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The van der Waals mixture construct of a $p - x$ 2-component gas $\rightleftharpoons$ liquid phase diagram

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Abstract

The van der Waals model, when applied to a mixture, is used to construct tie-line points on a liquid $\rightleftharpoons$ vapor two phase $p - x$ diagram.

Introduction

p-x and T-x two component phase diagrams are a standard part of the Physical Chemistry curriculum. The 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 van der Waals fluid model, the first (and perhaps only) model for fluids introduced after the ideal gas model, is widely taught in physical chemistry classes (a modern introduction can be found on the web[1]). It is the first model which introduces phase changes, liquid versus gas concepts, critical constants, the existence of a critical point, and the law of corresponding states. Unfortunately, the model when applied to mixtures loses its simplicity, and becomes intractable and therefore unavailable to most chemists.

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. 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 (last) 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 seek a graphical expression of the results for a van der Waals mixture when two phases are present.

Practical Considerations

The van der Waals equation for a pure substance is given by the equation:

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

which allows us to write a reduced variable form of the equation whose analysis proceeds cleanly no matter what the value of the van der Waals constants happen to be:

$$\left(p_r + \frac{3}{v_r^2}\right)(3v_r - 1) = 8T_r$$

But when we generalize to mixtures, all this generality is lost.

Mixture Specificity

In treating a mixture of two substances, A and B, we create pseudo van der Waals “constants” $a(x_A)$ and $b(x_A)$ so that the van der Waals equation becomes

$$\left(p+\frac{n^2a\left(x_A\right)}{V}\right)\left(V-nb\left(x_A\right)\right)=nRT$$

(for an overview of van der Waals mixtures, see Senger's[2] review). Specifying the new functions $a(x_A)$ and $b(x_A)$ becomes an exercise in model building. In virtually every case, tractability is lost no matter what the choice for either of these two functions is made. An example might be:

$$a\left(x_A\right) \;=\; x_A\; a_{AA} \;+\; x_A x_B a_{AB} \;+\; x_B a_{BB}$$

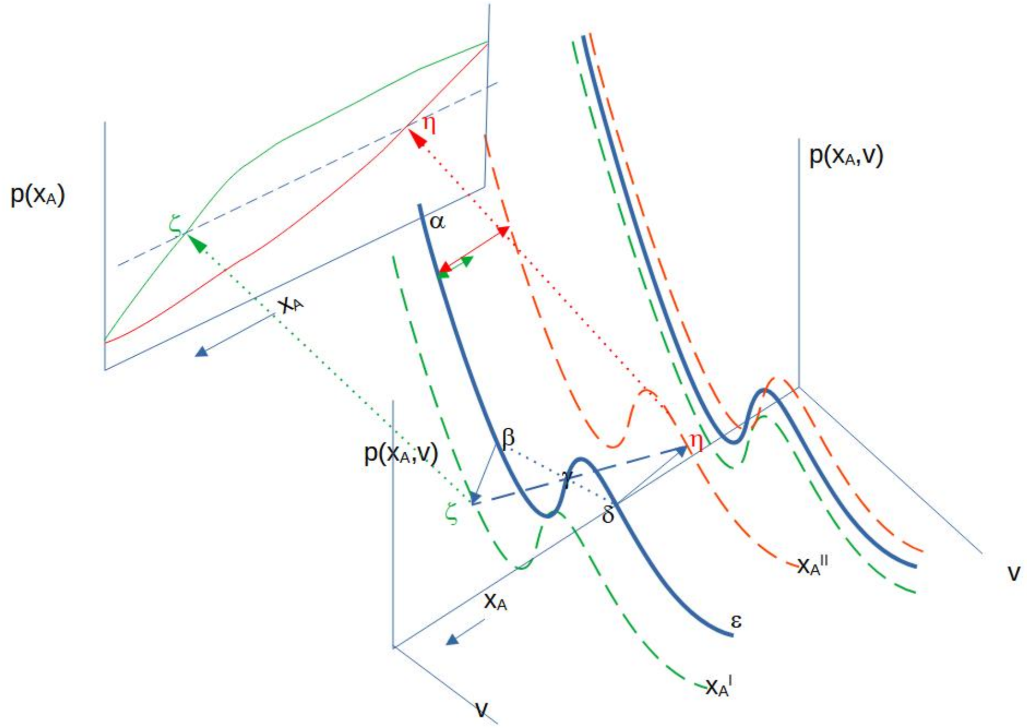
with a similar expression for $b(x_A)$. One should know that a fully quadratic in mole fraction expression seems more popular in the literature, i.e.,

$$a\left(x_A\right) \;=\; x_A^2\; a_{AA} \;+\; x_A x_B a_{AB} \;+\; x_B^2 a_{BB}$$

Treating a mixture as if it were pure

Graphically, one can understand the behavior of the system without explicitly solving the underlying equations, hence this communication. Consider Figure 1, in which the solid blue curve represents the van der Waals curve of a mixture (treated as pure) with $a(x_A)$ and $b(x_A)$ values fixed as determined by x_A. Again, assuming this curve represents a pure compound, the points β and δ represent *liquid* $\rightleftharpoons$ *vapor* equilibrium (as determined by a pseudo-Maxwell construction). Since this is not a pure substance, point γ bifurcates into two points, ζ and η, one intersecting with the (I) curve, the other with the (II) curve.

Figure 1: The construction of the $p - x_A$ two component phase diagram from the van der Waals isoconcentration/isotherm (blue) and two others (green and red) whose positions on the x_A axis are determined by the relevant chemical potentials.



The construct

A van der Waals constant composition isotherm (blue) with two others from which the liquid and vapor data translate to a $p-x$ diagram composition where a mixture of fixed composition x_A of substances A and B at a high pressure, shown as point α as a liquid, is allowed to have its pressure reduced following a path shown for the central (blue) van der Walls curve. Since x_A is fixed, we can treat this mixture as if it wasn't a mixture and so when the pressure is reduced to one in which two phases are classically possible, we get the separation shown as points β and δ. If this pseudo liquid and vapor were pure, these two phases would be in equilibrium. Since these two phases are not pure, but a mixture of identical composition, it is possible that A will transfer from one to the other phase, while B does the same thing, attempting to bring their chemical potentials, μ_A and μ_B, in the two phases, equal to each other, i.e.,

$$\mu_A^I = \mu_A^{II}$$

. This results in two points, ζ and η. Each lie on different van der Waals isotherms corresponding to different compositions (x_A^I and x_A^{II}), hence the double headed arrows indicating that their positions on the x_A axis are not fixed. Symbolically,

$$\beta \rightarrow \zeta$$

and

$$\delta \rightarrow \eta$$

These points, when translated backward (in the diagram) to a $p-x_A$ diagram, provide points at the end of a tie-line connecting the liquid curve to the vapor curve, as shown in every physical chemistry textbook.

Epilogue

There is another way of bifurcating from γ to ζ and η, with ζ on the II curve and η on the I curve. Which mode is chosen depends on the vapor pressures of the pure components at the fixed temperature being considered, as well as on the relevant chemical potentials.

Secondarily, one notes that the van der Waals gas need not be employed in this discussion if one uses discontinuous isotherms including a segment for the gaseous mixture and another segment for the liquid mixture, perhaps connected with a ”straight” or ”dotted” connector, along which bifurcation points are addressed.

Finally, we remember the difference between one and two component isotherms; the two component $p - v$ isotherm is not ”horizontal” when two phases are present. Figure 2 shows the isotherm.

Acknowledgements

An earlier version of this manuscript was rejected by the editor of J. Chem. Ed. for no reason that made sense to me. Another version was accepted by The Chemical Educator, but has not yet appeared (and may not ever appear during this COVID crisis), and resides behind a pay wall. Until it appears, it can be found at.[3]

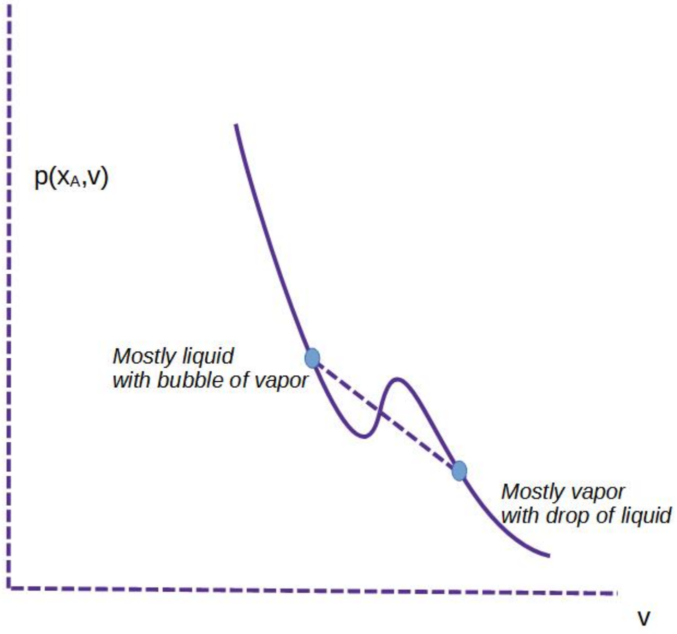
Since knowledge should be free, I am publishing this version on the University of Connecticut web site. It differs slightly from the earlier version.

References

(1) Suzuki, M. S.; Suzuki, I. `http://bingweb.binghamton.edu/~suzuki/GeneralPhysNote_PDF/TOP08.pdf`, accessed january, 2021.

(2) Sengers, J. L. `https://www.dwc.knaw.nl/wp-content/HSSN/2002-4-Sengers-How%20fluids%20unmix.pdf`, accessed january, 2021.

Figure 2: The $p - v$ isotherm for the two component mixture, following the dotted (slanted) path rather than the full path when two phases are present.



(3) David, C. The van der Waals mixture construct of a p-x 2-component gas - liquid phase diagram. `https://www.dropbox.com/s/g8n7zse3h665i1w/van%20der%20waals%20chem%20educator%20%20Galley%20Proof.pdf?dl=0`.