TOWARDS A CLEVER OPTIMIZATION OF MODELS

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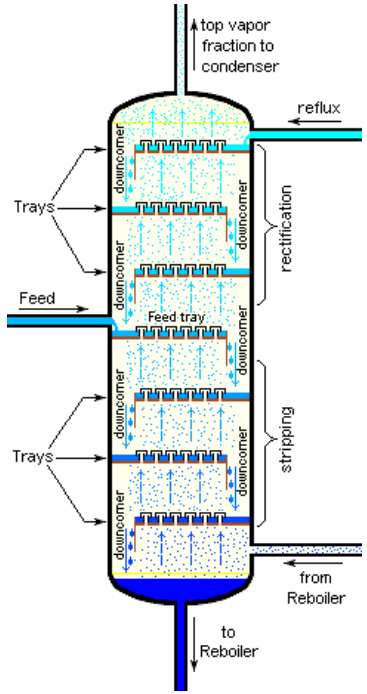
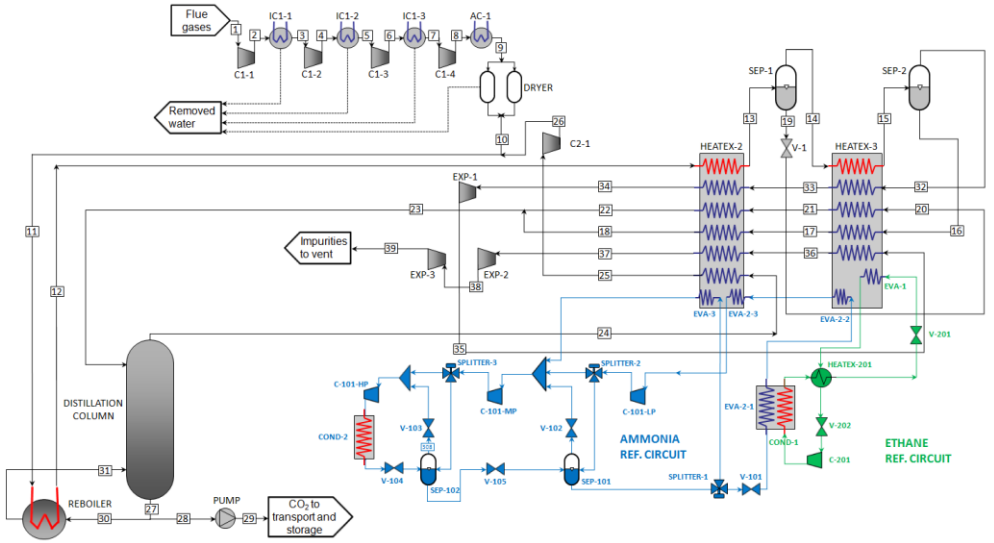
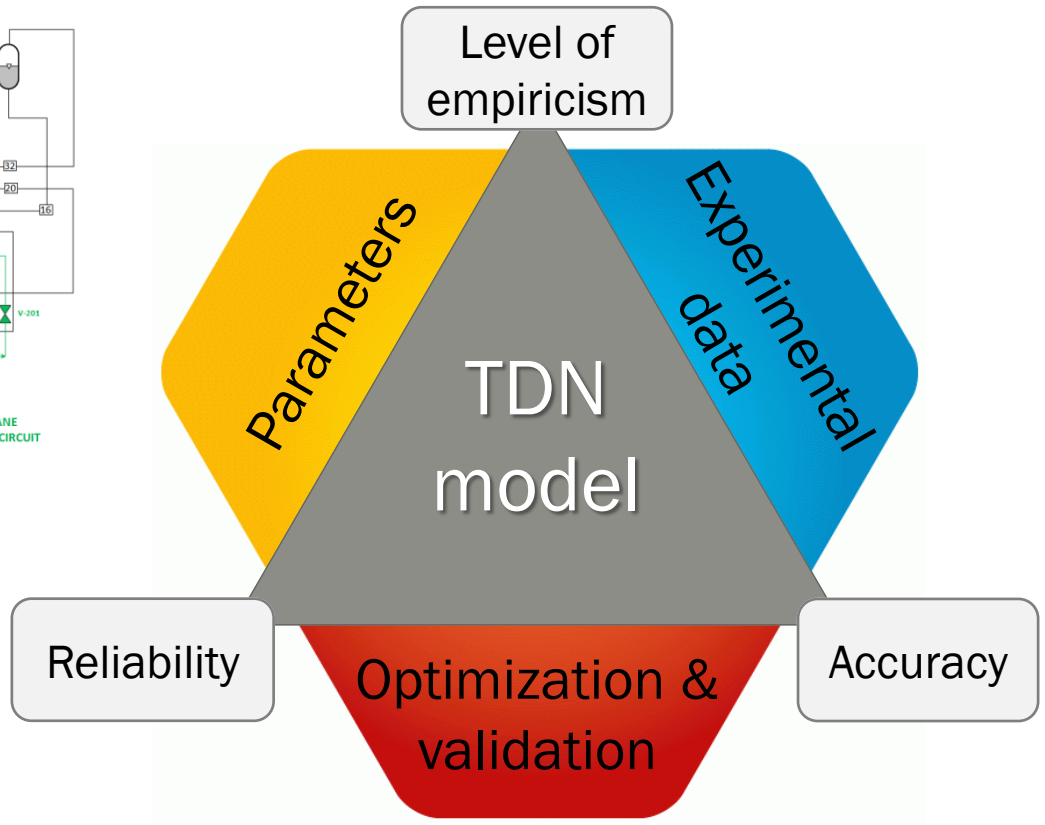
Introduction







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Introduction

Cascade of pivotal questions …

? What types of data should be used to perform the model optimization?

? How do characteristics of data influence the optimization problem?

? How to set up a clever optimization, considering the characteristics of available data?

? What is the role played by experimental uncertainties? How important they are in the optimization process?

? How to account for the uncertainty of models?

? …

This presentation is an attempt to answer these questions

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Outline

- **Key characteristics of experimental data**
- **The optimization process. Main considerations**
  - *Types of optimization processes*
  - *The role played by uncertainties of molar fractions*
  - *The uncertainty of model's parameters*
  - *The effect of the numerosity and dispersion of experimental data on optimization results of different types of systems*
- **In conclusion … how to set up a clever optimization of models?**

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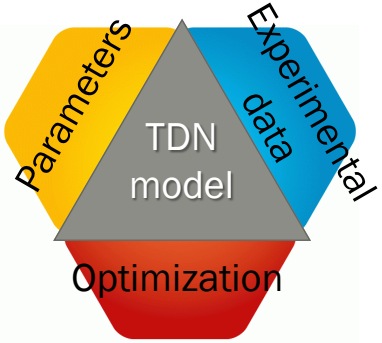
Optimization of model parameters

Experimental data for parameters optimization



What *kind of parameters* to be optimized?

⇩

What *type of data* for model's optimization?

- Empirical parameters

  Optimization over different types of experimental data (multi-property data: phase-equilibrium, p-ρ-T, h^M, $c_p{}^M$, …, of pure, binary and multi-component systems)

- Theoretically-based parameters

  Optimization over experimental data that macroscopically reflect the theoretical significance of parameters (typical example: saturation VLE data for regressing binary interaction parameters)

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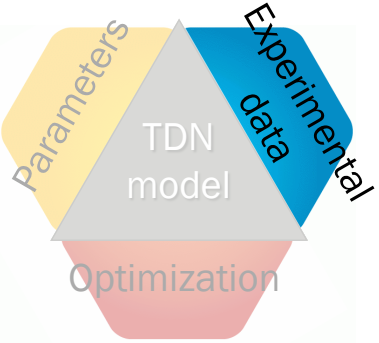
Optimization of model parameters

General characteristics of experimental data

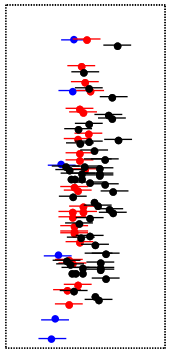


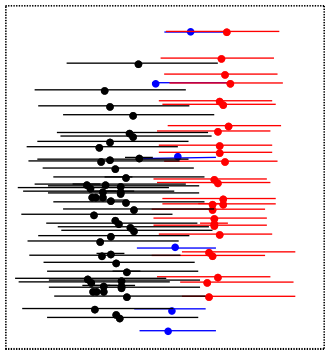
Analysis of general characteristics of experimental data

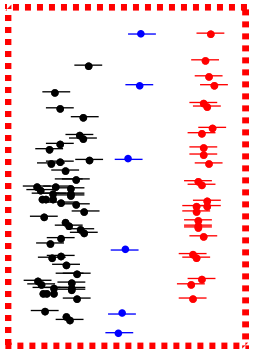
- The numerosity
- The dispersion
- The (availability of) experimental uncertainties

→ Enable the analysis of the **compatibility** between measurements and determination of the **uncertainty of the whole sample** of data.

Different types of samples of experimental data







THE KNOWLEDGE OF EXPERIMENTAL UNCERTAINTIES IS FUNDAMENTAL TO COMPREHEND AND TO QUANTIFY THE CAUSE OF THE DISPERSION OF EXPERIMENTAL DATA

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Optimization of model parameters

The role of experimental uncertainties

Do available *data* sets incorporate *uncertainties*?

Yes

⇩

It is possible to:

- compare experimental data on the basis of their compatibility
- optimize model parameters by weighting data over their uncertainties
- define a reasonable lower bound of the residuals between model's calculations and experimental data

No

⇩

It would be preferable to select only data that:

- belong to numerous populations
- are measured by different authors and with different experimental equipment

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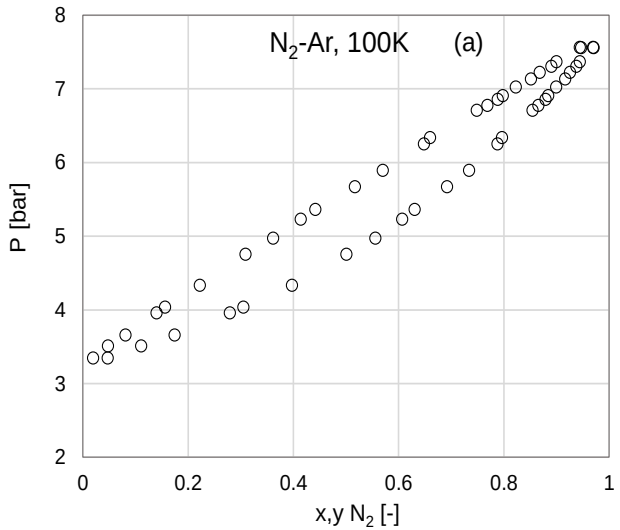
Optimization of model parameters

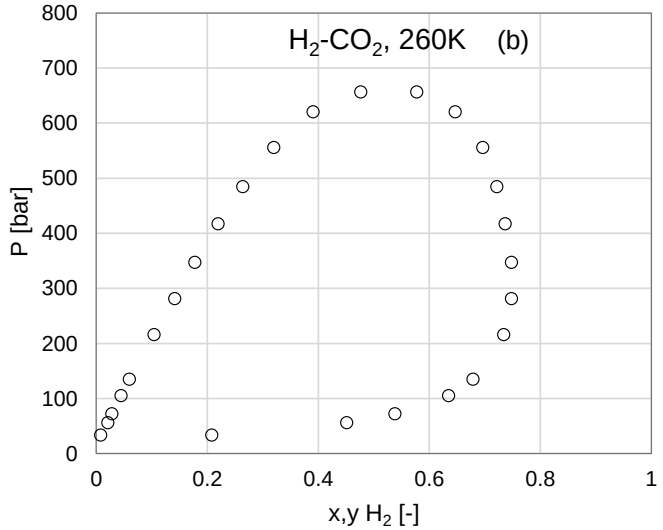
Preliminary analysis. Treating VLE data

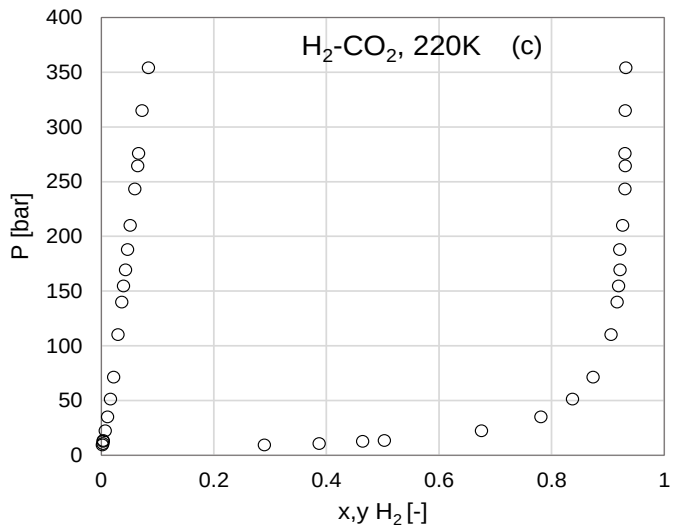
- The numerosity
- The dispersion
- The (availability of) experimental uncertainty
- The type of data (and, thus, of system)

More in particular, characteristics of VLE data

- The *"shape" of the phase diagram*
- The *homogeneity of the distribution of experimental data* along the whole phase diagram
- The availability of both *dew and bubble points* or just one of the two







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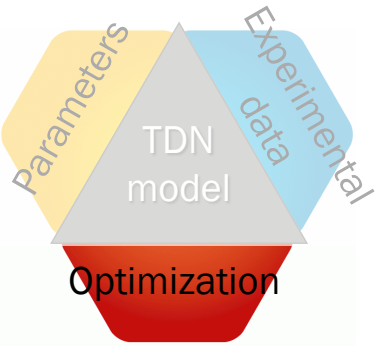
Optimization of model parameters

The selection of the optimization process



The results of **any optimization process** depend on:

- characteristics of experimental data
- the complexity of the analysed thermodynamic system
- the thermodynamic model under optimization
- the selected optimization process

⇨ ***Is there a specific optimization process that allows the optimal treatment of a group of data characterized by specific features ?***

The best is to apply methods (objective functions to be optimized) that account for the uncertainty of experimental data and to determine the uncertainty of optimal model's parameters.

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Optimization of models over VLE data

The selection of the objective function.

- Simple or weighted least squared methods

Optimization method	Example of LS objective functions $S(\bar{\beta})$
Simple least squared method	$\frac{1}{n_e}\sum_{i=1}^{n_e}(\hat{z}_{1i}-\tilde{z}_{1i})^2$ *with z being either x or y*
Simple least squared method	$\frac{1}{n_e}\sum_{i=1}^{n_e}(\hat{x}_{1i}-\tilde{x}_{1i})^2+\frac{1}{n_e}\sum_{i=1}^{n_e}(\hat{y}_{1i}-\tilde{y}_{1i})^2$
Weighted least squared method	$\frac{1}{n_e}\sum_{i=1}^{n_e}\left(\frac{\hat{z}_{1i}-\tilde{z}_{1i}}{u^e_{\hat{z}_{1i}}}\right)^2$ *with z being either x or y*
Weighted least squared method	$\frac{1}{n_e}\sum_{i=1}^{n_e}\left(\frac{\hat{x}_{1i}-\tilde{x}_{1i}}{u^e_{\hat{x}_i}}\right)^2+\frac{1}{n_e}\sum_{i=1}^{n_e}\left(\frac{\hat{y}_{1i}-\tilde{y}_{1i}}{u^e_{\hat{y}_{1i}}}\right)^2$

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Optimization of models over VLE data

The selection of the objective function

$$S(\bar{\beta}) = \frac{1}{n_e}\sum_{i=1}^{n_e}\left[\left(\frac{\widehat{P}_i - \widetilde{P}_i}{u^e_{\widehat{P}_i}}\right)^2 + \left(\frac{\widehat{T}_i - \widetilde{T}_i}{u^e_{\widehat{T}_i}}\right)^2 + \frac{1}{NC}\sum_{j=1}^{NC}\left(\left(\frac{\hat{x}_{ji} - \tilde{x}_{ji}}{u^e_{\hat{x}_{j,i}}}\right)^2 + \left(\frac{\hat{y}_{ji} - \tilde{y}_{ji}}{u^e_{\hat{y}_{j,i}}}\right)^2\right)\right]$$

Complete weighted least squared method

≡

Maximum likelihood method

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Optimization of models over VLE data

The selection of the objective function

- The maximum likelihood method for a binary mixture:

$$S(\bar{\beta}) = \frac{1}{n_e}\left[\sum_{i=1}^{n_e}\left(\frac{\hat{x}_{1i}-\tilde{x}_{1i}}{\sigma_{x_{1,i}}}\right)^2 + \sum_{i=1}^{n_e}\left(\frac{(\hat{y}_{1i}-\tilde{y}_{1i})\sigma_{x_{1,i}}^2}{\sigma_{x_{1,i}}\sqrt{\sigma_{x_{1,i}}^2\sigma_{y_{1,i}}^2-cov(x_{1,i},y_{1,i})^2}} - \frac{(\hat{x}_{1i}-\tilde{x}_{1i})cov(x_{1,i},y_{1,i})}{\sigma_{x_{1,i}}\sqrt{\sigma_{x_{1,i}}^2\sigma_{y_{1,i}}^2-cov(x_{1,i},y_{1,i})^2}}\right)^2\right]$$

$$\sigma_{y_{1,i}}^2 = \left(u_{y_{1,i}}^e\right)^2 + \left(\frac{\partial y_1}{\partial P}\right)_{T,\beta}^2 \left(u_{P_i}^e\right)^2 + \left(\frac{\partial y_1}{\partial T}\right)_{P,\beta}^2 \left(u_{T_i}^e\right)^2$$

$$\sigma_{x_{1,i}}^2 = \left(u_{x_{1,i}}^e\right)^2 + \left(\frac{\partial x_1}{\partial P}\right)_{T,\bar{\beta}}^2 \left(u_{P_i}^e\right)^2 + \left(\frac{\partial x_1}{\partial T}\right)_{P,\bar{\beta}}^2 \left(u_{T_i}^e\right)^2$$

$$cov(x_{1,i},y_{1,i}) = \left(\frac{\partial x_1}{\partial T}\right)_{P,\bar{\beta}}\left(\frac{\partial y_1}{\partial T}\right)_{P,\bar{\beta}} \left(u_{T_i}^e\right)^2 + \left(\frac{\partial x_1}{\partial P}\right)_{T,\bar{\beta}}\left(\frac{\partial y_1}{\partial P}\right)_{T,\bar{\beta}} \left(u_{P_i}^e\right)^2$$

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Optimization of models over VLE data

Experimental uncertainties of molar fractions

Considering a stream of NC components, **chromatography** allows the measurements of:

- *The number of moles of each specie, n_i*
- *The uncertainty, $u(n_i)$, of each measured n_i: $u(n_i) = \overline{b_i} \cdot n_i + \overline{c_i}$*

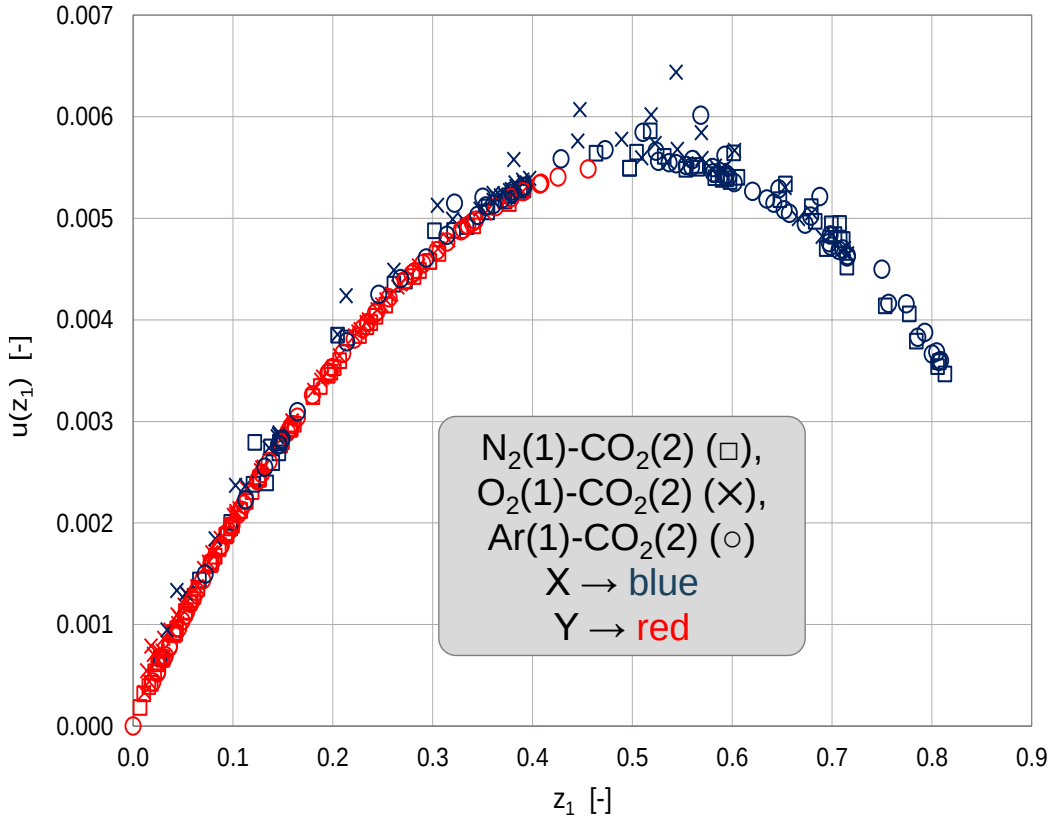
The uncertainty of molar fraction z_i is determined applying the Error Propagation formula:

$$u^2(z_i) = \sum_{j=1}^{NC} \left[\frac{\partial f(n_1, \ldots, n_{NC})}{\partial n_j} \right]^2_{n_{i=j}} \cdot u^2(n_j) \quad ; \quad f: z_i = \frac{n_i}{\sum_j^{NC} n_j}$$

For a binary mixture

$$u_{z_1}^2 = \frac{n_2^2}{(n_1+n_2)^4} u_{n_1}^2 + \frac{n_1^2}{(n_1+n_2)^4} u_{n_2}^2$$

$$u_{z_2}^2 = \frac{n_2^2}{(n_1+n_2)^4} u_{n_1}^2 + \frac{n_1^2}{(n_1+n_2)^4} u_{n_2}^2$$



Similar considerations are derived for **gravimetric compositional measurements**

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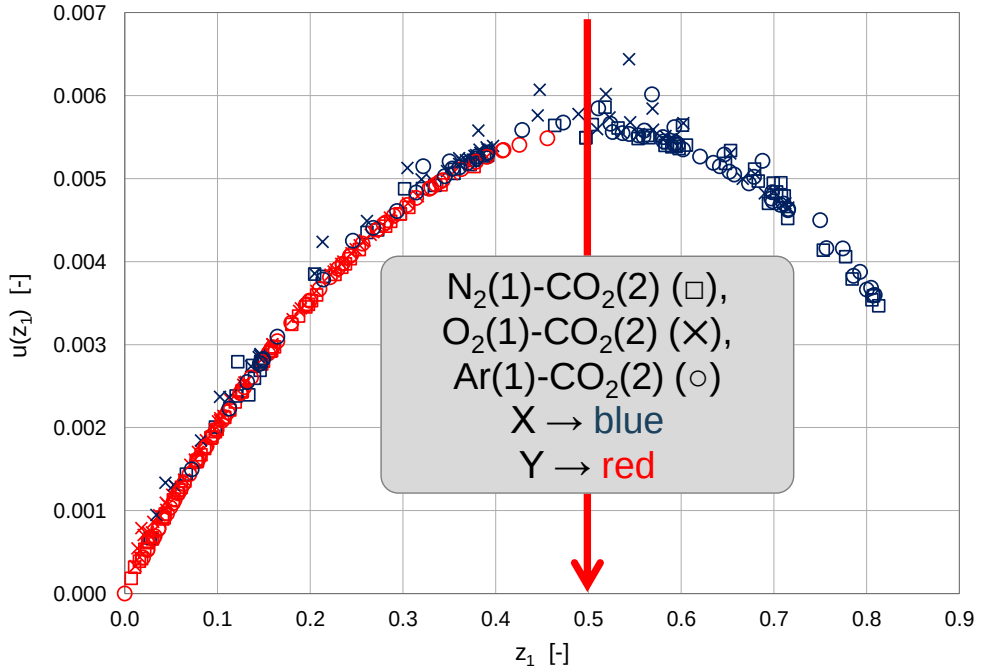
Optimization of models over VLE data

Experimental uncertainties of molar fractions

The analysis of our results has shown that:

1. In general, $\boldsymbol{u(z_i) = a \cdot z_i^2 + b \cdot z_i}$
2. Molar fractions of 0.5 have a maximum uncertainty: $\boldsymbol{(du(z_i)/dz_i)_{z_i=0.5} = 0}$
3. At the critical point ($x_i^{cr} = y_i^{cr}$):
$$\boldsymbol{u(x_i^{cr}) = u(y_i^{cr})}$$
4. In general, at non-critical conditions:
$$\boldsymbol{u(x_i) \neq u(y_i)}$$



The application of these outcomes enables the estimation of molar fractions uncertainty ($u(z_i)$) of literature data for which it is only specified a **maximum molar fraction uncertainty, associated to the specific mole fraction z***, $u_{max}(z^*)$:

$$u(z_i) = u_{max}(z_i^*)\frac{z_i^2 - z_i}{z_i^{*2} - z_i^*}$$

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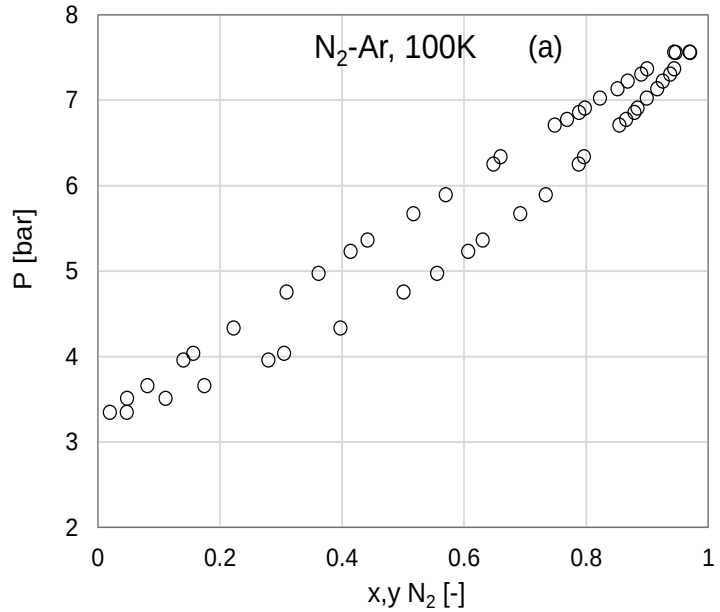
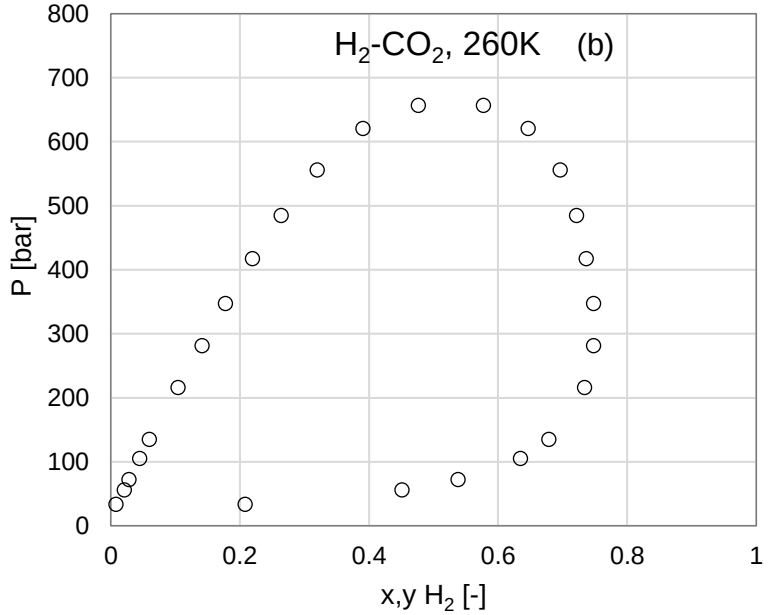
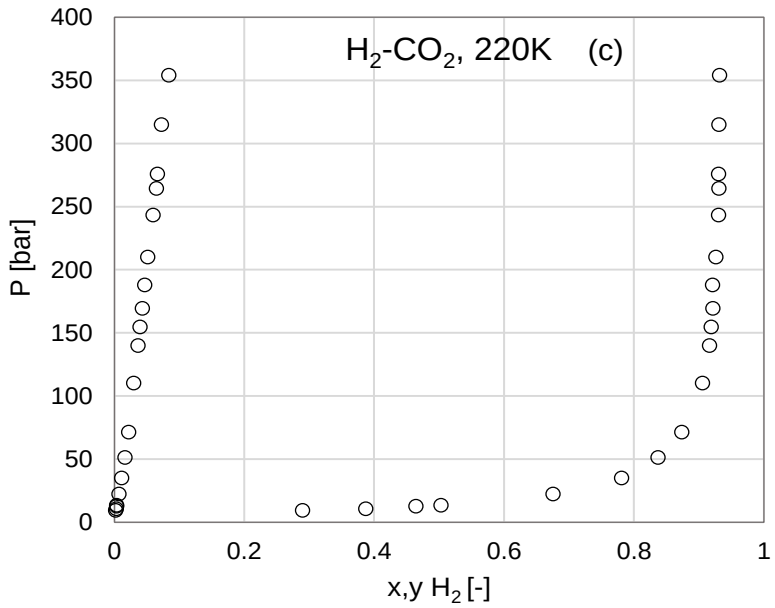
Optimization of models over VLE data

Maximum likelihood method and experimental uncertainties







$$\sigma^2_{y_{1,i}} = \left(u^e_{y_{1,i}}\right)^2 + \left(\frac{\partial y_1}{\partial P}\right)^2_{T_i,\beta} \left(u^e_{P_i}\right)^2 + \left(\frac{\partial y_1}{\partial T}\right)^2_{P_i,\beta} \left(u^e_{T_i}\right)^2$$

$$\sigma^2_{x_{1,i}} = \left(u^e_{x_{1,i}}\right)^2 + \left(\frac{\partial x_1}{\partial P}\right)^2_{T_i,\overline{\beta}} \left(u^e_{P_i}\right)^2 + \left(\frac{\partial x_1}{\partial T}\right)^2_{P_i,\overline{\beta}} \left(u^e_{T_i}\right)^2$$

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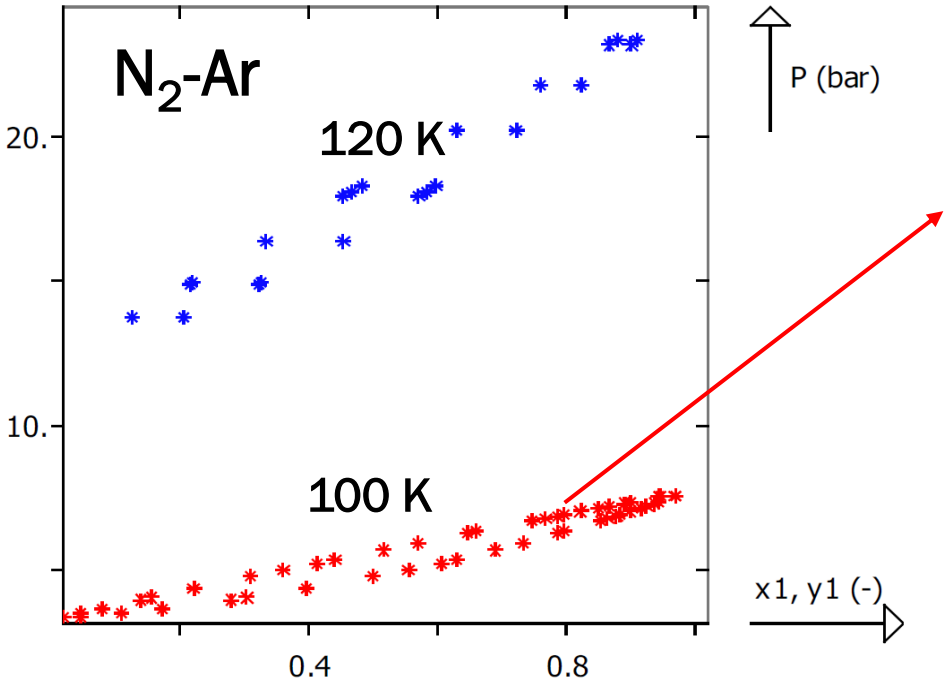
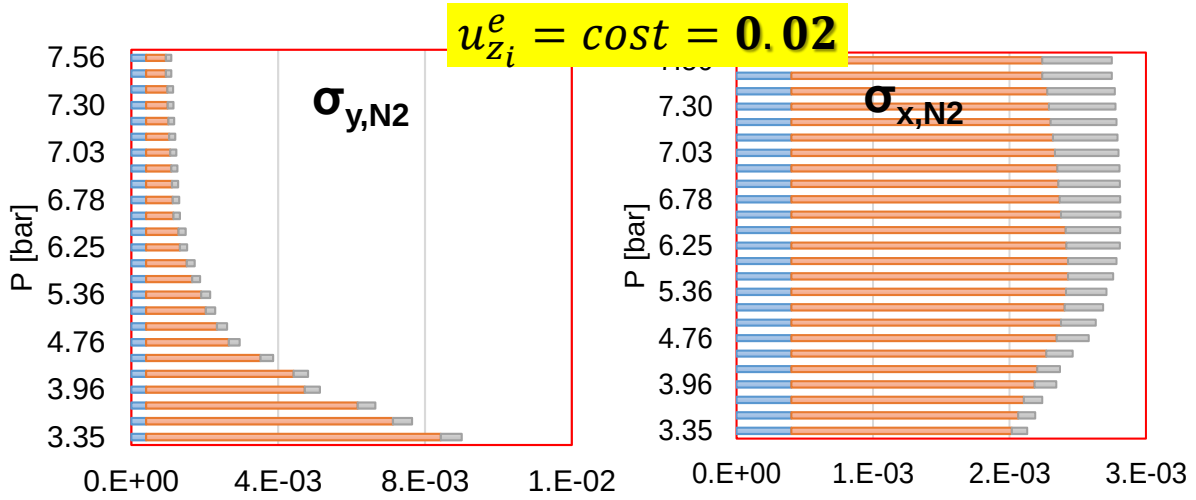
Optimization of models over VLE data

Maximum likelihood method and experimental uncertainties

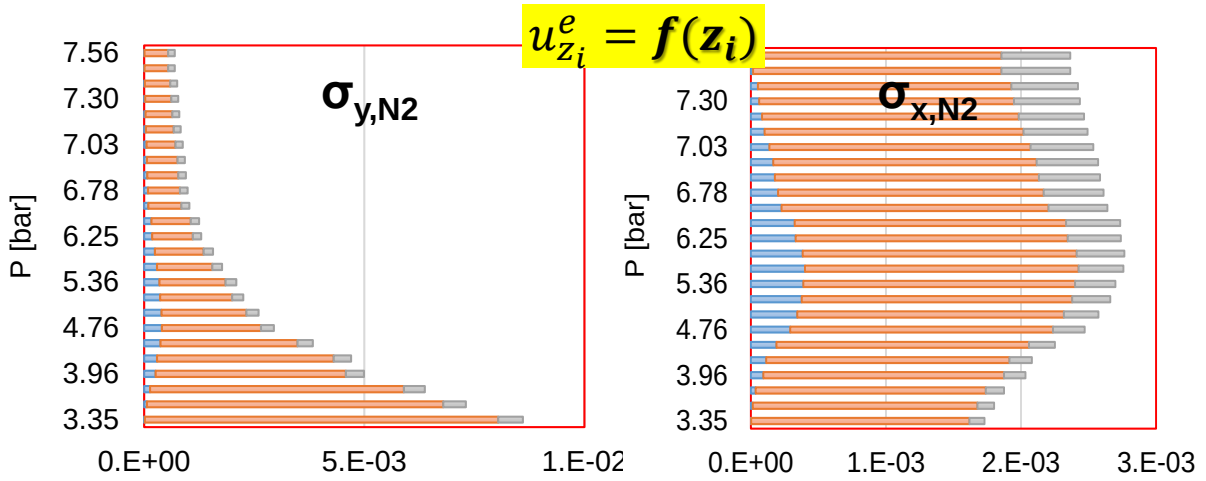
$$\sigma^2_{z_{1,i}} = \left(u^e_{z_{1,i}}\right)^2 + \left(\frac{\partial z_1}{\partial P}\right)^2_{T_i,\bar{\beta}} \left(\underbrace{u^e_{P_i}}_{\mathbf{0.2bar}}\right)^2 + \left(\frac{\partial z_1}{\partial T}\right)^2_{P_i,\bar{\beta}} \left(\underbrace{u^e_{T_i}}_{\mathbf{0.2K}}\right)^2$$



$u^e_{z_i} = cost = \mathbf{0.02}$



$u^e_{z_i} = \boldsymbol{f(z_i)}$



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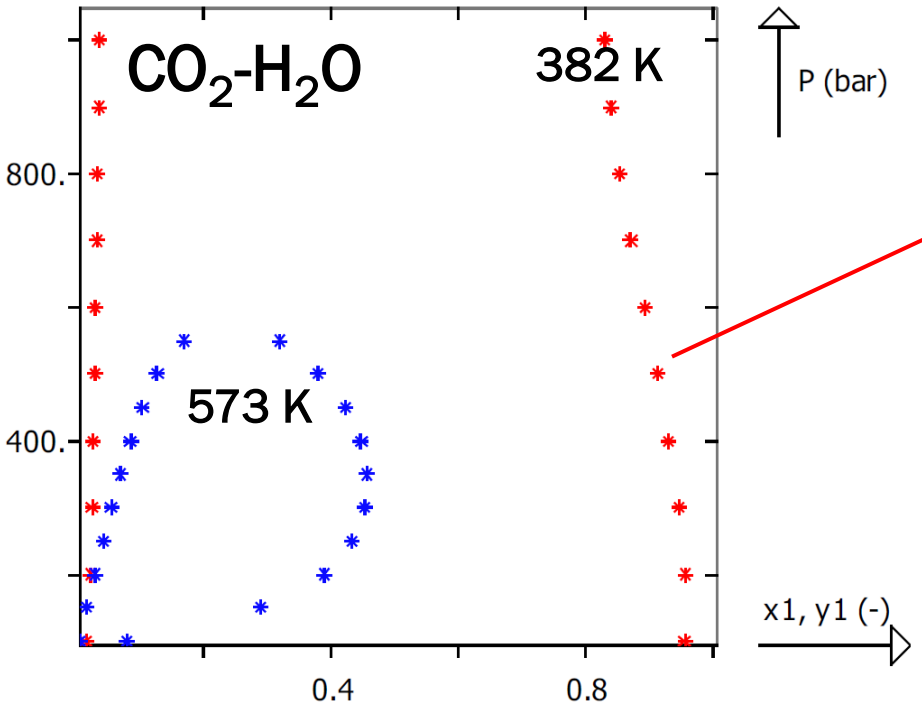
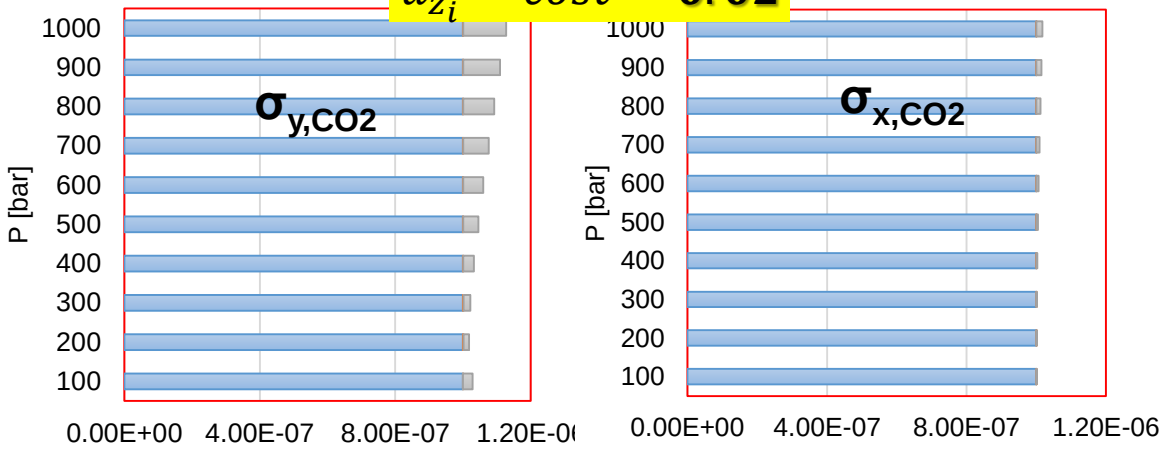
Optimization of models over VLE data

Maximum likelihood method and experimental uncertainties

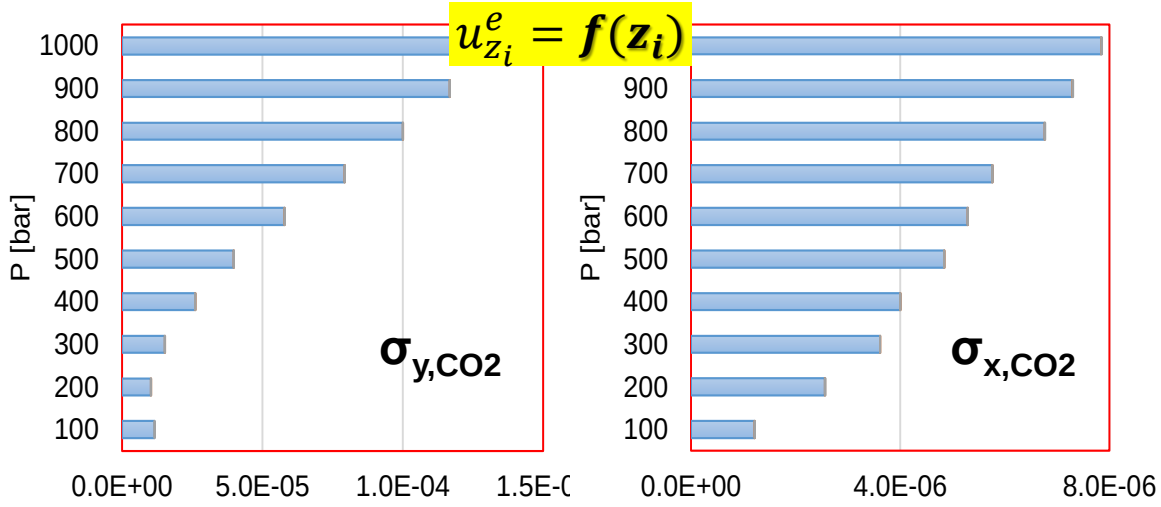
$$\sigma^2_{z_{1,i}} = \left(u^e_{z_{1,i}}\right)^2 + \left(\frac{\partial z_1}{\partial P}\right)^2_{T_i,\bar{\beta}} \left(\underbrace{u^e_{P_i}}_{0.2bar}\right)^2 + \left(\frac{\partial z_1}{\partial T}\right)^2_{P_i,\bar{\beta}} \left(\underbrace{u^e_{T_i}}_{0.2K}\right)^2$$



$u^e_{z_i} = cost = 0.02$



$u^e_{z_i} = f(z_i)$



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Optimization of models over VLE data
Maximum likelihood method and experimental uncertainties

- It can be stated that the application of MLM positively damps the highest non-linearities of the optimization problem, under-weighting in a more relevant way the deviations at the critical region of the phase diagram.
- Thus, we have seen that the contribution of molar fraction uncertainties:
  - *is comparable to that of pressure and temperature* ***in binary VLE systems containing two subcritical components***
  - *is much greater than that of pressure and temperature uncertainties, in the definition of molar fraction variances,* ***in binary VLE systems containing supercritical components***
- The use of uncertainties specific to each molar fraction, rather than overall constant uncertainties defined for a global set of data, leads to different results of the optimization (different optimal parameters).

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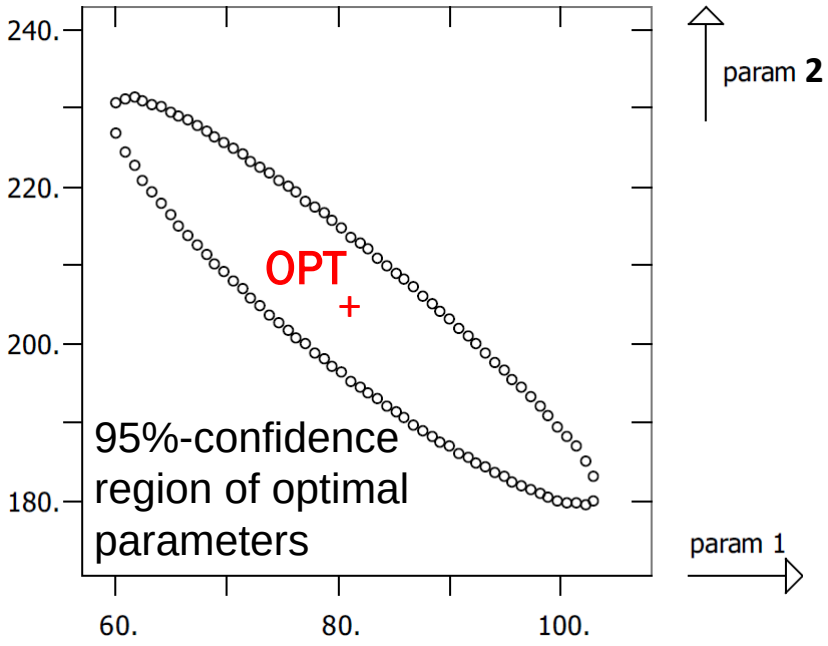
Optimization of models over VLE data

The uncertainty of optimal parameters β_{opt}



$$S(\boldsymbol{\beta})_\alpha = S(\boldsymbol{\beta}_{opt})\left[1 + \frac{NP}{n_e - NP} F_\alpha(NP, n_e - NP)\right]$$

- ⇧ **numerosity (NP)** $\Longrightarrow$ ⇩ $S(\beta)_\alpha$
- ⇩ $\boldsymbol{S(\beta_{opt})}$ $\Longrightarrow$ ⇩ $S(\beta)_\alpha$
- ⇧ **data uncertainty** $\Longrightarrow$ ⇧ difference between the curvature of the MLM and LSM objective functions around the minimum:
  - when the EoS is able to represent experimental data, MLM and LSM optimal parameters are similar but **MLM** leads to **more extended regions of uncertainties**
  - when the model is not able to represent experimental data, the conclusion is not straightforward. However, **MLM** leads **more regular uncertainty regions**.

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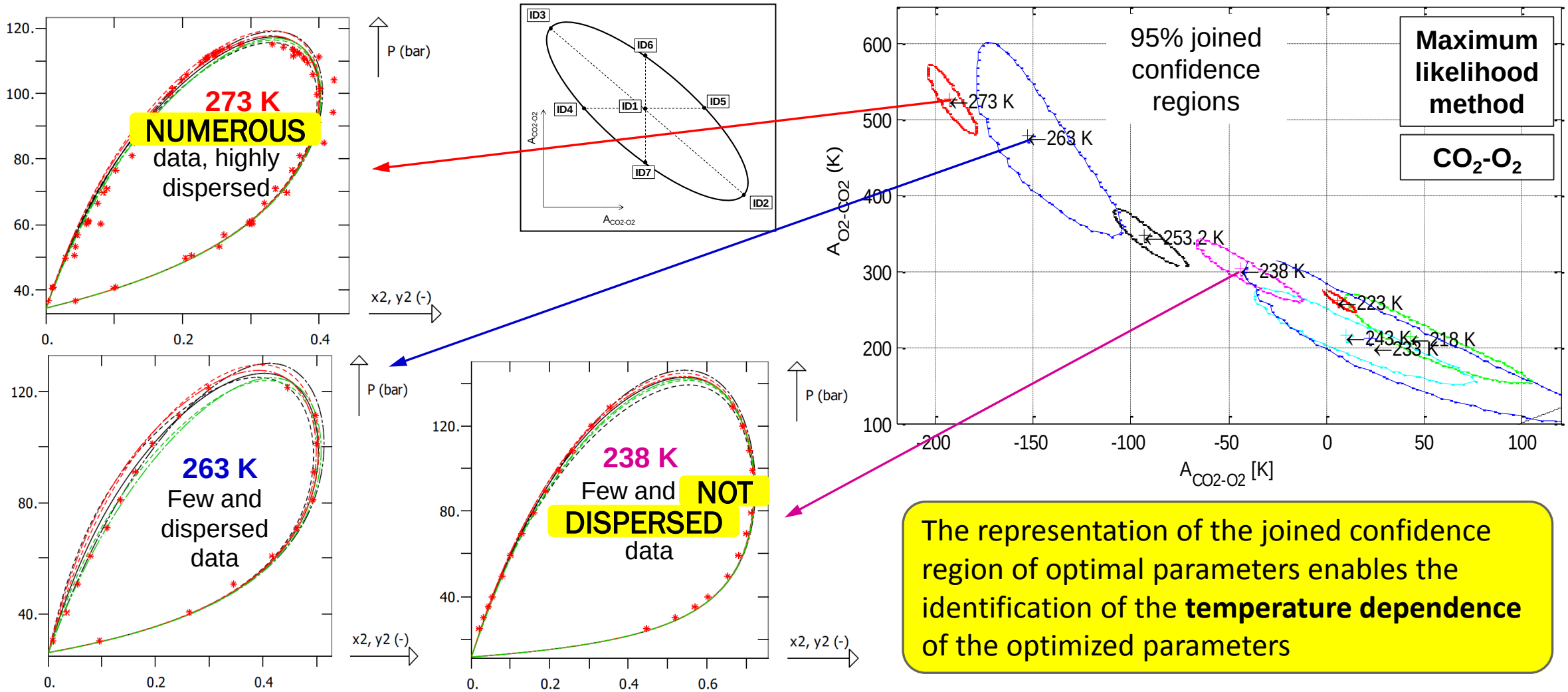
Optimization of models over VLE data

The effect of the numerosity and dispersion of data



The representation of the joined confidence region of optimal parameters enables the identification of the **temperature dependence** of the optimized parameters

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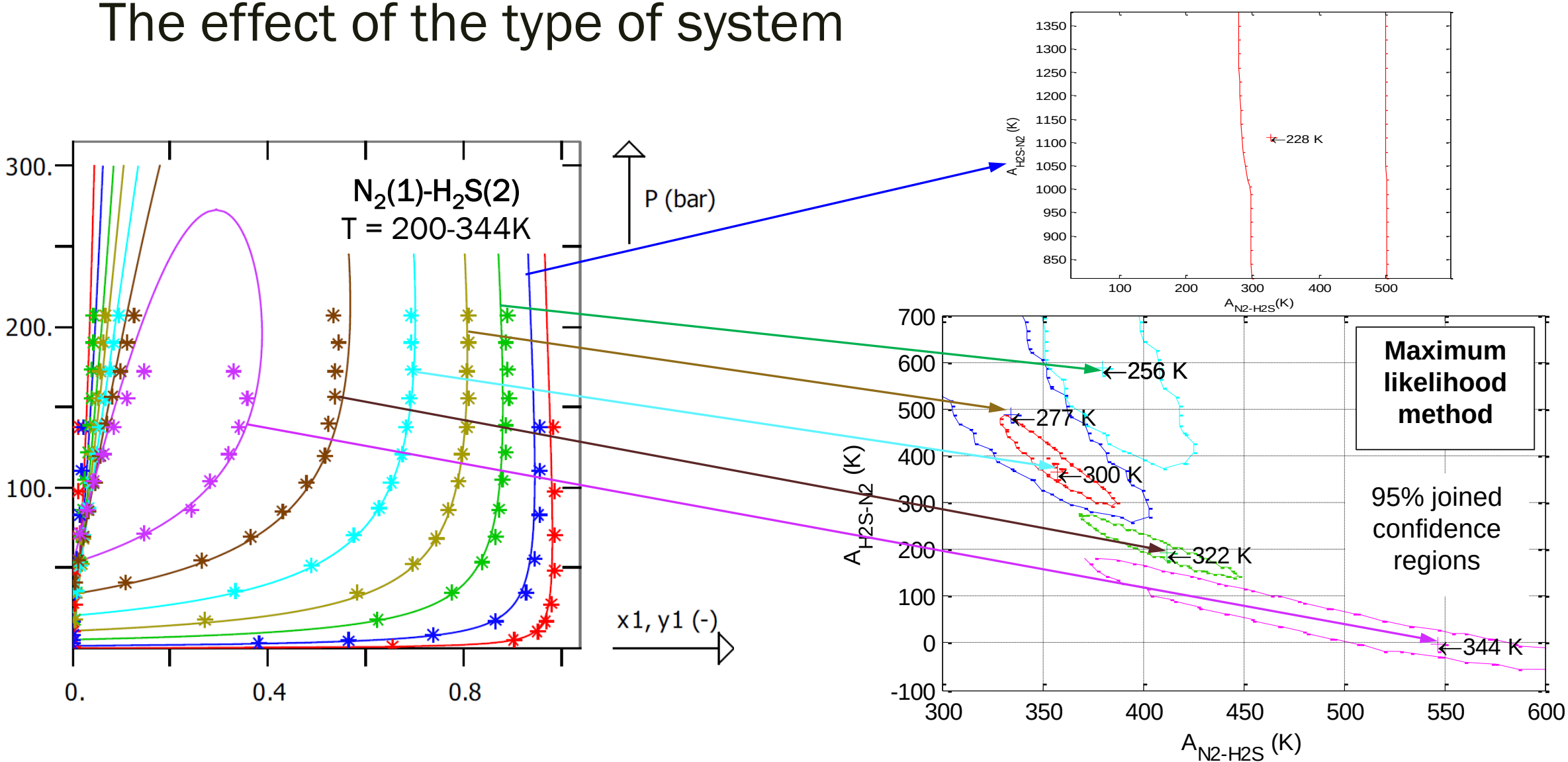
Optimization of models over VLE data

The effect of the type of system



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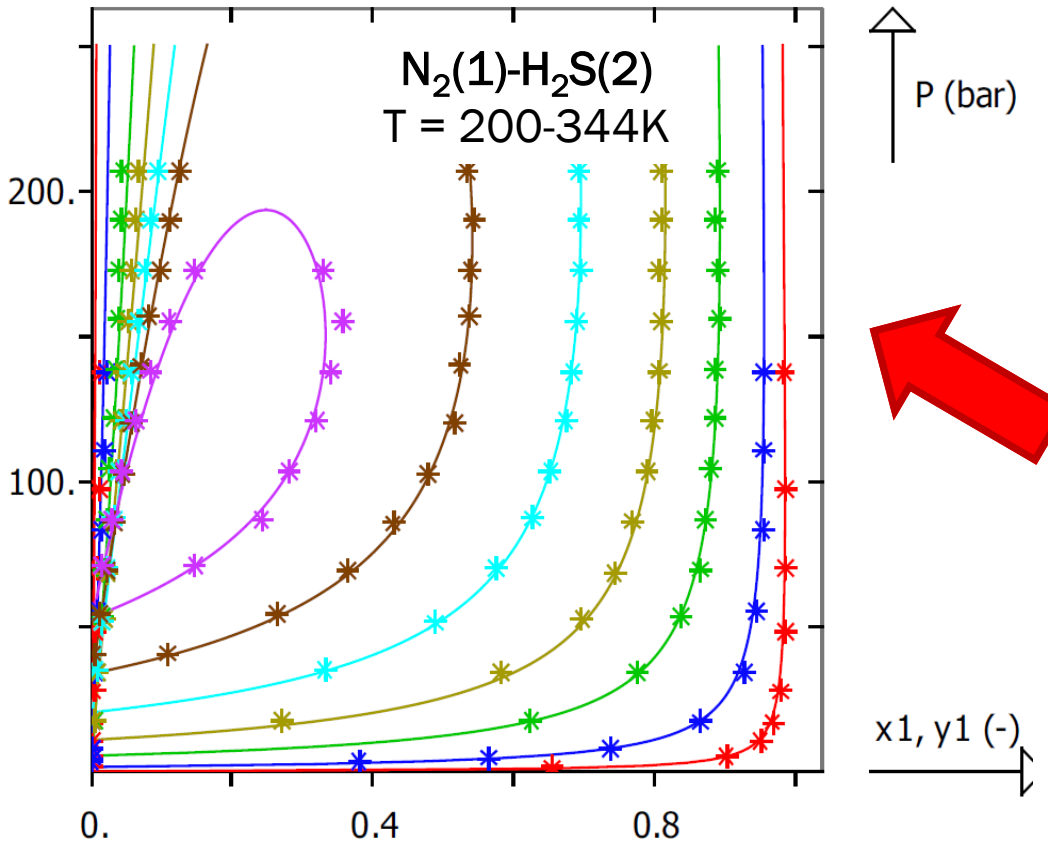
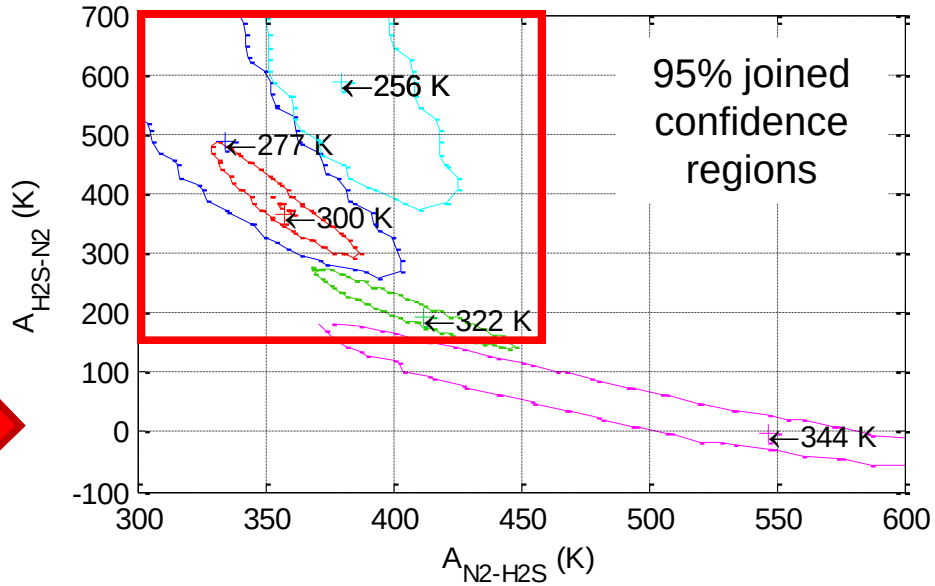
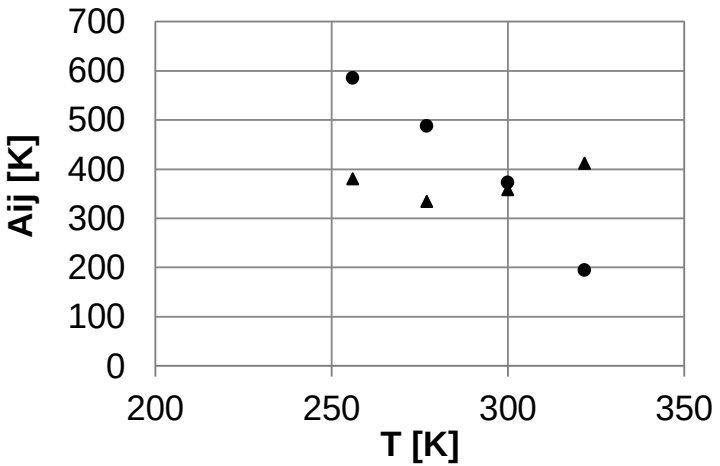
Optimization of models over VLE data

The effect of the type of system







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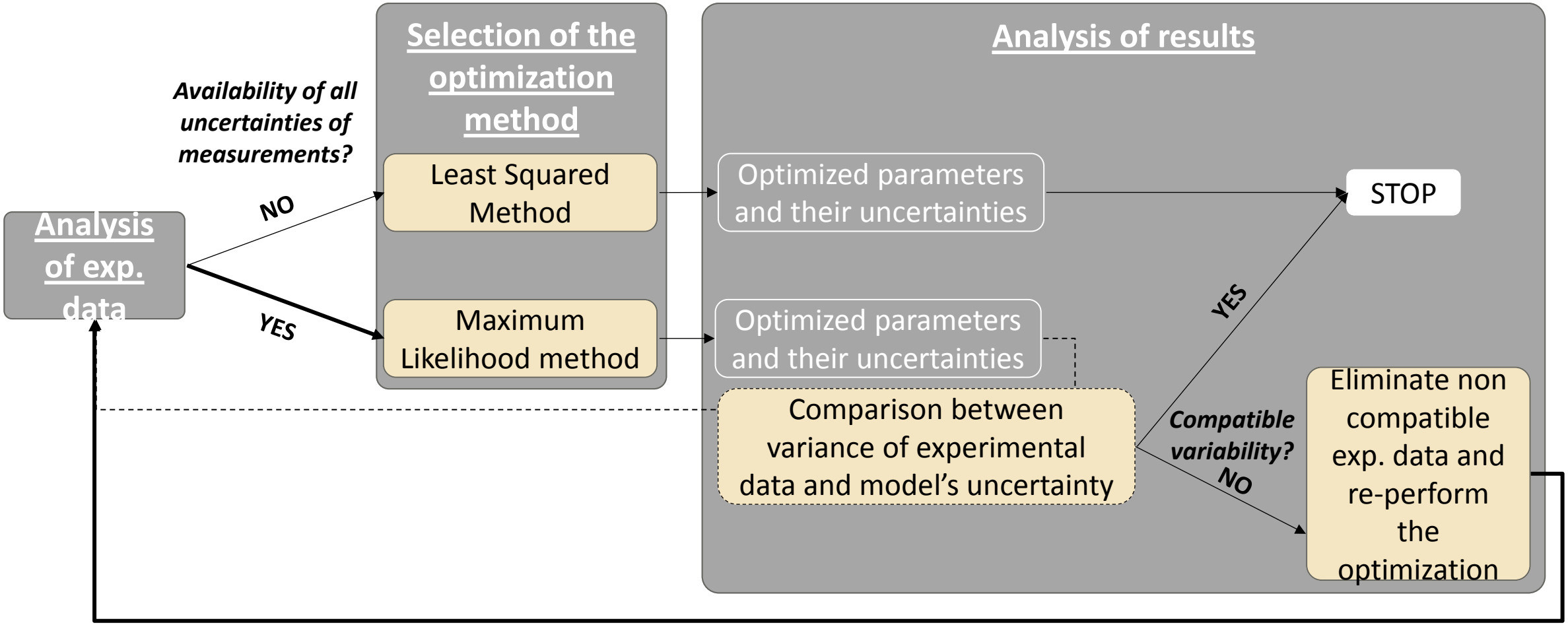
Optimization of model parameters
Conclusions



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THANKS

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