

*CHE221 – Computational Assignment 1 Report***Equation of State: Vander Waal's Equation****Substance:** Methane (CH<sub>4</sub>)

**Vander Waal's Equation:** 
$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

**System Parameters:**

- P: Pressure (unit used for assignment “bar”)
- V: Volume (unit used for assignment “L/mol”)
- T: Temperature
- a: Vander Waal's constant which takes into account the intermolecular forces between gas molecules ignored in ideal gas equation =  $2.283 \frac{L^2 bar}{mol^2}$  (for methane)
- b: Vander Waal's constant which denotes that the total volume of a container is not available for the gas molecules to occupy =  $0.04278 \frac{L}{mol}$  (for methane)

**About Vander Waal's EOS:** (Source: <http://www.thermopedia.com/content/1232/>)

The van der Waals equation was proposed in the year 1873. It was a first step towards taking into account interaction forces that are acting between real gas molecules.

The equation of state of the perfect gas refers to a gas consisting of point-like items which do not interact with one another.

Instead of this Vander Waals proposed an equation

$$(v-b) \left( p + \frac{a}{v^2} \right) = RT,$$

where a and b are the so-called van der Waals constants and which have different values for each gas.

The b correction takes into account the fact that, according to van der Waals. The real gas molecules can move not in the total volume occupied by the gas, but only in a part of this volume, which is defined by subtracting what he called the molecules own volume. The correction  $a/v^2$  —proportional to the square of density—takes into account the attraction forces existing between gas molecules. According to the van der Waals assumption, these forces decrease the pressure against the vessel walls, because the molecules which are close to the wall are subjected to the attraction of other molecules.

The a and b constants are to be considered as empirical; they have to be derived from experimental data on the density, temperature, and pressure interdependence. For several technically important gases, the van der Waals constants are tabulated.

According to the method of allowing for deviation of a real gas from a perfect gas, the van der Waals equation supposedly would be valid only for small deviations, i.e., for moderate pressures. But it turned out that this equation qualitatively satisfactorily describes the real gases behavior in a wide range of parameters, including the critical region.

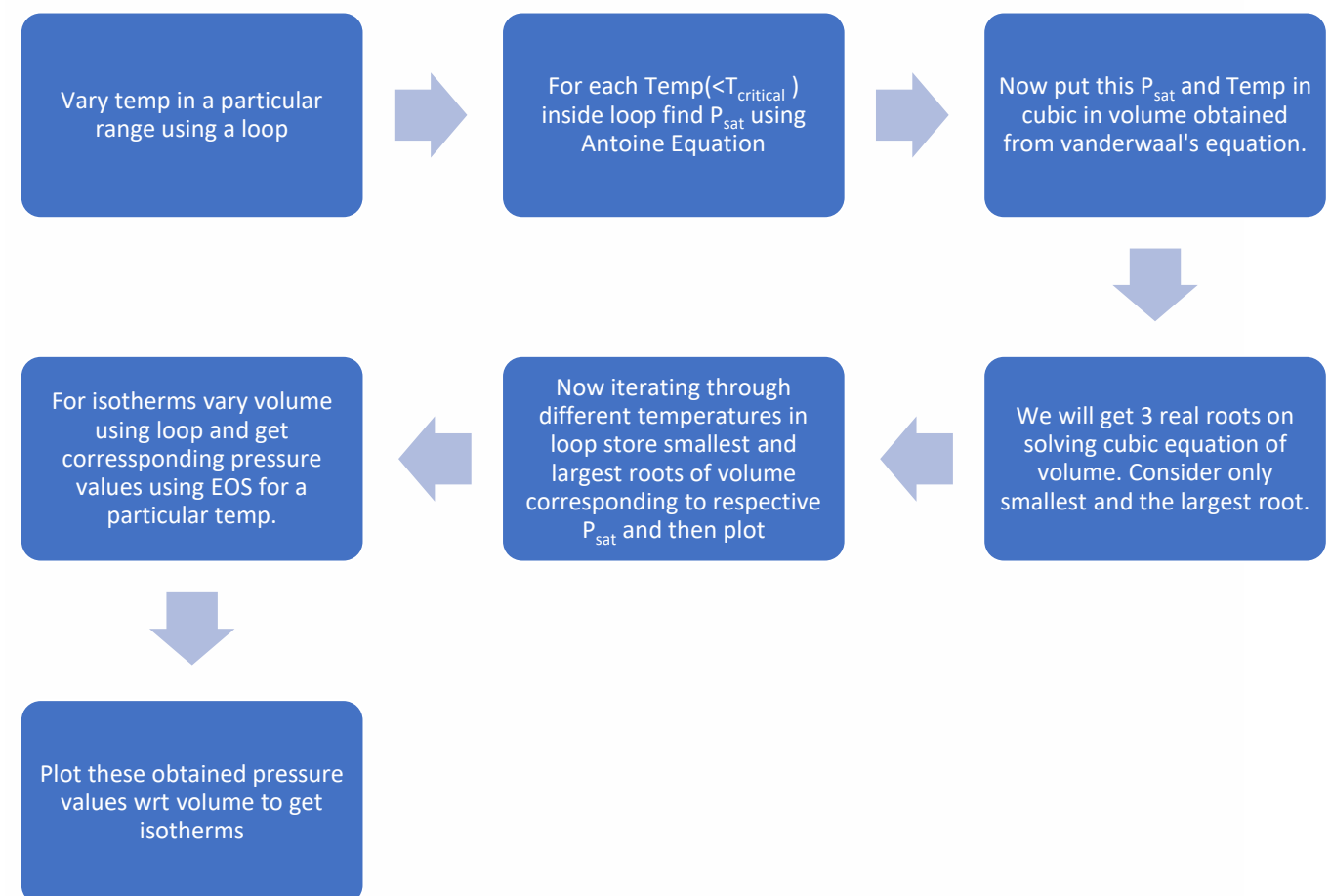
The van der Waals equation is a cubic one for the specific volume. This means that in general, at a given temperature, each pressure value corresponds to three specific volume values— $v_1$ ,  $v$ ,  $v_2$ . The values  $v_1$  and  $v_2$  correspond to physically existing states of liquid and vapor. The

value  $v$ , where  $(\partial p / \partial v)_T > 0$ , corresponds to an unstable state and does not exist physically. As the temperature increases, the values  $v_1$  and  $v_2$  get closer, and finally, at the critical point, all three roots coincide at the critical volume  $v_c$ . At higher temperatures, only one root of the van der Waals equation remains real, the two other being imaginary. These supercritical isotherms reveal inflections at  $v = v_c$ , which is close to the behavior of real substances.

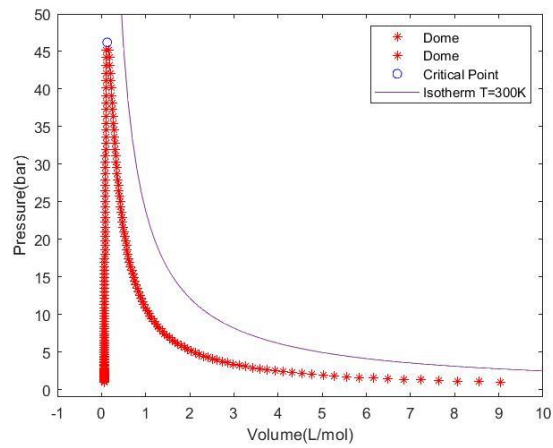
### History of EOS: (Source: [https://en.wikipedia.org/wiki/Van\\_der\\_Waals\\_equation](https://en.wikipedia.org/wiki/Van_der_Waals_equation))

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 on statistical thermodynamics.

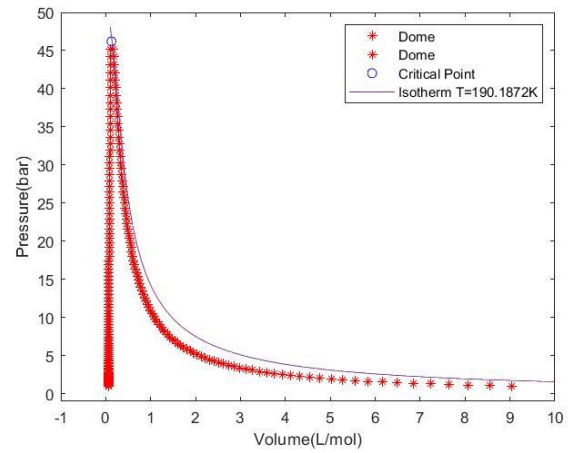
### Algorithm:



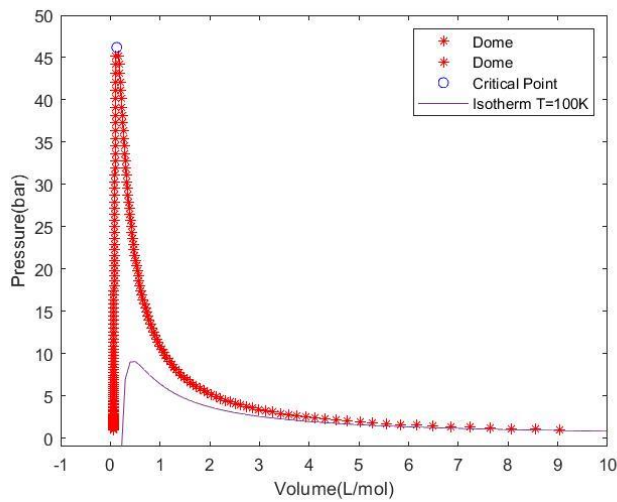
## Plots:



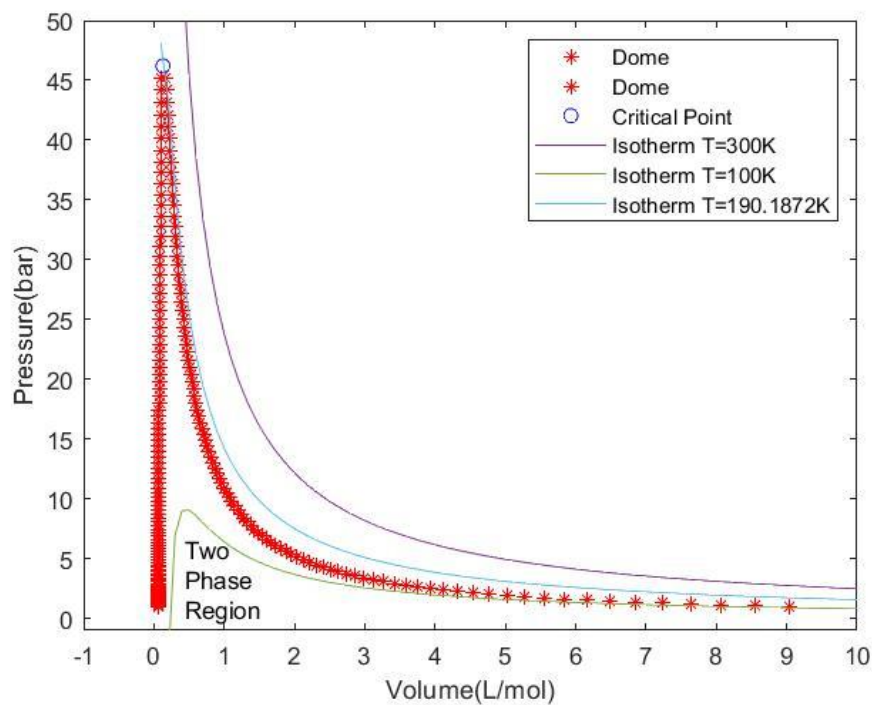
$T > T_{\text{critical}}$



$T = T_{\text{critical}}$



$T < T_{\text{critical}}$



## Analysis:

- $T > T_{\text{critical}}$  : Methane exists in a superheated state. Only one real root of Vander Waal's equation exists.
- $T = T_{\text{critical}}$  : 3 real roots exist of which 2 are equal. At this point, it is difficult to distinguish between vapor and liquid state of the substance
- $T < T_{\text{critical}}$  : 3 real and unequal roots exist. Smallest and largest roots among these correspond to saturated liquid and vapor state, respectively.
- In between bell-shaped dome, methane exists in both liquid and vapor state

**Antoine Equation:**  $\log_{10} p_{\text{sat}} = A - \frac{B}{C+T}$

A = 4.22061; B = 4.22061; C = 11.223 for temperature range : 110.0 – 190.5 K [for methane]

(Source: <https://webbook.nist.gov/cgi/cbook.cgi?ID=C74828&Mask=4&Type=ANTOINE&Plot=on>)

## Code:

```
a = 2.283; % Vanderwaal constant
b = 0.04278;
R = 0.08314; % gas constant
A = 4.22061; % antoine constant
B = 516.689;
C = 11.223;
Tc = (8*a)/(27*b*R); % critical temp
Pc = a/(27*(b^2)); %critical pressure
T = linspace(Tc-79,Tc,100); %divison of range of temp in 100
parts
Vol = linspace(0.1,10,100);
Xc = [3*b]; % critical volume
Yc = [Pc];

for i = 1:100
    Psat = (10^(A-(B/(C+T(i))))); % antoine equation
    V = [1 (-Psat*b-R*T(i))/Psat a/Psat -(a*b)/Psat];
    %vanderwaal equation
    v = roots(V);
    X1(i) = v(1);
    X2(i) = v(3);
    Y(i) = Psat;
end

%T = 300K Isotherm
for j = 1:100
    P1(j) = ((R*300)/(Vol(j)-b)) - (a/(Vol(j)^2));
end

%T = 100K Isotherm
for j = 1:100
    P2(j) = ((R*100)/(Vol(j)-b)) - (a/(Vol(j)^2));
end

%T = 150K Isotherm
for j = 1:100
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    P3(j) = ((R*150)/(Vol(j)-b)) - (a/(Vol(j)^2));
end

%T = 190K Isotherm
for j = 1:100
    P4(j) = ((R*190)/(Vol(j)-b)) - (a/(Vol(j)^2));
end

%T = 200K Isotherm
for j = 1:100
    P5(j) = ((R*200)/(Vol(j)-b)) - (a/(Vol(j)^2));
end

%T = 170K Isotherm
for j = 1:100
    P6(j) = ((R*170)/(Vol(j)-b)) - (a/(Vol(j)^2));
end

plot(X1,Y,'*','MarkerEdgeColor','r','DisplayName','Dome','LineStyle','None');
xlim([-1,10]);
ylim([-1,50]);
xlabel('Volume(L/mol)');
ylabel('Pressure(bar)');
hold on;
plot(X2,Y,'*','MarkerEdgeColor','r','DisplayName','Dome','LineStyle','None');
hold on;
plot(Xc,Yc,'o','MarkerEdgeColor','b','DisplayName','Critical Point');
hold on;
plot(Vol,P1,'DisplayName','Isotherm T=300K');
hold on;
plot(Vol,P2,'DisplayName','Isotherm T=100K');
hold on;
plot(Vol,P3,'DisplayName','Isotherm T=150K');
hold on;
plot(Vol,P4,'DisplayName','Isotherm T=190K');
hold on;
plot(Vol,P5,'DisplayName','Isotherm T=200K');
hold on;
plot(Vol,P6,'DisplayName','Isotherm T=170K');
legend;

```