→ Ideal Gas

$$P = \frac{nRT}{V} = \frac{RT}{V_m}$$

van der Waals

$$P = \frac{nRT}{V_{\cancel{m}} - bn} - a\left(\frac{n}{V}\right)^2$$

$$P = \frac{RT}{V_m - b} - a\frac{1}{V_m^2}$$

Redlich-Kwong

$$P = \frac{nRT}{V - nb} - \frac{a}{\sqrt{T}}\frac{n^2}{V_{\cancel{m}}(V + nb)}$$

$$P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}}\frac{1}{V_m(V_m + b)}$$

Viral Equation

$$P(V_m) = RT\left\{\frac{1}{V_m} + \frac{B(T)}{V_m^2} + \frac{C(T)}{V_m^3} + \cdots\right.$$

CONDENSATION HAPPENS AT CONSTANT PRESSURE AND INVOLVES A CHANGE IN VOLUME

CRITICAL P_c, T_c, and V_c

$\Rightarrow$ INFLEXION POINT FOR THE EQUATION OF STATE

$$\left.\begin{aligned}\left(\frac{\partial P}{\partial V_m}\right)_T &= 0\\ \left(\frac{\partial^2 P}{\partial V_m^2}\right)_T &= 0\end{aligned}\right\} \Rightarrow \begin{aligned}&a(T_c, V_c)\\ &b(T_c, V_c)\end{aligned}$$

van der WAALS

$$b = \frac{V_c}{3}$$

$$a = \frac{9}{8} R T_c V_c$$

$$\frac{R T_c}{P_c V_c} = \frac{8}{3}$$

REDUCED VARIABLES

$$P_r = \frac{P}{P_c} \qquad T_r = \frac{T}{T_c} \qquad V_r = \frac{V_m}{V_c}$$

SUBSTITUTE

$$P_c P_r = \frac{R T_c T_r}{V_c V_r - b} - \frac{a}{V_c^2 V_r^2}$$

$$P_r = \frac{RT_c}{P_c V_c}\left\{\frac{3T_r}{3V_r - 1} - \frac{9}{8V_r^2}\right\}$$

$$\boxed{P_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}}$$

NO FREE PARAMETERS

DEVIATION FROM IDEAL BEHAVIOR

COMPRESSION FACTOR

$$Z \equiv \frac{PV_m}{RT}$$

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$PV_m = \frac{RTV_m}{V_m - b} - \frac{a}{V_m}$$

$$\boxed{Z = \frac{PV_m}{RT} = \frac{V_m}{V_m - b} - \frac{a}{RT}\frac{1}{V_m}}$$

$$Z = \frac{P_r V_r}{T_r}\left(\frac{P_c V_c}{R T_c}\right) = Z_r\left(\frac{P_c V_c}{R T_c}\right)$$

$$= \frac{V_c V_r}{V_c V_r - \frac{V_c}{3}} - \left(\frac{a}{R T_c V_c}\right)\frac{1}{T_r V_r}$$

$$\boxed{Z_r = \frac{8 V_r}{3 V_r - 1} - \frac{3}{\cancel{8}}\,\frac{1}{T_r V_r}}$$

$$\frac{P_c V_c}{R T_c} = \frac{3}{8}$$

$$a = \frac{9}{8} R T_c V_c$$

Real Gases

```
Date[]
```

Out[243]= {2006, 4, 2, 15, 28, 46.606370}

Equations of state

```
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van der Waals

Equation of state

$$\text{pvdW[v\_, t\_, a\_, b\_, r\_]} := \frac{r\,t}{v-b} - a\left(\frac{1}{v}\right)^2$$

First derivative with respect to volime at constant temperature

```
eq1 = D[pvdW[v, t, a, b, r], v]
```

$$\frac{2\,a}{v^3} - \frac{r\,t}{(-b+v)^2}$$

Second derivative with respect to volime at constant temperature

```
eq2 = D[pvdW[v, t, a, b, r], {v, 2}]
```

$$-\frac{6\,a}{v^4} + \frac{2\,r\,t}{(-b+v)^3}$$

At the critical point both derivatives vanish defining an inflexion point, and the equation's parameters as a function of the critical values are obtaines as follows:

```
paravdW = Solve[{eq1 == 0, eq2 == 0}, {a, b}]
```

$$\left\{\left\{a \to \frac{9\,r\,t\,v}{8},\ b \to \frac{v}{3}\right\}\right\}$$

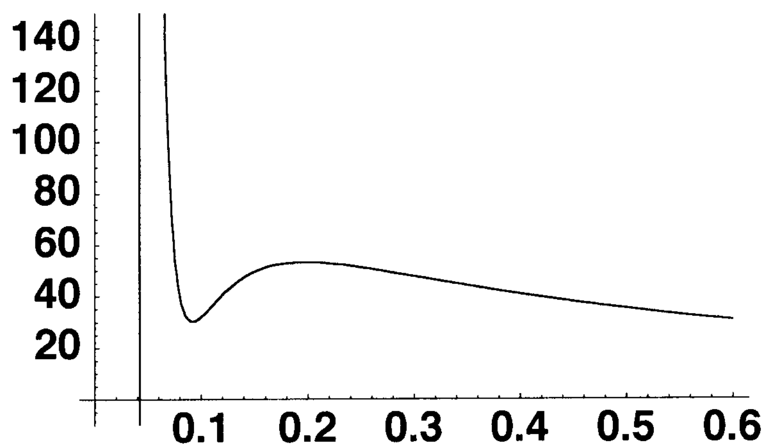
In these equations t and v represent the critical temperature and volume, and these values can now be used to reexpress the equation of state as a function of the reduced variables.

■ Carbon dioxide

Before we consider the critical values and the reduced variables, we use the van der waals eqaution in a more traditional manner. Since the van der Waals equtions, as wellas any equation of stae, is substance dependent, and we have to specify the parameters.

For Carbon dioxide we use the values for a nad b

```
Plot[pvdW[v, 273, 3.658, 0.0429, 0.0831451],
  {v, 0.01, 0.6}, PlotRange → {-10, 150}];
```



The surface P(V,T) is another approch