

## **SOLUTIONS MANUAL**

# **Molecular Thermodynamics of Fluid-Phase Equilibria, Third Edition**

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## P R E F A C E

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*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](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.

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# 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

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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  $\alpha_P$  and  $\kappa_T$  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,

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

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

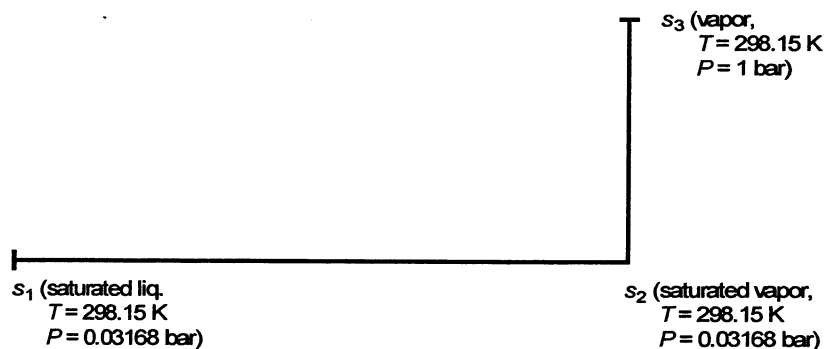
$$\Delta U = \int_{P_1}^{P_2} \left[ \left(-\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T \right] dP = 0$$

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

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

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

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),

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

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

$$= 147.19 - 28.70 + 69.96$$

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

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  $100 \text{ g mol}^{-1}$ ,

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

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

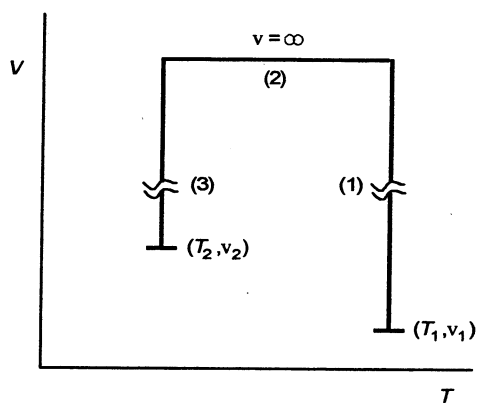
$$= -\left(1 \frac{\text{kg m}}{\text{N s}^2}\right) \times (1.4) \times \left(\frac{1}{100 \times 10^{-3}} \frac{\text{mol}}{\text{kg}}\right) \times \left(2.3 \times 10^{-3} \frac{\text{m}^3}{\text{mol}}\right)^2 \times \left(-3.3245 \times 10^8 \frac{\text{N mol}}{\text{m}^2 \text{ m}^3}\right)$$

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

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

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

$$du = Tds - Pd v$$

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

As

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

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

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

Then,

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

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

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