

Problem 5

10.213

a) NIST Database

Use your browser to point to <http://webbook.nist.gov/chemistry/fluid>. Select methane as the species of interest. Choose Celsius, bar, and m³/mol for the units and select isothermal properties. Continue to the next page in which you enter 27°C as the required temperature. Since we only need information for two points, we choose

$$\begin{aligned}P_{\text{low}} &= 1 \\P_{\text{high}} &= 200 \\P_{\text{inc}} &= 199\end{aligned}$$

Continue to the next page in which you will find a plot indicating that the first point is in the vapor range and the last point (200 bar) is in the supercritical range. Click the “view table” button to get the required results:

$$\begin{aligned}\text{At 1 bar, } V &= 0.024914 \text{ m}^3/\text{mol} \\ \text{At 200 bar, } V &= 0.00010341 \text{ m}^3/\text{mol}\end{aligned}$$

To calculate the volume of the tank, we need to calculate the number of moles using the information given at 1 bar.

$$n = \frac{V^t}{V} = \frac{40 \text{ m}^3}{0.024914 \text{ m}^3/\text{mol}} = 1605.5 \text{ mol}$$

The required tank volume

$$V^t = 1605.5 * .00010341 = 0.166 \text{ m}^3$$

b) The ideal gas law

Using n from part a, we apply the ideal gas law at 200 bar

$$V_{\text{ig}}^t = \frac{n R T}{P} = \frac{1605.5 \text{ mol} * 83.14 \text{ cm}^3 \text{ bar} / (\text{mol K}) * 300 \text{ K}}{200 \text{ bar}} \left(\frac{\text{m}}{100 \text{ cm}} \right)^3 = 0.200 \text{ m}^3$$

c) Lee/Kesler generalized correlation

Critical properties of Methane from S+VN Appendix B

$$\begin{aligned}T_c &= 190.6 \text{ K} \\P_c &= 45.99 \text{ bar} \\ \omega &= 0.012\end{aligned}$$

Calculate the reduced variables:

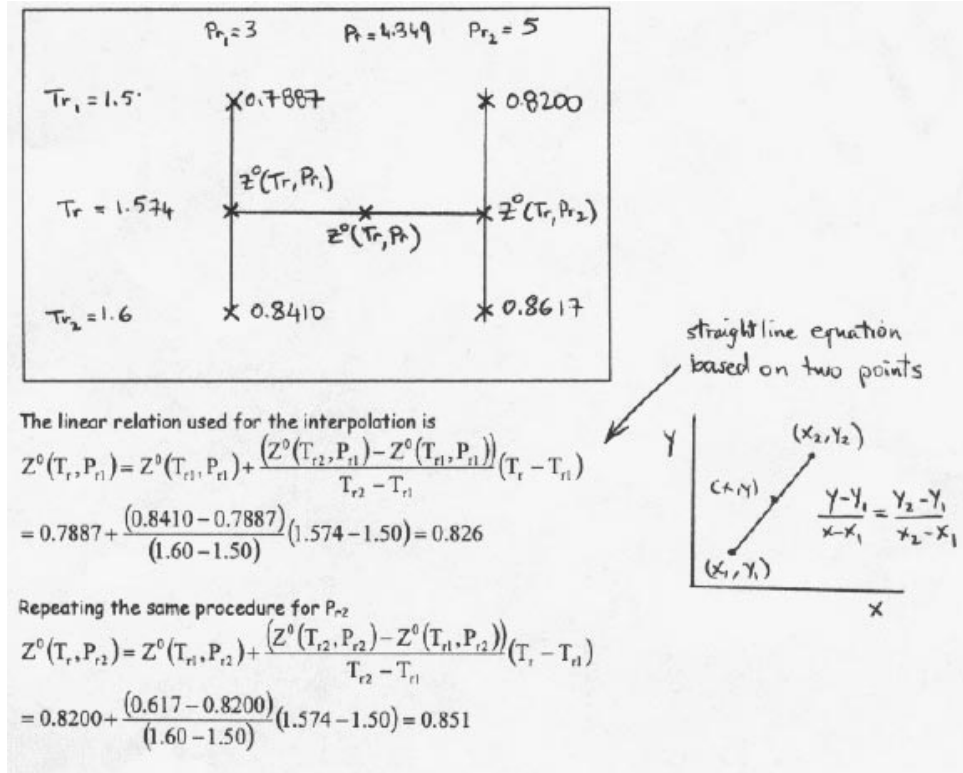
$$T_r = \frac{300 \text{ K}}{190.6 \text{ K}} = 1.574$$

$$P_r = \frac{200 \text{ bar}}{45.99 \text{ bar}} = 4.349$$

We use Lee/Kesler tables in Appendix E to get Z^0 and Z^1 for the equation

$$Z = Z^0 + \omega Z^1$$

There are no columns in the table for P_r of 4.35 nor there are any rows for T_r of 1.57. So we need to interpolate between the values given in the table. We can estimate a value based on our intuition without doing any calculations (e.g. 0.83) but it is better to linearly interpolate between the given values to get Z^0 at the needed T_r and P_r . To do this we will interpolate as illustrated in the diagram.



Interpolating between the two values of pressure

$$Z^0(T_r, P_r) = Z^0(T_r, P_{r1}) + \frac{(Z^0(T_r, P_{r2}) - Z^0(T_r, P_{r1}))}{P_{r2} - P_{r1}} (P_r - P_{r1})$$

$$= 0.826 + \frac{(0.851 - 0.826)}{(5.0 - 3.0)} (4.349 - 3.0) = 0.843$$

We can do the same to get $Z^1(T_r, P_r)$ of 0.250 (left as an exercise)

$$Z(T_r, P_r) = 0.843 + 0.012 * 0.250 = 0.846$$

We now can calculate the volume

$$V_{LK}^t = Z V_{ig}^t = 0.846 * 0.200 \text{ m}^3 = 0.169 \text{ m}^3$$

d) Van der Waals EOS

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

The constants a and b can be estimated from the critical constants of methane

$$a = \frac{27 R^2 T_c^2}{64 P_c} = \frac{27 * (83.14 \text{ cm}^3 \text{ bar} / (\text{mol K}))^2 * 190.6^2 \text{ K}}{64 * 45.99 \text{ bar}} \left(\frac{\text{m}}{100 \text{ cm}} \right)^6 = 2.3035 * 10^{-6} \left(\frac{\text{m}^3}{\text{mol}} \right)^2 \text{ bar}$$

$$b = \frac{R T_c}{8 P_c} = \frac{83.14 \text{ cm}^3 \text{ bar} / (\text{mol K}) 190.6 \text{ K}}{8 * 45.99 \text{ bar}} \left(\frac{\text{m}}{100 \text{ cm}} \right)^3 = 4.307 * 10^{-5} \frac{\text{m}^3}{\text{mol}}$$

Multiplying Van der Waals equation through by (V-b)/P to give

$$V-b = \frac{RT}{P} - \frac{a(V-b)}{V^2 P}$$

For iteration, we write

$$V_{i+1} = b + \frac{RT}{P} - \frac{a(V_i - b)}{V_i^2 P}$$

Using Excel spreadsheet to iterate for V (see the section on how to use formulas in Excel), we get

a	b	R	T	P
2.30E-06	0.00004307	0.00008314	300	200
iteration	Vi	Vi+1		
0	1.0000E-04	1.0221E-04		
1	1.0221E-04	1.0258E-04		
2	1.0258E-04	1.0264E-04		
3	1.0264E-04	1.0265E-04		
4	1.0265E-04	1.0266E-04		
5	1.0266E-04	1.0266E-04		

The tank volume is

$$V_{vdw}^t = 1605.5 \text{ mol} * 1.0266 * 10^{-4} \text{ m}^3 / \text{mol} = 0.1648 \text{ m}^3$$

e) The Redlich-Kwong EOS

Calculate a and b using equations (3.40) and (3.41) and iterate using equation (3.37) in an Excel spreadsheet as follows

Tc	Pc	a	b	R	T	P
190.6	45.99	3.2224E-05	2.99E-05	8.31E-05	300	200
iteration	Vi	Vi+1				
0	1.0000E-04	1.0431E-04				
1	1.0431E-04	1.0507E-04				
2	1.0507E-04	1.0521E-04				
3	1.0521E-04	1.0523E-04				
4	1.0523E-04	1.0524E-04				
5	1.0524E-04	1.0524E-04				

The tank volume is

$$V_{RK}^t = 1605.5 \text{ mol} * 1.0524 * 10^{-4} \text{ m}^3 / \text{mol} = 0.1690 \text{ m}^3$$

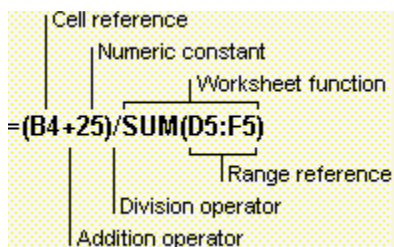
f)

Method	Ease of Use	Accuracy	V	% error (compared to a)
NIST	Very easy to use Limited to small number of compounds	Best accuracy because it is a compilation of experimental data	0.166	0
Ideal Gas Law	Very easy	Bad	0.2	20
Lee/Kesler	Easy if points are found, otherwise requires interpolation	Good	0.169	1.8
VdW	Tedious as it requires iteration for V	Good	0.1648	0.7
RK	Tedious as it requires iteration for V	Good	0.169	1.8

Excel help on how to use formulas

How formulas calculate values

A formula is an equation that analyzes data on a worksheet. Formulas perform operations such as addition, multiplication, and comparison on worksheet values; they can also combine values. Formulas can refer to other cells on the same worksheet, cells on other sheets in the same workbook, or cells on sheets in other workbooks. The following example adds the value of cell B4 and 25 and then divides the result by the sum of cells D5, E5, and F5.



About formula syntax

Formulas calculate values in a specific order that is known as the syntax. The syntax of the formula describes the process of the calculation. A formula in Microsoft Excel begins with an equal sign (=), followed by what the formula calculates. For example, the following formula subtracts 1 from 5. The result of the formula is then displayed in the cell.

`=5-1`

About cell references

A formula can refer to a cell. If you want one cell to contain the same value as another cell, enter an equal sign followed by the reference to the cell. The cell that contains the formula is known as a dependent cell; its value depends upon the value in another cell. Whenever the cell that the formula refers to changes, the cell that contains the formula also changes. The following formula multiplies the value in cell B15 by 5. The formula will recalculate whenever the value in cell B15 changes.

`=B15*5`

Formulas can refer to cells or ranges of cells, or to names or labels that represent cells or ranges.

About worksheet functions

Microsoft Excel contains many predefined, or built-in, formulas known as functions. Functions can be used to perform simple or complex calculations. The most common function in worksheets is the SUM function, which is used to add ranges of cells. Although you can create a formula to calculate the total value of a few cells that contain values, the SUM worksheet function calculates several ranges of cells.

The difference between relative and absolute references

When you create a formula, references to cells or ranges are usually based upon their position relative to the cell that contains the formula. In the following example, cell B6 contains the formula =A5; Microsoft Excel finds the value one cell above and one cell to the left of B6. This is known as a relative referencing.

	A	B
5	100	
6	200	=A5
7		

When you copy a formula that uses relative references, the references in the pasted formula update and refer to different cells relative to the position of the formula. In the following example, the formula in cell B6 has been copied to cell B7. The formula in cell B7 has changed to =A6, which refers to the cell that is one cell above and to the left of cell B7.

	A	B
5	100	
6	200	=A5
7		=A6

If you don't want references to change when you copy a formula to a different cell, use an absolute reference. For example, if your formula multiplies cell A5 with cell C1 (=A5*C1) and you copy the formula to another cell, both references will change. You can create an absolute reference to cell C1 by placing a dollar sign (\$) before the parts of the reference that do not change. To create an absolute reference to cell C1, for example, add dollar signs to the formula as follows:

=A5*\$C\$1