An azeotrope is a mixture that exhibits the same concentration in the vapor phase and the liquid phase. This is in contrast to ideal solutions with one component typically more volatile than the other; this is how we use distillation to separate materials. If the mixture forms an azeotrope, the vapor and the liquid concentrations are the same, which preventing separation via this approach.

**Introduction**

Azeotropes are a mixture of at least two different liquids. Their mixture can either have a higher boiling point than either of the components or they can have a lower boiling point. Azeotropes occur when fraction of the liquids cannot be altered by distillation. Typically when dealing with mixtures, components can be extracted out of solutions by means of Fractional Distillation, or essentially repeated distillation in stages (hence the idea of "fractional"). The more volatile component tends to vaporize and is collected separately while the least volatile component remains in the distillation container and ultimately, the result is two pure, separate solutions.

**Ideal Solutions vs. Azeotropes**

Ideal solutions are uniform mixtures of components that have physical properties connected to their pure components. These solutions are supported by Raoult’s law stating that interactions between molecules of solute and molecules of solvent are the same as those molecules each are by themselves. An example of ideal solutions would be benzene and toluene. Azeotropes fail to conform to this idea because, when boiling, the component ratio of unvaporized solution is equal to that of the vaporized solution. So an azeotrope can be defined as a solution whose vapor has the same composition its liquid. As you can imagine, it is extremely difficult to distil this type of substance. In fact, the most concentrated form of ethanol, an azeotrope, is around 95.6% ethanol by weight because pure ethanol is basically nonexistent.

Azeotropes exist in solution at a boiling point specific for that component. This is best represented graphically and the phase diagram of a maximum-boiling point azeotrope can be seen in the following figure. The point Z represents where the azeotrope exists at a certain boiling point. Imagine that at point Z, the A-B solution is 64% B by mass while component A is water. If that same solution contained any less than 64%, the solution would then be water + the azeotrope. Conversely, if it were to be greater than 64% then the solution would be component B + the azeotrope. This demonstrates that an azeotrope can only exist at one temperature because any higher or lower temperature would result in a different concentration of component A or B.

Also, a maximum-boiling point azeotrope is said to be a negative azeotrope because the boiling point of the azeotrope itself is higher than the boiling point of its components. As you can imagine, a positive azeotrope would have a lower boiling point than any of its components.

**Example 1**

If pure ethanol has a boiling point of 78.3 °C and its azeotrope has a boiling point of 78.174 °C, what would its graph look like?

**Solution**
Since the azeotrope BP $<$ pure ethanol BP, the azeotrope is a positive azeotrope and would have a graph that looks like the above figure upside-down (U shaped).

References


Contributors and Attributions

- Megan Doyle