

Chapter 13 Problems

1. Here are some data for CO₂:

critical T	304.21 K
critical P	73.825 bars
critical V	94.43 cm ³ mol ⁻¹

(a) Calculate the van der Waals a and b parameters from the critical data.

(b) Calculate

- the ideal gas molar volume, and
- the van der Waals molar volume

for CO₂, at 298.15 K and pressures of 10, 20, 30 40, 50, and 60 bars. One way to do this is to solve for V in $P = [RT/(V - b) - a/V^2]$, where $P = 10, 20, \dots$ using a spreadsheet solver or other iterative method.

(c) Do the same using the Redlich-Kwong equation.

2. Carry the calculations up to 100 bars. This entails passing through the liquid-vapor transition, which means you must solve the cubic VdW equation for its three roots in this region.

For comparison, experimental data from Michels et al. (1935)¹ are shown in Table 1.

3. Some van der Waals constants are listed in Table 2. There is quite a bit of variation in these values from different sources, as well as a variety of units.

In many experimental petrology labs, argon is used to pressurize reaction vessels. The argon comes in cylinders 1.55 m long, 11 cm in diameter (internal dimensions). The argon pressure in the cylinders is 2200 psi (pounds per square inch) at 25°C.

- What is the mass of the gas in the cylinder, assuming it is an ideal gas?
- What is the mass, assuming it is a van der Waals gas?
- What is the ideal gas molar volume?
- If the argon is released into a reaction vessel until it reaches a pressure of 1000 psi, what is the maximum amount of work it can do during that process if it acts as an ideal gas? Under what circumstances would this maximum amount of work be done?
- What is the maximum work if it acts as a van der Waals gas?
- What is the minimum amount of work that could be done. Under what circumstances?

¹Michels, A., Blaisse, B. and Michels, C., 1935, The isotherms of CO₂ in the neighbourhood of the critical point and round the coexistence line. Proc. Roy. Soc. London, v. A160, pp. 358–375.

P bars	V cm ³ mol ⁻¹
18.5374	1195.41
22.5716	957.581
26.3707	795.511
29.8654	683.723
33.3074	595.719
36.4942	528.334
39.4066	475.643
42.1695	431.734
63.114	187.502
63.247	185.762
63.403	183.526
63.451	180.148
63.446	175.219
63.450	162.526
63.468	118.662
63.467	77.056
63.456	76.590
63.474	62.292
63.513	62.261
63.593	62.208
63.760	62.090
64.151	61.840
65.259	61.200
65.370	61.120
67.514	60.119
74.739	57.956
109.870	53.081

Table 1: Data for CO₂ from Michels et al. (1935).

Substance	a J m ³ mol ⁻²	b m ³ mol ⁻¹	P_c Mpa	T_c K
Air	0.1358	3.64×10^{-5}	3.77	133
CO ₂	0.3643	4.27×10^{-5}	7.39	304.2
N ₂	0.1361	3.85×10^{-5}	3.39	126.2
H ₂	0.0247	2.65×10^{-5}	1.30	33.2
Ar	0.1340	3.22×10^{-5}	7.383	304.2

Table 2: van der Waals constants for a few gases.

- (g) How high could the maximum amount of work lift a 100 kg weight, assuming an ideal gas?
 - (h) Use the van der Waals equation to plot P vs. V from $V_1 = 149$ to $V_2 = 340$, and calculate the reversible work by calculating the area under the curve by some numerical method such as trapezoidal approximation. Compare with the previous result.
4. The equation of state of Duan et al. (1992)² looks complex but is actually quite easy to program, even in a spreadsheet, where the solver tool can be used to solve for V_R for given values of P and T . Use this equation to determine the compressibility coefficient (Z) and the fugacity coefficient of CO_2 at 25°C and from 10 to 100 bars, and compare with the other results. Be careful to note that V_c in this equation is not the normal critical volume.

²Duan, Z., N. Møller, and J.H. Weare, 1992, An equation of state for the $\text{CH}_4\text{-CO}_2\text{-H}_2\text{O}$ system: I. Pure systems from 0 to 1000°C and 0 to 8000 bar. *Geochim. et Cosmochim. Acta*, v. 56, pp. 2605–2617.