

So far, we have studied pure substances. These are not so relevant in chemistry. Almost always the solution(system) is a mixtures of liquids. How we handle that. Let us first look the gas partial pressures next to the mixed ideal solution. The partial pressure of mixture is, the **Raoult's la**

$$P_i = x_i P_i^*$$

where the P_i^* is the partial pressure of pure gas. In this model we assume that the components will interact similarly. This model is not very good since the two liquid components usually have different interactions.

We can now compute the solution chemical potential. The liquid and gas are in equilibrium.

$$\mu_{solution,i} = \mu_{gas,i}$$

there are few lines in the book

$$\mu_{solution,i} = \mu^* + RT \ln \frac{P_i}{P_i^*} = \mu^* + RT \ln x_i$$

the * always denote the pure system.

For an ideal solution $\Delta H_{mix} = 0$, $\Delta V_{mix} = 0$ and $\Delta G_{mix} = nRT \sum_i x_i \ln x_i$. Because $x_i < 1$ the ideal system mixed Gibbs energy is always negative and the process is spontaneous.

An example: water vapor pressure, $\Delta H_f^0(\text{liq}) = -285.8 \text{ kJ/mol}$, $\Delta H_f^0(\text{gas}) = -241.8 \text{ kJ/mol}$, $\Delta G_f^0(\text{liq}) = -237.1 \text{ kJ/mol}$, $\Delta G_f^0(\text{gas}) = -228.8 \text{ kJ/mol}$.

At room temp. $\mu^o(w, \text{liq}) = \mu^o(w, \text{gas}) + RT \ln \frac{P_w}{P^o} \Rightarrow \frac{P_w}{P^o} = \exp\left(\frac{\Delta\mu}{RT}\right)$ insert the numbers

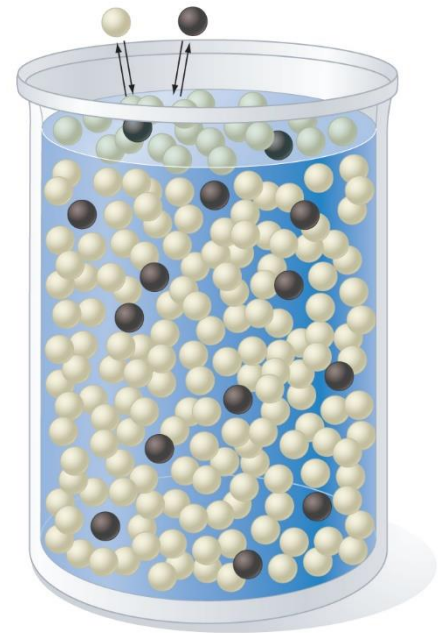
$p(\text{gas}) = 0.0324 \text{ atm}$.

Ethanol vapor pressure, $\Delta H_f^0(\text{liq}) = -277.6 \text{ kJ/mol}$, $\Delta H_f^0(\text{gas}) = -234.8 \text{ kJ/mol}$, $\Delta G_f^0(\text{liq}) = -174.8 \text{ kJ/mol}$, $\Delta G_f^0(\text{gas}) = -167.9 \text{ kJ/mol}$. Note the liq values are values in pure ethanol not water-ethanol mixture.

At room temp. Same equations as above, insert the numbers

$p(\text{gas}) = 0.0618 \text{ atm}$.

The ethanol partial pressure is higher.



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The Raoult's law is very simple for binary solutions. The total pressure is

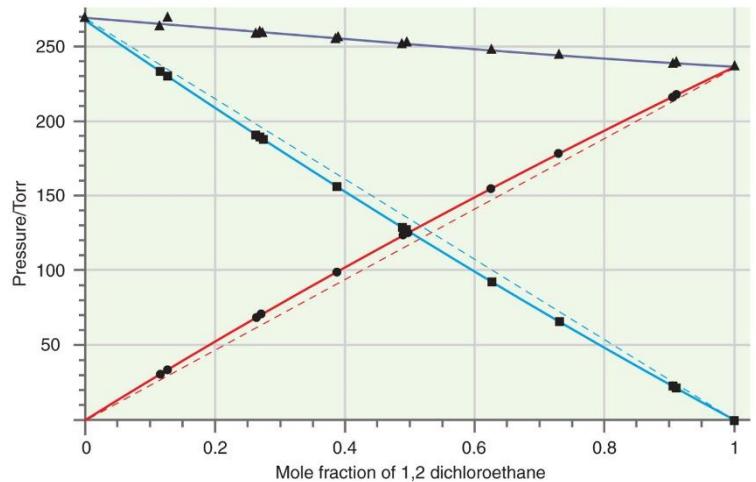
$$P_{tot} = P_1 + P_2 = x_1 P_1^* + (1 - x_1) P_2^* = P_2^* + (P_1^* - P_2^*) x_1$$

where x_1 is the solution mole fraction of component 1. We can also define the **gas mole fractions**, y .

$$y_1 = \frac{P_1}{P_{tot}} = \frac{x_1 P_1^*}{P_2^* + (P_1^* - P_2^*) x_1}$$

Note that the x and y are NOT the same because one of the gases are more volatile.

The figure 9.2. shows the gas pressures of mixture of benzene (blue) and dichloroethane (red). The dots are the experiments and dashed lines from the Raoult's law. The mole fraction refers to the solution. This system is close to ideal.



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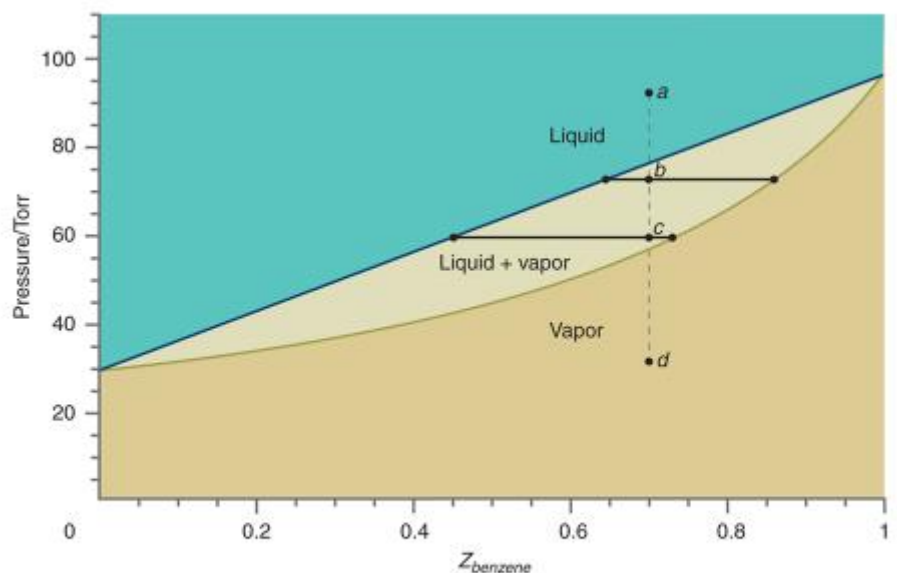
The vapor-liquid coexistence with respect to the total pressure is bit complex. We will first define average composition of one component. We use benzene-toluene system as an example.

$$Z_{benz} = \frac{n_{benz,liq} + n_{benz,gas}}{n_{benz,liq} + n_{benz,gas} + n_{tolu,liq} + n_{tolu,gas}} = \frac{n_{benz}}{n_{tot}}$$

Now the P-Z diagram can be drawn. At high pressures the system is liquid (bluish are) and at low pressures gas (brown are). In between, the liquid and vapor coexist.

Follow the example 9.3

Solution of 5 mol of benzene and 3.25 mol toluene at 298 K, ($x_{benz} = 0.606$). The pressure is reduced from 0.12 atm (90 Torr) to ca. 20 Torr. The pure substance vapor pressures are 96.4 Torr (benzene) and 28.9 Torr (toluene).



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What is the pressure in the vapor-liquid coexistence? (in line a--d)

The total vapor pressure is $(0.606 \cdot 96.4 + 0.394 \cdot 28.9)$ Torr = 69.8 Torr

What is the gas composition at this pressure? $y_{\text{benz}} = 0.827$ and $y_{\text{tolu}} = 0.163$. These values are quite different than in the solution. The gas is enriched with component that is more volatile (and have higher vapor pressure).

At point b what is the gas liquid ratio. It can be computed with the lever rule. (read the book)

$$\frac{n_{\text{tot,liq}}}{n_{\text{tot,gas}}} = \frac{Z_B - x_B}{y_B - Z_B}$$

The parameters of the example were not given. I used values $Z(\text{benz})=0.7$ and $P(\text{tot})=72$ Torr, then I got $x(\text{ben})=0.63852$ and $y(\text{ben})=0.8549$ and $n(\text{liq})/n(\text{gas})=2.52$. The total amount of liquid is 71.6 % and gas 28.4 %. The $x(\text{ben})$:

$$P_{\text{tot}} = x_b P_b^* + (1 - x_b) P_t^* \Rightarrow x_b = (P_{\text{tot}} - P_t^*) / (P_b^* - P_t^*), \quad y_b = \frac{x_b P_b^*}{P_{\text{tot}}}$$

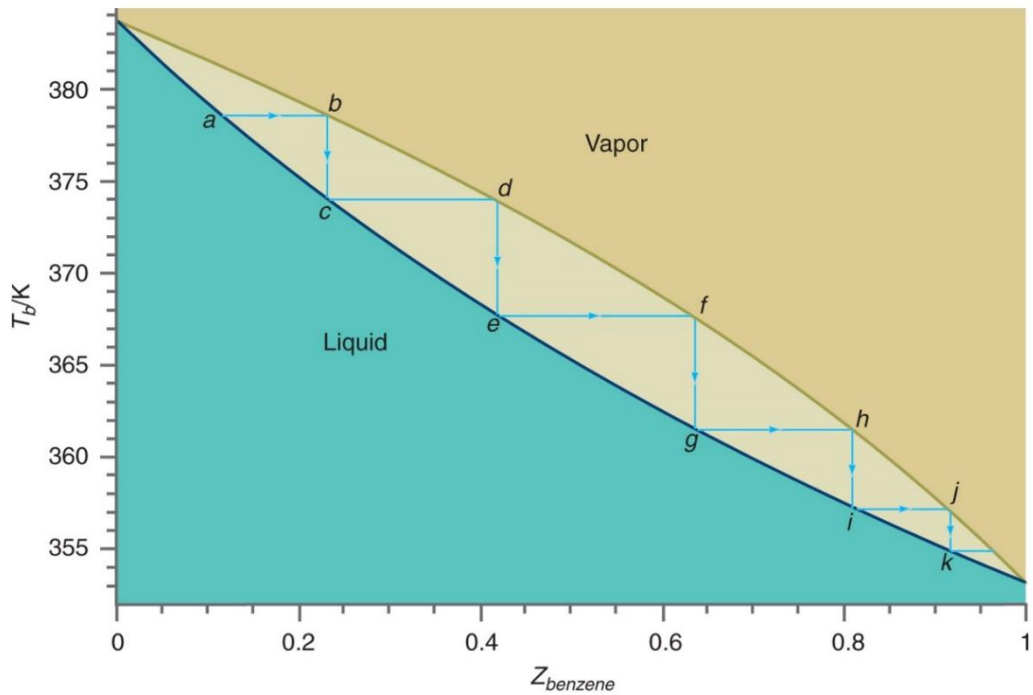
Repeat the calculations at $Z=0.7$ and $P=60$ Torr (point c)

Answer: $x(\text{ben})=0.46074$ and $y(\text{ben})=0.74026$ and $n(\text{liq})/n(\text{gas})=0.1683$. The total liquid is 14.4 % and gas 85.6 %.

Fractional distillation

Engel & Reid chapter 9.4

The T-Z diagram is useful for distillation. In this diagram, the relevant temperatures are the liquids boiling temperatures with respect to Z. Also in this diagram, the liquid and gas coexist. Here the diagram is used to illustrate the fractional distillation. If we start around point a, the benzene liquid coexist with gas at point b. The gas at point b have higher benzene concentration than at a. If this gas (mixture of benzene and toluene) is collected and cooled to temperature at c and then then the gas is collected that point d with again is richer in benzene than at c. The procedure can be repeated several times and at the end, very pure benzene can obtain.

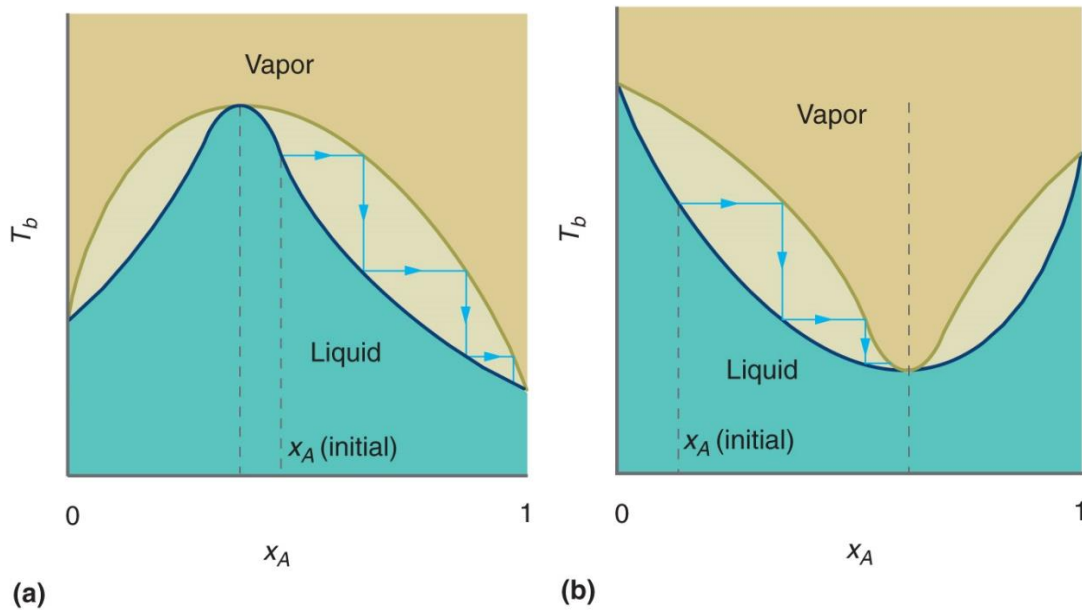


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The benzene-toluene mixture is a rather rare example of almost ideal mixtures. Most real liquid mixtures have more complex boiling point. At some mixtures the boiling point can be even higher or lower than the pure substances boiling points. These are called azeotropes.

See the table 9.1. In the case (b) with low boiling point around $x=0.66$ it is not possible to get compound A richer than ca. 66 % (at this pressure).

What is the maximum concentration of ethanol you can get from water-ethanol distillation?



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TABLE 9.1 Composition and Boiling Temperatures of Selected Azeotropes

Azeotropic Mixture	Boiling Temperature of Components (°C)	Mole Fraction of First Component	Azeotrope Boiling Point (°C)
Water–ethanol	100./78.5	0.096	78.2
Water–trichloromethane	100./61.2	0.160	56.1
Water–benzene	100./80.2	0.295	69.3
Water–toluene	100./111	0.444	84.1
Ethanol–hexane	78.5/68.8	0.332	58.7
Ethanol–benzene	78.5/80.2	0.440	67.9
Ethyl acetate–hexane	78.5/68.8	0.394	65.2
Carbon disulfide–acetone	46.3/56.2	0.608	39.3
Toluene–acetic acid	111/118	0.625	100.7

Source: Lide, D. R., ed. *Handbook of Chemistry and Physics*. 83rd ed. Boca Raton, FL: CRC Press, 2002.

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The next interesting thing is the effect of mixtures to freezing and boiling points. In general, the mixture (solute-solvent) will have lower melting point and higher boiling point than the pure system. As an example, the water-ethanol will freeze at lower temperatures than pure water. The boiling point is more difficult to observe since most of the ethanol will evaporate before water boils, but the mixture will have higher boiling point.

We also assume that the solid and gas are of pure compound A (solvent). The latter is realistic if the compound B (solute) have higher boiling temperature. In freezing we assume that the compound A and B separates which is very often the case. It is reasonable to assume that there is much more solvent than solute.

The derivation of the equations are bit tricky. The details are in the book. The final result for melting is

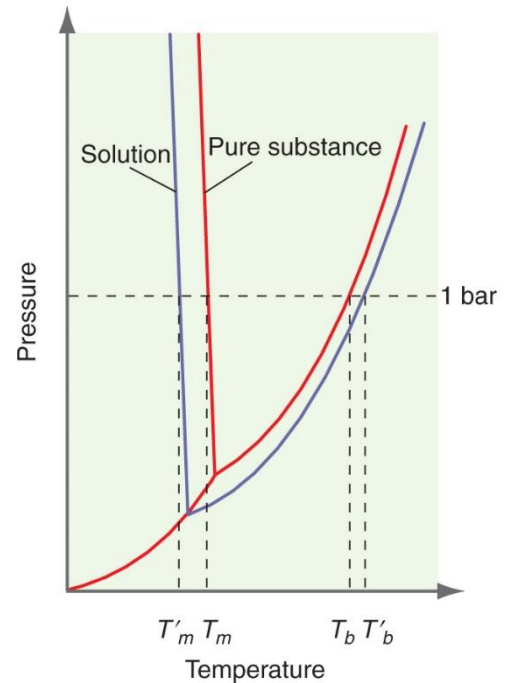
$$\Delta T_f = -\frac{RM_{\text{solvent}}T_{\text{melt}}^2}{\Delta H_{\text{melt}}}m_{\text{solute}} = -K_f m_{\text{solute}}$$

where the M_{solvent} is the mass of solvent molecules, the m_{solute} is the molality (moles of solute per kg of solvent). In principle the K_f do not depend on the solute. It is reasonable to assume that m is small.

For boiling point an identical equation hold

$$\Delta T_b = \frac{RM_{\text{solvent}}T_{\text{vapor}}^2}{\Delta H_{\text{vapor}}}m_{\text{solute}} = K_b m_{\text{solute}}$$

In real systems and especially at higher solute concentrations the solute matters.



(b)

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TABLE 9.2 Freezing Point Depression and Boiling Point Elevation Constants

Substance	Standard Freezing Point (K)	K_f (K kg mol ⁻¹)	Standard Boiling Point (K)	K_b (K kg mol ⁻¹)
Acetic acid	289.6	3.59	391.2	3.08
Benzene	278.6	5.12	353.3	2.53
Camphor	449	40.	482.3	5.95
Carbon disulfide	161	3.8	319.2	2.40
Carbon tetrachloride	250.3	30.	349.8	4.95
Cyclohexane	279.6	20.0	353.9	2.79
Ethanol	158.8	2.0	351.5	1.07
Phenol	314	7.27	455.0	3.04
Water	273.15	1.86	373.15	0.51

Source: Lide, D. R., ed. *Handbook of Chemistry and Physics*, 83rd ed. Boca Raton, FL: CRC Press, 2002.

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Note that for water the coefficients K_f and K_b are rather small.

Real solutions

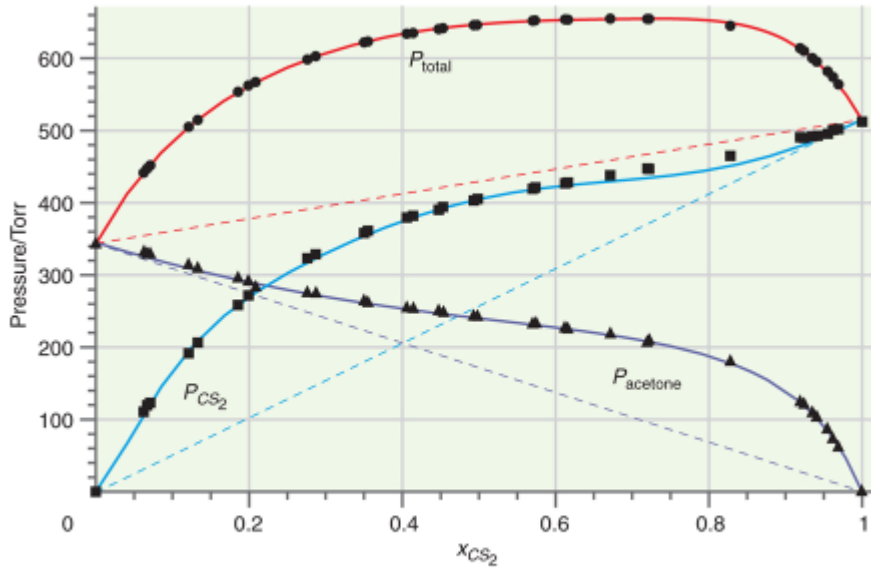
Engel & Reid chapter 9.9

The ideal gas is a good approximation on normal pressures but the not so good at high pressures. The densities of liquids are much higher than on high pressure gases, so the molecular interactions are even more important. From this point of view the ideal solutions are rather rare. There are no unique equations that could describe the real solution properties. The modern approach is data based. There are several (usually commercial) data bases of solutions properties and reliable numerical fitting tools for the data.

Some examples of open tools. For solid systems. OpenCalphad: <http://www.openalphad.com/>

ThermoCalc have also a free student license.

Below is the partial pressures and total pressure of CS₂ and acetone mixture. The dashed lines are from the Raoult's law. The deviations are quite large, especially on both ends. This means that the pure substances (either CS₂ or acetone) do not "like" the impurity molecules very much and they will evaporated easier.

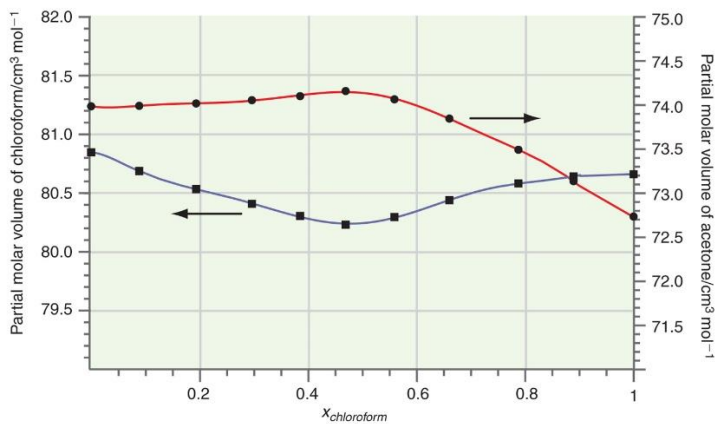


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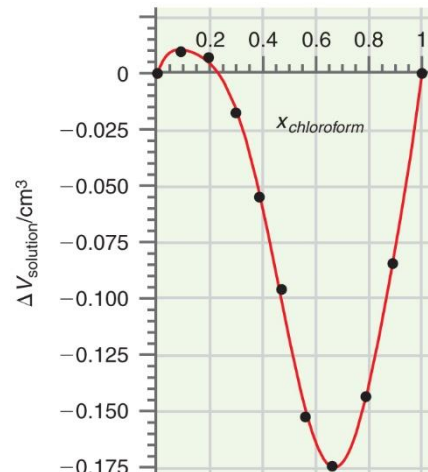
Similarly, to the partial pressure also the molar volume can deviate from the ideal. On the left there is the molar volume deviation from the ideal chloroform-acetone system.

The total molar volume will not tell the volumes of individual molecules. At small concentration interval, we can use Gibbs-Duhem equation to estimate the individual volume changes.

$$dV_1 = -\frac{x_2}{x_1} dV_2$$



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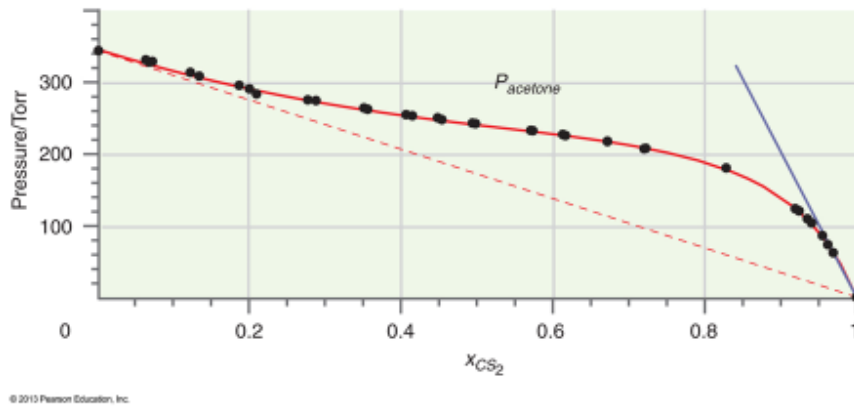


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Often we are interested of real solutions with one major component (solvent) and one dilute component (solute). We can compute the chemical potential as

$$\mu_{i,solution} = \mu_i^* + RT \ln P_i/P_i^*$$

remember that for non-ideal solution $P_i \neq x_i P_i^*$ now we can define an **activity** $a_i = P_i/P_i^*$ and activity coefficient $a_i = \gamma_i x_i$. The activity coefficient is an experimental parameter and at dilute system it has a simple interpretation. It is the slope of $P(x)$ curve at low concentrations. At high acetone concentrations the acetone is close to ideal (the slope is ca. 1)



$$P_i = k_{i,H} x_i$$

this is the Henry's law and the k_H is the Henry's constant. Note that the γ is valid in all mixtures and k_H only on dilute systems. For this system there are two Henry's constants. One for acetone in pure acetone (on the left, the normal Henry's constant) and the other in almost pure CS_2 on the right. They are rather different.

For dilute systems we can also write

$$\mu_{i,solution} = \mu_i^* + RT \ln \frac{P_i}{P_i^*} = \mu_i^* + RT \ln \frac{k_{i,H} x_i}{P_i^*} = \mu_i^H + RT \ln x_i \quad \text{where} \quad \mu_i^H = \mu_i^* + RT \ln \frac{k_{i,H}}{P_i^*}$$

Now the μ_i^H will replace the μ_i^* .

The activity coefficient can be much higher than 1.

Examine example 9.8. (there is also a quiz of this)

$$\gamma_{\text{CS}_2} = 1.997$$

We can use the Henry's law to estimate the solubility of gases to liquid. An interesting example is nitrogen to water, $\text{N}_2(\text{gas}) \leftrightarrow \text{N}_2(\text{aqueous})$ the nitrogen pressure

$P(\text{N}_2) = k_H(\text{N}_2)x(\text{N}_2)$ and nitrogen do not dissolve well to water $x(\text{N}_2) = n(\text{N}_2)/(n(\text{N}_2) + n(\text{H}_2\text{O})) \approx n(\text{N}_2)/n(\text{H}_2\text{O})$ then

$$n(\text{N}_2) = n(\text{H}_2\text{O}) \frac{P(\text{N}_2)}{k(\text{N}_2)}$$

Examine example 9.12.

70 kg human have ca. 5 L of blood (mostly water). How much she/he have nitrogen in blood at 1 atm. The k_H is $9.04 \cdot 10^4$ bar. In air the N_2 concentration is ca. 80 % so at 1 atm the $P(\text{N}_2) = 0.8$ bar.

$$n(\text{N}_2) \approx 2.5 \text{ mmol.}$$

What is the case for a diver using compressed air at 50 bar pressure? $n(\text{N}_2) \approx 0.125$ mol.

At normal pressure what is the volume of this gas? $V = 3.06$ L

This is the cause of divers' disease. The volume is a significant fraction of the blood circulation system. (ca. 5 L)

Chemical equilibrium on surface

Engel & Reid chapter 9.13

As before we can write the chemical reaction equilibrium using the chemical potentials.

$$\sum_i \nu_i \mu_i = 0 \Rightarrow \sum_i \nu_i \mu_i^* + RT \sum_i \ln(a_i^{\nu_i}) = 0$$

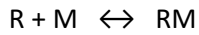
The first part of this equation is ΔG_{react} so $\Delta G_{\text{react}} = -RT \sum_i \ln(a_i^{\nu_i}) = -RT \ln K$

and the equilibrium constant is

$$K = \prod_i a_i^{\nu_i} = \prod_i \gamma_i^{\nu_i} \left(\frac{c_i}{c^0} \right)^{\nu_i}$$

This equation is not so simple to use since we need to know the γ 's for each substance. Often for most substances the γ is close to 1.

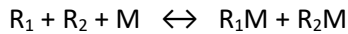
As an example we can look a simple binding reaction. We have a free molecule R and a binding site M and the bound molecule RM and they are in equilibrium. The binding site can be surface, like Pt catalyst, protein, etc.



the equilibrium constant $K = c_{RM}/c_R c_M$ (the γ 's are assumed to be 1). The fraction of bound molecules

$$v = \frac{c_{RM}}{c_M + c_{RM}} = \frac{K c_R}{1 + K c_R}$$

this is very simple equation and it depend only on K and c_R . K has dimension of $1/c$. This model assumes that all the binding sites are identical and independent. This naïve model can be used in gas phase by replacing c with p . It can be generalized to multiple species adsorption. For two species



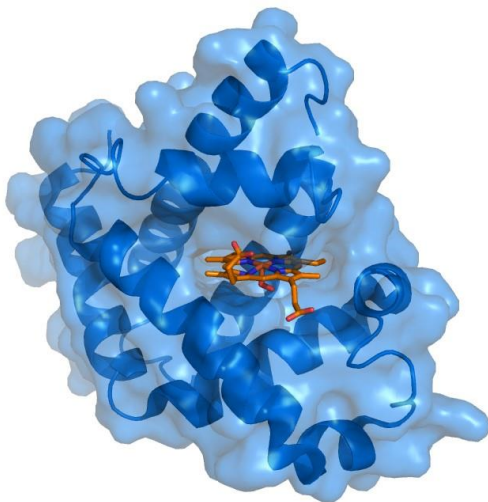
the equilibrium constants are $K_i = c_{R_iM}/c_{R_i} c_M$

and fraction of bound molecules are ($i=1,2$)

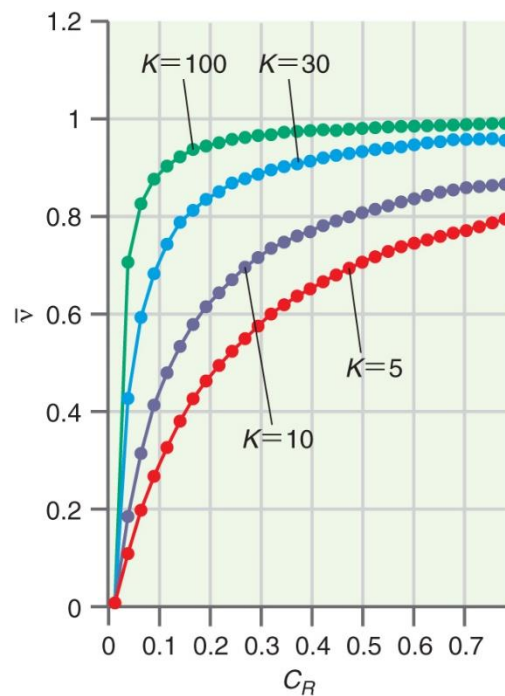
$$v_i = \frac{c_{R_iM}}{c_M + c_{R_1M} + c_{R_2M}} = \frac{K_i c_{R_i}}{1 + K_1 c_{R_1} + K_2 c_{R_2}}$$

From the figure on right we can see that the adsorbed molecules fraction reaches 1 rather slowly.

This model is surprisingly useful. On surfaces it is used to estimate the molecular coverage and it is called Langmuir isotherm. It can also be used on biochemistry to model molecule-protein binding.



[Myoglobin](#) (blue) with its ligand [heme](#) (orange) (from Wikipedia)



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The model can be extend to case where several sites (N) are needed to bind a molecule.

$$v = \frac{N K c_R}{1 + K c_R}$$

This can be written in form

$$\frac{v}{c_R} = -Kv + NK$$

this has now two parameters, but they are easy to fit to numerical data.

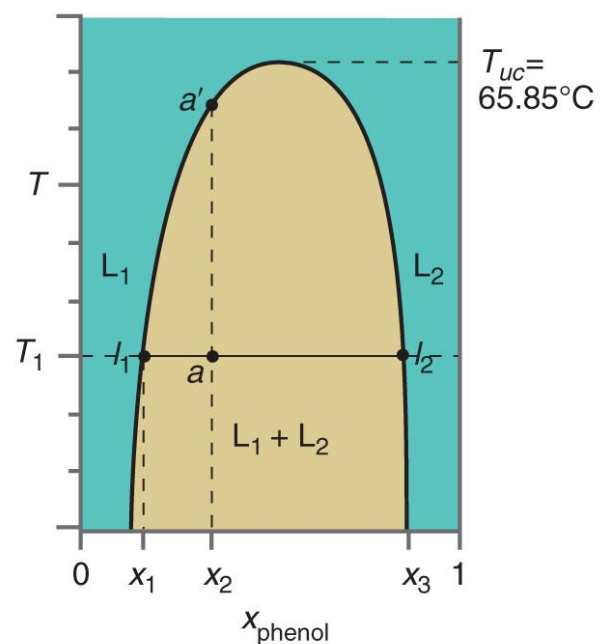
Examine the example 9.14

Partially miscible liquids

Engel & Reid chapter 9.14

So far we have assumed that the liquids will fully mix but this is not always the case. If the liquids are fully immiscible, the situation is rather easy – they can be studied separately. The challenging case are the partially miscible liquids.

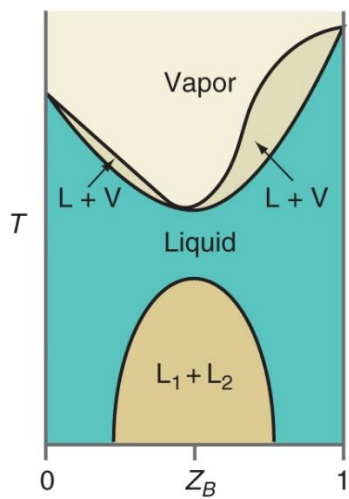
On the right there is phase diagram of water-phenol system. One can investigate the line at temperature T_1 . If we start from 100 % phenol system and add water to it, we will have homogenous liquid (L_2) up to concentration x_3 . Then the water and phenol will separate to liquids L_1 and L_2 . At concentrations between x_1 and x_3 the ratio of the two liquids can be estimated with lever rule. Below the concentration x_1 (quite watery system) the liquids mix again. Often the separated liquids can be below some temperature. This temperature is called the upper consolute temperature T_{uc} .



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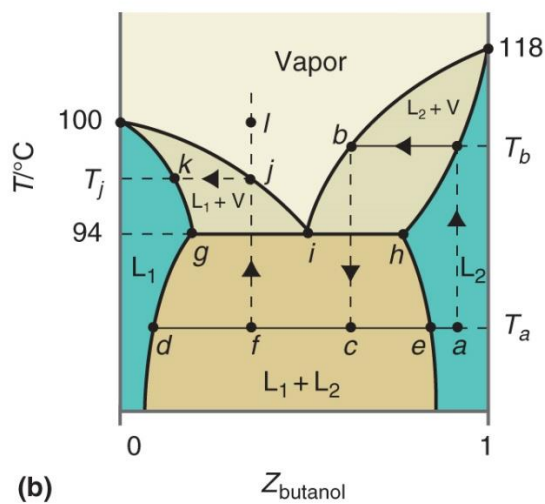
Why at high temperature the liquids mix well ?

If the temperature is increased further the liquids start to boil. In the figure (a) below the T_{uc} is lower than the lowest boiling point and in figure (b) the boiling happen below T_{uc} . The behavior of this type of liquids mixture is complex. You can read the book the get some idea what the lines means.



(a)

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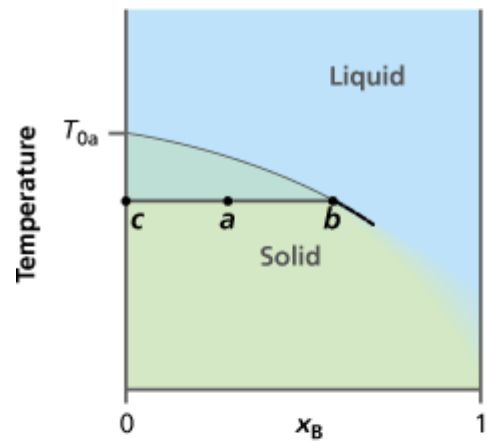
(b)

Solid liquid equilibrium	Engel & Reid chapter 9.15
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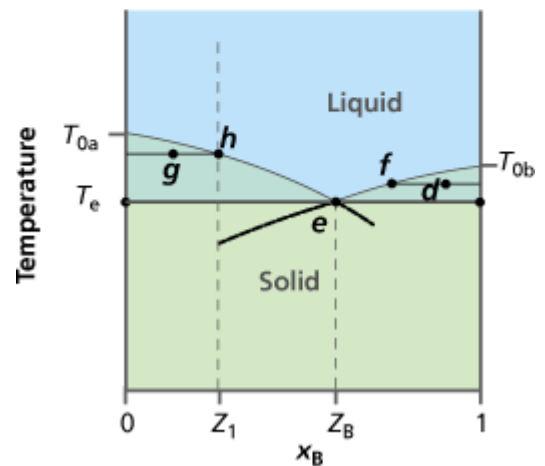
The solid liquid equilibrium of mixed system is an interesting phenomenon. The melting temperature will depend on the concentrations of the components (A and B and their fractions x_A and x_B). At low fractions of B. The melting temperature will be

$$\frac{1}{T} = \frac{1}{T_{fus}(A)} - \frac{R \ln x_B}{\Delta_{fus}H(A)}$$

Here the T_{fus} and H_{fus} are the melting temperature and enthalpy of fusion of the pure system. In figure (a) the lowering of the melting point with respect of fraction x_B is demonstrated. The equation is valid to some value of x_B then one could use a similar equation with reversing A and B. (figure (b) right side). Note that below the horizontal line (c-a) the system is solid. In the area between the melting line and c-a the solid and liquid co-exist.



(a)



(b)