Sustainable Energy Systems

2. Systems Modeling

Project

Aim: Critical evaluation of a technology (from a patent, an article, a news story…etc.) related to energy or sustainability. You should analyze (qualitatively and quantitatively) whether an idea or technology is feasible (technology scale) and can lead to a scalable solution (system scale) for an energy related issue. What are the bottlenecks? Can these bottlenecks be addressed, etc?

- The project is done in groups of 2-3 (self-assembled)
- Timeline:
  - April 1st: Make the groups, and present and discuss at least 1 proposal for a technology and a source with the assistant
  - April 17th: Submit proposed outline and plan of work
  - May 30th at midnight: Submit report (max 15 pages with figures but not references, 12 font size, no formatting tricks)
  - Week after classes: oral presentation of report + questions (they will be scheduled individually for each group)

Literature

Systems

- Biegler, L. T., I. E. Grossmann, and A. W. Westerberg. *Systematic Methods for Chemical Process Design*. New Jersey: Prentice-Hall, 1997.
- Smith, Robin M. *Chemical Process: Design and Integration*. New Jersey: John Wiley & Sons, 2005.
- Turton, R. *Analysis, Synthesis, and Design of Chemical Processes.* New York: Prentice-Hall, 1998.

Thermodynamics

- Prausnitz, John M., Rudiger N. Lichtenthaler, and Edmundo Gomes de Azevedo. *Molecular Thermodynamics of Fluid-Phase Equilibria*. Upper Saddle River, NJ: Pearson Education, 1998.
- Haynes, William M. *CRC Handbook of Chemistry and Physics, 95th Edition*. Boca Raton: CRC Press, 2014.
- Poling, Bruce E., J. M. Prausnitz, and John Paul O'Connell. *The Properties of Gases and Liquids*. New York: McGraw-Hill, 2001.

Heat integration

- Kemp, Ian C. *Pinch Analysis and Process Integration: A User Guide on Process Integration for the Efficient Use of Energy*. Oxford: Butterworth-Heinemann, 2011.
- Maréchal, Francois. *Process integration techniques for improving the energy efficiency of industrial processes*. Lecture Notes for EPFL course *Advanced Energetics* (ME-451), 2015.

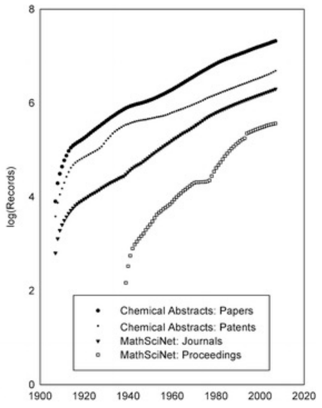
Uncertainty analysis and Life Cycle Assessment

- Tester, Jefferson W. *Sustainable Energy: Choosing Among Options*. Cambridge, Mass: MIT Press, 2012.
- Baumann, Henrikke, and Anne-Marie Tillman. *The Hitch Hiker's Guide to LCA: An Orientation in Life Cycle Assessment Methodology and Application*. Lund: Studentlitteratur, 2004.

Growth in knowledge

Knowledge is growing exponentially!

Growth in records per year



Source: *Scientometrics*. 2010 Sep; 84(3): 575–603

More knowledge will be published in the next 20 years than in all of history up to now.

What does this mean for scientists and engineers?

You cannot work alone anymore.

You need large teams!

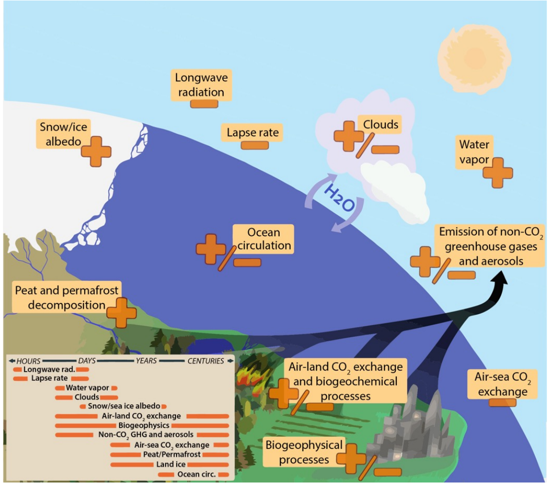
You need computers!

Systems modeling: required for complex questions

For example: How much will Temperature rise in the future?

Many different factors influence the answer

The required models/theory and fields of knowledge largely surpasses that of one person



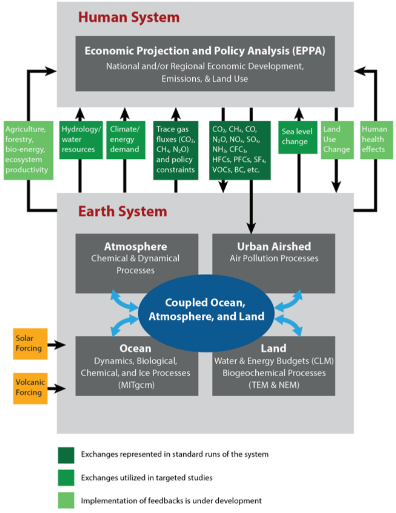
Source: *IPCC 2013, AR4, WG1*

Example: How much will Temperature rise in the future?

Let’s look at a complex model: The Integrated Global System Modeling framework (MIT)

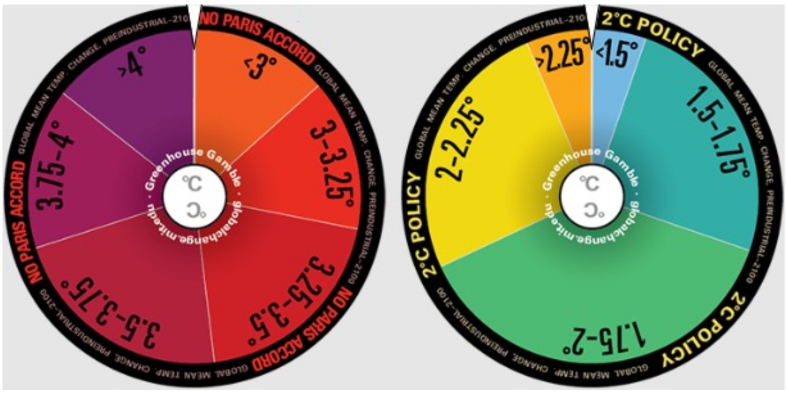
→ Special emphasis on society-climate interactions

Requires extensive collaboration across fields



Source: *MIT Global Change*

Example: How much will Temperature rise in the future?

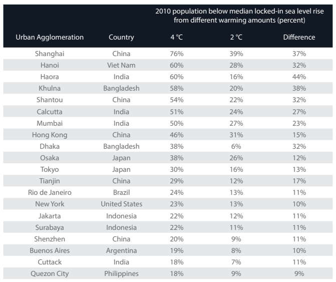


Source: *MIT Global Change*

Example: How much will Temperature rise in the future?

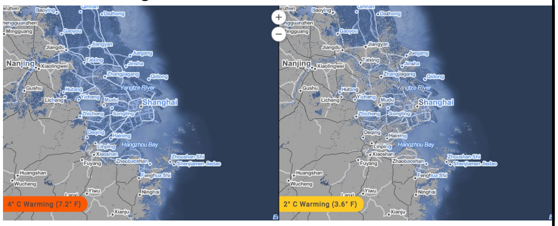
Starting at 4°C rise, effects are dramatic!

Cities of more than 10 million inhabitants with significant populations at risk:

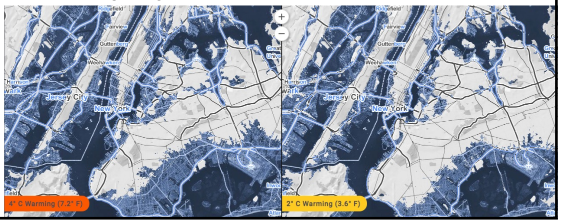


Urban Agglomeration	Country	2010 population below median locked-in sea level rise from different warming amounts (percent) 4 °C	2 °C	Difference
Shanghai	China	76%	39%	37%
Hanoi	Viet Nam	60%	28%	32%
Haora	India	60%	16%	44%
Khulna	Bangladesh	58%	20%	38%
Shantou	China	54%	22%	32%
Calcutta	India	51%	24%	27%
Mumbai	India	50%	27%	23%
Hong Kong	China	46%	31%	15%
Dhaka	Bangladesh	38%	6%	32%
Osaka	Japan	38%	26%	12%
Tokyo	Japan	30%	16%	13%
Tianjin	China	29%	12%	17%
Rio de Janeiro	Brazil	24%	13%	11%
New York	United States	23%	13%	10%
Jakarta	Indonesia	22%	12%	11%
Surabaya	Indonesia	22%	11%	11%
Shenzhen	China	20%	9%	11%
Buenos Aires	Argentina	19%	8%	10%
Cuttack	India	18%	7%	11%
Quezon City	Philippines	18%	9%	9%

Shanghai:

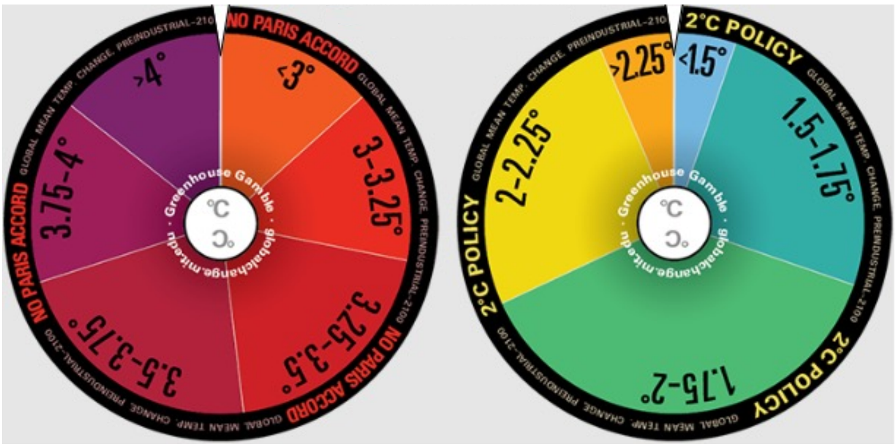


New York:



Source: *Climate central, Maping choices, 2015*

Example: How much will Temperature rise in the future?



Source: *MIT Global Change*

How does this concern you?

Most engineering decisions have always had an **energetic** component. More and more have an **environmental** component as well.

- You might participate in climate modeling efforts
- You are very likely to participate in technology/process choices that include energetic/environmental components

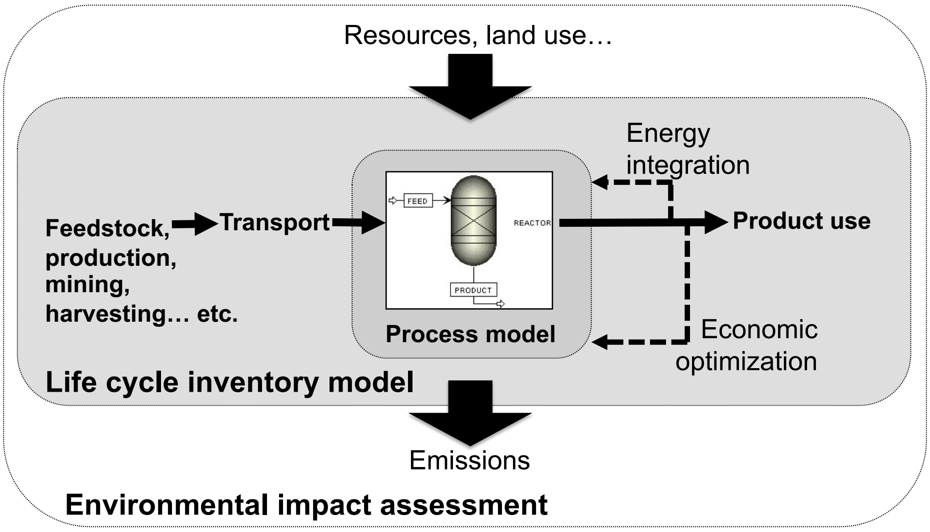
→ This part of the course is designed to help you make these choices.

Main themes of part 2

In this part of the course, we will answer these questions:

- Process systems modeling → What are the material/energy flows?
- Heat Integration → What is the process energy requirement?
- Life Cycle Assessment → What is the process environmental impact?
- Uncertainty analysis → How sure are we of the results?

Overview of the approach



Resources, land use…

Energy integration

Feedstock, production, mining, harvesting… etc. → **Transport** → **Process model** → **Product use**

Economic optimization

Life cycle inventory model

Emissions

Environmental impact assessment

Outline of Part 2

Objective: Cover the basic principles of Systems Modeling for a Renewable Energy Process and be able to model a simple system.

- Importance of Systems Modeling in Renewable Energy
- Modeling systems
  - Stream properties
  - Thermodynamic relationships
  - Unit models
- Heat integration & Pinch Analysis
  - Basic Principles
  - Composite Curves
  - The Heat Cascade and the Grand Composite Curve
- Life Cycle Assessment
  - Goal & Scope Definition
  - Life Cycle Inventory
  - Life Cycle Impact Assessment
- Uncertainty Analysis & The Monte Carlo Method

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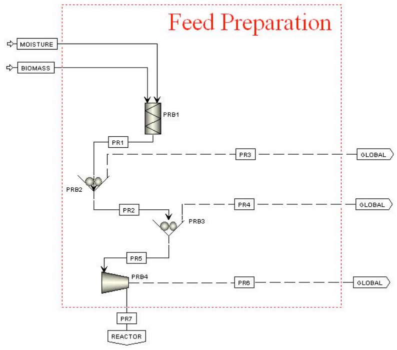
Process Modeling

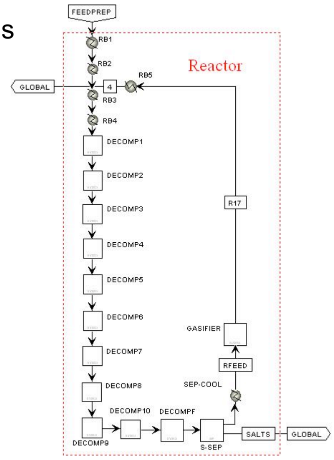
Processes = assemblies of interconnected unit operations

Process models are usually represented as **Flowsheets**

Biomass size reduction and pressurization



Biomass gasification



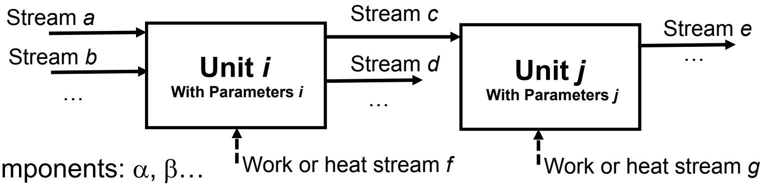
These are just sets of equations!

Process Modeling

Our view in the course:

Processes = assemblies of interconnected unit operations

Our nomenclature for the course:



Stream *a*

Stream *b*

…

Unit *i*
With Parameters *i*

Stream *c*

Stream *d*

…

Unit *j*
With Parameters *j*

Stream *e*

…

Work or heat stream *f*

Work or heat stream *g*

Components: α, β…

The approach:

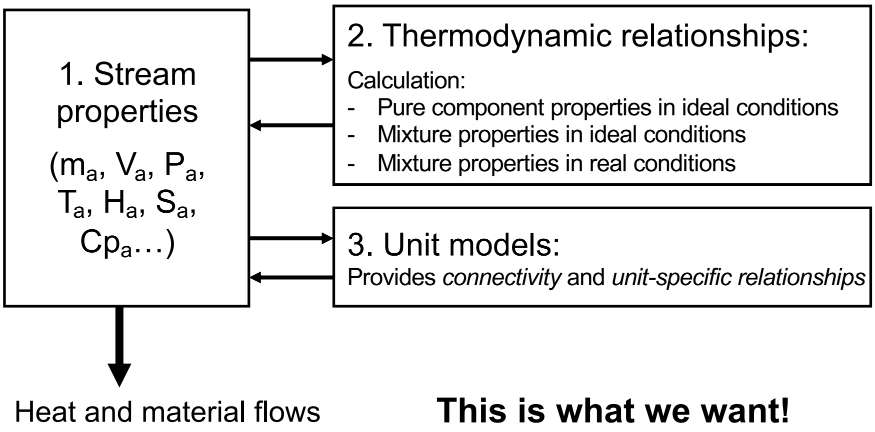
We will model processes directly as sets of equations, split into 3 categories:

- Stream properties
- Thermodynamic relationships
- Unit models

A real system to model and analyze…

Process Modeling

The approach:



1. Stream properties (m_a, V_a, P_a, T_a, H_a, S_a, Cp_a…)

2. Thermodynamic relationships:

Calculation:
- Pure component properties in ideal conditions
- Mixture properties in ideal conditions
- Mixture properties in real conditions

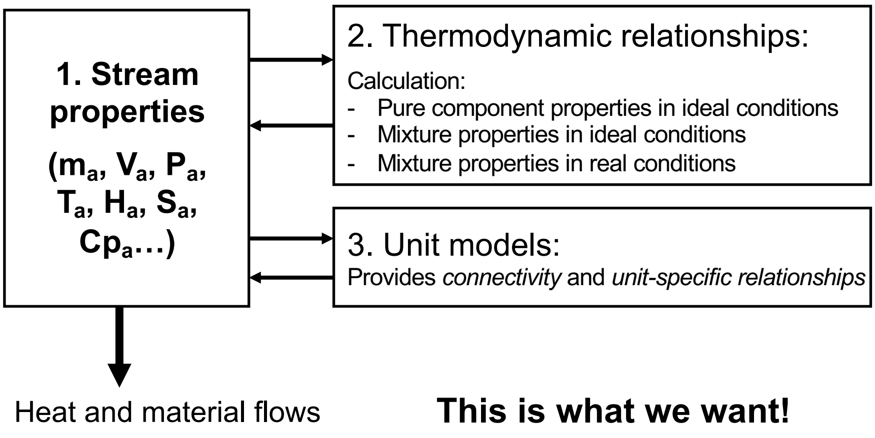
3. Unit models:
Provides *connectivity* and *unit-specific relationships*

Heat and material flows

This is what we want!

Process Modeling

The approach:



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Heat and material flows

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Stream properties

Types of streams:

- Heat streams
  - Completely characterized by their energetic flux (energy/time)
  - For heat integration, the temperature of heat exchange is needed
- Non-heat energetic streams: mechanical and electrical
  - Characterized by their energetic power (energy/time)
  - For mechanical work, shaft rotation speed must be specified
- Material streams

  Are characterized by:
  - Intensive properties (=independent of stream size/quantity), includes T, P, …
  - Extensive properties (=dependent on stream size/quantity): includes m, V, …

Material streams

A material stream is completely characterized when:

$$N_{\text{S.P.}} = N_{\text{S.P.I.}} + N_{\text{S.P.E.}} = 2 + N_c$$

Number of required specified properties

Number of specified intensive properties

Number of specified extensive properties

Number of components in the stream

Additional conditions:

$N_{\text{S.P.E.}} \geq 1 \longrightarrow$ Some indication of size is required.

→ Variables must be independent

Material streams: variable independence

How many intensive variables can be specified independently of each other?

Gibbs phase rule: $F_{\text{int.}} = 2 + N_c - N_p$

Degree of freedom for intensive variables

Number of components in the stream

Number of phases

What is $F_{int.}$ for liquid water at 1 atm? 2+1-1=2 → you can specify any T°

What is $F_{int.}$ for boiling water at 1 atm? 2+1-2=1→ T° is already specified

→ **Phases reduce $F_{int.}$ by imposing equilibrium conditions!**

Stream properties

Total number of specifications:

$$N_{Specifications} = N_{streams,Q} + N_{streams,W_{el}} + 2N_{streams,W_{mech.}} + N_{streams,material}(2+N_c)$$

Total number of specifications

Heat streams (1 specification per stream)

Electrical work streams (1 specification per stream)

Mechanical work streams (2 specification per stream)

Material streams

This will take the form of a stream specification matrix. For stream a, we would have (**S**$\mathbf{S_a}$):

$$\mathbf{S_a}(m_a, P_a, h_{\alpha,a,}, x_{\alpha,a}, x_{\beta,a}, \ldots) = 0$$

Mass flow

Pressure

Enthalpy of component α in stream a

Molar (or mass) fractions of components α or β in stream a

An overall specification matrix ***S*** is constructed by putting together all of these stream matrices.

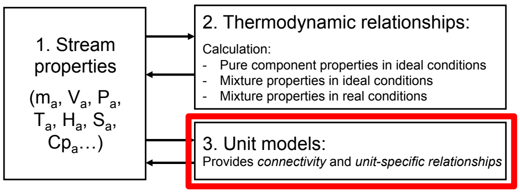
Stream properties

Total number of specifications:

$$N_{Specifications} = N_{streams,Q} + N_{streams,W_{el}} + 2N_{streams,W_{mech.}} + N_{streams,material}(2+N_c)$$

This number of specifications is only needed for isolated streams. Units connecting these streams will reduce their degree of freedom through:

- Mass balances
- Energy balances
- Momentum balances
- Unit-specific relations



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Stream properties

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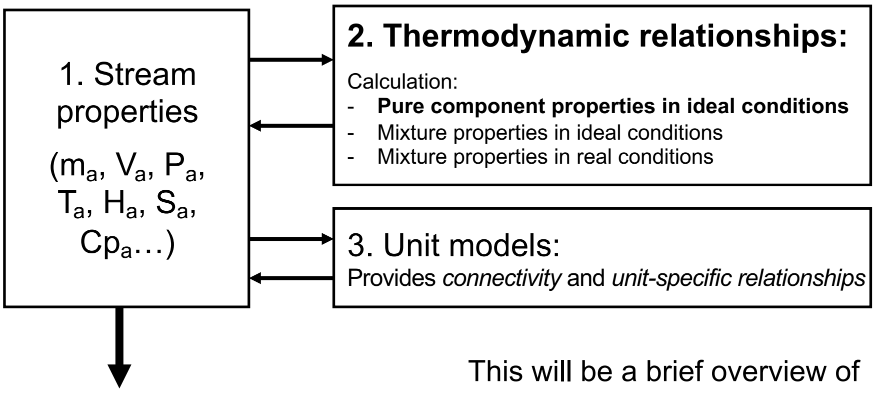
Once a stream is specified, you might not have all of the properties you need (e.g. you might have T, P, H and m but need V to size the equipment or S to calculate the entropic efficiency). How do you calculate the properties you need?

→ **Thermodynamic relationships**

Process Modeling

The approach:



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Heat and material flows

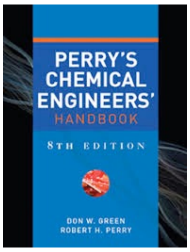
This will be a brief overview of thermodynamic property calculations, not a detailed review!

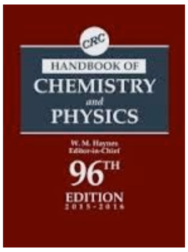
Thermodynamic relationships: 1. Pure components in ideal conditions

The first step: consider individual components

Individual properties are available from databases. I strongly recommend:

http://webbook.nist.gov/chemistry/





Typical properties that are considered: Enthalpy, Entropy, Cp, viscosity etc…

At this point, we ignore non-ideal behaviors like pressure or mixing effects.

Thermodynamic relationships: 1. Pure components in ideal conditions

Enthalpy

We start with a reference state: Elemental species in the gas phase (298 K, 1 bar)

But before we start, we need to know:

Gas or liquid phase? → The Antoine equation will tell us!

Antoine parameters of α

$$\log_{10}(P_{sat,\alpha}) = A_{\alpha} - \left(B_{\alpha} / \left[T_{sat,\alpha} + C_{\alpha}\right]\right)$$

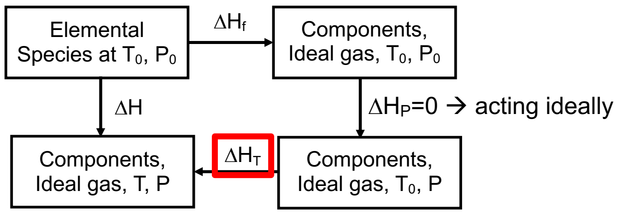
Saturation pressure of α in bar

Saturation temperature of α in K

Thermodynamic relationships: 1. Pure components in ideal conditions

Enthalpy

In the gas phase:



ΔH
$=\Delta H_f+\Delta H_P+\Delta H_T$
$=\Delta H_f+\Delta H_T$

ΔH_f: The enthalpy of formation. This is the difference between elemental species in an ideal gas state at T_0, P_0 (298 K, 1 bar) and the desired component at T_0, P_0

→ Find it in a database!

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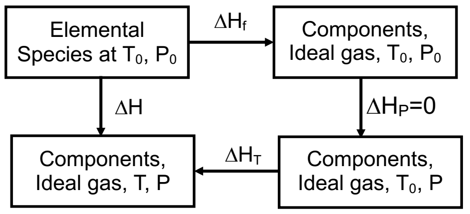
Thermodynamic relationships: 1. Pure components in ideal conditions

Enthalpy

In the gas phase:



$$\Delta H_T(T)=\int_{T_0}^{T} Cp(T')\,dT'$$

$$Cp_\alpha(T)=$$
$$A_\alpha+B_\alpha T+C_\alpha T^2+D_\alpha T^3+E_\alpha/T^2$$

Cp parameters for component α (Not the same as Antoine parameters!)

To summarize:

$$\Delta H_{v,\alpha}(T)=\Delta H^0_{f,\alpha}+\int_{T_0}^{T} Cp_\alpha(T')\,dT'$$

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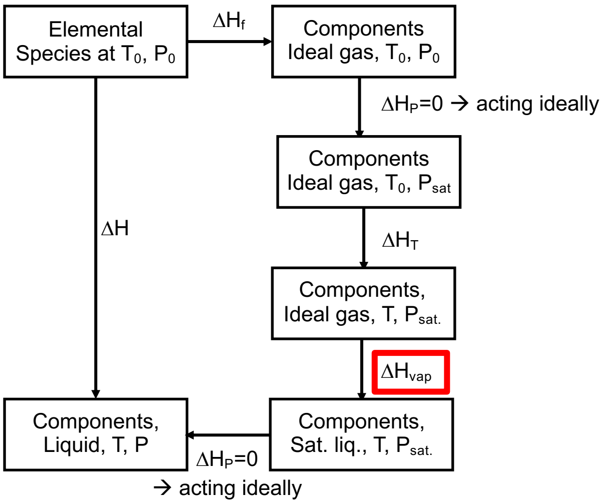
Thermodynamic relationships: 1. Pure components in ideal conditions

Enthalpy

In the liquid phase:

$$\boldsymbol{\Delta H = \Delta H_f + \Delta H_P + \Delta H_T - \Delta H_{vap} + \Delta H_P = \Delta H_f + \Delta H_T - \Delta H_{vap}}$$



Thermodynamic relationships: 1. Pure components in ideal conditions

Enthalpy

In the liquid phase:

We can calculate ΔH_{vap} with the Watson correlation:

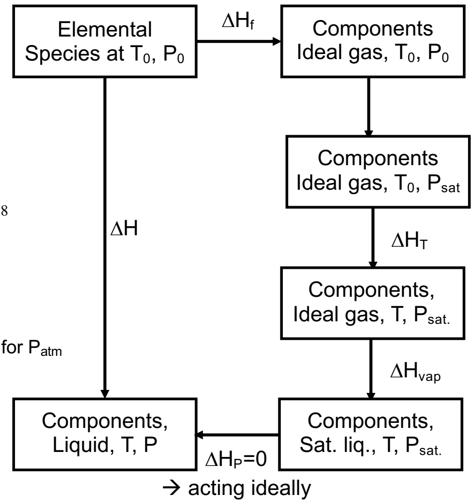
$$\Delta H_{vap,\,\alpha}(T) = \Delta H_{vap,\,\alpha}(T_{\alpha,b})\left[\frac{T_{\alpha,c}-T}{T_{\alpha,c}-T_{\alpha,b}}\right]^{\eta\approx 0.38}$$

Vaporization enthalpy of α at temperature T

Vaporization enthalpy of α at T_{sat} for P_{atm}

Critical temperature for component α

T_{sat} for P_{atm}



Thermodynamic relationships: 1. Pure components in ideal conditions

Enthalpy

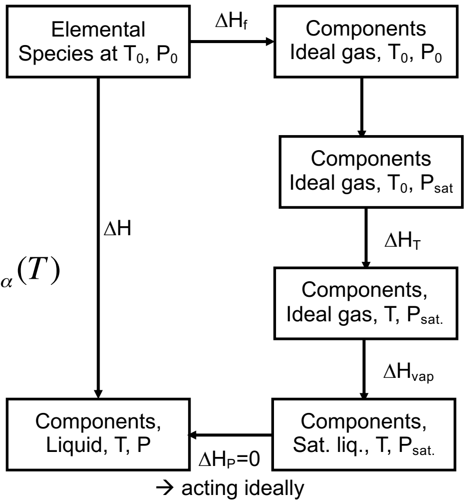
In the liquid phase:

To summarize:

$$\Delta H_{L,\alpha}(T) =$$

$$\Delta H^0_{f,\alpha} + \int_{T_0}^{T} Cp_\alpha(T')dT' - \Delta H_{Vap,\alpha}(T)$$

is subtracted because we are going from vapor to liquid.



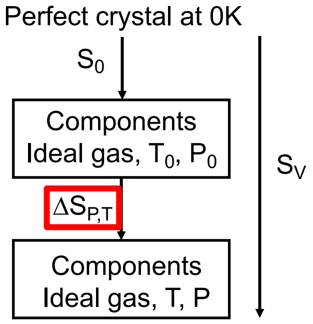
Thermodynamic relationships: 1. Pure components in ideal conditions

Entropy

In the gas phase:

Entropy does not need a reference state. It has an absolute value based a perfect crystal at 0K.

S_0: Standard molar entropies based on the perfect crystal at 0K



Thermodynamic relationships: 1. Pure components in ideal conditions

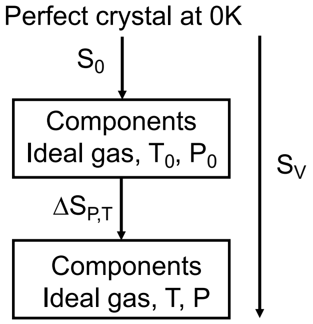
Entropy

In the gas phase:

$$\Delta S_{v,\alpha}(T,P) =$$

$$S_{0,\alpha} + \int_{T_0}^{T} \frac{Cp_{\alpha}(T')}{T'} dT' - R\ln\left(\frac{P}{P_0}\right)$$

As we saw previously, even for ideal gases, pressure effects on entropy cannot be discounted.


Perfect crystal at 0K

S_0

Components Ideal gas, T_0, P_0

$\Delta S_{P,T}$

Components Ideal gas, T, P

S_V

T and P terms are separate because they can be changed separately (S is path independent!)

Thermodynamic relationships: 1. Pure components in ideal conditions

Entropy (liquid phase)

At equilibrium:

$$\Delta G = 0 = \Delta H - T\Delta S \rightarrow \Delta S = \Delta H / T$$

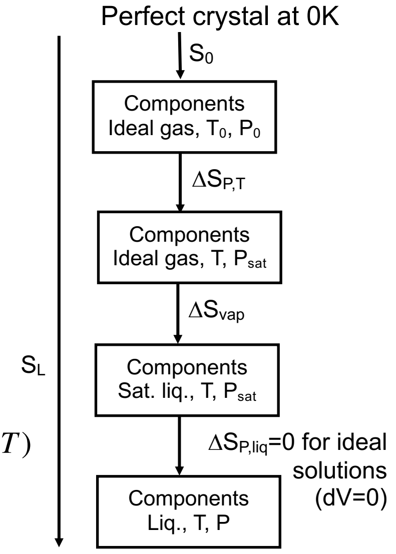
Phase change is an equilibrium:

$$\Delta S_{vap,\,\alpha}(T) = \frac{\Delta H_{vap,\,\alpha}(T)}{T}$$

Overall:

$$\Delta S_{L,\alpha}(T,P) =$$

$$S_{0,\alpha} + \int_{T_0}^{T} \frac{Cp_{\alpha}(T')}{T'} dT' - R\ln\left(\frac{P_{sat}}{P_0}\right) - \Delta S_{Vap,\alpha}(T)$$


Perfect crystal at 0K

S_0

Components Ideal gas, T_0, P_0

$\Delta S_{P,T}$

Components Ideal gas, T, P_{sat}

ΔS_{vap}

Components Sat. liq., T, P_{sat}

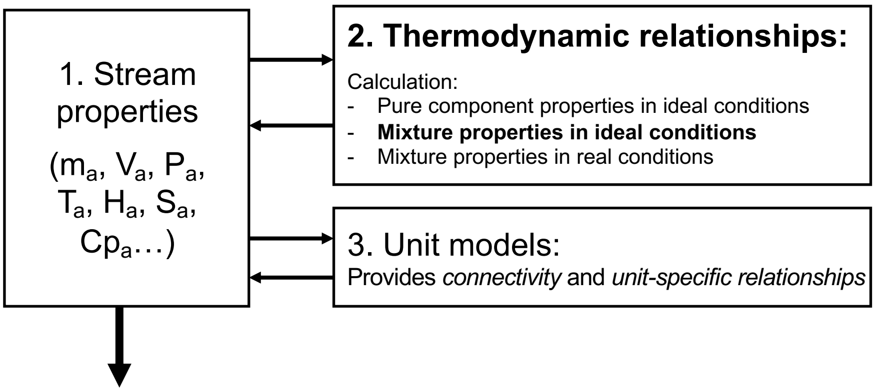
$\Delta S_{P,liq}$=0 for ideal solutions (dV=0)

Components Liq., T, P

S_L

Process Modeling

The approach:



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Heat and material flows

Ideal mixtures

We know how to calculate S, H, G or U for pure components. How do we calculate them for mixtures?

Let's start with an easy case: an **ideal mixture**.

In ideal mixtures, U and H are simply additive:

$$U_{L\,or\,V,tot} = \sum_{\alpha} U_{L\,or\,V,\alpha} \quad \text{and} \quad H_{L\,or\,V,tot} = \sum_{\alpha} H_{L\,or\,V,\alpha}$$

For the total mixture of *liquid* or *vapor*

Sum over all components (α, β, …)

Extensive property of component α

For Entropy, we have to account for the entropy of mixing as well:

$$S_{L\,or\,V,tot} = \sum_{\alpha} S_{L\,or\,V,\alpha} - \sum_{\alpha} n_{\alpha} R \ln x_{\alpha}$$

Mole fraction of α

Number of moles of α

G is simply found with:
$G = H - TS$

Vapor liquid equilibriums

A key property of mixtures is to calculate their vapor liquid equilibria (VLLEs).

This is important in:

- Chemical processes: distillation, extraction…etc.
- Environmental processes: atmospheric and ocean modeling

We want to find the state **at equilibrium**. What is the thermodynamic definition of an equilibrium?

$$dG = 0$$

Total free energy change of the system

Change of the quantity of component α in phase *p*

$$dG = -SdT + VdP + \sum_p \sum_\alpha \mu_{p,\alpha} dn_{p,\alpha}$$

Phase Component Chemical potential of component α in phase *p*

Vapor liquid equilibriums

$$dG = -SdT + VdP + \sum_p \sum_\alpha \mu_{p,\alpha} dn_{p,\alpha} = \sum_p \sum_\alpha \mu_{p,\alpha} dn_{p,\alpha} = 0$$

@ an equilibrium @ a given T and P

@ cst T and P, the only variable is n_α → To minimize *G* we have to find the point where:

$$\left(\frac{dG}{dn_\alpha}\right)_{T,P,n_{\alpha\neq\beta}} = 0 \quad = \sum_p \mu_{p,\alpha}$$

For independent components (e.g. no reactions)

$$\rightarrow \mu_{1,\alpha} = \mu_{2,\alpha} = \mu_{3,\alpha} \cdots$$

The chemical potentials of each component **must be equal across phases.**