

9.22: The Entropy Change for A Spontaneous Process at Constant H and P

For any spontaneous process, we have

$$dH = dE + PdV + VdP = dq^{spon} - P_{applied}dV + dw_{NPV}^{spon} + PdV + VdP$$

If the pressure is constant ($P = P_{applied} = \text{constant}$), this becomes $dq^{spon} = dH - dw_{NPV}^{spon}$. Substituting our result from [Section 9.15](#), we have

$$\hat{T}(dS)_P > dH - dw_{NPV}^{spon}$$

(spontaneous process, constant P)

If the enthalpy of the system is also constant throughout the process, we have

$$\hat{T}(dS)_{HP} > -dw_{NPV}^{spon}$$

(spontaneous process, constant H and P)

Dividing by \hat{T} and repeating our earlier result for a reversible process, we have the parallel relationships

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

(spontaneous process, constant H and P)

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

(reversible process, constant H and P)

If it is also true that the temperature of the surroundings is constant, summing the incremental contributions to a finite change of state produces the parallel relationships

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

(spontaneous process, constant H , P , and \hat{T})

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

(reversible process, constant H , P , and $\hat{T} = T$)

If only pressure–volume work is possible, we have $dw_{NPV}^{spon} = 0$, and

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

(spontaneous process, constant H , P , only PV work)

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

(reversible process, constant H and P , only PV work)

and for a finite change of state,

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

(spontaneous process, only PV work)

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

(reversible process, only PV work)

In this and earlier sections, we develop criteria for spontaneous change that are based on dE and dH . We are now able to develop similar criteria for a spontaneous change in a system that is in thermal contact with constant-temperature surroundings. These

criteria are based on dA and dG . However, before doing so, we develop a general relationship between the isothermal work in a spontaneous process and the isothermal work in a reversible process, when these processes take a system from a common initial state to a common final state.

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