Equations of State

BIG NOTE: the Octave code needs to be reworked and the numbers should be reviewed as well

Background

The Equations of State are equations which seek to relate various parameters concerning gasses in a single equation. These are parameters such as temperature, pressure and volume. The original and base equation is the so-called Ideal Gas Law, which has the following form:

PV = nRT

Where P is pressure, V is volume, n is the number of moles, R is the gas constant and T is the temperature. This equation works okay in certain circumstances and with some gasses, but it is far too limited to be useful in the general case. For example, it doesn't take into account the fact that gas molecules are not infinitely compressible, or the fact that there are attractive forces between the gas molecules.

There have been several new equations created since the Ideal Gas law which seek to capture the greater complexity involved in gasses. One such equation is called the Van der Waals Equation. It is still relatively simple and only a small step up from the Ideal Gas Law. But it does take into account attractive forces between molecules and the fact that molecules have volume. The equation has the following forms:

$$\left(P+\frac{a}{V_m^2}\right)\left(V_m-b\right)=RT$$

$$\left(P+\frac{n^2 a}{V_m^2}\right)\left(V_m-bn\right)=RT$$

The first equation is for the case where there is one mole of the gas and the second equation is for the other cases where there are n moles of the gas (in fact, the first equation is merely a special case of the second when $n = 1$).

The constant a is used to account for the attractive forces between molecules. The constant b is used to account for the volume of the gas molecules (which, in the Ideal Gas Law, was treated as negligible). These constants can be calculated or determined empirically and can be found in tables, an example of which is provided below:

Gas	***a***	***b***
H2	0.2444	0.02661
O2	1.360	0.03183
N2	1.390	0.03913
CO2	3.592	0.04267
Cl2	6.493	0.05622

Gas	*a*	*b*
A	1.345	0.03219
Ne	0.2107	0.01709
He	0.03412	0.02370

Octave is a useful tool for investigating the relationship between the parameters pressure, temperature and volume for a given gas using the Van der Waals equation. We will also use Newton's Method, which was discussed in a previous case study.

Objectives

1. Learning objectives
   a) Chemistry/Gas Laws
   b) Equation solving and graphing
2. Octave objectives
   a) Loops
   b) Functions
   c) Using previous work

Step-by-Step

1) Define functions for Van der Waals equation (need the equation itself and the derivative for use in Newton's method):

```
function ret = vdw(a,b,n,P,V,T)
  R = 0.08206;
  ret = (P + ((n .^ 2) .* a) ./ (V .^ 2)) .* (V – n .* b) – R
  .* T;
endfunction
function ret = vdwprime(b,n,V)
  ret = V – n .* b;
endfunction
```

2) Define solver function, which will solve Van der Waals equations for different values of P, V, T, a and b:

```
function ret = solve_P(guess,a,b,n,V,T)
  x(1) = guess;
  for i = 1:10
    x(i+1) = x(i) – vdw(a,b,n,x(i),V,T) ./ vdwprime(b,n,V);
  endfor
  ret = x(10);
endfunction
function ret = solve_P_over_V(a,b,n,V,T)
  for j = 1:20
    guess = a / V(j) + b / (V(j) ^ 2);
    P(j) = solve_P(guess,a,b,n,V(j),T);
```

```
    endfor
    ret = P;
  endfunction
  function ret = solve_P_over_T(a,b,n,V,T)
    for j = 1:20
      guess = a / V(j) + b / (V(j) ^ 2);
      P(j) = solve_P(guess,a,b,n,V,T(j));
    endfor
    ret = P;
  endfunction
```

3) Use solver function to plot, e.g., the relationship between pressure and volume.

```
> a = 3.592;
> b = 0.04267;
> n = 1;
> V = linspace(10,20,20);
> P = solve_P_over_V(a,b,n,V,T);
> plot(V,P);
```

The result is the following graph, which shows pressure (y-axis) vs. volume (x-axis):