2.16: Appendix III- Useful Mathematical Relations

Consider a set of n independent variables $\{x_1, \ldots, x_n\}$, which can be thought of as a point in n-dimensional space. Let $\{y_1, \ldots, y_n\}$ and $\{z_1, \ldots, z_n\}$ be other choices of coordinates. Then

$$\frac{\partial x_i}{\partial z_k} = \frac{\partial x_i}{\partial y_j} \frac{\partial y_j}{\partial z_k} \,. \tag{2.16.1}$$

Note that this entails a matrix multiplication: $A_{ik} = B_{ij} C_{jk}$, where $A_{ik} = \partial x_i / \partial z_k$, $B_{ij} = \partial x_i / \partial y_j$, and $C_{jk} = \partial y_j / \partial z_k$. We define the determinant

$$det\left(\frac{\partial x_i}{\partial z_k}\right) \equiv \frac{\partial(x_1, \ldots, x_n)}{\partial(z_1, \ldots, z_n)} \,. \tag{2.16.2}$$

Such a determinant is called a Jacobian. Now if $A = BC$, then $det(A) = det(B) \cdot det(C)$. Thus,

$$\frac{\partial(x_1, \ldots, x_n)}{\partial(z_1, \ldots, z_n)} = \frac{\partial(x_1, \ldots, x_n)}{\partial(y_1, \ldots, y_n)} \cdot \frac{\partial(y_1, \ldots, y_n)}{\partial(z_1, \ldots, z_n)} \,. \tag{2.16.3}$$

Recall also that

$$\frac{\partial x_i}{\partial x_k} = \delta_{ik} \,. \tag{2.16.4}$$

Consider the case $n = 2$. We have

$$\frac{\partial(x, y)}{\partial(u, v)} = det \begin{pmatrix} \left(\frac{\partial x}{\partial u}\right)_v & \left(\frac{\partial x}{\partial v}\right)_u \\ \left(\frac{\partial y}{\partial u}\right)_v & \left(\frac{\partial y}{\partial v}\right)_u \end{pmatrix} = \left(\frac{\partial x}{\partial u}\right)_v \left(\frac{\partial y}{\partial v}\right)_u - \left(\frac{\partial x}{\partial v}\right)_u \left(\frac{\partial y}{\partial u}\right)_v \,. \tag{2.16.5}$$

We also have

$$\frac{\partial(x, y)}{\partial(u, v)} \cdot \frac{\partial(u, v)}{\partial(r, s)} = \frac{\partial(x, y)}{\partial(r, s)} \,. \tag{2.16.6}$$

From this simple mathematics follows several very useful results.

1) First, write

$$\frac{\partial(x, y)}{\partial(u, v)} = \left[\frac{\partial(u, v)}{\partial(x, y)}\right]^{-1} \,. \tag{2.16.7}$$

Now let $v = y$:

$$\frac{\partial(x, y)}{\partial(u, y)} = \left(\frac{\partial x}{\partial u}\right)_y = \frac{1}{\left(\frac{\partial u}{\partial x}\right)_y} \,. \tag{2.16.8}$$

Thus,

$$\left(\frac{\partial x}{\partial u}\right)_y = 1 \Big/ \left(\frac{\partial u}{\partial x}\right)_y \tag{2.16.9}$$

2) Second, we have

$$\begin{aligned}\frac{\partial(x,y)}{\partial(u,y)} &= \left(\frac{\partial x}{\partial u}\right)_y \\ &= \frac{\partial(x,y)}{\partial(x,u)}\cdot\frac{\partial(x,u)}{\partial(u,y)} \\ &= -\left(\frac{\partial y}{\partial u}\right)_x \left(\frac{\partial x}{\partial y}\right)_u ,\end{aligned}$$

which is to say

$$\left(\frac{\partial x}{\partial y}\right)_u \left(\frac{\partial y}{\partial u}\right)_x = -\left(\frac{\partial x}{\partial u}\right)_y . \tag{2.16.10}$$

Invoking Equation [boxone], we conclude that

$$\left(\frac{\partial x}{\partial y}\right)_u \left(\frac{\partial y}{\partial u}\right)_x \left(\frac{\partial u}{\partial x}\right)_y = -1 . \tag{2.16.11}$$

3) Third, we have

$$\frac{\partial(x,v)}{\partial(u,v)} = \frac{\partial(x,v)}{\partial(y,v)}\cdot\frac{\partial(y,v)}{\partial(u,v)} , \tag{2.16.12}$$

which says

$$\left(\frac{\partial x}{\partial u}\right)_v = \left(\frac{\partial x}{\partial y}\right)_v \left(\frac{\partial y}{\partial u}\right)_v \tag{2.16.13}$$

This is simply the chain rule of partial differentiation.

4) Fourth, we have

$$\begin{aligned}\frac{\partial(x,y)}{\partial(u,y)} &= \frac{\partial(x,y)}{\partial(u,v)}\cdot\frac{\partial(u,v)}{\partial(u,y)} \\ &= \left(\frac{\partial x}{\partial u}\right)_v \left(\frac{\partial y}{\partial v}\right)_u \left(\frac{\partial v}{\partial y}\right)_u - \left(\frac{\partial x}{\partial v}\right)_u \left(\frac{\partial y}{\partial u}\right)_v \left(\frac{\partial v}{\partial y}\right)_u ,\end{aligned}$$

which says

$$\left(\frac{\partial x}{\partial u}\right)_y = \left(\frac{\partial x}{\partial u}\right)_v - \left(\frac{\partial x}{\partial y}\right)_u \left(\frac{\partial y}{\partial u}\right)_v \tag{2.16.14}$$

5) Fifth, whenever we differentiate one extensive quantity with respect to another, holding only intensive quantities constant, the result is simply the ratio of those extensive quantities. For example,

$$\left(\frac{\partial S}{\partial V}\right)_{p,T} = \frac{S}{V} . \tag{2.16.15}$$

The reason should be obvious. In the above example, $S(p,V,T) = V\phi(p,T)$, where ϕ is a function of the two intensive quantities p and T. Hence differentiating S with respect to V holding p and T constant is the same as dividing S by V. Note that this implies

$$\left(\frac{\partial S}{\partial V}\right)_{p,T} = \left(\frac{\partial S}{\partial V}\right)_{p,\mu} = \left(\frac{\partial S}{\partial V}\right)_{n,T} = \frac{S}{V} , \tag{2.16.16}$$

where $n = N/V$ is the particle density.

6) Sixth, suppose we have a function $\Phi(y,v)$ and we write

$$d\Phi = x\,dy + u\,dv . \tag{2.16.17}$$

That is,

$$x=\left(\frac{\partial\Phi}{\partial y}\right)_v\equiv\Phi_y \qquad , \qquad u=\left(\frac{\partial\Phi}{\partial v}\right)_y\equiv\Phi_v\ . \tag{2.16.18}$$

Now we may write

$$\begin{aligned} dx&=\Phi_{yy}\,dy+\Phi_{yv}\,dv\\ du&=\Phi_{vy}\,dy+\Phi_{vv}\,dv\ . \end{aligned}$$

If we demand $du=0$, this yields

$$\left(\frac{\partial x}{\partial u}\right)_v=\frac{\Phi_{yy}}{\Phi_{vy}}\ . \tag{2.16.19}$$

Note that $\Phi_{vy}=\Phi_{yv}$. From the equation $du=0$ we also derive

$$\left(\frac{\partial y}{\partial v}\right)_u=-\frac{\Phi_{vv}}{\Phi_{vy}}\ . \tag{2.16.20}$$

Next, we use Equation [due] with $du=0$ to eliminate dy in favor of dv, and then substitute into Equation [dxe]. This yields

$$\left(\frac{\partial x}{\partial v}\right)_u=\Phi_{yv}-\frac{\Phi_{yy}\,\Phi_{vv}}{\Phi_{vy}}\ . \tag{2.16.21}$$

Finally, Equation [due] with $dv=0$ yields

$$\left(\frac{\partial y}{\partial u}\right)_v=\frac{1}{\Phi_{vy}}\ . \tag{2.16.22}$$

Combining the results of eqns. [pxuv], [pyvu], [pxvu], and [pyuv], we have

$$\begin{aligned} \frac{\partial(x,y)}{\partial(u,v)}&=\left(\frac{\partial x}{\partial u}\right)_v\left(\frac{\partial y}{\partial v}\right)_u-\left(\frac{\partial x}{\partial v}\right)_u\left(\frac{\partial y}{\partial u}\right)_v\\ &=\left(\frac{\Phi_{yy}}{\Phi_{vy}}\right)\left(-\frac{\Phi_{vv}}{\Phi_{vy}}\right)-\left(\Phi_{yv}-\frac{\Phi_{yy}\,\Phi_{vv}}{\Phi_{vy}}\right)\left(\frac{1}{\Phi_{vy}}\right)=-1\ . \end{aligned}$$

Thus, if $\Phi=E(S,V)$, then $(x,y)=(T,S)$ and $(u,v)=(-p,V)$, we have

$$\frac{\partial(T,S)}{\partial(-p,V)}=-1\ . \tag{2.16.23}$$

Nota bene: It is important to understand what other quantities are kept constant, otherwise we can run into trouble. For example, it would seem that Equation [jacob] would also yield

$$\frac{\partial(\mu,N)}{\partial(p,V)}=1\ . \tag{2.16.24}$$

But then we should have

$$\frac{\partial(T,S)}{\partial(\mu,N)}=\frac{\partial(T,S)}{\partial(-p,V)}\cdot\frac{\partial(-p,V)}{\partial(\mu,N)}=+1 \qquad \text{(WRONG!)} \tag{2.16.25}$$

when according to Equation [jacob] it should be -1. What has gone wrong?

The problem is that we have not properly specified what else is being held constant. In Equation [detTSpV] it is N (or μ) which is being held constant, while in Equation [detmuNpV] it is S (or T) which is being held constant. Therefore a naive application of the chain rule for determinants yields the wrong result, as we have seen.

Let's be more careful. Applying the same derivation to $dE=x\,dy+u\,dv+r\,ds$ and holding s constant, we conclude

$$\frac{\partial(x,y,s)}{\partial(u,v,s)}=\left(\frac{\partial x}{\partial u}\right)_{v,s}\left(\frac{\partial y}{\partial v}\right)_{u,s}-\left(\frac{\partial x}{\partial v}\right)_{u,s}\left(\frac{\partial y}{\partial u}\right)_{v,s}=-1\ . \tag{2.16.26}$$

Thus, if

$$dE = T\,dS + y\,dX + \mu\,dN \quad , \tag{2.16.27}$$

where $(y, X) = (-p, V)$ or (H^α, M^α) or (E^α, P^α), the appropriate thermodynamic relations are

$$\begin{aligned} \frac{\partial(T,S,N)}{\partial(y,X,N)} &= -1 & \qquad \frac{\partial(T,S,\mu)}{\partial(y,X,\mu)} &= -1 \\ \frac{\partial(\mu,N,X)}{\partial(T,S,X)} &= -1 & \qquad \frac{\partial(\mu,N,y)}{\partial(T,S,y)} &= -1 \\ \frac{\partial(y,X,S)}{\partial(\mu,N,S)} &= -1 & \qquad \frac{\partial(y,X,T)}{\partial(\mu,N,T)} &= -1 \end{aligned}$$

For example,

$$\frac{\partial(T,S,N)}{\partial(-p,V,N)} = \frac{\partial(-p,V,S)}{\partial(\mu,N,S)} = \frac{\partial(\mu,N,V)}{\partial(T,S,V)} = -1 \tag{2.16.28}$$

and

$$\frac{\partial(T,S,\mu)}{\partial(-p,V,\mu)} = \frac{\partial(-p,V,T)}{\partial(\mu,N,T)} = \frac{\partial(\mu,N,-p)}{\partial(T,S,-p)} = -1\ . \tag{2.16.29}$$

If we are careful, then the results in eq. [TSyXN] can be quite handy, especially when used in conjunction with Equation [chain]. For example, we have \[\pabc{S}{V}{T,N}={\pz(T,S,N)\over\pz(T,V,N)}=\stackrel{=\,1}{\overbrace

} \cdot{\pz(p,V,N)\over\pz(T,V,N)}=\pabc{p}{T}{V,N}\ ,\] which is one of the Maxwell relations derived from the exactness of $dF(T,V,N)$. Some other examples include \[\begin{aligned} \pabc{V}{S}{p,N}&={\pz(V,p,N)\over\pz(S,p,N)}=\stackrel{=\,1}{\overbrace}\cdot{\pz(S,T,N)\over\pz(S,p,N)}=\pabc{T}{p}{S,N}\\ \pabc{S}{N}{T,p}&={\pz(S,T,p)\over\pz(N,T,p)}=\stackrel{=\,1}{\overbrace} \cdot{\pz(\mu,N,p)\over\pz(N,T,p)}=-\pabc{\mu}{T}{p,N}\ ,\bvph\end{aligned}\] which are Maxwell relations deriving from $d\mathcal{H}(S,p,N)$ and $dG(T,p,N)$, respectively. Note that due to the alternating nature of the determinant – it is antisymmetric under interchange of any two rows or columns – we have

$$\frac{\partial(x,y,z)}{\partial(u,v,w)} = -\frac{\partial(y,x,z)}{\partial(u,v,w)} = \frac{\partial(y,x,z)}{\partial(w,v,u)} = \ldots\ . \tag{2.16.30}$$

In general, it is usually advisable to eliminate S from a Jacobian. If we have a Jacobian involving T, S, and N, we can write

$$\frac{\partial(T,S,N)}{\partial(\bullet\,,\,\bullet\,,N)} = \frac{\partial(T,S,N)}{\partial(p,V,N)}\,\frac{\partial(p,V,N)}{\partial(\bullet\,,\,\bullet\,,N)} = \frac{\partial(p,V,N)}{\partial(\bullet\,,\,\bullet\,,N)}\ , \tag{2.16.31}$$

where each $\bullet$ is a distinct arbitrary state variable other than N.

If our Jacobian involves the S, V, and N, we write

$$\frac{\partial(S,V,N)}{\partial(\bullet\,,\,\bullet\,,N)} = \frac{\partial(S,V,N)}{\partial(T,V,N)}\cdot\frac{\partial(T,V,N)}{\partial(\bullet\,,\,\bullet\,,N)} = \frac{C_V}{T}\cdot\frac{\partial(T,V,N)}{\partial(\bullet\,,\,\bullet\,,N)}\ . \tag{2.16.32}$$

If our Jacobian involves the S, p, and N, we write

$$\frac{\partial(S,p,N)}{\partial(\bullet\,,\,\bullet\,,N)} = \frac{\partial(S,p,N)}{\partial(T,p,N)}\cdot\frac{\partial(T,p,N)}{\partial(\bullet\,,\,\bullet\,,N)} = \frac{C_p}{T}\cdot\frac{\partial(T,p,N)}{\partial(\bullet\,,\,\bullet\,,N)}\ . \tag{2.16.33}$$

For example, \[\begin{aligned} \pabc{T}{p}{S,N}&={\pz(T,S,N)\over\pz(p,S,N)}=\stackrel{=\,1}{\overbrace

} \cdot{\pz(p,V,N)\over\pz(p,T,N)}\cdot {\pz(p,T,N)\over\pz(p,S,N)}={T\over C\ns_p}\pabc{V}{T}{p,N}\bvph\\ \pabc{V}{p}{S,N}&={\pz(V,S,N)\over\pz(p,S,N)}={\pz(V,S,N)\over\pz(V,T,N)}\cdot{\pz(V,T,N)\over\pz(p,T,N)}\cdot{\pz(p,T,N)\over\pz(p,S,N)} ={C\ns_V\over C\ns_p}\,\pabc{V}{p}{T,N}\ .\bvph\end{aligned}\] With $\kappa \equiv -\frac{1}{V}\,\frac{\partial V}{\partial p}$ the compressibility, we see that the second of these equations says $\kappa_T\, c_V = \kappa_S\, c_p$, relating the isothermal and adiabatic compressibilities and the molar heat capacities at constant volume and constant pressure. This relation was previously established in Equation [cpcvktks]