Solução dos exercícios do capítulo 5, p. 90

Exercício 1. Usando a regra (5.19)

$$\left(\frac{\partial u}{\partial v}\right)_T = \left(\frac{\partial u}{\partial v}\right)_s + \left(\frac{\partial u}{\partial s}\right)_v \left(\frac{\partial s}{\partial v}\right)_T$$

Mas $(\partial u/\partial v)_s = -p$ e $(\partial u/\partial s)_v = T$ e usando a relao de Maxwell $(\partial s/\partial v)_T = (\partial p/\partial T)_v$ obtemos

$$\left(\frac{\partial u}{\partial v}\right)_T = -p + T\left(\frac{\partial p}{\partial T}\right)_v$$

Derivando $u(T, v) = cT - r(v)$ e $p(T, v) = Tw(v) - q(v)$ relativamente a v e T, respectivamente, e substituindo nessa equao, obtemos

$$-r'(v) = -p + Tw(v) \qquad \rightarrow \qquad -r'(v) = q(v)$$

Para $q(v) = a/v^2$, obtemos

$$r'(v) = -\frac{a}{v^2} \qquad \rightarrow \qquad r(v) = \frac{a}{v} + k$$

Exercício 2.

a)

$$\left(\frac{\partial T}{\partial p}\right)_V = -\frac{\left(\frac{\partial V}{\partial p}\right)_T}{\left(\frac{\partial V}{\partial T}\right)_p} = \frac{\kappa_T}{\alpha}$$

b)

$$\left(\frac{\partial V}{\partial S}\right)_p = \frac{1}{\left(\frac{\partial S}{\partial V}\right)_p} = \frac{1}{\left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial T}{\partial V}\right)_p} = \frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial S}{\partial T}\right)_p} = \frac{TV\alpha}{C_p}$$

c)

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{\left(\frac{\partial U}{\partial V}\right)_T}{\left(\frac{\partial U}{\partial T}\right)_V} = \frac{p - T\left(\frac{\partial S}{\partial V}\right)_T}{T\left(\frac{\partial S}{\partial T}\right)_V} = \frac{p - T\left(\frac{\partial p}{\partial T}\right)_V}{C_v} = \frac{p - T\frac{\alpha}{\kappa_T}}{C_v}$$

d)

$$\left(\frac{\partial T}{\partial p}\right)_H = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p} = -\frac{T\left(\frac{\partial S}{\partial p}\right)_T + V}{T\left(\frac{\partial S}{\partial T}\right)_p} = \frac{T\left(\frac{\partial V}{\partial T}\right)_p - V}{C_p} = \frac{TV\alpha - V}{C_p}$$

e)

$$\left(\frac{\partial T}{\partial p}\right)_U = -\frac{\left(\frac{\partial U}{\partial p}\right)_T}{\left(\frac{\partial U}{\partial T}\right)_p} = -\frac{T\left(\frac{\partial S}{\partial p}\right)_T - p\left(\frac{\partial V}{\partial p}\right)_T}{T\left(\frac{\partial S}{\partial T}\right)_p - p\left(\frac{\partial V}{\partial T}\right)_p} =$$

$$= \frac{T\left(\frac{\partial V}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial p}\right)_T}{T\left(\frac{\partial S}{\partial T}\right)_p - p\left(\frac{\partial V}{\partial T}\right)_p} = \frac{TV\alpha - pV\kappa_T}{C_p - pV\alpha} =$$

f)

$$\left(\frac{\partial V}{\partial p}\right)_S = -\frac{\left(\frac{\partial S}{\partial p}\right)_V}{\left(\frac{\partial S}{\partial V}\right)_p} = -\frac{\left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial T}{\partial p}\right)_V}{\left(\frac{\partial S}{\partial T}\right)_p\left(\frac{\partial T}{\partial V}\right)_p} = -\frac{C_V\left(\frac{\partial T}{\partial p}\right)_V}{C_p\left(\frac{\partial T}{\partial V}\right)_p} = \frac{C_V}{C_p}\left(\frac{\partial V}{\partial p}\right)_T$$

Notar que dessa identidade segue a relaço

$$\kappa_S = \frac{C_V}{C_p}\kappa_T$$

Exercício 4. Para mostrar que a energia interna molar u depende do volume mostramos que a derivada $(\partial u/\partial V)_T$ no nula. Para isso usamos a relaço

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_v - p$$

e calculamos o lado direito para cada equaço de estado.

a) Para a equaço de van der Waals

$$p = \frac{RT}{v-b} - \frac{a}{v^2} \qquad \rightarrow \qquad \left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v-b}$$

Logo

$$\left(\frac{\partial u}{\partial v}\right)_T = \frac{a}{v^2}$$

b) Para a equaço de Dieterici

$$p = \frac{RT}{v-b} e^{-a/RTv} \qquad \rightarrow \qquad \left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v-b} e^{-a/RTV} + \frac{a}{Tv(v-b)} e^{-a/RTv}$$

Logo

$$\left(\frac{\partial u}{\partial v}\right)_T = \frac{a}{v(v-b)} e^{-a/RTv}$$

c) Para a equaço de Berthelot

$$p = \frac{RT}{v-b} - \frac{a}{Tv^2} \qquad \rightarrow \qquad \left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v-b} + \frac{a}{T^2 v^2}$$

Logo

$$\left(\frac{\partial u}{\partial v}\right)_T = \frac{2a}{Tv^2}$$

d) Para a expanso virial

$$p = RT\{\rho + B_2\rho^2 + B_3\rho^3 + B_4\rho^4 + \ldots\} \qquad\qquad \rho = \frac{1}{v}$$

onde B_n s depende de T, temos

$$\left(\frac{\partial p}{\partial T}\right)_v = R\{\rho + B_2\rho^2 + B_3\rho^3 + B_4\rho^4 + \ldots\} +$$

$$+ RT\{B_2'\rho^2 + B_3'\rho^3 + B_4'\rho^4 + \ldots\}$$

onde B_n' denonta a derivada de B_n relativamente temperatura. Logo

$$\left(\frac{\partial u}{\partial v}\right)_T = RT^2\{B_2'\rho^2 + B_3'\rho^3 + B_4'\rho^4 + \ldots\}$$

Exercício 5.

a) Usando $v = 1/\rho$ escrevemos a equaço de van der Waals na forma

$$p = \frac{RT\rho}{1-b\rho} - a\rho^2$$

Expandindo $1/(1-b\rho)$ at termos lineares em ρ,

$$p = RT\rho(1+b\rho) - a\rho^2 = RT\rho + (RTb - a)\rho^2$$

b) Para a equaço de Dieterici

$$p = \frac{RT\rho}{1 - b\rho} e^{-a\rho/RT}$$

temos

$$p = RT\rho(1 + b\rho)(1 - \frac{a\rho}{RT}) = RT\rho(1 + b\rho - \frac{a\rho}{RT})$$

ou

$$p = RT\rho + (RTb - a)\rho^2$$

c) Para a equaço de Berthelot

$$p = \frac{RT\rho}{1 - b\rho} - \frac{a\rho^2}{T}$$

Expandindo $1/(1 - b\rho)$ at termos lineares em ρ,

$$p = RT\rho(1 + b\rho) - \frac{a\rho^2}{T} = RT\rho + (RTb - \frac{a}{T})\rho^2$$