

9.20: The Enthalpy Change for A Spontaneous Process at Constant S and P

From $H = E + PV$, we have $dH = dE + d(PV)$. For a spontaneous process in which both pressure–volume and non-pressure–volume work are possible, we can write this as $dH = dq^{spon} + dw_{PV}^{spon} + dw_{NPV}^{spon} + d(PV)$, which we can rearrange to $dH - dw_{PV}^{spon} - dw_{NPV}^{spon} - d(PV) = dq^{spon}$. For a spontaneous constant-entropy change that occurs while the system is in contact with its surroundings, we have $dq^{spon} < 0$, so that

$$(dH)_S - dw_{PV}^{spon} - dw_{NPV}^{spon} - d(PV) < 0.$$

Now, let us introduce the additional constraint that the system is subjected to a constant applied pressure, $P_{applied}$, throughout the process. Thus $P_{applied}$ is a well-defined property that can be measured at any stage of the process. The incremental pressure–volume work done by the surroundings on the system is $dw_{PV}^{spon} = -P_{applied}dV$. In principle, the system can undergo spontaneous change so rapidly that there can be a transitory difference between the system pressure and the applied pressure. In practice, pressure adjustments occur very rapidly. Except in extreme cases, we find that $P = P_{applied}$ is a good approximation at all times. Then the change in the pressure volume product is $d(PV) = P_{applied}dV$. Making these substitutions, the enthalpy inequality becomes

$$(dH)_{SP} < dw_{NPV}^{spon}$$

(spontaneous process, constant S and $P_{applied}$)

From our earlier discussion of reversible processes, we have the parallel relationship

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

(any reversible process, constant S and $P_{applied}$)

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

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

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

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

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

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

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