

Examples

Example 1.1 The atmosphere consists of 78.08% by volume of N_2 , and 20.95% of O_2 . Calculate the partial pressures due to the two gases.

The specification "% by volume" may be interpreted as follows. If the components of the atmosphere were to be separated, at the pressure of 1 atm, the volume occupied by each component is specified by the volume %. Thus, if we isolate the N_2 in 1.000 L of dry air, at a pressure of 1 atm its volume will be 0.781 L. According to the ideal gas law, at a fixed pressure and temperature, the amount of gas in moles $N = V(p/RT)$, i.e. the amount in moles is proportional to the volume. Hence percentage by volume is the same as percentage in N , i.e. 1.000 moles of air consists of 0.781 moles of N_2 . According to the Dalton's law (see (1.3.5)) the partial pressure is proportional to the N , the partial pressure of N_2 is 0.781 atm and that of O_2 is 0.209 atm.

Example 1.2 Using the ideal gas approximation, estimate the change in the total internal energy of 1.00 L of N_2 at $p=2.00$ atm and $T = 298.15$ K, if its temperature is increased by 10.0 K. What is the energy required to heat 1.00 mole of N_2 from 0.0 K to 298 K ?

The energy of an ideal gas depends only on the amount of gas N and the temperature. For a diatomic gas such as N_2 the energy per mole equals $(5/2)RT+U_0$. Hence, for N moles of N_2 the change in energy ΔU for a change in temperature from T_1 to T_2 is:

$$\Delta U = N(5/2)R(T_2 - T_1)$$

$$\text{In the above case } N = pV/RT = \frac{2.00 \text{ atm} \times 1.00 \text{ L}}{0.0821 \text{ L} \cdot \text{atm} \cdot \text{mol}^{-1} \text{K}^{-1} (298.15)} = 8.17 \times 10^{-2} \text{ mol}.$$

$$\begin{aligned} \text{Hence: } \Delta U &= 8.17 \times 10^{-2} \text{ mol} \frac{5}{2} (8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) (10.0 \text{ K}) \\ &= 17.0 \text{ J} \end{aligned}$$

(Note the different units of R used in this calculation.)

The energy required to heat 1.00 mol of N_2 from 0 K to 298 K is
 $= (5/2)RT = (5/2)(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) 298 \text{ K} = 6.10 \text{ kJ} \cdot \text{mol}^{-1}.$

Example 1.3 At $T=300\text{ K}$, 1.00 mol of CO_2 occupies a volume of 1.50 L . Calculate the pressures given by the ideal gas equation and the van der Waals equation. (The van der Waals constants a and b can be obtained from Table 1.1)

Ideal gas pressure
$$p = \frac{1.00\text{mol} \cdot 0.0821\text{atm}\cdot\text{L}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \times 300\text{K}}{1.50\text{L}} = 16.4\text{atm}$$

The pressure according to van der Waals equation:

$$p = \frac{NRT}{V - Nb} - a \frac{N^2}{V^2}$$

Since the van der Waals constants a and b given in Table 1.1 are in units of $\text{L}^2\cdot\text{atm}\cdot\text{mol}^{-2}$ and $\text{L}\cdot\text{mol}^{-1}$ respectively, we will use the value of $R=0.0821\text{atm}\cdot\text{L}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. This will give the pressure in atm.

$$p = \frac{1.00(0.0821)300}{1.50 - 1.00(0.0421)} - 3.59 \frac{1.00}{1.50^2} = 15.3\text{atm}$$

Exercises

1.1 Describe an experimental method, based on the ideal gas law, to obtain the molecular mass of a gas.

Answer: By measuring p , V and T of a gas, its mole number can be determined because $N=(pV/RT)$. If a flask of volume V is filled with the given gas of mass m , and if the p and T are its pressure and temperature respectively, then the molar mass of the gas

$$M = \frac{m}{N} = \frac{mRT}{pV}$$

1.2 The density of dry air at $p=1.0$ bar and $T = 300$ K is 1.161 kg/m³. Assuming that it consists entirely of N_2 and O_2 and using the ideal gas law, determine amount of each gas in moles in a volume of 1m^3 and their mole fractions.

Answer: Using the ideal gas law we see that the total amount of gas (N_2 plus O_2) is equal to:

$$N_{N_2} + N_{O_2} = N = \frac{pV}{RT} = \frac{1.0\text{bar} \times 10^3\text{L}}{0.08314(\text{barL/molK}) \times 300\text{K}} = 40.09\text{mol} \quad (\text{a})$$

The total mass of the two gasses

$$M_{N_2}N_{N_2} + M_{O_2}N_{O_2} = 1.161\text{kg} \quad (\text{b})$$

in which is the molar masses $M_{N_2}=28.01 \times 10^{-3}\text{kg/mol}$ and $M_{O_2}=32.00 \times 10^{-3}\text{kg/mol}$. Solving the two simultaneous equations (a) and (b) for N_{N_2} and N_{O_2} , we find: $N_{N_2} = 30.55$ mol and $N_{O_2} = 9.54$ mol. The corresponding mole fractions are $x_{N_2} = 0.762$ and $x_{O_2} = 0.238$.

1.3. The density of interstellar gas clouds is about 10^4 molecules/mL. The temperature is approximately 10K. Calculate the pressure. (The lowest vacuum obtainable in the lab is about 3 orders of magnitude larger.)

Answer: The pressure $p=(N/V)RT$. In this case, $\frac{N}{V} = \frac{10^4 / N_A}{10^{-6}\text{m}^3} = 1.66 \times 10^{-14} \text{ mol/m}^3$. Hence the interstellar pressure $p=(1.66 \times 10^{-14} \text{ mol/m}^3) \times (8.314 \text{ J/molK}) \times 10\text{K} = 1.38 \times 10^{-12} \text{ Pa}$.

1.4 A sperm whale dives to a depth of more than a 1.5 km into the ocean to feed. Estimate the pressure the sperm whale must withstand at this depth. (Express your answer in atm).

Answers: At a depth h , the pressure $p = h\rho g$, in which ρ is the liquid density and $g = 9.8 \text{ m s}^{-2}$. The density of sea water is about 1027 kg/m^3 . Hence the pressure:

$$p = 1.5 \times 10^3 \text{ m} (1027 \text{ kg/m}^3) (9.8 \text{ m s}^{-2}) = 1.5 \times 10^7 \text{ Pa} = 149.5 \text{ atm}$$

($1.0 \text{ atm} = 101.3 \text{ kPa}$). In the oceans, the pressure increases by about 1 atm for every 10 m of depth.

1.5 (a) Calculate the amount of gas in moles per m^3 of atmosphere at $p=1 \text{ atm}$ and $T=298 \text{ K}$ using the ideal gas equation.

(b) The atmospheric content of CO_2 is about 360 ppmv (parts per million by volume). Assuming a pressure of 1.00 atm, estimate the amount of CO_2 in 10.0 km layer of the atmosphere at the surface of the Earth. The radius of the Earth is 6370 km. (The actual amount of CO_2 in the atmosphere is about 6.0×10^{16} moles).

(c) The atmospheric content of O_2 is 20.946 % by volume. Using the result in part (b), estimate the total amount of O_2 in the atmosphere.

(d) Life on Earth consumes about 0.47×10^{16} moles of O_2 per year. What percent of the O_2 in the atmosphere does life consume in a year?

Answers:

(a) Since $1.0 \text{ m}^3 = 10^3 \text{ L}$, the number of moles of gas in 1.0 m^3 is:

$$N = \frac{pV}{RT} = \frac{1.0 \text{ atm} \times 10^3 \text{ L}}{0.0820 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 298} = 40.9 \text{ mol}$$

(b) At a given temperature and pressure, the number of moles is proportional to the volume. Since the CO_2 is 360 ppm by volume, the number of moles of CO_2 per m^3 is:

$$N_{\text{CO}_2} = 40.9 \times 360 \times 10^{-6} = 0.0147 \text{ moles/m}^3$$

If $R_E = 6370 \times 10^3 \text{ m}$ is the radius of the earth, the "volume" of the atmosphere in a layer of height h can be approximated by:

$$4\pi R_E^2 h = 4 \times 3.141 \times (6370 \times 10^3 \text{ m})^2 (10 \times 10^3 \text{ m}) = 5.098 \times 10^{18} \text{ m}^3.$$

$$(\text{the exact volume is } (4/3)\pi[(6380 \times 10^3)^3 - (6370 \times 10^3)^3] = 5.1061 \times 10^{18})$$

$$\begin{aligned}\text{Number of moles of CO}_2 \text{ in this layer} &= 0.0147 \text{ moles/m}^3 \times 5.1 \times 10^{18} \text{ m}^3 \\ &= 7.4 \times 10^{16} \text{ moles.}\end{aligned}$$

(this estimate is larger than the actual value of 6.0×10^{16} moles because the pressure decrease with height).

(c) $360 \text{ ppm} = 3.6 \times 10^{-4} = 3.6 \times 10^{-2} \%$. Since 20.9 % of the atmosphere is O_2 , the amount of O_2 in the 10 km layer = $\frac{20.9}{3.6 \times 10^{-2}} \times 7.4 \times 10^{16} = 4.3 \times 10^{19} \text{ mol}$.

(d) Since the consumption of O_2 by life on the planet is approximately $0.47 \times 10^{16} \text{ mol/year}$ the oxygen should last about :

$$\frac{4.3 \times 10^{19} \text{ mol}}{0.47 \times 10^{16} \text{ mol/year}} = 9100 \text{ years!}$$

1.6 The production of fertilizers begins with the Haber processes which is the reaction

$3 \text{ H}_2 + \text{N}_2 \rightarrow 2\text{NH}_3$ conducted at about 500 K and a pressure of about 300 atm. Assume that this reaction occurs in a container of fixed volume and temperature. If the initial pressure due to 300.0 mol H_2 and 100.0 mol N_2 is 300.0 atm, what will the final pressure be ? What will the final pressure be if initially the system contained 240.0 mol H_2 and 160.0 mol N_2 ? (use the ideal gas equations even though the pressures are high)

Answers:

Initially there are 400 mol of gas at $T=500\text{K}$ and $p=300\text{atm}$. After the reaction, there are only 200.0 moles of NH_3 . Since molar amount of gas, N , decreased by a factor of 2, for the same V and T , the pressure will also decrease by a factor of 2, i.e. $p=150 \text{ atm}$.

If initially there are 240.0 mol H_2 and 160 mol N_2 , 80 mol of N_2 will react with the H_2 and produce 160 mol NH_3 and 80 mol of N_2 will remain. Hence the total number of moles in the volume is 240 mol. Thus the number of moles has decreased by a factor $(240/400)=3/5$. Hence the pressure will also decrease by a factor of $3/5$, i.e. the final pressure will be $(3/5)300.0\text{atm} = 180.0 \text{ atm}$

1.7 The van der Waals constants for N_2 are: $a = 1.370 \text{ L}^2 \cdot \text{atm} \cdot \text{mol}^{-2}$ $b = 0.0387 \text{ L} \cdot \text{mol}^{-1}$. Consider 0.5 moles of $N_2(g)$ is in a vessel of volume 10.0L. Assuming that the temperature is 300 K, compare the pressures predicted by the ideal gas equation and the van der Waals equation.

- (a) What is the percent error in using the ideal gas equation instead of van der Waals equation?
- (b) Keeping $V = 10.0\text{L}$, use Maple/Mathematica to plot p vs N for $N = 1$ to 100, using the ideal gas and van der Waals equations. What do you notice regarding the difference between the pressure predicted by the two equations ?

Answers:

- (a) The pressure predicted by ideal gas equation:

$$p = NRT/V = 1.231 \text{ atm.}$$

The pressure predicted by van der Waals equation:

$$p = \frac{NRT}{(V - Nb)} - a\left(\frac{N^2}{V^2}\right) = 1.230 \text{ atm}$$

$$\text{The percent error} = \frac{1.231 - 1.230}{1.230} \times 100 = 0.08\%$$

Mathematica Code

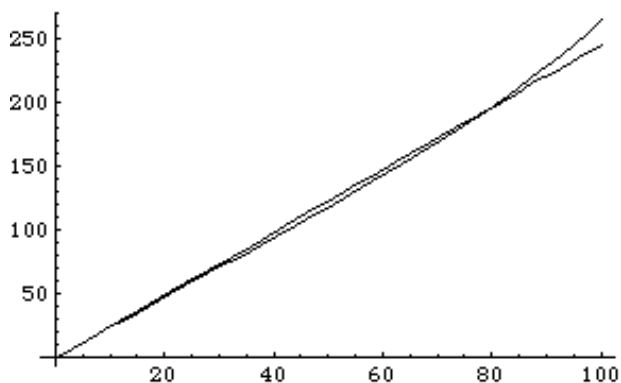
(* Exc. 1.7(b)*)

Clear[a, b, R, T];

a = 1.390; b = 0.039; R = 0.0821; T = 300;

vwp[N_] := (N*R*T/(10.0 - b*N)) - (a*(N/10.0)^2)

idp[N_] := N*R*T/10.0 Plot[{vwp[N], idp[N]}, {N, 1, 100}]



Maple Code

#Exc 1.7 (b);

restart;

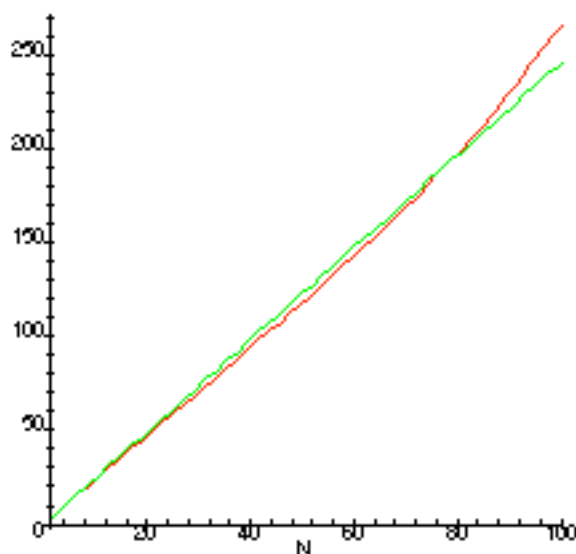
VWP:= N->(0.082*300*N/(10.0-0.0391*N))-1.390*(N/10.0)^2;

$$\text{VWP} := N \rightarrow 24.600 \frac{N}{10.0 - .0391 N} - .01390000000 N^2$$

> IDP:= N->0.082*300*N/10.0;

IDP := N -> 2.460000000 N

> plot([VWP(N),IDP(N)],N=1..100);



1.8 For 1.00 mol of Cl_2 in a volume of 2.50 L, calculate the difference in the energy between U_{ideal} and U_{vw} . What is the % difference when compared to U_{ideal} ?

Answer: From equation (1.3.11) it follows that:

$$U_{\text{ideal}} - U_{\text{vw}} = a(N^2/V) = 6.51 \text{ L}^2 \text{ atm mol}^{-2} \frac{1.00 \text{ mol}^2}{2.50 \text{ L}} = 2.60 \text{ atm.L}$$

$$\text{Note: } 1.0 \text{ atm.L} = (101.3 \times 10^3 \text{ Pa}) \times (10^{-3} \text{ m}^3) = 101.3 \text{ J}$$

$$\text{Hence: } 2.60 \text{ atm.L.} = 263 \text{ J}$$

$$U_{\text{ideal}} = (5/2)RT = (5/2) (8.314 \text{ JK}^{-1})(298\text{K}) = 6.19 \text{ kJ}$$

$$\frac{U_{\text{ideal}} - U_{\text{vw}}}{U_{\text{ideal}}} \times 100 = \frac{263 \text{ J}}{6.19 \times 10^3 \text{ J}} \times 100 = 4.2\%$$

1.9 (a) Using the ideal gas equation calculate the volume of one mole of a gas at temperature of 25°C and pressure of 1 atm. This volume is called the *Avogadro volume*.

(b) The atmosphere of Venus is 96.5% CO₂(g). The surface temperature is about 730 K and the pressure is about 90 atm. Using the ideal gas equation calculate the volume of one mole of CO₂(g) under these conditions (Avogadro volume on Venus).

(c) Use Maple/Mathematica and van der Waals equation to obtain the Avogadro volume on Venus and compare it (find the % difference) with the result obtained using the ideal gas equation.

Answers:

(a) $V_{\text{avgd}} = RT/P = R^*T = (1.00 \text{ mol}) (0.0821 \text{ atm.L.mol}^{-1}.\text{K}^{-1}) 298\text{K}/1.00\text{atm}$
 $= 24.5\text{L}$

(b) On Venus, $V_{\text{avgd}} = (1.00 \text{ mol}) (0.0821 \text{ atm.L.mol}^{-1}.\text{K}^{-1}) 750\text{K}/(90.0\text{atm})$
 $= 0.684 \text{ L}$

(c) Mathematica Code

In[3]:=

(*Exc. 1.9(c)*)

Clear[a,b,R,T];

a=3.59; b=0.0427; R=0.0821; T=750;

eq:=(1.0*R*T/(V-1.0*b))-a*(1/V^2)-90

Solve[eq==0,V]

Out[4]=

{{V -> 0.0278235 - 0.0419929 I}, {V -> 0.0278235 + 0.0419929 I}, {V -> 0.67122}}

Since the above equation is a third degree equation, there are 3 roots, two of them being complex. The real root $V=0.671\text{L}$ is the Avogadro volume on Venus.

Maple Code:

```
> #Exc 1.9(c);
> restart;R:=0.0821;T:=750;a:=3.59;b:=0.0427;
> eq:=(1.0*R*T/(V-1.0*b))-a*((1.0/V)^2)=90;
> solve(eq,V);
```

R := .0821

T := 750

a := 3.59

b := .0427

$$\text{eq} := \frac{61.57500}{V - .04270} - \frac{3.5900}{V^2} = 90$$

.02782347980 - .04199293909 I, .02782347980 + .04199293909 I,
.6712197071

Since the above equation is a third degree equation, there are 3 roots, two of them being complex. The real root $V=0.671\text{L}$ is the Avogadro volume on Venus.

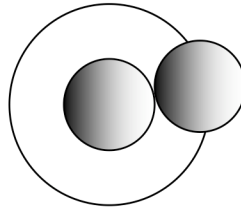
1.10 The van der Waals parameter b is a measure of the volume excluded due to the finite size of the molecules. Estimate the size of a single molecule from the data in Table 1.1.

Answer: A crude estimate of the size of the molecule can be obtained by assuming that it is spherical and by equating b to the total volume of N_A molecules. For CO_2 , for example this gives:

$$\frac{4}{3}\pi r^3 N_A = 0.0427 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$$

This gives a radius $r = 2.5 \times 10^{-10} \text{ m}$.

A better estimate is obtained by identifying the "excluded volume" by the finite size of the molecules. As shown in figure below, in a gas, each pair of molecules "excludes" a



volume equal to $\frac{4}{3}\pi(2r)^3$. Hence the total reduction in the available volume is

$$\frac{4}{3}\pi(2r)^3 \frac{1}{2} N_A = 0.0427 \times 10^{-3} m^3 mol^{-1}.$$

This gives a radius $r = 1.6 \times 10^{-10} m$.

1.11 For the van der Waals equation, express the pressure as a power series in $(1/V_m)$. Using this expression determine the Boyle Temperature, T_B , at which $p \approx RT_B/V_m$.

Answer: For the van der Waals equation

$$p = \frac{RT}{(V_m - b)} - \frac{a}{V_m^2}$$

The factor $1/(V_m - b)$ can be written as:

$$\frac{1}{V_m} \left[1 - \frac{b}{V_m} \right]^{-1} = \frac{1}{V_m} \left[1 + \frac{b}{V_m} + \left(\frac{b}{V_m} \right)^2 + \dots \right]$$

Substituting this expression in the expression in the expression for p we obtain:

$$p = \frac{RT}{V_m} + [RTb - a] \frac{1}{V_m^2} + \frac{RT}{V_m} \left[\left(\frac{b}{V_m} \right)^2 + \left(\frac{b}{V_m} \right)^3 + \dots \right]$$

The Boyle temperature, T_B , is the temperature at which the coefficient of the term $1/V_m^2$ is zero so that to the leading approximation, $p = RT/V_m$. By setting the coefficient of $1/V_m^2$ to zero we obtain:

$$T_B = a / bR$$

1.12 For the Redlich-Kwong equation $p = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T} V_m (V_m - b)}$ show that there is a critical point, i.e., show that for large T, p does not have an extremum.

Answer: At a fixed T, p has an extremum when $\left(\frac{\partial p}{\partial V_m}\right)_T = 0$. This implies:

$$\left(\frac{\partial p}{\partial V_m}\right)_T = \frac{-RT}{(V_m - b)^2} + \frac{a}{\sqrt{T}} \frac{(2V_m - b)}{V_m^2 (V_m - b)^2} \quad (1.12.1)$$

For large T, the second term becomes much smaller than the first making it impossible for the right hand side of the above equation to equal zero.

Alternatively one can equate the right-hand side of (1.12.1) to zero and look for the solutions when T is large. Equating the right-hand side of (1.12.1) zero we obtain:

$$RT^{3/2}V_m^2 - 2aV_m + ab = 0$$

Writing the solutions of this quadratic equation, it is easy to see that there are no real solutions when T is large.

1.13 Though van der Waals equation was a big improvement over the ideal gas equation, its validity is also limited. Compare following experimental data with the predictions of the van der Waals equation for one mole of CO₂ at T= 40°C. (Data source I. Prigogine and R. Defay, "Chemical Thermodynamics". 1967, London: Longmans.)

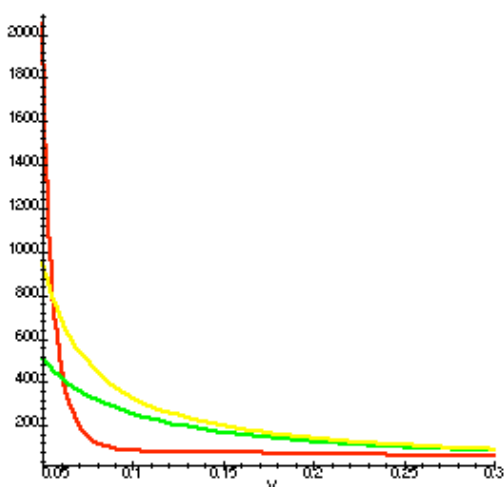
<u>p/atm</u>	<u>V_m/L.mol⁻¹</u>
1	25.574
10	2.4490
25	0.9000
50	0.3800
80	0.1187
100	0.0693
200	0.0525
500	0.0440
1000	0.0400

1.14 (a) Use Mathematica/Maple to plot the van der Waals p-V curves for Ar, N₂ and C₃H₈ using data listed in Table 1.1 (see Appendix 1.3 for sample programs). In particular, compare the van der Waals curves for CO₂ and He and the ideal gas equation.

Mathematica Codes are shown in the Appendix 1.3.

Maple Code:

```
> # Exc 1.10 Maple code for plotting van der Waals curves for CO2;
> restart;
> VWCO2:= (V,T)->(0.0821*T*1.0/(V-0.0427))-3.59*(1.0/(V^2));
> ID:=V->0.082*310/V;
> VWHe:= V->(0.082*310*1.0/(V-0.0237))-0.034*(1.0/V^2);
> plot([VWCO2(V,310),ID(V),VWHe(V)],V=0.05..0.3, thickness=2);
```



1.15 For CO₂, plot the compressibility factor $Z=pV_m/RT$ as function of the reduced pressure p_r for fixed reduced temperatures $T_r = 1.2$ and $T_r=1.7$. Verify that the Z - p_r curves are the same for all van der Waals gases. (This can be plotted using Parametric Plots)

1.16 Using Table 1.1 and the relations (1.5.4) obtain the critical temperature T_c , critical pressure p_c and critical molar volume V_{mc} for CO_2 , H_2 and CH_4 . Write a Maple/Mathematica code to calculate the van der Waals constants a and b given T_c , p_c and V_{mc} for any gas.

Gas	T_c /K	p_c /atm	V_{mc} /L
CO_2	303.4	72.9	0.128
H_2	33.1	12.7	0.0798
CH_4	189.7	45.5	0.128

Mathematica Code

```
=====
Clear[a,b]
a=3.59;b=0.0427;R=0.0821;
T=8*a/(27*R*b)
p=a/(27*b^2)
v=3*b
=====
```

Maple Code

```
=====
restart;
> a:=3.59;b:=0.0427;R:=0.0821;
> T=8*a/(27*R*b);
> p=a/(27*b^2);
> v=3*b;
=====
```

1.17 (a) For the van der Waals equation, using (1.5.2) obtain (1.5.3) and (1.5.4). (These calculations may also be done using Mathematica/Maple). (b) Show that $Z_c = (p_c V_{mc} / RT_c) = 3/8$ a constant for all gases.

Answer

(a) For the van der Waals equation:

$$p = \frac{RT}{(V_m - b)} - \frac{a}{V_m^2}$$

At the critical point:

$$\left(\frac{\partial p}{\partial V} \right)_T = \frac{-RT_c}{(V_{mc} - b)^2} + \frac{2a}{V_{mc}^3} = 0 \quad (1.17.1)$$

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = \frac{2RT_c}{(V_{mc} - b)^3} - \frac{6a}{V_{mc}^4} = 0 \quad (1.17.2)$$

Solving these two equations for V_{mc} and T_c we find:

$$V_{mc} = 3b \quad \text{and} \quad T_c = 8a/27Rb$$

Substituting these values in the van der Waals equation we get:

$$p_c = a/27b^2.$$

From these equations, (1.5.3) and (1.5.4) follow.

1.18 Using Mathematica/Maple obtain the equation (1.5.6) from (1.5.5).

Answer

The Mathematica code is in Appendix 1.2, Code C.

Maple Code

```
=====
> #Exc 1.13
> restart;
> p:=(T,V)->(R*T/(V-b))-(a/V^2);
> T:=(Tr*8*a)/(27*b*R); V:=Vr*3*b; pc:=a/(27*b^2);
> eq:=p(T,V)/pc;

> eq1:=simplify(eq);

> convert(eq1,parfrac,Vr);
```

$$8 \frac{\text{Tr}}{3 \text{ Vr} - 1} - \frac{3}{2 \text{ Vr}}$$

=====

1.19 For CO₂, plot p-V isotherms for van der Waals and Redlich-Kwong equations on the same graph for T=200K, 300K and 400K. The table below lists some constants a and b for the Redlich-Kwong equation (Source: J.H. Noggle, "Physical Chemistry", 1996, Harper Collins):

	a (bar L ² /mol K ^{1/2})	b (L/mol)
Ar	16.71	0.0219
CO ₂	64.48	0.0296
O ₂	17.36	0.0221

1.20 Show that Lennards-Jones energy $U_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$ has a minimum value equal to $-\epsilon$ at $r=2^{1/6}\sigma$.

Answer

The value of r at which U takes its the minimum value can be obtained by solving the equation:

$$\frac{\partial U_{LJ}(r)}{\partial r} = 0. \text{ Evaluating the derivative, we obtain:}$$

$$\frac{\partial U_{LJ}(r)}{\partial r} = 4\epsilon \left[\frac{-12\sigma^{12}}{r^{13}} + \frac{6\sigma^6}{r^7} \right] = 0$$

Which can be simplified to:

$$-12 \frac{\sigma^6}{r^6} + 6 = 0. \text{ That is } r = 2^{1/6} \sigma.$$

Substituting $r = 2^{1/6} \sigma$ into the expression for we see:

$$\frac{\partial U_{LJ}(r)}{\partial r} = 4\epsilon \left[\left(\frac{1}{2^{1/6}} \right)^{12} - \left(\frac{1}{2^{1/6}} \right)^6 \right] = -4\epsilon \frac{1}{4} = -\epsilon$$

1.21 . Estimate the average distance between molecules at $T=300\text{K}$ and $p=1.0\text{atm}$. (Hint: Consider a cube of side 10 cm in which the molecules occupy points on a 3-dimensional cubic lattice)

Answer

At $p=1.0\text{ atm}$ and $T=300\text{K}$, in volume of 1.0L there the amount of gas can be calculated:

$$N = \frac{pV}{RT} = \frac{1.0\text{atm} \cdot 1.0\text{L}}{0.0821 \frac{\text{atm L}}{\text{mol K}} \cdot 300\text{K}} = 0.0406\text{mol}$$

Let us assume, $0.0406N_A$ molecules to be in a cube of side 10.0 cm, arranged in an 3D array with n molecules along each side of the cube. Then $n^3 = 0.0406N_A = 0.0406 (6.023 \times 10^{23})$. Hence

$$n = [0.0406 (6.023 \times 10^{23})]^{1/3} = 2.89 \times 10^6.$$

The distance between the molecules is : $10\text{ cm} / 2.89 \times 10^6 = 3.4 \times 10^{-7}\text{ cm} = 3.4\text{ nm} = 34\text{ \AA}$.

1.22 According to the Graham's law of diffusion, the rate of diffusion of gas molecules is inversely proportional to the square root of its mass. Explain why this is so using the kinetic theory of gases. How would you expect the diffusion coefficient to depend on the temperature?

Answer

Diffusion is a consequence of random motion of molecules. Hence, the rate at which molecules diffuse can be expected to be proportional to the average speed of molecules. We have seen that the average kinetic energy of a molecule:

$$\langle mv^2/2 \rangle = (3/2) kT$$

From this it follows that $\sqrt{\langle v^2 \rangle} = \sqrt{3kT/m}$. Hence, we may surmise that the average speed is inversely proportional to the square root of the molecule's mass. This explains Graham's law. From this expression it is also clear that the rate of diffusion is proportional to the square root of the temperature T .

1.23 (a) Using the integrals in Appendix 1.2, obtain the average speed (1.6.19) and kinetic energy (1.6.20) of a gas molecule.

(b) Using the Maxwell probability distribution $f(v)$, obtain the most probable speed of a molecule of molar mass M at a temperature T .

Answer

(a) The average speed is given by the integral:

$$\langle v \rangle = \frac{4\pi}{z} \int_0^{\infty} v^3 e^{-\beta v^2} dv \quad 1.23.1$$

in which $\beta = M/2RT$ and $\frac{1}{z} = \left(\frac{M}{2\pi RT} \right)^{3/2}$. The integral can be evaluated using the integral (d) in the

appendix: $\int_0^{\infty} x^3 e^{-ax^2} dx = 1/2a^2$. Using this integral we see that:

$$\begin{aligned} \langle v \rangle &= \frac{4\pi}{z} \int_0^{\infty} v^3 e^{-\beta v^2} dv = \frac{4\pi}{z} \frac{1}{2\beta^2} = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} \frac{1}{2} \left(\frac{2RT}{M} \right)^2 \\ &= \left(\frac{8RT}{\pi M} \right)^{1/2} \end{aligned}$$

(b) The Maxwell probability distribution (1.6.15):

$$f(v)dv = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\beta v^2} v^2 dv$$

The most probable velocity is the one at which $f(v)$ reaches its maximum value. At its maximum value the derivative of the function $f(v) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\beta v^2} v^2$ must equal zero. Setting the derivative of $f(v)$ to zero we obtain:

$$-\beta 2v e^{-\beta v^2} v^2 + 2v e^{-\beta v^2} = 0$$

Solving for v we obtain: $v^2 = 1/\beta = 2k_B T/m$. Hence when v satisfies this equation, the function $f(v)$ reaches its maximum value, i.e. the most probable velocity $v = \sqrt{2k_B T/m}$.