

# Van der Waal's Equation of State

## History

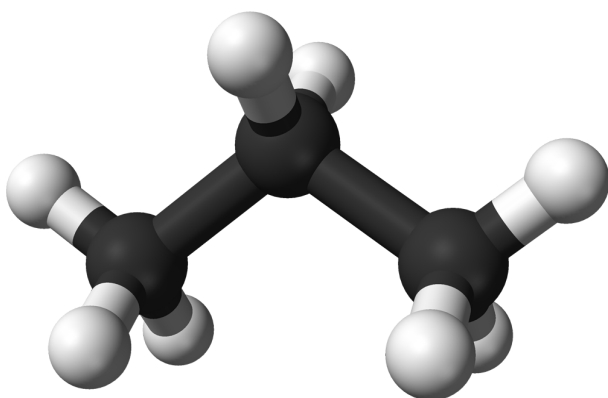
The van der Waals equation is a thermodynamic equation of state based on the theory that fluids are composed of particles with non-zero volumes, and subject to a (not necessarily pairwise) inter-particle attractive forces. It was based on work in theoretical physical chemistry performed in the late 19th century by Johannes Diderik van der Waals, who did related work on the attractive force that also bears his name. The equation is known to be based on a traditional set of derivations deriving from van der Waals' and related efforts, as well as a set of derivation based in statistical thermodynamics.

The ideal gas law treats the molecules of a gas as point particles with perfectly elastic collisions. This works well for dilute gases in many experimental circumstances. But gas molecules are not point masses, and there are circumstances where the properties of the molecules have an experimentally measurable effect. A modification of the ideal gas law was proposed by Johannes D. van der Waals in 1873 to take into account molecular size and molecular interaction forces. It is usually referred to as the van der Waals equation of state.

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

The constants *a* and *b* have positive values and are characteristic of the individual gas. The van der Waals equation of state approaches the ideal gas law  $PV=nRT$  as the values of these constants approach zero. The constant '*a*' provides a correction for the intermolecular forces. Constant '*b*' is a correction for finite molecular size and its value is the volume of one mole of the atoms or molecules.

## For Propane (C<sub>3</sub>H<sub>8</sub>)



$$a = 8.779 \text{ L}^2\text{bar/mol}^2$$

$$b = 0.08445 \text{ L/mol}$$

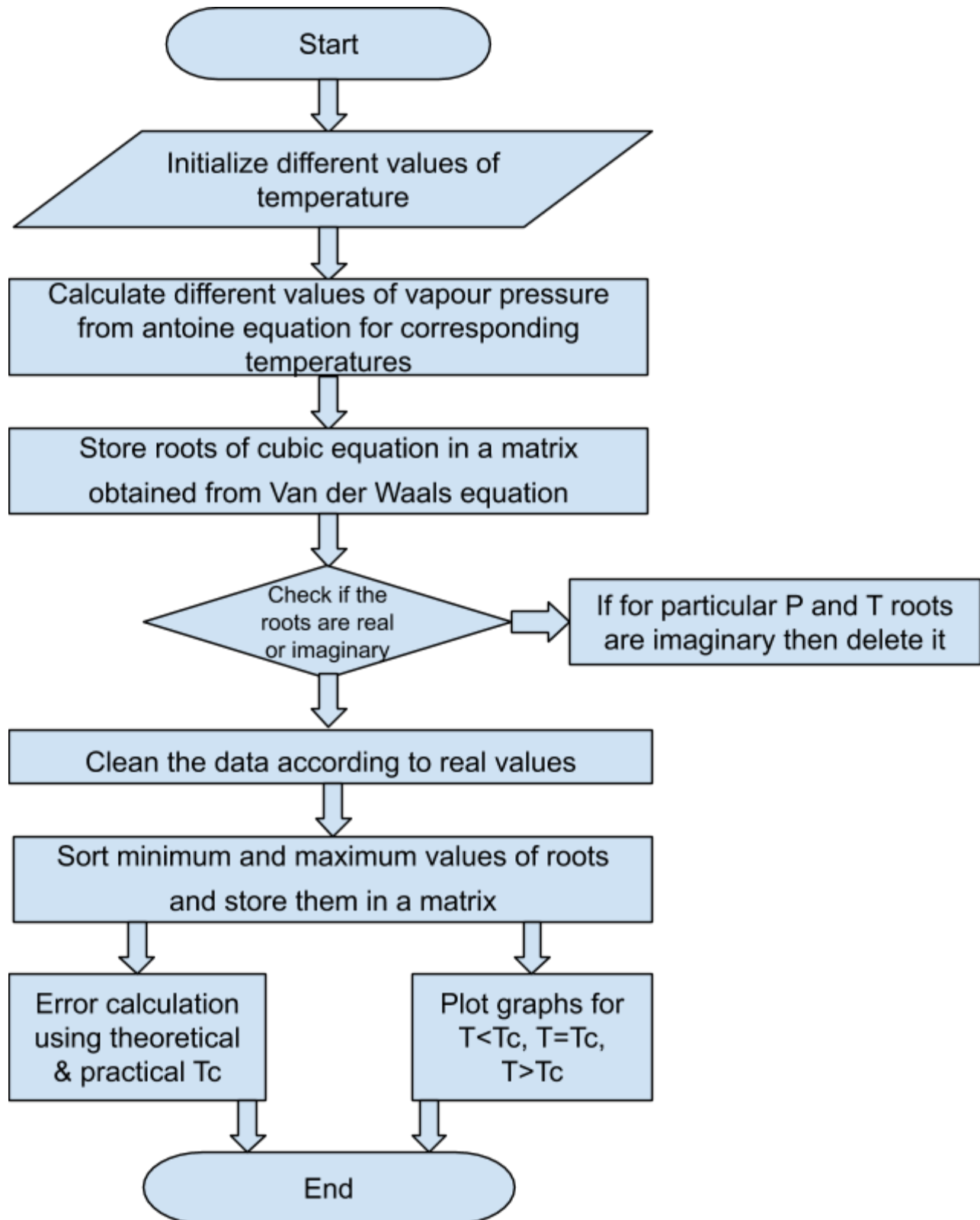
$$\text{Antoine Equation } \log_{10} P = A - B/(T+C)$$

$$P = \text{Vapour Pressure (bar)}$$

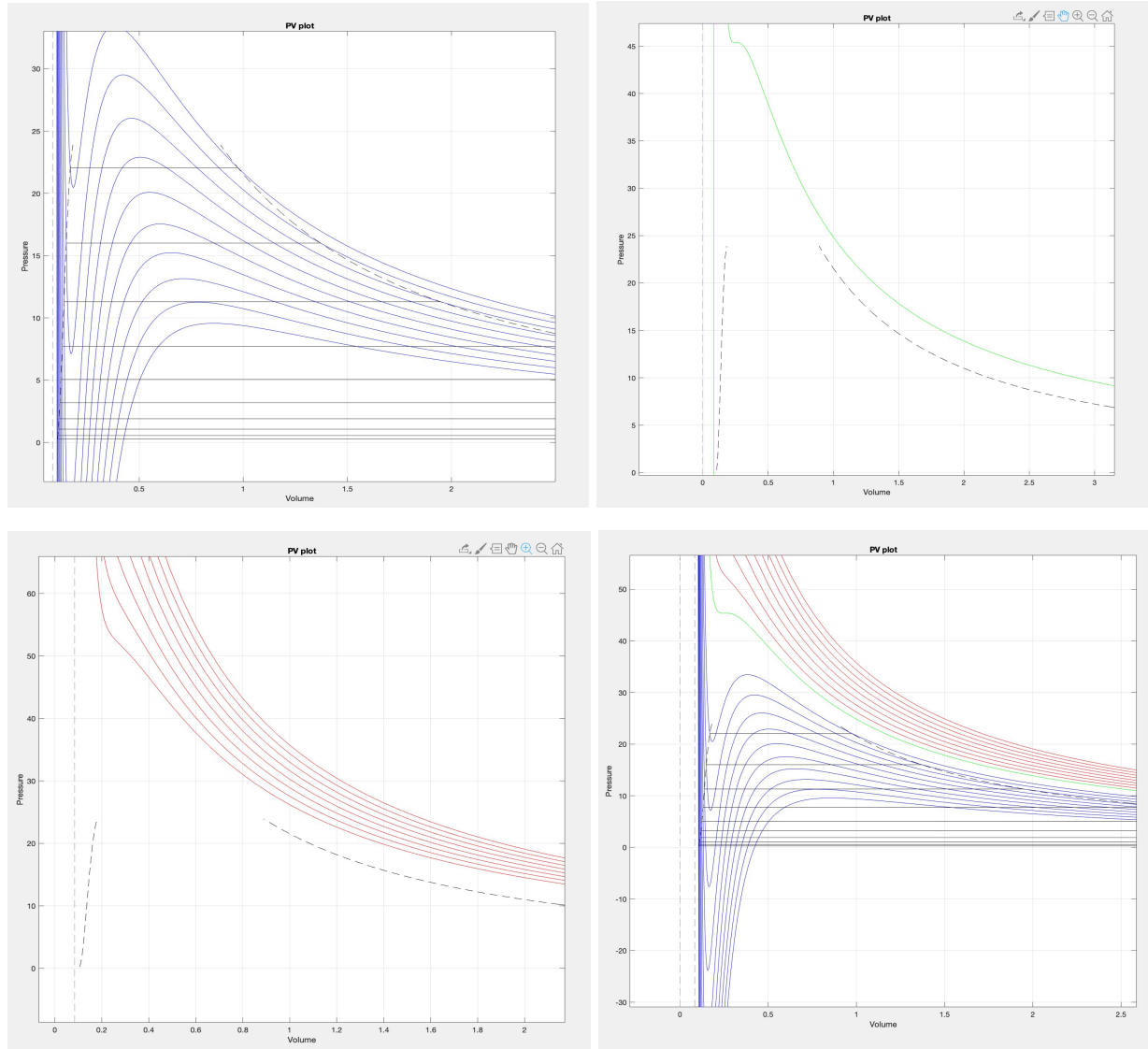
$$T = \text{Temperature (K), (277.6 - 360.8)K}$$

$$A = 4.53678, B = 1149.36, C = 24.906$$

## Algorithm Flowchart



# Graphs of Different Plots



## Analysis of Plot

In the above plot, the red lines represent isotherms for  $T > T_c$ , the green line represent isotherm for  $T = T_c$ , the blue lines represent isotherm for  $T < T_c$ . Liquid Vapour dome is symbolized by dashed black lines in all the 4 plots, which are basically the minimum and maximum real volume (roots) of the Van der Waals equation for a given pressure and temperature. Black coloured lines represent the actual property of propane in liquid vapour composition.

Critical Temperature comes to be 340 K, the theoretical critical temperature is 370K, therefore, the error comes out to be 0.0823.

## Why this error?

As the Antoine equation has the temperature range of 277.6 - 360.8 K and theoretical critical temperature is 370K, so we cannot find vapour pressure accurately at 370K. This error is due to the system chosen. If we have used any better way of finding vapour pressure other than Antoine equation, our error would have reduced significantly.

## Code

```
a = 8.779; %(L^2bar/mol^2)
b = 0.08445; %(L/mol)
R = 0.08314; %((L*bar)/(K*mol))
P = 0;
A = 4.53678;
B = 1149.36;
C = 24.906;
x = zeros; %different values of pressure
y = zeros; %different values of temperature
for T = 200 : 1 : 400
    x(T - 199) = 10^(A - (B / (T + C))); % Antoine's Equation
    y(T - 199) = T;
end
r = zeros(201, 3);
for i = 1 : 201
    coeff = [x(i), -(x(i) * b + R * y(i)), a, -a*b]; % Van der Waals equation in coefficient form
    r(i, :) = roots(coeff);
end
s = zeros(201,3);
for i = 1 : 201 % check for real data
    c = isreal(r(i,2));
    if c == 1
        s(i,:) = r(i,:);
    end
end
t = 201;
while t > 0 % eliminate imaginary roots and clean data
    if s(t, 1) == 0
        s(t, :) = [];
        x(t) = [];
        y(t) = [];
    end
    t = t - 1;
end
m = zeros(140,2);
for i = 1 : 140 % initiale min and max root
    m(i,2) = max(r(i,:));
    m(i,1) = min(r(i,:));
end
Tc = y(140) + 1; % critical temperature form the graph % error calculation
TcT = (8 * a) / (27 * R * b); % Theoretical critical temperature
error = (TcT - Tc)/TcT;
disp(error);
for i = 1 : 15 : 140 % plot for (T < Tc)
    fplot(@(V) ((R * y(i)) / (V-b)) - (a/(V^2)), 'blue');
```

```

title('PV plot');
xlabel('Volume');
ylabel('Pressure');
line([m(i,1) m(i,2)], [x(i) x(i)], 'color', 'black');
hold on;
plot(m,x,'k--');
hold on;
grid on;
end
for i = 370 % plot for (T = Tc)
    fplot(@(V) ((R * i) / (V-b)) - (a/(V^2)), 'green');
    title('PV plot');
    xlabel('Volume');
    ylabel('Pressure');
    hold on;
    plot(m,x,'k--');
    hold on;
    grid on;
end
for i = 385 : 15 : 490 % plot for (T > Tc)
    fplot(@(V) ((R * i) / (V-b)) - (a/(V^2)), 'red');
    hold on;
    title('PV plot');
    xlabel('Volume');
    ylabel('Pressure');
    hold on;
    plot(m,x,'k--');
    hold on;
    grid on;
end
end

```

## References

[https://en.wikipedia.org/wiki/Van\\_der\\_Waals\\_equation](https://en.wikipedia.org/wiki/Van_der_Waals_equation)  
<http://hyperphysics.phy-astr.gsu.edu/hbase/Kinetic/waal.html>  
[https://en.wikipedia.org/wiki/Van\\_der\\_Waals\\_constants\\_\(data\\_page\)](https://en.wikipedia.org/wiki/Van_der_Waals_constants_(data_page))  
[#ANTOINE](https://webbook.nist.gov/cgi/cbook.cgi?ID=C74986&Mask=4&Type=ANTOINE&Plot=on)  
<https://www.mathworks.com/help/matlab/>