

10.3: Expressing Thermodynamic Functions with Other Independent Variables

We have found simple differential expressions for E , S , H , A , and G that apply to closed, reversible systems in which only pressure–volume work is possible. From $dE = TdS + PdV$, we infer that $E = E(S, V)$. From $dH = TdS + VdP$, we infer that $H = H(S, P)$. An argument parallel to that above leads us to the conclusion that specifying the changes in S and P is sufficient to specify the change in the state of the system. Similarly, from $dA = -SdT + PdV$ and $dG = -SdT + VdP$, we see that it is sufficient to specify the changes in either V and T or P and T . These total differentials show that specifying the change in two state functions is sufficient to specify the change that occurs in the state of a closed system, when the change is reversible and all of the work is pressure–volume work. We have now found seven pairs of state functions that are sufficient; they are $\{S, V\}$, $\{S, E\}$, $\{E, V\}$, and the four pairs in which we choose one variable from the set $\{S, T\}$ and one from the set $\{P, V\}$. However, each of the equations we have obtained so far uses a different pair of independent variables.

Evidently, we should be able to express any thermodynamic function using various pairs of state functions. We can do this by transforming the equations that we have already derived. We are particularly interested in P , V , and T as independent variables, because these quantities are readily measured for most systems. In the sections below, we find exact differentials for dS , dE , dH , dA , and dG with V and T and with P and T as the independent variables.

While specifying the change in some pair of variables is always sufficient to specify the change in the state of a closed reversible system, we should note that it is not always necessary. If the system has only one degree of freedom, specifying some single variable is sufficient. For example, so long as both phases remain present, the change in the state of a pure substance at liquid–vapor equilibrium can be specified by specifying the change in the temperature, the pressure, the volume, or the number of moles of either phase. We discuss this further in [Section 10.7](#).

At present, we are developing relationships among state functions that are valid for any closed reversible system in which all work is pressure–volume work. The next several chapters explore the implications of these results. If the composition of the closed reversible system changes during these processes, this composition change does not affect the relationships we develop here. Of course, any composition change that occurs during a reversible process must be reversible; if the components of the system can react, this reaction must be at equilibrium throughout the process. In [Chapter 14](#), we extend the relationships that we develop here to explicitly include molar compositions as independent variables. This enables us to express our theory for equilibrium using composition variables.

In [Section 6.10](#), we assume—infer from experience—that specifying the changes in P and T is sufficient to specify a change in the state of a closed equilibrium system whose phase composition is fixed and in which only pressure–volume work is possible. We use this assumption to give a partial proof of Duhem’s theorem. In [Section 10.5](#), we see that this assumption is also a consequence of the theory we have developed. This is another check on the internal consistency of the theory.

Finally, it is time to consider a question we have thus far avoided: Is any arbitrary pair of state functions a sufficient set? The answer is no. In [Section 10.8](#), we find that neither $\{P, V\}$ nor $\{S, T\}$ is a sufficient pair in all cases.

This page titled [10.3: Expressing Thermodynamic Functions with Other Independent Variables](#) is shared under a [CC BY-SA 4.0](#) license and was authored, remixed, and/or curated by [Paul Ellgen](#) via [source content](#) that was edited to the style and standards of the LibreTexts platform.