

Thermodynamics of solutions

Two component systems

Ideal solutions

Raoult's law

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Chemical potential of a solution

For pure component j the equation becomes

$$\mu_j^*(l) = \mu_j^*(\text{vap}) = \mu_j^\circ(T) + RT \ln P_j^*$$

Thus

$$\mu_j^{\text{sln}} = \mu_j^* + RT \ln P_j/P_j^*.$$

This is a central result for the study of liquid. This result uses information from the vapor phase chemical potential above the liquid to give us information on the chemical potential in the liquid.

Ideal Solutions

Ideal solutions obey Raoult's law

$$P_j = x_j P_j^*$$

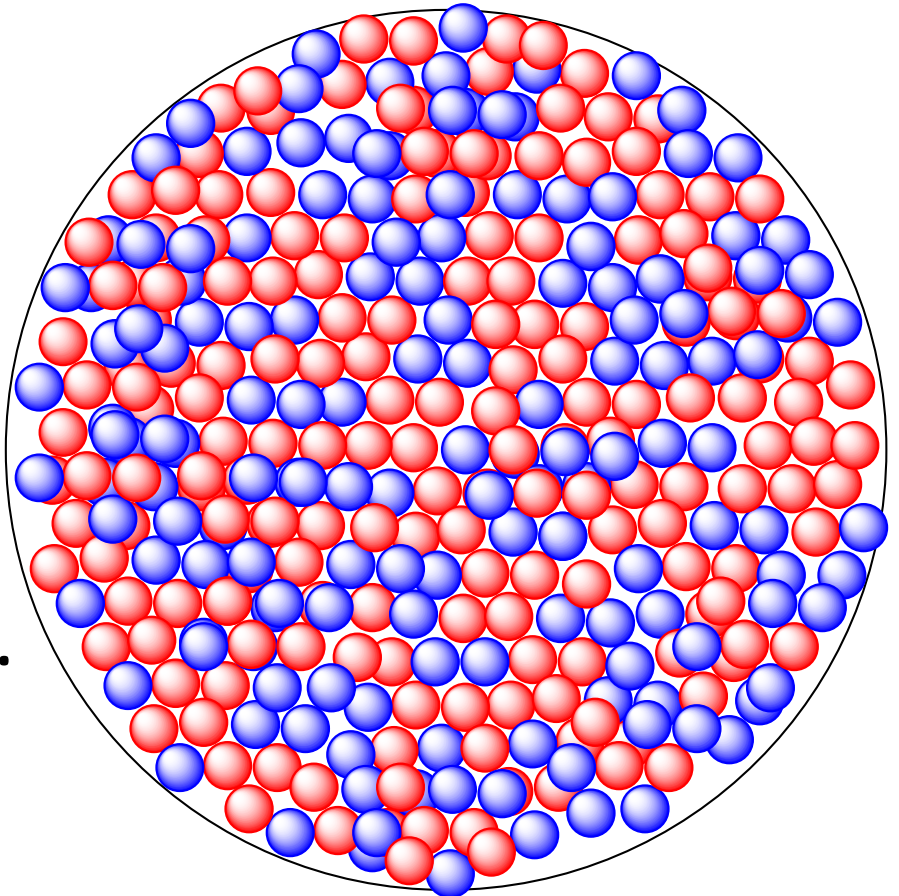
We choose as our first example a binary solution. Imagine that the two types of molecules in a binary solution are randomly distributed throughout the solution.

Raoult's law states that the partial pressure of liquid 1 above the liquid is equal to the mole fraction of the liquid in a solution times the partial pressure of the pure liquid. This holds for ideal solutions. An ideal solution is approached by binary solutions of molecules that have similar properties (e.g. benzene and toluene).

Geometric considerations

We can understand Raoult's law by means of a physical picture of the surface of a liquid.

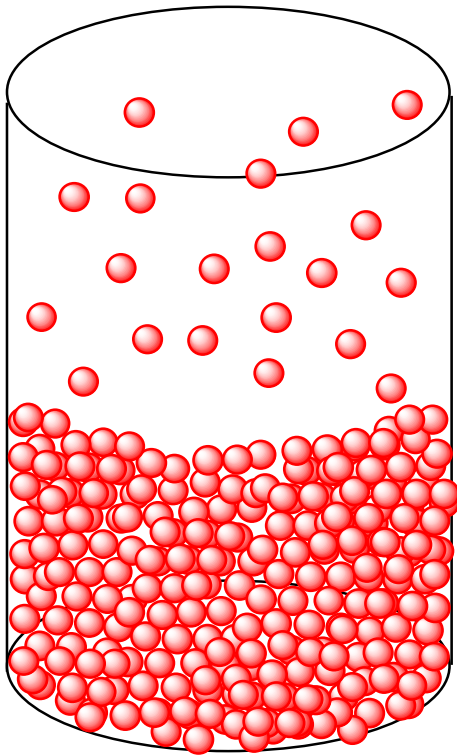
The two types of molecules can only enter the vapor phase if they reach the surface.



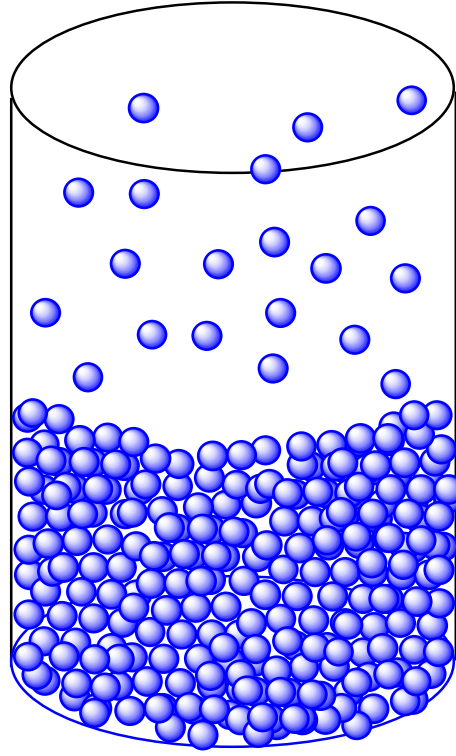
The red and blue spheres represent molecules of two species in a binary solution. Since the surface area is approximately proportional to the mole fraction (assuming that the molecules have the same size) then the ability of the molecule to jump into the vapor phase is proportional to its concentration (mole fraction at the surface).

We can consider the red and blue spheres to be two molecules in an ideal binary solution. We represent the vapor pressure of each of the pure liquids by P_{red}^* or P_{blue}^* .

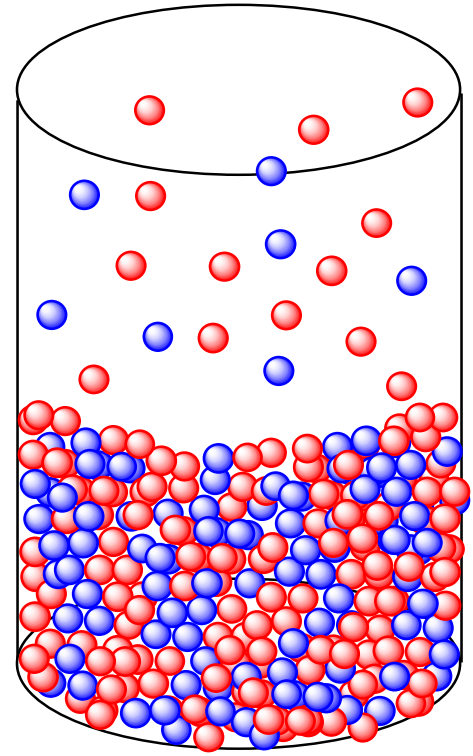
Vapor pressure in a two-component mixture



P^*



P^*



$xP^* + xP^*$

Interpreting Raoult's law

We can rewrite Raoult's law as

$$x_j = \frac{P_j}{P_j^*}$$

This leads to an expression for the chemical potential

$$\mu_j = \mu_j^* + RT \ln x_j$$

Calculated ideal vapor pressure plot

The total vapor pressure over an ideal solution is

$$P_{\text{total}} = P_1 + P_2 = x_1 P_1^* + x_2 P_2^* = (1 - x_2) P_1^* + x_2 P_2^* = P_1^* + x_2 (P_2^* - P_1^*)$$

We can make a plot of vapor pressure vs. composition for

benzene and toluene as follows. We plot $x_{\text{benzene}} P_{\text{benzene}}^*$ from

$x_{\text{benzene}} = 0$ to 1 where $P_{\text{benzene}}^* = 60$ torr and likewise we plot

x_{toluene} from 1 to 0 noting that $x_{\text{toluene}} = 1 - x_{\text{benzene}}$. Note that

$P_{\text{toluene}}^* = 180$ torr. Both of the vapor pressures quoted here are

temperature dependent. Note that on the abscissa we choose

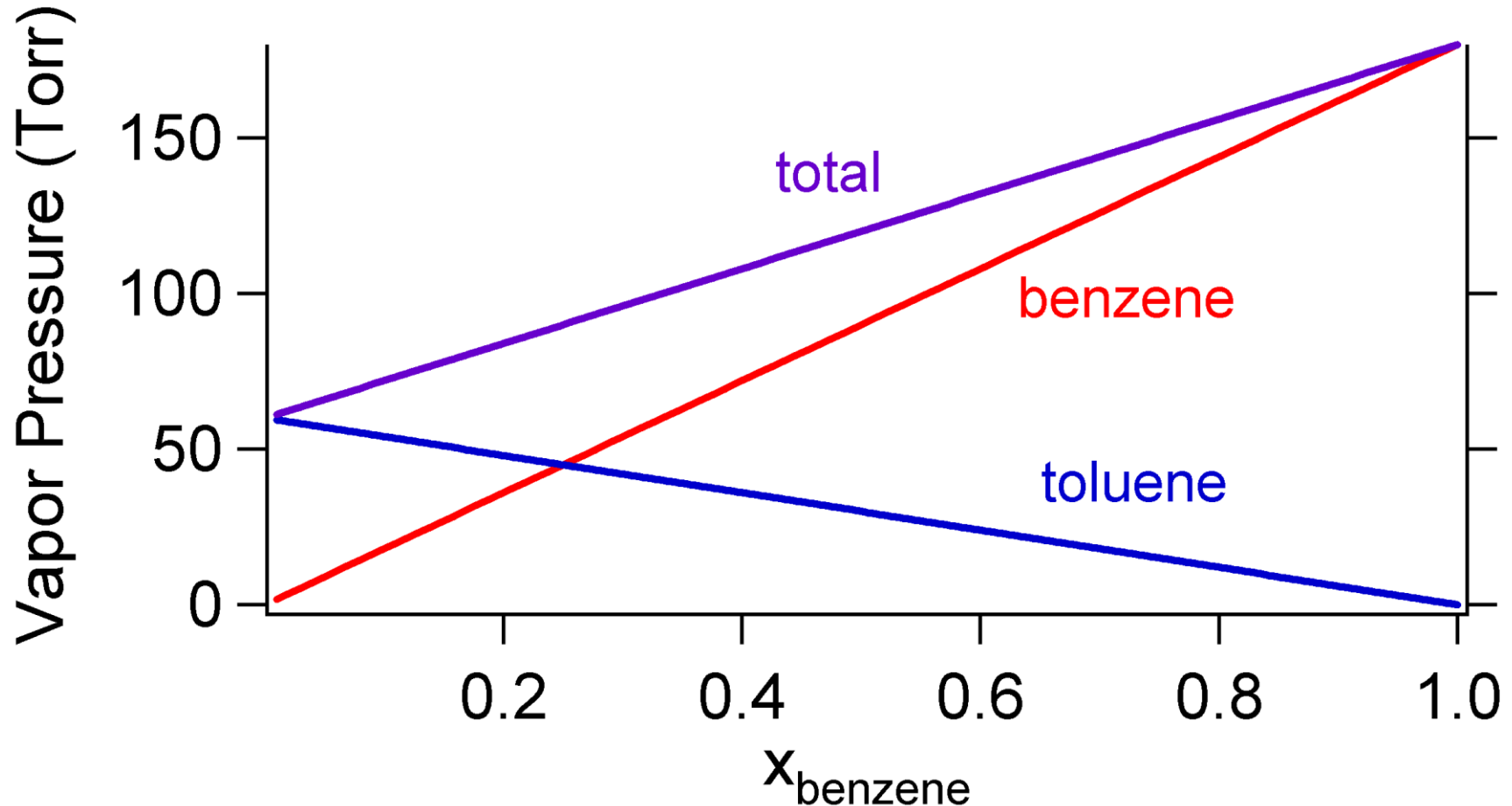
one of the mole fractions and plot each of the vapor pressures as

a function of that mole fraction. In the figure we have chosen

benzene, but we could have chosen toluene and the diagram

would have the same information.

Calculated ideal vapor pressure plot



Calculated ideal vapor pressure plot

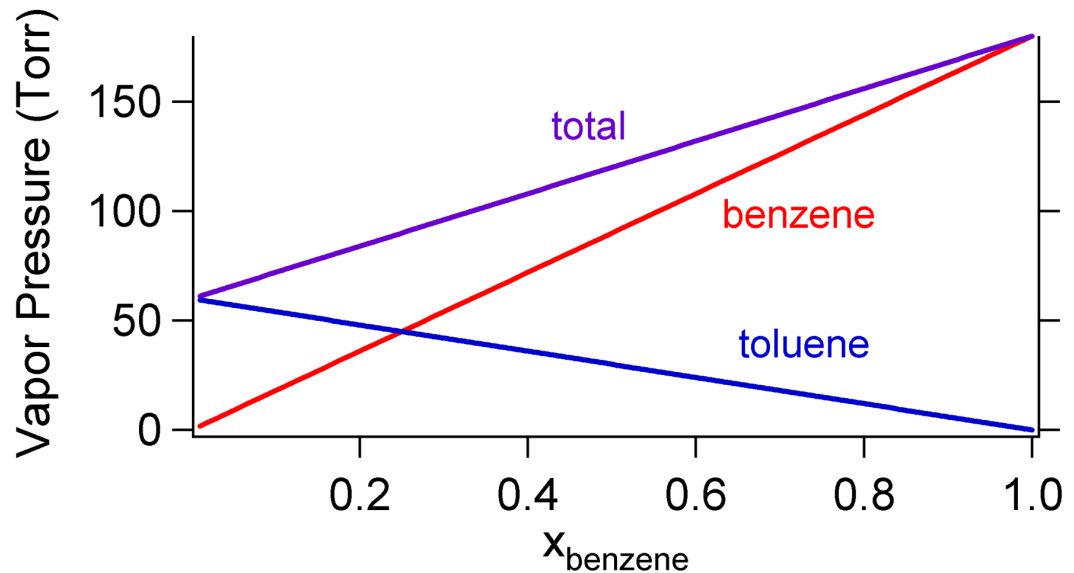
Vapor pressure-composition diagram of an ideal solution of benzene and toluene. The equations used to generate the lines on the plot are

$$P_{\text{total}} = P_1^* + x_2(P_2^* - P_1^*)$$

$$P_1 = x_1 P_1^*$$

$$P_2 = x_2 P_2^*$$

where 1 is benzene
and 2 is toluene.



Thinking in terms of the vapor pressure

In a binary solution the composition of the vapor is not the same as the composition of the liquid. The more volatile component will have a larger vapor pressure and so there is more of that component in the vapor above the liquid. In our figures above we have shown the red substance to be more volatile and therefore there are relatively more red molecules in the gas phase. Considering benzene and toluene, the vapor pressure of benzene is larger and so the mole fraction of benzene in the vapor will be larger than the mole fraction of benzene in solution.

Composition of the vapor

To calculate the mole fraction in the vapor we use Dalton's law. Dalton's law states that the partial pressure (here read vapor pressure as well) of a gas is equal to the mole fraction y_1 of component 1 in the gas phase times the total pressure.

$$P_1 = y_1 P_{\text{total}}$$

Note that we have a way to calculate both P_1 and P_{total} from the equations above

$$P_1 = x_1 P_1^* \text{ and } P_{\text{total}} = P_1^* + x_2 (P_2^* - P_1^*)$$

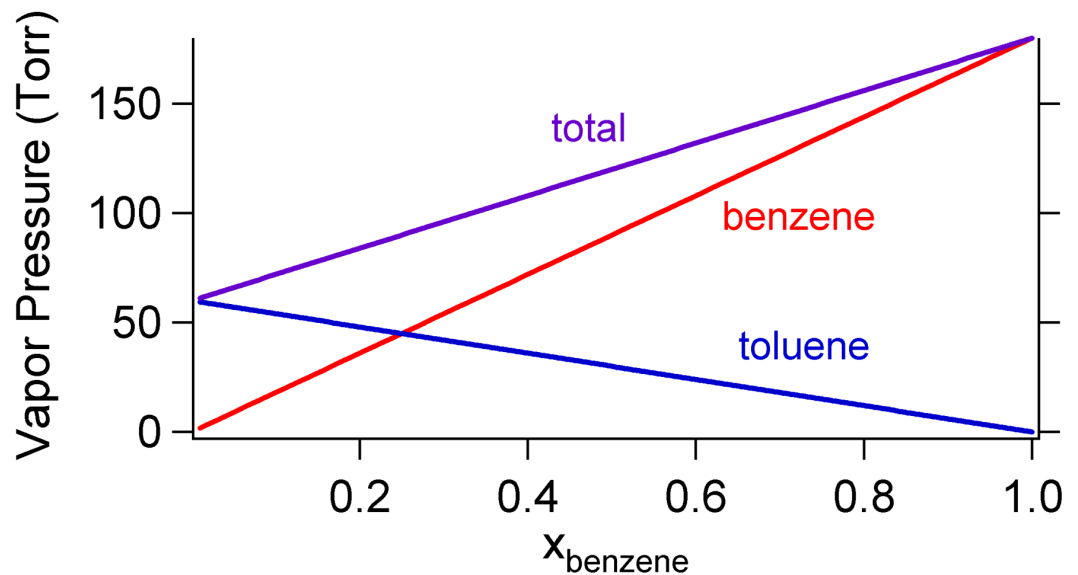
so

$$y_1 = x_1 P_1^* / P_{\text{total}}$$

Considering the composition of the vapor

We can expand on the plot above for benzene and toluene by plotting a vapor curve that represents the total vapor pressure as a function of the mole fraction in the vapor phase. Note that the violet total line in the figure above represents the vapor pressure as a function of the mole fraction in the liquid phase.

To plot this we need to solve for P_{total} in terms of y_1 , y_2 , P_1^* and P_2^* .



Derivation of the vapor curve

$$P_{\text{total}} = x_2 P_2^* / y_2 \text{ and } x_2 = (P_{\text{total}} - P_1^*) / (P_2^* - P_1^*)$$

$$P_{\text{total}} = (P_{\text{total}} - P_1^*) P_2^* / (P_2^* - P_1^*) y_2$$

$$P_{\text{total}} - P_{\text{total}} P_2^* / (P_2^* - P_1^*) y_2 = -P_1^* P_2^* / (P_2^* - P_1^*) y_2$$

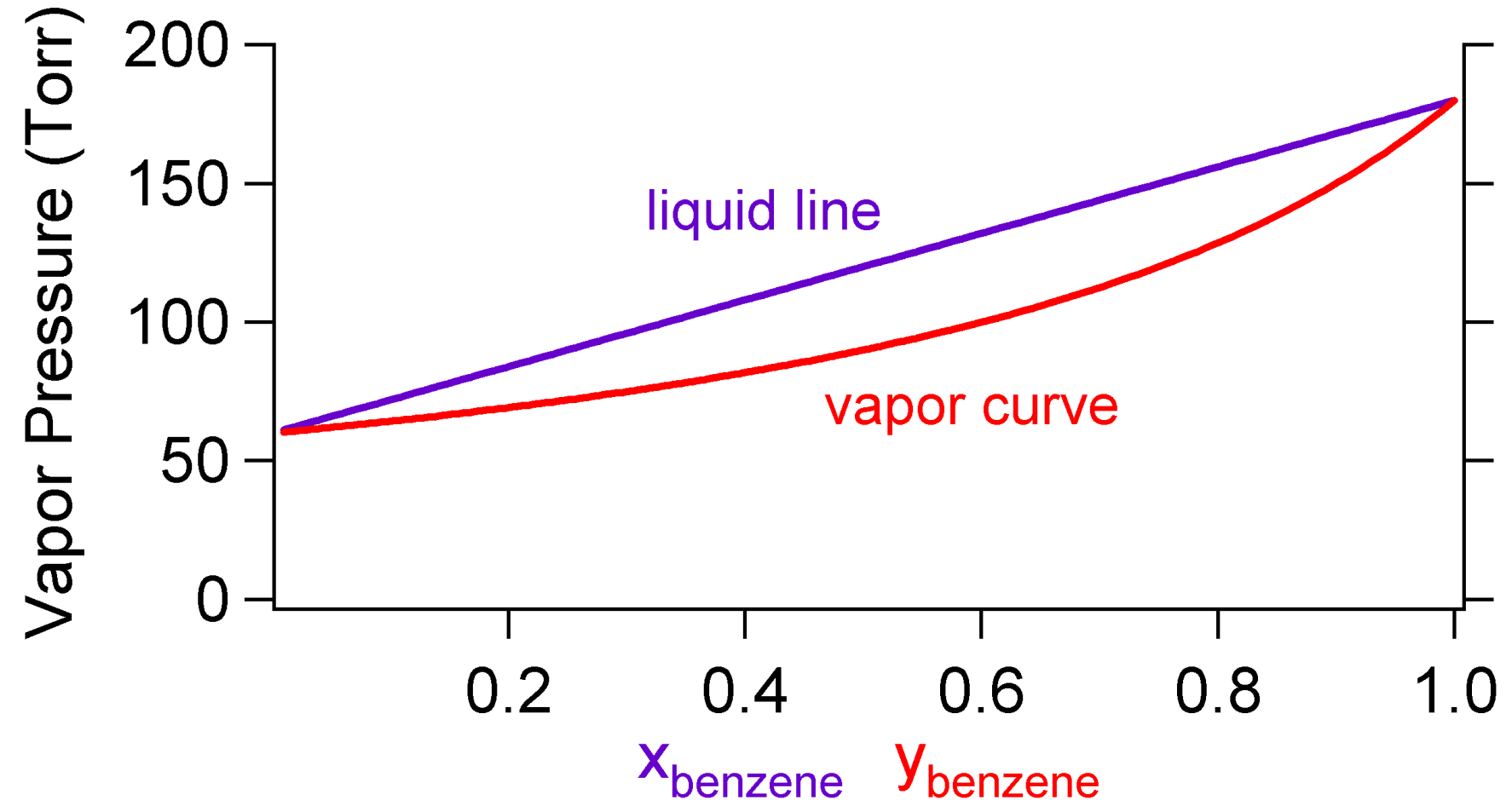
$$P_{\text{total}} [1 - P_2^* / (P_2^* - P_1^*) y_2] = -P_1^* P_2^* / (P_2^* - P_1^*) y_2$$

$$P_{\text{total}} [(P_2^* - P_1^*) y_2 - P_2^*] / (P_2^* - P_1^*) y_2 = -P_1^* P_2^* / (P_2^* - P_1^*) y_2$$

$$P_{\text{total}} [(P_2^* - P_1^*) y_2 - P_2^*] = -P_1^* P_2^*$$

$$P_{\text{total}} = P_1^* P_2^* / (P_2^* + (P_1^* - P_2^*) y_2)$$

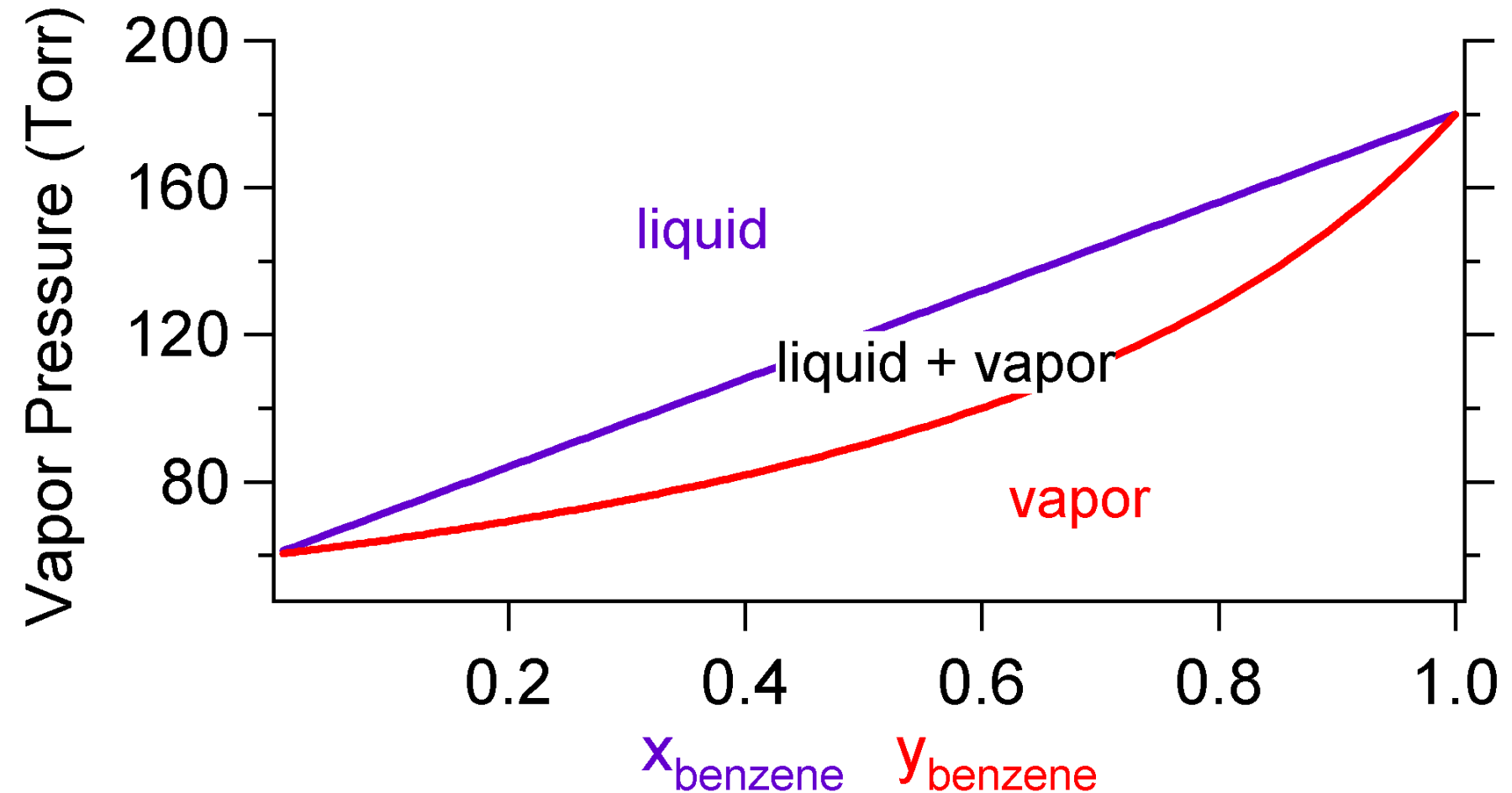
Plot of the vapor curve



Explanation of the liquid and vapor curves

The plot shown is a pressure-composition diagram. This can be shown by labeling the regions of the diagram. The upper region (at sufficiently high pressure) is the liquid region above the liquid line. The low region is completely vapor. The region between the curves is a region where the liquid is in equilibrium with vapor. That is to say that two phases coexist in this region.

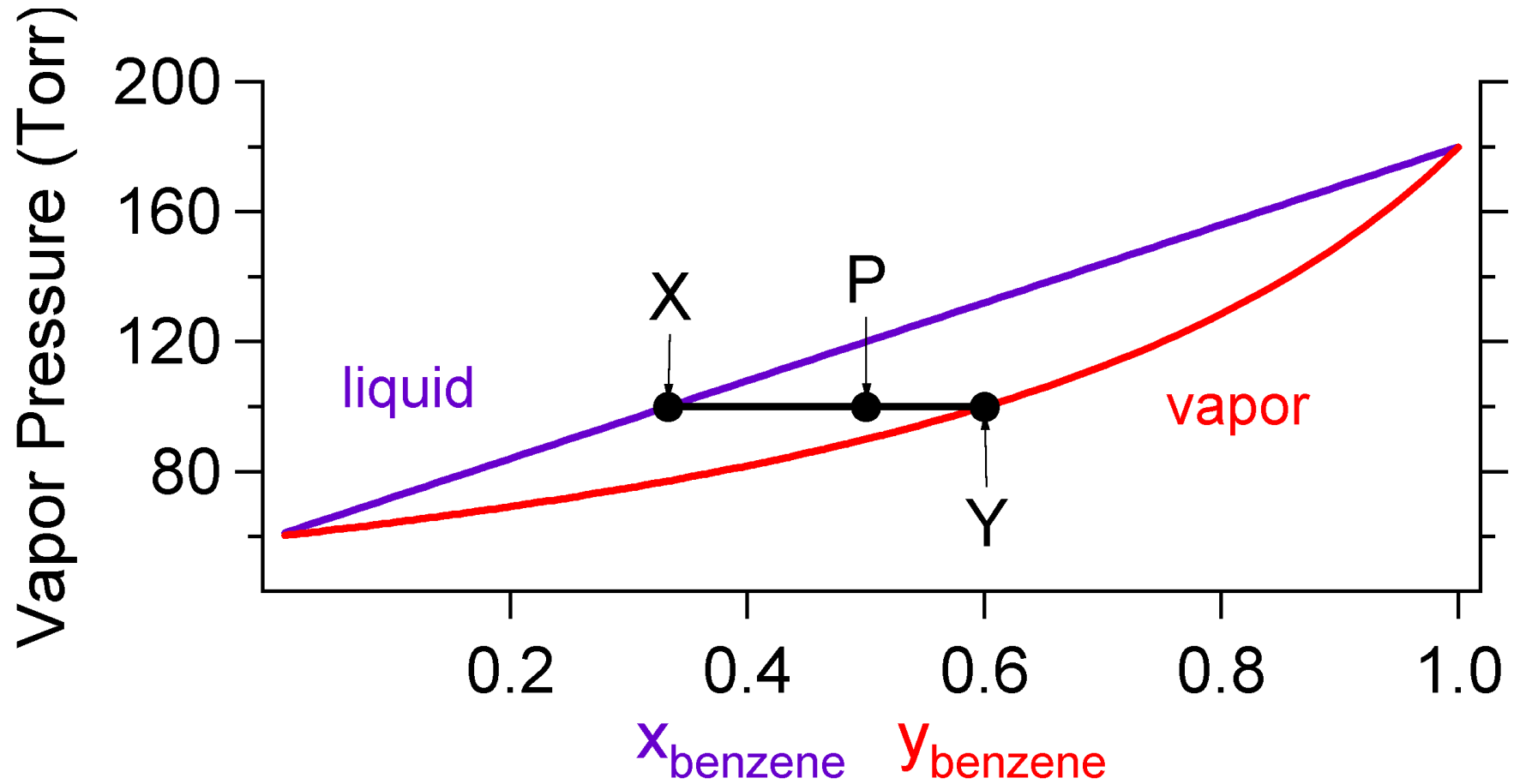
The two-phase region



Explanation of the two phase region

In the liquid region the composition is x_{benzene} (and the implied $x_{\text{toluene}} = 1 - x_{\text{benzene}}$) or more generally x_2 and $x_1 = 1 - x_2$. In the vapor region the composition is y_{benzene} (and the implied $y_{\text{toluene}} = 1 - y_{\text{benzene}}$) or more generally y_2 and $y_1 = 1 - y_2$. But what about the composition in the two phase region. We examine a point in the two phase region labeled P. The overall mole fraction at this point is z . At point P we draw a line connecting the liquid line and the vapor curve. This line is known as a tie line. It represents the fact that the composition of the liquid and vapor at this particular overall composition can be read from the vapor pressure-composition diagram by examining points X and Y.

The tie line



Calculating amount in each phase

We can define the mole fractions of liquid and vapor, respectively as

$$x_1 = \frac{n_1^l}{n_1^l + n_2^l} = \frac{n_1^l}{n^l} \quad \text{and} \quad y_1 = \frac{n_1^{vap}}{n_1^{vap} + n_2^{vap}} = \frac{n_1^{vap}}{n^{vap}}$$

Where n^l and n^{vap} are the total number of moles in the liquid and vapor phases, respectively. The overall mole fraction is given by

$$z_1 = \frac{n_1^l + n_1^{vap}}{n^l + n^{vap}}$$

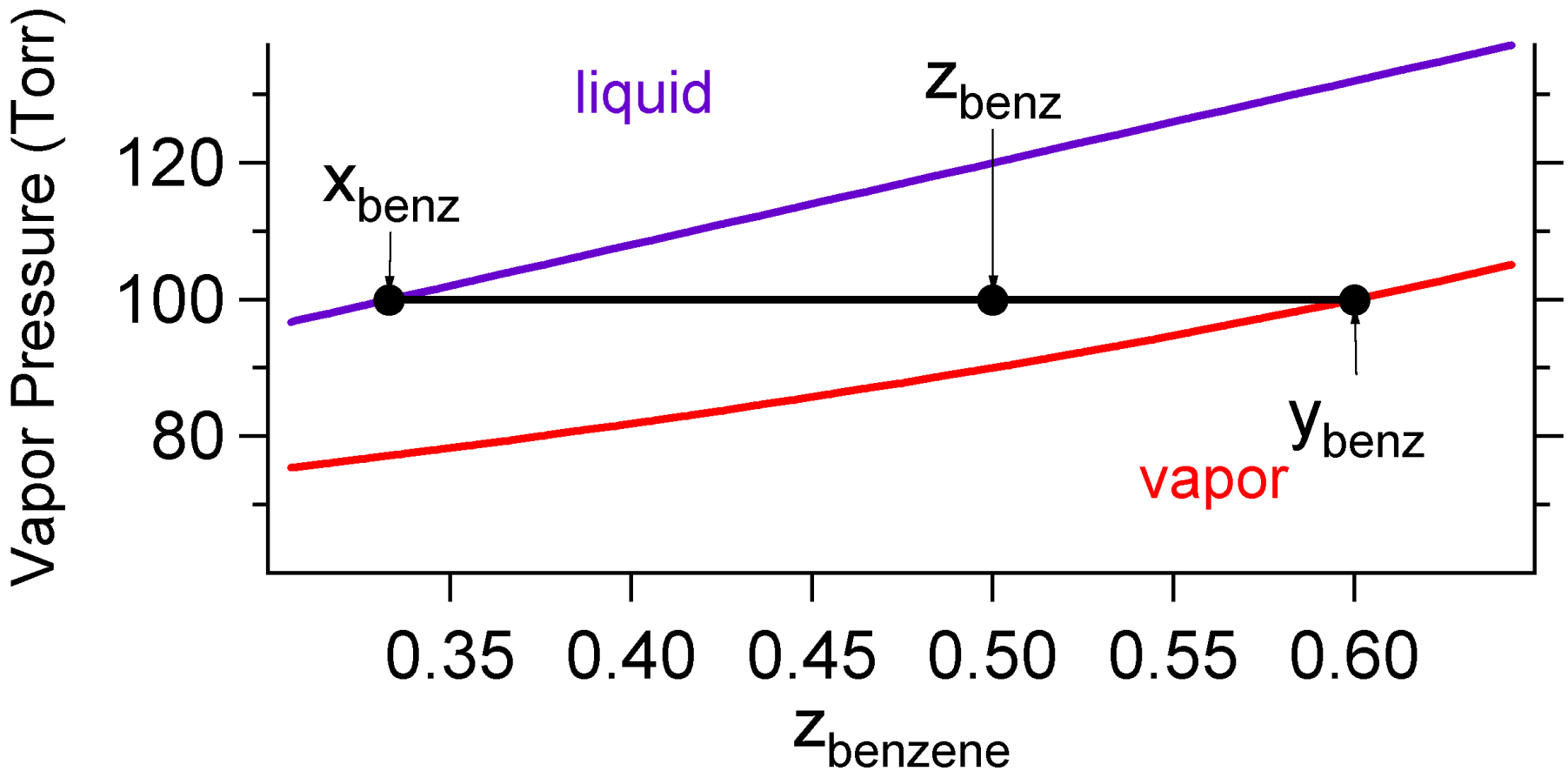
Using the fact that $z_1(n^l + n^{vap}) = x_1 n^l + y_1 n^{vap}$

We can calculate the relative amount of liquid and vapor:

$$\frac{n^l}{n^{vap}} = \frac{y_1 - z_1}{z_1 - x_1}$$

Illustration of the lever rule

This equation has a graphical interpretation. We look at an expansion of the region around P on the benzene/toluene vapor pressure-composition plot.



Example calculation using the lever rule

The above equation for $n^{\text{liq}}/n^{\text{vap}}$ is called the lever rule. If $z_1 = 0.5$ (and therefore $z_2 = 0.5$) and the vapor pressure is $P_{\text{total}} = 100$ Torr we can calculate both y_{benzene} and x_{benzene} that will give the limits of the tie line.

$$x_{\text{benz}} = (P_{\text{total}} - P_{\text{tol}}^*) / (P_{\text{benz}}^* - P_{\text{tol}}^*) = (100 - 60) / (180 - 60) \\ = 40/120 = 0.333$$

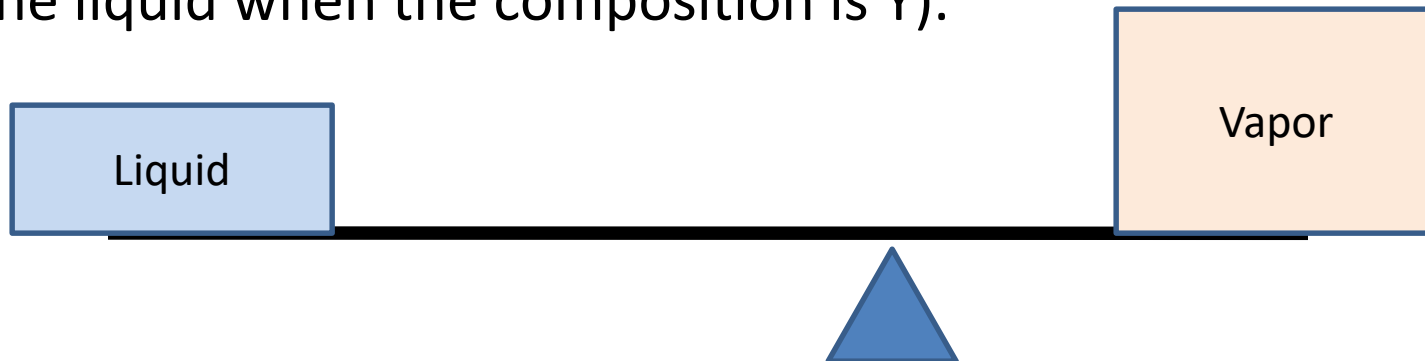
$$y_{\text{benz}} = x_{\text{benz}} P_{\text{benz}}^* / P_{\text{total}} = (1/3)(180)/100 = 0.6$$

In this case given that $z_{\text{benz}} = 0.5$ as shown in the figure we have

$$\frac{n^l}{n^{\text{vap}}} = \frac{0.6 - 0.5}{0.5 - 0.333} = \frac{0.1}{0.167} = 0.6$$

Graphical interpretation of the lever rule

Notice that there is an inverse relationship between the distance along the tie line to a phase and the amount of that phase. Point P is closer to the vapor curve and this means that there is more of the liquid. This seems counterintuitive at first. If we were to increase z to 0.6 along this line then we would move to point Y. Point Y represents the composition of the vapor in equilibrium with liquid (i.e. there is a negligible amount of vapor compared to the liquid when the composition is Y).



Temperature-component phase diagrams

We can display the composition of the solution and vapor phases at various temperatures on a temperature-composition diagram.

To construct a temperature-composition diagram we choose a total pressure. For example, the ambient pressure may be 760 torr. If this pressure is considered P_{total} for a solution then

$$x_2 = (P_{\text{total}} - P_1^*) / (P_2^* - P_1^*) \text{ or } x_2 = (760 \text{ torr} - P_1^*) / (P_2^* - P_1^*)$$

The magnitude of P_1^* and P_2^* are determined from the Clausius-Clapeyron equation for the two species.

$$P_1^* = P_1' \exp \left\{ \frac{\Delta_{\text{vap}} H}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right\}$$

The pressure P_1' and temperature T_1' are reference temperature and pressure such as the normal boiling point of the pure liquid. The equation allows us to calculate P_1^* at the temperature of interest. A similar calculation for P_2^* is then combined and input into the equation above to yield x_2 which determines the liquid composition curve.

Example: benzene and methanol

Molecule	T_{vap}	$\Delta_{\text{vap}}H$
Benzene	353.2	30.8
Methanol	337.2	35.3

$$P_1^* = (760 \text{ Torr}) \exp\{3.70(0.00283 - 1/T)\} \text{ for benzene}$$

$$P_2^* = (760 \text{ Torr}) \exp\{4.23(0.00296 - 1/T)\} \text{ for methanol}$$

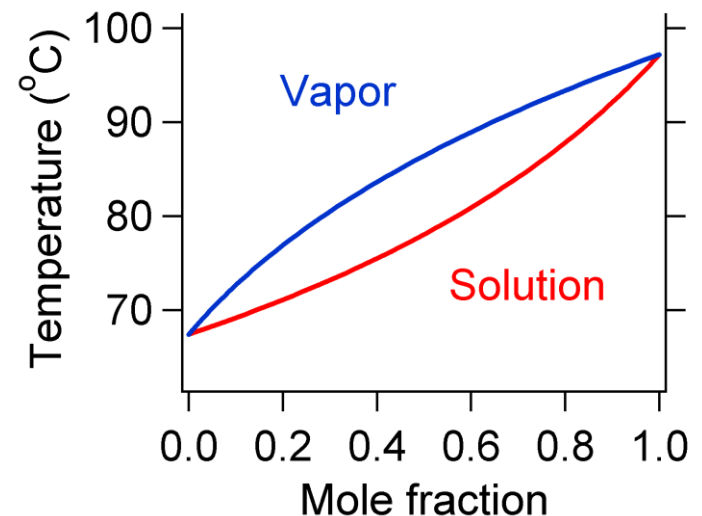
$$x_2 = (1 - \exp\{3.70(0.00283 - 1/T)\}) / (\exp\{4.23(0.00296 - 1/T)\} - \exp\{3.70(0.00283 - 1/T)\})$$

Calculating the vapor curve

As was described above for the vapor pressure-composition diagram we can relate y_2 to x_2 and thereby obtain a vapor curve.

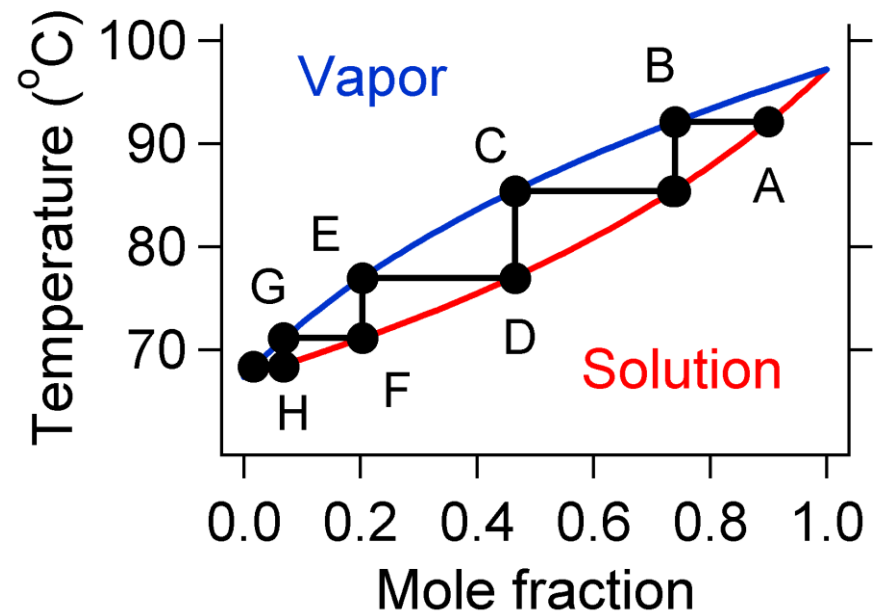
$$y_2 = x_2 P_2^* / P_{\text{total}}$$

The region between the liquid composition curve and the vapor composition curve is a two phase region and the lever rule applies there as was seen above for the vapor pressure-composition phase diagram.



Fractional distillation

The temperature composition diagram shows how fractional distillation works. If the initial composition of the liquid is A, then the composition of the vapor is B when this solution boils. If we were to collect the vapor and condense it we would be at point C. By boiling the solution with the composition at point C, the vapor has composition D. We can continue this process until we have essentially pure 1-propanol (the leftmost point on the phase diagram).



Practical note

In practice the process of distillation can be done in a single apparatus using a column of beads such that the temperature is lowered gradually ascending the column. The composition changes gradually as the vapor moves up the column. The beads create a nucleus for condensation of the vapor so that an equilibrium between liquid and vapor can be maintained.