

10.4: Expressing Thermodynamic Functions with Independent Variables V and T

If we choose V and T as the independent variables, we can express the differential of E as a function of V and T . We also have the differential relationship $dE = TdS - PdV$. These expressions for dE must be equal:

$$dE = \left(\frac{\partial E}{\partial V}\right)_T dV + \left(\frac{\partial E}{\partial T}\right)_V dT = TdS + PdV$$

Rearranging, we find a total differential for dS with V and T as the independent variables:

$$dS = \frac{1}{T} \left(\frac{\partial E}{\partial T}\right)_V dT + \frac{1}{T} \left[\left(\frac{\partial E}{\partial V}\right)_T + P \right] dV$$

From the coefficient of dT , we have

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T} \left(\frac{\partial E}{\partial T}\right)_V = \frac{C_V}{T}$$

where we use the definition $(\partial E/\partial T)_V = C_V$. (When we write " C_V ," we usually think of it as a property of a pure substance. The relationship above is valid for any reversible system. When we are describing a system that is not a pure substance, C_V is just an abbreviation for $(\partial E/\partial T)_V$.) From the coefficient of dV , we have

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \left[\left(\frac{\partial E}{\partial V}\right)_T + P \right] = \left(\frac{\partial P}{\partial T}\right)_V$$

where we use the relationship $(\partial S/\partial V)_T = (\partial P/\partial T)_V$ that we find in §1. Substituting into the expression for dS , we find

$$dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

Now, from $dE = TdS - PdV$, we have

$$dE = C_V dT + \left[T \left(\frac{\partial P}{\partial T}\right)_V + P \right] dV$$

From $H = E + PV$, we have

$$\begin{aligned} dH &= dE + d(PV) \\ &= dE + \left(\frac{\partial(PV)}{\partial T}\right)_V dT + \left(\frac{\partial(PV)}{\partial V}\right)_T dV \\ &= dE + V \left(\frac{\partial P}{\partial T}\right)_V dT + \left[P + V \left(\frac{\partial P}{\partial V}\right)_T \right] dV \\ &= \left[C_V + V \left(\frac{\partial P}{\partial T}\right)_V \right] dT + \left[T \left(\frac{\partial P}{\partial T}\right)_V + V \left(\frac{\partial P}{\partial V}\right)_T \right] dV \end{aligned}$$

Of course, we already have

$$dA = -SdT + PdV$$

From $G = H - TS$, by an argument that parallels the above derivation of dH , we obtain

$$dG = \left[V \left(\frac{\partial P}{\partial T}\right)_V + S \right] dT + V \left(\frac{\partial P}{\partial V}\right)_T dV$$

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

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

P , T , V , C_V , $(\partial P/\partial T)_V$, and $(\partial P/\partial V)_T$ are all experimentally accessible for any reversible system. If we have this information for a system that undergoes a change from a state specified by T_1 and V_1 to a second state specified by T_2 and V_2 , we can use these relationships to calculate ΔE , ΔS , and ΔH . To do so, we calculate the appropriate line integral along a reversible path. One such path is an isothermal reversible change, at T_1 , from V_1 to V_2 , followed by a constant-volume change, at V_2 , from T_1 to T_2 . In principle, the same procedure can be used to calculate ΔA and ΔG . However, because S appears in the differentials dA and dG , this requires that we first find S as a function of V and T .

If the system is a pure substance for which we have an equation of state, we can find $(\partial P/\partial T)_V$, and $(\partial P/\partial V)_T$ by straightforward differentiation. When the substance is a gas, an equation of state may be available in the literature. When the substance is a liquid or a solid, these partial derivatives can still be related to experimentally accessible quantities. The compressibility of a substance is the change in its volume that results from a change in the applied pressure, at a constant temperature. The thermal expansion of a substance is the change in its volume that results from a change in its temperature, at a constant applied pressure. It is convenient to convert measurements of these properties into intensive functions of the state of the substance by expressing the volume change as a fraction of the original volume. That is, we define the **coefficient of thermal expansion**:

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

and the **coefficient of isothermal compressibility**:

$$\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

Coefficients of thermal expansion and isothermal compressibility are available in compilations of thermodynamic data for many liquids and solids. In general, both coefficients are weak functions of temperature. We have

$$\left(\frac{\partial P}{\partial V} \right)_T = -\frac{1}{\beta V}$$

and

$$\left(\frac{\partial P}{\partial T} \right)_V = -\left(\frac{\partial V}{\partial T} \right)_P / \left(\frac{\partial V}{\partial P} \right)_T = \frac{\alpha}{\beta}$$

Using these coefficients, we can estimate a pressure change, for example, as a line integral of

$$dP = \left(\frac{\alpha}{\beta} \right) dT - \left(\frac{1}{\beta V} \right) dV$$

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