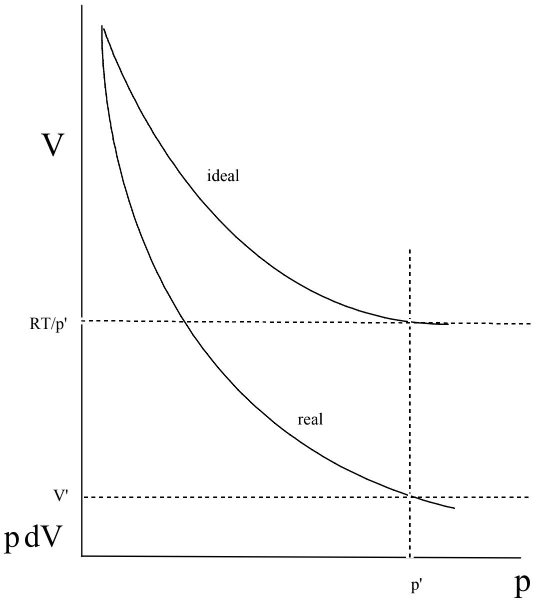
Fugacity Coefficient for Vander Waals Gas **Chemistry BC3254y**



The fugacity coefficient γ for a gas obeying Van der Waals' equation of state is given by

$$\ln \gamma = -\ln p + \ln\{RT/(V_m-b)\} - 2a/RTV_m + b/(V_m-b)$$

How is this obtained? For simplicity, set n=1.

$$-RT\ln\gamma = \int_0^{p'} (V_{id} - V)dp$$

The problem in doing this integral directly is that the van der Waals equation of state does not have an explicit solution for V as a function of p. However you can solve for p vs. V.

Let p′ be the upper limit of the original integral, and V′ the real volume at p′. (The ideal volume is at p′ is RT/p′).

Looking at the diagram:

$$\int_0^{p'} (V_{id} - V)dp = \int_{RT/p'}^{\infty} (p_{id} - p)dV + p'\{RT/p' - V'\} - \int_{V'}^{RT/p'} p\,dV$$

$$= \{RT - p'V'\} + \int_{RT/p'}^{\infty} p_{id}dV - \int_{V'}^{\infty} p\,dV$$

The upper limit of infinity is a problem. But as V gets very large, (V_{id}–V) approaches zero, so the integral is bound. To handle this, set the upper limit to V*; later we will let V* → ∞. Then

$$\int_0^{p'} (V_{id} - V)\,dp = \{RT - p'V'\} + RT\int_{RT/p'}^{V^*} (1/V)\,dV - \int_{V'}^{V^*} p\,dV$$

$$= \{RT - p'V'\} + RT\ln V^* - RT\ln(RT/p') - \int_{V'}^{V^*} p\,dV$$

From the van der Waals equation, $p = RT/(V-b) - a/V^2$ so

$\int (RT/(V-b) - a/V^2)\,dV = [RT\ln(V-b) + a/V]$

$$\int_0^{p'} (V_{id} - V)\,dp = \{RT - p'V'\} + RT\ln V^* - RT\ln(\frac{RT}{p'}) - RT\ln(V^* - b) + RT\ln(V' - b) - \frac{a}{V^*} + \frac{a}{V'}$$

If V* → ∞, (V*–b) = V*, so the two RT ln(V*..) terms cancel. Also (a/V*) → 0, so

$$\int_0^{p'} (V_{id} - V)dp = \{RT - p'V'\} - RT\ln(RT/p') + RT\ln(V' - b) + \frac{a}{V'}$$

$$\text{so } -\ln\gamma = \{1 - p'V'/RT\} + \ln p' + \ln(\frac{V' - b}{RT}) + \frac{a}{RTV'}$$

$p'V' = RTV'/(V'-b) - a/V' \rightarrow p'V'/RT = V'/(V'-b) - a/RTV'$ and $1 - V'/(V'-b) = -b/(V'-b)$

So

$$\ln\gamma = -\ln p' + \left(\frac{b}{V' - b}\right) - \ln(\frac{V' - b}{RT}) - \frac{2a}{RTV'} = -\ln p' + \ln(\frac{RT}{V' - b}) - \frac{2a}{RTV'} + \left(\frac{b}{V' - b}\right)$$