

9.14: The Fundamental Equation and Other Criteria for Reversible Change

To begin exploring the possibilities for stating the criteria for change using only the properties of the system, let us consider how some thermodynamic functions change when a process is reversible. We consider a closed system and focus on making incremental changes in the state of the system. For a reversible process, we have $dq^{rev} = TdS$. The reversible pressure–volume work is $dw_{PV}^{rev} = -PdV$. If non-pressure–volume work is also possible, the reversible work becomes $dw^{rev} = -PdV + dw_{NPV}^{rev}$, where dw_{NPV}^{rev} is the increment of reversible, non-pressure–volume work. The energy change is

$$dE = dq^{rev} + dw^{rev} = TdS - PdV + dw_{NPV}^{rev}$$

(any reversible process)

This equation is of central importance. It is sometimes called **the combined first and second laws of thermodynamics** or the **fundamental equation**. It applies to any closed system that is undergoing reversible change. It specifies a relationship among the changes in energy, entropy, and volume that must occur if the system is to remain at equilibrium while an increment of non-pressure–volume work, dw_{NPV}^{rev} , is done on it. The burden of our entire development is that any reversible process must satisfy this equation. Conversely, any process that satisfies this equation must be reversible.

For a reversible process at constant entropy, we have $dS = 0$, so that $(dE)_S = -PdV + dw_{NPV}^{rev}$. Since $-PdV$ is the reversible pressure–volume work, dw_{PV}^{rev} , and the sum $dw_{net}^{rev} = -PdV + dw_{NPV}^{rev}$ is the net work, we have

$$(dE)_S = dw_{net}^{rev}$$

(reversible process, constant S)

where the subscript “S” specifies that the entropy is constant. For a reversible process in which all of the work is pressure–volume work, we have $dw_{NPV}^{rev} = 0$, and the fundamental equation becomes

$$dE = TdS - PdV$$

(reversible process, only pressure–volume work)

For a reversible process in which only pressure–volume work is possible, this equation gives the amount, dE , by which the energy must change when the entropy changes by dS and the volume changes by dV .

Now, let us apply the fundamental equation to an arbitrary process that occurs reversibly and at constant entropy and constant volume. Under these conditions, $dS = 0$ and $dV = 0$. Therefore, at **constant entropy and volume**, a necessary and sufficient condition for the process to be reversible—and hence to be continuously in an equilibrium state as the process takes place—is that

$$(dE)_{SV} = dw_{NPV}^{rev}$$

(reversible process)

and if only pressure–volume work is possible,

$$(dE)_{SV} = 0$$

(reversible process, only pressure–volume work)

where the subscripts indicate that entropy and volume are constant.

If we consider an arbitrary reversible process that occurs at **constant energy and volume**, we have $dE = 0$ and $dV = 0$, and the fundamental equation reduces to

$$(dS)_{EV} = -\frac{dw_{NPV}^{rev}}{T}$$

(reversible process)

and if only pressure–volume work is possible,

$$(dS)_{EV} = 0$$

(reversible process, only pressure–volume work)

In this case, as noted in §7, the system is isolated. In §1-6, we note that an isolated system in an equilibrium state can undergo no further change. Thus, the condition $(dS)_{EV} = 0$ defines a unique or primitive equilibrium state.

If a closed system behaves reversibly, any composition changes that occur in the system must be reversible. For chemical applications, composition changes are of paramount importance. We return to these considerations in Chapter 14, where we relate the properties of chemical substances—their chemical potentials—to the behavior of systems undergoing both reversible and spontaneous composition changes.

If a closed system behaves reversibly and only pressure–volume work is possible, we see from the fundamental equation that specifying the changes in any two of the three variables, E , S , and V , is sufficient to specify the change in the system. In particular, if energy and entropy are constant, $dE = dS = 0$, the volume is also constant, $dV = 0$, and the system is isolated. Thus, the state of an equilibrium system whose energy and entropy are fixed is unique; $dE = dS = 0$ specifies a primitive equilibrium state. We see that the internal consistency of our model passes a significant test: From the entropy-based statement of the second law, we deduce the same proposition that we introduce in §7 as a heuristic conjecture. In Chapter 10, we expand on this idea.

Starting from the fundamental equation, we can find similar sets of relationships for enthalpy, the Helmholtz free energy, and the Gibbs free energy. We define $H = E + PV$. For an incremental change in a system we, have

$$dH = dE + PdV + VdP$$

Using the fundamental equation to substitute for dE , this becomes

$$dH = TdS - PdV + dw_{NPV}^{rev} + PdV + VdP = TdS + VdP + dw_{NPV}^{rev}$$

For a reversible process in which all of the work is pressure–volume work, we have

$$dH = TdS + VdP$$

(reversible process, only pressure–volume work)

For a reversible process in which only pressure–volume work is possible, this equation gives the amount, dH , by which the enthalpy must change when the entropy changes by dS and the pressure changes by dP . If a reversible process occurs at constant entropy and pressure, then $dS = 0$ and $dP = 0$. At **constant entropy and pressure**, the process is reversible if and only if

$$(dH)_{SP} = dw_{NPV}^{rev}$$

(reversible process)

If only pressure–volume work is possible,

$$(dH)_{SP} = 0$$

(reversible process, only pressure–volume work)

where the subscripts indicate that entropy and pressure are constant.

If we consider an arbitrary reversible process that occurs at **constant enthalpy and pressure**, we have $dH = 0$ and $dP = 0$, and the total differential for dH reduces to

$$(dS)_{HP} = -\frac{dw_{NPV}^{rev}}{T} \text{ (reversible process)}$$

and if only pressure–volume work is possible,

$$(dS)_{HP} = 0$$

(reversible process, only pressure–volume work)

From $A = E - TS$, we have $dA = dE - TdS - SdT$. Using the fundamental equation to substitute for dE , we have

$$dA = TdS - PdV + dw_{NPV}^{rev} - TdS - SdT = -PdV - SdT + dw_{NPV}^{rev}$$

For a reversible process in which all of the work is pressure–volume work,

$$dA = -SdT - PdV$$

(reversible process, only pressure–volume work)

For a reversible process in which only pressure–volume work is possible, this equation gives the amount, dA , by which the Helmholtz free energy must change when the temperature changes by dT and the volume changes by dV . For a reversible isothermal process, we have $dT = 0$, and from $dA = -PdV - SdT + dw_{NPV}^{rev}$ we have

$$(dA)_T = -PdV + dw_{NPV}^{rev} = dw_{PV}^{rev} + dw_{NPV}^{rev} = dw_{net}^{rev}$$

(reversible isothermal process)

where we recognize that the reversible pressure–volume work is $dw_{PV}^{rev} = -PdV$, and the work of all kinds is $dw_{net}^{rev} = dw_{PV}^{rev} + dw_{NPV}^{rev}$. We see that $(dA)_T$ is the total of all the work done on the system in a reversible process at constant temperature. This is the reason that “ A ” is used as the symbol for the Helmholtz free energy: “ A ” is the initial letter in “Arbeit,” a German noun whose meaning is equivalent to that of the English noun “work.”

If a reversible process occurs at constant temperature and volume, we have $dT = 0$ and $dV = 0$. At **constant temperature and volume**, a process is reversible if and only if

$$(dA)_{TV} = dw_{NPV}^{rev}$$

(reversible process)

If only pressure–volume work is possible,

$$(dA)_{TV} = 0$$

(reversible process, only pressure–volume work)

where the subscripts indicate that volume and temperature are constant. (Of course, these conditions exclude all work, because constant volume implies that there is no pressure–volume work.)

From

$$G = H - TS = E + PV - TS$$

and the fundamental equation, we have

$$\begin{aligned} dG = dE + PdV + VdP - SdT - TdS &= TdS - PdV + dw_{NPV}^{rev} & -TdS + PdV + VdP \\ -SdT &= -SdT + VdP + dw_{NPV}^{rev} \end{aligned}$$

For a reversible process in which all of the work is pressure–volume work,

$$dG = -SdT + VdP$$

(reversible process, only pressure–volume work)

For a reversible process in which only pressure–volume work is possible, this equation gives the amount, dG , by which the Gibbs free energy must change when the temperature changes by dT and the pressure changes by dP . For a reversible process that occurs at constant temperature and pressure, $dT = 0$ and $dP = 0$. At **constant temperature and pressure**, the process will be reversible if and only if

$$(dG)_{TP} = dw_{NPV}^{rev}$$

(any reversible process)

If only pressure–volume work is possible,

$$(dG)_{TP} = 0$$

(reversible process, only pressure–volume work)

where the subscripts indicate that temperature and pressure are constant.


In this section, we develop several criteria for reversible change, stating these criteria as differential expressions. Since each of these expressions applies to every incremental part of a reversible change that falls within its scope, corresponding expressions apply to finite changes. For example, we find $(dE)_S = dw_{net}^{rev}$ for every incremental part of a reversible process in which the

entropy has a constant value. Since we can find the energy change for a finite amount of the process by summing up the energy changes in every incremental portion, it follows that

$$(\Delta E)_S = w_{net}^{rev}$$

(reversible process)

Each of the other differential-expression criteria for reversible change also gives rise to a corresponding criterion for a finite reversible change. These criteria are summarized in §25.

In developing the criteria in this section, we stipulate that various combinations of the thermodynamic functions that characterize the system are constant. We develop these criteria for systems undergoing reversible change; consequently, the requirements imposed by reversibility must be satisfied also. In particular, the system must be composed of homogeneous phases and its temperature must be the same as that of the surroundings. The pressure of the system must be equal to the pressure applied to it by the surroundings. When we specify that a reversible process occurs at constant temperature, we  mean that $T = \hat{T} = \text{constant}$. When we specify that a reversible process occur at constant pressure, we mean that $P = P_{applied} = \text{constant}$.

This page titled [9.14: The Fundamental Equation and Other Criteria for Reversible Change](#) 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.