

SOLUTIONS MANUAL

Molecular Thermodynamics of Fluid-Phase Equilibria, Third Edition

**John M. Prausnitz
Rudiger N. Lichtenthaler
Edmundo Gomes de Azvedo**

The authors and publisher have taken care in the preparation of this book but make no expressed or implied warranty of any kind and assume no responsibility for errors or omissions. No liability is assumed for incidental or consequential damages in connection with or arising out of the use of the information or programs contained herein.

Visit us on the Web: www.informit.com

Copyright © 2008 Pearson Education, Inc.

This work is protected by United States copyright laws and is provided solely for the use of instructors in teaching their courses and assessing student learning. dissemination or sale of any part of this work (including the World Wide Web) will destroy the integrity of the work and is not permitted. The work and materials from it should never be made available to students except by instructors using the accompanying text in their classes. All recipients of this work are expected to abide by these restrictions and to honor the intended pedagogical purposes and the needs of other instructors who rely on these materials.

ISBN-10: 0-13-018388-1

ISBN-13: 978-0-13-018388-0

Text printed in the United States at OPM in Laflin, Pennsylvania

C O N T E N T S

Preface	i
Solutions to Problems Chapter 2	1
Solutions to Problems Chapter 3	17
Solutions to Problems Chapter 4	29
Solutions to Problems Chapter 5	49
Solutions to Problems Chapter 6	81
Solutions to Problems Chapter 7	107
Solutions to Problems Chapter 8	121
Solutions to Problems Chapter 9	133
Solutions to Problems Chapter 10	153
Solutions to Problems Chapter 11	165
Solutions to Problems Chapter 12	177

P R E F A C E

This manual provides detailed solutions to all problems presented in the third edition of the textbook *Molecular Thermodynamics of Fluid-Phase Equilibria* (Prentice-Hall, 1999).

This manual was prepared according to the corrections presented on the third (and subsequent) printing of the textbook. For those who have copies of the first and second printings, an errata is available for download at http://www.phptr.com/ptrbooks/ptr_0139777458.html or at <http://alfa.ist.utl.pt/~ejsga>.

Although we have carefully checked all solutions presented here, we would appreciate being informed of any misprints or errors that the text may contain.

We gratefully acknowledge the contribution of Van Nguyen that checked all the solutions presented here.

Berkeley, August 1999

J. M. Prausnitz
Berkeley, California

R. N. Lichtenthaler
Heidelberg, Germany
R.Lichtenthaler@urz.uni-heidelberg.de

E. Gomes de Azevedo
Lisbon, Portugal
egazevedo@ist.utl.pt
http://alfa.ist.utl.pt/~ejsga

S O L U T I O N S T O P R O B L E M S

C H A P T E R **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 $\Delta T = 1^\circ\text{C}$, we get

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

2. Given the equation of state,

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

we find:

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

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

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

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

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

For an isothermal change,

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

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

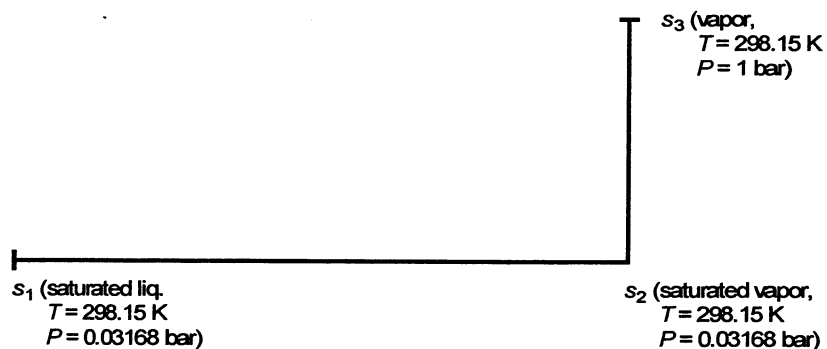
$$\Delta U = \int_{P_1}^{P_2} \left[\left(-\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T \right] dP = 0$$

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

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

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

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



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

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

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

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

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

$$s_3 = s^0(\text{H}_2\text{O}, \text{vapor})$$

$$= 147.19 - 28.70 + 69.96$$

$$= 188.45 \text{ J K}^{-1} \text{ mol}^{-1}$$

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

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

or

$$P = \frac{RTv^2}{2v^2 - 3 + v^3}$$

$$\left(\frac{\partial P}{\partial v}\right)_T = -\frac{RTv(v^3 + 6)}{(2v^2 - 3 + v^3)^2}$$

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

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

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

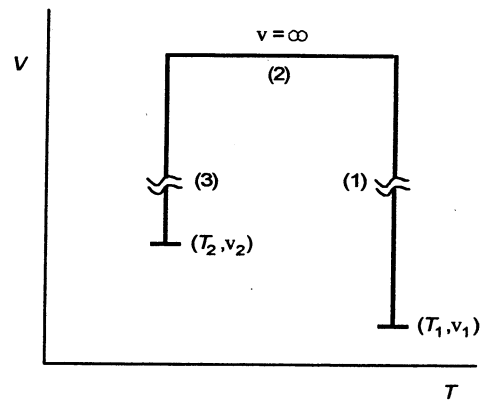
$$= -\left(1 \frac{\text{kg m}}{\text{N s}^2}\right) \times (1.4) \times \left(\frac{1}{100 \times 10^{-3}} \frac{\text{mol}}{\text{kg}}\right) \times \left(2.3 \times 10^{-3} \frac{\text{m}^3}{\text{mol}}\right)^2 \times \left(-3.3245 \times 10^8 \frac{\text{N mol}}{\text{m}^2 \text{ m}^3}\right)$$

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

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

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

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

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

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,

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

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

$$T_2 = 203 \text{ K}$$

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

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

Thus,

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

or

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

Because

$$z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \dots$$

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

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

7. Starting with

$$\begin{aligned} du &= Tds - Pdv \\ \left(\frac{\partial u}{\partial P}\right)_T &= T\left(\frac{\partial s}{\partial P}\right)_T - P\left(\frac{\partial v}{\partial P}\right)_T \\ &= -T\left(\frac{\partial v}{\partial T}\right)_P - P\left(\frac{\partial v}{\partial P}\right)_T \end{aligned}$$

As

$$\begin{aligned} v &= \frac{RT}{P} + B = \frac{RT}{P} + b - \frac{a}{T^2} \\ \left(\frac{\partial v}{\partial T}\right)_P &= \frac{R}{P} + \frac{2a}{T^3} \\ \left(\frac{\partial v}{\partial T}\right)_T &= -\frac{RT}{P^2} \end{aligned}$$

Then,

$$\begin{aligned} \left(\frac{\partial u}{\partial P}\right)_T &= -\frac{2a}{T^2} \\ \Delta u &= \int_0^\pi -\left(\frac{2a}{\tau^2}\right) dP \\ \Delta u &= -\frac{2a\pi}{\tau^2} \end{aligned}$$