

Winter 3-10-2022

The phase diagram of a non-ideal mixture's $p - v - x$ 2-component gas=liquid representation, including azeotropes

Carl W. David
University of Connecticut, Carl.David@uconn.edu

Follow this and additional works at: https://opencommons.uconn.edu/chem_educ

 Part of the [Physical Chemistry Commons](#)

Recommended Citation

David, Carl W., "The phase diagram of a non-ideal mixture's $p - v - x$ 2-component gas=liquid representation, including azeotropes" (2022). *Chemistry Education Materials*. 107.
https://opencommons.uconn.edu/chem_educ/107

The phase diagram of a non-ideal mixture's $p - v - x$ 2-component gas \rightleftharpoons liquid representation, including azeotropes

Carl W. David*

*Department of Chemistry,
University of Connecticut,
Storrs, Connecticut 06269-3060*

E-mail: Carl.David@uconn.edu

Abstract

The liquid \rightleftharpoons vapor two phase $p-v-x$ diagram is constructed for non-ideal solutions including azeotropes.

Introduction

$p-x$ and $T-x$ two component phase diagrams are a standard part of the Physical Chemistry curriculum. These diagrams serve as an introduction to poly-component systems, distillation, and chromatography.

Their construction is usually presented using words alone along with some hand-waving. The $p - v - x$ diagram is never shown, and perhaps has not been considered to be useful. An alternate method has been shown (https://opencommons.uconn.edu/chem_educ/106).¹

One needs 5 dimensions to describe binary mixtures, p, V, T, n_A and n_B where the pressure, volume and temperature are familiar from simple pure gases, and n_A and n_B are the

number of moles of substances A and B respectively. Introducing the mole fraction of, say, A , i.e., x_A , and forcing the total number of moles to 1, we reduce the number of variables to 4 (p, V, T, x_A). To reduce the number of variables one more time, we agree to continue the discussion at fixed temperature.

With 3 variables, one can plot in pseudo 3 dimensions on a 2 dimensional surface, which is our intent here.

We present such a diagram for a solution which follows Raoult's law and whose vapor obeys Dalton's law. Then, we present an extreme variation from ideality, a diagram illustrating azeotrope formation.

Practical Considerations

Raoult's law is

$$p_{total} = x_A p_A^o + (1 - x_A) p_B^o$$

and Dalton's law, in this context would be

$$y_A = \frac{x_A p_A^o}{x_A p_A^o + (1 - x_A) p_B^o}$$

Combining these two to treat *an ideal* solution is oxymoronic.

The surface depicted between the Raoult's law representation of the total pressure, and the resultant Dalton's law representation of the mole fraction in the vapor (y_A), is a ruled surface constituting tie lines between a chosen liquid composition and the resultant vapor composition at that same pressure (see Figure 1).

It is never stated explicitly that if during expansion (or compression) one chooses *not* to separate the two phases, then at the end of the evaporation (condensation) process, the pressure will be lower (higher) but the composition will be the same, constant, overall value (see Figure 3).

The projection of the ruled surface (see Figure 2) onto the $p - x$ plane yields the common phase diagram. The following code shows how this figure was constructed using SageMath/CoCalc:

```
x, y, pt,pt2, i= var('x,y,pt,pt2,i')
pa0,pb0 = var('pa0,pb0')
pa0 = 2
pb0 = 10
pt = pb0
def f(i): return (i/10)*pa0 + (1-i/10)*pb0
p = line([(0,1,pt),(1/10,1,f(1))])
for i in range(10):
#   print(i)
    pt = (i/10)*pa0 + (1-i/10)*pb0
    p = p + line([(i/10,1,f(i)),((i+1)/10,1,f(i+1))], rgbcolor=(1/4,1/4,3/4))
    x = (i/10)*pa0
    y = x/f(i)
    yy = (i+1)/10*pa0/f(i+1)
    p = p + line([(i/10,1,f(i)),(y,10,f(i))],rgbcolor=(3/4, 1/4, 1/8))
    p = p + line([(y,10,f(i)),(yy,10,f(i+1))],rgbcolor=(1/4,3/4,1/8))
```

As can be seen, picking an x_A value and finding the vapor pressure of that composition solution, allows one to construct a tie line to the other curve, and read out the composition of the vapor y_A that would be in equilibrium with that solution. Of course, a tiny bubble of gas would have this composition in equilibrium with an enormous amount of liquid of composition x_A .

Evaporation without composition changes

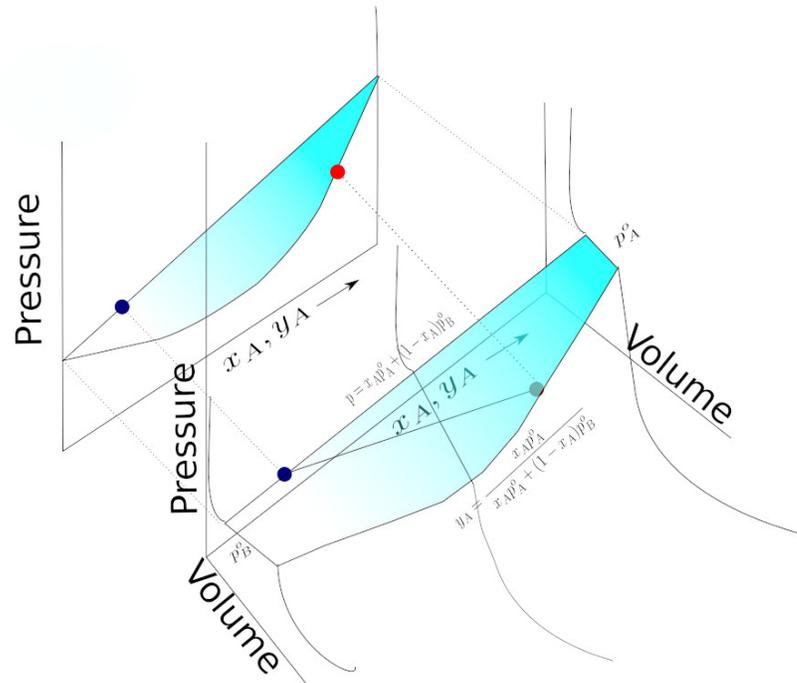
Figure 3 shows the effect of increasing the volume about a solution of the type discussed above, without separating phases (distillation). The dotted line indicates the actual isotherm, contrasting with the (horizontal) constant pressure path if the material under consideration were pure.

Azeotropic mixtures

There are two kinds of azeotropic mixtures in liquid phase, maximum and minimum boiling. The former manifests itself as a minimum vapor pressure azeotrope, while we illustrate here a maximum pressure azeotrope. The Raoult's law annotation is still shown, to illustrate the deviation from ideality. The center (long dashed) constant composition p-v isotherm is the azeotrope. It has a constant pressure two phase region, contrary to other composition isotherms.

Figures

Figure 1: The $p - v - x$ diagram for an ideal liquid (Raoult) and an ideal gas (Dalton) mixtures



References

- (1) David, C. The van der Waals mixture construct of a p-x two-component gas=liquid phase diagram. https://opencommons.uconn.edu/chem_educ/106.

Figure 2: The two phase region as drawn by Sagemath/CoCalc. The red lines are tie lines joining the straight line (Raoult locus, blue) and the curved (Dalton, green) loci.

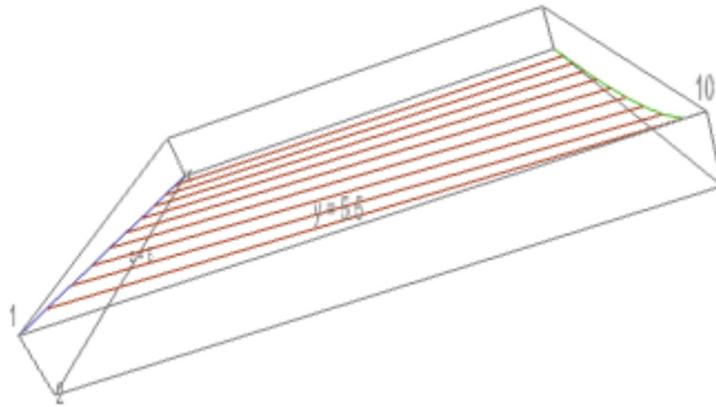


Figure 3: The evaporation/condensation path at constant (fixed) composition without phase separation.

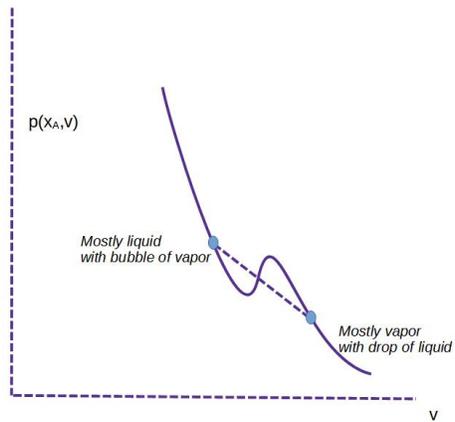


Figure 4: The construction of the $p - v - x_A$ two component phase diagram of an azeotropic mixture.

