

Vapor Pressure Diagrams and Boiling Diagrams

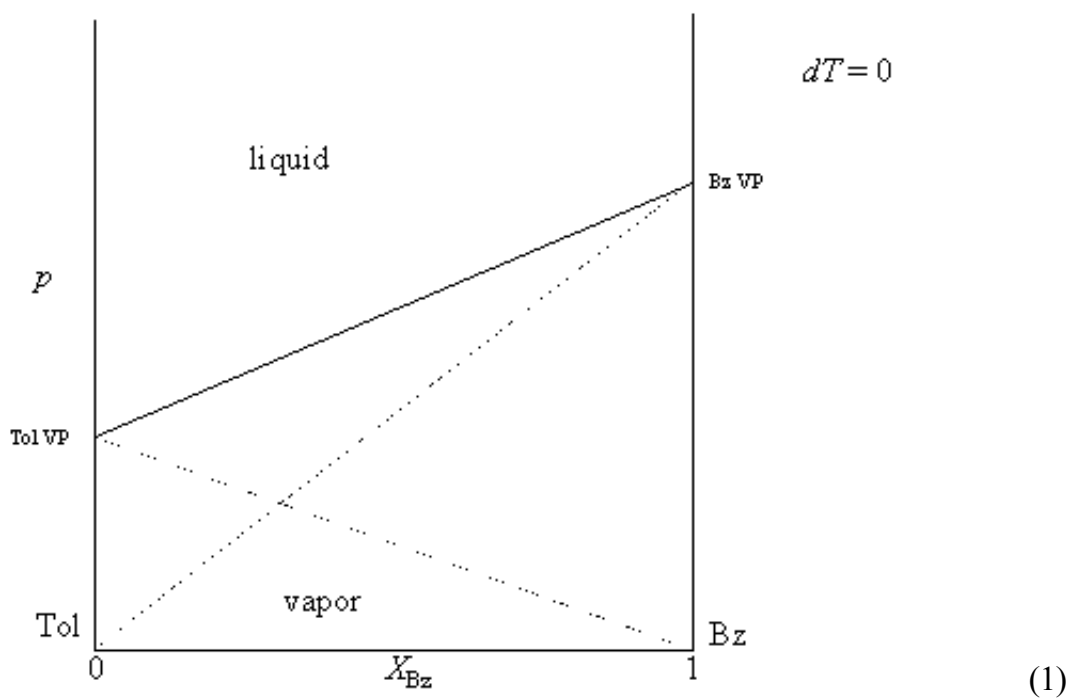
We are now ready to begin talking about phase diagrams involving two components. Our first few phase diagrams will involve only the liquid and gas (or vapor) phases. Later we will discuss two-component phase diagrams involving liquids and solids.

Consider a solution of two liquids, say benzene and toluene held at a constant temperature. Benzene and toluene form very nearly ideal solutions so we shall regard the solution as ideal. We know that an ideal solution obeys Raoult's law, so for each component we must have,

$$p_i = X_i p_i^* \quad (1)$$

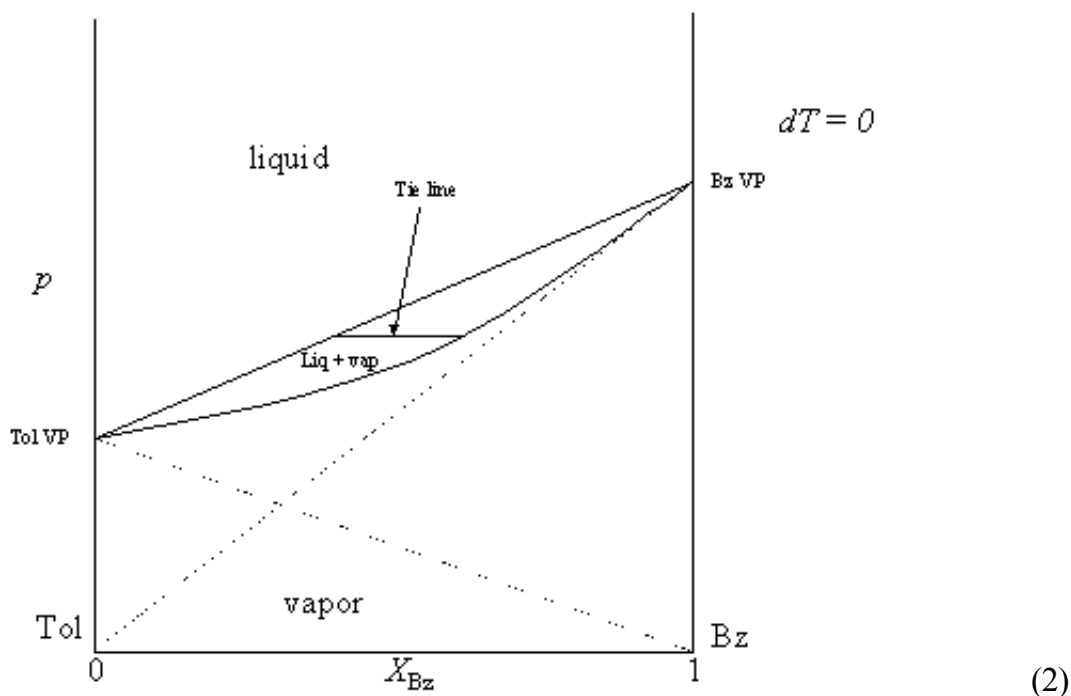
where p_i is the partial pressure of component i above the liquid mixture (or the vapor pressure of i in the mixture), X_i is the mole fraction of component i in the liquid, and p_i^* is the vapor pressure of pure component i .

If we now hold temperature constant and plot the vapor pressure of a benzene-toluene solution as a function of composition we would get a graph that looked something like this,



On this diagram (Figure 1) the dotted line that runs from "Tol VP" to lower right Bz corner is the Raoult's law vapor pressure of toluene. The dotted line that runs from the lower left Tol corner to "Bz VP" is the Raoult's law vapor pressure of benzene. The solid line from "Tol VP" to "Bz VP" is the total vapor pressure of the solution which is just the sum of the two Raoult's law vapor pressures (the sum of two straight lines is a straight line).

There is no indication on the above diagram what the composition of the vapor is at each pressure. We know that at any given pressure the vapor will be richer in the more volatile component, in this case richer in benzene. In our initial discussion of Raoult's law we worked a problem in which the composition of a benzene-toluene solution was 0.400 mole fraction benzene, but the vapor in equilibrium with the liquid was 0.649 mole fraction benzene. This means that we must draw another line to indicate the composition of the vapor at each pressure.



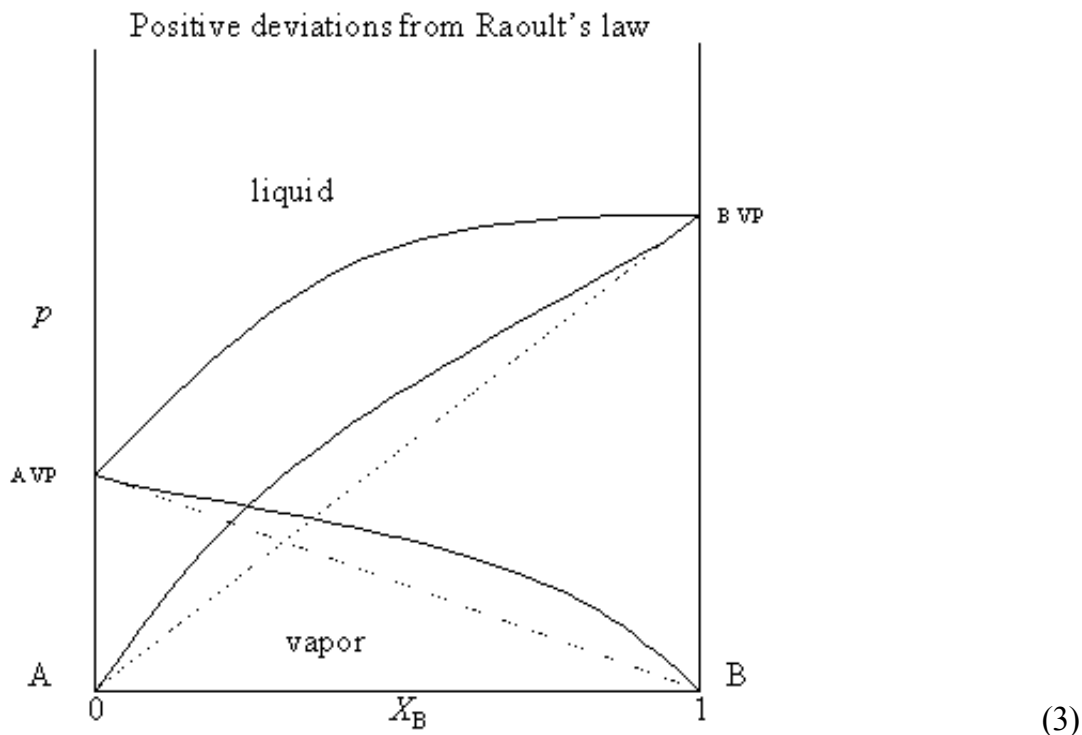
In Figure 2 we have added the lower curved line from "Tol VP" to "Bz VP" to show the composition of the vapor at each pressure. The region between the curved line and the straight total vapor pressure line is a two phase region. A single point inside this region does not correspond to a state of the system because in the two-phase region we have a vapor phase and a liquid phase in equilibrium with each other. Thus, a point in this region must correspond to two different compositions. The way we find these two different compositions is to draw a "tie line."

Although a point inside the two phase region does not give us the composition of either the liquid or the vapor phase, it does give the overall composition of the whole system. The tie line is a horizontal line through that point which intersects the two boundary lines of the two phase region. The intersection of our horizontal line (the tie line) with the boundary line on the liquid side of the region tells us the composition of the liquid and the intersection of the tie line with the boundary curve on the vapor side tells us the composition of the vapor phase.

Now we have to deal with nonideal solutions. We will distinguish two cases: positive deviations from Raoult's law and negative deviations from Raoult's law. Nonideal solutions which have positive deviations from Raoult's law have vapor pressures which are higher than Raoult's law would predict. This is because the attractive forces between the unlike molecules are weaker than the attractive forces between the like molecules.

Nonideal solutions which have negative deviations from Raoult's law have vapor pressures which are lower

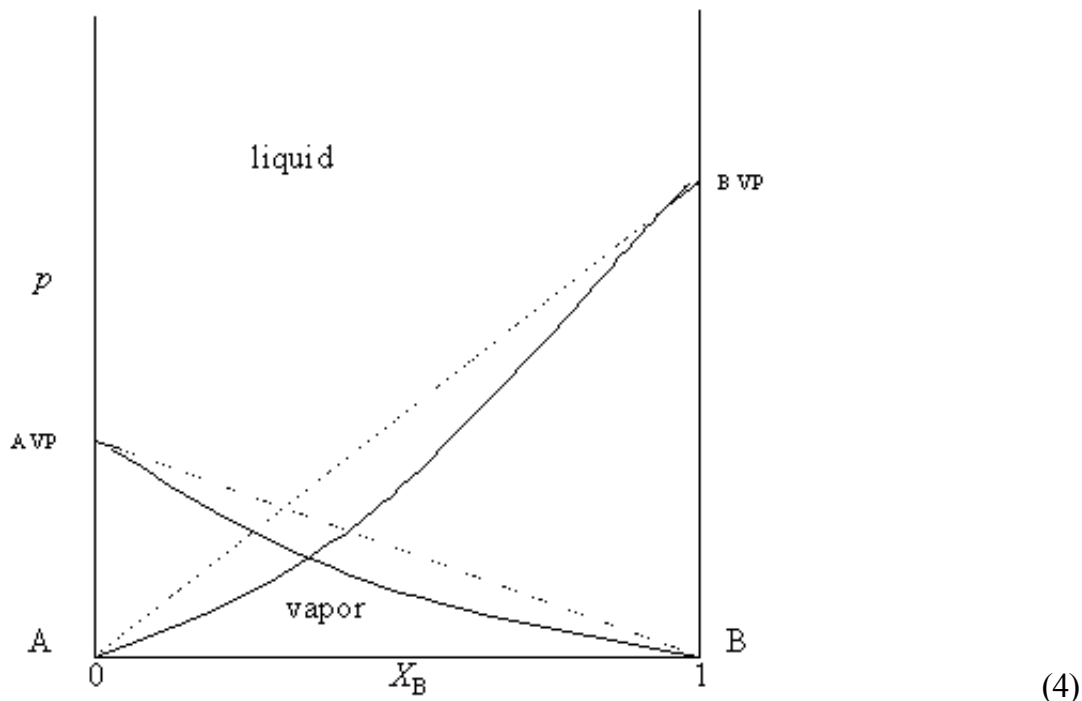
than Raoult's law would predict. This is because the attractive forces between the unlike molecules are stronger than the attractive forces between like molecules. A vapor pressure diagram for a system with positive deviations from Raoult's law might look qualitatively like the following:



This vapor pressure diagram shows qualitatively how the vapor pressures vary with composition for positive deviations from Raoult's law. We have not tried to draw the vapor composition curve on the diagram. We have tried to show that each component obeys Raoult's law in the limit as its mole fraction goes to one. Also, the vapor pressures of the individual components becomes linear in mole fraction as that mole fraction approaches zero. This latter phenomenon is known as "Henry's law" and will be discussed further below.

Negative deviations from Raoult's law might look qualitatively like the following diagram.

Negative deviations from Raoult's law



Once again we have tried to show that each component obeys Raoult's law as its mole fraction approaches one and becomes linear in its mole fraction as that mole fraction approaches zero. We have not shown the total vapor curve or the vapor composition curve. The total vapor pressure curve would just be the sum of the two individual vapor pressures. Since the solution does not obey Raoult's law it would require experimental data or a more sophisticated theory to construct the vapor composition curve.

Henry's law

We alluded above to the fact that as $X_i \rightarrow 1$ for each component in a binary mixture the vapor pressure of that component obeys Raoult's law. That is,

$$p_i = X_i p_i^* \quad (1)$$

even for nonideal solutions is the limit as $X_i \rightarrow 1$.

However, at the other end of the scale, for small mole fractions, p_i becomes proportional to X_i , but the proportionality constant is not p_i^* . That is, for small mole fractions

$$p_i = K_i X_i \quad (2)$$

Equation 2 is called Henry's law and the constant, K_i , is the Henry's law constant. The Henry's law constant depends on the nature of both the solvent and the solute.

It can be shown thermodynamically that in a concentration region where one component obeys Raoult's law the other will necessarily obey Henry's law.

Henry's law is most often used to describe the solubility of gases in liquids.

Example Calculation

Let's calculate the solubility of N_2 gas in water at $25^\circ C$ and 4.0 atm pressure. From a table of Henry's law constants we find the constant for nitrogen gas in water is 6.51×10^7 Torr. From equation 2 we get

$$\begin{aligned} X_{N_2} &= \frac{P}{K} \\ &= \frac{4.0 \times 760}{6.51 \times 10^7} \\ &= 4.7 \times 10^{-5}. \end{aligned} \quad (3a, b, c)$$

This amounts to about 0.0026 mol of N_2 per liter of water or 0.073 g/L.

One can use Henry's law to calculate the amount of oxygen gas dissolved in water which is exposed to the atmosphere. The Henry's law constant for O_2 gas in water at $25^\circ C$ is 3.3×10^7 . Since air is about 21 mole % oxygen, at an air pressure of one atmosphere the partial pressure of O_2 would be about 0.21 atm. It is easy to use Henry's law to calculate the oxygen content of water in contact with air at one atmosphere pressure,

$$\begin{aligned} X_{O_2} &= \frac{P}{K} \\ &= \frac{0.21 \times 760}{3.30 \times 10^7} \\ &= 4.8 \times 10^{-6}. \end{aligned} \quad (4a, b, c)$$

This corresponds to about 0.00027 moles of O_2 per liter of water, or 0.0086 g/L.

This does not seem like very much oxygen dissolved in water, but we note two things: Thermodynamically, the chemical potential of the dissolved O_2 is the same as the chemical potential of the O_2 in the gas in equilibrium with the water solution. Second, this seems to be enough to keep fish alive because fish use their gills to extract the oxygen and use it to metabolize food and produce energy.

(There are other issues involved in keeping fish alive in water. At equilibrium there is enough oxygen to keep fish alive, but as the fish remove the oxygen with their gills the concentration of oxygen decreases. The dissolution and diffusion of O_2 through water are relatively slow processes. Unless a way is found to replenish the oxygen the fish will die. In large bodies of water this is no problem, but in small fish tanks it can be fatal to

the fish. This is why most fish tanks have a "bubbler" in them. The bubbler increases the exposure of the water to the oxygen in air and gently stirs the water to hasten the saturation of water with oxygen.)

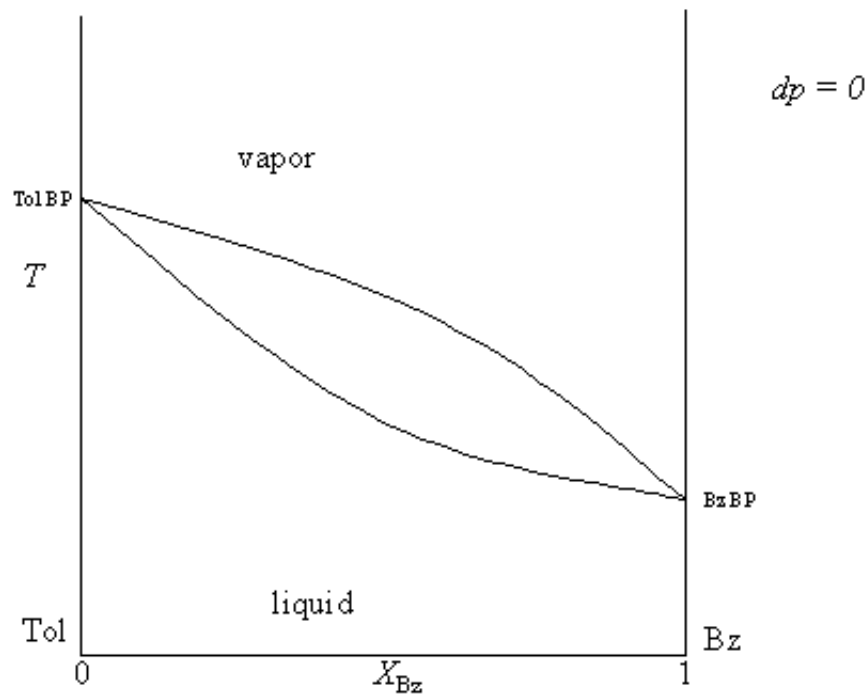
(One other comment about the solubility of gases in water. A condition known to deep sea divers as the "bends" is caused by the solubility of nitrogen in water. We know from Henry's law that the solubility increases with pressure. At the high pressures produced by deep sea diving [and some scuba diving] nitrogen gas dissolves in the blood. If the diver rises from the depths very slowly, over a period of many hours, the blood will gradually release the nitrogen and remain at equilibrium with the surrounding gas pressure. However, if the diver rises too fast the nitrogen will come out of solution as the pressure is released and form bubbles of nitrogen gas in the blood and other body fluids. The bubbles accumulate at the joints, producing great pain, and causing the diver to "double over in pain," Thus the condition is referred to as "the bends." The bends can even lead to death unless a way is found to redissolve the nitrogen gas. Commercial and military diving support ships carry a decompression chamber so that a diver can be brought up quickly and then recompressed in the chamber. [See the James Bond movie, *Licensed to Kill*.] In the decompression chamber the pressure can be released gradually allowing the nitrogen to escape the blood stream without forming the bubbles and making it unnecessary to remain at the diving site to bring the diver up slowly.)

Boiling diagrams

The diagrams shown above, where we are plotting vapor pressures as a function of composition at constant temperature are not the most useful diagrams. Since we live in a more-or-less constant pressure environment it is more useful and interesting to plot the properties of the solution as temperature versus composition.

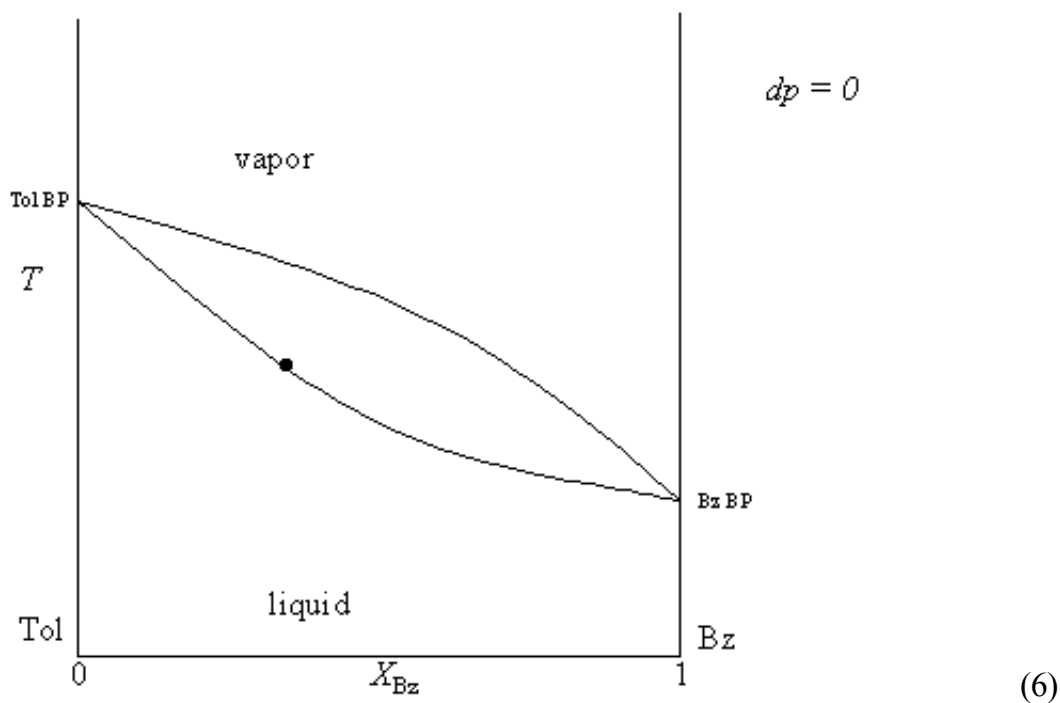
Think of the vapor pressure diagrams we showed above as slices at constant temperature through a three-dimensional diagram showing the properties of the mixture as a function of temperature, pressure, and composition. The lines in the above vapor pressure diagrams will appear on this three-dimensional diagram as surfaces, and the points, such as boiling points will be curved lines. (Because the boiling point changes with changing pressure.)

Now, instead of taking slices at constant temperature, let's take slices through our three-dimensional diagram at constant pressure. If we take our slice at a pressure of one atmosphere the new diagram, called a boiling diagram, would look something like,

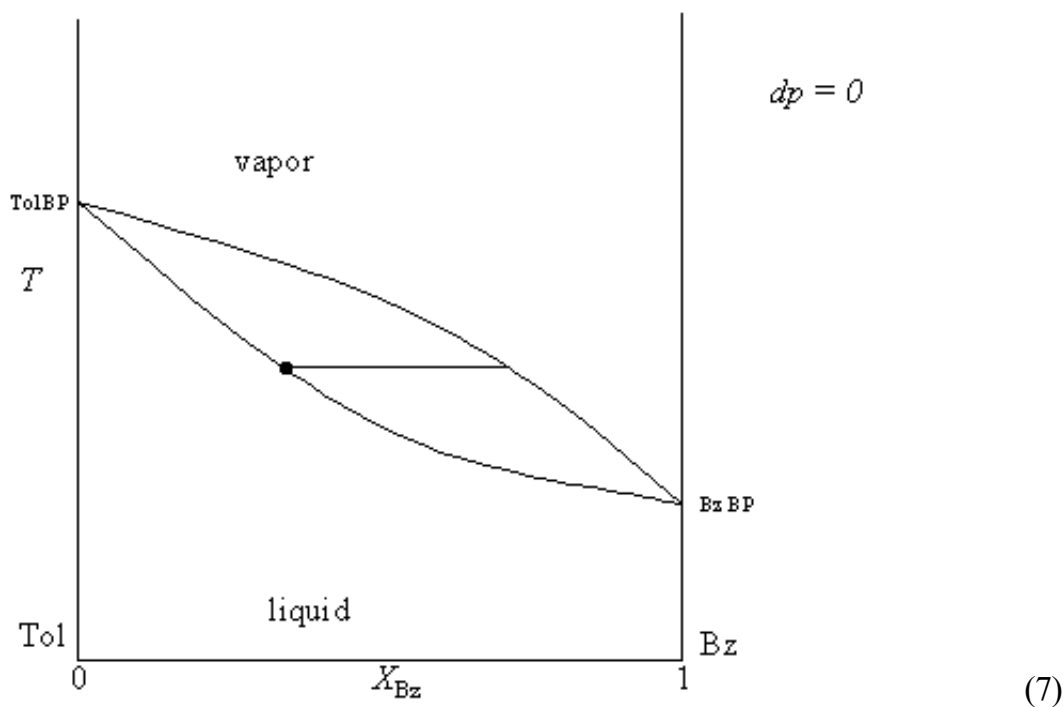


This diagram is called a "boiling diagram." Notice that at the edges we have points representing the boiling points of the pure components. The lower curve gives the boiling point of the liquid mixture as a function of composition.

Suppose we pick a point on the lower curve at, say, a mole fraction of benzene of about 0.33.



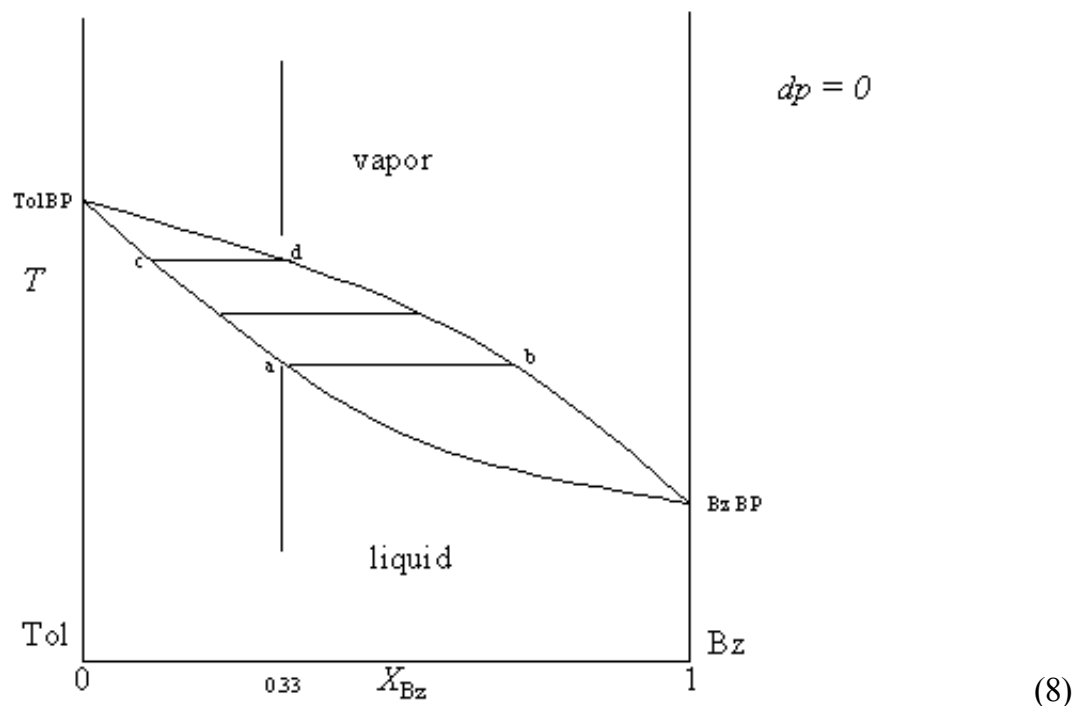
This point gives the boiling point of a mixture which is 0.33 mole percent benzene. We can ask, what is the composition of the vapor which is in equilibrium with the liquid at this temperature? Since we are asking a question about something at this temperature, the temperature of the point, clearly the vapor composition must lie on a horizontal (constant temperature) line going through this point. We know that at any given temperature and pressure the composition of the vapor must be richer in the more volatile component and benzene is the more volatile component. Thus we must draw our constant temperature line from the point proceeding to the right.



We call this line a **tie line** and it intersects the upper curve at the composition of the vapor in equilibrium with the liquid at the same temperature. The region between the two curves is a two-phase region. In this region two phases, liquid and gas, are in equilibrium with each other and we must be able to keep track of the compositions of both phases.

Above the upper curve the sample has fully evaporated and the system is entirely a gas. Below the lowest curve none of the sample has evaporated and the system is entirely a liquid. Between the two curved lines the system is composed of two phases in equilibrium and we must draw the tie line to keep track of the composition of both phases.

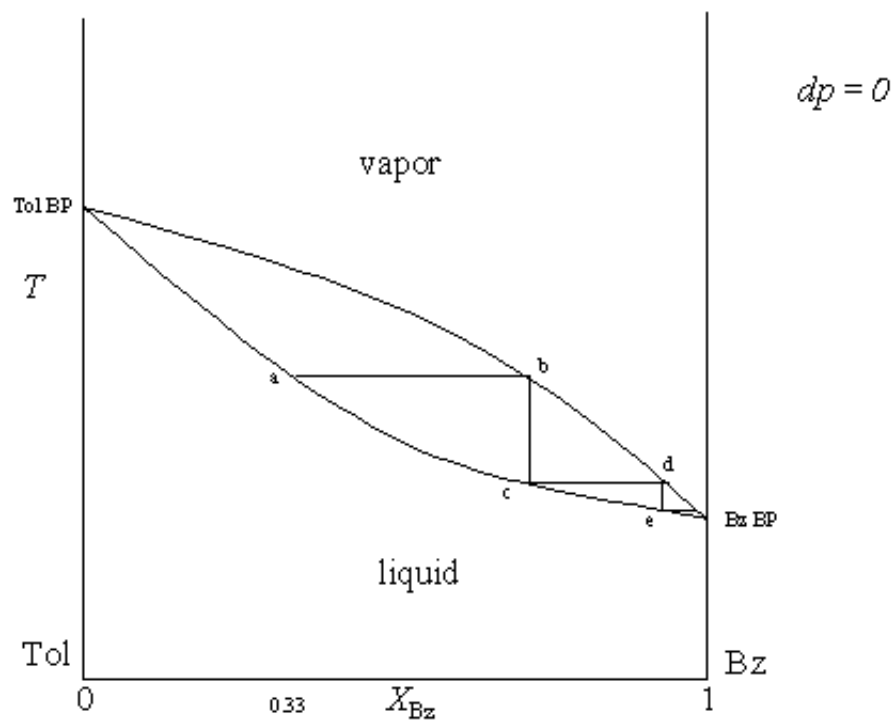
If we heat a liquid mixture at a composition of about 0.33 mole fraction benzene the liquid will have the composition shown at point "a" when the liquid first begins to boil.



The first vapor to come off will have the composition shown at point "b." As we continue to heat the system the more volatile component will evaporate preferentially and the liquid phase will become richer in the less volatile component (toluene, here). As we continue to heat the mixture the toluene will gradually catch up to the benzene in the vapor phase. The very last bit of liquid to evaporate will have the composition shown at point "c," and the vapor will have the original composition that we started with, "d" (or "a"). Notice that as we heat the system the tie line "tracks" with the lower and upper curves to give the composition of liquid and vapor in equilibrium.

Fractional distillation

Boiling diagrams provide an explanation for fractional distillation. Suppose we start with a liquid mixture with 0.33 mole fraction benzene.

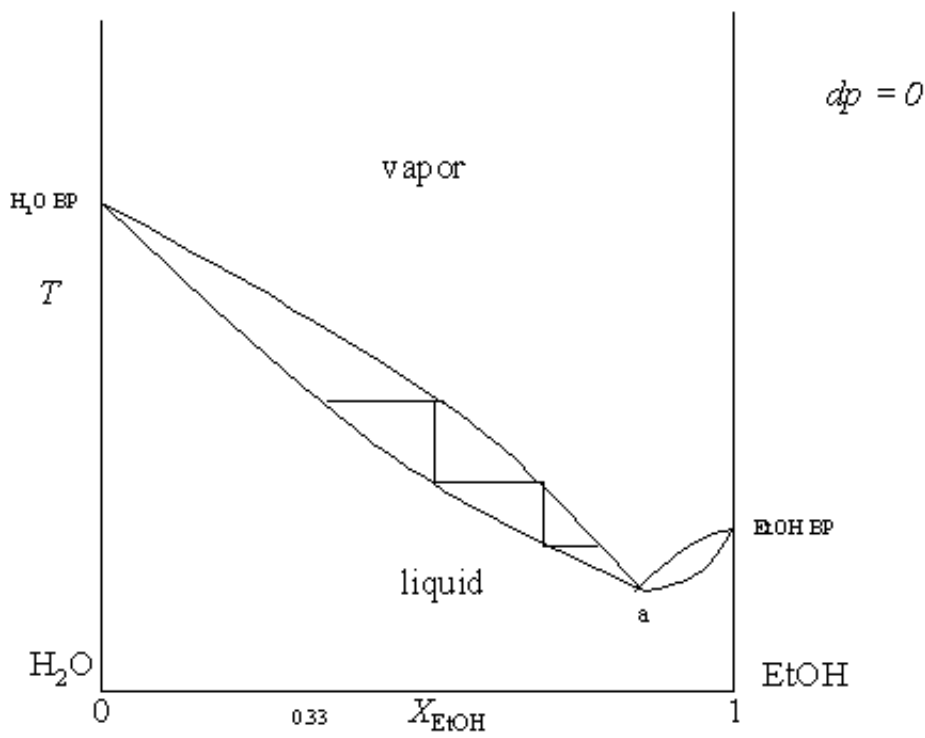


As we heat the liquid it will begin to boil when the temperature reaches the temperature of point "a." The first vapor to come off has the composition shown at point "b." Capture the vapor, condense it, and heat it up. The new liquid will boil at point "c" giving a vapor with composition at point "d." Capture this vapor, cool it, and boil it at point, "e," and so on. by continuing this process the vapor can be made as pure in benzene as desired.

This is what fractional distillation does. There are more modern ways to separate mixtures, for example, chromatography, but fractional distillation still has industrial and some laboratory importance.

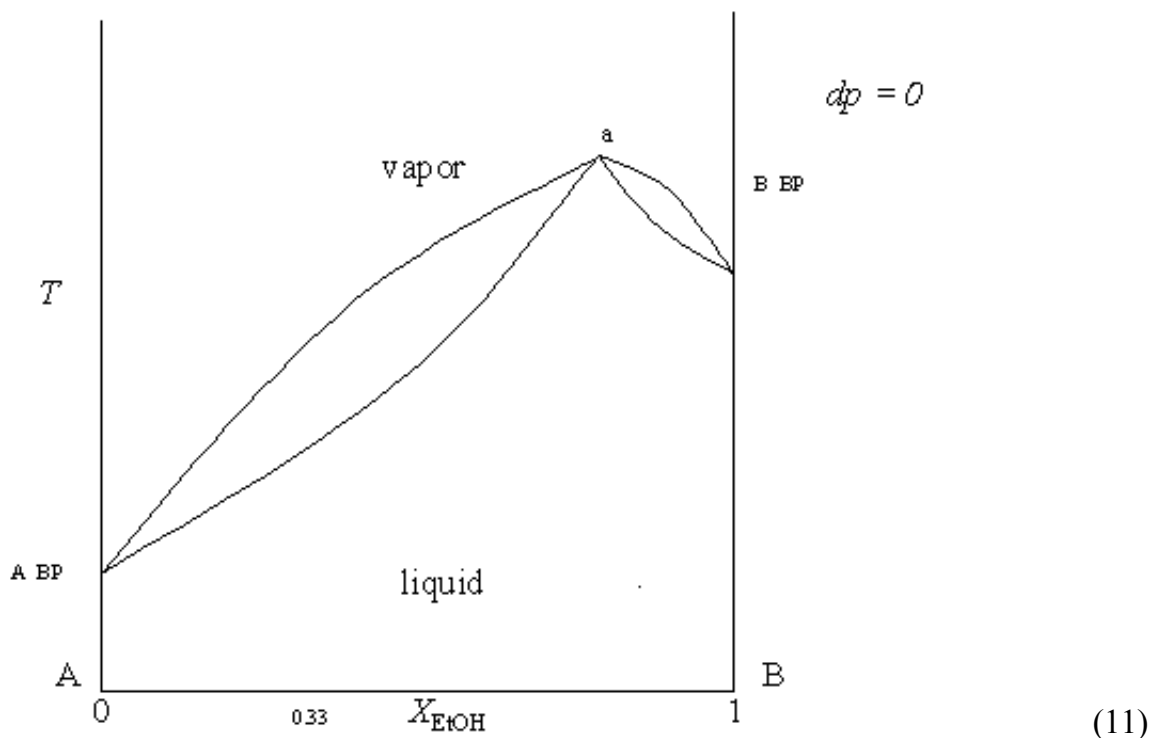
Boiling diagrams for nonideal solutions

We saw above that a solution with positive deviations from Raoult's law has a higher vapor pressure than would be given by Raoult's law. That means that the solution would boil at a lower temperature than would be expected from Raoult's law. A boiling diagram for such a substance might look like the following:



Point "a" denotes a constant boiling mixture called an "azeotrope." In this case it is a "low boiling azeotrope." We have drawn in some "zig-zag" lines to show why fractional distillation will not give complete separation of the mixture into its components.

In a mixture with negative deviations from Raoult's law the vapor pressure is lower than would be expected from Raoult's law which will produce boiling points higher than expected and a high boiling azeotrope.



On Figure 11 the point "a" indicates the high boiling azeotrope.

It turns out that the composition of the azeotrope is a function of the pressure. One can obtain a solution with very accurately known composition by letting it boil until the high boiling azeotrope is reached. For example, there are tables in the literature that give the composition of the high boiling HCl-H₂O azeotrope as a function of pressure. By measuring the local atmospheric pressure and going to the table you can obtain the composition of the high boiling azeotrope to an accuracy sufficient for acid-base analytical work.

For example, consider the following data from Harris, *Quantitative Chemical Analysis*, 6th Ed, Freeman, 2003.
:

P(Torr)	gHCl/100g solution
770	20.196
760	20.220
750	20.244
740	20.268
730	20.292

See also, Foulk and Hollingsworth, *J. Am. Chem. Soc.*, **45**, 1223 (1923).

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