

Rossmat, Frank & Adrain — for your interest

to get from $\circ$:

$$RT \ln \frac{f_i}{y_i p} = \int_0^p \left[\left(\frac{\partial v}{\partial n_i} \right)_{T, p, n_{j \neq i}} - \frac{RT}{p} \right] dp \quad (1)$$

to $\circ$:

$$= \int_v^\infty \left[\left(\frac{\partial f}{\partial n_i} \right)_{T, v, n_{j \neq i}} - \frac{RT}{v} \right] dv - RT \ln Z \quad (2)$$

Integration is at const T and composition.
Assume only

$$p(V, T, n_1, \dots, n_m) \quad (3)$$

without a specific functional form

Now in a multicomponent mixture of m species with species i varying, and all other species j held constant then at constant temperature

$$p(V, n_i)_{T, n_{j \neq i}} \quad (4)$$

so that

$$\left[\left(\frac{\partial p}{\partial v} \right)_{n_i} \left(\frac{\partial v}{\partial n_i} \right)_p \left(\frac{\partial n_i}{\partial p} \right)_v \right]_{T, n_{j \neq i}} = -1$$

or on solving for $(\partial v / \partial n_i)_{T, p, j \neq i}$

$$\left[\left(\frac{\partial v}{\partial n_i} \right)_p \right]_{T, n_{j \neq i}} = - \left[\left(\frac{\partial v}{\partial p} \right)_{n_i} \left(\frac{\partial p}{\partial n_i} \right)_v \right]_{T, n_{j \neq i}} \quad (6)$$

Substitute (6) in (1) and get

$$RT \ln \frac{f_i}{p} = \int_0^p - \left[\left(\frac{\partial v}{\partial p} \right)_{n_i} \left(\frac{\partial p}{\partial n_i} \right)_v \right]_{T, n_{j \neq i}} dp - \int_0^p \frac{RT}{p} dp \quad (7)$$

$$= - \int_0^p \left(\frac{\partial p}{\partial n_i} \right)_{T, n_{j \neq i}} dv - \int_0^p \frac{RT}{p} dp \quad (8)$$

$$\text{let } \frac{RT}{p} = \frac{V}{nZ} \quad dp = d \left(\frac{nRTZ}{V} \right)$$

$$= - \int_0^p \left(\frac{\partial p}{\partial n_i} \right)_{T, n_{j \neq i}} dv - \int_0^p \frac{V}{nZ} d \left(\frac{nRTZ}{V} \right)$$

$$= - \int_0^p \left(\frac{\partial p}{\partial n_i} \right)_{T, n_{j \neq i}} dv - \int_0^p \frac{V n RT}{nZ} \left[\frac{V dz - Z dv}{V^2} \right]$$

$$= - \int_0^p \left(\frac{\partial p}{\partial n_i} \right)_{T, n_{j \neq i}} dv - \int_0^p \frac{vRT}{z} \left(\frac{1}{v} dz - \frac{z}{v^2} dv \right)$$

$$= - \int_0^p \left(\frac{\partial p}{\partial n_i} \right)_{T, n_{j \neq i}} dv + \int_0^p \frac{RT}{v} dv - \int_0^p \frac{RT}{z} dz$$

gather and change the limits

$$\text{as } p \rightarrow 0 \quad v \rightarrow \infty \quad \text{and } z \rightarrow 1$$

$$= - \int_{\infty}^v \left[\left(\frac{\partial p}{\partial n_i} \right)_{T, n_{j \neq i}} + \frac{RT}{v} \right] dv - \int_1^z \frac{RT}{z} dz$$

$$= \int_v^{\infty} \left[\left(\frac{\partial p}{\partial n_i} \right)_{T, n_{j \neq i}} - \frac{RT}{v} \right] dv - RT \ln z$$

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