

9.21: The Entropy Change for A Spontaneous Process at Constant E and V

For any spontaneous process, we have $dE = dq^{spont} + dw^{spont}$, which we can rearrange to $dq^{spont} = dE - dw^{spont}$. Substituting our result from [Section 9.15](#), we have

$$\hat{T} dS > dE - dw^{spont}$$

(spontaneous process)

If the energy of the system is constant throughout the process, we have $dE = 0$ and

$$\hat{T} (dS)_E > -dw^{spont}$$

(spontaneous process, constant energy)

The spontaneous work is the sum of the pressure–volume work and the non-pressure–volume work, $dw^{spont} = dw_{PV}^{spont} + dw_{NPV}^{spont}$. If we introduce the further condition that the spontaneous process occurs while the volume of the system remains constant, we have $dw_{PV}^{spont} = 0$. Making this substitution and repeating our earlier result for a reversible process, we have the parallel relationships

$$(dS)_{EV} > \frac{-dw_{NPV}^{spont}}{\hat{T}}$$

(spontaneous process, constant E and V)

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

(reversible process, constant E and V)

(For a reversible process, $T = \hat{T}$.) If the spontaneous process occurs while \hat{T} is constant, summing the incremental contributions to a finite change of state produces the parallel relationships

$$(\Delta S)_{EV} > \frac{-w_{NPV}^{spont}}{\hat{T}}$$

(spontaneous process, constant E , V , and \hat{T})

$$(\Delta S)_{EV} = \frac{-w_{NPV}^{spont}}{\hat{T}}$$

(reversible process, constant E , V , and \hat{T})

Constant \hat{T} corresponds to the common situation in chemical experimentation in which we place a reaction vessel in a constant-temperature bath. If we introduce the further condition that only pressure–volume work is possible, we have $dw_{NPV}^{spont} = 0$. The parallel relationships become

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

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

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

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

If the energy and volume are constant for a system in which only pressure–volume work is possible, the system is isolated. The conditions we have just derived are entirely equivalent to our earlier conclusions that $dS = 0$ and $dS > 0$ for an isolated system that is at equilibrium or undergoing a spontaneous change, respectively. Summing the incremental contributions to a finite change of state produces the parallel relationships

$$(\Delta S)_{EV} > 0$$

(spontaneous process, only PV work)

$$(\Delta S)_{EV} = 0$$

(reversible process, only PV work)

The validity of these expressions is independent of any variation in either T or \hat{T} .

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