

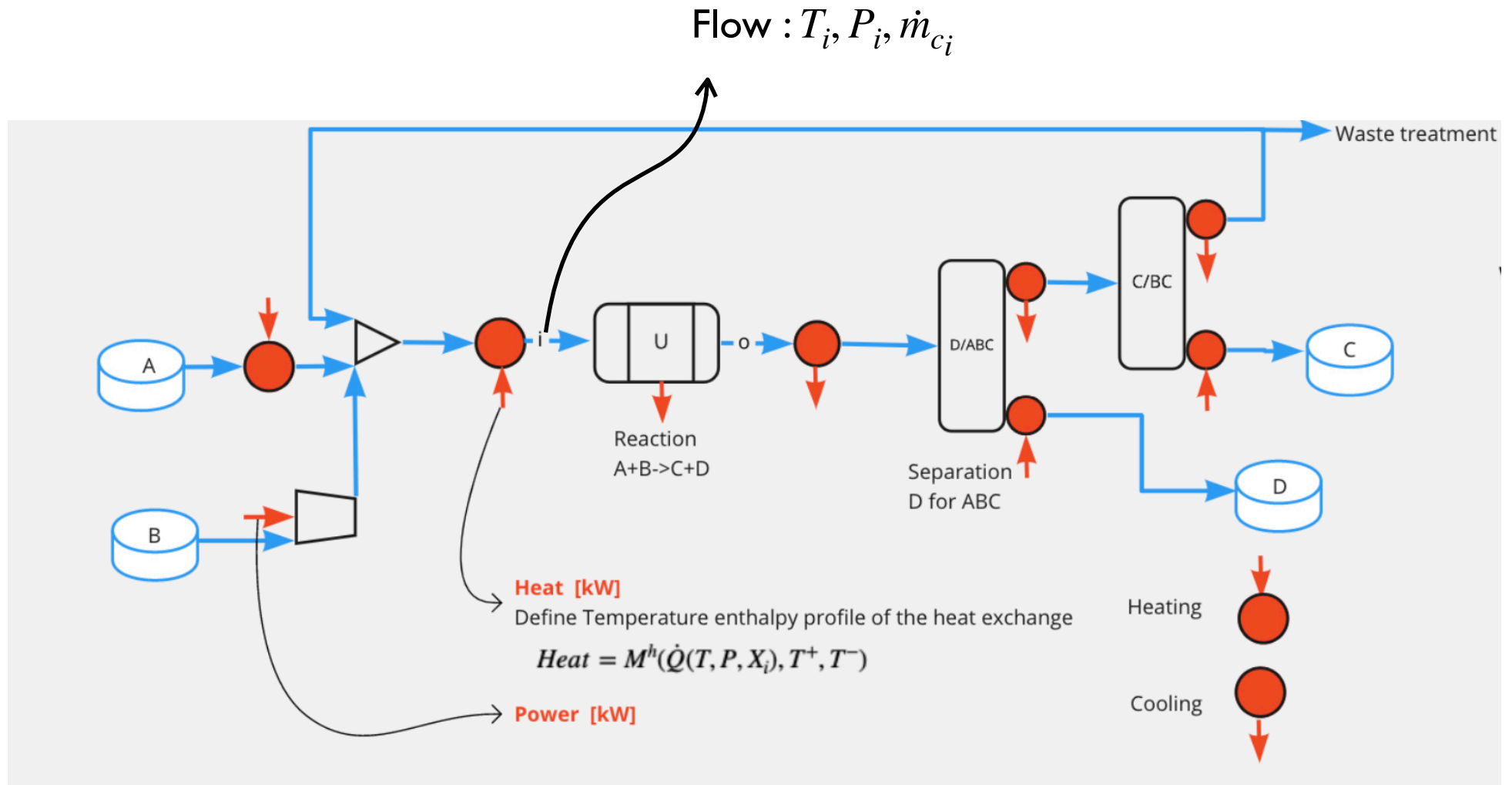
Constitutive equations

Equation of states

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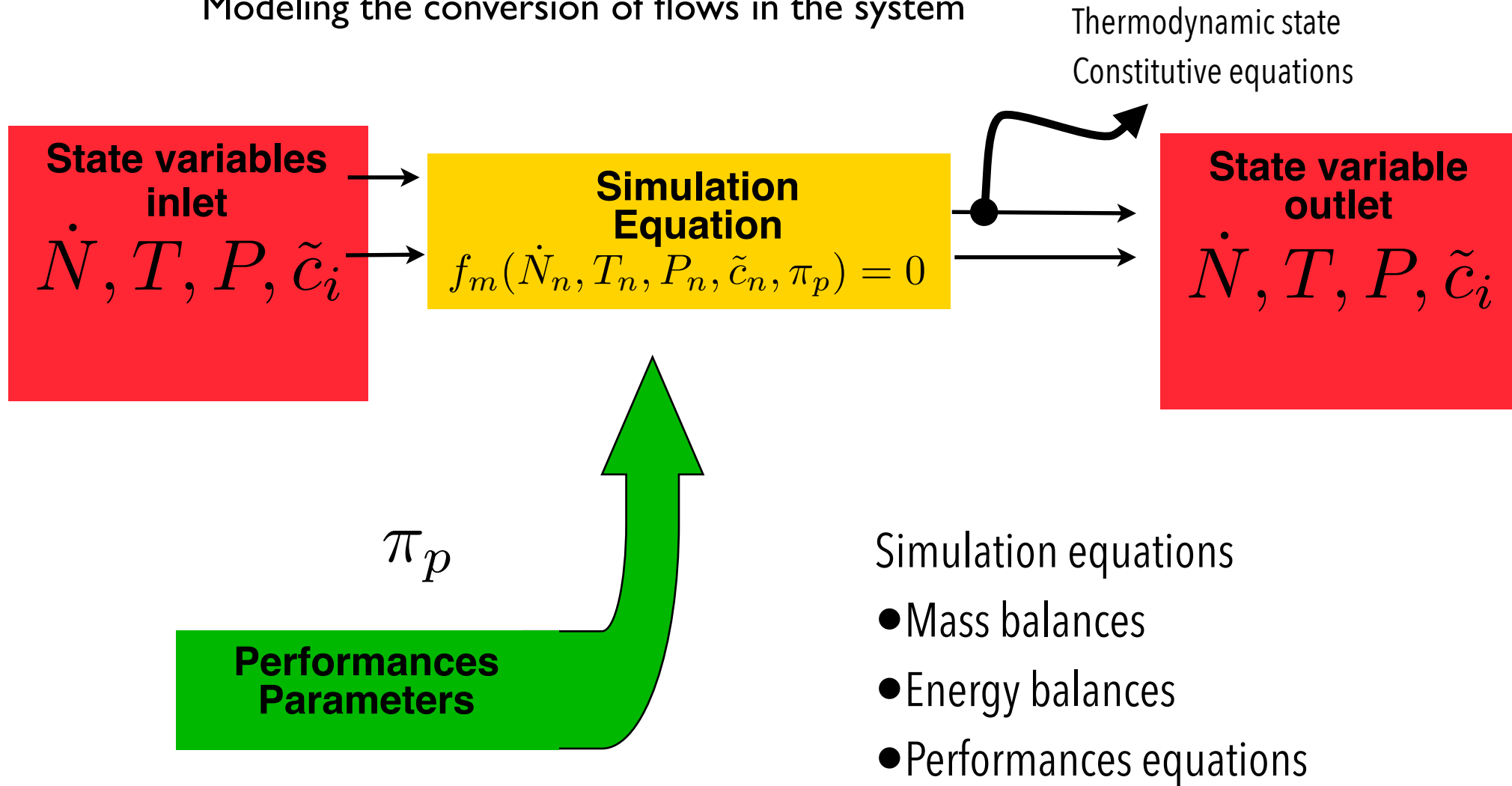
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Flowsheet State characterisation



Process unit models

Modeling the conversion of flows in the system



State variables of a flow : Gibbs Phase rule

- Degrees of freedom of a flow
 - For a flow 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 :

$$\begin{aligned} &T, P, \dot{m}_i \\ &P, h, \dot{m}, c_i \quad \text{for} \quad i = 1, \dots, N - 1 \\ &P, \dot{V}, \dot{m}_i \quad \text{for} \quad i = 1, \dots, N \end{aligned}$$

- **Other State variables**

- Density, Specific volume (v)
- Enthalpy (h), entropy (s), Specific Heat (c_p)
- Viscosity, thermal conductivity, diffusion coefficient, surface tension

- **Phase equilibrium (L-V, L-L, L-L-V)**

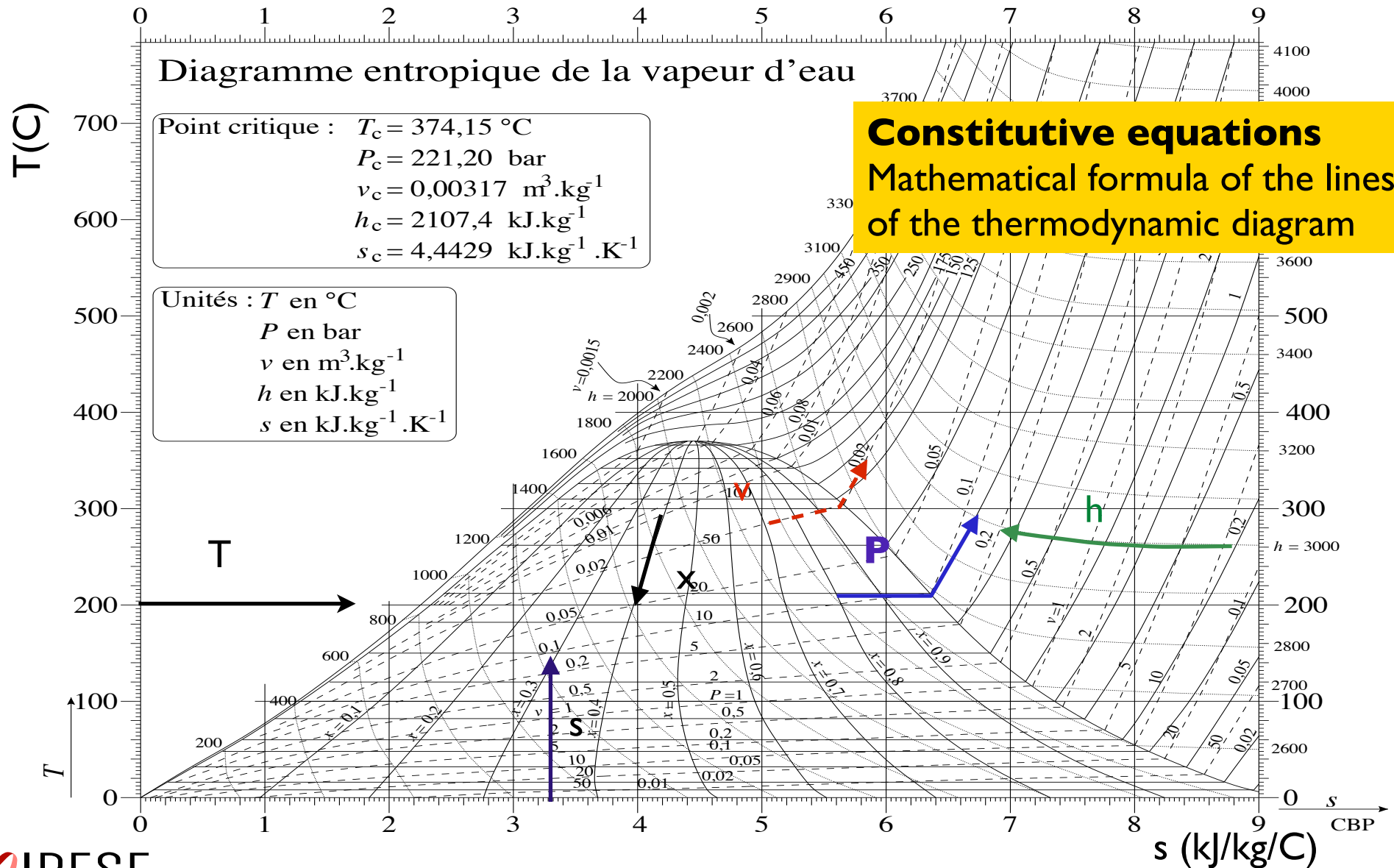
- Saturation point, dew point
- Heat of vaporisation
- Saturating pressure
- Phase distribution coefficient

- **Chemical reactions**

- Heat of reaction
- Equilibrium constants

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

Constitutive equation : Equation of state



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 C_p , 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 :

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

- Molecular structure analysis

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

- Substance sub-sets
 - Group contributions

- **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

T_0 : reference temperature
Perfect gas : 25 C | atm

Gas ideal

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

$$C_{p_i}(T) = a_i + b_i * T + c_i * T^2 + d_i * T^3 \quad a_i, b_i, c_i, d_i \text{ from data bases}$$

Liquid ideal

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

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

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

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

- For a gas state

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

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

- 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 type of 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

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

- 2 equations to calculate a and b at $T=T_c$
- a and/or b may be a function of T
- e.g. $b(T)$ calibrated to fit a given property like P_{vap}

Soave example cont.

Equations of state detailed example

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

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

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

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

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

$$\frac{H - H^0}{RT} = Z - 1 + \int_{\infty}^V \left\{ T \left(\frac{\partial P}{\partial T} \right)_V - P dV \right\}$$

Thermodynamics
& Maths

Properties of pure components

- Where to find the properties of the pure components
 - 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
 - T_c, P_c, V_c
 - Acentric Factor ω
 - Boiling temperature T_{eb}
 - Fusion temperature T_{fus}

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

Corresponding states

- Reduced coordinates
 - $Tr = T/T_c$ $Pr = P/P_c$ $vr = v/v_c$
- 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

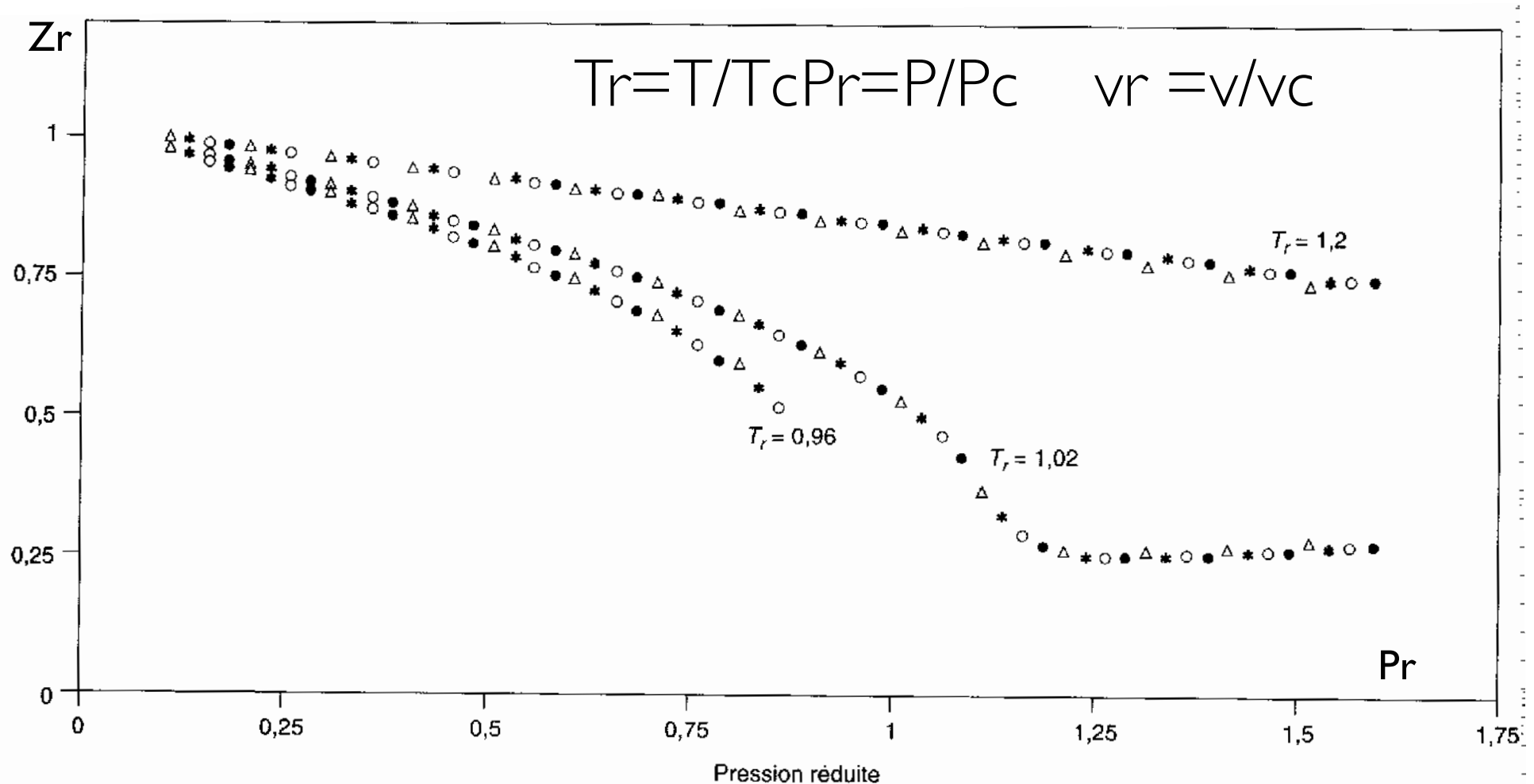


Fig. 3.3 Facteur de compressibilité du méthane (Δ), de l'éthane ($*$), du propane ($\circ$) et du *n*-butane ($\bullet$); représentation en coordonnées réduites.

Corresponding states

- Two detailed equations for two compounds
 - acentric factor of 1 (ω_1) near 0 (e.g. argon)
 - acentric factor of 2 (ω_2) near 1 (e.g. n-butane)
- The estimation of a given thermodynamic property $F(T,P)$ for a compounds with known ω, T_c and P_c is calculated by :
 - $T_r = T / T_c$ et $P_r = P / P_c$
- F is computed by corresponding state :
 - $F = F_1 + (\omega - \omega_1) / (\omega_2 - \omega_1) (F_2 - F_1)$
 - $F_1 = F(T_r, P_r)$ for reference compound 1
 - $F_2 = F(T_r, P_r)$ for reference compound 2

Equation of Soave : estimating properties

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

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

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

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

acentric facor

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>

EPFL 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 +++++
(1)  7.11714 1210.595  229.644 -13-  55 C   METHOD 1  *
(2)  6.91058 1189.640  226.280 -30- 170 C   METHOD 2  *
  
```

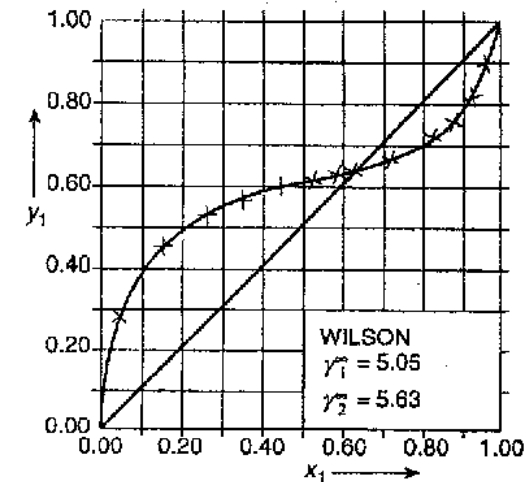
TEMPERATURE= 45.00 DEGREE C

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

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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	-0.0030	-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	-0.0053	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 $a=a(T, x_i)$ and $b=b(x_i)$
 - Compute A and B
 - Compute Z in liquid phase
 - Compute fugacity in the liquid state : ϕ_i^L
 - Gas phase
 - Compute $a=a(T, y_i)$ and $b=b(y_i)$
 - Compute A and B
 - Compute Z gas phase
 - Compute fugacity in the gas phase : ϕ_i^V
- $\Rightarrow K_i = \phi_i^L / \phi_i^V$

Soave example cont. : fugacity coefficient

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

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

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

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

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

$$\begin{aligned} \ln \phi &= Z - 1 - \ln Z - \int_{\infty}^V \frac{Z-1}{V} \\ &= Z - 1 - \ln(Z - B) - \frac{A}{B} \ln \frac{Z+B}{Z} \end{aligned}$$

Liquid-Vapor Equilibrium

Relation between the composition in the liquid and the gas
Equilibrium : $liquid \rightleftharpoons gas$

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

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

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

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

with:
 f_i^{*LS}
 φ_i^{*S}
 P_i^S

fugacity of pure substance at saturation at the temperature of the mixture
fugacity coefficient of saturated vapor under the same conditions
saturated vapor pressure of component i (calculated using the vapor equation of state)

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

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

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

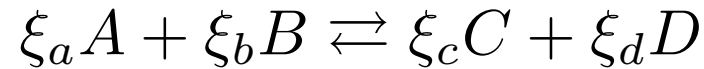
with

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

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

			Solution idéale $f_i^L = x_i \cdot f_i'^L$	Solution non idéale $f_i^L = \gamma_i \cdot x_i \cdot f_i'^L$
C o m p o s i t i o n e n t p h a s e v a p e u r	M é l a n g e i d é a l	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	$K_i = \frac{f_i^{*L} \cdot \gamma_i}{\varphi_i^* \cdot P}$

- Chemical reactions



- Equilibrium : Min Gibbs free energy

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

- **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).**
- **Aspen gives hints on choosing thermodynamic models**
 - based on the type of compounds
 - see Aspen Tutorials