

9.24: The Free Energy Changes for A Spontaneous Process at Constant T

Now let us consider the change in the Helmholtz free energy when a system undergoes a spontaneous change while in thermal contact with surroundings whose temperature remains constant at \hat{T} . We begin by considering an arbitrarily small increment of change in a process in which the temperature of the system remains constant at $T = \hat{T}$. The change in the Helmholtz free energy for this process is $(dA)_T = dE - TdS$. Substituting $dE = dq^{spont} + dw^{spont}$ gives

$$(dA)_T = dq^{spont} + dw^{spont} - TdS$$

(spontaneous process, constant T)

Rearranging, we have $(dA)_T - dw^{spont} + TdS = dq^{spont}$. Using the inequality $dq^{spont} < \hat{T}dS$, we have

$$(dA)_T - dw^{spont} + TdS < \hat{T}dS$$

When we stipulate that $T = \hat{T} = \text{constant}$, this becomes

$$(dA)_T < dw^{spont}$$

(spontaneous process, constant T)

where dw^{spont} is all of the work of any kind done on the system during a small increment of the spontaneous process. If we introduce the still further requirement that the volume is constant, we have $dw_{PV}^{spont} = 0$ and $dw^{spont} = dw_{NPV}^{spont}$. Then

$$(dA)_{TV} < dw_{NPV}^{spont}$$

(spontaneous process, constant T and V)

and if only pressure–volume work is possible,

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

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

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

$$(dA)_T = dw_{net}^{rev}$$

(reversible isothermal process)

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

(reversible process at constant T and V)

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

(reversible process at constant T and V , only PV work)

Similarly, under these conditions, the change in the Gibbs free energy for a spontaneous isothermal process is

$$\begin{aligned}(dG)_T &= dH - TdS \\ &= dE + d(PV) - TdS \\ &= dq^{spont} + dw_{PV}^{spont} + dw_{NPV}^{spont} + d(PV) - TdS\end{aligned}$$

Rearranging, we have

$$(dG)_T - dw_{PV}^{spont} - dw_{NPV}^{spont} - d(PV) + TdS = dq^{spont} < \hat{T}dS$$

and since $T = \hat{T} = \text{constant}$,

$$(dG)_T < dw_{pv}^{spont} + dw_{npv}^{spont} + d(pv)$$

(spontaneous process, constant T)

As we did when considering the enthalpy change for a spontaneous process, we introduce the additional constraints that the system is subjected to a constant applied pressure, P_{applied} , and that $P = P_{\text{applied}}$ throughout the process. The irreversible pressure–volume work done by the surroundings on the system becomes $dw_{PV}^{\text{spn}} = -P_{\text{applied}}dV$, and the change in the pressure volume product becomes $d(PV) = P_{\text{applied}}dV$. The Gibbs free energy inequality becomes

$$(dG)_{TP} < dw_{npv}^{\text{spn}}$$

(spontaneous process, constant P_{applied} and T)

If only pressure–volume work is possible, this becomes

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

(spontaneous process, constant P_{applied} and T , only PV work)

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

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

(reversible process, constant P and T)

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

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

Since each of these differential-expression criteria applies to every incremental part of a reversible change that falls within its scope, we have the following criteria for finite spontaneous changes when the temperature of the system is constant:

$$(\Delta A)_T < w^{\text{spn}}$$

(spontaneous process, constant T)

$$(\Delta A)_{TV} < w_{npv}^{\text{spn}}$$

(spontaneous process, constant T and V)

$$(\Delta A)_{TV} < 0$$

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

$$(\Delta G)_{TP} < w_{npv}^{\text{spn}}$$

(spontaneous process, constant P_{applied} and T)

$$(\Delta G)_{TP} = 0$$

(spontaneous process, constant P_{applied} and T , only PV work)

While the development we have just made assumes that the system temperature is strictly constant, the validity of these finite-change inequalities is not restricted to the condition of strictly constant system temperature. We can derive these finite-change inequalities by essentially the same argument from less restrictive conditions.

Let us consider a spontaneous process in which a system goes from state B to state C while in contact with surroundings whose temperature remains constant at \hat{T} . We suppose that in both state B and state C the system temperature is equal to the surroundings temperature; that is, $T_B = T_C = \hat{T} = \text{constant}$. However, at any intermediate point in the process, the system can have any temperature whatsoever. In states B and C, the Helmholtz free energies are $A_B = E_B - \hat{T}S_B$ and $A_C = E_C - \hat{T}S_C$. The change in the Helmholtz free energy is $(A_C - A_B) = (E_C - E_B) - \hat{T}(S_C - S_B)$ or $(\Delta A)_{\hat{T}} = \Delta E - \hat{T}\Delta S = q^{\text{spn}} + w^{\text{spn}} - \hat{T}\Delta S$. Rearranging, and using $q^{\text{spn}} < \hat{T}\Delta S$, we have

$(\Delta A)_{\hat{T}} - w^{\text{spn}} + \hat{T}\Delta S = q^{\text{spn}} < \hat{T}\Delta S$, so that

$$(\Delta A)_{\hat{T}} < w^{\text{spn}}$$

(spontaneous process, constant \hat{T})

If we require further that the system volume remain constant, there is no pressure–volume work, and we have

$$(\Delta A)_{V\hat{T}} < w_{npv}^{spon}$$

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

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

$$(\Delta A)_{V\hat{T}} < 0$$

(spontaneous process, constant \hat{T} and V , only PV work)

Under the same temperature assumptions, and assuming that $P_B = P_C = P_{applied} = \text{constant}$, the Gibbs free energies are $G_B = E_B + P_{applied}V_B - \hat{T}S_B$ and $G_C = E_C + P_{applied}V_C - \hat{T}S_C$. So that $(G_C - G_B) = (E_C - E_B) + P_{applied}(V_C - V_B) - \hat{T}(S_C - S_B)$ or

$$\begin{aligned} (\Delta G)_{P\hat{T}} &= \Delta E + P_{applied}\Delta V - \hat{T}\Delta S \\ &= q^{spon} + w_{PV}^{spon} + w_{NPV}^{spon} + P_{applied}\Delta V - \hat{T}\Delta S \end{aligned}$$

The pressure–volume work is $w_{PV}^{spon} = -P_{applied}\Delta V$. Cancelling and rearranging, we have

$$(\Delta G)_{P\hat{T}} - w_{NPV}^{spon} + \hat{T}\Delta S = q^{spon} < \hat{T}\Delta S$$

and

$$(\Delta G)_{P\hat{T}} < w_{npv}^{spon}$$

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

If only pressure–volume work is possible,

$$(\Delta G)_{P\hat{T}} < 0$$

(spontaneous process, constant \hat{T} and P , only PV work)

We find $(\Delta G)_{P\hat{T}} < w_{npv}^{spon}$ for any spontaneous process that occurs at constant pressure, while the system is in contact with surroundings at the constant temperature \hat{T} , and in which the initial and final system temperatures are equal to \hat{T} . These are the most common conditions for carrying out a chemical reaction. Consider the situation after we mix non-volatile reactants in an open vessel in a constant-temperature bath. We suppose that the initial temperature of the mixture is the same as that of the bath. The atmosphere applies a constant pressure to the system. The reaction is an irreversible process. It proceeds spontaneously until its equilibrium position is reached. Until equilibrium is reached, the reaction cannot be reversed by an arbitrarily small change in the applied pressure or the temperature of the surroundings. $(\Delta G)_{P\hat{T}} < w_{npv}^{spon}$ and $(\Delta G)_{P\hat{T}} < 0$ are criteria for spontaneous change that apply to this situation whatever the temperature of the system might be during any intermediate part of the process.

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