Solutions Manual to Accompany

Molecular Thermodynamics of Fluid-Phase Equilibria

Third Edition

John M. Prausnitz
Rüdiger N. Lichtenthaler
Edmundo Gomes de Azevedo

Prentice Hall PTR
Upper Saddle River, New Jersey 07458
http://www.phptr.com

Prentice Hall, Inc.
Upper Saddle River, NJ 07458

Electronic Typesetting: Edmundo Gomes de Azevedo

Printed in the United States of America
10 9 8 7 6 5 4 3 2

ISBN 0-13-018388-1

Prentice-Hall International (UK) Limited, *London*
Prentice-Hall of Australia Pty. Limited, *Sydney*
Prentice-Hall Canada Inc., *Toronto*
Prentice-Hall Hispanoamericana, S.A., *Mexico*
Prentice-Hall of India Private Limited, *New Delhi*
Prentice-Hall of Japan, Inc., *Tokyo*
Simon & Schuster Asia Pte. Ltd., *Singapore*
Editora Prentice-Hall do Brasil, Ltda., *Rio de Janeiro*

CONTENTS

SOLUTIONS TO PROBLEMS

CHAPTER 2

1. From problem statement, we want to find $(\partial P / \partial T)_v$.

Using the product-rule,

$$\left(\frac{\partial P}{\partial T}\right)_v = -\left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial P}{\partial v}\right)_T$$

By definition,

$$\alpha_P = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P$$

and

$$\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$$

Then,

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{\alpha_P}{\kappa_T} = \frac{1.8 \times 10^{-5}}{5.32 \times 10^{-6}} = 33.8 \text{ bar } ^\circ\text{C}^{-1}$$

Integrating the above equation and assuming α_P and κ_T constant over the temperature range, we obtain

$$\Delta P = \frac{\alpha_P}{\kappa_T} \Delta T$$

For $\Delta T = 1°\text{C}$, we get

$$\Delta P = \mathbf{33.8\ bar}$$

2. Given the equation of state,

$$P\left(\frac{V}{n}-b\right)=RT$$

we find:

$$\left(\frac{\partial S}{\partial V}\right)_T=\left(\frac{\partial P}{\partial T}\right)_V=\frac{nR}{V-nb}$$

$$\left(\frac{\partial S}{\partial P}\right)_T=-\left(\frac{\partial V}{\partial T}\right)_P=-\frac{nR}{P}$$

$$\left(\frac{\partial U}{\partial V}\right)_T=T\left(\frac{\partial P}{\partial T}\right)_V-P=0$$

$$\left(\frac{\partial U}{\partial P}\right)_T=\left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial P}\right)_T=0$$

$$\left(\frac{\partial H}{\partial P}\right)_T=-T\left(\frac{\partial V}{\partial T}\right)+V=nb$$

For an isothermal change,

$$\Delta S=\int_{V_1}^{V_2}\left(\frac{\partial P}{\partial T}\right)_V dV=nR\ln\frac{V_2-nb}{V_1-nb}$$

$$=-nR\ln\frac{P_1}{P_2}$$

$$\Delta U=\int_{P_1}^{P_2}\left[\left(-\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial P}\right)_T\right]dP=0$$

$$\Delta H=\int_{P_1}^{P_2}\left[-T\left(\frac{\partial V}{\partial T}\right)_P+V\right]dP=nb\left(P_2-P_1\right)$$

$$\Delta G=\Delta H-T\Delta S=nb\left(P_2-P_1\right)-nRT\ln\left(\frac{P_1}{P_2}\right)$$

$$\Delta A=\Delta U-T\Delta S=-nRT\ln\left(\frac{P_1}{P_2}\right)$$

3. This entropy calculation corresponds to a series of steps as follows:

$$s_3 = \Delta s_{1\to 2} + \Delta s_{2\to 3} + s_1$$

$$\Delta s_{1\to 2} = \Delta_{\text{vap}} s = \frac{\Delta_{\text{vap}} h}{T} = \frac{(2436)\times(18.015)}{298.15} = 147.19 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta s_{2\to 3} = \int_{P_2}^{P_3} \left[-\left(\frac{\partial v}{\partial T} \right)_P \right] dP$$

Because $v = \frac{RT}{P}$ (ideal gas),

$$\begin{aligned} \Delta s_{2\to 3} &= -R \ln\left(\frac{P_3}{P_2} \right) \\ &= -(8.31451)\times \ln\left(\frac{1.0}{0.03168} \right) \\ &= -28.70 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} s_3 &= s^0(\text{H}_2\text{O}, \text{vapor}) \\ &= 147.19 - 28.70 + 69.96 \\ &= \mathbf{188.45 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

4. Because $\alpha = \frac{RT}{P} - \upsilon$,

$$P = \frac{RT}{\alpha + \upsilon} = \frac{RT}{2 - 3/\upsilon^2 + \upsilon}$$

or

$$P = \frac{RT\upsilon^2}{2\upsilon^2 - 3 + \upsilon^3}$$

$$\left(\frac{\partial P}{\partial \upsilon}\right)_T = -\frac{RT\upsilon\,(\upsilon^3 + 6)}{(2\upsilon^2 - 3 + \upsilon^3)^2}$$

As $\upsilon = 2.3$ L mol^{-1}, T = 373.15 K, R = 0.0831451 bar L K^{-1} mol^{-1}, and molar mass is 100 g mol^{-1},

$$\left(\frac{\partial P}{\partial \upsilon}\right)_T = -3.3245 \text{ bar L}^{-1} \text{ mol} = -3.3245 \times 10^8 \text{ Pa m}^{-3} \text{ mol}$$

$$w^2 = -g_c k \upsilon^2 \left(\frac{\partial P}{\partial \upsilon}\right)_T$$

$$= -\left(1\,\frac{\text{kg m}}{\text{N s}^2}\right) \times (1.4) \times \left(\frac{1}{100 \times 10^{-3}}\,\frac{\text{mol}}{\text{kg}}\right) \times \left(2.3 \times 10^{-3}\,\frac{\text{m}^3}{\text{mol}}\right)^2 \times \left(-3.3245 \times 10^8\,\frac{\text{N mol}}{\text{m}^2\text{ m}^3}\right)$$

$$= 24{,}621 \text{ m}^2 \text{ s}^{-2}$$

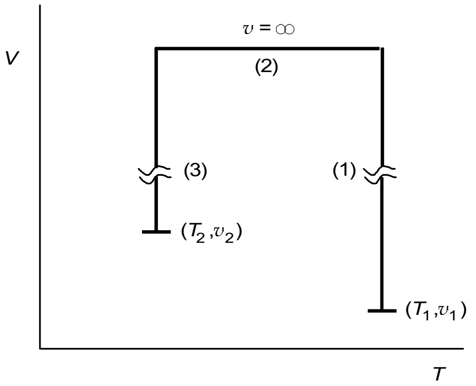
$$\boldsymbol{w = 157 \text{ m s}^{-1}}$$

5. Assume a three-step process:

(1) Isothermal expansion to $v = \infty$ (ideal gas state)

(2) Isochoric (v is constant) cooling to T_2

(3) Isothermal compression to v_2



For an isentropic process,

$$\Delta s = \Delta s_1 + \Delta s_2 + \Delta s_3 = 0$$

Because $s = s(v, T)$,

$$ds = \left(\frac{\partial s}{\partial v}\right)_T dv + \left(\frac{\partial s}{\partial T}\right)_v dT$$

or

$$ds = \left(\frac{\partial P}{\partial T}\right)_v dv + \frac{c_v}{T} dT$$

by using the relations

$$\left(\frac{\partial S}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v \qquad \text{(Maxwell relation)}$$

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{1}{T}\left(\frac{\partial u}{\partial T}\right)_v = \frac{c_v}{T}$$

then,

$$\Delta s = \int_{v_1}^{v=\infty} \left(\frac{\partial P}{\partial T}\right)_v dv + \int_{T_1}^{T_2} \frac{c_v^0}{T} dT + \int_{v=\infty}^{v_2} \left(\frac{\partial P}{\partial T}\right)_v dv$$

Using van der Waals' equation of state,

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v-b}$$

Thus,

$$\Delta s = R\ln\left(\frac{v_2-b}{v_1-b}\right) + \int_{T_1}^{T_2}\frac{c_v^0}{T}dT$$

To simplify, assume

$$c_v^0 = c_p^0 - R$$

$$v_2 = \frac{RT_2}{P_2}$$

Then,

$$\ln\frac{\frac{RT_2}{P_2}-b}{v_1-b} = \left(\frac{c_p^0-R}{R}\right)\ln\left(\frac{T_1}{T_2}\right)$$

$$\ln\left[\frac{(82.0578)\times(T_2)-45}{600-45}\right] = (3.029)\times\ln\frac{623.15}{T_2}$$

$$\boldsymbol{T_2 = 203\ \mathrm{K}}$$

6.

$$P = \frac{RT}{v-b} - \frac{a}{v^2} = \frac{RT}{v}\left[\frac{1}{1-\frac{b}{v}} - \frac{a}{RTv}\right]$$

Because $\frac{b^2}{v^2} < 1$,

$$\left(1-\frac{b}{v}\right)^{-1} = 1 + \frac{b}{v} + \frac{b^2}{v^2} + \cdots$$

Thus,

$$P = \frac{RT}{v}\left[1 + \left(b - \frac{a}{RT}\right)\frac{1}{v} + \frac{b^2}{v^2} + \cdots\right]$$

or

$$\frac{Pv}{RT} = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{v} + \frac{b^2}{v^2} + \cdots$$

Because

$$z = \frac{P\upsilon}{RT} = 1 + \frac{B}{\upsilon} + \frac{C}{\upsilon^2} + \cdots$$

the second virial coefficient for van der Waals equation is given by

$$B = b - \frac{a}{RT}$$

7. Starting with

$$du = Tds - Pd\upsilon$$

$$\left(\frac{\partial u}{\partial P}\right)_T = T\left(\frac{\partial s}{\partial P}\right)_T - P\left(\frac{\partial \upsilon}{\partial P}\right)_T$$

$$= -T\left(\frac{\partial \upsilon}{\partial T}\right)_P - P\left(\frac{\partial \upsilon}{\partial P}\right)_T$$

As

$$\upsilon = \frac{RT}{P} + B = \frac{RT}{P} + b - \frac{a}{T^2}$$

$$\left(\frac{\partial \upsilon}{\partial T}\right)_P = \frac{R}{P} + \frac{2a}{T^3}$$

$$\left(\frac{\partial \upsilon}{\partial T}\right)_T = -\frac{RT}{P^2}$$

Then,

$$\left(\frac{\partial u}{\partial P}\right)_T = -\frac{2a}{T^2}$$

$$\Delta u = \int_0^{\pi} -\left(\frac{2a}{\tau^2}\right) dP$$

$$\Delta u = -\frac{2a\pi}{\tau^2}$$

8. The equation

$$\left(P+\frac{n}{v^2T^{1/2}}\right)(v-m)=RT$$

can be rewritten as

$$(PT^{1/2})v^3-(PmT^{1/2})v^2+nv-nm=RT^{3/2}v^2$$

$$v^3-\left(m+\frac{RT}{P}\right)v^2+\left(\frac{n}{PT^{1/2}}\right)v-\frac{nm}{PT^{1/2}}=0 \tag{1}$$

At the critical point, there are three equal roots for $v = v_c$, or, equivalently,

$$\left(\frac{\partial P}{\partial v}\right)_{T=T_c}=\left(\frac{\partial^2 P}{\partial v^2}\right)_{T=T_c}=0$$

$$(v-v_c)^3=v^3-3v_cv^2+3v_c{}^2v-v_c{}^3=0 \tag{2}$$

Comparing Eqs. (1) and (2) at the critical point,

$$m+\frac{RT_c}{P_c}=3v_c \tag{3}$$

$$\frac{n}{P_cT_c^{1/2}}=3v_c^2 \tag{4}$$

$$\frac{nm}{P_cT_c^{1/2}}=v_c^3 \tag{5}$$

From Eqs. (3), (4), and (5) we obtain

$$m=\frac{v_c}{3} \tag{6}$$

$$v_c=\frac{3RT_c}{8P_c} \qquad \text{or} \qquad m=\frac{RT_c}{8P_c}$$

$$n=3v_c^2P_cT_c^{1/2}=\frac{27}{64}\frac{R^2T_c^{5/2}}{P_c}$$

The equation of state may be rewritten:

$$P = \frac{RT}{v}\left(\frac{1}{1-\frac{m}{v}} - \frac{n}{RT^{3/2}v}\right)$$

or

$$z = \frac{Pv}{RT} = \frac{1}{1-\frac{m}{v}} - \frac{n}{RT^{3/2}v}$$

From critical data,

$$m = 0.0428 \text{ L mol}^{-1}$$

$$n = 63.78 \text{ bar (L mol}^{-1})^2 \text{ K}^{1/2}$$

At 100°C and at $v = (6.948)\times(44)/1000 = 0.3057$ L mol^{-1},

$$\mathbf{z = 0.815}$$

This value of z gives $P = 82.7$ bar. Tables of Din for carbon dioxide at 100°C and $v = 6.948$ cm^3 g^{-1}, give $P = 81.1$ bar or $z = 0.799$.

9. We want to find the molar internal energy $u(T,v)$ based on a reference state chosen so that

$$u(T_0, v \to \infty) = 0$$

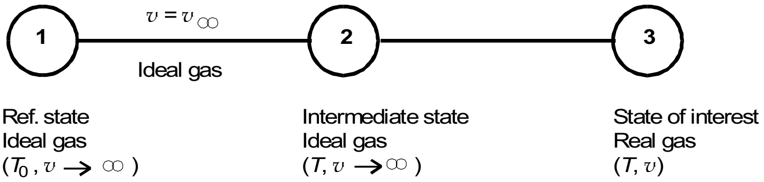
Then,

$$u(T,v) = u(T,v) - u(T_0, v \to \infty)$$

$$= u(T,v) - u(T, v\to\infty) + u(T, v\to\infty) - u(T_0, v\to\infty) \quad (1)$$

$$= \lim_{v\to\infty}\int_{v_\infty}^{v}\left(\frac{\partial u}{\partial v}\right)_T dv + \lim_{v\to\infty}\int_{T_0}^{T}\left(\frac{\partial u}{\partial T}\right)_{v=v_\infty} dT$$

Schematically we have:



In Eq. (1) we are taking 1 mol of gas from the reference state **1** to the state of interest **3** through an intermediate state **2**, characterized by temperature T and volume $v \to \infty$, in a two-step process consisting of an isochoric step and an isothermal step.

In the step **1** → **2** the gas is infinitely rarified, and hence exhibits ideal gas behavior. Then, the second integral in Eq. (1) gives:

$$\lim_{v\to\infty}\int_{T_0}^{T}\left(\frac{\partial u}{\partial v}\right)_{v=v_\infty} dT = \int_{T_0}^{T} c_v^0\, dT = \int_{T_0}^{T}(c_p^0 - R)\, dT = (c_p^0 - R)(T - T_0) \tag{2}$$

because for an ideal gas $c_p^0 - c_v^0 = R$ and because, by the problem statement, the heat capacity at constant pressure of the gas is temperature independent.

We have now to calculate the first integral in Eq. (1). To make this calculation, we first transform the derivative involved in the integral to one expressed in terms of volumetric properties.

By the fundamental equation for internal energy (see Table 2-1 of the text),

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial v}\right)_T - P \tag{3}$$

Making the derivative using the equation of state give we obtain

$$\left(\frac{\partial u}{\partial v}\right)_T = \frac{RT}{v-b} - \frac{RT}{v-b} + \frac{a}{v(v-b)} = \frac{a}{v(v-b)} \tag{4}$$

Then,

$$\begin{aligned}\int_{v_\infty}^{v}\left(\frac{\partial u}{\partial v}\right) dv &= \frac{a}{b}\int_{v_\infty}^{v}\left[\frac{1}{v-b} - \frac{1}{v}\right] dv = \frac{a}{b}\left[\ln\left(\frac{v-b}{v_\infty - b}\right) - \ln\frac{v}{v_\infty}\right] \\ &= \frac{a}{b}\ln\left(\frac{v-b}{v}\frac{v_\infty}{v_\infty - b}\right)\end{aligned} \tag{5}$$

and

$$\lim_{v\to\infty}\int_{v_\infty}^{v}\left(\frac{\partial u}{\partial v}\right)_T dv = \frac{a}{b}\ln\left(\frac{v-b}{v}\right) \tag{6}$$

Combining Eqs. (1), (2) and (6) we obtain the desired expression for the molar internal energy,

$$u(T,v) = (c_p^0 - R)(T - T_0) + \frac{a}{b}\ln\left(\frac{v-b}{v}\right)$$

10.

$$\ln\gamma_w = A(1-x_w)^2 \quad \text{such that} \quad \gamma_w \to 1 \quad \text{as} \quad x_w \to 1$$

Using Gibbs-Duhem equation,

$$x_w d\ln\gamma_w + x_s d\ln\gamma_s = 0$$

or, because $dx_w = -dx_s \quad (x_w + x_s = 1)$,

$$x_w \frac{d\ln\gamma_w}{dx_w} = x_s \frac{d\ln\gamma_s}{dx_s}$$

$$\frac{d\ln\gamma_w}{dx_w} = 2A(1-x_w)(-1) = -2A(1-x_w)$$

Then,

$$d\ln\gamma_s = \frac{-2Ax_s(1-x_s)}{x_s}dx_s = -2A(1-x_s)\,dx_s$$

$$\int_0^{\ln\gamma_s} d\ln\gamma_s = -2A\int_0^{x_s}(1-x_s)\,dx_s$$

$$\ln\gamma_s = -2A\left(x_s - \frac{x_s^2}{2}\right)$$

$$\ln\gamma_s = A(x_w^2 - 1)$$

---

11. Henry's law for component 1, at constant temperature, is

$$f_1 = k_1 x_1 \qquad (\text{for} \quad 0 < x_1 < a)$$

where k_1 is Henry's constant.

For a liquid phase in equilibrium with its vapor, $f_i^L = f_i^V$. If the vapor phase obeys ideal-gas law, $f_i^V = y_i P$.

Henry's law can then be written:

$$y_1 P = k_1 x_1$$

Taking logarithms this becomes

$$\ln(y_1 P) = \ln k_1 + \ln x_1$$

Differentiation at constant temperature gives

$$\frac{d\ln(y_1P)}{dx_1} = \frac{d\ln x_1}{dx_1} = \frac{1}{x_1}$$

Using the Gibbs-Duhem equation

$$x_1\frac{d\ln P_1}{dx_1} + x_2\frac{d\ln P_2}{dx_1} = 0$$

gives

$$1 + x_2\frac{d\ln(y_2P)}{dx_1} = 0$$

or, because $dx_2 = -dx_1$,

$$x_2\frac{d\ln(y_2P)}{dx_2} = 1$$

or,

$$d\ln(y_2P) = d\ln x_2$$

Integration gives

$$\ln(y_2P) = \ln x_2 + \ln C$$

where $\ln C$ is the constant of integration.

For $x_2 = 1$, $y_2 = 1$, and $P = P_2^s$. This gives $C = P_2^s$ and we may write

$$\ln(y_2P) = \ln x_2 + \ln P_2^s = \ln(x_2P_2^s)$$

or

$$y_2P = P_2 = x_2P_2^s \qquad \text{[for } (1-a) < x_2 < 1\text{]}$$

which is Raoult's law for component 2.

12. Starting from $dg_i = RTd\ln f_i$,

$$\Delta g_{i_{P^*\to P}} = RT\ln\frac{f_i\ (\text{at } P)}{f_i\ (\text{at } P^*)} \qquad \text{(}P^*\text{ is a low pressure where gas } i \text{ is ideal)}$$

From the Steam Tables we obtain Δh and Δs at T and P to calculate Δg from

$$\Delta g = \Delta h - T\Delta s$$

Choose $P^* = 1$ bar.

$$\Delta h = h_{70\text{ bar}} - h_{1\text{ bar}} = -196 \text{ J g}^{-1}$$

$$\Delta s = s_{70\text{ bar}} - s_{1\text{ bar}} = -2.215 \text{ J g}^{-1}{}^\circ\text{C}^{-1}$$

Then, at 320°C,

$$\Delta g = 1117.8 \text{ J g}^{-1} = 20137 \text{ J mol}^{-1}$$

Thus,

$$\ln f_{i\,(70\text{ bar, }320^\circ\text{C})} = \frac{20137}{(8.31451)\times(593.15)} = 4.08$$

or

$$\boldsymbol{f = 59.1 \text{ bar}}$$

---

13. The virial equation for a van der Waals gas can be written (as shown in Problem 6)

$$v = \frac{RT}{P} + b - \frac{a}{RT} \tag{1}$$

At the Boyle temperature,

$$B = b - \frac{a}{RT} = 0$$

or

$$b = \frac{a}{RT}$$

The Boyle temperature then, is given by

$$T_\text{B} = \frac{a}{bR} \tag{2}$$

The Joule-Thomson coefficient is

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H$$

or

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = -\frac{\left(\frac{\partial T}{\partial H}\right)_P}{\left(\frac{\partial P}{\partial H}\right)_T} = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{c_p}$$

Because

$$\left(\frac{\partial H}{\partial P}\right)_T = -\upsilon + T\left(\frac{\partial \upsilon}{\partial T}\right)_P$$

and because c_p is never zero, when $\mu = 0$, $\left(\frac{\partial H}{\partial P}\right)_T = 0$.

Substitution in Eq. (1) gives

$$\left(\frac{\partial H}{\partial P}\right)_T = -\frac{RT}{P} - b + \frac{a}{RT} + \left(\frac{RT}{P} + \frac{a}{RT}\right)$$

$$= -b + \frac{2a}{RT}$$

The inversion temperature is

$$T_{\mathrm{JT}} = \frac{2a}{Rb}$$

Comparison with Eq. (2) gives

$$T_{\mathrm{JT}} = 2T_{\mathrm{B}}$$

14. At equilibrium,

$$f_1^G = f_1^L$$

where subscript 1 stands for the solute.

At constant pressure, a change in temperature may be represented by

$$\left(\frac{d\ln f_1^G}{dT}\right)_P dT = \left(\frac{d\ln f_1^L}{dT}\right)_P dT \tag{1}$$

Since the solvent is nonvolatile, f_1^G (at constant pressure) depends only on *T* (gas composition does not change.) However, f_1^L (at constant pressure) depends on *T* and x_1 (or $\ln x_1$):

$$\left(\frac{d\ln f_1^L}{dT}\right)_P dT = \left(\frac{\partial \ln f_1^L}{\partial T}\right)_{P,x} dT + \left(\frac{\partial \ln f_1^L}{\partial \ln x_1}\right)_{T,P} d\ln x_1 \tag{2}$$

Further,

$$\left(\frac{d\ln f_1^G}{dT}\right)_P = \frac{h_1^0 - h_1^G}{RT^2} \tag{3}$$

$$\left(\frac{d\ln f_1^L}{\partial T}\right)_{P,x} = \frac{h_1^0 - \bar{h}_1^L}{RT^2} \tag{4}$$

where:

h_1^0 = ideal-gas enthalpy of 1;

h_1^G = real-gas enthalpy of 1;

$\bar{h}_1^L$ = partial molar enthalpy of 1 in the liquid phase.

Assuming Henry's law,

$$\frac{f_1}{x_1} = \text{constant}$$

or

$$\left(\frac{\partial \ln f_1^L}{\partial \ln x_1}\right)_{T,P} = 1 \tag{5}$$

Substituting Eqs. (2), (3), (4), and (5) into Eq. (1), we obtain

$$\frac{d\ln x_1}{d(1/T)} = -\frac{\Delta\bar{h}_1}{R}$$

From physical reasoning we expect $h_1^G > \bar{h}_1^L$. Therefore x_1 falls with rising temperature. This is true for most cases but not always.

SOLUTIONS TO PROBLEMS

CHAPTER 3

1. The Gibbs energy of a mixture can be related to the partial molar Gibbs energies by

$$g - g_{\text{o}} = \sum_{i=1}^{m} y_i \left(\bar{g}_i - \bar{g}_i^{\text{o}} \right) \tag{1}$$

Since, at constant temperature, $dg = RTd\ln f$, we may integrate to obtain

$$g - g_{\text{o}} = RT \ln f_{\text{mixt}} - RT \ln f_{\text{mixt}}^{\text{o}}$$

or

$$g - g_{\text{o}} = RT \ln f_{\text{mixt}} - RT \ln P \tag{2}$$

where subscript mixt stands for mixture.

For a component in a solution, $d\bar{g}_i = RTd\ln f_i$. Integration gives

$$\bar{g}_i - \bar{g}_i^{\text{o}} = RT \ln f_i^{\text{o}}$$

$$\bar{g}_i - \bar{g}_i^{\text{o}} = RT \ln(y_i P) \tag{3}$$

Substituting Eqs. (2) and (3) into Eq. (1) gives

$$\ln f_{\text{mixt}} - \ln P = \sum_{i=1}^{m} y_i \ln f_i - \sum_{i=1}^{m} y_i \ln(y_i P)$$

$$\ln f_{\text{mixt}} - \ln P = \sum_{i=1}^{m} y_i \ln\left(\frac{f_i}{y_i} \right) - \sum_{i=1}^{m} y_i \ln P \tag{4}$$

Because

$$\sum_{i=1}^{m} y_i \ln P = \ln P\left(\sum_{i=1}^{m} y_i\right) = \ln P$$

Eq. (4) becomes

$$\ln f_{\text{mixt}} = \sum_{i=1}^{m} y_i \ln\left(\frac{f_i}{y_i}\right) \tag{5}$$

Assuming the Lewis fule, $f_i = y_i f_{\text{pure } i}$, Eq. (5) becomes

$$\ln f_{\text{mixt}} = \sum_{i=1}^{m} y_i \ln f_{\text{pure } i}$$

or

$$f_{\text{mixt}} = \prod_{\text{i}=1}^{m} f_{\text{pure } i}^{y_i}$$

---

2. As shown in Problem 1,

$$\ln f_{\text{mixt}} = \sum_{i=1}^{m} y_i \ln\left(\frac{f_i}{y_i}\right)$$

This result is rigorous. It does *not* assume the Lewis fugacity rule.
Using fugacity coefficients,

$$f_i = \varphi_i y_i P$$

and

$$\ln f_{\text{mixt}} = y_A \ln \varphi_A + y_B \ln \varphi_B + \ln P$$

$$f_{\text{mixt}} = \varphi_A^{y_A} \varphi_B^{y_B} P$$

$$= (0.65)^{0.25} \times (0.90)^{0.75} \times (50)$$

$$\boldsymbol{f_{\text{mixt}} = 41.5 \text{ bar}}$$

---

3. Pure-component saturation pressures show that water is relatively nonvolatile at 25°C. Under these conditions the mole fraction of ethane in the vapor phase (y_E) is close to unity.

Henry's law applies:

$$f_E = H(T)x_E$$

The equilibrium condition is

$$f_E^V = f_E^L$$

or

$$y_E \varphi_E P = H(T)x_E$$

At 1 bar, $\varphi_E \approx 1$ and $H(T) = P/x_E$:

$$H(T) = \frac{1}{0.33\times 10^{-4}} = 3.03\times 10^4 \text{ bar}$$

At 35 bar we must calculate φ_E:

$$\ln\varphi_E = \int_0^P \frac{z-1}{P}dP$$

Using

$$z = 1 - 7.63\times 10^{-3}P - 7.22\times 10^{-5}P^2$$

we obtain

$$\varphi_E = 0.733$$

Because Henry's constant H is not a strong function of pressure,

$$x_E = \frac{f_E}{H} = \frac{\varphi_E P}{H}$$

$$x_E = x_{\text{Ethane}} = \frac{(0.733)\times(35)}{3.03\times 10^4} = \mathbf{8.47\times 10^{-4}}$$

4. The change in chemical potential can be written,

$$\Delta\mu_1 = \mu_1 - \mu_1^0 = RT\ln\left(\frac{f_1}{f_1^0}\right) \qquad (f_1^0 = 1 \text{ bar}) \tag{1}$$

The chemical potential may be defined as[1]:

$$\mu_1 - \mu_1^0 = \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2} - \left(\frac{\partial G^0}{\partial n_1}\right)_{T,n_2}$$

$$= \left(\frac{\partial A}{\partial n_1}\right)_{T,V,n_2} - \left(\frac{\partial A^0}{\partial n_1}\right)_{T,n_2} - RT \qquad (2)$$

Combining Eqs. (1) and (2):

$$\ln f_1 = \frac{1}{RT}\left(\frac{\partial \Delta A}{\partial n_1}\right)_{T,V,n_2} - 1$$

Using total volume, $V = n_T v$, $n_T = n_1 + n_2$,

$$\frac{\Delta A}{RT} = n_T \ln\left(\frac{V}{V - n_T b}\right) - n_1 \ln\left(\frac{V}{n_1 RT}\right) - n_2 \ln\left(\frac{V}{n_2 RT}\right)$$

Taking the partial derivative and substituting gives

$$\ln \frac{f_1}{\dfrac{y_1 RT}{v-b}} = \frac{b_1}{v-b}$$

or

$$f_1 = \frac{y_1 RT}{v-b} \exp\left(\frac{b_1}{v-b}\right)$$

The same expression for the fugacity can be obtained with an alternative (but equivalent) derivation:

---

[1] $$A^0 = U^0 - TS^0; \quad G^0 = U^0 + PV^0 - TS^0; \quad PV^0 = n_T RT$$

$$\mu_1^0 = \left(\frac{\partial G^0}{\partial n_1}\right)_{T,n_j \neq 1} = \left(\frac{\partial U^0}{\partial n_1}\right)_{T,n_j \neq 1} + RT - T\left(\frac{\partial S^0}{\partial n_1}\right)_{T,n_j \neq 1}$$

and

$$\left(\frac{\partial A^0}{\partial n_1}\right)_{T,n_j \neq 1} = \left(\frac{\partial U^0}{\partial n_1}\right)_{T,n_j \neq 1} + RT - T\left(\frac{\partial S^0}{\partial n_1}\right)_{T,n_j \neq 1}$$

then

$$\mu_1^0 = \left(\frac{\partial A^0}{\partial n_1}\right)_{T,n_j \neq 1} + RT$$

$$\mu_1 - \mu_1^0 = RT\ln\left(\frac{f_1}{f_1^0}\right) \qquad (f_1^0 = 1 \text{ bar})$$

By definition, $\mu_1 = \left(\frac{\partial A}{\partial n_1}\right)_{T,V,n_{j\neq 1}}$. The Helmholtz energy change Δa can be written as

$$n_T \Delta a = A - \sum_i n_i a_i^0$$

$$= A - \sum_i n_i(\mu_1^0 - RT)$$

Then,

$$\left(\frac{\partial n_T \Delta a}{\partial n_1}\right)_{n_{j\neq 1},T,V} = \left(\frac{\partial A}{\partial n_1}\right)_{n_{j\neq 1},T,V} - \mu_1^0 - RT$$

$$= \mu_1 - \mu_1^0 - RT$$

and

$$\frac{\mu_1 - \mu_1^0}{RT} = \left[\frac{\partial(n_T \Delta a / RT)}{\partial n_1}\right]_{n_{j\neq 1},T,V} - 1$$

Using the equation for Δa,

$$\left[\frac{\partial(n_T \Delta a / RT)}{\partial n_1}\right]_{n_{j\neq 1},T,V} = \ln\frac{V}{V - n_T b} - \ln\frac{V}{n_1 RT} + 1 + \frac{n_T b_1}{V - n_T b}$$

or

$$\ln f_1 = \ln\left(\frac{\mu_1 - \mu_1^0}{RT}\right) = \left[\frac{\partial(n_T \Delta a / RT)}{\partial n_1}\right]_{n_{j\neq 1},T,V} - 1$$

$$= \ln\frac{n_1 RT}{V - n_T b} + \frac{n_T b_1}{V - n_T b}$$

$$f_1 = \frac{n_1 RT}{V - n_T b}\exp\left(\frac{n_T b_1}{V - n_T b}\right)$$

Hence,

$$f_1 = \frac{y_1 RT}{v - b}\exp\left(\frac{b_1}{v - b}\right)$$

5.

a) Starting with Eq. (3-51):

For a pure component $(n_i = n_T)$:

$$\mu_i = \frac{G}{n_i}; \quad \mu_i^0 = \frac{G_i^0}{n_i}$$

Because

$$G = U + PV - TS$$

$$\mu_i^0 = \mu_i^0 - Ts_i^0 + RT \tag{1}$$

From Eq. (3-52),

$$\mu_i = \int_V^{\infty}\left(\frac{P}{n_i} - \frac{RT}{V}\right)dV - RT\ln\frac{V}{n_iRT} + \mu_i^0 - Ts_i^0 + \frac{PV}{n_i} \tag{2}$$

From Eqs. (1) and (2),

$$\mu_i - \mu_i^0 = \int_V^{\infty}\left(\frac{P}{n_i} - \frac{RT}{V}\right)dV - RT\ln\frac{V}{n_iRT} + \frac{PV - n_iRT}{n_i}$$

But,

$$RT\ln f_i = \mu_i - \mu_i^0$$

and

$$\frac{V}{n_iRT} = \frac{z_i}{P}$$

Substitution gives

$$RT\ln\left(\frac{f}{P}\right)_i = \int_V^{\infty}\left(\frac{P}{n_i} - \frac{RT}{V}\right)dV - RT\ln z_i + RT(z_i - 1)$$

b) Starting with Eq. (3-53):
For a pure component, $y_i = 1.$ To use Eq. (3-53), we must calculate

$$\left(\frac{\partial P}{\partial n_i}\right)_{T,V,\text{pure component } i}$$

Pressure *P* is a function of *T*, *V*, and n_i and

$$\left(\frac{\partial P}{\partial n_i}\right)_V \left(\frac{\partial n_i}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_{n_i} = -1$$

$$\left(\frac{\partial P}{\partial n_i}\right)_V = -\left(\frac{\partial V}{\partial n_i}\right)_P \left(\frac{\partial P}{\partial V}\right)_{n_i}$$

$$= \frac{P}{n_i} - \left[\frac{P}{n_i} + \frac{V}{n_i}\left(\frac{\partial P}{\partial V}\right)_{n_i}\right]$$

But,

$$\frac{P}{n_i} + \frac{V}{n_i}\left(\frac{\partial P}{\partial V}\right)_{n_i} = \frac{1}{n_i}\left[\frac{\partial (PV)}{\partial V}\right]_{n_i}$$

Then,

$$\int_V^\infty \left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_{j\neq 1}} = \int_V^\infty \frac{P}{n_i} dV - \frac{1}{n_i}\int_{PV}^{n_i RT} d(PV)$$

$$= \int_V^\infty \frac{P}{n_i} dV - RT + \frac{PV}{n_i}$$

$$= \int_V^\infty \frac{P}{n_i} dV - RT(z-1)$$

Now Eq. (3-54) follows directly.

---

6. The solubility of water in oil is described by

$$f_1 = H(T)x_1$$

Henry’s constant can be evaluated at 1 bar where $f_1 = 1\text{ bar}$.
Then,

$$H(T) = \frac{f_1}{x_1} = \frac{1}{35\times 10^{-4}} = 286\text{ bar} \qquad (t = 140^\circ\text{C})$$

To obtain f_1 at 410 bar and 140°C, use the Steam Tables (e.g., Keenen and Keyes). Alternatively, get f at saturation (3.615 bar) and use the Poynting factor to correct to 410 bar.

At 140°C,

$$RT\ln f_1 = \Delta g_{1\to 410\ \text{bar}} = \Delta h_{1\to 410\ \text{bar}} - T\Delta s_{1\to 410\ \text{bar}}$$

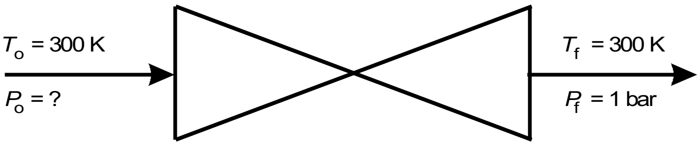
$$RT\ln f_1 = 282\ \text{J g}^{-1} \quad \text{(from Steam Tables)}$$

$$\ln f_1 = \frac{(282)\times(18)}{(8.31451)\times(413)} = 1.48$$

Then, f_1 = 4.4 bar at 410 bar and 140°C and

$$x_1 = \frac{f_1}{H(T)} = \frac{4.4}{286} = 0.0154$$

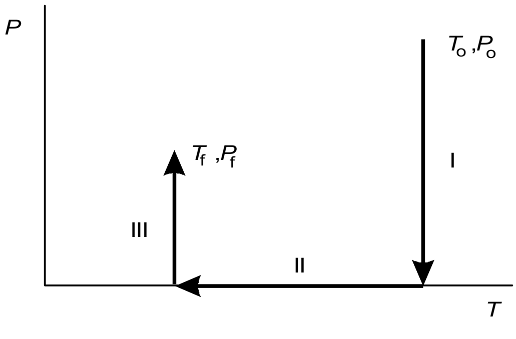
7.



Applying an energy balance to this process,

$$\Delta h = h_f - h_o = 0$$

This may be analyzed on a *P*-*T* plot. Assume 1 mole of gas passing through the valve.



A three-step process applies:

I. Isothermal expansion to the ideal-gas state.

II. Isobaric cooling of the ideal gas.

III. Compression to the final pressure.

For this process,

$$\Delta h = \Delta h_{\mathrm{I}} + \Delta h_{\mathrm{II}} + \Delta h_{\mathrm{III}} = 0$$

Since $h = h(T,P)$,

$$dh = \left(\frac{\partial h}{\partial P}\right)_T dP + \left(\frac{\partial h}{\partial T}\right)_P dT$$

$$\Delta h = \int_{T_\mathrm{o}P_\mathrm{o}}^{T_f P_f} dh$$

$$= \int_{P_\mathrm{o}}^{0}\left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right]_{T_\mathrm{o}} dP + \int_{T_\mathrm{o}}^{T_f} c_p^0\, dT + \int_{0}^{P_f}\left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right]_{T_\mathrm{f}} dP$$

But,

$$v = \frac{RT}{P} + 50 - \frac{10^5}{T}$$

Then,

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P} + \frac{10^5}{T^2}$$

and

$$c_p^0 = y_\mathrm{A} c_{p,\mathrm{A}}^0 + y_\mathrm{B} c_{p,\mathrm{B}}^0$$

$$\Delta h = 0 = \left(50 - \frac{2\times 10^5}{T_\mathrm{o}}\right)\left(-P_\mathrm{o}\right) + \left(y_\mathrm{A} c_{p,\mathrm{A}}^0 + y_\mathrm{B} c_{p,\mathrm{B}}^0\right)\left(T_\mathrm{f} - T_\mathrm{o}\right) + \left(50 - \frac{2\times 10^5}{T_\mathrm{f}}\right) P_\mathrm{f}$$

Substitution gives

$$(-616.7)\times P_\mathrm{o} = (33.5 \text{ J mol}^{-1}\text{ K}^{-1})\times(10 \text{ bar cm}^3\text{ J}^{-1})\times(200-300\text{ K}) + (-950)\times(1\text{ bar})$$

$$\boldsymbol{P_\mathrm{o} = 55.9\ \textbf{bar}}$$

---

8. From the Gibbs-Helmholtz equation:

$$\frac{\partial\left(\frac{g}{T}\right)}{\partial T} = -\frac{h}{T^2}$$

or, alternately,

$$\frac{\partial\left(\frac{\Delta g}{T}\right)}{\partial\left(\frac{1}{T}\right)} = \Delta h = h^{\text{real}} - h^{\text{ideal}} \tag{1}$$

Because, at constant temperature,

$$d(\Delta g) = RTd\ln\left(\frac{f}{P}\right) \tag{2}$$

we may substitute Eq. (2) into Eq. (1) to obtain

$$R\frac{\partial\ln\left(\frac{f}{P}\right)}{\partial\left(\frac{1}{T}\right)} = \Delta h$$

From the empirical relation given,

$$\ln\frac{f}{P} = 0.067P - \frac{30.7}{T}P - 0.0012P^2 + \frac{0.416P^2}{T}$$

$$R\frac{\partial\ln\left(\frac{f}{P}\right)}{\partial\left(\frac{1}{T}\right)} = -30.7P + 0.416P^2 = \frac{\Delta h}{R}$$

At P = 30 bar,

$$\Delta h = (8.31451)\times[(-30.7)\times(30) + (0.416)\times(30)^2]$$

$$\boldsymbol{\Delta h = -4545\ \mathrm{J\ mol^{-1}}}$$

---

9. Consider mixing as a three-step process:

(I) Expand isothermally to ideal-gas state.
(II) Mix ideal gas.
(III) Compress mixture isothermally.

Starting with

$$du = c_v dT + \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right]dv$$

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P$$

Because, $P = \frac{RT}{v-b} - \frac{a}{v^2}$,

$$\left(\frac{\partial u}{\partial v}\right)_T = \frac{a}{v^2}$$

Integration of this equation to the ideal-gas state $(v = \infty)$ gives

$$\Delta u = \int_v^\infty \frac{a}{v^2} dv = \frac{a}{v}$$

Therefore,

$$\Delta u_{\mathrm{I}} = \frac{x_1 a_1}{v_1} + \frac{x_2 a_2}{v_2} = 5914 \text{ J mol}^{-1}$$

$$[(1 \text{ bar})\times(1 \text{ cm}^3) \approx 0.1 \text{ Joule}]$$

$\Delta u_{\mathrm{II}} = 0$ (because is the mixing of ideal gases)

$$\Delta u_{\mathrm{III}} = -\frac{a_{\mathrm{mixt}}}{v_{\mathrm{mixt}}} = \frac{-[x_1^2 a_{11} + 2x_1 x_2 \sqrt{a_{11}a_{22}} \times (1-0.1) + x_2^2 a_{22}]}{x_1 v_1 + x_2 v_2}$$

$$= -5550 \text{ J mol}^{-1}$$

$$\Delta_{\mathrm{mix}} h = \Delta_{\mathrm{mix}} u = \Delta u_{\mathrm{I}} + \Delta u_{\mathrm{II}} + \Delta u_{\mathrm{III}} = \mathbf{364\ J\ mol^{-1}}$$

SOLUTIONS TO PROBLEMS

CHAPTER 4

1. At 25 Å we can neglect repulsive forces.

The attractive forces are London forces and induced dipolar forces; we neglect (small) quadrupolar forces. (There are no dipole-dipole forces since N_2 is nonpolar.)

Let 1 stand for N_2 and 2 stand for NH_3.

London force:

$$\Gamma_{12} = -\frac{3}{2}\frac{\alpha_1\alpha_2}{r^6}\frac{I_1 I_2}{I_1 + I_2}$$

$$F_{12} = -\frac{d\Gamma}{dr} = -\frac{9\alpha_1\alpha_2}{r^7}\frac{I_1 I_2}{I_1 + I_2}$$

Since,

$$\alpha_1 = 17.6 \times 10^{-25}\ \text{cm}^3$$

$$\alpha_2 = 22.6 \times 10^{-25}\ \text{cm}^3$$

$$I_1 = 15.5\ \text{eV} = 2.48 \times 10^{-18}\ \text{N m}$$

$$I_2 = 11.5\ \text{eV} = 1.84 \times 10^{-18}\ \text{N m}$$

then

$$F_{12}^{\text{London}} = -62.0 \times 10^{-18}\ \text{N}$$

Induced dipole force:

$$\Gamma_{12} = -\frac{\alpha_1 \mu_2^2}{r^6}$$

$$F_{12} = -\frac{6\alpha_1 \mu_2^2}{r^7}$$

$$1\ \text{D} = 1\times 10^{-18}(\text{erg cm}^3)^{1/2}$$

$$\mu_2 = 1.47\ \text{D} = 1.47\times 10^{-18}(\text{erg cm}^3)^{1/2}$$

$$F_{12}^{\text{ind}} = -3.8\times 10^{-18}(\text{erg cm}^3)^{1/2}$$

Neglecting all forces due to quadrupoles (and higher poles),

$$F^{\text{tot}} = F^{\text{London}} + F^{\text{ind}}$$

$$\boldsymbol{F^{\text{tot}} = -65.8\times 10^{-18}\ \text{N}}$$

2. From the Lennard-Jones model:

$$\text{Attractive potential} = -4\varepsilon\frac{\sigma^6}{r^6} = \Gamma$$

$$\text{Attractive force} = -\frac{d\Gamma}{dr} = -24\varepsilon\frac{\sigma^6}{r^7}$$

Assume force of form,

$$\text{Force} = -\frac{d\Gamma}{dr} = (\text{constant})\left(\frac{\varepsilon}{k}\right)\frac{\sigma^6}{r^7}$$

Using corresponding states:

$$\left(\frac{\varepsilon}{k}\right) = (\text{constant})\times T_c = \alpha\, T_c \qquad \sigma^6 = (\text{constant}\times \upsilon_c)^2 = \beta\upsilon_c^2$$

where α and β are universal constants.

$$\frac{\text{force CH}_4}{\text{force substance B}} = \frac{(\text{constant})}{(\text{constant})}\frac{(\varepsilon/k)_{\text{CH}_4}}{(\varepsilon/k)_{\text{B}}}\frac{\dfrac{(\sigma_{\text{CH}_4})^6}{(r_{\text{CH}_4})^7}}{\dfrac{(\sigma_{\text{B}})^6}{(r_{\text{B}})^7}}$$

$$\frac{2\times10^{-8}}{\text{force substance B}} = \frac{\alpha(T_{c_{\text{CH}_4}})}{\alpha(T_{c_{\text{B}}})}\times\frac{\dfrac{\beta(\upsilon_{c_{\text{CH}_4}})^2}{(1\times10^{-7}\,\text{cm})^7}}{\dfrac{\beta(\upsilon_{c_{\text{B}}})^2}{(2\times10^{-7}\,\text{cm})^7}}$$

$$\text{Force substance B} = -4\times10^{-10}\ \text{dyne}$$

$$\mathbf{Force = -4\times10^{-15}\ N}$$

3.

$$\Gamma_{\text{AA}} = -8\times10^{-16}\ \text{erg}$$

By the molecular theory of corresponding states:

$$\frac{\Gamma_{ii}}{\varepsilon_i} = f\left(\frac{r}{\sigma_i}\right) \qquad (r = 2\sigma)$$

$$\frac{\Gamma_{\text{BB}}}{\Gamma_{\text{AA}}} = \left(\frac{\varepsilon_{\text{B}}}{\varepsilon_{\text{A}}}\right)\left[\frac{f(2)}{f(2)}\right] = \frac{\varepsilon_{\text{B}}}{\varepsilon_{\text{A}}} \qquad (f \text{ is a universal function})$$

Since $\varepsilon/k = 0.77T_c$ (taking the generalized function f as the Lennard-Jones (12-6) potential),

$$\Gamma_{\text{BB}} = \Gamma_{\text{AA}}\frac{T_{c_{\text{B}}}}{T_{c_{\text{A}}}}$$

$$= (-8\times10^{-16}\ \text{erg})\times(180\ \text{K}/120\ \text{K})$$

$$\Gamma_{\text{BB}} = -12.0\times10^{-16}\ \text{erg}$$

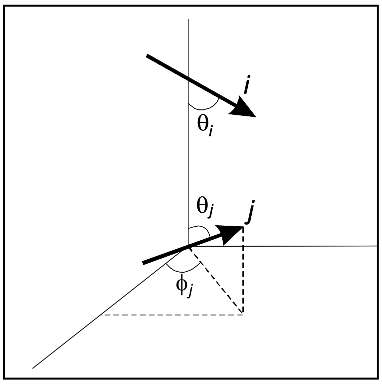
$$= \mathbf{-12.0\times10^{-23}\ J}$$

4. For dipole-dipole interaction:

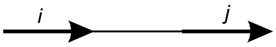
$$\Gamma(dd) = \frac{\mu_i \mu_j}{(4\pi\varepsilon_o r^3)} f(\theta_i, \theta_j, \phi)$$

with

$$f(\theta_i, \theta_j, \phi) = 2\cos\theta_i \cos\theta_j + \sin\theta_i \sin\theta_j \cos(\phi_i + \phi_j)$$



For the relative orientation:



$\theta_i = 0°$ $\phi_i = 0°$

$\theta_j = 180°$ $\phi_j = 0°$

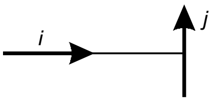
$$\Gamma(dd) = \frac{\mu_i \mu_j}{(4\pi\varepsilon_o r^3)} \times [2 \times 1 \times (-1)] = \frac{-2\mu_i \mu_j}{(4\pi\varepsilon_o r^3)}$$

For $\mu_i = \mu_j = 1.08$ D $= 3.603\times10^{-30}$ C m and $r = 0.5\times10^{-9}$ m,

$$\Gamma(dd) = \frac{(-2)\times(3.603\times10^{-30})^2}{(4\pi)\times(8.8542\times10^{-12})\times(0.5\times10^{-9})^3}$$

$$= \mathbf{-1.87\times10^{-21}\ J}$$

For the relative orientation:



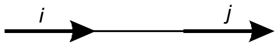
$\theta_i = 0°$ $\phi_i = 0°$

$\theta_j = 90°$ $\phi_j = 0°$

For the dipole-induced dipole interaction:

$$\Gamma(dd_i) = -\frac{\mu_i^2 \alpha_j}{2(4\pi\varepsilon_o)^2 r^6}(3\cos^2\theta_i + 1) - \frac{\mu_j^2 \alpha_i}{2(4\pi\varepsilon_o)^2 r^6}(3\cos^2\theta_j + 1)$$

For the relative orientation:

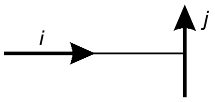


$\theta_i = 0°$ $\theta_j = 90°$

$$\Gamma(dd_i) = 2\times\left[\frac{-(3.603\times10^{-30})^2\times(2.60\times10^{-30})}{2\times(1.1124\times10^{-10})\times(0.5\times10^{-9})^6}\times(4)\right]$$

$$= -7.77\times10^{-23}\,\text{J} \approx \mathbf{-8.0\times10^{-23}\,J}$$

For the relative orientation:



$\theta_i = 0°$ $\theta_j = 90°$

$$\Gamma(dd_i) = -\frac{(3.603\times10^{-30})^2\times(2.60\times10^{-30})}{2\times(1.1124\times10^{-10})\times(0.5\times10^{-9})^6}\times(4+1)$$

$$= -4.85\times10^{-23}\,\text{J} \approx \mathbf{-4.8\times10^{-23}\,J}$$

---

5. The energy required to remove the molecule from the solution is

$$E = \frac{1}{a^3}\left(\frac{\varepsilon_r - 1}{2\varepsilon_r + 1}\right)\mu^2$$

$\varepsilon_r = 3.5$ $a = 3.0\times10^{-8}$ cm $\mu = 2$ D

(See, for example, C. J. E. Böttcher, 1952, *The Theory of Electric Polarization*, Elsevier)

$E = 4.61\times10^{-21}$ J/molecule = **2777 J mol^{-1}**

6.

a) The critical temperatures and critical volumes of N_2 and CO are very similar, more similar than those for N_2 and argon (see Table J-4 of App. J). Therefore, we expect N_2/CO mixtures to follow Amagat's law more closely than N_2/Ar mixtures.

b) Using a harmonic oscillator model for CO, $F = -Kx$, where F is the force, x is the displacement (vibration) of nuclei from equilibrium position and K is the force constant. This constant may be measured by relating it to characteristic frequency υ through:

$$\upsilon = \frac{1}{2\pi}\sqrt{\frac{K(m_C + m_O)}{m_C m_O}}$$

where m_C and m_O are, respectively, the masses of carbon and oxygen atoms.

Infrared spectrum will show strong absorption at υ.

Argon has only translational degrees of freedom while CO has, in addition, rotational and vibrational degrees of freedom. Therefore, the specific heat of CO is larger than that of argon.

---

7. Electron affinity is the energy released when an electron is added to a neutral atom (or molecule).

Ionization potential is the energy required to remove an electron from a neutral atom (or molecule).

Lewis acid = electron acceptor (high electron affinity).

Lewis base = electron donor (low ionization potential).

Aromatics are better Lewis bases than paraffin. To extract aromatics from paraffins we want a good Lewis acid. SO_2 is a better a Lewis acid than ammonia.

---

8. From Debye's equation:

$$\underbrace{v\left[\frac{\varepsilon_r - 1}{\varepsilon_r + 2}\right]}_{\text{Total polarization}} = \underbrace{\frac{4}{3}\pi N_A \alpha}_{\substack{\text{Static polarization} \\ \text{independent of } T}} + \frac{4}{3}\pi N_A \left(\frac{\mu^2}{3kT}\right)$$

Measurement of molar volume, v, and relative permitivity, ε_r, in a dilute solution as a function of T, allows μ to be determined (plot total polarization versus $1/T$; slope gives μ).

---

9. We compare the attractive part of the LJ potential ($r >> \sigma$) with the London formula. The attractive LJ potential is

$$\Gamma_{11} = -4\varepsilon_{11}\left(\frac{\sigma_{11}}{r}\right)^6$$

$$\Gamma_{22} = -4\varepsilon_{22}\left(\frac{\sigma_{22}}{r}\right)^6$$

$$\Gamma_{12} = -4\varepsilon_{12}\left(\frac{\sigma_{12}}{r}\right)^6$$

We assume that $\sigma_{12} = 1/2(\sigma_{11} + \sigma_{22})$. The London formula is

$$\Gamma_{11} = -\frac{3\alpha_1^2 I_1}{4r^6}$$

$$\Gamma_{22} = -\frac{3\alpha_2^2 I_2}{4r^6}$$

$$\Gamma_{12} = -\frac{3}{2}\left(\frac{\alpha_1\alpha_2}{r^6}\right)\left(\frac{I_1 I_2}{I_1 + I_2}\right)$$

Substitution gives

$$\varepsilon_{12} = (\varepsilon_{11}\varepsilon_{22})^{1/2}\left[\frac{\sqrt{\sigma_{11}\sigma_{22}}}{\frac{1}{2}(\sigma_{11} + \sigma_{22})}\right]^6\left[\frac{\sqrt{I_1 I_2}}{\frac{1}{2}(I_1 + I_2)}\right]$$

Only when $\sigma_{11} = \sigma_{22}$ and $I_1 = I_2$ do we obtain

$$\varepsilon_{12} = (\varepsilon_{11}\varepsilon_{22})^{1/2}$$

Notice that both correction factors (in brackets) are equal to or less than unity. Thus, in general,

$$\varepsilon_{12} \le (\varepsilon_{11}\varepsilon_{22})^{1/2}$$

---

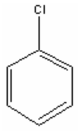
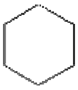
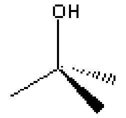
10. See Pimentel and McClellan, *The Hydrogen Bond*, Freeman (1960).
Phenol has a higher boiling point and a higher energy of vaporization than other substituted benzenes such as toluene or chlorobenzene. Phenol is more soluble in water than other substituted benzenes. Distribution experiments show that phenol is strongly associated when dissolved in

nonpolar solvents like CCl_4. Infrared spectra show absorption at a frequency corresponding to the $-OH \cdots H$ hydrogen bond.

11. $\gamma_{\text{acetone}(\text{CCl}_4)} > \gamma_{\text{acetone}(\text{CHCl}_3)}$ because acetone can hydrogen-bond with chloroform but not with carbon tetrachloride.

12.

a)

$CHCl_3$	Chloroform is the best solvent due to hydrogen bonding which is not present in pure chloroform or in the polyether (PPD).
	Chlorobenzene is the next best solvent due to its high polarizability and it is a Lewis acid while PPD is a Lewis base.
	Cyclohexane is worst due to its low polarizability.
	*n*-butanol is probably a poor solvent for PPD. Although it can hydrogen-bond with PPD, this requires breaking the H-bonding network between *n*-butanol molecules.
	*t*-butanol is probably better. Steric hindrance prevents it from forming H-bonding networks; therefore, it readily exchanges one H-bond for another when mixed with PPD. The lower boiling point of *t*-butanol supports the view that it exhibits weaker hydrogen bonding with itself than does *n*-butanol.

b) Cellulose nitrate (nitrocellulose) has *two* polar groups: ONO_2 and OH. For maximum solubility, we want one solvent that can "hook up" with the ONO_2 group (e.g., an aromatic hydrocarbon) and another one for the OH group (e.g., an alcohol or a ketone).

c) Using the result of Problem 5,

$$E = \frac{1}{a^3}\left(\frac{\varepsilon_r - 1}{2\varepsilon_r + 1}\right)\mu^2$$

At 20°C, the dielectric constants are

$$\varepsilon_r(\text{CCl}_4) = 2.238 \qquad \varepsilon_r(\text{C}_8\text{H}_{18}) = 1.948$$

Thus,

$$\frac{\varepsilon_r(\text{CCl}_4)}{\varepsilon_r(\text{C}_8\text{H}_{18})} = 1.17$$

It takes more energy to evaporate HCN from CCl_4 than from octane.

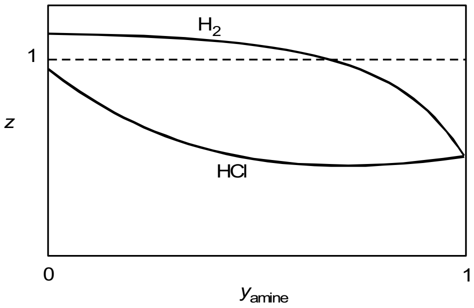
---

13. At 170°C and 25 bar:

z_{H_2} is above 1

z_{amine} is well below 1

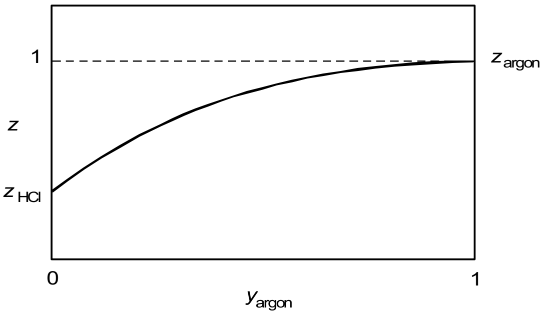
z_{HCl} is slightly below 1



a) A mixture of amine and H_2 is expected to exhibit positive deviations from Amagat's law.

b) Since amine and HCl can complex, mixtures will exhibit negative deviations from Amagat's law.

c)



The strong dipole-dipole attractive forces between HCl molecules cause $z_{\text{HCl}} < 1$, while argon is nearly ideal. Addition of argon to HCl greatly reduces the attractive forces experienced by the HCl molecules, and the mixture rapidly approaches ideality with addition of argon. Addition of HCl to Ar causes induced dipole attractive forces to arise in argon, but these forces are much smaller than the dipole-dipole forces lost upon addition of Ar to HCl. Thus the curve is convex upwards.

14.

a) Acetylene has acidic hydrogen atoms while ethane does not. Acetylene can therefore complex with DMF, explaining its higher solubility. No complexing occurs with octane.

b) At the lower pressure (3 bar), the gas-phase is nearly ideal. There are few interactions between benzene and methane (or hydrogen). Therefore, benzene feels equally “comfortable” in both gases.

However, at 40 bar there are many more interactions between benzene and methane (or hydrogen) in the gas phase. Now benzene does care about the nature of its surroundings. Because methane has a larger polarizability than hydrogen, benzene feels more “comfortable” with methane than with hydrogen. Therefore, K_{B} (in methane) > K_{B} (in hydrogen).

c) Under the same conditions, CO_2 experiences stronger attractive forces with methane than with hydrogen due to differences in polarizability. This means that CO_2 is more “comfortable” in methane than in H_2 and therefore has a lower fugacity that explains the condensation in H_2 but not in CH_4.

d) It is appropriate to look at this from a corresponding-states viewpoint. At 100°C, for ethane $T_R \approx 1.2$, for helium, $T_R \approx 80$.

At lower values of T_R (near unity) the molecules have an average thermal (kinetic) energy on the order of ε (because T_R is on the order of kT/ε). The colliding molecules (and molecules near one another, of which there will be many at 50 bar) can therefore be significantly affected by the attractive portion of the potential, leading to $z < 1$. At higher T_R, the molecules have such high thermal energies that they are not significantly affected by the attractive part. The molecules look like hard spheres to one another, and only the repulsive part of the potential is important. This leads to $z > 1$.

e) Chlorobenzene would probably be best although cyclohexane might be good too because both are polar and thus can interact favorably with the polar segment of poly(vinyl chloride). Ethanol is not good because it hydrogen bonds with itself and *n*-heptane will be poor because it is nonpolar.

f) i) Dipole.
ii) Octopole.
iii) Quadrupole.
iv) Octopole.

g) Lowering the temperature lowers the vapor pressure of heptane and that tends to lower solvent losses due to evaporation. However, at 0°C and at 600 psia, the gas phase is strongly nonideal, becoming more nonideal as temperature falls. As the temperature falls, the solubility of heptane in high-pressure ethane and propane rises due to increased attraction between heptane and ethane on propane. In this case, the effect of increased gas-phase nonideality is more important than the effect of decreased vapor pressure.

15.

a) They are listed in Page 106 of the textbook:

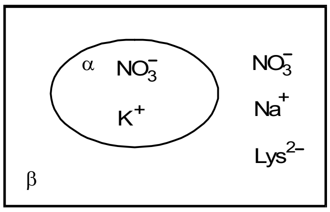
1. Q can be factored so that Q_{int} is independent of density.
2. Classical (rather than quantum) statistical mechanics is applicable.
3. $\Gamma_{\text{total}} = \sum(\Gamma_{\text{Pairs}})$ (pairwise additivity).
4. $\Gamma / \varepsilon = F(r / \sigma)$ (universal functionality).

b) In general, assumption 4 is violated. But if we fix the core size to be a fixed fraction of the collision diameter, then Kihara potential is a 2-parameter (σ, ε) potential that satisfies corresponding states.

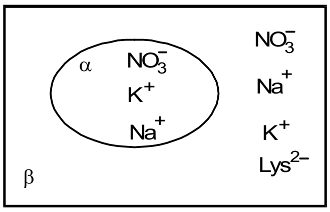
c) Hydrogen (at least at low temperatures) has a de Broglie wavelength large enough so that quantum effects must be considered and therefore assumption 2 is violated. Assumption 1 is probably pretty good for H_2; assumption 4 is violated slightly. All substances violate assumption 3, but H_2 isn't very polarizable so it might be closer than the average substance to pairwise additivity.

d) Corresponding states (and thermodynamics in general) can only give us functions such as $c_p - c_p^0$. Values of c_p^0 (for isolated molecules) cannot be computed by these methods, because the contributions to c_p^0 (rotation, vibration, translational kinetic energy) appear in Q_{int} and the kinetic energy factor, not in the configuration integral.

16. Let α represent the phase inside the droplet and β the surrounding phase.
Schematically we have for the initial state and for the final (equilibrium) state:



Initial state



Equilibrium state

Because the molar mass of lysozyme is above the membrane's cut-off point, lysozyme cannot diffuse across the membrane.

Let:

δ represent the change in K^+ concentration in α;

φ represent the change in Na^+ concentration in β.

The final concentrations (f) of all the species in α and β are:

In α: $c^{f\alpha}_{Lys^{-2}} = 0 \quad c^{f\alpha}_{K^+} = c^{0\alpha}_{K^+} - \delta \quad c^{f\alpha}_{Na^+} = \varphi \quad c^{f\alpha}_{NO_3^-} = c^{0\alpha}_{NO_3^-} - \delta + \varphi$

In β: $c^{f\beta}_{Lys^{2-}} = c^{0\beta}_{Lys^{2-}} \quad c^{f\beta}_{K^+} = \delta \quad c^{f\beta}_{Na^+} = c^{0\beta}_{Na^+} - \varphi \quad c^{f\beta}_{NO_3^-} = c^{0\beta}_{NO_3^-} + \delta - \varphi$

The equilibrium equations for the two nitrates are

$$\begin{gathered} \mu^{\alpha}_{K^+} + \mu^{\alpha}_{NO_3^-} = \mu^{\beta}_{K^+} + \mu^{\beta}_{NO_3^-} \\ \mu^{\alpha}_{Na^+} + \mu^{\alpha}_{NO_3^-} = \mu^{\beta}_{Na^+} + \mu^{\beta}_{NO_3^-} \end{gathered} \tag{1}$$

Similar to the derivation in the text (pages 102-103), Eq. (1) yields

$$\begin{gathered} c^{\beta}_{K^+} c^{\beta}_{NO_3^-} = c^{\alpha}_{K^+} c^{\alpha}_{NO_3^-} \\ c^{\beta}_{Na^+} c^{\beta}_{NO_3^-} = c^{\alpha}_{Na^+} c^{\alpha}_{NO_3^-} \end{gathered} \tag{2}$$

where, for clarity, superscript f has been removed from all the concentrations.

Substituting the definitions of δ and φ gives:

$$\begin{gathered} \left(c^{0\alpha}_{K^+} - \delta\right)\left(c^{0\alpha}_{NO_3^-} - \delta + \varphi\right) = (\delta)\left(c^{0\beta}_{NO_3^-} + \delta - \varphi\right) \\ \left(c^{0\beta}_{Na^+} - \varphi\right)\left(c^{0\beta}_{NO_3^-} + \delta - \varphi\right) = (\varphi)\left(c^{0\alpha}_{NO_3^-} - \delta + \varphi\right) \end{gathered} \tag{3}$$

where

$$c^{0\alpha}_{\mathrm{K^+}} = c^{0\alpha}_{\mathrm{NO_3^-}} = \frac{0.01\ \mathrm{mol}}{1\ \mathrm{kg\ water}} = 9.970\times 10^{-3}\ \mathrm{mol\ L^{-1}}$$

(using the mass density of water at 25°C: 0.997 g $\mathrm{cm^{-3}}$)

and

$$c^{0\beta}_{\mathrm{Na^+}} = c^{0\alpha}_{\mathrm{NO_3^-}} = 0.01\ \mathrm{mol\ L^{-1}}$$

Solving for δ and φ gives

$$\begin{gathered} \delta = 4.985\times 10^{-3}\,\mathrm{mol\ L^{-1}} \\ \varphi = 5.000\times 10^{-3}\,\mathrm{mol\ L^{-1}} \end{gathered} \tag{4}$$

Because both solutions are dilute, we can replace the activities of the solvent by the corresponding mole fractions. The osmotic pressure is thus given by [cf. Eq. (4-50) of the text]

$$\pi = \frac{RT}{\upsilon_s} \ln \frac{x_s^\beta}{x_s^\alpha} \tag{5}$$

where x_s is the mole fraction of the solvent (water) given by

$$\begin{gathered} x_s^\alpha = x_w^\alpha = 1 - (x^\alpha_{\mathrm{NO_3^-}} + x^\alpha_{\mathrm{K^+}} + x^\alpha_{\mathrm{Na^+}}) \\ x_s^\beta = x_w^\beta = 1 - (x^\beta_{\mathrm{NO_3^-}} + x^\beta_{\mathrm{K^+}} + x^\beta_{\mathrm{Na^+}} + x^\beta_{\mathrm{Lys}}) \end{gathered} \tag{6}$$

Because solutions are dilute, we expand the logarithmic terms in Eq. (5), making the approximation $\ln(1-A) \approx -A$:

$$\pi = \frac{RT}{\upsilon_w}\left[-(x^\beta_{\mathrm{NO_3^-}} + x^\beta_{\mathrm{K^+}} + x^\beta_{\mathrm{Na^+}} + x^\beta_{\mathrm{Lys}}) + (x^\alpha_{\mathrm{NO_3^-}} + x^\alpha_{\mathrm{K^+}} + x^\alpha_{\mathrm{Na^+}})\right]$$

Again, because solutions are very dilute,

$$x_i = \frac{c_i}{\sum_i c_i} \approx \frac{c_i}{c_w}$$

with

$$\upsilon_w c_w \approx 1$$

Therefore, with these simplifying assumptions, the osmotic pressure is given by

$$\pi = RT[c^\alpha_{\mathrm{NO_3^-}} + c^\alpha_{\mathrm{K^+}} + c^\alpha_{\mathrm{Na^+}} - c^\beta_{\mathrm{NO_3^-}} - c^\beta_{\mathrm{K^+}} - c^\beta_{\mathrm{Na^+}} - c^\beta_{\mathrm{Lys}}]$$

Using the relationships with the original concentrations, we have

$$\pi = RT[(c^{0\alpha}_{\mathrm{NO}_3^-} - \delta + \varphi) + (c^{0\alpha}_{\mathrm{K}^+} - \delta) + (\varphi) - (c^{0\beta}_{\mathrm{NO}_3^-} + \delta - \varphi) - (c^{0\beta}_{\mathrm{Na}^+} - \varphi) - (c^{0\beta}_{\mathrm{Lys}})]$$

Because

$$c^{0\alpha}_{\mathrm{NO}_3^-} = c^{0\alpha}_{\mathrm{K}^+}$$

$$c^{0\beta}_{\mathrm{NO}_3^-} = c^{0\beta}_{\mathrm{Na}^+}$$

we obtain

$$\pi = RT(2c^{0\alpha}_{\mathrm{K}^+} - 2c^{0\beta}_{\mathrm{Na}^+} - c^{0\beta}_{\mathrm{Lys}} - 4\delta + 4\varphi) \tag{7}$$

The lysozyme concentration is

$$c^{0\beta}_{\mathrm{Lys}} = \frac{2\ \mathrm{g}}{1\ \mathrm{L}} = \frac{(2/14{,}000)\ \mathrm{mol}}{1\ \mathrm{L}} = 1.429\times10^{-4}\ \mathrm{mol\ L^{-1}}$$

Substitution of values in Eq. (7) gives the osmotic pressure

$$\pi = (8314.51\ \mathrm{Pa\ L\ mol^{-1}\ K^{-1}})\times(298\ \mathrm{K})\times[(2\times9.97\times10^{-3}) - (2\times0.01) - (1.429\times10^{-4})$$

$$-(4\times4.985\times10^{-3}) + (4\times5.000\times10^{-3})\ (\mathrm{mol\ L^{-1}})]$$

$$= \mathbf{-354\ Pa}$$

---

17. Because only water can diffuse across the membrane, we apply directly Eq. (4-41) derived in the text:

$$-\ln a_w = -\ln(x_w\gamma_w) = \frac{\pi v_{\mathrm{pure}\,w}}{RT} \tag{1}$$

where subscript *w* indicates water.

Since the aqueous solution in part α is dilute in the sense of Raoult's law, $\gamma_w \approx 1$. This reduces Eq. (1) to:

$$-\ln x_w = -\ln(1 - x_{\mathrm{A}} - x_{\mathrm{A}_2}) \approx (x_{\mathrm{A}} + x_{\mathrm{A}_2}) = \frac{\pi v_{\mathrm{pure}\,w}}{RT} \tag{2}$$

or equivalently,

$$\pi = \frac{RT(x_A + x_{A_2})}{v_{\text{pure } w}}$$

At $T = 300$ K, $v_{\text{pure } w} = 0.018069$ mol L^{-1}.

Mole fractions x_A and x_{A_2} can be calculated from the dimerization constant and the mass balance on protein A:

$$K = 10^5 = \frac{a_{A_2}}{a_A^2} \approx \frac{x_{A_2}}{x_A^2} \tag{4}$$

$$v_w = \frac{M_w}{d_w} = \frac{18.015}{0.997} = 18.069 \text{ cm}^3 \text{ mol}^{-1}$$

$$\frac{(5/5{,}000)}{(1000/18.069)} \frac{\text{mol A}}{\text{mol water}} = 1.81 \times 10^{-5} = x_A + 2x_{A_2} \tag{5}$$

Solving Eqs. (4) and (5) simultaneously gives

$$x_A = 7.34 \times 10^{-6}$$

$$x_{A_2} = 5.38 \times 10^{-6}$$

Substituting these mole fractions in Eq. (3), we obtain

$$\pi = \frac{(0.0831451) \times (300) \times (5.38 \times 10^{-6} + 7.34 \times 10^{-6})}{(0.018069)}$$

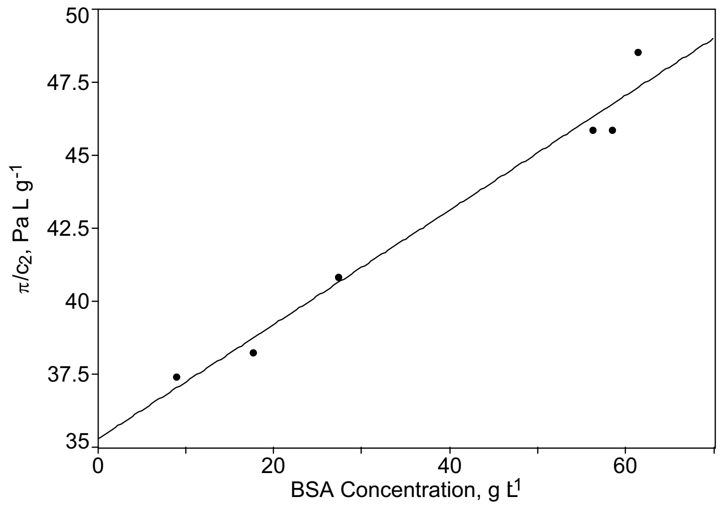
$$= 0.01756 \text{ bar} = \mathbf{1756 \ Pa}$$

18.

a) From Eq. (4-45):

$$\frac{\pi}{c_2} = \frac{RT}{M_2} + RTB^* c_2 + \cdots$$

Ploting π / c_2 (with π in pascal and c_2 in g L^{-1}) as a function of c_2, we obtain the protein's molecular weight from the intercept and the second virial osmotic coefficient from the slope.



From a least-square fitting we obtain:
Intercept = RT/M_2 = 35.25 Pa L g^{-1} = 35.25 Pa m^3 kg^{-1} from which we obtain

$$M_2 = \frac{RT}{35.25} = \frac{(298.15)\times(8.314)}{35.25}$$

$$= 70.321 \text{ kg mol}^{-1} = 70{,}321 \text{ g mol}^{-1}$$

Slope = 0.196 = RTB^*. Therefore, $B^* = 7.92\times10^{-8}$ L mol g^{-2}.
The protein's specific volume is given by the ratio molecular volume/molecular mass.
The mass per particle is

$$m = \frac{M_2}{N_A} = \frac{70{,}321}{6.022\times10^{23}} = 1.17\times10^{-19} \text{ g molecule}^{-1}$$

Because protein molecule is considered spherical, the actual volume of the particle is 1/4 of the excluded volume. Therefore the actual volume of the spherical particle is

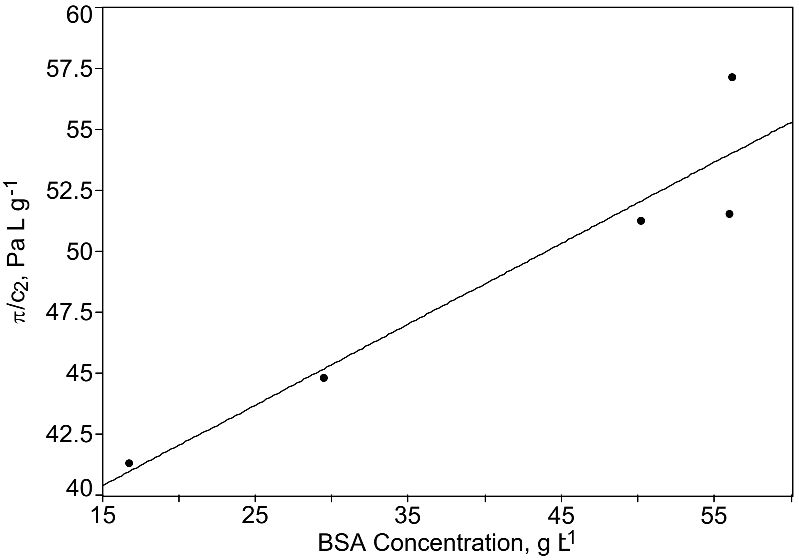
$$\frac{1.18\times10^{-24}}{4} = 2.95\times10^{-25} \text{ m}^3 \text{ molecule}^{-1}$$

which corresponds to a molecular radius of 4.13×10^{-9} m or 4.13 nm.
For the specific volume:

$$\frac{2.95\times10^{-25}}{1.17\times10^{-19}} = 2.52\times10^{-6} \text{ m}^3 \text{ g}^{-1} = 2.52 \text{ cm}^3 \text{ g}^{-1}$$

b) Comparison of this value with the nonsolvated value of 0.75 cm^3 g^{-1}, indicates that the particle is hydrated.

c) Plotting π / c_2 (with π in pascal and c_2 in g L^{-1}) as a function of c_2 for the data at pH = 7.00, we obtain:



Slope = 0.3317, which is steeper that at pH = 5.34, originating a larger second virial osmotic coefficient: $B^* = 1.338\times10^{-7}$ L mol g^{-2} = 13.38×10^{-8} L mol g^{-2}.

At pH = 7.00, the protein is charged. The charged protein particles require counterions so electroneutrality is obtained. The counterions form an ion atmosphere around a central protein particle and therefore this particles and its surrounding ion atmosphere have a larger excluded volume than the uncharged particle.

It is the difference between the value of B^* at pH = 7.00 and that at pH = 5.37 for the uncharged molecule gives the contribution of the charge to B^*:

$$(13.38 - 7.92)\times10^{-8} \text{ L mol g}^{-2} = \frac{1000z^2}{4M_2^2\rho_1 m_{\text{MX}}}$$

In this equation, we take the solution mass density $\rho_1 \approx \rho_{\text{water}} \approx 1\text{ g cm}^{-3}$. Moreover, M_2 = 70,321 g mol^{-1}, and $m_{\text{MX}} \approx 0.15$ mol kg^{-1}:

$$z^2 = \frac{4\times(5.46\times10^{-8})\times(70{,}321)^2\times(1.0)\times(0.15\times10^3)}{1000} \approx 162$$

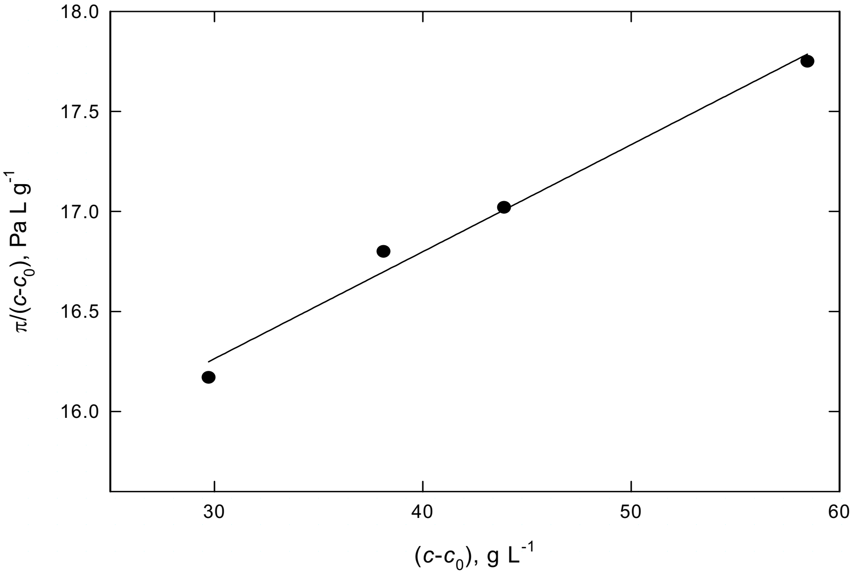
or $z = \pm 13$. Because pH is higher than the protein's isoelectric point, the BSA must be negatively charged. Hence, z **= -13**.

19.

a) From Eq. (4-45) and according to the data:

$$\frac{\pi}{c - c_0} = \frac{RT}{M_2} + RTB^*(c - c_0) + \cdots$$

Ploting $\pi/(c-c_0)$ (with π in pascal and c_2 in g L^{-1}) as a function of $c - c_0$, we obtain the solute's molecular weight from the intercept and the second virial osmotic coefficient from the slope.



From a least-square fitting we obtain:

Intercept = RT/M_2 = 14.658 Pa L g^{-1} = 14.658 Pa m^3 kg^{-1} from which we obtain

$$M_2 = \frac{RT}{14.659} = \frac{(298.15)\times(8.314)}{14.659}$$

$$= 169.109 \text{ kg mol}^{-1} = \mathbf{169{,}109 \text{ g mol}^{-1}}$$

Slope = 0.053495 = RTB^*. Therefore, $\boldsymbol{B^* = 2.16\times10^{-8}}$ **L mol $\mathbf{g^{-2}}$**.

b) The number of molecules in the aggregate is obtained by comparison of the molecular weight of the original ether (M = 390 g mol^{-1}) with that obtained in a):

$$\text{Number of molecules in the aggregate} = \frac{169{,}109}{390} \approx \mathbf{434}$$

Assuming that the colloidal particles are spherical, we obtain the molar volume of the aggregates from the value of the second virial osmotic coefficient B^*. It can be shown (see, e.g., *Principles of Colloid and Surface Chemistry*, 1997, P.C. Hiemenz, R. Rajagopalan, 3rd. Ed., Marcel Dekker) that B^* is related to the excluded volume V^{ex} through

$$B^* = \frac{N_A V^{\text{ex}}}{2M_2^2}$$

From a), $B^* = 2.16\times10^{-8}$ L mol g^{-2} = 2.16×10^{-5} m^3 mol kg^{-2} and M_2 = 169,109 g mol^{-1} = 169.109 kg mol^{-1}. The above equation gives V^{ex} that is 4 times the actual volume of the particles (we assume that the aggregates are spherical). Calculation gives for the aggregate's volume, 5.13×10^{-25} m^3 (or **30.90 dm^3 mol^{-1}**) with a radius of 4.97×10^{-9} m or **5 nm**.

SOLUTIONS TO PROBLEMS

CHAPTER 5

1. Initial pressure P_{i}:

- for n_1 moles of gas 1 at constant T and V:

$$\frac{P_{\mathrm{i}}V}{n_1RT} = 1 + n_1\frac{B_{11}}{V}$$

or

$$P_{\mathrm{i}} = \frac{n_1RT}{V} + \frac{n_1^2RTB_{11}}{V^2}$$

Final pressure P_{f}:

- after addition of n_2 moles of gas 2 at same T and V:

$$P_{\mathrm{f}} = \frac{(n_1+n_2)RT}{V} + \frac{(n_1+n_2)^2\,RTB}{V^2}$$

where $(n_1+n_2)^2B = n_1^2B_{11} + 2n_1n_2B_{12} + n_2^2B_{22}$

Pressure change ΔP:

$$\Delta P = P_{\mathrm{f}} - P_{\mathrm{i}} = \frac{n_2RT}{V} + (2n_1n_2B_{12} + n_2^2B_{22})\frac{RT}{V^2}$$

Solving for B_{12}:

$$B_{12} = \frac{1}{2n_1n_2}\left(\frac{V^2\Delta P}{RT} - n_2V - n_2^2B_{22}\right)$$

---

2. For precipitation to occur,

$$f^{V}_{CO_2} > f^{s}_{CO_2}$$

To obtain $f^{s}_{CO_2}$,

$$\ln \frac{f^{s}_{CO_2}}{(0.1392)} = \frac{1}{(83.1451)\times(173)} \int_{0.1392}^{60} (27.6)\, dP$$

$$f^{s}_{CO_2} = 0.156 \text{ bar} \quad \text{(at 60 bar, 173 K)}$$

Next, find the vapor mole fraction of CO_2 that is in equilibrium with the solid at the specified *P* and *T*:

$$y_{CO_2} = \frac{f^{V}_{CO_2}}{\varphi_{CO_2} P}$$

Using the virial equation for the vapor,

$$\ln \varphi^{V}_{CO_2} = \frac{2}{v}(y_{CO_2} B_{CO_2} + y_{H_2} B_{H_2\text{-}CO_2}) - \ln z$$

Because $y_{CO_2} << 1$, we may make the approximations

$$z = z_{H_2} \quad \text{and} \quad v = v_{H_2} = \frac{z_{H_2} RT}{P}$$

From data for H_2 (see App. C) at –100°C,

$$B_{H_2} = 8.8 \text{ cm}^3 \text{ mol}^{-1}$$

which indicates that $z_{H_2} = 1$.

From correlations:

$$B_{CO_2} = -460 \text{ cm}^3 \text{ mol}^{-1}$$

$$B_{CO_2-H_2} = -32.1 \text{ cm}^3 \text{ mol}^{-1}$$

At equilibrium

$$f^{V}_{CO_2} = f^{s}_{CO_2}$$

and then

$$y_{CO_2} = \frac{f_{CO_2}^{S}}{\exp\left\{\frac{2P}{RT}\left[y_{CO_2}B_{CO_2} + (1-y_{CO_2})B_{H_2\text{-}CO_2}\right]\right\} P}$$

$$y_{CO_2} = 0.00344$$

Because $y_{CO_2} < 0.01$ at equilibrium, CO_2 precipitates.

To find out how much, assume solid is pure CO_2. Let n be the number of moles of CO_2 left in the gas phase. From the mass balance and, as basis, 1 mole of mixture,

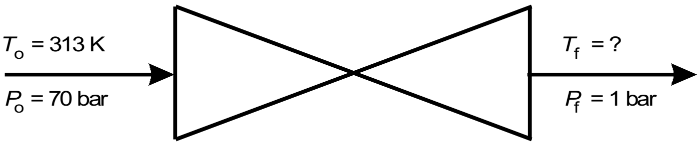
$$0.00344 = \frac{n}{n + 0.99}$$

$$n = 0.003417$$

The number of moles precipitating is

$$0.01 - 0.003417 = \mathbf{0.0066\ moles\ CO_2}$$

3.

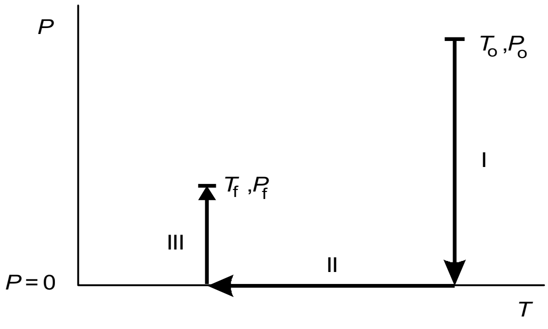


Condensation will occur in the outlet if $f_{CO_2}^{V} > f_{CO_2}^{L}$.

First it is necessary to find the outlet temperature, assuming no condensation. Joule-Thomson throttling is an isenthalpic process that may be analyzed for 1 mole of gas through a 3-step process:

I, III: Isothermal pressure changes.

II: Isobaric temperature change.



Then

$$\Delta h_{\text{total}} = 0 = \Delta h_{\text{I}} + \Delta h_{\text{II}} + \Delta h_{\text{III}} \tag{1}$$

$$\Delta h_{\text{I}} = \int_{P_{\text{o}}}^{0} \left[\upsilon - T_{\text{o}} \left(\frac{\partial \upsilon}{\partial T} \right)_P \right] dP \tag{2}$$

$$\Delta h_{\text{II}} = \int_{T_{\text{o}}}^{T_{\text{f}}} c_{p,\text{mixt}}\, dT \tag{3}$$

$$\Delta h_{\text{III}} = \int_{0}^{P_{\text{f}}} \left[\upsilon - T_{\text{f}} \left(\frac{\partial \upsilon}{\partial T} \right)_P \right] dP \tag{4}$$

Assuming that the volumetric properties of the gaseous mixture are given by the virial equation of state truncated after the second term,

$$\upsilon = \frac{RT}{P} + B_{\text{mixt}}$$

then,

$$\left(\frac{\partial \upsilon}{\partial T} \right)_P = \frac{R}{P} + \left(\frac{dB_{\text{mixt}}}{dT} \right)_P$$

where B_{mixt} is the second virial coefficient of the mixture.

Because

$$B_{\text{mixt}} = y_1^2 B_{11} + 2 y_1 y_2 B_{12} + y_2^2 B_{22} \tag{5}$$

$$(1 = \text{CH}_4; \quad 2 = \text{CO}_2)$$

$$\frac{dB_{\text{mixt}}}{dT} = y_1^2 \frac{dB_{11}}{dT} + 2 y_1 y_2 \frac{dB_{12}}{dT} + y_2^2 \frac{dB_{22}}{dT} \tag{6}$$

If

$$B = c^{(0)} + \frac{c^{(1)}}{T} + \frac{c^{(2)}}{T^2}$$

then

$$\frac{dB}{dT} = -\frac{c^{(1)}}{T^2} - \frac{2c^{(2)}}{T^3} \tag{7}$$

Assume

$$c_{p,\text{mixt}}^0 = y_{\text{CH}_4} c_{p,\text{CH}_4}^0 + y_{\text{CO}_2} c_{p,\text{CO}_2}^0 \tag{8}$$

then,

$$0=\int_{P_o}^{0}\left[B_{\text{mixt}}-T_o\left(\frac{dB_{\text{mixt}}}{dT}\right)_P\right]dP+\int_{T_o}^{T_f}c_{p,\text{mixt}}\,dT+\int_{0}^{P_f}\left[B_{\text{mixt}}-T_f\left(\frac{dB_{\text{mixt}}}{dT}\right)_P\right]dP$$

$$0=\left(c_{\text{mixt}}^{(0)}+\frac{2c_{\text{mixt}}^{(1)}}{T_o}+\frac{3c_{\text{mixt}}^{(2)}}{T_o^2}\right)(-P_o)+c_{p,\text{mixt}}(T_f-T_o)+\left(c_{\text{mixt}}^{(0)}+\frac{2c_{\text{mixt}}^{(1)}}{T_f}+\frac{3c_{\text{mixt}}^{(2)}}{T_f^2}\right)(P_f) \qquad (9)$$

From data:

As $y_1=0.7$, $y_2=0.3$, $c_{p,\text{mixt}}=36.22\text{ J K}^{-1}\text{ mol}^{-1}$ according to Eq. (8).
From Eqs. (5), (6) and (7),

$$c_{\text{mixt}}^{(0)}=41.849$$

$$c_{\text{mixt}}^{(1)}=-18683$$

$$c_{\text{mixt}}^{(2)}=-34.12\times10^5$$

Substitution in Eq. (9) gives $T_f=278.4\text{ K}$.

<u>Second</u>, the fugacities of liquid and vapor phases may be calculated.

$$f_{CO_2}^L=x_{CO_2}\gamma_{CO_2}P_{CO_2}^s\varphi_{CO_2}^s\exp\left[\int_{P_{CO_2}^s}^{P}\frac{v_{CO_2}^L}{RT}dP\right]$$

This equation may be simplified assuming that x_{CO_2}, γ_{CO_2}, $\varphi_{CO_2}^s$ equal to unity.

At 278 K, $P_{CO_2}^s=39.8$ bar and $v_{CO_2}^L=49.0\text{ cm}^3\text{mol}^{-1}$.

$$f_{CO_2}^L=(39.8)\times\exp\left[\frac{(49.0)\times(1-39.8)}{(83.1451)\times(278)}\right]=36.6\text{ bar}$$

Fugacity of vapor is calculated from

$$f_{CO_2}^V=\varphi_{CO_2}y_{CO_2}P$$

with

$$\ln\varphi_{CO_2}=\left[2(y_{CO_2}B_{CO_2}+y_{CH_4}B_{CO_2\text{-}CH_4})-B_{\text{mixt}}\right]\frac{P}{RT}$$

$$\ln\varphi_{CO_2}=\left[2\times(0.3)\times(-139)+2\times(0.7)\times(-77)+(69)\right]\frac{P}{RT}$$

$$\varphi_{CO_2} = 0.995 \approx 1$$

Then

$$f^V_{CO_2} = 0.3 \text{ bar}$$

Because

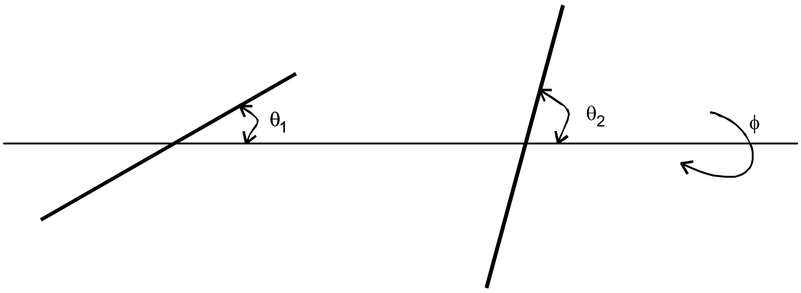
$$f^V_{CO_2} < f^L_{CO_2}$$

<u>no</u> condensation occurs.

4. The Stockmayer potential is

$$\Gamma = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - (\left(\frac{\sigma}{r}\right)^{6}\right] - \frac{\mu^2}{r^3} g(\theta_1, \theta_2, \phi_2 - \phi_1)$$

where μ is the dipole moment.



We can write the potential in dimensionless form:

$$\frac{\Gamma}{\varepsilon} = f\left(\frac{r}{\sigma}, \frac{\mu^2}{\varepsilon\sigma^3}\right) \qquad \text{where } f \text{ is a universal function.}$$

Therefore, we can write the compressibility factor z in terms of the reduced quantities:

$$z = f(\tilde{T}, \tilde{P}, \tilde{\mu})$$

with

$$\tilde{T} = \frac{kT}{\varepsilon}$$

$$\tilde{P} = \frac{P\sigma^3}{\varepsilon}$$

$$\tilde{\mu} = \frac{\mu}{\sqrt{\varepsilon\sigma^3}}$$

5.

a) For acetylene: $T_c = 308.3\ \text{K}$, $\omega = 0.184$. At 0°C, $T_R = 0.886 \approx 0.90$. Using Lee-Kesler charts (see, e.g., *AIChE J.*, 21: 510 [1975]):

$\Delta s^{(0)}/R = 3.993$ $\qquad z_V^{(0)} = 0.78$ $\qquad z_L^{(0)} = 0.10$

$\Delta s^{(1)}/R = 3.856$ $\qquad z_V^{(1)} = -0.11$ $\qquad z_L^{(1)} = -0.04$

$$\Delta_{\text{vap}}s = (8.31451)\times[3.993 + (0.184)\times(3.856)] = 39.1\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$\Delta_{\text{vap}}h = T\,\Delta_{\text{vap}}s = (273)\times(39.1) = 10.67\ \text{kJ mol}^{-1}$$

$$\Delta_{\text{vap}}u = \Delta_{\text{vap}}h - RT(z_V - z_L) = 10.67 - (8.31451)\times(273)\times(0.76 - 0.092)\times 10^{-3}$$

$$\Delta_{\text{vap}}u = 9.15\ \text{kJ mol}^{-1}$$

b)

C_4H_{10}: $T_c = 425.2\ \text{K}$ $\qquad N_2$: $T_c = 126.2\ \text{K}$

$P_c = 38.0\ \text{bar}$ $\qquad P_c = 33.7\ \text{bar}$

$\omega = 0.193$ $\qquad \omega = 0.04$

$v_c = 255\ \text{cm}^3\ \text{mol}^{-1}$ $\qquad v_c = 89.5\ \text{cm}^3\ \text{mol}^{-1}$

At 461 K: $\qquad T_R = 1.084$ $\qquad T_R = 3.65$

Using the Pitzer-Tsonopoulos equation (see Sec. 5.7):

$B_{C_4H_{10}} = -267\ \text{cm}^3\ \text{mol}^{-1}$ $\qquad B_{N_2} = 15.5\ \text{cm}^3\ \text{mol}^{-1}$

For B_{12}:

$$\omega_{12} = \frac{1}{2}(\omega_1 + \omega_2) = 0.1165$$

$$T_{c_{12}} = (T_{c_1} T_{c_2})^{1/2} = 231.6\ \text{K} \qquad (T_{R_{12}} = 1.990)$$

$$z_{c_{12}} = 0.291 - 0.08\omega_{12} = 0.2817$$

$$P_{c_{12}} = \frac{z_{c12} R T_{c12}}{\frac{1}{8}(v_{c_1}^{1/3} + v_{c_2}^{1/3})^3} = 34.3\ \text{bar}$$

Then, $B_{12} = -21.6\ \text{cm}^3\ \text{mol}^{-1}$

$$B_{\text{mixt}} = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} = -177.2\ \text{cm}^3\ \text{mol}^{-1}$$

c)

	$CH_4(1)$: $T_c = 190.6\ \text{K}$	$N_2(2)$: $T_c = 126.2\ \text{K}$	$H_2(3)$: $T_c = 33.2\ \text{K}$
	$P_c = 46.0\ \text{bar}$	$P_c = 33.7\ \text{bar}$	$P_c = 13.0\ \text{bar}$
	$\omega = 0.008$	$\omega = 0.040$	$\omega = -0.22$
	$v_c = 99.0\ \text{cm}^3\ \text{mol}^{-1}$	$v_c = 89.5\ \text{cm}^3\ \text{mol}^{-1}$	$v_c = 65.0\ \text{cm}^3\ \text{mol}^{-1}$
At 200 K:	$T_R = 1.58$	$T_R = 6.02$	$T_R = 1.05$
At 100 bar:	$P_R = 2.97$	$P_R = 2.17$	$P_R = 7.69$

Using the mixing rules suggested by Lee and Kesler:

$$v_{c,\text{mixt}} = \frac{1}{8}\sum_j \sum_k x_j x_k (v_{c_j}^{1/3} + v_{c_k}^{1/3})^3$$

$$T_{c,\text{mixt}} = \frac{1}{8v_c}\sum_j \sum_k x_j x_k (v_{c_j}^{1/3} + v_{c_k}^{1/3})^3 (T_{c_j} T_{c_k})^{1/2}$$

$$\omega_{\text{mixt}} = \sum_j x_j \omega_j \cong 0$$

$$P_{c,\text{mixt}} = (0.291 - 0.08\omega_{\text{mixt}}) R T_{c,\text{mixt}} / v_{c,\text{mixt}}$$

$$v_{c,\text{mixt}} = 84.1\ \text{cm}^3\ \text{mol}^{-1}$$

$$T_{c,\text{mixt}} = 111.38\ \text{K} \ \ (T_R = 1.80)$$

$$P_{c,\text{mixt}} = 31.47\ \text{bar} \ \ (P_R = 3.18)$$

Enthalpy of mixing = $h^E = h_{\text{mixture}} - \frac{1}{3}(h_1 + h_2 + h_3)$.

Using the Lee-Kesler charts,

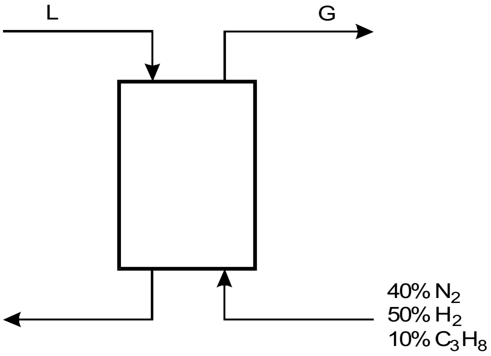
$$h^E = -922 - \frac{1}{3}(-5385 - 1383 + 0) = \mathbf{1334\ J\ mol^{-1}}$$

6.

$L/G = 5$

$P = 40$ bar

$t = 25\,°\mathrm{C}$



From the mass balance for C_3H_8:

$$y_{\mathrm{in}}G = y_{\mathrm{out}}G + x_{\mathrm{out}}(L + [y_{\mathrm{in}} - y_{\mathrm{out}}]G)$$

$$y_{\mathrm{out}}G = 0.05 y_{\mathrm{in}}G$$

$$0.10 = 0.005 + 5.005 x_{C_3}$$

$$x_{C_3} = 0.01898 = \text{mole fraction of } C_3H_8 \text{ in effluent oil.}$$

To find the driving force, note that

$$P_i = P_{C_3} = y_{C_3}P^{\mathrm{total}} = (0.10) \times (40) = 4\ \text{bar}$$

$$P_i^* = P_{C_3}^* = f_{C_3}^* / \varphi_{C_3}^*$$

where

$$f_{C_3}^* = x_{C_3}H = (0.01898) \times (53.3) = 1.012\ \text{bar}$$

and

$$\ln \varphi_{C_3}^* = \frac{2P}{z^*RT}[y_{C_3}B_{C_3} + y_{N_2}B_{C_3-N_2} + y_{H_2}B_{C_3-H_2}] - \ln z^*$$

Obtain virial coefficients from one of the generalized correlations:

$$B_{C_3} = -400.8 \text{ cm}^3 \text{ mol}^{-1}$$

$$B_{C_3-N_2} = -73.5 \text{ cm}^3 \text{ mol}^{-1}$$

$$B_{C_3-H_2} = -3.5 \text{ cm}^3 \text{ mol}^{-1}$$

We may estimate $z^* = 0.95$ (feed value).

To find $y^*_{C_3}$, $y^*_{N_2}$, and $y^*_{H_2}$, we know that ($y^*_{N_2}/y^*_{H_2}$) = 4/5. As first guess, assume $y^*_{C_3} = 0.10$. Then we calculate,

$$\varphi^*_{C_3} = 0.855 \quad \text{and} \quad y^*_{C_3} = \frac{1.012}{(40)\times(0.855)} = 0.0292$$

This gives

$$y^*_{N_2} + y^*_{H_2} = 0.9708 \quad \text{or} \quad y^*_{N_2} = 0.4308,\ y^*_{H_2} = 0.540$$

With these y^*'s, calculate $\varphi^*_{C_3}$ again:

$$\varphi^*_{C_3} = 0.924 \quad \text{and} \quad y^*_{C_3} = 0.027$$

That is close enough. Thus,

$$P^*_{C_3} = \frac{1.012}{0.924} = 1.095 \text{ bar}$$

Now we must check the assumption $z^* = 0.95$ was correct. Using the virial equation, the assumption is close enough.

$$\text{Driving force} = (P_{C_3} - P^*_{C_3}) = (4.00 - 1.095) = \mathbf{2.91\ bar}$$

---

7. Since $f_i^V = f_i^L$,

$$y_i \varphi_i P = x_i H_{i,\text{solv}} \exp\frac{\overline{v}_i^{\infty}(P - P^s_{\text{solv}})}{RT}$$

As $P^s_{\text{solv}} = 0$,

$$\frac{y_i}{x_i} = \frac{H_i \exp(\overline{v}_i^{\infty} P / RT)}{\varphi_i P}$$

Using the virial equation,

$$\ln \varphi_1 = \frac{2}{v}(y_1 B_{11} + y_2 B_{12}) - \ln z_{\text{mixt}}$$

$$\ln \varphi_2 = \frac{2}{v}(y_2 B_{22} + y_1 B_{12}) - \ln z_{\text{mixt}}$$

Because

$$\frac{Pv}{RT} = 1 + \frac{B_{\text{mixt}}}{v}$$

$$v^2 - \frac{RT}{P}v - \frac{B_{\text{mixt}}RT}{P} = 0$$

$$B_{\text{mixt}} = -3.23 \text{ cm}^3 \text{ mol}^{-1}$$

$$v = 524 \text{ cm}^3 \text{ mol}^{-1}, \quad z_{\text{mixt}} = 1.0067$$

Thus,

$$\varphi_1 = 0.8316 \qquad \varphi_2 = 0.9845$$

$$\frac{y_1}{x_1} = \frac{(100)\times \exp\left[\dfrac{(60)\times(50)}{(313)\times(83.14)}\right]}{(50)\times(0.8316)} = 2.70$$

and

$$\frac{y_2}{x_2} = 21.31$$

$$\alpha_{2,1} = \left(\frac{y_2}{x_2}\right)\left(\frac{x_1}{y_1}\right) = \mathbf{7.89}$$

---

8. For methane (1) and methanol (2), we may write

$$f_1^V = f_1^L$$

$$f_2^V = f_2^L$$

Neglecting the Poynting corrections [Note: the Poynting Correction is 1.035. Including this, we get $y_2 = 0.00268$],

$$y_1 \varphi_1 P = x_1 H_{1,2}$$

$$y_2\varphi_2 P = x_2\gamma_2 P_2^s \varphi_2^s$$

Because $x_2 = 1$, assume $\gamma_2 = 1$.
Use virial equation to get fugacity coefficients:

$$\varphi_2^s = \exp\frac{B_{22}P_2^s}{RT} = \exp\frac{(-4068)\times(0.0401)}{(83.14)\times(273)} = 0.993$$

Assuming $y_1 = 1$, $y_2 = 0$ as first estimate,

$$\varphi_1 = 0.954 \qquad \varphi_2 = 0.783$$

Thus,

$$x_1 = \frac{\varphi_1 P}{H_{1,2}} = 0.0187$$

$$y_2 = \frac{(1-x_1)P_2^s\varphi_2^s}{\varphi_2 P} = 0.00250$$

Using now $y_2 = 0.00250$, get

$$\varphi_1 = 0.954 \qquad \varphi_2 = 0.770$$

and

$$x_1 = 0.01867 \qquad y_2 = 0.00255$$

This calculation is important to determine solvent losses in natural gas absorbers using methanol as solvent.

9.

$$2(\text{monomer}) \rightleftharpoons \text{dimer}$$

The equilibrium constant is

$$K_a = \frac{a_\text{d}}{(a_\text{m})^2} = \frac{f_\text{d}/f_\text{d}^0}{(f_\text{m}/f_\text{m}^0)^2} = \frac{f_\text{d}}{f_\text{m}^2}\left(\frac{f_\text{m}^{0^2}}{f_\text{d}^0}\right)$$

where a_d is the activity of the dimer, and a_m is the activity of the monomer.

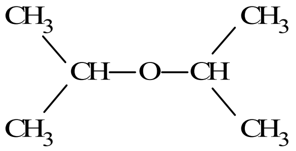
The quantity $f_\text{m}^{0^2}/f_\text{d}^0$ is a constant that depends on T, but not on P or y.

Then,

$$f_{\mathrm{d}} = k f_{\mathrm{m}}^2$$

where *k* is a constant.

10.



Di-isopropyl ether

$CH_3CH_2—O—CH_2CH_2CH_2CH_3$

Ethyl butyl ether

HCl can associate with the ether’s non-bonded electron pairs. However, the di-isopropyl ether will offer some steric hindrance. The cross-coefficient, B_{12}, is a measure of association. Both virial coefficients will be negative; B_{12} for ethyl butyl ether/HCl will be more negative.

11. Let α be the fraction of molecules that are dimerized at equilibrium.

$$\begin{array}{ccc} 2\mathrm{A} & \rightleftharpoons & \mathrm{A}_2 \\ 1-\alpha & & \alpha/2 \end{array}$$

$$n_T = 1-\alpha+\frac{\alpha}{2} = 1-\frac{\alpha}{2}$$

$$y_{\mathrm{A}_2} = \frac{\alpha/2}{1-\alpha/2}$$

$$y_{\mathrm{A}} = \frac{1-\alpha}{1-\alpha/2}$$

By assuming the vapor to be an ideal gas, we may write

$$K = \frac{P_{\mathrm{A}_2}}{(P_{\mathrm{A}})^2} = \frac{y_{\mathrm{A}_2}P}{(y_{\mathrm{A}}P)^2} = \frac{(\alpha/2)(1-\alpha/2)}{(1-\alpha)^2 P}$$

At the saturation pressure, $P = 2.026$ bar and

$$y_{\mathrm{A}} = 0.493 \qquad \alpha = 0.6726$$

Then

$$f_A^V = f_A^L = y_A P = (0.493)\times(2.026) = 0.999 \text{ bar}$$

The pressure effect on fugacity is given by

$$\left(\frac{\partial \ln f_i}{\partial P}\right)_T = \frac{\overline{v}_i}{RT}$$

Assuming the liquid to be incompressible in the range P^s to 50 bar,

$$\ln \frac{f_A(50 \text{ bar})}{f_A(2.026 \text{ bar})} = \frac{v_A \Delta P}{RT}$$

$$f_A(50 \text{ bar}) = \mathbf{1.1\ bar}$$

12.

a) The Redlich-Kwong equation is

$$z = \frac{Pv}{RT} = \frac{v}{v-b} - \frac{a}{RT^{1.5}}\left(\frac{1}{v+b}\right)$$

If z is expanded in powers of $1/v$:

$$z = 1 + \frac{B}{v} + \frac{C}{v^2} + \cdots$$

This gives

$$B = b - \frac{a}{RT^{1.5}}$$

$$C = b^2 + \frac{ab}{RT^{1.5}}$$

But,

$$B' = B/RT$$

$$C' = \frac{C - B^2}{(RT)^2}$$

Substitution gives

$$B' = \frac{1}{RT}\left(b - \frac{a}{RT^{1.5}}\right)$$

$$C' = \frac{a}{R^3T^{3.5}}\left(3b - \frac{a}{RT^{1.5}}\right)$$

b) Using an equation that gives fugacities from volumetric data, we obtain

$$\ln \varphi_1 = \frac{P}{RT}\left[b_1 + \frac{y_1^2 a_1 - 2y_1 a_1 + y_2^2 a_2 - 2y_2^2 (a_1 a_2)^{1/2}}{RT^{1.5}}\right]$$

Evaluate *a* and *b* using critical data:

Ethylene (1): T_c = 282.4 K P_c = 50.4 bar

Nitrogen (2): T_c = 126.2 K P_c = 33.7 bar

$$a_1 = 7.86\times10^7 \text{ bar cm}^6 \text{ K}^{1/2} \text{ mol}^{-2}$$

$$a_2 = 1.57\times10^7$$

$$b_1 = 40.4 \text{ cm}^3 \text{ mol}^{-1}$$

Substitution gives $\varphi_1 = 0.845$,

$$f_1 = y_1\varphi_1 P = \mathbf{8.44\ \ bar}$$

13. Using the virial equation,

$$P = \frac{RT}{v} + \frac{RTB_{\text{mixt}}}{v^2}$$

with

$$B_{\text{mixt}} = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \tag{1}$$

For maximum pressure,

$$\left(\frac{\partial P}{\partial y_1}\right)_{T,v} = \frac{RT}{v^2}\left(\frac{\partial B_{\text{mixt}}}{\partial y_1}\right)_T = 0 \tag{2}$$

Substituting Eq. (1) into Eq. (2) gives $(y_2 = 1 - y_1)$:

$$\left(\frac{\partial B_{\text{mixt}}}{\partial y_1}\right)_T = 2y_1 B_{11} - 2y_2 B_{12} + 2y_1 B_{22} - 2B_{22} = 0$$

At maximum,

$$y_1 = \frac{B_{22}}{B_{11} + B_{22} - B_{12}} \tag{3}$$

Using the correlations,

$$B_{11} = -126.7 \ \text{cm}^3\ \text{mol}^{-1} \ \ \text{(ethylene)}$$

$$B_{22} = -12.5 \ \ \text{cm}^3\ \text{mol}^{-1} \ \ \text{(argon)}$$

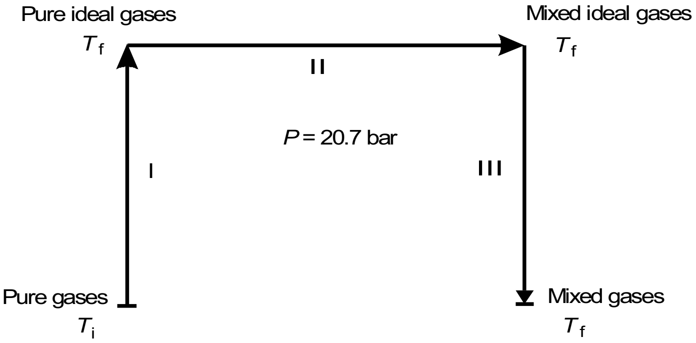
$$B_{12} = -45.9 \ \ \text{cm}^3\ \text{mol}^{-1}$$

Substitution in Eq. (3) gives

$$\mathbf{y_1 = 0.134}$$

---

14. Consider a 3-step process:



The overall enthalpy change is zero:

$$\Delta H_{\text{I}} + \Delta H_{\text{II}} + \Delta H_{\text{III}} = 0$$

$$\Delta H_{\text{I}} = n_1 \Delta H_1 + n_2 \Delta H_2 \qquad \text{(1 = hydrogen; 2 = ethylene)}$$

$$\Delta H_1 = c_{p1}^0 (T_f - T_i) + \frac{H^0 - H}{RT_{c_1}} (RT_{c_1})$$

$$\Delta H_2 = c_{p2}^0 (T_f - T_i) + \frac{H^0 - H}{RT_{c_2}} (RT_{c2})$$

where $\frac{H^0 - H}{RT_c}$ is evaluated using Lee-Kesler Tables.

For heat capacities, we can estimate

$$c^0_{p1} = 28.6\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$c^0_{p2} = 43.7\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$\Delta H_{\text{II}} = 0 \quad \text{(because we are mixing ideal gas)}$$

$$\Delta H_{\text{III}} = -\left(\frac{H^0 - H}{RT_{c,\text{mixt}}}\right) RT_{c,\text{mixt}} \quad \text{evaluated at } T_R = T_{\text{f}} / T_{c,\text{mixt}},\ P_R = 20.7/P_{c,\text{mixt}}$$

Find T_{f} by trial and error:

$$\boldsymbol{T_{\text{f}} = 247\ \text{K}}$$

---

15. At equilibrium,

$$f^V_{\text{A}} = f^{\ell}_{\text{A}}$$

$$y_{\text{A}}\varphi_{\text{A}}P = (1 - x_{\text{CO}_2}) P^s_{\text{A}} \varphi^s_{\text{A}} \exp \int_{P^s_{\text{A}}}^{P} \frac{\upsilon^{\ell}_{\text{A}}}{RT}\, dP$$

Assuming $x_{\text{CO}_2} \approx 0$,

$$\frac{(y_A P)\varphi_{\text{A}}}{P^s_{\text{A}}\varphi^s_{\text{A}}} = \exp\left[\frac{\upsilon^{\ell}_{\text{A}}(P - P^s_{\text{A}})}{RT}\right]$$

But

$$\varphi^s_{\text{A}} = \exp\left(\frac{B_{\text{AA}} P^s_{\text{A}}}{RT}\right) = 1.00$$

Because $y_{\text{A}} << y_{\text{CO}_2}$, $y_{\text{CO}_2} \cong 1$

$$\varphi_{\text{A}} = \exp\left[(2B_{\text{A-CO}_2} - B_{\text{CO}_2})\frac{P}{RT}\right]$$

$$\frac{y_{\text{A}}P}{P^s_{\text{A}}} = \exp\left[\frac{\upsilon^{\ell}_{\text{A}}(P - P^s_{\text{A}})}{RT} - \frac{(2B_{\text{A-CO}_2} - B_{\text{CO}_2})P}{RT}\right]$$

or

$$P = \left[P_{\mathrm{A}}^{s} \upsilon_{\mathrm{A}}^{\mathcal{S}} + RT \ln \frac{y_{\mathrm{A}} P}{P_{\mathrm{A}}^{s}} \right] / (\upsilon_{\mathrm{A}}^{\mathcal{S}} - 2B_{\mathrm{A-CO_2}} + B_{\mathrm{CO_2}})$$

Substitution gives

$$\boldsymbol{P = 68.7 \text{ bar}}$$

For this pressure, $y_{\mathrm{A}} = 1.9 \times 10^{-4} << 1$ and assumption $y_{\mathrm{A}} \approx 0$ is correct.

---

16. Let 1 = ethylene and 2 = naphthalene.
As, at equilibrium,

$$f_2^{\mathcal{S}} = f_2^V$$

and as

$$f_2^{\mathcal{S}} = P_2^s \varphi_2^s \exp \int_{P_2^2}^{P} \frac{\upsilon_2^{\mathcal{S}}}{RT} dP$$

$$f_2^V = y_2 \varphi_2 P$$

we may write

$$y_2 = (1 - x_1) P_2^s \varphi_2^s \exp[\upsilon_2^{\mathcal{S}} (P - P_2^s) / RT] / \varphi_2^V P$$

a) Using ideal-gas law:

$$\varphi_2^s = \varphi_2^V = 1$$

As $\upsilon_2^{\mathcal{S}} = \dfrac{128.174}{1.145} = 111.94 \text{ cm}^3\text{mol}^{-1}$,

$$y_2 = P_2^s \exp\left[\frac{\upsilon_2^{\mathcal{S}} (P - P_2^s)}{RT} \right] / P = 1.1 \times 10^{-5}$$

b) Using VDW constants:

$$a = 27R^2 T_c^2 / 64 P_c \qquad b = RT_c / 8P_c$$

$$a_1 = 4.62 \times 10^6 \text{ bar cm}^6 \text{ mol}^{-2} \qquad b_1 = 58.23 \text{ cm}^3 \text{ mol}^{-1}$$

$$a_2 = 4.03 \times 10^7 \text{ bar cm}^6 \text{ mol}^{-2} \qquad b_2 = 192.05 \text{ cm}^3 \text{ mol}^{-1}$$

$$B_{11} = b_1 - a_1 / RT = -122.2 \;\; \text{cm}^3 \text{ mol}^{-1}$$

$$B_{22} = -1382 \;\; \text{cm}^3 \text{ mol}^{-1}$$

Because $y_2 << y_1$, $y_1 \cong 1$ and $B_{\text{mixt}} \cong B_{11}$

$$\varphi_2^s = \exp\frac{B_{22}P_2^s}{RT} \cong 1$$

$$\ln\varphi_2^V = \left[2(y_1B_{12} + y_2B_{22}) - B_{\text{mixt}}\right]\frac{P}{RT} \cong (2B_{12} - B_{11})\frac{P}{RT}$$

$$B_{12} = b_{12} - a_{12} / RT \quad \text{with} \quad b_{12} = 1/2(b_1 + b_2) \quad \text{and} \quad a_{12} = \sqrt{(a_1a_2)}$$

$$b_{12} = 125.14 \;\; \text{cm}^3 \text{ mol}^{-1} \quad \text{and} \quad a_{12} = 1.36\times10^7 \text{ bar cm}^6 \text{ mol}^{-2}$$

Then B_{12} = -406 cm^3 mol^{-1}.

$$\varphi_2^V = \exp\left[(2B_{12} - B_{11})\frac{P}{RT}\right] = 0.446$$

$$y_2 = (2.80\times10^{-4}) \times \exp[(111.9\times30)/(83.1451\times308)]/(0.446\times30)$$

$$\boldsymbol{y_2 = 2.4\times10^{-5}}$$

---

17. Water will condense if $f_{\text{H}_2\text{O}}^V > f_{\text{H}_2\text{O}}^{\mathcal{S}}$.

Thus, the maximum moisture content, $y_{\text{H}_2\text{O}}$, is given by

$$f_{\text{H}_2\text{O}}^V = f_{\text{H}_2\text{O}}^{\mathcal{S}}$$

$$y_{\text{H}_2\text{O}}\varphi_{\text{H}_2\text{O}}^V P = x_{\text{H}_2\text{O}}P_{\text{H}_2\text{O}}^s \exp\int_{P_{\text{H}_2\text{O}}^s}^{P} \frac{v_{H_2O}^{\mathcal{S}}}{RT} dP$$

Assuming that the condensate is pure (solid) water,

$$x_{\text{H}_2\text{O}} = 1 \quad \text{and} \quad \varphi_{\text{H}_2\text{O}}^s = 1$$

Then

$$(y_{H_2O}\varphi^V_{H_2O})\times(30\text{ bar})=\frac{(1.95\text{ torr})}{(750.06\text{ torr/bar})}\exp\left[\frac{(18/0.92)\times\left(30-\frac{1.95}{750.06}\right)}{(83.1451)\times(263.15)}\right]$$

$$y_{H_2O}=\frac{8.90\times10^{-5}}{\varphi^V_{H_2O}}$$

Let 1 = N_2, 2 = O_2, and 3 = H_2O.
To get $\varphi^V_{H_2O}$ use the virial equation of state:

$$\ln\varphi^V_{H_2O}=\ln\varphi_3=[2(y_1B_{13}+y_2B_{23}+y_3B_{33})-B_{\text{mixt}}]\frac{P}{RT}$$

with

$$B_{\text{mixt}}=\sum_i\sum_j y_iy_jB_{ij}$$

Assume $y_3 << y_1$ where $y_1 = 0.80$ and $y_2 = 0.20$.
Then,

$$B_{\text{mixt}}=y_1^2B_{11}+y_2^2B_{22}+2y_1y_2B_{12}=-21.8\quad\text{cm}^3\text{ mol}^{-1}$$

Substitution in the equation for $\ln\varphi_3$ gives $\varphi_3=0.871.$
As

$$y_{H_2O}=\frac{8.90\times10^{-5}}{\varphi^V_{H_2O}}$$

then

$$\mathbf{y_{H_2O}=1.0\times10^{-4}}$$

---

18. The Joule-Thompson coefficient is defined as

$$\mu_H\equiv\left(\frac{\partial T}{\partial P}\right)_H \tag{1}$$

Applying the triple-product rule with T, P and H, we have

$$\left(\frac{\partial T}{\partial P}\right)_H\left(\frac{\partial P}{\partial H}\right)_T\left(\frac{\partial H}{\partial T}\right)_P = -1 \tag{2}$$

Because

$$\left(\frac{\partial H}{\partial T}\right)_P \equiv c_p$$

and

$$\left(\frac{\partial H}{\partial P}\right)_T = \frac{1}{\left(\frac{\partial P}{\partial H}\right)_T}$$

combining Eqs. (1) and (2) gives

$$\mu_H = -\frac{1}{c_p}\left(\frac{\partial H}{\partial P}\right)_T \tag{3}$$

From the fundamental equation $dH = TdS + VdP$, we have

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V \tag{4}$$

However, we also have Maxwell's relation:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Therefore,

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V \tag{5}$$

Substituting Eq. (5) into Eq. (3) gives

$$\mu_H = -\frac{1}{c_p}\left[-T\left(\frac{\partial V}{\partial T}\right)_P + V\right] \tag{6}$$

or, in terms of molar volume (υ) and molar heat capacity at constant pressure (c_p),

$$\mu_H = -\frac{1}{c_p}\left[-T\left(\frac{\partial \upsilon}{\partial T}\right)_P + \upsilon\right] \tag{7}$$

Because in this specific problem we want μ_H of the hydrogen-ethane mixture to be zero, Eq. (7) yields

$$\upsilon = T\left(\frac{\partial \upsilon}{\partial T}\right)_P \tag{8}$$

From the truncated-virial equation of state

$$\frac{Pv}{RT} = 1 + \frac{B}{v} \tag{9}$$

we have

$$\left(\frac{\partial T}{\partial v}\right)_P = \left(\frac{P}{R}\right)\left(\frac{v}{v+B}\right)\left(2 - \frac{v}{v+B}\right) = \left(\frac{P}{R}\right)\frac{v(v+2B)}{(v+B)^2} \tag{10}$$

Substituting the equation of state Eq. (9) and Eq. (10) into Eq. (8) yields

$$\frac{RT}{P}\left(1 + \frac{B}{v}\right) = T\left[\frac{R}{P}\frac{(v+B)^2}{v(v+2B)}\right] \tag{11}$$

or equivalently,

$$B = 0 \tag{12}$$

where B is the second virial coefficient of the hydrogen-ethane mixture at 300 K.

Using the McGlashan and Potter equation [Eq. (5-52)],

$$\frac{B}{v_c} = 0.430 - 0.866\left(\frac{T}{T_c}\right)^{-1} - 0.694\left(\frac{T}{T_c}\right)^{-2} \tag{13}$$

we obtain $B_{11} = 11.4$ cm^3 mol^{-1} for hydrogen, and $B_{22} = -173.3$ cm^3 mol^{-1} for ethane, and $B_{12} = B_{21} = 11.4$ cm^3 mol^{-1} for the cross term, respectively.

Applying

$$B_{\text{mixt}} = \sum_i \sum_j y_i y_j B_{ij}$$

and the material balance $y_1 + y_2 = 1,$, we have

$$B_{\text{mixt}}(\text{cm}^3\ \text{mol}^{-1}) = 11.4 y_1^2 + 22.8 y_1(1-y_1) - 173.3(1-y_1)^2 \tag{14}$$

Equations (12) and (14) yield $y_1 = 0.73$.

Consequently, if we start out with 1 mol of H_2, the amount of ethane that must be added to have a zero μ_H is **0.37 mol**.

---

19. Because methane does not significantly dissolve in liquid water at moderate pressures, the equation of equilibrium is

$$f_2^V = f_{\text{pure 2}}^L \tag{1}$$

or equivalently,

$$y_2\varphi_2 P = P_2^s \varphi_2^s \exp\left[\frac{v_2^L\left(P - P_2^s\right)}{RT}\right] \tag{2}$$

where subscript 2 denotes water.

The fugacity coefficient from the volume-explicit virial equation of state is given by Eq. (5-33):

$$\ln\varphi_2 = \left[2(y_1 B_{12} + y_2 B_{22}) - B_{\text{mixt}}\right]\frac{P}{RT} \tag{3}$$

with

$$B_{\text{mixt}} = y_1{}^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \tag{4}$$

Similarly, we also have

$$\ln\varphi_2^s = \frac{B_{22}P_2^s}{RT} \tag{5}$$

(i) At the inlet (60ºC, 20 bar):

Substitute Eqs. (3), (4), and (5) into Eq. (2). Solving Eq. (2) using $v_2^L = 18\ \text{cm}^3\ \text{mol}^{-1}$ and $P_2^s = 149\ \text{mmHg}$, we obtain

$y_2^{\text{i}} = 0.011$ (superscript i denotes inlet).

(ii) At the outlet (25ºC, 40 bar):

Similarly, with $v_2^L = 18\ \text{cm}^3\ \text{mol}^{-1}$ and $P_2^s = 24\ \text{mmHg}$, we obtain

$y_2^{\text{o}} = 0.000951$ (superscript o denotes outlet).

Because the gas phase is primarily methane, the amount of water that must be removed per mol methane is

$$\frac{\text{mol water removed}}{\text{mol methane}} = y_2^{\text{i}} - y_2^{\text{o}} \approx \mathbf{0.01}$$

20. Assuming negligible changes in potential and kinetic energies, the first law of thermodynamics for a steady-state flow process is

$$\Delta H = Q + W_s \tag{1}$$

where ΔH is the change in enthalpy, and Q and W_s are, respectively, the heat and the shaft work done on the system (by the surroundings).

Because we are given the initial and final state and enthalpy is a state function, ΔH is fixed in this problem. Consequently, minimum W_s corresponds to maximum Q. Maximum Q occurs when the process is reversible, or equivalently $Q = T\Delta S$.

Hence, Eq. (1) can be rewritten as

$$W_s = \Delta H - T\Delta S \tag{2}$$

where W_s is now the minimum amount of work required for the process.

To calculate ΔH and ΔS from the volume-explicit virial equation of state

$$\frac{PV}{n_T RT} = 1 + BP$$

we take an isothermal reversible path from the initial to the final state.

Expressions for enthalpy and entropy are given by Eqs. (3-9) and (3-10) in the text:

$$\begin{aligned} H &= \int_0^P \left[V - T\left(\frac{\partial V}{\partial T}\right)_{P,n_T} \right] dP + n_1 h_1^0 + n_2 h_2^0 \\ S &= \int_0^P \left[\frac{n_T R}{P} - \left(\frac{\partial V}{\partial T}\right)_{P,n_T} \right] dP - R(n_1 \ln y_1 P + n_2 \ln y_2 P) + n_1 s_1^0 + n_2 s_2^0 \end{aligned} \tag{3}$$

Substituting

$$\left(\frac{\partial V}{\partial T}\right)_{P,n_T} = \frac{n_T R}{P}(1 + BP)$$

from the virial equation of state gives

$$\begin{aligned} H &= n_1 h_1^0 + n_2 h_2^0 \\ S &= n_T RBP - R(n_1 \ln y_1 P + n_2 \ln y_2 P) + n_1 s_1^0 + n_2 s_2^0 \end{aligned} \tag{4}$$

Applying Eq. (4) to this specific problem, we have

$$\begin{aligned} \Delta H &= 0 \\ \Delta S &= RP(n_T B_{\text{mixt}} - n_1 B_{11} - n_2 B_{22}) - R(n_1 \ln y_1 + n_2 \ln y_2) \end{aligned} \tag{5}$$

At 298 K, second virial coefficients are

$$B_{11} = -41.9 \text{ cm}^3 \text{ mol}^{-1}$$

$$B_{12} = -122.2 \text{ cm}^3 \text{ mol}^{-1} \tag{6}$$

$$B_{22} = -66.0 \text{ cm}^3 \text{ mol}^{-1}$$

Hence, at 298 K,

$$B_{\text{mixt}} = \sum_i \sum_j y_i y_j B_{ij} = -74.0 \text{ cm}^3 \text{ mol}^{-1}$$

Taking a basis of $n_T = 1$ mol of the mixture initially, then $n_1 = n_2 = 0.5$ mol, Eq. (5) yields at 298 K

$$\Delta H = 0$$

$$T\Delta S = -248.5 \text{ kJ} \tag{7}$$

Substituting Eq. (7) into Eq. (2), the minimum amount of work required for this process is **$248.5 \text{ kJ mol}^{-1}$** of initial mixture.

21. The second virial coefficient for a square-well potential is given by Eq. (5-39) in the text

$$B = b_0 R^3 \left(1 - \frac{R^3 - 1}{R^3} \exp\frac{\varepsilon}{kT}\right) \tag{1}$$

with

$$b_0 = \frac{2}{3}\pi N_A \sigma^3 \tag{2}$$

Substituting $\varepsilon / k = 469 \text{ K}$, $\sigma = 0.429 \text{ nm}$ and $R = 0.337\sigma$ gives

$$B(423 \text{ K}) = 302 \text{ cm}^3 \text{ mol}^{-1}$$

Because, for a pure component,

$$\ln\varphi = \ln\frac{f}{P} = \frac{BP}{RT}$$

fugacity is given by

$$f = P\exp\left(\frac{BP}{RT}\right)$$

Hence, at 150ºC and 30 atm,

$$f = (30\text{ atm}) \times \exp\left[\frac{(30\text{ atm}) \times (301.8\text{ cm}^3\text{ mol}^{-1})}{(82.06\text{ atm cm}^3\text{ mol}^{-1}) \times (423\text{ K})}\right]$$

$$= 38.94\text{ atm} \approx \mathbf{39\ atm}$$

To obtain the standard enthalpy and entropy of dimerization of methyl chloride we assume a small degree of dimerization. In this case, the relation between the second virial coefficient and the dimerization constant is given by Eq. (5-113):

$$B = b - \frac{RTK}{P^0}$$

Applying $P^0 = RTc^0$ (where $c^0 = 1\text{ mol L}^{-1} = 10^{-3}\text{mol cm}^{-3}$ is the standard state) gives

$$10^3(\text{cm}^3\text{ mol}^{-1})K = B - b$$

Because we only have a weak dimerization,

$$b = b_0 = \frac{2}{3}\pi N_A \sigma^3 \qquad (3)$$

and the second virial coefficient is essentially that of pure methyl chloride [Eq. (1)].

Combining Eqs. (1) and (3) gives

$$10^3(\text{cm}^3\text{ mol}^{-1})K = \left(\frac{2}{3}\pi N_A \sigma^3\right)\left[R^3\left(1 - \frac{R^3 - 1}{R^3}\exp\frac{\varepsilon}{kT}\right) - 1\right] \qquad (4)$$

The following table shows $K(T)$ calculated from Eq. (4).

T (K)	K
100	10.74
200	0.939
300	0.376
400	0.222
500	0.155

Because the standard enthalpy and entropy of dimerization obey [Eq. (5-114)]

$$-R\ln K = \frac{\Delta h^0}{T} - \Delta s^0$$

plotting $-R\ln K$ as a function of $1/T$ gives Δh^0 as the slope, and $-\Delta s^0$ as the intercept.

Results are

$$\mathbf{\Delta h^0 = -4.34\ kJ\ mol^{-1}}$$

$$\mathbf{\Delta s^0 = -23.2\ J\ K^{-1}\ mol^{-1}}$$

22.

a) Substitution of given $\Gamma(r)$ in Eq. (5-19) gives

$$B = 2\pi N_A \left[\int_0^{\sigma} (1 - e^{-\infty / kT}) r^2 dr + \int_{\sigma}^{\infty} (1 - e^{A/kTr^n}) r^2 dr \right]$$

$$= 2\pi N_A \left[\int_0^{\sigma} r^2 dr + \int_{\sigma}^{\infty} (1 - e^{A/kTr^n}) r^2 dr \right] \tag{1}$$

$$= 2\pi N_A \left[\frac{\sigma^3}{3} + \int_{\sigma}^{\infty} (1 - e^{A/kTr^n}) r^2 dr \right]$$

At high temperatures, A/kTr^n is small.
Because

$$e^x \approx 1 + x + \frac{x^2}{2!} + \cdots \qquad \text{when } x \text{ is small,}$$

we expand the exponencial e^{A/kTr^n} :

$$e^{A/kTr^n} \approx 1 + \frac{A}{kTr^n} + \cdots$$

Substitution of this approximation into Eq. (1) gives:

$$\int_{\sigma}^{\infty} (1 - e^{A/kTr^n}) r^2 dr = \int_{\sigma}^{\infty} \left(1 - 1 - \frac{A}{kTr^n} \right) r^2 dr = \frac{-A}{kT} \int_{\sigma}^{\infty} (r^{-n}) r^2 dr$$

$$= \frac{-A}{kT} \int_{\sigma}^{\infty} (r^{2-n}) dr = \frac{-A}{kT} \left[\frac{r^{3-n}}{3-n} \right]_{\sigma}^{\infty} \tag{2}$$

$$= \frac{A}{kT} \left(\frac{\sigma^{3-n}}{3-n} \right) = \frac{-A\sigma^{3-n}}{kT(n-3)}$$

We substitute now this result in Eq. (1):

$$B = \frac{2}{3} \pi N_A \sigma^3 - 2\pi A N_A \left[\frac{\sigma^{3-n}}{kT(n-3)} \right]$$

Constant n is large (i.e., $n > 3$):

$$B = \frac{2}{3}\pi N_A \sigma^3 - 2\pi A N_A\left[\frac{\sigma^3}{kT(n-3)\sigma^n}\right]$$

$$= \frac{2}{3}\pi N_A \sigma^3 - \frac{2}{3}\pi N_A \sigma^3\left[\frac{3A}{kT(n-3)\sigma^n}\right] \qquad (3)$$

b) From Eq. (3) we see that it is the attractive part of the potential that causes negative *B* and is responsible for the temperature dependence of *B* [the first term on the right hand side of Eq. (3) is independent of temperature].

23. Substitution of the square-well potential [Eq. (5-39)] into Eq. (5-17) gives

$$B = 2\pi N_A \int_0^\infty (1 - e^{-\Gamma(r)/kT})\, r^2 dr$$

$$= 2\pi N_A\left[\int_0^\sigma (1-e^{-\infty/kT})r^2 dr + \int_\sigma^{R'} (1-e^{\varepsilon/kT})r^2 dr + \int_{R'}^\infty (1-e^{0/kT})r^2 dr\right]$$

$$= 2\pi N_A\left[\frac{\sigma^3}{3} + \int_\sigma^{R'} (1-e^{\varepsilon/kT})r^2 dr + 0\right]$$

$$= 2\pi N_A\left[\frac{\sigma^3}{3} + \left(\frac{R'^3}{3} - \frac{\sigma^3}{3}\right)(1-e^{\varepsilon/kT})\right]$$

$$= \frac{2}{3}\pi N_A \sigma^3 + \frac{2}{3}\pi N_A (1-e^{\varepsilon/kT})(R'^3 - \sigma^3)$$

In the equation above, $R' = R\sigma = 1.55\sigma$. For argon, $\sigma = 0.2989$ nm $= 0.2989\times10^{-9}$ m, $\varepsilon/k = 141.06$ K, and $R' = 1.55\sigma = 4.633\times10^{-10}$ m.

The above equation gives for $T = 273.15$ K,

$$B = 3.368\times10^{-5} + (-6.202\times10^{-5})$$

$$= -2.834\times10^{-5}\,\text{m}^3\text{mol}^{-1} \approx \mathbf{-28\ cm^3\ mol^{-1}}$$

The calculated value compares relatively well with the experimental *B* for argon at the same temperature: $B_{\text{exp}} = -22.08$ cm^3 mol^{-1}.

---

24. Substitution of Sutherland potential [Eq. (5-37)] in Eq. (5-19) with $N = N_A$ gives

$$B(T) = 2\pi N_A \left[\int_0^\sigma (1 - e^{-\infty/kT}) r^2 dr + \int_\sigma^\infty (1 - e^{K/kTr^6}) r^2 dr \right]$$

$$= \frac{2}{3}\pi N_A \sigma^3 + \int_\sigma^\infty (1 - e^{K/kTr^6}) r^2 dr \tag{1}$$

$$\exp\left(\frac{K}{kTr^6}\right) \approx 1 + \frac{K}{kTr^6} + \frac{K^2}{2(kT)^2 r^{12}} + \frac{K^3}{6(kT)^3 r^{18}} + \frac{K^4}{24(kT)^4 r^{24}} + \cdots \tag{2}$$

$$[\, e^x \approx 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \cdots \,]$$

We now have to replace the approximate result [Eq. (2)] in Eq. (1) and perform the necessary integrations.

The result is:

$$B(T) = \frac{2}{3}\pi N_A \sigma^3 - \frac{2\pi N_A K}{3kT\sigma^3} - \frac{2\pi N_A K^2}{18(kT)^2\sigma^9} - \frac{2\pi N_A K^3}{90(kT)^3\sigma^{15}} - \frac{2\pi N_A K^4}{504(kT)^4\sigma^{21}} - \cdots$$

This equation is best solved using an appropriate computer software such as Mathematica, TKSolver, MathCad, etc.

Making the necessary programming we obtain at 373 K,

B(methane) = -20 cm^3 mol^{-1}

B(n-pentane) = -634 cm^3 mol^{-1}

In both cases, the agreement with experiment is very good.

---

25. The equation of equilibrium for helium is

$$f_1^L = f_1^R \tag{1}$$

where superscripts L and R stand for left and right compartments, respectively.

Equivalently,

$$y_1^L {\varphi_1}^L P^L = y_1^R {\varphi_1}^R P^R \tag{2}$$

Equation (5-33) of the text gives the fugacity coefficients in both compartments from the volume-explicit virial equation of state:

$$\ln \varphi_1 = \left[2(y_1 B_{11} + y_2 B_{12}) - B_{\text{mixt}}\right]\frac{P}{RT} \tag{3}$$

with

$$B_{\text{mixt}} = {y_1}^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \tag{4}$$

Further, we also have material balances

$$\begin{aligned} y_1^L + y_2^L &= 1 \\ y_1^R + y_3^R &= 1 \end{aligned} \tag{5}$$

Applying Eqs. (3), (4), and (5) to both compartments yields

$$\begin{aligned} \ln \varphi_1^R &= \left\{2\left[{y_1}^L B_{11} + (1-y_1^L)B_{12}\right] - \left[(y_1^L)^2 B_{11} + 2{y_1}^L(1-y_1^L)B_{12} + (1-y_1^L)^2 B_{22}\right]\right\}\frac{P^L}{RT} \\ \ln \varphi_1^L &= \left\{2\left[{y_1}^R B_{11} + (1-{y_1}^R)B_{13}\right] - \left[({y_1}^R)^2 B_{11} + 2{y_1}^R(1-{y_1}^R)B_{13} + (1-{y_1}^R)^2 B_{33}\right]\right\}\frac{P^R}{RT} \end{aligned} \tag{6}$$

Total mole balance on helium gives

$$n_1^L + n_1^R = 0.02 \text{ mol} \tag{7}$$

Combining with mass balances on ethane and nitrogen gives

$$\begin{aligned} y_1^L &= \frac{n_1^L}{0.99 + n_1^L} \\ y_1^R &= \frac{n_1^R}{0.99 + n_1^R} = \frac{0.02 - n_1^L}{1.01 - n_1^L} \end{aligned} \tag{8}$$

Substituting Eqs. (6) and (8) into Eq. (2) yields

$$n_1^L = 0.013 \text{ mol}$$

Combining this result and Eq. (8) gives

$$\boldsymbol{y_1^L = 0.013}$$

$$\boldsymbol{y_1^R = 0.007}$$

26. Because the equilibrium constant is independent of pressure, the more probable reaction is the one that satisfies this condition.

(1) Assuming reaction (a) is more probable:

With this scheme, concentration of $(\mathrm{HF})_6$ is negligible compared to those of (HF) and $(\mathrm{HF})_4$.

The equilibrium constant $K_{(\mathrm{a})}$ is

$$K_{(\mathrm{a})} = \frac{y_{(\mathrm{HF})4}}{y^4_{(\mathrm{HF})} P^3} = \frac{y_{(\mathrm{HF})4}}{\left[1 - y_{(\mathrm{HF})4}\right]^4 P^3} \tag{1}$$

Total mass balance for (HF) gives

$$y_{(\mathrm{HF})4} n_T (4 \times M_{\mathrm{HF}}) + \left[1 - y_{(\mathrm{HF})4}\right] n_T M_{\mathrm{HF}} = V \times \rho_{\mathrm{HF}} \tag{2}$$

where V is the total volume; ρ_{HF} and M_{HF} are the mass density and the molar mass of hydrogen fluoride, respectively; n_T is the total number of moles that can be calculated by assuming that the gas phase is ideal:

$$n_T = \frac{PV}{RT} \tag{3}$$

Substituting Eqs. (2) and (3) into Eq. (1) yields

$$K_{(\mathrm{a})} = \frac{(1/3)\left(\dfrac{\rho_{\mathrm{HF}} RT}{P \times M_{\mathrm{HF}}} - 1\right)}{\left[1 - (1/3)\left(\dfrac{\rho_{\mathrm{HF}} RT}{P \times M_{\mathrm{HF}}} - 1\right)\right]^4 P^3} \tag{4}$$

Applying Eq. (4) at the two pressures, 1.42 and 2.84 bar, we obtain for $K_{(\mathrm{a})}$:

P (bar)	ρ_{HF} (g/L)	$K_{(\mathrm{a})}$
1.42	1.40	0.0595
2.84	5.45	0.453

Because $K_{(\mathrm{a})}$ depends on pressure, reaction (a) cannot be the more probable one.

Next we need to check for the pressure independence of $K_{(\mathrm{b})}$.

(2) Assuming reaction (b) is more probable:

In this case, concentration of $(\mathrm{HF})_4$ is negligible compared to those of (HF) and $(\mathrm{HF})_6$. The equilibrium constant $K_{(\mathrm{b})}$ is

$$K_{(\mathrm{b})} = \frac{y_{(\mathrm{HF})_6}}{y_{(\mathrm{HF})}^6 P^5} = \frac{y_{(\mathrm{HF})_6}}{\left[1 - y_{(\mathrm{HF})_6}\right]^6 P^5} \tag{5}$$

Mass balance for HF in this case is:

$$y_{(\mathrm{HF})_6} n_T (6 \times M_{\mathrm{HF}}) + \left[1 - y_{(\mathrm{HF})_6}\right] n_T M_{\mathrm{HF}} = V \times \rho_{\mathrm{HF}} \tag{6}$$

where all terms are defined in Eq. (2).

Substitution of Eqs. (3) and (6) into Eq. (5) gives

$$K_{(\mathrm{b})} = \frac{(1/5)\left(\dfrac{\rho_{\mathrm{HF}} RT}{P \times M_{\mathrm{HF}}} - 1\right)}{\left[1 - (1/5)\left(\dfrac{\rho_{\mathrm{HF}} RT}{P \times M_{\mathrm{HF}}} - 1\right)\right]^6 P^5} \tag{7}$$

Corresponding values of $K_{(\mathrm{b})}$ at 1.42 and 2.84 bar are:

P (bar)	ρ_{HF} (g/L)	$K_{(\mathrm{b})}$
1.42	1.40	0.017
2.84	5.45	0.017

Because $K_{(\mathrm{b})}$ is independent of pressure, reaction (b) is the more probable.

SOLUTIONS TO PROBLEMS

CHAPTER 6

1. The three equations of equilibrium (in addition to $T^L = T^V$ and $P^L = P^V$) are

$$y_1 \varphi_1^V P = x_1 \gamma_1 f_1^L$$

$$y_2 \varphi_2^V P = x_2 \gamma_2 f_2^L$$

$$y_3 \varphi_3^V P = x_3 \gamma_3 f_3^L$$

with (assuming the liquid incompressible)

$$f_1^L = P_1^s \varphi_1^s \exp \frac{v_1^L (P - P_1^s)}{RT}$$

We write similar expressions for f_2^L and f_3^L.

For φ^V we may write

$$RT \ln \varphi_1^V = P(2y_1 B_{11} + 2y_2 B_{12} + 2y_3 B_{13} - B_{\text{mixt}})$$

and similar expressions for φ_2^V and φ_3^V. In these equations,

$$B_{\text{mixt}} = y_1^2 B_{11} + y_2^2 B_{22} + y_3^2 B_{33} + 2y_1 y_2 B_{12} + 2y_1 y_3 B_{13} + 2y_2 y_3 B_{23}$$

2. Given $g^E = Ax_1x_2$ with $P_1^s / P_2^s = 1.649$, and assuming ideal vapor,

$$\gamma_1 = \frac{y_1 P}{x_1 P_1^s}$$

$$\gamma_2 = \frac{y_2 P}{x_2 P_2^s}$$

At azeotrope, $x_1 = y_1$:

$$\ln\gamma_1 = \ln\frac{P}{P_1^s}$$

$$\ln\gamma_2 = \ln\frac{P}{P_2^s}$$

or

$$\ln\frac{\gamma_1}{\gamma_2} = \ln\frac{P_2^s}{P_1^s} = -0.5$$

From the g^E expression,

$$\ln\gamma_1 = \frac{A}{RT}x_2^2$$

and

$$\ln\gamma_2 = \frac{A}{RT}x_1^2$$

Then

$$\ln\frac{\gamma_1}{\gamma_2} = \frac{A}{RT}(x_2^2 - x_1^2)$$

$$\frac{A}{RT} = \frac{-0.5}{x_2^2 - x_1^2} = \frac{-1}{4x_2 + 2}$$

or

$$x_2 = \frac{1}{2} - \frac{RT}{4A}$$

Because $0 \le x_2 \le 1$,

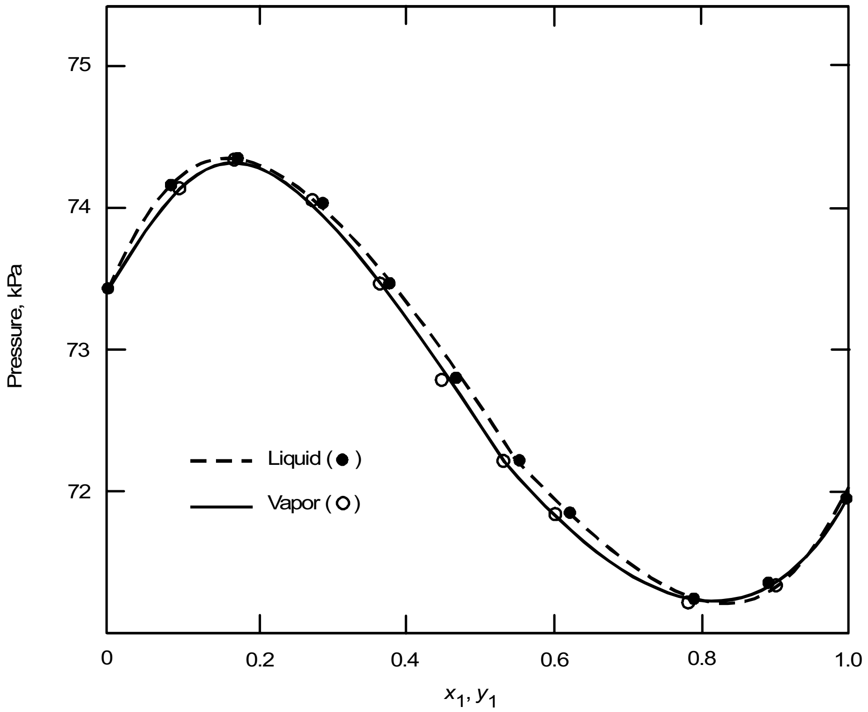
$$-\frac{1}{2} \le \frac{RT}{4A} \le \frac{1}{2}$$

Thus, if $|A| \ge \frac{1}{2}RT$, an azeotrope exists.

---

3. From the plot *P*-*x*-*y* we can see the unusual behavior of this system:

1. There is a double azeotrope
2. Liquid and vapor curves are very close to each other.



---

4. Neglecting vapor phase non-idealities,

$$P = x_1\gamma_1 P_1^s + x_2\gamma_2 P_2^s \tag{1}$$

At the maximum,

$$\left(\frac{\partial P}{\partial x_1}\right)_T = 0 = \gamma_1 P_1^s + x_1 P_1^s\left(\frac{\partial \gamma_1}{\partial x_1}\right)_T - x_2 P_2^s\left(\frac{\partial \gamma_2}{\partial x_2}\right)_T - \gamma_2 P_2^s \tag{2}$$

From the Gibbs-Duhem equation (at constant *T* and low pressure),

$$x_1\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)_T + x_2\left(\frac{\partial \ln\gamma_2}{\partial x_1}\right)_T = 0$$

or

$$\frac{x_1}{\gamma_1}\left(\frac{\partial\gamma_1}{\partial x_1}\right)_T = \frac{x_2}{\gamma_2}\left(\frac{\partial\gamma_2}{\partial x_2}\right)_T \tag{3}$$

Substituting Eq. (3) into Eq. (2) and simplifying,

$$(\gamma_1 P_1^s - \gamma_2 P_2^s)\left(1+\frac{x_1}{\gamma_1}\frac{\partial\gamma_1}{\partial x_1}\right) = 0$$

There are two possibilities:

(1) $\gamma_1 P_1^s - \gamma_2 P_2^s = 0$

Then

$$\frac{\gamma_2 P_2^s}{\gamma_1 P_1^s} = 1 = \frac{(y_2 / x_2)}{(y_1 / x_1)} = \alpha$$

$\alpha = 1$ corresponds to an azeotrope

(2) $1+\frac{x_1}{\gamma_1}\frac{\partial\gamma_1}{\partial x_1} = 0$

The solution to this differential equation is $x_1\gamma_1 = \text{constant}$.

To find the constant, use the boundary condition $\gamma_1 = 1$ when $x_1 = 1$.

Hence $\gamma_1 x_1 = 1$.

As $y_1 P = x_1\gamma_1 P_1^s$ if $\gamma_1 x_1 = 1$, then y_1 must be 1.[†]

Hence, the curve *P*-*x* goes through a maximum at $x_1 = 1$. This is also an azeotrope (but a trivial one).

5. Given

$$g^E = A_{12}x_1x_2 + A_{13}x_1x_3 + A_{14}x_1x_4 + A_{23}x_2x_3 + A_{24}x_2x_4 + A_{34}x_3x_4$$

where

[†] This may not be immediately obvious. But $\gamma_1 x_1$ is the activity, and the activity of component 1 cannot reach unity for any x_1 less than one because the solution will split into two phases of lower activity. See Fig. 6-25 in the text.

$$x_1 = n_1 / n_T$$

$$x_2 = x_2 / n_T$$

$$\vdots$$

with $n_T = n_1 + n_2 + n_3 + n_4$ the total number of moles.

Because

$$RT \ln \gamma_1 = \left(\frac{\partial n_T g^E}{\partial n_1} \right)_{P,T,n_2,n_3,n_4}$$

we find

$$RT \ln \gamma_1 = A_{12}x_2^2 + A_{13}x_3^2 + A_{14}x_4^2 + x_2x_3(A_{12} + A_{13} - A_{23})$$

$$+x_2x_4(A_{12} + A_{14} - A_{24}) + x_3x_4(A_{13} + A_{14} - A_{34})$$

---

6. Calculate *T*-*y* giving pressure and for $x = 0.1, 0.2, \ldots, 0.9$ – bubble-point calculation.
We have to solve the equilibrium equations:

$$\varphi_i y_i P = \gamma_i x_i P_i^s \tag{1}$$

Because total pressure is low (below atmospheric) we assume vapor phase as ideal: $\varphi_i \approx 1$.

The activity coefficients are obtained from the equation for G^E given in the data. Using Eq. (6-47) of the text we obtain

$$\begin{aligned} \ln \gamma_1 &= -2.1x_2^2 \\ \ln \gamma_2 &= -2.1x_1^2 \end{aligned} \tag{2}$$

As the pressure is fixed, temperature varies along with x_1 (and y_1) and is bounded by the saturation temperatures of the two components. These can be easily obtained from the vapor-pressure equations. They are given in the form,

$$\ln P^s = A - \frac{B}{T + C} \tag{3}$$

from which we obtain the saturation temperature

$$T^s = \frac{B}{A - \ln P^s} - C \tag{4}$$

For P^s = 30 kPa, we obtain $T_1^s = 387.26\ \text{K}$ for cyclohexanone (1) and $T_2^s = 415.59\ \text{K}$ for phenol (2).

To obtain the T-x_1-y_1 diagram we assign values for the liquid mole fraction x_1. Total pressure is

$$P = \gamma_1 x_1 P_1^s + \gamma_2 x_2 P_2^s$$

or

$$P_1^s = \frac{P}{\gamma_1 x_1 + \gamma_1 x_1 \dfrac{P_2^s}{P_1^s}} \tag{5}$$

To start the calculation we make an initial estimate of the temperature:

$$T = x_1 T_1^s + x_2 T_2^s \tag{6}$$

For example, let us fix $x_1 = 0.5$: $T = 0.5 \times 387.26 + 0.5 \times 415.59 = 401.42\ \text{K}$

With this temperature we obtain P_1^s and P_2^s from Eq. (3), the pure-component vapor pressure equations: $P_1^s = 47.243\ \text{kPa}$ and $P_2^s = 17.918\ \text{kPa}$ Because we fixed x_1, Eqs. (2) give $\gamma_1 = \exp(-2.1 \times 0.5^2) = 0.592$ and $\gamma_2 = 0.592$.

Next we recalculate $P_1^s = 73.482\ \text{kPa}$ from Eq. (5), which in turn gives a new temperature, T = 416.34 K, from the pure cyclohexanone vapor pressure equation.

The sequence of calculations is now repeated for this new temperature (we assume here that activity coefficients are independent of temperature), yielding:

$P_2^s = 30.786$ kPa; $P_1^s = 71.426$ kPa [from Eq.(5)]

$T_1^s = 415.34$ K [from Eq.(6)]

•
•
•

P_1^s = 71.552 kPa; T_1^s = 415.40 K; P_2^s = 29.798 kPa

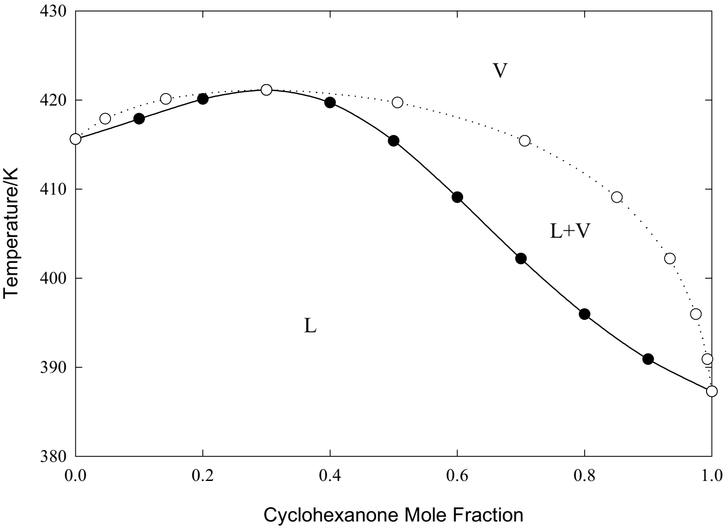
After these values, the change in temperature is small and therefore additional iterations leads to no significant further change in the remaining values.

We can now calculate the vapor phase mole fraction from

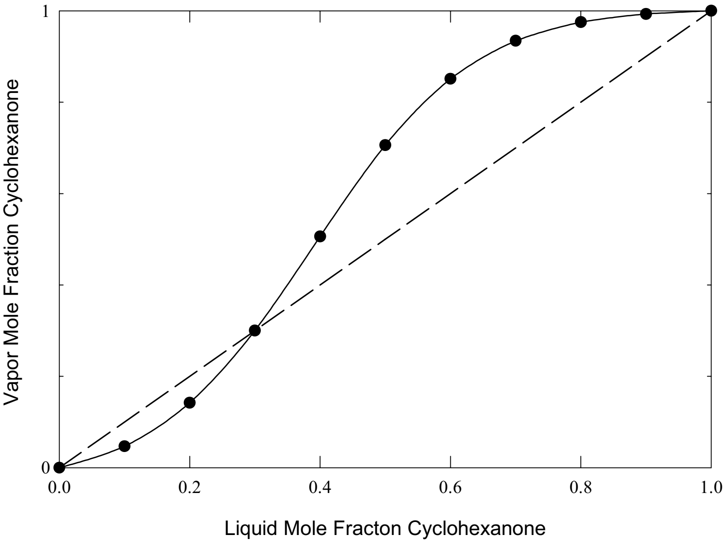
$$y_1 = \frac{x_1 \gamma_1 P_1^s}{P} = \frac{(0.5) \times (0.592) \times (71.552)}{30} = 0.706$$

The whole process is repeated for a new liquid mole fraction.

The following figure shows the computed T-x_1-y_1 diagram for this system at 30 kPa.



Similarly, with the data calculated we can easily draw the corresponding y_1-x_1 diagram, shown in the figure below.



As both figures show, this system has an azeotrope at $T^{\mathrm{az}} \approx 421\,\mathrm{K}$ and for the composition $x_1^{\mathrm{az}} \approx 0.3$.

7. Assume $g^E = Ax_1x_2$, where A is a function of temperature. Then,

$$RT\ln\gamma_1^\infty = RT\ln\gamma_2^\infty = A$$

But

$$\ln\gamma_1^\infty = 0.15 + \frac{10}{T-273} = \frac{A}{RT}$$

Because

$$\frac{\partial(g^E/T)}{\partial T} = \frac{-h^E}{T^2}$$

$$\frac{\partial(g^E/T)}{\partial T} = \frac{-10Rx_1x_2}{(T-273)^2} = \frac{-h^E}{T^2}$$

At $x_1 = x_2 = 0.5$ and $T = 333\text{K}$,

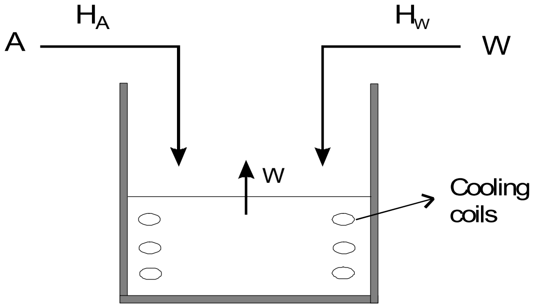
$$h^E = \Delta_{\text{mix}}h = \mathbf{641\ J\ mol^{-1}}$$

8.

a) From the equation for $\overline{H}_w$ we can obtain the infinite dilution partial molar enthalpy of water in sulfuric acid solutions at 293 K and 1 bar as:

$$\overline{H}_w^\infty = \lim_{x_w\to 0}\overline{H}_w = \lim_{x_A\to 1}\overline{H}_w = \mathbf{-41.44\ kJ\ mol^{-1}}$$

b) The mixing process is schematically shown below.



Taking the liquid in the vessel as the system, a first law balance gives for this flow process:

$$dU = dQ + dW + H_A dn_A + H_w dn_w$$

where work W is $dW = -PdV$, done on environment by the rising liquid level, under constant pressure.

Then,

$$d(U + PV) = dH = dQ + H_A dn_A + H_w dn_w$$

Integrating between initial state (empty vessel) and final state (full vessel), because $H_A = H_A(T,P)$ of the pure acid and $H_w = H_w(T,P)$ of the pure water are constant, we obtain

$$H = Q + n_A H_A + n_w H_w \quad \text{or} \quad Q = H - n_A H_A - n_w H_w$$

But $H = n_A \overline{H}_A + n_w \overline{H}_w$, and the equation above becomes

$$Q = n_A(\overline{H}_A - H_A) + n_w(\overline{H}_w - H_w) = n_A \Delta\overline{H}_A + n_w \Delta\overline{H}_w = \Delta H \tag{1}$$

where n_A = 1 mol and n_w = 2 mol in the final state.

In Eq. (1), the quantity $(\overline{H}_w - H_w)$ is given by the equation given in the data, because the reference state in that equation has been chosen to be pure water at system T and P:

$$\overline{H}_w - H_w = -\frac{134 x_A^2}{(1 + 0.7983 x_A)^2} \quad \text{kJ mol}^{-1} \tag{2}$$

We need now to calculate the quantity $(\overline{H}_A - H_A)$, knowing $(\overline{H}_w - H_w)$. This can be done by using the Gibbs-Duhem equation.

At constant T and P:

$$x_A d\overline{H}_A + x_w d\overline{H}_w = 0 \qquad \Rightarrow \qquad d\overline{H}_A = -\frac{x_w}{x_A} d\overline{H}_w = -\frac{1 - x_A}{x_A} d\overline{H}_w \tag{3}$$

Differentiating Eq. (2), at constant T and P, we obtain:

$$d\overline{H}_w = (-134 \text{ kJ mol}^{-1}) \times \frac{2x_A(1 + 0.7983x_A)^2 - 2(0.7983)x_A^2(1 + 0.7983x_A)}{(1 + 0.7983x_A)^4} dx_A$$

$$= \frac{-268 x_A}{(1 + 0.7983 x_A)^3} dx_A \qquad (\text{kJ mol}^{-1}) \tag{4}$$

Therefore, from Eqs. (3) and (4),

$$d\overline{H}_A = \frac{268(1 - x_A)}{(1 + 0.7983 x_A)^3} dx_A \qquad (\text{kJ mol}^{-1}) \tag{5}$$

Integrating Eq. (5) between composition x_A and composition x_A = 1 (pure acid) gives

$$\overline{H}_A - \overline{H}_A(x_A = 1) = \overline{H}_A - H_A = \int_1^{x_A} \frac{268(1-x_A)}{(1+0.7983x_A)^3} dx_A$$

$$= \left[\frac{335.71(x-0.1263)}{(1+0.7983x_A)^2}\right]_1^{x_A} = \frac{-74.51(1-x_A)^2}{(1+0.7983x_A)^2} \qquad (\text{kJ mol})^{-1} \tag{6}$$

We can now calculate the heat load Q in Eq. (1). Setting $n = n_A + n_w = 3$ mol, and using Eqs. (2) and (6) in (1),

$$Q = n\left[\frac{-74.51x_A(1-x_A)^2}{(1+0.7983x_A)^2} - \frac{134x_A^2(1-x_A)}{(1+0.7983x_A)^2}\right]$$

$$= n\left[\frac{-74.51x_A(1-x_A)(1-x_A+1.7983x_A)}{(1+0.7983x_A)^2}\right] \tag{7}$$

$$= n\left[\frac{-74.51x_A(1-x_A)}{1+0.7983x_A}\right] \qquad (\text{kJ mol}^{-1})$$

Substitution of $n = 3$ mol and $x_A = 1/3$ gives the desired heat load:

$$\boldsymbol{Q = -39.23\ \textbf{kJ}}$$

Q is negative because heat is removed *from* the system.

9.

a) Yes, it's possible. Slight positive deviations merely mean that the physical interaction between SO_2 and C_4H_8 makes a larger contribution to the excess Gibbs energy than does the chemical interaction.

b)

$$g^E_{SO_2-\text{isobutene}} > g^E_{SO_2-n\text{-butene-2}}$$

because the tendency to complex (which tends to make g^E negative) is stronger with *n*-butene-2. Steric hindrance in isobutene is larger than in *n*-butene-2.

10. The suggested procedure is to integrate numerically a suitable form of the Gibbs-Duhem equation.

At low pressures, we may write the Gibbs-Duhem equation:

$$\frac{x_1}{\gamma_1}\left(\frac{\partial\gamma_1}{\partial x_1}\right)_T+\frac{x_2}{\gamma_2}\left(\frac{\partial\gamma_2}{\partial x_2}\right)_T=0$$

By assuming ideal-gas behavior,

$$\gamma_1=\frac{y_1P}{x_1P_1^s}=\frac{P_1}{x_1P_1^s}$$

$$\frac{\partial\gamma_1}{\partial x_1}=\frac{1}{x_1P_1^s}\left(\frac{\partial P_1}{\partial x_1}\right)-\frac{P_1}{x_1^2P_1^s}$$

Similarly,

$$\frac{\partial\gamma_2}{\partial x_1}=-\frac{1}{x_2P_2^s}\left(\frac{\partial P_2}{\partial x_2}\right)+\frac{P_2}{x_2^2P_2^s}$$

Substituting we find

$$\frac{x_1}{P_1}\frac{\partial P_1}{\partial x_1}=\frac{x_2}{P_2}\frac{\partial P_2}{\partial x_2}$$

Because $P=P_1+P_2$, $dP=dP_1+dP_2$, then

$$\frac{\partial P_2}{\partial x_2}=\frac{\partial P}{\partial x_2}\left[\frac{1}{1-\frac{x_2P_1}{x_1P_2}}\right]$$

In different form:

$$\frac{\Delta P_2}{\Delta x_2}=\frac{1}{1-\frac{x_2P_1}{x_1P_2}}\frac{\Delta P}{\Delta x_2}$$

For *P*-*x* data, we choose a small Δx_2 (say 0.05) and integrate to find ΔP_2 and thus P_2. We obtain P_1 by difference: $P_1=P-P_2$.

This method is described by Boissanas, quoted in Prigogine and Defay, *Chemical Thermodynamics,* page 346. It gives good agreement with experimental partial-pressure data for this particular system.

11. For a binary system, the Wilson equation gives

$$\ln\gamma_1 = -\ln(x_1 + x_2\Lambda_{12}) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right] \tag{1}$$

$$\ln\gamma_2 = -\ln(x_2 + x_1\Lambda_{21}) - x_1\left[\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right] \tag{2}$$

At infinite dilution these equations become

$$\ln\gamma_1^\infty = -\ln\Lambda_{12} + (1 - \Lambda_{21}) \tag{3}$$

$$\ln\gamma_2^\infty = -\ln\Lambda_{21} - (\Lambda_{12} - 1) \tag{4}$$

For $\gamma_1^\infty = 12.0,\ \gamma_2^\infty = 3.89,$ solve Eqs. (3) and (4) to find,

$$\Lambda_{21} = 0.6185$$

$$\Lambda_{12} = 0.1220$$

Assuming ideal-gas behavior and neglecting Poynting correction, we may write:

$$y_1 P = x_1\gamma_1 P_1^s \tag{5}$$

$$y_2 P = x_2\gamma_2 P_2^s \tag{6}$$

$$P = x_1\gamma_1 P_1^s + x_2\gamma_2 P_2^s \tag{7}$$

From Perry's, the saturation pressures at 45°C are:

$$P_1^s = 0.188 \text{ bar}$$

$$P_2^s = 0.0958 \text{ bar}$$

To construct the *P-x-y* diagram:

1. Choose x_1 (or x_2)
2. Calculate y_1 (or y_2) from Eq. (5) and using Eqs. (1) and (2)
3. Calculate P from Eq. (7).

12. The solution procedure would be:

1. Find P_1^s and P_2^s at each T.

2. At this low pressure, assume ideal-gas behavior and neglect Poynting correction:

$$y_1 P = x_1 \gamma_1 P_1^s$$

$$y_2 P = x_2 \gamma_2 P_2^s$$

For γ 's use the Wilson equation with two parameters: Λ_{12} and Λ_{21}. Assume that $(\lambda_{11} - \lambda_{12})$ and $(\lambda_{22} - \lambda_{12})$ are independent of temperature.

Λ_{12} and Λ_{21} are, however, temperature-dependent as given by Eqs. (6-107) and (6-108).

3. Assume value of $(\lambda_{11} - \lambda_{12})$ and $(\lambda_{22} - \lambda_{12})$ and calculate the total pressure:

$$P_{\text{calc}} = x_1 \gamma_1 P_1^s + x_2 \gamma_2 P_2^s$$

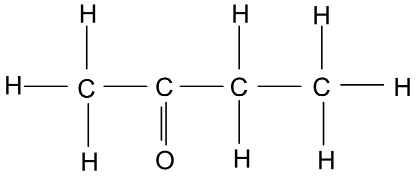
4. Repeat; assuming new values. Keep repeating until P_{calc} is very close to 0.5 bar for every point; that is until

$$\sum_{i=1}^{n} (P_{\text{calc}} - P)^2 \quad \text{is a minimum}$$

where n is the number of data points.

13.

a) 2-Butanone:



$CH_3-C(=O)-CH_2-CH_3$

Cyclohexane:

$$(CH_2)_6$$

6 groups CH_2: R = 0.6744; Q = 0.540

Molecule	Group	Number	R	Q
2-Butanone	CH_3CO	1	1.6724	1.488
	CH_3	1	0.9011	0.848
	CH_2	1	0.6744	0.540
Cyclohexane	CH_2	6	0.6744	0.540

b) We use UNIFAC activity coefficient equations to calculate γ_1 and γ_2 for the equimolar mixture at 75°C (for a detailed example of a similar UNIFAC calculation see Chapter 8 of *The Prop-*

erties of Gases and Liquids by R.C. Reid, J.M. Prausnitz, B. E Poling (4th. Ed., McGraw-Hill, 1988).

We obtain:

$$\ln\gamma_1 = \ln\gamma_1^{\text{comb}} + \ln\gamma_1^{\text{res}} = 0.01228 + 0.2595 = 0.27238 \quad \Rightarrow \quad \gamma_1 = 1.31$$

$$\ln\gamma_2 = \ln\gamma_2^{\text{comb}} + \ln\gamma_2^{\text{res}} = 0.01415 + 0.3420 = 0.35615 \quad \Rightarrow \quad \gamma_2 = 1.43$$

c) Using UNIFAC we can calculate the activity coefficients as a function of composition at 75°C.

Total pressure is calculated from

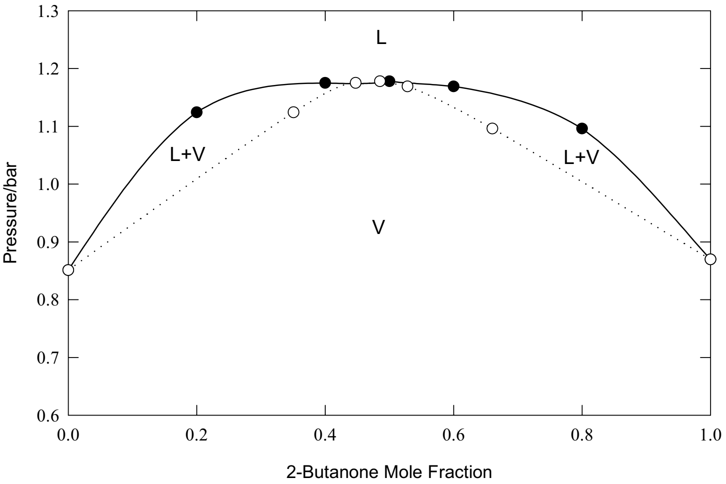
$$P = x_1\gamma_1 P_1^s + x_2\gamma_2 P_2^s$$

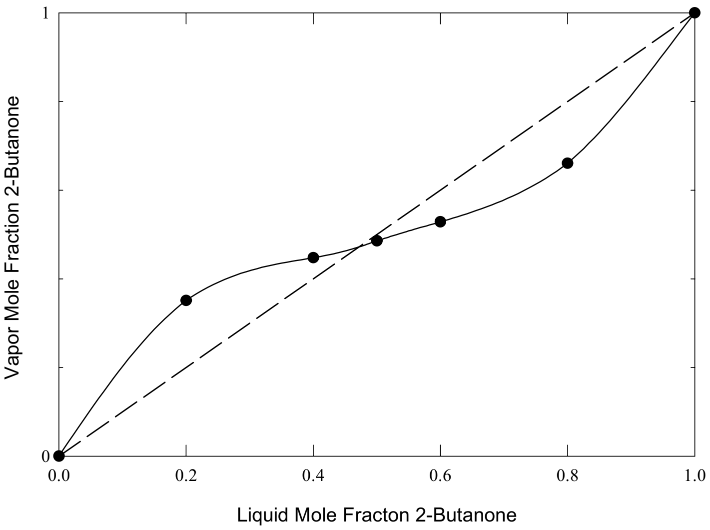
and the vapor-phase composition from

$$y_1 = \frac{x_1\gamma_1 P_1^s}{P}$$

Using Antoine vapor pressure equations at 75°C, we obtain for 2-butanone $P_1^s = 0.8695$ bar and for cyclohexane $P_2^s = 0.8651$ bar.

The following figures show the calculated results in the form of P-x_1-y_1 and y_1-x_1 diagrams.





The table below shows the calculated activity coefficients from UNIFAC, vapor composition and total pressure.

x_1	γ_1	γ_2	y_1	P/bar
0	4.38	1.00	0	0.8511
0.2	2.27	1.07	0.351	1.124
0.4	1.51	1.27	0.447	1.175
0.5	1.32	1.42	0.485	1.178
0.6	1.18	1.62	0.528	1.169
0.8	1.04	2.19	0.660	1.096
1.0	1.00	3.10	1.0	0.8695

Comparison of the calculated γ's in this table with those given in the data, indicate that the latter are actually UNIFAC predictions and not experimental data. In the tables, at $x_1 = 0$ and $x_1 = 1$ the activity coefficients listed are, respectively, γ_1^∞ and γ_2^∞. UNIFAC predicts $\gamma_1^\infty = 4.38$, which compares well with the experimental ebulliometry data at 77.6°C, $\gamma_1^\infty = 3.70$.

14. The UNIQUAC equation is

$$g^E = g^E_{\text{combinatorial}} + g^E_{\text{residual}}$$

$$\frac{g^E_{\text{comb}}}{RT} = x_1 \ln\frac{\Phi_1}{x_1} + x_2 \ln\frac{\Phi_2}{x_2} + \frac{z}{2}(x_1 q_1 \ln\frac{\theta_1}{\Phi_1} + x_2 q_2 \ln\frac{\theta_2}{\Phi_2})$$

$$\frac{g^E_{\text{res}}}{RT} = -x_1 q_1 \ln(\theta_1 + \theta_2 \tau_{21}) - x_2 q_2 \ln(\theta_2 + \theta_1 \tau_{12})$$

$$\Phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} \qquad \theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2}$$

$$\tau_{12} = \exp(-\frac{a_{12}}{T}) \qquad \tau_{21} = \exp(-\frac{a_{21}}{T})$$

The condition for instability of a binary liquid mixture is

$$\left(\frac{\partial^2 \Delta_{\text{mix}} g}{\partial x^2}\right)_{P,T} < 0 \tag{1}$$

where $\Delta_{\text{mix}} g$ is the molar change in Gibbs energy upon mixing, or

$$\left(\frac{\partial^2 g^E}{\partial x_1^2}\right)_{P,T} + RT\left(\frac{1}{x_1} + \frac{1}{x_2}\right) < 0$$

Incipient instability occurs at

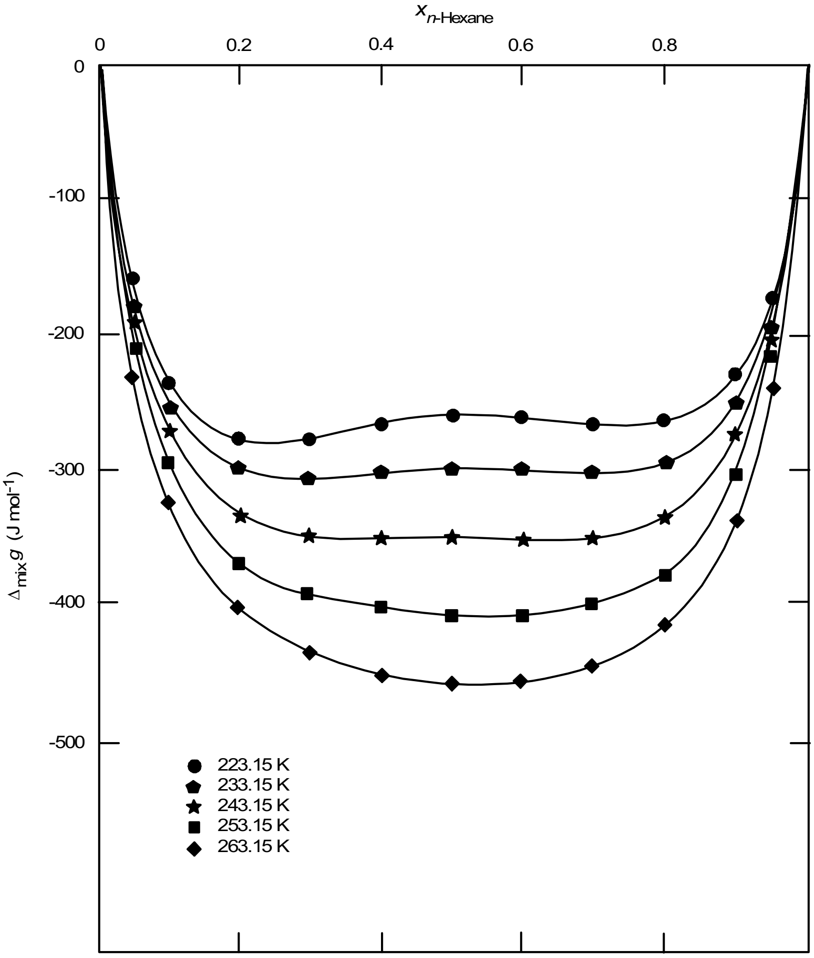
$$\left(\frac{\partial^2 \Delta_{\text{mix}} g}{\partial x^2}\right)_{P,T} = 0$$

and

$$\left(\frac{\partial^3 \Delta_{\text{mix}} g}{\partial x^3}\right)_{P,T} = 0$$

Given x_1, x_2 and all parameters, we could determine if Eq. (1) is satisfied. However, the procedure is long and tedious. It is easier to graph $\Delta_{\text{mix}} g$ over the composition range and to look for inflection points.

For the data given, phase separation occurs at -40°C.



---

15. If the two curves cross $\Delta_{\text{mix}}g/RT$ is zero because

$$\Delta_{\text{mix}}g = \Delta_{\text{mix}}h - T\Delta_{\text{mix}}s$$

This is <u>not</u> possible, because $\Delta_{\text{mix}}g$ must always be negative for two liquids to be miscible.

---

16. To relate γ_i^∞ to $H_{i,j}$:

$$\gamma_i = \frac{f_i}{x_i f_i^0}$$

then,

$$\gamma_i^\infty = \lim_{x_i \to 0}\left(\frac{f_i}{x_i f_i^0}\right) = \frac{1}{f_i^0}\lim\left(\frac{f_i}{x_i}\right) = \frac{H_{i,j}}{f_i^0}$$

Assuming $f_i^0 \cong P_i^s$,

$$\gamma_i^\infty = \frac{H_{i,j}}{P_i^s}$$

then,

$$\gamma_1^\infty = \frac{H_{1,2}}{P_1^s} = \frac{2}{1.07} = 1.869$$

$$\gamma_2^\infty = \frac{H_{2,1}}{P_2^s} = \frac{1.6}{1.33} = 1.203$$

Using the van Laar equations,

$$\ln\gamma_1 = \frac{A'}{\left(1 + \frac{A'}{B'}\frac{x_1}{x_2}\right)^2}$$

$$\ln\gamma_2 = \frac{B'}{\left(1 + \frac{B'}{A'}\frac{x_2}{x_1}\right)^2}$$

we get

$$\ln\gamma_1^\infty = A' = 0.625$$

$$\ln\gamma_2^\infty = B' = 0.185$$

To solve for vapor composition (assuming ideal vapor and neglecting Poynting corrections),

$$y_1 P = x_1 \gamma_1 P_1^s$$

$$y_2 P = x_2 \gamma_2 P_2^s$$

$$P = y_1 P + y_2 P$$

At $x_1 = x_2 = 0.5$,

$$\ln\gamma_1 = \frac{0.625}{\left(1+\dfrac{0.625}{0.185}\right)^2} = 0.033 \qquad \Rightarrow \qquad \gamma_1 = 1.033$$

$$\ln\gamma_2 = \frac{0.185}{\left(1+\dfrac{0.185}{0.625}\right)^2} = 0.110 \qquad \Rightarrow \qquad \gamma_2 = 1.116$$

Therefore,

$$y_1P = (0.5)\times(1.033)\times(1.07) = 0.55 \text{ bar}$$

$$y_2P = (0.5)\times(1.116)\times(1.33) = 0.74 \text{ bar}$$

$$P = 0.55 + 0.74 = 1.29 \text{ bar}$$

$$y_1 = 0.55/1.29 = \mathbf{0.426}$$

$$y_2 = \mathbf{0.574}$$

---

17. To estimate the vapor-phase composition, assume ideal vapor:

$$y_iP = x_i\gamma_iP_i^s \qquad (i\text{=1, 2, 3})$$

Then,

$$P = y_1P + y_2P + y_3P$$

To find the activity coefficients, assume that g^E/RT is given by a sum of Margules terms [Eq. (6-149)]. Then,

$$\ln\gamma_1 = A'_{12}x_2^2 + A'_{13}x_3^2 + (A'_{12} + A'_{13} - A'_{23})x_2x_3 \qquad (1)$$

$$\ln\gamma_2 = A'_{12}x_1^2 + A'_{23}x_3^2 + (A'_{12} + A'_{23} - A'_{13})x_1x_3 \qquad (2)$$

$$\ln\gamma_3 = A'_{13}x_1^2 + A'_{23}x_2^2 + (A'_{13} + A'_{23} - A'_{12})x_1x_2 \qquad (3)$$

We can find A'_{12}, A'_{13}, A'_{23} from binary data.

From (1-2) binary:

$$\ln \gamma_1^{\infty} = \frac{A}{RT} = \ln(1.3) = 0.262$$

$$A'_{12} = 0.262 \quad \text{at} \quad 320\text{K}$$

At 300K, $A'_{12} = (0.262) \times \left(\frac{320}{300}\right) = 0.280$ (assuming regular solution).

From (1-3) binary:

At azeotrope $x_1 = y_1, \; x_3 = y_3$

$$y_1 P = x_1 \gamma_1 P_1^s$$

$$y_3 P = x_3 \gamma_3 P_3^s$$

$$\gamma_1 = \gamma_3 = P / P_1^s = 1.126$$

$$\ln \gamma_1 = \frac{A}{RT} x_2^3$$

At $x_3 = 0.5$, $\frac{A}{RT} = A'_{13} = 0.475$.

From (2-3) binary:

$$\ln \gamma_2 = \frac{A}{RT} x_3^2$$

At incipient instability,

$$\frac{A}{RT^c} = 2$$

or

$$\frac{A}{R} = 2T^c$$

$$\frac{A}{RT} = \left(\frac{A}{RT^c}\right)\left(\frac{T^c}{T}\right) = (2) \times \left(\frac{270}{300}\right) = 1.80$$

$$A_{23} = 1.80$$

With $x_1 = x_2 = x_3$, from Eqs. (1), (2) and (3):

$$\ln\gamma_1 = -0.0322 \quad \Rightarrow \quad \gamma_1 = 0.968$$

$$\ln\gamma_2 = 0.409 \quad \Rightarrow \quad \gamma_1 = 1.506$$

$$\ln\gamma_3 = 0.475 \quad \Rightarrow \quad \gamma_1 = 1.607$$

$$y_1P = (1/3)\times(0.968)\times(0.533) = 0.172 \text{ bar}$$

$$y_2P = (1/3)\times(1.506)\times(0.400) = 0.201 \text{ bar}$$

$$y_3P = (1/3)\times(1.607)\times(0.533) = 0.286 \text{ bar}$$

$$P = 0.172 + 0.201 + 0.286 = 0.659 \text{ bar}$$

Then,

$$\mathbf{y_1 = 0.261}$$

$$\mathbf{y_2 = 0.305}$$

$$\mathbf{y_3 = 0.434}$$

18. Using the 3-suffix Margules equation,

$$g^E / RT = x_1x_2[A + B(x_1 - x_2)]$$

we obtain

$$\ln\gamma_1 = (A + 3B)x_2^2 - 4Bx_2^3$$

$$\ln\gamma_2 = (A - 3B)x_1^2 + 4Bx_1^3$$

At infinite dilution,

$$\ln\gamma_1^\infty = A - B$$

$$\ln\gamma_2^\infty = A + B$$

which gives

$$A = 1.89$$

$$B = -0.34$$

For instability to occur,

$$\left(\frac{\partial^2 g^E}{\partial x_1^2}\right)_{P,T} + RT\left(\frac{1}{x_1} + \frac{1}{x_2}\right) < 0$$

Rewriting g^E as

$$g^E = RT[(A-B)x_1 - (A-3B)x_1^2 - 2Bx_1^3]$$

$$\frac{\partial g^E}{\partial x_1} = RT[(A-B) - 2(A-3B)x_1 - 6Bx_1^2]$$

$$\frac{\partial^2 g^E}{\partial x_1^2} = RT[-2(A-3B) - 12Bx_1]$$

Thus, the condition for instability (at constant *T*) is:

$$RT\left[-2A + 6B - 12Bx_1 + \frac{1}{x_1} + \frac{1}{1-x_1}\right] < 0$$

Finding the zeros of the function in brackets,

$x_1 = 0.421$ and $x_1 = 0.352$ in the range $0 < x_1 < 1$.

Thus, instability at *T* is in the range

$$\mathbf{0.352 < x_1 < 0.421}$$

19.

a) At the azeotrope

$$\left(\frac{\partial P}{\partial x_A}\right)_T = 0$$

With g^E / RT of the form $g^E / RT = Ax_A x_B$,

$$\ln\gamma_A = Ax_B^2$$

$$\ln\gamma_B = Ax_A^2$$

Assuming an ideal vapor phase,

$$y_A P = x_A \gamma_A P_A^s$$

$$y_B P = x_B \gamma_B P_B^s$$

$$P = x_A \gamma_A P_A^s + x_B \gamma_B P_B^s$$

$$P = x_A \exp(A x_B^2) P_A^s + x_B \exp(A x_A^2) P_B^s$$

$$\left(\frac{\partial P}{\partial x_A} \right) = P_A^s \exp(A x_B^2)(1 - 2 x_A x_B A) + P_B^s \exp(A x_A^2)(-1 + 2 x_B x_A A) = 0$$

$$P_A^s \exp(A x_B^2) = P_B^s \exp(A x_A^2)$$

$$A x_B^2 = \ln(P_B^s / P_A^s) + A x_A^2$$

At 30°C,

$$P_A^s = 0.235 \text{ bar}; \quad P_B^s = 0.658 \text{ bar}; \quad A = 0.415$$

Then, $x_A = 0.30$.

At 50°C,

$$P_A^s = 0.539 \text{ bar}; \quad P_B^s = 0.658 \text{ bar}; \quad A = 0.415$$

Then $x_A = 0.26$.

At 70°C,

$$P_A^s = 1.119 \text{ bar}; \quad P_B^s = 1.367 \text{ bar}; \quad A = 0.330$$

Then $x_A = 0.20$.

b) Assuming ideal vapor,

$$\gamma_A = y_A P / x_A P_A^s$$

$$\gamma_B = y_A P / x_B P_B^s$$

At azeotrope, $x_A = y_A$, $x_B = y_B$. Then

$$\gamma_A = P / P_A^s$$

$$\gamma_B = P / P_B^s$$

Taking the ratio

$$\gamma_A / \gamma_B = P_B^s / P_A^s$$

$$\ln(\gamma_A / \gamma_B) = \ln P_B^s - \ln P_A^s$$

$$= 12.12 - \frac{4050}{T} - 11.92 + \frac{4050}{T}$$

$$= 0.20$$

Because

$$\ln \gamma_A = Ax_B^2 \qquad \text{and} \qquad \ln \gamma_B = Ax_A^2,$$

$$\ln(\gamma_A / \gamma_B) = A(x_B^2 - x_A^2) = 0.2$$

$$A = \frac{1}{5 - 10x_A} \qquad \text{because} \quad 0 < x_A < 1$$

If |A| > 0.2 there is an azeotrope.
The pure component boiling points are:

$$t_b^A = 67°\text{C}$$

$$t_b^B = 61°\text{C}$$

In the range 61°C < t < 67°C, A is always larger than 0.2. Therefore, the azeotrope exists.

c) The enthalpy of mixing equation cannot be totally consistent since the expression for g^E is quadratic in mole fraction and the expression for $\Delta_{\text{mix}}h$ is cubic. However, they may be close. To check this, we use the Gibbs-Helmholtz equation:

$$\frac{\partial g^E / RT}{\partial T} = \frac{-h^E}{RT^2}$$

$$\frac{g^E}{RT} = A(T)x_A x_B$$

$$\frac{\partial g^E / RT}{\partial T} = x_A x_B \frac{\partial A}{\partial T} \cong x_A x_B(-0.00425)$$

Because $h^E = \Delta_{\text{mix}} h$,

$$\frac{\Delta_{\text{mix}} h^{(1)}}{RT} = (323) \times (0.00425) x_A x_B = 1.373 x_A x_B$$

The other data indicate

$$\frac{\Delta_{\text{mix}} h^{(2)}}{RT} = (1.020 + 0.112 x_A) x_A x_B$$

Looking at selected values:

x_A	$\Delta_{\text{mix}} h^{(1)}/RT$	$\Delta_{\text{mix}} h^{(2)}/RT$
0.1	0.123	0.093
0.2	0.220	0.167
0.3	0.288	0.221
0.4	0.330	0.256
0.5	0.343	0.269
0.6	0.330	0.261
0.7	0.288	0.231
0.8	0.220	0.178
0.9	0.123	0.101

The above shows the degree of inconsistency of the two sets of data.

SOLUTIONS TO PROBLEMS

CHAPTER 7

1. Using regular-solution theory and data for A in CS_2 we find the solubility parameter for A. Then, we predict vapor-liquid equilibria for the A/toluene system.

Let B refer to toluene and C refer to CS_2. From regular-solution theory,

$$RT\ln\gamma_A = v_A\Phi_C^2(\delta_A - \delta_C)^2 \qquad \text{(for A in CS}_2\text{)}$$

Further, assuming ideal vapor phase, we have

$$y_A P = P_A = x_A\gamma_A P_A^s$$

$$\gamma_A = \frac{8}{(0.5)\times(13.3)} = 1.203$$

or

$$\ln\gamma_A = 0.185$$

Then,

$$\delta_A - \delta_C = \pm\left[\frac{RT\ln\gamma_A}{v_A}\right]^{1/2}\frac{1}{\Phi_C}$$

with

$$v_A = 200 \text{ cm}^3 \text{ mol}^{-1} \qquad \text{and} \qquad \Phi_C = 0.234$$

$$\delta_A - \delta_C = \pm 6.30 \ (\text{J cm}^{-3})^{1/2}$$

For liquid hydrocarbons, δ is approximately 12-18 (J cm^{-3})$^{1/2}$. Therefore, we take the smaller value.

For A in toluene,

$$RT\ln\gamma_A = \upsilon_A\Phi_B^2(\delta_A-\delta_B)^2$$

or

$$\gamma_A = 1.18$$

$$RT\ln\gamma_B = \upsilon_B\Phi_A^2(\delta_A-\delta_B)^2$$

or

$$\gamma_B = 1.37$$

For ideal vapor,

$$P = P_A + P_B = x_A\gamma_A P_A^s + x_B\gamma_B P_B^s = 25.3\ \text{kPa}$$

Hence,

$$y_A = 0.31$$

$$\mathbf{y_B = 0.69}$$

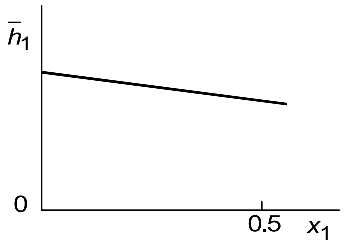
---

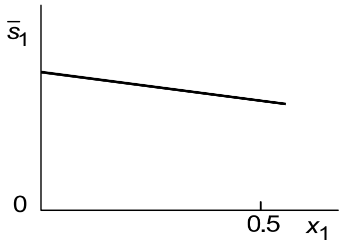
2. Excess properties (h^E, s^E) are defined in reference to an ideal (in the sense of Raoult's law) mixture of pure components.

The partial molar quantities $\bar{h}^E$ and $\bar{s}^E$ are the contributions to these excess properties per differential amount added to the solution.

The "pure" acetic acid is highly dimerized, so as the first bits go into solution thse dimers must be broken up. This will require energy ($\bar{h}_1^E > 0$) and will increase the entropy more than is accounted for by the ideal mixing term ($\bar{s}_1^E > 0$).

As x_1 gets larger, some dimer will begin to exist in the solution, so these effects will diminish. Therefore, at small x_1, the curves should look something like this:





3. The K factors for hexane (1) and benzene (2) (neglecting Poynting corrections and assuming ideal-vapor phase) are:

$$K_1 = \frac{\gamma_1 P_1^s}{P}$$

$$K_2 = \frac{\gamma_2 P_2^s}{P}$$

where

$$P = x_1\gamma_1 P_1^s + x_2\gamma_2 P_2^s$$

Using regular-solution theory,

$$RT\ln\gamma_1 = \upsilon_1\Phi_2^2(\delta_1 - \delta_2)^2$$

$$RT\ln\gamma_2 = \upsilon_2\Phi_1^2(\delta_1 - \delta_2)^2$$

The volume fractions are

$$\Phi_1 = 0.389 \qquad \Phi_2 = 0.611$$

From the above equations,

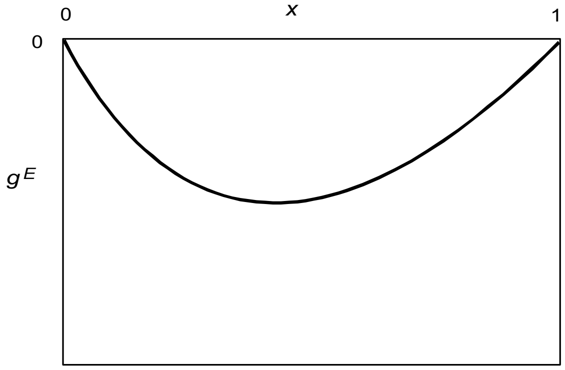
$$\gamma_1 = 1.32 \qquad \gamma_2 = 1.08$$

$$P = (0.3)\times(1.32)\times(0.533) + (0.7)\times(1.08)\times(0.380) = 0.498 \text{ bar}$$

$$K_1 = K_{C_6H_{14}} = \frac{(1.32)\times(0.533)}{0.498} = \mathbf{1.41}$$

$$K_2 = K_{C_6H_6} = \frac{(1.08)\times(0.38)}{0.498} = \mathbf{0.82}$$

4. Ether and pentachloroethane hydrogen bond with each other (but not with themselves). Then, $g^E < 0$.



5. The relative volatility of A and B is

$$\alpha_{A,B} = \frac{(y_A / x_A)}{(y_B / x_B)}$$

Assuming ideal vapor phase and neglecting Poynting corrections,

$$y_A P = x_A \gamma_A P_A^s$$

$$y_B P = x_B \gamma_B P_B^s$$

At the azeotrope, $x_A = y_A$ and

$$\alpha_{A,B} = 1 = \frac{\gamma_A P_A^s}{\gamma_B P_B^s}$$

From regular-solution theory,

$$RT \ln \gamma_A = v_A \Phi_B^2 (\delta_A - \delta_B)^2$$

$$RT \ln \gamma_B = v_B \Phi_A^2 (\delta_A - \delta_B)^2$$

Because $\upsilon_A = \upsilon_B$, $\gamma_A = \gamma_B$, then $P_A^s = P_B^s$.
For the ternary mixture,

$$RT \ln \gamma_i = \upsilon_i (\delta_i - \overline{\delta})^2$$

$$\overline{\delta} = \sum_i \Phi_i \delta_i$$

As $\Phi_A = \Phi_B = 0.2$ and $\Phi_C = 0.6$, $\overline{\delta} = 17.2 \ (\text{J cm}^{-3})^{1/2}$.
Then

$$\ln \gamma_A = \frac{(100) \times (14.3 - 17.2)^2}{(8.31451) \times (300)} \qquad \Rightarrow \qquad \gamma_A = 1.40$$

$$\ln \gamma_B = \frac{(100) \times (16.4 - 17.2)^2}{(8.31451) \times (300)} \qquad \Rightarrow \qquad \gamma_B = 1.03$$

$$\alpha_{A,B} = \frac{\gamma_A P_A^s}{\gamma_B P_B^s} = \frac{\gamma_A}{\gamma_B} = \frac{1.40}{1.03} = \mathbf{1.36}$$

6. Assuming ideal vapor phase and neglecting Poynting corrections,

$$y_1 P = x_1 \gamma_1 P_1^s$$

$$y_2 P = x_2 \gamma_2 P_2^s$$

$$P = x_1 \gamma_1 P_1^s + x_2 \gamma_2 P_2^s \tag{1}$$

Using regular-solution theory,

$$RT \ln \gamma_1 = \upsilon_1 \Phi_2^2 (\delta_1 - \delta_2)^2$$

$$RT \ln \gamma_2 = \upsilon_2 \Phi_1^2 (\delta_1 - \delta_2)^2$$

Because $\upsilon_1 = \upsilon_2$, we can rewrite [Eqs. (7-25) and (7-26)]:

$$RT \ln \gamma_1 = \upsilon_1 x_2^2 (\delta_1 - \delta_2)^2$$

$$RT \ln \gamma_2 = \upsilon_2 x_1^2 (\delta_1 - \delta_2)^2$$

As $\upsilon_1 = \upsilon_2 = 160 \ \text{cm}^3 \ \text{mol}^{-1}$,

$$\gamma_1 = \exp(0.616 x_2^2)$$

$$\gamma_2 = \exp(0.616 x_1^2)$$

Substitution in Eq. (1) gives

$$P = 0.533 \exp(0.616 x_2^2) + 0.800 \exp(0.616 x_1^2)$$

At the azeotrope,

$$\left(\frac{\partial P}{\partial x_1}\right)_T = 0$$

Thus, after differentiation,

$$0.616 x_2^2 = 0.40547 + 0.16 x_1^2$$

Solving for x_1,

$$\mathbf{x_1 = 0.171}$$

---

7. Neglecting vapor-phase non-idealities and Poynting corrections, the total pressure, P, is

$$P = x_\mathrm{A} \gamma_\mathrm{A} P_\mathrm{A}^s + x_\mathrm{B} \gamma_\mathrm{B} P_\mathrm{B}^s$$

Because the two fluids are similar in size, simple and nonpolar, we can assume that γ's are given by two-suffix Margules equations:

$$\ln \gamma_\mathrm{A} = \frac{A}{RT} x_\mathrm{B}^2$$

$$\ln \gamma_\mathrm{B} = \frac{A}{RT} x_\mathrm{A}^2$$

As $x_\mathrm{A} = x_\mathrm{B} = 0.5$,

$$P = 0.667 = 0.5 \times \left[\exp\left(\frac{A}{4RT}\right)\right] \times (0.427 + 0.493)$$

$$A = 4696 \text{ J mol}^{-1}$$

From Eq. (6-144) of the text,

$$T^c = \frac{A}{2R}$$

$$T^c = 282\ \mathrm{K}$$

If one considers the effect of non-randomness (based on the quasichemical approximation), Eq. (7-110) gives

$$T^c = \frac{A}{2.23R} = 253\ \mathrm{K}$$

(assuming that $\dfrac{A}{2R} = \dfrac{w}{2k} = \text{constant}$ and that the temperature dependence is given by $\ln\gamma$ proportional to $1/T$).

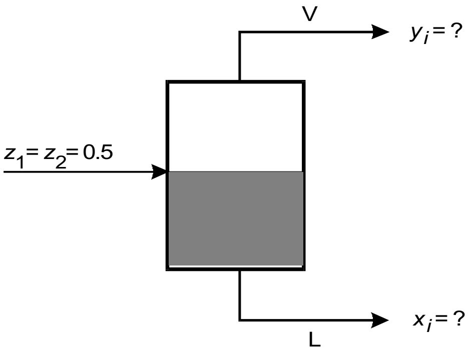
Thus, random mixing predicts a value higher than that given by quasichemical theory. The observed consolute temperature is likely to be lower than both.

8.

Let:

1 = benzene

2 = *n*-butane



There are three unknowns: $x_1, y_1,$ and V/F.

To solve for them, we use two equilibrium equations and one mass balance.

Assuming ideal vapor and neglecting Poynting corrections:

$$y_1 P = x_1 \gamma_1 P_1^s$$

$$(1-y_1)P = (1-x_1)\gamma_2 P_2^s$$

$$z_1 = \left(\frac{V}{F}\right) y_1 + \left(1 - \frac{V}{F}\right) x_1$$

Using regular-solution theory,

$$RT \ln\gamma_i = v_i \Phi_j^2 (\delta_i - \delta_j)^2$$

with υ_1 = 92 cm^3 mol^{-1} and υ_2 = 106 cm^3 mol^{-1}.

Then,

$$\gamma_1 = \exp(0.828\Phi_2^2)$$

$$\gamma_2 = \exp(0.950\Phi_1^2)$$

Substitution gives

$$y_1 = 0.368 x_1 \exp(0.828\Phi_2^2) \tag{1}$$

$$(1-y_1) = 4.76(1-x_1)\exp(0.950\Phi_1^2) \tag{2}$$

$$0.5 = \left(\frac{V}{F}\right) y_1 + \left(1-\frac{V}{F}\right) x_1 \tag{3}$$

Φ_1 and Φ_2 are related to x_1 and x_2 by Eqs. (7-25) and (7-26).

To solve Eqs. (1), (2), and (3) for $x_1, y_1,$ and $V/F,$ assume first that $\gamma_i = 1.$ This gives,

$$x_1 = 0.856 \qquad y_1 = 0.315 \qquad \frac{V}{F} = 0.658$$

A second approximation ($\gamma_i \neq 1$) gives

$$x_1 = x_{C_6H_6} = \mathbf{0.94}$$

$$y_1 = \mathbf{0.35}$$

$$\frac{V}{F} = 0.741$$

9. As derived in Sec. 7.2 of the text, the regular-solution equations can be written in the van Laar form

$$g^E = \frac{A x_1 x_2}{\frac{A}{B} x_1 + x_2} \tag{1}$$

where parameters *A* and *B* are related to pure-component liquid molar volume and solubility parameters as follows [Eqs. (7-38) and (7-39)]:

$$A = \upsilon_A(\delta_A - \delta_B)^2$$

$$B = \upsilon_B(\delta_A - \delta_B)^2 \tag{2}$$

Substituting the given liquid molar volumes and solubility parameters, we obtain

$$A = (120 \ \text{cm}^3 \ \text{mol}^{-1}) \times [(18-12)^2 \text{J cm}^{-3}] = 4320 \quad \text{J mol}^{-1}$$

$$B = (180 \ \text{cm}^3 \ \text{mol}^{-1}) \times [(18-12)^2 \text{J cm}^{-3}] = 6480 \quad \text{J mol}^{-1} \tag{3}$$

As discussed in Section 6-12, the temperature and composition at the consolute point are found from solving:

$$\left(\frac{\partial \ln a_\text{A}}{\partial x_\text{A}}\right)_{T,P} = \left(\frac{\partial^2 \ln a_\text{A}}{\partial x_\text{A}^2}\right)_{T,P} = 0 \tag{4}$$

Upon substitution of Eq. (1) into Eq. (4), the results are given in Eq. (6-146) in the text:

$$x_\text{A}^c = \frac{[(A/B)^2 + 1 - (A/B)]^{1/2} - (A/B)}{1-(A/B)}$$

$$T^c = \frac{2x_\text{A}^c(1-x_\text{A}^c)(A^2/B)}{R[(A/B)x_\text{A}^c + (1-x_\text{A}^c)]^3} \tag{5}$$

where superscript c denotes consolute.

Substituting Eq. (3) into Eq. (5), we finally obtain

$$x_\text{A}^c = 0.646$$

$$\boldsymbol{T^c = 328 \ \textbf{K}}$$

10. For each phase we choose the standard-state fugacity for cyclohexane as its pure subcooled liquid at 25ºC. The equation of equilibrium is

$$x_3^{(1)}\gamma_3^{(1)} = x_3^{(2)}\gamma_3^{(2)} \tag{1}$$

where subscript 3 denotes cyclohexane and superscripts (1) and (2) denote, respectively, carbon disulfide phase and perfluoro-*n*-heptane phase.

Rearrangement of Eq. (1) gives

$$K \equiv \frac{x_3^{(1)}}{x_3^{(2)}} = \frac{\gamma_3^{(2)}}{\gamma_3^{(1)}} \tag{2}$$

Because phase (1) contains only carbon disulfide and a trace amount of cyclohexane, whereas phase (2) contains only perfluoro-*n*-heptane and a trace amount of cylohexane, $\gamma_3^{(1)}$ and $\gamma_3^{(2)}$ are essentially activity coefficients at the infinite-dilution limit of cyclohexane.

Hence, we can write

$$K \equiv \frac{x_3^{(1)}}{x_3^{(2)}} = \left[\frac{\gamma_3^{(2)}}{\gamma_3^{(1)}}\right]^{\infty} \tag{3}$$

where superscript ∞ denotes the infinite-dilution limit of cyclohexane.

From the regular-solution theory [Eq. (7-37)], $\left[\gamma_3^{(1)}\right]^{\infty}$ and $\left[\gamma_3^{(2)}\right]^{\infty}$ are given by:

$$\begin{aligned} \ln\left[\gamma_3^{(1)}\right]^{\infty} &= \frac{v_3}{RT}(\delta_1 - \delta_3)^2 \\ \ln\left[\gamma_3^{(2)}\right]^{\infty} &= \frac{v_3}{RT}(\delta_2 - \delta_3)^2 \end{aligned} \tag{4}$$

Substituting the pure-component liquid molar volumes and solubility parameters, we obtain

$$\begin{aligned} \ln\left[\gamma_3^{(1)}\right]^{\infty} &= \frac{(109 \text{ cm}^3 \text{ mol}^{-1})}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})\times(298 \text{ K})} \times \left[(20.5-16.8)^2 \text{ J cm}^{-3}\right] = 0.602 \\ \ln\left[\gamma_3^{(2)}\right]^{\infty} &= \frac{(109 \text{ cm}^3 \text{ mol}^{-1})}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})\times(298 \text{ K})} \times \left[(12.3-16.8)^2 \text{ J cm}^{-3}\right] = 0.891 \end{aligned} \tag{10}$$

Substituting Eq. (5) into Eq. (3), we have

$$\boldsymbol{K = 1.34}$$

---

11. From the definition of the solubility parameter, δ,

$$\delta^2 = \frac{\Delta u_{\text{complete vaporization}}}{v^L}$$

[Complete vaporization means going from saturated liquid to ideal gas at constant *T*.]
Then,

$$\delta^2 = \frac{\left(\frac{h^0 - h^L}{RT_c}\right)RT_c - RT(1 - z^L)}{\frac{z^L RT}{P^s}}$$

$$\frac{\delta^2}{P_c} = \left[\frac{\frac{h^0 - h^L}{RT_c}}{z^L T_R} + 1 - \frac{1}{z^L}\right] P_R^s$$

Because

$$\frac{h^0 - h^L}{RT_c} = f(T_R, \omega)$$

and

$$z^V = f(T_R, \omega) \qquad z^L = f(T_R, \omega) \qquad P_R^s = f(T_R, \omega)$$

for $T_R \leq 1$,

$$\frac{\delta^2}{P_c} = f^{(0)}(T_R) + \omega f^{(1)}(T_R) + (\text{higher terms})$$

[Reference: Lyckman *et al.*, 1965, *Chem. Eng. Sci.*, 20: 703].

12.

a) Pure methanol is hydrogen-bonded to dimers, trimers, etc. In dilute solution (in iso-octante), methanol is a monomer. For an order-of-magnitude estimate, we can assume that, to make a monomer, approximately one hydrogen bond must be broken. Thus $\bar{h}^E$ = 12 kJ mol^{-1}.

b) From solubility parameters we get (roughly) an *endothermic* heat of 263 J mol^{-1}. The molar specific heat is (roughly) 125 J K^{-1} mol^{-1} . Thus, $\Delta t \approx -2°$C.

c) We want a Lewis acid that can hook on to the double bond in hexene.

Good Solvents are:

$$\left.\begin{array}{l}\text{Dimethyl sulfoxide}\\ \text{Sulfur Dioxide}\\ \text{Acetonitrile}\end{array}\right\}\ \text{Strong Lewis acids}$$

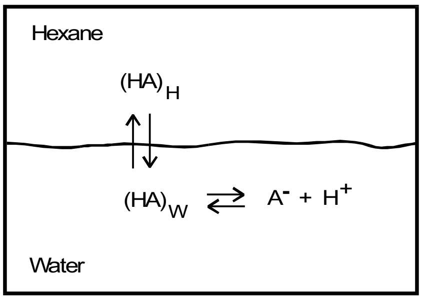
Poor Solvents are:

$$\left.\begin{array}{l}\text{Ammonia}\\ \\ \text{Aniline}\end{array}\right\}\ \text{Weak Lewis acids}$$

It is also important that the solvent should not be something that prefers self-interaction than that with hexene molecules. Strongly hydrogen-bonded liquids (e.g. water and most alcohols) would therefore be poor solvents.

13. Let (HA) be the acid. In ionized form,

$$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$$



Equilibrium constants are defined as

$$K_1 = \frac{(\text{HA})_\text{W}}{(\text{HA})_\text{H}}$$

$$K_2 = \frac{(\text{H}^+)(\text{H}^-)}{(\text{HA})_\text{W}} = \frac{(\text{A}^-)^2}{(\text{HA})_\text{W}}$$

In hexane: $C_\text{H} = (\text{HA})_\text{H}$

In water: $C_\text{W} = (\text{HA})_\text{W} + (\text{A}^-) = (\text{HA})_\text{W} + \sqrt{K_2(\text{HA})_\text{W}}$

$$= K_1(\text{HA})_\text{H} + \sqrt{K_1K_2(\text{HA})_\text{H}}$$

$$C_\text{W} = K_1C_\text{H} + \sqrt{K_1K_2C_\text{H}}$$

Thus,

$$\frac{\sqrt{C_H}}{C_W} = \frac{1}{\sqrt{K_1 K_2}}\left(1 - K_1 \frac{C_H}{C_W}\right)$$

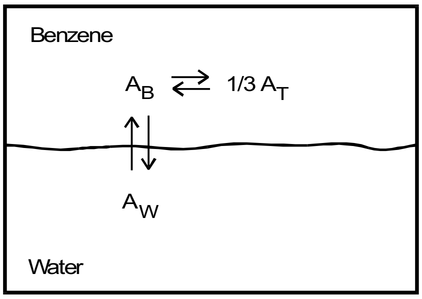
with

$$\frac{1}{\sqrt{K_1 K_2}} = a$$

and

$$K_1 = b$$

14.



Assume constant distribution coefficient and “reaction” equilibrium.

$$K_1 = \frac{A_B}{A_W}$$

$$K_2 = \frac{A_T}{(A_B)^3}$$

In water:

$$C_W = A_W$$

In benzene:

$$C_B = A_B + 3A_T$$

$$C_B = K_1 C_W + 3K_2 K_1^3 C_W^3$$

$$\frac{C_B}{C_W} = K_1 + 3K_2 K_1^3 C_W^2$$

Thus, plot $\frac{C_B}{C_W}$ as a function of C_W^2 .

Slope is $3K_2K_1^3$ and intercept is K_1.

15.

a) Pure CH_2Cl_2 and acetone do not hydrogen bond themselves but some hydrogen bonding is likely to occur between dissimilar pairs, which explains the negative deviations from Raoult's law observed for this system.

Pure methanol is highly hydrogen bonded. However, in dilute solutions of CH_2Cl_2, methanol exists primarily as monomer. Hydrogen bonding between methanol and CH_2Cl_2 is likely to be weak. (Note that at infinite dilution, activity coefficient γ_1^∞ indicates the effect on a molecule 1 when surrounded by molecules of the other component).

b) Nitroethane has a large dipole moment. Both *n*-hexane and benzene are non-polar but, due to π electrons, benzene is more polarizable. Therefore, we expect nitroethane/benzene interactions to be stronger than those for nitroethane/*n*-hexane. Thus $\gamma_{\text{nitroethane}}$ in *n*-hexane is larger than that in benzene.

c) Both $CHCl_3$ and methanol are polar and slightly acidic. Although methanol has a slightly higher dipole moment, $CHCl_3$ is likely to solvate the coal tar more easily because methanol tends to form strong hydrogen bonds with itself.

SOLUTIONS TO PROBLEMS

CHAPTER 8

1. Given

$$\ln \Gamma_1^{\infty} = \left(1 - \frac{1}{r}\right) + \chi$$

For $r >> 1$,

$$\ln \Gamma_1^{\infty} = 1 + \chi$$

If $\chi = 0.44$,

$$\ln \Gamma_1^{\infty} = 1.44 \qquad \Rightarrow \qquad \Gamma_1^{\infty} = 4.22$$

As defined,

$$\Gamma_1^{\infty} = \frac{a_1}{\Phi_1} = \frac{a_1}{10^{-4}} = 4.22 \qquad \Rightarrow \qquad a_1 = 4.22 \times 10^{-4}$$

Because

$$a_1 = \frac{P_1}{P_1^s}$$

$$P_1 = (4.22 \times 10^{-4}) \times (4.49) = 0.0019 \text{ bar}$$

For a non-volatile polymer, $P_2 = 0$. Therefore,

$$P \cong P_1 = \mathbf{0.0019\ bar}$$

---

2. We can use the data for the Henry's-law region to evaluate the Flory interaction parameter, χ, and then predict results at higher concentration.

Let:

1 = solvent
2 = polymer
w_i = weight fraction
Φ_i = volume fraction

Then,

$$\Phi_1 = \frac{v_1}{v_1 + v_2} = \frac{\dfrac{w_1}{\rho_1}}{\dfrac{w_1}{\rho_1} + \dfrac{w_2}{\rho_2}}$$

In the Henry's law region,

$$w_1 \rightarrow 0, \qquad w_2 \rightarrow 1$$

$$\frac{a_1}{\Phi_1} = \frac{f_1}{\Phi_1 f_1^0} = \frac{w_1 H_{1,2}}{\Phi_1 f_1^0}$$

But, as $w_1 \rightarrow 0$,

$$\Phi_1 = w_1 \rho_2 / \rho_1$$

$$\Phi_2 = 1$$

Then,

$$\frac{a_1}{\Phi_1} = \frac{\rho_1 H_{1,2}}{\rho_2 f_1^0}$$

If $f_1^0 = P_1^s$,

$$\frac{a_1}{\Phi_1} = \frac{f_1}{\Phi_1 f_1^0} = \frac{\rho_1 H_{1,2}}{\rho_2 P_1^s} = \frac{(0.783) \times (18.3)}{(1.11) \times (3340 / 760)} = 2.94$$

From Flory-Huggins theory (r is large),

$$\ln \frac{a_1}{\Phi_1} = \Phi_2 + \chi \Phi_2^2$$

If $\Phi_1 \rightarrow 1$,

$$\ln(2.94) = 1 + \chi \qquad \Rightarrow \qquad \chi = 0.078$$

At higher concentrations ($w_1 = 0.5$), assume $\chi \neq \chi(w_1)$:

$$\Phi_2 = \frac{(0.5)\times(1/1.11)}{(0.5)\times(1/1.11)+(0.5)\times(1/0.783)} = 0.414 \qquad (\Phi_1 = 0.586)$$

Then,

$$\ln\frac{a_1}{\Phi_1} = 0.414 + 0.078\times(0.414)^2$$

$$\frac{a_1}{\Phi_1} = 1.53 \qquad \text{or} \qquad a_1 = 0.898$$

$$P \approx f_1 = a_1 f_1^0 \approx a_1 P_1^s = (0.898)\times(3340) = 3000 \text{ torr}$$

$$P = 3000 \text{ torr} \approx \mathbf{3.9\ bar}$$

3.

a) The generalized van der Waals partition is given by [Eq. (8-39)]

$$Q(T,V,N) = \frac{1}{N!}\left(\frac{V_f}{\Lambda^3}\right)^N \left[q_{\text{ext}}(V)\right]^N \left[q_{\text{int}}(T)\right]^N \left[\exp\left(-\frac{E_0}{2kT}\right)\right]^N \tag{1}$$

Following the discussion on pages 442 and 443 of the textbook, we further have

$$\frac{V_f}{\Lambda^3} q_{\text{ext}} = \left(\frac{V_f}{\Lambda^3}\right)^{rc}$$

$$\frac{E_0}{2} = \frac{-rs\eta}{2v}$$

$$V_f = \tau r v^* \left[\left(\frac{v}{v^*}\right)^{1/3} - 1\right]^3 \tag{2}$$

$$v = \frac{V}{Nr}$$

Substituting Eq. (2) into Eq. (1) yields

$$\ln Q = -\ln N! - Nrc\ln \Lambda^3 + Nrc\ln(\tau r v^*)$$

$$+\,3Nrc\ln\left[\left(\frac{v}{v^*}\right)^{1/3} - 1\right] + N\ln q_{\text{int}} + \frac{Nrs\eta}{2vkT} \tag{3}$$

Because the first, second, third and fifth terms on the right-hand side of Eq. (3) are only functions of temperature, the equation of state is given by

$$\frac{P}{kT} = \left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} = \frac{1}{Nr}\left(\frac{\partial \ln Q}{\partial v}\right)_{N,T}$$

$$= \frac{1}{Nr}\left[\frac{3Nrc}{(\tilde{v}^{1/3} - 1)}\left(\frac{1}{3}\frac{v^{-2/3}}{v^{*1/3}}\right) + \frac{Nrs\eta}{2kT}\left(-\frac{1}{v^2}\right)\right] \tag{4}$$

We can rewrite Eq. (4) as

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3} - 1} - \frac{1}{\tilde{T}\tilde{v}} \tag{5}$$

where the reduced properties are defined by

$$\tilde{T} = \frac{T}{T^*} = \frac{2v^* ckT}{s\eta}$$

$$\tilde{P} = \frac{P}{P^*} = \frac{2{v^*}^2 P}{s\eta} \tag{6}$$

$$\tilde{v} = \frac{v}{v^*}$$

Equation (5) is the Flory equation of state [Eq. (8-45) of the textbook].

b) The configurational partition function [Eqs. (8-82) and (8-83]

$$Q = Q^C \exp\left(-\frac{E}{kT}\right)$$

$$Q^C = (\text{constant})^N \frac{(V/v^*)^N}{N_0!\,N!}\frac{1}{(V/v^*)^{N(r-1)}} \tag{7}$$

where

$$\frac{V}{v^*} = N_0 + rN$$

$$E = -\frac{z}{2}\varepsilon N_r \left[\frac{rN}{(V/\upsilon^*)}\right] \tag{8}$$

Combining Eqs. (7) and (8) gives

$$\begin{aligned} \ln Q &= \ln(\text{constant}) + \frac{V}{\upsilon^*}\ln\left(\frac{V}{\upsilon^*}\right) - \frac{V}{\upsilon^*} \\ &\quad - \ln N_0\,! - \ln N! - N(r-1)\ln\left(\frac{V}{\upsilon^*}\right) \\ &\quad + \varepsilon^*(\upsilon^* rN)^2\left(\frac{V}{\upsilon^*}\right)V^{-2} \end{aligned} \tag{9}$$

where

$$\begin{aligned} \varepsilon^* &= \frac{z}{2}\frac{\varepsilon}{kT} \\ \ln N_0\,! &= \ln\left[\left(\frac{V}{\upsilon^*}\right) - rN\right]! \\ &= \left[\left(\frac{V}{\upsilon^*}\right) - rN\right]\ln\left[\left(\frac{V}{\upsilon^*}\right) - rN\right] - \left[\left(\frac{V}{\upsilon^*}\right) - rN\right] \end{aligned} \tag{10}$$

The equation of state is thus given by

$$\begin{aligned} \frac{P}{kT} &= \left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} \\ &= \frac{1}{\upsilon^*}\ln\left(\frac{V}{\upsilon^*}\right) + \left(\frac{V}{\upsilon^*}\right)\frac{\upsilon^*(1/\upsilon^*)}{V} - \frac{1}{\upsilon^*} \\ &\quad - \frac{1}{\upsilon^*}\ln\left(\frac{V}{\upsilon^*} - rN\right) - \left(\frac{V}{\upsilon^*} - rN\right)\frac{1/\upsilon^*}{\frac{V}{\upsilon^*} - rN} + \frac{1}{\upsilon^*} \\ &\quad - N(r-1)\frac{1/\upsilon^*}{V/\upsilon^*} + \varepsilon^*(\upsilon^* rN)^2\left(-\frac{V^{-2}}{\upsilon^*}\right) \end{aligned} \tag{11}$$

We can rewrite

$$\left(\frac{PV}{kT}\right)\left(\frac{1}{rN}\right)=\frac{\tilde{P}\tilde{v}}{\tilde{T}}$$

$$=\tilde{v}\ln\left(\frac{V}{v^*}\right)-\tilde{v}\ln\left(\frac{V}{v^*}-rN\right)-(\tilde{v}-1)\left(\frac{\frac{V}{v^*}}{\frac{V}{v^*}-rN}\right)$$

$$+\tilde{v}-1+\frac{1}{r}-\varepsilon^*\frac{rN}{V/v^*} \tag{12}$$

$$=\frac{1}{r}-\left[1+\tilde{v}\ln\left(1-\frac{1}{\tilde{v}}\right)\right]-\frac{1}{\tilde{T}\tilde{v}}$$

where

$$\tilde{T}=\frac{T}{T^*}=\frac{T}{z\varepsilon/2k}$$

$$\tilde{P}=\frac{P}{P^*}=\frac{P}{z\varepsilon/2v^*} \tag{13}$$

$$\tilde{v}=\frac{v}{v^*}$$

Equation (12) is the Sanchez-Lacombe lattice-fluid equation of state [Eq. (8-84) of the textbook].

4. The Flory-Huggins equation for the activity of the solvent [Eq. (8-11)] is

$$\ln a_1=\ln(1-\Phi_2^*)+\left(1-\frac{1}{r}\right)\Phi_2^*+\chi\Phi_2^{*2} \tag{1}$$

Conditions for incipient instability give [analogous to Eqs. (6-141) and (6-142)]:

$$\left(\frac{\partial\ln a_1}{\partial\Phi_1^*}\right)_{P,T}=0$$

$$\left(\frac{\partial^2\ln a_1}{\partial\Phi_1^{*2}}\right)_{P,T}=0$$

Equivalently, we have

$$\left(\frac{\partial \ln a_1}{\partial \Phi_2^*}\right)_{P,T} = 0$$

$$\left(\frac{\partial^2 \ln a_1}{\partial \Phi_2^{*2}}\right)_{P,T} = 0 \tag{2}$$

because

$$\Phi_1^* + \Phi_2^* = 1$$

Substituting Eq. (1) into Eq. (2), we obtain

$$\frac{1}{1-\Phi_2^{*c}} - \left(1-\frac{1}{r}\right) - 2\chi^c \Phi_2^{*c} = 0$$

$$\left(\frac{1}{1-\Phi_2^{*c}}\right)^2 - 2\chi^c = 0$$

where superscript c stands for critical.

Hence, we obtain

$$\Phi_2^{*c} = \frac{1}{1+r^{1/2}}$$

$$\chi^c = \frac{1}{2}\left(1+\frac{1}{r^{1/2}}\right)^2$$

---

5. The Flory-Huggins equation for the activity coefficient of HMDS (1) [Eq. (8-12)] with $\chi = 0$ is

$$\ln \gamma_1 = \ln\left[1-\left(1-\frac{1}{r}\right)\Phi_2^*\right] + \left(1-\frac{1}{r}\right)\Phi_2^*$$

Using data in Table 8-5 of the text, calculated molecular characteristic volumes V^*, ratios of molecular segments r and activity coefficients of HMDS (at $\Phi_2^* = 0.8$) are given in the following table:

Substance	$V^* = v_{sp}^* \bar{M}_n$ (cm^3 mol^{-1})	$r = V_2^* / V_1^*$	$\ln\gamma_1$ ($\Phi_2^* = 0.8$)
HMDS	162.30	–	–
PDMS 3	521.53	3.21	-0.249
PDMS 10	832.89	5.13	-0.389
PDMS 20	1313.8	8.09	-0.528
PDMS 100	3507.8	21.61	-0.677
PDMS 350	5530.1	34.07	-0.722
PDMS 1000	6604.8	40.70	-0.735
PDMS ∞	∞	∞	-0.809

As we increase the molecular weight of PDMS, $\ln\gamma_1$ becomes more negative. γ_1 is smaller than unity and increasingly deviates from unity as the molecular weight of PDMS is increased.

This example illustrates the effect of differences in molecular sizes of HMDS and various PDMS with $\chi = 0$ (Fig. 8-3).

---

6. The flux of gas i through the membrane is given by, Eq. (8-118)

$$J_i = \frac{D_i}{\delta_M}\left(S_{iF}^G P_{iF} - S_{iP}^G P_{iP}^G\right) \tag{1}$$

Because solubility coefficients for both O_2 and N_2 in the feed and permeate are assumed to be equal and the permeate pressure is vacuum, Eq. (1) reduces to

$$\begin{aligned} J_i &= \frac{D_i S_i^G}{\delta_M} P_{iF} \\ &= \frac{D_i S_i^G}{\delta_M} y_i P_F \end{aligned} \tag{2}$$

where y_i and P_F ($P_F = 2\times 10^5$ Pa) denote, respectively, the mole fraction of component i and the total pressure of the feed.

For the feed mixture (air) we have

$$\begin{aligned} y_{O_2} &\cong 0.21 \\ y_{N_2} &\cong 0.79 \end{aligned} \tag{3}$$

Substituting Eq. (3) and the given data for membrane thickness, solubility and diffusion coefficients into Eq. (2), the corresponding fluxes of O_2 and N_2 are

$$J_{O_2} = 0.148 \times 10^{-5} \quad \text{m}^3 \text{ m}^{-2} \text{ s}^{-1}$$

$$J_{N_2} = 0.197 \times 10^{-5} \quad \text{m}^3 \text{ m}^{-2} \text{ s}^{-1}$$

The separation factor is defined by [Eq. (8-121)]

$$\alpha_{O_2/N_2} = \frac{D_{O_2} S^G_{O_2}}{D_{N_2} S^G_{N_2}}$$

$$= \mathbf{2.79}$$

Although $\alpha_{O_2/N_2} > 1$, the net flux of N_2 is larger than that of O_2 due to the difference in partial pressures in the feed.

---

7. If the feed pressure were low, we could use Eq. (8-112) to calculate J_1, the flux of carbon dioxide, and J_2, the flux of methane. Equation (8-113) then gives the composition (y) of the permeate.

However, because the pressure of the feed is high, we must allow for the effect of pressure on nonideality of the gas phase.

Equation (8-111) is

$$J_1 = \frac{D_1}{\delta_M}\left(c^M_{1F} - c^M_{1P}\right) \tag{1}$$

where c^M_1 is the concentration of carbon dioxide in the membrane; subscripts F and P refer to feed and permeate.

To find c^M_{1F}, we use the equilibrium relation

$$(y_1 P \varphi_1)_F = \left[H_1 c^M_1 \exp\left(\frac{\overline{v}_1 P}{RT}\right)\right]_F \tag{2}$$

where H_1 and $\overline{v}_1$ are Henry's constant and partial molar volume for carbon dioxide in the membrane, both at 300 K and 100 bar.

Fugacity coefficient φ_1 is given by the virial equation of state, truncated after the second virial coefficient [Eq. (5-33)]:

$$\ln \varphi_1 = \left(2\sum_{i=1}^{2} y_i B_{1i} - B_{\text{mixt}} \right) \frac{P}{RT}$$

$$B_{\text{mixt}} = \sum_{i=1}^{2}\sum_{j=1}^{2} y_i y_j B_{ij} \tag{3}$$

Substituting the given temperature, pressure and second virial coefficients into Eq. (3), we obtain

$$\varphi_1 = 0.729$$

Substituting Eq. (4) and all other given data into Eq. (2) yields

$$c_{1F}^M = 0.314 \quad \text{mol L}^{-1} \tag{4}$$

To find c_{1P}^M we use the equilibrium relation

$$(y_1 P \varphi_1)_P = (H_1 c_1^M)_P \tag{5}$$

where $P_P = 1$ bar and $\varphi_{1P} = 1$.

Hence, Eq. (5) reduces to

$$c_{1P}^M = \frac{y_{1P}}{19} \quad \text{mol L}^{-1} \tag{6}$$

The quantity y_{1P} is an unknown in this problem.

Substituting Eqs. (4) and (6) into Eq. (1) gives

$$J_1 \left(\frac{\text{mol}}{\text{cm}^2\text{s}} \right) = \frac{5\times10^{-6}}{0.1} \left(0.314\times10^{-3} - \frac{y_{1P}}{19}\times10^{-3} \right) \tag{7}$$

Applying the same procedure for methane (2), we obtain

$$J_2 \left(\frac{\text{mol}}{\text{cm}^2\ \text{s}} \right) = \frac{50\times10^{-6}}{0.1} \left(0.155\times10^{-3} - \frac{y_{2P}}{50}\times10^{-3} \right) \tag{8}$$

The (steady-state) mole fraction of carbon dioxide in the permeate is given by [Eq. (8-113)]

$$y_{1P} = \frac{J_1}{J_1 + J_2} \tag{9}$$

Further, the mass conservation gives

$$y_{1P} + y_{2P} = 1 \tag{10}$$

Substituting Eqs. (7), (8) and (10) into Eq. (9) gives $\boldsymbol{y_{1P} = 0.168}$ for carbon dioxide in the permeate.

Therefore, for methane in the permeate, $\boldsymbol{y_{2P} = 0.832}$.

8.

a) Flux of water through the membrane is given by Eq. (8-128):

$$J_w = \left(\frac{\text{permeability}}{\text{thickness}}\right) \times \left\{ x_{wF}^L - x_{wP}^L \exp\left[-\frac{\bar{v}_w (P_F - P_P)}{RT} \right] \right\} \tag{1}$$

where $x_{wP}^L = 1$ (pure water in the permeate); $P_P = P_w^s = 0.0312$ atm.

To calculate concentration of water in the feed, we use

$$(P_w)_F = (x_w^L P_w^s)_F \tag{2}$$

with

$$P_w^s = 0.0312 \text{ atm}$$

$$P_{wF} = (1 - 0.0184) \times (0.0312) \text{ atm}$$

Therefore, we obtain

$$x_{wF}^L = 0.9816$$

Because the permeate is pure water, we obtain

$$\bar{v}_w \approx v_w = \frac{18.015 \text{ g mol}^{-1}}{0.997 \text{ g cm}^{-3}} = 18.069 \text{ cm}^3 \text{ mol}^{-1}$$

The feed pressure is thus given by

$$7.2 \times 10^{-4} \text{ g cm}^{-2} \text{ s}^{-1} = \left(\frac{2.6 \times 10^{-5} \text{ g cm cm}^{-2} \text{ s}^{-1}}{10 \times 10^{-4} \text{ cm}} \right)$$

$$\times \left\{ 0.9816 - (1) \times \exp\left[-\frac{(18.069 \text{ cm}^3 \text{ mol}^{-1}) \times (P_F - 0.0312 \text{ atm})}{(82.06 \text{ atm L K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})} \right] \right\}$$

Therefore, the feed pressure is

$$\boldsymbol{P_F = 63.93 \text{ atm}}$$

b)

$$1 \times 10^6 \text{ gallons/day} = 3785.4 \text{ m}^3\text{/day} = 0.0438 \text{ m}^3\text{/s} = 43.67 \text{ kg/s}$$

$$\text{Flux} = 7.2\times10^{-4}\ \text{g cm}^{-2}\ \text{s}^{-1} = \frac{43.67\times10^{3}\ \text{g s}^{-1}}{(A\ \text{cm}^{2})} \qquad (3)$$

where A is the membrane area needed.

Solving Eq. (3) for the area, we get

$$A = 6.07\times10^{7}\ \text{cm}^{2} = 6.07\times10^{3}\ \text{m}^{2} = \mathbf{6.5\times10^{4}\ ft^{2}}$$

SOLUTIONS TO PROBLEMS

CHAPTER 9

1. The solubility product is the equilibrium constant for the reaction

$$\underset{\text{Solid}}{\text{AgCl}} \rightleftharpoons \underset{\text{Aqueous solution}}{\text{Ag}^+ + \text{Cl}^-}$$

defined as

$$K_{SP} = (a_{\text{Ag}^+})(a_{\text{Cl}^-})$$

being the standard states the pure solid AgCl and the ideal dilute 1-molal aqueous solution for each ion.

a) Let S be the solubility of AgCl in pure water, in $\dfrac{\text{mol AgCl}}{\text{kg water}}$ (a molality).

$$a_{\text{Ag}^+} = \gamma_{\text{Ag}^+} S \qquad a_{\text{Cl}^-} = \gamma_{\text{Cl}^-} S$$

$$K_{SP} = (a_{\text{Ag}^+})(a_{\text{Cl}^-}) = (\gamma_{\text{Ag}^+})(\gamma_{\text{Cl}^-})S^2 = (\gamma_\pm S)^2 \tag{1}$$

Because the solution is very dilute, $\gamma_\pm \approx 1$ and $S \approx \sqrt{K_{SP}}$ and is of the order of 10^{-5} molal and therefore the ionic strength is also very low: $I \approx 1.31 \times 10^{-5}$ molal. Therefore we may apply the Debye-Hückel limiting law.

$$I = \frac{1}{2}[m \times (+1)^2 + m \times (-1)^2] = m = S$$

Using Eq. (9-50a) of the text,

$$\log\gamma_{\pm}^{(m)} = -0.510 \times |(1)\times(-1)| I^{1/2} = -0.510\, S^{1/2} \qquad (2)$$

We now replace $\gamma_{\pm}$ given by Eq. (2) into Eq. (1) and solve for the solubility S:

$$[(10^{-0.510 S^{1/2}})S]^2 = 1.72\times10^{-10}$$

$$\boldsymbol{S = 1.31\times10^{-5}\ \mathrm{mol\ kg^{-1}}} \qquad (\gamma_{\pm}\approx 1.0\,)$$

b) With the addition of NaCl the ionic strength increases and we need to evaluate $\gamma_{\pm}$ because now the solution is not very dilute and therefore we don't have $\gamma_{\pm}\approx 1.0$.

Let S be the new solubility of AgCl in this aqueous solution that contains NaCl. The molalities are

$$m_{\mathrm{Ag^+}} = S \qquad m_{\mathrm{Cl^-}} = S + 0.01$$

The total ionic strength (due almost exclusively to NaCl because S is small) is

$$I = \frac{1}{2}[S\times(+1)^2 + S\times(-1)^2 + 0.01\times(+1)^2 + 0.01\times(-1)^2] \approx 0.01\ \mathrm{mol\ kg^{-1}}$$

We use in this case the extended limiting law [Eq. (9-52)] with $A_{\gamma} = 1.174\ \mathrm{kg^{1/2}\ mol^{-1/2}}$:

$$\ln\gamma_{\pm} = -\frac{1.174\times(0.01)^{1/2}}{1+(0.01)^{1/2}} \qquad\Rightarrow\qquad \gamma_{\pm} = 0.90$$

As in a),

$$K_{SP} = (a_{\mathrm{Ag^+}})(a_{\mathrm{Cl^-}}) = (\gamma_{\mathrm{Ag^+}})(\gamma_{\mathrm{Cl^-}})(m_{\mathrm{Ag^+}})(m_{\mathrm{Cl^-}})$$

$$= (\gamma_{\pm})^2(S)(S+0.01) = 1.72\times10^{-10}$$

or substituting $\gamma_{\pm} = 0.90$,

$$S(S+0.01) = 2.12\times10^{-10}$$

Because S is small and $S \ll 0.01$, we obtain $\boldsymbol{S \approx 2.12\times10^{-8}\ \mathrm{mol\ kg^{-1}}}$.

The addition of NaCl reduces the AgCl solubility from 1.31×10^{-5} mol kg^{-1} [as calculated in a) for pure water] to 2.12×10^{-8} mol kg^{-1} (in a 0.01 molal NaCl aqueous solution). This is the common ion ("salting out") effect.

c) Similarly, let S be the new AgCl solubility.

Molalities are:

$$m_{\mathrm{Ag^+}} = S \qquad m_{\mathrm{Cl^-}} = S$$

Again, the ionic strength is almost exclusively due to $NaNO_3$:

$$I \approx 0.01 \text{ mol kg}^{-1} \qquad \text{and} \qquad \gamma_{\pm} = 0.90$$

$$K_{SP} = (a_{\text{Ag}^+})(a_{\text{Cl}^-}) = (\gamma_{\text{Ag}^+})(\gamma_{\text{Cl}^-})(m_{\text{Ag}^+})(m_{\text{Cl}^-})$$

$$= (\gamma_{\pm})^2 (S)^2 = 1.72 \times 10^{-10}$$

$$\mathbf{S = 1.46 \times 10^{-5} \ mol\ kg^{-1}}$$

Compared to the solubility of AgCl in pure water, the solubility of AgCl in a 0.01 molal $NaNO_3$ aqueous solution increases by roughly 10%, because the higher ionic strength reduces the activity of Ag^+ and Cl^- ions and causes more AgCl to dissolve ("salting in" effect).

---

2. The solubility product is the equilibrium constant for the reaction (PbI_2 is a 1-2 electrolyte)

$$\underset{\text{Solid}}{PbI_2} \rightleftharpoons \underset{\text{Aqueous solution}}{Pb^{2+} + 2I^-}$$

defined as

$$K_{SP} = (a_{\text{Pb}^{2+}})(a_{\text{I}^-})^2 = (\gamma_{\pm})^3 S^3$$

being the standard states the pure solid PbI_2 and the ideal dilute 1-molal aqueous solution for each ion. In the above equation, S is the solubility of PbI_2 in pure water, in $\frac{\text{mol PbI}_2}{\text{kg water}}$ (a molality). Because the solution is very dilute, $\gamma_{\pm} \approx 1$ and

$$K_{SP} = (S)^3 = (1.66 \times 10^{-3})^3 = 4.57 \times 10^{-9}$$

For the solution with KI the ionic strength increases and we need to evaluate $\gamma_{\pm}$ because now the solution is not very dilute and therefore we may not have $\gamma_{\pm} \approx 1.0$.

Let S be the new solubility of PbI_2 in this aqueous solution that contains KI. The molalities are

$$m_{\text{Pb}^{2+}} = S \qquad m_{\text{I}^-} = 2S + 0.01 \qquad m_{\text{K}^+} = 0.01$$

The total ionic strength is

$$I = \frac{1}{2}[2S \times (-1)^2 + S \times (+2)^2 + 0.01 \times (+1)^2 + 0.01 \times (-1)^2] = (3S + 0.01) \text{ mol kg}^{-1} \qquad (1)$$

We use in this case the extended limiting law [Eq. (9-52)] with $A_{\gamma} = 1.174 \text{ kg}^{1/2} \text{ mol}^{-1/2}$:

$$\ln\gamma_{\pm} = -\frac{1.174\times(3S+0.01)^{1/2}}{1+(3S+0.01)^{1/2}} \tag{2}$$

Simultaneous solution of Eqs. (1) and (2) gives

$$\gamma_{\pm} = 0.88$$

$$\boldsymbol{S = 1.89\times10^{-3}\ \ \text{mol kg}^{-1}}$$

---

3. The solubility product for PbI_2 in an aqueous solution is

$$\log K_{SP} = 3\log m_{\pm} + 3\log\gamma_{\pm} \tag{1}$$

where

$$m_{+} = m_{\text{Pb}^{2+}} = m$$

$$m_{-} = m_{\text{I}^{-}} = 2m \tag{2}$$

$$m_{\pm} = \left[m(2m)^2\right]^{1/3} = 1.587m$$

With $I = \frac{1}{2}(2^2 m + 2m) = 3m$ Eq. (9-50a) gives

$$\log\gamma_{\pm} = -0.510\times(2)\times(3m)^{1/2} \tag{3}$$

With $m = 1.66\times10^{-3}$ mol kg^{-1} we obtain

$$\log K_{SP} = -7.953 \tag{4}$$

For the solutions containing sodium chloride or potassium iodide saturated with PbI_2, we have

$$\log K_{SP} = -7.953 = 3\times\log m_{\pm} - 0.510\times(2)\times I^{1/2} \tag{5}$$

For the NaCl solution, we write

$$m_{\mathrm{Pb}^{2+}} = m \qquad m_{\mathrm{I}^-} = 2m \qquad m_{\mathrm{Na}^+} = m_{\mathrm{Cl}^-} = 0.01$$

$$m_\pm = \left[m \times (2m)^2 \right]^{1/3} = 1.587m$$

$$I = \frac{1}{2}\left[2^2 m + 2m + 2 \times (0.01) \right] = 3m + 0.01$$

Substitution in Eq. (1) yields

$$m = 1.89 \text{ mol kg}^{-1}$$

For the KI solution, we write

$$m_{\mathrm{Pb}^{2+}} = m \qquad m_{\mathrm{I}^-} = 2m + 0.01 \qquad m_{\mathrm{K}^+} = 0.01$$

$$m_\pm = \left[m \times (2m + 0.01)^2 \right]^{1/3}$$

$$I = \frac{1}{2}\left[(2^2) \times m + 2m + 2 \times (0.01) \right] = 3m + 0.01$$

Substitution in Eq. (1) yields

$$m = 0.24 \text{ mol kg}^{-1}$$

For both systems, calculated and experimental values are in good agreement. The large decrease in PbI_2 solubility in the KI solution follows because all iodide ions are included in $m_\pm$. This reduction in solubility is called the common-ion effect.

---

4. The dissociation of acetic acid is represented by

$$CH_3COOH \rightleftharpoons H^+ + CH_3COOH^-$$

or schematically

$$AH \rightleftharpoons H^+ + A^-$$

The dissociation constant is

$$K = 1.758 \times 10^{-5} = \frac{(a_{\mathrm{H}^+})(a_{\mathrm{H}^-})}{a_{\mathrm{AH}}}$$

$$= \frac{(m_+^{\nu+})(m_-^{\nu-})}{m_{\mathrm{AH}}^{(\mathrm{m})}} \frac{(\gamma_\pm^{(\mathrm{m})})^{\nu}}{\gamma_{\mathrm{AH}}^{(\mathrm{m})}} = \frac{(m_{\mathrm{H}^+})(m_{\mathrm{A}^-})}{m_{\mathrm{AH}}^{(\mathrm{m})}} \frac{(\gamma_\pm^{(\mathrm{m})})^{2}}{\gamma_{\mathrm{AH}}^{(\mathrm{m})}}$$

Designating by α the extent of ionization, and by m the stoichiometric molality of acetic acid, in dilute solutions we may assume $a_{\mathrm{H}^+} = a_{\mathrm{A}^-} = \alpha$ and $a_{\mathrm{AH}^+} = m - \alpha$. Further, the activity of undissociated acetic acid approaches its molality at infinite dilution.

Assuming that the activity coefficients are unity (very dilute solutions) we have

$$K = 1.758 \times 10^{-5} = \frac{(\alpha)(\alpha)}{m - \alpha} = \frac{\alpha^2}{m - \alpha}$$

For a $m = 10^{-3}$ molal aqueous solution, the equation above gives $\alpha = 1.24 \times 10^{-4}$.

The fraction of acetic acid ionized is:

$$\frac{\alpha}{m} = \frac{1.24 \times 10^{-4}}{1 \times 10^{-3}} = \mathbf{0.124}$$

5. In SI units, the Debye length is defined by Eq. (9-47) of the text:

$$\kappa^{-1} = \left(\frac{RT\varepsilon_0 \varepsilon_r}{2 d_s N_A^2 e^2 I} \right)^{1/2}$$

where d_s is the density of the solvent in kg m^{-3}. For water at 25ºC, d_s = 997 kg m^{-3}.

The ionic strength is $I \approx$ 0.001 mol kg^{-1} for the 0.001 M solution and $I \approx$ 0. 1 mol kg^{-1} for the 0.1 M solution.

Substitution of values gives the values for the Debye length κ^{-1} (in nm) presented in the following table:

Solution	Water	Methanol
0.001 M	9.6	6.1
0.1 M	0.96	0.61

We see that κ^{-1} decreases ten times with a hundredfold increase in concentration. For the solutions at higher concentrations, shielding effects are more important and κ^{-1} is low. Further, the Debye length increases with increasing dielectric constant: when ε_r is large (as in water), the ionic atmosphere is weak and the coulombic interactions are strongly reduced.

6.

a) The molality of NaCl in seawater is

$$m_{\text{NaCl}} = \frac{\left(\frac{3.5}{58.5}\right) \text{ mol NaCl}}{(100-3.5) \text{ g water}}$$

$$= \frac{\left(\frac{3.5}{58.5}\right)}{(100-3.5)} \times 1000 \ \frac{\text{mol}}{\text{kg}}$$

$$= 0.620 \quad \text{mol/kg water}$$

The ionic strength is given by

$$I = \frac{1}{2}(m_{\text{Na}^+} z^2_{\text{Na}^+} + m_{\text{Cl}^-} z^2_{\text{Cl}^-}) = m = 0.620 \quad \text{mol / kg water}$$

which is a relatively high value.

Also,

$$\nu = \nu_{\text{Na}^+} + \nu_{\text{Cl}^-} = 2$$

The molar volume of water at 25ºC is

$$v_w = \frac{M_w}{d_w} = \frac{18}{0.997} \ \frac{\text{g / mol}}{\text{g / cm}^3} = 18.05 \text{ cm}^3 \text{ mol}^{-1}$$

To obtain the molal osmotic coefficient, ϕ, we need an expression for $\gamma_\pm$ in terms of the ionic strength I (= m).

Since solution is not dilute, we use Bromley's model:

$$\ln \gamma_\pm = -\frac{A_\gamma I^{1/2}}{1+I^{1/2}} + \frac{(0.138+1.38B)I}{(1+1.5I)^2} + 2.303BI$$

with, for NaCl at 25ºC, $A_\gamma = 1.174 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ and $B = 0.0574 \text{ kg}^{1/2} \text{ mol}^{-1/2}$.

From Eq. (9-11) of the text (reminding that in this case $I = m$),

$$\phi = 1 + \frac{1}{I}\int_0^I I\, d\ln\gamma_\pm$$

$$= 1 - \frac{A}{I}\int_0^I \frac{I^{1/2}}{2(1+I^{1/2})^2}dI + (0.138 + 1.38B)\frac{I}{(1+1.5I)^2}$$

$$-\frac{(0.138+1.38B)}{I}\int_0^I \frac{I}{(1+1.5I)^2}dI + \frac{B}{2.303}\int_0^I dI$$

Performing the integrations, we obtain:

$$\phi = 1 - \frac{A}{I}\left[1 + I^{1/2} - 2\ln(1+I^{1/2}) - \frac{1}{1+I^{1/2}}\right]$$

$$+\frac{(0.138+1.38B)}{1.5}\left[\frac{1+3I}{(1+1.5I)^2} - \frac{1}{1.5I}\ln(1+1.5I)\right] + 2.303\frac{IB}{2}$$

Substituting $A_\gamma = 1.174$, $B = 0.0574$, and $I = 0.62$ we obtain $\boldsymbol{\phi} = \mathbf{0.924}$.

b) From the expression that relates the osmotic pressure, π, to the molal osmotic coefficient, ϕ, we obtain

$$\pi = \frac{\nu RTM_w}{1000 v_w}\phi m$$

$$= \frac{(2)\times(8.314\text{ J K}^{-1}\text{ mol}^{-1})\times(298.15\text{ K})\times(18\text{ g mol}^{-1})}{(1000)\times(18.05\times10^{-6})}\times(0.924)\times(0.620\text{ mol kg}^{-1})$$

$$= 2.83\times10^6\text{ Pascal} = 28.3\text{ bar} \approx \mathbf{28\,atm}$$

Linear interpolation from osmotic pressure data of aqueous NaCl listed in Perry gives for $m = 0.62$ mol kg^{-1}, 28.0 atm, in good agreement with our calculated osmotic pressure.

7. For K_2SO_4, which is a 2-1 electrolyte, we have

$$m_+ = m_{K^+} = 2m \quad ; \quad z_+ = 1$$

$$m_- = m_{SO_4^{2-}} = m \quad ; \quad z_- = -2$$

$$I = \frac{1}{2}(2m + 2^2 m) = 3m \; ; \quad \nu_+ = 2, \quad \nu_- = 1, \quad \nu = 3$$

$$\ln \gamma_\pm^{(m)} = \frac{A_\gamma |z_+ z_-| I^{1/2}}{1 + BaI^{1/2}} + bI \qquad \Rightarrow \qquad b = \frac{1}{3m}\left[\ln \gamma_\pm^{(m)} + \frac{A_\gamma |z_+ z_-| (3m)^{1/2}}{1 + Ba(3m)(3m)^{1/2}}\right]$$

With

$\gamma_\pm^{(m)} = 0.4$ for $m = 0.12$ mol kg^{-1}; $A_\gamma = 1.174$ kg$^{1/2}$ mol$^{-1/2}$; $B = 0.33$ kg$^{1/2}$ mol$^{-1/2}$Å^{-1}; $a = 4$ Å

we obtain

$$b = \frac{1}{0.36}\left[\ln 0.4 + \frac{(1.174)\times(2)\times(0.36)^{1/2}}{1 + (0.33)\times(4)\times(0.36)^{1/2}}\right] \text{ kg mol}^{-1}$$

$$= -0.362 \text{ kg mol}^{-1}$$

For $m = 0.33$ mol kg^{-1}, we obtain $\gamma_\pm = 0.25$ (the experimental value is 0.275).

To use Eq. (9-25) for calculating the activity of water, we first need to calculate the osmotic coefficient, ϕ.

$$\phi = 1 - \frac{1.174}{3}(2)\times(3\times 0.33)^{1/2}\sigma(y) - \frac{0.3615\times(3\times 0.33)}{2}$$

where

$$y = (0.33)\times 4 \times (3\times 0.33)^{1/2} = 1.32$$

and

$$\sigma(y = 1.32) = \frac{3}{(1.32)^3}\left[1 + 1.32 - 2\ln(1 + 1.32) - \frac{1}{1 + 1.32}\right] = 0.257$$

$$\phi = 0.618 = -\left[\frac{1000 \text{ (g/kg)}}{3\times 0.33 \text{ (mol/kg) } \times 18 \text{ (g/mol)}}\right]\times \ln a_w$$

$$\ln a_w = -0.011 \qquad \Rightarrow \qquad a_w = 0.989$$

$$P_w / P_w^{sat} = 0.989 \qquad \Rightarrow \qquad \boldsymbol{P_w = 0.0314} \textbf{ bar}$$

The vapor pressure has not changed much; it is only about 1% lower than that of pure water because m is still small.

8.

$$\frac{\pi}{RT} = c_{\mathrm{BSA}} + c_{\mathrm{CI}} + Bc_{\mathrm{BSA}}^2$$

c = concentration in mol L^{-1}

CI = counter ion

Because the charge on BSA is –20, there are 20 counter ions (protons) for each molecule of BSA.

B is the osmotic second virial coefficient characterizing the BSA-BSA interaction in a 1 M aqueous NaCl medium. We neglect contributions from proton-proton and proton-BSA interactions, and also contributions from interactions with NaCl.

Because the concentration (1 M) of NaCl is the same in both sides and because 1 M is much larger than the concentration of counter ions, we neglect any (tiny) charges that might occur in NaCl concentration due to interactions of Na$^+$ and Cl$^-$ with counter ions or with BSA.

$$\pi = \frac{224}{13} = 17.2 \text{ mmHg}; \;\; T = 298 \text{ K}; \;\; R = 62.36 \text{ mmHg L mol}^{-1} \text{ K}^{-1}$$

$$c_{\mathrm{BSA}} = \frac{44.6}{66,000} = 6.76 \times 10^{-4} \text{ mol L}^{-1}; \;\; c_{\mathrm{CI}} = (20) \times (6.76 \times 10^{-4}) \text{ mol L}^{-1}$$

Substitution gives

$$\boldsymbol{B = -29040 \text{ L mol}^{-1}}$$

9.

a) To calculate the activity coefficients of water we use the Gibbs-Duhem equation:

$$d\ln\gamma_w = -\frac{x_s}{x_w} d\ln\gamma_\pm \tag{1}$$

where subscripts w and s refer to water and salt, respectively.

Integration of Eq. (1) between mole fractions $x_s = 0$ (or $x_w = 1$, for which $\gamma_w = 1$) and x_s, gives

$$\ln\gamma_w(x_s)=\int_0^{x_s}\frac{-x_s}{1-x_s}\,d\ln\gamma_\pm$$

or

$$\ln\gamma_w(x_s)=\int_0^{x_s}\frac{-x_s}{1-x_s}\left(\frac{d\ln\gamma_\pm}{dx_s}\right)dx_s \tag{2}$$

The derivative in Eq. (2) can be obtained from the truncated Pitzer equation given:

$$\ln\gamma_\pm=\frac{-8.766x^{1/2}+124.598x^{3/2}}{1+9x^{1/2}} \tag{3}$$

We made $I = x_s$, because being NaBr a 1-1 electrolyte, the solution ionic strength is

$$I_x=\frac{1}{2}\sum_i x_i z_i^2=\frac{1}{2}(x_s+x_s)=x_s \tag{4}$$

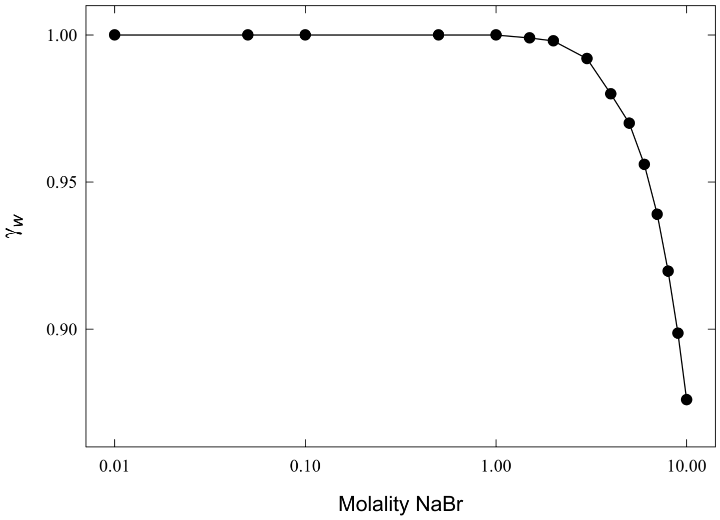
Differentiation of ln $\gamma_\pm$ in Eq. (3) in order of x and substitution in Eq. (2) gives

$$\ln\gamma_w(x_s)=\int_0^{x_s}\frac{-x_s}{1-x_s}\left[\frac{-4.383{x_s}^{-1/2}+186.897{x_s}^{1/2}+1121.382x_s}{(1+9{x_s}^{1/2})^2}\right]dx_s \tag{5}$$

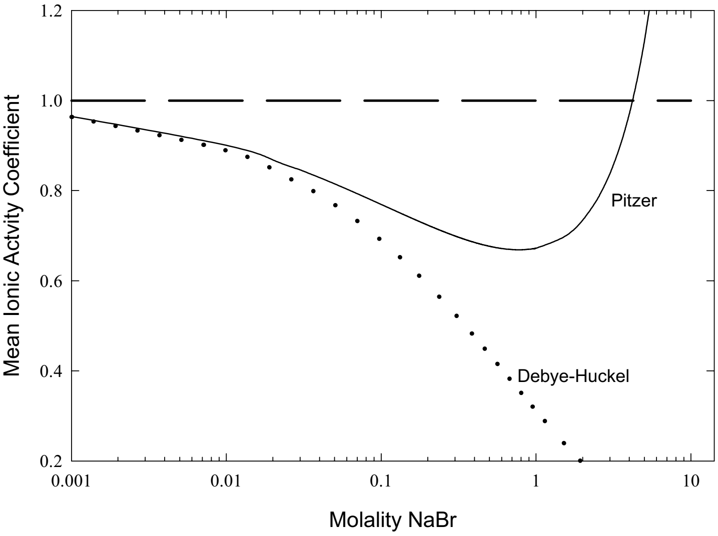
The salt mole fractions are easily calculated from the given molalities (between m = 0 and m = 5 mol kg^{-1}) from:

$$x_s=\frac{n_{\mathrm{NaBr}}}{n_w+n_{\mathrm{NaBr}}}=\frac{m_{\mathrm{NaBr}}}{\dfrac{1000}{18.015}+m_{\mathrm{NaBr}}}=\frac{m_{\mathrm{NaBr}}}{55.51+m_{\mathrm{NaBr}}} \tag{6}$$

The following figure shows the activity coefficients of water in different NaBr aqueous solutions at 25ºC, calculated using the Sympson rule to evaluate the integral in Eq. (5). As the figure shows, $\gamma_w \approx 1$ until about m = 1.5 mol kg^{-1} and becomes less than one after that concentration. For example, γ_w = 0.92 for m = 8 mol kg^{-1} and γ_w = 0.88 for m =10 mol kg^{-1}.



b) The mean ionic activity coefficients for NaBr aqueous solutions at 25ºC are calculated from Debye-Hückel equation, $\ln\gamma_{\pm} = -A_x\sqrt{I_x}$, and from the Pitzer equation as given in this problem. The following figure compares both predictions. As expected, they agree only at very low salt concentrations.



c) Equation (4-44) gives the Van't Hoff equation for the osmotic pressure: (valid for ideal, dilute solutions):

$$\pi V = n_s RT \tag{7}$$

where V is the total volume and n_s the number of moles of the salt.

Taking into consideration the nonideality of the liquid phase we write [Eq. (4-41)]:

$$-\ln a_w = -\ln(\gamma_w x_w) = \frac{\pi v_w}{RT} \tag{8}$$

where v_w is the molar volume of the pure solvent (water).

We use Eq. (7) to calculate the osmotic pressure for the simplest case (Van't Hoff equation) and Eq. (8) for the more correct calculation that takes into account the solution nonideality, with γ_w obtained from Eq. (5).

Assuming that NaBr is completely dissociated into Na^+ and Br^- in water, we rewrite Eq. (7) as

$$\pi = 2c_s RT \quad \text{with} \quad c_s = \frac{n_s}{V} \quad \text{mol L}^{-1} \tag{9}$$

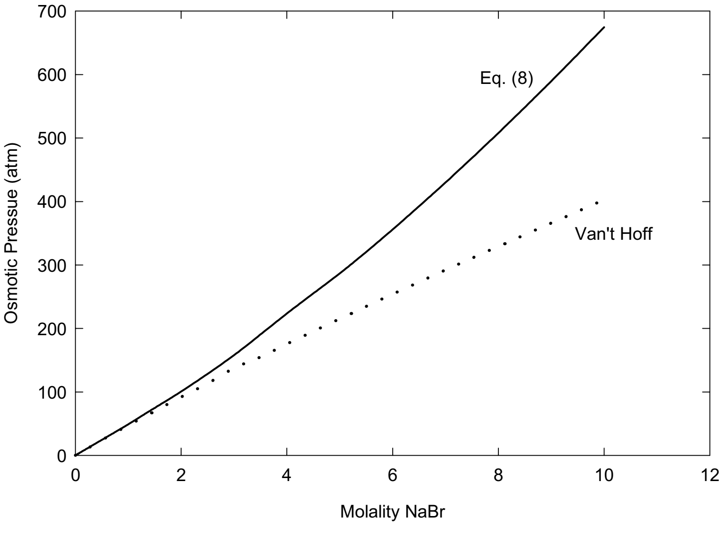
We obtain the salt concentrations (molarities) from the given molalities (m_2) from

$$c_s(\text{mol L}^{-1}) = \frac{d\, m_s}{1 + 0.001 M_s m_s}$$

where d is the mass density (in g cm^{-3}) of the solution and M_s is the molar mass of NaBr (in g mol^{-1}).

To use Eq. (8) we take the molar volume of pure water as $v_w = 18.015$ cm^3 mol^{-1}, $x_w = 1 - 2x_s$ with γ_w given by Eq. (5).

The following figures compares the results obtained from the Van't Hoff equation [Eq. (9)] with the equation that takes into account the solution nonideality [Eq. (8)].



As the figure shows, the solution behaves as an ideal solution (i.e. Van't Hoff equation is valid) up to a concentration of about $m_{\text{NaBr}} = 2$ mol kg^{-1}. However, for more concentrated solutions ($m_{\text{NaBr}} > 2$ mol kg^{-1}), the effect of thermodynamic nonideality can not be neglected anymore.

10. For the dissociation reaction

$$\mathrm{AB} \rightleftharpoons \mathrm{A}^+ + \mathrm{B}^-$$

the equilibrium constant is

$$K = \frac{(a_{\mathrm{A}^+})(a_{\mathrm{B}^-})}{a_{\mathrm{AB}}} = 5\times 10^{-3} \text{ mol kg}^{-1}$$

The equilibrium equation is

$$f_{\mathrm{AB}}^{L} = f_{\mathrm{AB}}^{V} \tag{1}$$

where f denotes fugacity.

Equation (1) is equivalent to (Henry's constant $H_{\mathrm{AB,w}} = 30$ bar kg mol^{-1}, $y_{\mathrm{AB}} = 1$)

$$m_{\mathrm{AB}} H_{\mathrm{AB,w}} \exp\left[\int_{P_{\mathrm{w}}^{sat}}^{P} \frac{\overline{v}_{\mathrm{AB}}^{\infty}}{RT} dP\right] = \varphi_{\mathrm{AB}} P \tag{2}$$

Component AB in the vapor phase is in equilibrium with the undissociated AB dissolved in water. The total molality of AB (solubility) in water is:

$$m_T = m_{\mathrm{AB}} + m_{\mathrm{A}^+}$$

If α is the fraction dissociated, we obtain

$$m_{\mathrm{A}^+} = \alpha m_T \qquad \text{and} \qquad m_{\mathrm{AB}} = (1-\alpha) m_T$$

The equilibrium constant then is

$$K = 5\times 10^{-3} \text{ mol kg}^{-1} = \frac{\gamma_{\pm}^{2}\, \alpha^2 m_T}{1-\alpha} \tag{3}$$

and Eq. (2) becomes

$$(1-\alpha) m_T H_{\mathrm{AB,w}} \exp\left[\frac{\overline{v}_{\mathrm{AB}}^{\infty}(P - P_w^{sat})}{RT}\right] = \varphi_{\mathrm{AB}} P \tag{2a}$$

where $P - P_{\mathrm{w}}^{sat} \cong P$ because $P = 50 \text{ bar} >> P_{\mathrm{w}}^{sat}$.

The fugacity coefficient at 50 bar is

$$\varphi_{\mathrm{AB}} = \exp\left[\frac{P B_{\mathrm{AB,AB}}}{RT}\right]$$

$$= \exp\left[\frac{(50 \text{ bar})\times(-200 \text{ cm}^3\text{mol}^{-1})}{(83.14 \text{ cm}^3 \text{ bar K}^{-1} \text{ mol}^{-1})\times(298 \text{ K})}\right] = 0.668$$

With $I = \frac{1}{2}(m_{\mathrm{A}^+} + m_{\mathrm{B}^-}) = m_{\mathrm{A}^+} = \alpha \times m_T$, the mean ionic activity coefficient is [Eq. (9-52)]

$$\ln \gamma_{\pm} = -\frac{A_{\gamma}\sqrt{\alpha m_T}}{1+\sqrt{\alpha m_T}} \tag{4}$$

where $A_{\gamma} = 1.174\ \text{kg}^{1/2}\ \text{mol}^{-1/2}$.

We have now three equations [Eqs. (2a), (3), (4)] and three unknowns m_T, α, and $\gamma_{\pm}$. Solving these gives:

$$m_T = 1.038\ \text{mol kg}^{-1}$$

$$\alpha = 0.0871$$

$$\gamma_{\pm} = 0.762$$

Iteration procedure is:

Start with $\alpha = 0$ in Eq. (2a) and calculate m_T.

Then calculate a first approximation for α with $\gamma_{\pm} = 1$ using Eq. (3).

Use m_T and α in Eq. (4) to obtain better $\gamma_{\pm}$, etc.

---

11. In his theory of absolute reaction rates, Eyring states that reactants A and B form an activated complex (AB) as an intermediate state in the reaction

$$\text{A} + \text{B} \rightleftharpoons \text{(AB)} \rightarrow \text{Products} \tag{1}$$

By assumption, reactants A and B are in equilibrium with the activated complex (AB), so that

$$K = \frac{a_{(\text{AB})}}{a_{\text{A}}a_{\text{B}}} \tag{2}$$

The reaction rate is proportional to the concentration of (AB), i.e., $\text{constant} \times c_{(\text{AB})}$.

Replacing the activities by the products of concentrations and activity coefficients in Eq. (2) we obtain

$$c_{(\text{AB})} = Kc_{\text{A}}c_{\text{B}}\frac{\gamma_{\text{A}}\gamma_{\text{B}}}{\gamma_{(\text{AB})}} \tag{3}$$

Hence,

$$\text{Rate of reaction} = (\text{constant})Kc_{\text{A}}c_{\text{B}}\frac{\gamma_{\text{A}}\gamma_{\text{B}}}{\gamma_{(\text{AB})}} \tag{4}$$

The rate of reaction can also be expressed in the usual manner by kc_Ac_B, where *k* is the observed specific rate. Hence, from Eq. (4), we can write

$$k = (\text{constant})K\frac{\gamma_A\gamma_B}{\gamma_{(AB)}} = k_o\frac{\gamma_A\gamma_B}{\gamma_{(AB)}} \tag{5}$$

Equivalently, we can write

$$\log k = \log k_o + \log\frac{\gamma_A\gamma_B}{\gamma_{(AB)}} \tag{6}$$

To calculate the second term on the right side of Eq. (6), we use Eq. (9-50a)

$$\log\frac{\gamma_A\gamma_B}{\gamma_{(AB)}} = -0.510\sqrt{I}\times(z_A^2 + z_B^2 - z_{(AB)}^2) \tag{7}$$

Substituting $z_{(AB)} = z_A + z_B$ gives

$$\log\frac{\gamma_A\gamma_B}{\gamma_{(AB)}} = 0.510\sqrt{I}\times(2z_Az_B) \tag{8}$$

Combining Eqs. (6) and (8) gives

$$\log k = \log k_o + 1.02z_Az_B\sqrt{I} \tag{9}$$

Therefore, a plot of $\log k$ versus $\sqrt{I}$ is a straight line with slope $1.02z_Az_B$.

Reaction	z_Az_B	Change of k
I	-2	Decreases with increasing I
II	0	Constant

When the inert salt NaCl is added, I changes.
For $m_{\text{NaCl}} = 0.01$ and negligible molalities of reactants, we obtain

$$\begin{aligned} m_+ &= m_{\text{Na}^+} = 0.01 \qquad z_+ = 1 \\ m_- &= m_{\text{Cl}^-} = 0.01 \qquad z_- = -1 \end{aligned} \tag{10}$$

and

$$I = \frac{1}{2}(0.01 + 0.01) = 0.01\ \text{M} \tag{11}$$

Combining Eqs. (9) and (11) gives

Reaction	$z_A z_B$	k
I	-2	-0.204
II	0	0

12. Some helpful relations for single-electrolyte solutions (i.e., one cation M and one anion X)

$$\nu = \nu_M + \nu_X \quad \text{or} \quad 1 = \frac{\nu_M}{\nu} + \frac{\nu_X}{\nu} \tag{1}$$

$$\nu_M z_M + \nu_X z_X = 0 \quad \text{or} \quad \nu_M |z_M| = \nu_X |z_X| \tag{2}$$

$$m\nu = m_M + m_X = m\nu_M + m\nu_X$$

$$\sum_i m_i = \nu\, m$$

$$\sum_i m_i |z_i| = m(\nu_M |z_M| + \nu_X |z_X|)$$

$$I = \frac{1}{2}\sum_i m_i z_i^2 = \frac{1}{2} m(\nu_M z_M^2 + \nu_X z_X^2)$$

a) Eq. (9-59) from Eq. (I-13):

For a single electrolyte: $c = 1 = \mathrm{M}$ and $a = 1 = \mathrm{X}$
All Φ's, Ψ's, and λ's are zero. Equations (I-14), (I-15), (9-61) and Eq. (I-13) give

$$\ln \gamma_{\pm} = \underline{|z_M z_X| f^{\gamma}} + |z_M z_X| m_M m_X B'_{MX}$$

$$+ \frac{\nu_M}{\nu} m_X \left(2B_{MX} + \sum_i m_i |z_i| c_{MX} \right)$$

$$+ \frac{\nu_X}{\nu} m_M \left(2B_{MX} + \sum_i m_i |z_i| c_{MX} \right)$$

$$+ \frac{m_M m_X}{\nu} 2\nu_M |z_M| c_{MX}$$

where B_{MX} and B'_{MX} are given by Eq. (I-19a) and Eq. (I-19b), respectively, and C_{MX} is given by Eq. (I-18).

Equations (I-16), (I-19), and (9-62) – (9-65) give

$$2B_{MX} + I\,B'_M = B^{\gamma}_{MX}$$

and

$$C_{MX} = \frac{2}{3} C^{\gamma}_{MX} / (2|z_M z_X|^{1/2})$$

From Eq. (9-45), the terms with B_{MX} or B'_{MX} can be summarized as:

$$|z_M z_X| m_M m_X B'_{MX} + 2\left(\frac{\nu_M m_X + \nu_X m_M}{\nu} \right) B_{MX}$$

$$= \frac{2I}{m\nu} m^2 \nu_M \nu_X B'_{MX} + \frac{1}{\nu} (\nu_M \nu_X m + \nu_X \nu_M m) 2B_{MX}$$

$$= \frac{2\nu_M \nu_X}{\nu} m (IB'_{MX} + 2B_{MX})$$

$$\underline{= m^2 \left(\frac{2\nu_M \nu_X}{\nu} \right) B^{\gamma}_{MX}}$$

Summarizing the C_{MX} terms gives:

$$\left[\left(\frac{\nu_\mathrm{M}}{\nu}m_\mathrm{X}+\frac{\nu_\mathrm{X}}{\nu}m_\mathrm{M}\right)(m_\mathrm{M}|z_\mathrm{M}|+m_\mathrm{X}|z_\mathrm{X}|)+\frac{m_\mathrm{M}m_\mathrm{X}}{\nu}2\nu_\mathrm{M}z_\mathrm{M}\right]\frac{2}{3}\frac{1}{2|z_\mathrm{M}z_\mathrm{X}|^{1/2}}C^{\gamma}_\mathrm{M}$$

$$=\left[\left(\frac{\nu_\mathrm{M}\nu_\mathrm{X}}{\nu}m+\frac{\nu_\mathrm{X}\nu_\mathrm{M}}{\nu}m\right)(\nu_\mathrm{M}|z_\mathrm{M}|+\nu_\mathrm{X}|z_\mathrm{X}|)m+\frac{m^2\nu_\mathrm{M}\nu_\mathrm{X}}{\nu}2\nu_\mathrm{M}z_\mathrm{M}\right]\frac{C^{\gamma}_\mathrm{MX}}{3|z_\mathrm{M}z_\mathrm{X}|^{1/2}}$$

$$\underline{=m^2\left[\frac{2(\nu_\mathrm{M}\nu_\mathrm{X})^{3/2}}{\nu}\right]C^{\gamma}_\mathrm{MX}}$$

The 3 terms above marked with ______ are identical to the 3 terms in Eq. (9-59).

b) <u>Eq. (9-60) from Eq. (I-10):</u>

As before c = 1 = M and a = 1 = X and all Φ's, Ψ's, and λ's are zero.
Equations (9-64) and (I-18) and Eq. (I-10) give

$$\begin{aligned}\phi-1&=\underbrace{\left(2I/\textstyle\sum m_i\right)f^{\phi}}_{(1)}\\ &+\underbrace{\frac{2}{\sum m_i}m_\mathrm{M}m_\mathrm{X}\,B^{\phi}_\mathrm{MX}}_{(2)}\\ &+\underbrace{\frac{2}{\sum m_i}\sum m_i|z_i|\frac{m_\mathrm{M}m_\mathrm{X}}{2|z_\mathrm{M}z_\mathrm{X}|^{1/2}}C^{\phi}_\mathrm{MX}}_{(3)}\end{aligned}\tag{1}$$

Term (1):

$$\begin{aligned}2I/\textstyle\sum m_i&=2\frac{1}{2}m(\nu_\mathrm{M}z_\mathrm{M}^2+\nu_\mathrm{X}z_\mathrm{X}^2)\\ &=\frac{\nu_\mathrm{M}z_\mathrm{M}^2+\nu_\mathrm{X}z_\mathrm{X}^2}{\nu}\end{aligned}$$

With $\nu_\mathrm{M}|z_\mathrm{M}|=\nu_\mathrm{X}|z_\mathrm{X}|$, it follows

$$\text{Term (1)} = \frac{1}{\nu}\left(\nu_{\mathrm{M}}\left|z_{\mathrm{M}}\right|\frac{\nu_{\mathrm{X}}}{\nu_{\mathrm{M}}}\left|z_{\mathrm{X}}\right| + \nu_{\mathrm{X}}\left|z_{\mathrm{X}}\right|\frac{\nu_{\mathrm{M}}}{\nu_{\mathrm{X}}}\left|z_{\mathrm{M}}\right| \right)$$

$$= \left|z_{\mathrm{M}}\right|\left|z_{\mathrm{X}}\right|\left(\frac{\nu_{\mathrm{X}}}{\nu} + \frac{\nu_{\mathrm{M}}}{\nu} \right)$$

$$= \left|z_{\mathrm{M}}\right|\left|z_{\mathrm{X}}\right|\left(\frac{\nu_{\mathrm{X}}}{\nu} + \frac{\nu_{\mathrm{M}}}{\nu} \right)$$

$$= \left|z_{\mathrm{M}}\right|\left|z_{\mathrm{X}}\right|$$

Term (2):

$$\frac{2}{\sum m_i} m_{\mathrm{M}} m_{\mathrm{X}} = \frac{2m^2 \nu_{\mathrm{M}}\nu_{\mathrm{X}}}{\nu m} = m\left(\frac{2\nu_{\mathrm{M}}\nu_{\mathrm{X}}}{\nu} \right)$$

Term (3):

$$\frac{2}{\sum m_i}\sum m_i \left|z_i\right| \frac{m_{\mathrm{M}} m_{\mathrm{X}}}{2\left|z_{\mathrm{M}} z_{\mathrm{X}}\right|^{1/2}} = \frac{\nu_{\mathrm{M}}\nu_{\mathrm{X}} m^2}{\nu m} \frac{m(\nu_{\mathrm{M}}\left|z_{\mathrm{M}}\right| + \nu_{\mathrm{X}}\left|z_{\mathrm{X}}\right|)}{\left|z_{\mathrm{M}} z_{\mathrm{X}}\right|^{1/2}}$$

Again using $\nu_{\mathrm{M}}\left|z_{\mathrm{M}}\right| = \nu_{\mathrm{X}}\left|z_{\mathrm{X}}\right|$ gives

$$\nu_{\mathrm{M}}\left|z_{\mathrm{M}}\right|\left|z_{\mathrm{X}}\right| = \nu_{\mathrm{X}}\left|z_{\mathrm{X}}\right|\left|z_{\mathrm{X}}\right| \qquad \Rightarrow \qquad \left|z_{\mathrm{M}} z_{\mathrm{X}}\right|^{1/2} = \left(\frac{\nu_{\mathrm{X}}}{\nu_{\mathrm{M}}} \right)^{1/2} \left|z_{\mathrm{X}}\right|$$

and

$$\nu_{\mathrm{M}}\left|z_{\mathrm{M}}\right| + \nu_{\mathrm{X}}\left|z_{\mathrm{X}}\right| = 2\nu_{\mathrm{X}}\left|z_{\mathrm{X}}\right|$$

Therefore,

$$\text{Term (3)} = \frac{\nu_{\mathrm{M}}\nu_{\mathrm{X}}}{\nu} m^2 \frac{2\nu_{\mathrm{X}}\left|z_{\mathrm{X}}\right|}{\nu_{\mathrm{X}}^{1/2}\nu_{\mathrm{M}}^{-1/2}\left|z_{\mathrm{X}}\right|} = m^2\left[\frac{2(\nu_{\mathrm{M}}\nu_{\mathrm{X}})^{3/2}}{\nu} \right]$$

Comparison of the results for the terms (1), (2), and (3) with those in Eq. (9-60) shows that they are identical.

SOLUTIONS TO PROBLEMS

CHAPTER 10

1. Let 1 = methane, 2 = benzene, 3 = *m*-xylene, and 4 = hexane.
Neglecting Poynting corrections and vapor non-idealities,

$$K_1 = \frac{y_1}{x_1} = \frac{\gamma_1 f^L_{\text{pure 1}}}{\varphi_1 P}$$

From Fig. 10-13 of the text we obtain $f^L_{\text{pure 1}}$ at 366 K and 13.8 bar.

Because $y_1 \cong 1$ we can use Lewis' fugacity rule to obtain φ_1 by writing $\varphi_1 = (f/P)_{\text{pure 1}}$.

We find γ_1 from

$$\ln\gamma_1 = \frac{v_1(\delta_1 - \bar{\delta})^2}{RT}$$

In the first iteration, find $\bar{\delta}$ using $x_1 = 0$.

For a second estimate, first calculate y_1 from $y_1 = 1 - y_1 - y_3 - y_4$, where

$$y_2 = \frac{x_2\gamma_2 f_2^0}{P}, \qquad \text{etc.}$$

Then,

$$x_1 = \frac{y_1}{K_1} \qquad \text{(other } x_i \text{ from relative amounts)}$$

Recalculate $\bar{\delta}$ for second estimate of γ_1 to find

$$K_1 = K_{\mathrm{CH_4}} = \mathbf{34}$$

2. Let 1 = argyle acetate and 2 = helium.
Because we have two data points, we can use the Krichevsky-Kasarnovsky equation to evaluate the two parameters $H_{2,1}$ and $\overline{v}_2^\infty$.

$$\ln\left(\frac{f_2}{x_2}\right) = \ln H_{2,1}^{(P_1^s)} + \frac{\overline{v}_2^\infty (P - P_1^s)}{RT}$$

Assume:

1. $\gamma_2^* = 1$
2. $P_1^s << P$

Then, for helium,

$$f_2 = y_2 \varphi_2 P$$

From data given in App. C for helium,

$$B_{22}(293 \text{ K}) = 12.1 \text{ cm}^3 \text{ mol}^{-1}$$

Using the virial equation and assume $y_2 = 1$,

$$\ln \varphi_2 = \frac{B_{22} P}{RT}$$

Find f_2 at different pressures:

P (bar)	φ_2	f_2 (bar)
25	1.012	25.3
75	1.038	77.8
150	1.077	161.5

At 25 bar,

$$\ln\frac{f_2}{x_2} = \ln(25.3 \times 10^4)$$

$$= \ln H_{2,1} + \frac{(25) \times (\overline{v}_2^\infty)}{(83.14) \times (293)}$$

$$\ln(27 \times 10^4) = \ln H_{2,1} + \frac{(75) \times (\overline{v}_2^\infty)}{(83.14) \times (293)}$$

These equations give

$$\bar{v}_2^{\infty} = 32.4 \text{ cm}^3 \text{ mol}^{-1}$$

and

$$\ln H_{2,1} = 12.4$$

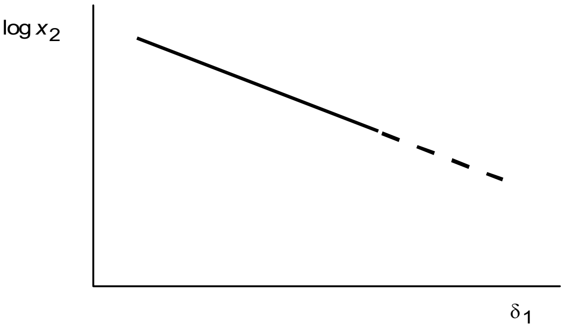
At 150 bar,

$$\ln x_2 = \ln f_2 - 12.62$$

$$x_2 = x_{\text{He}} = \mathbf{5.37 \times 10^{-4}}$$

---

3. Over a small range of values for δ, Hildebrand has shown that $\log x_2$ is linear (approximately) in δ_1. A plot of $\log x_2$ vs. δ_{solvent} gives x_2 in liquid air.



Because

$$\delta_i = \left(\frac{\Delta_{\text{vap}} u_i}{v_i}\right)^{1/2} \approx \left(\frac{\Delta_{\text{vap}} h_i - RT}{v_i}\right)^{1/2}$$

we can calculate δ's from data given:

$$\delta_{\text{CH}_4} = 15.0 \text{ (J cm}^{-3})^{1/2}$$

and

$$\delta_{\text{CO}} = 1.4 \text{ (J cm}^{-3})^{1/2}$$

For air, assume a mixture of N_2 and O_2:

$$\bar{\delta}_{\text{air}} = 11.4 \text{ (J cm}^{-3})^{1/2}$$

From plot of $\log x_2$ vs. δ_1 we find for $\bar{\delta} = 11.4$ (J cm^{-3})$^{1/2}$,

$$x_2(\text{in air}) = \boldsymbol{x_{\mathrm{H_2}} = 2.63 \times 10^{-3}}$$

Note that in this case we hit one of our known points. In general, we must interpolate or extrapolate.

4.

a) The equilibrium equation between the gaseous phase containing oxygen and the liquid phase saturated in dissolved oxygen is:

$$f_{\mathrm{O_2}}^{G} = f_{\mathrm{O_2}}^{L} \tag{1}$$

At the low pressures of interest here, we assume the gas phase as an ideal gas mixture:

$$f_{\mathrm{O_2}}^{G} = y_{\mathrm{O_2}} P \tag{2}$$

Moreover, because oxygen is sparingly soluble, i.e., oxygen is present at very low concentrations in the liquid phase, Henry's law holds:

$$f_{\mathrm{O_2}}^{L} = x_{\mathrm{O_2}} k_{\mathrm{O_2}} \tag{3}$$

From Eqs. (1), (2) and (3),

$$y_{\mathrm{O_2}} P = x_{\mathrm{O_2}} k_{\mathrm{O_2}} \tag{4}$$

Equation (4) is the condition for phase equilibrium that characterizes the dissolution of a sparingly soluble gas. Under the given pressure and gaseous composition, Henry's law constant $k_{\mathrm{O_2}}$ can be determined, once the solubility $x_{\mathrm{O_2}}$ is known. This solubility is given here by the Bunsen coefficient α.

Substituing t = 20ºC in the equation for α we obtain,

$$\alpha = 31.01 \times 10^{-3} \ \frac{\mathrm{Ncm^3(O_2)}}{\mathrm{cm^3(H_2O)}}$$

where Ncm^3 stands for *normal* cubic centimeters, i.e., cubic centimeters of gas measured at 0ºC and 1 atm.

We convert normal cubic centimeters of gas to moles using the ideal gas law:

$$v_{O_2} = \frac{RT}{P} = \frac{(8.31451)\times(293.15)}{101325}$$

$$= 0.022414 \text{ m}^3 \text{ mol}^{-1}$$

$$= 22414 \text{ cm}^3 \text{ mol}^{-1}$$

The molar density of water at 20°C and 1 atm is

$$\frac{1}{v_{H_2O}} = \frac{\rho_{H_2O}}{M_{H_2O}} = \frac{0.9982}{18.015} = 0.0554 \text{ mol cm}^{-3}$$

Under the conditions of the Bunsen experiment, we have:

$$\text{Dissolved oxygen} = \frac{\alpha}{v_{O_2}} = \frac{31.01\times10^{-3}}{22414} = 1.3835\times10^{-6}\ \frac{\text{mol } O_2}{\text{cm}^3\ H_2O}$$

The liquid phase is made exclusively of H_2O and O_2. Then the mole fraction of O_2 in the liquid is

$$x_{O_2} = \frac{\left(\dfrac{\alpha}{v_{O_2}}\right)}{\left(\dfrac{\alpha}{v_{O_2}}\right)+\left(\dfrac{1}{v_{H_2O}}\right)} = \frac{1.3835\times10^{-6}}{1.3835\times10^{-6}+0.0554}$$

$$\approx \frac{1.3835\times10^{-6}}{0.0554} = 2.497\times10^{-5}\ \frac{\text{mol } O_2}{\text{mol } O_2 + \text{mol } H_2O}$$

By the definition of α, $y_{O_2} = 1.0$ and P = 1 atm = 1.01325 bar.

From Eq. (4),

$$k_{O_2} = \frac{y_{O_2}P}{x_{O_2}} = \frac{(1.0)\times(1.01325)}{(2.497\times10^{-5})} = 4.058\times10^4 \text{ bar}$$

b) Here we want to determine x_{O_2} given y_{O_2}, P and k_{O_2}, using again Eq. (4).

The atmospheric air above the water phase is a mixture of water vapor, oxygen and other atmospheric gases (predominantly nitrogen).

Assuming that the air is saturated in water vapor,

$$y_{H_2O} = \frac{P^s_{H_2O}}{P} = \frac{17.5}{760} = 0.0230$$

The mole fraction of oxygen in the vapor phase is then

$$y_{O_2} = \frac{p_{O_2}}{P} = \frac{(0.2095)\times[(760)-(17.5)]}{(760)} = 0.02047$$

For the ambient pressure we obtain form Eq. (4),

$$x_{O_2} = \frac{y_{O_2}P}{k_{O_2}} = \frac{(0.2047)\times(1.01325)}{(4.057\times10^4)} = 5.112\times10^{-6}\ \frac{\text{mol O}_2}{\text{mol liquid}}$$

This solubility can now be expressed as mass of gas per volume of liquid, making the simplifying assumption that the liquid phase is pratically pure water:

$$\text{Solubility} = \frac{(5.112\times10^{-6}\text{mol O}_2/\text{mol liquid})\times(32.0\text{ g O}_2/\text{mol O}_2)}{(18.015\text{ g H}_2\text{O/mol H}_2\text{O})\times\left(\dfrac{1}{0.9982\text{ g H}_2\text{O/cm}^3\text{ H}_2\text{O}}\right)\times(1\text{ mol H}_2\text{O}/\text{mol liquid})}$$

$$= 9.06\times10^{-6}\text{g O}_2\text{/cm}^3\ \text{H}_2\text{O} = 9.06\ \text{mg dm}^{-3} = \mathbf{9.06\ ppm}$$

---

5. The number of moles for each component is

$$n_1 = \frac{180}{18.015} = 10.0\ \text{mol} \qquad n_2 = \frac{420}{84.16} = 5.0\ \text{mol} \qquad n_3 = \frac{28}{28.012} = 1.0\ \text{mol}$$

The volume available for the vapor phase is

$$V = 3.0 - \left(\frac{420}{0.774} + \frac{180}{0.997}\right)\times10^{-6} = 2.28\times10^{-3}\ \text{m}^3$$

Therefore the pressure inside the vessel is (assuming vapor – formed almost exclusively by nitrogen whose second virial coefficient at 25ºC is zero – as ideal),

$$P = \frac{n_3RT}{V} = \frac{(1)\times(8.314)\times(298.15)}{(2.28\times10^{-6})}$$

$$= 10.88\times10^5\,\text{Pa} = 10.88\ \text{bar}$$

Because the solubilities are very small, we use Henry's law to describe the fugacity of cyclohexane in gas phase:

$$f_3 \approx p_3 = y_3P = x_3H_{3,i}\,.$$

Further, because we neglect mutual solubility of water and cyclohexane, we obtain for the solubility of nitrogen in water,

$$x_{3,w} = \left(\frac{H_{3,1}}{p_3}\right)^{-1} = \left(\frac{86{,}000}{10.88}\right)^{-1} = 1.26\times 10^{-4}$$

and for the solubility of nitrogen in cyclohexane,

$$x_{3,c} = \left(\frac{H_{3,2}}{p_3}\right)^{-1} = \left(\frac{1{,}300}{10.88}\right)^{-1} = 8.37\times 10^{-3}$$

---

6. Let 1 = N_2 and 2 = H_2.
From Orentlicher's correlation,

$$\ln\frac{f_2}{x_2} = \ln H_{2,1}^{(P_1^s)} + \frac{A}{RT}(x_1^2 - 1) + \frac{\bar{v}_2^{\infty}(P - P_1^s)}{RT}$$

Assuming that the vapor is pure H_2:

$$f_2 = f_2^V = y_2\varphi_2 P = 88 \text{ bar} \qquad \text{(with } y_2 = 1\text{)}$$

Because,

$$P_1^s = 1 \quad \text{bar}$$

$$A = 7.1 \quad \text{L bar mol}^{-1}$$

$$H_{2,1} = 467 \quad \text{bar}$$

$$\bar{v}_2^{\infty} = 31.3 \quad \text{cm}^3 \text{ mol}^{-1}$$

by trial and error we find

$$\boldsymbol{x_2 = 0.17}$$

---

7. From Fig. 10-11 with $\delta_1 = 14.9 \text{ (J cm}^{-3})^{1/2}$, at 25°C and at 1.01325 bar partial pressure,

$$\log x_2 = -3.1 \qquad \Rightarrow \qquad x_2 = 8\times 10^{-4}$$

For t = 0°C, use Eq. (10-26):

$$\ln\frac{x_2(T_2)}{x_2(T_1)} \cong \frac{\Delta\bar{s}_2}{R}\ln\frac{T_2}{T_1}$$

But at 25°C and 1.01325 bar,

$$-R\ln x_2 = 59.29 \text{ J mol}^{-1}\text{ K}^{-1}$$

and from Fig. 10-7,

$$\bar{s}_2^L - s_2^G \cong 17 \text{ J mol}^{-1}\text{ K}^{-1}$$

Then,

$$\Delta\bar{s}_2 = \bar{s}_2^L - s_2^G = 17 \text{ J mol}^{-1}\text{ K}^{-1}$$

$$\ln\frac{x_2}{8\times10^{-4}} = \frac{17}{8.31451}\ln\frac{273}{298}$$

$$x_2 = 6.7\times10^{-4} \qquad \text{(at 1 bar)}$$

Assuming

$$\frac{x_2(P_2)}{x_2(P_1)} = \frac{(y_2P)_2}{(y_2P)_1}$$

we obtain at 0°C and 2 bar partial pressure,

$$\boldsymbol{x_2 = 1.34\times10^{-3}}$$

---

8. Let 1 = ethylene oxide and 2 = CH_4.
Then,

$$\ln\frac{f_2}{x_2} = \ln H_{2,1}^{(P_1^s)} + \frac{\bar{v}_2^{\infty}(P-P_1^s)}{RT}$$

From Tables 10-2 and 10-3 at 10°C,

$$H_{2,1} = 621 \text{ bar}$$

$$\bar{v}_2^{\infty} = 45 \text{ cm}^3\text{ mol}^{-1}$$

At 10°C, $P_1^s \approx 1$ bar. Then,

$$\ln\frac{f_2}{x_2} = 6.5$$

$$\frac{f_2}{x_2} = 665 \text{ bar}$$

But

$$f_2 = \varphi_2 y_2 P$$

Assuming $y_2 \approx 1$,

$$\ln\varphi_2 = \frac{B_{22}P}{RT}$$

with $B_{22} = -49 \text{ cm}^3 \text{ mol}^{-1}$ (Table 10-3)

$$\varphi_2 = 0.949$$

$$f_2 = (0.949) \times (25) = 23.7 \text{ bar}$$

$$x_{\mathrm{CH_4}} = x_2 = \frac{f_2}{665} = \mathbf{0.036}$$

9.

a) Henry's constant $H_{2,1}$ is calculated from [Eq. (10-21)]:

$$H_{2,1}^{(P_1^s)} = P_1^s \varphi_2^{L,\infty}$$

where $\varphi_2^{L,\infty}$ is the fugacity coefficient of solute 2 in the liquid phase at infinite dilution ($x_2 = 0$); φ_2 may be obtained from Eq. (12-64) of the text with

$$b_{\text{mixture}} \approx b_1$$

$$v_{\text{mixture}} \approx v_1^s$$

$$P \approx P_1^s$$

$$x_2 \approx 0$$

Then, $H_{2,1}$ is given by

$$\ln H_{2,1} = \ln\frac{RT}{v_1 - b_1} + \frac{b_2}{v_1 - b_1} - \frac{a_1 b_2 v_1}{RTb_1[v_1(v_1+b_1)+b_1(v_1-b_1)]}$$

$$+\frac{a_1 b_2}{2\sqrt{2}RTb_1^2}\ln\frac{(v_1+2.414b_1)}{(v_1-0.414b_1)} - \frac{a_{12}}{RT\sqrt{2}b_1}\ln\frac{(v_1+2.414b_1)}{(v_1-0.414b_1)}$$

where

$$a_{12} = (a_1 a_2)^{1/2}(1-k_{12})$$

$$k_{12} = 0.0867$$

Constants a_1 and a_2 are obtained from Eqs. (12-61) to (12-63) and constants b_1 and b_2 from Eq. (12-60). Substitution gives

$$\boldsymbol{H_{2,1} = 360\ \textbf{bar}}$$

b) From Eq. (10-22),

$$\overline{v}_2^{\infty} = -\left[\frac{\left(\dfrac{\partial P}{\partial n_2}\right)_{T,V,n_1}}{\left(\dfrac{\partial P}{\partial V}\right)_{T,n_1,n_2}}\right]_{n_2=0}$$

Using Peng-Robinson equation of state [Eq. (12-59)], we find

$$\overline{v}_2^{\infty} = \frac{\dfrac{RT(b_2+v_1^s-b_1)}{(v_1^s-b_1)^2} - \dfrac{2a_{12}}{v_1^s(v_1^s+b_1)+b_1(v_1^s-b_1)} + \dfrac{2a_1 b_2(v_1^s-b_1)}{[v_1^s(v_1^s+b_1)+b_1(v_1^s-b_1)]^2}}{\dfrac{RT}{(v_1^s-b_1)^2} - \dfrac{2a_1(v_1^s+b_1)}{[v_1^s(v_1^s+b_1)+b_1(v_1^s-b_1)]^2}}$$

Substitution gives

$$\boldsymbol{\overline{v}_2^{\infty} = 69.5\ \textbf{cm}^3\ \textbf{mol}^{-1}}$$

c) Margules parameter A can be found from Eq. (10-23):

$$A = -\frac{RT}{2}\left(\frac{\partial \ln \varphi_2^L}{\partial x_2}\right)_{P=P_1^s,T,x_2=0}$$

The result is:

$$A = -\frac{RT}{2}\left\{\frac{b_2(b_2-b_1)-v' b_2}{(v_1^s-b_1)^2} - \frac{a_1 b_2 v' + 2b_2 v_1^s(a_{12}-a_1)}{RTb_1[v_1^s(v_1^s+b_1)+b_1(v_1^s-b_1)]} - \frac{v' - (b_2-b_1)}{v_1^s-b_1}\right.$$

$$+\frac{a_1 b_2 v_1^s\left[(b_2-b_1)\left\{v_1^s(v_1^s+b_1)+b_1(v_1^s-b_1)\right\}+2b_1\left\{v'(v_1^s+b_1)+(v_1^s-b_1)(b_2-b_1)\right\}\right]}{RT\left\{b_1\left[v_1^s(v_1^s+b_1)+b_1(v_1^s-b_1)\right]\right\}^2}$$

$$-\frac{2b_1(a_{12}-a_1)-a_1(b_2-b_1)}{2\sqrt{2}RTb_1^2}\left(\frac{2a_{12}}{a_1}-\frac{b_2}{b_1}\right)\ln\frac{v_1^s+2.414b_1}{v_1^s-0.414b_1}$$

$$-\frac{a_1}{\sqrt{2}RTb_1}\left[\frac{a_1(a_2-a_{12})-2a_{12}(a_{12}-a_1)}{a_1^2}+\frac{b_2(b_2-b_1)}{2b_1^2}\right]\ln\frac{v_1^s+2.414b_1}{v_1^s-0.414b_1}$$

$$\left.-\frac{a_1}{RTb_1}\left(\frac{2a_{12}}{a_1}-\frac{b_2}{b_1}\right)\frac{v_1^s(b_2-b_1)-b_1v'}{(v_1^s+2.414b_1)(v_1^s-0.414b_1)}\right\}$$

with

$$v'=\left(\frac{\partial v}{\partial x_2}\right)_{x_2=0}=\overline{v}_2^{\infty}-v_1^s$$

Substitution gives

$$\boldsymbol{A}=13{,}900 \text{ bar cm}^{-3}\text{ mol}^{-1}$$

SOLUTIONS TO PROBLEMS

CHAPTER 11

1. Assuming

$$f_i^{s} = f_{\text{pure } i}^{s}$$

and

$$f_i^{L} = x_i f_{\text{pure } i}^{L} \qquad (\text{i.e. } \gamma_i = 1)$$

with $T_t = T_m$, $\Delta c_p = 0$,

$$\ln \frac{f_{\text{pure } i}^{L}}{f_{\text{pure } i}^{s}} = \ln\left(\frac{1}{x_i}\right) = \frac{\Delta_{\text{fus}} h_i}{RT}\left[1 - \frac{T}{T_m}\right]$$

Rearranging,

$$T = \left(\frac{\Delta_{\text{fus}} h_i}{R}\right)\left[\frac{1}{\ln\left(\frac{1}{x_i}\right) + \frac{\Delta_{\text{fus}} h_i}{RT_{m,i}}}\right]$$

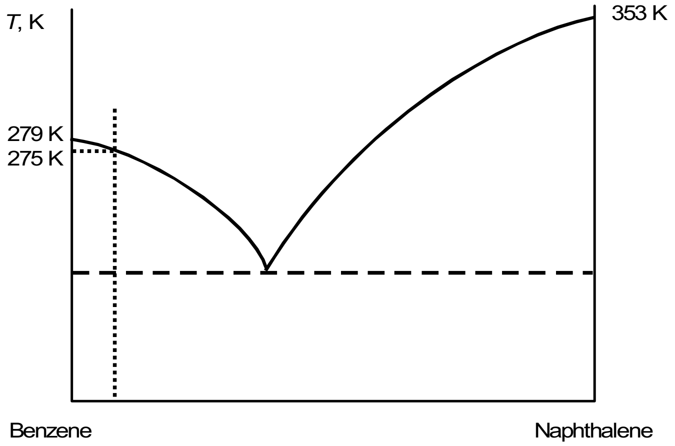
For i = benzene, $\Delta_{\text{fus}} h_i = 9843$ J mol^{-1}, $x_i = 0.95$, $T_{m,i} = 278.7$ K, we obtain

$$T = 275 \text{ K}$$

For i = naphthalene, $\Delta_{\text{fus}} h_i = 19008$ J mol^{-1}, $x_i = 0.05$, $T_{m,i} = 353.4$ K, we obtain

$$T = 241 \text{ K}$$

We choose the higher temperature (i.e., benzene precipitates first).



At $T = 275$ K, a solid phase appears.

2. We need activity a_A at $x_\text{A} = x_\text{A}^\text{sat}/2$.

At saturation,

$$f_\text{A}^L = f_\text{A}^S = f_\text{pure A}^S$$

Because

$$f_\text{A}^L = a_\text{A} f_\text{pure A}^L$$

$$-\ln a_\text{A}^\text{sat} = \ln\left(\frac{f_\text{A}^L}{f_\text{A}^S}\right)_\text{pure} = \frac{\Delta_\text{fus}h}{RT}\left(1-\frac{T}{T_t}\right) - \frac{\Delta c_p}{R}\left(\frac{T_t - T}{T}\right) + \frac{\Delta c_p}{R}\ln\frac{T_t}{T}$$

Assuming, $T_m = T_t$, we find $a_\text{A}^\text{sat} = 0.118$.

Because $x_\text{A}^\text{sat} = 0.05$, $\gamma_\text{A} = 2.36$.

To find the activity at another composition, assume that

$$RT\ln\gamma_\text{A} = D(1-x_\text{A})^2$$

Using the above data, we find $D = 2357 \text{ J mol}^{-1}$.

Hence at $x_\text{A} = x_\text{A}^\text{sat}/2$,

$$\gamma_\text{A} = 2.47$$

$$a_A = x_A \gamma_A = 0.0618$$

Then

$$\frac{\theta}{1-\theta} = 8.04 \qquad \Rightarrow \qquad \theta = 0.89$$

Thus, **89%** of sites are occupied.

---

3. Klatt's data are really at 0^0C, not -70^0C. This is above the freezing points of toluene and xylene and near that of benzene.

Let HF be component 1 and the solute (2) be A (benzene), B (toluene), and C (m-xylene). The order of increasing substitution (basicity) is A, B, C. To simplify things, ignore the solubility of 1 in 2.

Then:

$$f_{\text{pure }2} = f_{2,\text{in }1} = x_2 \gamma_2 f_2^0$$

But, $f_2^0 = f_{\text{pure }2}$, so this reduces to: $1 = x_2 \gamma_2$. Therefore, x_2 is inversely proportional to γ_2.

We might think that γ_2 depends only on the 1-2 interaction. On this basis, we expect $\gamma_C < \gamma_B < \gamma_A$, and thus $x_C > x_B > x_A$. Klatt's data show the reverse.

There is, however, another factor: the strength of the 2-2 interactions. At 0^0C, $P_A^s \approx 0.036$ bar, $P_B^s \approx 0.009$ bar and $P_C^s \approx 0.002$ bar. This means that pure C "holds on" to its molecules more tightly than B which in turn has a tighter grip than A.

In other words, the more volatile solute (that has the weakest 2-2 interactions) exerts more "pressure" to enter the solvent phase. This is discussed in a qualitative manner by Hildebrand, 1949, *J. Phys. Coll. Chem.,* 53: 973.

It may be helpful to look at this from a lattice theory (interchange energy) perspective. Using the simplest form of this theory, we can say:

$$\ln \gamma_2 = \frac{w}{kT} x_1^2$$

$$w = z[\Gamma_{12} - \tfrac{1}{2}(\Gamma_{11} + \Gamma_{22})]$$

where w is the interchange energy.

With the attractive interaction, we expect $\Gamma_{1A} > \Gamma_{1B} > \Gamma_{1C}$.

This produces a higher w (and hence a higher γ_2 and lower x_2) for the less-substituted molecule.

But, if we look at the vapor pressures we see that the less-substituted molecules have less attractive 2-2 interactions. Hence, $\Gamma_{AA} > \Gamma_{BB} > \Gamma_{CC}$. This produces a higher w (and hence a higher γ_2 and lower x_2) for the more-substituted molecule. Sometimes, this effect is greater than that of the 1-2 interactions; that is apparently true in this case.

---

4. Let 1 = naphthalene, 2 = iso-pentane, and 3 = CCl_4.
At saturation,

$$f_1^{s} = f_1^{L} = x_1\gamma_1 f_{1,\text{ pure}}^{L}$$

Assuming, $f_{1,\text{ pure}}^{s} = f_1^{s}$,

$$\ln\left(\frac{f_1^L}{f_1^{s}}\right)_{\text{pure}} = -\ln a_1 = \frac{\Delta_{\text{fus}}h}{RT}\left(1-\frac{T}{T_t}\right) = -\ln x_1\gamma_1$$

From the regular-solution theory, assuming $x_1 = 0$ initially, we obtain

$$\bar{\delta} = 14.9\ \ (\text{J cm}^{-3})^{1/2}$$

and

$$\ln\gamma_1 = \frac{v_1(\delta_1-\bar{\delta})^2}{RT} = 1.45$$

$$\delta_1 = 20.3\ \ (\text{J cm}^{-3})^{1/2}$$

$$\ln a_1 = 1.18$$

$$x_1 = 0.073$$

Now repeat the calculation using $x_1 = 0.073$ and $\frac{x_2}{x_3} = \frac{7}{3}$, to obtain

$$\bar{\delta} = 15.3\ \ (\text{J cm}^{-3})^{1/2}$$

and

$$x_1 = 0.093$$

One more iteration gives $x_1 = x_{\text{naphthalene}} \approx 0.10$.

---

5. The equilibrium equation for benzene (B) is

$$\text{Partial pressure of B} = y_\text{B}P = x_\text{B}\gamma_\text{B}P_{\text{liquid B}}^{s} \qquad (1)$$

where x_B ($x_B = 0.10$) and γ_B denote liquid-phase mole fraction and activity coefficient of benzene; $P^s_{\text{liquid B}}$ is the vapor pressure of pure, subcooled liquid benzene at 260 K.

To find $P^s_{\text{liquid B}}$, we use the approximation

$$\frac{P^s_{\text{liquid B}}}{P^s_{\text{solid B}}} = \left(\frac{f^L}{f^S}\right)_{\text{pure B}} \tag{2}$$

where $P^s_{\text{solid B}}$ ($P^s_{\text{solid B}} = 0.0125 \text{ bar at } 260 \text{ K}$) is the vapor pressure of pure solid benzene at 260 K; the fugacity ratio for pure benzene is calculated from Eq. (11-13) neglecting Δc_p for benzene

$$\ln\left(\frac{f^L}{f^S}\right)_{\text{pure B}} = \frac{\Delta_{\text{fus}} h}{RT_m}\left(\frac{T_m}{T} - 1\right) \tag{3}$$

Substituting $\Delta_{\text{fus}} h = 30.45 \text{ cal g}^{-1} = 9944.07 \text{ J mol}^{-1}$, $T_m = 278.7 \text{ K}$, $T = 260 \text{ K}$ and $R = 8.314$ J K^{-1} mol^{-1} into Eqs. (2) and (3), we obtain

$$\frac{P^s_{\text{liquid B}}}{P^s_{\text{solid B}}} = 1.362 \tag{4}$$

Hence,

$$P^s_{\text{liquid B}} = 1.362 \times (0.0125 \text{ bar}) = 0.0170 \text{ bar} \tag{5}$$

To calculate γ_B in Eq. (1), we use Eq. (7-55):

$$\ln \gamma_B = \frac{v_B}{RT}(\delta_B - \bar{\delta})^2 \tag{6}$$

where

$$\begin{gathered} \bar{\delta} = \sum_{i=1}^{3} \Phi_i \delta_i \\ \Phi_i = \frac{x_i v_i}{\sum_{j}^{3} x_j v_j} \end{gathered} \tag{7}$$

Substituting $T = 260 \text{ K}$, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ and the given liquid-phase mole fractions, pure-component molar volumes and solubility parameters into Eqs. (6) and (7), we obtain

$$\gamma_B = 1.305 \tag{8}$$

Combining $x_B = 0.10$ and Eqs. (1), (5) and (8) yields

$$\text{Partial pressure of B} = y_B P = \mathbf{0.0022 \text{ bar}}$$

---

6. This is similar to Problem 1, but includes activity coefficients.

$$f_i^{s} = f_{i,\text{pure}}^{s} = f_i^L = x_i \gamma_i f_{i,\text{pure}}^L$$

Then, considering $\Delta c_p = 0$ and $T_t = T_m$,

$$\ln\left(\frac{f_i^L}{f_i^{s}}\right)_{\text{pure}} = \frac{\Delta_{\text{fus}} h_i}{RT}\left(1 - \frac{T}{T_{m,i}}\right) = \ln\left(\frac{1}{x_i \gamma_i}\right)$$

Using the regular-solution theory,

$$\ln \gamma_i = \frac{v_i (\delta_1 - \delta_2)^2 \Phi_j^2}{RT}$$

Let 1 = benzene and 2 = *n*-heptane

$$\Phi_2 = 0.935$$

$$\ln \gamma_1 = \frac{(89) \times (18.8 - 15.1)^2 \times (0.935)^2}{(8.31451) \times (T)} = \frac{128}{T}$$

Then,

$$\frac{9843}{RT}\left(1 - \frac{T}{278.7}\right) = -\ln\left[(0.1) \times \exp\left(\frac{128}{T}\right)\right]$$

Solving for T,

$$T = 200 \text{ K}$$

Similarly, for *n*-heptane,

$$\Phi_1 = 0.065$$

$$\ln \gamma_2 = \frac{(148) \times (18.8 - 15.1)^2 \times (0.065)^2}{(8.31451) \times (T)} = \frac{1.03}{T}$$

Then,

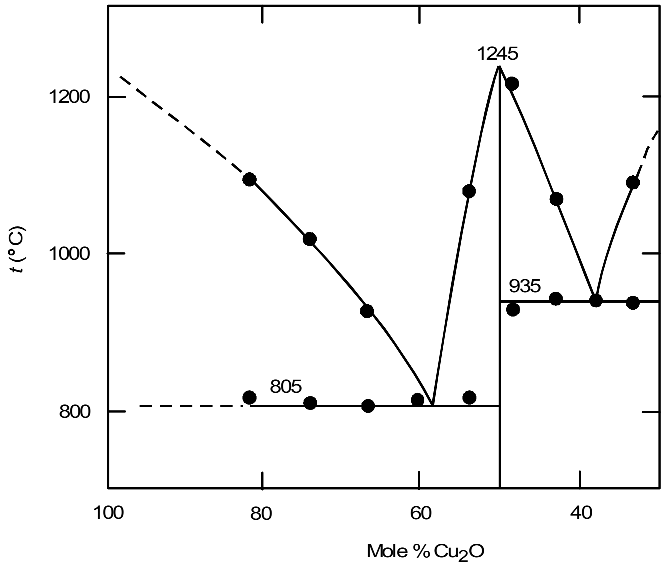
$$\frac{14067}{RT}\left(1 - \frac{T}{182.6}\right) = -\ln\left[(0.9) \times \exp\left(\frac{1.03}{T}\right)\right]$$

Solving for T,

$$T = 181 \text{ K}$$

As temperature decreases, benzene starts to precipitate at **200 K**.

7. Plotting the data we obtain:



A compound, $Cu_2OP_2O_5$, is formed with a congruent melting point at 1518 K. Eutectics occur at 1208 K and 1078 K.

8.

a) According to the ideal solubility equation, T_m of the solvent has no influence on the solubility. Any difference would have to come from nonideality (i.e. activity coefficients).

If we look at solubility parameters, we find that the solubility parameter of CS_2 is closer to that of benzene. Therefore, we expect greater solubility in CS_2.

b) Let 1 = benzene, 2 = CS_2 and 3 = *n*-octane.

Assuming

$$f_1^{\mathcal{S}} = f_{\text{pure 1}}^{\mathcal{S}} = f_1^L = x_1\gamma_1 f_{\text{pure 1}}^L$$

and

$$\Delta c_p = 0$$

$$T_t \cong T_m$$

we have

$$-\ln \gamma_1 x_1 = \frac{\Delta_{\text{fus}} h}{RT}\left(1 - \frac{T}{T_f}\right) \tag{1}$$

Using the regular-solution theory,

$$\ln \gamma_1 = \frac{\upsilon_1(\delta_1 - \bar{\delta})^2}{RT} \tag{2}$$

with

$$\bar{\delta} = \sum_{i=1}^{3} \Phi_i \delta_i$$

From Tables:

Component	δ (J cm^{-3})$^{1/2}$	υ (cm^3 mol^{-1})
1	18.8	89
2	20.4	61
3	15.3	164

From Eq. (1) with $x_1 = 0.3$,

$$\ln \gamma_1 = 0.144$$

Then, from Eq. (2),

$$\ln \gamma_1 = 0.144 = \frac{\upsilon_1(\delta_1 - \bar{\delta})}{RT}$$

$\bar{\delta} = 17.1$ (or 20.6; this value is probably meaningless since it is higher than δ's of pure components).

$$\bar{\delta} = \sum_{i=1}^{3} \Phi_i \delta_i$$

$$\Phi_1 = \frac{x_1 \upsilon_1}{x_1 \upsilon_1 + x_2 \upsilon_2 + x_3 \upsilon_3}, \quad \text{etc.}$$

Solving for x_2 and x_3,

$$x_1 = 0.30$$

$$x_2 = x_{\mathrm{CS}_2} = 0.32$$

$$x_3 = 0.38$$

9. At $x_2 = 0.25$,

$$f_2^{\mathscr{s}} = f_{\text{pure }2}^{\mathscr{s}} = f_2^L = x_2\gamma_2 f_{\text{pure }2}^L$$

$$x_2\gamma_2 = (f^{\mathscr{s}} / f^L)_{\text{pure }2} = 0.56$$

$$\gamma_2 = 2.24$$

Because $f_{\text{pure }2}^{\mathscr{s}} = P_2^{\mathscr{s},sat} = 0.99$ bar,

$$f_{\text{pure }2}^L = 1.77 \text{ bar}$$

Assuming $\ln\gamma_2 = Ax_1^2$, at $x_2 = 0.25$, then $\gamma_2 = 2.24$, and

$$A = 1.434$$

At $x_2 = 0.05$,

$$f_2^V = f_2^L = x_2\gamma_2 f_{\text{pure }2}^L$$

$$\ln\gamma_2 = (1.434)\times(0.95)^2$$

$$\gamma_2 = 3.65$$

$$P_2 = P_{\mathrm{CO}_2} = (0.05)\times(3.65)\times(1.77) = \mathbf{0.323\ bar}$$

10. At 250 K, we need a standard-state fugacity for a hypothetical liquid.

$$\ln\left(\frac{f_{\mathrm{A}}^{L}}{f_{\mathrm{A}}^{s}}\right)_{\text{pure}} = \frac{\Delta_{\text{fus}}h}{RT}\left(1-\frac{T}{T_m}\right)$$

$$= \frac{(13000)}{(8.31451)\times(250)}\times\left(1-\frac{250}{300}\right)$$

Hence,

$$\frac{f_{\mathrm{A}}^{L}}{f_{\mathrm{A}}^{s}} = 2.84$$

Because solid is pure,

$$f_{\mathrm{A}}^{s} = f_{\text{pure A}}^{s} = P_{\mathrm{A}}^{s,sat} = 35 \text{ torr}$$

$$f_{\text{pure A}}^{L} = \left(\frac{35}{750.06}\right)\times(2.84) = 0.1325 \text{ bar}$$

For the A-CCl_4 system,

$$f_{\mathrm{A}}^{V} = f_{\mathrm{A}}^{L} = x_{\mathrm{A}}\gamma_{\mathrm{A}} f_{\text{pure A}}^{L}$$

Neglecting vapor-phase non idealities and the Poynting correction factor,

$$y_{\mathrm{A}}P = x_{\mathrm{A}}\gamma_{\mathrm{A}} f_{\text{pure A}}^{L}$$

$$\gamma_{\mathrm{A}} = \frac{(5/750.06)}{(0.03)\times(0.1325)} = 1.677$$

Using the regular-solution theory,

$$RT\ln\gamma_{\mathrm{A}} = \upsilon_{\mathrm{A}}(\delta_{\mathrm{A}}-\delta_{\mathrm{CCl4}})^2\Phi_{\mathrm{CCl4}}^2$$

Thus,

$$(\delta_{\mathrm{A}}-\delta_{\mathrm{CCl_4}})^2 = \frac{(8.31451)\times(250)\times(\ln 1.677)}{(95)\times\left[\frac{(0.97)\times(97)}{(0.03)\times(95)+(0.97)\times(97)}\right]^2}$$

$$\delta_{\mathrm{A}}-\delta_{\mathrm{CCl4}} = 3.4 \ \ (\mathrm{J\ cm^{-3}})^{1/2}$$

As for $\delta_{\mathrm{CCl4}} = 17.6 \ \ (\mathrm{J\ cm^{-3}})^{1/2}$,

$$\delta_{\mathrm{A}} = 21.0 \ \ (\mathrm{J\ cm^{-3}})^{1/2}$$

or

$$\delta_{\mathrm{A}} = 14.2 \;\; (\mathrm{J\ cm^{-3}})^{1/2}$$

Because A is a branched hydrocarbon, we choose $\delta_{\mathrm{A}} = 14.2\,(\mathrm{J\ cm^{-3}})^{1/2}$. For the A-hexane system,

$$y_{\mathrm{A}}P = x_{\mathrm{A}}\gamma_{\mathrm{A}} f^{L}_{\text{pure A}}$$

$$\ln\gamma_{\mathrm{A}} = \frac{\upsilon_{\mathrm{A}}(\delta_{A} - \delta_{\text{hex}})^2}{RT}\Phi^2_{\text{hex}}$$

$$= \frac{(95)\times(14.2-14.9)^2 \times \left[\dfrac{(0.99)\times(132)}{(0.01)\times(95)+(0.99)\times(132)}\right]^2}{(8.31451)\times(250)}$$

$$\gamma_{\mathrm{A}} = 1.02$$

Then,

$$y_{\mathrm{A}}P = P_{\mathrm{A}} = (0.01)\times(1.02)\times(0.1325)$$

$$\boldsymbol{P_{\mathrm{A}} = 0.00135\ \mathbf{bar}}$$

---

11. Let

$$f^{L}_{\mathrm{A}} = x_{\mathrm{A}} f^{L}_{\text{pure A}} \qquad (\gamma_{\mathrm{A}} = 1)$$

$$f^{L}_{\mathrm{B}} = x_{\mathrm{B}} f^{L}_{\text{pure B}} \qquad (\gamma_{\mathrm{B}} = 1)$$

From Eq. (11-13) with $T \cong T_m$, $\Delta c_p \cong 0$,

$$\ln\left(\frac{f^{L}_{\text{pure A}}}{f^{\mathcal{S}}_{\text{pure A}}}\right) = \frac{\Delta_{\text{fus}}h_{\mathrm{A}}}{RT}\left(1 - \frac{T}{T_{m,\mathrm{A}}}\right)$$

$$\ln\left(\frac{f^{L}_{\text{pure B}}}{f^{\mathcal{S}}_{\text{pure B}}}\right) = \frac{\Delta_{\text{fus}}h_{\mathrm{B}}}{RT}\left(1 - \frac{T}{T_{m,\mathrm{B}}}\right)$$

Because solids A and B are mutually insoluble,

$$f^{\mathcal{S}}_{\mathrm{A}} = f^{\mathcal{S}}_{\text{pure A}}$$

$$f_{\mathrm{B}}^{S} = f_{\text{pure B}}^{S}$$

At equilibrium,

$$f_{\mathrm{A}}^{S} = x_{\mathrm{A}} f_{\text{pure A}}^{L}$$

$$f_{\mathrm{B}}^{S} = x_{\mathrm{B}} f_{\text{pure B}}^{L}$$

Then,

$$\ln\left(\frac{f_{\text{pure A}}^{L}}{f_{\text{pure A}}^{S}}\right) = \ln\left(\frac{1}{x_{\mathrm{A}}}\right) = \frac{(8000)}{(8.31451)\times(T)}\times\left(1-\frac{T}{293}\right)$$

$$\ln\frac{1}{x_{\mathrm{B}}} = \frac{(12000)}{(8.31451)\times(T)}\times\left(1-\frac{T}{278}\right)$$

with $x_{\mathrm{B}} = 1 - x_{\mathrm{A}}$.

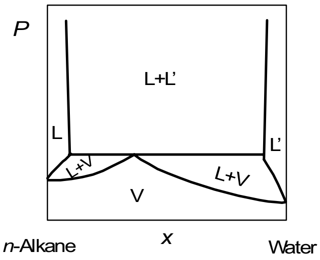
Solving the above equations, we obtain $x_{\mathrm{A}} = 0.516$ (or **51.6 mol % A**), $x_{\mathrm{B}} = 0.484$ and ***T* = 244 K**.

SOLUTIONS TO PROBLEMS

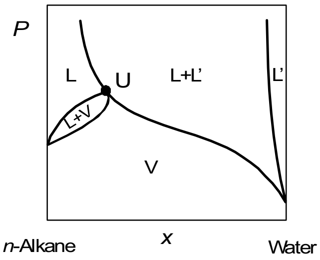
CHAPTER 12

1.

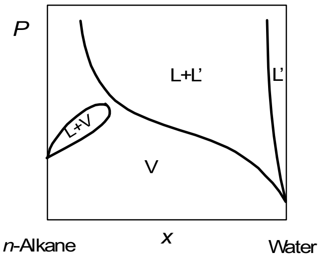
i) $T < T_U$



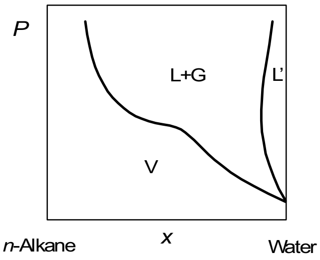
ii) $T = T_U$



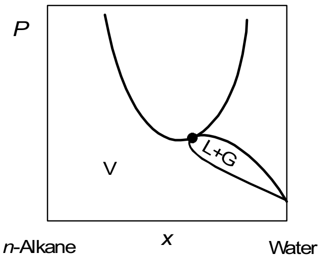
iii) $T_U < T < T_{C_n}$



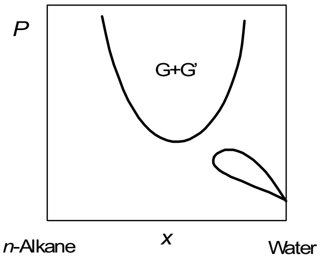
iv) $T_{C_n} < T < T_{C_b}$



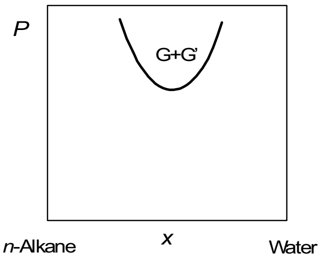
v) $T = T_{C_b}$



vi) $T_{C_b} < T < T_{C_{H_2O}}$

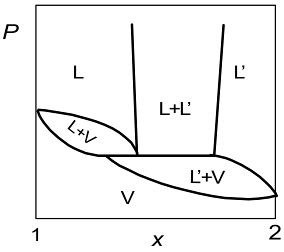


vii) $T > T_{C_{H_2O}}$

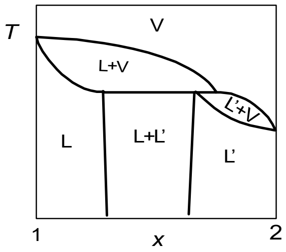


2.

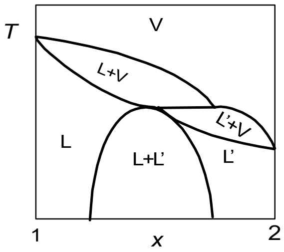
a) $T = T_1$



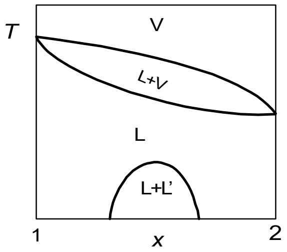
b) $P_1 < P_{UCEP}$



$P_2 = P_{\text{UCEP}}$



$P_3 > P_{\text{UCEP}}$



---

3. Let A stand for alcohol.
For alcohol distributed between phases ' and ''

$$x'_A \gamma'_A = x''_A \gamma''_A$$

Then,

$$K = \lim_{x_A \to 0} \left(\frac{x'_A}{x''_A} \right) = \lim_{x_A \to 0} \left(\frac{\gamma''_A}{\gamma'_A} \right)$$

At 0°C and 1 bar,

$$\ln \gamma'_A = \frac{2400}{RT}(1 - x'_A)^2$$

$$\ln \gamma''_A = \frac{320}{RT}(1 - x''_A)^2$$

The pressure correction to γ_A is

$$\gamma_A(P_2) = \gamma_A(P_1) \exp \int_{P_1}^{P_2} \frac{\overline{v}^E}{RT} dP$$

The temperature correction is:

$$\gamma_A(T_2) = \gamma_A(T_1) \exp \int_{T_1}^{T_2} \frac{-\overline{h}^E}{RT^2} dT$$

Thus, we can write,

$$\ln\gamma'_{\mathrm{A}} = \Big[\frac{2400}{(8.31451)\times(273)} + \int_{1}^{100}\frac{16}{(8.31451)\times(273)}\,dP$$

$$-\int_{273}^{303}\frac{4800}{(8.31451)\times(T^2)}\,dT\Big]\times(1-x'_{\mathrm{A}})^2$$

$$= 0.9178\times(1-x'_{\mathrm{A}})^2$$

$$\ln\gamma''_{\mathrm{A}} = \Big[\frac{320}{(8.31451)\times(273)} + \int_{1}^{100}\frac{-10}{(8.31451)\times(273)}\,dP$$

$$-\int_{273}^{303}\frac{600}{(8.31451)\times(T^2)}\,dT\Big]\times(1-x''_{\mathrm{A}})^2$$

$$= 0.0712(1-x''_{\mathrm{A}})^2$$

This gives

$$K = \lim_{x_{\mathrm{A}}\to 0}\frac{\gamma''_{\mathrm{A}}}{\gamma'_{\mathrm{A}}} = \mathbf{0.429}$$

---

4. For pure benzene, neglecting fugacity coefficients and assuming constant density of each phase with respect to pressure,

$$f_{\mathrm{B}}^{L} = f_{\mathrm{B}}^{\mathscr{s}}$$

$$P_{\mathrm{B}}^{s,L}\exp\frac{v^{L}(P-P_{\mathrm{B}}^{s,L})}{RT} = P_{\mathrm{B}}^{s,\mathscr{s}}\exp\frac{v^{\mathscr{s}}(P-P_{\mathrm{B}}^{s,\mathscr{s}})}{RT}$$

with $v^{L} = 87.7\ \mathrm{cm^3\,mol^{-1}}$ and $v^{\mathscr{s}} = 77.4\ \mathrm{cm^3\,mol^{-1}}$, as obtained from density data.

$$P_{\mathrm{B}}^{s,L}\exp\left[\frac{(87.7)\times(200-P_{\mathrm{B}}^{s,L})}{(83.1451)T}\right] = P_{\mathrm{B}}^{s,\mathscr{s}}\exp\left[\frac{(77.4)\times(200-P_{\mathrm{B}}^{s,\mathscr{s}})}{(83.1451)T}\right]$$

Temperature T can be found from the intercept of the curves obtained by representing each side of the last equation as a function of temperature.

In an alternate way, we can express $P_{\mathrm{B}}^{s,L}$ and $P_{\mathrm{B}}^{s,\mathscr{s}}$ from vapor-pressure equations:

$$P_{\mathrm{B}}^{s,L} = \frac{10^{(7.9622-1785/T)}}{750.06}$$

$$P_{\mathrm{B}}^{s,\mathcal{S}} = \frac{10^{(9.846-2310/T)}}{750.06}$$

which, together with the last equation, can be solved for T:

$$T_m(200 \text{ bar}) = \mathbf{284.4\ K}$$

---

5. The Redlich-Kwong equation is:

$$P = \frac{RT}{v-b} - \frac{a}{T^{1/2}v(v+b)}$$

with

$$a = \sum_i \sum_j z_i z_j a_{ij} = z_{\mathrm{A}}^2 a_{\mathrm{AA}} + 2 z_{\mathrm{A}} z_{\mathrm{B}} a_{\mathrm{AB}} + z_{\mathrm{B}}^2 a_{\mathrm{BB}}$$

$$b = \sum_i z_i b_i = z_{\mathrm{A}} b_{\mathrm{A}} + z_{\mathrm{B}} b_{\mathrm{B}}$$

Assuming that a_{AB} is given by the geometric rule,

$$a_{\mathrm{AB}} = (a_{\mathrm{AA}} a_{\mathrm{BB}})^{1/2}$$

we get for $z_{\mathrm{A}} = z_{\mathrm{B}} = 0.5$,

$$a = 4.35 \times 10^{8} \text{ bar (cm}^3\text{ mol}^{-1}\text{) K}^{1/2}$$

$$b = 91.5 \text{ cm}^3 \text{ mol}^{-1}$$

Substitution in the R-K equation gives for total pressures:

$$P = -41.3 \text{ bar}$$

Because this result is absurd, we use Henry's constant data to find a_{AB}.
For infinitely dilute solutions of A in B,

$$H_{\mathrm{A,B}} = (P\varphi_{\mathrm{A}})_{x_{\mathrm{A}}=0} = P_{\mathrm{B}}^{s} \varphi_{\mathrm{B}}^{\infty}$$

At infinite dilution, $P_{\text{total}} \cong P_{\text{pure B}}^{s}$ which can be obtained from the R-K equation with the appropriate constants [$a = 4.53 \times 10^{8}$ bar (cm^3 mol^{-1})^2 K$^{1/2}$ and $b = 82.8$ cm^3 mol^{-1}].

This gives,

$$P_B^s = 1.13 \text{ bar}$$

Therefore,

$$\varphi_A^\infty = \frac{H_{A,B}}{P_B^s} = \frac{7.01}{1.13} = 6.195$$

For the R-K equation, fugacity coefficients are given by:

$$\ln\varphi_A^\infty = \ln\frac{v}{v-b} + \frac{b_A}{v-b} - \frac{2a_{AB}}{RT^{3/2}b}\ln\frac{v+b}{v} + \frac{ab_A}{RT^{3/2}b^2}\left[\ln\frac{v+b}{v} - \frac{b}{v+b}\right] - \ln\frac{Pv}{RT}$$

Using $b \cong b_B$, $a \cong a_B$ and $v \cong v_B$ (infinite dilution of A).
Solving for a_{AB},

$$a_{AB} = 3.963\times10^8 \text{ bar (cm}^3\text{ mol}^{-1})^2\text{ K}^{1/2}$$

Then, for the mixture,

$$a = 4.159\times10^8 \text{ bar (cm}^3\text{ mol}^{-1})\text{ K}^{1/2}$$

$$b = 91.5 \text{ cm}^3\text{ mol}^{-1}$$

Calculating again the pressure we obtain,

$$\boldsymbol{P = 4.14 \textbf{ bar}}$$

6. Let 1 = C_2H_6 and 2 = C_6H_6.
The K factor of component i is defined as

$$K_i = \frac{y_i}{x_i} = \frac{\varphi_i^L(P,x)}{\varphi_i^V(P,y)}$$

with

$$\varphi = c^{(0)} + c^{(1)}P + c^{(2)}z_i$$

Thus, we need to solve for P and y_1 (or y_2).
At equilibrium,

$$y_1\varphi_1^V = x_1\varphi_1^L \tag{1}$$

$$(1-y_1)\varphi_2^V = (1-x_1)\varphi_2^L \tag{2}$$

From the given equations, we rewrite Eqs.(1) and (2) for x_1 = 0.263:

$$(1.2545 - 2.458\times 10^{-4}P - 0.4091y_1)y_1 = 1.1699 - 0.008345P$$

$$[0.74265 - 7.0069\times 10^{-3}P + 0.50456(1-y_1)](1-y_1) = 0.24596 - 0.001874P$$

The above equations can be solved (either graphically or numerically) for P and y_1:

$$P = 59 \text{ atm}$$

$$y_1 = 0.715 \qquad (y_2 = 0.285)$$

Then,

$$K_1 = \frac{y_1}{x_1} = \frac{0.715}{0.263} = 2.72$$

$$K_2 = \frac{y_2}{x_2} = \frac{0.285}{0.737} = 0.387$$

[From Kay's data: $K_1 = 2.73$ and $K_2 = 0.41$].

---

7. The stability criterion is [see Eq. (6-131) of text]:

$$\left(\frac{\partial^2 g^E}{\partial x_1^2}\right)_{T,P} + RT\left(\frac{1}{x_1}+\frac{1}{x_2}\right) < 0$$

We need an expression for g^E valid at high pressures.
Because

$$\left(\frac{\partial g^E}{\partial P}\right)_{T,x} = v^E$$

we write

$$g^E(T,P,x) = g^E(T,P=1\text{ atm},x) + \int_1^P v^E\,dP$$

$$= (RT)\times(1.877)x_1x_2 + \int_1^P x_1x_2(4.026 - 0.233\ln P)dP$$

Thus,

$$g^E(T,P,x) = (RT)\times(1.877)x_1x_2 + (P-1)\times(4.026)x_1x_2$$

$$+(P-1)\times(0.233)x_1x_2 - 0.233P(\ln P)x_1x_2$$

$$= (42043 + 4.259P - 0.233P\ln P)x_1x_2 = Ax_1x_2$$

For g^E of this form ($g^E = Ax_1x_2$, where A is a constant), the stability criterion is (see Sec. 6.12):

$$\frac{A}{RT} > 2$$

or

$$42043 + 4.259P - 0.233P\ln P > (2)\times(82.0578)\times(273)$$

Solving for *P*,

$$P = 1046 \text{ atm} \quad \text{(or 1060 bar)}$$

At pressures higher than 1060 bar, the system splits into two phases.
To solve for the composition at a higher pressure, we use:

$$x_1^{'}\gamma_1^{'} = x_1^{''}\gamma_1^{''}$$

$$(1-x_1^{'})\gamma_2^{'} = (1-x_1^{''})\gamma_2^{''}$$

where

$$RT\ln\gamma_i = (42043 + 4.259P - 0.233P\ln P)x_j^2$$

At 1500 atm (or 1520 bar) and 273 K,

$$\ln\gamma_i = 2.0477x_j^2$$

Thus,

$$x_1^{'}\exp[2.0477(1-x_1^{'})^2] = x_1^{''}\exp[2.0477(1-x_1^{''})^2]$$

$$(1-x_1^{'})\exp[2.0477(x_1^{'})^2] = (1-x_1^{''})\exp[2.0477(x_1^{''})^2]$$

Solving (either graphically or numerically), we obtain

$$\boldsymbol{x_1^{'} = 0.37} \qquad (x_2^{'} = 0.63)$$

$$\boldsymbol{x_1^{''} = 0.63} \qquad (x_2^{''} = 0.37)$$

8. We want to relate h^E to volumetric data. Relations given in Chapter 3 of the text may be used. We write h^E at any pressure P relative to h^E at 1 bar as:

$$h^E(P) - h^E(1\text{ bar}) = \int_1^P \left[v^E - T\left(\frac{\partial v^E}{\partial T}\right)_P \right] dP$$

Thus, we need the above integrand as a function of pressure at 333 K.
From volumetric data, using linear regression at each pressure between 323 K and 348 K,

$$\left(\frac{\partial v^E}{\partial T}\right)_{1\text{ bar}} = 0.0186 \qquad \left(\frac{\partial v^E}{\partial T}\right)_{100\text{ bar}} = 0.0154$$

$$\left(\frac{\partial v^E}{\partial T}\right)_{250\text{ bar}} = 0.01239 \qquad \left(\frac{\partial v^E}{\partial T}\right)_{500\text{ bar}} = 0.00963$$

Using linear interpolation, at 333 K,

$$v^E(1\text{ bar}) = 1.091 \qquad v^E(100\text{ bar}) = 0.9638$$

$$v^E(250\text{ bar}) = 0.8284 \qquad v^E(500\text{ bar}) = 0.6846$$

If

$$F(P) = v^E - T\left(\frac{\partial v^E}{\partial T}\right)_P$$

then:

P (bar)	1	100	250	500
$F(P)$ (J bar mol^{-1})	-0.5102	-0.4164	-0.3297	-0.2522

Using a trapezoid-rule approximation,

$$\int_1^{360} F(P)dP = -128\text{ J mol}^{-1}$$

Therefore, at 333K

$$h^E(360\text{ bar}) = h^E(1\text{ bar}) + \int_1^{360} F(P)dP$$

$$= 1445 - 128$$

$$\boldsymbol{h^E(360\text{ bar, } 333\text{K}) = 1317\text{ J mol}^{-1}}$$

9. For condensation to occur,

$$f_{\mathrm{W}}^{L} > f_{\mathrm{W}}^{V}$$

To find the temperature for condensation (at constant pressure and vapor composition), we solve the equilibrium relation

$$f_{\mathrm{W}}^{L} = f_{\mathrm{W}}^{V}$$

The liquid phase is assumed to be pure water. Its fugacity is given by

$$f_{\mathrm{W}}^{L} = f_{\mathrm{pure}}^{L} \exp \int_{P_{\mathrm{W}}^{s}}^{P} \frac{\upsilon_{\mathrm{W}}}{RT} dP$$

As a good approximation, let

$$f_{\mathrm{W}}^{L} \cong P_{\mathrm{W}}^{s} \exp \frac{\upsilon_{\mathrm{W}}^{s}(P - P_{w}^{s})}{RT} \qquad \text{(obtain data from Steam Tables)}$$

Thus, we are neglecting φ_{W}^{s} and we assume that (liquid) water is incompressible over the pressure range between P_{W}^{s} and P (150 atm).

The vapor phase is described by an equation of state. Therefore,

$$f_{\mathrm{W}}^{V} = y_{\mathrm{W}} \varphi_{\mathrm{W}}^{V} P$$

To obtain φ_{W}^{V}, we use the Redlich-Kwong equation of state:

$$P = \frac{RT}{\upsilon - b} - \frac{a}{T^{1/2}\upsilon(\upsilon + b)} \tag{1}$$

from which we obtain

$$\begin{aligned} \ln \varphi_{\mathrm{W}} = \ln \frac{\upsilon}{\upsilon - b} + \frac{b_{\mathrm{W}}}{\upsilon - b} - (2\sum_{j} y_j a_{\mathrm{W}j})(RT^{1.5}b)^{-1} \ln\left(\frac{\upsilon + b}{\upsilon}\right) \\ + \frac{ab_{\mathrm{W}}}{RT^{1.5}b^2}\left(\ln \frac{\upsilon + b}{\upsilon} - \frac{b}{\upsilon + b}\right) - \ln \frac{P\upsilon}{RT} \end{aligned} \tag{2}$$

where υ is the molar volume of the mixture and

$$a = \sum_i \sum_j y_i y_j a_{ij}$$

$$b = \sum_i y_i b_i$$

In these equations, a_{W} and $a_{\mathrm{CO_2}}$ are given as functions of temperature; the cross-coefficient is

$$a_{ij} = (a_i^{(0)} a_j^{(0)})^{1/2} + 0.5 R^2 T^{2.5} K$$

With a trial-and-error procedure, we can calculate f_{W}^{V}. Use the following procedure:

1. Guess temperature.
2. Calculate υ from equation of state [Eq. (1)].
3. Use T and υ (along with P and y) to calculate φ_{W} from Eq. (2).
4. Calculate the fugacity of vapor.
5. Compare f_{W}^{V} with saturation pressure of water at that temperature.

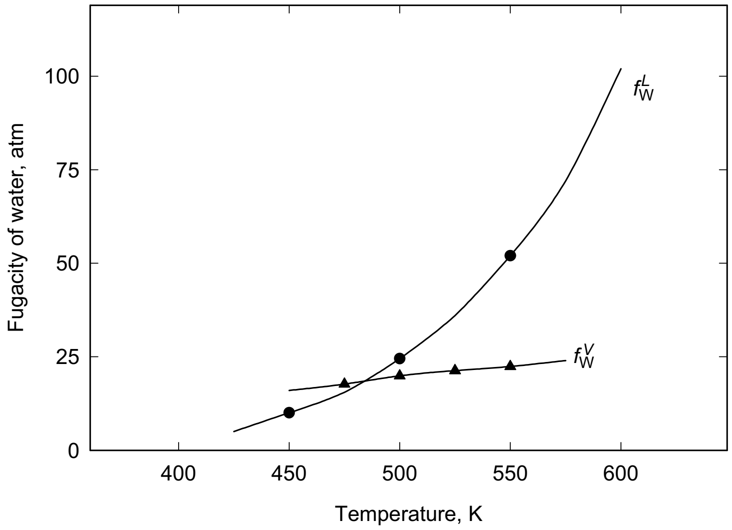
Typical results are:

T (K)	φ_{W}	f_{W}^{V} (atm)
475	0.588	17.7
500	0.633	19.9
525	0.711	21.3
550	0.746	22.4

Plotting f_{W}^{V} and f_{W}^{L} as a function of temperature (see figure), we see that

$$f_{\mathrm{W}}^{L} = f_{\mathrm{W}}^{V}$$

at $T \approx 482\,\mathrm{K}$. That is the temperature where condensation first occurs (dew-point temperature of the mixture).



Fugacity of water in vapor phase and in liquid phase at P = 150 atm.

10.

a) For equilibrium between solid solute and solute dissolved in the supercritical fluid,

$$f_2^{s}(P,T) = f_2^{f}(P,T,y_2)$$

or

$$d\ln f_2^{s} = d\ln f_2^{f} \tag{1}$$

where subscript 2 refers to solute and superscript *f* to fluid phase.

Expanding Eq. (1) with respect to *T*, *P* and composition (see Sec. 12.4), we obtain (temperature is constant):

$$\left(\frac{\partial \ln f_2^{s}}{\partial T}\right)_{P,y} = 0$$

$$\left(\frac{\partial \ln f_2^{f}}{\partial T}\right)_{P,y} = 0$$

$$\left(\frac{\partial \ln f_2^{s}}{\partial x_2}\right)_{P,T} = 0 \qquad \text{(pure solid solute)}$$

$$\left(\frac{\partial \ln f_2^{s}}{\partial P}\right)_{T} dP = \left(\frac{\partial \ln f_2^{f}}{\partial P}\right)_{T,y} dP + \left(\frac{\partial \ln f_2^{f}}{\partial y_2}\right)_{T,P} dy_2 \tag{2}$$

But because

$$\left(\frac{\partial \ln f_2^{s}}{\partial P}\right)_{T} = \frac{v_2^{s}}{RT}$$

$$\left(\frac{\partial \ln f_2^{f}}{\partial P}\right)_{T} = \frac{\overline{v}_2^{f}}{RT}$$

Equation (2) becomes:

$$\frac{(v_2^{s} - \overline{v}_2^{f})}{RT} dP = \left(\frac{\partial \ln f_2^{f}}{\partial y_2}\right)_{T,Pdy} dy_2 = \left(\frac{\partial \ln f_2^{f}}{\partial \ln y_2}\right)_{T,P} d(\ln y_2) \tag{3}$$

Finally, because

$$f_2^{f} = y_2 \varphi_2 P$$

Equation (3) becomes

$$\left(\frac{\partial \ln y_2}{\partial P}\right)_{T} = \frac{\dfrac{v_2^{s} - \overline{v}_2^{f}}{RT}}{1 + \left(\dfrac{\partial \ln \varphi_2}{\partial \ln y_2}\right)_{T,P}} \tag{4}$$

b) Maxima (or minima) occur when

$$\left(\frac{\partial \ln y_2}{\partial P}\right)_{T} = 0$$

Because $\partial \ln \varphi_2 / \partial \ln y_2$ is always greater than –0.4, the above derivative is zero when $v_2^{s} = \overline{v}_2^{f}$.

It is necessary, then, to calculate $\overline{v}_2^{f}$ as a function of pressure.

Using Eq. (12-41),

$$\overline{v}_2 = -\frac{\left(\dfrac{\partial P}{\partial n_2}\right)_{T,V,n_1}}{\left(\dfrac{\partial P}{\partial V}\right)_{T,\text{ all } n}}$$

and the Redlich-Kwong equation of state with the mixing rules,

$$a = \sum_i \sum_j x_i x_j a_{ij}$$

$$b = \sum_i x_i b_i$$

we obtain

$$\overline{v}_2 = \frac{\dfrac{RT}{v-b}\left(1+\dfrac{b_2}{v-b}\right) - \dfrac{2(\sum_i x_i a_{2i}) - ab_2/(v+b)}{v(v+b)T^{1/2}}}{\dfrac{RT}{(v-b)^2} - \dfrac{a}{T^{1/2}}\left[\dfrac{2v+b}{v^2+(v+b)^2}\right]}$$

Assuming that the fluid phase is almost pure solvent, v, a and b are those for pure solvent 1. Cross parameter a_{12} is given by:

$$a_{12} = (a_{11}a_{22})^{1/2}(1-k_{12})$$

Constants are:

$$a_{11} = 0.7932\times 10^{8} \quad \text{bar (cm}^3\text{ mol}^{-1})^2\text{ K}^{1/2}$$
$$a_{22} = 0.11760\times 10^{10} \quad \text{bar (cm}^3\text{ mol}^{-1})^2\text{ K}^{1/2}$$
$$a_{12} = 0.3264\times 10^{9} \quad \text{bar (cm}^3\text{ mol}^{-1})^2\text{ K}^{1/2}$$
$$b_1 = 40.683 \text{ cm}^3\text{ mol}^{-1} \qquad b_2 = 140.576 \text{ cm}^3\text{ mol}^{-1}$$

Using volumetric data for ethylene at 318 K (IUPAC Tables), and because

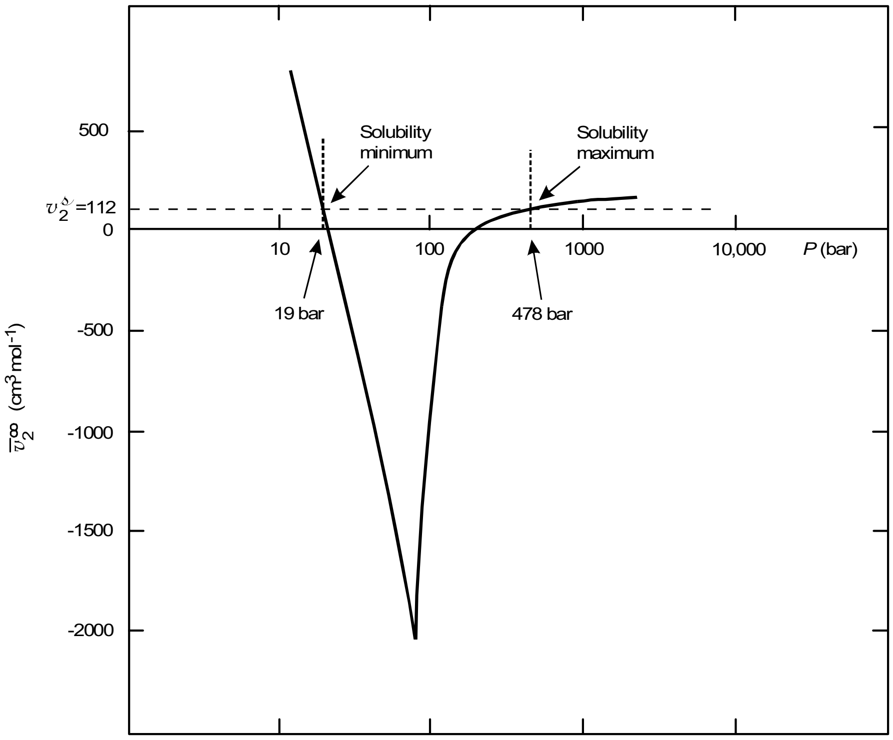
$$v_2^{s} = \frac{128.174}{1.144} = 112 \text{ cm}^3\text{ mol}^{-1}$$

the maximum (and minimum) occurs $(\overline{v}_2 = v_2^{s})$ at (see figure below)

minimum = 19 bar

maximum = 478 bar

These values are in good agreement with results shown in Fig. 5-39 of the text.



Partial molar volumes of naphthalene infinitely dilute in ethylene at 318 K calculated from Redlich-Kwong equation of state with $k_{12} = -0.0182$.