2.43 ADVANCED THERMODYNAMICS

Spring Term 2024
LECTURE 11

Room 3-442
Tuesday, March 12, 2:30pm - 4:30pm

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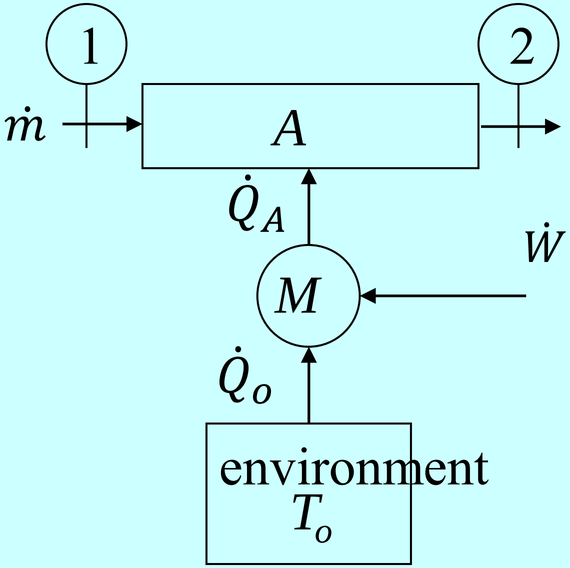
Room 3-351d

Review of basic concepts:

Exergies
and
first and second law efficiencies

in
energy conversion technologies

Review of basic concepts: Exergy in heating and cooling bulk flows



Heating of a flow with a heat pump

$$\dot Q_A = \dot m(h_2 - h_1)$$

$$\mathrm{COP} = \frac{\dot m(h_2 - h_1)}{\dot W} = \frac{\dot Q_A}{\dot W}$$

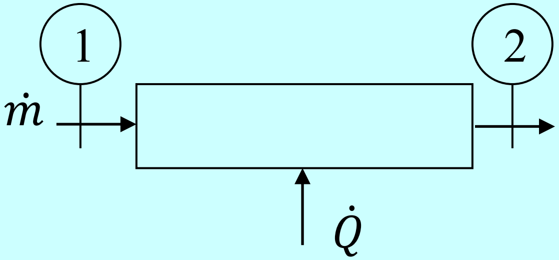
$$\eta_{\mathrm{II}} = \frac{\dot m[(h_2 - h_1) - T_o(s_2 - s_1)]}{\dot W} = \frac{\dot Q_A\left(1 - T_o\dfrac{s_2 - s_1}{h_2 - h_1}\right)}{\dot W} = \mathrm{COP}\left(1 - \frac{T_o}{T_{\mathrm{lm},12}}\right)$$

$$\mathrm{COP}_{\max} = \frac{1}{\left(1 - T_o\dfrac{s_2 - s_1}{h_2 - h_1}\right)} = \frac{1}{\left(1 - \dfrac{T_o}{T_{\mathrm{lm},12}}\right)} \qquad \text{where } T_{\mathrm{lm},12} = \frac{h_2 - h_1}{s_2 - s_1}$$

Review of basic concepts: Minimum exergy for low temperature heating a liquid or ideal-gas flow

Ratio between exergy and energy content for a liquid flow:

$$\Delta\dot{E}x_{12} \approx \dot{Q}\left[1 - \frac{T_a \ln(T_2/T_1)}{T_2 - T_1}\right]$$



For example, for the heating of pressurized water from 60°C to 120°C (in an environment at 300 K)

$$\frac{\Delta\dot{E}x_{12}}{\dot{Q}} = 1 - \frac{T_a \ln(T_2/T_1)}{T_2 - T_1} = 1 - \frac{300 \ln(393/333)}{60} = 0.172$$

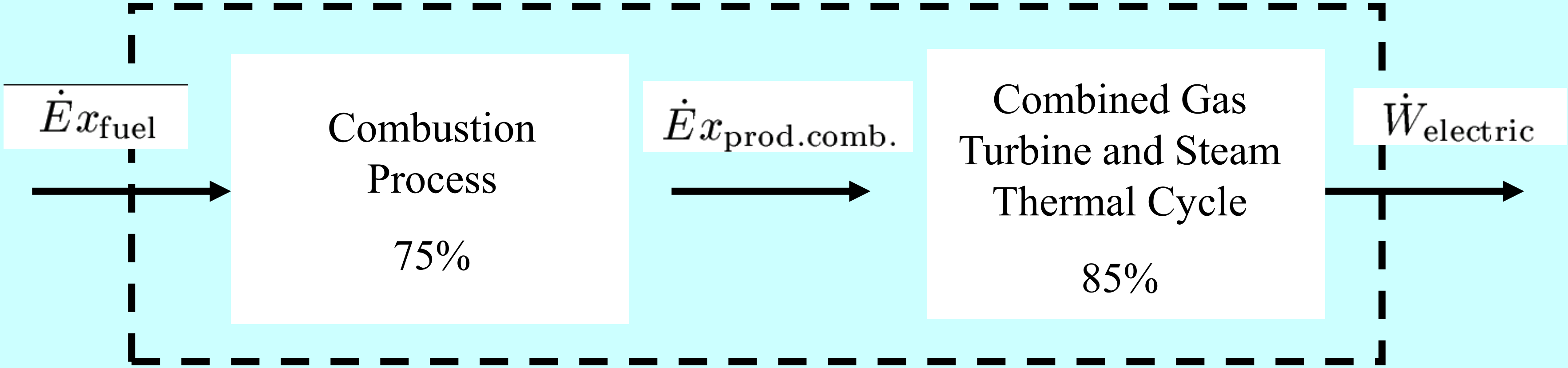
$$\mathrm{COP}_{\max} = \frac{1}{0.172} = 5.8$$

For the heating of water from 20°C to 60°C (in an environment at 300 K)

$$\frac{\Delta\dot{E}x_{12}}{\dot{Q}} = 1 - \frac{T_a \ln(T_2/T_1)}{T_2 - T_1} = 1 - \frac{300 \ln(333/293)}{40} = 0.040$$

$$\mathrm{COP}_{\max} = \frac{1}{0.04} = 25$$

Review of basic concepts: Power-plant philosophy of best available flame-based fuel-to-power conversion technology



$\dot{E}x_{\rm fuel}$

Combustion Process

75%

$\dot{E}x_{\rm prod.comb.}$

Combined Gas Turbine and Steam Thermal Cycle

85%

$\dot{W}_{\rm electric}$

$$\eta_{\rm II-combustion} = \frac{\dot{E}x_{\rm prod.comb.}}{\dot{E}x_{\rm fuel}} \approx 75\%$$

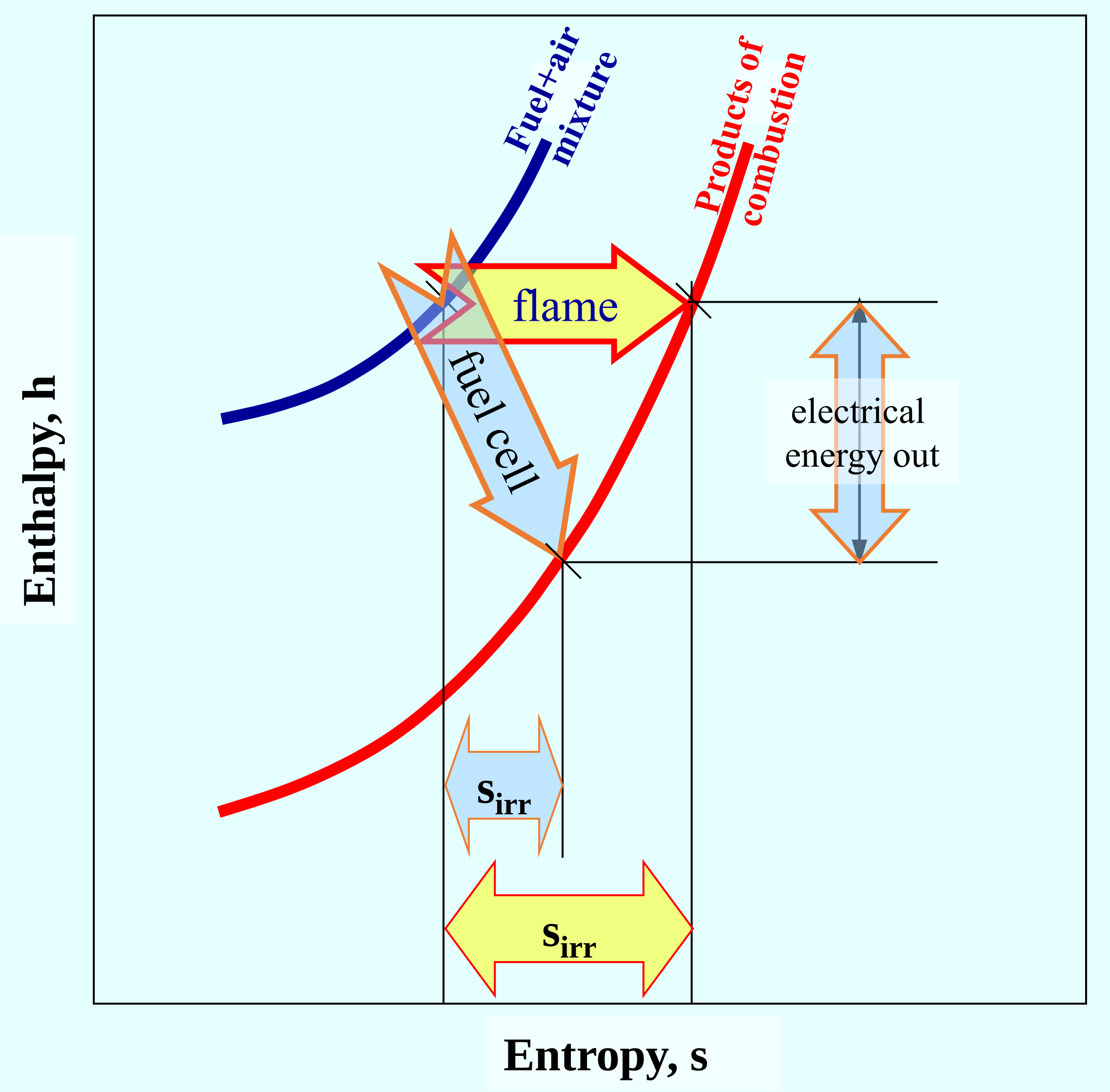
$$\eta_{\rm II-thermal-cycle} = \frac{\dot{W}_{\rm electric}}{\dot{E}x_{\rm prod.comb.}} \approx 85\%$$

Overall thermodynamic efficiency

64%

$$\eta_{\rm II-overall} = \frac{\dot{W}_{\rm electric}}{\dot{E}x_{\rm fuel}} = \eta_{\rm II-combustion} \times \eta_{\rm II-thermal-cycle} \approx 64\%$$

Review of basic concepts: one way to get around the inherent irreversibility of flames is by oxidating the fuel in fuel cells



Integrating SOFC in Thermal Cycles (without CO2 sequestration) may yield:

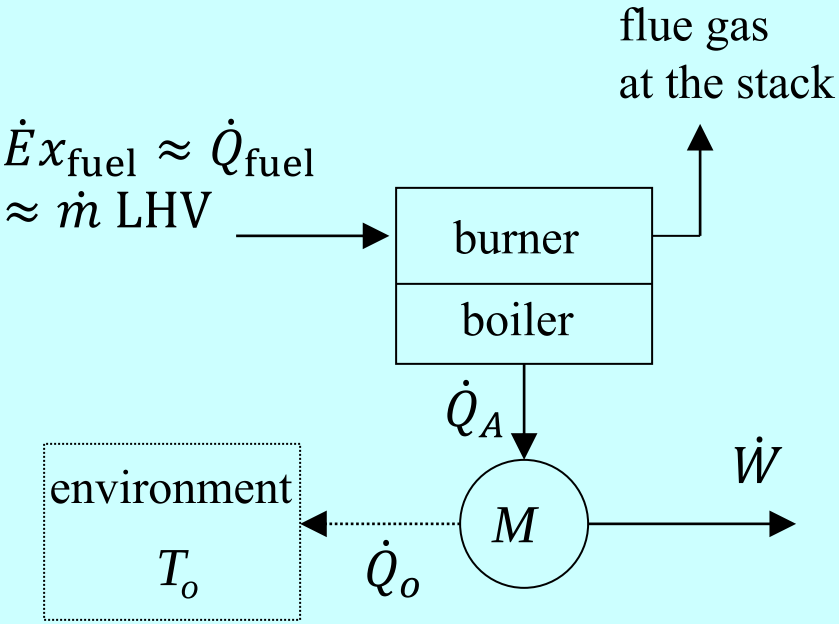
Fuel-Cell Rankine Cycle, 72%

Fuel-Cell Combined Brayton-Rankine Cycle, 75%

Fuel-Cell Regenerative Brayton Cycle, 76%

Review of basic concepts: Typical (efficient and inefficient) uses of fossil fuels

Separate production of electricity (simple thermoelectric generation)



$$\eta_{\text{I}} = \frac{\dot{W}}{\dot{Q}_{\text{fuel}}}$$

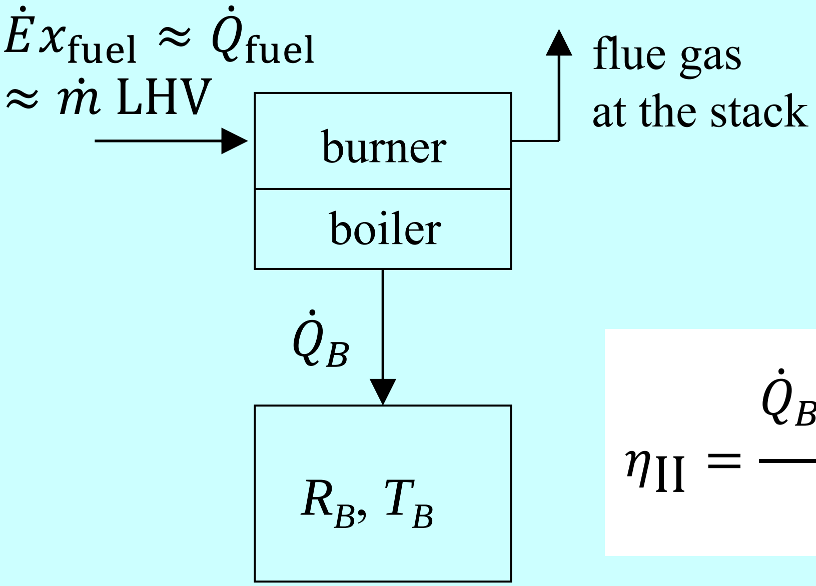
$$\eta_{\text{II}} = \frac{\dot{W}}{\dot{E}x_{\text{fuel}}} \approx \frac{\dot{W}}{\dot{Q}_{\text{fuel}}} = \eta_{\text{I}}$$

Note that in this particular case, $\eta_{\text{II}} \approx \eta_{\text{I}}$ is a consequence of the fact that

$$\dot{E}x_{\text{fuel}} \approx \dot{Q}_{\text{fuel}} \approx \dot{m}\,\text{LHV}$$

Review of basic concepts: Typical (efficient and inefficient) uses of fossil fuels

Separate production of heat at a fixed temperature



$\dot{E}x_{\text{fuel}} \approx \dot{Q}_{\text{fuel}} \approx \dot{m}\,\text{LHV}$

burner

boiler

flue gas
at the stack

$\dot{Q}_B$

R_B, T_B

$$\eta_{\text{I}} = \frac{\dot{Q}_B}{\dot{Q}_{\text{fuel}}}$$

$$\eta_{\text{II}} = \frac{\dot{Q}_B\left(1-\frac{T_o}{T_B}\right)}{\dot{E}x_{\text{fuel}}} \approx \frac{\dot{Q}_B\left(1-\frac{T_o}{T_B}\right)}{\dot{Q}_{\text{fuel}}} = \eta_{\text{I}}\left(1-\frac{T_o}{T_B}\right)$$

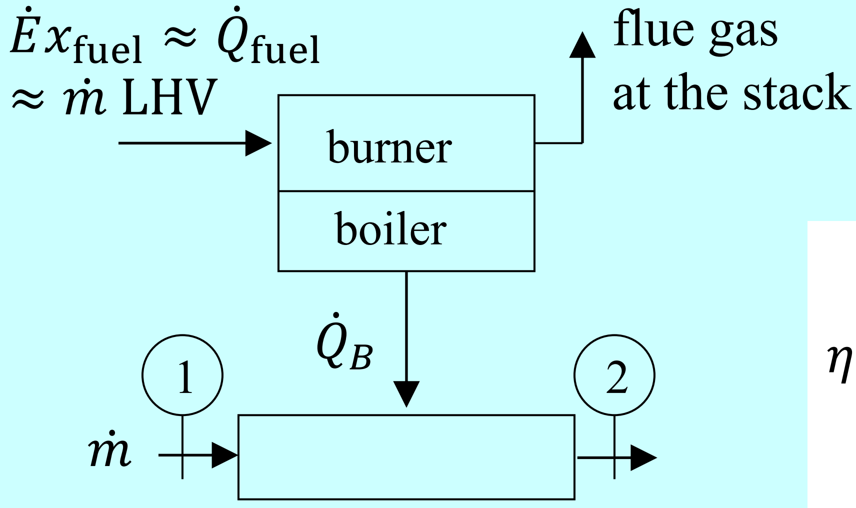
- The value of η_{I} for a boiler for an industrial production of process steam is around 95%. But remember that this does not mean that there is only a 5% margin of improvement. In fact..

- The value of η_{II} for an industrial boiler that produces steam at 120°C is equal to 0.95*(1-283/393) = 27% (for T_o = 283 K), so there is a large margin for improvement!

Review of basic concepts: Typical (efficient and inefficient) uses of fossil fuels

Separate production of hot water (simple boiler)

Recall: $T_{\mathrm{lm}12} = \dfrac{(T_2 - T_1)}{\ln(T_2/T_1)}$



$$\dot{E}x_{\mathrm{fuel}} \approx \dot{Q}_{\mathrm{fuel}} \approx \dot{m}\,\mathrm{LHV}$$

$$\dot{Q}_B \qquad \dot{m}$$

$$\dot{Q}_B = \dot{m}(h_2 - h_1) = \dot{m}c(T_2 - T_1)$$

$$\eta_{\mathrm{I}} = \frac{\dot{Q}_B}{\dot{Q}_{\mathrm{fuel}}}$$

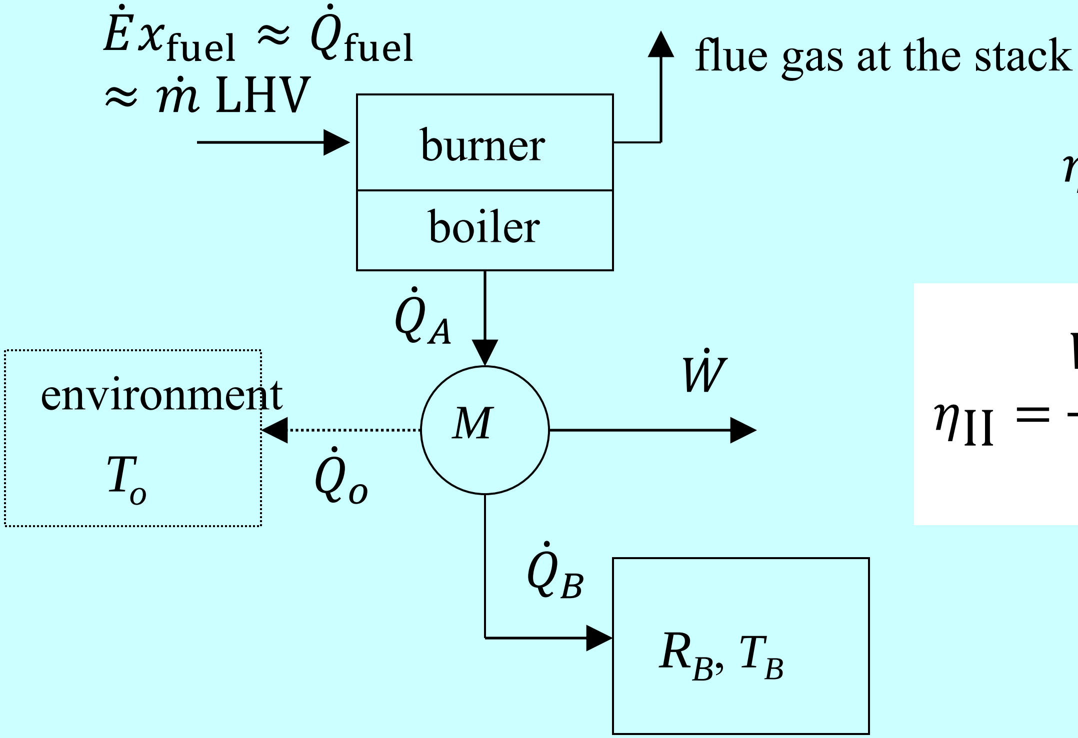
$$\eta_{\mathrm{II}} = \frac{\dot{Q}_B\left[1 - \dfrac{T_o \ln(T_2/T_1)}{T_2 - T_1}\right]}{\dot{E}x_{\mathrm{fuel}}}$$

$$\approx \frac{\dot{Q}_B\left(1 - \dfrac{T_o}{T_{\mathrm{lm}12}}\right)}{\dot{Q}_{\mathrm{fuel}}} = \eta_{\mathrm{I}}\left(1 - \frac{T_o}{T_{\mathrm{lm}12}}\right)$$

- The value of η_{II} for an 85% efficient domestic boiler which heats water from 20 to 60°C is around 4% (for T_o = 298 K) or 11% (for T_o = 273 K).
- For a 95% efficient industrial boiler that heats pressurized water from 20 to 120°C, η_{II} is around 12% (for T_o = 298 K) or 19% (for T_o = 273 K).
- There are ample margins for improvement, obtained for example with cogeneration.

Review of basic concepts: Typical (efficient and inefficient) uses of fossil fuels

Combined production of heat and mechanical energy (cogeneration)

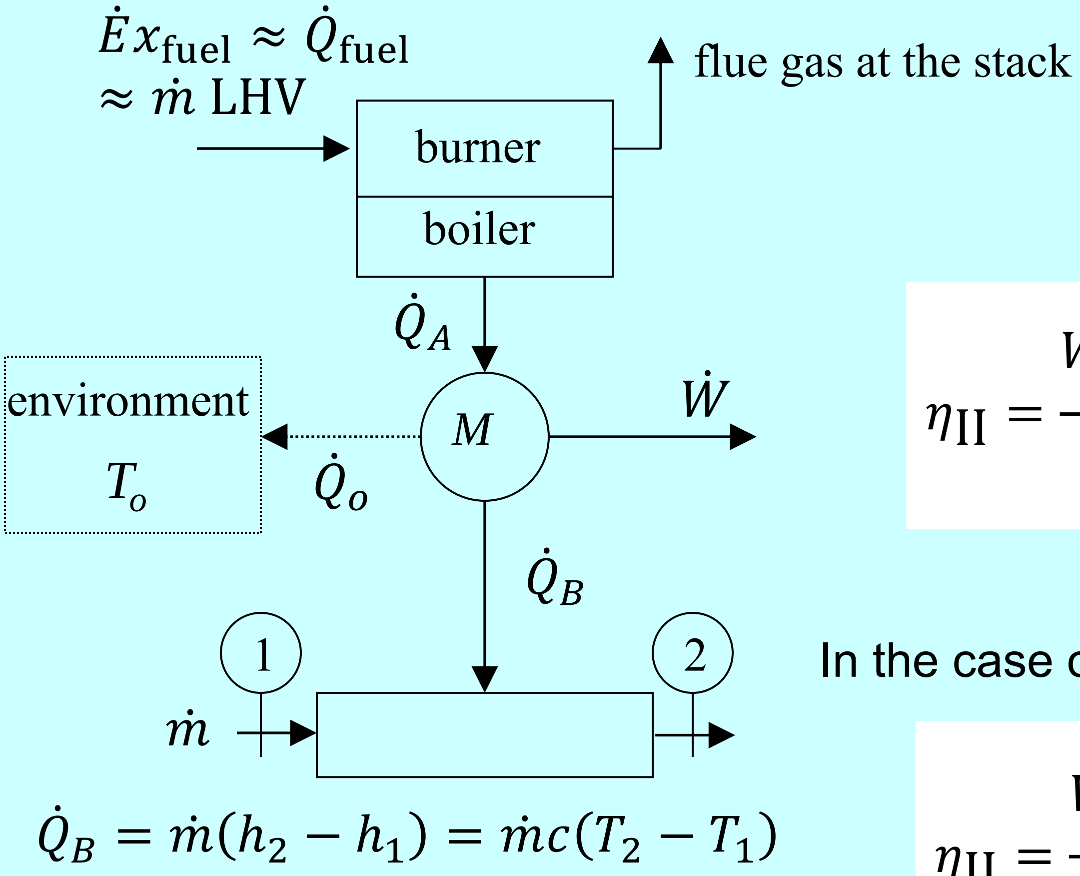


$$\eta_{\text{I}} = \frac{\dot{W} + \dot{Q}_B}{\dot{Q}_{\text{fuel}}}$$

$$\eta_{\text{II}} = \frac{\dot{W} + \dot{Q}_B\left(1 - \frac{T_o}{T_B}\right)}{\dot{E}x_{\text{fuel}}}$$

Review of basic concepts: Typical (efficient and inefficient) uses of fossil fuels

Combined production of heat and mechanical energy (cogeneration)



$$\dot{Q}_B = \dot{m}(h_2 - h_1) = \dot{m}c(T_2 - T_1)$$

$$\eta_{\text{I}} = \frac{\dot{W} + \dot{Q}_B}{\dot{Q}_{\text{fuel}}}$$

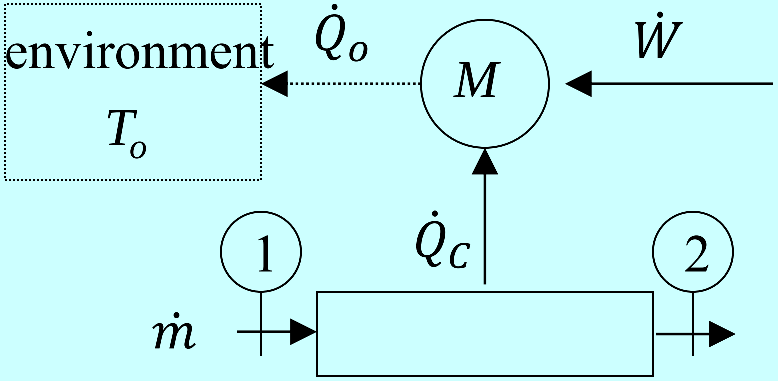
$$\eta_{\text{II}} = \frac{\dot{W} + \dot{Q}_B \left[1 - T_o \dfrac{s_2 - s_1}{h_2 - h_1}\right]}{\dot{E}x_{\text{fuel}}}$$

In the case of heating of water or air:

$$\eta_{\text{II}} = \frac{\dot{W} + \dot{Q}_B \left[1 - \dfrac{T_o \ln(T_2/T_1)}{T_2 - T_1}\right]}{\dot{E}x_{\text{fuel}}}$$

Review of basic concepts: Typical (efficient and inefficient) uses of fossil fuels

Separate production of chilled water (simple industrial refrigeration)



$$\dot{Q}_C = \dot{m}(h_1 - h_2) = \dot{m}c(T_1 - T_2)$$

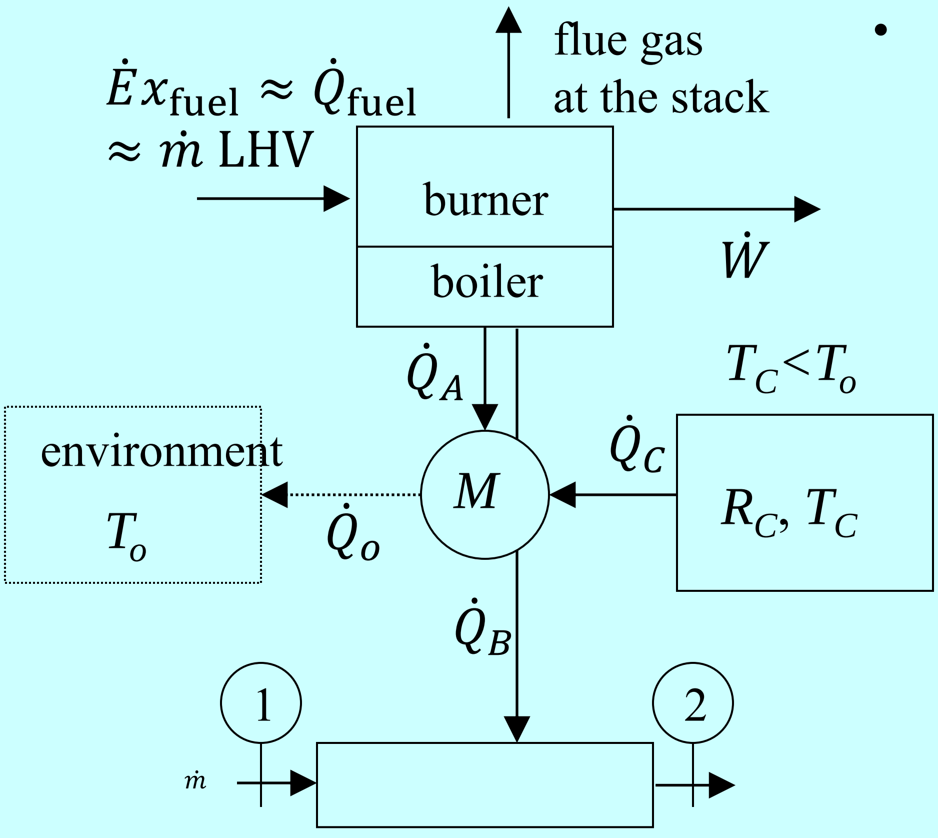
$$\mathrm{COP_{refr}} = \frac{\dot{Q}_C}{\dot{W}}$$

$$\eta_{\mathrm{II}} = \frac{\dot{Q}_C\left[\frac{T_o \ln(T_1/T_2)}{T_1 - T_2} - 1\right]}{\dot{W}}$$

$$= \mathrm{COP_{refr}}\left(1 - \frac{T_o}{T_{\mathrm{lm12}}}\right)$$

The value of COP for industrial refrigerators used for air conditioning, which cool water from 12 to 7°C, can be around 5, so (for T_o = 303 K) η_{II} is around 36%.

Review of basic concepts: Typical (efficient and inefficient) uses of fossil fuels



$$\dot{Q}_B = \dot{m}(h_2 - h_1) = \dot{m}c(T_2 - T_1)$$

- **Combined production of mechanical energy, thermal and cooling (trigeneration)**

$$\eta_{\rm I} = \text{not defined}$$

You must first allocate the shares of fuel used for the different products, and then define

$$\eta_{\rm I,\dot{W}} = \frac{\dot{W}}{\dot{Q}_{\rm fuel,\dot{W}}}$$

$$\mathrm{COP}_{\dot{\rm Q}_{\rm B}} = \frac{\dot{Q}_B}{\dot{Q}_{\rm fuel,\dot{Q}_B}}$$

$$\mathrm{COP}_{\dot{\rm Q}_{\rm C}} = \frac{\dot{Q}_C}{\dot{Q}_{\rm fuel,\dot{Q}_C}}$$

$$\eta_{\rm II} = \frac{\dot{W} + \dot{Q}_B\left[1 - \dfrac{T_o\ln(T_2/T_1)}{T_2 - T_1}\right] + \dot{Q}_C\left(\dfrac{T_o}{T_C} - 1\right)}{\dot{E}x_{\rm fuel}}$$

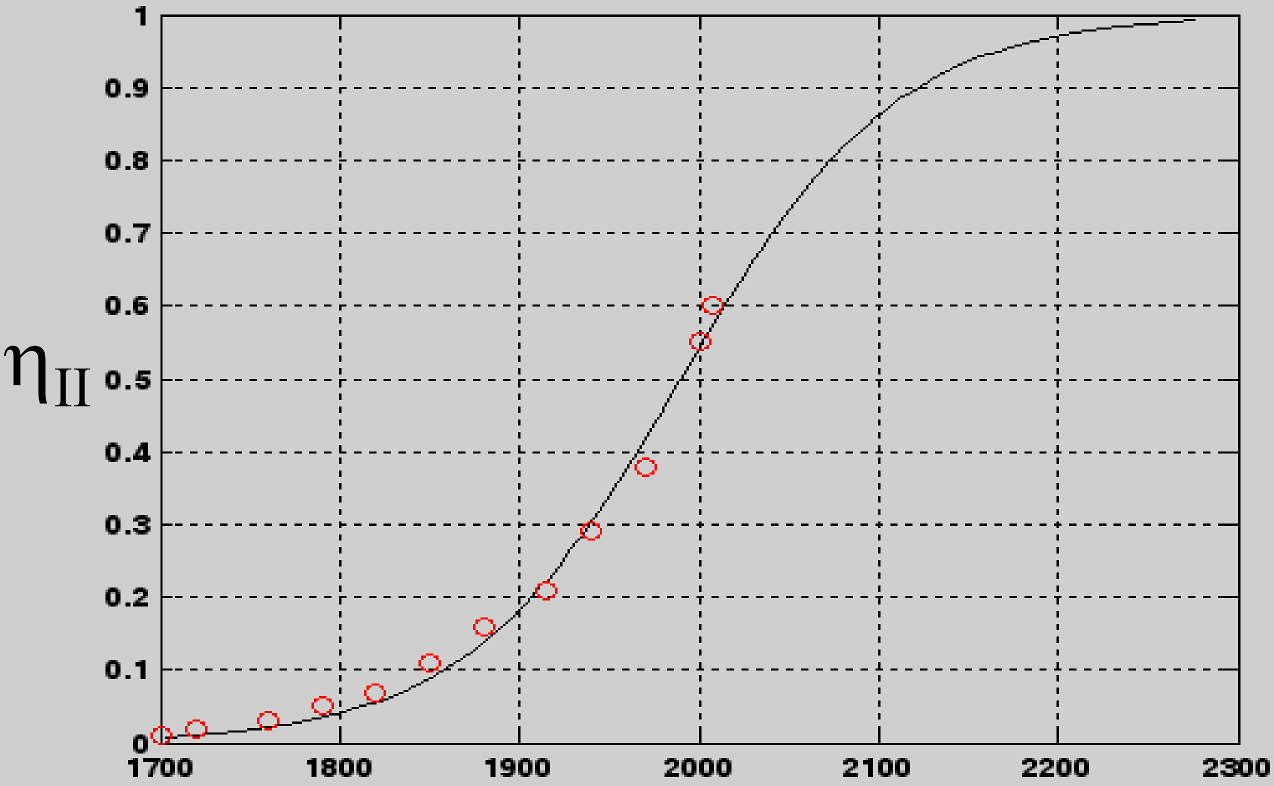
Review of basic concepts: Typical (efficient and inefficient) uses of fossil fuels

Try to fill this table for your own country!

Method:	SP = Separate production		CHP = combined heat and power		HYB = hybrid fuel and renewable	
Second-law efficiency of the conversion of fuel energy to:	Ave 🇮🇹	BAT	Ave 🇮🇹	BAT	Ave 🇮🇹	BAT
Electrical power	45%?	65%?	55%?	70%?	48%?	?
Residential heat (20-60°C @T_a=0°C)	11%?		14%?			
Residential heat (20-60°C @T_a=25°C)	4%?		5%?			
Industrial heat (60-120°C @T_a=0°C)	23%?		32%?			
Industrial heat (60-120°C @T_a=25°C)	17%?		23%?			
... (other energy products)						

Review of basic concepts:

The learning curve of fuel-to-power conversion technologies



$$\frac{d\eta_{II}}{dt} = \frac{1}{\tau}\eta_{II}(1-\eta_{II}) \quad \text{with} \quad \tau \approx 60\,\text{yr}$$

η_{II}

Thermodynamic efficiency of the best-available mature technology for primary energy conversion to work or electricity

Methods for the ALLOCATION

of

energy consumption and **CO_2 production**

in

combined heat and power (CHP) production

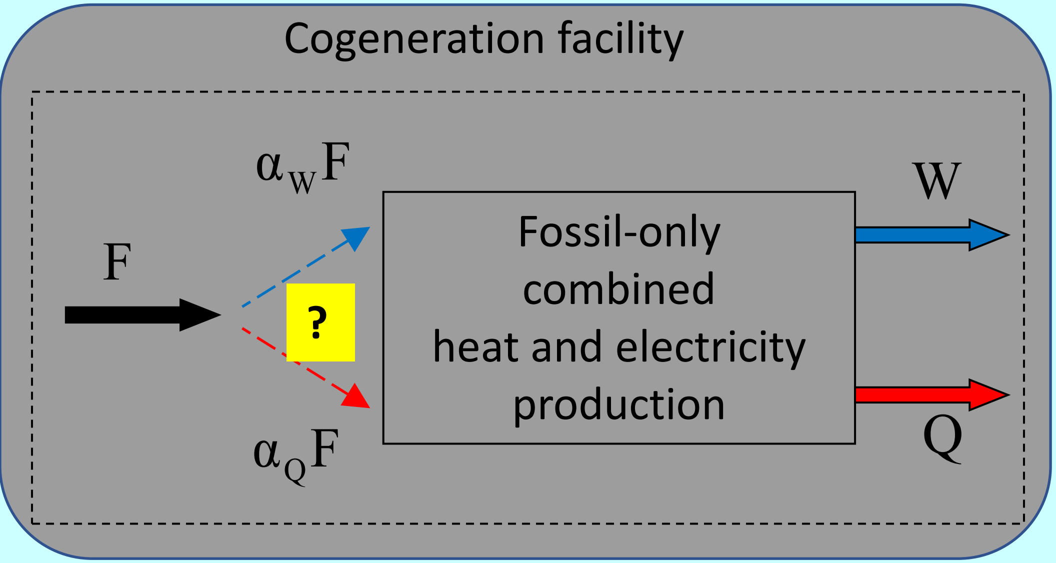
and of

heat and/or power production

in

hybrid multi-resource facilities

Allocation problem in Heat&Power Cogeneration: α_W, α_Q, partial efficiencies, and PES



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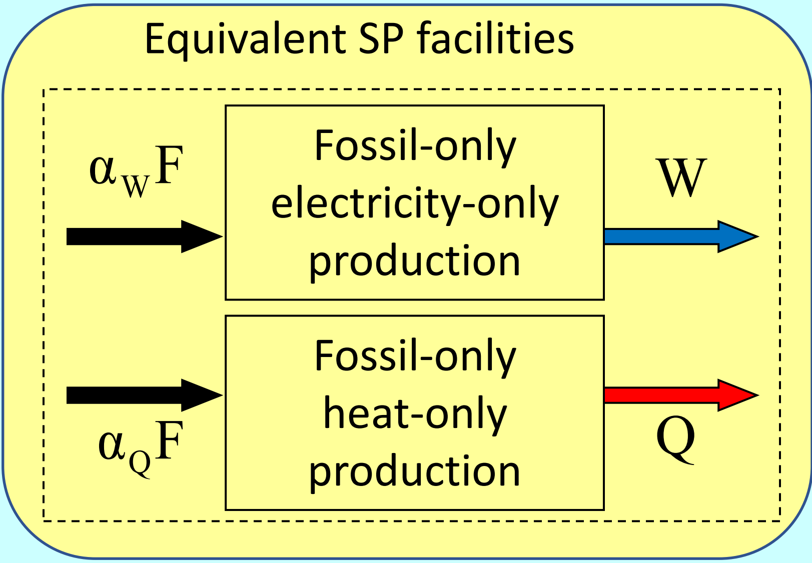


Partial Efficiencies

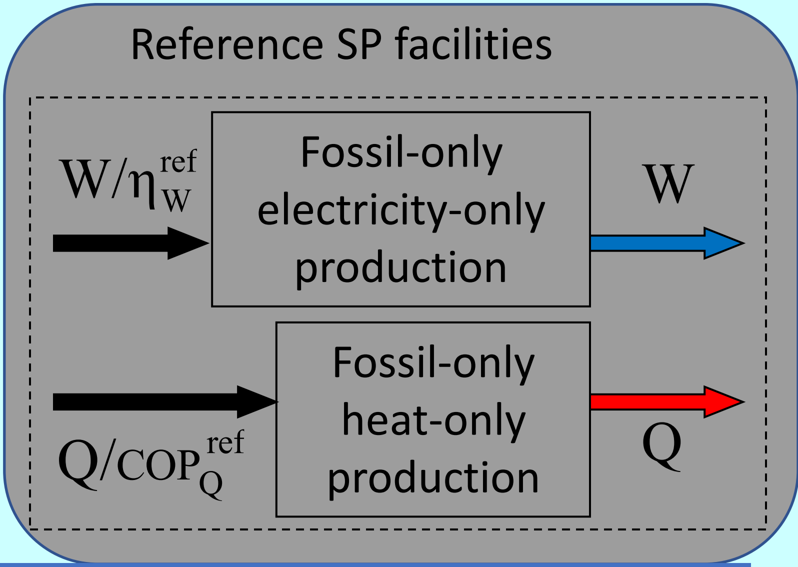
$$\eta_W^{\rm chp} = \frac{W}{\alpha_W F}$$

$$\mathrm{COP}_Q^{\rm chp} = \frac{Q}{\alpha_Q F}$$

Primary Energy Savings vs SP facilities

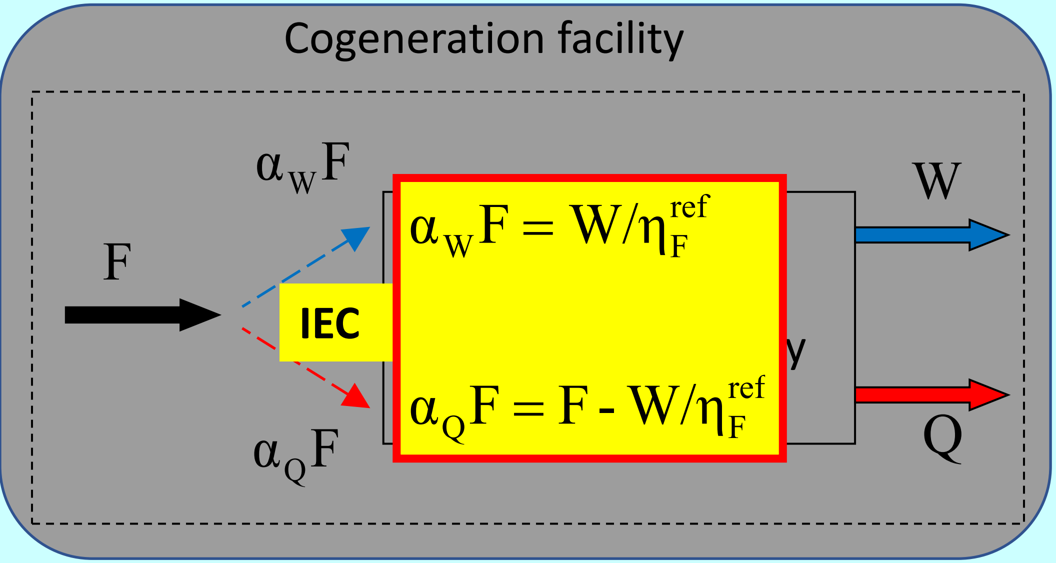
$$\mathrm{PES}_W = \frac{W/\eta_W^{\rm ref} - \alpha_W F}{W/\eta_W^{\rm ref}}$$

$$\mathrm{PES}_Q = \frac{Q/\mathrm{COP}_Q^{\rm ref} - \alpha_Q F}{Q/\mathrm{COP}_Q^{\rm ref}}$$



$$\mathrm{PES} = \frac{W/\eta_W^{\rm ref} + Q/\mathrm{COP}_Q^{\rm ref} - F}{W/\eta_W^{\rm ref} + Q/\mathrm{COP}_Q^{\rm ref}} = \frac{W/\eta_W^{\rm ref}}{W/\eta_W^{\rm ref} + Q/\mathrm{COP}_Q^{\rm ref}}\mathrm{PES}_W + \frac{Q/\mathrm{COP}_Q^{\rm ref}}{W/\eta_W^{\rm ref} + Q/\mathrm{COP}_Q^{\rm ref}}\mathrm{PES}_Q$$

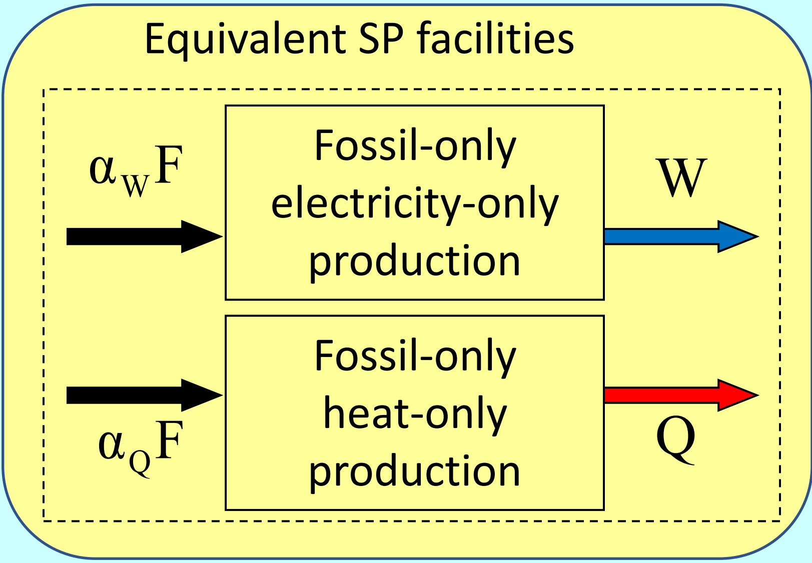
Allocation problem in CHP: Incremental Electricity-Centered Allocation



$$\alpha_W F = W/\eta_F^{ref}$$

$$\alpha_Q F = F - W/\eta_F^{ref}$$

=



Partial Efficiencies

$$COP_Q^{chp} = \frac{Q}{F - W/\eta_W^{ref}}$$

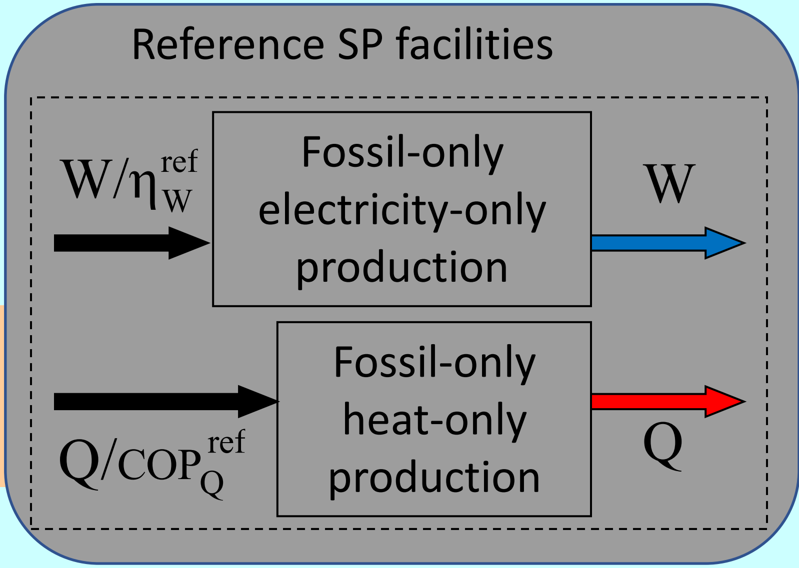
$$\eta_W^{chp} = \eta_W^{ref}$$

Primary Energy Savings vs SP facilities

$$PES_W = 0$$

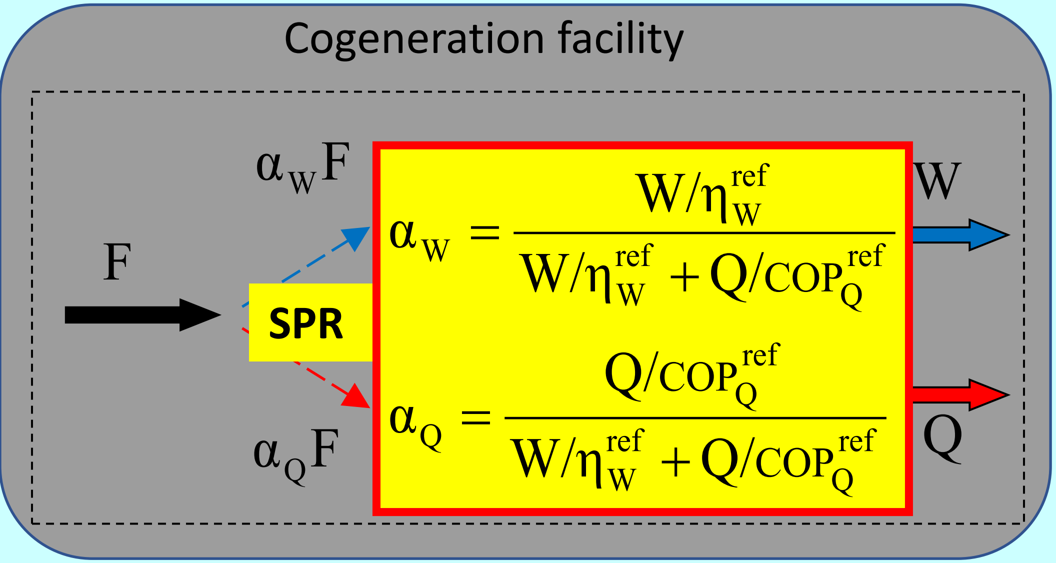
$$PES_Q = \frac{Q/COP_Q^{ref} - (F - W/\eta_W^{ref})}{Q/COP_Q^{ref}}$$

$$PES_Q = \frac{W/\eta_W^{ref} + Q/COP_Q^{ref}}{Q/COP_Q^{ref}} PES > PES\,!$$



No allotment of the benefits of cogeneration between W and Q! COP_Q may be negative!

Allocation problem in CHP: Separate Production Reference Allocation



Cogeneration facility

F

SPR

$\alpha_W F$

$\alpha_Q F$

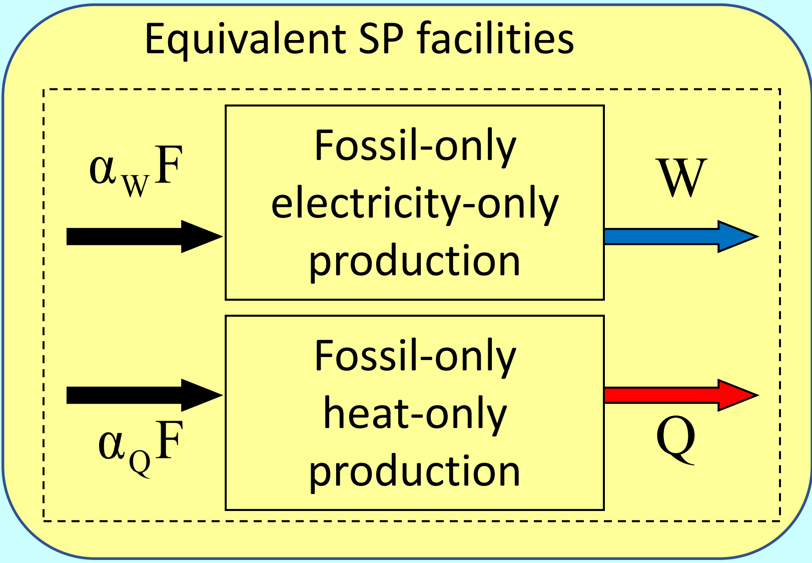
$$\alpha_W = \frac{W/\eta_W^{ref}}{W/\eta_W^{ref} + Q/COP_Q^{ref}}$$

$$\alpha_Q = \frac{Q/COP_Q^{ref}}{W/\eta_W^{ref} + Q/COP_Q^{ref}}$$

W

Q

$=$



Equivalent SP facilities

$\alpha_W F$

Fossil-only electricity-only production

W

$\alpha_Q F$

Fossil-only heat-only production

Q

Partial Efficiencies

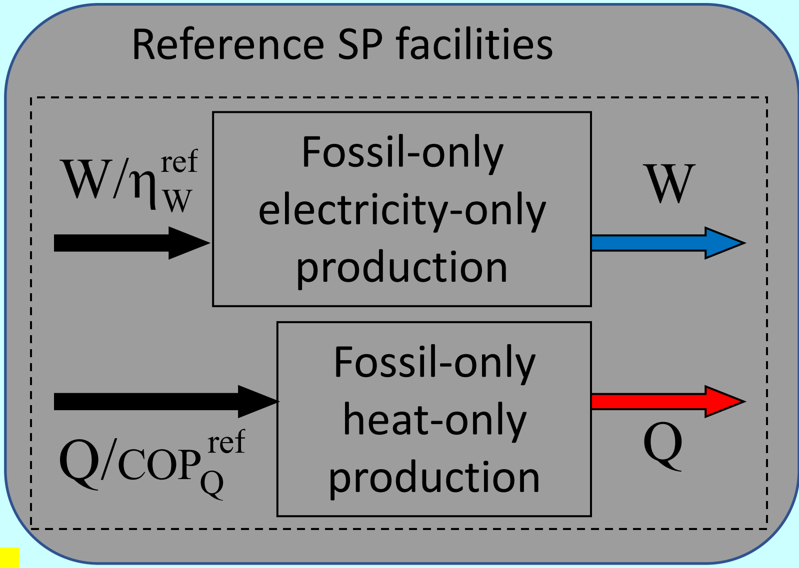
$$\eta_W^{chp} = \frac{W}{\alpha_W F}$$

$$COP_Q^{chp} = \frac{Q}{\alpha_Q F}$$

Primary Energy Savings vs SP facilities

$$PES_W = \frac{W/\eta_W^{ref} - \alpha_W F}{W/\eta_W^{ref}}$$

$$PES_Q = \frac{Q/COP_Q^{ref} - \alpha_Q F}{Q/COP_Q^{ref}}$$



Reference SP facilities

W/η_W^{ref}

Fossil-only electricity-only production

W

Q/COP_Q^{ref}

Fossil-only heat-only production

Q

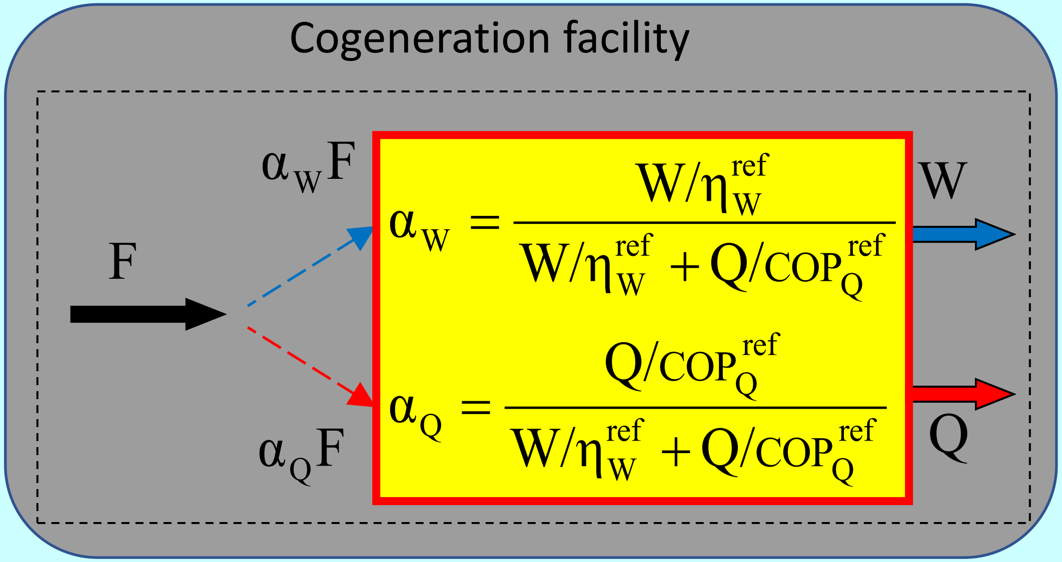
$$PES = \frac{W/\eta_W^{ref} + Q/COP_Q^{ref} - F}{W/\eta_W^{ref} + Q/COP_Q^{ref}} = PES_W = PES_Q$$

Fair allotment of the benefits of cogeneration between W and Q provided reference values…!!

Allocation problem in CHP: Choice of reference values for $\eta_{\mathrm{W}}^{\mathrm{ref}}$ and $\mathrm{COP}_{\mathrm{Q}}^{\mathrm{ref}}$

SPR method:

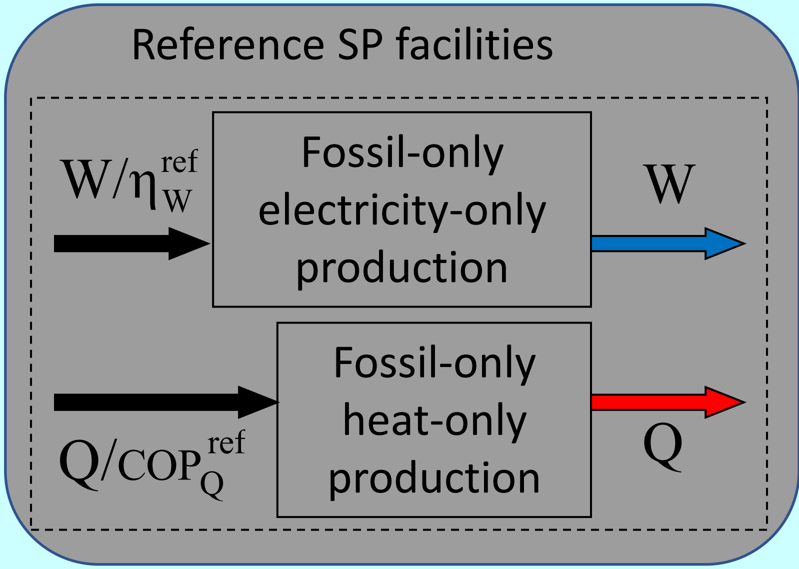
Fixed values set by some local Authority



Cogeneration facility

$$\alpha_{\mathrm{W}} = \frac{\mathrm{W}/\eta_{\mathrm{W}}^{\mathrm{ref}}}{\mathrm{W}/\eta_{\mathrm{W}}^{\mathrm{ref}} + \mathrm{Q}/\mathrm{COP}_{\mathrm{Q}}^{\mathrm{ref}}}$$

$$\alpha_{\mathrm{Q}} = \frac{\mathrm{Q}/\mathrm{COP}_{\mathrm{Q}}^{\mathrm{ref}}}{\mathrm{W}/\eta_{\mathrm{W}}^{\mathrm{ref}} + \mathrm{Q}/\mathrm{COP}_{\mathrm{Q}}^{\mathrm{ref}}}$$



Reference SP facilities

Fossil-only electricity-only production

Fossil-only heat-only production

Exergy method:

Fixed values set by Thermodynamics

Effectively takes as references
the REVERSIBLE heat engines!

$$\eta_{\mathrm{W}}^{\mathrm{ref}} \approx 1 \qquad \mathrm{COP}_{\mathrm{Q}}^{\mathrm{ref}} = 1 \bigg/ \left(1 - \frac{T_{\mathrm{env}}}{T_{\mathrm{Q}}}\right)$$

Allocation problem in CHP: “fair” reference values in a given local area

STALPR Method*: Self-Tuned-Average-Local-Productions-Reference

Adopt reference efficiencies

η_W^{ref} COP_Q^{ref}

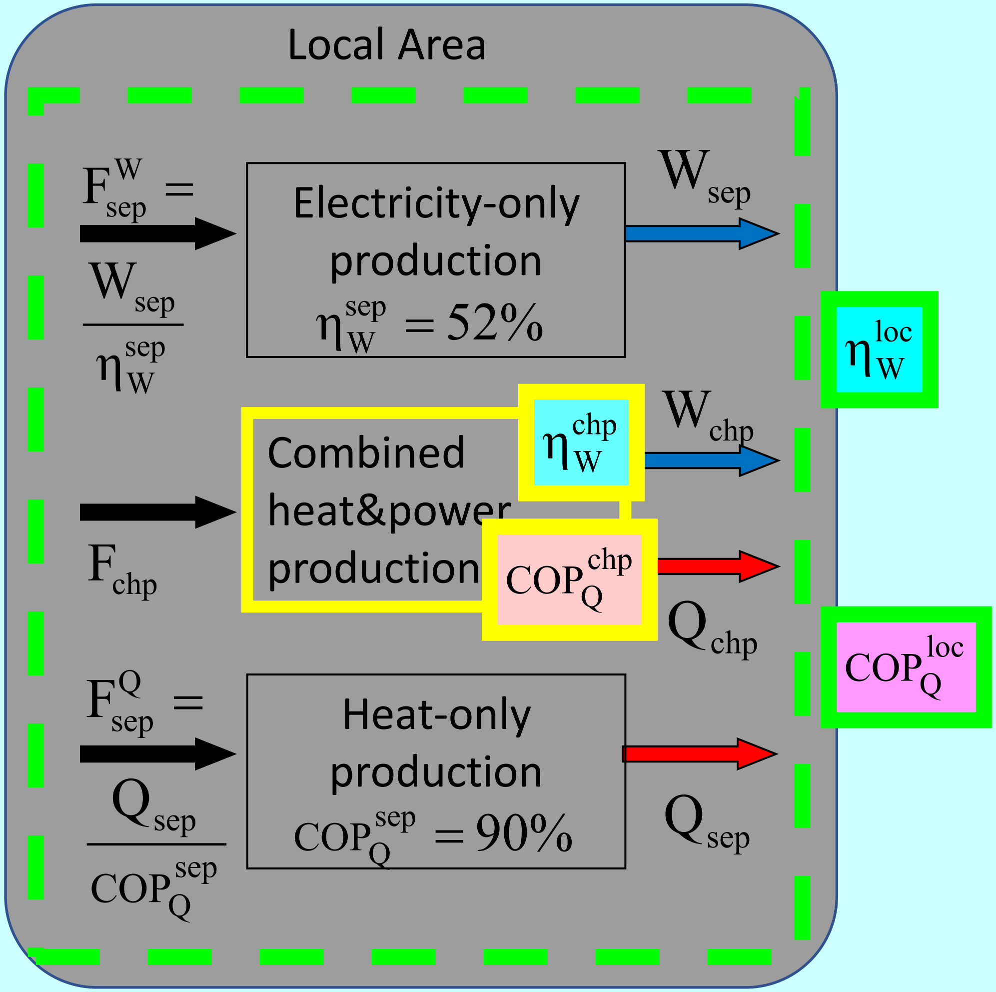
that are representative of the actual average efficiencies

η_W^{loc} COP_Q^{loc}

of the energy production portfolio (typically the local area where the cogenerator itself is located) with which the resulting efficiencies of the cogenerator

η_W^{chp} COP_Q^{chp}

are to be compared.



Local Area

$F_{sep}^W = \dfrac{W_{sep}}{\eta_W^{sep}}$

Electricity-only production $\eta_W^{sep} = 52\%$

W_{sep}

η_W^{loc}

F_{chp}

Combined heat&power production

η_W^{chp}

W_{chp}

COP_Q^{chp}

Q_{chp}

COP_Q^{loc}

$F_{sep}^Q = \dfrac{Q_{sep}}{COP_Q^{sep}}$

Heat-only production $COP_Q^{sep} = 90\%$

Q_{sep}

$$\eta_W^{loc} = \frac{W_{sep} + W_{chp}}{F_{sep}^W + \alpha_W F_{chp}}$$

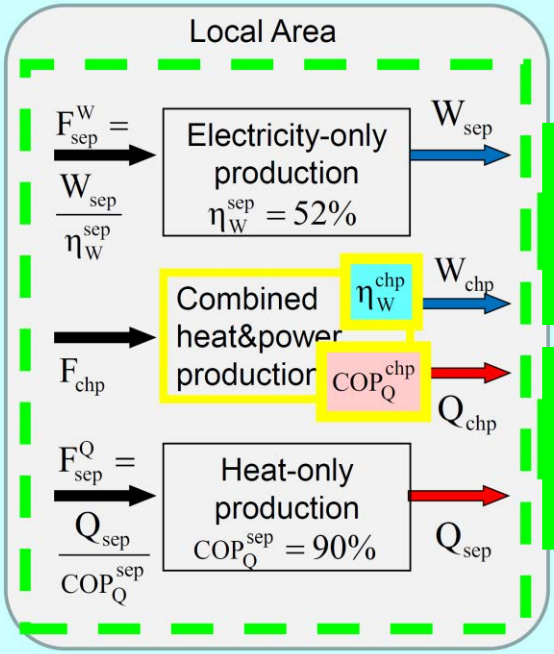
$$COP_Q^{loc} = \frac{Q_{sep} + Q_{chp}}{F_{sep}^Q + \alpha_Q F_{chp}}$$

* G.P. Beretta, P. Iora, and A.F. Ghoniem, Energy, Vol. 44, pp. 1107-1120 (2012)

Allocation Example in CHP: a comparison between allocation methods

Parameters of the local area	
$\sigma_{loc} = \dfrac{W_{sep} + W_{chp}}{Q_{sep} + Q_{chp}}$	50 %
$\gamma^{Q}_{chp} = \dfrac{Q_{chp}}{Q_{sep} + Q_{chp}}$	40 %

Average efficiencies based on SPR	CC	BPST
η^{loc}_{W}	68.3 %	52.4 %
COP^{loc}_{Q}	90.8 %	92.2 %
$\gamma^{W}_{chp} = \dfrac{W_{chp}}{W_{sep} + W_{chp}}$	96 %	16 %
Reference values for SPR		
η^{ref}_{W}	68.3 %	52.4 %
COP^{ref}_{Q}	90.8%	92.2 %

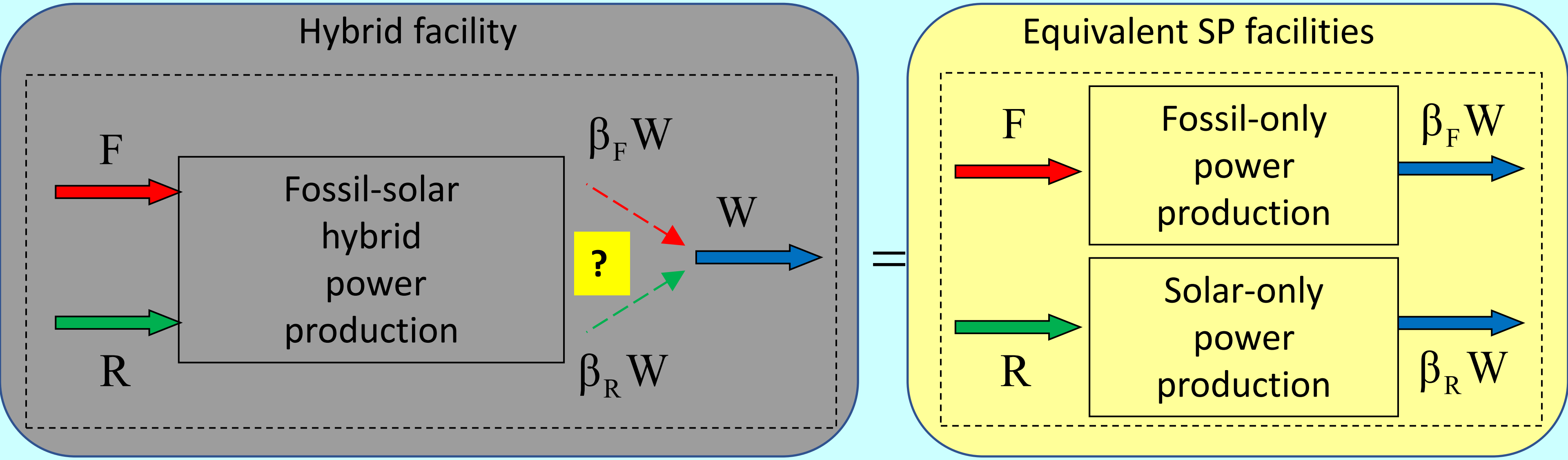


$$\boxed{\eta^{loc}_{W} = \frac{W_{sep} + W_{chp}}{F^{W}_{sep} + \alpha_{W} F_{chp}}}$$

$$\boxed{COP^{loc}_{Q} = \frac{Q_{sep} + Q_{chp}}{F^{Q}_{sep} + \alpha_{Q} F_{chp}}}$$

%	IEC		Exergy		STALPR	
	η^{chp}_{W}	COP^{chp}_{Q}	η^{chp}_{W}	COP^{chp}_{Q}	η^{chp}_{W}	COP^{chp}_{Q}
CC	52	354	50	234	69.2	92.0
BPST	52	101	29	137	54.4	95.8

Allocation problem in Hybrid Facilities: β_F, β_Q, partial efficiencies, and PES



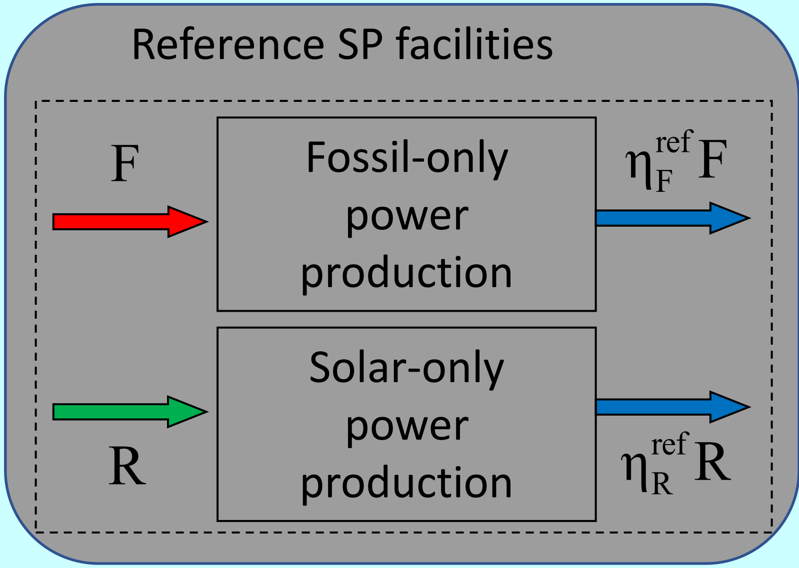
Hybrid facility

Fossil-solar hybrid power production

Equivalent SP facilities

Fossil-only power production

Solar-only power production



Reference SP facilities

Fossil-only power production

Solar-only power production

Partial Efficiencies

$$\eta_F^{hyb} = \frac{\beta_F W}{F}$$

$$\eta_R^{hyb} = \frac{\beta_R W}{R}$$

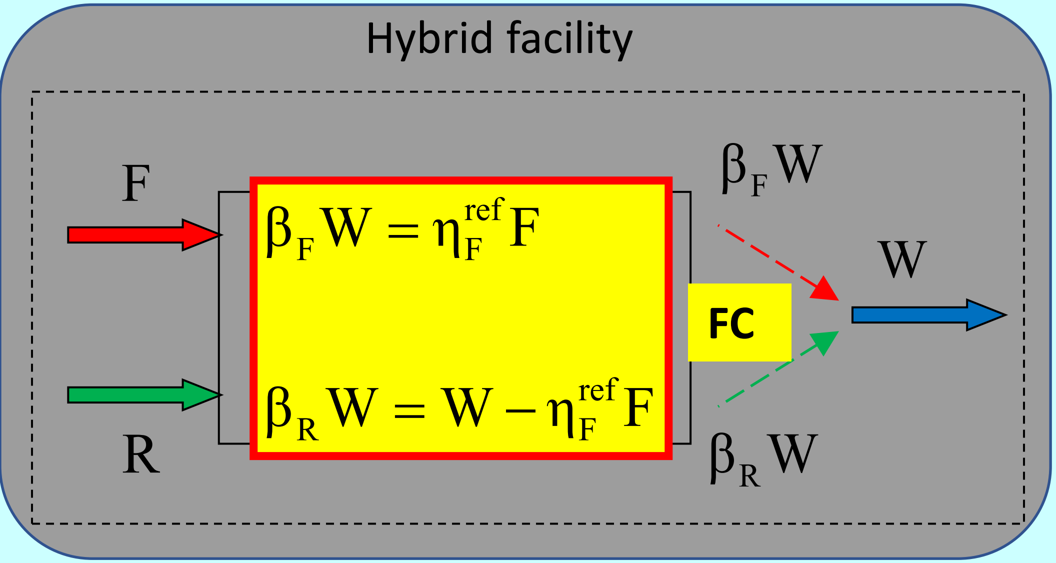
Primary Energy Savings vs SP facilities

$$PES_F = \frac{\beta_F W - \eta_F^{ref} F}{\beta_F W}$$

$$PES_R = \frac{\beta_R W - \eta_R^{ref} R}{\beta_R W}$$

$$PES = \frac{\beta_F W/\eta_F^{ref} + \beta_R W/\eta_R^{ref} - F - R}{\beta_F W/\eta_F^{ref} + \beta_R W/\eta_R^{ref}} = \frac{\beta_F W/\eta_F^{ref}}{\beta_F W/\eta_F^{ref} + \beta_R W/\eta_R^{ref}} PES_F + \frac{\beta_R W/\eta_R^{ref}}{\beta_F W/\eta_F^{ref} + \beta_R W/\eta_R^{ref}} PES_R$$

Allocation problem in Hybrid Facilities: Incremental Fossil-Centered Allocation

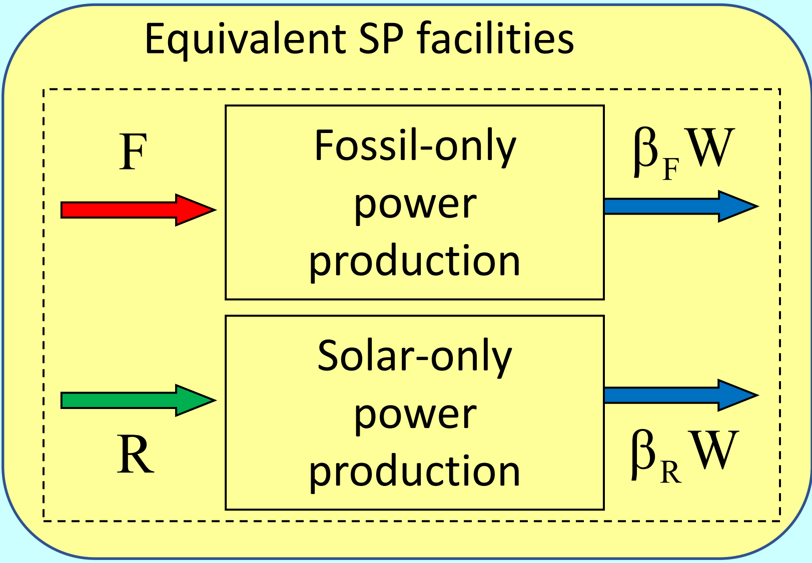


Hybrid facility

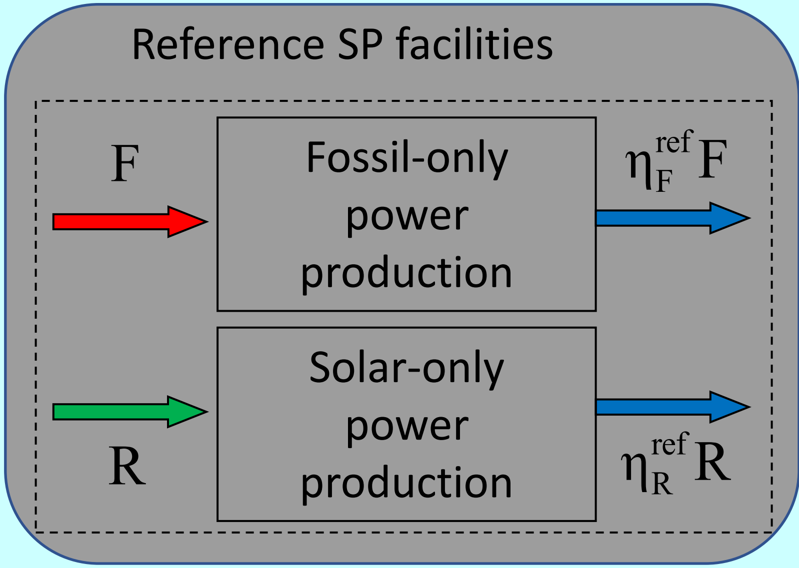
$\beta_F W = \eta_F^{ref} F$

$\beta_R W = W - \eta_F^{ref} F$

$=$



Equivalent SP facilities



Reference SP facilities

Partial Efficiencies

$$\eta_F^{hyb} = \eta_F^{ref}$$

$$\eta_R^{hyb} = \frac{W - \eta_F^{ref} F}{R}$$

Primary Energy Savings vs SP facilities

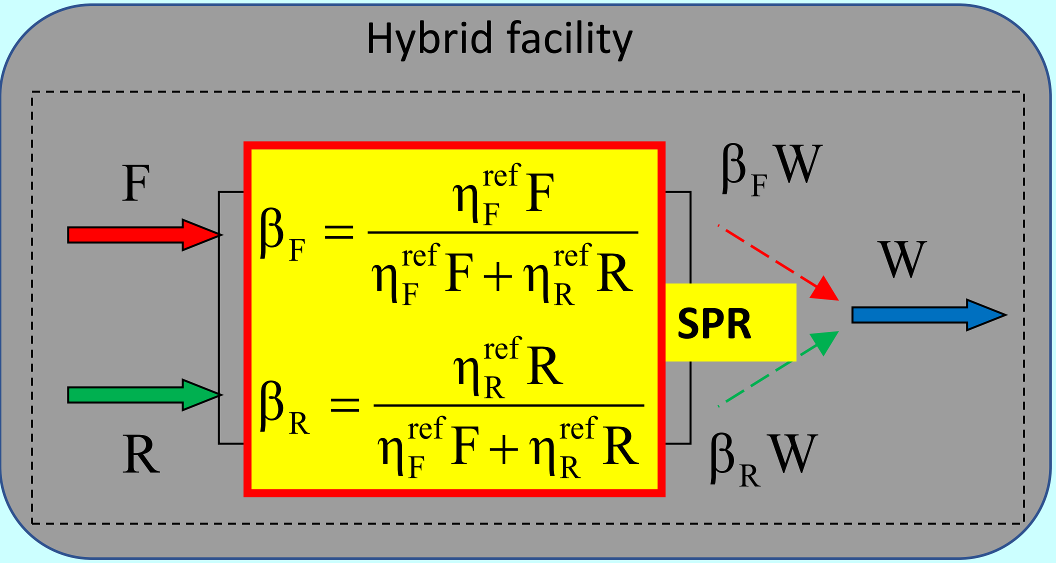
$$\mathrm{PES}_F = 0$$

$$\mathrm{PES}_R = \frac{W - \eta_F^{ref} F - \eta_R^{ref} R}{W - \eta_F^{ref} F}$$

$$\mathrm{PES}_R = \left(1 + \frac{\eta_R^{ref} F}{\beta_R W}\right) \mathrm{PES} > \mathrm{PES}\,!$$

No allottment of the benefits of hybridization between F and R!

Allocation problem in Hybrid Facilities: Separate Production Reference Allocation



Hybrid facility

F

R

$$\beta_F = \frac{\eta_F^{ref} F}{\eta_F^{ref} F + \eta_R^{ref} R}$$

$$\beta_R = \frac{\eta_R^{ref} R}{\eta_F^{ref} F + \eta_R^{ref} R}$$

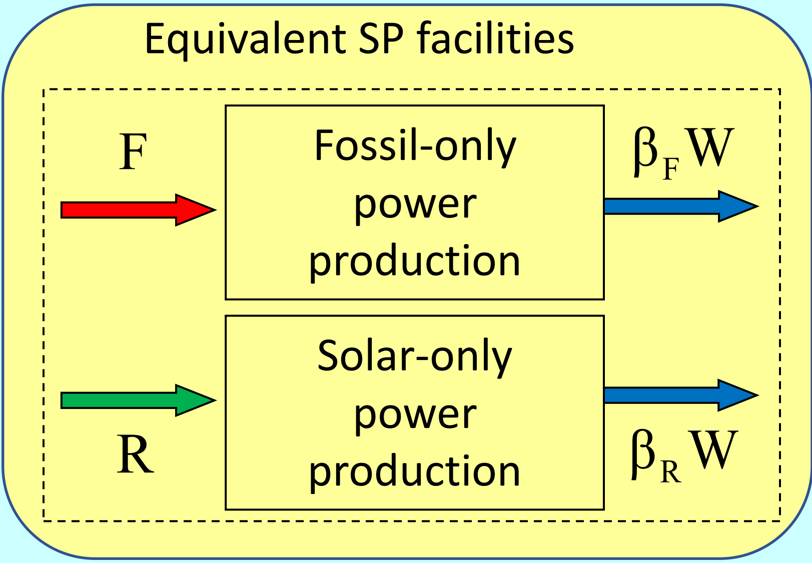
SPR

$\beta_F W$

$\beta_R W$

W

$=$



Equivalent SP facilities

F → Fossil-only power production → $\beta_F W$

R → Solar-only power production → $\beta_R W$

Partial Efficiencies

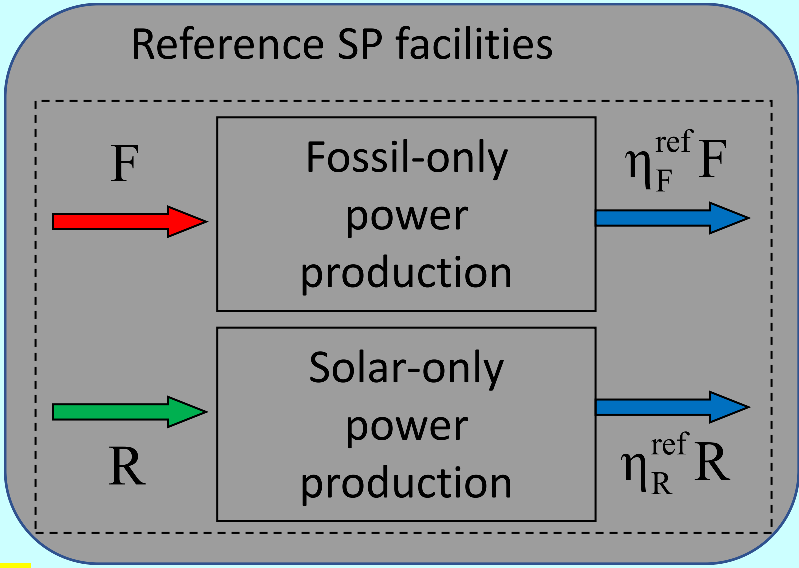
$$\eta_F^{hyb} = \frac{\beta_F W}{F}$$

$$\eta_R^{hyb} = \frac{\beta_R W}{R}$$

Primary Energy Savings vs SP facilities

$$PES_F = \frac{\beta_F W - \eta_F^{ref} F}{\beta_F W}$$

$$PES_R = \frac{\beta_R W - \eta_R^{ref} R}{\beta_R W}$$



Reference SP facilities

F → Fossil-only power production → $\eta_F^{ref} F$

R → Solar-only power production → $\eta_R^{ref} R$

$$PES = \frac{\beta_F W/\eta_F^{ref} + \beta_R W/\eta_R^{ref} - F - R}{\beta_F W/\eta_F^{ref} + \beta_R W/\eta_R^{ref}} = PES_F = PES_R$$

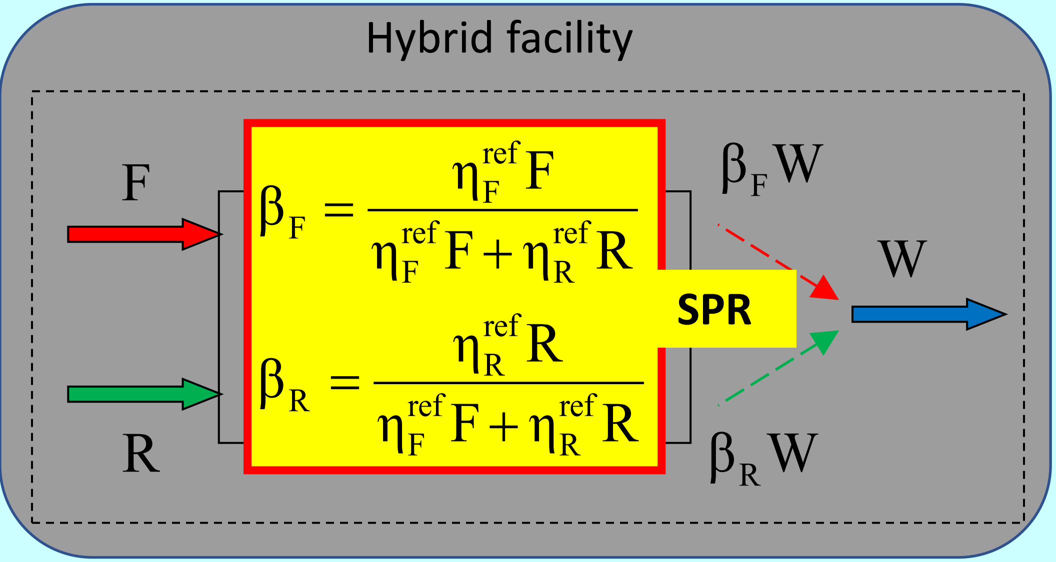
Allottment of the hybridization benefits between F and R is fair only for fair reference values…!!

Choice of reference values η_F^{ref} a η_R^{ref} .

SPR method:

Fixed values set by some <u>local Authority</u>

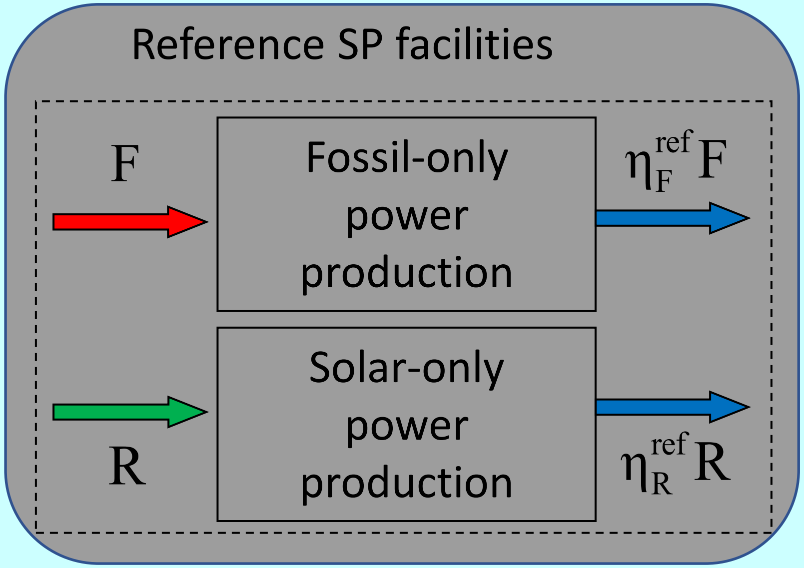
Hybrid facility



$$\beta_F = \frac{\eta_F^{ref} F}{\eta_F^{ref} F + \eta_R^{ref} R}$$

$$\beta_R = \frac{\eta_R^{ref} R}{\eta_F^{ref} F + \eta_R^{ref} R}$$

Reference SP facilities



Exergy method:

Fixed values set by <u>Thermodynamics</u>

Effectively takes as references
the REVERSIBLE heat engines!

$$\eta_F^{ref} \approx 1 \qquad \eta_R^{ref} \approx 0.93$$

Allocation problem in Hybrid Facilities: “fair” reference values in a given local area

STALPR Method*: Self-Tuned-Average-Local-Productions-Reference

Adopt reference efficiencies

η_F^{ref} η_R^{ref}

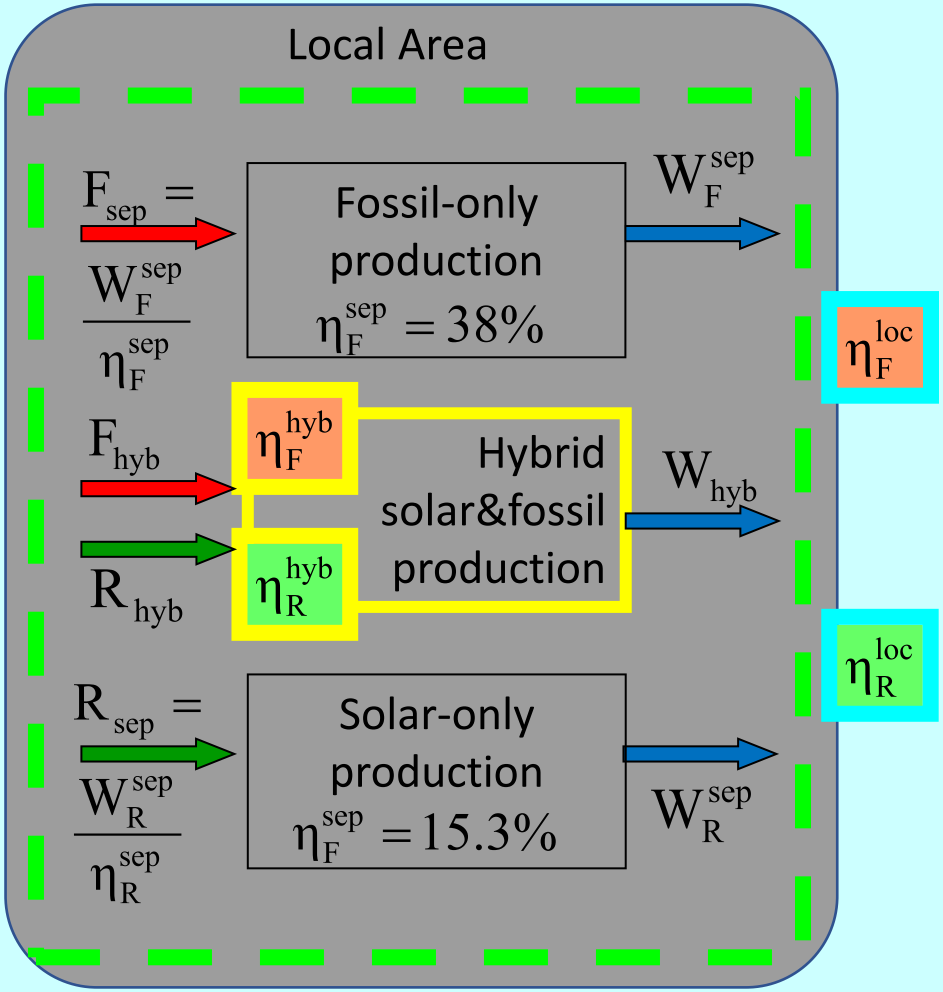
that are representative of the actual average efficiencies

η_F^{loc} η_R^{loc}

of the energy production portfolio (typically the local area where the hybrid plant itself is located) with which the resulting efficiencies of the hybrid plant

η_F^{hyb} η_R^{hyb}

are to be compared.



Local Area

$F_{sep} = \dfrac{W_F^{sep}}{\eta_F^{sep}}$

Fossil-only production $\eta_F^{sep} = 38\%$

W_F^{sep}

η_F^{loc}

F_{hyb}

R_{hyb}

η_F^{hyb} η_R^{hyb} Hybrid solar&fossil production

W_{hyb}

η_R^{loc}

$R_{sep} = \dfrac{W_R^{sep}}{\eta_R^{sep}}$

Solar-only production $\eta_F^{sep} = 15.3\%$

W_R^{sep}

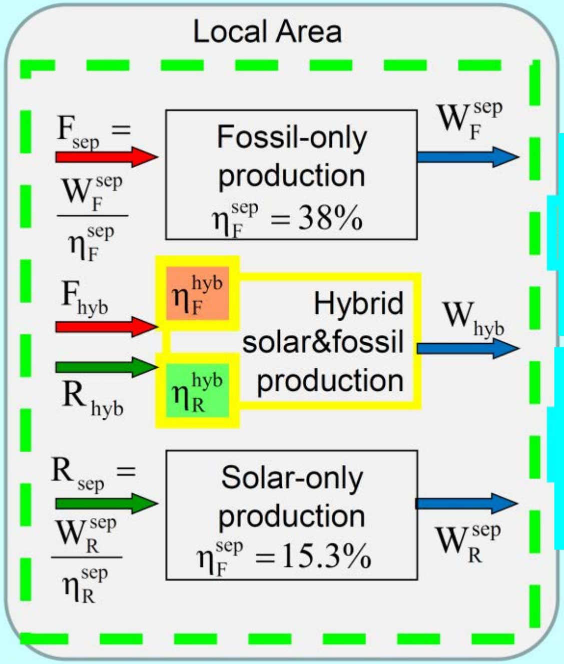
$$\eta_F^{loc} = \frac{W_F^{sep} + \beta_F W_{hyb}}{F_{sep} + F_{hyb}}$$

$$\eta_R^{loc} = \frac{W_R^{sep} + \beta_R W_{hyb}}{R_{sep} + R_{hyb}}$$

* G.P. Beretta, P. Iora, and A.F. Ghoniem, Energy, Vol. 60, pp. 344-360 (2013)

Allocation Example in Hybrid Facilities: a comparison between allocation methods

Parameters of the local area	
$\dfrac{W_{hyb}}{W_{hyb}+W_F^{sep}+W_R^{sep}}$	45 %
$\dfrac{W_R^{sep}}{W_{hyb}+W_F^{sep}+W_R^{sep}}$	10 %
Reference values for SPR	
η_F^{ref}	40.8 %
η_R^{ref}	16.2 %
Average local area efficiencies	
η_F^{loc}	40.8 %
η_R^{loc}	16.2 %



$$\eta_F^{loc} = \frac{W_F^{sep} + \beta_F W_{hyb}}{F_{sep} + F_{hyb}}$$

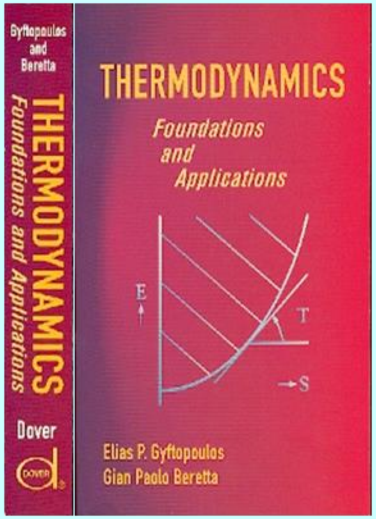
$$\eta_R^{loc} = \frac{W_R^{sep} + \beta_R W_{hyb}}{R_{sep} + R_{hyb}}$$

%	FC			Exergy			SPR (38%,15.3%)			STALRP		
	η_F^{hyb}	η_R^{hyb}	β_R^{hyb}	η_F^{hyb}	η_R^{hyb}	β_R^{hyb}	η_F^{hyb}	η_R^{hyb}	β_R^{hyb}	η_F^{hyb}	η_R^{hyb}	β_R^{hyb}
	38	204	25.2	42	35.5	17.4	46.2	18.6	9.11	46.1	18.7	9.19

Part II: chemical potentials and multicomponent equilibria

Contents:

- Modeling ideal and nonideal gas mixtures and solutions
- Mutual equilibrium across semi-permeable membranes
- Minimum work of separation, maximum work of mixing
- Osmotic pressure
- Liquid-vapor and liquid-liquid phase equilibria
- Metastable states and spinodal decomposition
- Modeling chemically reacting mixtures
- Chemical equilibrium
- Chemical kinetics standard model
- Electrochemical potentials



Stable-equilibrium properties of MIXTURES (within the simple-system model)

Partial properties
Gibbs-Dalton ideal mixtures
Mixing and separation
Osmotic pressure and blue energy
Stratification

Summary of SES relations: (small systems) (Mixtures)

Specific properties in general depend on *n* ...

$$Eu = E - TS + pV - \boldsymbol{\mu}\cdot\boldsymbol{n} = F + pV - \boldsymbol{\mu}\cdot\boldsymbol{n} = G - \boldsymbol{\mu}\cdot\boldsymbol{n} = H - TS - \boldsymbol{\mu}\cdot\boldsymbol{n}$$

$$\mathrm{d}Eu = -S\,\mathrm{d}T + V\,\mathrm{d}p - \boldsymbol{n}\cdot\mathrm{d}\boldsymbol{\mu} \quad\Rightarrow\quad Eu = Eu(T,p,\boldsymbol{\mu})$$

$$eu = \frac{Eu}{n} = e - Ts + pv - \boldsymbol{\mu}\cdot\boldsymbol{y} = g - \boldsymbol{\mu}\cdot\boldsymbol{y} = f + pv - \boldsymbol{\mu}\cdot\boldsymbol{y} = h - Ts - \boldsymbol{\mu}\cdot\boldsymbol{y}$$

$$\mathrm{d}eu = \frac{1}{n}\mathrm{d}Eu - Eu\frac{\mathrm{d}n}{n^2} = -s\,\mathrm{d}T + v\,\mathrm{d}p - \boldsymbol{y}\cdot\mathrm{d}\boldsymbol{\mu} - eu\frac{\mathrm{d}n}{n} \quad\Rightarrow\quad eu = eu(T,p,\boldsymbol{\mu},n) = \frac{n_0}{n}eu(T,p,\boldsymbol{\mu},n_0)$$

$$\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n} \quad\Rightarrow\quad E = E(S,V,n\boldsymbol{y}) \quad\Rightarrow\quad \mu_i = \left(\frac{\partial E}{\partial n_i}\right)_{S,V,\boldsymbol{n}'_i} = \mu_i(S,V,\boldsymbol{n})$$

$$\mathrm{d}e = \frac{1}{n}\mathrm{d}E - E\frac{\mathrm{d}n}{n^2} = T\,\mathrm{d}s - p\,\mathrm{d}v + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{y} - eu\frac{\mathrm{d}n}{n} \quad\Rightarrow\quad e = e(s,v,\boldsymbol{y},n)$$

$$\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n} \quad\Rightarrow\quad \begin{aligned} F &= E - TS \\ &= F(T,V,n\boldsymbol{y}) \end{aligned} \quad\Rightarrow\quad \mu_i = \left(\frac{\partial F}{\partial n_i}\right)_{T,V,\boldsymbol{n}'_i} = \mu_i(T,V,\boldsymbol{n})$$

$$\mathrm{d}f = \frac{1}{n}\mathrm{d}F - F\frac{\mathrm{d}n}{n^2} = -s\,\mathrm{d}T + p\,\mathrm{d}v + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{y} - eu\frac{\mathrm{d}n}{n} \quad\Rightarrow\quad f = f(T,v,\boldsymbol{y},n)$$

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n} \quad\Rightarrow\quad \begin{aligned} G &= E - TS + pV \\ &= G(T,p,n\boldsymbol{y}) \end{aligned} \quad\Rightarrow\quad \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,\boldsymbol{n}'_i} = \mu_i(T,p,\boldsymbol{n})$$

$$\mathrm{d}g = \frac{1}{n}\mathrm{d}G - G\frac{\mathrm{d}n}{n^2} = -s\,\mathrm{d}T + v\,\mathrm{d}p + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{y} - eu\frac{\mathrm{d}n}{n} \quad\Rightarrow\quad g = g(T,p,\boldsymbol{y},n)$$

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n} \quad\Rightarrow\quad \begin{aligned} H &= E + pV \\ &= H(S,p,n\boldsymbol{y}) \end{aligned} \quad\Rightarrow\quad \mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,\boldsymbol{n}'_i} = \mu_i(S,p,\boldsymbol{n})$$

$$\mathrm{d}h = \frac{1}{n}\mathrm{d}H - H\frac{\mathrm{d}n}{n^2} = T\,\mathrm{d}s + v\,\mathrm{d}p + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{y} - eu\frac{\mathrm{d}n}{n} \quad\Rightarrow\quad h = h(s,p,\boldsymbol{y},n)$$

Summary of SES relations: (large *n* limit: simple-system approximation) (Mixtures)

... but that dependence vanishes for large *n*

$\mathit{Eu} = 0 \quad \Rightarrow \quad E - TS + pV - \boldsymbol{\mu}\cdot\boldsymbol{n} = 0$ **Euler relation**

$$\Rightarrow \quad \boldsymbol{\mu}\cdot\boldsymbol{n} = G = H - TS = F + pV = E - TS + pV$$

$\mathrm{d}\mathit{Eu} = -S\,\mathrm{d}T + V\mathrm{d}p - \boldsymbol{n}\cdot\mathrm{d}\boldsymbol{\mu} = 0$ **Gibbs-Duhem relation**

$$\mathit{eu} = 0 = e - Ts + pv - \boldsymbol{\mu}\cdot\boldsymbol{y} \quad \Rightarrow \quad \boldsymbol{\mu}\cdot\boldsymbol{y} = g = h - Ts = f + pv = e - Ts + pv$$

$$\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n} \quad \Rightarrow \quad E = E(S,V,n\boldsymbol{y}) \quad \Rightarrow \quad \mu_i = \left(\frac{\partial E}{\partial n_i}\right)_{S,V,\boldsymbol{n}'_i} = \mu_i(S,V,\boldsymbol{n})$$

$$\mathrm{d}e = \frac{1}{n}\mathrm{d}E - E\frac{\mathrm{d}n}{n^2} = T\,\mathrm{d}s - p\,\mathrm{d}v + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{y} \quad \Rightarrow \quad e = e(s,v,\boldsymbol{y})$$

$$\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n} \quad \Rightarrow \quad \begin{aligned} F &= E - TS \\ &= F(T,V,n\boldsymbol{y}) \end{aligned} \quad \Rightarrow \quad \mu_i = \left(\frac{\partial F}{\partial n_i}\right)_{T,V,\boldsymbol{n}'_i} = \mu_i(T,V,\boldsymbol{n})$$

$$\mathrm{d}f = \frac{1}{n}\mathrm{d}F - F\frac{\mathrm{d}n}{n^2} = -s\,\mathrm{d}T + p\,\mathrm{d}v + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{y} \quad \Rightarrow \quad f = f(T,v,\boldsymbol{y})$$

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n} \quad \Rightarrow \quad \begin{aligned} G &= E - TS + pV \\ &= G(T,p,n\boldsymbol{y}) \end{aligned} \quad \Rightarrow \quad \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,\boldsymbol{n}'_i} = \mu_i(T,p,\boldsymbol{n})$$

$$\mathrm{d}g = \frac{1}{n}\mathrm{d}G - G\frac{\mathrm{d}n}{n^2} = -s\,\mathrm{d}T + v\,\mathrm{d}p + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{y} \quad \Rightarrow \quad g = g(T,p,\boldsymbol{y})$$

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n} \quad \Rightarrow \quad \begin{aligned} H &= E + pV \\ &= H(S,p,n\boldsymbol{y}) \end{aligned} \quad \Rightarrow \quad \mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,\boldsymbol{n}'_i} = \mu_i(S,p,\boldsymbol{n})$$

$$\mathrm{d}h = \frac{1}{n}\mathrm{d}H - H\frac{\mathrm{d}n}{n^2} = T\,\mathrm{d}s + v\,\mathrm{d}p + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{y} \quad \Rightarrow \quad h = h(s,p,\boldsymbol{y})$$

Summary of SES relations: (small systems) (Pure substances)

Specific properties in general depend on *n*

$$\mathit{Eu} = E - TS + pV - \mu n = F + pV - \mu n = G - \mu n = H - TS - \mu n$$

$$\mathrm{d}\mathit{Eu} = -S\,\mathrm{d}T + V\,\mathrm{d}p - n\,\mathrm{d}\mu \quad \Rightarrow \quad \mathit{Eu} = \mathit{Eu}(T, p, \mu)$$

$$\mathit{eu} = \frac{\mathit{Eu}}{n} = e - Ts + pv - \mu = g - \mu = f + pv - \mu = h - Ts - \mu$$

$$\mathrm{d}\mathit{eu} = \frac{1}{n}\mathrm{d}\mathit{Eu} - \mathit{Eu}\frac{\mathrm{d}n}{n^2} = -s\,\mathrm{d}T + v\,\mathrm{d}p - \mathrm{d}\mu - \mathit{eu}\frac{\mathrm{d}n}{n} \quad \Rightarrow \quad \mathit{eu} = \mathit{eu}(T, p, \mu, n) = \frac{n_0}{n}\mathit{eu}(T, p, \mu, n_0)$$

$$\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}n \quad \Rightarrow \quad E = E(S, V, n) \quad \Rightarrow \quad \mu = \left(\frac{\partial E}{\partial n}\right)_{S,V} = \mu(S, V, n)$$

$$\mathrm{d}e = \frac{1}{n}\mathrm{d}E - E\frac{\mathrm{d}n}{n^2} = T\,\mathrm{d}s - p\,\mathrm{d}v - \mathit{eu}\frac{\mathrm{d}n}{n} \quad \Rightarrow \quad e = e(s, v, n)$$

$$\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V + \mu\,\mathrm{d}n \quad \Rightarrow \quad \begin{aligned} F &= E - TS \\ &= F(T, V, n) \end{aligned} \quad \Rightarrow \quad \mu = \left(\frac{\partial F}{\partial n}\right)_{T,V} = \mu(T, V, n)$$

$$\mathrm{d}f = \frac{1}{n}\mathrm{d}F - F\frac{\mathrm{d}n}{n^2} = -s\,\mathrm{d}T + p\,\mathrm{d}v - \mathit{eu}\frac{\mathrm{d}n}{n} \quad \Rightarrow \quad f = f(T, v, n)$$

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \mu\,\mathrm{d}n \quad \Rightarrow \quad \begin{aligned} G &= E - TS + pV \\ &= G(T, p, n) \end{aligned} \quad \Rightarrow \quad \mu = \left(\frac{\partial G}{\partial n}\right)_{T,p} = \mu(T, p, n)$$

$$\mathrm{d}g = \frac{1}{n}\mathrm{d}G - G\frac{\mathrm{d}n}{n^2} = -s\,\mathrm{d}T + v\,\mathrm{d}p - \mathit{eu}\frac{\mathrm{d}n}{n} \quad \Rightarrow \quad g = g(T, p, n)$$

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p + \mu\,\mathrm{d}n \quad \Rightarrow \quad \begin{aligned} H &= E + pV \\ &= H(S, p, n) \end{aligned} \quad \Rightarrow \quad \mu = \left(\frac{\partial H}{\partial n}\right)_{S,p} = \mu(S, p, n)$$

$$\mathrm{d}h = \frac{1}{n}\mathrm{d}H - H\frac{\mathrm{d}n}{n^2} = T\,\mathrm{d}s + v\,\mathrm{d}p - \mathit{eu}\frac{\mathrm{d}n}{n} \quad \Rightarrow \quad h = h(s, p, n)$$

Summary of SES relations: (large n limit: simple-system approximation) (Pure substances)

... but that dependence vanishes for large n

$$Eu = 0 \quad \Rightarrow \quad E - TS + pV - \mu n = 0$$ **Euler relation**

$$\Rightarrow \quad \mu n = G = H - TS = F + pV = E - TS + pV$$

$$\mathrm{d}Eu = -S\,\mathrm{d}T + V\,\mathrm{d}p - n\,\mathrm{d}\mu = 0 \quad \Rightarrow \quad \mathrm{d}\mu = -s\,\mathrm{d}T + v\mathrm{d}p$$ **Gibbs-Duhem relation**

$$eu = 0 = e - Ts + pv - \mu \quad \Rightarrow \quad \mu = g = h - Ts = f + pv = e - Ts + pv = \mu(T,p)$$

$$\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}n \quad \Rightarrow \quad E = E(S,V,n) \quad \Rightarrow \quad \mu = \left(\frac{\partial E}{\partial n}\right)_{S,V} = \mu(S,V,n)$$

$$\mathrm{d}e = \frac{1}{n}\mathrm{d}E - E\frac{\mathrm{d}n}{n^2} = T\,\mathrm{d}s - p\,\mathrm{d}v \quad \Rightarrow \quad e = e(s,v)$$

$$\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V + \mu\,\mathrm{d}n \quad \Rightarrow \quad \begin{aligned} F &= E - TS \\ &= F(T,V,n) \end{aligned} \quad \Rightarrow \quad \mu = \left(\frac{\partial F}{\partial n}\right)_{T,V} = \mu(T,V,n)$$

$$\mathrm{d}f = \frac{1}{n}\mathrm{d}F - F\frac{\mathrm{d}n}{n^2} = -s\,\mathrm{d}T + p\,\mathrm{d}v \quad \Rightarrow \quad f = f(T,v)$$

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \mu\,\mathrm{d}n \quad \Rightarrow \quad \begin{aligned} G &= E - TS + pV \\ &= G(T,p,n) \end{aligned} \quad \Rightarrow \quad \mu = \left(\frac{\partial G}{\partial n}\right)_{T,p} = \mu(T,p,n)$$

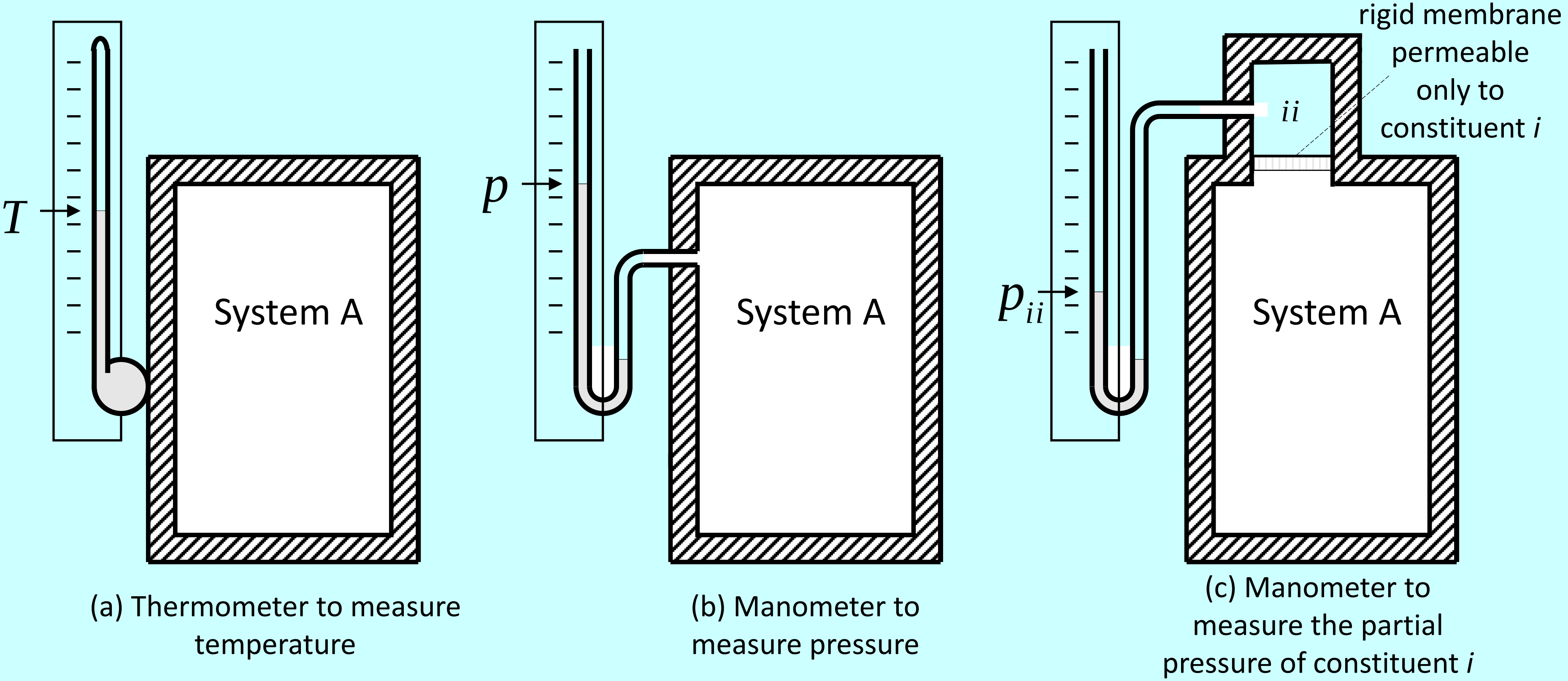
$$\mathrm{d}g = \frac{1}{n}\mathrm{d}G - G\frac{\mathrm{d}n}{n^2} = -s\,\mathrm{d}T + v\,\mathrm{d}p \quad \Rightarrow \quad g = g(T,p) \quad \Rightarrow \quad \mu = \mu(T,p)$$

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p + \mu\,\mathrm{d}n \quad \Rightarrow \quad \begin{aligned} H &= E + pV \\ &= H(S,p,n) \end{aligned} \quad \Rightarrow \quad \mu = \left(\frac{\partial H}{\partial n}\right)_{S,p} = \mu(S,p,n)$$

$$\mathrm{d}h = \frac{1}{n}\mathrm{d}H - H\frac{\mathrm{d}n}{n^2} = T\,\mathrm{d}s + v\,\mathrm{d}p \quad \Rightarrow \quad h = h(s,p)$$

Experimental measurement of SES properties of mixtures:

Partial pressures to measure chemical potentials



(a) Thermometer to measure temperature

(b) Manometer to measure pressure

(c) Manometer to measure the partial pressure of constituent *i*

Recall the definition of partial pressure of constituent i in the mixture

$$\mu_i(T,p,\boldsymbol{n}) = \mu_{ii}(T,p_{ii},n_{ii}) \quad \Rightarrow \quad p_{ii} = p_{ii}(T,p,\boldsymbol{n},n_{ii}) \quad \xrightarrow{n \text{ large}} \quad p_{ii} = p_{ii}(T,p,\boldsymbol{y})$$

For large n, within the SS model, recall that for the pure substance $\mu = g$, hence,

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

Experimental measurement of SES properties of mixtures:

Partial properties from the chemical potentials

$$G = E - TS + pV = G(T,p,\boldsymbol{n}) \qquad \mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n}$$

$$\left(\frac{\partial G}{\partial T}\right)_{T,p,\boldsymbol{n}} = -S(T,p,\boldsymbol{n}) \quad \left(\frac{\partial G}{\partial p}\right)_{T,p,\boldsymbol{n}} = V(T,p,\boldsymbol{n}) \quad \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,\boldsymbol{n}'_i} = \mu_i(T,p,n\boldsymbol{y})$$

$$\mathrm{d}\mu_i = \underbrace{\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\boldsymbol{n}}}_{-s_i}\mathrm{d}T + \underbrace{\left(\frac{\partial \mu_i}{\partial p}\right)_{T,\boldsymbol{n}}}_{v_i}\mathrm{d}p + \sum_{j=1}^{r}\underbrace{\left(\frac{\partial \mu_i}{\partial n_j}\right)_{T,p,\boldsymbol{n}'_j}}_{\mu_{i,j}\,=\,\mu_{i,j}}\mathrm{d}n_j = -s_i\,\mathrm{d}T + \underbrace{v_i\,\mathrm{d}p + \textstyle\sum_{j=1}^{r}\mu_{i,j}\,\mathrm{d}n_j}_{\mathrm{d}\mu_i|_T}$$

where we define

$$-\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\boldsymbol{n}} = -\left(\frac{\partial^2 G}{\partial T\partial n_i}\right)_{p,\boldsymbol{n}'_i} = \left(\frac{\partial S}{\partial n_i}\right)_{T,p,\boldsymbol{n}'_i} = s_i(T,p,n\boldsymbol{y}) \quad \textbf{Partial entropy of constituent } i$$

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,\boldsymbol{n}} = \left(\frac{\partial^2 G}{\partial p\partial n_i}\right)_{T,\boldsymbol{n}'_i} = \left(\frac{\partial V}{\partial n_i}\right)_{T,p,\boldsymbol{n}'_i} = v_i(T,p,n\boldsymbol{y}) \quad \textbf{Partial volume of constituent } i$$

$$\left(\frac{\partial \mu_i}{\partial n_j}\right)_{T,p,\boldsymbol{n}'_j} = \left(\frac{\partial^2 G}{\partial n_j\partial n_i}\right)_{T,p,\boldsymbol{n}'_{ij}} = \left(\frac{\partial \mu_j}{\partial n_i}\right)_{T,p,\boldsymbol{n}'_{ij}} = \mu_{i,j}(T,p,n\boldsymbol{y}) = \mu_{j,i}(T,p,n\boldsymbol{y})$$

notice that, from $\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n}$ and $\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n}$ we also have

$$\left(\frac{\partial E}{\partial n_i}\right)_{T,p,\boldsymbol{n}'_i} = e_i(T,p,n\boldsymbol{y}) = T\,s_i - p\,v_i + \mu_i \quad \textbf{Partial energy of constituent } i$$

$$\left(\frac{\partial H}{\partial n_i}\right)_{T,p,\boldsymbol{n}'_i} = h_i(T,p,n\boldsymbol{y}) = T\,s_i + \mu_i = \left(\frac{\partial(\mu_i/T)}{\partial(1/T)}\right)_{p,\boldsymbol{n}} \quad \textbf{Partial enthalpy of constituent } i$$

All partial properties can be evaluated once we know the chemical potentials as functions of T, p, $\boldsymbol{y}$ and n, i.e., $\mu_i = \mu_i(T,p,n\boldsymbol{y})$.

Of course, the dependence on n vanishes for large n and $\mu_i = \mu_i(T,p,\boldsymbol{y})$.

Experimental measurement of SES properties of mixtures:

Mixture properties from the partial properties

$$\mathit{Eu} = E - TS + pV - \boldsymbol{\mu}\cdot\boldsymbol{n} = \mathit{Eu}(T,p,\boldsymbol{\mu})$$

$$\mathrm{d}\mathit{Eu} = -S\,\mathrm{d}T + V\,\mathrm{d}p - \boldsymbol{n}\cdot\mathrm{d}\boldsymbol{\mu} \qquad \Rightarrow \quad \left(\frac{\partial \mathit{Eu}}{\partial T}\right)_{p,\boldsymbol{\mu}} = -S \quad \left(\frac{\partial \mathit{Eu}}{\partial p}\right)_{T,\boldsymbol{\mu}} = V \quad \left(\frac{\partial \mathit{Eu}}{\partial \mu_i}\right)_{T,p,\boldsymbol{\mu}_i'} = -n_i$$

Substituting $\boldsymbol{\mu} = \boldsymbol{\mu}(T,p,\boldsymbol{n})$ we may view Eu as a function of T, p, $\boldsymbol{n}$

$$\mathit{Eu} = \mathit{Eu}(T,p,\boldsymbol{\mu}(T,p,\boldsymbol{n})) = \mathit{Eu}(T,p,\boldsymbol{n})$$

using the chain rule and the definitions of partial entropies and volumes, its partial derivatives are

$$\left(\frac{\partial \mathit{Eu}}{\partial T}\right)_{p,\boldsymbol{n}} = \left(\frac{\partial \mathit{Eu}}{\partial T}\right)_{p,\boldsymbol{\mu}} + \sum_{i=1}^{r}\left(\frac{\partial \mathit{Eu}}{\partial \mu_i}\right)_{T,p,\boldsymbol{\mu}_i'}\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\boldsymbol{n}} = -S + \sum_{i=1}^{r} n_i\, s_i$$

$$\left(\frac{\partial \mathit{Eu}}{\partial p}\right)_{T,\boldsymbol{n}} = \left(\frac{\partial \mathit{Eu}}{\partial p}\right)_{T,\boldsymbol{\mu}} + \sum_{i=1}^{r}\left(\frac{\partial \mathit{Eu}}{\partial \mu_i}\right)_{T,p,\boldsymbol{\mu}_i'}\left(\frac{\partial \mu_i}{\partial p}\right)_{T,\boldsymbol{n}} = V - \sum_{i=1}^{r} n_i\, v_i$$

$$\left(\frac{\partial \mathit{Eu}}{\partial n_j}\right)_{T,p,\boldsymbol{n}_j'} = \sum_{i=1}^{r}\left(\frac{\partial \mathit{Eu}}{\partial \mu_i}\right)_{T,p,\boldsymbol{\mu}_i'}\left(\frac{\partial \mu_i}{\partial n_j}\right)_{T,\boldsymbol{n}_j'} = -\sum_{i=1}^{r} n_i\, \mu_{i,j}$$

Therefore, in general (i.e., for small and large systems) we have

$$S = \sum_{i=1}^{r} n_i\, s_i - \left(\frac{\partial \mathit{Eu}}{\partial T}\right)_{p,\boldsymbol{n}} \qquad \xrightarrow{n \text{ large}} \qquad S = \sum_{i=1}^{r} n_i\, s_i$$

$$V = \sum_{i=1}^{r} n_i\, v_i + \left(\frac{\partial \mathit{Eu}}{\partial p}\right)_{T,\boldsymbol{n}} \qquad \xrightarrow{n \text{ large}} \qquad V = \sum_{i=1}^{r} n_i\, v_i$$

$$\sum_{i=1}^{r} n_i\, \mu_{i,j} = -\left(\frac{\partial \mathit{Eu}}{\partial n_j}\right)_{T,p,\boldsymbol{n}_j'} \qquad \xrightarrow{n \text{ large}} \qquad \sum_{i=1}^{r} n_i\, \mu_{i,j} = 0$$

Duhem-Margules relation

Experimental measurement of SES properties of mixtures:

Mixture properties from the partial properties

So, in general (i.e., for small and large systems) we proved

$$S = \sum_{i=1}^{r} n_i\, s_i - \left(\frac{\partial Eu}{\partial T}\right)_{p,\boldsymbol{n}} \quad \xrightarrow{n \text{ large}} \quad \boxed{S = \sum_{i=1}^{r} n_i\, s_i}$$

$$V = \sum_{i=1}^{r} n_i\, v_i + \left(\frac{\partial Eu}{\partial p}\right)_{T,\boldsymbol{n}} \quad \xrightarrow{n \text{ large}} \quad \boxed{V = \sum_{i=1}^{r} n_i\, v_i}$$

$$\sum_{i=1}^{r} n_i\, \mu_{i,j} = -\left(\frac{\partial Eu}{\partial n_j}\right)_{T,p,\boldsymbol{n}'_j} \quad \xrightarrow{n \text{ large}} \quad \boxed{\sum_{i=1}^{r} n_i\, \mu_{i,j} = 0}$$

Duhem-Margules relation

Moreover, recalling the definitions of Eu and partial properties

$$Eu = E - TS + pV - \boldsymbol{\mu}\cdot\boldsymbol{n} = F + pV - \boldsymbol{\mu}\cdot\boldsymbol{n} = G - \boldsymbol{\mu}\cdot\boldsymbol{n} = H - TS - \boldsymbol{\mu}\cdot\boldsymbol{n}$$

$$\mu_i = e_i - Ts_i + pv_i = f_i + pv_i = g_i = h_i - Ts_i$$

we also find the following relations, which justify calling partial properties that way:

$$E = \sum_{i=1}^{r} n_i\, e_i + Eu - T\left(\frac{\partial Eu}{\partial T}\right)_{p,\boldsymbol{n}} - p\left(\frac{\partial Eu}{\partial p}\right)_{T,\boldsymbol{n}} \quad \xrightarrow{n \text{ large}} \quad \boxed{E = \sum_{i=1}^{r} n_i\, e_i}$$

$$F = \sum_{i=1}^{r} n_i\, f_i + Eu - p\left(\frac{\partial Eu}{\partial p}\right)_{T,\boldsymbol{n}} \quad \xrightarrow{n \text{ large}} \quad \boxed{F = \sum_{i=1}^{r} n_i\, f_i}$$

$$G = \sum_{i=1}^{r} n_i\, g_i + Eu = \sum_{i=1}^{r} n_i\, \mu_i + Eu \quad \xrightarrow{n \text{ large}} \quad \boxed{G = \sum_{i=1}^{r} n_i\, g_i = \sum_{i=1}^{r} n_i\, \mu_i}$$

$$H = \sum_{i=1}^{r} n_i\, h_i + Eu - T\left(\frac{\partial Eu}{\partial T}\right)_{p,\boldsymbol{n}} \quad \xrightarrow{n \text{ large}} \quad \boxed{H = \sum_{i=1}^{r} n_i\, h_i}$$

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