

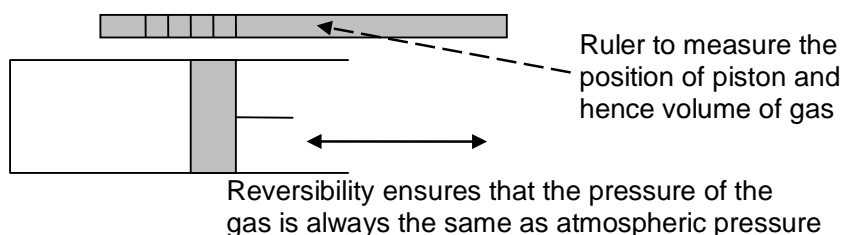
Tutorial Sheet: PVT Relationships

1. The coefficient of isothermal compressibility (β) is defined as:

$$\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T,m}$$

For water at 50°C and 1 bar, the coefficient of isothermal compressibility (β) is $44 \times 10^{-6} \text{ bar}^{-1}$. To what pressure must the water be compressed to increase the density by 1%? You may assume that β is independent of pressure.

2. One way of measuring temperature is to place a certain amount of an ideal gas in a perfectly sealed frictionless piston–cylinder arrangement, where the pressure of the gas remains **constant**. In this case, as the temperature is increased, the volume increases.



- (a) Calculate the value of the thermal expansivity for the gas, which is defined by

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{P,m}$$

at a temperature of 25°C and compare this with typical values for a liquid such as water.

- (b) Why is this value so much greater than the corresponding value for water?

3. Consider a constant-volume process. For this to occur it is necessary to change both the pressure **and** the temperature. This variation is quantified by the **thermal-pressure**

coefficient, defined by $\left(\frac{\partial P}{\partial T} \right)_{V,m}$.

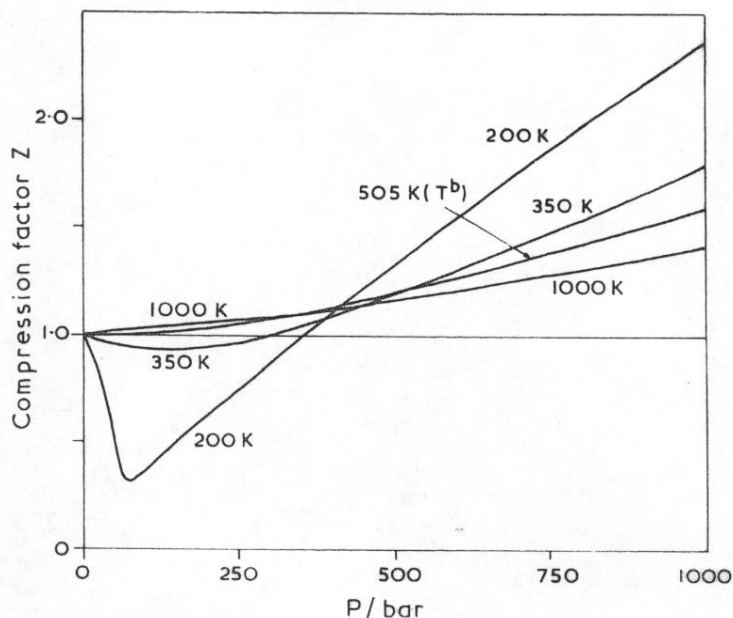
- (a) Show that the thermal-pressure coefficient can be written in terms of the thermal expansion coefficient (α) and the isothermal compressibility coefficient (β). You should start from the general expression for volume changes (i.e., the total volume differential):

$$dV = \left(\frac{\partial V}{\partial P} \right)_{T,m} dP + \left(\frac{\partial V}{\partial T} \right)_{P,m} dT$$

- (b) For acetone at 20°C and 1 bar, the values of α and β are $1.5 \times 10^{-3} \text{ K}^{-1}$ and $62 \times 10^{-6} \text{ bar}^{-1}$ respectively. Calculate the value of the coefficient at these conditions.

- (c) Calculate the pressure generated when acetone is heated at constant volume from 20°C and 1 bar to 30°C.

4. The picture below shows the variation of the compressibility factor (Z) of methane against pressure (P) with temperature (T) as a parameter.



- (a) Estimate the value of Z for methane at 250 bar and 350 K, and use this to obtain the volume occupied by 120 kg of methane at 250 bar and 350 K.
- (b) Using the same graph, estimate the pressure which would be developed by storing 120 kg of methane in a vessel of 0.5 m^3 at a temperature of 350 K. This form of question is slightly more difficult to solve than (a) because here, we start with *two* unknowns: pressure (P) and the compressibility (Z).

Hint: Starting with the non-ideal equation-of-state

$$PV = nZRT$$

*You should be able to develop a **straight-line equation** which can be plotted on the picture.*

CP203 -Thermodynamics Tutorial Solutions Week 1

Group 17

1.

$$\begin{aligned}\beta &= -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T,m} \\ \Delta V &= \beta \Delta P + \alpha \Delta T \xrightarrow{0} \\ \Delta V &= \beta \Delta P \\ \left(\frac{m}{V_2} \right) - \left(\frac{m}{V_1} \right) &= \beta \Delta P \\ 1.01 - 1 &= \beta \Delta P \\ \Delta P &= \frac{0.01}{44 \times 10^{-6}} = 227.27 \text{ Bar}\end{aligned}$$

This method uses the approximation, $\log(1+x) \approx x$, when $x \ll 1$ to simplify the relationship. This is a valid approximation as we are told in the question that we must find the pressure change that corresponds to only a 1% increase in density.

The ΔT term can be cancelled to zero as we are told that the system is isothermal meaning the difference in temperature between states is zero.

We also assume that the system is closed, meaning that there is no transfer of material across the boundary meaning that mass is constant.

2. a)

$$\begin{aligned}PV &= nRT \\ V &= \frac{nRT}{P} \\ \left(\frac{\partial V}{\partial T} \right) &= \frac{nR}{P} \\ \alpha &= \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{P,m} \\ \alpha &= \frac{1}{V} \frac{nR}{P} \\ \alpha &= \frac{P}{nRT} \frac{nR}{P} \\ \alpha &= \frac{\cancel{P}}{\cancel{nRT}} \frac{\cancel{nR}}{\cancel{P}} = \frac{1}{T} \\ \alpha &= 3.35 \times 10^{-3} \text{ K}^{-1}\end{aligned}$$

b) The coefficient of thermal expansion for a gas is larger than for a liquid because the particles in a gas are farther apart and have more room to move, allowing them to expand more when heated. In contrast, the particles in a liquid are closer together and have less room to move, so they expand less when heated. Additionally, since gases are typically less dense than liquids, they tend to expand more upon heating.

3. a)

$$\begin{aligned}dV &= \left(\frac{\partial V}{\partial P}\right)_{T,m} dP + \left(\frac{\partial V}{\partial T}\right)_{P,m} dT \\dV &= 0 \text{ for constant volume} \\0 &= \left(\frac{\partial V}{\partial P}\right)_{T,m} dP + \left(\frac{\partial V}{\partial T}\right)_{P,m} dT \\0 &= \alpha V dT + (-\beta V dP) \\\alpha V dT &= \beta V dP \\\frac{dP}{dT} &= \frac{\alpha}{\beta}\end{aligned}$$

b)

$$\frac{\alpha}{\beta} = \frac{1.5 \times 10^{-3}}{6.2 \times 10^{-5}} = 24.2 \text{ K}^{-1} \text{Bar}^{-1}$$

c)

$$dP = \frac{\alpha}{\beta} dT = 24.2 \cdot 10 = 242 \text{ Bar}$$

4. a)

$$\begin{aligned}n &= \frac{m}{MW} = \frac{120 \times 10^3}{16} = 7500 \text{ moles} \\V &= \frac{nRTZ}{P} \\Z &\approx 0.9 \text{ from graph} \\V &\approx \frac{7500 \cdot 8.3145 \cdot 350 \cdot 0.9}{250 \times 10^5} \\V &\approx 0.786 \text{ m}^3\end{aligned}$$

b) We can turn $PV = nRTZ$ into a linear equation by rearranging for Z:

$$Z = \frac{PV}{nRT}$$

Then if we plot Z on the y -axis, and P on the x -axis, we get an equation for a line with a slope of $\frac{V}{nRT}$ and an intercept of zero.

$$Z = \frac{V}{nRT} P + 0$$

Since the only two unknown values are Z and P , we can plug in the values to find the gradient, giving:

$$Z = 2.3 \times 10^{-8} P + 0$$

We know that at $P = 0$, $Z = 0$, so when $Z = 2$,

$$P = \frac{2}{2.3 \times 10^{-8}} = 86,956,521.74 \text{ Pa} = 869.57 \text{ Bar}$$

Plotting this we see that the pressure is ≈ 531 Bar, at the intersection with the 350 K line:

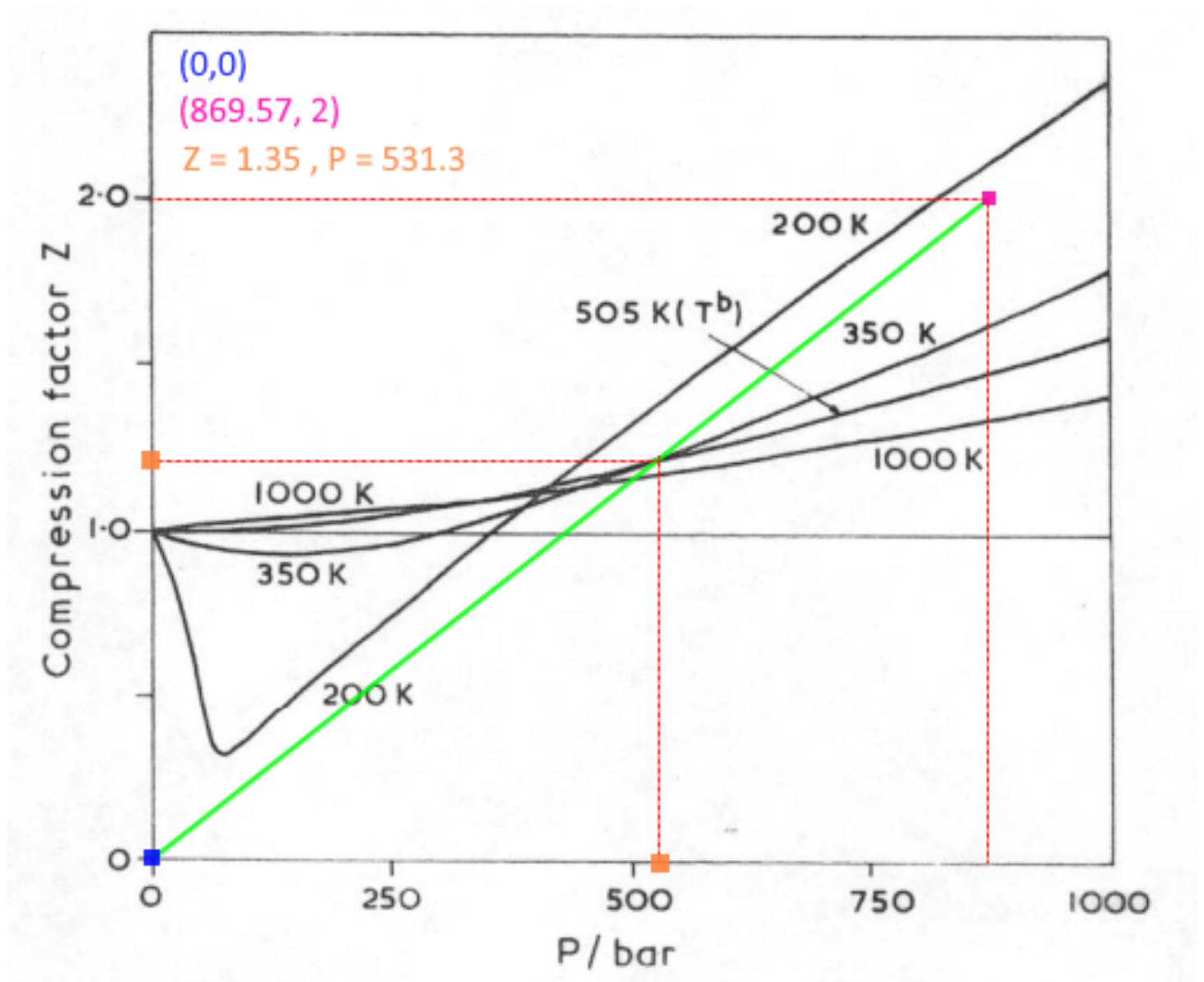


Figure 1: Graph With Estimated Values