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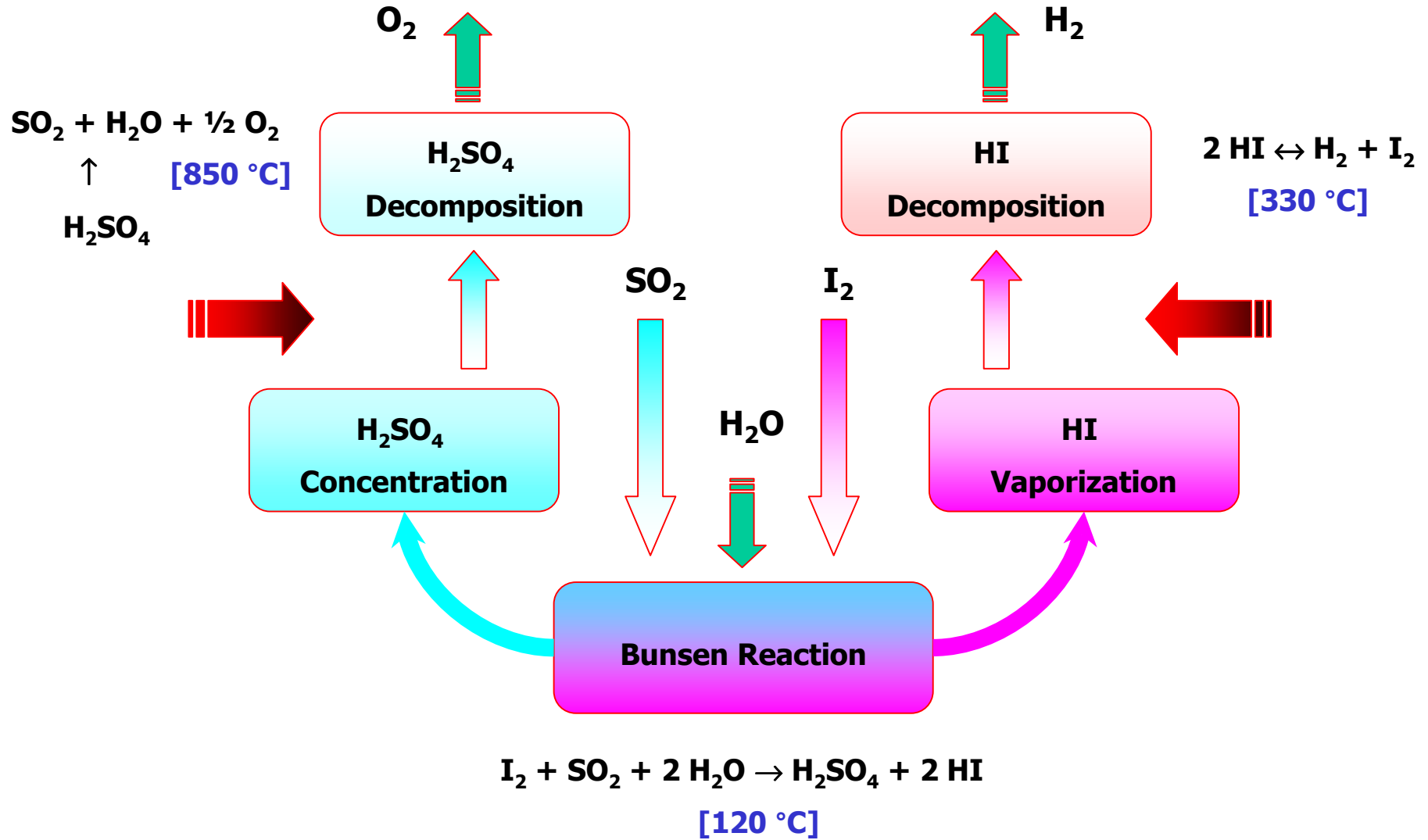
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# Thermodynamics modeling of the HIx part of the Iodine – Sulfur thermocycle

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# Iodine – sulfur thermocycle for hydrogen production



# Thermodynamics challenges of HIX system

“ ...The sulfuric acid decomposition section of this process can be simulated accurately, but other sections (acid generation and hydrogen iodide decomposition) illustrate the difficulty of modeling phase behavior, particularly liquid-phase immiscibility, in complex electrolyte systems.”

(Mathias 2005, Fluid Phase Equilibria)

**HIX = HI/H<sub>2</sub>O/I<sub>2</sub>** (nominal : HI / 5 H<sub>2</sub>O / 4 I<sub>2</sub>)

- ✓ Multiphase behavior (vapor – liquid – liquid – solid),
- ✓ H<sub>2</sub>O – I<sub>2</sub> : highly immiscible liquid – liquid equilibrium system,
- ✓ HI – I<sub>2</sub> : solid – liquid equilibrium system,
- ✓ H<sub>2</sub>O – HI
  - Maximum boiling / low pressure azeotrope,
  - Strong electrolytic system,
  - Liquid – liquid equilibrium,
- ✓ The ternary mixture has two separate liquid – liquid regions,
- ✓ Solvation reactions occur as well as poly-iodides formation in the solution.

# Outline

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- ✓ Iodine-Sulfure thermochemical cycle for hydrogen production
- ✓ HIX modeling Challenges
- ✓ **Proposed model and identification methodology**
- ✓ **Validation vs experimental literature data**
- ✓ **Conclusions and perspectives**

# Hix modeling

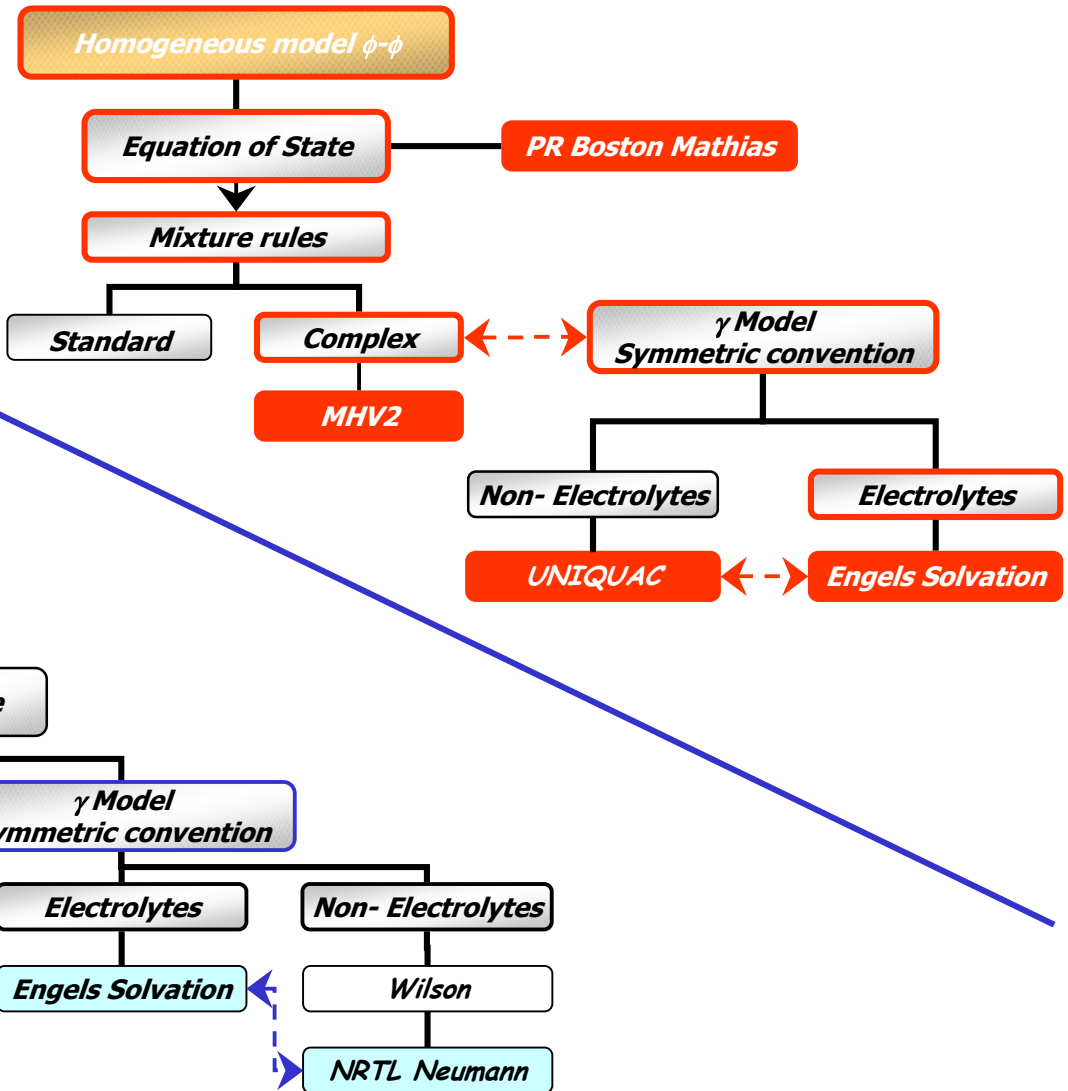
## New models:

**UNIQUAC Solvation (UQSolv)**

## Literature models:

**Neumann : Engels + NRTL**

**Mathias et al. : electrolyte**



# Advantages of the model

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- ✓  $\phi$ - $\phi$  approach:
  - No extrapolation of the vapor pressure law above critical points
  - Correct handling of mixture phase behavior above HI critical point ( $T_c=423\text{K}$ )
- ✓ Equation of state: Peng Robinson w/ Boston Mathias  $\alpha$  function
  - Accurate behavior of pure components above critical points
- ✓ Mixing rule: MHV2 including non ideal liquid phase behavior via a  $G^{\text{ex}}$  model
- ✓ Activity coefficient model: Engels solvation
  - Electrolytic model but with symmetric convention so as to span the whole composition range
  - Introduces solvation complexes with several solvents
- ✓ Activity coefficient model: UNIQUAC vs NRTL:
  - Combinatorial term handles steric effect
  - Residual term accounts for non ideal liquid phase behavior (as NRTL)

# Simulis Thermodynamics component

**Editeur de calculator thermodynamique**

### Actions et propriétés du calculator

**Packages de calculator**

- Ouvrir le gestionnaire de package...
- Importer un package...
- Construire un package...
- Sélectionner un package CAPE-OPEN

**Modifications**

- Défaire
- Refaire

**Services**

- Calculer
- Générer un fichier PSF

Nom:

Commentaires:

CAPE-OPEN

### Calculator

Cette fenêtre permet de spécifier le contexte de votre calculator thermodynamique.

Nom:

Profil:

Assistant thermodynamique

Utiliser un modèle spécifique eau pure

**Avancé**

Modèle eau-hydrocarbures

Sol A:

Sol B:

Modèle thermodynamique:

Règles de mélange:

Volume molaire liquide:

Equation d'état phase gaz:

Modèle des coefficients d'activité:

Fugacité liquide pur état standard:

Propriétés de transport:

Modèle thermodynamique utilisateur:

Index du modèle:

Calcul enthalpique:

Commentaires:

Constituants | **Modèle** | Paramètres

OK Annuler



# Model parameter identification procedure

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## ✓ Three binary mixtures

- $\text{H}_2\text{O} - \text{I}_2$ : only UNIQUAC binary interaction parameters
- $\text{HI} - \text{I}_2$ : only UNIQUAC binary interaction parameters
- $\text{H}_2\text{O} - \text{HI}$ :
  - $\text{HI}$  solvation by  $\text{H}_2\text{O} \rightarrow$  equilibrium constant and solvation number



- UNIQUAC binary interaction parameters for  $\text{H}_2\text{O}$ ,  $\text{HI}$  and the solvation complex  $\text{C}$

## ✓ Ternary mixture

- $\text{H}_2\text{O} - \text{HI} - \text{I}_2$ : refined parameter values

# Available experimental data



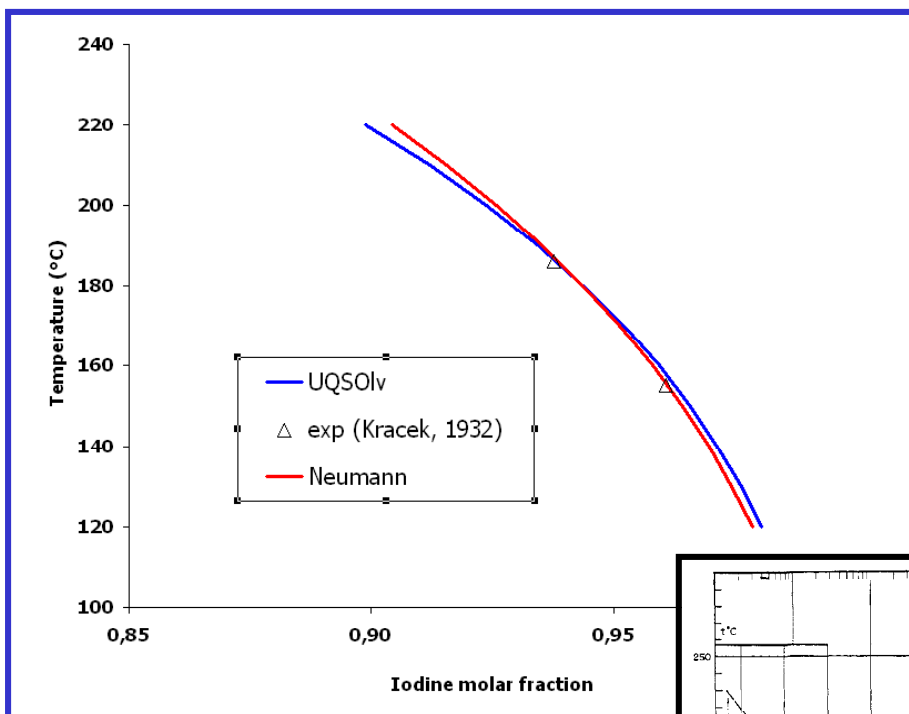
Fitting data



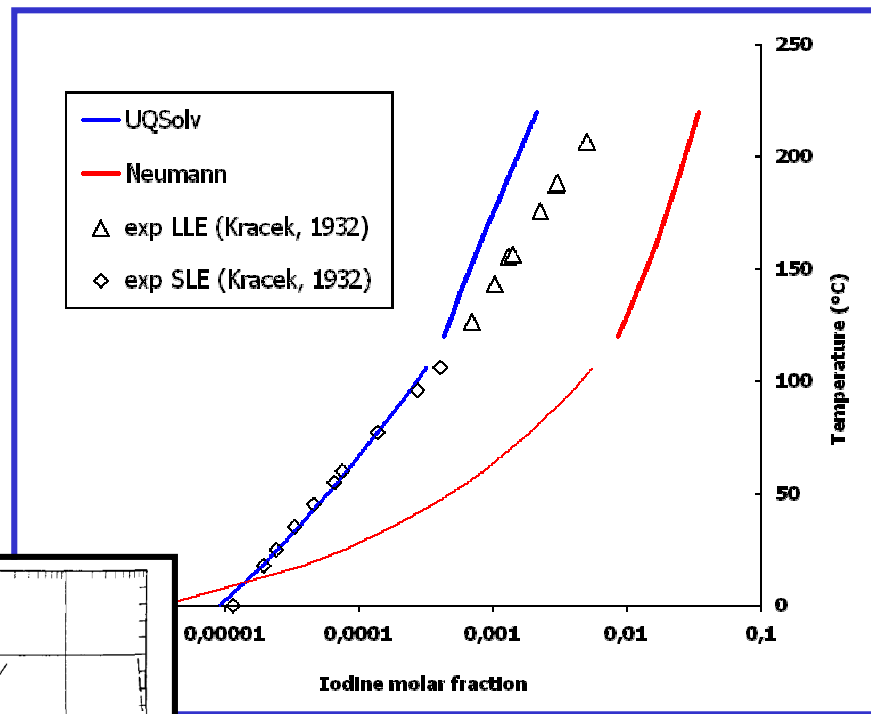
validation

	Data	Data number	Data sources
<b>H<sub>2</sub>O – HI</b>	VLE	38 $T = f(P, \mathbf{x}, \mathbf{y})$	Pascal (1926)
	VLE	21 $P = f(T, \mathbf{x}, \mathbf{y})$	Haase (1963)
	VLE	80 $P = f(T, \mathbf{x})$	Wüster (1979)
	$\Delta H$	13	Vanderzee & Gier (1974)
	LLE	6 $T = f(\mathbf{x})$	Haase (1963) / Norman (1985)
<b>H<sub>2</sub>O – I<sub>2</sub></b>	LLE	10 $T = f(\mathbf{x})$	Kracek (1932)
	LSE	10 $T = f(\mathbf{x})$	Kracek (1932)
<b>HI – I<sub>2</sub></b>	LSE	5 $T = f(\mathbf{x})$	O'keefe & Norman (1982)
<b>H<sub>2</sub>O – HI – I<sub>2</sub></b>	VLE	280 $P = f(T, \mathbf{x})$	Neumann (1986)
	LLE	12	Norman (1984)

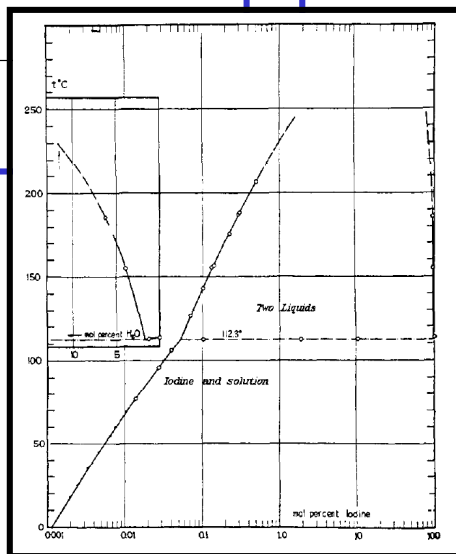
# H<sub>2</sub>O – I<sub>2</sub> identification results



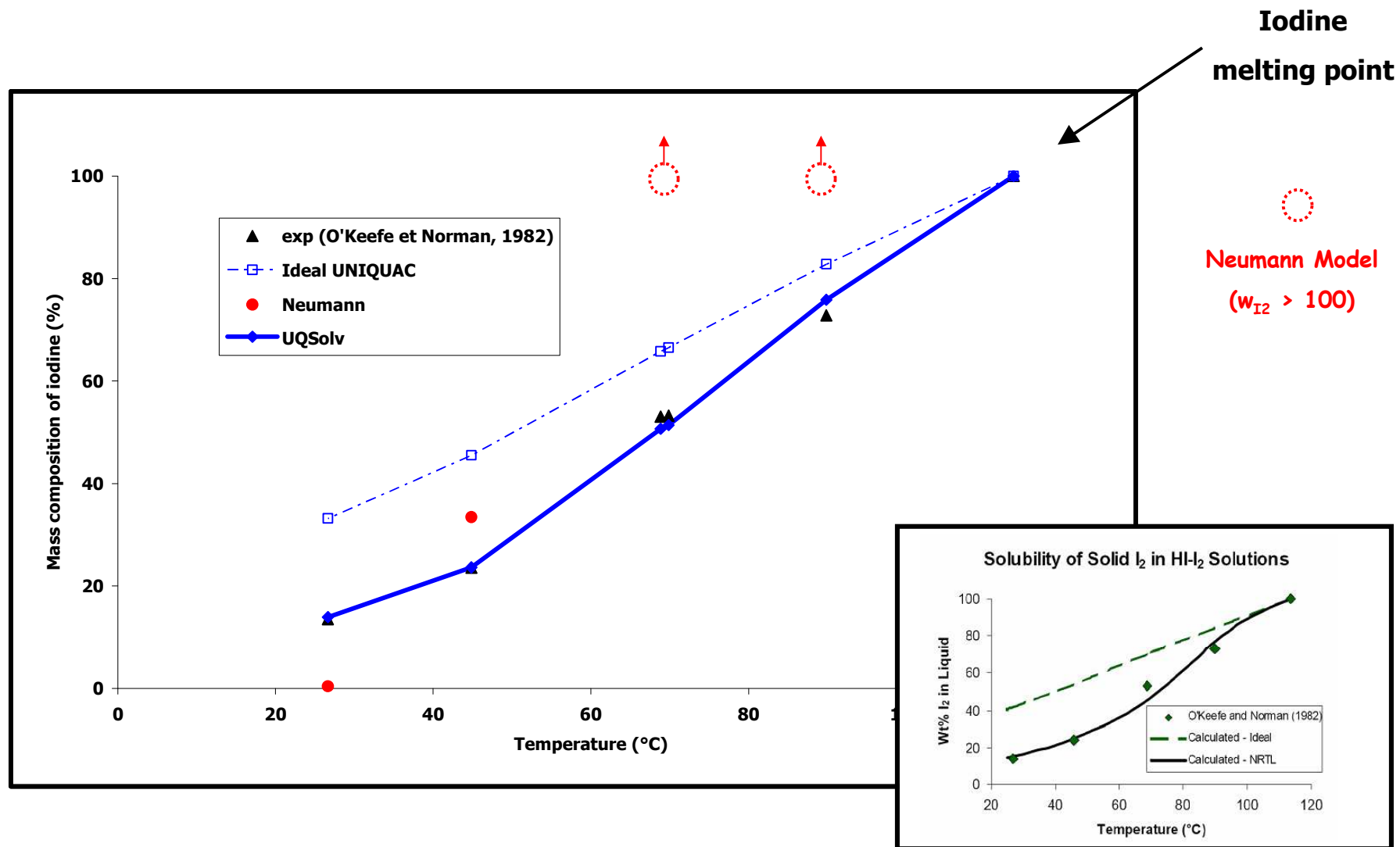
Iodine phase



Model prediction of iodine solubility in aqueous solution

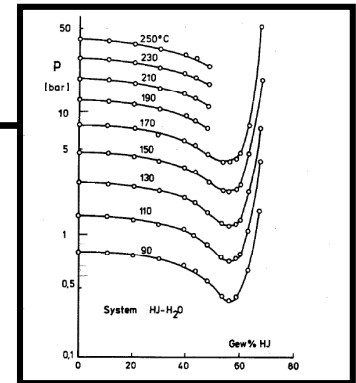
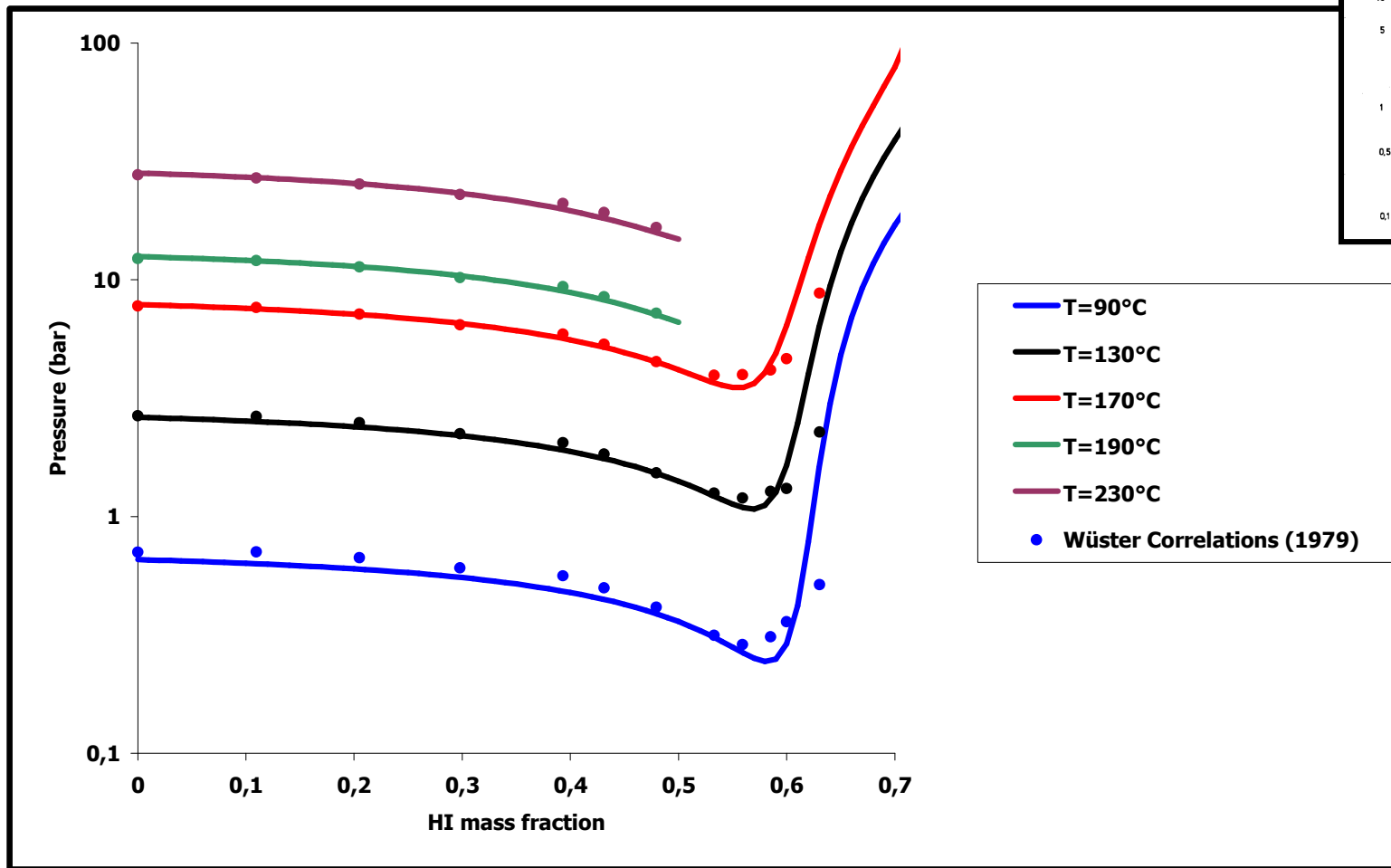


# HI – I<sub>2</sub> identification results



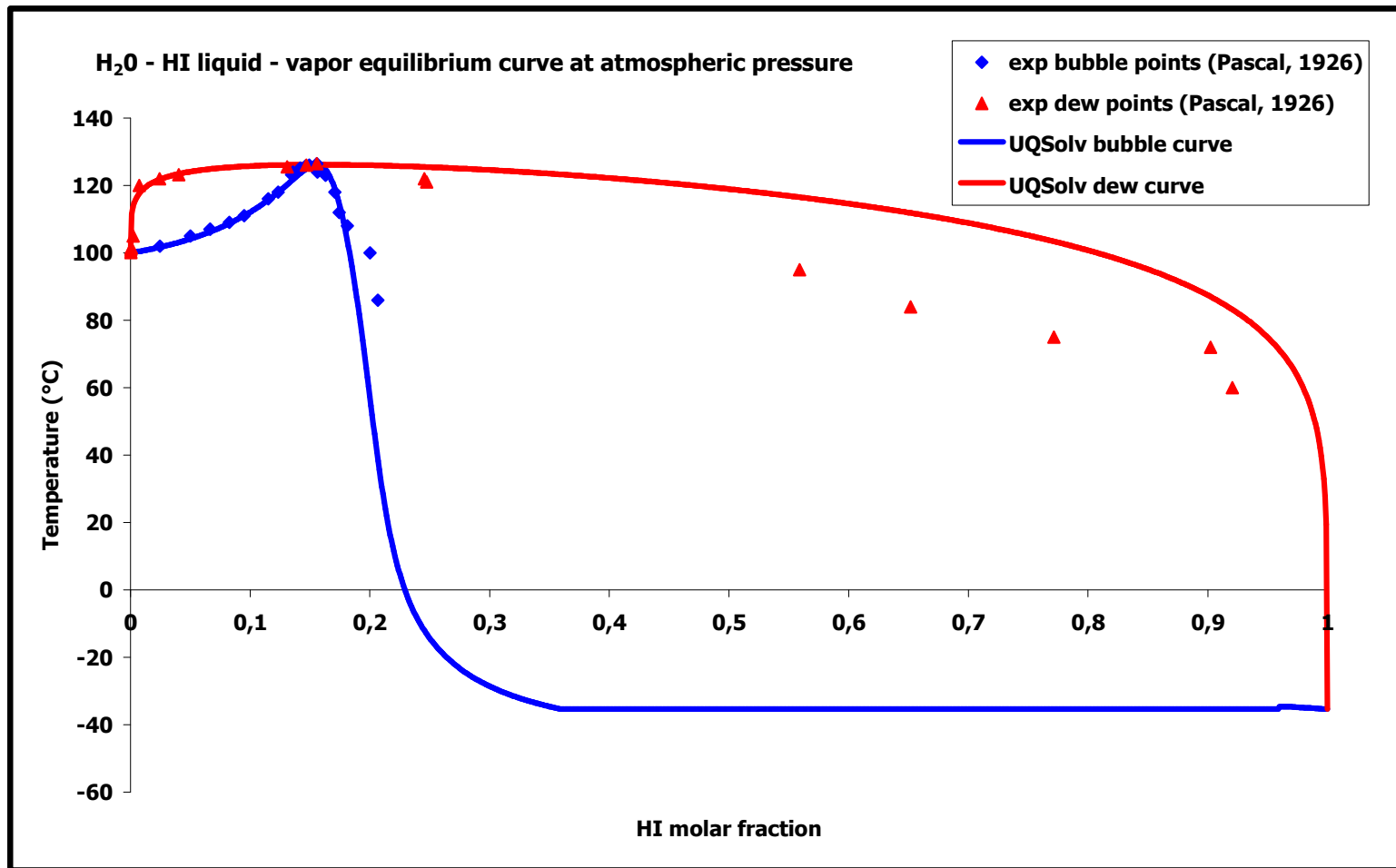
# H<sub>2</sub>O – HI identification results 1/2

Good agreement up to the azeotrope



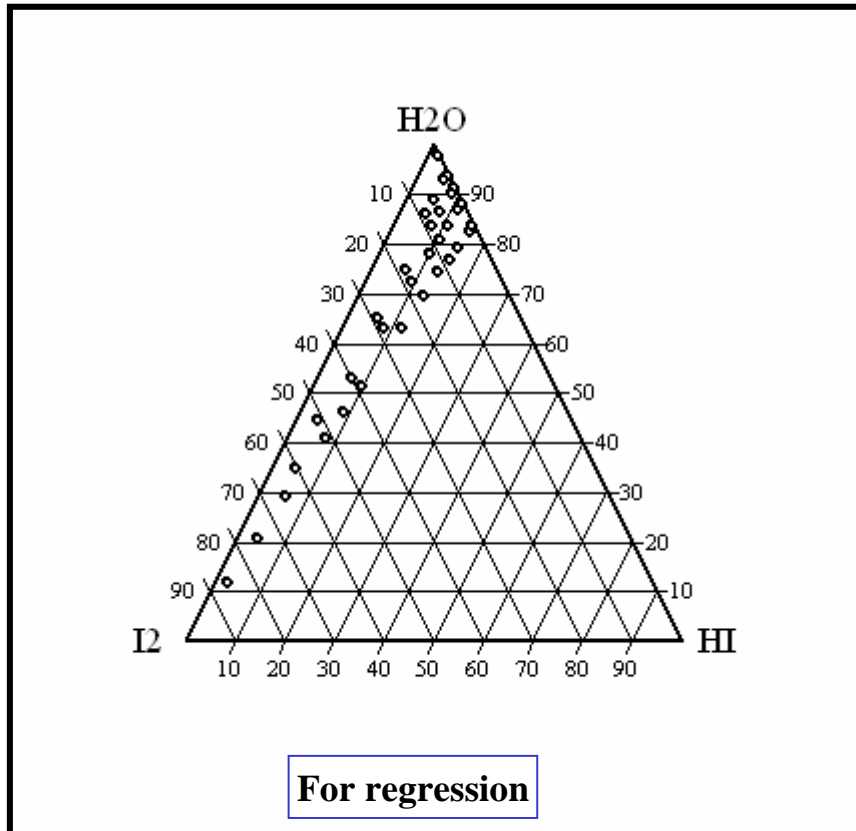
- T=90°C
- T=130°C
- T=170°C
- T=190°C
- T=230°C
- Wüster Correlations (1979)

## H<sub>2</sub>O – HI identification results 2/2

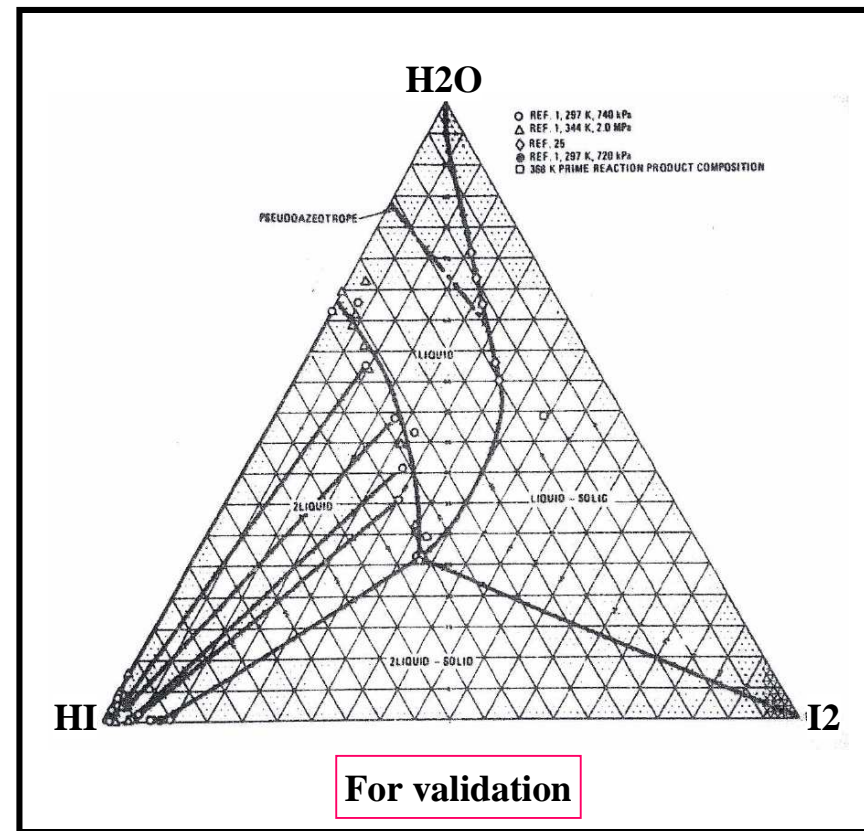


Model prediction of LVE curve at atmospheric pressure

# Ternary system H<sub>2</sub>O – HI – I<sub>2</sub>



Engels experimental data  
(0,017 < x<sub>HI</sub> < 0,159)



Liquid – liquid equilibrium data  
(Norman, 1984)

## H<sub>2</sub>O – HI – I<sub>2</sub> identification results 1/2

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Keeping identified parameters for :

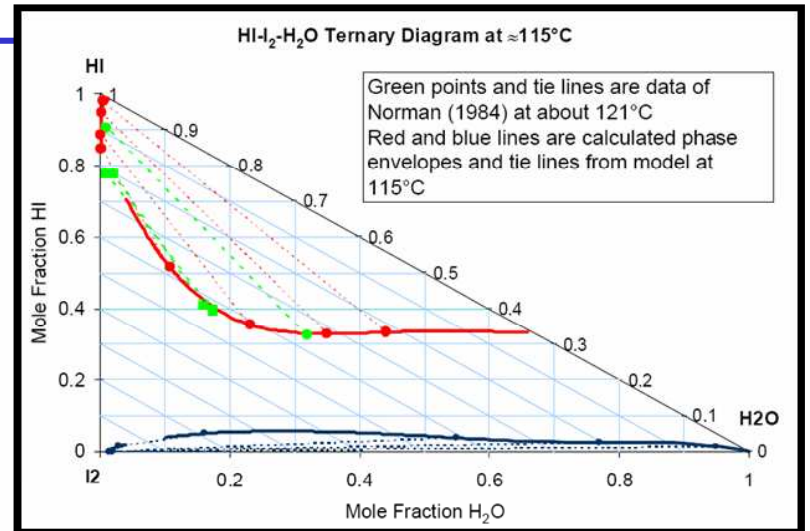
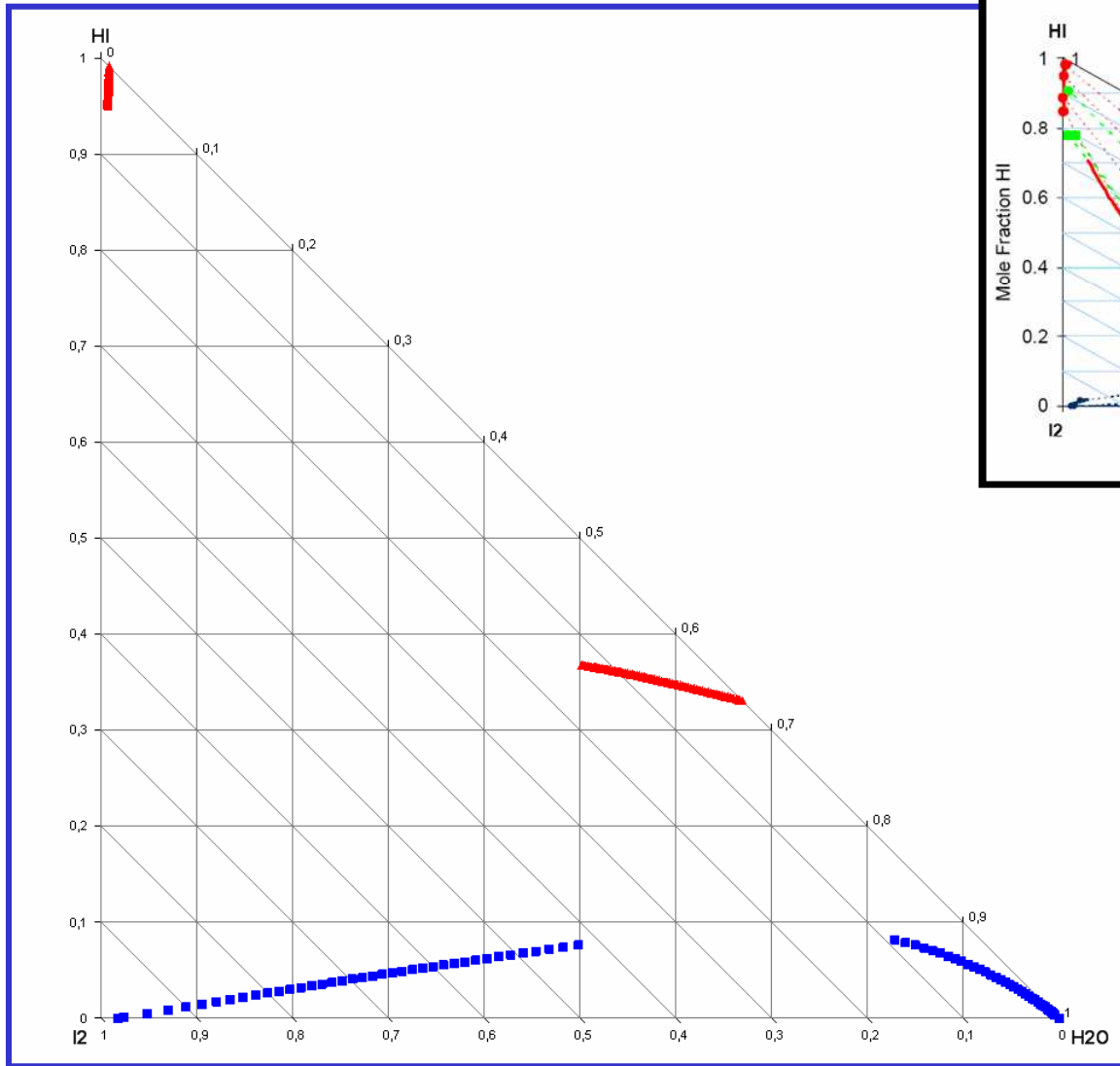
- ✓ Liquid – liquid equilibrium (H<sub>2</sub>O – I<sub>2</sub>)
- ✓ Solid – liquid equilibrium (HI – I<sub>2</sub>)
- ✓ Vapor – liquid equilibrium (H<sub>2</sub>O – HI) with solvation (m H<sub>2</sub>O + HI ⇌ 2C)

$$\text{Criterion} = \sum_{N_p} \left( \frac{P_{\text{exp}} - P_{\text{cal}}}{P_{\text{exp}}} \right)^2$$

	Average error (%)	Max error (%)	criterion
<b>Neumann</b>	9.53	62.24	6.50
<b>UQSolv</b>	8.18	44.83	3.73



# H<sub>2</sub>O – HI – I<sub>2</sub> identification results 2/2



## Conclusion and perspectives

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- ✓ HIx non ideal and electrolytic system is modeled by an equation of state (EOS) approach with complex mixing rules including  $G^{\text{EX}}$  models.
- ✓ The EOS approach is well suited with expected process T and P conditions that may be higher than the HI critical point.
- ✓ The liquid phase non ideal behavior is modelled combining Engels solvation equations suitable for any electrolyte composition and activity coefficient UNIQUAC equation.
- ✓ The resulting UQsolv model predict accurately most of the experimental data available and accurate, incl. LLE, LSE and LLVE for each binary and ternary system.
- ✓ Largest discrepancy is found for high HI concentration mixtures where experimental data is lacking or is uncertain.
- ✓ Improvements are under investigation:
  - Polyiodide ion formation
  - HI decomposition in  $I_2$  and  $H_2$  for the vapor phase rich in HI