

## Problem 1. Simple steps

Each of these consists of small algebra and definitions.

- (a) The probability of a system being in the  $i$ th microstate is

$$P_i = e^{-\beta E_i} / Z, \quad (1)$$

where  $E_i$  is the energy of the  $i$ th microstate and  $\beta$  and  $Z$  are constants. From the Gibbs expression for the entropy  $S = -k_B \sum_m P_m \ln P_m$  show that the entropy is related to  $Z$

$$\frac{S}{k_B} = \ln Z + \beta U \quad (2)$$

where  $U = \sum P_i E_i$ . Also show that

$$Z = e^{-\beta F} \quad F = -k_B T \log Z \quad (3)$$

- (b) Starting from the first Law  $dE = TdS - pdV$  derive the expression for  $dG$  in terms of its natural variables  $(T, P)$

- (c) Show the following

$$U = -T^2 \left( \frac{\partial(F/T)}{\partial T} \right)_V \quad (4)$$

$$C_V = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_V \quad (5)$$

$$H = -T^2 \left( \frac{\partial(G/T)}{\partial T} \right)_P \quad (6)$$

$$C_P = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_P \quad (7)$$

## Problem 2. van der Waal gas

Real gasses don't quite obey the ideal gas law. A systematic way to account for deviations from ideal behavior at low densities (large volumes) is the *virial expansion*, where the pressure reads

$$Pv = RT \left( 1 + \frac{B(T)}{v} + \frac{C(T)}{v^2} + \dots \right), \quad (8)$$

The functions  $B(T)$ ,  $C(T)$ , are called the second and third virial coefficients, respectively. When the density of the gas is low, the third (and higher) terms can often be omitted. Here  $v = V/n_{\text{ml}}$  is the volume per mole. The second virial coefficient for diatomic nitrogen  $N_2$  is given below

$T$ (K)	$B$ (cm <sup>3</sup> /mol)
100	-160
200	-35
300	-4.2
400	9.0
500	16.9
600	21.3

Table 1: Table of the second virial coefficient of diatomic nitrogen

- Determine the % correction to the ideal gas pressure at a temperature 200 K and atmospheric pressure due to the first term in the virial expansion (i.e. the term due to  $B$ .) Estimate the size of higher order corrections due to  $C$ .
- Give a brief hand-wavy qualitative explanation why  $B(T)$  might be negative at low temperatures, but positive at high temperatures.
- A well motivated parametrization of a non-ideal gas is known as the van der Waals equations of state, which reads

$$P = \frac{RT}{v - b} - \frac{a}{v^2}, \quad (9)$$

Here  $v = V/n_{\text{ml}}$  is the volume for one mole of substance (i.e. a measure of the volume per particle). The motivation for this equation of state is the following<sup>1</sup>:

First, we recognize that the particles are not point particles, but that each has a nonzero volume  $b/N_A$ . Accordingly the volume  $v$  in the ideal gas equation is replaced by  $v - N_A(b/N_A)$ ; the total volume diminished by the volume  $b$  occupied by the molecules themselves.

The second correction arises from the existence of forces between the molecules. If the forces are attractive this will tend to reduce the pressure on the container walls. This diminution of the pressure should be proportional to the number of *pairs* of molecules, or upon the square of the number of particles per volume ( $1/v^2$ ); hence the second term proportional to  $a$  in the van der Waals equation.

Determine the second and third virial coefficients ( $B$  and  $C$ ) for a gas obeying the van der Waals equation, in terms of  $b$  and  $a$ .

*Hint:* In the ideal gas limit the volume per particle  $v$  is very large, so you may expand  $1/(v - b)$  for large  $v$ .

- Experimental fits to real gasses with the van der Waals eos give the coefficients  $a$ , and  $b$  (and also  $c$  discussed below), and are shown in Fig. 1. Make a graph of the prediction for  $B(T)$  from the van der Waals equation of state for diatomic nitrogen and compare with the experimental data in given in Table. 1. The plot I get is shown below in Fig. 2

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<sup>1</sup>This discussion paraphrases Callen

TABLE 3.1  
Van der Waals Constants and Molar Heat  
Capacities of Common Gases<sup>a</sup>

Gas	$a$ (Pa·m <sup>6</sup> )	$b$ (10 <sup>-6</sup> m <sup>3</sup> )	$c$
He	0.00346	23.7	1.5
Ne	0.0215	17.1	1.5
H <sub>2</sub>	0.0248	26.6	2.5
A	0.132	30.2	1.5
N <sub>2</sub>	0.136	38.5	2.5
O <sub>2</sub>	0.138	32.6	2.5
CO	0.151	39.9	2.5
CO <sub>2</sub>	0.401	42.7	3.5
N <sub>2</sub> O	0.384	44.2	3.5
H <sub>2</sub> O	0.544	30.5	3.1
Cl <sub>2</sub>	0.659	56.3	2.8
SO <sub>2</sub>	0.680	56.4	3.5

<sup>a</sup> Adapted from Paul S Epstein, *Textbook of Thermodynamics*, Wiley, New York, 1937.

Figure 1:

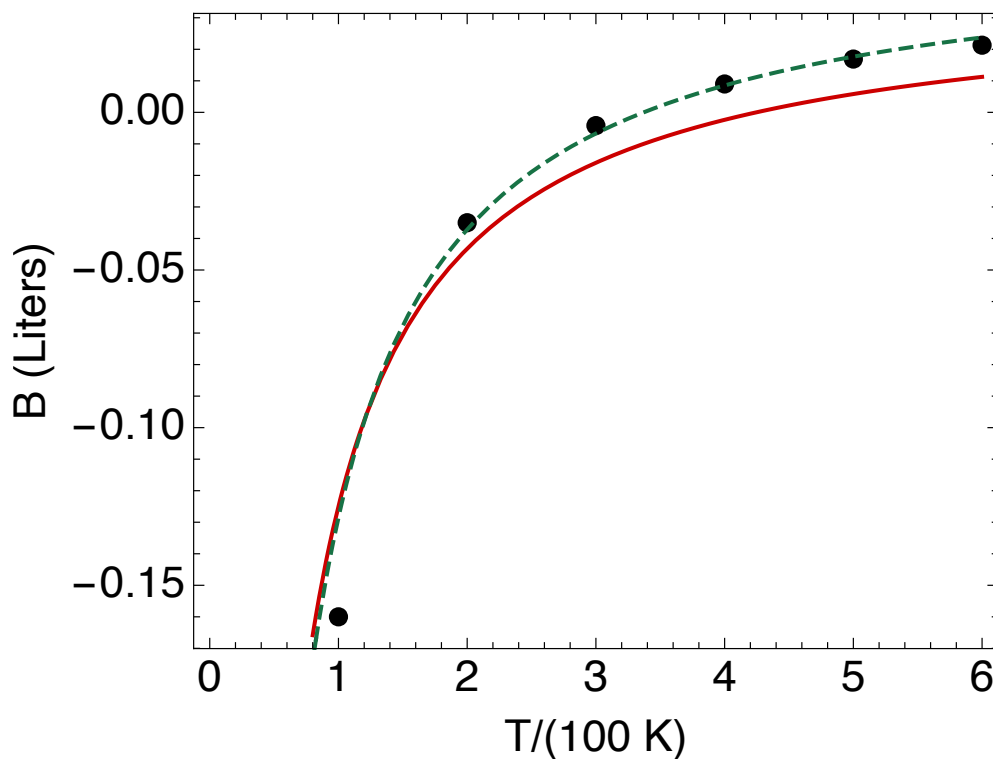


Figure 2: A plot comparing the van der Waal prediction to the data. The red curve is the uses the  $a$  and  $b$  from Table. 1, while in the green line I have increased  $b$  to a somewhat different value of  $b = 54.2 \times 10^{-6} \text{ m}^3$  and  $a = 0.152 \text{ Pa m}^6$ , which gives a better description.

### Problem 3. Energy in the van der Waals (based on Blundell 16.)

Recall that the temperature of the ideal gas is related to the energy via  $U = C_V T$ , with  $C_v^{1\text{mol}} = \frac{3}{2}R$  for a monoatomic gas, and  $\frac{5}{2}R$  for a diatomic gas. A commonly used parametrization of the energy temperature relation of a van der Waals gas is

$$u = cRT - \frac{a}{v} \quad (10)$$

Here  $u$  is the energy for one mole and  $c$  is typically  $3/2$  or  $5/2$  depending on molecule type. Some data on  $c$  is shown in the table below.

(a) Show that for any substance we have

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V} \left[ T \left(\frac{\partial p}{\partial T}\right)_V - p \right] \quad (11)$$

$$= -\frac{1}{C_V} \left[ T \frac{\beta_p}{\kappa_T} - p \right] \quad (12)$$

*Hint:* Entropy is a function of  $S(U, V)$

(b) Show that Eq. (11) is satisfied for a van der Waals gas. What is  $\left(\frac{\partial T}{\partial V}\right)_U$  for an ideal gas?

(c) Show that for any substance we have:

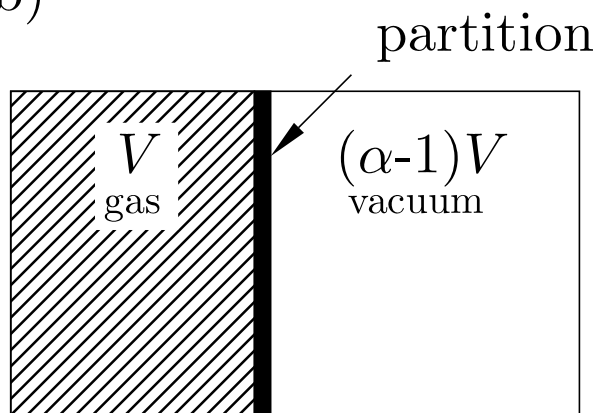
$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{1}{C_V} \left[ T \left(\frac{\partial p}{\partial T}\right)_V \right] \quad (13)$$

$$= -\frac{1}{C_V} \left[ \frac{\beta_p}{\kappa_T} \right] \quad (14)$$

Show that this implies that for that an ideal gas undergoing an adiabatic expansion that  $pV^\gamma = \text{const.}$

### Problem 4. Temperature change during a free expansion

(b)



One mole of a van der Waal gas is contained in a vessel of volume  $V_i = V$  at temperature  $T_i$ . A valve is opened, permitting the gas to expand into an initially evacuated vessel of volume  $(\alpha - 1)V$ , so that the final volume is  $\alpha V$  (i.e.  $\alpha$  is a constant greater than one). The walls of the vessels do not allow for heat flow.

- (a) Find the final temperature  $T_f$ , and compare to the ideal gas case. You should find that the temperature falls by an amount proportional to  $(\alpha - 1)/\alpha$ . Compare with the ideal gas case.

For definiteness evaluate your result for  $V_i = 2\text{ L}$  and  $V = 5\text{ L}$  and  $T_i = 300\text{ K}$  and the van der Waals constants of argon. I find

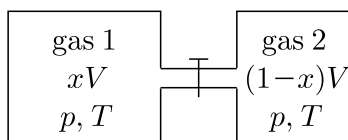
$$\Delta T = -3.2\text{ K} \quad (15)$$

- (b) Find the change in entropy during the expansion for a van der Waal gas. Assume the temperature is nearly constant during the expansion. (You should have found that the temperature change is only 1% in part (a).) .

You should find

$$\Delta S = R \log \left( \frac{\alpha V - b}{V - b} \right) - \frac{a}{T_i V} \left( \frac{\alpha - 1}{\alpha} \right) \quad (16)$$

## Problem 5. (Optional) Entropy of Mixing from Gibbs Formula



**Fig. 14.6** Gas 1 is confined in a vessel of volume  $xV$ , while gas 2 is confined in a vessel of volume  $(1-x)V$ . Both gases are at pressure  $p$  and temperature  $T$ . Mixing occurs once the tap on the pipe connecting the two vessels is opened.

- (a) (Optional) Consider the entropy of mixing described previously. Two gasses initially separated into two containers which have equal temperature and pressure. When the valve is opened the two gasses mix with each other and fill the entire container, as shown in the figure above. Follow the argument given in the text (Eq. 14.39) and show that the entropy produced during the process is

$$\Delta S = -Nk_B [x \log x + (1 - x) \log(1 - x)] \quad (17)$$

(b) Use the Gibbs formula for the entropy

$$S = -k_B \sum_m P_m \log P_m \quad (18)$$

to rederive the result for  $\Delta S$ .

*Hint:* For each molecule of the gasses define two states, i.e. in left container or in right container, and work out the probabilities both before and after the valve is opened.