Assigned questions for Lecture 13 are listed below. The questions occur in the following editions of “Physical Chemistry” by P.W. Atkins:

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<tbody>
<tr>
<td>Note: The letter “P” in front of a number indicates that the question is in the “Problem” category as opposed to the “Exercise” category in Atkins’ books.</td>
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<tr>
<td>Note: There are two separate problem sets associated with Lecture 13.</td>
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<tr>
<td>Note: There are a lot of questions that are now missing, which is unfortunate.</td>
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**Set 1**

**Question 13.01**

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<td>(Ex. 5.4a, 7th edition)</td>
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<td>(Ex. 5.4b, 7th edition)</td>
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**Question 13.02**

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<tr>
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<th>3E.1</th>
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<th>3.16</th>
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<tbody>
<tr>
<td>Same question format, variation in numbers between 10th and 11th Eds. vs. 8th and 9th Eds.</td>
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<tr>
<td>3.16(a) Suppose that 3.0 mmol N₂(g) occupies 36 cm³ at 300 K and expands to 60 cm³. Calculate ΔG for the process.</td>
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<tr>
<td>3.16(b) Suppose that 2.5 mmol Ar(g) occupies 72 dm³ at 298 K and expands to 100 dm³. Calculate ΔG for the process.</td>
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<tr>
<td>3E.1(a) Suppose that 2.5 mmol N₂(g) occupies 42 cm³ at 300 K and expands isothermally to 600 cm³. Calculate ΔG for the process.</td>
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<tr>
<td>3E.1(b) Suppose that 6.0 mmol Ar(g) occupies 52 cm³ at 298 K and expands isothermally to 122 cm³. Calculate ΔG for the process.</td>
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**Question 13.03**

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<tbody>
<tr>
<td>Same questions.</td>
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<tr>
<td>3D.2(a) The change in the Gibbs energy of a certain constant–pressure process was found to fit the expression ΔG/J = −85.40 + 36.5(T/K). Calculate the value of ΔS for the process.</td>
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<tr>
<td>3D.2(b) The change in the Gibbs energy of a certain constant–pressure process was found to fit the expression ΔG/J = −73.1 + 42.8(T/K). Calculate the value of ΔS for the process.</td>
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</table>
Question 13.04*

n/a | n/a | 3.18 | 3.18

*Missing from 10th and 11th Eds. No idea why.*

3.18(a) Calculate the change in Gibbs energy of 35 g of ethanol (mass density 0.789 g cm\(^{-3}\)) when the pressure is increased isothermally from 1 atm to 3000 atm.

3.18(b) Calculate the change in Gibbs energy of 25 g of methanol (mass density 0.791 g cm\(^{-3}\)) when the pressure is increased isothermally from 100 kPa to 100 MPa. Take \(\kappa_T = 1.26 \times 10^{-9}\) Pa\(^{-1}\).

Question 13.05*

n/a | n/a | n/a | n/a

*Missing in all editions after 7th Ed.*

(Ex. 5.8a, 7th edition). When 2.00 mol of has at 330 K and 3.50 atm is subject to isothermal compression, its entropy decreases by 25.0 J K\(^{-1}\). Calculate (a) the final pressure of the gas and (b) the \(\Delta G\) for the compression.

(Ex. 5.8b, 7th edition). When 3.00 mol of has at 230 K and 150 kPa is subject to isothermal compression, its entropy decreases by 15.0 J K\(^{-1}\). Calculate (a) the final pressure of the gas and (b) the \(\Delta G\) for the compression.

Question 13.06*

n/a | n/a | 3.19 | 3.19

*Missing from the 10th and 11th Eds. Not sure why. But: See E3E.6 in 11th Ed. for something similar (see Q13.09 below).*

3.19(a) Calculate the change in chemical potential of a perfect gas when its pressure is increased isothermally from 1.8 atm to 29.5 atm at 40\(^\circ\)C.

3.19(b) Calculate the change in chemical potential of a perfect gas that its pressure is increased isothermally from 92.0 kPa to 252.0 kPa at 50\(^\circ\)C.

Question 13.07*

n/a | n/a | 3.2 | 3.2

*Missing from the 10th Ed. Not sure why.*

3.20(a) The fugacity coefficient of a certain gas at 200 K and 50 bar is 0.72. Calculate the difference of its molar Gibbs energy from that of a perfect gas in the same state.

3.20(b) The fugacity coefficient of a certain gas at 290 K and 2.1 MPa is 0.68. Calculate the difference of its molar Gibbs energy from that of a perfect gas in the same state.
Question 13.08

3E.3 | 3D.3 | 3.21 | 3.21

Sort of the same style question. Use of mass density in 10th Ed. is similar to Question 13.04.

3.21(a) Estimate the change in the Gibbs energy of 1.0 dm$^3$ of benzene when the pressure acting on it is increased from 1.0 atm to 100 atm.

3.21(b) Estimate the change in the Gibbs energy of 1.0 dm$^3$ of water when the pressure acting on it is increased from 100 kPa to 300 kPa.

3E.3(a) Estimate the change in the Gibbs energy and molar Gibbs energy of 1.0 dm$^3$ of octane when the pressure acting on it is increased from 1.0 atm to 100 atm. The mass density of octane is 0.703 g cm$^{-3}$.

3E.3(b) Estimate the change in the Gibbs energy and molar Gibbs energy of 100 cm$^3$ of water when the pressure acting on it is increased from 100 kPa to 500 kPa. The mass density of water is 0.997 g cm$^{-3}$.

Question 13.09

3E.6 | 3D.4 | 3.22 | 3.22

Same question in 10th and earlier editions.

3D.4(a) Calculate the change in the molar Gibbs energy of hydrogen gas when its pressure is increased isothermally from 1.0 atm to 100.0 atm at 298 K.

3D.4(b) Calculate the change in the molar Gibbs energy of oxygen when its pressure is increased isothermally from 50.0 kPa to 100.0 kPa at 500 K.

Changed in 11th Ed.

3E.6(a) Calculate the change in the molar Gibbs energy of a perfect gas when its pressure is increased isothermally from 1.0 atm to 100.0 atm at 298 K.

3E.6(b) Calculate the change in the molar Gibbs energy of a perfect gas when its pressure is increased isothermally from 50.0 kPa to 100.0 kPa at 500 K.
Set 2

Question 13.10*

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*Part (a) is missing in all editions after the 7th Ed, in 9th-11th Eds.*

(Ex. 5.14a, 7th edition). The molar Helmholtz energy of a certain gas is given by

\[ A_m = -\frac{a}{V_m} - RT (\ln V_m - b) + f(T) \]

where \( a \) and \( b \) are constants and \( f(T) \) is a function of temperature only. Obtain the equation of state of the gas.

(Ex. 5.14b, 7th edition). The molar Gibbs energy of a certain gas is given by

\[ G_m = RT \ln p + A + Bp + \frac{1}{2} Cp^2 + \frac{1}{3} Dp^3 \]

where \( A, B, C \) and \( D \) are constants. Obtain the equation of state of the gas.

Question 13.11

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9th Ed. and earlier:

P3.23 Evaluate \((\partial S/\partial V)_T\) for (a) a van der Waals gas, (b) a Dieterici gas (see Lecture 4, real gases). For an isothermal expansion, for which kind of gas (and a perfect gas) will \( \Delta S \) be greatest? Explain your conclusion.

Changed in the 10th:

3D.4 Two empirical equations of state of a real gas are as follows:

\[
\text{van der Waals: } p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \\
\text{Dieterici: } p = \frac{RT e^{-a/RTV_m}}{V_m - b}
\]

Evaluate \((\partial S/\partial V)_T\) for each gas. For an isothermal expansion, for which kind of gas (also consider a perfect gas) will \( \Delta S \) be greatest? Explain your conclusion.

And yet again in the 11th (see next page):
Question 13.12*

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*Missed in 8th and 9th Eds.*

(P5.1, 7th edition). Calculate $\Delta_r G^o (375 \text{ K})$ for the reaction $2\text{CO(g)} + \text{O}_2(g) \rightarrow 2\text{CO}_2(g)$ from the Gibbs-Helmholz equation, and the values of $\Delta_r G^o (298 \text{ K})$ and $\Delta_r H^o (298 \text{ K})$.

*11th Ed.:

P3E.1 (a) By integrating the Gibbs–Helmholtz equation between temperature $T_1$ and $T_2$, and with the assumption that $\Delta H$ is independent of temperature, show that

$$\frac{\Delta G(T_2)}{T_2} = \frac{\Delta G(T_1)}{T_1} + \Delta H \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where $\Delta G(T)$ is the change in Gibbs energy at temperature $T$. (b) Using values of the standard Gibbs energies and enthalpies of formation from the Resource section, determine $\Delta_r G^o$ and $\Delta_r H^o$ at 298 K for the reaction $2\text{CO(g)} + \text{O}_2(g) \rightarrow 2\text{CO}_2(g)$. (c) Hence estimate $\Delta_r G^o$ at 375 K.
Question 13.13*

| n/a   | n/a   | P3.24 | P3.24 |

Missing from the 10th ed. Not sure why.

**P3.24** Show that, for a perfect gas, \( (\partial U / \partial S)_V = T \) and \( (\partial U / \partial V)_S = -p \).

Question 13.14*

| n/a   | P3D.5 | P3.25 | P3.25 |

Same questions in 10th and earlier. Missing in 11th. However, this is just what is asked of you in classes for L13, and part of this is covered in tutorial.

**3D.5** Two of the four Maxwell relations were derived in the text, but two were not. Complete their derivation by showing that \( (\partial S / \partial V)_T = (\partial p / \partial T)_V \) and \( (\partial T / \partial p)_S = (\partial V / \partial S)_p \).

Question 13.15*

| n/a   | 3D.6a,b | P3.26, P3.30 | P3.26, P3.30 |

In the 10th Ed, the problems are joined together into one (a and b). Missing from the 11th Ed.

**P3.26** Use the Maxwell relations to express the derivatives (a) \( (\partial S / \partial V)_T \) and \( (\partial V / \partial S)_p \) and (b) \( (\partial p / \partial S)_V \) and \( (\partial V / \partial S)_p \) in terms of the heat capacities, the expansion coefficient \( \alpha \), and the isothermal compressibility, \( \kappa_T \).

**P3.30** The Joule coefficient, \( \mu_J \), is defined as \( \mu_J = (\partial T / \partial V)_U \). Show that \( \mu_J C_V = p - \alpha T / \kappa_T \).

**3D.6** (a) Use the Maxwell relations to express the derivatives \( (\partial S / \partial V)_T \), \( (\partial V / \partial S)_p \), \( (\partial p / \partial S)_V \), and \( (\partial V / \partial S)_p \) in terms of the heat capacities, the expansion coefficient \( \alpha = (1 / V)(\partial V / \partial T)_p \), and the isothermal compressibility, \( \kappa_T = -(1 / V)(\partial V / \partial p)_T \).

(b) The Joule coefficient, \( \mu_J \), is defined as \( = (\partial T / \partial V)_U \). Show that \( \mu_J C_V = p - \alpha T / \kappa_T \).

Question 13.16*

| n/a   | n/a   | P3.27 | P3.27 |

Missing from the 10th ed. Not sure why.

**3.27** Use the Maxwell relations to show that the entropy of a perfect gas depends on the volume as \( S \propto R \ln V \).
Question 13.17*

| n/a | n/a | P3.28 | P3.28 |

Missing from the 10th ed. Not sure why.

**P3.28** Derive the thermodynamic equation of state

\[
\left( \frac{\partial H}{\partial T} \right)_p = V - T \left( \frac{\partial V}{\partial T} \right)_p
\]

Derive an expression for \( (\partial H/\partial p)_T \) for (a) a perfect gas and (b) a van der Waals gas. In the latter case, estimate its value for 1.0 mol Ar(g) at 298 K and 10 atm. By how much does the enthalpy of the argon change when the pressure is increased isothermally to 11 atm?

Question 13.18*

| n/a | P3D.7 | P3.33 | P3.33 |

Same questions, except for addition of highlighted term in 10th Ed, which seems to be a misprint. And of course...missing from the illustrious 11th Ed.

**3D.7** Suppose that \( S \) is regarded as a function of \( p \) and \( T \). Show that \( TdS = C_v dT - \alpha TV dp \). Hence, show that the energy transferred as heat when the pressure on an incompressible liquid or solid is increased by \( \Delta p \) is equal to \( \alpha TV \Delta p \), where \( Q = (1/V)(\partial V/\partial T)_p \). Evaluate \( q \) when the pressure acting on 100 cm\(^3\) of mercury at 0 °C is increased by 1.0 kbar. \((\alpha = 1.82 \times 10^{-4} \text{ K}^{-1})\)

**10th Ed. misprint (online Ed).** Likely, this is suppose to be: \( \alpha = (1/V)(\partial V/\partial T)_p \)

**Note for F2018:**

It seems that the Atkins editing team has removed most question involving partial derivatives and the second-law toolbox - contrary to most of major texts on thermodynamics. Lots more unhelpful discussion questions though!
Answer 13.01*

| n/a | n/a | n/a | n/a |

Missing after 7th Ed. (not sure why).

**M 3.8 (5.4 a, 7th Ed.) - ANSWER**

Express \( \left( \frac{\partial S}{\partial V} \right)_T \) in terms of \( \alpha \) and \( \kappa_T \).

\[
\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial p}{\partial T} \right)_V \quad \text{M.R.}
\]

\[
\left( \frac{\partial p}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_p \left( \frac{\partial V}{\partial p} \right)_T = -1 \quad \text{C.R.}
\]

\[
\left( \frac{\partial p}{\partial T} \right)_V = - \left( \frac{\partial V}{\partial T} \right)_p \quad \kappa_T = - \frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T
\]

\[
\left( \frac{\partial p}{\partial T} \right)_V = \frac{\alpha}{\kappa_T}
\]

**M 3.8b (5.4b, 7th Ed.)**

\( \left( \frac{\partial S}{\partial p} \right)_T \) in terms of \( \alpha \)

\[
\left( \frac{\partial S}{\partial p} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_p = - \frac{V}{V} \left( \frac{\partial V}{\partial T} \right)_p = -V \alpha
\]
Answer 13.04*

Missing from 10th and 11th Eds. No idea why.

**E3.18(a)** \( dG = -SdT + Vdp \) [3.52]; at constant \( T \), \( dG = Vdp \), therefore

\[
\Delta G = \int_{p_i}^{p_f} Vdp
\]

The change in volume of a condensed phase under isothermal compression is given by the isothermal compressibility (eqn 2.43).

This small isothermal compressibility (typical of condensed phases) tells us that we can expect a small change in volume from even a large increase in pressure. So we can make the following approximations to obtain a simple expression for the volume as a function of the pressure

\[
\kappa_T \approx -\frac{1}{V} \left( \frac{V - V_i}{p - p_i} \right) = -\frac{1}{V_i} \left( \frac{V - V_i}{p} \right) \quad \text{so} \quad V = V_i(1 - \kappa_T p),
\]

where \( V_i \) is the volume at 1 atm, namely the sample mass over the density, \( m/\rho \).

\[
\Delta G = m \int_{1 \text{ atm}}^{3000 \text{ atm}} \frac{1}{\rho} (1 - \kappa_T p) dp
\]

\[
= m \left( \int_{1 \text{ atm}}^{3000 \text{ atm}} dp - \kappa_T \int_{1 \text{ atm}}^{3000 \text{ atm}} p dp \right)
\]

\[
= m \left( \rho \left( \frac{3000 \text{ atm}}{1 \text{ atm}} \right) - \frac{1}{2} \kappa_T p^2 \right)_{1 \text{ atm}}^{3000 \text{ atm}}
\]

\[
= \frac{35 \text{ g}}{0.789 \text{ g cm}^{-3}} \left( 2999 \text{ atm} - \frac{1}{2} (76.8 \times 10^{-6} \text{ atm}^{-1}) \times (9.00 \times 10^6 \text{ atm}^2) \right)
\]

\[
= 44.4 \text{ cm}^3 \times \left( \frac{1 \text{ m}}{100 \text{ cm}} \right)^3 \times 2653 \text{ atm} \times (1.013 \times 10^5 \text{ Pa atm}^{-1})
\]

\[
= 1.19 \times 10^4 \text{ J} = 12 \text{ kJ}
\]

**Note:** You will not have to decide whether to integrate or assume that the volume is constant in an exam situation. This will be made very clear.
E3.18(b) \[ dG = -SdT + VdP \text{ [3.52]} \]; at constant \( T \), \( dG = VdP \), therefore

\[ \Delta G = \int_{P_i}^{P_f} VdP \]

The change in volume of a condensed phase under isothermal compression is given by the isothermal compressibility (eqn 2.43):

\[ \kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = 1.26 \times 10^{-9} \text{ Pa}^{-1} \]

This small isothermal compressibility (typical of condensed phases) tells us that we can expect a small change in volume from even a large increase in pressure. So we can make the following approximations to obtain a simple expression for the volume as a function of the pressure:

\[ \kappa_T = -\frac{1}{V} \left( \frac{V - V_i}{P - P_i} \right) \approx -\frac{1}{V_i} \left( \frac{V - V_i}{P} \right) \]

so \( V = V_i (1 - \kappa_T P) \)

where \( V_i \) is the volume at 1 atm, namely the sample mass over the density, \( m/\rho \):

\[ \Delta G = \int_{100 \text{ kPa}}^{100 \text{ MPa}} \frac{m}{\rho} (1 - \kappa_T P) dP \]

\[ = \frac{m}{\rho} \left[ \int_{100 \text{ kPa}}^{100 \text{ MPa}} dP - \kappa_T \int_{100 \text{ kPa}}^{100 \text{ MPa}} PdP \right] \]

\[ = \frac{m}{\rho} \left[ \frac{1}{2} \left( \frac{100 \text{ MPa}}{100 \text{ kPa}} \right) - \kappa_T \left( \frac{100 \text{ MPa}}{100 \text{ kPa}} \right)^2 \right] \]

\[ = \frac{25 \text{ g}}{0.791 \text{ g cm}^{-3}} \left( 9.99 \times 10^7 \text{ Pa} - \frac{1}{2} (1.26 \times 10^{-9} \text{ Pa}^{-1}) \times (1.00 \times 10^{16} \text{ Pa}^2) \right) \]

\[ = 31.6 \text{ cm}^3 \times \left( \frac{1 \text{ m}}{100 \text{ cm}} \right)^3 \times 9.36 \times 10^7 \text{ Pa} \]

\[ = 2.96 \times 10^3 \text{ J} \]
Answer 13.05*

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Missing in all editions after 7th Ed.

\[ M_3.9 (E5.8a, 3K) \]

\[ n = 2.00 \text{ mole, } T = 330 \text{ K, } p = 3.50 \text{ atm} \]

\[ \Delta S = -25.0 \text{ JK}^{-1} \]

(a) **ideal process**

\[ \Delta S = nR \ln \left( \frac{p_f}{p_i} \right) = nR \ln \left( \frac{p_f}{p_i} \right) \]

\[ \frac{p_i}{p_f} = e^{\frac{\Delta S}{nR}} \quad \therefore \quad p_f = p_i e^{-\frac{\Delta S}{nR}} \]

\[ p_f = 3.50 \text{ atm} \exp \left( -\frac{-25.0 \text{ JK}^{-1}}{2.00 \text{ mol}/8.314 \text{ JK}^{-1} \text{ mol}^{-1}} \right) \]

\[ p_f = 15.2 \text{ atm} \]

(b) **\( \Delta G \)**

\[ \Delta G = nRT \ln \left( \frac{p_f}{p_i} \right) = -T \Delta S \]

(\( \Delta H = 0 \), const. \( T \), p.g.)

\[ \Delta G = (-330 \text{ K})(-25.0 \text{ JK}^{-1}) = 8250 \text{ J} = 8.25 \text{ kJ} \]
Answer 13.06*

| n/a  | n/a  | 3.19 | 3.19 |

*Missing from the 10th Ed. Not sure why.*

\[ \Delta G_m = G_{m,f} - G_{m,i} = RT \ln \left( \frac{p_f}{p_i} \right) \]

\[ = +7.3 \text{ kJ mol}^{-1} \]

\[ \Delta G_m = G_{m,f} - G_{m,i} = RT \ln \left( \frac{p_f}{p_i} \right) \]

\[ = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (313 \text{ K}) \times \ln \left( \frac{252.0}{92.0} \right) \approx 2.71 \text{ kJ mol}^{-1} \]

Answer 13.07*

| n/a  | n/a  | 3.2  | 3.2  |

*Missing from the 10th Ed and later. Not sure why.*

\[ \Delta G_m = G_{m,f} - G_{m,i} = RT \ln \left( \frac{p_f}{p_i} \right) \]

\[ \text{But for a real gas, } \Delta G_m = G_{m,f}^o + RT \ln f \left( \frac{p_f}{p_i} \right) \]

\[ = RT \ln \phi = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (200 \text{ K}) \times (0.72) = -0.55 \text{ kJ mol}^{-1} \]

\[ \Delta G_m = G_{m,f}^o + RT \ln f \left( \frac{p_f}{p_i} \right) \]

\[ \text{But for a real gas, } \Delta G_m = G_{m,f}^o + RT \ln f \left( \frac{p_f}{p_i} \right) \]

\[ = RT \ln \phi = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (200 \text{ K}) \times (0.68) \approx -0.93 \text{ kJ mol}^{-1} \]
**Answer 13.10a**

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Part (a) is missing in all edition after the 7th Ed in 9th and 10 Eds.

**E5.14(a)** An equation of state is a functional relationship between the state properties, $p$, $V_m$, and $T$. From the definition

$$A = U - TS \quad \Rightarrow \quad \frac{\partial A}{\partial V_m} = \frac{1}{V_m} - \frac{a}{V_m^2}$$

Using [5.2] in eqn 4.31a, $dA = -SdT - p dV_m$; hence

$$p = -\left(\frac{\partial A}{\partial V_m}\right)_T = -\frac{a}{V_m^2} + RT \times \left(\frac{1}{V_m - b}\right) = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

which is the van der Waals equation.

**E5.14(b)**

$$V = \left(\frac{\partial G}{\partial p}\right)_T [5.10] = \frac{RT}{p} + B' + C'p + D'p^2$$

which is the virial equation of state.
### Answer 13.12*

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*Missing in all editions after 7th Ed.*

#### P5.1

The Gibbs–Helmholtz equation [5.11] may be recast into an analogous equation involving $\Delta G$ and $\Delta H$, since

$$
\left( \frac{\partial \Delta G}{\partial T} \right)_p = \left( \frac{\partial G_f}{\partial T} \right)_p - \left( \frac{\partial G_i}{\partial T} \right)_p
$$

and $\Delta H = H_f - H_i$

Thus, $$
\left( \frac{\partial}{\partial T} \frac{\Delta r G^\Theta}{T} \right)_p = - \frac{\Delta r H^\Theta}{T^2}
$$

$$
d \left( \frac{\Delta r G^\Theta}{T} \right) = \left( \frac{\partial}{\partial T} \frac{\Delta r G^\Theta}{T} \right)_p dT \text{[constant pressure]} = - \frac{\Delta r H^\Theta}{T^2} dT
$$

$$
\Delta \left( \frac{\Delta r G^\Theta}{T} \right) = - \int_{T_c}^{T} \frac{\Delta r H^\Theta}{T^2} dT
$$

$$
\approx - \Delta r H^\Theta \int_{T_c}^{T} \frac{dT}{T^2} = \Delta r H^\Theta \left( \frac{1}{T} - \frac{1}{T_c} \right) \quad [\Delta r H^\Theta \text{ assumed constant}]
$$

Therefore, $$
\frac{\Delta r G^\Theta(T)}{T} - \frac{\Delta r G^\Theta(T_c)}{T_c} \approx \Delta r H^\Theta \left( \frac{1}{T} - \frac{1}{T_c} \right)
$$

and so

$$
\Delta r G^\Theta(T) = \frac{T}{T_c} \Delta r G^\Theta(T_c) + \left(1 - \frac{T}{T_c}\right) \Delta r H^\Theta(T_c)
$$

$$
= \tau \Delta r G^\Theta(T_c) + (1 - \tau) \Delta r H^\Theta(T_c) \quad \tau = \frac{T}{T_c}
$$

For the reaction

$$
2\text{CO}(g) + \text{O}_2(g) \rightarrow 2\text{CO}_2(g)
$$

$$
\Delta r G^\Theta(T_c) = 2\Delta r G^\Theta(\text{CO}_2, g) - 2\Delta r G^\Theta(\text{CO}, g)
$$

$$
= [2 \times (-394.36) - 2 \times (-137.17)] \text{kJ mol}^{-1} = -514.38 \text{kJ mol}^{-1}
$$

$$
\Delta r H^\Theta(T_c) = 2\Delta r H^\Theta(\text{CO}_2, g) - 2\Delta r H^\Theta(\text{CO}, g)
$$

$$
= [2 \times (-393.51) - 2 \times (-110.53)] \text{kJ mol}^{-1} = -565.96 \text{kJ mol}^{-1}
$$

Therefore, since $\tau = \frac{375}{298.15} = 1.258$

$$
\Delta r G^\Theta(375 \text{K}) = \{(1.258) \times (-514.38) + (1 - 1.258) \times (-565.96)\} \text{kJ mol}^{-1}
$$

$$
= \boxed{-501 \text{kJ mol}^{-1}}
$$
Answer 13.13*

Missing from the 10th ed and later. Not sure why.

\[ P3.24 \quad (dU)_s, \quad P5.5 \quad (dH)_s \]

\[ (\frac{\partial U}{\partial S})_V = T; \quad (\frac{\partial U}{\partial V})_S = -p \]

Since \( dq + dw = TdS - pdV \)

And

\[ dU = (\frac{\partial U}{\partial S})_V dS + (\frac{\partial U}{\partial V})_S dV \]

Then

\[ (\frac{\partial U}{\partial S})_V = T \quad \text{and} \quad (\frac{\partial U}{\partial V})_S = -p \]

\[ \alpha : \quad dU = C_v dT; \quad dS = \frac{dq - pdV}{T} = \frac{C_v dT}{T} \quad \text{const.} \]

\[ (\frac{\partial Y}{\partial S})_V = \frac{C_v dT}{C_v dT} = T \]

And

\[ dw = -pdV; \quad (\frac{\partial U}{\partial V})_S = -p \]
Answer 13.15*

In the 10th Ed, the problems are joined together into one (a and b). Missing from the 11th Ed.

\[
\alpha = \left( \frac{1}{V} \right) \times \left( \frac{\partial V}{\partial T} \right)_p \quad [2.42]; \quad \kappa_T = -\left( \frac{1}{V} \right) \times \left( \frac{\partial V}{\partial p} \right)_T \quad [2.43]
\]

(a) \[
\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial p}{\partial T} \right)_V \quad \text{[Maxwell relationship]}
\]

\[
\left( \frac{\partial p}{\partial T} \right)_V = -\left( \frac{\partial V}{\partial T} \right)_p \quad \left( \frac{\partial p}{\partial V} \right)_T \quad \text{[Euler chain relation MB2.3c]}
\]

\[
= -\left( \frac{\partial V}{\partial T} \right)_p \quad \text{[reciprocal identity, MB2.3b]}
\]

\[
= -\left( \frac{1}{V} \right) \left( \frac{\partial V}{\partial T} \right)_p = \frac{\alpha}{\kappa_T}
\]

\[
\left( \frac{\partial V}{\partial S} \right)_p = \left( \frac{\partial T}{\partial p} \right)_S \quad \text{[Maxwell relationship]}
\]

\[
\left( \frac{\partial T}{\partial S} \right)_p = -\left( \frac{\partial V}{\partial T} \right)_p \quad \text{[Euler chain]} = -\left( \frac{\partial S}{\partial T} \right)_p \quad \text{[reciprocal]}
\]

First, treat the numerator:

\[
\left( \frac{\partial S}{\partial p} \right)_T = -\left( \frac{\partial V}{\partial T} \right)_p \quad \text{[Maxwell relation]} = -\alpha V
\]

As for the denominator, at constant \( p \)

\[
dS = \left( \frac{\partial S}{\partial T} \right)_p \ dT \quad \text{and} \quad dS = \frac{dq_{rev}}{T} = \frac{dH}{T} = \frac{C_p dT}{T} \quad [dq_{rev} = dH]
\]

Therefore, \( \left( \frac{\partial S}{\partial T} \right)_p = \frac{C_p}{T} \) and \( \left( \frac{\partial V}{\partial S} \right)_p = \frac{\alpha T V}{C_p} \)
(b) \( \frac{\partial p}{\partial S} \) \bigg|_p = -\frac{\partial T}{\partial V} \bigg|_T [Maxwell relationship]

\[-\left( \frac{\partial T}{\partial V} \right)_S = \frac{1}{\frac{\partial S}{\partial T} \frac{\partial V}{\partial S} _T} \] [Euler chain] = \frac{\frac{\partial S}{\partial T}}{\frac{\partial V}{\partial T}} \bigg|_T [reciprocal]

\[= \frac{\frac{\partial p}{\partial T} _V}{\frac{\partial S}{\partial U} \frac{\partial U}{\partial T} _V} \bigg|_T [Maxwell relation] = -\frac{\frac{\partial p}{\partial V} _T}{\frac{\partial S}{\partial T} \frac{\partial U}{\partial T} _V} \bigg|_T [Euler chain]

\[-\left( \frac{\partial V}{\partial T} \right)_S \left( \frac{\partial U}{\partial T} \right)_V \bigg|_T \text{ [reciprocal identity, twice]} = \frac{\alpha T}{\kappa_T} \left[ \frac{\partial U}{\partial S} \right]_V = T \]

P3.30

\[\mu_f = \left( \frac{\partial T}{\partial V} \right)_U \quad C_V = \left( \frac{\partial U}{\partial T} \right)_V\]

\[\mu_f C_V = \left( \frac{\partial T}{\partial V} \right)_U \left( \frac{\partial U}{\partial T} \right)_V = -\frac{1}{\left( \frac{\partial T}{\partial V} \right)_T} \bigg|_V \text{ [Euler chain relation]}

\[= -\left( \frac{\partial U}{\partial V} \right)_T \text{ [reciprocal identity]} = p - T \left( \frac{\partial p}{\partial T} \right)_T \bigg|_V \text{ [3.51]}

\[\left( \frac{\partial p}{\partial T} \right)_V = -\frac{1}{\left( \frac{\partial T}{\partial V} \right)_p \left( \frac{\partial p}{\partial V} \right)_T} \bigg|_p \text{ [Euler chain]} = \frac{\left( \frac{\partial V}{\partial T} \right)_p}{\left( \frac{\partial V}{\partial p} \right)_T} = \frac{\alpha}{\kappa_T}\]

Therefore, \[\mu_f C_V = p - \frac{\alpha T}{\kappa_T}\]
Answer 13.16*

| n/a | P3.27 | P3.27 |

*Missing from the 10th ed. Not sure why.*

\[ \left( \frac{\partial S}{\partial V} \right) _T = \left( \frac{\partial p}{\partial T} \right) _V \text{ [Maxwell relation]; } \left( \frac{\partial p}{\partial T} \right) _V = \left\{ \frac{\partial}{\partial T} \left( \frac{nRT}{V} \right) \right\} _V = \frac{nR}{V}. \]

\[ dS = \left( \frac{\partial S}{\partial V} \right) _T dV \text{ [constant temperature] } = nR \frac{dV}{V} = nR d\ln V. \]

\[ S = \int dS = \int nR d\ln V. \]

\[ S = nR \ln V + \text{constant} \quad \text{or} \quad S \propto R \ln V. \]

---

Answer 13.17*

| n/a | P3.28 | P3.28 |

*Missing from the 10th ed. Not sure why.*

\[ P.3.28 \text{ (PS.10)} \]

\[ \max : \left( \frac{\partial H}{\partial p} \right) _T = V - T \left( \frac{\partial V}{\partial T} \right) _p \]

\[ dH = dU + pdV + Vdp = Tds - nRTd\mu + n\mu dV + Vdp = Tds + Vdp \]

\[ dH = \left( \frac{\partial H}{\partial S} \right) _p ds + \left( \frac{\partial H}{\partial V} \right) _p dv ; \quad \left( \frac{\partial H}{\partial S} \right) _p = T \quad \text{and} \quad \left( \frac{\partial H}{\partial p} \right) _S = V \]

\[ \left( \frac{\partial H}{\partial p} \right)_T = \left( \frac{\partial H}{\partial S} \right) _p \left( \frac{ds}{dV} \right)_T + V \left( \frac{dv}{dV} \right)_T \quad \text{since} \quad \left( \frac{\partial S}{\partial p} \right)_T = -\left( \frac{\partial V}{\partial T} \right)_p \]

\[ = \left[ -T \left( \frac{\partial V}{\partial T} \right)_p + V \right] \]

\[ a) \quad \text{for } p, \mu \quad V = nRT/p \]

\[ \left( \frac{\partial H}{\partial p} \right)_T = -T \left( \frac{\partial (nRT/p)}{\partial T} \right)_p + V = -\frac{nRT}{p} + V = 0 \]

\[ b) \quad \text{ignore - algebra too long.} \]
**Answer 13.18*\**

<table>
<thead>
<tr>
<th>n/a</th>
<th>P3D.7</th>
<th>P3.33</th>
<th>P3.33</th>
</tr>
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</table>

Same questions, except for addition of highlighted term in 10th Ed, which seems to be a misprint. And of course…missing from the illustrious 11th Ed.

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**P3D.7**

If $S=S(T,p)$

then

$$dS = \frac{\partial S}{\partial T} dT + \frac{\partial S}{\partial p} dp$$

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_p dT + T\left(\frac{\partial S}{\partial p}\right)_T dp$$

Use

$$\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p = \frac{1}{T} C_p \left[\left(\frac{\partial H}{\partial S}\right)_T = T\right]$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$ [Maxwell relation]

Hence,

$$TdS = C_P dT - \left(\frac{\partial V}{\partial T}\right)_p dp = C_P dT - \alpha TV dp$$

For reversible, isothermal compression, $T dS = dq_{rev}$ and $dT = 0$; hence

$$dq_{rev} = -\alpha TV dp$$

$$q_{rev} = \int_{P_i}^{P_f} -\alpha TV dp = -\alpha TV \Delta P$$ \[\alpha \text{ and } V \text{ assumed constant}\]

---

For mercury

$$q_{rev} = \left(-1.82 \times 10^{-4} \text{ K}^{-1}\right) \times (273 \text{ K}) \times (1.00 \times 10^{-4} \text{ m}^3) \times (1.0 \times 10^8 \text{ Pa}) = -0.50 \text{ kJ}$$