SOLUTIONS MANUAL

Molecular Thermodynamics of Fluid-Phase Equilibria, Third Edition

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

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ISBN-10: 0-13-018388-1
ISBN-13: 978-0-13-018388-0
Text printed in the United States at OPM in Laflin, Pennsylvania

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PREFACE

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

SOLUTIONS TO PROBLEMS

CHAPTER 2

1. From problem statement, we want to find $(\partial P/\partial T)_{\mathrm{v}}$.
Using the product-rule,

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

By definition,

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

and

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

Then,

$$\left(\frac{\partial P}{\partial T}\right)_{\mathrm{v}}=\frac{\alpha_P}{\kappa_T}=\frac{1.8\times10^{-5}}{5.32\times10^{-6}}=33.8\ \text{bar}\ {}^\circ\text{C}^{-1}$$

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

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

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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,

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

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

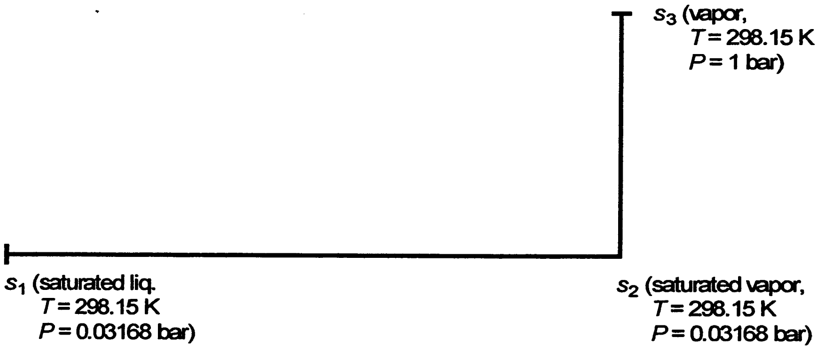
$$\Delta U=\int_{P_1}^{P_2}\left[\left(-\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial P}\right)_T\right]dP=0$$

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

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

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

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



$$s_3 = \Delta s_{1\to2} + \Delta s_{2\to3} + s_1$$

$$\Delta s_{1\to2} = \Delta_{\text{vap}} s = \frac{\Delta_{\text{vap}} h}{T} = \frac{(2436)\times(18.015)}{298.15} = 147.19 \text{ J K}^{-1}\text{ mol}^{-1}$$

$$\Delta s_{2\to3} = \int_{P_2}^{P_3}\left[-\left(\frac{\partial \text{v}}{\partial T}\right)_P\right]dP$$

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

$$\begin{aligned}\Delta s_{2\to3} &= -R\ln\left(\frac{P_3}{P_2}\right)\\ &= -(8.31451)\times\ln\left(\frac{1.0}{0.03168}\right)\\ &= -28.70 \text{ J K}^{-1}\text{ mol}^{-1}\end{aligned}$$

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

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

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

or

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

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

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

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

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

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

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

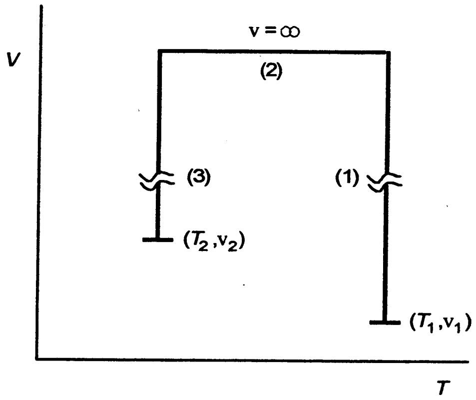
$$\boldsymbol{w = 157\ \mathrm{m\ s^{-1}}}$$

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,

$$\Delta s = R\ln\left(\frac{\mathrm{v}_2 - b}{\mathrm{v}_1 - b}\right) + \int_{T_1}^{T_2} \frac{c_\mathrm{v}^0}{T} dT$$

To simplify, assume

$$c_\mathrm{v}^0 = c_p^0 - R$$

$$\mathrm{v}_2 = \frac{RT_2}{P_2}$$

Then,

$$\ln\frac{\frac{RT_2}{P_2} - b}{\mathrm{v}_1 - b} = \left(\frac{c_p^0 - R}{R}\right)\ln\left(\frac{T_1}{T_2}\right)$$

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

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

6.

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

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

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

Thus,

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

or

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

Because

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

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

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

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7. Starting with

$$du=Tds-Pdv$$

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

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

As

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

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

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

Then,

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

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

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