Chapter 10

Vapor/Liquid Equilibrium: Introduction

Preceding chapters have dealt largely with pure substances or with constant-composition mixtures. e.g., air. However, composition changes are the desired outcome, not only of chemical reactions, but of a number of industrially important mass-transfer operations.

The most commonly encountered coexisting phases in industrial practice are vapour and liquid, although liquid/liquid, vapour/solid, and liquid/solid systems are also found.

10.1 THE NATURE OF EQUILIBRIUM

Equilibrium is a static condition in which no changes occur in the macroscopic properties of a system with time. This implies a balance of all potentials that may cause change. In engineering practice, the assumption of equilibrium is justified when it leads to results of satisfactory accuracy. For example, in the reboiler for a distillation column, equilibrium between vapour and liquid phases is commonly assumed. For finite vaporization rates this is an approximation, but it does not introduce significant error into engineering calculations. An isolated system consisting of liquid and vapour phases in intimate contact eventually reaches a final state wherein no tendency exists for change to occur within the system. The temperature, pressure, and phase compositions reach final values which thereafter remain fixed. The system is in equilibrium.

Measures of Composition

The three most common measures of composition are mass fraction, mole fraction, and molar concentration. Mass or mole fraction is defined as the ratio of the mass or number of moles of a particular chemical species in a mixture or solution to the total mass or number of moles of the mixture or solution:

$$x_i \equiv \frac{m_i}{m} = \frac{\dot{m}_i}{\dot{m}} \qquad \text{or} \qquad x_i \equiv \frac{n_i}{n} = \frac{\dot{n}_i}{\dot{n}}$$

Molar concentration is defined as the ratio of the mole fraction of a particular chemical species in a mixture or solution to its molar volume:

$$C_i \equiv \frac{x_i}{V}$$

This quantity has units of moles of i per unit volume. For flow processes convenience suggests its expression as a ratio of rates. Multiplying and dividing by molar flow rate $\dot{n}$ gives:

$$C_i = \frac{\dot{n}_i}{q}$$

where $\dot{n}_i$ is molar flow rate of species i, and q is volumetric flow rate.

The molar mass of a mixture or solution is, by definition, the mole-fraction-weighted sum of the molar masses of all species present:

$$M \equiv \sum_i x_i M_i$$

10.4 SIMPLE MODELS FOR VAPOR/LIQUID EQUILIBRIUM

The preceding section has described what is observed through experimental observation. When thermodynamics is applied to vapour/liquid equilibrium, the goal is to find by calculation the temperatures, pressures, and compositions of phases in equilibrium. Indeed, thermodynamics provides the mathematical framework for the systematic correlation, extension, generalization, evaluation, and interpretation of data. Moreover, it is the means by which the predictions of various theories of molecular physics and statistical mechanics may be applied to practical purposes. None of this can be accomplished without models for the behaviour of systems in vapour/liquid equilibrium. The two simplest are Raoult's law and Henry's law.

Raoult's Law

The two major assumptions required to reduce VLE calculations to Raoult's law are:

- The vapor phase is an ideal gas.
- The liquid phase is an ideal solution (Sec. 11.8).

The first assumption means that Raoult's law can apply only for low to moderate pressures. The second implies that it can have approximate validity only when the species that comprise the system are chemically similar. Just as the ideal gas serves as a standard to which real-gas behaviour may be compared, the ideal solution represents a standard to which real-solution behaviour may be compared. Ideal-solution behaviour is often approximated by liquid phases wherein the molecular species are not too different in size and are of the same chemical nature. Thus, a mixture of isomers, such as ortho-, meta-, and para-xylene, conforms very closely to ideal-solution behaviour. So do mixtures of adjacent members of a homologous series, as for example, n-hexane/n-heptane, ethanol/propanol, and benzene/toluene. Other examples are acetone/acetonitrile and acetonitrile/nitromethane.

The mathematical expression which reflects the two listed assumptions and which therefore gives quantitative expression to Raoult's law is

$$\boxed{y_i P = x_i P_i^{\text{sat}} \qquad (i = 1, 2, \ldots, N)} \qquad (10.1)$$

where x_i is a liquid-phase mole fraction, y_i is a vapour-phase mole fraction, and P_i^{sat} is the vapour pressure of pure species i at the temperature of the system. The product yi P on the left side of Eq. (10.1) is known as the partial pressure of species i (Sec. 11.4).

A limitation of Raoult's law is that it can be applied only to species for which a vapor pressure is known, and this requires that the species be "subcritical," i.e., that the temperature of application be below the critical temperature of the species.

An important and useful feature of Raoult's law is that it is valid for any species present at a mole fraction approaching unity, provided only that the vapour phase is an ideal gas. Chemical similarity of the constituent species is not here a requirement.

Dewpoint and Bubblepoint Calculations with Raoult's Law

Although VLE problems with other combinations of variables are possible, engineering interest centres on dewpoint and bubblepoint calculations; there are four classes:

BUBL P: Calculate $\{y_i)$ and P, given $\{x_i\}$ and T
DEW P: Calculate $\{x_i\}$ and P, given $\{y_i\}$ and T
BUBL T: Calculate $\{y_i\}$ and T, given $\{x_i\}$ and P
DEW T: Calculate $\{x_i\}$ and T, given $\{y_i\}$ and P

Because $\sum$ yi = 1, Eq. (10.1) may be summed over all species to yield:

$$P = \sum_i x_i P_i^{sat} \qquad (10.2)$$

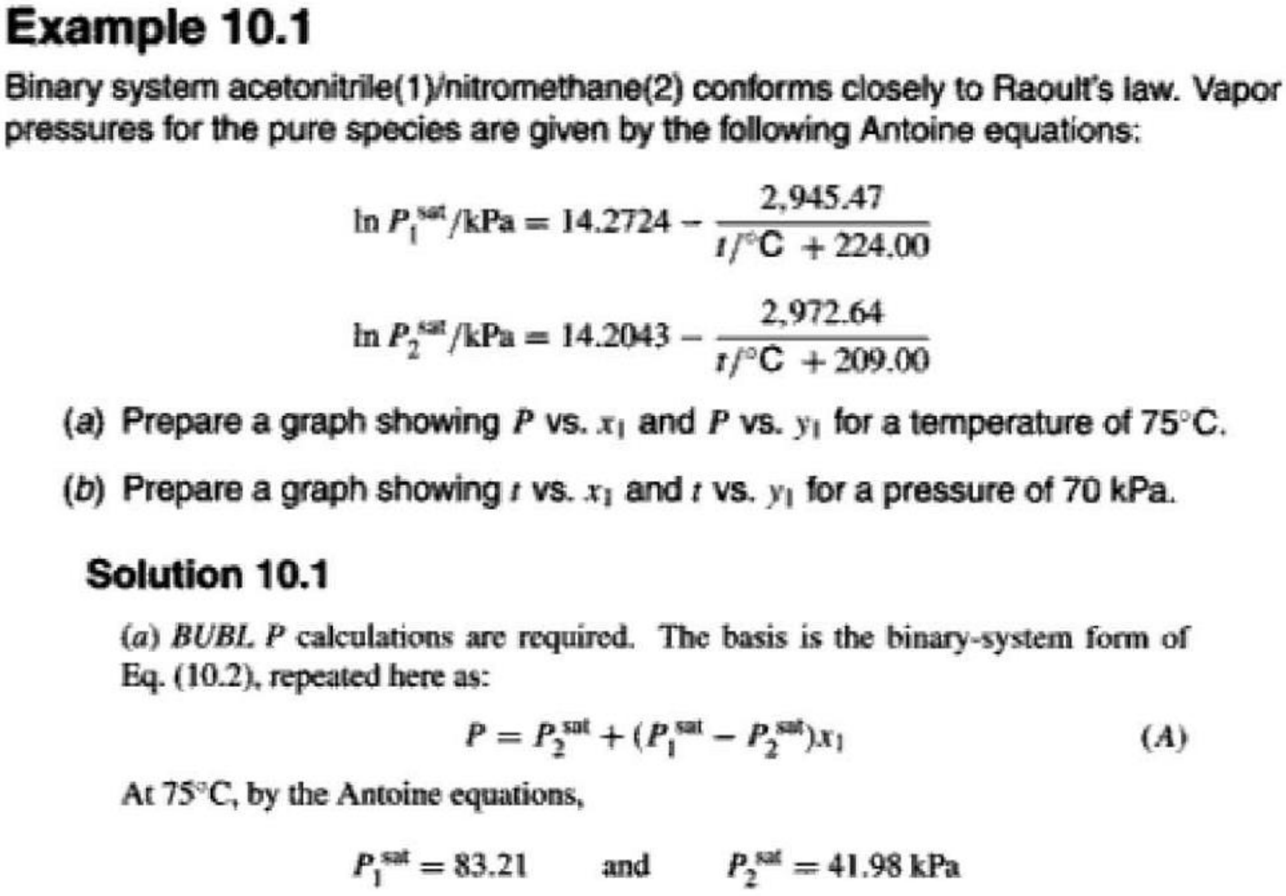
This equation finds application in bubblepoint calculations, where the vapour-phase composition is unknown. For a binary system with $x_2 = 1 - x_l$,

$$P = P_2^{sat} + (P_1^{sat} - P_2^{sat})x_1$$

and a plot of P vs. x_l at constant temperature is a straight line connecting p_2^{sat} at $x_l = 0$ with p_1^{sat} at $x_l = 1$. The P-x-y diagrams of Fig. 10.8 show this linear relation.
Equation (10.1) may also be solved for xi and summed over all species. With $\sum$ xi = 1, this yields:

$$P = \frac{1}{\sum_i y_i / P_i^{sat}} \qquad (10.3)$$

an equation applied in dewpoint calculations, where liquid-phase compositions are not known.



Example 10.1

Binary system acetonitrile(1)/nitromethane(2) conforms closely to Raoult's law. Vapor pressures for the pure species are given by the following Antoine equations:

$$\ln P_1^{sat}/\text{kPa} = 14.2724 - \frac{2{,}945.47}{t/^\circ\text{C} + 224.00}$$

$$\ln P_2^{sat}/\text{kPa} = 14.2043 - \frac{2{,}972.64}{t/^\circ\text{C} + 209.00}$$

(*a*) Prepare a graph showing P vs. x_1 and P vs. y_1 for a temperature of 75°C.

(*b*) Prepare a graph showing t vs. x_1 and t vs. y_1 for a pressure of 70 kPa.

Solution 10.1

(*a*) *BUBL P* calculations are required. The basis is the binary-system form of Eq. (10.2), repeated here as:

$$P = P_2^{sat} + (P_1^{sat} - P_2^{sat})x_1 \qquad (A)$$

At 75°C, by the Antoine equations,

$$P_1^{sat} = 83.21 \qquad \text{and} \qquad P_2^{sat} = 41.98 \text{ kPa}$$

Calculations are here very simple, as illustrated for $x_1 = 0.6$:

$$P = 41.98 + (83.21 - 41.98)(0.6) = 66.72 \text{ kPa}$$

The corresponding value of y_1 is then found from Eq. (10.1):

$$y_1 = \frac{x_1 P_1^{\text{sat}}}{P} = \frac{(0.6)(83.21)}{66.72} = 0.7483$$

These results mean that at 75°C a liquid mixture of 60 mol-% acetonitrile and 40 mol-% nitromethane is in equilibrium with a vapor containing 74.83 mol-% acetonitrile at a pressure of 66.72 kPa. The results of calculations for 75°C at a number of values of x_1 are tabulated as follows:

x_1	y_1	P/kPa	x_1	y_1	P/kPa
0.0	0.0000	41.98	0.6	0.7483	66.72
0.2	0.3313	50.23	0.8	0.8880	74.96
0.4	0.5692	58.47	1.0	1.0000	83.21

These same results are shown by the P-x_1-y_1 diagram of Fig. 10.11. This figure is a phase diagram on which the straight line labeled P-x_1 represents states of saturated liquid; the subcooled-liquid region lies above this line. The curve

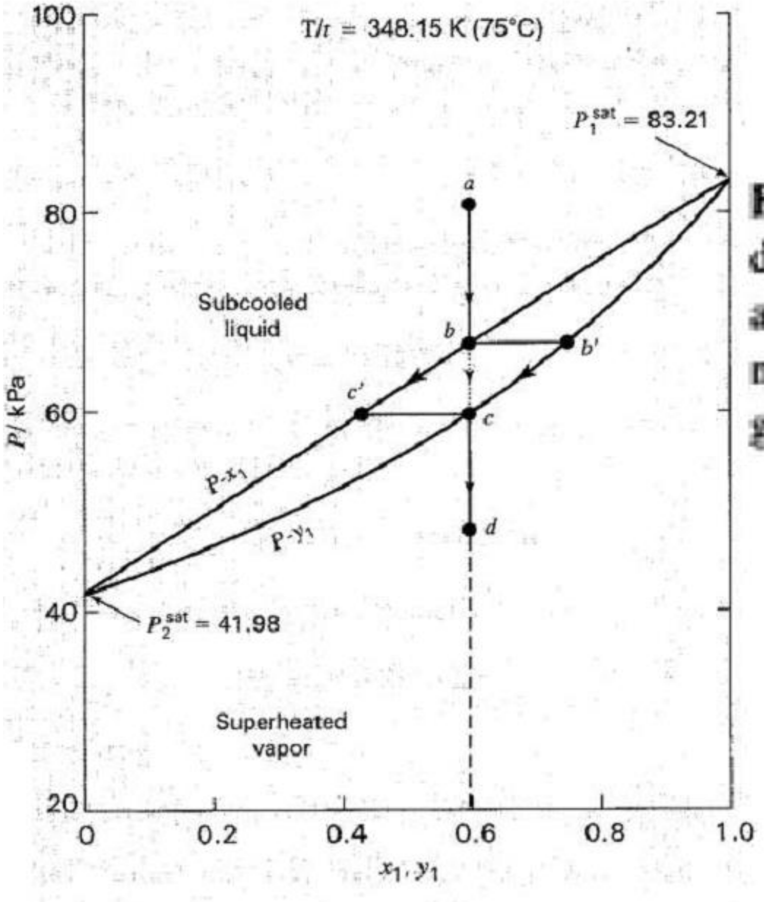


Figure 10.11: *Pxy* diagram for acetonitrile(1)/nitromethane(2) at 75°C as given by Raoult's law.

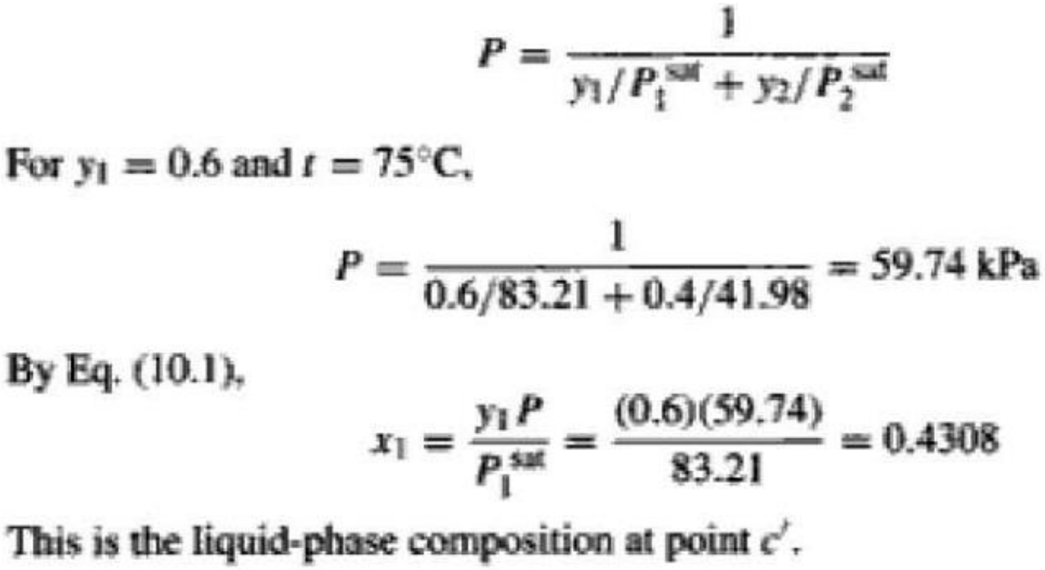
labelled P-yi represents states of saturated vapour: the superheated- vapour region lies below this curve points lying between the saturated-liquid and saturated vapour lines are in the two-phase region. What saturated liquid and saturated vapour coexists in equilibrium? The P-x_l and P-y_1 lines meet at the edges of the diagram what saturated liquid and saturated vapour of the pure species coexist ad the vapour pressures P_1^{sat} and P_2^{sat}.

To illustrate the nature of phase behaviour in this binary system we follow the course of a constant-temperature expansion process on the P -x_l -y_1 diagram, A subcooled liquid mixture of 60 mol-% acetonitrile and 40 mot-% nitmmethane exists in a piston/cylinder arrangement at 75 ^{o}C. Its state is represented by point a in Fig. 10.11. Withdrawing the piston slowly enough reduces the pressure while maintaining the system at equilibrium at 75^{o}C. Because the system is closed, the overall composition remains constant during the process and the states of the system as a whole fall on the vertical line descending from point a. When the pressure reaches the value at point b, the system is saturated liquid on the verge of vaporizing. A minuscule further decrease in pressure produces a bubble of vapour, represented by point $\acute{b}$. The two points b and $\acute{b}$ (x_1 =0.6, P = 66.72 kpa. and yi = 0.7483) together represent the state determined by earlier calculations.

Point b is a bubble point, and the P-x_1 line is the locus of bubble points.

As the pressure is further reduced, the amount of vapour increases and the amount of liquid decreases, with the states of the two phases following paths b'c and bc' respectively. The dotted line from point b to point c represents the overall states of the two-phase system. Finally, as point c is approached, the liquid phase, represented by point c', has almost disappeared, with only droplets (dew) remaining. Point c is therefore a dew point and the P-y_1 curve is the locus of dew points. Once the dew has evaporated, only saturated vapour at point c remains, and further pressure reduction leads to superheated vapour at point d.

The composition of the vapour at point c is y_i = 0.6, but the composition of the liquid at point c' and the pressure must either be read from the graph or calculated. This is a DEW P calculation, and by Eq. (10.3),



$$P = \frac{1}{y_1/P_1^{sat} + y_2/P_2^{sat}}$$

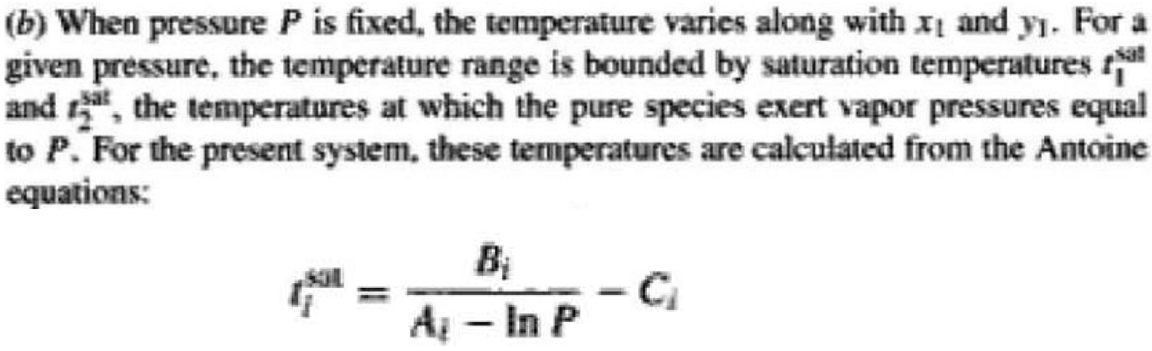
For $y_1 = 0.6$ and $t = 75°\text{C}$,

$$P = \frac{1}{0.6/83.21 + 0.4/41.98} = 59.74 \text{ kPa}$$

By Eq. (10.1),

$$x_1 = \frac{y_1 P}{P_1^{sat}} = \frac{(0.6)(59.74)}{83.21} = 0.4308$$

This is the liquid-phase composition at point c'.



(*b*) When pressure P is fixed, the temperature varies along with x_1 and y_1. For a given pressure, the temperature range is bounded by saturation temperatures t_1^{sat} and t_2^{sat}, the temperatures at which the pure species exert vapor pressures equal to P. For the present system, these temperatures are calculated from the Antoine equations:

$$t_i^{sat} = \frac{B_i}{A_i - \ln P} - C_i$$

For $P = 70$ kPa, $t_1^{sat} = 69.84$°C and $t_2^{sat} = 89.58$°C. The simplest way to prepare a t-x_1-y_1 diagram is to select values of t between these two temperatures, calculate P_1^{sat} and P_2^{sat} for these temperatures, and evaluate x_1 by Eq. (A), written:

$$x_1 = \frac{P - P_2^{sat}}{P_1^{sat} - P_2^{sat}}$$

For example, at 78°C, $P_1^{sat} = 91.76$ kPa, $P_2^{sat} = 46.84$ kPa, and

$$x_1 = \frac{70 - 46.84}{91.76 - 46.84} = 0.5156$$

By Eq. (10.1),

$$y_1 = \frac{x_1 P_1^{sat}}{P} = \frac{(0.5156)(91.76)}{70} = 0.6759$$

The results of this and similar calculations for $P = 70$ kPa are as follows:

x_1	y_1	t/°C	x_1	y_1	t/°C
0.0000	0.0000	89.58 (t_2^{sat})	0.5156	0.6759	78
0.1424	0.2401	86	0.7378	0.8484	74
0.3184	0.4742	82	1.0000	1.0000	69.84 (t_1^{sat})

Figure 10.12 is the t-x_1-y_1 diagram showing these results. On this phase diagram, drawn for a constant pressure of 70 kPa, the t-y_1 curve represents states of saturated vapor, with states of superheated vapor lying above it. The t-x_1 curve represents states of saturated liquid, with states of subcooled liquid lying below it. The two-phase region lies between these curves.

With reference to Fig. 10.12, consider a constant-pressure heating process leading from a state of subcooled liquid at point a to a state of superheated vapor at point d. The path shown on the figure is for a constant overall composition of 60 mol-% acetonitrile. The temperature of the liquid increases as the result of heating from point a to point b, where the first bubble of vapor appears. Thus point b is a bubblepoint, and the t-x_1 curve is the locus of bubblepoints.

For $x_1 = 0.6$ and $P = 70$ kPa, t is determined by a *BUBL T* calculation, which requires iteration. Equation (10.2) is here written:

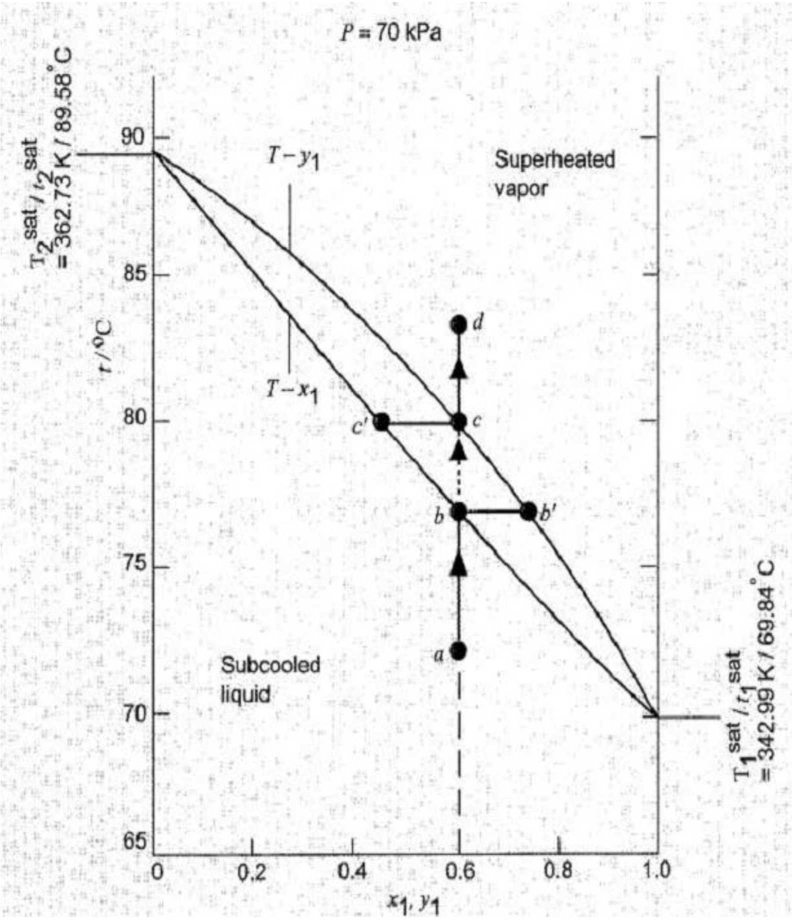


Figure 10.12: *txy* diagram for acetonitrile(1)/nitromethane(2) at 70 kPa as given by Raoult's law.

$$P_2^{sat} = \frac{P}{x_1\alpha + x_2} \tag{B}$$

where $\alpha \equiv P_1^{sat}/P_2^{sat}$. Subtracting $\ln P_2^{sat}$ from $\ln P_1^{sat}$ as given by the Antoine equations yields:

$$\ln\alpha = 0.0681 - \frac{2{,}945.47}{t + 224.00} + \frac{2{,}972.64}{t + 209.00} \tag{C}$$

The reason for introducing α is that as the controlling variable it is far less sensitive to t than an individual vapor pressure. An initial value of α is found for an arbitrary intermediate temperature. Iteration is then as follows:

- With the current value of α, calculate P_2^{sat} by Eq. (B).
- Calculate t from the Antoine equation for species 2:

$$t = \frac{2{,}972.64}{14.2043 - \ln P_2^{sat}} - 209.00$$

- Find a new value of α by Eq. (C).
- Return to the initial step and iterate to convergence for a final value of t.

The result is $t = 76.42$°C, the temperature of points b and b'. From the Antoine equation, $P_1^{sat} = 87.17$ kPa, and by Eq. (10.1) the composition at point b' is:

$$y_1 = \frac{x_1 P_1^{sat}}{P} = \frac{(0.6)(87.17)}{70} = 0.7472$$

Vaporizing a mixture at constant pressure, unlike vaporizing a pure species, does not in general occur at constant temperature. As the heating process continues beyond point b, the temperature rises, the amount of vapor increases, and the amount of liquid decreases. During this process, the vapor- and liquid-phase compositions change as indicated by paths $b'c$ and bc', until the dewpoint is reached at point c, where the last droplets of liquid disappear. The t-y_1 curve is the locus of dewpoints.

The vapor composition at point c is $y = 0.6$; because the pressure is also known ($P = 70$ kPa), a *DEW T* calculation is possible. With $\alpha \equiv P_1^{sat}/P_2^{sat}$, Eq. (10.3) is written:

$$P_1^{sat} = P(y_1 + y_2\alpha)$$

The iteration steps are as before, but are based on P_1^{sat} rather than P_2^{sat}, with

$$t = \frac{2{,}945.47}{14.2724 - \ln P_1^{sat}} - 224.00$$

The result here is $t = 79.58$°C, the temperature of points c and c'. From the Antoine equation, $P_1^{sat} = 96.53$ kPa, and Eq. (10.1) gives the composition at point c':

$$x_1 = \frac{y_1 P}{P_1^{sat}} = \frac{(0.6)(70)}{96.53} = 0.4351$$

Thus the temperature rises from 76.42 to 79.58°C during the vaporization step from point b to point c. Continued heating simply superheats the vapor to point d.