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:

\[
\ln \left( \frac{p_1}{p_2} \right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

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

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

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 \(P = P_0 e^{-\frac{Mgh}{RT}}\), in which \(M=0.0289\) kg. mol\(^{-1}\), and \(g = 9.81\) ms\(^{-2}\). Assume that the enthalpy of vaporization of water is \(\Delta H_{\text{vap}} = 40.6\) kJ mol\(^{-1}\) and predict at what temperature water will boil at a height of 2.5 miles.

Answer

Using the formula \(P = P_0 e^{-\frac{Mgh}{RT}}\), 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:

\[
\ln \left( \frac{0.62}{1.0} \right) = \frac{40.6 \times 10^3 \text{J.mol}^{-1}}{8.314 \text{J.K}^{-1}} \left( \frac{1}{373.15} - \frac{1}{T_1} \right)
\]
Solving for $T_1 = 360.0 \, \text{K} = 86.85^\circ \text{C}$ as the boiling point of water at an altitude of 4.0 km:

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### 7.3 At atmospheric pressure, CO$_2$ turns from solid to gas, i.e., it sublimes. Given that the triple point of CO$_2$ is at $T=216.58 \, \text{K}$ and $p=518.0 \, \text{kPa}$, how would obtain liquid CO$_2$?

**Answer**

![Phase diagram](image)

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.

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### 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, $P=4$.

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### 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$_2$O(g) $\rightleftharpoons$ 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) \( \text{Fe}(s) + \text{H}_2\text{O}(g) \rightleftharpoons \text{FeO}(s) + \text{H}_2(g) \)
Since there is one reaction, \( R=1 \). Also, \( C = 4 \), \( P = 2 \).
Hence, \( f = C-P+2-R = 3 \)
But amounts of \( \text{FeO} \) and \( \text{H}_2 \) are generated only by this reaction, they are not independent, their amounts are in the ratio 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**

![Triangular Representation Diagram](image)

We need to show that: \( \frac{AP}{BP} = \frac{A'P'}{B'P'} \). 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: \( \frac{AP}{A'P'} = \frac{PZ}{P'Z} \).

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

Hence \( \frac{AP}{A'P'} = \frac{BP}{B'P'} \), from which we get the needed result: \( \frac{AP}{BP} = \frac{A'P'}{B'P'} \).

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).

\[
\begin{array}{ccc}
\text{L} & \text{S} & \text{P} \\
V_1 & V_s & V_g
\end{array}
\]

\textbf{Answer}

\(x\) is the mole fraction of the gas. \(V_s = xV_g + (1-x)V_1\)

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

\[\frac{1 - x}{x} = \frac{SP}{SL}\]

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 \(\delta V\) is proportional to \((\delta p)^{1/3}\). This corresponds to the classical prediction (7.5.2).

\textbf{Answer}

The reduced van der Waals equation is:

\[p_r = \frac{8T_r}{3V_r} - \frac{3}{V_r^2}\]

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

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

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