10.40 Thermodynamics **Fall 2003**
Problem Set 4

Problem 5.4 Text

Solution:

(a) $(\partial \underline{S}/\partial P)_{T,N}$

Use $y^{(2)}$, thus

$$dy^{(2)} = d\underline{G} = -\underline{S}dT + \underline{V}dP + \Sigma\mu_j\, dN_j$$

$$(\partial \underline{S}/\partial P)_{T,N} = -(\partial \underline{V}/\partial T)_{P,N}$$

(b) $(\partial \underline{H}/\partial P)_{T,N}$ in terms of $\underline{G}$ and its derivatives

$$\underline{G} = \underline{U} - T\underline{S} + P\underline{V} = \underline{H} - T\underline{S}$$

$$\underline{H} = \underline{G} + T\underline{S}$$

$$(\partial \underline{H}/\partial P)_{T,N} = (\partial \underline{G}/\partial P)_{T,N} + T(\partial \underline{S}/\partial P)_{T,N}$$

$$(\partial \underline{G}/\partial P)_{T,N} = G_P = \underline{V}$$

$$(\partial \underline{S}/\partial P)_{T,N} = -G_{TP} = \partial^2 \underline{G}/\partial T \partial P = -G_{PT} = -(\partial \underline{V}/\partial T)_{P,N}$$

Therefore,

$$(\partial \underline{H}/\partial P)_{T,N} = G_P + T(-G_{PT}) = \underline{V} - T(\partial \underline{V}/\partial T)_{P,N}$$

(c) $\partial[(\underline{A}/T)/\partial(1/T)]_{\underline{V},N}$ as a function of $\underline{U}$

$$= -T^2\left[\frac{\partial(A/T)}{\partial T}\right]_{\underline{V},N} = -T^2\left[\frac{1}{T}\left(\frac{\partial A}{\partial T}\right)_{P,N} - \frac{\underline{A}}{T^2}\right]$$

but $(\partial \underline{A}/\partial T)_{\underline{V},N} = -\underline{S}$. Therefore,

$$\left|\frac{\partial(A/T)}{\partial(1/T)}\right|_{\underline{V},N} = -T(-\underline{S}) + \underline{U} - T\underline{S} = \underline{U}$$

which is similar to the Gibbs-Helmholtz relationship (Eq. (5-113))

(e) $(\partial T/\partial N_A)_{\underline{V}, \underline{S}, \mu_B, N_C, \ldots}$ in terms of $\underline{U}$

Let us define $\underline{U}$ as the basis function but order as

$y^{(0)} = \underline{U} = f(N_B, \underline{S}, N_A, \underline{V}, N_C, \ldots)$

$y^{(1)} = f(\mu_B, \underline{S}, N_A, \underline{V}, N_c, \ldots)$

$y^{(0)}$

	x_i	ξ_i
1	N_B	μ_B
2	$\underline{S}$	T
3	N_A	μ_A
4	$\underline{V}$	$-P$
5	N_C	μ_C

$y^{(1)}$

	x_i	ξ_i
1	μ_B	$-N_B$
2	$\underline{S}$	T
3	N_A	μ_A
4	$\underline{V}$	$-P$
5	N_C	μ_C

and $y_2^{(1)} = T$; $y_{23}^{(1)} = (\partial T/\partial N_A)_{\mu_B, \underline{S}, \underline{V}, N_C, \ldots}$
but,

$$y_{23}^{(1)} = y_{23}^{(0)} - \frac{y_{12}^{(0)} y_{13}^{(0)}}{y_{11}^{(0)}}$$

where

$$y_{23}^{(0)} = \underline{U}_{\underline{S}N_A} = (\partial T/\partial N_A)_{N_B, \underline{S}, \underline{V}, N_C \ldots}$$

$$y_{12}^{(0)} = \underline{U}_{N_B\underline{S}} = (\partial \mu_B/\partial \underline{S})_{N, \underline{V}}$$

$$y_{13}^{(0)} = \underline{U}_{N_BN_A} = (\partial \mu_B/\partial N_A)_{\underline{S}, \underline{V}, N[A]}$$

$$y_{11}^{(0)} = \underline{U}_{N_BN_B} = (\partial \mu_B/\partial N_B)_{\underline{S}, \underline{V}, N[B]}$$