$$\left(\frac{\partial nb}{\partial n_1}\right)_{T,\underline{V},n_{j\neq k}} = b_1 \quad \text{and} \quad \left(\frac{\partial nb}{\partial n_2}\right)_{T,\underline{V},n_{j\neq k}} = b_2 \qquad 10.21$$

and the general result is

$$\left(\frac{\partial nb}{\partial n_k}\right)_{T,\underline{V},n_{j\neq k}} = b_k \qquad 10.22$$

The second type of derivative which we will encounter is of the form

$$\left(\frac{\partial n^2 a}{\partial n_k}\right)_{T,\underline{V},n_{j\neq k}} \qquad 10.23$$

$n^2 a$ may be written as $n^2 \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j a_{ij}$. For a binary mixture, $n_1^2 a_{11} + 2n_1 n_2 a_{12} + n_2^2 a_{22}$. Taking the appropriate derivative,

$$\left(\frac{\partial n^2 a}{\partial n_1}\right)_{T,\underline{V},n_2} = 2n_1 a_{11} + 2n_2 a_{12} \quad \text{and} \quad \left(\frac{\partial n^2 a}{\partial n_2}\right)_{T,\underline{V},n_1} = 2n_1 a_{12} + 2n_2 a_{22} \qquad 10.24$$

The general result is

$$\left(\frac{\partial n^2 a}{\partial n_k}\right)_{T,\underline{V},n_{j\neq k}} = 2\sum_j n_j a_{jk} \qquad 10.25$$

For the virial equation, we need to differentiate a function that will look like:

$$\left(\frac{\partial nB}{\partial n_k}\right)_{T,n_{j\neq k}} = \left(\frac{\partial\left(\frac{1}{n}\right)\left(\sum_i \sum_j n_i n_j B_{ij}\right)}{\partial n_k}\right)_{T,P,n_{j\neq k}} \qquad 10.26$$

Differentiation by the product rule gives

$$\frac{1}{n}\left(\frac{\partial\left(\sum_i \sum_j n_i n_j B_{ij}\right)}{\partial n_k}\right)_{T,P,n_{j\neq k}} - \frac{\sum_i \sum_j n_i n_j B_{ij}}{n^2} \qquad 10.27$$

The double sum in the derivative is n^2B which we have evaluated in equivalent form in Eqn 10.24. The second term is just B given by Eqn. 10.1. Therefore we have for a binary mixture

$$\left(\frac{\partial nB}{\partial n_1}\right)_{T,P,n_2} = \left(\frac{\partial\left(\frac{1}{n}\right)\left(\sum_i\sum_j n_i n_j B_{ij}\right)}{\partial n_1}\right)_{T,P,n_2} = 2y_1B_{11} + 2y_2B_{12} - B \text{ and}$$

$$\left(\frac{\partial nB}{\partial n_2}\right)_{T,P,n_1} = \left(\frac{\partial\left(\frac{1}{n}\right)\left(\sum_i\sum_j n_i n_j B_{ij}\right)}{\partial n_2}\right)_{T,P,n_1} = 2y_1B_{12} + 2y_2B_{22} - B \qquad 10.28$$

The general result is,

$$\left(\frac{\partial\left(\frac{1}{n}\right)\left(\sum_i\sum_j n_i n_j B_{ij}\right)}{\partial n_k}\right)_{T,P,n_{j\neq k}} = 2\sum_j y_j B_{jk} - B \qquad 10.29$$

Example 10.3 Fugacity coefficient from the virial equation

For moderate deviations from the ideal-gas law, a common method is to use the virial equation given by:

$$Z = 1 + BP/RT$$

where $B = \sum_i\sum_j y_i y_i B_{ij}$

Develop an expression for the fugacity coefficient.

Solution: For the virial equation, we have the result of Eqn. 8.28

$$\frac{G - G^{ig}}{RT} = \ln\varphi = \frac{BP}{RT}$$