On Integration of the Coexistence Equation for Binary Vapor-Liquid Equilibrium

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Numerical integration of the coexistence equation for isothermal *P-x* data can be carried out by standard techniques. Two questions are considered with respect to this procedure: (a) Do continuous, analytic *P-x* relations exist which fail to provide thermodynamically acceptable results? (b) Does it matter from what point one starts the numerical integration? It is the purpose of this paper to demonstrate in each case that the answer is affirmative.

Vapor compositions for binary vapor-liquid equilibria may be computed by several methods from vapor pressures measured as a function of liquid composition at fixed temperature. The direct method for carrying out these calculations by solution of the coexistence equation is described in detail by Van Ness (*2*). No attention will be given here to $T - x$ data at fixed pressure.

The coexistence equation is based on the Gibbs-Duhem equation, and in its general form is completely rigorous. It is not necessary here to use this general form, for the equation applicable at low pressures adequately illustrates the points to be made. This equation results from the Gibbs-Duhem equation when one assumes that the vapor phase is an ideal gas and that the properties of the liquid phase are independent of pressure:

$$\frac{dP}{dy_1} = \frac{P(y_1 - x_1)}{y_1(1 - y_1)} \tag{1}$$

For a given set of $P - x_1$ data the objective is to determine the $P - y_1$ (or $x_1 - y_1$) relation which satisfies this equation. Since no general analytical solution is possible, Equation (1) is integrated by a numerical marching procedure which starts at one of the limiting points of the $P - x_1$ relation with a known value of dP/dy_1. Although this equation has been previously discussed by Stein and Voetter (*1*), the ease of numerical solution by automatic computer makes its use especially attractive and prompts this re-examination.

It is the purpose of this paper to discuss two questions with respect to integration of the coexistence equation: (a) Do there exist continuous, analytic $P - x_1$ relations, single valued in P, which do not provide thermodynamically acceptable solutions to Equation (1) for binary systems in stable, two-phase, vapor-liquid equilibrium? (b) Does it matter from what point one starts the numerical procedure for integration of Equation (1)?

Consider the first question initially with respect to $P - x_1$ relations which show a maximum in P and for which the curvature (second derivative) is everywhere negative. Two such curves are illustrated in Figure 1. One might well suppose that pairs of mutually soluble liquids could exist whose mixtures would exhibit vapor pressures at some temperature conforming to each of these curves. This is indeed the case for Curve A, but not for Curve B. However, there is nothing evident in the curves themselves to suggest this distinction. It is necessary to solve for the $P - y_1$ relations that correspond to each of these sets of $P - x_1$ data. The results of the numerical calculations for Curve A (Figure 1) appear in Figure 2. Not only is the resulting $P - y_1$ curve shown, but in addition the partial pressure curves appear. These latter curves must conform to the Gibbs-Duhem equation

$$x_1 \frac{d \ln (Py_1)}{dx_1} + x_2 \frac{d \ln (Py_2)}{dx_1} = 0 \tag{2}$$

because Equation (1) results from it merely by rearrangement.

The numerical procedure used to produce these results is not in question, for in this particular case the results are subject to direct confirmation. The $P - x_1$ data used were generated by the regular solution equations:

$$\Delta G^E/RT = Ax_1x_2, \quad \gamma_1 = \exp\, Ax_2^2, \quad \text{and} \quad \gamma_2 = \exp\, Ax_1^2$$

Since

$$P = x_1P_1^\circ\gamma_1 + x_2P_2^\circ\gamma_2$$

$$P = x_1P_1^\circ \exp\, Ax_2^2 + x_2P_2^\circ \exp\, Ax_1^2 \tag{3}$$

The choice of $P_1^\circ = P_2^\circ = 100$ and $A = 1.95$ led to the $P - x_1$ relation employed. Since

$$y_1 = \frac{x_1P_1^\circ \exp\, Ax_2^2}{P}$$

the values of y_1 found through Equation (1) were directly checked and found to be correct. As explained later, the marching procedure by which Equation (1) is solved cannot pass through a point of positive azeotropy. Thus one starts at either end of the $P - x_1$ relation and marches toward the point of maximum pressure.

Curve B of Figure 1 is seen to be a distortion of Curve A which destroys its symmetry. The results of numerical solution of Equation (1) for this $P - x_1$ relation are shown in Figure 3. Here we find unexpected features. The two branches of the $P - y_1$ curve fail to meet at the point of maximum pressure, but rather they cross. Moreover, the $P - y_1$ curve fails to become tangent to the $P - x_1$ curve at its maximum. In short, the Gibbs-Konowalow laws are violated. These laws might be considered as boundary conditions on Equation (1). However, this equation is first-order and admits but one independent boundary condition, which is imposed at the start of the marching procedure by setting $y_1 = x_1 = 0$ or $y_1 = x_1 = 1$. Thus the Gibbs-Konowalow laws must automatically be satisfied whenever integration of Equation (1) leads to the expected behavior at an azeotrope (as in Figure 2). Where it does not (as in Figure 3), some other consideration must enter.

This additional consideration is that of material stability, which played no part whatever in the derivation of Equation (1). The stability condition requires that a binary liquid phase at constant T must always exhibit a positive value for $d^2(\Delta G/RT)/dx_1^2$, where it is presumed that $\Delta G/RT$ is a continuous, analytic function of x_1 essentially independent of pressure. Any real or imagined violation of this condition presupposes that the liquid phase considered is unstable with respect to a split into two other liquid phases, which would represent the equilibrium condition.

The implications of the stability requirement for the binary vapor-liquid equilibrium problem considered here are demonstrated as follows. Basic relations for the liquid phase are (2)

$$\Delta G/RT = \Delta G^E/RT + \Delta G^{id}/RT$$
$$\Delta G^E/RT = x_1 \ln\gamma_1 + x_2 \ln\gamma_2$$
$$\Delta G^{id}/RT = x_1 \ln x_1 + x_2 \ln x_2$$

Combination of these yields:

$$\Delta G/RT = x_1 \ln x_1\gamma_1 + x_2 \ln x_2\gamma_2 \tag{4}$$

For vapor-liquid equilibrium at low pressures where the vapor phase is an ideal gas and the liquid-phase properties are independent of pressure,

$$\gamma_i = y_iP/x_iP_i^o$$

Substitution into Equation (4) gives

$$\Delta G/RT = x_1 \ln \frac{y_1P}{P_1^o} + x_2 \ln \frac{y_2P}{P_2^o} \tag{5}$$

Differentiation of this equation with respect to x_1 and combination with the Gibbs-Duhem equation [Equation (2)] yields

$$d(\Delta G/RT)/dx_1 = \ln \frac{y_1P}{P_1^o} - \ln \frac{y_2P}{P_2^o}$$

A second differentiation gives

$$d^2(\Delta G/RT)/dx_1^2 = \frac{d \ln (y_1P)}{dx_1} - \frac{d \ln (y_2P)}{dx_1} \tag{6}$$

Again employing the Gibbs-Duhem equation, we get

$$d^2(\Delta G/RT)dx_1^2 = \frac{1}{x_2}\,\frac{d \ln (y_1P)}{dx_1} = \frac{-1}{x_1}\,\frac{d \ln (y_2P)}{dx_1} \tag{7}$$

In addition, Equation (6) is readily rearranged to the form

$$d^2(\Delta G/RT)dx_1^2 = \frac{1}{y_1(1-y_1)}\,\frac{dy_1}{dx_1} \tag{8}$$

Thus we have from Equations (1), (7), and (8)

$$d^2(\Delta G/RT)dx_1^2 = \frac{1}{x_2}\,\frac{d \ln (y_1P)}{dx_1} = \frac{-1}{x_1}\,\frac{d \ln (y_2P)}{dx_1}$$
$$= \frac{1}{y_1(1-y_1)}\,\frac{dy_1}{dx_1} = \frac{1}{y_1-x_1}\,\frac{d \ln P}{dx_1}$$

For stability it is clear that every member of this set of equations must be positive. Thus the stability condition requires that

$$d(y_1P)/dx_1 > 0, \quad d(y_2P)/dx_1 < 0, \quad dy_1/dx_1 > 0$$

and that dP/dx_1, dP/dy_1, and $(y_1 - x_1)$ all have the same sign. These apply to low-pressure binary vapor-liquid equilibrium at constant T.

It is interesting that none of these conditions is actually violated by the curves of Figure 3 if one disregards the discontinuities. Moreover, if one calculates $\Delta G/RT$ as a function of x_1 from the $x_1 - y_1 - P$ data of Figure 3 by means of Equation (5), one obtains the results shown by Figure 4. Again there is a discontinuity in the $\Delta G/RT$ vs. x_1 curve, but otherwise there is no point where the primary stability condition

$$d^2(\Delta G/RT)/dx_1^2 > 0$$

is violated. Note however in the statement containing this condition the presumption that $\Delta G/RT$ is a continuous, analytic function of x_1. Clearly in the case considered it is not. The problem is that the complete condition for stability is difficult to represent by a single, simple mathematical expression. This complete condition is discussed by Van Ness (2), and is given by the statement that for a stable liquid phase the $\Delta G/RT$ vs. x_1 curve is such that no external straight line can be drawn which is tangent to the curve at more than one point. If one postulates a $\Delta G/RT$ vs. x_1 curve such that an external straight line can be drawn which is tangent to the curve at two points, then any single liquid phase whose composition lies between those of the tangent points cannot be stable. Moreover, the stable state is a mixture of two liquid phases having the compositions given by the tangent points.

Returning now to Figure 4, we see that an external straight line can be drawn tangent to the $\Delta G/RT$ vs. x_1 curve at $x_1 = 0.24$ and at $x_1 = 0.62$. Thus any single liquid phase of an intermediate composition cannot be stable, and the $P - x_1$ diagram of Figure 3 between $x_1 = 0.24$ and 0.62 must represent a system, real or imagined, which is not stable. Truncation of this curve between the given values of x_1 results in a diagram which conforms to physical reality for stable equilibrium, as shown in Figure 5. Note that the horizontal line which represents the $P - x_1$ behavior in the immiscible region passes exactly through the intersection of the two branches of the calculated $P - y_1$ curve, as it should.

One concludes from this discussion that any set of experimental $P - x_1$ data for binary vapor-liquid equilibrium which leads to results, such as those of Figure 3, from a correct integration of the coexistence equation must be in error.

Clearly, there is a large class of $P - x_1$ curves of the maximum-pressure type which cannot represent binary vapor-liquid equilibria for any stable system. Often it is not possible to distinguish a curve which conforms to physical reality from one which does not, except by carrying out the integration of Equation (1). However, one can absolutely exclude all curves for which $P_{\max} \geqq P_1^o + P_2^o$. The reason for this is that as a result of the stability requirements (see Figure 2, for example)

$$Py_1 \leqq P_1^o \quad \text{and} \quad Py_2 \leqq P_2^o$$

Thus

$$P = Py_1 + Py_2 < P_1^o + P_2^o$$

An additional restraint on $P - x_1$ relations of the maximum-pressure type, which has nothing to do with stability, is treated in the Appendix. What of $P - x_1$ curves which exhibit minima only or no extrema at all? Systems characterized by these types of curves do not show phase separa-

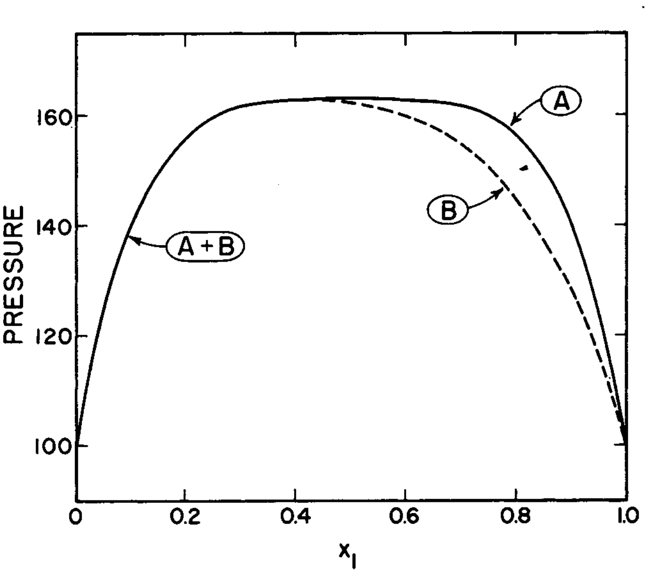

Fig. 1. Two P-x_1 relations. Curve A is for a regular solution with $A = 1.95$.

tion as a limiting behavior, and therefore all such curves represent physically possible systems which would satisfy the criteria of material stability. Curves of greater complexity are possible, but no attempt at a complete classification is presented here. Their admissibility is to be judged by the general criteria already discussed.

The second question posed at the beginning of this paper can be considered on purely mathematical grounds. In the numerical marching procedure for integration of the coexistence equation, one starts at one of the limiting points of the $P - x_1$ relation where $(x_1 - y_1) \rightarrow 0$, and thus imposes a boundary condition such as $y_1 = x_1 = 0$ or $y_1 = x_1 = 1$. Let us expand our view so as to treat the whole family of curves representing solutions to Equation (1), for a given $P - x_1$ relation, without restriction to a particular boundary condition. Equation (1) requires that $dP/dy = 0$ whenever $x - y = 0$, provided that neither y nor $1 - y$ approaches zero. (For simplicity, the subscript 1 is suppressed here and in what follows.) Thus the $P - x$ curve divides the $P - y$ plane into a region where $(y - x)$ and dP/dy are positive and a region where both are negative.

Consider now the slope dP/dy of solution curves which cross the constant-pressure line at $P = P_2^o$. Since this pressure obtains only when $x = 0$, we have

$$\left(\frac{dP}{dy}\right)_{\substack{x=0\\ y\neq 0}} = \frac{P_2^o}{1-y} \tag{9}$$

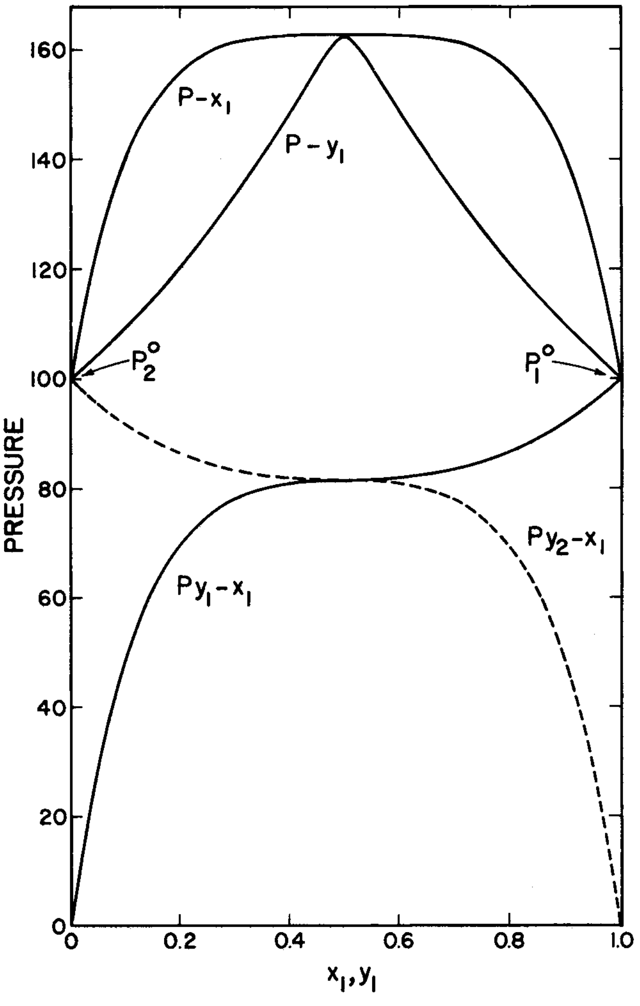

Fig. 2. Results of numerical integration of Equation (1) for curve A of Figure 1.

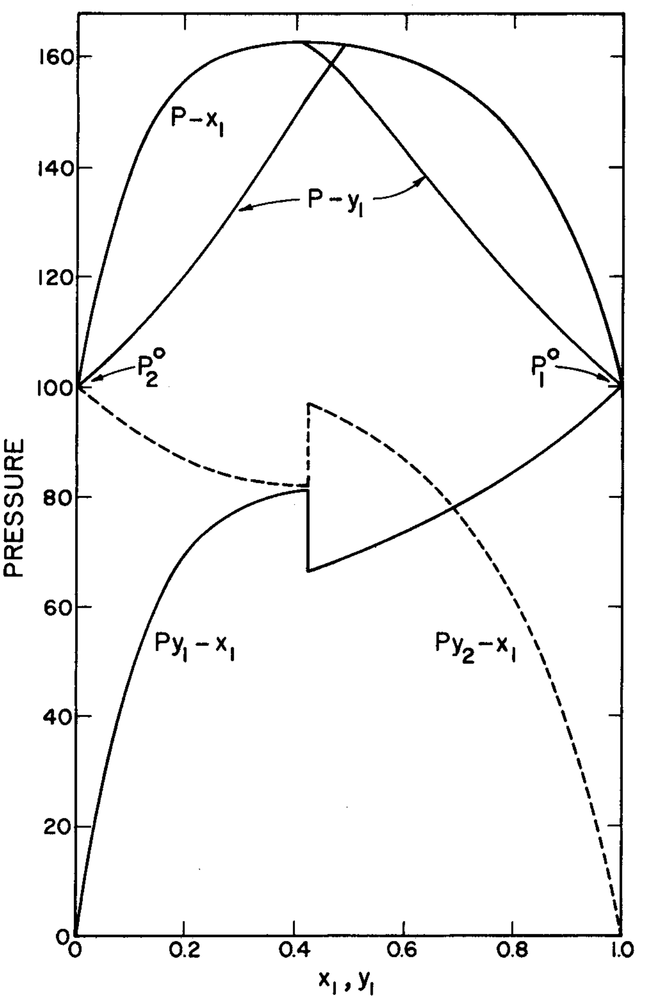

Fig. 3. Results of numerical integration of Equation (1) for curve B of Figure 1.

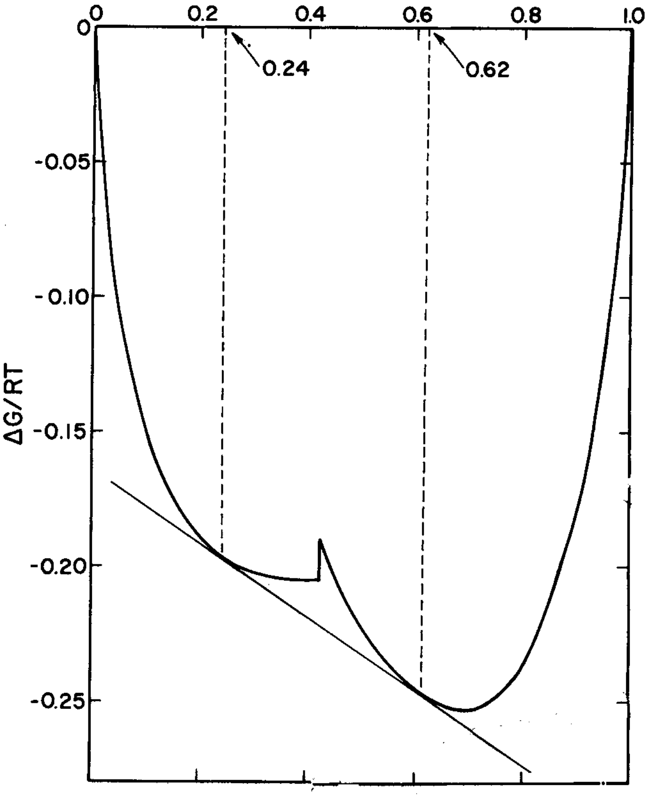

Fig. 4. Gibbs function change of mixing from results of Figure 3.

Thus the slopes of solution curves are clearly defined along the line $P = P_2^o$ except where $y = 0$.

When both x and y approach zero, dP/dy is indeterminate, but by application of l'Hôpital's rule to Equation (1) and subsequent rearrangement a limiting value is determined:

$$\left(\frac{dP}{dy}\right)_{x=y=0} = \frac{1}{\dfrac{1}{(dP/dx)_{x=0}} + \dfrac{1}{P_2^o}} \tag{10}$$

Equation (1) may now be integrated numerically for various starting values of x, y, and P. The simplest example is that of a solution obeying Raoult's law, for which P is linear in x. A particular case is illustrated in Figure 6, where the heavy line represents the linear $P - x$ relation and the lighter lines are solutions to Equation (1). The circles show the points at which numerical integration was started in each case. It is seen that all solution curves converge to the point $y = x = 1$, $P = P_1^o$. Furthermore, all curves approach the same slope at this point. This slope is again determined by application of l'Hôpital's rule to Equation (1)

$$\left(\frac{dP}{dy}\right)_{x=y=1} = \frac{1}{\dfrac{1}{(dP/dx)_{x=1}} - \dfrac{1}{P_1^o}} \tag{11}$$

Equation (1) clearly requires that $y \rightarrow x$ as $y \rightarrow 1$ if $(dP/dy)_{y=1}$ is to be finite. As a consequence of the convergence of all solution curves to the same slope at $x = y = 1$, one cannot start a numerical integration at this point, for there is no way to predetermine which solution curve will be followed. Since only one solution curve passes through the point $x = y = 0$, it is from this point that integration must start. Of course, only the curve passing through this point has physical significance.

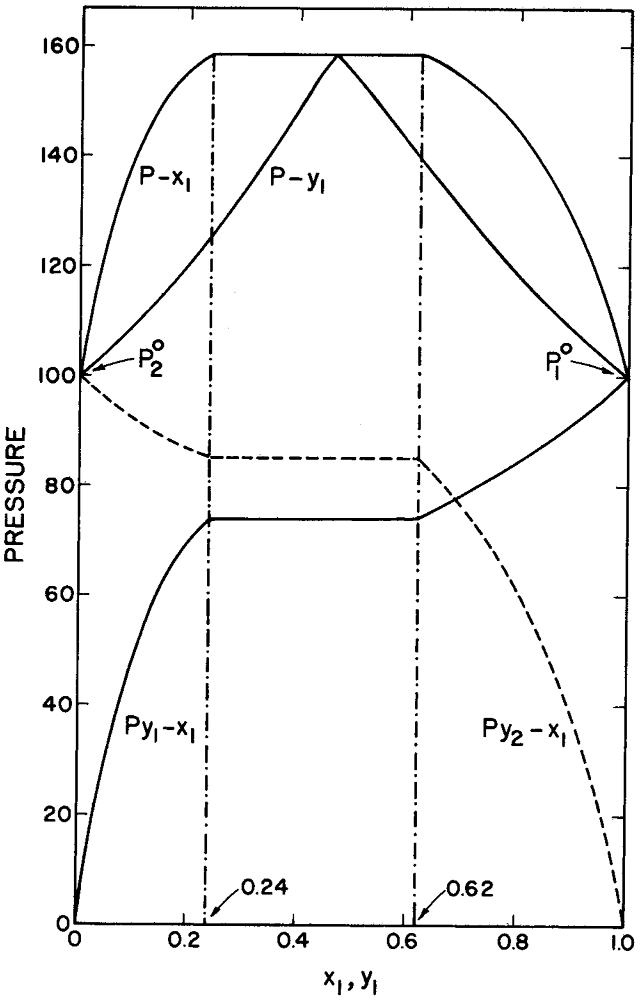

Fig. 5. Results of Figure 3 modified to show region of partial miscibility.

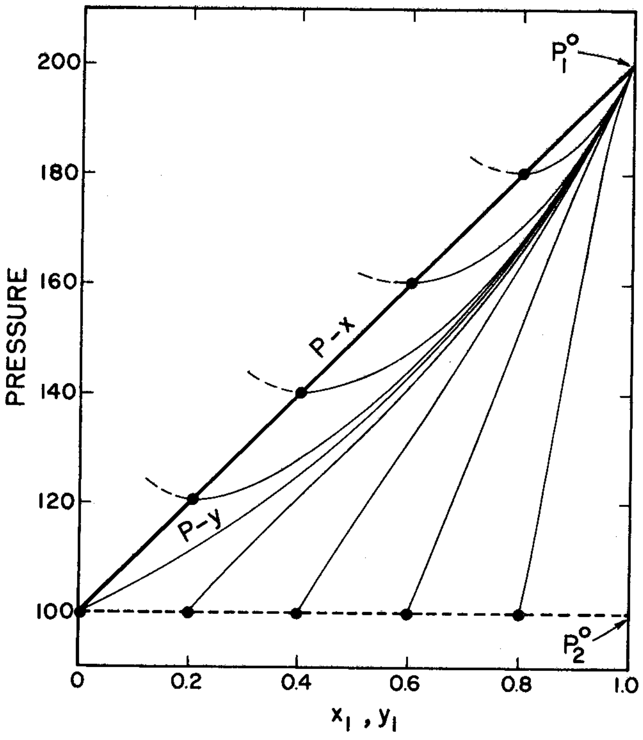

Fig. 6. Sketch of solution curves to Equation (1) (light lines) for linear P-x relation (heavy line). Circles indicate points at which integration started.

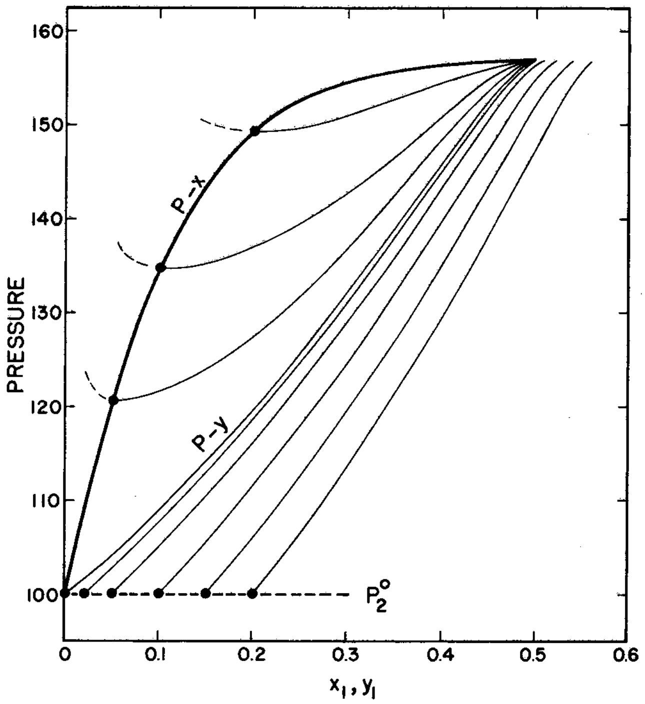

Fig. 7. Sketch of solution curves to Equation (1) (light lines) for P-x relation generated for regular solution with $A = 1.8$ (heavy line). Circles indicate points at which integration started. Only the left half of the diagram is shown.

Although Figure 6 illustrates just the Raoult's law case, the results are the same for $P-x$ curves showing both positive and negative deviations from Raoult's law provided no azeotrope exists. If one plots the Raoult's law case for exactly the same system as shown in Figure 6 but lets x and y represent the other component, then the diagram is the mirror image of the one shown, with the solution curves again converging at the higher pressure end. Thus for non-azeotropic systems one must integrate from the lowest to the highest pressure.

For systems which exhibit maximum pressure azeotropes, it is convenient to divide the problem into two parts and to consider the left region from $x = 0$ to the azeotropic composition first. The expressions for dP/dy for $x = y$ and along the line $P = P_2^o$ are as before. The difference comes in that a maximum in the $P-x$ curve is reached at $x = x_{az} < 1$. There is nothing about Equation (1) that forces y to approach x as x approaches x_{az} and dP/dx approaches zero. What Equation (1) does require is that dP/dy approach zero if y approaches x. All the necessary information is readily available to allow integration of Equation (1) for various starting values of x, y, and P. The simplest example of a system exhibiting a maximum pressure (positive) azeotrope is the regular solution. This case is illustrated in Figure 7 where the constants of Equation (3) have been taken as $P_1^o = P_2^o = 100$ and $A = 1.8$. The heavy line represents the $P-x$ relation and the lighter lines are solutions to Equation (1) for various initial (boundary) conditions as indicated by the circles. It is seen that all solution curves which lie above and include the one passing through $y = x = 0$, $P = P_2^o$ converge with zero slope at $y = x = x_{az}$, $P = P_{max}$. So do solution curves that lie below but close to this curve which represents physically reality. Curves lying still lower are not convergent. However, the existence of a family of curves which converge with zero slope at the azeotrope makes it impossible to start numerical integration at the azeotrope. Integration must start at $y = x = 0$, $P = P_2^o$. For the regular solution case considered, the other half of Figure 7 is its mirror image, with convergence of the solution curves occurring at the maximum pressure. Thus one cannot pass through a point of positive azeotropy, for although it can be approached from one side along a particular solution curve, this solution curve joins with a whole family of curves that converge from the other side. Again integration must proceed from the lowest to the highest pressure.

The choice of $A = 1.8$ for the regular solution characterized by Equation (3) guaranteed that we were dealing with a thermodynamically stable system with respect to the $P-y$ curve of physical reality that originates at $y = x = 0$, $P = P_2^o$. It is well known that the value of $A = 2$ separates stable from unstable systems that are regular. Had A been taken greater than 2 the convergent family of solution curves would not have included the physically real one originating at the point cited. This merely reinforces the conclusions reached earlier with respect to unstable systems. The conclusions drawn for regular solutions apply to all systems which show positive azeotropy.

Systems exhibiting minimum-pressure (negative) azeotropes are less easily characterized by a simple example. However, it is not difficult to demonstrate that solution curves converge at $y = x = 0$, $P = P_2^o$ and at $y = x = 1$, $P = P_1^o$, rather than at the azeotrope. Thus integration must start at the azeotrope and proceed toward higher pressures and toward the edges of a $P-x-y$ diagram.

The general conclusion to be drawn from this discussion is that the numerical integration of the coexistence equation must in all cases proceed in the direction of increasing pressure.

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NOTATION

A = a constant
ΔG = Gibbs function change of mixing of liquid phase
ΔG^{id} = Gibbs function change of mixing for an ideal solution
ΔG^E = Gibbs function change of mixing over and above that for an ideal solution
P = vapor pressure of a solution
P_i^o = vapor pressure of pure i
R = universal gas constant
T = absolute temperature
x_i = mole fraction of component i in liquid phase
y_i = mole fraction of component i in vapor phase
γ_i = activity coefficient of component i in liquid phase

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APPENDIX

An additional restraint on $P-x_1$ curves which exhibit positive azeotropy may be demonstrated as follows. Multiplication of Equation (1) by dy/dx gives

$$\frac{P(dy/dx)}{y(1-y)} = \frac{dP/dx}{(y-x)}$$

At an azeotrope both dP/dx and $(y-x)$ approach zero, and the right-hand side is indeterminate. Application of l'Hôpital's rule gives

$$\frac{P_{az}(dy/dx)_{az}}{y_{az}(1-y)_{az}} = \lim_{x \to y} \frac{dP/dx}{(y-x)} = \frac{(d^2P/dx^2)_{az}}{(dy/dx-1)_{az}}$$

or

$$(dy/dx)^2_{az} - (dy/dx)_{az} - \frac{y_{az}(1-y_{az})}{P_{az}} \left(\frac{d^2P}{dx^2}\right)_{az} = 0$$

Let

$$(dy/dx)_{az} = z \text{ and } \frac{y_{az}(1-y_{az})}{P_{az}} \left(\frac{d^2P}{dx^2}\right)_{az} = -m$$

Then

$$z^2 - z + m = 0$$

and

$$z = \frac{1}{2} \pm \sqrt{\frac{1}{4} - m}$$

For a positive azeotrope $(d^2P/dx^2)_{az}$ is negative, and therefore m is positive. To avoid imaginary roots we must have $m < 1/4$. Thus

$$-\left(\frac{d^2P}{dx^2}\right)_{az} < \frac{P_{az}}{4y_{az}(1-y_{az})}$$

This is a rather restrictive condition, which for positive azeotropes occurring at mole fractions not close to zero or unity limits $-(d^2P/dx^2)_{az}$ to the order of P_{az}. Thus maximum-pressure azeotropes generally are rather flat at the top. For minimum-pressure azeotropes m is negative, and the question of imaginary roots does not arise.