

9.19: The Energy Change for A Spontaneous Process at Constant S and V

From the fundamental equation, $dE - TdS + PdV = dw_{NPV}^{rev}$ for a reversible process. We find that the criterion for reversible change at constant entropy is $(dE)_S = dw_{net}^{rev}$. For a reversible process at constant entropy and volume, we find $(dE)_{SV} = dw_{NPV}^{rev}$.

To consider the energy change for a spontaneous process, we begin with $dE = dq + dw$, which is independent of whether the change is spontaneous or reversible. For a spontaneous process in which both pressure–volume, dw_{PV}^{spon} , and non-pressure–volume work, dw_{NPV}^{spon} , are possible, we have $dE = dq^{spon} + dw_{PV}^{spon} + dw_{NPV}^{spon}$, which we can rearrange to

$$dE - dw_{PV}^{spon} - dw_{NPV}^{spon} = dq^{spon}$$

For a spontaneous, constant-entropy change that occurs while the system is in contact with its surroundings, we have $dq^{spon} < 0$. Hence, we have $(dE)_S - dw_{PV}^{spon} - dw_{NPV}^{spon} < 0$. Letting $dw_{net}^{spon} = dw_{PV}^{spon} + dw_{NPV}^{spon}$, we can express this as

$$(dE)_S < dw_{net}^{spon}$$

(spontaneous process, constant S)

If we introduce the further condition that the spontaneous process occurs while the volume of the system remains constant, we have $dw_{PV}^{spon} = 0$. Making this substitution and repeating our earlier result for a reversible process, we have the parallel relationships

$$(dE)_{SV} < dw_{NPV}^{spon}$$

(spontaneous process, constant S and V)

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

(reversible process, constant S and V)

If we introduce the still further requirement that only pressure–volume work is possible, we have $dw_{NPV}^{spon} = 0$. The parallel relationships become

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

(spontaneous process, constant S and V, only PV work)

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

(reversible process, constant S and V, only PV work)

These equations state the criteria for change under conditions in which the entropy and volume of the system remain constant. If the process is reversible, the energy change must be equal to the non-pressure–volume work. If the process is spontaneous, the energy change must be less than the non-pressure volume work. If only pressure–volume work is possible, the energy of the system must decrease in a spontaneous process and remain constant in a reversible process. Each of these differential-expression criteria applies to every incremental part of a change that falls within its scope. In consequence, corresponding criteria apply to finite spontaneous changes. These criteria are listed in the summary in [Section 9.25](#).

Now the question arises: What sort of system can undergo a change at constant entropy? If the process is reversible and involves no heat, the entropy change will be zero. If we have a system consisting of a collection of solid objects at rest, we can rearrange the objects without transferring heat between the objects and their surroundings. For such a process, the change in the energy of the system is equal to the net work done on the system. Evidently, reversible changes in mechanical systems occur at constant entropy and satisfy the criterion

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

For a change that occurs reversibly and in which the entropy of the system is constant, the energy change is equal to the net work (of all kinds) done on the system. A spontaneous change in a mechanical system dissipates mechanical energy as heat by friction. If this heat appears in the surroundings and the thermal state of the system remains unchanged, such a spontaneous processes satisfies the criterion

$$(dE)_S < dw_{net}^{spon}$$

We have arrived at the criterion for change that we are accustomed to using when we deal with a change in the potential energy of a constant-temperature mechanical system: A spontaneous change can occur in such a system if and only if the change in the system's energy is less than the net work done on it. The excess work is degraded to heat that appears in the surroundings. This convergence notwithstanding, the principles of mechanics and those of thermodynamics, while consistent with one another, are substantially independent. We address this issue briefly in [Section 12.2](#).

In the next section, we develop spontaneous-change criteria based on the enthalpy change for a constant-entropy process. In subsequent sections, we consider other constraints and find other criteria. We find that the Helmholtz and Gibbs free energy functions are useful because they provide criteria for spontaneous change when the process is constrained to occur isothermally.

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