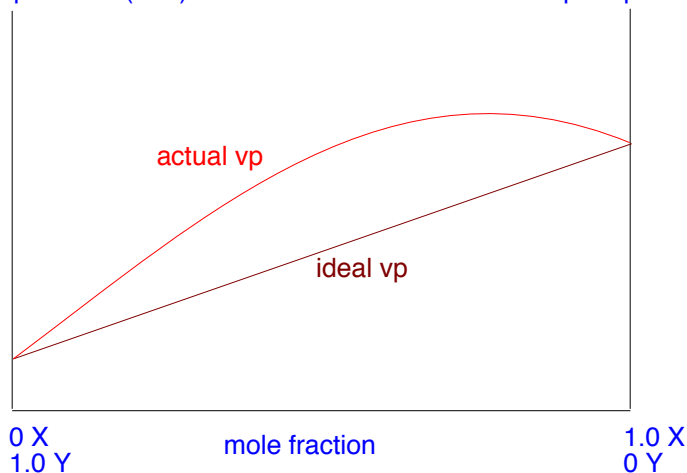


Chemguide – answers

NON-IDEAL MIXTURES OF LIQUIDS

1. a) vapour pressure (kPa) vapour pressure (kPa)

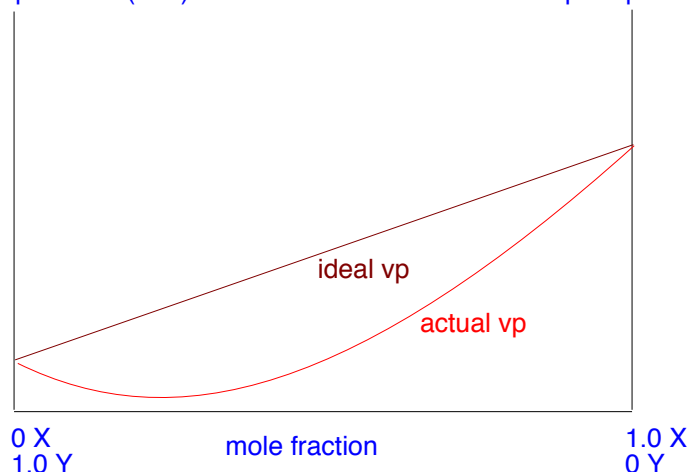


You don't actually need to include the ideal vapour pressure line. It doesn't matter where you draw the maximum point of the actual vapour pressure curve - but it should have a maximum higher than the vapour pressure of X. If you drew this curve with a minimum rather than a maximum, remember that a **positive** deviation from Raoult's law means that the **vapour pressure** of a mixture is always **higher** than ideal.

b) A positive deviation means that the vapour pressure is higher than ideal. That means that the particles in the mixture are escaping more easily into the vapour than they would do in the ideal case. That means that the forces of attraction between the particles in the mixture must be weaker than they are in the individual liquids.

c) Look at the enthalpy change of mixing. Heat is needed to break the attractions between the molecules of X and the molecules of Y; heat is given out when new attractions are made between X and Y. If the new attractions are weaker, less heat will be given out when the new attractions are made than was used to break the original ones. That means that the mixing will be endothermic, and the temperature will decrease when you mix X and Y together.

- d) vapour pressure (kPa) vapour pressure (kPa)

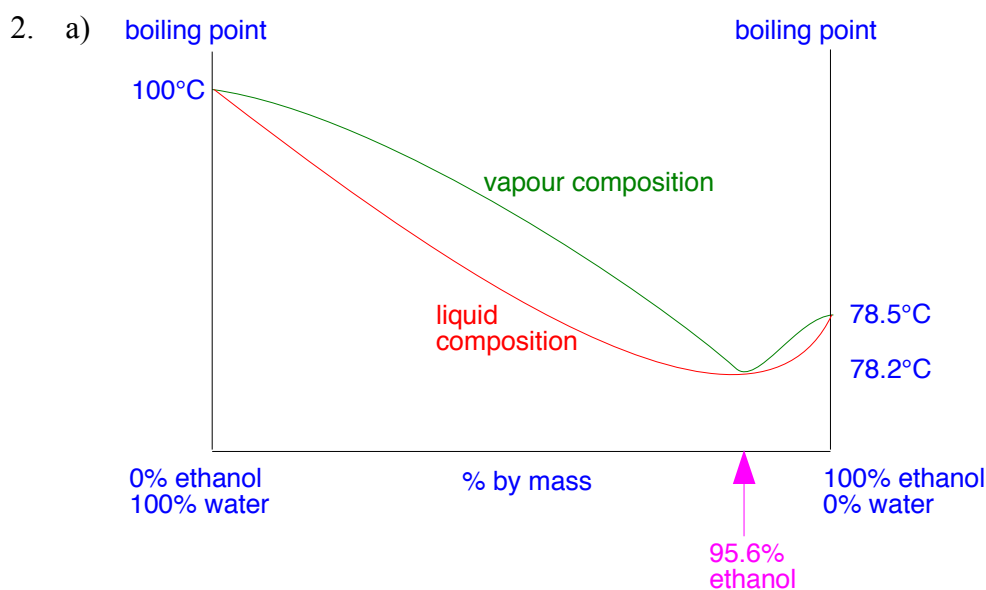


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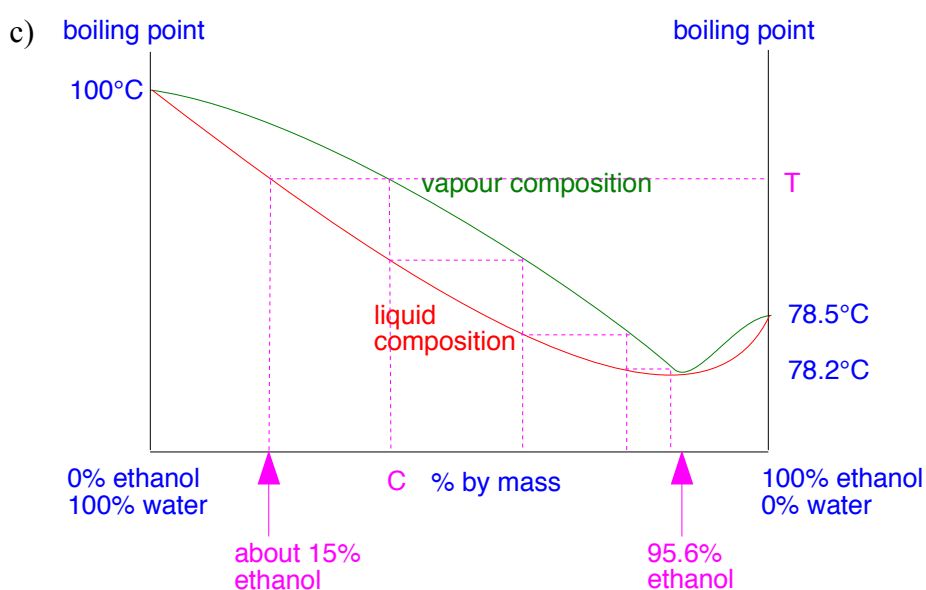
Again, you don't need to include the ideal vapour pressure line, and it doesn't matter where you put the minimum of the actual vapour pressure curve, as long as there is a minimum.

e) A negative deviation means that the vapour pressure is lower than ideal. That means that the particles in the mixture are escaping less easily into the vapour than they would do in the ideal case. That means that the forces of attraction between the particles in the mixture must be stronger than they are in the individual liquids.

f) In this case there would be heat evolved on mixing. The heat evolved when the new stronger attractions are set up will be greater than the heat needed to break the old ones. There will be a temperature increase on mixing.



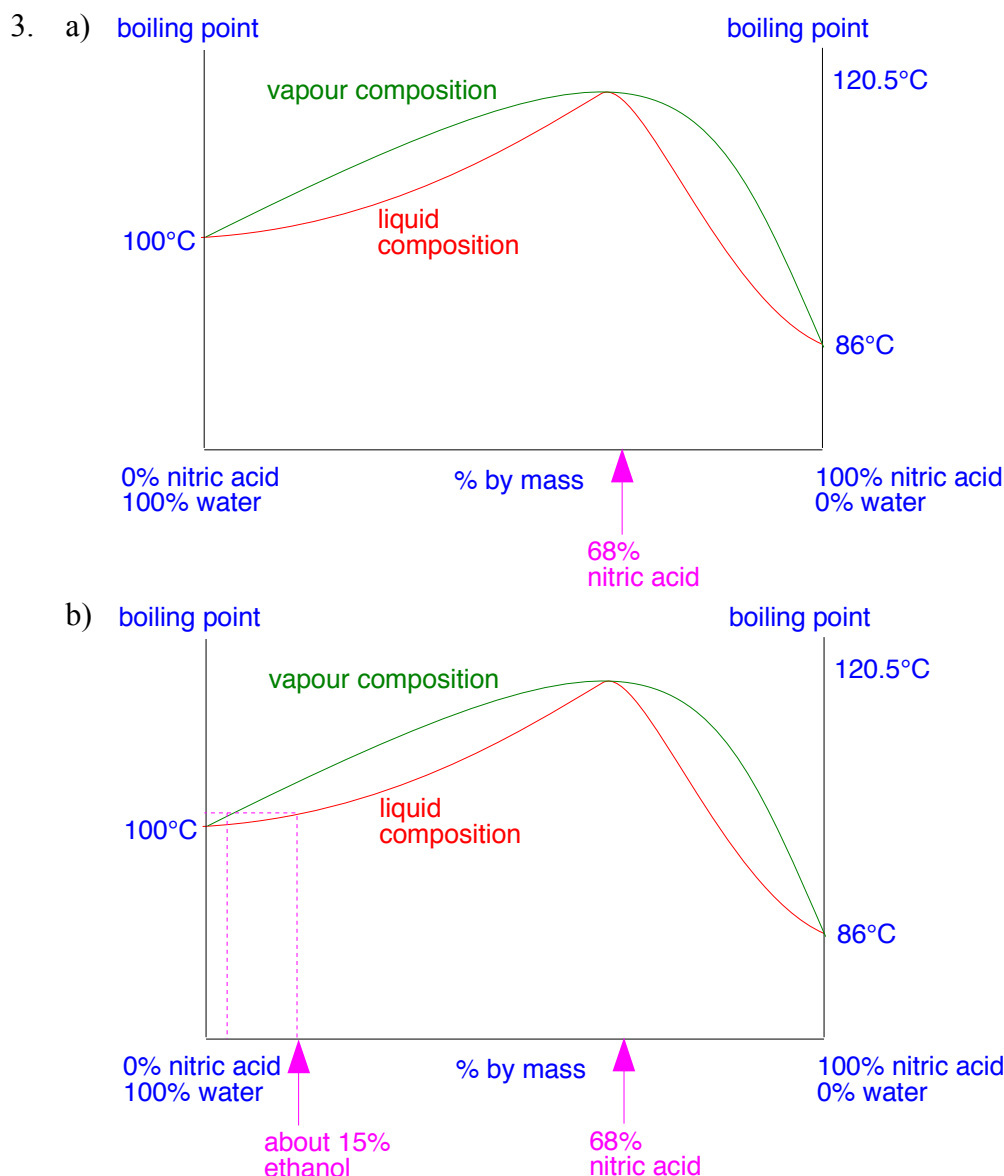
b) An azeotropic mixture is one which has a constant boiling point, and where the vapour over the top of the liquid has exactly the same composition as the liquid itself. If you boil such a mixture, it will simply boil away with no change in boiling point, just as if it was a single pure substance.



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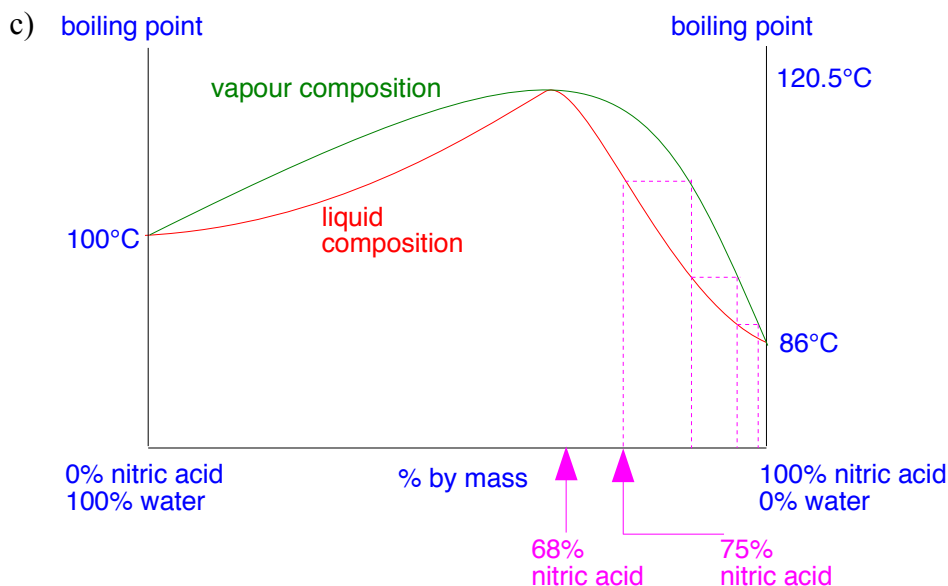
The mixture would first boil at a temperature of T_1 , giving a vapour richer in ethanol. This would condense to give a liquid of composition C. As this is constantly reboiled and recondensed, the composition of the condensing liquid will move closer and closer to the azeotropic mixture.

When it reaches the azeotropic composition, there will be no further change in the composition of the vapour. That means that the most concentrated ethanol that you could obtain from the top of the fractionating column would be 95.6%. However, eventually the liquid left in the flask would be 100% water.



If you boil a mixture containing 15% nitric acid, it will produce a vapour richer in water. Condensing and reboiling this will soon lead to pure water at the top of the fractionating column. As the liquid loses water, it will gradually become more concentrated until it reaches the azeotropic mixture, at which point there will be no further changes in its composition. The flask will eventually contain the azeotropic mixture.

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This time, on boiling, the vapour is richer in nitric acid. If you condense this, and boil it again, the vapour will be even richer in nitric acid. That means that by carefully controlling the temperature, you will be able to get pure nitric acid out of the top of the fractionating column.

Meanwhile, because the liquid in the flask is gradually losing nitric acid, its concentration will drift back to the azeotropic mixture, at which point there will be no further changes. The flask will again contain the azeotropic mixture.

(If you think about this, whatever mixture of nitric acid and water you boil, you will always end up with a liquid in the boiling flask with the azeotropic composition. Note also that once you have got the azeotropic mixture in the flask, the output from the top of the column will also now contain the azeotropic mixture if you allow the temperature at the top to increase to 120.5°C. Once you have got the azeotropic mixture, it behaves just like a pure single liquid as far as boiling is concerned.)