10.6: The Transformation of Thermodynamic Variables in General

Let us suppose that M, Q, R, X, and Y are state functions and that we know the total differentials

$$dM = \left(\frac{\partial M}{\partial X}\right)_Y dX + \left(\frac{\partial M}{\partial Y}\right)_X dY$$

$$dQ = \left(\frac{\partial Q}{\partial X}\right)_Y dX + \left(\frac{\partial Q}{\partial Y}\right)_X dY$$

$$dR = \left(\frac{\partial R}{\partial X}\right)_Y dX + \left(\frac{\partial R}{\partial Y}\right)_X dY$$

To find the total differential of $M\left(Q,R\right)$,

$$dM = \left(\frac{\partial M}{\partial Q}\right)_R dQ + \left(\frac{\partial M}{\partial R}\right)_Q dR$$

we solve the total differentials of $Q\left(X,Y\right)$ and $R\left(X,Y\right)$ to find dX and dY in terms of dQ and dR. Since dQ and dR are simultaneous equations in the variables dX and dY, we can apply Cramer’s rule to obtain

$$dX = \frac{\begin{vmatrix} dQ & \left(\partial Q/\partial Y\right)_X \\ dR & \left(\partial R/\partial Y\right)_X \end{vmatrix}}{J\left(\dfrac{Q,R}{X,Y}\right)} = \frac{\left(\dfrac{\partial R}{\partial Y}\right)_X dQ - \left(\dfrac{\partial Q}{\partial Y}\right)_X dR}{J\left(\dfrac{Q,R}{X,Y}\right)}$$

and

$$dY = \frac{\begin{vmatrix} \left(\partial Q/\partial X\right)_Y & dQ \\ \left(\partial R/\partial X\right)_Y & dR \end{vmatrix}}{J\left(\dfrac{Q,R}{X,Y}\right)} = \frac{-\left(\dfrac{\partial R}{\partial X}\right)_Y dQ + \left(\dfrac{\partial Q}{\partial X}\right)_Y dR}{J\left(\dfrac{Q,R}{X,Y}\right)}$$

where $J\left(\left(Q,R\right)/\left(X,Y\right)\right)$ is the Jacobian of the transformation of variables X and Y to variables Q and R:

$$\begin{aligned} J\left(\frac{Q,R}{X,Y}\right) &= \begin{vmatrix} \left(\partial Q/\partial X\right)_Y & \left(\partial Q/\partial Y\right)_X \\ \left(\partial R/\partial X\right)_Y & \left(\partial R/\partial Y\right)_X \end{vmatrix} \\ &= \left(\frac{\partial Q}{\partial X}\right)_Y \left(\frac{\partial R}{\partial Y}\right)_X + \left(\frac{\partial Q}{\partial Y}\right)_X \left(\frac{\partial R}{\partial X}\right)_Y \end{aligned}$$

To find

$$dM = \left(\frac{\partial M}{\partial Q}\right)_R dQ + \left(\frac{\partial M}{\partial R}\right)_Q dR$$

We substitute these results for dX and dY into the total differential of $M = M\left(X,Y\right)$:

$$
\begin{aligned}
dM &= \left(\frac{\partial M}{\partial X}\right)_Y dX + \left(\frac{\partial M}{\partial Y}\right)_X dY \\
&= \frac{\left(\frac{\partial M}{\partial X}\right)_Y \left[\left(\frac{\partial R}{\partial Y}\right)_X dQ - \left(\frac{\partial Q}{\partial Y}\right)_X dR\right]}{J\left(\frac{Q,R}{X,Y}\right)} + \frac{\left(\frac{\partial M}{\partial Y}\right)_X \left[-\left(\frac{\partial R}{\partial X}\right)_Y dQ + \left(\frac{\partial Q}{\partial X}\right)_Y dR\right]}{J\left(\frac{Q,R}{X,Y}\right)} \\
&= \left[\frac{\left(\frac{\partial M}{\partial X}\right)_Y \left(\frac{\partial R}{\partial Y}\right)_X - \left(\frac{\partial M}{\partial Y}\right)_X \left(\frac{\partial R}{\partial X}\right)_Y}{J\left(\frac{Q,R}{X,Y}\right)}\right] dQ + \left[\frac{-\left(\frac{\partial M}{\partial X}\right)_Y \left(\frac{\partial Q}{\partial Y}\right)_X + \left(\frac{\partial M}{\partial Y}\right)_X \left(\frac{\partial Q}{\partial X}\right)_Y}{J\left(\frac{Q,R}{X,Y}\right)}\right] dR
\end{aligned}
$$

where the coefficients of dQ and dR are $(\partial M/\partial Q)_R$ and $(\partial M/\partial R)_Q$, respectively. In §5, we find the other total differentials in terms of dP and dT. If we set $X = T$ and $Y = P$, we can use these relationships to find the total differential for any state function expressed in terms of any two other state functions.

To illustrate this point, let us use these relationships to find the total differential of S expressed as a function of P and V, $S = S(P,V)$. In this case, we are transforming from the variables (P,T) to the variables (P,V). This is a one-variable transformation. To effect it, we make the additional substitutions $M = S$, $Q = V$, and $R = P$. Since we have $Y = R = P$, the transformation equations simplify substantially. We have

$$
\begin{aligned}
\left(\frac{\partial R}{\partial Y}\right)_X &= \left(\frac{\partial P}{\partial P}\right)_X = 1 \\
\left(\frac{\partial R}{\partial X}\right)_Y &= \left(\frac{\partial P}{\partial T}\right)_P = 0 \\
\left(\frac{\partial Q}{\partial Y}\right)_X &= \left(\frac{\partial V}{\partial P}\right)_T \\
\left(\frac{\partial Q}{\partial X}\right)_Y &= \left(\frac{\partial V}{\partial T}\right)_P
\end{aligned}
$$

The Jacobian becomes

$$
J\left(\frac{Q,R}{X,Y}\right) = \left(\frac{\partial V}{\partial T}\right)_P
$$

and the partial derivatives of S become

$$
\left(\frac{\partial S}{\partial V}\right)_P = \left(\frac{\partial S}{\partial T}\right)_P \Big/ \left(\frac{\partial V}{\partial T}\right)_P = \frac{C_P}{T}\left(\frac{\partial T}{\partial V}\right)_P
$$

and

$$
\left(\frac{\partial S}{\partial P}\right)_V = \frac{-\left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial T}\right)_P} \tag{10.6.1}
$$

$$
= \frac{C_P}{T}\left(\frac{\partial T}{\partial P}\right)_V + \left(\frac{\partial S}{\partial P}\right)_T \tag{10.6.2}
$$

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