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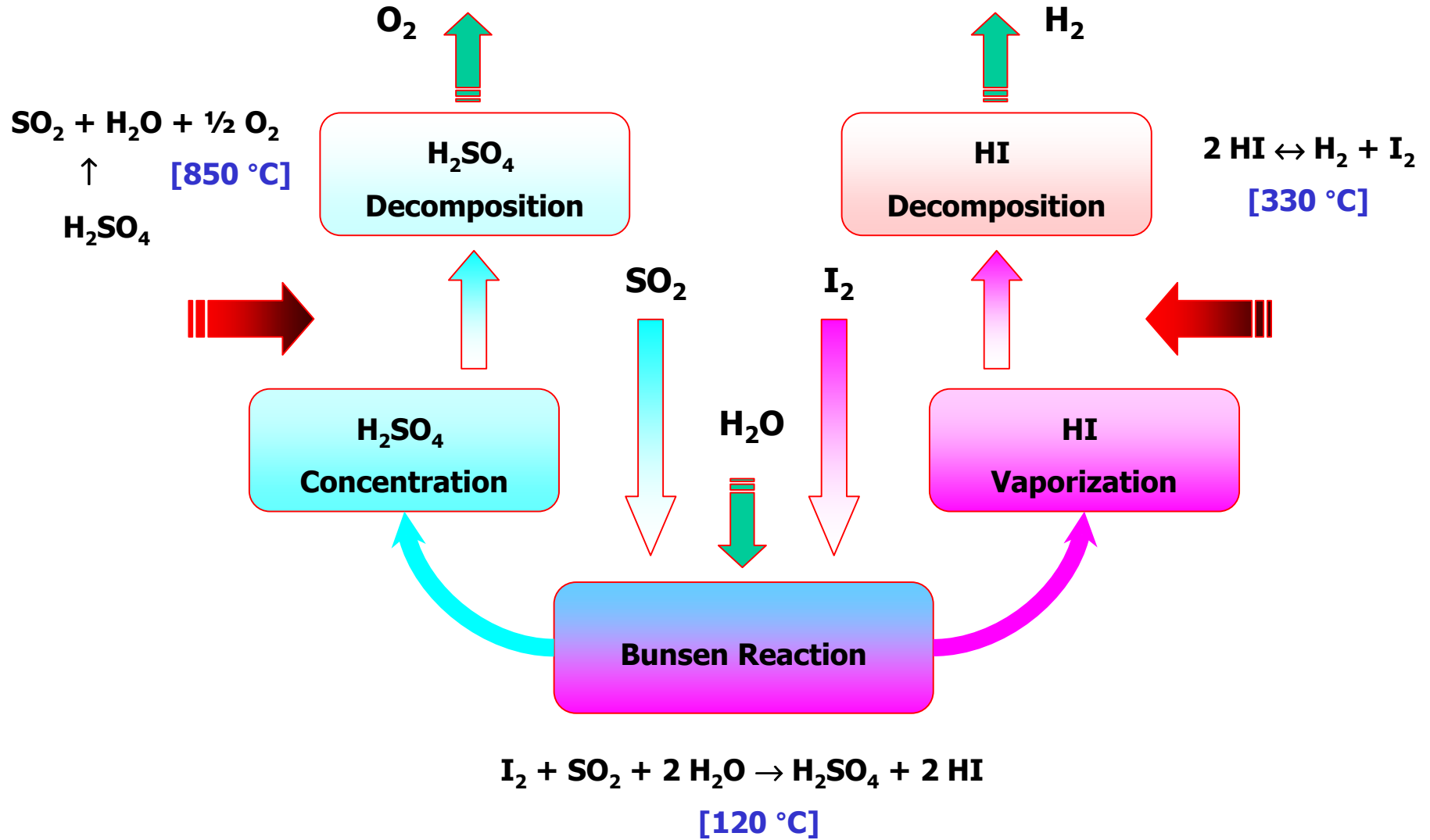
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Thermodynamics modeling of the HIx part of the Iodine – Sulfur thermocycle

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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)



- ✓ Multiphase behavior (vapor – liquid – liquid – solid),
- ✓ H₂O – I₂ : highly immiscible liquid – liquid equilibrium system,
- ✓ HI – I₂ : solid – liquid equilibrium system,
- ✓ H₂O – 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

- ✓ 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

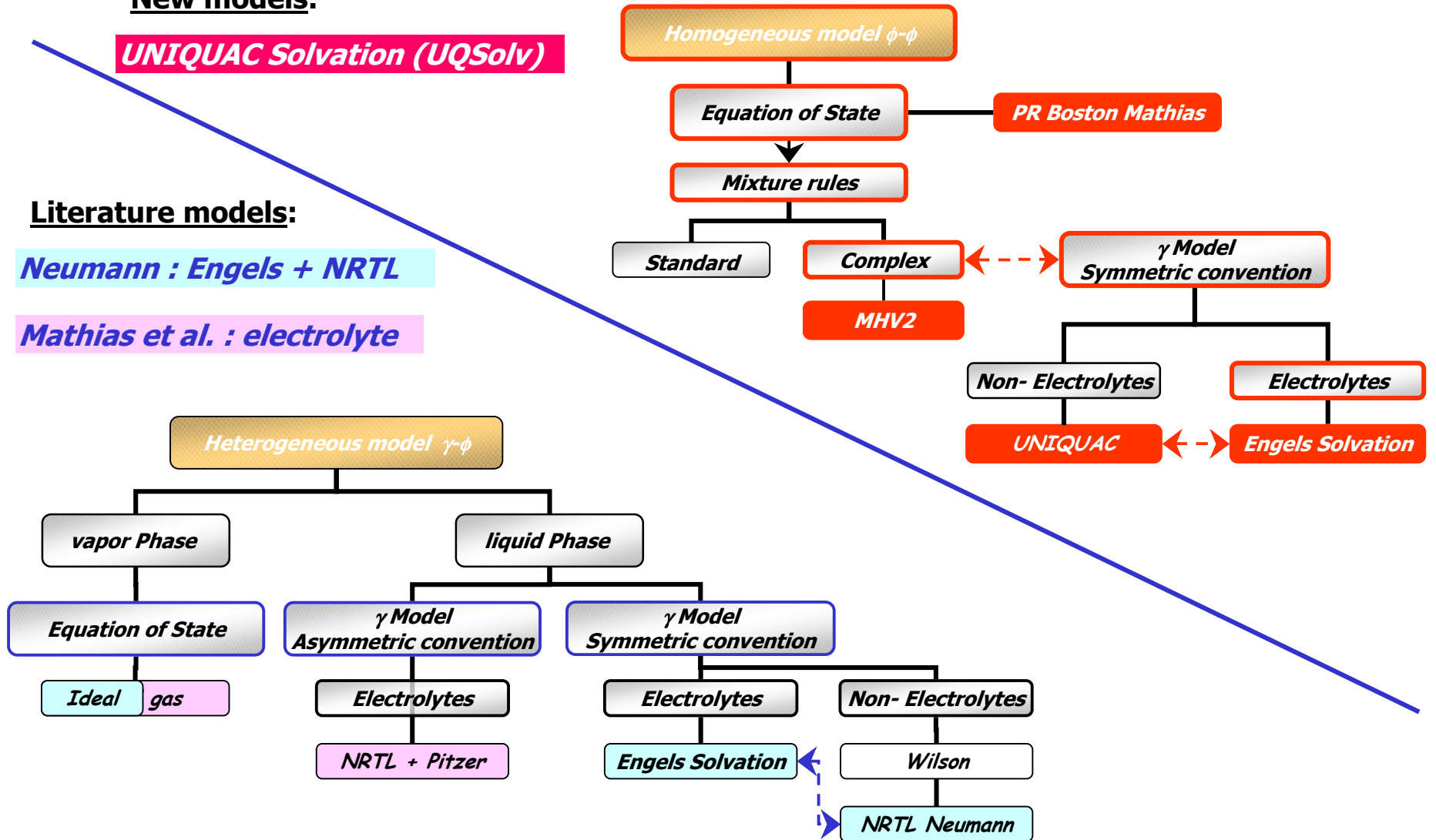
New models:

UNIQUAC Solvation (UQSolv)

Literature models:

Neumann : Engels + NRTL

Mathias et al. : electrolyte



Advantages of the model

- ✓ ϕ - ϕ 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 α function
 - Accurate behavior of pure components above critical points
- ✓ Mixing rule: MHV2 including non ideal liquid phase behavior via a G^{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

✓ 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
- $\text{H}_2\text{O} - \text{HI}$:
 - HI solvation by $\text{H}_2\text{O} \rightarrow$ equilibrium constant and solvation number



- UNIQUAC binary interaction parameters for H_2O , HI and the solvation complex C

✓ Ternary mixture

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

Available experimental data



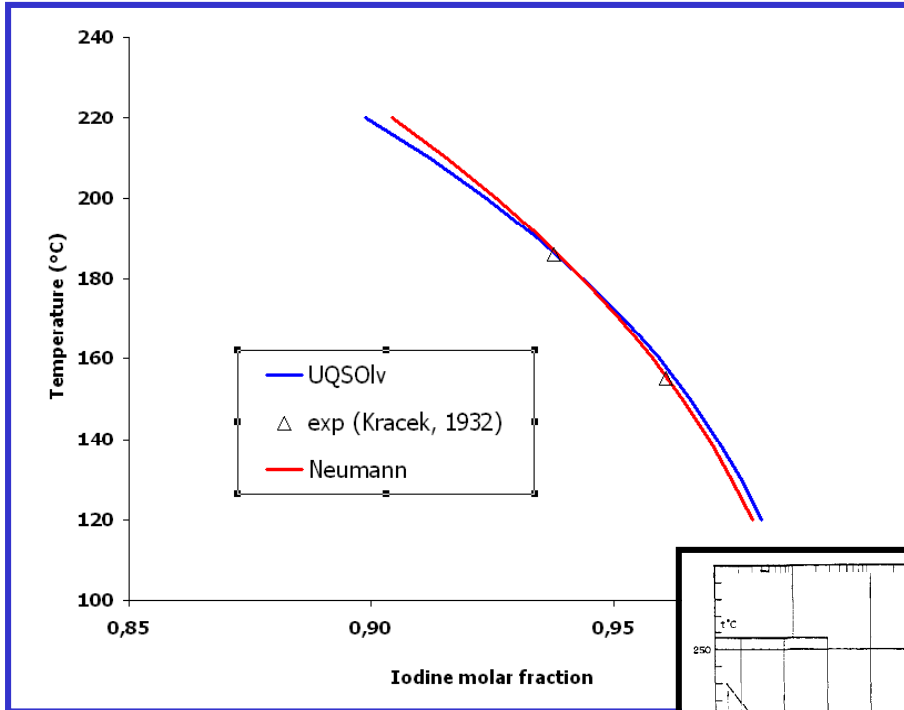
Fitting data



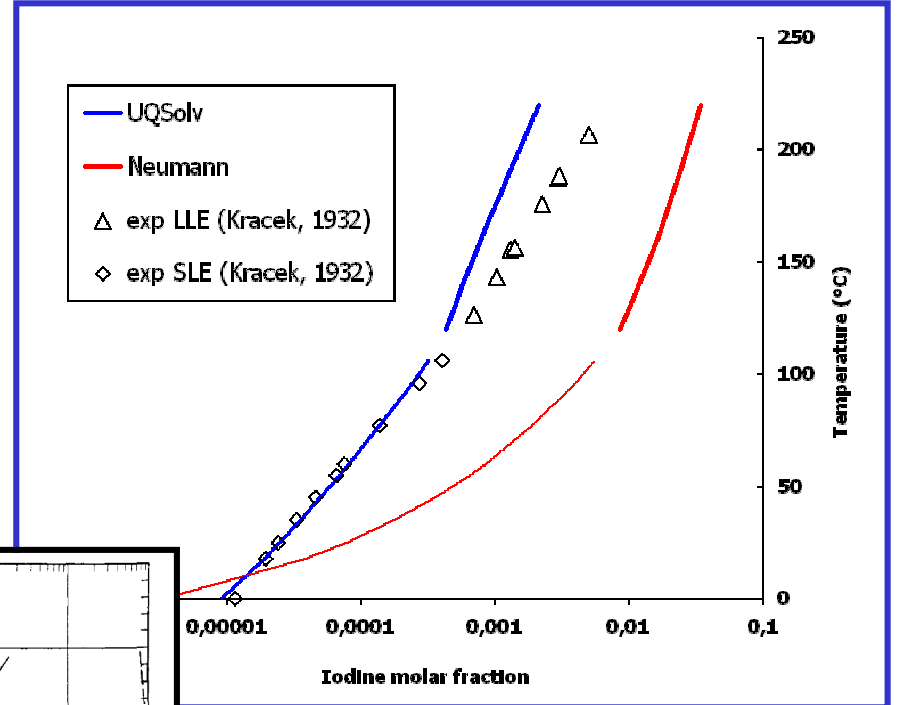
validation

| | Data | Data number | Data sources |
|--|------------|---------------------------------------|------------------------------|
| H₂O – HI | 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) |
| | ΔH | 13 | Vanderzee & Gier (1974) |
| | LLE | 6 $T = f(\mathbf{x})$ | Haase (1963) / Norman (1985) |
| H₂O – I₂ | LLE | 10 $T = f(\mathbf{x})$ | Kracek (1932) |
| | LSE | 10 $T = f(\mathbf{x})$ | Kracek (1932) |
| HI – I₂ | LSE | 5 $T = f(\mathbf{x})$ | O'keefe & Norman (1982) |
| H₂O – HI – I₂ | VLE | 280 $P = f(T, \mathbf{x})$ | Neumann (1986) |
| | LLE | 12 | Norman (1984) |

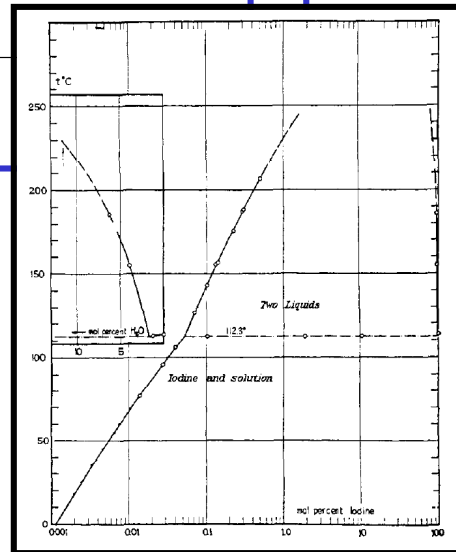
H₂O – I₂ identification results



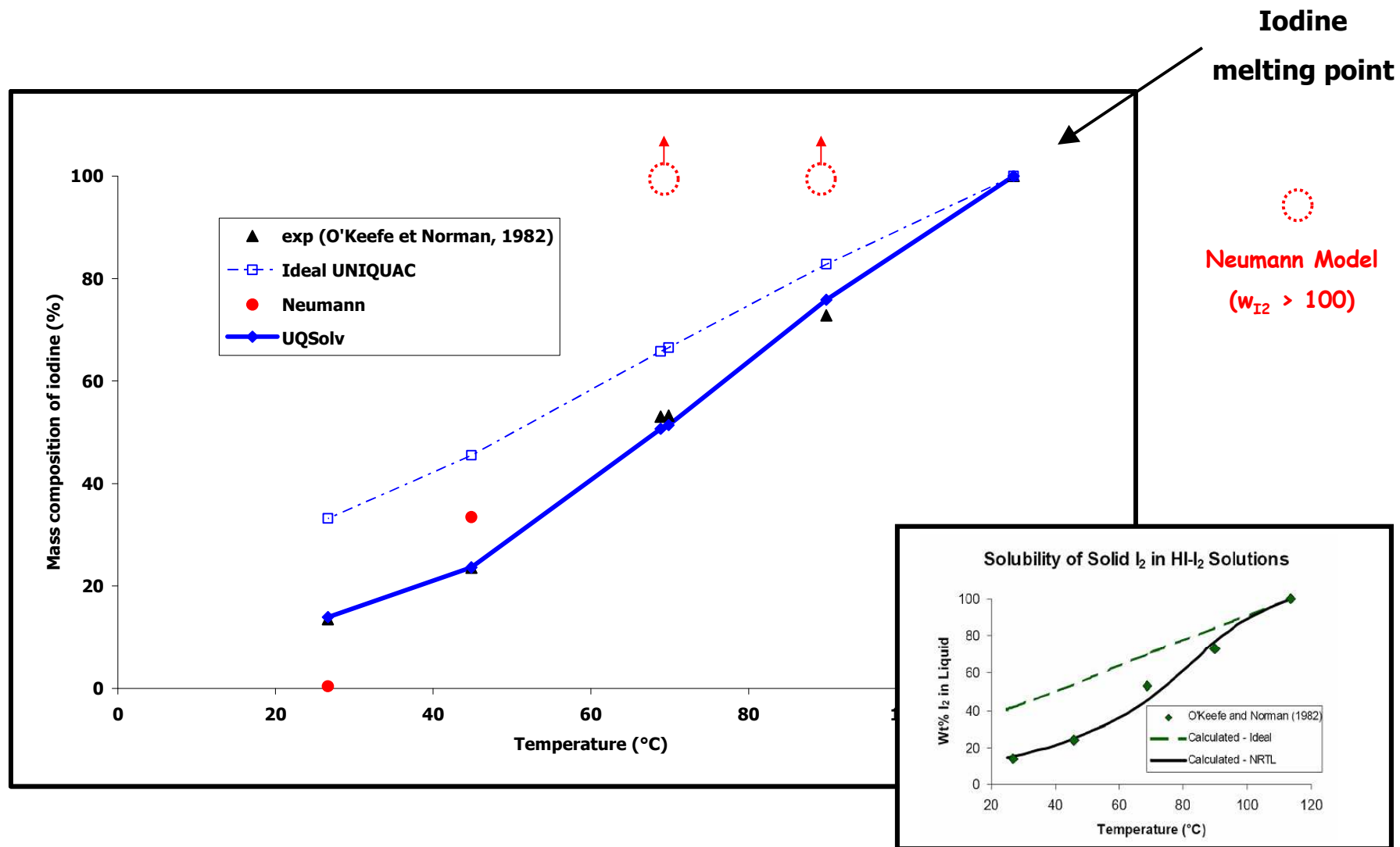
Iodine phase



Model prediction of iodine solubility in aqueous solution

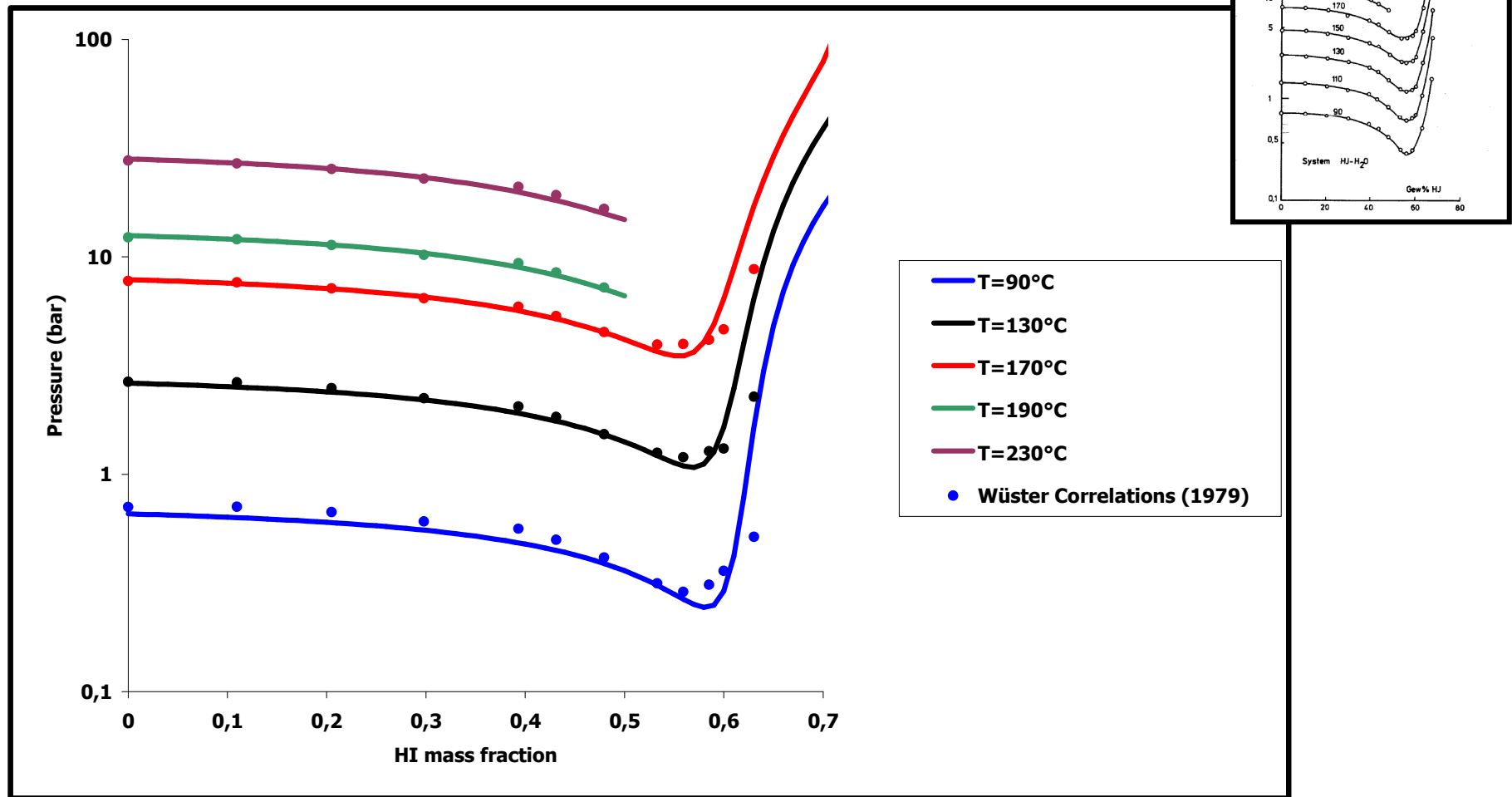


HI – I₂ identification results

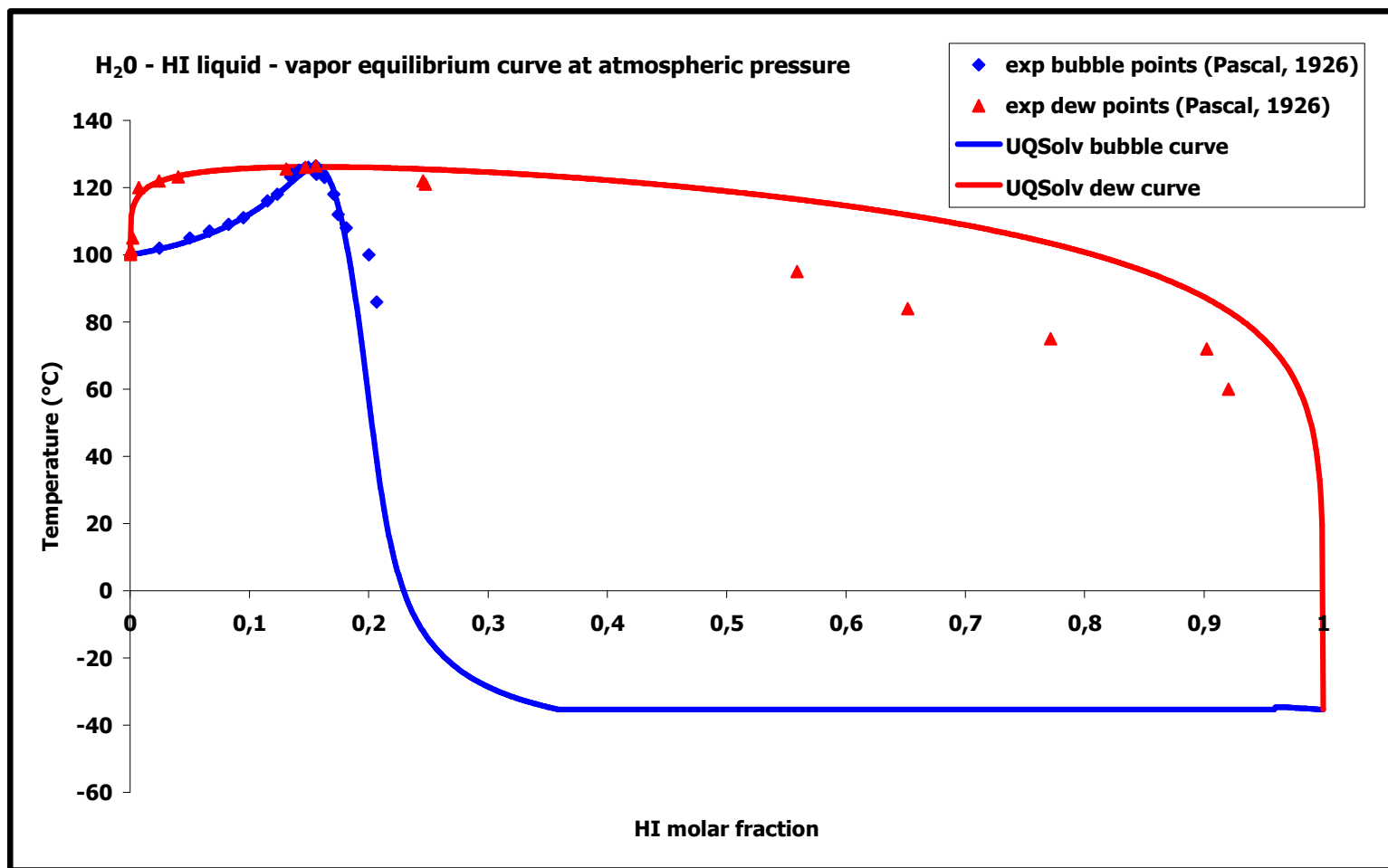


H₂O – HI identification results 1/2

Good agreement up to the azeotrope

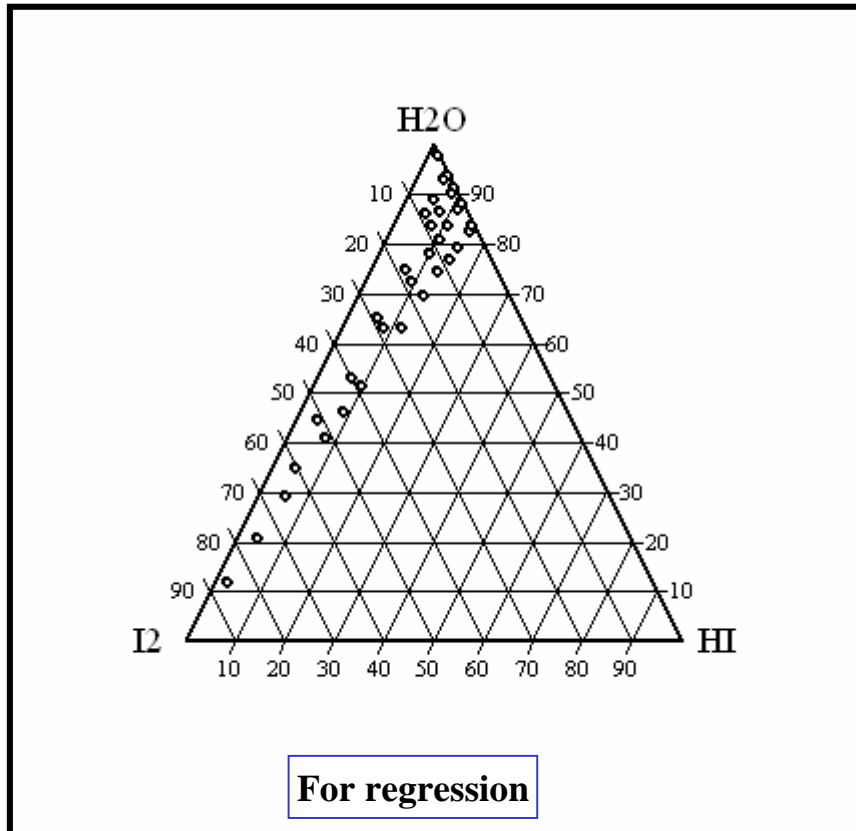


H₂O – HI identification results 2/2

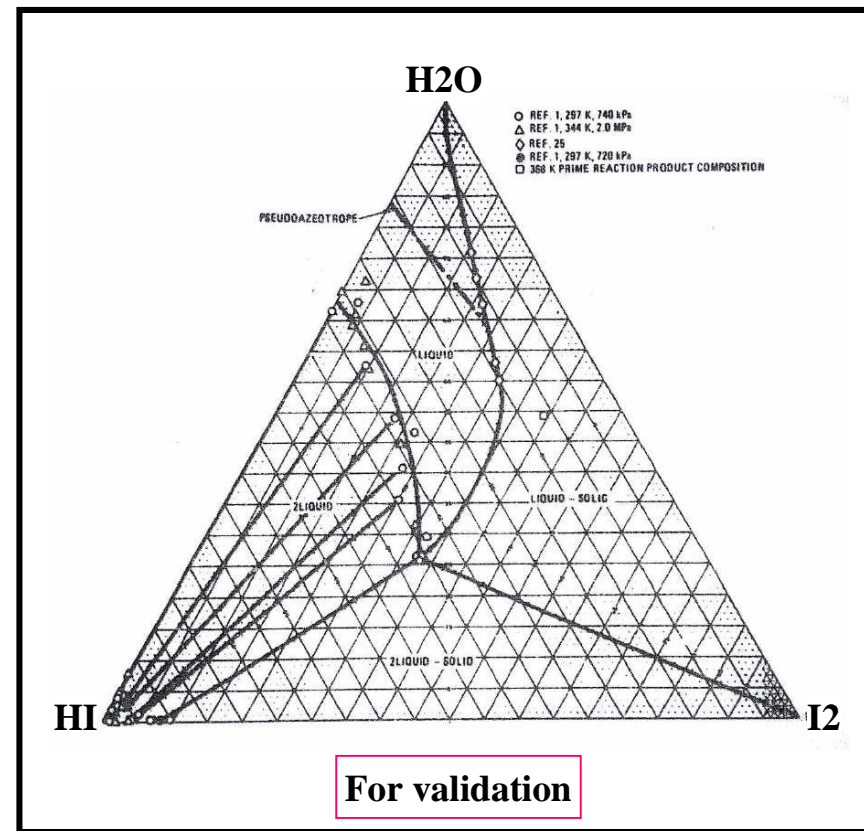


Model prediction of LVE curve at atmospheric pressure

Ternary system H₂O – HI – I₂



Engels experimental data
(0,017 < x_{HI} < 0,159)



Liquid – liquid equilibrium data
(Norman, 1984)

H₂O – HI – I₂ identification results 1/2

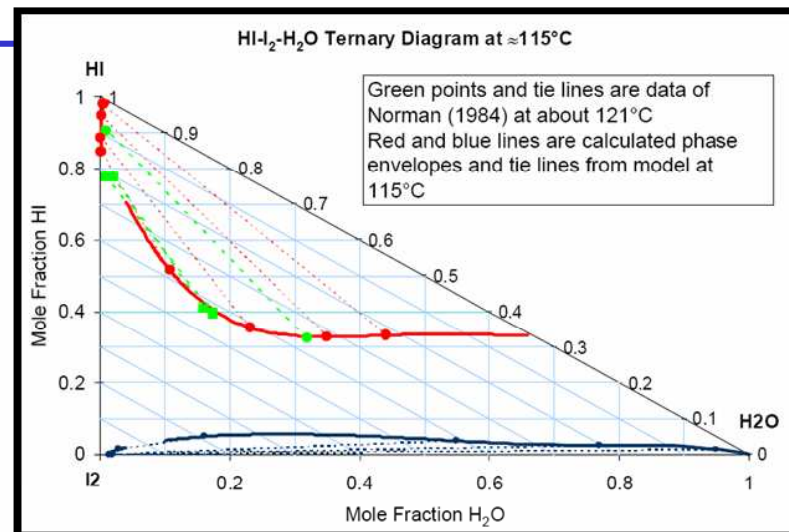
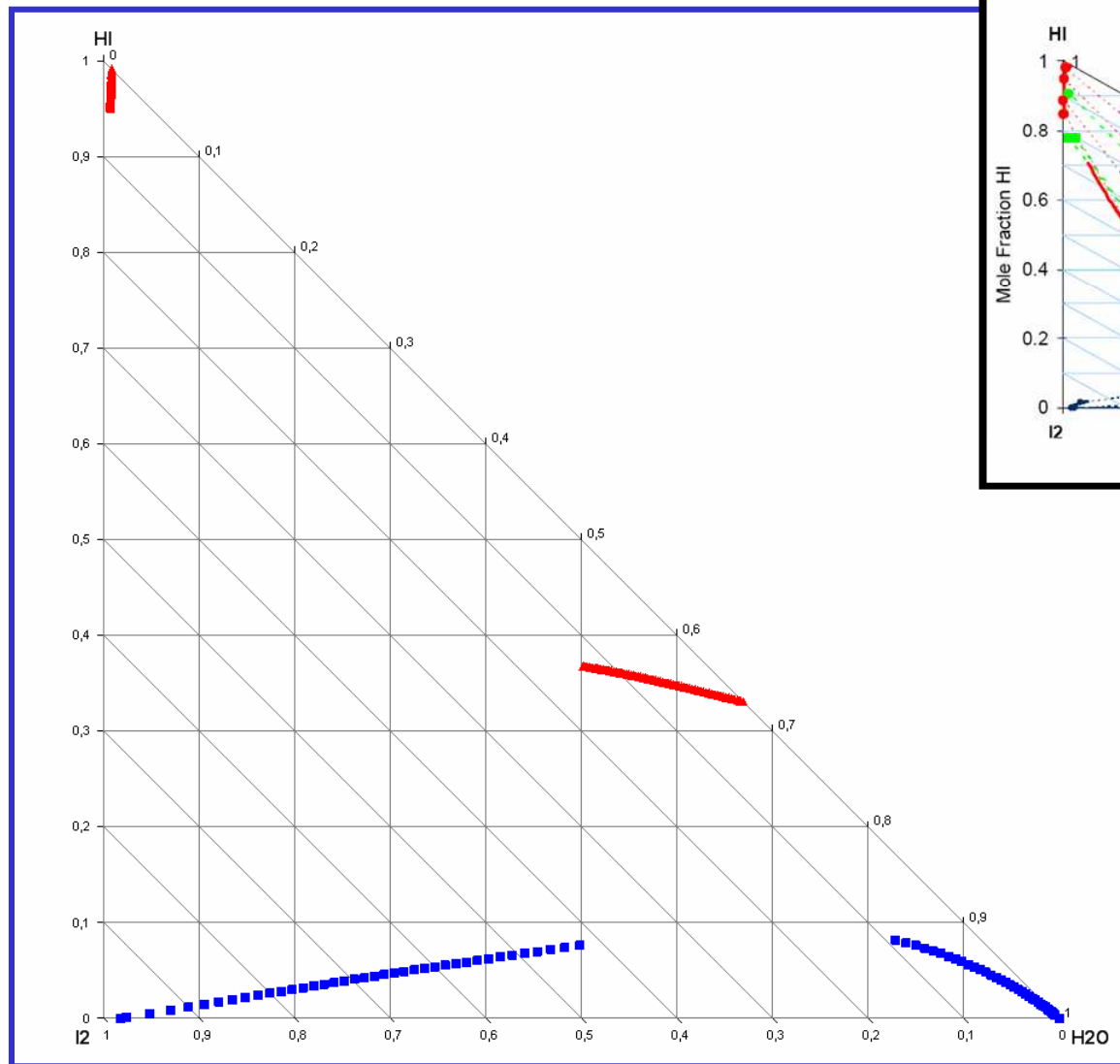
Keeping identified parameters for :

- ✓ Liquid – liquid equilibrium (H₂O – I₂)
- ✓ Solid – liquid equilibrium (HI – I₂)
- ✓ Vapor – liquid equilibrium (H₂O – HI) with solvation (m H₂O + 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 |
|----------------|-------------------|---------------|-----------|
| Neumann | 9.53 | 62.24 | 6.50 |
| UQSolv | 8.18 | 44.83 | 3.73 |

H₂O – HI – I₂ identification results 2/2



Conclusion and perspectives

- ✓ HIx non ideal and electrolytic system is modeled by an equation of state (EOS) approach with complex mixing rules including G^{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