

**10.40 Thermodynamics****Fall 2003****Problem Set 5**

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**Problem #1**

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Let's compare the pressure-temperature behavior of two important expansion processes that are used for refrigeration and cooling applications:

- (i) expansion across a Joule-Thompson valve
- (ii) expansion in an adiabatic turbine

To carryout this comparison it is helpful to construct an equation to express the ratio of how temperature varies with pressure for each process. Defining this ratio as follows:

$$\alpha \equiv \frac{(\partial T / \partial P)_{process (i)}}{(\partial T / \partial P)_{process (ii)}}$$

We will also need to specify the type of fluid to be expanded. To keep things simple, let's limit our analysis to pure CO<sub>2</sub> which can be represented by four constitutive property models whose accuracy will depend on the *PVT* region where the expansion is carried out. The four models are:

- (1) ideal gas
- (2) The Law of Corresponding States  
(Hint: Express  $\alpha$  in terms of  $Z$  and its derivatives)
- (3) PR EOS
- (4) Thermodynamic charts given in Figures 8.12 a,b

- (a) What is the initial value of  $\alpha$  for each model above for the expansion of pure CO<sub>2</sub> from an initial state of 100 bar and 37°C?
- (b) Which process would you expect to liquefy a greater fraction of the entering CO<sub>2</sub> gas if the final pressure state for the expansion is 10 bar?
- (c) What technological and economic issues would be important in selecting a process for practical use?

Physical property data for carbon dioxide are given at the end of the problem set and in Appendix G of the text.

**Solution:**

(a)

For case (i), expansion across a Joule-Thompson valve is isenthalpic, so that:

$$\left(\frac{\partial T}{\partial P}\right)_{\text{process (i)}} = \left(\frac{\partial T}{\partial P}\right)_H = \alpha_H \quad (1)$$

For case (ii), we must assume that expansion across an adiabatic turbine is reversible in order to proceed. Then, the expansion becomes reversible, so we can say that it is an isentropic expansion:

$$\left(\frac{\partial T}{\partial P}\right)_{\text{process (ii)}} = \left(\frac{\partial T}{\partial P}\right)_S = \alpha_S \quad (2)$$

From Example 5.2 or Example 8.1 in the book, we get:

$$\alpha_H = \frac{T\left(\frac{\partial V}{\partial T}\right)_P - V}{C_p} \quad (3)$$

$$\alpha_S = \frac{T\left(\frac{\partial V}{\partial T}\right)_P}{C_p}$$

Therefore, taking the ratio of the expressions in equation (3):

$$\alpha = \frac{T\left(\frac{\partial V}{\partial T}\right)_P - V}{T\left(\frac{\partial V}{\partial T}\right)_P} = 1 - \frac{V}{T}\left(\frac{\partial T}{\partial V}\right)_P \quad (4)$$

We can now determine  $\alpha$  for each of the given models:(i) Ideal Gas Model  $PV=RT$ 

For an ideal gas:

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \quad (5)$$

$$\alpha = \frac{RT/P - V}{RT/P} = \frac{V - V}{V} = 0 \quad (6)$$

Therefore,  $\alpha = 0$  always for an ideal gas. This should be obvious since for an ideal gas,  $H = H(T)$  only, so for an isenthalpic process where  $H$  is constant,  $T$  must also be constant and  $\alpha_H = 0$ .

(ii) Law of Corresponding States  $Z=PV/RT$ We can re-write  $Z$  in terms of  $V$ :

$$V = \frac{RTZ}{P} \quad (7)$$

Plugging this into the derivative in our expression for  $\alpha$ :

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \left(\frac{\partial(TZ)}{\partial T}\right)_P = \frac{R}{P} \left[ T \left(\frac{\partial Z}{\partial T}\right)_P + Z \underbrace{\left(\frac{\partial T}{\partial T}\right)_P}_{=1} \right] \quad (8)$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \left[ T \left(\frac{\partial Z}{\partial T}\right)_P + Z \right] \quad (9)$$

Substituting equation (9) into  $\alpha$  and multiplying the numerator and denominator by P/RT gives:

$$\alpha = \frac{\frac{RT}{P} \left[ T \left(\frac{\partial Z}{\partial T}\right)_P + Z \right] - V}{\frac{RT}{P} \left[ T \left(\frac{\partial Z}{\partial T}\right)_P + Z \right]} = \frac{T \left(\frac{\partial Z}{\partial T}\right)_P + Z - Z}{T \left(\frac{\partial Z}{\partial T}\right)_P + Z} \quad (10)$$

$$\alpha = \frac{T \left(\frac{\partial Z}{\partial T}\right)_P}{T \left(\frac{\partial Z}{\partial T}\right)_P + Z} \quad (11)$$

To calculate  $\alpha$ , we need values of Z and its derivative with respect to T at our conditions of interest, namely P = 100 bar = 10 MPa and T = 37°C = 310 K. Using the handout included in the problem statement, we can use the PVT data given to calculate Z and then estimate its derivative using a finite differences argument. Data is given in the table below.

P (MPa)	T (K)	$\rho$ (kg/m <sup>3</sup> )	Z
10	305	751.67	0.2200
10	310	685.77	0.2412
10	315	586.02	0.2822

Thus:

$$\left(\frac{\partial Z}{\partial T}\right)_P \approx \frac{\Delta Z}{\Delta T} = \frac{0.282 - 0.220}{10 \text{ K}} = 0.00622 \text{ K}^{-1} \quad (12)$$

$$\alpha = \frac{(310 \text{ K})(0.00622 \text{ K}^{-1})}{0.2412 + (310 \text{ K})(0.00622 \text{ K}^{-1})} = 0.889$$

The isentropic process cools down the CO<sub>2</sub> more during expansion initially.

(iii) Peng-Robinson EOS

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)} \quad (13)$$

where:

$$a = a_c \left( 1 + \kappa \left( 1 - \sqrt{T/T_c} \right) \right)^2 \quad (14)$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (15)$$

and b and a<sub>c</sub> are defined in terms of the critical constants (see Equation (8-47)-(8-51) in the text).

Since we are working with a pressure-explicit equation of state, we can not evaluate  $(\partial V/\partial T)_P$  directly. However, making use of the triple-product rule:

$$\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T = -1$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{-\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial P}{\partial V}\right)_T} \quad (16)$$

Now we have two derivatives of the pressure explicit EOS. Analytically evaluating the numerator and denominator of equation (16):

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} - \frac{\left(\frac{\partial a}{\partial T}\right)_V}{V(V+b) + b(V-b)} \quad (17)$$

where:

$$\left(\frac{\partial a}{\partial T}\right)_V = \frac{-a\kappa}{(\alpha T T_c)^{1/2}} \quad (18)$$

and

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{-RT}{(V-b)^2} + \frac{2a(V+b)}{(V^2 + 2bV - b^2)^2} \quad (19)$$

We can now proceed with determining values for the derivatives in equations (17-19) at the temperature and pressure of interest. Values for the critical constants, acentric factor, and intermediate calculation values are given in the table below. The volume at this condition is found using equation (13) by finding the roots of the cubic equation. Since at 100 bar and 37°C we are above the critical point of CO<sub>2</sub>, there should be only one real root.

Conditions	Constants	Intermediate Calcs
T = 37°C = 310 K	T <sub>C</sub> = 304.2 K	κ = 0.707984
P = 100 bar = 10 MPa	P <sub>C</sub> = 73.8 bar = 73.8 x 10 <sup>5</sup> Pa	a = 0.39086 Pa(m <sup>3</sup> /mol) <sup>2</sup>
V = 7.099 x 10 <sup>-5</sup> m <sup>3</sup> /mol	a <sub>c</sub> = 0.3963 Pa(m <sup>3</sup> /mol) <sup>2</sup>	(∂a/∂T) <sub>V</sub> = -9.07 x 10 <sup>-4</sup> (Pa/K)(m <sup>3</sup> /mol) <sup>2</sup>
	ω = 0.225	(∂P/∂T) <sub>V</sub> = 2.993 x 10 <sup>5</sup> Pa/K
	b = 2.666 x 10 <sup>-5</sup> m <sup>3</sup> /mol	(∂P/∂V) <sub>T</sub> = -1.528 x 10 <sup>11</sup> Pa-mol/m <sup>3</sup>

Finally, after plugging in all our calculations, we get

$$\alpha = 0.883$$

Once again, we find that the isentropic process cools more rapidly initially.

(iv) Thermodynamic Charts in Fig. 8.12 a and b

We can calculate  $(\partial T/\partial V)_P$  by following an isobar, or a line of constant P, and reading values for the temperature and volume just before and after the initial starting point. Then we estimate the derivative using the same method employed for case (ii). Notice that we can not graphically find the derivative at the initial point because the figure axes are not in our units of interest. We must use Fig. 8.12b since Fig. 8.12a does not have isochors that extend over to the initial point. The values read from the figure are given in the table below.

P (MPa)	T (K)	$\rho$ (kg/m <sup>3</sup> )	Z
10	301	600	
10	310	675	0.25
10	315	800	

$$\left(\frac{\partial T}{\partial V}\right)_P \approx \frac{\Delta T}{\Delta V} = \frac{315 \text{ K} - 301 \text{ K}}{\left(\frac{1}{600} - \frac{1}{800}\right) \frac{\text{m}^3}{\text{kg}}} = 33600 \frac{\text{K} \cdot \text{kg}}{\text{m}^3} \quad (20)$$

$$\alpha = 1 - \frac{\left(\frac{1}{675}\right) \left(\frac{\text{m}^3}{\text{kg}}\right)}{310 \text{ K}} 33600 \frac{\text{K} \cdot \text{kg}}{\text{m}^3} = 0.839 = \alpha \quad (21)$$

This is consistent with the calculations from the previous EOS. The reason for the discrepancy is most probably due to difficulties in reading the figure.

## (b)

We can use Figures 18.12a and b to answer this question. For the isenthalpic process, we use Fig. 18.12a and follow a line of constant enthalpy vertically down from the initial point at 1450 psia and about 100°F to the final pressure of 14.5 psia. We end up in the vapor-liquid region, and from the chart we can see that the mixture is 42% liquid (58% vapor). For the isentropic process, we use Fig. 18.12b and follow a line of constant entropy vertically down from the initial point at 10 MPa and 310 K down to 1 MPa. Once again, we are in the vapor-liquid region, and from the chart see that mixture is about 53% liquid (47% vapor). We conclude that the isentropic process produces more liquid CO<sub>2</sub>.

This conclusion is supported by our models and makes sense practically. A turbine would extract work from the gas as it expands, whereas the valve does not, thus lowering its total internal energy more.

## (c)

Economically, a simple valve is less expensive than a turbine and all its moving parts (although you could generate electricity from the turbine, which may defray some of its costs).

Technically, the turbine will not be reversible as we have assumed, so we will not get as great a  $(\partial T/\partial V)_P$  as predicted. Plus, if the CO<sub>2</sub> were to liquefy in the turbine, it would cause cavitation and corrosion, thus quickly destroying the turbine as well as greatly reducing its efficiency.

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