

10.1: Thermodynamic Relationships from dE, dH, dA and dG

In Chapter 9, we substitute $dq^{rev} = TdS$, from the second law, into

$$dE = dq + PdV$$

from the first law, to obtain, for any closed system undergoing a reversible change in which the only work is pressure–volume work, the fundamental equation, $dE = TdS + PdV$. In view of the mathematical properties of state functions that we develop in Chapter 7, this result means that we can express the energy of the system as a function of entropy and volume, $E = E(S, V)$. With this choice of independent variables, the total differential of E is

$$(dE = (\partial E / \partial S)_V dS + (\partial E / \partial V)_S dV).$$

Equating these expressions for dE , we find

$$\left[\left(\frac{\partial E}{\partial S} \right)_V + T \right] dS + \left[\left(\frac{\partial E}{\partial V} \right)_S + P \right] dV = 0$$

for any such system. Since S and V are independent variables, this equation can be true for any arbitrary state of the system only if the coefficients of dS and dV are each identically equal to zero. It follows that

$$\left(\frac{\partial E}{\partial S} \right)_V = T$$

and

$$\left(\frac{\partial E}{\partial V} \right)_S = -P$$

Moreover, because dE is an exact differential, we have

$$\frac{\partial}{\partial V} \left(\frac{\partial E}{\partial S} \right)_V = \frac{\partial}{\partial S} \left(\frac{\partial E}{\partial V} \right)_S$$

so that

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V$$

Using the result $dH = TdS + VdP$, parallel arguments show that enthalpy can be expressed as a function of entropy and pressure, $H = H(S, P)$, so that

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

and

$$\left(\frac{\partial H}{\partial P} \right)_S = V$$

and

$$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P$$

Since $dA = -SdT + PdV$, the Helmholtz free energy must be a function of temperature and volume, $A = A(T, V)$, and we have

$$\left(\frac{\partial A}{\partial T} \right)_V = -S$$

and

$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$

and

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Likewise, $dG = -SdT + VdP$ implies that the Gibbs free energy is a function of temperature and pressure, $G = G(P, T)$, so that

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

and

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

and

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

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