9.25: Summary- Thermodynamic Functions as Criteria for Change

For a spontaneous process, we conclude that the entropy change of the system must satisfy the inequality $\Delta S+\Delta\hat{S}>0$. For any process that occurs reversibly, we conclude that $\Delta S+\Delta\hat{S}=0$. For every incremental part of a reversible process that occurs in a closed system, we have the following relationships:

$$dE=TdS-PdV+dw_{NPV}^{rev}$$

$$dH=TdS+VdP+dw_{NPV}^{rev}$$

$$dA=-SdT-PdV+dw_{NPV}^{rev}$$

$$dG=-SdT+VdP+dw_{NPV}^{rev}$$

At constant entropy, the energy relationship becomes:

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

$$(\Delta E)_S=w_{net}^{rev}$$

At constant temperature, the Helmholtz free energy relationship becomes:

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

$$(\Delta A)_T=w_{net}^{rev}$$

For reversible processes in which all work is pressure–volume work:

$$dE=TdS-PdV$$

$$dH=TdS+VdP$$

$$dA=-SdT-PdV$$

$$dG=-SdT+VdP$$

From these general equations, we find the following relationships for reversible processes when various pairs of variables are held constant:

$$(dS)_{EV}=-dw_{NPV}^{rev}/T(\Delta S)_{EV}=-w_{NPV}^{rev}/T$$

$$(dS)_{HP}=-dw_{NPV}^{rev}/T(\Delta S)_{HP}=-w_{NPV}^{rev}/T$$

$$(dE)_{SV}=dw_{NPV}^{rev}(\Delta E)_{SV}=w_{NPV}^{rev}$$

$$(dH)_{SP}=dw_{NPV}^{rev}(\Delta H)_{SP}=w_{NPV}^{rev}$$

$$(dA)_{TV}=dw_{NPV}^{rev}(\Delta A)_{TV}=w_{NPV}^{rev}$$

$$(dG)_{TP}=dw_{NPV}^{rev}(\Delta G)_{TP}=w_{NPV}^{rev}$$

If the only work is pressure–volume work, then $dw_{NPV}^{rev}=0$, $w_{NPV}^{rev}=0$, and these relationships become:

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

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

$$(dE)_{SV}=0(\Delta E)_{SV}=0$$

$$(dH)_{SP}=0(\Delta H)_{SP}=0$$

$$(dA)_{TV}=0(\Delta A)_{TV}=0$$

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

For every incremental part of an irreversible process that occurs in a closed system at constant entropy:

$$dq^{spon} < 0$$

and

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

and

$$q^{spon} < 0$$

and

$$(\Delta E)_S < w_{net}^{spon}$$

For an irreversible process at constant temperature:

$$dq^{spon} < \hat{T} dS$$

and

$$(dA)_{\hat{T}} < dw_{net}^{spon}$$

and

$$q^{spon} < \hat{T} \Delta S$$

and

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

When an irreversible process occurs with various pairs of variables held constant, we find:

$$(dS)_{EV} > -dw_{NPV}^{spon}/\hat{T}(\Delta S)_{EV} = -w_{NPV}^{spon}/\hat{T}$$

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

$$(dE)_{SV}$$

$$(dH)_{SP}$$

$$(dA)_{\hat{T}V}$$

$$(dG)_{\hat{T}P}$$

For irreversible processes in which the only work is pressure–volume work, these inequalities become:

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

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

$$(dE)_{SV} < 0(\Delta E)_{SV} < 0$$

$$(dH)_{SP} < 0(\Delta H)_{SP} < 0$$

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

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