APPENDIX 3

Rearrangement of independent variables.

given $\quad X = X(P,T) \qquad$ eg: $\rho = \rho(P,T)$

$\qquad\quad Y = Y(P,T) \qquad\qquad h = h(P,T)$

we often need:

$$\left.\frac{\partial Y}{\partial X}\right)_P \quad \text{or} \quad \left.\frac{\partial Y}{\partial X}\right)_T \quad \text{or} \quad \left.\frac{\partial Y}{\partial P}\right)_X \quad \text{etc}$$

We can easily rearrange as follows:

step 1: expand:

$$dX = \left.\frac{\partial X}{\partial P}\right)_T dP + \left.\frac{\partial X}{\partial T}\right)_P dT$$

$$dY = \left.\frac{\partial Y}{\partial P}\right)_T dP + \left.\frac{\partial Y}{\partial T}\right)_P dT$$

step 2: solve for dP & dT:

$$dP = \frac{\left.\frac{\partial Y}{\partial T}\right)_P dX - \left.\frac{\partial X}{\partial T}\right)_P dY}{\left.\frac{\partial X}{\partial P}\right)_T \left.\frac{\partial Y}{\partial T}\right)_P - \left.\frac{\partial X}{\partial T}\right)_P \left.\frac{\partial Y}{\partial P}\right)_T}$$

$$dT = \frac{\left.\frac{\partial Y}{\partial P}\right)_T dX - \left.\frac{\partial X}{\partial P}\right)_T dY}{-\left[\left.\frac{\partial X}{\partial P}\right)_T \left.\frac{\partial Y}{\partial T}\right)_P - \left.\frac{\partial X}{\partial T}\right)_P \left.\frac{\partial Y}{\partial P}\right)_T\right]}$$

Selected differentials from a condensed collection of thermodynamic formulas by P. W. Bridgman

Any partial derivative of a state variable of a thermodynamic system, with respect to any other state variable, a third variable being held constant [for example, $(\partial u/\partial v)_T$] can be written, from Eq. (4-20), in the form

$$(\partial u/\partial v)_T = \frac{(\partial u/\partial z)_T}{(\partial v/\partial z)_T}$$

where z is any arbitrary state function. Then if one tabulates the partial derivatives of all state variables with respect to an arbitrary function z, any partial derivative can be obtained by dividing one tabulated quantity by another. For brevity, derivatives of the form $(\partial u/\partial z)_T$ are written in the table below in the symbolic form $(\partial u)_T$. Then, for example,

$$\left(\frac{\partial u}{\partial v}\right)_T = \frac{(\partial u)_T}{(\partial v)_T} = \frac{T(\partial v/\partial T)_P + P(\partial v/\partial P)_T}{-(\partial v/\partial P)_T} = \frac{T\beta}{\kappa} - P,$$

which agrees with Eq. (6-9). Ratios (not derivatives) such as $d'q_P/dv_P$ can be treated in the same way. For a further discussion, see *A Condensed Collection of Thermodynamics Formulas* by P. W. Bridgman (Harvard University Press, 1925), from which the table below is taken.

P constant

$(\partial T)_P = 1$
$(\partial v)_P = (\partial v/\partial T)_P$
$(\partial s)_P = c_P/T$
$(\partial q)_P = c_P$
$(\partial w)_P = P(\partial v/\partial T)_P$
$(\partial u)_P = c_P - P(\partial v/\partial T)_P$
$(\partial h)_P = c_P$
$(\partial g)_P = -s$
$(\partial f)_P = -s - P(\partial v/\partial T)_P$

T constant

$(\partial P)_T = -1$
$(\partial v)_T = -(\partial v/\partial P)_T$
$(\partial s)_T = (\partial v/\partial T)_P$
$(\partial q)_T = T(\partial v/\partial T)_P$
$(\partial w)_T = -p(\partial v/\partial P)_T$
$(\partial u)_T = T(\partial v/\partial T)_P + P(\partial v/\partial P)_T$
$(\partial h)_T = -v + T(\partial v/\partial T)_P$
$(\partial g)_T = -v$
$(\partial f)_T = P(\partial v/\partial P)_T$

h constant

$(\partial P)_h = -c_P$
$(\partial T)_h = v - T(\partial v/\partial T)_P$
$(\partial v)_h = -c_P(\partial v/\partial P)_T - T(\partial v/\partial T)_P^2 + v(\partial v/\partial T)_P$
$(\partial s)_h = vc_P/T$
$(\partial q)_h = vc_P$
$(\partial w)_h = -P[c_P(\partial v/\partial P)_T + T(\partial v/\partial T)_P^2 - v(\partial v/\partial T)_P]$

s constant

$(\partial P)_s = -c_P/T$
$(\partial T)_s = -(\partial v/\partial T)_P$
$(\partial v)_s = -\frac{1}{T}[c_P(\partial v/\partial P)_T + T(\partial v/\partial T)_P^2]$
$(\partial q)_s = 0$
$(\partial w)_s = -\frac{P}{T}[c_P(\partial v/\partial P)_T + T(\partial v/\partial T)_P^2]$
$(\partial u)_s = \frac{P}{T}[c_P(\partial v/\partial P)_T + (T\,\partial v/\partial T)_P^2]$
$(\partial h)_s = -vc_P/T$
$(\partial g)_s = -\frac{1}{T}[vc_P - sT(\partial v/\partial T)_P]$
$(\partial f)_s = \frac{1}{T}[Pc_P(\partial v/\partial P)_T + PT(\partial v/\partial T)_P^2 + sT(\partial v/\partial T)_P]$

g constant

$(\partial P)_g = s$
$(\partial T)_g = v$
$(\partial v)_g = v(\partial v/\partial T)_P + s(\partial v/\partial P)_T$
$(\partial s)_g = \frac{1}{T}[vc_P - sT(\partial v/\partial T)_P]$
$(\partial q)_g = -sT(\partial v/\partial T)_P + vc_P$
$(\partial w)_g = P[v(\partial v/\partial T)_P + s(\partial v/\partial P)_T]$

v constant

$(\partial P)_v = -(\partial v/\partial T)_P$
$(\partial T)_v = (\partial v/\partial P)_T$
$(\partial s)_v = \frac{1}{T}[c_P(\partial v/\partial P)_T + T(\partial v/\partial T)_P^2]$
$(\partial q)_v = c_P(\partial v/\partial P)_T + T(\partial v/\partial T)_P^2$
$(\partial w)_v = 0$
$(\partial u)_v = c_P(\partial v/\partial P)_T + T(\partial v/\partial T)_P^2$
$(\partial h)_v = c_P(\partial v/\partial P)_T + T(\partial v/\partial T)_P^2 - v(\partial v/\partial T)_P$
$(\partial g)_v = -v(\partial v/\partial T)_P - s(\partial v/\partial P)_T$
$(\partial f)_v = -s(\partial v/\partial P)_T$