Constitutive Equations in Process flowsheeting

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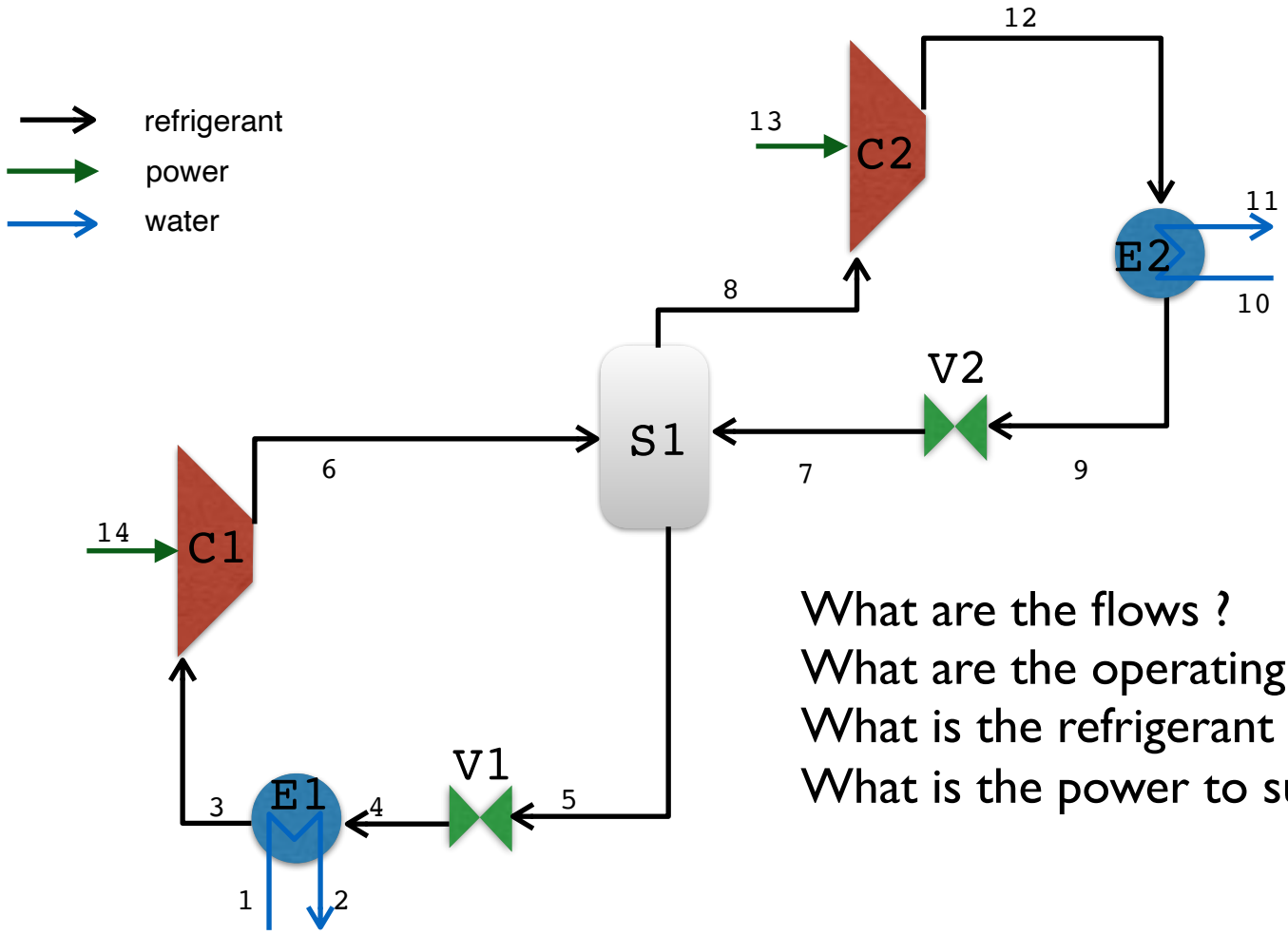
Two stages heat pump flow sheet



What are the flows ?
What are the operating conditions (P,T)
What is the refrigerant ?
What is the power to supply $\dot{Q}_{10-11}$ with $\dot{Q}_{1-2}$

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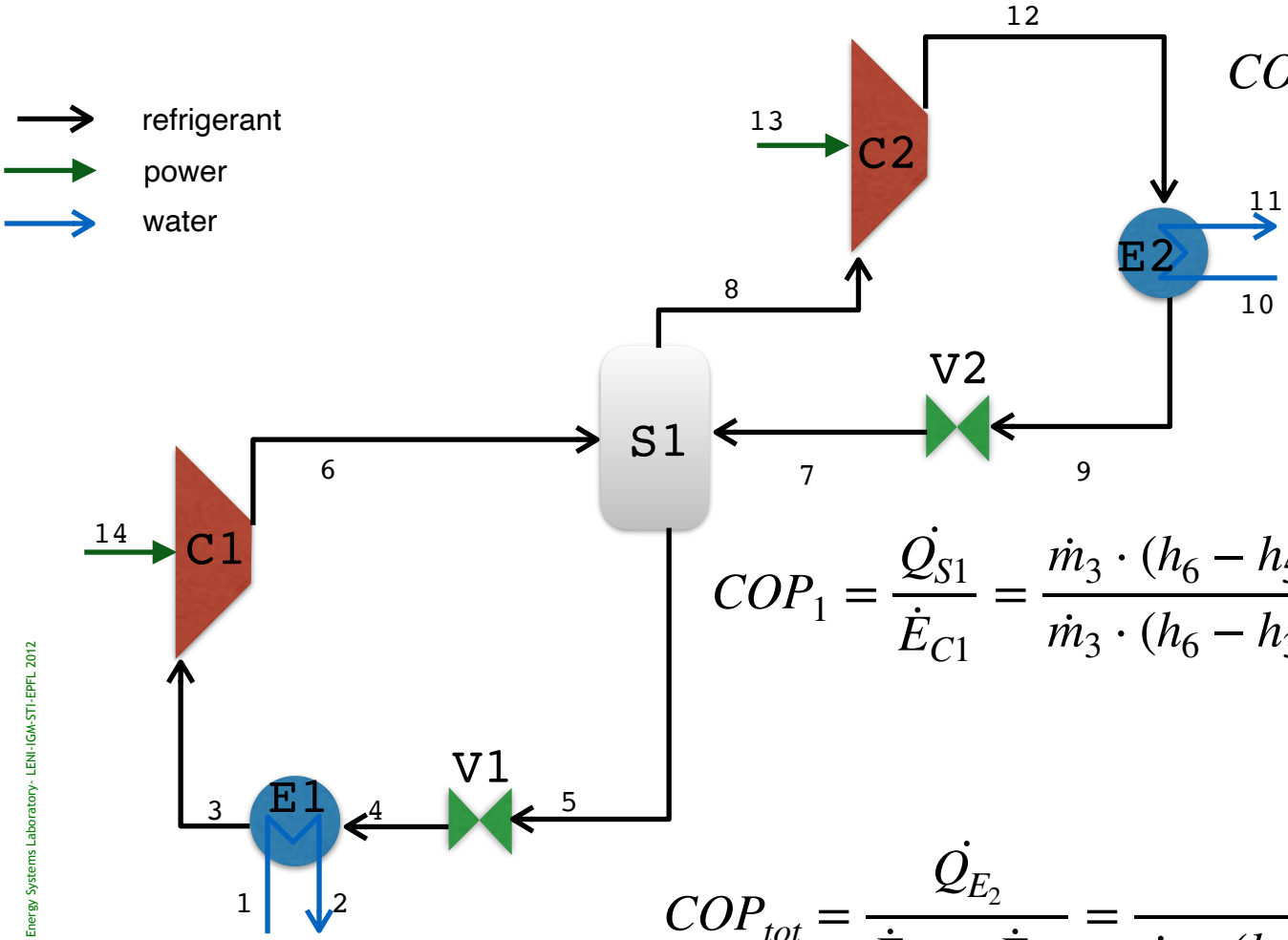
Two stages heat pump flow sheet



$$COP_2 = \frac{\dot{Q}_{E2}}{\dot{E}_{C2}} = \frac{\dot{m}_8 \cdot (h_{12} - h_9)}{\dot{m}_8 \cdot (h_{12} - h_8)}$$

$$COP_1 = \frac{\dot{Q}_{S1}}{\dot{E}_{C1}} = \frac{\dot{m}_3 \cdot (h_6 - h_5)}{\dot{m}_3 \cdot (h_6 - h_3)}$$

$$COP_{tot} = \frac{\dot{Q}_{E_2}}{\dot{E}_{14} + \dot{E}_{13}} = \frac{\dot{m}_3 \cdot (h_{12} - h_9)}{\dot{m}_8 \cdot (h_12 - h_8) + \dot{m}_3 \cdot (h_6 - h_3)}$$

$$\dot{Q}_{S1} = \dot{m}_3 \cdot (h_6 - h_5) = \dot{m}_8 \cdot (h_8 - h_7)$$

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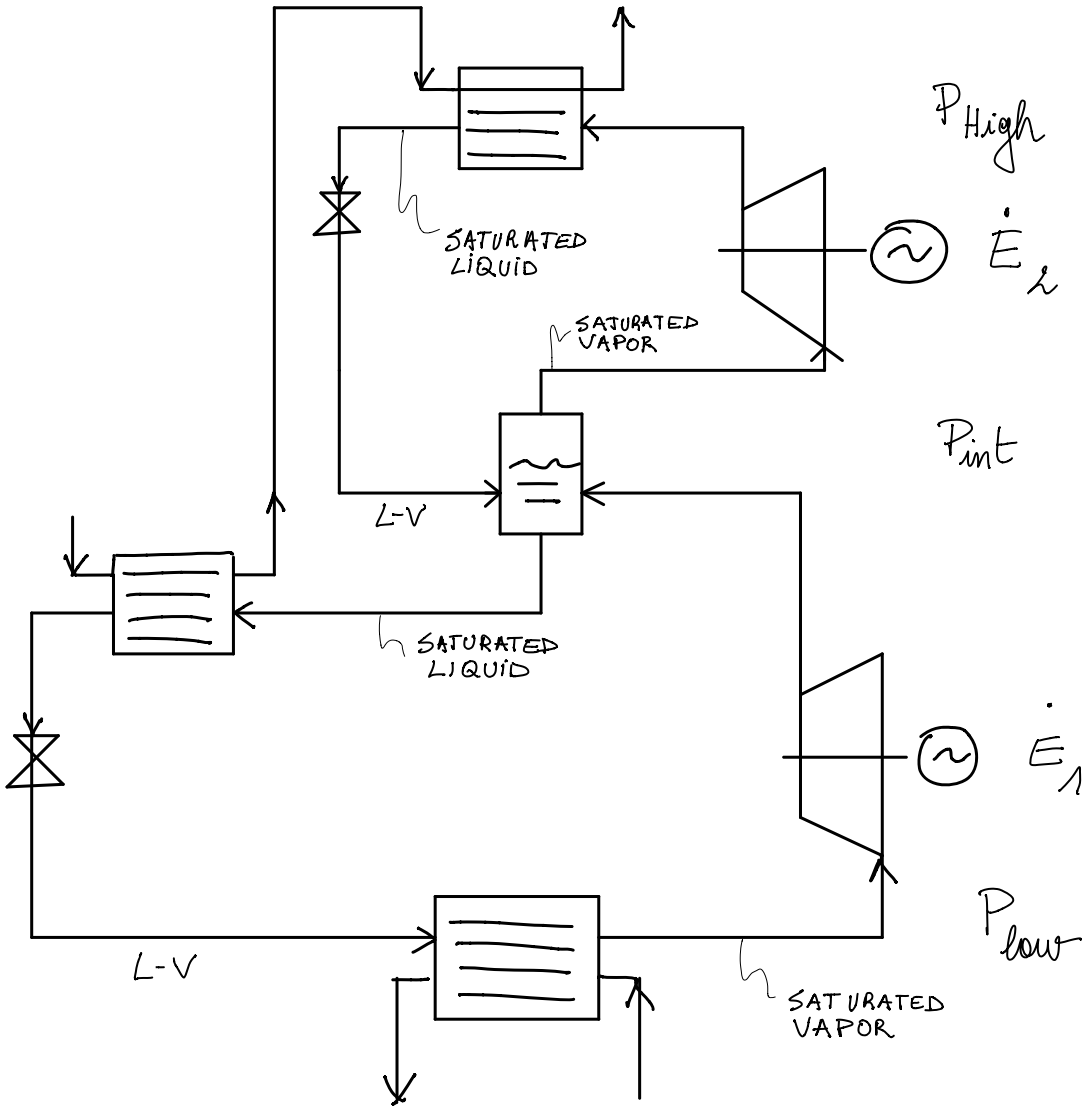
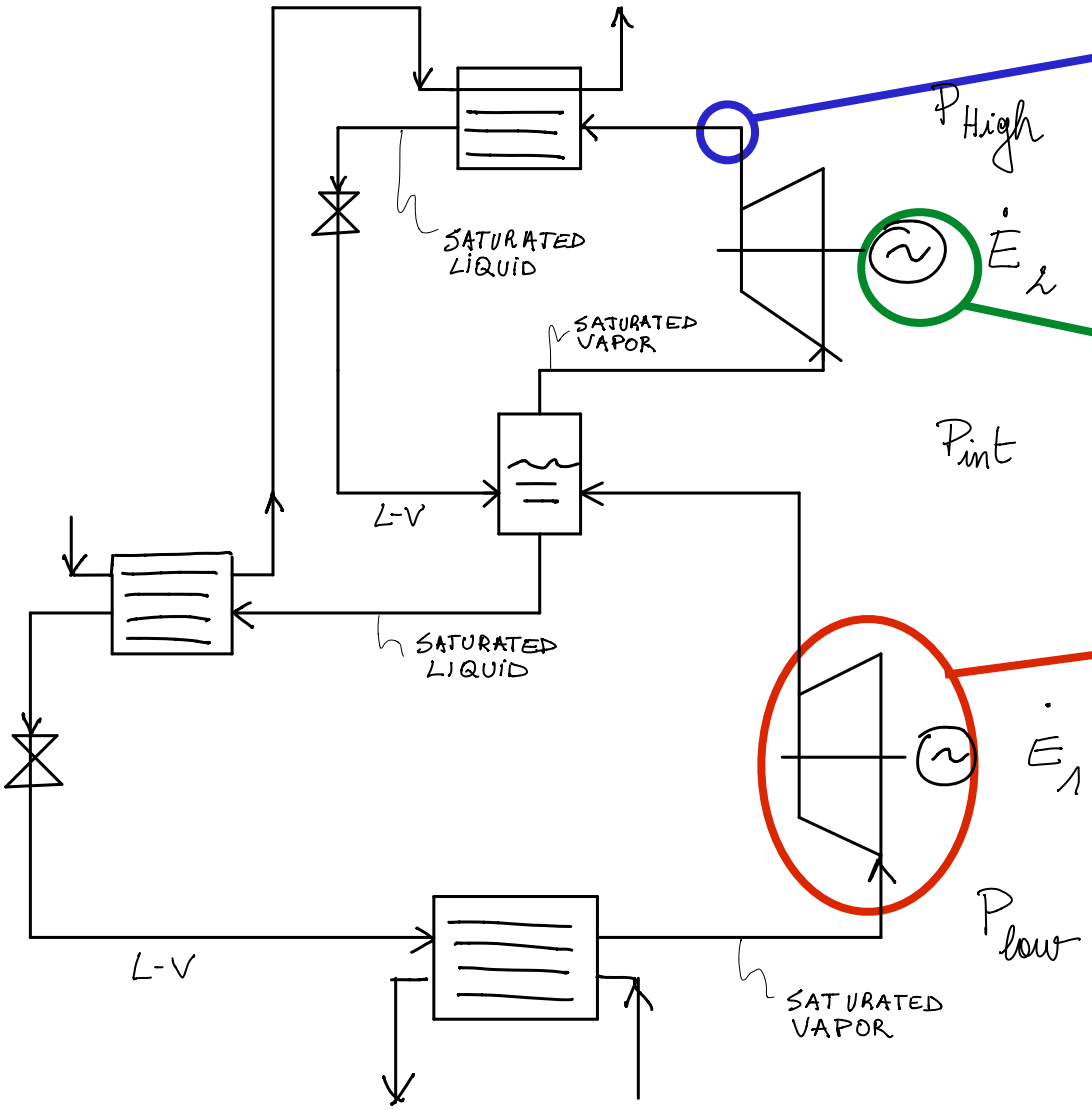
EPFL

Double stage heat pump



- **What is needed ?**
  - flows
  - temperatures
  - pressures
  - mechanical power

Double stage heat pump Flowsheet



Flows interconnecting units
- Flowrate
- Thermodynamic State T, P, X

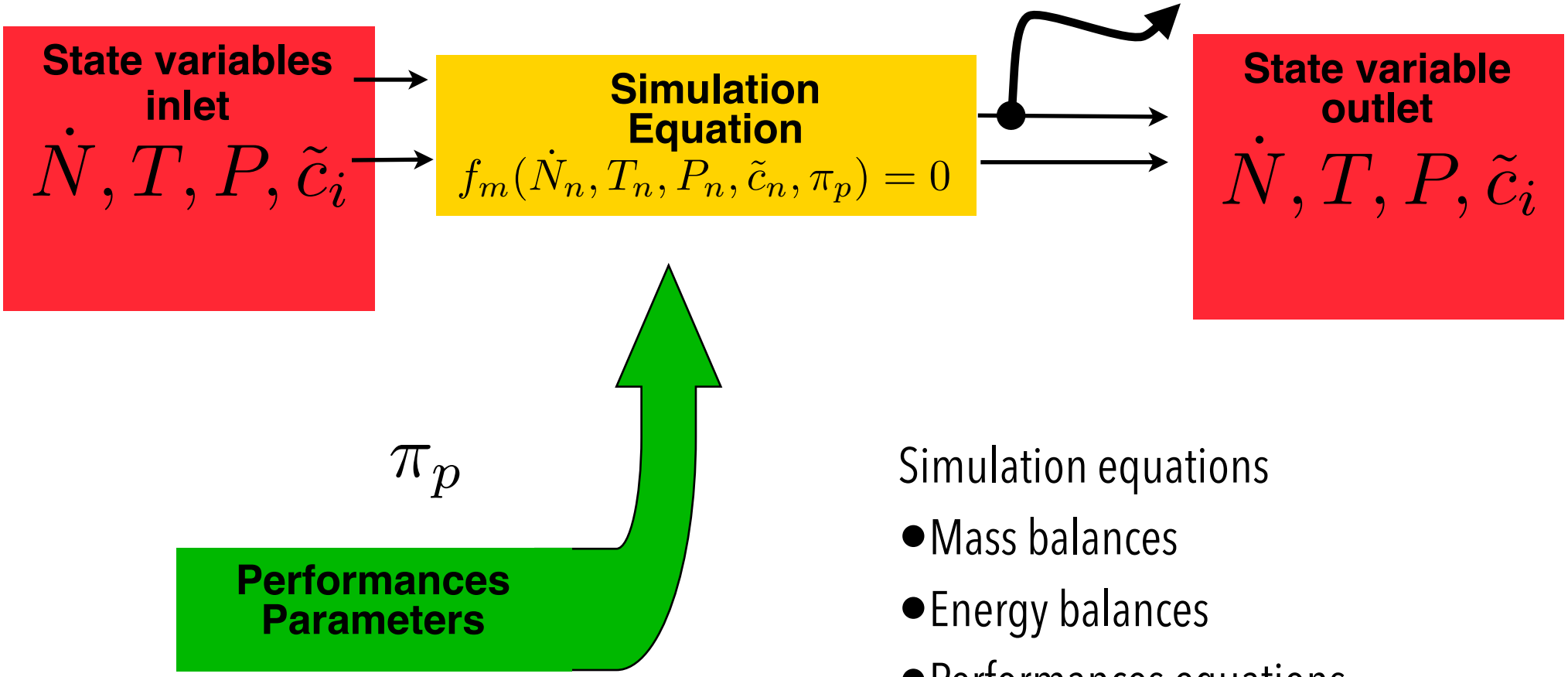
Power

Process unit : converting flows
- Size
- Type
- Conversion of mass and energy

A process unit model

Modeling the conversion
Characterising the flows in the system

Thermodynamic state
Constitutive equations



Simulation equations

- Mass balances
- Energy balances
- Performances equations

Constitutive Equations

- How to characterize the flow between two unit operations ?
  - what is the state of the flow ?
- How to calculate the thermodynamic state of a stream ?
- How to know what is the temperature, the pressure, the enthalpy, the entropy, the volume, the fugacity, the state (liquid or vapor), the viscosity, the Gibbs free energy ?
- How to define the properties when the flow is a mixture of several compounds ?
- How to calculate the thermodynamic transformations in the process units : separation, reaction, compression, expansion, pressure drop ?

State variables of a stream : Gibbs Phase rule

- **Degrees of freedom of a streams**
  - **For a stream with N compounds**
  - only **N+2** variables are required to characterise the state. (Gibbs phase rule, Degree of freedom of a flow)
  - in which at least one will characterise a flow
    - i.e. **1 extensive variable**
- **Examples :**

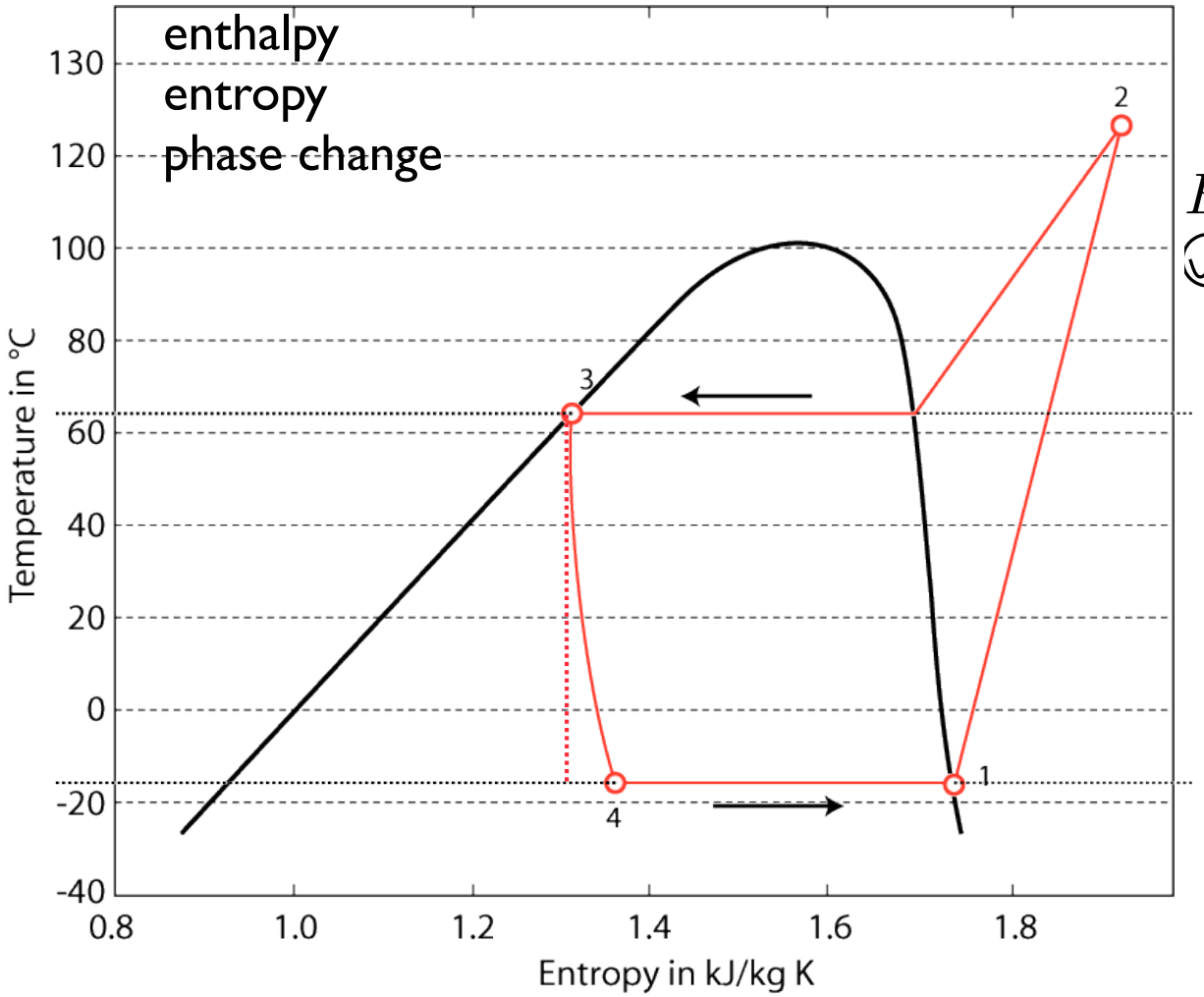
$$T, P, \dot{m}_i$$
$$P, h, \dot{m}, c_i \quad for \quad i = 1, \ldots, N-1$$
$$P, \dot{V}, \dot{m}_i \quad for \quad i = 1, \ldots, N$$

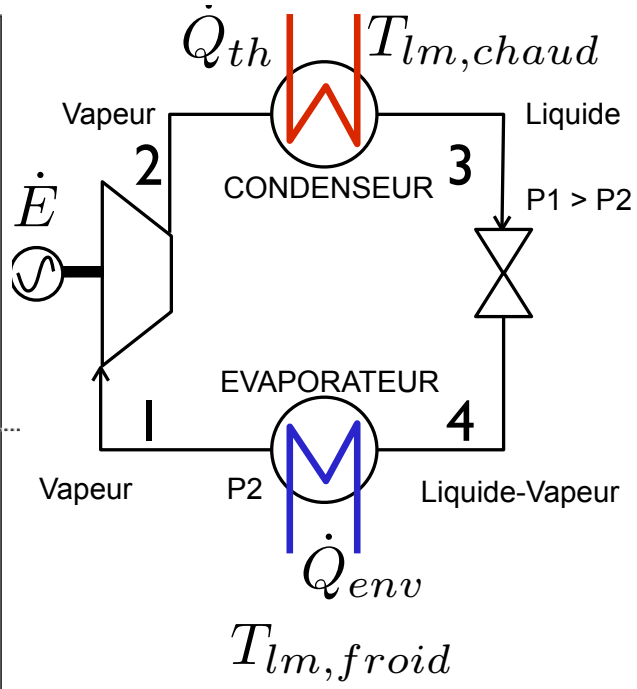
Thermodynamic properties (other state variables)

- **Other State variables**
  - Density, Specific volume (v)
  - Enthalpy (h), entropy (s), Specific Heat (s)
  - Viscosity, thermal conductivity, diffusion coefficient,surface tension
- **Phase equilibirum (L-V, L-L, L-L-V)**
  - Saturation point,dew point
  - Heat of vaporisation
  - Saturating pressure
  - Phase distribution coefficient
- **Chemical reactions**
  - Heat of reaction
  - Equilibrium constants

- **To be calculated by the constitutive equations when N+2 state variables are known**

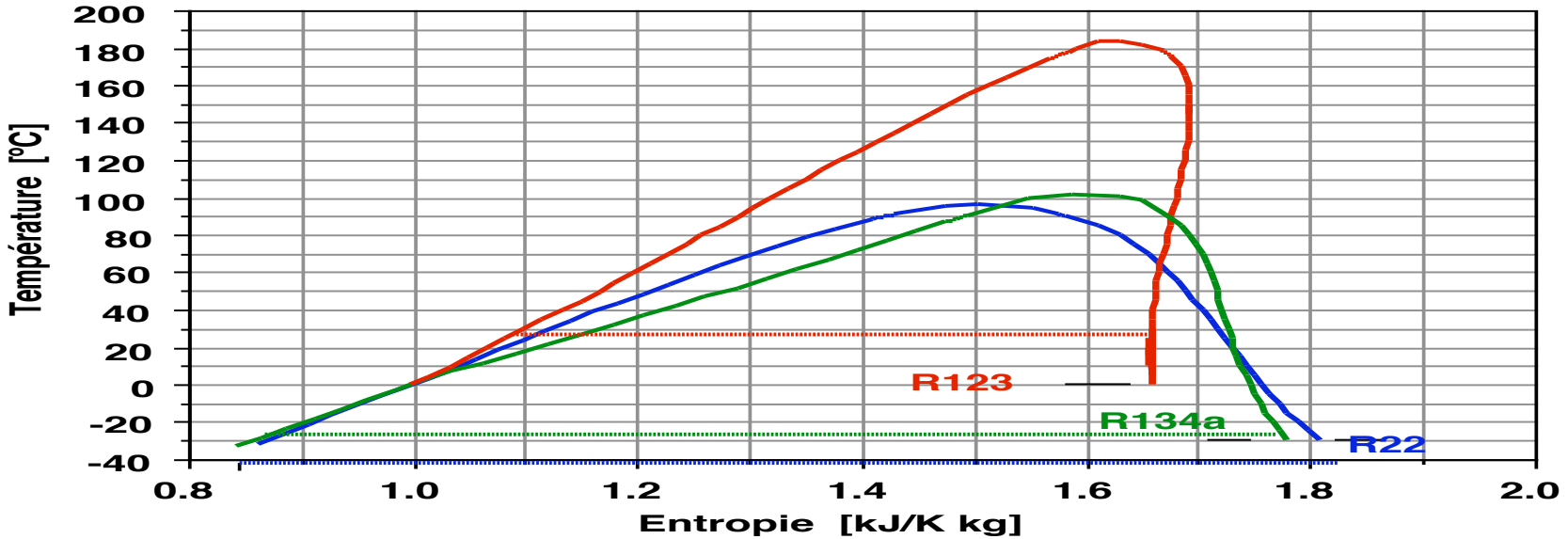
Single stage Heat pump

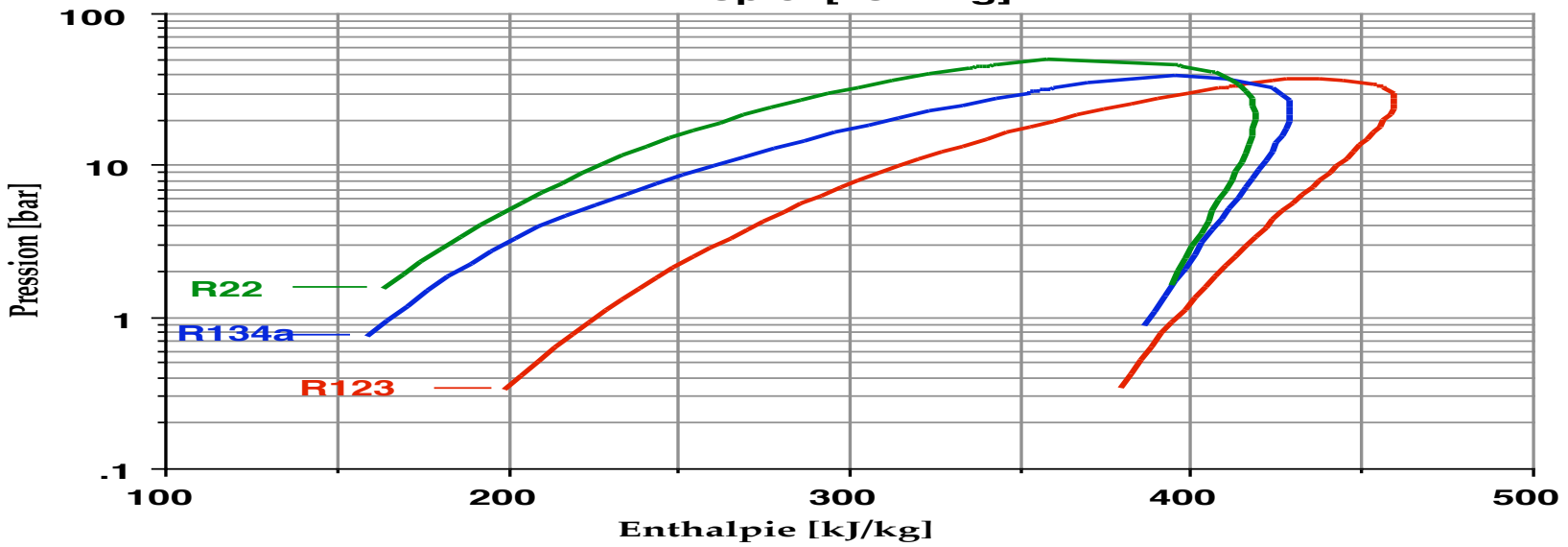




For a given refrigerant, the state of the flows can be obtained by using the state diagram of the refrigerant. States can be calculated if we know P and T (or α) of some flows and the models of the units

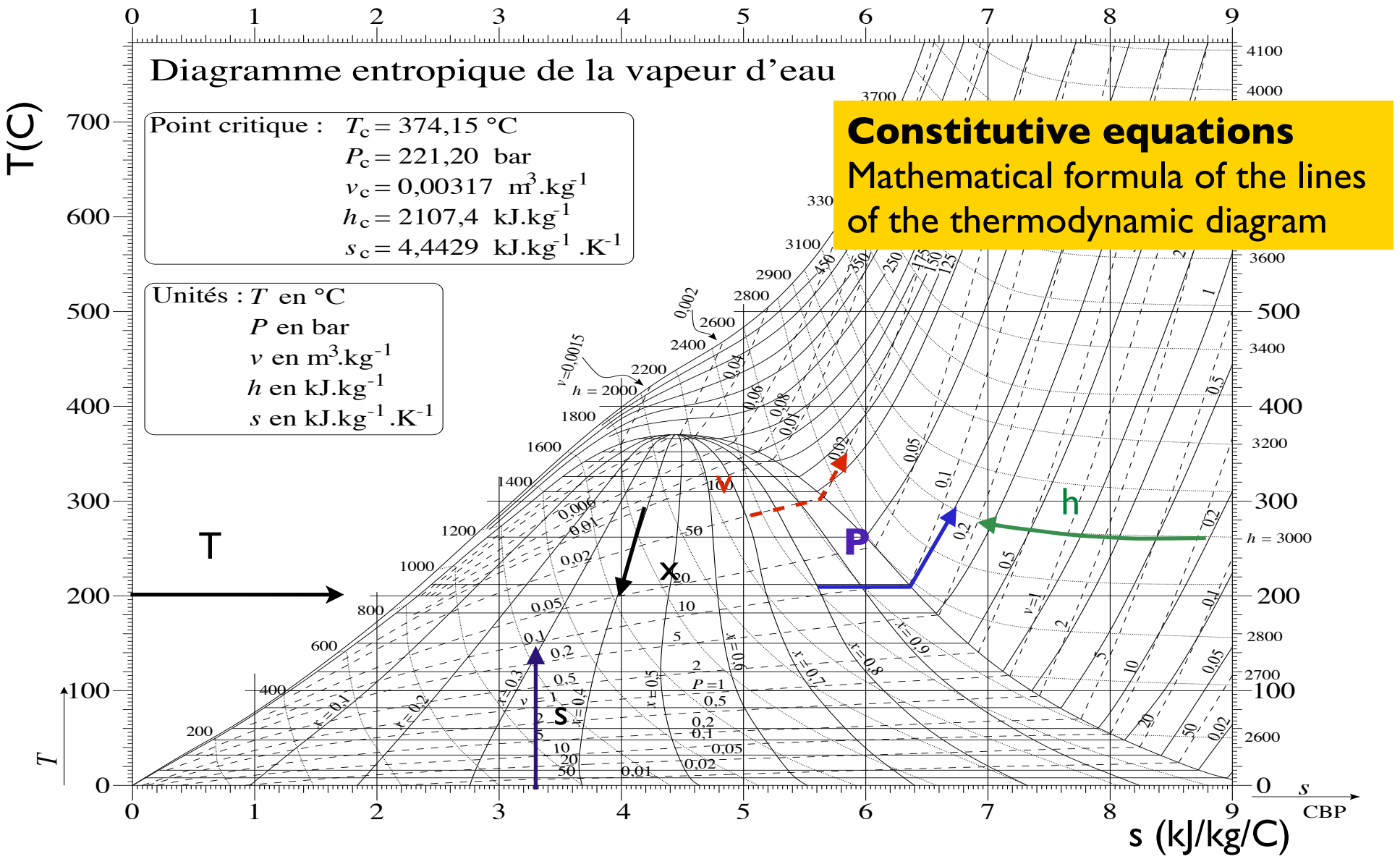
Different fluids





Refrigerants have different relationships between T,P,s,h

Constitutive equation : Equation of state



Constitutive equations
Mathematical formula of the lines of the thermodynamic diagram

Constitutive equations

- **To represent properties of the molecule and the interactions forces between the molecules**
  - Thermodynamic properties are related with the energy storage mode in the molecules.
    - Nuclear forces
    - Links between atoms in a molecule (vibration modes)
      - Specific heat
      - Heat of formation
  - Interactions between molecules
    - Attraction/repulsion
    - affinity -> equilibrium
    - Reactivity

Relation micro/macro scales

- **Energy of the molecules**
  - Translation : perfect gases
  - Rotation, vibration
    - Contributions to Cp, H, S
- **Interactions between molecules**
  - Attraction, repulsion
    - Equations of State
    - Corrections wrt perfect gases
    - Phase changes
    - transport phenomena

- **Correlations between properties**
  - Thermodynamic Theory
    - Example : Clapeyron

$$\frac{dP_{vp}}{dT} = \frac{\Delta H_v}{T\Delta V_v} = \frac{\Delta H_v}{\left(RT^2 / P_{vp}\right)\Delta Z_v}$$

$$\frac{d\ln P_{vp}}{d(1/T)} = \frac{-\Delta H_v}{R\Delta Z_v}$$

  - Observations : polynomial correlation on experiments :

$$cp_i(T) = a_i + b_i \cdot T + c_i \cdot T^2 + d_i \cdot T^3 + \frac{e_i}{T}$$

$$T_{min_i} \leq T \leq T_{max_i}$$

  - Molecular structure analysis
    - Substance sub-sets
    - Group contributions

Constitutive equations : Empirical

- **Represent properties and interactions forces between the molecules**
  - For specific substances
    - i.e. see NIST web book, refprop, coolprop
    - http://webbook.nist.gov/chemistry/
  - May be really detailed, according to the amount of experiments available
    - Applied for pure components
  - Difficult to implement in a systematic manner in a software (not generic)
- **Example : Refprop/Coolprop softwares**

- **Equation of state**
  - Generic mathematical expression with parameters
  - Independent of the components
  - Mixtures of components
  - Constrained by the theory of thermodynamics
- **Model parameters**
  - Fitted from experiments : Compounds data base
  - Calculated by "educated" models
    - Scientific intelligence

Systematic implementation : Enthalpy calculations

T0 : reference temperature
Perfect gas : 25 C 1 atm

Gas ideal

$$H_{id}^{g}(T,P,x_i) = \sum_i x_i * \Delta H^{0f}{}_i + \int_{T^\circ}^{T} \left(\sum_i x_i * Cp_i(T) \right) .dT$$

$$Cp_i(T) = a_i + b_i * T + c_i * T^2 + d_i * T^3$$

a_i, b_i, c_i, d_i from data bases

Liquid ideal

$$H_{id}^{l}(T,P,x_i) = \sum_i x_i * \Delta H^{0f}{}_i + \int_{T^\circ}^{T} \left(\sum_i x_i * Cp_i(T) \right) dT - \sum_i x_i * \Delta Hvap_i(T)$$

$$\Delta Hvap_i(T) = \Delta Hvap_i(T_i^b) * \left(\frac{T_i^{crit} - T}{T_i^{crit} - T_i^b} \right)^{0.38}$$

Mixture liquid - vapor $T = T^{sat}(P, x_i)$

$$\boxed{H_{id}^{l-v}(T,P,x_i) = \alpha * H_{id}^{g}(T,P,x_i) + (1-\alpha) * H_{id}^{l}(T,P,x_i)}$$

Systematic implementation : Entropy calculation

- **For a gas state**

$$ds = cp\frac{dT}{T} - \left(\frac{\delta v}{\delta T}\right)_P dP$$

$$s_i = s_i^{0f} + \int_{T_0}^{T} \frac{cp_i(T)}{T} dT - \Re ln \frac{P_i}{P^0}$$

- **This shows that the properties can be deduced if we know**
  - the correlation equations
  - the data characterising the components
  - the fundamental rules of thermodynamics.

Equation of state : explanation

- **Interactions between molecules :**
  - Attraction : lowers the pressure for the same volume
  - Repulsion : minimum volume, quasi incompressible
- **Perfect gases : link between T, P, V**

$$PV = n\Re T \Rightarrow PV - n\Re T = 0$$

- **Example : van der Waals equation**

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

Repulsion Attraction

Equation of state : derived from van der Waals eq.

Redlich-Kwong

$$P = \frac{RT}{V-b} - \frac{a}{\sqrt{T}V(V+b)}$$

Soave

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)}$$

Peng-Robinson

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)}$$

The best equation depends on the type of fluid

Parameters calibration : Values of a(T) and b

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)}$$

- At the critical point

$$\left(\frac{\partial P}{\partial V}\right)_{T=Tc} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T=Tc} = 0$$

- 2 equations to calculate a and b at T=Tc
- a and/or b may be a function of T
- e.g. a(T) calibrated to fit a given property like Pvap

The value of a and b can be calculated if we know the critical conditions (Tc and Pc) of the fluid. When there is a dependence to the T, experiments are needed.

Soave example cont.

Equations of state detailed example

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)}$$

$$Z = \frac{PV}{RT} \qquad A = \frac{aP}{(RT)^2} \qquad B = \frac{bP}{RT}$$

Z is the conpressibility factor

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0$$

$$\frac{H-H^0}{RT} = \frac{U-U^0}{RT} + \frac{PV-RT}{RT} = \frac{\int_{\infty}^{V}\left(\frac{\partial U}{\partial V}\right)_T dv}{RT} + \frac{PV-RT}{RT}$$

Thermodynamics & Maths

$$\frac{H-H^0}{RT} = \frac{\int_{\infty}^{V}\left(T\frac{\partial P}{\partial T}\right)_V - P)dv}{RT} + \frac{PV-RT}{RT}$$

$$\frac{H-H^\circ}{RT} = Z - 1 + \int_{\infty}^{V}\left\{T\left(\frac{\partial P}{\partial T}\right)_V - P\right\}dV$$

Properties of pure components

- **Where to find the properties of the pure components (e.g. parameters a and b of a compound in the equation of state)**
  - Literature : dedicated papers
  - Compilations : Tables & Graphs
    - e.g. ASHRAE (http://www.ashrae.org)
  - Thermodynamic Data bases
    - e.g. DIPPR (www.aiche.org/dippr **)**
  - Estimation methods is required because
    - Millions of substances…
    - mixtures …
    - extrapolate properties using models
    - to predict missing information

$$cp_i(T) = a_i + b_i \cdot T + c_i \cdot T^2 + d_i \cdot T^3 + \frac{e_i}{T}$$

$$T_{min_i} \leq T \leq T_{max_i}$$

Single component values

- **Minimum information needed (values used in empirical correlations)**
  - Critical properties
    - Tc, Pc, Vc
  - Acentric Factor **ω** (how far of a sphere the molecule is ?)

$$\omega_i = -log_{10}(\frac{P_i^{sat}(T = 0.7 \cdot T_{c_i})}{P_{c_i}}) - 1$$

  - Boiling temperature Teb
  - Fusion temperature Tfus

Corresponding states

- Reduced coordinates
  - Tr=T/Tc Pr=P/Pc vr =v/vc
- in reduced coordinates phase diagrams coincide for simple compounds :Ar,CH4,N2,O2
- For non polar substances or non spherical substances a 3rd parameter is needed.

Example : corresponding states

Properties of CH4, C2H6, C3H8 and C4H10 are identical in reduced coordinates

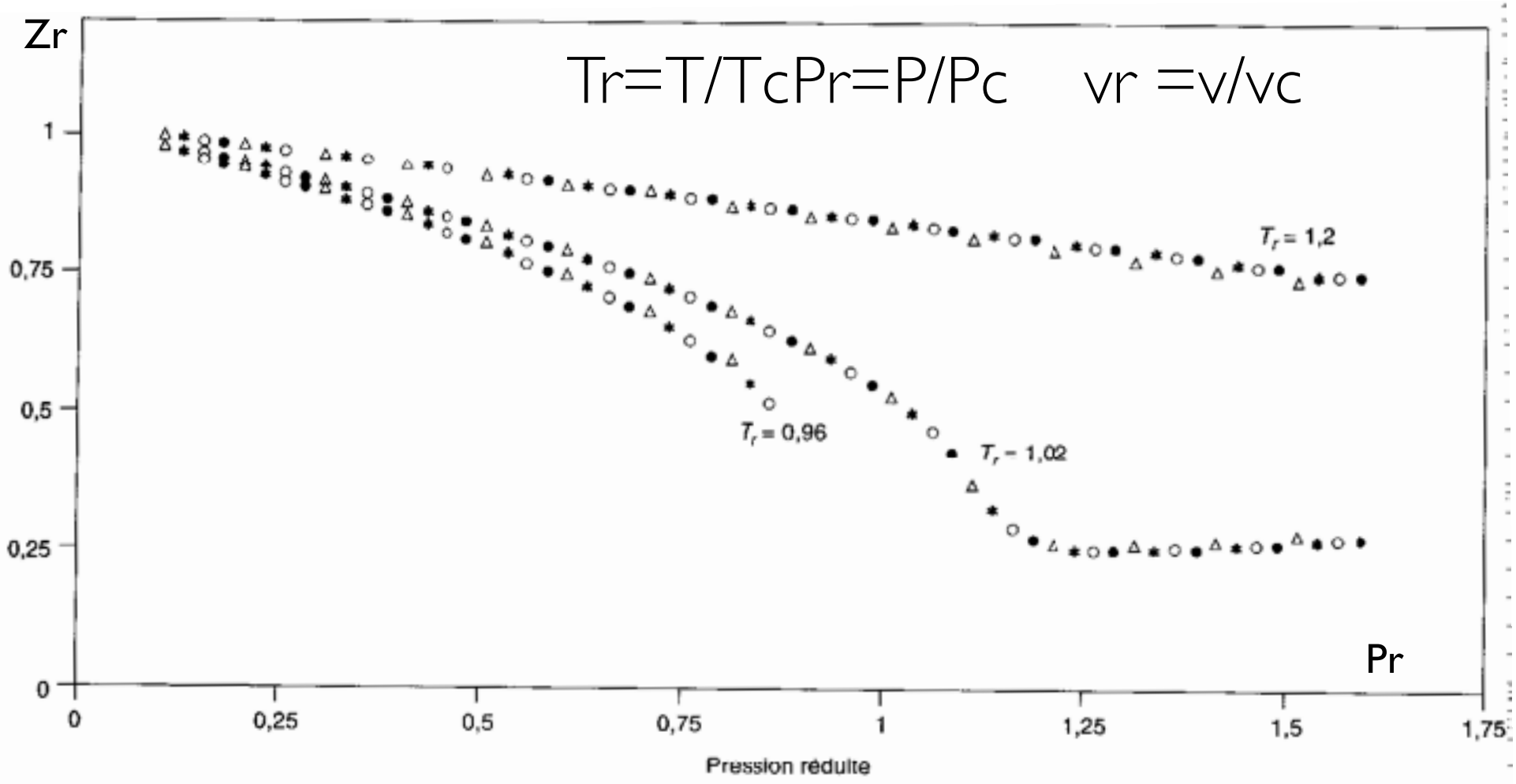


Fig. 3.3 Facteur de compressibilité du méthane (Δ), de l'éthane (∗), du propane (○) et du *n*-butane (●); représentation en coordonnées réduites.

Corresponding states

- **Two detailed equations for the property F of two compounds**
  - F1 for **ω**1 near 0 (e.g. argon : Spheric)
  - F2 for **ω**2 near 1 (e.g. n-butane : Non spheric)
- **The estimation of a given thermodynamic property F(T,P) for a compounds with known ω,Tc and Pc is calculated by :**
  - Tr=T/ Tc et Pr=P/ Pc
- **property F is computed by corresponding state :**
  - F=F1+(**ω**-**ω**1) /(**ω**2-**ω**1) (F2 - F1)
    - F1 = F(Tr, Pr) for reference compound 1
    - F2 = F(Tr, Pr) for reference compound 2

Equation of Soave : estimating properties

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)}$$

$$a_c = 0.42748 \frac{(RT_c)^2}{P_c}$$

$$a = a_c\left[1 + \left(0.48 + 1.574\omega - 0.176\omega^2\right)\left(1 - \sqrt{T_r}\right)\right]^2$$

acentric facor

$$b = 0.08664 \frac{RT_c}{P_c}$$

T_c, P_c, ω are characteristics of the molecules

Group Contribution

- **When a compound is unknown**
  - group contribution methods : a molecule is represented by constitutive groups :
    - CH3, CH2, CH and C
    - CH3CO, CH2CO
  - Properties are calculated by correlations between groups contributions
  - see UNIFAC method for thermodynamic properties https://en.wikipedia.org/wiki/UNIFAC

Extending the equations to mixture

Mixing rules

$$a = \sum_{i}^{N} x_i \sum_{j}^{N} x_j a_{i,j}$$

$$b = \sum_{i}^{N} x_i b_i$$

Combinaison rules

$$a_{i,j} = \sqrt{a_i a_j (1 - \delta_{i,j})}$$

$\delta_{i,j}$ are interaction coefficient between compound i and j

$\delta_{i,j}$ parameters are calibrated to fit measurements using parameter identification techniques

Parameter identification

- Fit parameters $\delta_{i,j}$ to represent measured data (e.g. Dechema)

(1) ACETONE — C3H6O

(2) HEXANE — C6H14

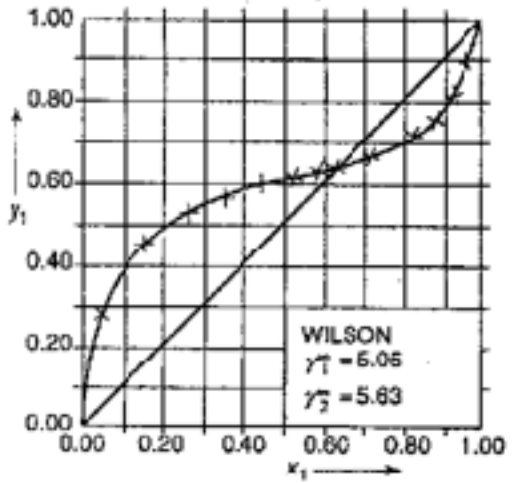
***** ANTOINE CONSTANTS ***** REGION ***** CONSISTENCY

(1)	7.11714	1210.595	229.664	-13- 55 C	METHOD 1 *
(2)	6.91058	1189.640	226.280	-30- 170 C	METHOD 2 *

TEMPERATURE= 45.00 DEGREE C

LIT: SCHAEFER K.,RALL W.,Z.ELEKTROCHEM.62,1090(1958).

CONSTANTS:	A12	A21	ALPHA12
MARGULES	1.5061	1.6352	
VAN LAAR	1.5055	1.6399	
WILSON	962.8113	341.4214	
NRTL	699.6735	599.8547	0.4817
UNIQUAC	-42.4860	485.5658	



EXPERIMENTAL DATA			MARGULES		VAN LAAR		WILSON		NRTL		UNIQUAC	
P MM HG	X1	Y1	DIFF P	DIFF Y1	DIFF P	DIFF Y1	DIFF P	DIFF Y1	DIFF P	DIFF Y1	DIFF P	DIFF Y1
339.40	0.0	0.0	4.21	0.0	4.21	0.0	4.21	0.0	4.21	0.0	4.21	0.0
444.60	0.0651	0.2828	3.10	-0.0032	3.25	-0.0033	-3.48	-0.0122	-2.44	-0.0109	2.36	-0.0042
545.80	0.1592	0.4442	10.11	-0.0104	10.42	-0.0101	9.40	-0.0065	9.34	-0.0074	10.16	-0.0098
590.20	0.2549	0.5163	3.32	-0.0163	3.63	-0.0161	7.95	-0.0063	7.12	-0.0080	4.07	-0.0149
617.30	0.3478	0.5560	4.90	-0.0177	5.12	-0.0177	10.83	-0.0078	9.82	-0.0094	5.78	-0.0165
632.60	0.4429	0.5866	7.17	-0.0133	7.29	-0.0135	12.06	-0.0074	11.16	-0.0084	7.82	-0.0128
639.60	0.5210	0.6068	8.65	-0.0096	8.70	-0.0100	12.30	-0.0083	11.55	-0.0087	9.07	-0.0098
633.80	0.5907	0.6258	0.26	-0.0049	0.28	-0.0051	3.12	-0.0077	2.48	-0.0075	0.55	-0.0057
637.10	0.6202	0.6339	3.05	-0.0034	3.06	-0.0039	5.69	-0.0079	5.09	-0.0073	3.30	-0.0044
631.00	0.7168	0.6662	-1.42	0.0011	-1.45	0.0007	0.79	-0.0069	0.24	-0.0056	-1.25	-0.0002
627.80	0.7923	0.7034	2.88	0.0041	2.79	0.0038	4.26	-0.0037	3.81	-0.0021	2.88	0.0029
623.30	0.8022	0.7292	0.04	0.0240	-0.07	0.0238	1.22	0.0165	0.80	0.0182	-0.00	0.0230
603.40	0.8692	0.7583	-2.33	0.0010	-2.52	0.0010	-3.16	-0.0025	-3.22	-0.0014	-2.71	0.0007
583.20	0.9288	0.8255	6.82	-0.0075	6.58	-0.0072	3.82	-0.0052	4.30	-0.0054	6.17	-0.0069
543.30	0.9658	0.9003	-4.81	-0.0044	-5.00	-0.0041	-7.90	0.0001	-7.26	-0.0008	-5.38	-0.0035
505.00	1.0000	1.0000	-7.38	0.0	-7.38	0.0	-7.38	0.0	-7.38	0.0	-7.38	0.0
	MEAN DEVIATION:		4.21	0.0086	4.30	0.0086	6.14	0.0071	5.62	0.0072	4.39	0.0082
	MAX. DEVIATION:		10.11	0.0240	10.42	0.0238	12.30	0.0165	11.55	0.0182	10.16	0.0230

Liquid-Vapour equilibrium

- **repartition between gas and liquid state :** $K_i = \frac{y_i}{x_i} = f(T, P, x, y)$
  - Liquid
    - Compute a=a(T,xi) and b=b(xi)
    - Compute A and B
    - Compute Z in liquid phase
    - Compute fugacity in the liquid state : ΦiL
  - Gas phase
    - Compute a=a(T,yi) and b=b(yi)
    - Compute A and B
    - Compute Z gas phase
    - Compute fugacity in the gas phase : ΦiV
- **=>Ki = φiL/φiV**

Soave example cont. : fugacity coefficient

$$Z = \frac{PV}{RT} \qquad A = \frac{aP}{(RT)^2} \qquad B = \frac{bP}{RT}$$

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)}$$

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0$$

$$RTd(\ln\phi) = VdP = d(PV) - PdV$$

$$\Rightarrow \ln\phi = \int \frac{d(PV) - PdV}{RT} = \frac{PV}{RT} - \int \frac{1}{V-b}dV + \int \frac{a(T)}{RT * V(V+b)}dV$$

$$\ln\phi = Z - 1 - \ln Z - \int_{\infty}^{V} \frac{Z-1}{V}$$

$$= Z - 1 - \ln(Z - B) - \frac{A}{B}\ln\frac{Z+B}{Z}$$

Liquid-Vapor Equilibrium

Relation between the composition in the liquid and the gas

Equilibrium : $liquid \rightleftarrows gas$

$$\varphi_i \cdot y_i \cdot P = \gamma_i \cdot x_i \cdot f_i^{*L}$$

$$K_i = \frac{y_i}{x_i} = \frac{f_i^{*L} \cdot \gamma_i}{P \cdot \varphi_i}$$

$$f_i^{*L} = f_i^{*LS} \cdot exp\left[\frac{v_i^s \cdot (P - P^s)}{RT}\right]$$

$$f_i^{*LS} = P_i^S \cdot \varphi_i^{*S}$$

			Solution idéale $f_i^L = x_i \cdot f_i^{'L}$	Solution non idéale $f_i^L = \gamma_i \cdot x_i \cdot f_i^{'L}$
Comportement phase vapeur	Mélange idéal	Gaz parfait $\varphi_i^* = \varphi_i^{*s} = 1$	$K_i = \frac{P_i^s}{P}$ $K = K^r = f(P,T)$	$K_i = \frac{P_i^s \cdot \gamma_i}{P}$
		Gaz réel $f_i^V = y_i \cdot f_i^{'V}$ $f_i^{'V} = \varphi_i^* \cdot P$	$K_i = \frac{f_i^{*L}}{\varphi_i^* \cdot P}$ $K = K^{id} = f(P,T)$	$K_i = \frac{f_i^{*L} \cdot \gamma_i}{\varphi_i^* \cdot P}$
	Mélange non idéal		Impossible	$K_i = \frac{f_i^{*L} \cdot \gamma_i}{\varphi_i^* \cdot P}$

with:

f_i^{*LS} fugacity of pure substance at saturation at the temperature of the mixture

φ_i^{*S} fugacity coefficient of saturated vapor under the same conditions

P_i^S saturated vapor pressure of component i (calculated using the vapor equation of state)

P_i^S with Lee-Kesler Method : $P_i^S = f^{(0)} + \omega \cdot f^{(1)}$

$$f^{(0)} = 5.92714 - \frac{6.09648}{T_r} - 1.28862 \cdot \ln T_r + 0.169347 \cdot T_r^6$$

$$f^{(1)} = 15.2518 - \frac{15.6875}{T_r} - 13.4721 \cdot \ln T_r + 0.43577 \cdot T_r^6$$

with

$P_r = \frac{P}{P_c}$ (reduced pressure) and $T_r = \frac{T}{T_c}$ (reduced temperature).

$$ln\varphi_i^{*S} = Z - 1 - lnZ - \int_\infty^V \frac{Z-1}{V} = Z - 1 - ln(Z - B) - \frac{A}{B} ln\frac{Z+B}{Z}$$

f is the fugacity : the trend that the molecule has to escape (fugare) from the state it is.

https://en.wikipedia.org/wiki/Lee–Kesler_method

- **Chemical reations**

$$\xi_a A + \xi_b B \rightleftarrows \xi_c C + \xi_d D$$

  - **Equilibrium : Min Gibbs free energy**

$$g - g_{ref} = RT\ln(\phi) = \left[PV\right]_{P0->0}^{P} - \int_{V0->\infty}^{V} PdV - \int_{P0->0}^{P} \frac{RT}{P} dP$$

Conclusion : Constitutive equations

- **Equations of state**
  - computes thermodynamic properties knowing the N+2 state variables (one is defining the flow)
- **Parameters of the equations**
  - Data bases (measures + calibration)
  - Corresponding states (estimates by interpolation)
  - Group contribution (based on the chem. formula)
  - Mixing rules to represent behaviour of mixtures
- **Standard form => easy to change fluid without changing equations (only values of parameters are changed).**
- **Flowsheeting software like Aspen give hints on choosing thermodynamic models**
  - based on the type of compounds and the typical conditions (high P for example)

Constitutive equation

- The choice of the dependent state variable is important

$$h = f(T, P, x_i)$$

$$s = f(h, P, x_i)$$

?