

10.5: Expressing Thermodynamic Functions with Independent Variables P and T

We can follow a parallel development to express these thermodynamic functions with P and T as the independent variables. We have the differential relationship $dH = TdS + VdP$. We expand dH with P and T as the independent variables. Equating these, we obtain

$$dH = \left(\frac{\partial H}{\partial P} \right)_T dP + \left(\frac{\partial H}{\partial T} \right)_P dT \quad (10.5.1)$$

$$= TdS + VdP \quad (10.5.2)$$

so that we have

$$dS = \frac{1}{T} \left(\frac{\partial H}{\partial T} \right)_P dT + \frac{1}{T} \left[\left(\frac{\partial H}{\partial P} \right)_T - V \right] dP$$

From the coefficient of dT and the definition $(\partial H / \partial T)_P = C_P$, we have

$$\left(\frac{\partial S}{\partial T} \right)_P = \frac{1}{T} \left(\frac{\partial H}{\partial T} \right)_P = \frac{C_P}{T}$$

(When we are describing a reversible system that is not a pure substance, C_P is just an abbreviation for $(\partial H / \partial T)_P$.) From the coefficient of dP and the relationship $(\partial S / \partial P)_T = -(\partial V / \partial T)_P$ that we find in [Section 10.1](#), we have

$$\left(\frac{\partial S}{\partial P} \right)_T = \frac{1}{T} \left[\left(\frac{\partial H}{\partial P} \right)_T - V \right] = - \left(\frac{\partial V}{\partial T} \right)_P$$

Substituting into the expression for dS , we find

$$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T} \right)_P dP$$

Using the same approach as in the previous section, we can now obtain

$$dE = \left[C_P - P \left(\frac{\partial V}{\partial T} \right)_P \right] dT - \left[P \left(\frac{\partial V}{\partial P} \right)_T + T \left(\frac{\partial V}{\partial T} \right)_P \right] dP \quad (10.5.3)$$

$$dH = C_P dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP \quad (10.5.4)$$

$$dA = - \left[S + P \left(\frac{\partial V}{\partial T} \right)_P \right] dT - P \left(\frac{\partial V}{\partial P} \right)_T dP \quad (10.5.5)$$

and, we already have

$$dG = VdP - SdT$$

Finally, we can write $V = V(P, T)$ to find

$$dV = \left(\frac{\partial V}{\partial P} \right)_T dP + \left(\frac{\partial V}{\partial T} \right)_P dT$$

so that we have total differentials for all of the principal thermodynamic functions when they are expressed as functions of P and T . If an equation of state is not known but the coefficients of thermal expansion and isothermal compressibility are available, we have $(\partial V / \partial T)_P = \alpha V$ and $(\partial V / \partial P)_T = -\beta V$. Then we can estimate a volume change, for example, as a line integral of

$$dV = \alpha V dT - \beta V dP$$

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