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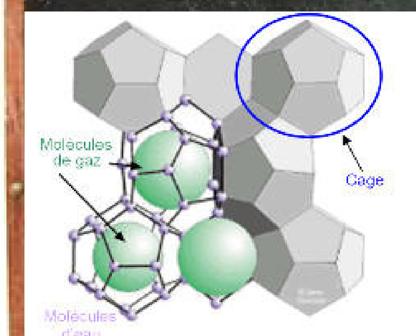
SAINT-ETIENNE

Gas Hydrates and CO_2 capture

Amara Fezoua
ENS des Mines de Saint-Etienne



Roma, 6th - 10th, July 2009

The team

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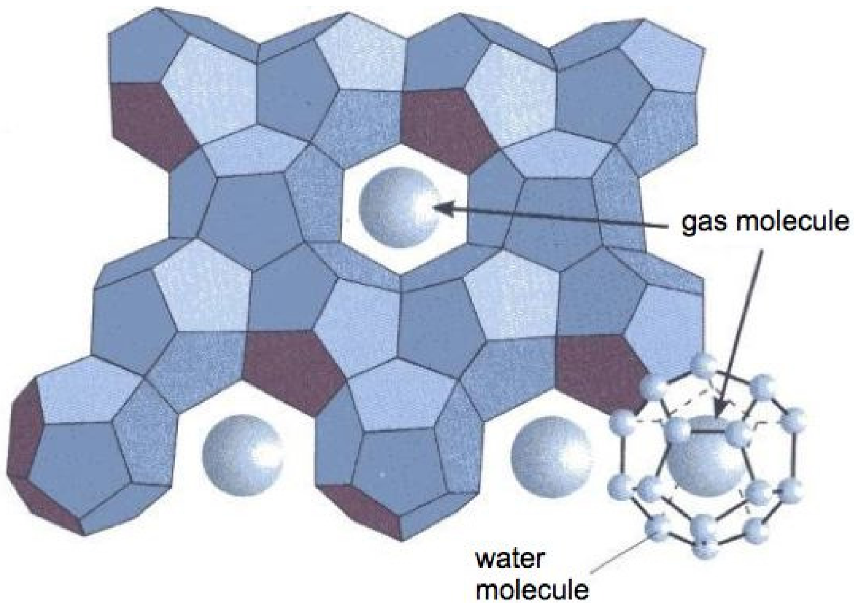
Gas hydrates



Methane hydrate

- Ice-like Crystalline Substances Made Up of Two or More Components
- Host Component (Water) - Forms an Expanded Framework with Void Spaces
- Van der Waals Forces Hold the Lattice Together

Gas hydrates formation

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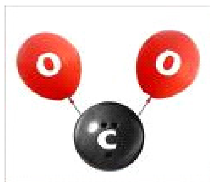

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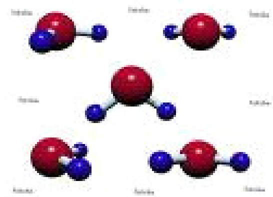
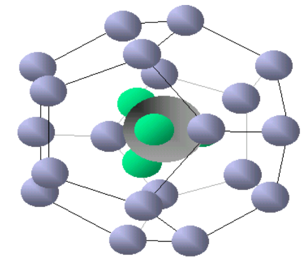


P ↗ (10-100 bar)

→

T ↘ (0-5 °C)

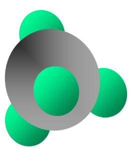


gas

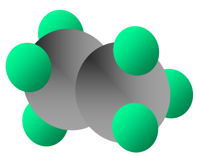
water

Gas hydrate

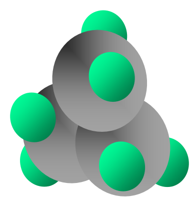
➡ hydrocarbones can form hydrates



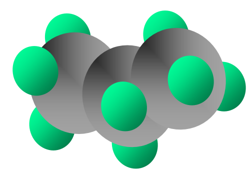
Methane



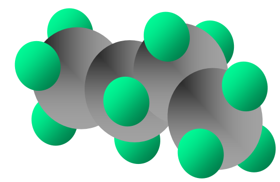
Ethane



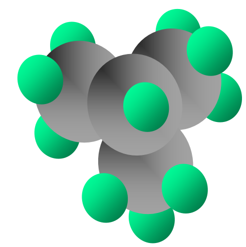
Cyclo-Propane



propane



butane



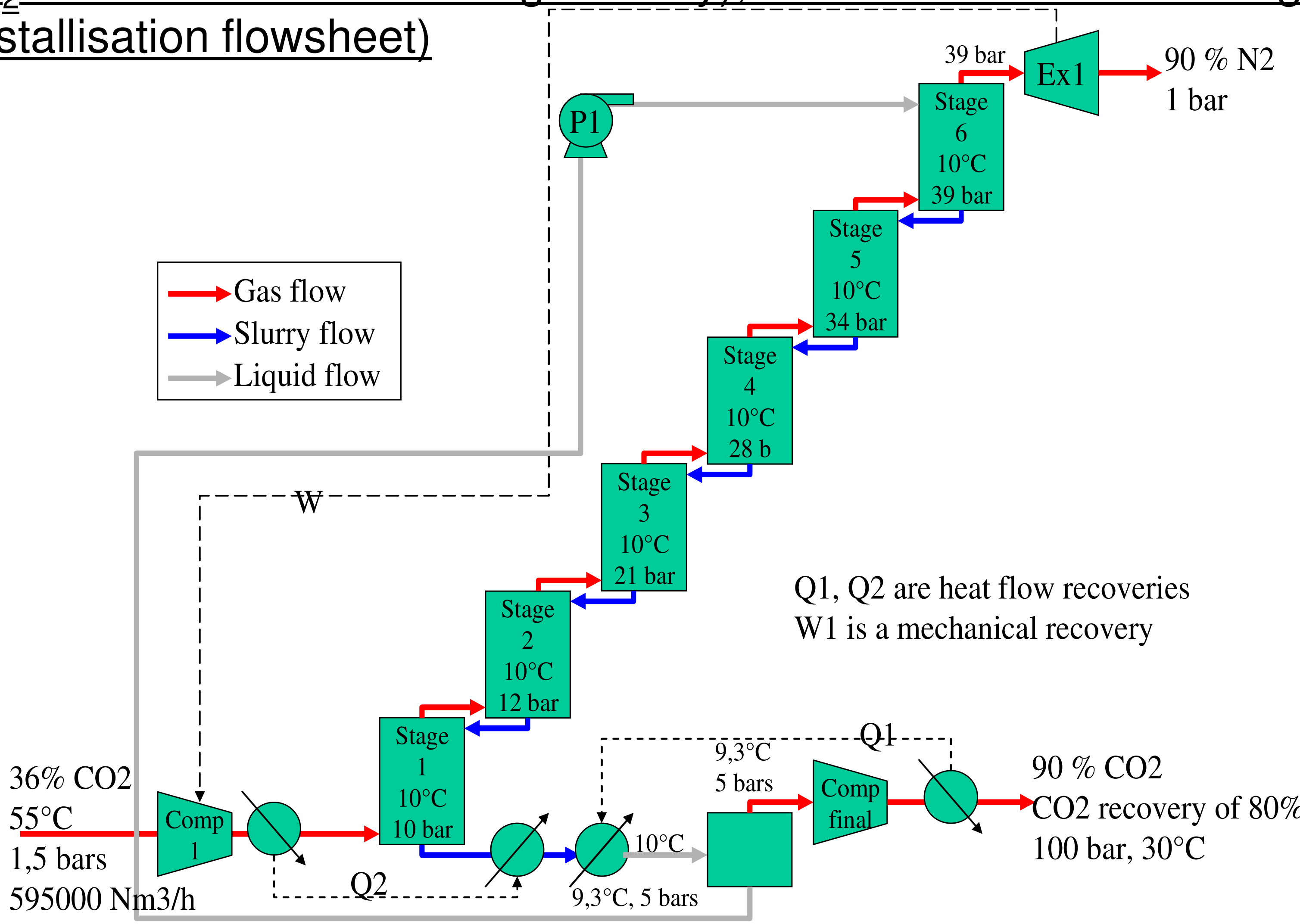
isobutane

But also

AIR CO_2 H_2S Ar, Kr, Xe and quaternary ammonimums

CO_2 capture project

In the framework of the 6PCRDT (Integrated Program ULCOS : Ultra Low CO_2 emission for Steelmaking industry), we have costed a mutistages crystallisation flowsheet)



Nguyen Hong Duc, Fabien Chauvy, Jean-Michel Herri, Energy Conversion and Management 48 (2007) 1313–1322

CO_2 capture project

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Preliminary economic evaluation:

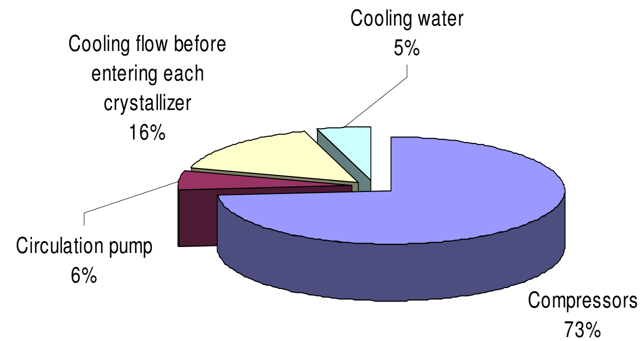
Utilities : electricity 40 euro/MW
cooling water (20°C) 40 euro/1000 m3

Compressors consumption (efficacity 80 %) : 128 MW – 21 MW (recovered in EX1) = 107 MW

Pump (P1) consumption (efficacity of 80 %) : 8.1 MW

Heat exchangers : 23 MW

Water cooling (at 20 °C) : 7000 m3/h



Energy cost of the process : **17 euros/tonne CO_2**
Recovery rate of CO_2 80 %, purity of CO_2 90 %

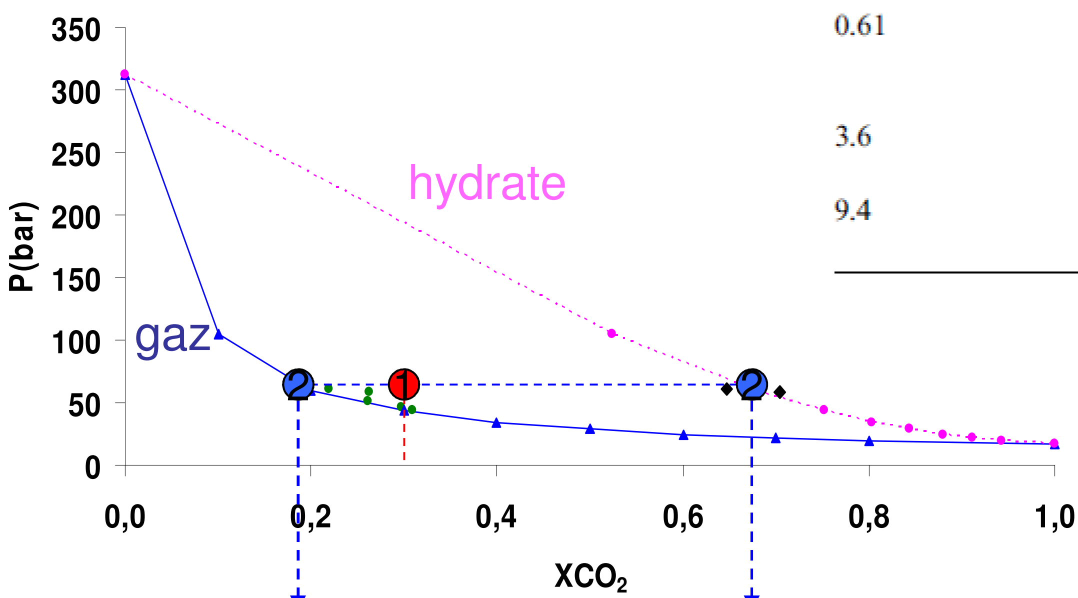
CO_2 capture project

Separation is based on a equilibrium between a solid phase (hydrates slurry) and a gas phase :

Role of the quaternary ammoniums

Equilibrium pressure of CO_2 hydrate with and without TBAB

% TBAB (mol)	T (K)	P (bar)	P (without TBAB) (bar)
0.29	279.3	2.73	35
	282	6.4	36.9
	284	8.4	143.6
0.61	286.1	10.7	270
	286.2	11.2	372
3.6	290.9	33.2	1220
9.4	284	8.15	143.6
	285	9.86	243



Vapeur phase

(18% CO_2, 82% N_2)

Hydrate phase

(68% CO_2, 32% N_2)

What are we doing?

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- National program ANR-SECOHYA (academic program)
- National program FUI-ACACIA (industrial program)
- European program PI-7PCRDT iCAP (both academic and industrial program)

IFP-Rhodia-LAFARGE-Veolia-Solvay-ARKEMA

- ➢ Doing experiments about thermodynamics of equilibrium and kinetics of crystallization in different contexts (water based systems, and water in oil based systems)
- ➢ Modeling thermodynamic
- ➢ Implementing the thermo on the web

Experimental Set Up

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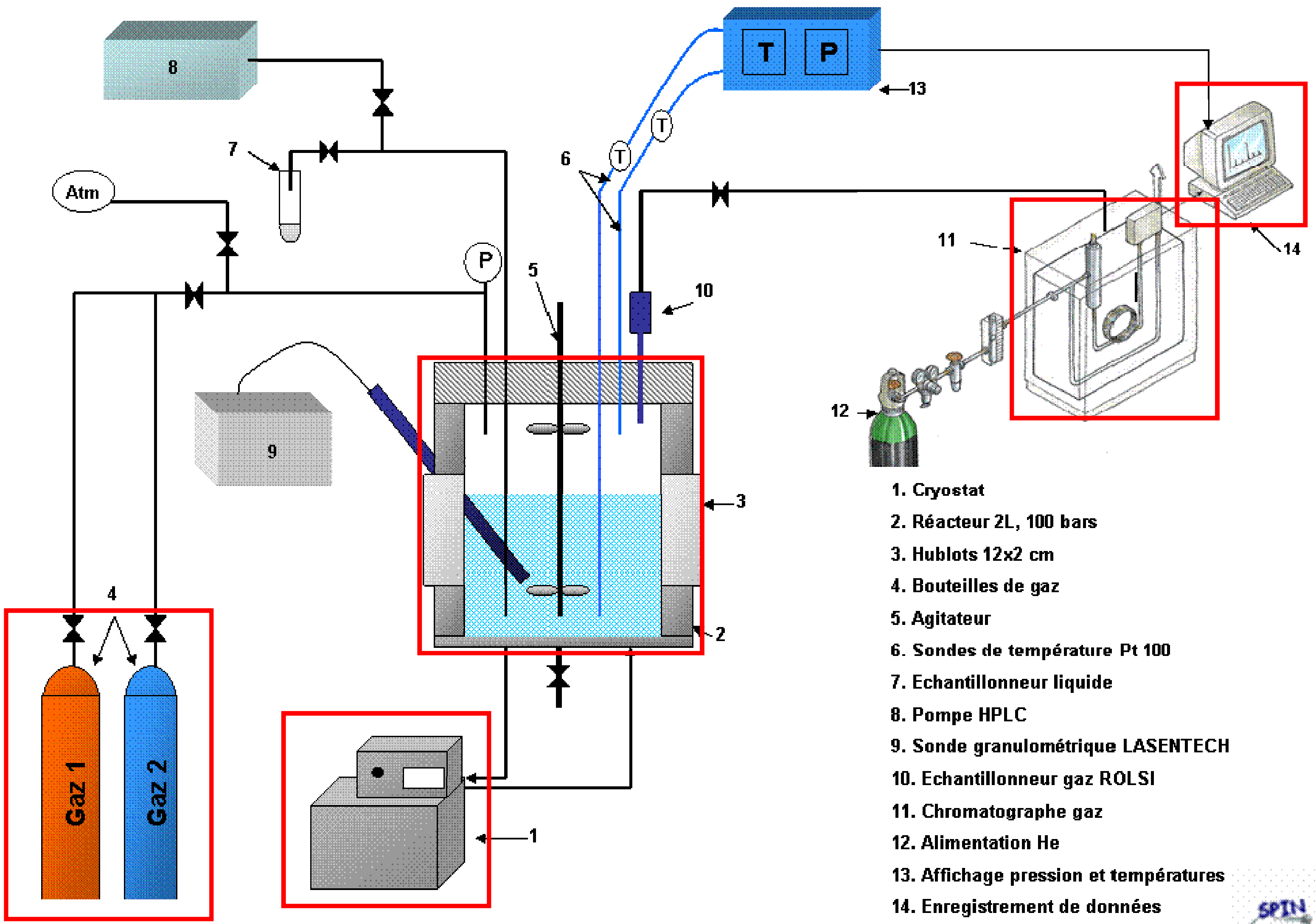

1. Cryostat
2. Réacteur 2L, 100 bars
3. Hublots 12x2 cm
4. Bouteilles de gaz
5. Agitateur
6. Sondes de température Pt 100
7. Echantillonneur liquide
8. Pompe HPLC
9. Sonde granulométrique LASENTECH
10. Echantillonneur gaz ROLSI
11. Chromatographe gaz
12. Alimentation He
13. Affichage pression et températures
14. Enregistrement de données

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Objectifs:

- representation and prediction of the equilibrium conditions (P,T,x,y,z);
- formation/dissociation conditions

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Equilibrium conditions

- P and T constant
- $\mu_i^\alpha = \mu_i^\beta$

α , β : phases , i : component

⬆

Modélisation

- calcul of the chemical potential in the ≠ phases

Modeling the thermodynamic

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<u>Vander Waals and Platteuuws model:</u>

- based on the equality : $\mu_w^H = \mu_w^L$ ➡ $\Delta\mu_w^{\beta\text{-}H} = \Delta\mu_w^{\beta\text{-}L}$

$\Delta\mu_w^{\beta\text{-}H}$: is the difference of chemical potential of water between the hydrate phase and the reference phase β;

$\Delta\mu_w^{\beta\text{-}L}$: is the difference of chemical potential of water in the liquid phase and the reference phase

- Assumptions :
  - There is no interaction between the guest molecules in diffrent cavities
  - Each cavity contains at most one guest molecule.
  - The interaction between a gas and water molecule can be described by a pair potential function
  - The cavity and the guest molecules can be treated as perfectly spherical.
  - analogy with the Langmuir adsorption ➡ θ_j^i (occupancy fraction of the cavities)

Modeling the thermodynamic

Vander Waals and Platteuuws model:

➡ $\Delta\mu_w^{\beta\text{-}H}$: *statistical thermodynamic*

$$\Delta\mu_w^{\beta-H} = RT\sum_i \nu_i \ln(1-\sum_j C_j^i f_j(T,P))$$

$$C_j^i = \frac{4\pi}{kT}\int_0^R \exp\left(\frac{-w(r)}{kT}\right) r^2 dr$$

$$C_j^i = \frac{A_j^i}{T}\exp\left(\frac{B_j^i}{T}\right)$$

(Parrish & Prausnit)

$$\ln\phi = \ln\frac{f}{P} = \int_0^P (Z-1)\frac{dP}{P}$$

Calculated by EoS (SRK,PR,PT,…)

Modeling the thermodynamic

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➡ $\Delta\mu_w^{\beta\text{-}L}$: *Classical thermodynamic*

$$\left(\frac{\Delta\mu_w^{\beta-L}}{RT}\right)_{T,P} = \left(\frac{\Delta\mu_w}{RT}\right)_{T0,P0} - \int_{T0}^{T}\frac{\Delta h_w}{RT^2}dT + \int_{P0}^{P}\frac{\Delta V_w}{RT}dP - \ln(\gamma_w * X_w)$$

$$\Delta h_w = \Delta hw_0 + \int_{Tref}^{T}\Delta Cp dT$$

and

$$\Delta Cp = \Delta Cp_0 + a(T - T_0)$$

$\Delta\mu_{w0}$, ΔC_{p0}, Δh_{w0}, a et ΔV_{w0} are determined experimentally

GasHyDyn Software

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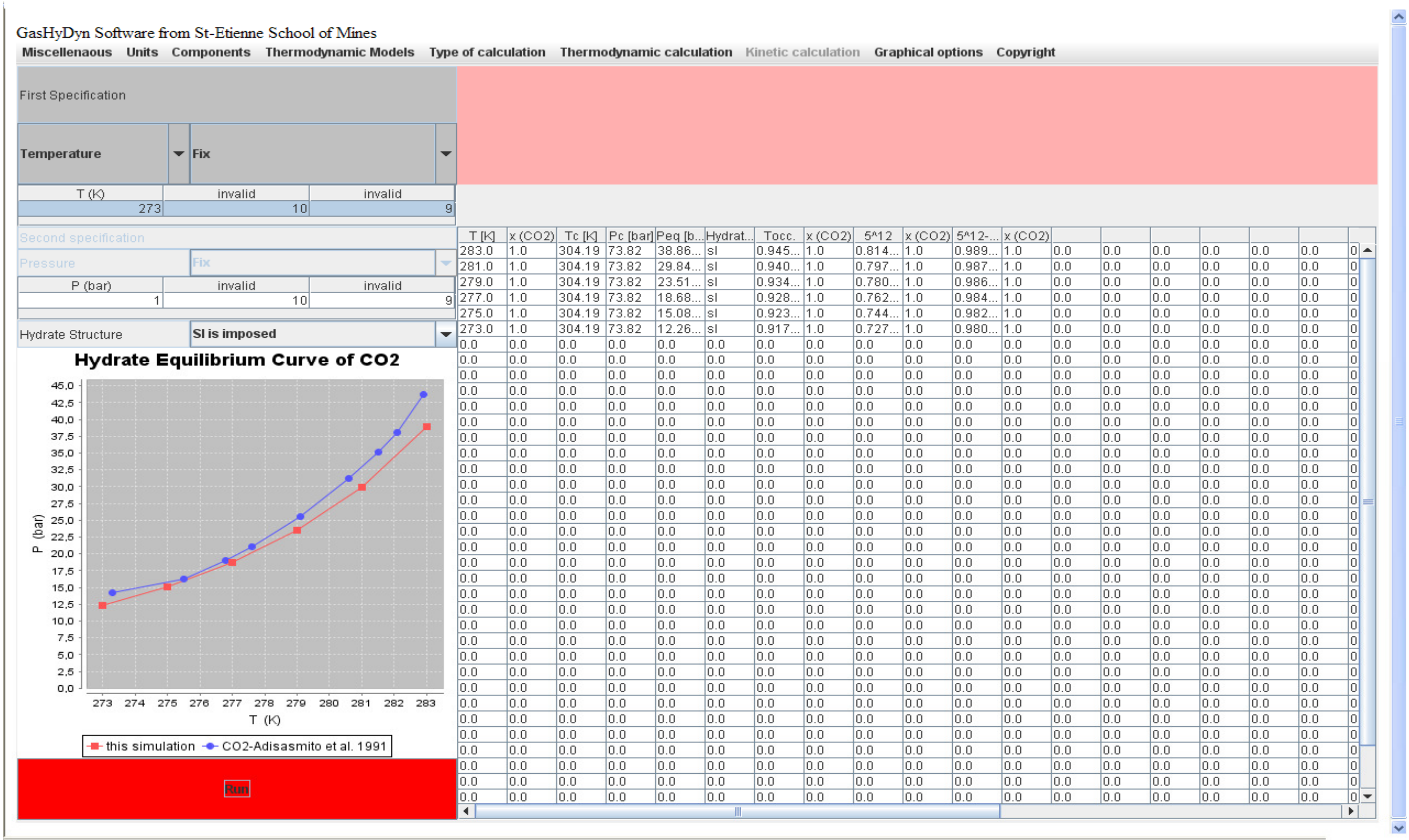
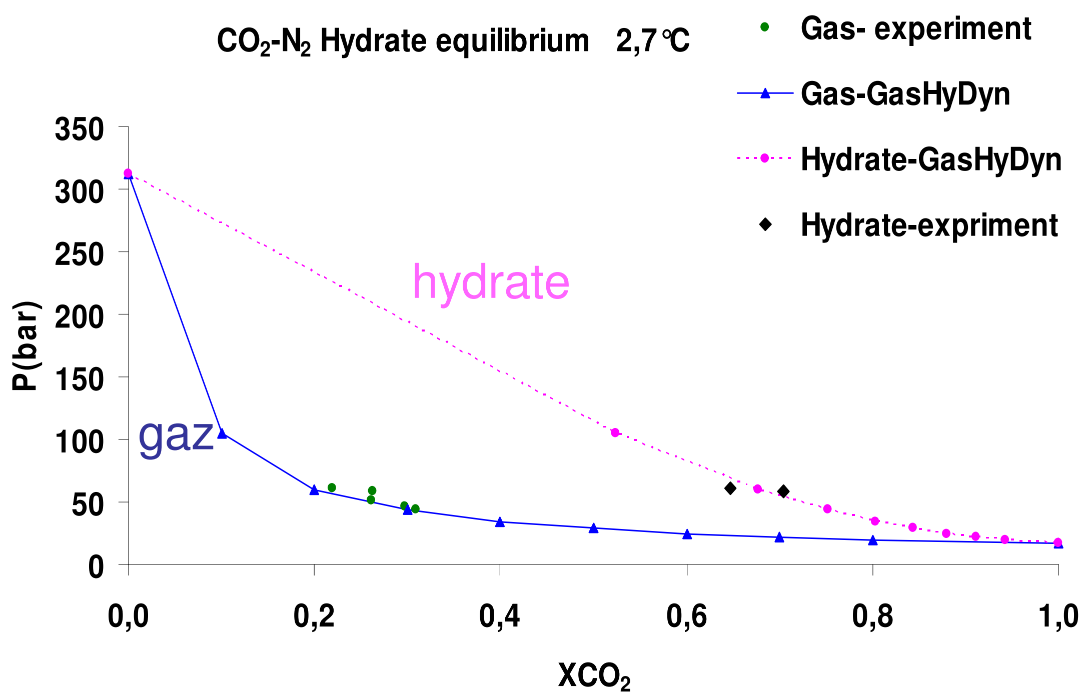
Examples : pur CO2 gas



http://www.emse.fr/fr/transfert/spin/depscientifiques/GENERIC/hydrates/logiciel_jmh/GasHyDyn.html

GasHyDyn Software

Examples : gas mixture



The model describe well experiments

GasHyDyn Software : examples

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Pressure calculations

T(K)	P(Mpa)	Chapoy	%dev.	Sloan	%dev	z N2	z CO2
273,8	**4,2**	4,1	3,2	4,0	-0,7	0,246	0,754
275,6	**4,4**	4,2	5,3	4,1	-1,2	0,309	0,691
275,9	**4,5**	4,3	3,5	4,3	-1,2	0,309	0,691
275,8	**4,5**	4,3	5,1	4,2	-1,4	0,308	0,692
275,8	**4,7**	4,4	5,3	4,4	-1,1	0,297	0,703
275,8	**4,8**	4,5	7,0	4,4	-1,2	0,295	0,705
273,8	**4,8**	4,6	3,3	4,6	-0,6	0,207	0,793
274,9	**5,1**	4,6	10,9	4,6	-0,9	0,245	0,755
275,9	**5,2**	5,0	5,2	4,9	-1,3	0,261	0,739
277,8	**6,3**	5,8	8,0	5,7	-2,1	0,291	0,709
278,1	**6,4**	6,0	6,2	5,8	-2,4	0,295	0,705
278,4	**6,4**	6,2	2,7	6,1	-2,3	0,295	0,705
278,6	**6,5**	6,3	2,8	6,1	-2,3	0,301	0,699
279,8	**6,8**	6,7	0,9	6,5	-3,1	0,337	0,663
273,4	**6,1**	5,5	11,3	5,4	-0,6	0,157	0,843
274,5	**6,2**	6,0	2,2	6,0	-0,4	0,164	0,836
275,4	**6,4**	6,2	3,6	6,1	-1,4	0,185	0,815
276,5	**6,6**	6,7	-1,9	6,6	-1,7	0,200	0,800
280,1	**5,3**	4,5	17,1	4,4	-2,7	0,559	0,441
281,1	**5,6**	5,0	13,3	4,8	-3,7	0,585	0,416
281,9	**6,2**	5,3	15,7	5,1	-4,8	0,617	0,383
			12,2		-1,8		

Relative errors

Composition calculations

P(Mpa)	T(K)	XCO2	Sloan	%dev
6,0	273,2	0,658	0,643	2,4
6,1	274,3	0,657	0,646	1,9
6,3	275,2	0,656	0,665	1,3
6,5	276,3	0,584	0,674	13,3
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
6,3	278,2	0,715	0,738	3,0
6,4	278,4	0,695	0,740	6,0
6,0	275,2	0,670	0,683	1,8
6,1	275,8	0,648	0,694	6,7
5,2	279,9	0,845	0,852	0,8
5,6	280,9	0,819	0,858	4,5
6,1	281,7	0,571	0,866	34,0
				5,9

Relative errors

Good agreement between model and experiments!!!

Perspectives

Working with quaternary ammonimums

⬇

We need to calculate :

$\Delta\mu_{w0}$, ΔC_{p0}, Δh_{w0}, a et ΔV_{w0}

And also modeling γ_w

$$\left(\frac{\Delta\mu_w^{\beta-L}}{RT}\right)_{T,P} = \left(\frac{\Delta\mu_w}{RT}\right)_{T0,P0} - \int_{T0}^{T}\frac{\Delta h_w}{RT^2}dT + \int_{P0}^{P}\frac{\Delta V_w}{RT}dP - \ln(\gamma_w * X_w)$$

Thank you for your attention