How good is the Ideal Gas Approximation? A comparison with the Van der Walls' Equation.

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Constants:

$$R := 8.31441 \cdot \frac{joule}{mole \cdot K} \qquad molecule := \frac{1}{6.02 \cdot 10^{23} \cdot mole}$$

Molecules: (Index to link different molecules to array for constants)

$He := 0 \qquad O2 := 3 \qquad CO2 := 6$

$Xe := 1 \qquad H2O := 4 \qquad SO2 := 7$

$H2 := 2 \qquad Cl2 := 5 \qquad CH4 := 8$

Van der Walls' Constants

Units in Kask and Rawn

SI Units

$$a := \begin{bmatrix} 0.0341 \\ 4.19 \\ 0.244 \\ 1.36 \\ 5.46 \\ 6.49 \\ 3.59 \\ 6.71 \\ 2.25 \end{bmatrix} \cdot liter^2 \cdot atm \cdot mole^{-2} \quad a = \begin{bmatrix} 3.455 \cdot 10^{-3} \\ 0.425 \\ 0.025 \\ 0.138 \\ 0.553 \\ 0.658 \\ 0.364 \\ 0.68 \\ 0.228 \end{bmatrix} \cdot m^6 \cdot Pa \cdot mole^{-2} \quad a = \begin{bmatrix} 0 \\ 1.171 \cdot 10^{-48} \\ 6.822 \cdot 10^{-50} \\ 3.802 \cdot 10^{-49} \\ 1.527 \cdot 10^{-48} \\ 1.815 \cdot 10^{-48} \\ 1.004 \cdot 10^{-48} \\ 1.876 \cdot 10^{-48} \\ 6.291 \cdot 10^{-49} \end{bmatrix} \cdot m^3 \cdot mole^{-4} \cdot joule \cdot molecule^{-}$$

$$b := \begin{bmatrix} 0.0237 \\ 0.0510 \\ 0.0266 \\ 0.0318 \\ 0.030 \\ 0.0562 \\ 0.0427 \\ 0.056 \\ 0.0428 \end{bmatrix} \cdot liter \cdot mole^{-1} \quad b = \begin{bmatrix} 2.37 \cdot 10^{-5} \\ 5.1 \cdot 10^{-5} \\ 2.66 \cdot 10^{-5} \\ 3.18 \cdot 10^{-5} \\ 3 \cdot 10^{-5} \\ 5.62 \cdot 10^{-5} \\ 4.27 \cdot 10^{-5} \\ 5.6 \cdot 10^{-5} \\ 4.28 \cdot 10^{-5} \end{bmatrix} \cdot m^3 \cdot mole^{-1} \quad b = \begin{bmatrix} 3.937 \cdot 10^{-29} \\ 8.472 \cdot 10^{-29} \\ 4.419 \cdot 10^{-29} \\ 5.282 \cdot 10^{-29} \\ 4.983 \cdot 10^{-29} \\ 9.336 \cdot 10^{-29} \\ 7.093 \cdot 10^{-29} \\ 9.302 \cdot 10^{-29} \\ 7.11 \cdot 10^{-29} \end{bmatrix} \cdot m^3 \cdot mole^{-2} \cdot molecule^{-1}$$

Comparison of Van der Walls' with Ideal Gas

Conditions

Gas $x := He$

Equations

Ideal Gas $$p_{ideal}(v,t) := \frac{R\cdot(t+273.15)\cdot K}{v}$$

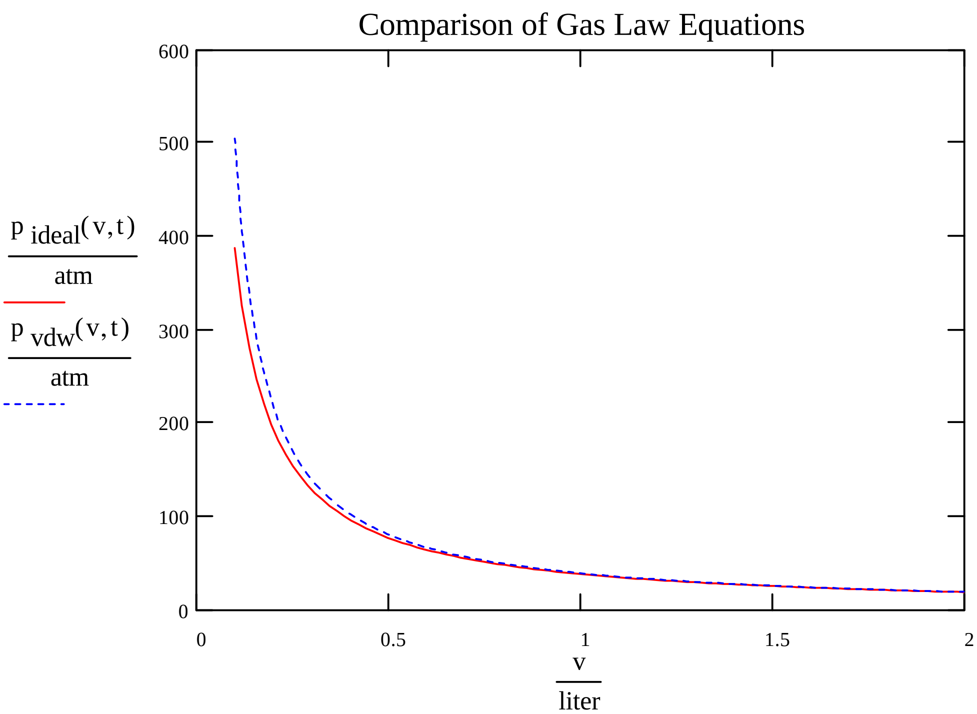
Van der Walls' Gas $$p_{vdw}(v,t) := \left[\frac{R\cdot(t+273.15)\cdot K}{v-b_x} - \frac{a_x}{v^2}\right]$$

Molar Volume

$$v_{initial} := 0.1\cdot\frac{liter}{mole} \qquad v_{final} := 2\cdot\frac{liter}{mole}$$

$$v := v_{initial}, v_{initial} + \left(\frac{v_{final} - v_{initial}}{100}\right) .. v_{final}$$

Temperature (C) $t := 200$



Temperature Comparisons for Gases

Gas $x := CO2$

Temperature

$t_{initial} := 0 \qquad t_{final} := 40$

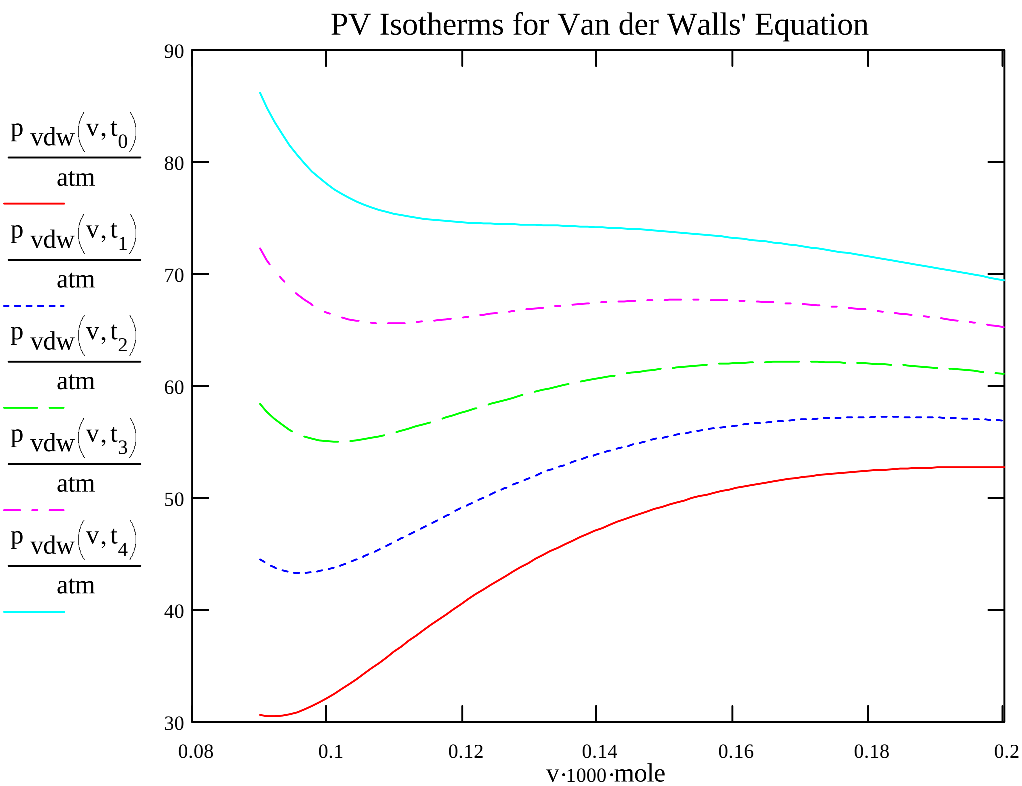
Equations

$$p_{vdw}(v,t) := \left[\frac{R\cdot(t+273.15)\cdot K}{v-b_x} - \frac{a_x}{v^2}\right] \qquad i := 0,1..5 \qquad t_i := \left[t_{initial} + \left(\frac{t_{final} - t_{initial}}{5}\right)\cdot i\right]$$

Molar Volume

$$v_{initial} := 0.090\cdot\frac{liter}{mole} \qquad v_{final} := 0.2\cdot\frac{liter}{mole}$$

$$v := v_{initial}, v_{initial} + \left(\frac{v_{final} - v_{initial}}{100}\right) .. v_{final}$$



Temp (C)

$t_0 = 0$

$t_1 = 8$

$t_2 = 16$

$t_3 = 24$

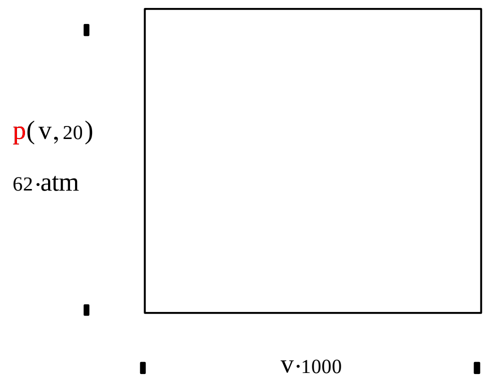
$t_4 = 32$

(b) liquid liquid & gas gas

(c) The boundaries of the two-phase region are the extreme intersections of constant P such that equal areas lie between P and the p(v) curve. For this, estimate the volumes from this graph and use to solve numerically

$$v := 90\cdot\frac{cm^3}{mole}, 92\cdot\frac{cm^3}{mole} .. 240\cdot\frac{cm^3}{mole}$$

from this graph and use to solve numerically for precise volumes. Then vary P, by trial and error, to obtain equal volumes.



Find the pressure, P, at which CO_2 boils at a temperature of 20 degrees Celcius.

$t := 20$ $\quad P := 6.4015 \cdot 10^6 \cdot Pa$ $\quad$ Vary this pressure until the integral becomes zero.

Liquid volume: $\quad P = 63.178 \circ atm$

$f(v) := p(v, t) - P$

(guess) $\quad v := .09 \cdot dm^3$

$v0 := root(f(v), v) \quad v0 = \ \circ dm^3$

Gas volume: $\quad v := v0 + .11 \cdot dm^3$ (guess from graph)

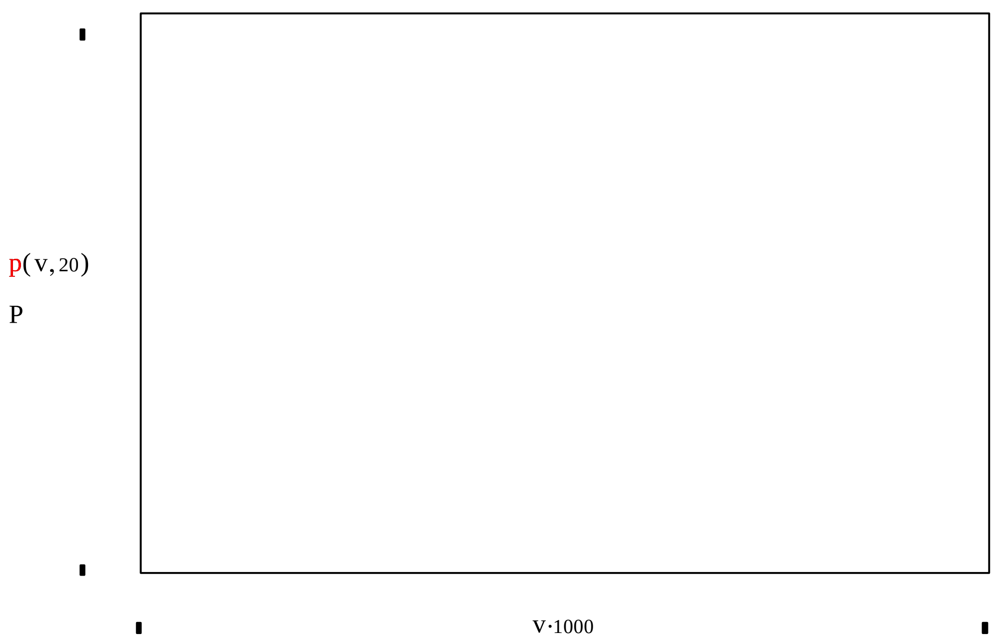
$v1 := root(f(v), v) \quad v1 = \ \circ dm^3$

This is the equal areas integral:

$$\int_{v0}^{v1} p(v, t) - P \, dv = \ \circ joule$$

Graph again to check:

$P := 6.4015 \cdot 10^6 \cdot Pa$ $\quad v := 90 \cdot \frac{cm^3}{mole}, 92 \cdot \frac{cm^3}{mole} .. 240 \cdot \frac{cm^3}{mole}$



(d) Density of liquid and gas at 20Celcius and boiling pressure:

$$\rho liq := \frac{(12.011 + 2\cdot 15.9994)\cdot gm}{v0} \qquad \rho liq = \circ \frac{gm}{dm^3}$$

$$\rho gas := \frac{(12.011 + 2\cdot 15.9994)\cdot gm}{v1} \qquad \rho gas = \circ \frac{gm}{dm^3}$$

$$\Delta\rho := \rho liq - \rho gas \qquad \Delta\rho = \circ \frac{gm}{dm^3}$$

Units: $dm \equiv \frac{m}{10}$