

**Problem 1.4 [FOR ASSIGNMENT 1; max 10 points]**

**Carbon Dioxide as a van der Waals gas.**

Consider the behaviour of carbon dioxide ( $\text{CO}_2$ ) as approximated by the van der Waals equation:

$$\left(P + \frac{a}{(V/n)^2}\right)(V/n - b) = RT,$$

where  $a = 0.44 \text{ Nm}^4/\text{mol}^2$  and  $b = 5.2 \times 10^{-5} \text{ m}^3/\text{mol}$ .

- (a) Confirm that the equation is dimensionally consistent—in other words, confirm that the units on the left side equal the units on the right side.
- (b) What is the work done on 1 mol of  $\text{CO}_2$  during an isothermal expansion at  $T = 290\text{K}$  from an initial volume of  $100 \text{ cm}^3$  to a final volume of  $200 \text{ cm}^3$ , according to the van der Waals equation?
- (c) Calculate the work again but this time use the ideal gas law. How does this result compare to your result from part (b)? Can we treat  $\text{CO}_2$  as an ideal gas under these conditions?  
(HINT: the work done on a gas is given by  $W = -\int_{V_i}^{V_f} P dV$ .)

a) LHS:

$$\left(P + \frac{a}{\left(\frac{V}{n}\right)^2}\right)\left(\frac{V}{n} - b\right)$$
$$= \left(\frac{N}{\text{m}^2} + \frac{Nm^4}{\text{mol}^2 \left(\frac{\text{m}^3}{n}\right)^2}\right)\left(\frac{\text{m}^3}{\text{mol}} - \frac{\text{m}^3}{\text{mol}}\right)$$
$$= \left(\frac{N}{\text{m}^2} + \frac{N}{\text{m}^2}\right)\left(\frac{\text{m}^3}{\text{mol}}\right)$$
$$= \frac{Nm}{\text{mol}} = \frac{J}{\text{mol}}$$

RHS:  $\frac{J}{\text{mol} \cdot K} K$   
 $= \frac{J}{\text{mol}}$

QED  
LHS = RHS

b) We understand  $W = - \int_{V_i}^{V_f} P dV$

Rearranging van der Waals:

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

$$\therefore W = - \int_{V_i}^{V_f} \frac{RT}{\frac{V}{n} - b} dV + \int_{V_i}^{V_f} anV^{-2} dV$$

Note  $V_f = 0.02 \text{ m}^3$   $V_i = 0.01 \text{ m}^3$   $T = 290 \text{ K}$

$$= -RT \left[ n \ln \left( \frac{V}{n} - b \right) \right]_{0.01}^{0.02} + an \left[ -\frac{1}{V} \right]_{0.01}^{0.02}$$

$$= -8.3145 \times 290 \left[ \ln(V - 5.2 \times 10^{-5}) \right]_{0.01}^{0.02} + 0.44 \left[ -\frac{1}{V} \right]_{0.01}^{0.02}$$

$$= -1676.9 + 22 = -1654.9 \text{ J}$$

c) Ideal gas law:  $PV = nRT$

$$P = \frac{nRT}{V}$$

$$W = - \int_{V_i}^{V_f} \frac{nRT}{V} dV$$

$$= - \int_{0.01}^{0.02} \frac{R \times 290}{V} dV = -290R \left[ \ln(V) \right]_{0.01}^{0.02}$$

$$= -290R (\ln(0.02) - \ln(0.01))$$

$$= -1671.3 \text{ J}$$

We notice that the ideal gas law overestimated the work done by 16.4 J when compared to the van der Waals gas equation.

However, given the discrepancy is minor compared to the work's magnitude, we can estimate  $\text{CO}_2$  to be an ideal gas under these conditions.

**Problem 1.5** [FOR ASSIGNMENT 1; max 10 points]

**Internal energy change for an isothermal process**

The internal energy  $U$  of a substance can be related to changes in temperature  $T$ , volume  $V$  and pressure  $P$  via

$$dU = C_V dT + \left( T \left( \frac{\partial P}{\partial T} \right)_V - P \right) dV,$$

where  $C_V$  is the heat capacity at constant volume.

- (a) Consider a van der Waals gas that undergoes a change in volume and pressure at constant temperature. Use the above relationship to show that the change in internal energy is

$$\Delta U_T = an^2 \left( \frac{1}{V_i} - \frac{1}{V_f} \right),$$

where  $a$  is the constant used to introduce attractive forces in the van der Waals equation,  $n$  is the number of moles of gas, and the subscripts  $i$  and  $f$  label the state variables in the initial and final states, respectively.

(HINT: the van der Waals equation can be written as  $P = \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2$ .)

- (b) Compare the results from (a) to what you would expect for an ideal gas, and suggest reasons for any differences. You should explicitly refer to the dependence on  $a$  in your value for  $\Delta U_T$  computed for the van der Waals gas.

a) Given  $P = \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2$   $\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V-nb}$

$$dU = C_V dT + \left( \frac{nRT}{V-nb} - \frac{nRT}{V-nb} + a\left(\frac{n}{V}\right)^2 \right) dV$$

$$dU = C_V dT + a\left(\frac{n}{V}\right)^2 dV$$

$$\Delta U_T = \int_{V_i}^{V_f} C_V dT + \int_{V_i}^{V_f} a\left(\frac{n}{V}\right)^2 dV$$

Given the temperature is constant, this term goes to 0.

$$\begin{aligned} \int_{V_i}^{V_f} an^2 V^{-2} dV &= an^2 \left[ -\frac{1}{V} \right]_{V_i}^{V_f} \\ &= an^2 \left( -\frac{1}{V_f} + \frac{1}{V_i} \right) \end{aligned}$$

$$\therefore \text{QED} \quad \Delta U_T = an^2 \left( \frac{1}{V_i} - \frac{1}{V_f} \right)$$

b) In the case of an ideal case, we find:

$$dU = C_v dT + \left( T \left( \frac{\partial P}{\partial T} \right)_v - P \right) dV$$

$$\left( \frac{\partial P}{\partial T} \right)_v = \frac{\partial}{\partial T} \frac{nRT}{v} = \frac{nR}{v}$$

$$\therefore dU = C_v dT + \left( \frac{nRT}{v} - P \right) dV$$

$$\text{as } P = \frac{nRT}{v}, \quad \searrow = 0$$

$$\therefore \Delta U = \int C_v dT + 0$$

= 0 For Isothermal process

In the van der Waals case, we find that  
as  $P = \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V-nb}$$

$$\therefore \int \frac{nR}{V-nb} - \frac{nR}{V-nb} - a\left(\frac{n}{V}\right)^2 dV$$

As such, it is the dependence on  
the  $a\left(\frac{n}{V}\right)^2$  that results in a non-zero  
 $\Delta U$ .

In theory, this term rectifies the  
ideal gas law into evaluating the  
overlooked intermolecular forces,  
such that:

As volume increases, the space  
between the molecules also  
increases and so the forces  
decrease. This leads to an  
increase in internal energy  $\Delta U$ .  
And Vice Versa.

Problem 2.4 [FOR ASSIGNMENT 1; max 10 points]

Expansion of an ideal diatomic gas.

One mole of an ideal diatomic gas at pressure  $P_1 = 20$  bar expands from a volume  $V_1 = 2 \times 10^{-3} \text{ m}^3$  to a volume  $V_2 = 4 \times 10^{-3} \text{ m}^3$ . During the expansion, the pressure follows the relation  $PV^3 = k$ , with  $k$  a constant. Determine:

- (a) the temperature of the gas in the initial and final state;
- (b) the change in the internal energy of the gas; and
- (c) the amount of heat exchanged.

(HINT: the value of the constant you can determine using the initial values of  $P$  and  $V$ .)

$$n=1 \quad P_i = 2000 \text{ kPa} \quad V_i = 2 \times 10^{-3} \text{ m}^3 \quad V_f = 4 \times 10^{-3} \text{ m}^3$$

$$PV^3 = k$$

a) Given  $PV = nRT$   
initially:  $T_i = \frac{PV}{nR} = \frac{2000 \cdot 2 \times 10^{-3} \times 10^3}{1 \times R} = 481.1^\circ \text{K}$

Given initial  $P$  and  $V$ :

$$k = PV^3 = 2000 \times 10^3 \cdot (2 \times 10^{-3})^3 \\ = 0.016$$

And thus finally:

$$0.016 = P(4 \times 10^{-3})^3$$

$$P = 2.5 \times 10^5$$

Therefore the final temperature is:

$$T_f = \frac{2.5 \times 10^5 \times 4 \times 10^{-3}}{1 \times R} = 120.27^\circ \text{K}$$

b)

$$\Delta U = \frac{f}{2} n R \Delta T$$

We understand that as this is an ideal diatomic gas it has three translational and two vibrational degrees of freedom:

$$f = 5$$

$$\begin{aligned} \therefore \Delta U &= \frac{5}{2} \times 1 \times R \times (T_f - T_i) \\ &= \frac{5R}{2} (120.27 - 481.1) \\ &= -7499.9 \text{ J} \approx -7.5 \text{ kJ} \end{aligned}$$

c) Given  $\Delta U = W + Q$ :

$$Q = \Delta U - W$$

$$W = \int_{V_i}^{V_f} P dV$$



$$\text{As } PV^3 = k = 0.016$$

$$P = \frac{0.016}{V^3}$$

$$W = \int_{2 \times 10^{-3}}^{4 \times 10^{-3}} \frac{0.016}{V^3} dV$$

$$= 0.016 \left[ -\frac{1}{2} V^{-2} \right]_{2 \times 10^{-3}}^{4 \times 10^{-3}}$$

$$= 1500 \text{ J} = 1.5 \text{ kJ}$$

We notice that this work was done by the system as the volume increased, thus:

$$Q = -7499.9 - 1500$$

$$= -5999.9 \text{ J}$$

$$\approx -6 \text{ kJ}$$

$\therefore$  -6 kJ exchange from the system to the environment.

Problem 2.5 [FOR ASSIGNMENT 1; max 10 points]

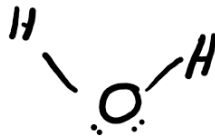
Heating of water: theory vs. experiment.

Four kilograms of water vapour (corresponding to 221 moles) is heated from 300 K to 800 K at a constant pressure of 10 kPa.

- (a) How many quadratic degrees of freedom would you expect to be active for each water molecule? Explain your answer.
- (b) Assuming that the water vapour behaves as an ideal gas with this number of degrees of freedom, calculate its heat capacity at constant pressure  $C_P$ . From this determine the heat  $Q$  required to increase the temperature to 800 K.
- (c) Check your calculation by also calculating the  $Q$  from the data in Table 1. Discuss the level of agreement, and what might cause any discrepancies.

$$\begin{array}{llll} \text{H}_2\text{O}: & n = 221 & T_i = 300\text{K} & T_f = 800\text{K} \\ & P = 10\text{kPa} & & \end{array}$$

a) water is a bent polar molecule:



We understand that a water molecule has 3 translational degrees of freedom ( $x, y, z$ ). Additionally, given its non-linear make-up, it has 3 rotational degrees of freedom. Finally, we also understand that the molecule will have:

$$\begin{array}{l} \text{Number of atoms.} \nearrow 3N - 6 = \text{Vibrational degrees of freedom} \\ = 3 \end{array}$$

We understand that the translational and rotational degrees only contribute quadratically to the kinetic energy.

The vibrational degrees however contribute to both the kinetic and potential energy and thus we find the total number of quadratic degrees of freedom to be:

$$\begin{array}{ccccc} & \nearrow & & \nearrow & \\ & 3 & + & 3 & + & (3 \times 2) & = & 12 \\ \text{Translational} & & & \text{Rotational} & & \text{Vibrational} \end{array}$$

However, we must not overlook the fact that at low temperatures, water experiences "freezing-out" such that not enough heat energy is available to activate all 3 degrees of vibrational freedom.

It is understood that the measure for vibrations is given by:

$$kT = kT$$

And, that by general rule, rotation is activated at 100K, and vibrational at 1000K.

Thus, we find that for this system (300 to 800K) the translational and vibrational degrees are active and thus we have 6 active quadratic degrees of freedom.

b) At constant pressure :

$$C_p = C_v + nR$$

$$C_v = \left( \frac{\partial U}{\partial T} \right)_v \Rightarrow C_p = \frac{\partial U}{\partial T} + nR$$

Since  $U = \frac{f}{2} nRT$

$$\left( \frac{\partial U}{\partial T} \right)_p = \left( \frac{\partial U}{\partial T} \right)_v = \frac{f}{2} nR = C_v$$

$$V = nRT/p \Rightarrow \left( \frac{\partial V}{\partial T} \right)_p = \frac{nR}{p}$$

$$\therefore C_p = C_v + nR = \left( \frac{f}{2} + 1 \right) nR$$

$$C_p = \left( \frac{f}{2} + 1 \right) nR$$

$n = 1$  for  
molar specific  
heat

For the 6 degrees  
previously stated.

$$= \left( \frac{6}{2} + 1 \right) nR$$

$$C_p = 33.25 \frac{\text{J}}{\text{mol K}}$$

Finally given  $Q = nC_p \Delta T$

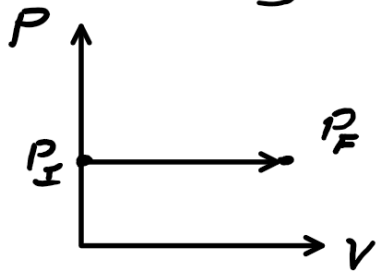
$$Q = 221 \times 33.25 \times (800 - 300) \\ = 3674.1 \text{ kJ}$$

Thus, it required 3674.1 kJ  
of heat to increase the  
system from 300K to 800K.

c) We define enthalpy as:

$$H = U + PV$$

For a constant pressure process with increasing volume:



$$H_F - H_I = U_F + pV_F - U_I - pV_I$$

$$= Q_F - W_F + pV_F - Q_I + W_I - pV_I$$

Note that:  $W_F = pV_F$

$$W_I = pV_I$$

$\therefore \Delta H = \Delta Q$  Thus for:

$$300\text{ K}: H = 2584.6 \frac{\text{kJ}}{\text{kg}}$$

$$800\text{ K}: H = 3489.0 \frac{\text{kJ}}{\text{kg}}$$

$$\Delta H = 3489 - 2584.6$$

$$= 904.4 \frac{\text{kJ}}{\text{kg}}$$

For 4 kg:

$$\Delta Q = 904.4 \times 4 = 3617.6 \text{ kJ}$$

As observed a relatively small discrepancy was found, with the theoretical energy change being 56.5 kJ larger than that calculated by the table of experimental values. There are two apparent reasons for this.

Firstly, our theoretical value assumed 6 degrees of freedom. However, primarily for the lower temperatures, it is probable that not all rotational degrees of freedom were active for every molecule, resulting in lower  $C_p$  and  $Q$  values.

Secondly, and perhaps more importantly we must consider the likely heat loss in the experimental results. Likely a product of an impossibly ideal isolator, the system would have lost heat to the environment, resulting in inaccurate enthalpy measurements and further causing a discrepancy in the calculated  $\Delta Q$  value.

