

Physical Chemistry II - Homework 1

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January 23rd 2019

1. SO_2 is a serious air pollutant, produced through the combustion of fossil fuel. However, volcanic emissions can also be a significant source of SO_2 . Since the Mt. Kilauea eruption ended last fall, the latest measured emissions of SO_2 gas are $35t/d$ ($t = 103kg$). If the gas is emitted at $800^\circ C$ and $1atm$, what volume of SO_2 has been emitted in the last 90 days? State your assumptions.

Molar mass of $SO_2 = 64.066g/mol$

$$90d \times \frac{35t}{1d} \times \frac{10^3kg}{1t} \times \frac{10^3g}{1kg} \times \frac{1mol SO_2}{64.066g SO_2} = 49168045 mol SO_2$$

$$Ideal Gas Law: PV = nRT \rightarrow V = \frac{nRT}{P}$$

$$V = \frac{49168045mol \times 0.082057 L.atm.K^{-1}.mol^{-1} \times (800 + 273.15)K}{1atm} = \boxed{4.33 \times 10^9 L}$$

Assumptions making when using Ideal Gas law

- (1) the gas consists of a large number of molecules, which are in random motion and obey Newton's laws of motion
- (2) the volume of the molecules is negligibly small compared to the volume occupied by the gas
- (3) no forces act on the molecules except during elastic collisions of negligible duration.

2. A mixture of H_2 and NH_3 has a volume at $25^\circ C$, $1bar$ of $153.2cm^3$. To separate the mixture, it is chilled with liquid nitrogen. Some gas condenses, and the remaining gas is drawn off. The volume of the removed gas (when rewarmed to $25^\circ C$, $1bar$) is $98.7cm^3$. Calculate the mole fraction of ammonia in the original mixture.

| Gas | Boiling Point |
|--------|------------------|
| H_2 | $-432.2^\circ F$ |
| N_2 | $-320.4^\circ F$ |
| NH_3 | $-28.01^\circ F$ |

At the temperature of liquid nitrogen ($-320.4^\circ F$), NH_3 condenses, therefore, the remaining gas must be H_2 , which is removed and has the volume of $98.7cm^3$.

The volume of NH_3 in the mixture = $153.2cm^3 - 98.7cm^3 = 54.5cm^3$

The mole fraction of a gas to its mixture is directly proportional to the volume fraction, therefore, the mole fraction of NH_3 in the above mixture can be calculated as:

$$\chi_{NH_3} = \frac{V_{NH_3}}{V_{mixture}} \frac{54.5}{153.2} = \boxed{0.356}$$

3. Prepare plots of $f(v)$ vs. v for (a) Kr at 25, 225, 425, and $625^\circ C$ and (b) He, Ne, Ar, and Kr at $25^\circ C$. Make sure to label axes clearly, including units. Comment on the notable features of the plots.

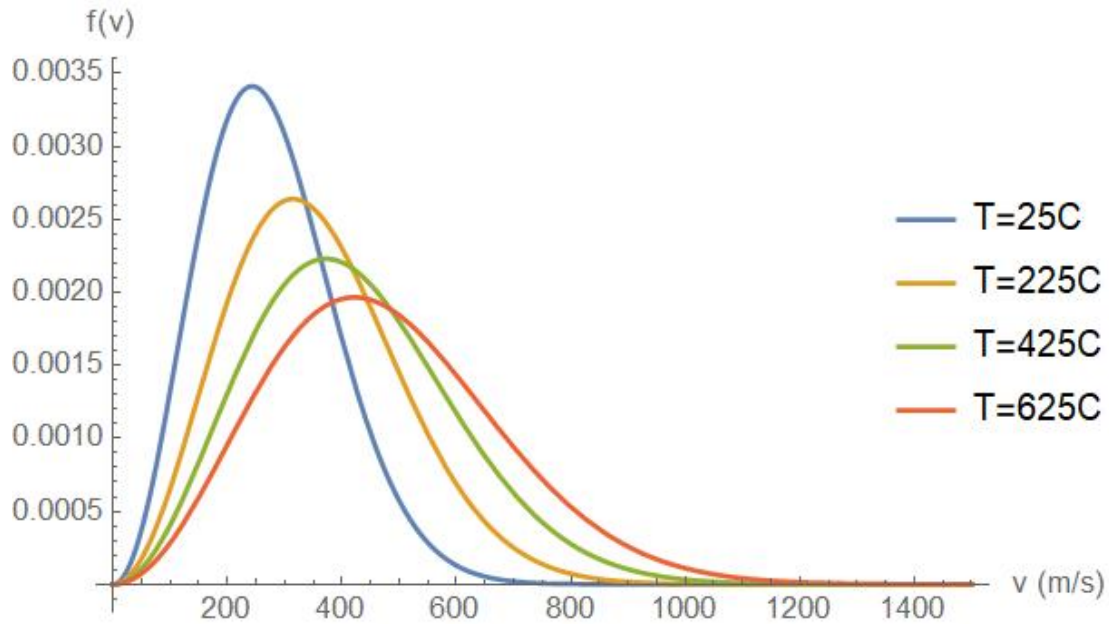
| Gas | Molar mass (kg) |
|-----|-----------------|
| He | 0.0040026 |
| Ne | 0.020180 |
| Ar | 0.039948 |
| Kr | 0.083798 |

Using the Maxwell-Boltzmann distribution of speeds

$$f(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-\frac{Mv^2}{2RT}}$$

for plotting, in which, v is the speed of gas, M is molar mass, $R = 8.3144621 kg.m^2.s^{-2}.K^{-1}.mol^{-1}$ is the gas constant, and T in temperature in Kelvin.

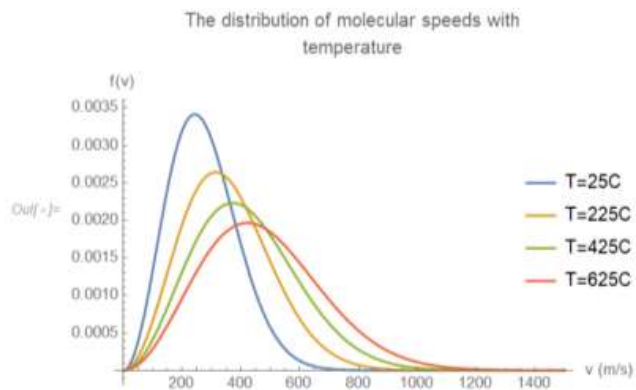
The distribution of molecular speeds with temperature



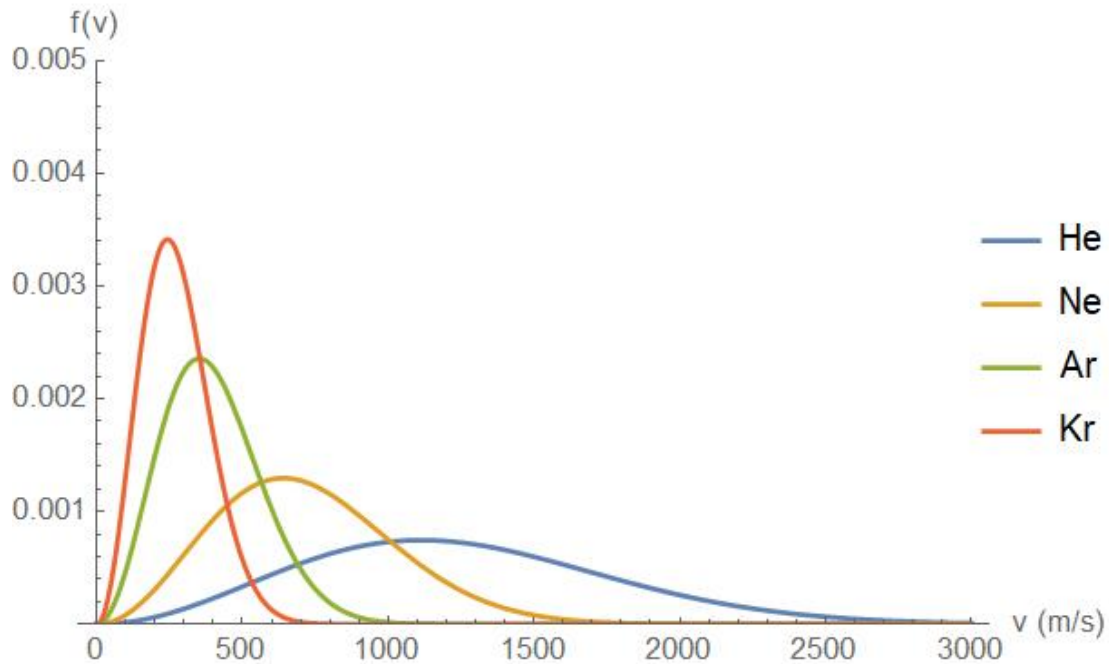
Graph is done by using Mathematica



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Plot[{4*Pi*x^2*(Kr/(2*Pi*R*298.15))^(3/2)*E^(-Kr*x^2/(2*R*298.15)),
4*Pi*x^2*(Kr/(2*Pi*R*498.15))^(3/2)*E^(-Kr*x^2/(2*R*498.15)),
4*Pi*x^2*(Kr/(2*Pi*R*698.15))^(3/2)*E^(-Kr*x^2/(2*R*698.15)),
4*Pi*x^2*(Kr/(2*Pi*R*898.15))^(3/2)*E^(-Kr*x^2/(2*R*898.15))}, {x, 0, 1500}, PlotRange -> All,
PlotLegends -> Placed[{"T=25C", "T=225C", "T=425C", "T=625C"}, p], AxesLabel -> {"v (m/s)", "f(v)"},
PlotLabel -> "The distribution of molecular speeds with temperature"]
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The distribution of molecular speeds with molar mass



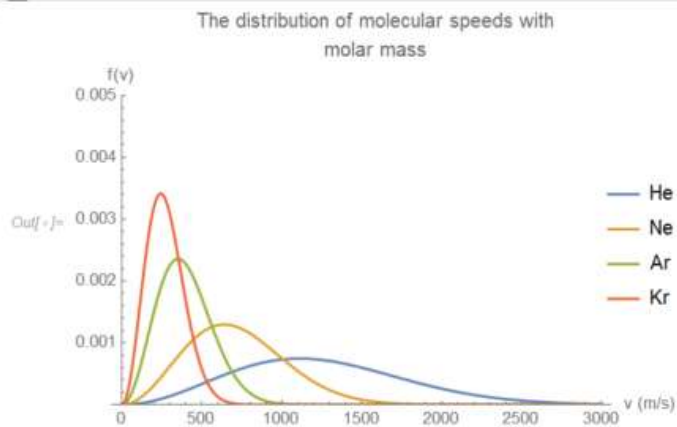
Graph is done by using Mathematica



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In[ ]:= Plot[{4*Pi*x^2*(He/(2*Pi*R*298.15))^(3/2)*E^(-He*x^2/(2*R*298.15)),
  4*Pi*x^2*(Ne/(2*Pi*R*498.15))^(3/2)*E^(-Ne*x^2/(2*R*498.15)),
  4*Pi*x^2*(Ar/(2*Pi*R*298.15))^(3/2)*E^(-Ar*x^2/(2*R*298.15)),
  4*Pi*x^2*(Kr/(2*Pi*R*298.15))^(3/2)*E^(-Kr*x^2/(2*R*298.15))}, {x, 0, 3000},
  PlotLegends -> Placed[{"He", "Ne", "Ar", "Kr"}, pos], AxesLabel -> {"v (m/s)", "f(v)"},
  PlotRange -> {0, 0.005}, PlotLabel -> "The distribution of molecular speeds with
  molar mass"]

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From the graphs above, we can conclude that heavy molecules are unlikely to be found with very high speeds and vice versa; gas molecules are more likely to travel faster at higher temperature than at low temperature; the area under each curve is expected to equal to 1; there are less molecules traveling at slow speeds regardless to their mass, and there is no molecule has the speed of 0 m/s.

4. A gas confined to move in two dimensions (i.e. molecules on a surface) has a speed distribution of

$$f(v) = \left(\frac{m}{kT}\right) v e^{-\frac{mv^2}{2kT}}$$

Use this distribution to find v_{mp} , v_{mean} , and v_{rms} for a 2D gas.

$$R = kN_A = k \times \frac{M}{m} \implies \frac{R}{M} = \frac{k}{m}$$

For v_{mean} :

$$v_{mean} = \int_0^\infty v f(v) dv = \left(\frac{m}{kT}\right) \int_0^\infty v^2 e^{-\frac{mv^2}{2kT}} dv$$

$$= \left(\frac{m}{kT}\right) \left(\frac{1}{4}\right) \left(\frac{\pi}{\left(\frac{m}{2kT}\right)^3}\right)^{1/2} = \boxed{\sqrt{\frac{\pi kT}{2m}}} \text{ or } \boxed{\sqrt{\frac{\pi RT}{2M}}}$$

For v_{rms} :

$$\left[\int_0^\infty v^2 f(v) dv\right]^{1/2} = \left[\left(\frac{m}{kT}\right) \int_0^\infty v^3 e^{-\frac{mv^2}{2kT}} dv\right]^{1/2}$$

$$= \left[\left(\frac{m}{kT}\right) \left(\frac{1}{2\left(\frac{m}{2kT}\right)^2}\right)\right]^{1/2} = \boxed{\sqrt{\frac{2kT}{m}}} \text{ or } \boxed{\sqrt{\frac{2RT}{M}}}$$

For v_{mp} :

v_{mp} can be obtained by optimizing the function of distribution of molecular speeds:

$$\frac{d f(v)}{dv} = \frac{d\left[\left(\frac{m}{kT}\right) v e^{-\frac{mv^2}{2kT}}\right]}{dv} = \left(v \cdot e^{-\frac{mv^2}{2kT}}\right)' = e^{-\frac{mv^2}{2kT}} - (v)(2v\left(\frac{m}{2kT}\right))e^{-\frac{mv^2}{2kT}}$$

$$= e^{-\frac{mv^2}{2kT}} \left(1 - 2\left(\frac{m}{2kT}\right)v^2\right) = 0$$

Since $e^{-\frac{mv^2}{2kT}}$ cannot be 0, $f(v)$ is maximized when

$$\left(1 - 2\left(\frac{m}{2kT}\right)v^2\right) = 0 \leftrightarrow v_{mp} = \sqrt{\frac{1}{2\left(\frac{m}{2kT}\right)}} = \boxed{\sqrt{\frac{kT}{m}}} \text{ or } \boxed{\sqrt{\frac{RT}{M}}}$$

5. What fraction of air (assume $M = 29g/mole$) is traveling below 100mph at $30^\circ C$?

$$\frac{100miles}{hour} \times \frac{1hour}{3600s} \times \frac{1609.34km}{1mile} = 44.704m/s$$

Fraction of air ($M = 0.029kg$) traveling below 44.704m/s at $30^\circ C$ or (303.15K) :

$$P(0; 44.704) = \int_0^{44.704} f(v) dv = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} \int_0^{44.704} v^2 e^{\left(\frac{-Mv^2}{2RT}\right)} dv$$

The numerical value of this integral can be solved by using the website <https://www.zweigmedia.com/RealWorld/integral/integral.html>

Just enter the function you want to integrate and/or graph, and click on the action you want. [Click here for some examples of function formatting.](#)

$$f(x) = 4 \cdot 3.14159654 \cdot ((0.029)/(2 \cdot 3.141592654 \cdot 8.3144621 \cdot 303.15))^{(3/2)} \cdot (x^2) \cdot e^{((-0.029 \cdot x^2)/(2 \cdot 3.141592654 \cdot 8.3144621 \cdot 303.15))}$$

Lower limit: $a = 0$

Upper limit: $b = 44.704$

Number of subdivisions (required for left- and right-Riemann sums, trapezoid sum and Simpson's rule) $n =$

☐ Fractions

Rounding: 7

significant digits ▾

Left sum

Right sum

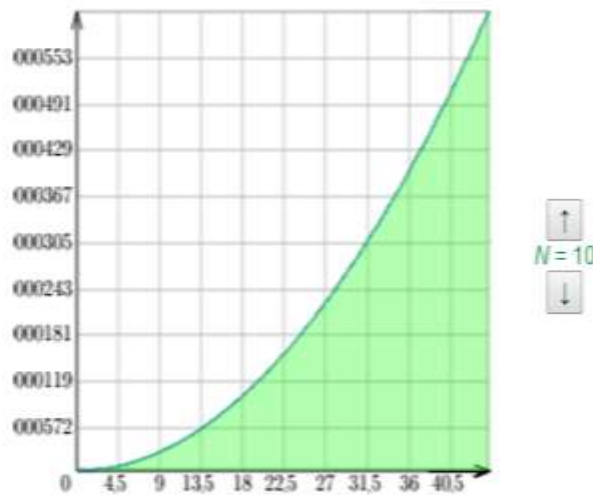
Trapezoid sum

Simpson sum

Integral

Clear

$$\int_a^b f(x) dx \approx 0.0009209247$$



$$P(0; 44.704) = 0.00092 = 0.092\%$$

6. Argon at 25°C is confined between two parallel plates 1mm apart. At what pressure does the mean free path equal the plate separation?

$$\sigma_{Ar} = 0.36\text{nm}^2 = 3.6 \times 10^{-19}\text{m}^2; T = 25^\circ\text{C} = 298.15\text{K}; \lambda = 1\text{mm} = 1 \times 10^{-3}\text{m}$$

$$\text{Mean free path : } \lambda = \frac{v_{rel}}{z} = \frac{kT}{\sigma P}$$

$$\text{therefore } P = \frac{kT}{\lambda\sigma} = \frac{1.3806 \times 10^{-23} Pa.m^3.K^{-1} \times 298.15K}{3.6 \times 10^{-19}m^2 \times 1 \times 10^{-3}m} = \boxed{11.43Pa}$$

7. For N_2 at $25^\circ C$, $1bar$, calculate: v_{mean} , number density of the molecules (\mathcal{N}), collision frequency (z), mean free path (λ), and ratio of the mean free path to molecular diameter. Interpret these values in brief explanations.

$$25^\circ C = 298.15K; 1bar = 10^5 Pa; \text{molecular mass of } N_2 = 0.028kg;$$

$$\sigma_{N_2} = 0.43nm^2 = 4.3 \times 10^{-19}m^2; d_{N_2} = 364pm = 3.64 \times 10^{-10}m$$

$$v_{mean} = \left(\frac{8RT}{\pi M} \right)^{1/2} = \left(\frac{8 \times 8.3144621 K.g.m^2.s^{-1}.K^{-2}.mol^{-1} \times 298.15K}{\pi \times 0.028 Kg/mol} \right)^{1/2} = \boxed{474.816m/s}$$

$$v_{rel} = \sqrt{2} \times v_{mean} = (\sqrt{2})(474.816m/s) = \boxed{671.49m/s}$$

$$\mathcal{N} = \frac{N}{V} = \frac{nN_A}{\frac{nRT}{P}} = \frac{P}{kT} = \frac{10^5 Pa}{(1.3806 \times 10^{-23} Pa.m^3.K^{-1})(298.15K)} = \boxed{2.429 \times 10^{25}m^{-3}}$$

$$z = \sigma v_{rel} \mathcal{N} = (4.3 \times 10^{-19}m^2)(671.49m/s)(2.429 \times 10^{25}m^{-3}) = \boxed{7.014 \times 10^9 s^{-1}}$$

$$\lambda = \frac{v_{rel}}{z} = \frac{671.49m/s}{7.014 \times 10^9 s^{-1}} = 9.574 \times 10^{-8} = \boxed{95.74nm}$$

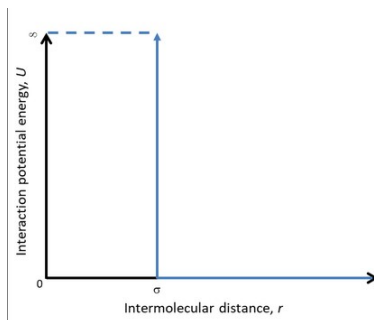
$$\frac{\lambda}{d} = \frac{95.74 \times 10^{-9}m}{3.64 \times 10^{-10}m} = \boxed{263}$$

Physical Chemistry II - Homework 2

Hao Anh Nguyen

January 30th 2019

1. Use the relationship between intermolecular potential and second virial coefficient $B(T) = 2\pi N_A \int_0^\infty \left(1 - e^{\frac{-U}{kT}}\right) r^2 dr$ to find the second virial coefficient of a hard sphere potential. How is the result connected to van der Waals constants and the second virial coefficient in terms of the van der Waals constants?



For hard-sphere potential:

$$U = 0 \quad \text{when } r > \sigma$$

$$U = \infty \quad \text{when } 0 \leq r \leq \sigma$$

$$\begin{aligned}
 B(T) &= 2\pi N_A \int_0^\infty \left(1 - e^{\frac{-U}{kT}}\right) r^2 dr \\
 &= 2\pi N_A \left[\int_0^\sigma \left(1 - e^{\frac{-U}{kT}}\right) r^2 dr + \int_\sigma^\infty \left(1 - e^{\frac{-U}{kT}}\right) r^2 dr \right] \\
 &= 2\pi N_A \left[\int_0^\sigma \left(1 - e^{\frac{-\infty}{kT}}\right) r^2 dr + \int_\sigma^\infty \left(1 - e^{\frac{0}{kT}}\right) r^2 dr \right] \\
 &= 2\pi N_A \left[\int_0^\sigma (1 - 0) r^2 dr + \int_\sigma^\infty (1 - 1) r^2 dr \right] \\
 &= 2\pi N_A \left. \frac{r^3}{3} \right|_0^\sigma \\
 &= \boxed{2\pi N_A \frac{\sigma^3}{3}}
 \end{aligned} \tag{1}$$

Virial equation: $p = \frac{RT}{V_m} \left(1 + B \frac{1}{V_m} + C \frac{1}{V_m^2} + \dots \right)$

Van der Waals equation:

$$\begin{aligned}
 p &= \frac{RT}{V_m - b} - \frac{a}{V_m^2} \\
 &= \frac{RT}{V_m} \times \frac{V_m}{V_m - b} - \frac{a}{V_m^2} \\
 &= \frac{RT}{V_m} \times \left(\frac{V_m - b}{V_m} \right)^{-1} - \frac{a}{V_m^2} \\
 &= \frac{RT}{V_m} \times \left(1 - \frac{b}{V_m} \right)^{-1} - \frac{a}{V_m^2} \quad (\text{with } \frac{b}{V_m} < 1) \\
 &= \frac{RT}{V_m} \times \left(1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} + \frac{b^3}{V_m^3} + \dots \right) - \frac{a}{V_m^2} \\
 &= \frac{RT}{V_m} \times \left(1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} + \frac{b^3}{V_m^3} + \dots - \frac{a}{V_m RT} \right) \\
 &= \frac{RT}{V_m} \times \left(1 + \left(b - \frac{a}{RT} \right) \frac{1}{V_m} + \frac{b^2}{V_m^2} + \frac{b^3}{V_m^3} + \dots \right)
 \end{aligned} \tag{2}$$

Comparing the two equations with color codes we can conclude:

$$\boxed{B = b - \frac{a}{RT}} \text{ and } \boxed{C = b^2}$$

2. Plot PV van der Waals isotherms for SO_2 at 500 K, 430.5 K, 350 K. Also add the ideal gas isotherm at 500 K. (Pressure range from -2 to 10 MPa; Volume range from 0 to $3.6 \text{ cm}^3/\text{mol}$). Label regions of supercritical fluid, gas, liquid, and gas/liquid equilibrium. Cite your source for van der Waals constants. Comment on the features of the graph.

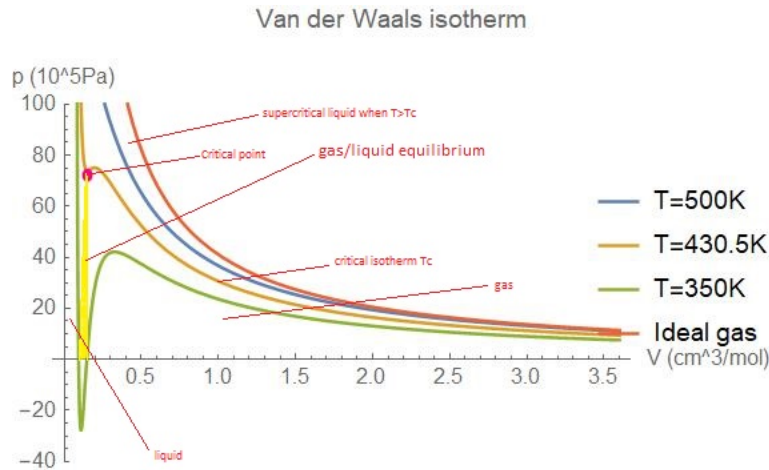
Van der Waals constants for SO_2 adapted from Atkins' Physical Chemistry Tenth Edition by Peter Atkins, Julio de Paula, and James Keele:

$$a = 6.775 \text{ atm dm}^6 \text{ mol}^{-2}; \quad b = 5.68 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$$

$$\text{Van der Waals equation: } P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$T_c = 430.5 \text{ K}$$

Perfect gas isotherms are obtained at high temperatures and large molar volumes. Liquids and gases coexist when the attractive and repulsive effects are in balance.



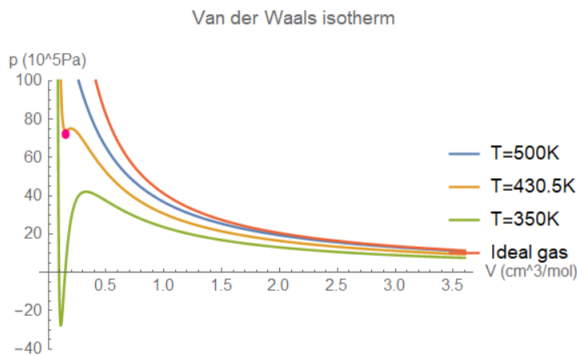
Graph is done by using Mathematica, edited by Paint

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In[90]= Plot[{((R*500)/(x-0.0568))-6.86476/x^2, ((R*430.5)/(x-0.0568))-6.86476/x^2,
  ((R*350)/(x-0.0568))-6.86476/x^2, ((R*500)/(x-0))-0/x^2}, {x, 0, 3.6}, PlotRange -> {-40, 100},
  PlotLegends -> Placed[{"T=500K", "T=430.5K", "T=350K", "Ideal gas"}, pos],
  AxesLabel -> {"V (cm^3/mol)", "p (10^5Pa)"}, PlotLabel -> "Van der Waals isotherm"]

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3. The critical temperature of nitrous oxide (N_2O) is $36.5^\circ C$, and its critical pressure is 71.7 atm. Using the law of corresponding states, estimate the molar volume of N_2O at 54.0 atm at 356 K.?

$$T_c = 36.5^\circ C = 309.65 K; P_c = 71.7 atm = 7265002.5 Pa; P = 54.0 atm = 5417155 Pa$$

$$P_r = \frac{54}{71.7} = 0.753138; T_r = \frac{356}{309.65} = 1.149685$$

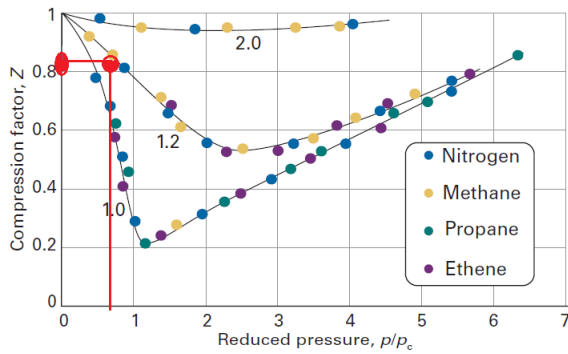


Figure 1C.9 The compression factors of four of the gases shown in Fig. 1C.3 plotted using reduced variables. The curves are labelled with the reduced temperature $T_r = T/T_c$. The use of reduced variables organizes the data on to single curves.

According to the diagram adapted from Atkins' Physical Chemistry Tenth Edition by Peter Atkins, Julio de Paula, and James Keele, approximation of the compress factor of Z at

$$P_r = 0.753138 \text{ and } T_r = 1.149685 \text{ is } z = 0.87$$

$$\begin{aligned} z &= \frac{PV_m}{RT} \\ V_m &= \frac{zRT}{P} \\ &= \frac{0.87 \times 8.3145 \text{ m}^3 \text{ Pa mol}^{-1} \text{ K}^{-1} \times 356 \text{ K}}{5417155 \text{ Pa}} \\ &= 0.00047537 \text{ m}^3 = \boxed{0.475 \text{ dm}^3} \end{aligned} \quad (3)$$

4. Find the expression for the Boyle temperature in terms of van der Waals constants. Use that expression to find the Boyle temperature for Xe. Explain the physical significance of this temperature.

At Boyle temperature, the second coefficient of the virial equation(B) becomes zero. Using the relationship between of the Van der Waals constants and virial coefficients shown at (2) in problem 1, we have:

$$B = b - \frac{a}{RT_B} = 0 \implies \boxed{T_B = \frac{a}{Rb}}$$

Van der Waals constants for Xenon adapted from Atkins' Physical Chemistry Tenth Edition by Peter Atkins, Julio de Paula, and James Keele:

$$a = 4.137 \text{ atm dm}^6 \text{ mol}^{-2}; b = 5.16 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}.$$

$$T_b = \frac{a}{Rb} = \frac{4.137 \text{ atm dm}^6 \text{ mol}^{-2}}{0.08205746 \text{ dm}^3 \text{ K}^{-1} \text{ atm mol}^{-1} \times 5.16 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}} = \boxed{977 \text{ K}}$$

At Boyle temperature, the attractive forces and the repulsive forces on the gas particles balance out, therefore, the gas behaves as a perfect gas.

5. Find the internal pressure, π , of a van der Waals gas. Explain the physical meaning of this parameter.

Internal pressure:

$$\begin{aligned}
 \pi &= \left(\frac{\partial U}{\partial V} \right)_T \\
 &= T \left(\frac{\partial P}{\partial T} \right)_V - P \\
 &= T \left(\frac{\partial \left[\frac{RT}{V_m - b} - \frac{a}{V_m^2} \right]}{\partial T} \right)_V - \frac{RT}{V_m - b} + \frac{a}{V_m^2} \\
 &= \frac{RT}{V_m - b} - \frac{RT}{V_m - b} + \frac{a}{V_m^2} \\
 &= \frac{a}{V_m^2}
 \end{aligned} \tag{4}$$

Internal pressure shows how the internal energy changes when volume is changed and temperature is constant.

6. a) Calculate the work done during the isothermal reversible expansion of a van der Waals gas.

b) Plot on the same graph the indicator diagrams (graphs of P vs. V) for the isothermal expansion of

i) a perfect gas, ii) a van der Waals gas in which $a = 0$ and $b = 5.11 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1}$, and iii) a van der Waals gas in which $a = 4.2 \text{ dm}^6 \text{ atm mol}^{-2}$ and $b = 0$. (The values exaggerate the imperfections but show up clearly on the indicator diagrams). Comment on the appearance of the indicator diagrams and the amount of work done in each process. Take $V_i = 1.0 \text{ dm}^3$, $V_f = 2.0 \text{ dm}^3$, $n = 1.0 \text{ mole}$, and $T = 298 \text{ K}$

For isothermal reversible expansion: Work done: $w = - \int_{V_i}^{V_f} P dV$

For Van der Waals equation: $P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$

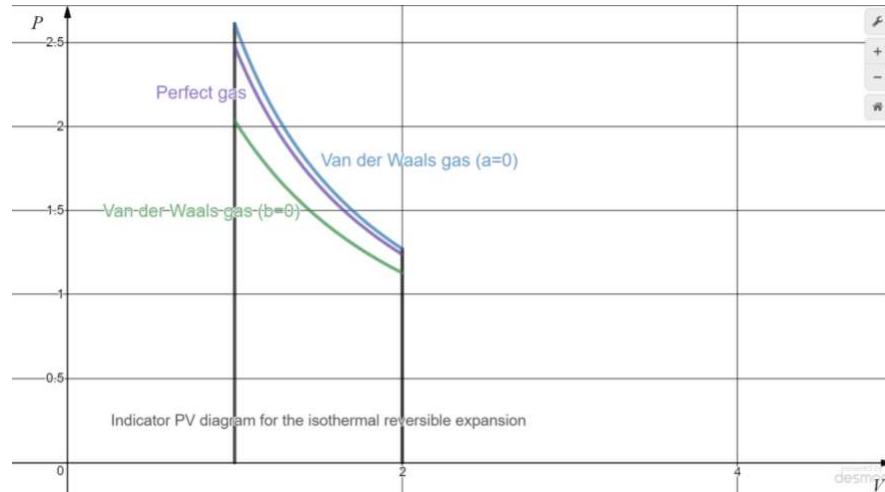
Therefore:

$$\begin{aligned}
 w &= - \int_{V_i}^{V_f} \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} dV \\
 &= - \int_{V_i}^{V_f} \frac{nRT}{V - nb} dV + \int_{V_i}^{V_f} \frac{n^2 a}{V^2} dV \\
 &= -nRT \ln(V - nb) \Big|_{V_i}^{V_f} - \frac{n^2 a}{V} \Big|_{V_i}^{V_f} \\
 &= -nRT \ln \frac{V_f - nb}{V_i - nb} - n^2 a \left(\frac{1}{V_f} - \frac{1}{V_i} \right)
 \end{aligned} \tag{5}$$

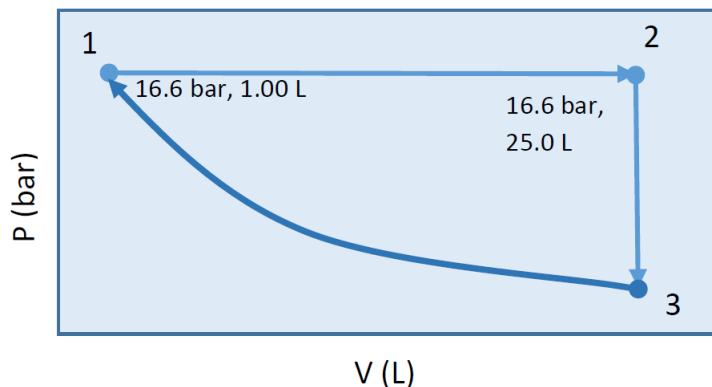
Constants and unit conversions: $R = 8.314462 \text{ m}^3 \text{ Pa mol}^{-1} \text{ K}^{-1}$, $a = 4.2 \text{ dm}^6 \text{ atm mol}^{-2} = 0.4242 \text{ m}^6 \text{ Pa mol}^{-2}$, $b = 5.11 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} = 5.11 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$, $V_i = 1.0 \times 10^{-3} \text{ m}^3$, $V_f = 2.0 \times 10^{-3} \text{ m}^3$, $n = 1 \text{ mole}$, $T = 298 \text{ K}$

| | a | b | w |
|---------------------|--|--|-------------------|
| ideal gas | 0 | 0 | -1717 J |
| Van der Waals gas 1 | 0 | $5.11 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ | -1724 J |
| Van der Waals gas 2 | $0.4242 \text{ m}^6 \text{ Pa mol}^{-2}$ | 0 | -1505 J |

Indicator diagram created by using Desmos



7. A system containing 2.50 moles of an ideal gas for which $C_{vm} = 20.79 \text{ J mol}^{-1} \text{ K}^{-1}$ is taken through a cycle in the following diagram in the direction indicated by the arrows. The curved path corresponds to $PV = nRT$, where $T = T_1 = T_3$.



Calculate q , w , ΔU , and ΔH for each segment and for the entire cycle. Identify what type of process occurs and each step, and explain your calculations. Explain how the values change if the path is reversed.

$$T_2 = \frac{P_2 V_2}{nR} = \frac{16.6 \text{ bar} \times 25.0 \text{ L}}{2.5 \text{ mol} \times 0.08314 \text{ bar L mol}^{-1} \text{ K}^{-1}} = 1996.6 \text{ K}$$

$$T_1 = T_3 = \frac{P_1 V_1}{nR} = \frac{16.6 \text{ bar} \times 1.00 \text{ L}}{2.5 \text{ mol} \times 0.08314 \text{ bar L mol}^{-1} \text{ K}^{-1}} = 79.9 \text{ K}$$

$$P_3 = \frac{nRT_3}{V_3} = \frac{2.5 \text{ mol} \times 0.08314 \text{ bar L mol}^{-1} \text{ K}^{-1} \times 79.9 \text{ K}}{25.0 \text{ L}} = 0.66 \text{ bar}$$

For process $1 \rightarrow 2$, which is a isobaric process:

$$\begin{aligned} \Delta U_{1 \rightarrow 2} &= C_{vm}(T_2 - T_1) \\ &= \frac{C_{vm}}{nR}(P_2 V_2 - P_1 V_1) \\ &= \frac{2.5 \text{ mol} \times 20.79 \text{ J mol}^{-1} \text{ K}^{-1}}{(2.5 \text{ mol})(0.08314462 \text{ L bar mol}^{-1} \text{ K}^{-1})}(16.6 \text{ bar} \times 25.0 \text{ L} - 16.6 \text{ bar} \times 1.00 \text{ L}) \\ &= 99618 \text{ J} = \boxed{99.6 \text{ kJ}} \end{aligned} \quad (6)$$

$$\begin{aligned} w &= -P_{ex}(V_2 - V_1) \\ &= -(16.6 \text{ bar} \times (25 \text{ L} - 1 \text{ L})) \\ &= -398.4 \text{ bar L} \\ &= \boxed{-39.8 \text{ kJ}} \end{aligned} \quad (7)$$

$$\begin{aligned} q &= \Delta U - w \\ &= 99.6 \text{ kJ} - (-39.8 \text{ kJ}) \\ &= \boxed{139.4 \text{ kJ}} \end{aligned} \quad (8)$$

$$\begin{aligned} \Delta H_{1 \rightarrow 2} &= \Delta U_{1 \rightarrow 2} + \Delta(PV) \\ &= \Delta U_{1 \rightarrow 2} + nR\Delta(T) \\ &= 99.6 \text{ kJ} + 2.5 \text{ mol} \times 8.3145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \times (1996.6 \text{ K} - 79.9 \text{ K}) = \boxed{139.4 \text{ kJ}} \end{aligned} \quad (9)$$

For process $2 \rightarrow 3$, which is a isochoric process:

$$\boxed{w = 0J} \text{ because } \Delta V = 0$$

$$\begin{aligned}
 q &= \Delta U_{2 \rightarrow 3} = C_{vm}(T_3 - T_2) \\
 &= \frac{C_{vm}}{nR}(P_3V_3 - P_2V_2) \\
 &= \frac{2.5mol \times 20.79J mol^{-1}K^{-1}}{(2.5mol)(0.08314462Lbar mol^{-1}K^{-1})}(0.66bar \times 25.0L - 16.6bar \times 25.0L) \\
 &= -99643J = \boxed{-99.6kJ}
 \end{aligned} \tag{10}$$

$$\begin{aligned}
 \Delta H_{2 \rightarrow 3} &= \Delta U_{2 \rightarrow 3} + \Delta(PV) \\
 &= \Delta U_{2 \rightarrow 3} + nR\Delta(T) \\
 &= -99.6kJ + 2.5mol \times 8.3145 \times 10^{-3}kJK^{-1}mol^{-1} \times (79.9K - 1996.6K) = \boxed{-139.4kJ}
 \end{aligned} \tag{11}$$

For process 3 → 1, which is a isothermal process:

$$\Delta U_{3 \rightarrow 1} = \Delta H_{3 \rightarrow 1} = \boxed{0kJ} \text{ because } \Delta T = 0$$

$$w = -nRT_1 \ln \frac{V_1}{V_3} = -2.5mol \times 8.134 \times 10^{-3}kJmol^{-1}K^{-1} \times 79.9 \ln \frac{1.0L}{25.0L} = \boxed{5.35kJ} \tag{12}$$

$$q = \Delta U - w = 0 - 5.35 = \boxed{-5.35kJ}$$

For the entire process

$$q = \Sigma q = 139.4kJ - 99.6kJ - 5.35kJ = \boxed{34.5kJ}$$

$$w = \Sigma w = -39.8kJ + 0kJ + 5.35kJ = \boxed{-34.5kJ}$$

$$\Delta U = \Sigma \Delta U = 99.6kJ - 99.6kJ = \boxed{0kJ}$$

$$\Delta H = \Sigma \Delta H = 139.4kJ - 139.4kJ = \boxed{0kJ}$$

If the path is reversed, the sign of the values will also be reversed.

8. Calculate ΔH and ΔU for the transformation of 1mol of ideal gas from 27.0°C at 1.00atm to 327°C and 17.0atm if $C_{p,m} = 20.9 + 0.042T$ (in units of $JK^{-1}mol^{-1}$).

Unit conversions: 27°C = 300.15K, 327°C = 600.15K

$$\begin{aligned}
 \Delta H &= n \int_{T_i}^{T_f} C_{p,m} dT = n \int_{300.15}^{600.15} (20.9 + 0.042T) dT \\
 &= 1mol \times \left(20.9T + 0.042 \times \frac{T^2}{2} \right) \Big|_{300.15}^{600.15} \\
 &= 20.9(600.15 - 300.15) + 0.042 \times \frac{(600.15 - 300.15)^2}{2} \\
 &= 11941.89J = \boxed{11.9kJ}
 \end{aligned} \tag{13}$$

$$\begin{aligned}
\Delta U &= \Delta H - \Delta(PV) \\
&= \Delta H - nR\Delta T \\
&= 11.9kJ - 1mol \times 8.314 \times 10^{-3}kJmol^{-1}K^{-1} \times (600.15K - 300.15K) \\
&= \boxed{9.41kJ}
\end{aligned} \tag{14}$$

For extra practice on shorter problems, work on the following exercises: 1A: 3a; 4a; 5a; 7a; 8a;; 1C: 1a, 3a, 6a, 7a, 8a

1. Consider a 20.0 L sample of moist air at 60 °C and 1 atm in which the partial pressure of water vapor is 0.120 atm. Assume that *dry air* has the composition of 78.0 mole % N₂, 21.0 mole % O₂, and 1.00 mole % Ar. State any assumptions made in solving the following problems.
 - a. What are the mole percentages of each of the gases in the moist air sample?
 - b. The percent relative humidity (%RH) = $\frac{P_{H_2O}}{P_{H_2O}^*}$, is a measure of the actual amount of water vapor in the air compared to the total amount of vapor that can exist in the air at its current temperature. In this case, P_{H_2O} is the partial pressure of water in the sample, and $P_{H_2O}^* = 0.197 \text{ atm}$ is the equilibrium vapor pressure of water at 60 °C. (See <https://www.weather.gov/lmk/humidity> for more on %RH.) The gas is compressed at 60 °C until the relative humidity is 100%. What volume does the mixture contain now?
 - c. What fraction of the water will be condensed if the total pressure of the mixture is isothermally (no change in temperature) increased to 200 atm?

(Ans. N₂ 68.8%, O₂ 18.5%, Ar 8.8%, H₂O 12.0%; 12.2 L; 0.992)

Solutions:

a. Assuming ideal gas and Dalton's Law

The sum of the partial pressures of each gas gives the total pressure

$$P_{\text{moist air}} = P_{\text{water}} + P_{\text{dry air}} = P_{\text{water}} + P_{N_2} + P_{O_2} + P_{Ar}$$

By subtraction, the pressure of the dry air component can be determined

$$1 \text{ atm} = 0.120 \text{ atm} + P_{N_2} + P_{O_2} + P_{Ar}$$

$$P_{\text{dry air}} = P_{N_2} + P_{O_2} + P_{Ar} = 0.880 \text{ atm}$$

The mole fraction of water is determined by Dalton's Law

$$X_{\text{water}} = \frac{P_{\text{water}}}{P_{\text{moist air}}} = 0.12$$

The mole fraction of each gas is determined from the total pressure of the dry air and the mole fraction in that air using Dalton's Law:

$$X_{N_2} = \frac{P_{N_2}}{P_{\text{moist air}}} = \frac{X_{N_2} P_{\text{air}}}{P_{\text{moist air}}} = \frac{0.78 \cdot 0.880}{1} = 0.688$$

$$X_{O_2} = \frac{P_{O_2}}{P_{\text{moist air}}} = \frac{X_{O_2} P_{\text{air}}}{P_{\text{moist air}}} = \frac{0.21 \cdot 0.880}{1} = 0.185$$

$$X_{Ar} = \frac{P_{Ar}}{P_{\text{moist air}}} = \frac{X_{Ar} P_{\text{air}}}{P_{\text{moist air}}} = \frac{0.01 \cdot 0.880}{1} = 0.088$$

b. The relative humidity will be 100% when $P_{H_2O} = 0.197 \text{ atm}$

Neglecting intermolecular interactions, $P_1 V_1 = P_2 V_2$ as long as the temperature is unchanged.

$$0.120 \text{ atm} \cdot 20.0 \text{ L} = 0.197 \text{ atm} \cdot V_2$$

$$V_2 = 12.2 \text{ L}$$

c. Use ideal gas law to determine moles of water present in original mixture.

$$n = \frac{PV}{RT} = \frac{0.120 \text{ atm} \cdot 20 \text{ L}}{0.08206 \frac{\text{Latm}}{\text{K mole}} 333 \text{ K}} = 0.0878 \text{ moles water vapor}$$

To determine the volume of the mixture after compression, use $P_1 V_1 = P_2 V_2$, $1 \text{ atm} \cdot 20 \text{ L} = 200 \text{ atm} \cdot V_2$ gives $V_2 = 0.1 \text{ L}$

The amount of water vapor present at equilibrium at 60 °C is 0.197 atm. Use the pressure value with the final volume to determine the number of moles of water vapor present in the compressed mixture: $n =$

$$\frac{PV}{RT} = \frac{0.197 \text{ atm} \cdot 0.1 \text{ L}}{0.08206 \frac{\text{Latm}}{\text{Kmol}} \cdot 333\text{K}} = 0.000721 \text{ moles water vapor}$$

To determine the fraction that is condensed, subtract the fraction in the vapor phase from 1:

$$X_{\text{condensed}} = 1 - \frac{n(g)_{\text{water,compressed}}}{n(g)_{\text{water,original}}} = 1 - \frac{0.000721}{0.0878} = 0.992$$

2. a. Calculate the pressure exerted by N₂ at 300 K for molar volumes of 250 and 0.100 L using the ideal gas and the van der Waals equations of state. Use $a = 1.370 \text{ bar dm}^6 \text{ mol}^{-2}$ $b = 3.87 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$ for the N₂ vdW coefficients.
- b. Compare the results of your calculations at the two pressures. If P calculated using the vdW equation of state is greater than those calculated with the ideal gas law, the repulsive forces outweigh attractive forces at that density. A similar statement could be made for attractive forces. Is the attractive or repulsive interaction greater for N₂ at 300 K and $V_m = 250 \text{ L}$? For 300 K and 0.100 L?

(Ans. $9.98 \times 10^{-2} \text{ bar}$; 249 bar; $9.98 \times 10^{-2} \text{ bar}$; 270 bar)

Solution:

The pressure calculated from the ideal gas equation of state

$$P = \frac{nRT}{V} = \frac{1 \text{ mol} \times 8.314 \times 10^{-2} \frac{\text{Lbar}}{\text{molK}} \times 300\text{K}}{250\text{L}} = 9.98 \times 10^{-2} \text{ bar}$$

$$P = \frac{nRT}{V} = \frac{1 \text{ mol} \times 8.314 \times 10^{-2} \frac{\text{Lbar}}{\text{molK}} \times 300\text{K}}{0.100\text{L}} = 249 \text{ bar}$$

The pressure calculated from the vdW equation of state

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} = \frac{1 \text{ mol} \times 8.314 \times 10^{-2} \frac{\text{Lbar}}{\text{molK}} \times 300\text{K}}{250\text{L} - \left(1 \text{ mol} \times 3.87 \times 10^{-2} \frac{\text{L}}{\text{mol}}\right)} - \frac{(1 \text{ mol})^2 1.370 \frac{\text{barL}^2}{\text{mol}^2}}{(250\text{L})^2}$$

$$= 9.98 \times 10^{-2} \text{ bar}$$

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} = \frac{1 \text{ mol} \times 8.314 \times 10^{-2} \frac{\text{Lbar}}{\text{molK}} \times 300\text{K}}{0.100\text{L} - \left(1 \text{ mol} \times 3.87 \times 10^{-2} \frac{\text{L}}{\text{mol}}\right)} - \frac{(1 \text{ mol})^2 1.370 \frac{\text{barL}^2}{\text{mol}^2}}{(0.100\text{L})^2}$$

$$= 270 \text{ bar}$$

b. At 250 L, the pressures calculated with the ideal gas and vdW equation of state are the same, indicating that no intermolecular forces are predominant. At 0.100 L, the vdW equation of state predicts a higher pressure than that predicted by the ideal gas equation of state. Therefore, the repulsive interactions are more important than the attractive interactions at this temperature and volume.

3. Look up the van der Waals constants for the following substances: NH₃, N₂, CH₂Cl₂, Cl₂, CCl₄. (Give your source.) Which of the following substances has the smallest value of the van der Waals value a ? The largest value of b ? **Explain why.** (N₂; CCl₄)

Solution: (i) N₂

The value of the Van der Waals constant, a , of a given gaseous substance depends on the strength of attractions between its component molecules. Molecules experiencing the weakest attractive forces will have the smallest a constant while those with the strongest attractive forces will have the largest a values.

Of the molecules NH_3 ($a=4.169 \text{ atm L}^2\text{mol}^{-2}$; $b = 0.0371 \text{ Lmol}^{-1}$), N_2 ($a= 1.352 \text{ atm L}^2\text{mol}^{-2}$; $b= 0.0387 \text{ Lmol}^{-1}$), CH_2Cl_2 ($a=12.44 \text{ bar L}^2\text{mol}^{-2}$; $b = 0.0869 \text{ Lmol}^{-1}$), Cl_2 ($a =6.260 \text{ atm L}^2\text{mol}^{-2}$; $b= 0.0542 \text{ Lmol}^{-1}$), CCl_4 ($a=20.01 \text{ bar L}^2\text{mol}^{-2}$; $b = 0.1281 \text{ Lmol}^{-1}$), the two molecules nitrogen and chlorine alone have non-polar bonds between their component atoms. This results in weaker attractions between molecules, so N_2 and Cl_2 will have the smallest a values. The remaining molecules all have polar bonds between their component atoms and in the case of NH_3 , hydrogen bonds between molecules. These are factors that lead to increased a constants. As the N_2 molecule is smaller than the Cl_2 molecule and therefore has fewer electrons present, the attractive forces between N_2 molecules will be weaker than those between Cl_2 molecules and N_2 will have the smallest a constant. (van der Waals constants from Table 1C.3 and http://www2.ucdsb.on.ca/tiss/stretton/database/van_der_waals_constants.html)

(ii) CCl_4

The value of the van der Waals b constant is merely the actual volume of a mole of the molecules and this can be deduced by comparing the volumes of the molecules in the list. Small molecular volume results in small b values and a large molecular volume corresponds to a large b constant. From the compound in the list, CCl_4 is the largest and so it will have the greatest b constant.

4. a. Show that the virial coefficient B is related to the van der Waals constant b as $B = b - \frac{a}{RT}$. You will need to expand the van der Waals expression in a virial expansion in terms of $\frac{1}{V_m}$ and use the approximation $(1 - x)^{-1} = 1 + x + x^2 + x^3 + \dots \approx 1 + x$.
- b. Use the virial series with the vdW constants to identify the conditions for which $Z < 1$, and $Z > 1$. Do the results make sense physically? Explain. (**Ans. to part b: $Z > 1$ when $b > \frac{a}{RT}$. $Z < 1$ when $b < \frac{a}{RT}$.**)

Solution:

Start with the vdW equation: $P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$

Multiply both sides with the molar volume: $PV_m = \frac{RTV_m}{V_m - b} - \frac{a}{V_m}$

Rewriting gives: $PV_m = RT \left(\frac{V_m}{V_m - b} \right) - \frac{a}{V_m}$

Dividing the numerator and denominator of the first term by the molar volumes gives

$$PV_m = RT \left(\frac{1}{1 - \frac{b}{V_m}} \right) - \frac{a}{V_m}$$

Using the series approximation for the term in parentheses gives

$$PV_m = RT \left(1 + \frac{b}{V_m} \right) - \frac{a}{V_m}$$

Combining the terms in molar volume gives

$$PV_m = RT + (bRT - a) \frac{1}{V_m}$$

Dividing through by RT gives

$$\frac{PV_m}{RT} = 1 + \left(b - \frac{a}{RT} \right) \frac{1}{V_m}$$

The term on the left is just Z , but the virial series shows that the coefficient in front of the reciprocal of the molar volume is the virial coefficient B

$$Z = \frac{PV_m}{RT} = 1 + B \frac{1}{V_m}$$

Comparison of the two expressions shows that

$$B = b - \frac{a}{RT}$$





b. Start with $Z = 1 + \left(b - \frac{a}{RT} \right) \frac{1}{V_m}$

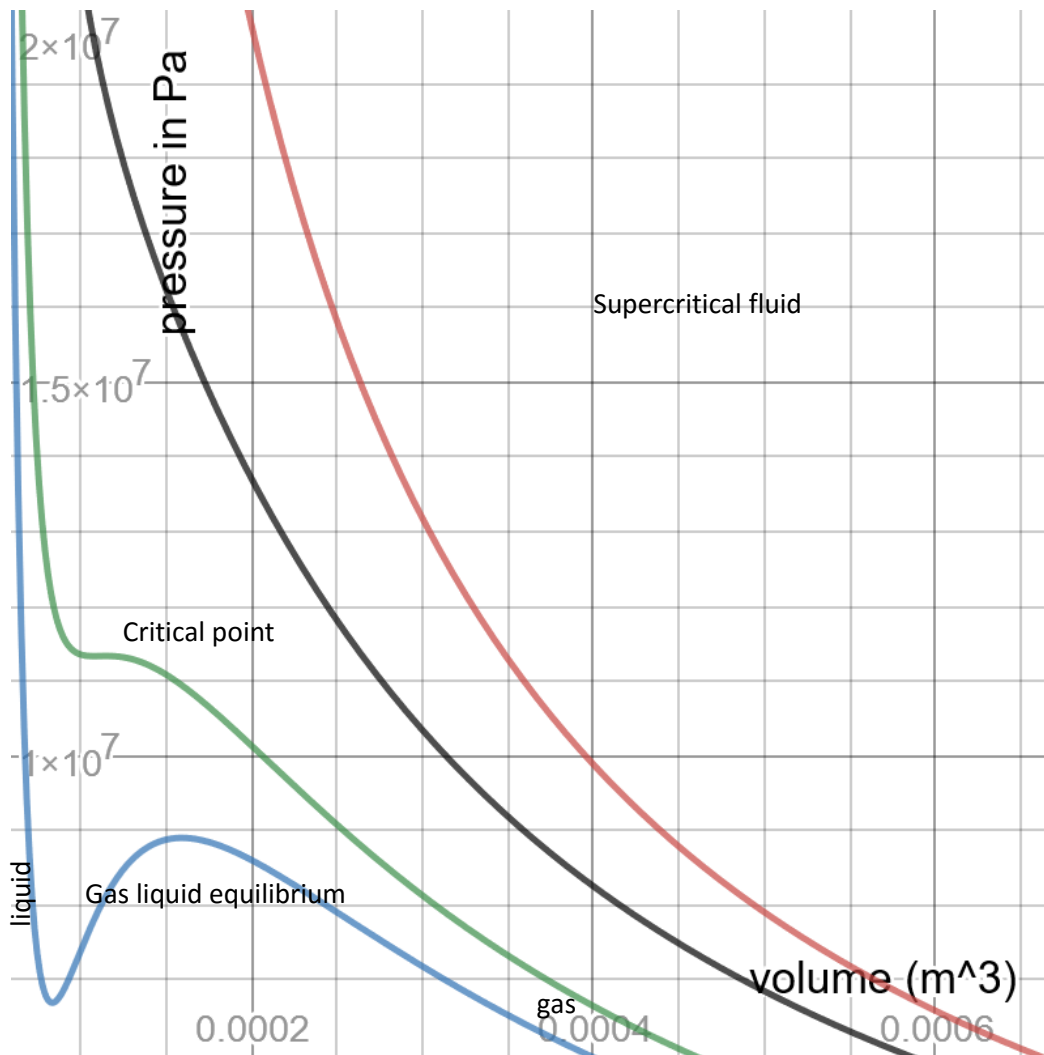
Since the molar volume can never be negative, it follows that $Z > 1$, when the second term is positive, i.e. $b > \frac{a}{RT}$. $Z < 1$ when the second term is negative, $b < \frac{a}{RT}$. Remember that another way of defining Z is $\frac{V_m}{V_m^\circ}$, where V_m° is the molar volume of a perfect gas. That means that the $Z > 1$ when the volume of the gas is larger than ideal. That will happen when repulsive forces predominate. $Z < 1$ when the volume of the gas is smaller than the ideal gas. That happens when attractive forces predominate.

5. Plot PV isotherms for NH_3 at the critical temperature, 30 degrees above the critical temperature, and 30 degrees below the critical temperature. Also plot the ideal gas isotherm at the highest temperature. Label the regions of supercritical fluid, gas, liquid, and gas/liquid equilibrium. Cite your sources for all constants. Comment on the features of the graph.

Solution: $T_c = 405.56 \text{ K}$; $P_c = 11.357 \text{ MPa}$ (critical constants from the CRC Handbook of Chemistry and Physics); $a = 4.225 \text{ bar L}^2\text{mol}^{-2}$; $b = 0.0371 \text{ L/mol}$ (vdw Constants from Wikipedia).

Plot made with desmos.com. (Be careful of units! I used P in Pa and V in m^3)

| | | |
|---|---|---|
| 1 |  | $y_1 = 8.3145 \cdot \frac{435}{X}$ |
| 2 |  | $y_2 = 8.314 \cdot \frac{435}{(X - 0.0371 \cdot 10^{-3})} - \left(\frac{(4.225 \cdot 10^{-1})}{X^2} \right)$ |
| 3 |  | $y_3 = 8.314 \cdot \frac{405}{(X - 0.0371 \cdot 10^{-3})} - \left(\frac{(4.225 \cdot 10^{-1})}{X^2} \right)$ |
| 4 |  | $y_4 = 8.314 \cdot \frac{375}{(X - 0.0371 \cdot 10^{-3})} - \left(\frac{(4.225 \cdot 10^{-1})}{X^2} \right)$ |



<https://www.desmos.com/calculator/ge7kx80qv>

Above the critical temperature, the vdW isotherm is similar to the ideal gas isotherm, though the vdW gas exhibits lower volumes at all pressures, indicating the importance of attractive interactions. At the critical temperature, there is an inflection at the critical point. Below the critical temperature, the isotherm exhibits van der Waals loops. In this region, the gas and liquid are in equilibrium. The largest volume represents the gas volume and the smallest volume represents the liquid volume.

6. a. Show that $r_m = 2^{1/6}\sigma$ for the Lennard-Jones potential.
- b. Determine the value of r_m for N_2 . (LJ values can be found in class notes.)
- c. Plot the potential energy (in units of K) for the interaction of two molecules of N_2 . Comment on the appearance of the graph.

(Ans to part b: $r_m = 415 \text{ pm}$)

Solutions:

a. r_m is the distance where the potential function is a minimum. To find the minimum, take the derivative of the potential function and set it to zero.

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

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

$$12 \left(\frac{\sigma^{12}}{r_m^{13}} \right) = 6 \left(\frac{\sigma^6}{r_m^7} \right)$$

$$2\sigma^6 = r_m^6$$

$$2^{1/6}\sigma = r_m$$

b. Using the values from the notes, $\sigma = 370 \text{ pm}$

$$2^{1/6}(370 \text{ pm}) = r_m$$

$$r_m = 415 \text{ pm}$$

c. Graph printed at desmos.com. Note that $U=0$ at 370 pm and U is at a minimum where $r=415 \text{ pm}$ as expected. Also, the well depth is -95 K , as given by the L-J parameter.

