


Since the system is simple, for the process to be internally reversible, the temperature must be uniform throughout the system (no gradients). So the system temperature has a single value throughout. On a molar basis, the fundamental property relation for dU is $dU_{rev} = T dS_{rev} - (PdV)_{rev}$. Noting that U , S , and V are all state functions, not path functions, we recognize that this relation applies whether the path is reversible or not. Consequently, the subscripts have been dropped.

$$dU = TdS - PdV$$

5.4  dU for a closed simple system.

The significance of this relation is that changes in one state variable, dU , have been related to changes in two other state variables, dS and dV . Therefore, the physical problem of relating heat flow and volume changes to energy changes has been transformed into a purely mathematical problem of the calculus of two variables. This transformation liberates us from having to think of a physical means of attaining some conversion of energy—instead if we know changes in S and V , we can apply some relatively simple rules of calculus.


Auxiliary Relations for Convenience Properties

Because dU is most simply written as a function of S and V it is termed a *natural function* of S and V . We can express changes of internal energy in terms of other state properties (such as $\{P, T\}$ or $\{T, V\}$), but when we do so, the expression always involves additional derivatives. We will show this in more detail in Example 5.9 on page 185. We also should explore the natural variables for the convenience properties.

We have defined enthalpy, $H \equiv U + PV$. Therefore, $dH = dU + PdV + VdP = TdS - PdV + PdV + VdP$,

$$dH = TdS + VdP$$

which shows H is a natural function of S and P ¹


5.5  dH for a reversible, closed simple system. Enthalpy is convenient when heat and pressure are manipulated.

Enthalpy is termed a *convenience* property because we have specifically *defined* it to be useful in problems where reversible heat flow and pressure are manipulated. By now you have become so used to using it that you may not stop to think about what the enthalpy really is. If you look back to our introduction of enthalpy, you will see that we defined it in an arbitrary way when we needed a new tool. The fact that it relates to the heat transfer in a constant-pressure closed system, and relates to the heat transfer/shaft work in steady-state flow systems, is a result of our careful choice of its definition.

We may want to control T, V for some problems, particularly in statistical mechanics, where we create a system of particles and want to change the volume (intermolecular separation) at fixed temperature. Situations like this also arise quite often in our studies of pistons and cylinders. Since U is not a natural function of T, V , such a state property is convenient. Therefore, we define *Helmholtz energy* $A \equiv U - TS$. Therefore, $dA = dU - TdS - SdT = TdS - PdV - TdS - SdT$,

$$dA = -SdT - PdV$$

which shows A is a natural function of T and V

5.6  Helmholtz energy is convenient when T, V are manipulated.

1. The mathematical manipulation used here is called a Legendre transformation. It involves addition of a conjugate pair like PV or TS , then differentiation and simplification. Details are given by J.W. Tester and M. Modell, *Thermodynamics and Its Applications*, 3rd Ed, Prentice Hall, Upper Saddle River, N.J., 1996.