Solutions to Exercises: Chapter 7

7.1 The heat of vaporization of hexane is 30.8 kJ. mol^{-1}. The boiling point of hexane at a pressure of 1.00 atm is 68.9°C. What will the boiling point be at a pressure of 0.50 atm?

Answer

From the Clausius-Clapeyron equation we see that:

$$\ln \frac{p_1}{p_2} = \frac{H_{vap}}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

In this problem, $p_1 = 0.50$ atm, $p_2 = 1.0$ atm, $H_{vap} = 30.8$ kJ.mol^{-1}, $T_2 = 342.0$K and we want to obtain T_1. Thus:

$$\ln \frac{0.5}{1.0} = \frac{30.8 \times 10^3 \text{J.mol}^{-1}}{8.314 \text{J.K}^{-1}} \left[\frac{1}{342.0} - \frac{1}{T_1} \right]$$

Solving for T_1 gives : $T_1 = 321.0$K $= 48.85$°C

7.2 The atmospheric pressure decreases with height. The pressure at a height h above sea level is given approximately by the barometric formula $P = P_0 \, e^{-Mgh/RT}$, in which M=0.0289 kg. mol^{-1}, and g=9.81 ms^{-2}. Assume that the enthalpy of vaporization of water is $H_{vap} = 40.6$ kJ mol^{-1} and predict at what temperature water will boil at a height of 2.5 miles.

Answer

Using the formula $P = P_0 \, e^{-Mgh/RT}$, we can determine the pressure at an altitude of 2.5 miles = 4.0 km.

$$P = 1.0\text{atm} \, e^{-\frac{(0.0289\text{kg.mol}^{-1})(9.8\text{m.s}^{-2})4000\text{m}}{(8.314\text{J.K}^{-1}.\text{mol}^{-1})(298.15\text{K})}} = 0.62\text{atm}$$
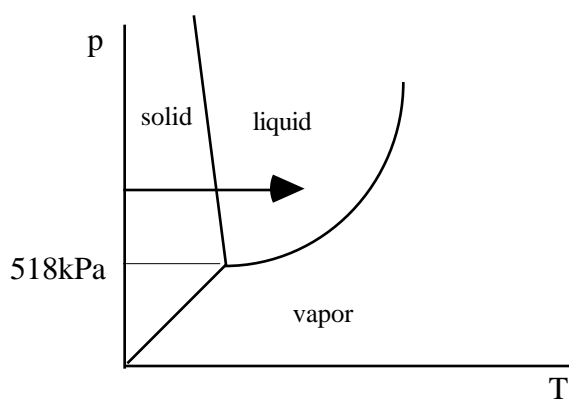
Using the Clausius-Clapeyron equation (as in Exc. 7.1) we see that:

$$\ln \frac{0.62}{1.0} = \frac{40.6 \times 10^3 \text{J.mol}^{-1}}{8.314 \text{J.K}^{-1}} \left[\frac{1}{373.15} - \frac{1}{T_1} \right]$$

Solving for $T_1 = 360.0K = 86.85°C$ as the boiling point of water at an altitude of 4.0 km :

7.3 At atmospheric pressure, CO_2 turns from solid to gas, i.e., it sublimates. Given that the triple point of CO_2 is at T=216.58K and p=518.0kPa, how would obtain liquid CO_2 ?

Answer

From the phase diagram shown above, we see that to convert CO_2 from a solid to a liquid, the temperature should be raised at a pressure above 518 kPa.

7.4 In a two-component system, what is the maximum number of phases that can be in equilibrium ?

Answer   According to the Gibbs phase rule, $f = C-P+2$. In this case, C=2. Maximum phases implies f=0. Hence, P=4.

7.5 Determine the number of degrees of freedom for the following systems:
    (a) Solid CO_2 in equilibrium with CO_2 gas.
    (b) An aqueous solution of fructose
    (c) $Fe(s) + H_2O(g) ==== FeO(s) + H_2(g)$

Answer

(a) C=1, P=2. Hence f = C-P+2 = 1

(b) Since fructose does not dissociate we have two components, water and fructose. Thus, C=2, P=1 and f= C-P+2 = 3

(c) $Fe(s) + H_2O(g) ==== FeO(s) + H_2(g)$
Since there is one reaction, R=1. Also, C =4 , P = 2.
Hence, f = C-P+2-R = 3
But amounts of FeO and H_2 are generated only by this reaction, they are not independent, their amounts are in the ration 1:1. Hence there is one less degree of freedom.

7.6 Qualitative figures of the azeotropes in Table 7.2.

Answer   All except HCl and HNO_3 are minimum-boiling-point azeotropes.

7.7 In Fig. 7.8, show that PA+PB+PC=1 for any point P.
Answer
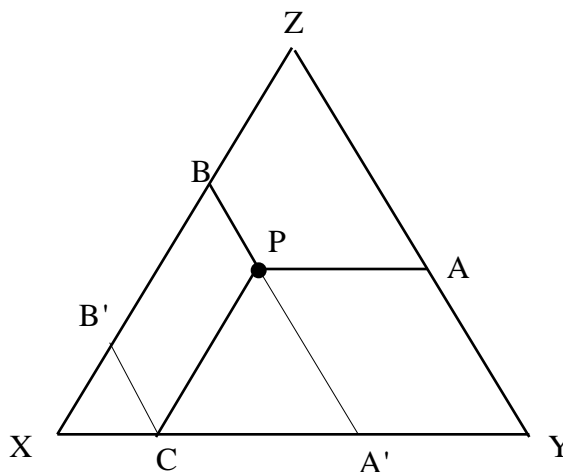

Extrapolate BP to intersect XY at A'. Then, from C draw a parallel to BP to intersect XZ at B'. Then, PA=A'Y, PC=A'C, and PB=CB'=CX. Hence,
$$PA+PB+PC = A'Y+A'C+CX = 1.$$

7.8 In the triangular representation of the mole fractions of ternary solution, show that along the line joining an apex and a point on the opposite side, the ratio of two of the mole fractions remain constant while mole fraction of the third component changes.

Answer
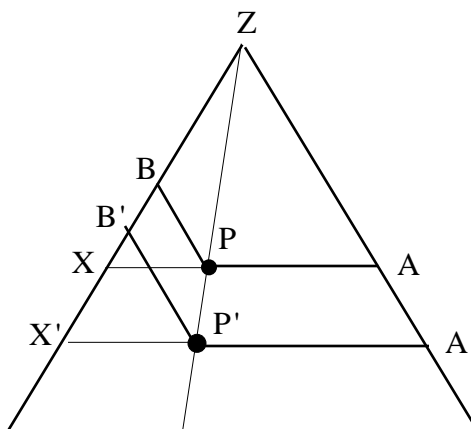
We need to show that: $\dfrac{AP}{BP} = \dfrac{A'P'}{B'P'}$. This can be seen as follows:

Extend AP to intersect the opposite side at X; similarly extend A'P' to X'. Then APZ and A'P'Z are similar triangles. Hence: $\dfrac{AP}{A'P'} = \dfrac{PZ}{P'Z}$.

Similarly, triangles BPZ and B'P'Z are similar. Hence: $\dfrac{BP}{B'P'} = \dfrac{PZ}{P'Z}$

Hence $\dfrac{AP}{A'P'} = \dfrac{BP}{B'P'}$, from which we get the needed result: $\dfrac{AP}{BP} = \dfrac{A'P'}{B'P'}$

7.9 On triangular graph, mark points representing the following compositions:

(a) $x_A = 0.2$, $x_B = 0.4$, $x_C = 0.4$

(b) $x_A = 0.5$, $x_B = 0$, $x_C = 0.5$

(c) $x_A = 0.3$, $x_B = 0.2$, $x_C = 0.5$

(d) $x_A = 0$, $x_B = 0$, $x_C = 1.0$

Answer

7.10 Obtain the lever rule (7.4.6) from (7.4.5).

$$
\begin{array}{ccc}
\text{L} & \text{S} & \text{P} \\
\vdash\!\!\!\!-\!\!\!\!-\!\!\!\!-\!\!\!\!-\!\!\!\!-\!\!\!\!+\!\!\!\!-\!\!\!\!-\!\!\!\!-\!\!\!\!-\!\!\!\!-\!\!\!\!-\!\!\!\!-\!\!\!\!-\!\!\!\!\dashv \\
V_l & V_s & V_g
\end{array}
$$
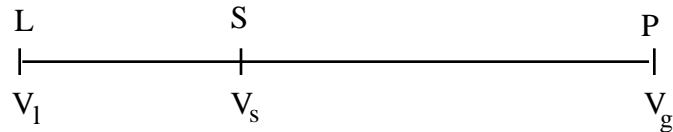
Answer

x is the mole fraction of the gas. $V_s = xV_g + (1-x)V_l$

Eqn. (7.4.5) is $x = \dfrac{SL}{LP}$. Hence $(1-x) = 1 - \dfrac{SL}{LP} = \dfrac{LP - SL}{LP} = \dfrac{SP}{LP}$

Hence $\dfrac{1-x}{x} = \dfrac{SP}{SL}$. This leads to (7.4.6): $x(SP) = (1-x)SL$.

7.11 When the der Waals equation in written in terms of the reduced variables p_r, V_r and T_r, the critical pressure, temperature and volume are equal to one. Consider small deviations from the critical point, $p_r = 1 + \delta p$ and $V_r = 1 + \delta V$ on the critical isotherm. Show that δV is proportional to $(\delta p)^{1/3}$. This corresponds to the classical prediction (7.5.2).

Answer

The reduced van der Waals equation is:

$$
p_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}
$$

At the critical point, $\left(\dfrac{\partial p}{\partial V}\right)_c = \left(\dfrac{\partial^2 p}{\partial V^2}\right)_c = 0$. The Taylor expansion of p as function of V at the critical point ($V_r = 1$, $p_r = 1$) for a deviation δV is:

$$
p(1 + \delta V) = 1 + \left(\frac{\partial p}{\partial V}\right)_c \delta V + \frac{1}{2}\left(\frac{\partial^2 p}{\partial V^2}\right)_c (\delta V)^2 + \frac{1}{2.3}\left(\frac{\partial^3 p}{\partial V^3}\right)_c (\delta V)^3 + \ldots
$$

Since the first two derivatives are zero, to the leading order:

$$
\delta p = \frac{1}{6}\left(\frac{\partial^3 p}{\partial V^3}\right)(\delta V)^3
$$

From which it follows that: $\delta V = 6 / \left(\dfrac{\partial^3 p}{\partial V^3}\right)^{1/3} (\delta p)^{1/3}$.