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Some comments on the double retrograde vaporization

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Abstract

The double retrograde vaporization in binary fluid mixtures under high pressure is studied by means of the Gibbs–Konowalow equations. It is shown that the phenomenon is related to the behavior of two functions, the slope of tie lines in a volume–mole fraction diagram and the composition derivative of the vapor volume, which in turn depends on the partial molar volume of the solute. Due to mathematical constraints these curves can intersect more than once, thus creating double retrograde behavior.

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1. Introduction

Recently Raeissi and Peters [1] called attention to a peculiar phenomenon occurring in high-pressure (vapor + liquid) phase equilibria – the so-called *double retrograde vaporization*: Upon compressing, a gas containing trace amounts of a low-volatile compound undergoes more than one condensation/vaporization transition until the liquid or compressed fluid state is reached. Up to four dew points have been reported for one composition. The phenomenon is caused by a sigmoid shape of the dew point curve in the vicinity of the critical point of the more volatile component.

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Experimental evidence of this phenomenon has been obtained by Peters and Raessi as well as several other authors; for an overview of the experimental work on this subject see [1]. In this publication [1] the authors model the phenomenon for two experimental systems (ethane + limonene) and (ethane + linalool) by means of a simple cubic equation of state with standard mixing rules and they conjecture that double retrograde vaporization should be a rather common phenomenon in fluid mixtures.

In this short contribution the phenomenon is investigated by means of classical thermodynamics, without any reference to a specific model.

2. Theory

A convenient starting point for this investigation is the Gibbs–Konowalow equations, which can be regarded as generalizations of the Clapeyron equation for mixtures. The Gibbs–Konowalow equation for an isothermal phase equilibrium curve of a two-component mixture is

$$\left(\frac{\partial p}{\partial x_1'}\right)_{T,\text{eq}} = -\frac{x_1'' - x_1'}{x_2''(x_1'(V_1' - V_1'') + x_2'(V_2' - V_2''))} \left(\frac{\partial \mu_1''}{\partial x_1''}\right)_{T,p}. \quad (1)$$

Here x_i denotes the mole fraction, V_i the partial molar volume, and μ_i the chemical potential of component i . The assignments of the phases and components are arbitrary, but here it is assumed that the subscript “1” indicates the volatile compound, “2” the low-volatile solute, a single prime the liquid and a double prime the vapor phase. The pressure derivative is taken at constant temperature along the phase envelope, here the dew point curve. Equation (1) is a differential equation for the dew point curve and can be used for the numerical calculation of phase diagrams. Here it will be used to determine some geometric properties of the dew point curve.

The double retrograde vaporization phenomenon requires a “wriggling” of the dew point curve. Hence, it is necessary to look for mole fraction extrema of this curve, *i.e.*, points at which the condition $(\partial x_1''/\partial p) = 0$ holds or at which equation (1) diverges.

The derivative of the chemical potential in this equation can be simplified as follows:

$$\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,p} = \frac{\partial}{\partial x_1} \left\{ G_m + x_2 \left(\frac{\partial G_m}{\partial x_1}\right)_{T,p} \right\} = x_2 \left(\frac{\partial^2 G_m}{\partial x_1^2}\right)_{T,p} = x_2 G_{2x}. \quad (2)$$

Here we have used the common shorthand notation for thermodynamic derivatives:

$$G_{ipkx} = \left(\frac{\partial^{i+k} G_m}{\partial p^i \partial x_1^k}\right)_T. \quad (3)$$

By taking the inverse of equation (1), the condition for mole fraction extrema can be formulated as

$$\left(\frac{\partial x_1''}{\partial p}\right)_{T,\text{eq}} = -\frac{1}{G_{2x}} \frac{x_1'(V_1' - V_1'') + x_2'(V_2' - V_2'')}{x_1'' - x_1'} \stackrel{!}{=} 0. \quad (4)$$

With the help of the Euler relation

$$V_m = x_1 V_1 + x_2 V_2, \quad (5)$$

equation (4) can be rearranged into

$$\left(\frac{\partial x_1''}{\partial p} \right)_{T,\text{eq}} = -\frac{1}{G_{2x}} \left(V_x'' - \frac{V_m'' - V_m'}{x_1'' - x_1'} \right) \stackrel{!}{=} 0. \quad (6)$$

This form of the Gibbs–Konowalow equations has been proposed by Rowlinson and Swinton [2]. G_{2x} is always finite and positive for single-phase state; it vanishes only at (binary) critical points. Hence it cannot be responsible for a zero of equation (4). The difference of the mole fractions is positive, too, unless there is azeotropy. The criterion for extrema along the dew point curve can therefore be reformulated as

$$V_x'' = \frac{\Delta V_m}{\Delta x_1}, \quad (7)$$

with $\Delta V_m = V_m'' - V_m'$ and $\Delta x_1 = x_1'' - x_1'$. The right hand side of this equation describes the slope of tie lines in a (V_m, x_1) diagram and will be referred to as the *volume slope function*. The left hand side of this equation is the derivative of the vapor volume with respect to the mole fraction, and will be referred to as the *volume derivative function*.

As the double retrograde vaporization takes place in mixtures containing trace amounts of component 2 only, it is permissible to approximate V_1'' by V_m'' , the molar volume of the gas phase:

$$V_x'' \approx V_m'' - V_2''. \quad (8)$$

The difficult property is the partial molar volume of the solute. It can be obtained from

$$V_2 = -\left(\frac{\partial V}{\partial p} \right)_{T,n_2} \left(\frac{\partial p}{\partial n_2} \right)_{T,V}. \quad (9)$$

The first derivative on the right hand side of this equation is related to the compressibility and must always be negative; in the vicinity of a critical point this factor $\rightarrow -\infty$. The divergence of V_2'' at the critical point of component 1 is therefore governed by the pressure derivative. If the addition of the low-volatile component lowers the pressure, $(\partial p/\partial n_2) < 0$, it is called an attractive solute. This behavior is usually attributed to the formation of dense solvation shells of component 1 around the molecules of the solute 2. The partial molar volume of the solute, V_2'' , will diverge towards $-\infty$. If the addition of the low-volatile component raises the pressure, $(\partial p/\partial n_2) > 0$, it is called a repulsive solute. The partial molar volume of the solute, V_2'' , will diverge towards $+\infty$.

2.1. The subcritical case

For temperatures below the critical temperature of the volatile component, $T < T_{c,1}$, the dew point curve and the bubble point curve meet at the vapor pressure

points of the pure fluids. Here Δx_1 vanishes, whereas ΔV_m remains positive. Therefore the volume slope function diverges (see figure 1).

The relation of the parts of equation (7) is shown in figure 1. Usually, the volume derivative function is below the volume slope function and no intersections and therefore no extrema along the dew point curve occur. But if a solute is strongly attractive, the two curves can intersect in two points, thus generating a mole fraction maximum and a minimum. Therefore three dew points become possible at a given concentration.

The volume derivative function in figure 1 was calculated for a fixed composition. One might argue that it should rather be calculated along the dew point curve. In this case the volume derivative function would terminate at the vapor pressure of pure component 1 (at the pole). But this would not affect the geometric relations leading to double retrograde behavior.

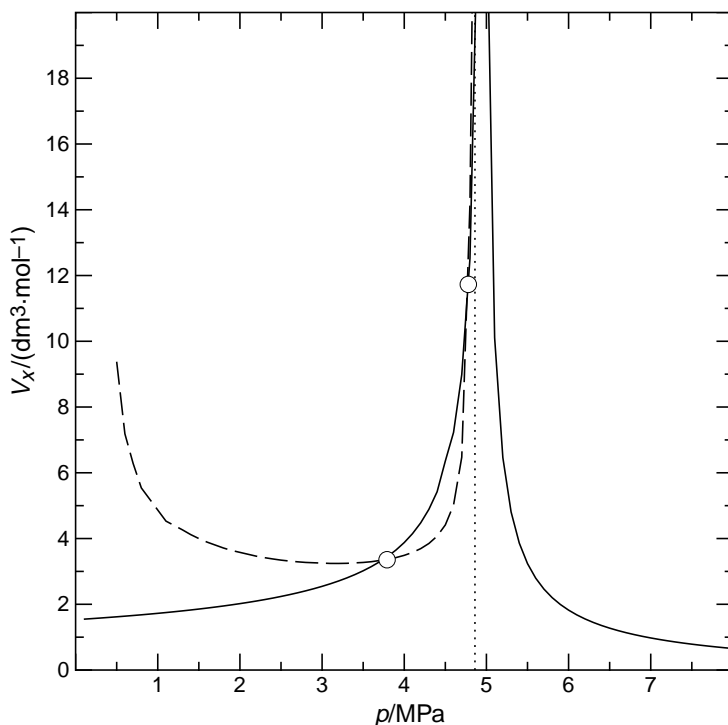


FIGURE 1. Comparison of the left and right hand side of equation (7), subcritical case. —, volume derivative function (V_x); ---, volume slope function ($(\Delta V_m/\Delta x_1)$); ···, pole marking the vapor pressure of the solute; ○, mole fraction extrema. The curves were calculated for (ethane + limonene) at $T = 305.2$ K from the Peng–Robinson equation of state, using the parameters of Raessi and Peters [1] and the thermoC program package [3].

2.2. The supercritical case

The dew point curve and the bubble point curve meet at a binary critical point when $\Delta x_1 \rightarrow 0$ and $\Delta V_m \rightarrow 0$. The ratio of these two can be determined from a series expansion of the molar Helmholtz energy at this point:

$$A_m = A_0^c + A_V^c \delta V + A_x^c \delta x + \frac{1}{2} A_{2V}^c (\delta V)^2 + A_{Vx}^c (\delta V)(\delta x) + \frac{1}{2} A_{2x}^c (\delta x)^2 + \dots \quad (10)$$

Here the A_{ik}^c denote derivatives of A_m taken at the binary critical point. Following a procedure described by Levelt Sengers [4], equation (10) is differentiated to obtain expressions for the pressure and the chemical potentials and these are inserted into the conditions for phase equilibrium

$$p' = p'' \text{ and} \\ \mu'_i = \mu''_i, \quad i = 1, 2. \quad (11)$$

By some lengthy algebra it can be shown that the phase envelopes are symmetrical in the vicinity of the critical point and

$$\delta V' = -\delta V'' \text{ and } \delta x' = -\delta x''. \quad (12)$$

Substituting equation (12) this into the pressure condition yields:

$$A_V^c + A_{Vx}^c \delta x + A_{2V}^c \delta V + \dots = A_V^c - A_{Vx}^c \delta x - A_{2V}^c \delta V + \dots \quad (13)$$

All even powers of δx and δV cancel in equation (13). With $\Delta V_m = \delta V'' - \delta V' = 2\delta V''$ and an analogous expression for Δx_1 , equation (13) leads to

$$A_{Vx}^c \Delta x_1 + A_{2V}^c \Delta V_m + O\left((\Delta x_1)^3, (\Delta V_m)^3\right) = 0, \quad (14)$$

and finally to

$$\lim_{\Delta x_1 \rightarrow 0} \frac{\Delta V_m}{\Delta x_1} = -\frac{A_{Vx}^c}{A_{2V}^c} = V_x. \quad (15)$$

From equation (15) two conclusions can be drawn: (1), The volume slope curve does not diverge, as in the subcritical case, but ends on the partial molar volume curve (see figure 2), and (2), because of the missing quadratic terms in equation (14), the volume slope curve ends with zero slope.

This explains the appearance of retrograde behavior: If the critical pressure of the mixture is above the critical pressure of the pure volatile component, the locus of the mixture critical point in figure 2 is on the declining (high-pressure) side of the peak of the partial molar volume curve. To reach its destination, the volume slope curve must cross the partial molar volume curve at least once and this gives rise to a mole fraction extremum on the dew point curve, and to (normal) retrograde behavior. Close to the pure fluid critical point the volume slope curve is rather steep, but then has to make a sharp bend in order to fulfill the zero slope condition at the binary critical point. If this bend collides with the partial molar volume curve, this creates two additional extrema along the dew point curve and the double retrograde behavior.

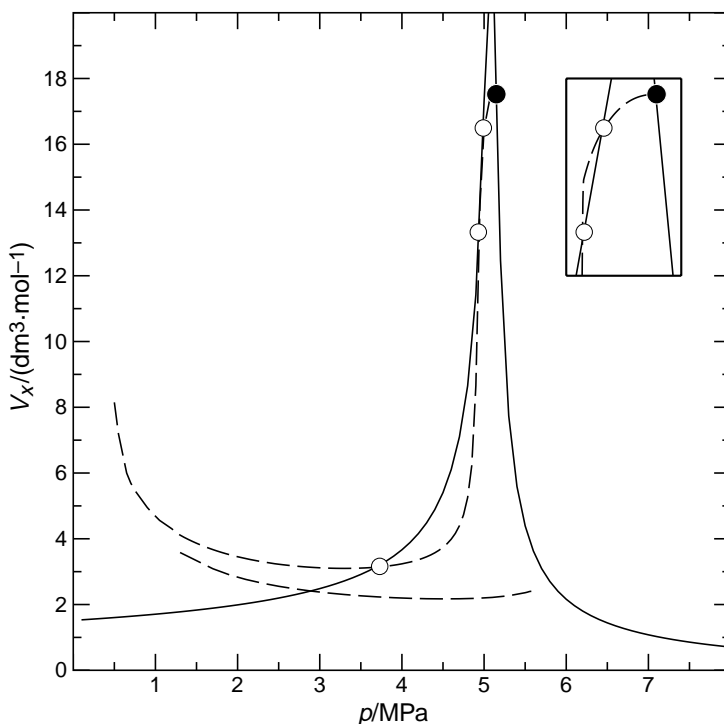


FIGURE 2. Comparison of the left and right hand side of equation (7), supercritical case. —, volume derivative function (V_x); ---, volume slope function ($(\Delta V_m/\Delta x_1)$); \cdots , pole marking the vapor pressure of the solute; O, mole fraction extrema; ●, binary critical point. The insert shows an enlargement of its vicinity. The curves were calculated for (ethane + limonene) at $T = 307$ K, except for the lower dashed curve, which corresponds to $T = 320$ K and illustrates the behavior of volume slope curves at higher temperatures.

3. Conclusions

Multiple retrograde vaporization can be explained by the intersection of two curves whose general shape is more or less fixed: the volume slope curve, which represents the volume and composition differences between the coexisting phases as a function of pressure, and the partial molar volume curve, which represents the difference of the molar volume of the vapor phase and the partial molar volume of the solute. Normally these curves do not intersect (subcritical case) or have only one intersection (supercritical case).

The bend of the volume slope curve that is responsible for additional intersections in the supercritical state can only appear in the vicinity of the pure fluid critical point. Likewise, the diverging volume slope curve in the subcritical case can only intersect with the partial molar volume curve, if the latter is already rather large, *i.e.*, close to the critical point. In both cases the behavior of the curves is governed by their limiting behavior and not by special features of the underlying model or equation of state.

Therefore, any reasonably accurate equation of state should be able to model double retrograde behavior. Furthermore, it seems rather unlikely that more than one additional pair of extrema along the dew point curve will ever be observed.

In the argumentations above mostly attractive solutes have been considered. Strongly repulsive solutes will make the partial molar volume curve run towards a negative peak, but they will also cause azeotropic behavior, so that the sign of the volume slope curve is changed, too, and the geometric relations between the curves are analogous to the normal case.

Although the Gibbs–Konowalow equations are powerful tools for the construction of phase diagrams, most modern textbooks in physical chemistry or chemical engineering do not mention them any more. The author is very grateful to G. M. Schneider (University of Bochum, Germany) for calling his attention to these (and many other) treasures of thermodynamics. He furthermore thanks C. J. Peters (TU Delft, The Netherlands) for making available preprints on the topic of double retrograde vaporization.

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