2.43 ADVANCED THERMODYNAMICS

Spring Term 2024
LECTURE 05

Room 3-442
Tuesday, February 20, 2:30pm - 4:30pm

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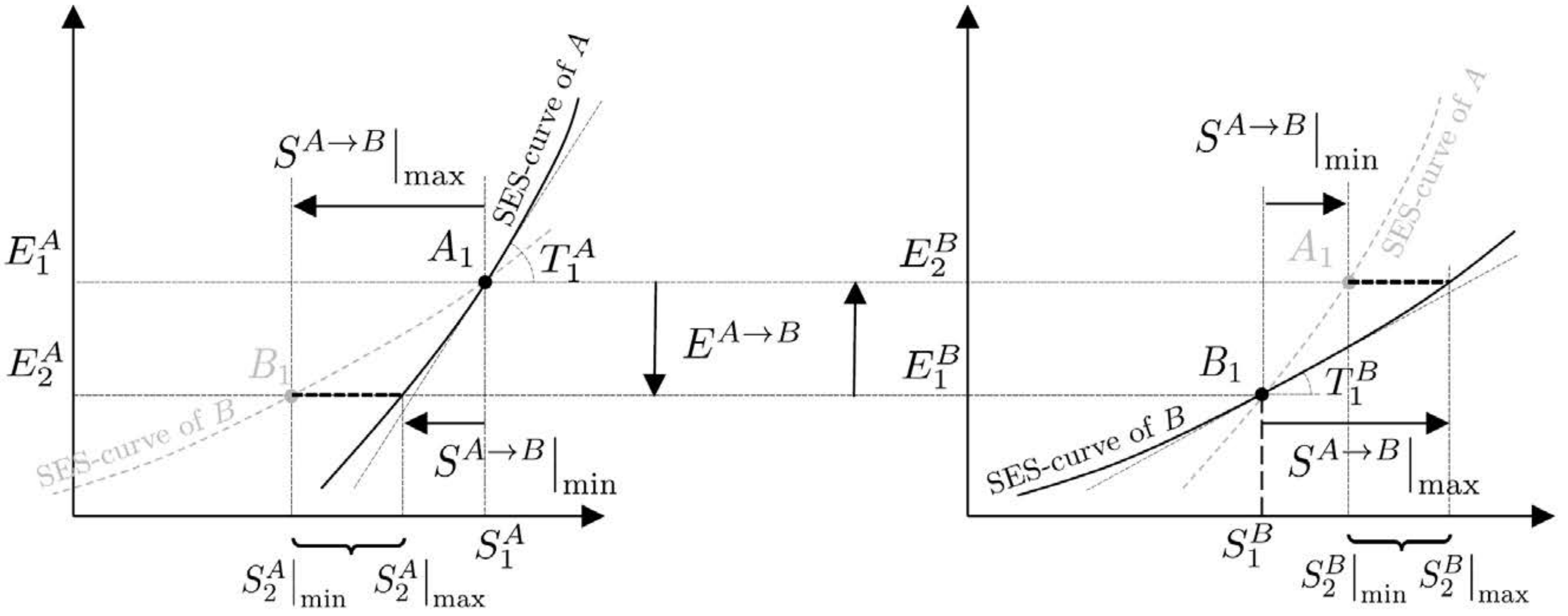
graphical proof of a more precise Clausius inequality

valid for finite transfers of energy and entropy

$$S^B_{\text{SES}}(E^B_1 + E^{A\to B}, V^B, n^B) - S^B_1 \leq S^{A\to B} \leq S^A_1 - S^A_{\text{SES}}(E^A_1 - E^{A\to B}, V^A, n^A)$$

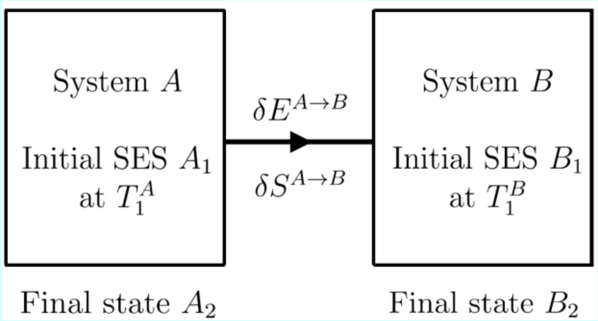


Systems A and B are initially in SES and interact directly without other effects by exchanging a finite amount $E^{A\to B}$ of energy. Such exchange can occur only if there is also an entropy $S^{A\to B}$ transfer, at least $S^{A\to B}|_{\min}$ but no more than $S^{A\to B}|_{\max}$.

Review of basic concepts:

Work interactions
Adiabatic process

Non-Work interactions
Heat interactions



Review of basic concepts: types of interactions: Work

Work interaction: when energy is exchanged with no exchange of entropy nor amounts of constituents. The exchanged energy is called *work*, denoted by $W^{\leftarrow}$ instead of $E^{\leftarrow}$:

$$\begin{cases} E_{12}^{\leftarrow} = W_{12}^{\leftarrow} = -W_{12}^{\rightarrow} \\ S_{12}^{\leftarrow} = 0 \end{cases}$$

Energy and entropy balances for a system *A* experiencing only a work interaction

$$E_2^A - E_1^A = -W_{12}^{A\rightarrow}$$

$$S_2^A - S_1^A = \left(S_{\mathrm{irr}}^A\right)_{12}$$

Adiabatic process: a process whereby the system experiences only work interactions (for example, a weight process may be adiabatic)

Review of basic concepts: types of interactions: Non-work and Heat

Non-work interaction: if there is an exchange of entropy or constituents (usually ther is also an exchange of energy)

$$S_{12}^{\leftarrow} \neq 0$$

Non-adiabatic process: if there are some non-work interactions

Heat interaction: a limiting case of a non-work interaction with no exchange of constituents in which the energy exchanged is entirely distinguishable from work. It occurs between two system initially in stable equilibrium states with

$$T_1^A \cong T_1^B \cong T_Q$$

- It entails an exchange of both energy and entropy between the two systems, such that

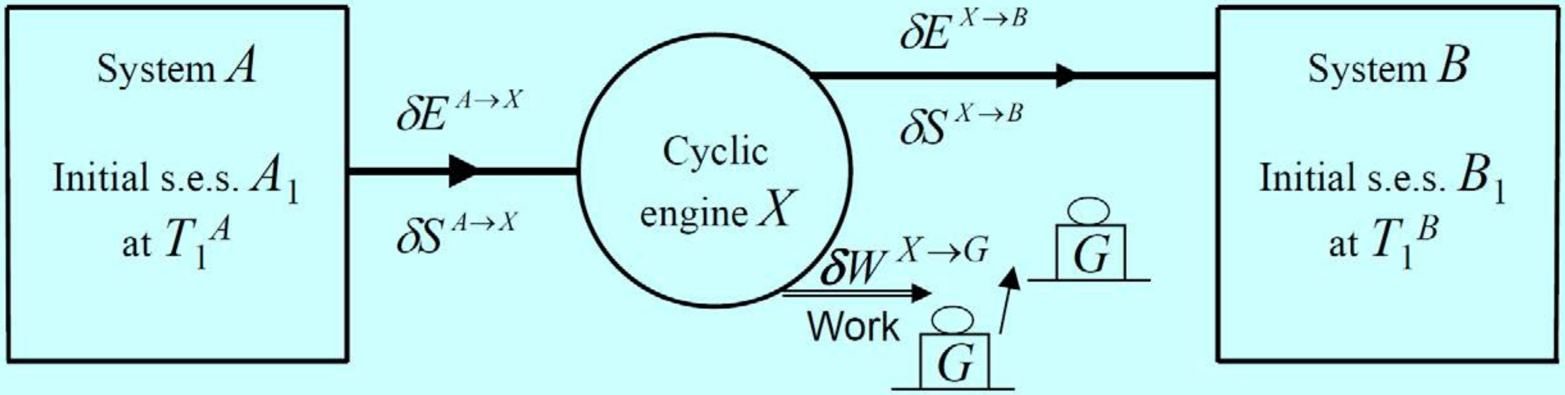
$$E_{12}^{\leftarrow} = T_Q S_{12}^{\leftarrow}$$

The exchanged energy is called *heat*, denoted by the symbol $Q^{\leftarrow}$ instead of $E^{\leftarrow}$:

$$Q_{12}^{\leftarrow} = T_Q S_{12}^{\leftarrow}$$

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:*

$$\left\{\begin{aligned} &0=\delta S^{A\to X}-\delta S^{X\to B}\\ &0=\delta E^{A\to X}-\delta W^{X\to G}-\delta E^{X\to B}\\ &\delta E^{A\to X}=-dE^A=-T_1^A dS^A=T_1^A\delta S^{A\to X}\\ &\delta E^{X\to B}=dE^B=T_1^B dS^B=T_1^B\delta S^{X\to B}\end{aligned}\right.$$

we get

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

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**.

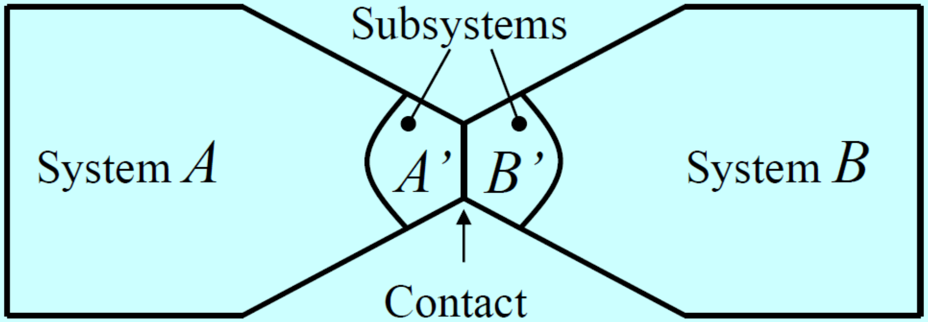
Review of basic concepts: Heat interactions

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

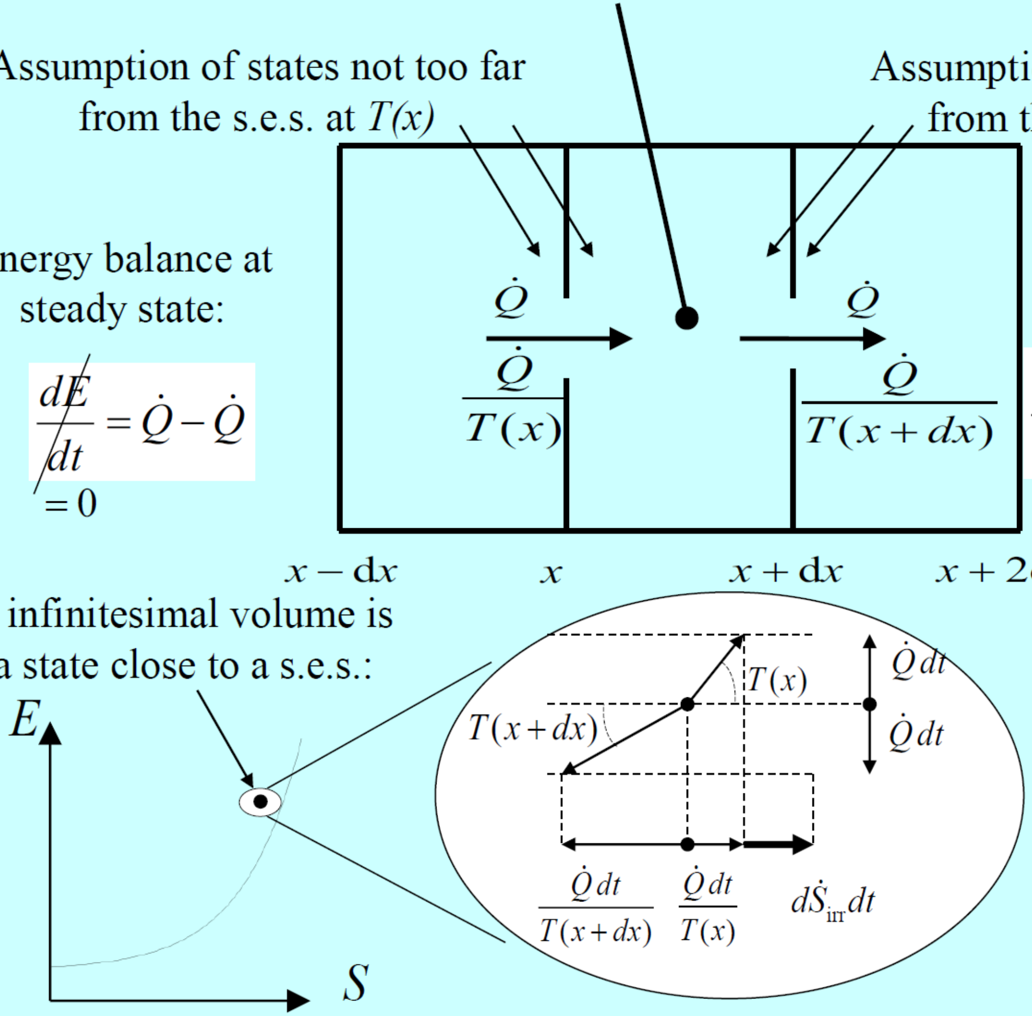
- The contact between two bodies at different temperatures produces nonequilibrium states in both systems
- To study these nonequilibrium states, we model each body as a continuum of infinitesimal volumes, and assume that each is in a state not to far from a s.e.s. (*local quasi-equilibrium assumption*)
- 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:

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

Entropy balance at steady state:

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

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

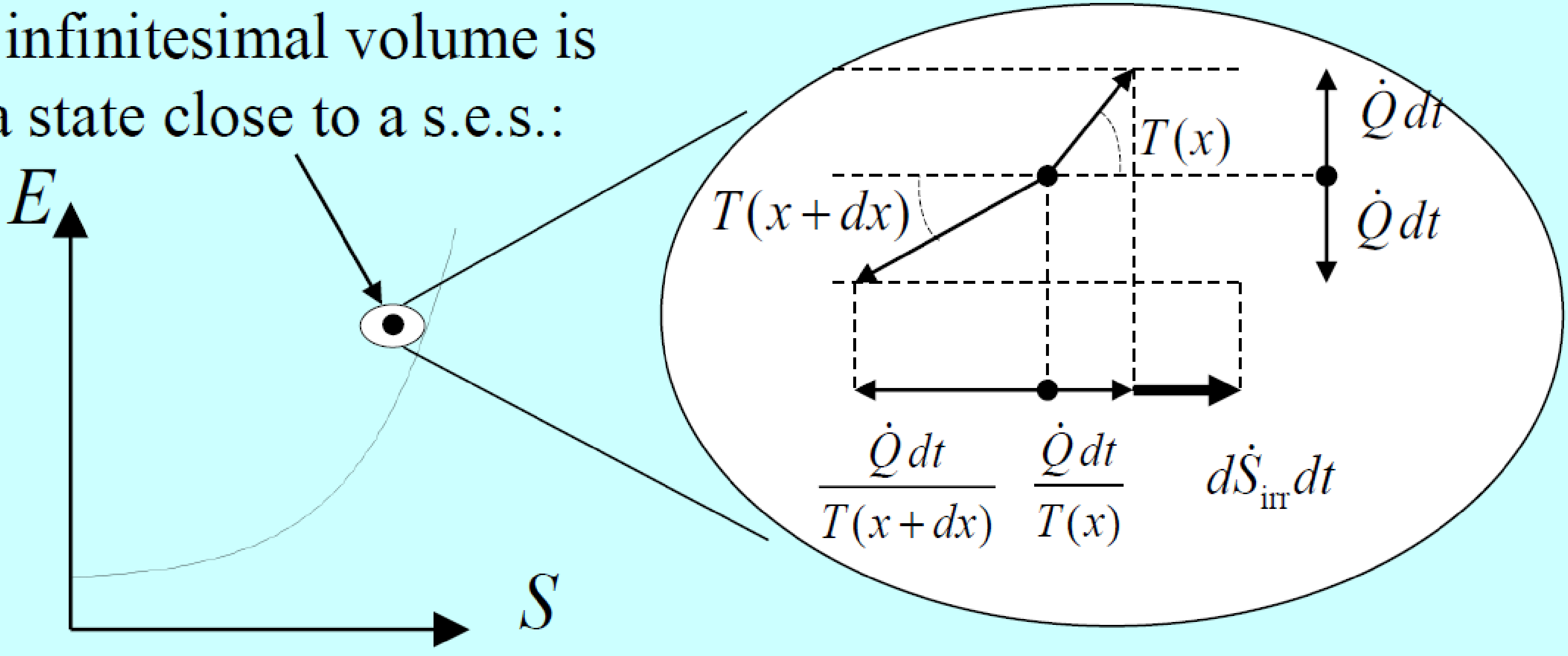
$$d\dot{S}_{\rm irr} = \frac{T(x)-T(x+dx)}{T(x)T(x+dx)}\dot{Q}$$

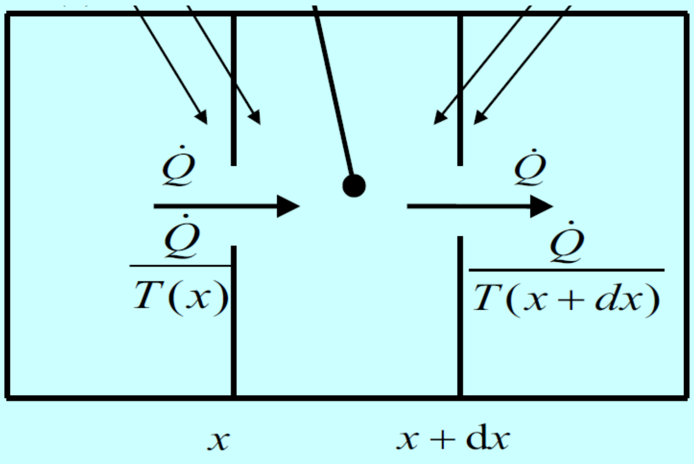
$$\approx -\frac{dT}{dx}\frac{\dot{Q}}{T^2}dx$$

Review of basic concepts: **Heat interactions**

steady state heat transfer requires non-equilibrium

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





$$d\dot S_{\rm irr} = \frac{T(x)-T(x+dx)}{T(x)T(x+dx)}\dot Q$$

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

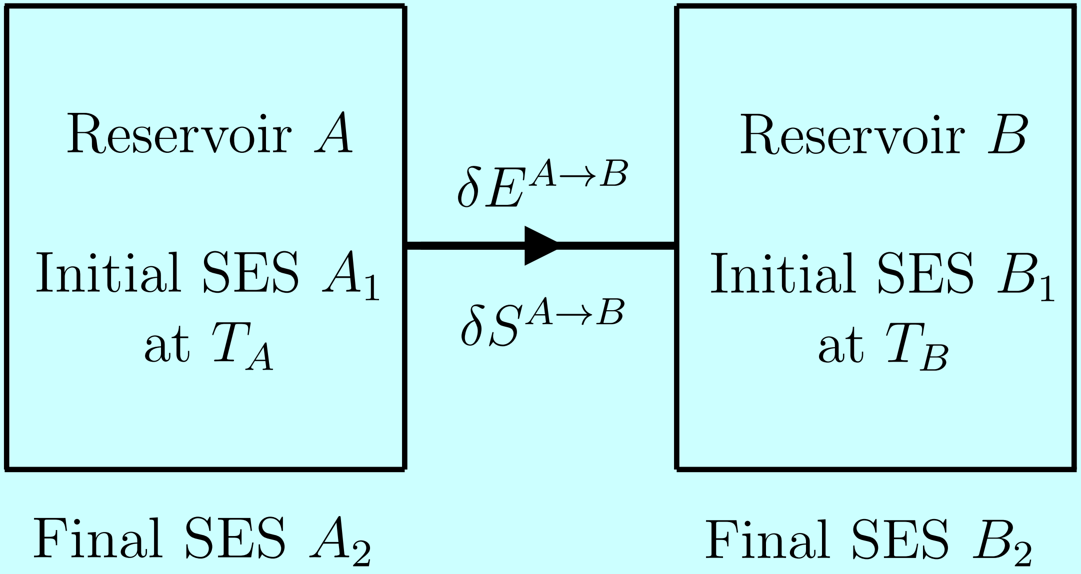
Review of basic concepts:

First and second law efficiency

in
heat engines
heat pumps
refrigeration

First and second law efficiencies: E and S exchanges between two reservoirs

Clausius inequalities impose irreversibilities in at least one



Reservoir A

Initial SES A_1 at T_A

$\delta E^{A\to B}$

$\delta S^{A\to B}$

Reservoir B

Initial SES B_1 at T_B

Final SES A_2

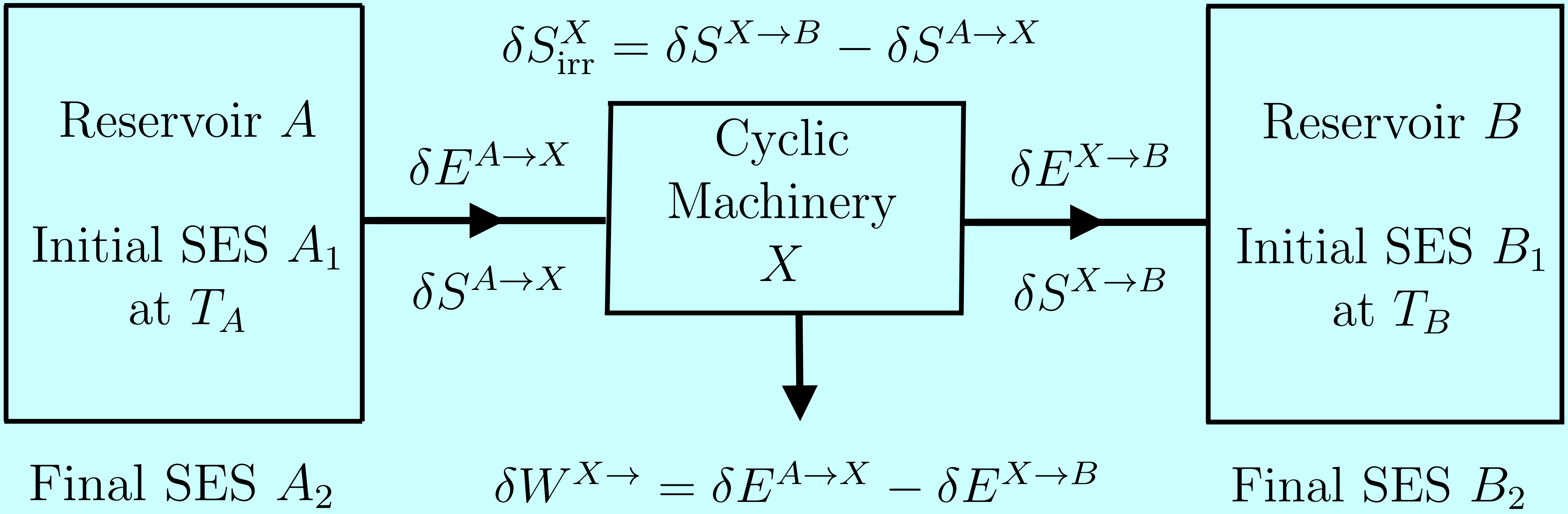
Final SES B_2

$$\frac{\delta E^{A\to B}}{T_A} \underset{2A,3A}{=} \delta S^{A\to B} - \delta S^{A}_{\rm irr} \underset{1A}{\le} \delta S^{A\to B} \underset{1B}{\le} \delta S^{A\to B} + \delta S^{B}_{\rm irr} \underset{2B,3B}{=} \frac{\delta E^{A\to B}}{T_B}$$

Impossible to operate reversibly.
Must have generation of S either in A or B or both.

First and second law efficiencies: E and S exchanges between two reservoirs

Interposing a third system makes reversibility possible



$$\delta S_{\rm irr}^{X} = \delta S^{X\to B} - \delta S^{A\to X}$$

Reservoir A

Initial SES A_1 at T_A

$\delta E^{A\to X}$

$\delta S^{A\to X}$

Cyclic Machinery X

$\delta E^{X\to B}$

$\delta S^{X\to B}$

Reservoir B

Initial SES B_1 at T_B

Final SES A_2

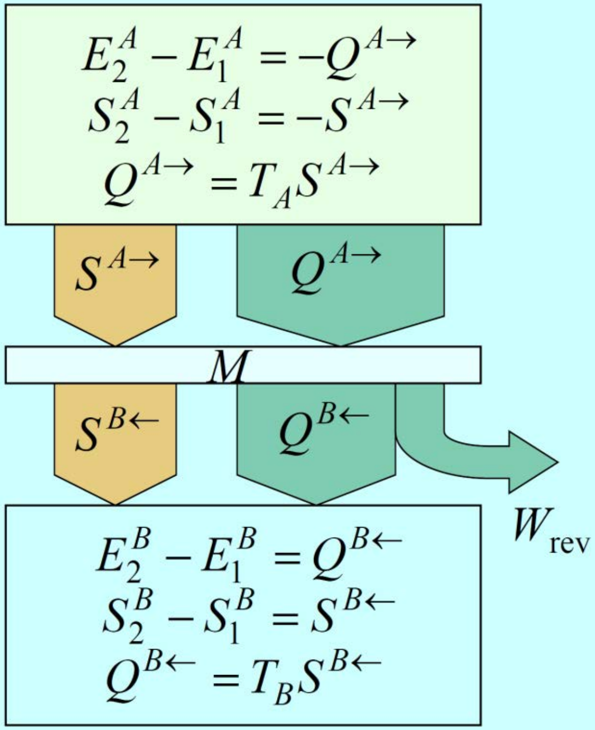
$$\delta W^{X\to} = \delta E^{A\to X} - \delta E^{X\to B}$$

Final SES B_2

$$\frac{\delta E^{A\to X}}{T_A} \underset{2A,3A}{=} \delta S^{A\to X} \le \delta S^{A\to X} + \delta S_{\rm irr}^{X} = \delta S^{X\to B} \underset{2B,3B}{=} \frac{\delta E^{X\to B}}{T_B}$$

The machinery can operate reversibly, by exchanging less energy with the reservoir at lower temperature than it exchanges with the reservoir a higher temperature. The difference is balanced with a work interaction (no entropy exchange).

First and second law efficiencies: Heat engine between two thermal reservoirs



$$\begin{aligned} E_2^A - E_1^A &= -Q^{A\to} \\ S_2^A - S_1^A &= -S^{A\to} \\ Q^{A\to} &= T_A S^{A\to} \end{aligned}$$

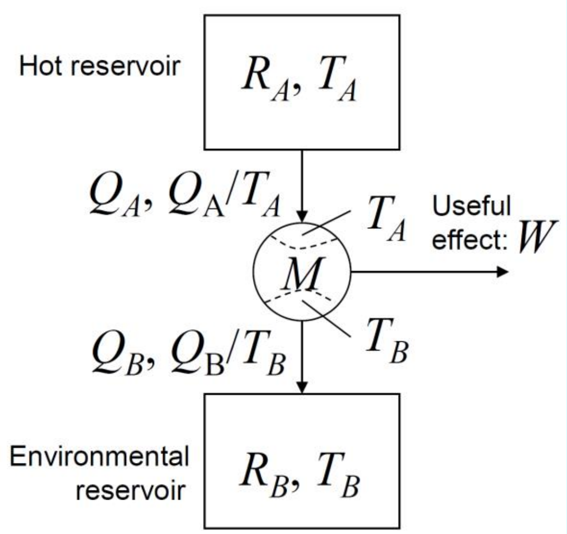
$$\begin{aligned} E_2^B - E_1^B &= Q^{B\leftarrow} \\ S_2^B - S_1^B &= S^{B\leftarrow} \\ Q^{B\leftarrow} &= T_B S^{B\leftarrow} \end{aligned}$$

Balance equations for reversible *M*

$$\begin{cases} 0 = Q^{A\to} - Q^{B\leftarrow} - W_{\text{rev}} \\ 0 = S^{A\to} - S^{B\leftarrow} \end{cases}$$

from which

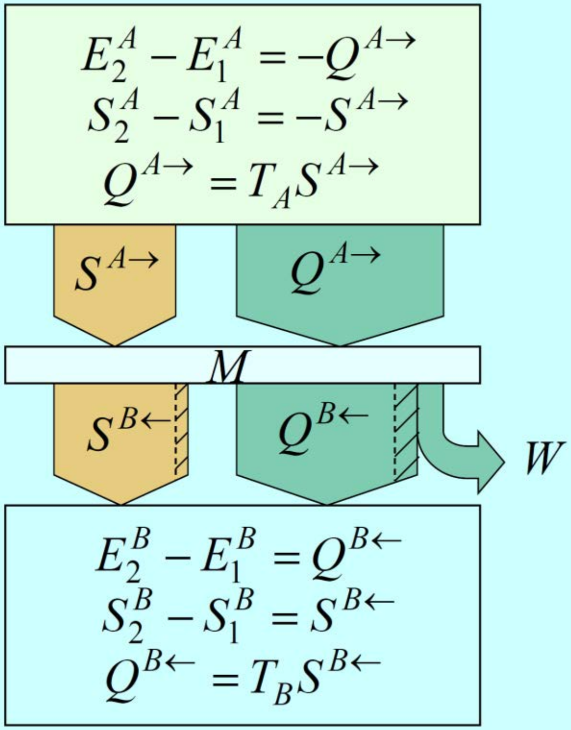
$$\begin{cases} W_{\text{rev}} = S^{A\to}(T_A - T_B) > 0 \\ S^{A\to} = S^{B\leftarrow} \end{cases}$$



$$W = Q_A\left(1 - \frac{T_B}{T_A}\right) - T_B\, S_{\text{irr}}$$

$$\eta_{\text{I}} = \frac{W^{\to}}{Q_A^{\leftarrow}} = \left(1 - \frac{T_B}{T_A}\right) - \frac{T_B\, S_{\text{irr}}}{Q_A^{\leftarrow}}$$

$$\eta_{\text{II}} = \left.\frac{W^{\to}}{W_{\text{rev}}^{\to}}\right|_{Q_A^{\leftarrow}} = \frac{W^{\to}}{Q_A^{\leftarrow}\left(1 - \frac{T_B}{T_A}\right)} = 1 - \frac{T_B\, S_{\text{irr}}}{Q_A^{\leftarrow}\left(1 - \frac{T_B}{T_A}\right)}$$



$$\begin{aligned} E_2^A - E_1^A &= -Q^{A\to} \\ S_2^A - S_1^A &= -S^{A\to} \\ Q^{A\to} &= T_A S^{A\to} \end{aligned}$$

$$\begin{aligned} E_2^B - E_1^B &= Q^{B\leftarrow} \\ S_2^B - S_1^B &= S^{B\leftarrow} \\ Q^{B\leftarrow} &= T_B S^{B\leftarrow} \end{aligned}$$

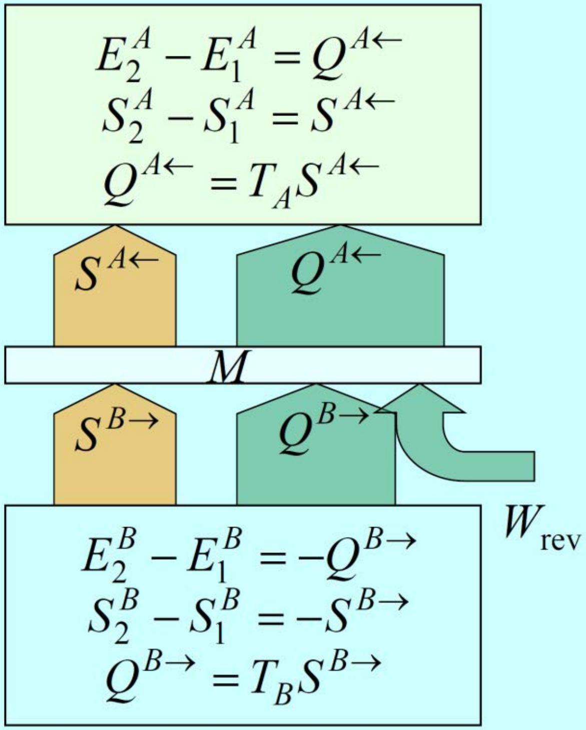
Balance equations for irreversible M

$$\begin{cases} 0 = Q^{A\to} - Q^{B\leftarrow} - W \\ 0 = S^{A\to} - S^{B\leftarrow} + S_{\text{irr}} \end{cases}$$

from which

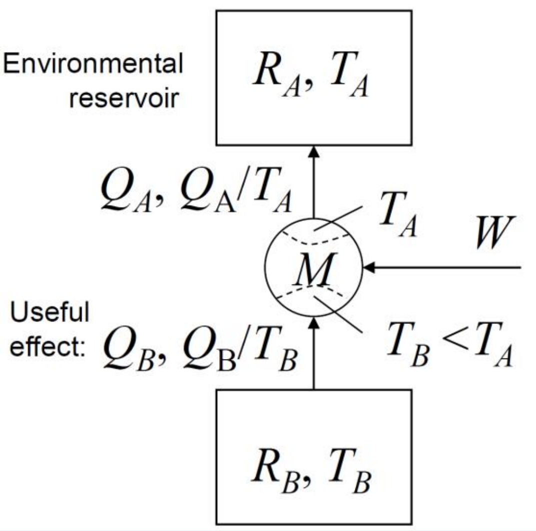
$$\begin{cases} W = S^{A\to}(T_A - T_B) - T_B S_{\text{irr}} < W_{\text{rev}} \\ S^{A\to} + S_{\text{irr}} = S^{B\leftarrow} \end{cases}$$

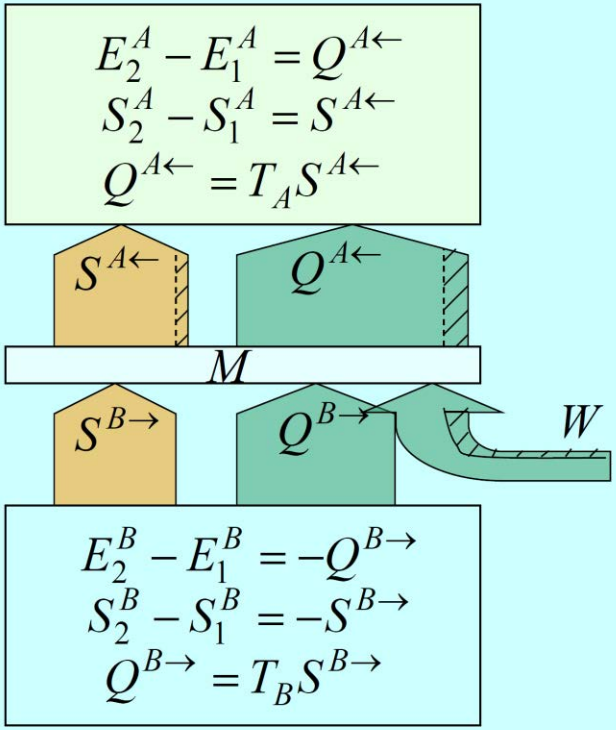
First and second law efficiencies: Refrigerator between two thermal reservoirs



$$E_2^A - E_1^A = Q^{A\leftarrow}$$
$$S_2^A - S_1^A = S^{A\leftarrow}$$
$$Q^{A\leftarrow} = T_A S^{A\leftarrow}$$

$$E_2^B - E_1^B = -Q^{B\rightarrow}$$
$$S_2^B - S_1^B = -S^{B\rightarrow}$$
$$Q^{B\rightarrow} = T_B S^{B\rightarrow}$$





$$E_2^A - E_1^A = Q^{A\leftarrow}$$
$$S_2^A - S_1^A = S^{A\leftarrow}$$
$$Q^{A\leftarrow} = T_A S^{A\leftarrow}$$

$$E_2^B - E_1^B = -Q^{B\rightarrow}$$
$$S_2^B - S_1^B = -S^{B\rightarrow}$$
$$Q^{B\rightarrow} = T_B S^{B\rightarrow}$$

$$Q_B = \frac{W}{(T_A/T_B - 1)} - \frac{T_A\, S_{\text{irr}}}{(T_A/T_B - 1)}$$

$$COP\big|_{\text{r.u.}} = \frac{Q_B^{\leftarrow}}{W^{\leftarrow}} = \frac{1}{\left(\dfrac{T_A}{T_B} - 1\right)} - \frac{T_A\, T_B}{T_A - T_B}\,\frac{S_{\text{irr}}}{W^{\leftarrow}}$$

$$\eta_{\text{II}}\big|_{\text{r.u.}} = \frac{Q_B^{\leftarrow}}{Q_{B,\text{rev}}^{\leftarrow}}\Bigg|_{W^{\leftarrow}} = \frac{-Q_B^{\leftarrow}\left(1 - \dfrac{T_A}{T_B}\right)}{W^{\leftarrow}} = 1 - \frac{T_A S_{\text{irr}}}{W^{\leftarrow}}$$

Balance equations for reversible M

$$\begin{cases} 0 = -Q^{A\leftarrow} + Q^{B\rightarrow} + W_{\text{rev}} \\ 0 = -S^{A\leftarrow} + S^{B\rightarrow} \end{cases}$$

from which

$$\begin{cases} W_{\text{rev}} = S^{B\rightarrow}(T_A - T_B) > 0 \\ S^{A\leftarrow} = S^{B\rightarrow} \end{cases}$$

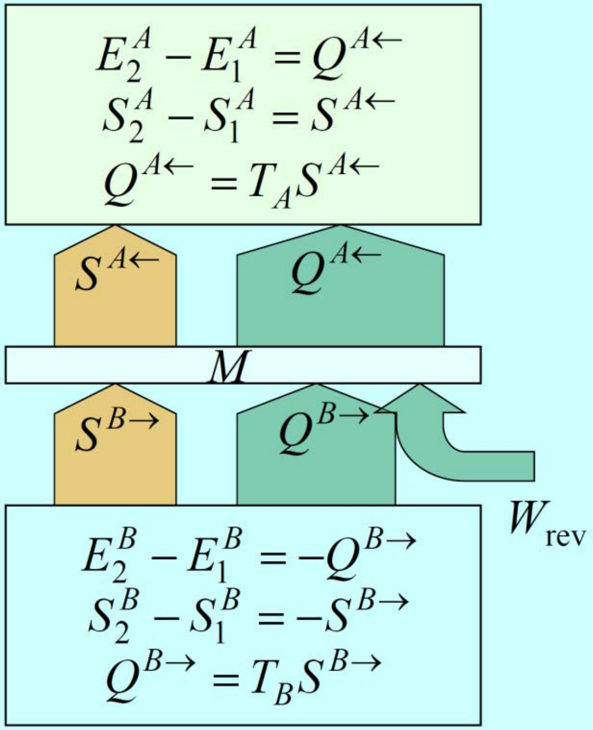
Balance equations for irreversible M

$$\begin{cases} 0 = -Q^{A\leftarrow} + Q^{B\rightarrow} + W \\ 0 = -S^{A\leftarrow} + S^{B\rightarrow} + S_{\text{irr}} \end{cases}$$

from which

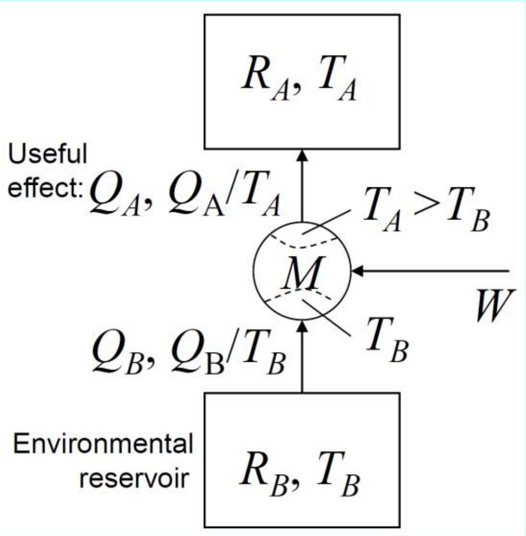
$$\begin{cases} W = S^{B\rightarrow}(T_A - T_B) + T_A S_{\text{irr}} > W_{\text{rev}} \\ S^{A\leftarrow} = S^{B\rightarrow} + S_{\text{irr}} \end{cases}$$

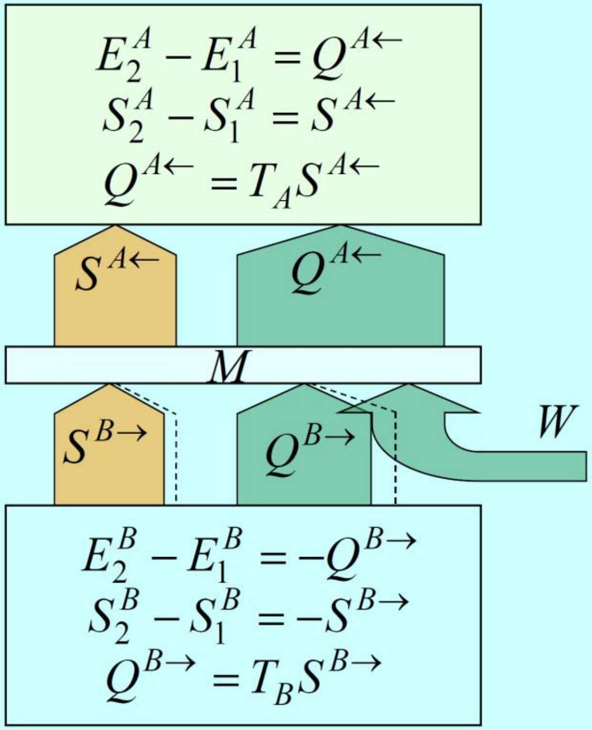
First and second law efficiencies: Heat pump between two thermal reservoirs



$$E_2^A - E_1^A = Q^{A\leftarrow}$$
$$S_2^A - S_1^A = S^{A\leftarrow}$$
$$Q^{A\leftarrow} = T_A S^{A\leftarrow}$$

$$E_2^B - E_1^B = -Q^{B\rightarrow}$$
$$S_2^B - S_1^B = -S^{B\rightarrow}$$
$$Q^{B\rightarrow} = T_B S^{B\rightarrow}$$





$$E_2^A - E_1^A = Q^{A\leftarrow}$$
$$S_2^A - S_1^A = S^{A\leftarrow}$$
$$Q^{A\leftarrow} = T_A S^{A\leftarrow}$$

$$E_2^B - E_1^B = -Q^{B\rightarrow}$$
$$S_2^B - S_1^B = -S^{B\rightarrow}$$
$$Q^{B\rightarrow} = T_B S^{B\rightarrow}$$

$$Q_A = \frac{W}{(1 - T_B/T_A)} - \frac{T_B\, S_{\text{irr}}}{(1 - T_B/T_A)}$$

$$COP\Big|_{\text{p.cal.}} = \frac{Q_A^{\rightarrow}}{W^{\leftarrow}} = \frac{1}{\left(1 - \dfrac{T_B}{T_A}\right)} - \frac{T_A\, T_B}{T_A - T_B}\,\frac{S_{\text{irr}}}{W^{\leftarrow}}$$

$$\eta_{\text{II}}\Big|_{\text{p.cal.}} = \left.\frac{Q_A^{\rightarrow}}{Q_{A,\text{rev}}^{\rightarrow}}\right|_{W^{\leftarrow}} = \frac{Q_A^{\rightarrow}\left(1 - \dfrac{T_B}{T_A}\right)}{W^{\leftarrow}}$$
$$= 1 - \frac{T_B S_{\text{irr}}}{W^{\leftarrow}}$$

Balance equations for reversible M

$$\begin{cases} 0 = -Q^{A\leftarrow} + Q^{B\rightarrow} + W_{\text{rev}} \\ 0 = -S^{A\leftarrow} + S^{B\rightarrow} \end{cases}$$

from which

$$\begin{cases} W_{\text{rev}} = S^{A\leftarrow}(T_A - T_B) > 0 \\ S^{A\leftarrow} = S^{B\rightarrow} \end{cases}$$

Balance equations for irreversible M

$$\begin{cases} 0 = -Q^{A\leftarrow} + Q^{B\rightarrow} + W \\ 0 = -S^{A\leftarrow} + S^{B\rightarrow} + S_{\text{irr}} \end{cases}$$

from which

$$\begin{cases} W = S^{A\rightarrow}(T_A - T_B) + T_B S_{\text{irr}} > W_{\text{rev}} \\ S^{A\leftarrow} - S_{\text{irr}} = S^{B\rightarrow} \end{cases}$$

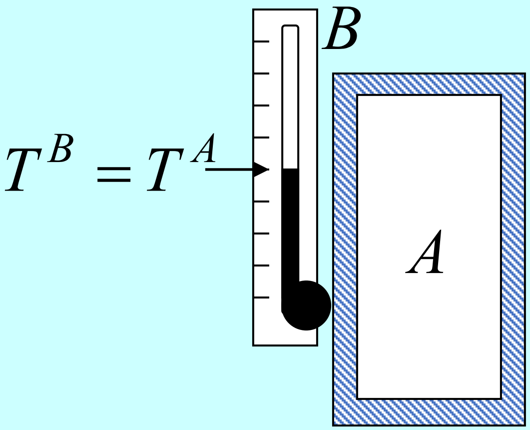
Review of basic concepts:

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, $T^B = T^A$.

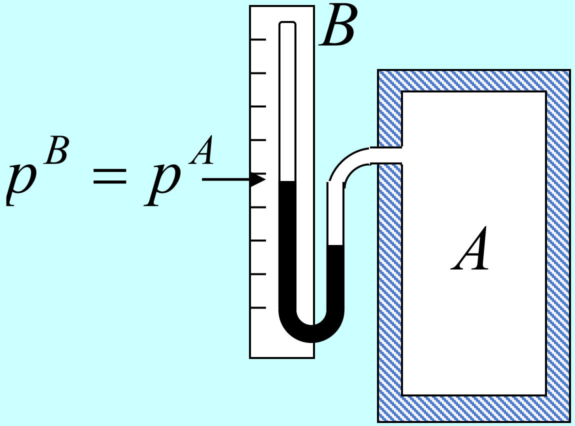


The temperature read by thermometer *B* is equal to that of system *A*, regardless of the details of system *A*.

Experimental measurement of SES properties: manometer

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

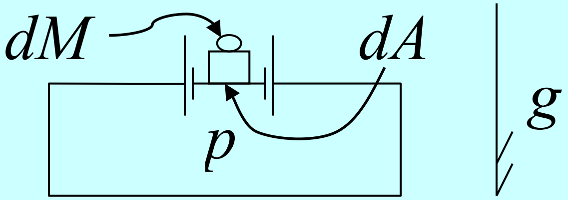
If a manometer *B* is brought into mutual equilibrium with a system *A*, through a piston or a movable interface, with a system A, $p^B = p^A$.



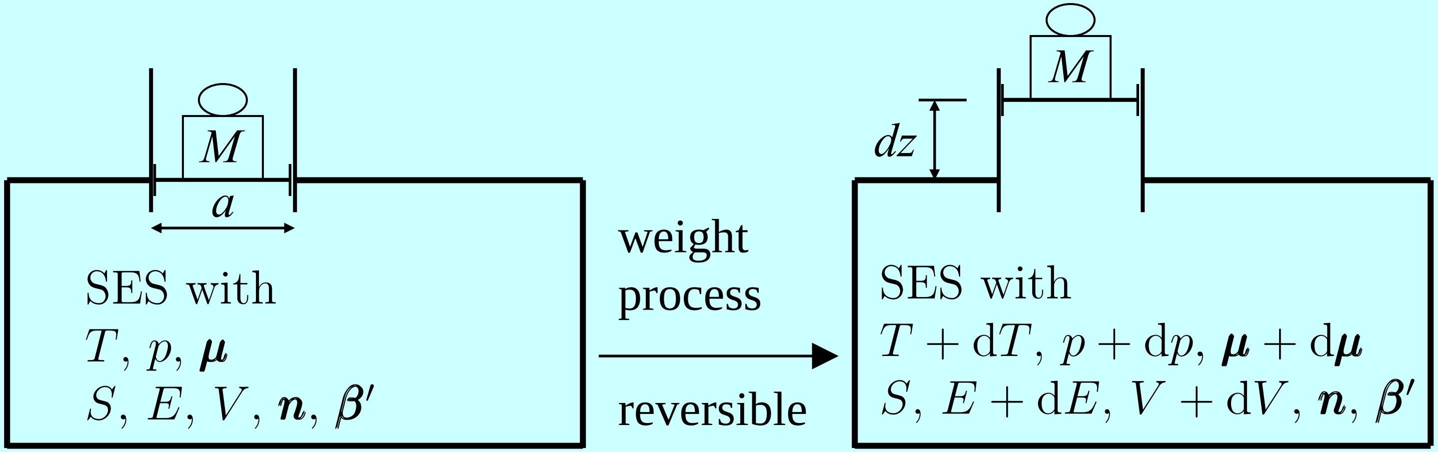
The pressure read by manometer *B* is equal to that of system *A*, regardless of details of system *A*.

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*.

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



Pressure vs force per unit area



SES with
T, p, $\boldsymbol{\mu}$
S, E, V, $\boldsymbol{n}$, $\boldsymbol{\beta}'$

weight
process

reversible

SES with
$T + \mathrm{d}T$, $p + \mathrm{d}p$, $\boldsymbol{\mu} + \mathrm{d}\boldsymbol{\mu}$
S, $E + \mathrm{d}E$, $V + \mathrm{d}V$, $\boldsymbol{n}$, $\boldsymbol{\beta}'$

Energy balance for the weight process (reversible: $\mathrm{d}S = 0$):

$$\mathrm{d}E|_{S,\boldsymbol{n},\boldsymbol{\beta}'} = -Mg\,\mathrm{d}z = -f\,\mathrm{d}V \qquad \text{where} \qquad f = \frac{Mg}{a} \qquad \mathrm{d}V = a\,\mathrm{d}z$$

and from the fundamental relation $E = E(S, V, \boldsymbol{n}, \boldsymbol{\beta}')$

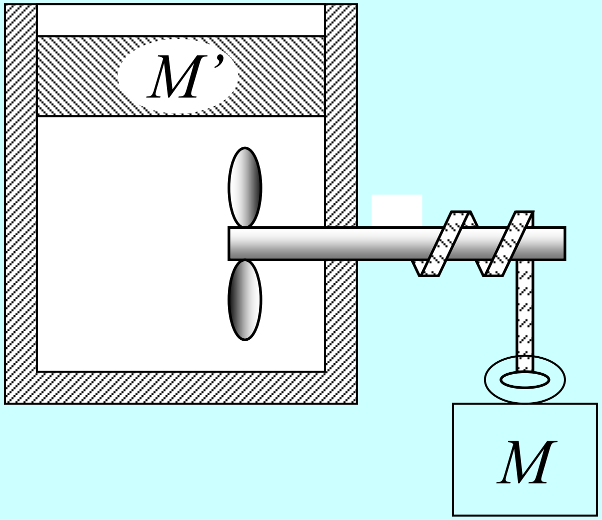
$$\mathrm{d}E|_{S,\boldsymbol{n},\boldsymbol{\beta}'} = -p\,\mathrm{d}V \qquad \text{where} \qquad p = -\left(\frac{\partial E}{\partial V}\right)_{S,\boldsymbol{n},\boldsymbol{\beta}'}$$

At SES, the pressure p is equal to the force per unit area exerted by the system anywhere on the walls confining its constituents in the volume V.
If the state is not a SES, we can still use the manometer to measure the force per unit area at various locations on the walls, but in general it may differ from location to location. Pressure is not defined because there is no fundamental relation.

Experimental measurement of SES properties: heat capacities

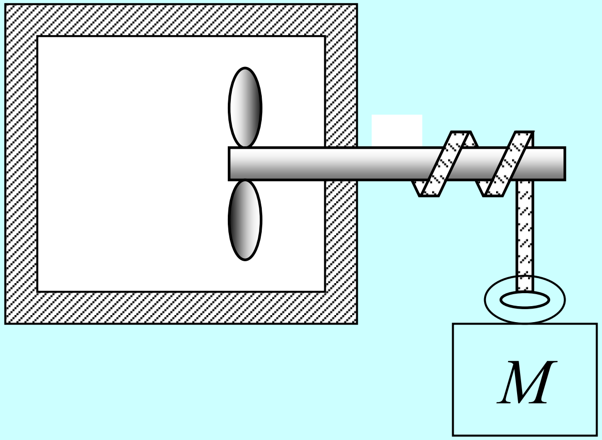
Heat capacity at constant pressure:

$$C_p = \left(\frac{\partial H}{\partial T}\right)_{p,\mathbf{n}} \approx \frac{Mg(-\Delta z)}{\Delta T}$$



Heat capacity at constant volume:

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{V,\mathbf{n}} \approx \frac{Mg(-\Delta z)}{\Delta T}$$



Enthalpy and heat capacity at constant pressure

From the fundamental relation, the Gibbs relation, the definition of enthalpy, and its partial derivatives:

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

$$dE = TdS - pdV + \boldsymbol{\mu} \cdot d\boldsymbol{n}$$

$$\boxed{H \equiv E + pV}$$

$$dH = dE + d(pV) = TdS + Vdp + \boldsymbol{\mu} \cdot d\boldsymbol{n}$$

$$\left.\begin{aligned} &H = H(S, p, \boldsymbol{n}) \\ &T = \left(\frac{\partial H}{\partial S}\right)_{p.\boldsymbol{n}} = T(S, p, \boldsymbol{n}) \end{aligned}\right\}$$

Eliminate *S*, to obtain:

$$H = H(T, p, \boldsymbol{n})$$

$$\boxed{C_p = \left(\frac{\partial H}{\partial T}\right)_{p,\boldsymbol{n}} = C_p(T, p, \boldsymbol{n})}$$

Heat capacity at constant volume and equation of state

From the fundamental relation and its partial derivatives:

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

$$T = \left(\frac{\partial E}{\partial S}\right)_{V.\boldsymbol{n}} = T(S, V, \boldsymbol{n})$$

Eliminate *S*, to obtain:

$$E = E(T, V, \boldsymbol{n})$$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{V,\boldsymbol{n}} = C_V(T, V, \boldsymbol{n})$$

$$T = \left(\frac{\partial E}{\partial S}\right)_{V.\boldsymbol{n}} = T(S, V, \boldsymbol{n})$$

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

Eliminate *S*, to obtain:

$$V = V(T, p, \boldsymbol{n})$$ ***Equation of state***

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,\boldsymbol{n}} = \alpha_p(T, p, \boldsymbol{n})$$

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

Equation of state

The equation of state

$$V = V(T, p, \boldsymbol{n})$$

has the advantage that only easily measurable properties appear.
Its differential is

$$(dV)_{\boldsymbol{n}} = \left(\frac{\partial V}{\partial T}\right)_{p,\boldsymbol{n}} dT + \left(\frac{\partial V}{\partial p}\right)_{T,\boldsymbol{n}} dp = V\alpha_p dT - V\kappa_T dp$$

where we define

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,\boldsymbol{n}} \qquad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,\boldsymbol{n}}$$

- The **coefficient of isobaric expansion** expresses the percentage increase in volume resulting from an increase in temperature at constant pressure.
- The **coefficient of isothermal compressibility** expresses the percentage reduction in volume resulting from an increase in pressure at constant temperature.

They are functions of temperature, pressure, and composition.

Experimental measurement of SES properties:
Mayer relation, Joule-Thomson coefficient, sound speed, etc

Definitions of other SES properties and their respective relations in terms of p, V, T, C_v, C_p, $\gamma = C_p/C_v$, κ_T, α_p.

$$C_p - C_V = \frac{VT\alpha_p^2}{\kappa_T}$$ **Mayer relation**

$$\mu_{\mathrm{JT}} = \left(\frac{\partial T}{\partial p}\right)_{H,\boldsymbol{n}} = \frac{V(\alpha_p T - 1)}{C_p}$$ **Joule–Thomson coefficient**

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{S,\boldsymbol{n}}$$ **isoentropic compressibility**

$$c_s^2 = \left(\frac{\partial p}{\partial \rho}\right)_{S,\boldsymbol{n}} = -\frac{v^2}{M}\left(\frac{\partial p}{\partial V}\right)_{S,\boldsymbol{n}} = \frac{1}{\rho\kappa_S} = \frac{\gamma}{\rho\kappa_T}$$ **speed of sound propagation**

$$c_{\mathrm{J}} = \left(\frac{\partial T}{\partial V}\right)_{U,\boldsymbol{n}} = \frac{p\kappa_T - T\alpha_p}{C_v\kappa_T}$$ **Joule coefficient**

$$\left(\frac{\partial C_p}{\partial p}\right)_{T,\boldsymbol{n}} = \left(\frac{\partial^2 H}{\partial T\partial p}\right)_{\boldsymbol{n}} = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_{p,\boldsymbol{n}} = -TV\alpha_p^2 - TV\left(\frac{\partial \alpha_p}{\partial T}\right)_{p,\boldsymbol{n}}$$

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

$$\left(\frac{\partial \alpha_p}{\partial p}\right)_{T,\boldsymbol{n}} = -\left(\frac{\partial \kappa_T}{\partial T}\right)_{p,\boldsymbol{n}} = \alpha_p\kappa_T + \frac{1}{V}\left(\frac{\partial^2 V}{\partial p\partial T}\right)_{\boldsymbol{n}}$$

Gibbs free energy and chemical potentials as functions of *T* and *p*

From the fundamental relation, the Gibbs relation, the definition of Gibbs free energy, and its partial derivatives:

$$E = E(S,V,n)$$

$$dE = TdS - pdV + \boldsymbol{\mu}\cdot d\mathbf{n}$$

$$\boxed{G \equiv E - TS + pV}$$

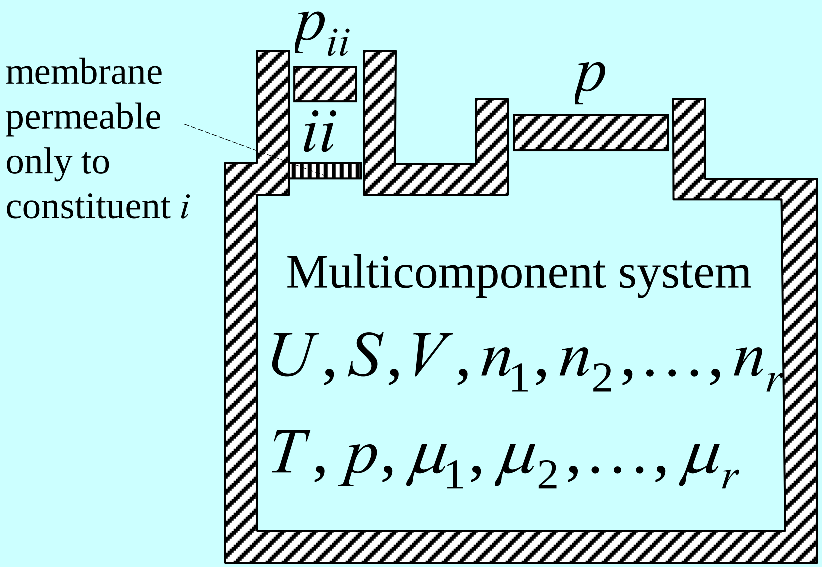
$$dG = dE - d(TS) + d(pV) = -SdT + Vdp + \boldsymbol{\mu}\cdot d\mathbf{n}$$

$$G = G(T,p,\mathbf{n})$$

$$\boxed{\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p.\mathbf{n}'} = \mu_i(T,p,\mathbf{n})}$$

The chemical potentials are functions of temperature, pressure, and composition.

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.

Summary of properties

Properties **defined for all states** (including SES and NES):

- Energy
- Entropy
- Volume
- Amounts of constituents
- Availabilities

$$E, S, V, \boldsymbol{n}$$

Properties **defined only for SES** (all of them):

- Temperature
- Pressure
- Chemical potentials
- Enthalpy
- Gibbs free energy

$$T, p, \boldsymbol{\mu}, H, G$$

Properties **defined only for some SES** (e.g., not for two-phase states):

- Specific heat at constant volume
- Specific heat at constant pressure
- Isobaric expansion coefficient
- Isothermal compressibility coefficient

$$C_V, C_p, \alpha_{p,} \kappa_T$$

Construction of the fundamental relation from measurements of T, p, α_p, κ_T, C_p, and μ_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 ***n*** we can reconstruct (by integration) the fundamental relation.

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

For example, at fixed amounts ***n*** we can integrate these general relations:

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

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

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

Next:

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

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

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 λ 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 $F = F(y)$

$$\boxed{L = L(\lambda)} = F(y(\lambda)) - \lambda\, y(\lambda)$$

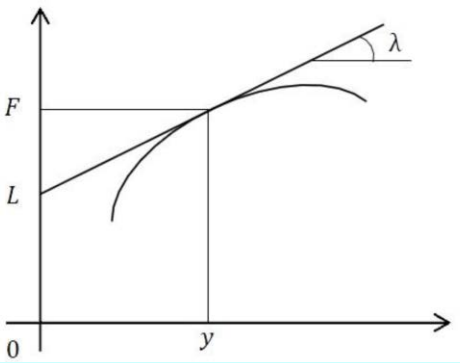
Notice that the Legendre transform of $L = L(\lambda)$ is the original $F = F(y)$. In fact, denoting the slope of its tangent line by η and its intercept by G,

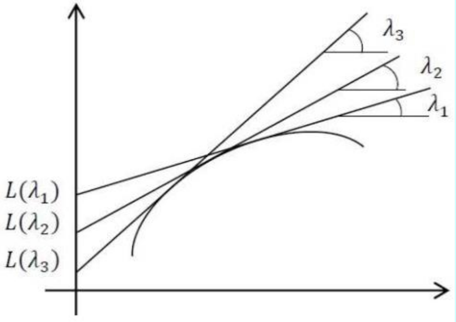
$$\eta(\lambda) = \frac{\partial L}{\partial \lambda} = \frac{\partial F}{\partial y}\frac{\partial y}{\partial \lambda} - y(\lambda) - \lambda \frac{\partial y}{\partial \lambda} = -y(\lambda) \quad \Rightarrow \quad \eta = -y$$

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

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

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





Examples:

$F(y) = e^y$

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

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

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

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

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

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