

Phase diagram of gas-hydrate slurries in gas-shortage

Michel Pons

LISN, Université Paris-Saclay, CNRS

Rue du Belvédère, bât 507, Campus, 91400 Orsay

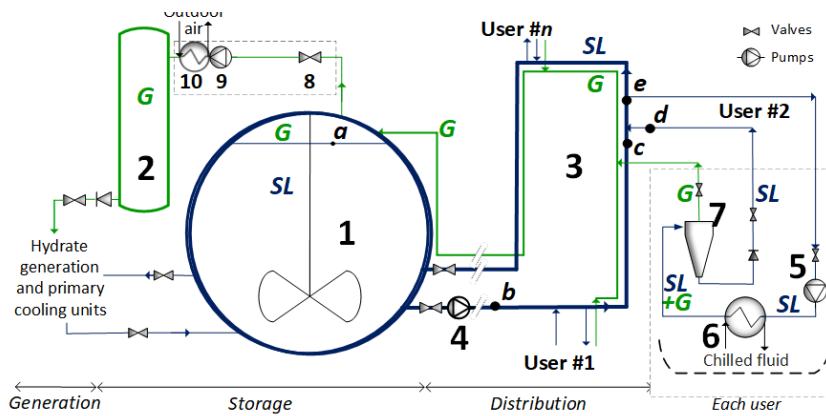
<https://perso.limsi.fr/mpons/>

Warning: bad motivations

- Severe addiction to Thermodynamics
 - Attraction for useless issues
- Neurotically excessive attention to tiny details

Context - 1

- Slurries of mixed-gas-hydrate (typically CO_2 +TBPB) in secondary refrigeration processes (storage and transport of cold): *numerical simulation, performance analysis.*



Laboratoire Interdisciplinaire des Sciences du Numérique



université
PARIS-SACLAY



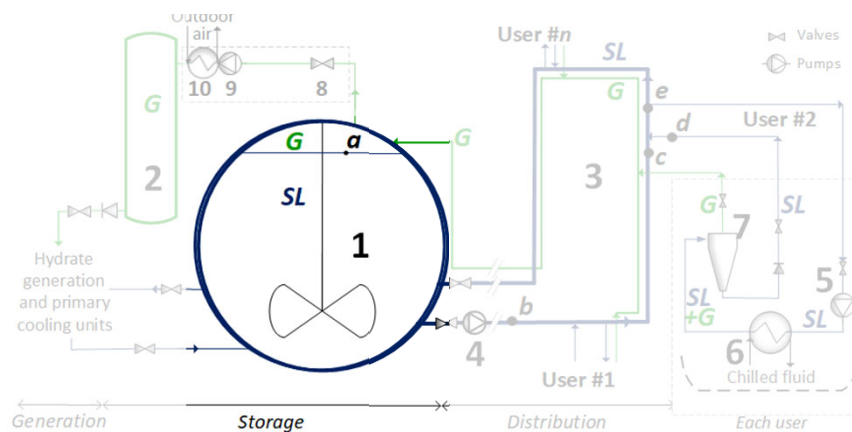
GDR2026
Hydrates de gaz

Journées Hydrates 2022
IFPEN, Rueil-Malmaison

3

Context - 2

- Storage tank **1**: Stirred slurry bath (**SL**) and Gas blanket (**G**), the point **a** is at the free surface.



Laboratoire Interdisciplinaire des Sciences du Numérique



université
PARIS-SACLAY



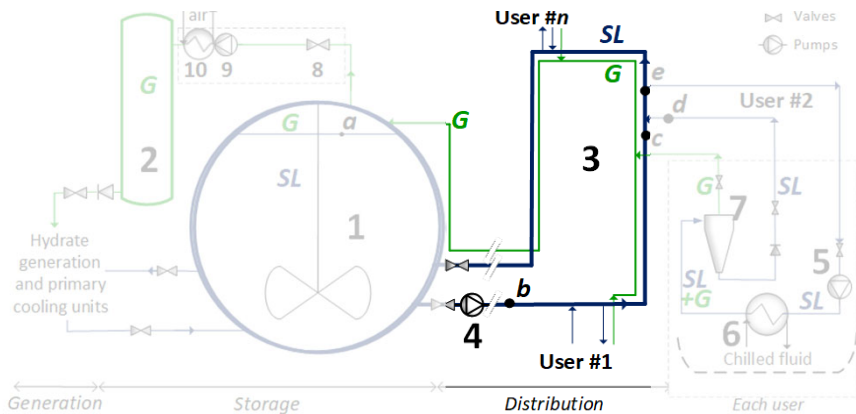
GDR2026
Hydrates de gaz

Journées Hydrates 2022
IFPEN, Rueil-Malmaison

4

Context - 3

- Distribution loop **3**: users in series, probably separate circuits for the gas (**G**) and the solid & liquid phases (slurry **SL**), point **b** at the outlet of the distribution pump **4**.



Laboratoire Interdisciplinaire des Sciences du Numérique



université
PARIS-SACLAY



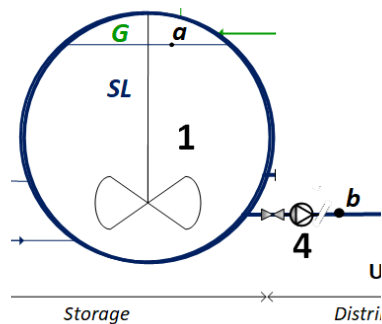
GDR2026
Hydrates de gaz

Journées Hydrates 2022
IFPEN, Rueil-Malmaison

5

What about pressurized slurries?

- Point **a** at the free surface: 3-phase equilibrium (**SLG**)
- Point **b** in the bulk of slurry: only two phases (**SL**),
- From **a** to **b**, the slurry is pressurized ...
... first by the hydrostatic pressure field,
... then by the distribution pump.
- Present issue: What is the thermodynamic state of the pressurized slurry at point **b**?



Laboratoire Interdisciplinaire des Sciences du Numérique



université
PARIS-SACLAY



GDR2026
Hydrates de gaz

Journées Hydrates 2022
IFPEN, Rueil-Malmaison

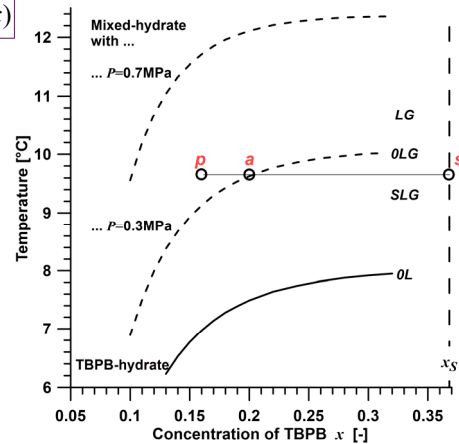
6

Mixed Hydrate of TBPB + CO₂: phase diagram

- Diagram T vs. x (x =TBPB concentration in the solution)

- For the hydrate crystal: Vertical line $x = x_s$

- EoS for the liquid solution $T = fT_{eq}(P, x)$
-> dashed (- - -) equilibrium curves with P as parameter.
- 3-phase equilibrium in the H₂O + TBPB + CO₂ system:
when $P \nearrow$ while $T \rightarrow$ (path $a \rightarrow p$)
then, x must \searrow
- This is obtained only when hydrate crystals (s) are generated
- Which requires supply of gaseous CO₂
- **But there is no gas available** between points a and b .



Laboratoire Interdisciplinaire des Sciences du Numérique



université
PARIS-SACLAY



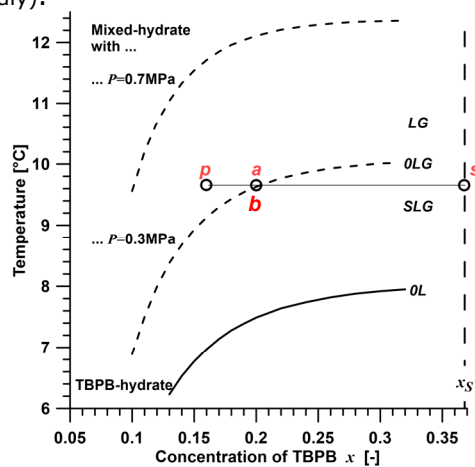
GDR2026
Hydrates de gaz

Journées Hydrates 2022
IFPEN, Rueil-Malmaison

7

What happens between points a and b ?

- Liquid and solid phases are not changed by mechanical pressurization (hardly).
- Point b (pressurized slurry) is very close to point a , and remains distant from equilibrium (point p).
- *The lack of gas prevents the system to move from b to p .*
- **The slurry is in gas-shortage.**
- Thermodynamic analysis, first for the 3-phase equilibrium.



Laboratoire Interdisciplinaire des Sciences du Numérique



université
PARIS-SACLAY



GDR2026
Hydrates de gaz

Journées Hydrates 2022
IFPEN, Rueil-Malmaison

8

Variance analysis - the Gibbs rule

$$V = C + 2 - \Phi$$

Equilibrium with 3 components and 3 phases

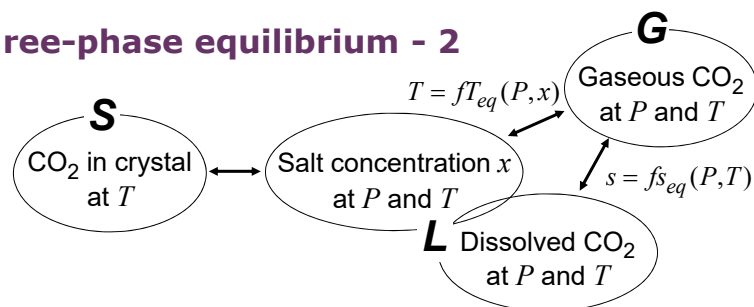
we are familiar with

$$V = 2.$$

• **Two degrees of freedom:**
typically *Temperature and Pressure*.

- The system of unknowns & equations can be solved only when **two equations of state** (EoS) are given:
 - One for the *3-phase equilibrium with hydrate*: $T = fT_{eq}(P, x)$
 - One for the *CO₂-dissolution equilibrium*: $s = fs_{eq}(P, T)$

Three-phase equilibrium - 2



- CO₂ is the only component present in the three phases.

Three-phase equilibrium \Leftrightarrow

CO₂ has the **same chemical potential** in each phase,
solid (part of hydrate crystal), liquid (dissolved) and gas.

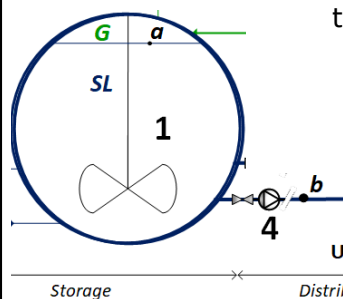
And when the gas phase is absent (i.e. for slurries in gas-shortage) ...

- $V = C + 2 - \Phi$

- With $\Phi=2$, $V=3$: there is an **additional degree of freedom**.
- **Although distant from the 3-phase equilibrium, the pressurized slurry *SL* is not out-of-equilibrium, it has its own equilibrium.**
- Herein, the amount of CO_2 contained in the slurry *SL* is chosen as the additional degree of freedom, if below the maximum allowed by crystals and dissolution at given T and P .

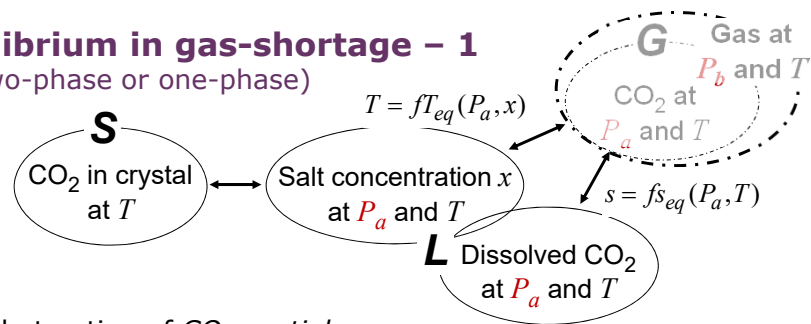
And when the gas phase is absent - 2

- With that additional degree of freedom, only **one** equation of state is needed.
- CO_2 has same chemical potential in the solid and liquid phases.



- Mechanical compression alone (without gas and adiabatic) does not change composition of the solid and liquid phases between **a** and **b**.
- The state at point **b** is described by the equations of state written at point **a**:
$$T = fT_{eq}(P_a, x) \quad \text{and} \quad s = fs_{eq}(P_a, T).$$
- P_a emerges as a kind of **CO_2 -partial-pressure at point **b****, obviously with $P_a < P_b$.

Equilibrium in gas-shortage - 1 (two-phase or one-phase)



- From that notion of CO_2 -partial-pressure one can **imagine a virtual gas** at total pressure P_b , consisting of CO_2 at partial pressure P_a plus a perfectly inert gas.
- CO_2 in that gas would have the **same chemical potential** as that of CO_2 in the liquid and solid phases (*solid when relevant*).
 - For the sake of generality, the CO_2 -partial-pressure is now P_{CD} , and the total pressure P_{tot} .

Laboratoire Interdisciplinaire des Sciences du Numérique



université
PARIS-SACLAY



GDR2026
Hydrates de gaz

Journées Hydrates 2022
IFPEN, Rueil-Malmaison

13

Equilibrium in gas-shortage - 2

- **THE equation of state is implicit:**
 - Three degrees of freedom: T, P_{tot}, χ_{CD} (total amount of CO_2)
 - For any value of the CO_2 -partial-pressure P_{CD} , one has:
 1. $s = fs_{eq}(P_{CD}, T)$ -> amount of CO_2 dissolved in the liquid,
 2. $T = fT_{eq}(P_{CD}, x)$ -> x salt concentration in the liquid phase, -> solid mass fraction, -> amount of CO_2 in the solid phase,
 - -> total amount of CO_2 .
 - For **one** value of P_{CD} , that total amount of CO_2 equates χ_{CD} .
- Note: $T, \chi_{CD}, P_{CD}, s,$ and x are fully coupled but P_{tot} is absolutely independent from them (mechanical compression of the slurry does keep concentrations x and s constant).

Laboratoire Interdisciplinaire des Sciences du Numérique



université
PARIS-SACLAY



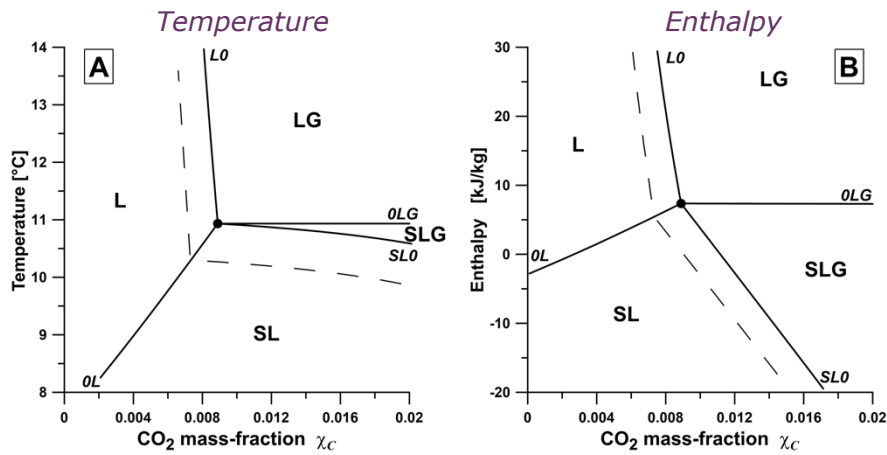
GDR2026
Hydrates de gaz

Journées Hydrates 2022
IFPEN, Rueil-Malmaison

14

Phase diagram of slurry in gas-shortage

- T and h vs. global CO_2 -mass-fraction (at $P=0.5$ MPa):
4 domains SLG, SL, LG & L; the dashed curves are for $P_{CD} = 0.8 \times P$.



Laboratoire Interdisciplinaire des Sciences du Numérique



université
PARIS-SACLAY



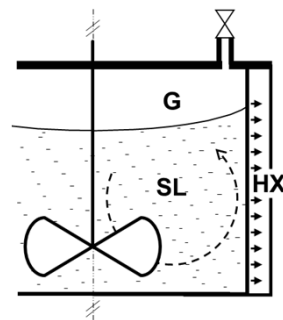
GDR2026
Hydrates de gaz

Journées Hydrates 2022
IFPEN, Rueil-Malmaison

15

Another case of gas-shortage

- When cooling a slurry (SL) in a stirred bath covered by a gas (G) blanket (e.g. when generating hydrate crystals), convection in the bath moves elements of slurry towards the cold heat-exchanger (HX); close to that heat-exchanger, hydrate crystals should form, but they can't, just because there is no gas below the free surface. (once again: gas-shortage).



- Next question: What happens when a slurry in gas-shortage is cooled?

Laboratoire Interdisciplinaire des Sciences du Numérique



université
PARIS-SACLAY



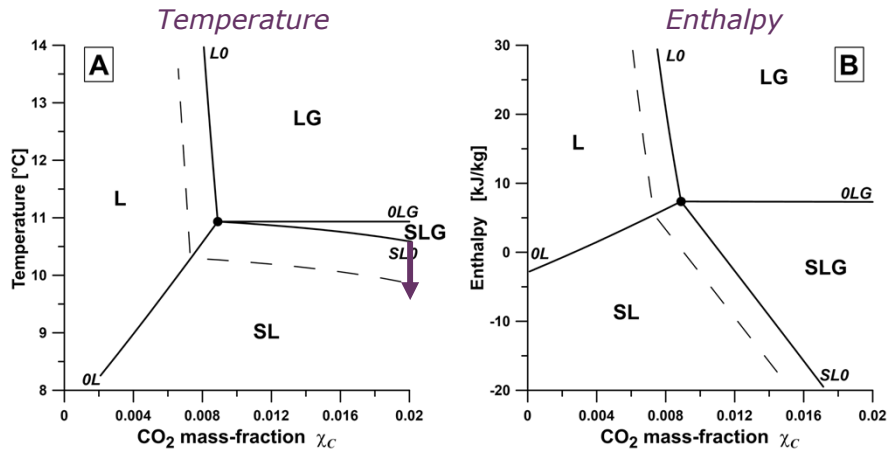
GDR2026
Hydrates de gaz

Journées Hydrates 2022
IFPEN, Rueil-Malmaison

16

Cooling a slurry in gas-shortage

- Let us reduce the temperature of a slurry in gas-shortage by 1K. First, the partial pressure P_{CD} decreases (by more than 20%).



Laboratoire Interdisciplinaire des Sciences du Numérique



université
PARIS-SACLAY



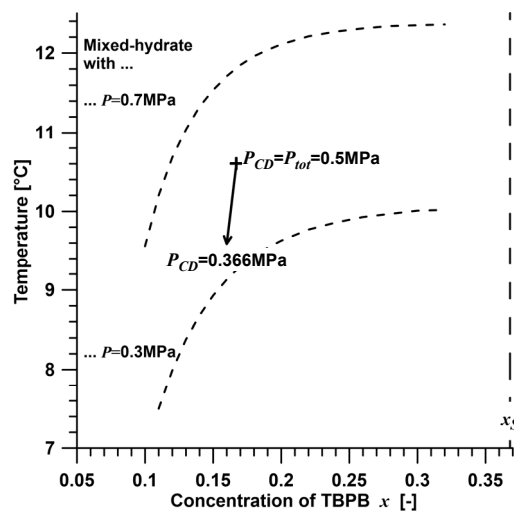
GDR2026
Hydrates de gaz

Journées Hydrates 2022
IFPEN, Rueil-Malmaison

17

... in the T - x diagram ... plus mass balances ...

- The value of x slightly decreases (from 0.167 to 0.160),
- $P_{CD} \searrow \Rightarrow$ the amount of dissolved CO_2 decreases (from 0.0078 to 0.0058)
- All that \Rightarrow crystals are generated (from 0.173 to 0.201, i.e. not few)
- Now, what about the enthalpy balance?



Laboratoire Interdisciplinaire des Sciences du Numérique



université
PARIS-SACLAY



GDR2026
Hydrates de gaz

Journées Hydrates 2022
IFPEN, Rueil-Malmaison

18

... and the enthalpy balance for $\Delta T = -1\text{K}$

- **Enthalpy change ...**
 - ... **by sensible heat** ($C_p.dT$) = **-3.7kJ/kg**
 - and **by latent heat** ($\Delta h.dm$) = **-5.0kJ/kg**, i.e. with ...
 - ... release of dissolved CO_2 (endothermal)
 - and generation of hydrate crystals (exothermal)
- Apparently, there is only a temperature drop.
 - However, some dissolved CO_2 is released for forming new hydrate crystals.
 - Big surprise: in that redistribution of CO_2 , the latent heat is larger than the sensible heat!

Other comments

- When **heating a slurry in gas-shortage**, there is no gas release, until $P_{CD} = P_{tot}$.
(a probably unexpected behaviour)
- Slurries of **single gas-hydrate** (CH_4 , CO_2 ...) may also be in gas-shortage
- Present analysis is on **equilibrium states only**.
Actual behaviours involve other effects, the understanding of which however always refers to equilibrium states.

Conclusion

- **Slurries in gas-shortage have their own equilibria** (independent from the 3-phase equilibrium).
 - There may be **transfers of CO₂** between **dissolved state** and **hydrate crystals**.
 - In such cases, the **latent heat** may be **more significant** than the sensible heat.
- **THANK YOU FOR YOUR ATTENTION**
to that tiny useless issue.

Imagine ...

- A 'system'
(= given amounts of
water, TBPB and CO₂)
enclosed in a balloon
submitted to external pressure
and temperature conditions
with increasing pressure
or decreasing temperature.

