^{-1}}$; this yields a total amount of 0.34 mol or 41.6 g Freon 12 left in the bottle.

The free energy of condensation at 25°C is given by (Eq. 8.2):

$$\Delta_{\mathrm{cond}}G_i = RT\ln\ p_i^* = (2.48\ \mathrm{kJ\ mol^{-1}})(\ln 6.51) = 4.6\ \mathrm{kJ\ mol^{-1}}$$

To get the enthalpy of condensation, calculate the linear regression of the five data points ($\ln\ p_i^*$ vs. 1/T):

$$\ln\ p_i^*\ (\mathrm{kPa}) = -2437\ (1/\mathrm{T}) + 14.65$$

Since $\Delta_{\mathrm{cond}}H_i = (\mathrm{slope})R$, you get an enthalpy of condensation of $-20.3\ \mathrm{kJ\ mol^{-1}}$, and an entropy of condensation, $\Delta_{\mathrm{cond}}S_i = (\Delta_{cond}H_i - \Delta_{\mathrm{cond}}G_i)/T = (-20.3\ \mathrm{kJ\ mol^{-1}} - 4.6\ \mathrm{kJ\ mol^{-1}})/298\mathrm{K}$ of $-83.6\ \mathrm{J\ mol^{-1}K^{-1}}$.

Problem 8.4 ***What Are the Differences Between Freon 12 And its Replacement HFC-134a? (From Roberts, 1995)***

The replacement was necessary because, due to its large residence time in the atmosphere, Freon 12 is both an "ozone killer" as well as a very potent greenhouse gas. HFC-134a does not react with stratospheric ozone and has a shorter residence time due to reaction with OH-radicals. However, it is still a potent greenhouse gas.

(a) The normal boiling point, T_b, is the temperature at which the vapor pressure is 1 bar or 100kPa (Section 8). From the vapor pressure temperature relationship derived for Freon 12 in Problem 8.3:

$$\ln\ p_i^*\,(\text{kPa}) = -2437\ (1/T) + 14.65$$

you obtain a boiling point of 242.8 K or –30.4°C for this compound. The relationship derived for HFC-134a is:

$$\ln\ p_i^*\,(\text{kPa}) = -2748\ (1/T) + 15.75$$

which yields a T_b value of 246.7 K or –26.5°C. Note that above the boiling point, the vapor pressure reflects the vapor pressure of the superheated liquid (see Fig. 8.2).

(b) Setting the two equations equal and solving for T yields a T_{equal} of 283K or about 10°C.

(c) As calculated in Problem 8.3, for Freon 12, $\Delta_{\text{vap}}H_i = 20.3\ \text{kJ mol}^{-1}$ and $\Delta_{\text{vap}}S_i = 83.6\ \text{J mol}^{-1}\ \text{K}^{-1}$ at 25°C). The same calculation for HFC-134a yields $\Delta_{\text{vap}}G_i = -5.5\ \text{kJ mol}^{-1}$, and thus $\Delta_{\text{vap}}H_i = 22.8\ \text{kJ mol}^{-1}$ and $\Delta_{\text{vap}}S_i = 94.0\ \text{J mol}^{-1}\ \text{K}^{-1}$ for HFC-143a.

(d) Insertion of T = 323.2K into the above equations yields the following vapor pressures at 50°C:

$$\text{Freon 12:}\quad p_i^* = 12.1\ \text{bar} \quad ; \quad \text{HFC-134a:}\ p_i^* = 13.9\ \text{bar}$$

Hence the difference is more than 10%, and some adjustments had to be made in the air conditioners in cars when Freon 12 was replaced by HFC-134a.

Problem 8.5 ***A* Public *Toilet Problem***

In Appendix C (Wiley website) you find the molecular weight (147.0 g mol^{-1}) and the Abraham parameters (V_i=0.96, L_i=4.44, S_i=0.75, A_i=0, B_i=0) of 1,4-DCB.

(a) At 20°C 1,4-DCB is a solid. Hence you can only use the first four data points for deriving the vapor pressure – temperature relationship:

$$\ln\ p^*_{is}\,(\text{kPa}) = -5458(1/T) + 17.08$$

Insertion of T = 293K yields p^*_{is} = 0.21 kPa or 2.1×10^{-3} bar, which corresponds to a maximum concentration of p^*_{is}/RT = 8.7×10^{-5} mol L^{-1} or about 13 g m^{-3}.

(b) Inserting T_b into Eq. 8-17 (with K_F=1; since dipole moment is zero for this compound, Fishtine, 1963) yields the vapor pressure of the subcooled liquid 1,4-DCB at 20°C: log p^*_{iL} (bar) = –2.8 or p^*_{iL} =1.5×10^{-3} bar. Using Eq. 8-21 with $\Delta_\text{fus}S_i(T_\text{m})$ = 45 J mol^{-1}K (Table 8.2) the yields a solid vapor pressure of 0.87×10^{-3} bar or 5.3 g m^{-3}.

(c) Using the pp-LFER Eqs. 8-19 and 8-14 yields a subcooled liquid vapor pressure at 20°C of 145 Pa or 1.45×10^{-3} bar, which is virtually the same value as predicted from the boiling point (b).

Hence, the predictions are about a factor of two smaller than the value obtained from the experimental data which is quite satisfactory.

In the Death Valley, 1,4-DCB is a liquid. Using the boiling point (100 kPa) and the vapor pressure at 99°C (10 kPa) given in the Table above, one obtains

$$\ln\ p^*_{iL}\,(\text{kPa}) = -5132(1/T) + 16.09$$

and thus p^*_{iL} (kPa) at 60°C = 1.97 kPa or 1.99×10^{-2} bar or about 105 g m^{-3} which is an eight times higher concentration than at 20°C, demonstrating the strong temperature dependence of the vapor pressure of the compound.

Problem 8.6 *True or False?*

In Appendix C you find
1,2-DCB: T_m = – 17°C, T_b = 180°C; 1,4-DCB: T_m = 53.1°C, T_b = 174°C. Hence, at 60°C both compounds are liquids, and you would expect that the one with the lower boiling point (1,4-DCB) would exhibit the higher vapor pressure, which is of course, reflected in the corresponding estimated vapor pressures. However, at 20°C, this is not obvious, since one has to take into account that, in contrast to 1,2-DCB, 1,4-DCB is a solid at this temperature.

For estimating the (subcooled) liquid vapor pressures, insert the respective T_b values (in K) into Eq. 8-17. Note, according to Fishtine (1963), for substituted benzenes the $K_F=1+2\mu/100$ where μ is a compound's dipole moment. Since the chlorine substituents on 1,4-DCB are symmetrically opposed to one another, μ for 1,4-DCB is 0 and $K_F = 1$. But 1,2-DCB has permanent dipole moment of 2.5 (Haynes, 2014), so it's K_F is 1.05). The resulting $p_{i\mathrm{L}}^*$ values are
at 60°C:
1,2-DCB : 1.2×10^{-2} bar
1,4-DCB : 1.8×10^{-2} bar

at 20°C:
1,2-DCB : 0.91×10^{-3} bar
1,4-DCB : 1.7×10^{-3} bar

However correcting the vapor pressure of the 1,4-DCB solid (Eq. 8-21 with $\Delta_{\mathrm{fus}}S_i(T_\mathrm{m})$ = 45 J mol^{-1}K; Table 8.2) yields the solid (real) vapor pressure of 0.92×10^{-3} bar.
The person is slightly wrong to the extent one can trust the estimates!

For determining at which temperature the two isomers exhibit the same vapor pressures, you need to have the vapor pressure – temperature relationship for the two compounds over the temperature range of the intersect of the two lines which has to be between 20°C and the melting point temperature of 1,4-DCB. For 1,2-DCB you can take the vapor pressures at 20°C and 60°C that you have already calculated. For 1,4-DCB you need to calculate the vapor pressure at the melting point, hence at 53.1°C (Eq. 8-17). The value is 1.28×10^{-2} bar. This yields the following vapor pressure-temperature relationships:

for 1,4-DCB:
$\ln\ p_{i\mathrm{s}}^*(\mathrm{bar}) = -7617(1/T) + 19.00$

and for 1,2-DCB:

$\ln\ p_{i\mathrm{L}}^*(\mathrm{bar}) = --6245(1/T) + 14.31$

setting the two equations equal yields the temperature at which the vapor pressures are equal.
T = 292.5K or 19.5°C

Problem 8.7 ***Vapor pressure of Alkyl Nitriles from Biomass Burning***

The melting temperature and boiling point indicate that dodecyl nitrile (DN) is a liquid at 25°C. So one may use Eq. 8-17 to estimate this compound's vapor pressure:

$$\log p^*_{\mathrm{DNL}}(\mathrm{bar}) = -(1/2.303)K_{\mathrm{F}}(4.4+\ln T_{\mathrm{b}})\left[1.8\left(\frac{T_{\mathrm{b}}}{T}-1\right)-0.8\ln\frac{T_{\mathrm{b}}}{T}\right]$$

where K_{F} is DN's "Fishtine" factor. For nitriles with long (>12C) alkyl chains like DN, the K_{F} value is 1.01 (Fishtine, 1963). Hence, one may use this small factor and DN's boiling temperature (277°C = 550 K) to estimate its vapor pressure:

$$\log p^*_{\mathrm{DNL}}(25^{\circ}\mathrm{C},\ \mathrm{bar}) = -(1/2.303)(1.01)(4.4+\ln 550)\left[1.8\left(\frac{550}{298}-1\right)-0.8\ln\frac{550}{298}\right] = 1.4\times 10^{-5}\ \mathrm{bar} = 1.4\ \mathrm{Pa}$$