# 2.43 ADVANCED THERMODYNAMICS

**Spring Term 2024**
**LECTURE 06**

Room 3-442
Friday, February 23, 11:00am - 1:00pm

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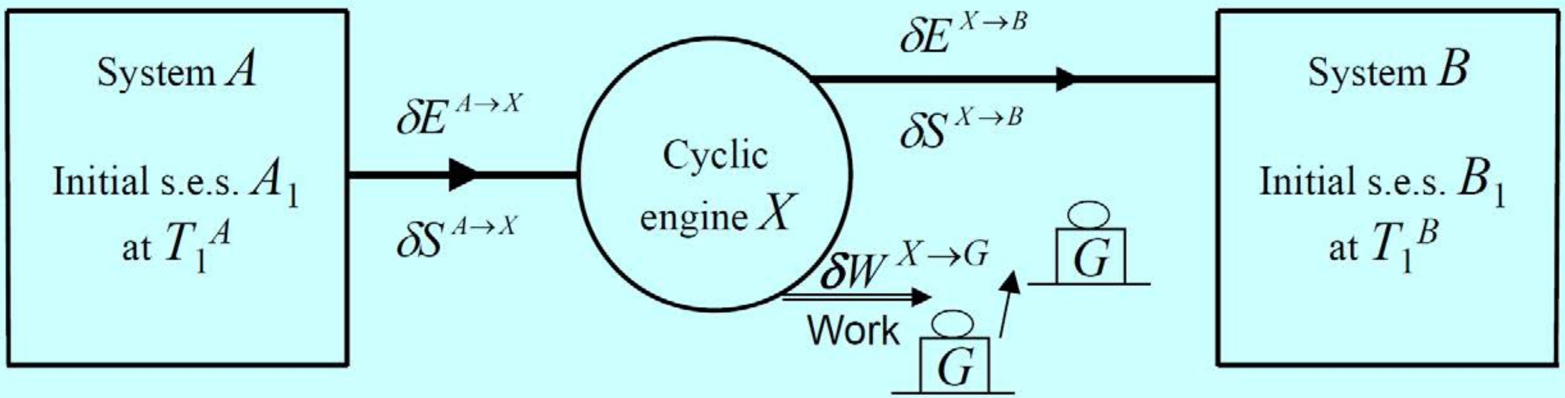
# Review of basic concepts: **Heat interactions:**
## when is the energy exchanged entirely distinguishable from Work?

The cyclic engine *X* intercepts the energy exchanged between *A* and *B* and tries to separate part of it as work.




*Energy and entropy balances for X, A and B (assuming **reversible** processes), and Gibbs relations for A and B:*

$$\begin{cases} 0 = \delta S^{A\to X} - \delta S^{X\to B} \\ 0 = \delta E^{A\to X} - \delta W^{X\to G} - \delta E^{X\to B} \\ \delta E^{A\to X} = -dE^A = -T_1^A dS^A = T_1^A \delta S^{A\to X} \\ \delta E^{X\to B} = dE^B = T_1^B dS^B = T_1^B \delta S^{X\to B} \end{cases}$$

we get

$$\frac{\delta W^{X\to G}}{\delta E^{A\to X}} = 1 - \frac{T_1^B}{T_1^A}$$

The max fraction of the exchanged energy that can be separated as work is negligible (<< 1) only in the limit $T_1^A \to T_1^B$ that is if

$$\frac{T_1^A - T_1^B}{T_1^A} << 1$$

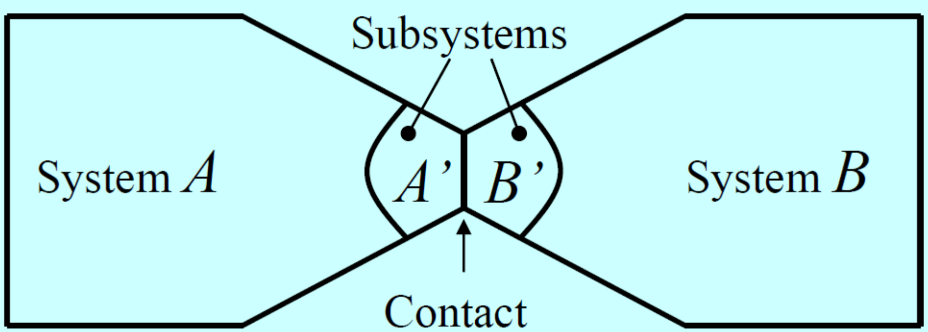
This condition defines therefore the **heat interaction**.

# is the definition of Heat compatible with the notions we learn in Heat Transfer

The strict definition of heat interaction just given may appear in contrast with the common notion that calls heat transfer the exchange of energy between systems at different temperatures.

**Heat Transfer**

- The contact between two bodies at different temperatures produces nonequilibrium states in both systems
- To study these nonequilibrium states, we model each body as a continuum of infinitesimal volumes, and assume that each is in a state not to far from a s.e.s. (*local quasi-equilibrium assumption*)
- The temperatures of two adjacent volume elements differ only slightly, therefore they interact via heat interactions
- We speak of *temperature field* within the two bodies



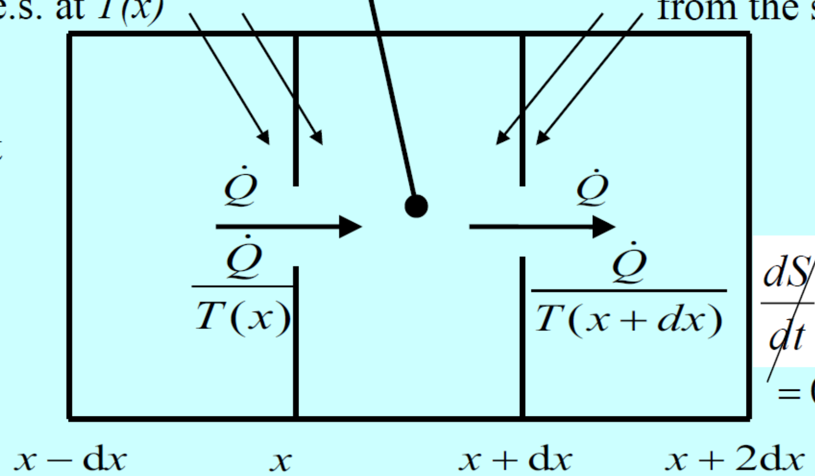
## Review of basic concepts: **Heat interactions**

# steady state heat transfer requires non-equilibrium

Infinitesimal volume in a nonequilibrium state.
Here the entropy needed to sustain the steady state is generated by irreversibility

Assumption of states not too far from the s.e.s. at *T(x)*

Assumption of states not too far from the s.e.s. at *T(x+dx)*



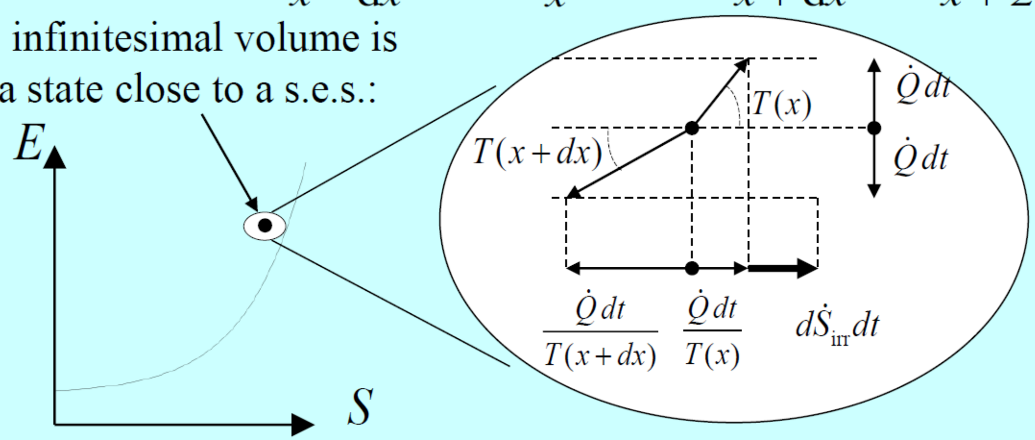

Energy balance at steady state:

$$\underbrace{\frac{dE}{dt}}_{=0} = \dot{Q} - \dot{Q}$$

Entropy balance at steady state:

$$\underbrace{\frac{dS}{dt}}_{=0} = \frac{\dot{Q}}{T(x)} - \frac{\dot{Q}}{T(x+dx)} + d\dot{S}_{\text{irr}}$$

The infinitesimal volume is in a state close to a s.e.s.:




$$d\dot{S}_{\text{irr}} = \frac{T(x)-T(x+dx)}{T(x)T(x+dx)}\dot{Q}$$

$$\approx -\frac{dT}{dx}\frac{\dot{Q}}{T^2}dx$$

Consequences of the **Principle of entropy nondecrease in weight processes:**

# Temperature (or -1/*T*) as escaping tendency for energy. Pressure as capturing tendency for volume

System $C = AB$

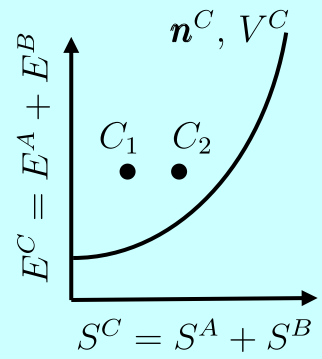
| System $A$ | System $B$ |
|---|---|
| SES $A_1$ | SES $B_1$ |
| $E_1^A$ | $E_1^B$ |
| $\boldsymbol{n}^A$, $T_1^A$ | $\boldsymbol{n}^B$, $T_1^B$ |
| $p_1^A$, $V_1^A$ | $p_1^B$, $V_1^B$ |

State $C_1 = A_1 B_1$

System $C = AB$

| System $A$ | System $B$ |
|---|---|
| SES $A_2$ | SES $B_2$ |
| $E_1^A + dE$ | $E_1^B - dE$ |
| $\boldsymbol{n}^A$ | $\boldsymbol{n}^B$ |
| $V_1^A + dV$ | $V_1^B - dV$ |

State $C_2 = A_2 B_2$




If $AB$ is isolated and states $A_1$ and $B_1$ are SES but not MES. Then, a spontaneous process for $C$ can occur only if $S_2^C \geq S_1^C$ i.e.

$$S_2^C - S_1^C \geq 0$$

from entropy additivity

$$0 \leq S_2^C - S_1^C = (S_2^A + S_2^B) - (S_1^A + S_1^B) = (S_2^A - S_1^A) + (S_2^B - S_1^B)$$

from the fundamental relations for $A$ and $B$ and the principle of maximum entropy

$$\leq \frac{1}{T_1^A} dE + \frac{p_1^A}{T_1^A} dV + \frac{1}{T_1^B}(-dE) + \frac{p_1^B}{T_1^B}(-dV)$$

$$= \underbrace{\left(\frac{1}{T_1^A} - \frac{1}{T_1^B}\right)}_{\substack{\text{must be } > 0 \\ \text{for } dV = 0 \\ \text{and } dE > 0}} dE + \underbrace{\left(\frac{p_1^A}{T_1^A} - \frac{p_1^B}{T_1^B}\right)}_{\substack{\text{must be } > 0 \\ \text{for } T_1^A = T_1^B \\ \text{and } dV > 0}} dV$$

Consequences of the **Principle of entropy nondecrease in weight processes:**

# Temperature (or -1/*T*) as escaping tendency for energy.
# Chemical potentials as escaping tendencies for constituents

System $C = AB$

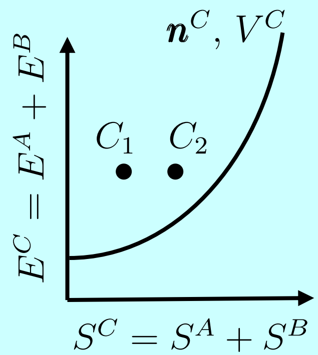
| System $A$ | System $B$ |
|---|---|
| SES $A_1$ | SES $B_1$ |
| $E_1^A$ | $E_1^B$ |
| $n_{i1}^A$, $T_1^A$ | $n_{i1}^B$, $T_1^B$ |
| $\boldsymbol{n}'^A$, $V^A$ | $\boldsymbol{n}'^B$, $V^B$ |

State $C_1 = A_1 B_1$

System $C = AB$

| System $A$ | System $B$ |
|---|---|
| SES $A_2$ | SES $B_2$ |
| $E_1^A + dE$ | $E_1^B - dE$ |
| $n_{i1}^A + dn_i$ | $n_{i1}^B - dn_i$ |
| $\boldsymbol{n}'^A$, $V^A$ | $\boldsymbol{n}'^B$, $V^B$ |

State $C_2 = A_2 B_2$




If $AB$ is isolated and states $A_1$ and $B_1$ are SES but not MES. Then, a spontaneous process for $C$ can occur only if $S_2^C \geq S_1^C$ i.e.

$$S_2^C - S_1^C \geq 0$$

from entropy additivity

$$0 \leq S_2^C - S_1^C = (S_2^A + S_2^B) - (S_1^A + S_1^B) = (S_2^A - S_1^A) + (S_2^B - S_1^B)$$

from the fundamental relations for $A$ and $B$ and the principle of maximum entropy

$$\leq \frac{1}{T_1^A} dE - \frac{\mu_{i1}^A}{T_1^A} dV + \frac{1}{T_1^B}(-dE) - \frac{\mu_{i1}^B}{T_1^B}(-dn_i)$$

$$= \underbrace{\left(\frac{1}{T_1^A} - \frac{1}{T_1^B}\right)}_{\substack{\text{must be } > 0 \\ \text{for } dn_i = 0 \\ \text{and } dE > 0}} dE + \underbrace{\left(\frac{\mu_{i1}^B}{T_1^B} - \frac{\mu_{i1}^A}{T_1^A}\right)}_{\substack{\text{must be } > 0 \\ \text{for } T_1^A = T_1^B \\ \text{and } dn_i > 0}} dn_i$$

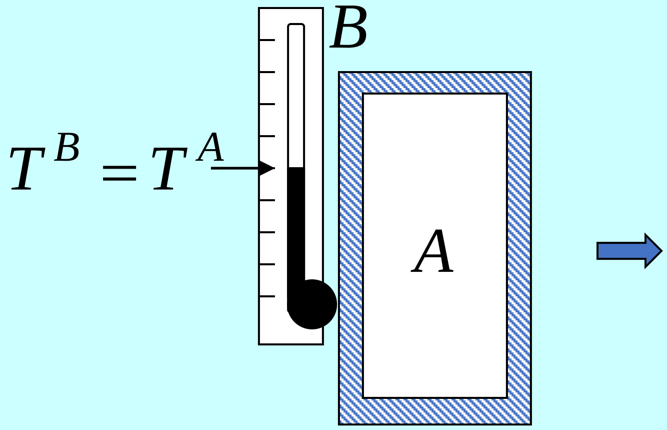
## Review of basic concepts:

## Experimental measurement of stable-equilibrium properties

# Experimental measurement of SES properties: thermometer

**Thermometer:** It is a system for which the temperature is easily readable on a scale.

If a thermometer *B* is placed in contact with a system *A* and we wait for mutual equilibrium to be reached, $T^B = T^A$.



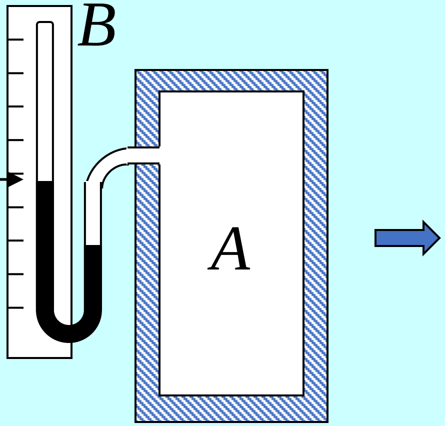

The temperature read by thermometer *B* is equal to that of system *A*, regardless of the details of system *A*.

# Experimental measurement of SES properties: manometer

**Manometer:** it is a system for which the pressure is easily readable on a scale.

If a manometer *B* is brought into mutual equilibrium with a system *A*, through a piston or a movable interface, with a system A, $p^B = p^A$.

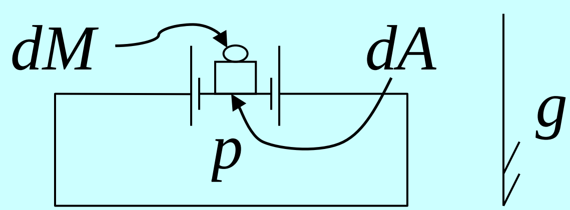
$$p^B = p^A$$



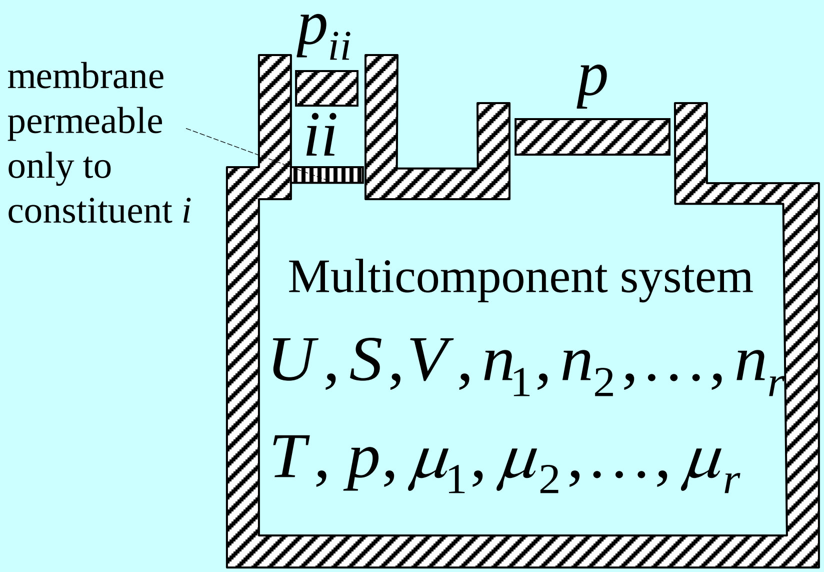

The pressure read by manometer *B* is equal to that of system *A*, regardless of details of system *A*.

**NOTE:** It can be proved (pp.158-159 of G&B) that the pressure *p* is equal to the force per unit area exerted by the system on the walls confining its constituents in the region of space with volume *V*.

$$p = \frac{g\,dM}{dA}$$



# Experimental measurement of SES properties: partial pressures and chemical potentials




Mutual stable equilibrium across the semi-permeable membrane implies:

$$T = T_{ii}$$

$$\mu_i(T, p, \boldsymbol{n}) = \mu_{ii}(T, p_{ii})$$

This measurement procedure defines the **partial pressure of constituent *i* in the mixture**.

If we know the chemical potential of **pure** constituent *i* as function of temperature and pressure, by evaluating it at the temperature and partial pressure of the mixture we obtain the chemical potential of the constituent *i* in the mixture.

# Construction of the fundamental relation from measurements of $T$, $p$, $\alpha_p$, $\kappa_T$, $C_p$, and $\mu_i$'s (through $p_{ii}$'s)

For SES's for which these properties are defined (e.g. single-phase states)...

... if we know them as functions of $T$, $p$ and $\boldsymbol{n}$ we can reconstruct (by integration) the fundamental relation.

$$\left.\begin{array}{l} \alpha_p = \alpha_p(T,p,\boldsymbol{n}) \\ \kappa_T = \kappa_T(T,p,\boldsymbol{n}) \\ C_p = C_p(T,p,\boldsymbol{n}) \\ \mu_i = \mu_i(T,p,\boldsymbol{n}) \end{array}\right\} \leftrightarrow \left\{\begin{array}{l} S = S(T,p,\boldsymbol{n}) \\ E = E(T,p,\boldsymbol{n}) \\ V = V(T,p,\boldsymbol{n}) \\ G = G(T,p,\boldsymbol{n}) \\ H = H(T,p,\boldsymbol{n}) \end{array}\right.$$

$$\left.\begin{array}{l} S = S(T,p,\boldsymbol{n}) \\ E = E(T,p,\boldsymbol{n}) \\ V = V(T,p,\boldsymbol{n}) \end{array}\right\} \quad S = S(E,V,\boldsymbol{n})$$

$$S = S(E,V,\boldsymbol{n}) \updownarrow H = H(S,V,\boldsymbol{n})$$

$$G = G(T,p,\boldsymbol{n}) \leftrightarrow H = H(S,V,\boldsymbol{n})$$

For example, at fixed amounts $\boldsymbol{n}$ we can integrate these general relations:

$$(dE)_{\boldsymbol{n}} = \left(C_p - pV\alpha_p\right)dT + \left(p\kappa_T - T\alpha_p\right)V\,dp$$

$$(dS)_{\boldsymbol{n}} = \frac{C_p}{T}\,dT - \alpha_p V\,dp$$

$$(dH)_{\boldsymbol{n}} = C_p\,dT + \left(1 - T\alpha_p\right)V\,dp$$

## Review of basic concepts:

## Characteristic SES functions

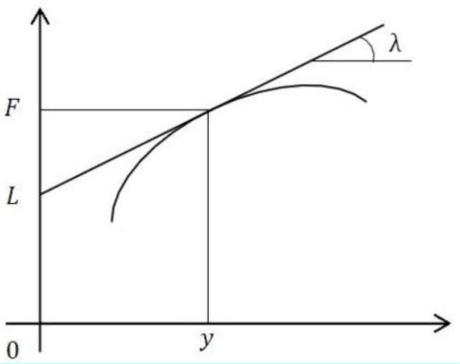
## from
## Legendre transforms
## of the fundamental relation

# Changing variables of the fundamental relation by means Legendre transform

**Legendre transform of a function of a single variable**

Consider a curve described by the convex or concave monotonic function

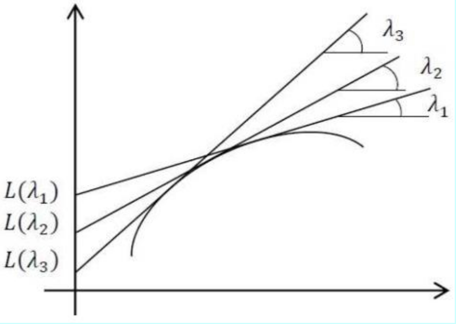
$$F = F(y) \qquad \lambda(y) = \frac{\partial F}{\partial y} \qquad L(y) = F(y) - \lambda(y)\, y$$




Legendre's observation is that we can describe the same curve also as the envelope of the family of its tangent lines, by the function that relates the slope $\lambda$ of each tangent line to its intercept $L$ at $y = 0$.

Since the $F(y)$ is convex or concave and monotonic, $\lambda = \lambda(y)$ is monotonic and hence invertible. Using its inverse, $y = y(\lambda)$, we find the Legendre transform of $F = F(y)$

$$L = L(\lambda) = F(y(\lambda)) - \lambda\, y(\lambda)$$




Notice that the Legendre transform of $L = L(\lambda)$ is the original $F = F(y)$. In fact, denoting the slope of its tangent line by $\eta$ and its intercept by $G$,

$$\eta(\lambda) = \frac{\partial L}{\partial \lambda} = \frac{\partial F}{\partial y}\frac{\partial y}{\partial \lambda} - y(\lambda) - \lambda \frac{\partial y}{\partial \lambda} = -y(\lambda) \quad \Rightarrow \quad \eta = -y$$

$$G = G(\eta) = L(\lambda(\eta)) - \eta\, \lambda(\eta)$$

$$G(y) = G(-\eta) = L(\lambda(y)) + y\, \lambda(y) = F(y(\lambda(y))) - \lambda(y)\, y(\lambda(y)) + y\, \lambda(y) = F(y)$$

where we used $y(\lambda(y)) = y$ since $y = y(\lambda)$ is the inverse of $\lambda = \lambda(y)$.

Examples:

$F(y) = e^y$

$L(\lambda) = \lambda - \lambda \ln \lambda$

$F(y) = \frac{1}{2} y^2$

$L(\lambda) = \frac{1}{2}\lambda^2$

$F(y) = \frac{1}{2} \underline{y} \cdot \underline{\underline{A}} \cdot \underline{y}$

$L(\lambda) = \frac{1}{2} \underline{\lambda} \cdot \underline{\underline{A}} \cdot \underline{\lambda}$

# Characteristic SES functions from Legendre transforms of the fundamental relation in energy form

| | | | | | |
|---|---|---|---|---|---|
| $E = E(S, V, \boldsymbol{n})$ | | | | $\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n}$ | fundamental relation |
| $F = F(y, \cdots)$ | $y$ | $\lambda = \dfrac{\partial F}{\partial y}$ | $L = F - \lambda\, y = L(\lambda, \cdots)$ | $\mathrm{d}L = -y\,\mathrm{d}\lambda + \cdots$ | |
| $E = E(S, V, \boldsymbol{n})$ | $S$ | $T$ | $F = E - TS = F(T, V, \boldsymbol{n})$ | $\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n}$ | Helmholtz free energy |
| $F = F(T, V, \boldsymbol{n})$ | $V$ | $-p$ | $G = F - (-p)V = E - TS + pV = G(T, p, \boldsymbol{n})$ | $\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n}$ | Gibbs free energy |
| $E = E(S, V, \boldsymbol{n})$ | $V$ | $-p$ | $H = E - (-p)V = H(S, p, \boldsymbol{n})$ | $\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n}$ | Enthalpy |
| $H = H(S, p, \boldsymbol{n})$ | $S$ | $T$ | $G = H - TS = E - TS + pV = G(T, p, \boldsymbol{n})$ | $\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n}$ | Gibbs free energy |
| $G = G(T, p, \boldsymbol{n})$ | $n_i$ | $\mu_i$ | $Eu_i = G - \mu_i n_i = E - TS + pV - \mu_i n_i = Eu_i(T, p, \mu_i, \boldsymbol{n}')$ | $\mathrm{d}Eu_i = -S\,\mathrm{d}T + V\,\mathrm{d}p - n_i\,\mathrm{d}\mu_i + \boldsymbol{\mu}'\cdot\mathrm{d}\boldsymbol{n}'$ | osmotic free energy |
| $G = G(T, p, \boldsymbol{n})$ | $\boldsymbol{n}$ | $\boldsymbol{\mu}$ | $Eu = G - \boldsymbol{\mu}\cdot\boldsymbol{n} = E - TS + pV - \boldsymbol{\mu}\cdot\boldsymbol{n} = Eu(T, p, \boldsymbol{\mu})$ | $\mathrm{d}Eu = -S\,\mathrm{d}T + V\,\mathrm{d}p - \boldsymbol{n}\cdot\mathrm{d}\boldsymbol{\mu}$ | Euler free energy |

# Maxwell relations

From $E(S,V,\boldsymbol{n})$, $T = \left(\frac{\partial E}{\partial S}\right)_{V,\boldsymbol{n}} = T(S,V,\boldsymbol{n})$ and $p = -\left(\frac{\partial E}{\partial V}\right)_{S,\boldsymbol{n}} = p(S,V,\boldsymbol{n})$

$$\left(\frac{\partial^2 E}{\partial S \partial V}\right)_{\boldsymbol{n}} = \left(\frac{\partial^2 E}{\partial V \partial S}\right)_{\boldsymbol{n}} \quad \Rightarrow \quad \boxed{-\left(\frac{\partial p}{\partial S}\right)_{V,\boldsymbol{n}} = \left(\frac{\partial T}{\partial V}\right)_{S,\boldsymbol{n}}}$$

From $F(T,V,\boldsymbol{n})$, $S = -\left(\frac{\partial F}{\partial T}\right)_{V,\boldsymbol{n}} = S(T,V,\boldsymbol{n})$ and $p = -\left(\frac{\partial F}{\partial V}\right)_{T,\boldsymbol{n}} = p(T,V,\boldsymbol{n})$

$$\left(\frac{\partial^2 F}{\partial T \partial V}\right)_{\boldsymbol{n}} = \left(\frac{\partial^2 F}{\partial V \partial T}\right)_{\boldsymbol{n}} \quad \Rightarrow \quad \boxed{\left(\frac{\partial p}{\partial T}\right)_{V,\boldsymbol{n}} = \left(\frac{\partial S}{\partial V}\right)_{T,\boldsymbol{n}}}$$

From $H(S,p,\boldsymbol{n})$, $T = \left(\frac{\partial H}{\partial S}\right)_{p,\boldsymbol{n}} = T(S,p,\boldsymbol{n})$ and $V = \left(\frac{\partial H}{\partial p}\right)_{S,\boldsymbol{n}} = V(S,p,\boldsymbol{n})$

$$\left(\frac{\partial^2 H}{\partial S \partial p}\right)_{\boldsymbol{n}} = \left(\frac{\partial^2 H}{\partial p \partial S}\right)_{\boldsymbol{n}} \quad \Rightarrow \quad \boxed{\left(\frac{\partial V}{\partial S}\right)_{p,\boldsymbol{n}} = \left(\frac{\partial T}{\partial p}\right)_{S,\boldsymbol{n}}}$$

From $G(T,p,\boldsymbol{n})$, $S = -\left(\frac{\partial G}{\partial T}\right)_{p,\boldsymbol{n}} = S(T,p,\boldsymbol{n})$ and $V = \left(\frac{\partial G}{\partial p}\right)_{T,\boldsymbol{n}} = V(T,p,\boldsymbol{n})$

$$\left(\frac{\partial^2 G}{\partial T \partial p}\right)_{\boldsymbol{n}} = \left(\frac{\partial^2 G}{\partial p \partial T}\right)_{\boldsymbol{n}} \quad \Rightarrow \quad \boxed{\left(\frac{\partial V}{\partial T}\right)_{p,\boldsymbol{n}} = -\left(\frac{\partial S}{\partial p}\right)_{T,\boldsymbol{n}}}$$

# Maxwell relations

From $G(T,p,\boldsymbol{n})$, $S=-\left(\frac{\partial G}{\partial T}\right)_{p,\boldsymbol{n}}=S(T,p,\boldsymbol{n})$, $V=\left(\frac{\partial G}{\partial p}\right)_{T,\boldsymbol{n}}=p(S,p,\boldsymbol{n})$ and $\mu_i=\left(\frac{\partial G}{\partial n_i}\right)_{T,p,\boldsymbol{n}_i'}=\mu_i(T,p,\boldsymbol{n})$ we obtain also these other useful relations:

$$\left(\frac{\partial^2 G}{\partial T\partial n_i}\right)_{p,\boldsymbol{n}_i'}=\left(\frac{\partial^2 G}{\partial n_i\partial T}\right)_{p,\boldsymbol{n}'}\quad\Rightarrow\quad -\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\boldsymbol{n}}=\left(\frac{\partial S}{\partial n_i}\right)_{T,p,\boldsymbol{n}_i'}=\underbrace{s_i(T,p,\boldsymbol{n})}$$

later we will call this the **partial entropy** of constituent $i$

$$\left(\frac{\partial^2 G}{\partial p\partial n_i}\right)_{T,\boldsymbol{n}_i'}=\left(\frac{\partial^2 G}{\partial n_i\partial p}\right)_{T,\boldsymbol{n}_i'}\quad\Rightarrow\quad \left(\frac{\partial \mu_i}{\partial p}\right)_{T,\boldsymbol{n}}=\left(\frac{\partial V}{\partial n_i}\right)_{T,p,\boldsymbol{n}_i'}=\underbrace{v_i(T,p,\boldsymbol{n})}$$

later we will call this the **partial volume** of constituent $i$

$$\left(\frac{\partial^2 G}{\partial n_i\partial n_j}\right)_{p,T,\boldsymbol{n}_{ij}''}=\left(\frac{\partial^2 G}{\partial n_j\partial n_i}\right)_{p,T,\boldsymbol{n}_{ij}''}\quad\Rightarrow\quad \left(\frac{\partial \mu_i}{\partial n_j}\right)_{T,p,\boldsymbol{n}_j'}=\left(\frac{\partial \mu_j}{\partial n_i}\right)_{T,p,\boldsymbol{n}_i'}$$

# Characteristic SES functions from Legendre transforms of the fundamental relation in entropy form

| | | | | | |
|---|---|---|---|---|---|
| $S = S(E, V, \boldsymbol{n})$ | | | | $\mathrm{d}S = \frac{1}{T}\,\mathrm{d}E + \frac{p}{T}\,\mathrm{d}V$ $-\frac{1}{T}\boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n}$ | fundamental relation |
| $F = F(y, \cdots)$ | $y$ | $\lambda = \dfrac{\partial F}{\partial y}$ | $L = F - \lambda\, y$ $= L(\lambda, \cdots)$ | $\mathrm{d}L = -y\,\mathrm{d}\lambda + \cdots$ | |
| $S = S(E, V, \boldsymbol{n})$ | $E$ | $\dfrac{1}{T}$ | $J = S - \frac{E}{T}$ $= J(\frac{1}{T}, V, \boldsymbol{n})$ $= -\frac{1}{T}F(T, V, , \boldsymbol{n})$ | $\mathrm{d}J = -E\,\mathrm{d}\frac{1}{T} + \frac{p}{T}\,\mathrm{d}V$ $-\frac{1}{T}\boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n}$ | Massieu free entropy |
| $J = J(\frac{1}{T}, V, \boldsymbol{n})$ | $V$ | $\dfrac{p}{T}$ | $K = J - \frac{p}{T}V$ $= S - \frac{E}{T} - \frac{p}{T}V$ $= K(\frac{1}{T}, \frac{p}{T}, \boldsymbol{n})$ $= -\frac{1}{T}G(T, p, \boldsymbol{n})$ | $\mathrm{d}K = -E\,\mathrm{d}\frac{1}{T} - V\,\mathrm{d}\frac{p}{T}$ $-\frac{1}{T}\boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n}$ | Horstmann-Planck free entropy |
| $K = K(\frac{1}{T}, \frac{p}{T}, \boldsymbol{n})$ | $\boldsymbol{n}$ | $-\dfrac{\boldsymbol{\mu}}{T}$ | $Su = K + \frac{1}{T}\boldsymbol{\mu}\cdot\boldsymbol{n}$ $= S - \frac{E}{T} - \frac{p}{T}V$ $+\frac{1}{T}\boldsymbol{\mu}\cdot\boldsymbol{n}$ $= Su(\frac{1}{T}, \frac{p}{T}, \frac{\boldsymbol{\mu}}{T})$ $= -\frac{1}{T}Eu(T, p, \boldsymbol{\mu})$ | $\mathrm{d}Su = -E\,\mathrm{d}\frac{1}{T} - V\,\mathrm{d}\frac{p}{T}$ $+\boldsymbol{n}\cdot\mathrm{d}\frac{\boldsymbol{\mu}}{T}$ | Euler free entropy |

# Maxwell relations

From $S(E,V,\boldsymbol{n})$, $\frac{1}{T}=\left(\frac{\partial S}{\partial E}\right)_{V,\boldsymbol{n}}=\frac{1}{T}(E,V,\boldsymbol{n})$ and $\frac{p}{T}=\left(\frac{\partial S}{\partial V}\right)_{E,\boldsymbol{n}}=\frac{p}{T}(E,V,\boldsymbol{n})$

$$\left(\frac{\partial^2 S}{\partial E\partial V}\right)_{\boldsymbol{n}}=\left(\frac{\partial^2 S}{\partial V\partial E}\right)_{\boldsymbol{n}} \quad\Rightarrow\quad \left(\frac{\partial p}{\partial E}\right)_{V,\boldsymbol{n}}=\left(\frac{\partial T}{\partial V}\right)_{E,\boldsymbol{n}}$$

From $M(\frac{1}{T},V,\boldsymbol{n})$, $E=-\left(\frac{\partial M}{\partial \frac{1}{T}}\right)_{V,\boldsymbol{n}}=E(\frac{1}{T},V,\boldsymbol{n})$ and $\frac{p}{T}=\left(\frac{\partial M}{\partial V}\right)_{T,\boldsymbol{n}}=\frac{p}{T}(\frac{1}{T},V,\boldsymbol{n})$

$$\left(\frac{\partial^2 M}{\partial \frac{1}{T}\partial V}\right)_{\boldsymbol{n}}=\left(\frac{\partial^2 M}{\partial V\partial \frac{1}{T}}\right)_{\boldsymbol{n}} \quad\Rightarrow\quad \left(\frac{\partial E}{\partial V}\right)_{T,\boldsymbol{n}}=-p+T\left(\frac{\partial p}{\partial T}\right)_{V,\boldsymbol{n}}$$

From $J(E,\frac{p}{T},\boldsymbol{n})$, $\frac{1}{T}=\left(\frac{\partial J}{\partial E}\right)_{\frac{p}{T},\boldsymbol{n}}=\frac{1}{T}(E,\frac{p}{T},\boldsymbol{n})$ and $V=-\left(\frac{\partial J}{\partial \frac{p}{T}}\right)_{E,\boldsymbol{n}}=V(E,\frac{p}{T},\boldsymbol{n})$

$$\left(\frac{\partial^2 J}{\partial E\partial \frac{p}{T}}\right)_{\boldsymbol{n}}=\left(\frac{\partial^2 J}{\partial \frac{p}{T}\partial E}\right)_{\boldsymbol{n}} \quad\Rightarrow\quad \left(\frac{\partial E}{\partial V}\right)_{\frac{p}{T},\boldsymbol{n}}=-p+T\left(\frac{\partial p}{\partial T}\right)_{E,\boldsymbol{n}}$$

From $K(\frac{1}{T},\frac{p}{T},\boldsymbol{n})$, $E=-\left(\frac{\partial K}{\partial \frac{1}{T}}\right)_{\frac{p}{T},\boldsymbol{n}}=E(\frac{1}{T},\frac{p}{T},\boldsymbol{n})$, $V=-\left(\frac{\partial K}{\partial \frac{p}{T}}\right)_{T,\boldsymbol{n}}=V(\frac{1}{T},\frac{p}{T},\boldsymbol{n})$

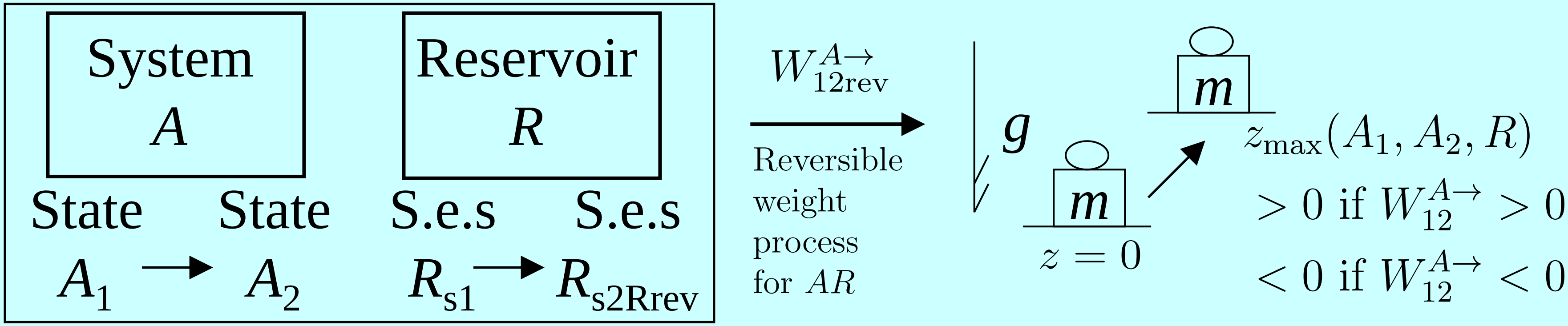
$$\left(\frac{\partial^2 K}{\partial \frac{1}{T}\partial \frac{p}{T}}\right)_{\boldsymbol{n}}=\left(\frac{\partial^2 K}{\partial \frac{p}{T}\partial \frac{1}{T}}\right)_{\boldsymbol{n}} \quad\Rightarrow\quad \left(\frac{\partial E}{\partial p}\right)_{T,\boldsymbol{n}}=-T\left(\frac{\partial V}{\partial T}\right)_{\frac{p}{T},\boldsymbol{n}}$$

**Review of basic concepts:**

**availabile energy with respect to various types of thermal reservoirs**

**availability functions**

# Available energy with respect to a thermal reservoir with fixed volume and amounts




Energy balance: $(E_2^A - E_1^A) + (E_2^R - E_1^R) = -W_{12}^{A\rightarrow}$

Entropy balance: $(S_2^A - S_1^A) + (S_2^R - S_1^R) = S_{\text{gen}}$

Fund.rel. for $R$: $E_2^R - E_1^R = T_R\,(S_2^R - S_1^R)$

Eliminate $(E_2^R - E_1^R)$ and $(S_2^R - S_1^R)$ from the above to yield:

$$W_{12}^{A\rightarrow} = E_1^A - E_2^A - T_R\,(S_1^A - S_2^A) - T_R\,S_{\text{gen}} = W_{12\text{rev}}^{A\rightarrow} - T_R\,S_{\text{gen}}$$

$$W_{12\text{rev}}^{A\rightarrow} = \left(\Omega^R\right)_1^A - \left(\Omega^R\right)_2^A = \Gamma_1^A - \Gamma_2^A$$

where $\left(\Omega^R\right)^A = E^A - E_R^A - T_R\,(S^A - S_R^A) = \Gamma^A - \Gamma_R^A$

we define the **canonical availability function** $\Gamma = E - T_R\,S$

Note that $\Gamma$ is **minimum at state** $A_R$ with $T_R^A = T_R$, where $\Gamma_R = F_R$

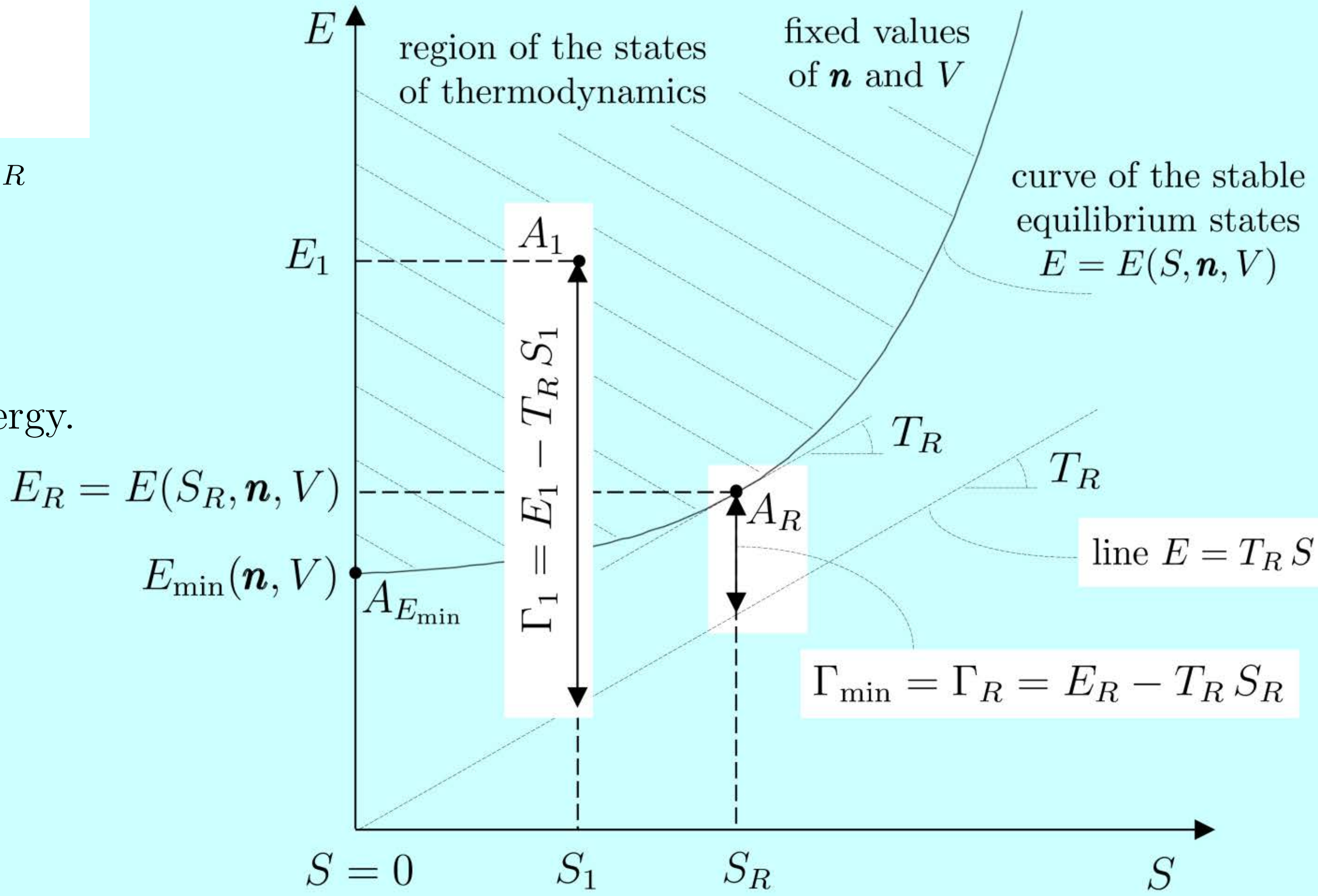
# Available energy with respect to a thermal reservoir with fixed volume and amounts

Availability function $\Gamma = E - T_R\,S$:

From $(\Omega^R)_1^A = \Gamma_1^A - \Gamma_R^A \begin{cases} = 0 \text{ if } A_1 = A_R \\ > 0 \text{ if } A_1 \neq A_R \end{cases}$

follows that $\Gamma > \Gamma_R$ for any state of $A$ that is not of MSE with $R$.

The minimum value $\Gamma_R$ is achieved only at the MSE state $A_R$, where $\Gamma_R = F_R$, the Helmholtz free energy.



# Stability conditions deriving from the available energy with respect to a thermal reservoir with fixed volume and amounts

If $A$ is in state $A_R$ (MSE with the thermal reservoir $R$), any possible variation to another state $A_1$ is such that

$$\Delta\Gamma^A = \Gamma^A_1 - \Gamma^A_R > 0$$

For example, choose $A_1$ to be the neighbouring SES with $\Delta S^A = dS$, and the same values of $V$ and $\boldsymbol{n}$, so that

$$\Delta E^A = E^A(S_R + dS, V, \boldsymbol{n}) - E^A_R = T_R dS + \tfrac{1}{2} d^2 E^A|_{V,\boldsymbol{n}} + \cdots$$

This implies

$$\Delta\Gamma^A = \Delta E^A - T_R \Delta S^A = \tfrac{1}{2} d^2 E^A|_{V,\boldsymbol{n}} + \cdots > 0 \quad \Rightarrow \quad \boxed{d^2 E^A|_{V,\boldsymbol{n}} \geq 0}$$

Again, choose instead $A_1$ to be the neighbouring SES with $\Delta E^A = dE$, and the same values of $V$ and $\boldsymbol{n}$, so that

$$\Delta S^A = S^A(E_R + dE, V, \boldsymbol{n}) - S^A_R = \frac{1}{T_R} dE + \tfrac{1}{2} d^2 S^A|_{V,\boldsymbol{n}} + \cdots$$

This implies

$$\Delta\Gamma^A = \Delta E^A - T_R \Delta S^A = -\tfrac{1}{2} d^2 S^A|_{V,\boldsymbol{n}} + \cdots > 0 \quad \Rightarrow \quad \boxed{d^2 S^A|_{V,\boldsymbol{n}} \leq 0}$$

 **Consequences of the Maximum Entropy Principle:**

# Concavity of the fundamental relation

In a similar way, we can prove that the fundamental relation is concave in all its independent variables, i.e., that in any SES **the Hessian of the fundamental relation** $S = S(E, \boldsymbol{n}, V)$ **is a negative semidefinite** matrix

$$\text{Hessian}(S) = \begin{bmatrix} \frac{\partial^2 S}{\partial E^2} & \frac{\partial^2 S}{\partial E \partial n_1} & \cdots & \frac{\partial^2 S}{\partial E \partial n_r} & \frac{\partial^2 S}{\partial E \partial V} \\ \frac{\partial^2 S}{\partial n_1 \partial E} & \frac{\partial^2 S}{\partial n_1^2} & \cdots & \frac{\partial^2 S}{\partial n_1 \partial n_r} & \frac{\partial^2 S}{\partial n_1 \partial V} \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \frac{\partial^2 S}{\partial n_r \partial E} & \frac{\partial^2 S}{\partial n_r \partial n_1} & \cdots & \frac{\partial^2 S}{\partial n_r^2} & \frac{\partial^2 S}{\partial n_r \partial V} \\ \frac{\partial^2 S}{\partial V \partial E} & \frac{\partial^2 S}{\partial V \partial n_1} & \cdots & \frac{\partial^2 S}{\partial V \partial n_r} & \frac{\partial^2 S}{\partial V^2} \end{bmatrix}$$

The full second-order differential of $S = S(E, \boldsymbol{n}, V)$ is

$$d^2 S_{E,\boldsymbol{n},V} = (dE, dn_1, \ldots, dn_r, dV) \cdot \text{Hessian}(S) \cdot (dE, dn_1, \ldots, dn_r, dV)^T \leq 0$$

From these properties it is possible to prove a number of general inequalities that must be satisfied by stable equilibrium properties.

# Stability conditions deriving from the available energy with respect to a thermal reservoir with fixed volume and amounts

If $V$ and $\boldsymbol{n}$ cannot change for system $A$, the **partial Hessian of the fundamental relation** $S = S^A(E, \boldsymbol{n}, V)$ is simply the second order derivative

$$\text{partialHessian}(S^A)|_{\boldsymbol{n},V} = \left(\frac{\partial^2 S}{\partial E^2}\right)^A_{\boldsymbol{n},V}$$

The partial second-order differential evaluated at state $A_R$ is

$$d^2 S^A|_{\boldsymbol{n},V} = dE \cdot \text{partialHessian}(S)|_{\boldsymbol{n},V}|_R \cdot dE = \left(\frac{\partial^2 S}{\partial E^2}\right)^A_{\boldsymbol{n},V}\Bigg|_R (dE)^2 \leq 0$$

Which, repeated for reservoirs at different $T_R$'s proves an important general concavity feature of the fundamental relation of any system $A$

$$\left(\frac{\partial^2 S}{\partial E^2}\right)_{\boldsymbol{n},V} \leq 0 \quad \Rightarrow \quad -\frac{1}{T^2}\left(\frac{\partial T}{\partial E}\right)_{\boldsymbol{n},V} = -\frac{1}{T^2 C_V} \leq 0 \quad \Rightarrow \quad C_V \geq 0$$

Similarly, from $d^2 E^A|_{\boldsymbol{n},V} \geq 0$ follows that in general, for any system $A$,

$$\left(\frac{\partial^2 E}{\partial S^2}\right)_{\boldsymbol{n},V} \geq 0 \quad \Rightarrow \quad \left(\frac{\partial T}{\partial S}\right)_{\boldsymbol{n},V} \geq 0$$

# Stability conditions and LeChatelier-Braun principle

The inequalities just seen, implied by stability conditions, give body to the general **LeChatelier-Braun theorem** (or **principle**).

So far, we have seen that

$$\left(\frac{\partial^2 S}{\partial E^2}\right)_{\boldsymbol{n},V} \leq 0 \quad \Rightarrow \quad \left(\frac{\partial T}{\partial E}\right)_{\boldsymbol{n},V} \geq 0$$

$$\left(\frac{\partial^2 E}{\partial S^2}\right)^A_{\boldsymbol{n},V} \geq 0 \quad \Rightarrow \quad \left(\frac{\partial T}{\partial S}\right)_{\boldsymbol{n},V} \geq 0$$

**Combined with the idea that $T$ is an escaping tendency for energy**, we may interpret this as follows.

If we change a SES to another SES with higher energy (or entropy), the temperature increases, hence enhancing the systems' tendency to give energy (or entropy) away. The increase of temperature can be interpreted as an attemp of the system to counteract the externally imposed increase of energy (or entropy) by enhancing its tendency to give energy (and entropy) away.

If the system is initially in MSE with a reservoir $R$, an injection (subtraction) of energy pushes its state away from MSE, but the consequent increase (decrease) of its temperature, away from the initial $T_R$, favors a spontaneous process whereby the system exchanges energy (and entropy) with $R$ so as to return to MSE.

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