

Example 1

Seawater consists of salt (the solute) and water (the solvent). Determine the boiling temperature of solution with an 8% salt concentration at 1 bar. Use both Raoult's Law, and the equality $\hat{g}_{\text{H}_2\text{O}(\ell)} = \hat{g}_{\text{H}_2\text{O}(\text{g})}$.

Solution

The partial pressure of water

$$p_{\text{H}_2\text{O}} = X_{\text{H}_2\text{O}(\ell)} P_{\text{H}_2\text{O}}^{\text{sat}}(T).$$

At 100 kPa, since $X_{\text{H}_2\text{O}(\ell)} = 0.92$,

$$100 = 0.92 P_{\text{H}_2\text{O}}^{\text{sat}}(T), \text{ i.e., } P_{\text{H}_2\text{O}}^{\text{sat}}(T) = 108.7 \text{ kPa.}$$

At this pressure, using the tables

$$T = 102.1^\circ\text{C},$$

which is the boiling point of the salt water.

At phase equilibrium

$$\hat{g}_{\text{H}_2\text{O}(\ell)}(T, P, X_{\text{H}_2\text{O}(\ell)}) = \hat{g}_{\text{H}_2\text{O}(\text{g})}(T, P, X_{\text{H}_2\text{O}}) \quad (\text{A})$$

Using the ideal solution model for the liquid phase in context of Eq. (A),

$$\hat{g}_{\text{H}_2\text{O}(\ell)}(T, P, X_{\text{H}_2\text{O}}) = \bar{g}_{\text{H}_2\text{O}(\ell)} + \bar{R}T \ln X_{\text{H}_2\text{O}}. \quad (\text{B})$$

Similarly, for the gas phase,

$$\hat{g}_{\text{H}_2\text{O}(\text{g})}(T, P, X_{\text{H}_2\text{O}}) = \bar{g}_{\text{H}_2\text{O}(\text{g})}(T, P) + \bar{R}T \ln X_{\text{H}_2\text{O}}. \quad (\text{C})$$

Assuming the gas phase to consist of only water vapor, i.e., $X_{\text{H}_2\text{O},\ell} = 1$, using Eqs. (A)–(C),

$$\bar{g}_{\text{H}_2\text{O}(\ell)} + \bar{R}T \ln X_{\text{H}_2\text{O}(\ell)} = \hat{g}_{\text{H}_2\text{O}(\text{g})}(T, P, 1). \quad (\text{D})$$

If we assume the boiling point to be 100°C ,

$$\begin{aligned} \hat{g}_{\text{H}_2\text{O}(\text{g})}(373 \text{ K}, 100 \text{ kPa}, 1) &= \bar{g}_{\text{H}_2\text{O}(\text{g})}(373 \text{ K}, 100 \text{ kPa}) \\ &= \bar{h}_{\text{H}_2\text{O}(\text{g})}(373 \text{ K}, 100 \text{ kPa}) - 373 \times \bar{s}_{\text{H}_2\text{O}(\text{g})}(373 \text{ K}, 100 \text{ kPa}) + 0 \\ &= 2676.1 \times 18.02 - 373 \times 7.3549 \times 18.02 = -1212 \text{ kJ kmole}^{-1}. \end{aligned} \quad (\text{E})$$

In the liquid state, $X_{\text{H}_2\text{O},\ell} = 0.92$, and using Eq. (B),

$$(373 \text{ K}, 100 \text{ kPa}, 0.92) = \bar{g}_{\text{H}_2\text{O}(\ell)}(373 \text{ K}, 100 \text{ kPa}) + 8.314 \times 373 \times \ln 0.92, \text{ and} \quad (\text{F})$$

$$\begin{aligned} \bar{g}_{\text{H}_2\text{O}(\ell)}(373 \text{ K}, 100 \text{ kPa}) &= \bar{h}_{\text{H}_2\text{O}(\ell)} - T \bar{s}_{\text{H}_2\text{O}(\ell)} \\ 419.04 \times 18.02 - 373 \times 1.3069 \times 18.02 &= -1212 \text{ kJ kmole}^{-1}. \end{aligned} \quad (\text{G})$$

Using Eqs. (E)–(G),

$$\begin{aligned} \hat{g}_{\text{H}_2\text{O}(\ell)}(373 \text{ K}, 100 \text{ kPa}, 0.92) &= -1212 - 8.314 \times 373 \ln 0.92 = -1407.6 \text{ kJ kmole}^{-1}, \\ \text{i.e.,} \end{aligned}$$

$$\hat{g}_{\text{H}_2\text{O}(\ell)} - \hat{g}_{\text{H}_2\text{O}(\text{g})} = -1470.6 - (-1212) = 258.6 \text{ kJ kmole}^{-1}.$$

The partial molal Gibbs free energy of the liquid phase water is lower than in the gas phase, since the water mole fraction in the liquid phase is lower than unity. The liquid temperature must be increased in order to raise the value of $\hat{g}_{\text{H}_2\text{O}(\ell)}$ so that it equals that of the vapor phase water.

In this context assume that the boiling point T_{BP} equals 110°C or 383 K. In that case, for the liquid phase water, Eq. (E) yields

$$\hat{g}_{\text{H}_2\text{O}(\ell)} (383 \text{ K}, 100 \text{ kPa}, 0.92) = \bar{g}_{\text{H}_2\text{O}(\ell)} (383 \text{ K}, 100 \text{ kPa}) + 8.314 \times 383 \times \ln 0.92. \quad (\text{H})$$

The Gibbs energy of liquid water at 383 K and 100 kPa is unavailable from the tables, since this is a superheated vapor state for pure water. The Gibbs energy of saturated liquid water at 383 K is available at a pressure of 143 kPa, i.e.

$$\begin{aligned} \bar{g}_{\text{H}_2\text{O}(\ell)} (483 \text{ K}, 143 \text{ kPa}) &= \bar{h}_{\text{H}_2\text{O}(\ell)} - T \bar{s}_{\text{H}_2\text{O}(\ell)} \\ &= 461.3 - 383 \times 1.4185 = -81.99 \text{ kJ kg}^{-1} = -1477.5 \text{ kJ kmole}^{-1}. \quad (\text{J}) \end{aligned}$$

We will use the relation

$$dg_T = v dP. \quad (\text{K})$$

Assuming the liquid to be incompressible, and integrating Eq. (K) between the limits (T, P^{sat}) and (T, P) , for the hypothetical liquid water state,

$$\bar{g}_{\text{H}_2\text{O}(\ell)} (T, P) - g_f(T, P^{\text{sat}}) = \bar{v}_f (P - P^{\text{sat}}).$$

where for water $\bar{v}_f = 0.018 \text{ m}^3 \text{ kmole}^{-1}$ at 373 K. Thus

$$\begin{aligned} \bar{g}_{\text{H}_2\text{O}(\ell)} (383 \text{ K}, 100 \text{ kPa}) &= \bar{g}_f(383 \text{ K}, 143 \text{ kPa}) + 0.018 \times (100 - 143) \\ &= -1477.5 + 0.018 \times (100 - 143) = -1478.2 \text{ kJ kmole}^{-1}, \text{ i.e.}, \quad (\text{L}) \end{aligned}$$

It is seen that $v_f (P - P^{\text{sat}})$ term is negligible. Hence

$$\bar{g}_{\text{H}_2\text{O}(\ell)} (T, P) \approx \bar{g}_f (T, P^{\text{sat}}) = -1477.5 \text{ kJ kmole}^{-1}. \quad (\text{K})$$

Using Eq. (B), the partial molal Gibbs function of liquid water can be determined, i.e.,

$$\hat{g}_{\text{H}_2\text{O}(\ell)} (383 \text{ K}, 100 \text{ kPa}, 0.92) = -1476.7 + \bar{R} T \ln (0.92) = -1742 \text{ kJ kmole}^{-1}. \quad (\text{M})$$

For the gaseous water,

$$\hat{g}_{\text{H}_2\text{O}(\text{g})} (383 \text{ K}, 100 \text{ kPa}) = \bar{g}_{\text{H}_2\text{O}(\text{g})} (383 \text{ K}, 100 \text{ kPa}) + \bar{R} T \ln (1).$$

In the gaseous state, water is superheated, and from the tables

$$\hat{g}_{\text{H}_2\text{O}(\text{g})} (383 \text{ K}, 100 \text{ kPa}) = 2696.4 \times 18.02 - 383 \times 7.41 \times 18.02 = -2580.5 \text{ kJ kmole}^{-1}. \quad (\text{N})$$

Therefore,

$$\hat{g}_{\text{H}_2\text{O}(\ell)}(383 \text{ K}, 100 \text{ kPa}, 0.92) - \hat{g}_{\text{H}_2\text{O}(\text{g})}(383 \text{ K}, 100 \text{ kPa}) = 838 \text{ kJ kmole}^{-1}.$$

Using Eqs. (H) and (N) we can interpolate for the temperature at which $(\hat{g}_{\text{H}_2\text{O}(\ell)} - \hat{g}_{\text{H}_2\text{O}(\text{g})}) = 0$. That temperature is 102.2°C.

Remarks

We have assumed the ideal solution model applies in the liquid phase. This model assumes that the attractive forces between water–water molecules equal those between water–salt molecules. Therefore, the change in the boiling temperature of water in the mixture compared to that of pure water is uninfluenced by attractive forces.

When additional salt is introduced into the solution the mole fraction of liquid water is reduced. At phase equilibrium, the random condensation rate of a component k of a mixture must equal the random evaporation of that component from the liquid phase. The surface of a mass of pure water exposed to the gas phase contains only liquid water molecules, and the condensation and evaporation rates equal one another at a gas–phase pressure of 100 kPa at a temperature of 373 K. In case of salt water the same area will accommodate a smaller number of liquid water molecules (due to the presence of salt molecules), which reduces the evaporation rate. Phase equilibrium considerations imply that a smaller number of vapor molecules consequently condense, and the vapor pressure at 373 K is lower than 100 kPa. In order to achieve the same vapor pressure as is generated by the pure component, the liquid temperature must be raised as salt is added to water in order for the same number of molecules to evaporate as for the pure component. (Similar arguments apply for the depression of the freezing point of a salt–water solution with salt addition).

We will now obtain a simple relation for change in boiling point when solute is added in a solvent. The application of Raoult's law yields,

$$P_{\text{H}_2\text{O}}^{\text{sat}} = (P/X_{k(\ell)}) \quad (\text{O})$$

Recall from Chapter 7 (Clausius Clapeyron relation) that we can approximately express $P_{\text{H}_2\text{O}}^{\text{sat}}$ in the form

$$\ln P_{\text{H}_2\text{O}}^{\text{sat}} = A - B/T. \quad (\text{P})$$

Employing Eqs. (O) and (P),

$$T = B/(A - \ln(P/X_{k(\ell)})). \quad (\text{Q})$$

For the pure component $X_{k(\ell)}=1$, and

$$T_{\text{pure}} = B/(A - \ln(P)). \quad (\text{R})$$

Using Eqs. (Q) and (R),

$$(1/T_{\text{pure}} - 1/T) = (1/B) \ln X_{k(\ell)}. \quad (\text{S})$$

Since $T = T_{\text{pure}} + \delta T$, and $\delta T/T_{\text{pure}} \ll 1$, the LHS of the above relation can be expanded in a binomial series. Retaining only the first order terms, Eq. (S) yields

$$\delta T = -(T_{\text{pure}}^2/B) \ln X_{k(\ell)} \quad (\text{T})$$

Recall from the Clausius Clapeyron relation, Chapter 7 that $B = h_{\text{fg}}/R$. Therefore,

$$\delta T = -(T_{\text{pure}}^2 R/h_{\text{fg}}) \ln X_{k(\ell)}. \quad (\text{U})$$

In case of water $B = 5205.2 \text{ K}$ and $T_{\text{pure}} = 373 \text{ K}$. For the case $X_{k(\ell)} = 0.92$, $\delta T = 2.23 \text{ K}$, i.e., the boiling temperature $T_{\text{BP}} = 102.3 \text{ C}$.

At a specified pressure, the boiling temperature is increased by the amount ΔT . In the current example, the salt concentration is much less compared to water. Thus $X_{\text{H}_2\text{O}(\ell)} = 1 - X_{\text{salt}}$, $X_{\text{salt}} \ll 1$, then $\ln X_{\text{H}_2\text{O}(\ell)} = \ln(1 - X_{\text{salt}}) \approx -X_{\text{salt}}$. Using this result in Eq. (U),

$$\delta T = (T_{\text{pure}}^2 R/h_{\text{fg}}) X_{\text{salt}}, \quad (\text{V})$$

Sometimes we write $\Delta T = k_b M_{\text{solute}}$, where M_{solute} is the molality of the solution (Eq.(1e), Chapter 8). Comparing this empirical expression with Eq. (V) and replacing the molal fraction with molality (See Example 1 in Chapter 8), we can show that

$$k_b = R T_{\text{pure}}^2 / (1000 \times h_{\text{fg}}) = (8.314/18.02) \times 373^2 / (1000 \times 2257) = 0.51 \text{ (W)}$$

Since gas phase consists of only H_2O , the salt water is purified by distillation process.

The anti-freeze in your car consists of glycol and water solution. The glycol is almost non-volatile while water is volatile. Thus we can use Eq. (U) to determine the rise in boiling temperature with addition of glycol. The freezing point depression with addition of salt can also be determined using similar derivation.

Example 2

A solution consists of 40% methanol (species 1) and 60% water (species 2). Assume that methanol is completely miscible in water and that the solution behaves according to Raoult's Law. The saturation pressure correlations for the pure components are:

$$\ln p_1^{\text{sat}} \text{ (mm of Hg)} = 20.61 - 4719.2/T \text{ K}, \text{ and} \quad (\text{A})$$

$$\ln p_2^{\text{sat}} \text{ (mm of Hg)} = 20.60 - 5205.2/T \text{ K}. \quad (\text{B})$$

If the temperature is maintained at 20°C , at what pressure will a vapor bubble begin to fall? (This pressure is the vapor pressure at 20°C and the pressure and temperature specify the saturated liquid state.)

At this pressure and at 20°C , determine the quality W , i.e., the ratio of moles of vapor in the vapor-liquid mixture, and the vapor-phase composition.

At 20°C , what is the pressure at which virtually the entire liquid has vaporized? Determine the liquid composition and the quality at this pressure.

Solution

Water is a low volatile substance and methanol is highly volatile. At 20°C a vapor bubble first appears in pure water at $p_2^{\text{sat}} = 17.03 \text{ mm of (0.0224 bars)}$, while for methanol it appears at a higher pressure $p_1^{\text{sat}} = 90.33 \text{ mm of Hg (0.119 bars)}$.

However we are interested in determining the pressure at which bubble is formed from a liquid mixture. A two-phase mixture forms when a bubble embryo first appears in the continuous mother phase of liquid, and Raoult's Law can be applied at this point. Applying Raoult's Law for each component in the mixture,

$$p_1 = X_{1(l)} P_1^{\text{sat}}, \quad (\text{C})$$

$$p_2 = X_{2(l)} P_2^{\text{sat}} \quad (\text{D})$$

Using Eq. (A), at $T = 20^\circ\text{C}$, $P_1^{\text{sat}} = 90.33$ mm of Hg, (0.119 bar) i.e., from eq. (C)

$$p_1 = 0.4 \times 90.33 = 36.13 \text{ mm of Hg} (0.048 \text{ bars}). \quad (\text{E})$$

Similarly from Eq.(D)

$$p_2 = 0.6 \times 17.03 = 10.22 \text{ mm of Hg} (0.013 \text{ bars}). \quad (\text{F})$$

Adding Eqs. (E) and (F), the pressure at which a vapor bubble forms

$$P = p_1 + p_2 = 46.35 \text{ mm of Hg} (0.061 \text{ bars}). \quad (\text{G})$$

Generalizing the result for a multicomponent mixture

$$P = \sum X_{k(l)} P_k^{\text{sat}} (T)$$

Since this state ($P, 20^\circ\text{C}$) lies on the saturated liquid line, at this pressure, the quality $W = 0$.

$$p_1 = X_1 P, \quad (\text{H})$$

where X_1 is the vapor phase mole fraction of species 1. From Eqs. (E), (G), and (H),

$$X_1 = 36.13 \div 46.35 = 0.78. \quad (\text{I})$$

Similarly,

$$X_2 = 10.22 \div 46.35 = 0.22. \quad (\text{J})$$

The vapor phase has a different composition as compared to the liquid composition.

Generalizing the result for a multicomponent mixture

$$X_k = X_{k(l)} P_k^{\text{sat}} / \sum X_{k(l)} P_k^{\text{sat}}. \quad (\text{K})$$

Applying Raoult's law,

$$X_1 = (X_{1(l)} P_1^{\text{sat}}) / (X_{1(l)} P_1^{\text{sat}} + X_{2(l)} P_2^{\text{sat}}), \text{ and} \quad (\text{L})$$

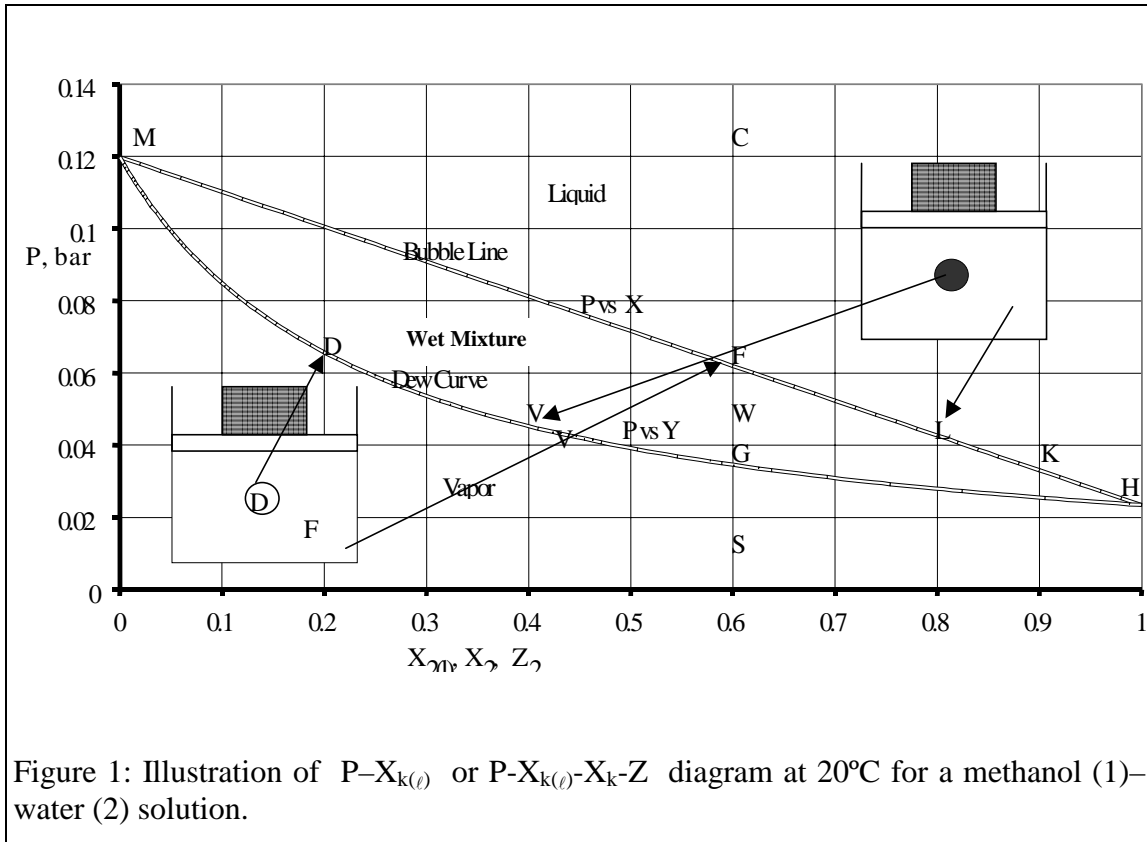
$$X_2 = (X_{2(l)} P_2^{\text{sat}}) / (X_{1(l)} P_1^{\text{sat}} + X_{2(l)} P_2^{\text{sat}}), \text{ i.e.,} \quad (\text{M})$$

When almost the entire liquid is vaporized $X_1 = 0.4$ and $X_2 = 0.6$, and from Eqs. (L) and (M) we have

$$X_{1(l)} = 0.112, X_{2(l)} = 0.888, \text{ and}$$

$$P = (X_{1(l)} P_1^{\text{sat}} + X_{2(l)} P_2^{\text{sat}}) = 0.112 \times 90.33 + 0.888 \times 17.03 = 25.24 \text{ mm of Hg.}$$

The last liquid drop contains 11% methanol and 89% water. One can alter the



liquid composition and obtain plots of P vs $X_{H_2O(l)}$ as shown by curve MFLKH in Figure 1.

Generalizing for K components, one can solve for $X_{k(P)}$ using the K linear relations (Eqs. (K)) and the known vapor phase mole fractions, X_k . At the saturated vapor state the quality $W=1$.

Remarks

Consider a 40% methanol and 60% water mixture at 20 °C in a PCW assembly so that pressure is at 0.132 bars (State C). As we start slowly removing smaller weights one after another, the first vapor bubble (embryo phase) appears in the liquid (mother phase) at a pressure of 46.35 mm of Hg (or 0.061 bars, Figure 1 point F). At phase equilibrium, inside that bubble, the mole fraction of water vapor is 0.22 and mole fraction of methanol is 0.78 (point D). The vapor in the embryo is still at 46.35 mm of Hg. Although water constitutes 60 % of the liquid phase (point F), it constitutes only 22 % of the vapor phase (Point D) , since it is less volatile due to a lower vapor pressure. By altering the composition, the $P-X_{k(P)}$ diagram can be obtained as M DVG H..

Now consider an 88.8% water and 11.2% methanol solution at 20°C. The first vapor bubble appears at a pressure of 24.36 mm of Hg (point K, 0.0325 bars) and the vapor composition is 60% water and 40% methanol (point G). Thus, for $X_{2(P)} = 0.6$, $P = 0.061$ bars, and $X_2 = 0.22$ while at $X_{2(l)} = 0.888$, $P = 0.0322$ bars, and $X_2 = 0.6$. As $X_{2(l)} \rightarrow 1.0$, $P \rightarrow P_2^{\text{sat}}$ (i.e., 17.03 mm of Hg or 0.0225 bars, point H). As $X_{2(l)} \rightarrow 0$ (and, consequently, $X_{1(l)} \rightarrow 1$) $P = P_2^{\text{sat}}$ (90.33 mm of Hg or 0.119 bars, point M). A line connecting the pressures through the bubble points is called the bubble line (saturated liquid line, MFKH) at which the first bubble appears

Consider a methanol–water mixture with $X_{2(l)} = 0.6$ at 20°C. The mixture is in compressed liquid state at a pressure of 100 mm of Hg (point C) (0.132 bars). As pressure is reduced below 0.061 bars (46.4 mm of Hg) (bubble pressure), say pressure of 0.0422 bars (32 mm Hg, point W), phase equilibrium requires $X_{2(l)} = 0.8$ and $X_2 = 0.43$, Representing the initial molal fraction of species 2 as Z_2 , then at “W” Figure 1

$$Z_2 = (N_2(l) + N_2(g))/N, \text{ i.e.,} \quad (\text{K})$$

Rewriting,

$$Z_2 = (X_{2(l)}N_l + X_2 N_g)/N = X_{2(l)}(1-W) + X_2W, \quad (\text{L})$$

where $W = N_g/N$ denotes the molal quality. Consequently,

$$W = (X_{2(l)} - Z_2)/(X_{2(l)} - X_2). \quad (\text{M})$$

Example 4

A fuel droplet contains a binary mixture of 60% n–heptane (species 1) and 40% hexadecane (species 2). Determine the partial pressures of the two species 297 K in air if the ambient pressure is 100 kPa. Assume that air (species 3) is insoluble in the liquid phase. The Cox–Antoine relation can be assumed to apply, i.e.,

$$\ln P_k^{\text{sat}} = E_k + F_k/(T + G_k), \quad k = 1, 2 \quad (\text{A})$$

where E_k , F_k , and G_k are constant for a specified fuel component. If the pressure is expressed in mm of Hg, $E_1 = 15.89$, $F_1 = -2911.32$, and $G_1 = -56.4$, and $E_2 = 24.66$, $F_2 = -10660.2$, and $G_2 = 54.1$ when $1 < P < 40$ mm of Hg. Determine the gas–phase composition.

Solution

Applying Raoult’s Law for miscible mixtures $p_k = x_k P_k^{\text{sat}}$, $k=1,2$, since

$$p_1 + p_2 + p_3 = P, \quad X_{1,\ell} P_1^{\text{sat}} + X_{2,\ell} P_2^{\text{sat}} + p_3 = P, \text{ i.e.,} \quad (\text{B})$$

$$p_3 = p_{\text{air}} = P - (X_{1,\ell} P_1^{\text{sat}} + X_{2,\ell} P_2^{\text{sat}}). \quad (\text{C})$$

At 20°C, $P_1^{\text{sat}} = 44.245$ mm of Hg, and $P_2^{\text{sat}} = 0.00338$ (i.e., species 2 is almost nonvaporizable). Therefore,

$$p_1 = X_{1,\ell} P_1^{\text{sat}} = 0.6 \times 44.245 = 26.55 \text{ mm of Hg, and}$$

$$p_2 = (1-X_{1,\ell}) P_2^{\text{sat}} = 0.4 \times 0.00338 = 0.001352 \text{ mm of Hg.}$$

Using Eq. (C),

$$p_{\text{air}} = 760 - (26.55 + 0.001335) = 733.45 \text{ mm of Hg, i.e.,}$$

$$X_1 = 26.55 \div 760 = 0.0349, \text{ and}$$

$$X_{\text{air}} = 733.45 \div 760 = 0.965,$$

(Since hexadecane is virtually nonvaporizing, we neglect its mole fraction.) The mass fraction of n-heptane

$$Y_1 = 0.0349 \times (7 \times 12 + 16 \times 1) \div (0.0349 \times 100 + 0.965 \times 28.97) = 0.11, \text{ i.e.,}$$

$$Y_3 = 0.89$$

The variation of the temperature of a droplet containing a binary mixture consisting of n-heptane (60 %) and hexadecane with respect to the n-heptane mole fraction is illustrated in Figure 2 at P=100 kPa.

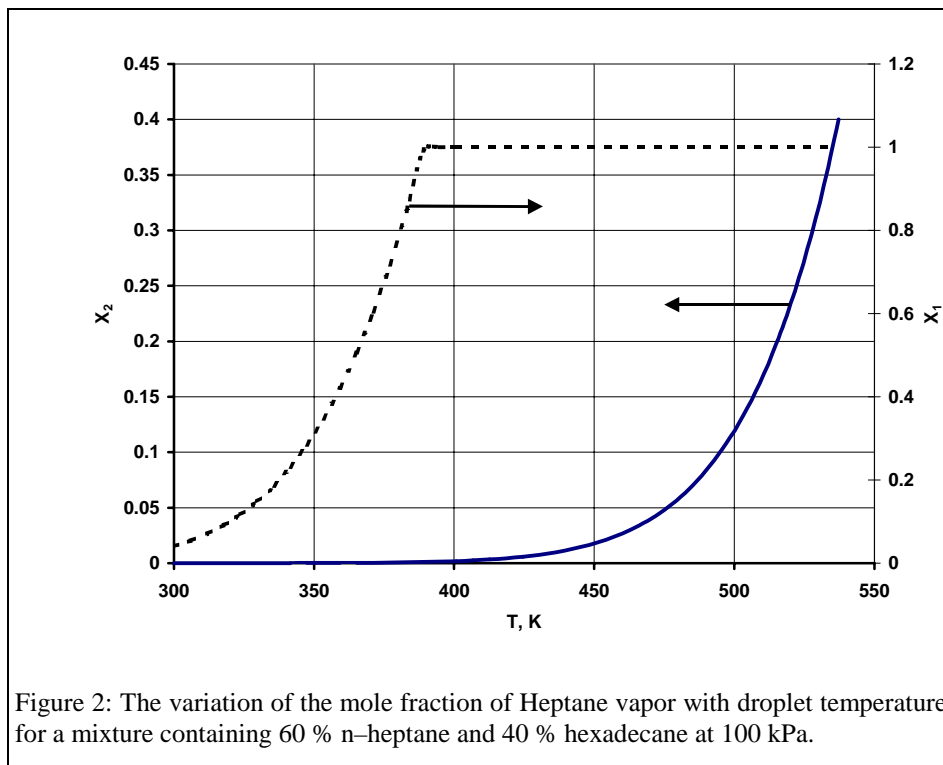


Figure 2: The variation of the mole fraction of Heptane vapor with droplet temperature for a mixture containing 60 % n-heptane and 40 % hexadecane at 100 kPa.

Example 5

A 20-liter rigid volume consists of 80% liquid and 20% vapor by mass at 111.4°C and 1.5 bar. A pin is placed on piston to prevent its motion. Gaseous nitrogen is isothermally injected into the volume until the pressure reaches 2 bar. What is the nitrogen mole fraction in the gas phase? Assume that N_2 does not dissolve in the liquid.

Discuss what happens if there is no pin during injection of N_2

Solution

$$P^{\text{sat}}(111.4\text{ C}) = 1.5\text{ bars. The total volume}$$

$$V = m_g v_g + m_f v_f = m (x v_g + (1-x) v_f) \quad (\text{A})$$

$$= m (0.2 \times 1.159 + 0.8 \times 0.001053) = m (0.233).$$

Therefore,

$$m = 20 \times 0.001 / 0.233 = 0.0858\text{ kg}$$

Using the ideal gas law for the vapor phase

$$m = V_f / v_f + (V - V_f) / (RT / P_o), \quad (\text{B})$$

$$V_f = (m - P_o V / RT) / (1/v_f - P_o / RT) \approx v_f (m - P_o V / RT). \quad (\text{C})$$

The pressure increases as additional gas is injected, thereby increasing the Gibbs energy of the liquid and vapor phases.

In case of liquid water,

$$g(T, P) = g_l(T, P^{\text{sat}}) + v_l (P - P^{\text{sat}}).$$

For an ideal gas mixture in the gas phase,

$$\hat{g}_{\text{H}_2\text{O}}(T, P, X_{\text{H}_2\text{O}}) = \bar{g}_{\text{H}_2\text{O}}(T, p_{\text{H}_2\text{O}}) = \bar{g}_{\text{H}_2\text{O}}(T, P^{\text{sat}}) + \int \bar{v}_{\text{H}_2\text{O}(\text{g})} dP = \bar{g}_g(T, P^{\text{sat}}) + \bar{R} T \ln(p_{\text{H}_2\text{O}} / P^{\text{sat}}).$$

It follows that

$$\bar{v} (P - P^{\text{sat}}) = RT \ln(p_{\text{H}_2\text{O}} / P^{\text{sat}}), \text{ or } \ln(p_{\text{H}_2\text{O}} / P^{\text{sat}}) = [v_l (P - P^{\text{sat}})] / (RT) \quad (\text{D})$$

This relation is known as the Kelvin–Helmholtz formula which shows the effect of total pressure on partial pressure of vapor.. Note that the partial pressure of H₂O is not same as saturation pressure at T

For water, $v_l = 0.001053\text{ m}^3\text{ kmole}^{-1}$, $P^{\text{sat}} = 1.5\text{ bar}$, and for this case $P = 2\text{ bar}$, and $T = 384.56\text{ K}$. Therefore, the partial pressure of H₂O in vapor phase,

$$p_{\text{H}_2\text{O}} = 1.500445\text{ bar.}$$

Consequently,

$$X_{\text{H}_2\text{O}} = 0.75022, \text{ and } X_{\text{N}_2} = 0.24798.$$

The vapor mass

$$m_v = p_v V_v / RT = p_v (V - V_f) / RT, \text{ and}$$

the liquid mass

$$m_f = V_f / v_f.$$

Adding the two masses,

$$m = p_v (V - V_f) / RT + V_f / v_f.$$

Therefore,

$$V_f = (m - p_v V / RT) / (1/v_f - p_v / RT) \approx v_f (m - p_v V / RT). \quad (\text{B})$$

Since P_v after N₂ injection $> P_v$ before N₂ injection, there should be more vapor; thus the volume of liquid decreases. . According to Le Chatelier, a composite system responds by decreasing the volume of liquid phase and, therefore, counteracts the pressure increase by increasing the volume of the vapor phase. If we ignore the term $[v_l (P - P^{\text{sat}})] / (RT)$, in Eq. (A) this implies that $p_{\text{H}_2\text{O}} = P^{\text{sat}}$ and $X_v = 0.75$.

The injection of nitrogen implies that $X_{\text{H}_2\text{O}} < 1$. Therefore, $\hat{g}_{\text{H}_2\text{O}} = \bar{g}_{\text{H}_2\text{O}}(T, P) + \bar{R} T \ln X_{\text{H}_2\text{O}}$. Since $X_{\text{H}_2\text{O}} < 1$, $\hat{g}_{\text{H}_2\text{O}} < \hat{g}_{\text{H}_2\text{O}(\ell)}(T, P)$, as long as the temperature and pressure are maintained, vaporization continues until all of the liquid vaporizes. The presence of

impurities causes the Gibbs function of the two phases to differ which causes the water molecules to cross over from the liquid into the vapor phase

Remarks

At a specified temperature, an increase in pressure causes the "g" of liquid to increase slightly. The Gibbs free energy of the vapor equals that of the liquid. If the vapor is an ideal gas, the enthalpy of the vapor will remain unchanged. The slight Gibbs energy increase must then cause the entropy of vapor to decrease which corresponds to an increase in the partial pressure of vapor.

Consider a component k of a liquid mixture that exists in equilibrium with a vapor phase that also contains a mixture of insoluble inert gases. In this case

$$\mu_{k(l)}(T,P) = \mu_{k(g)}(T, P).$$

If the vapor phase is isothermally pressurized, then

$$\mu_{k(l)}(T,P) + d\mu_{k(l)} = \mu_{k(g)}(T,P) + d\mu_{k(g)}, \quad v_{k(l)}dP_l = v_{k(g)} dP_g \quad \text{and} \quad dP_l/dP_g = v_{k(g)}/v_{k(l)}.$$

An increase in the pressure in the vapor phase requires a large change in the liquid phase pressure to ensure that liquid–vapor equilibrium is maintained.

Example 6

Consider binary vapor mixture of methanol (species 1) and water (species 2) that are assumed to be immiscible in the liquid phase. Illustrate their behavior with respect to pressure and temperature. You may assume that

$$\ln P_2^{\text{sat}} = 13.97 - 5205.2/T \text{ (K)}, \quad \text{and} \quad \text{(A)}$$

$$\ln P_1^{\text{sat}} = 13.98 - 4719.2/T \text{ (K)}. \quad \text{(B)}$$

Solution

Employing Eqs. (A) and (B), the normal boiling points of species 1 and 2 are, respectively, 64.4 and 100°C.

We will employ Raoult's Law, in which the liquid mole fractions for water and methanol are assumed to be unity, since they are immiscible. Therefore,

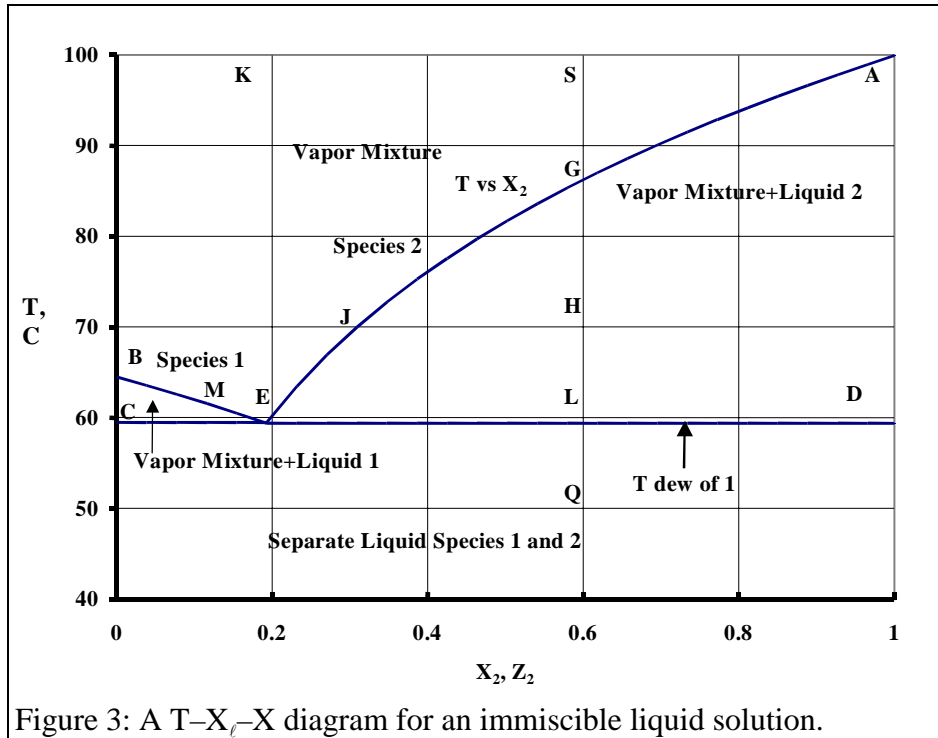


Figure 3: A $T-X_{\ell}-X$ diagram for an immiscible liquid solution.

$$P_2^{\text{sat}}(T) = X_2 P, \text{ and} \quad (\text{C})$$

$$P_1^{\text{sat}}(T) = X_1 P. \quad (\text{D})$$

Upon adding Eqs. (C) and (D), we obtain the expression

$$P_2^{\text{sat}}(T) + P_1^{\text{sat}}(T) = P. \quad (\text{E})$$

Figure 3 shows the $T- X_{k(\ell)}-X_k$ diagram.

Remarks

In case of immiscible mixtures, partial pressures are only a function of temperature alone. Irrespective of the liquid phase composition, at a specified temperature, P_2^{sat} can be obtained from Eq. (A), while P_1^{sat} can be, likewise, obtained using Eq. (B). Using Eqs. (C) and (D), we obtain the values of X_1 and X_2 for a specified pressure, and plots of temperature can be plotted with respect to composition, as shown in Figure 3. The lines BME and EJGA in that figure are called the dew lines for species 1 and 2, respectively. The region above the curve BMEJGA is the superheated vapor mixture region while that below the curve CELD is the compressed liquid region.

Consider the following scenario. A vapor mixture is contained in a piston-cylinder-weight assembly, such that $P = 1$ bar, $X_2 = 0.6$, and $T = 100^\circ\text{C}$ (cf. point S). Species 2 exists in the form of superheated vapor, since $p_2 = 0.6$ bar at $T = 100^\circ\text{C}$. The cylinder is now cooled. The saturation temperatures $T_2^{\text{sat}} = 86.5^\circ\text{C}$ at p_2

= 0.6 bar, and $T_1^{\text{sat}} = 43.87^\circ\text{C}$ at $p_1 = 0.4$ bar. The assembly contains a vapor mixture only, as long as $T > 86.5^\circ\text{C}$. As the vapor mixture is cooled, a liquid drop appears at $T = 86.5^\circ\text{C}$ (point G). If the gas phase composition is changed to $X_2 = 0.2$, in that case the first liquid drop appears at 61°C . If the mixture is cooled to 70°C (cf. point H), phase equilibrium – that is manifested in the form of Eq. (C) – implies that $X_2 = 0.3$ (cf. point J), i.e., more of species 2 must condense. It also implies that X_1 must increase to 0.7 from the initial mole fraction of 0.4. Eqs (D) and (B) dictate that $T_1^{\text{sat}} = 52^\circ\text{C}$, so that species 1 at 70°C exists in the form of a superheated vapor. Upon further cooling to 60°C , phase equilibrium requires that $X_2 = 0.19$ (cf. point E), and $T_1^{\text{sat}} = 60^\circ\text{C}$. Any further cooling causes both species 1 and 2 to condense, where the condensate phase is an immiscible binary mixture. Within the region AED (i.e., for $X_2 > 0.19$, $60 < T < 100^\circ\text{C}$), species 2 exists in both liquid and vapor forms. In region BEC ($X_2 < 0.19$, $60 < T < 64.7^\circ\text{C}$), only species 1 exists in the liquid and vapor phases. At 60°C , $X_2 = 0.19$, and both the liquid and vapor mixture coexist.

At point E there are two liquid phases and one vapor phase. According to Gibbs phase rule, $F = K + 2 - \pi = 2 + 2 - 3 = 1$. Therefore, there is one independent variable in the set (P, T, X_2). In case the pressure is fixed, then the temperature and X_1 are fixed (i.e., 60°C , and $X_2 = 0.19$) for coexistence the three phases to coexist. If the mixture is cooled from 100°C (cf. point K), species 1 condenses, increasing the mole fraction of species 2 until $X_2 = 0.19$.

Now assume that the liquid mixture is heated at the condition $X_{2(l)} = 0.6$ and $P = 1$ bar in a piston–cylinder–weight assembly. At low temperatures, the sum of the saturation pressures (cf. Eq. (E)) is insufficient to create the imposed 1 bar pressure. Therefore, at $T < 60^\circ\text{C}$ (point Q), the fluid exists as a compressed liquid. At $\approx 60^\circ\text{C}$ (cf. point L), the sum of the saturation pressures is roughly 1 bar. The temperature at this condition can be predicted using Eqs. (A), (B), and (E). Consequently, the values of X_1 and X_2 can be determined using Eqs. (C) and (D). Thus first vapor bubble at a 1 bar pressure appears at 60°C . The vapor composition can be determined by employing Eqs. (C) and (D), and at this condition is 81% and 19% for species 1 and 2, respectively. At this point there are three phases (two liquid phases, since they are immiscible, and a vapor phase). As more heat is isobarically added, the temperature cannot rise according to equation (E), but the vapor bubble can grow. If the heating process begins with 0.4 kmole of species 1 and 0.6 kmole of species 2 and vaporization occurs until the vapor phase is at state E (i.e., $T_1^{\text{sat}} = 60^\circ\text{C}$), since the vapor phase mole fraction of species 1 is 0.81, the ratio of the moles of species 2 that are vaporized to those of species 1 is $0.19 \div 0.81$. Therefore, for every 0.4 kmole of species 1 that are vaporized, the moles of species 2 that are vaporized equal $0.4 \times 0.19 \div 0.81 = 0.094$ kmole. Hence, the vapor contains 0.4 kmole of species 1 in the liquid phase and 0.094 kmole of species 2 in the vapor phase, and $0.6 - 0.094 = 0.506$ kmole of species 2 remain in the liquid phase. Once $T > 60^\circ\text{C}$, further vaporization of species 2 occurs, thereby increasing the mole fraction of species 2 in the vapor state, and it is possible to determine the value of X_2 along the curve EJGA. As the temperature reaches 86.5°C (cf. point G), all of the initial 0.6 kmole of species 2 in the liquid phase vaporize so that $X_2 = 0.6$.