TOWARD SUSTAINABLE CO_2 CAPTURE

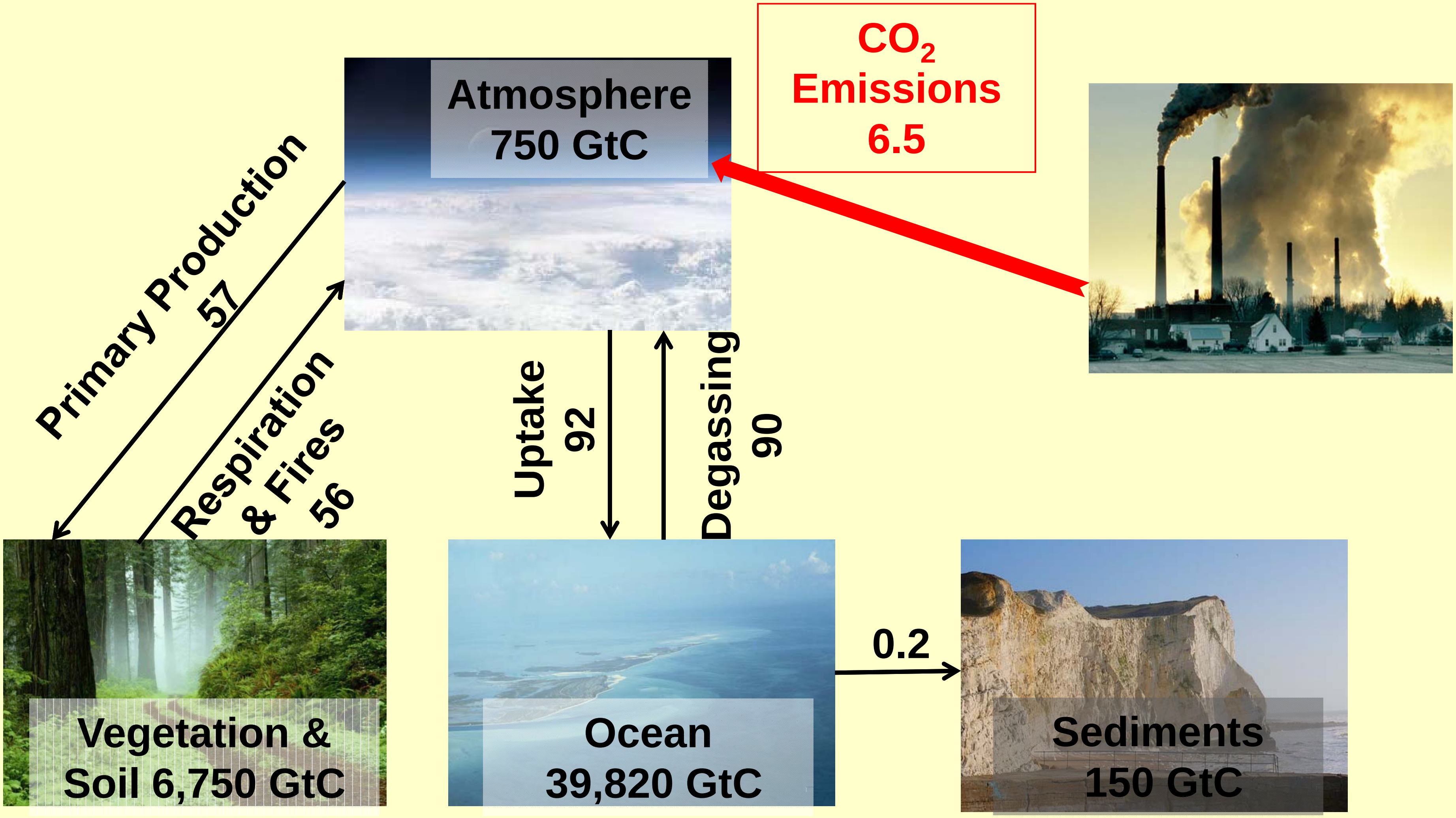
Jae W. Lee

Department of Chemical Engineering
Grove School of Engineering
The City College of New York, CUNY

CUNY
The City University of New York

the City College of New York

Global Carbon Cycle



CO$_2$ Emissions 6.5

Atmosphere 750 GtC

Primary Production 57

Respiration & Fires 56

Uptake 92

Degassing 90

Vegetation & Soil 6,750 GtC

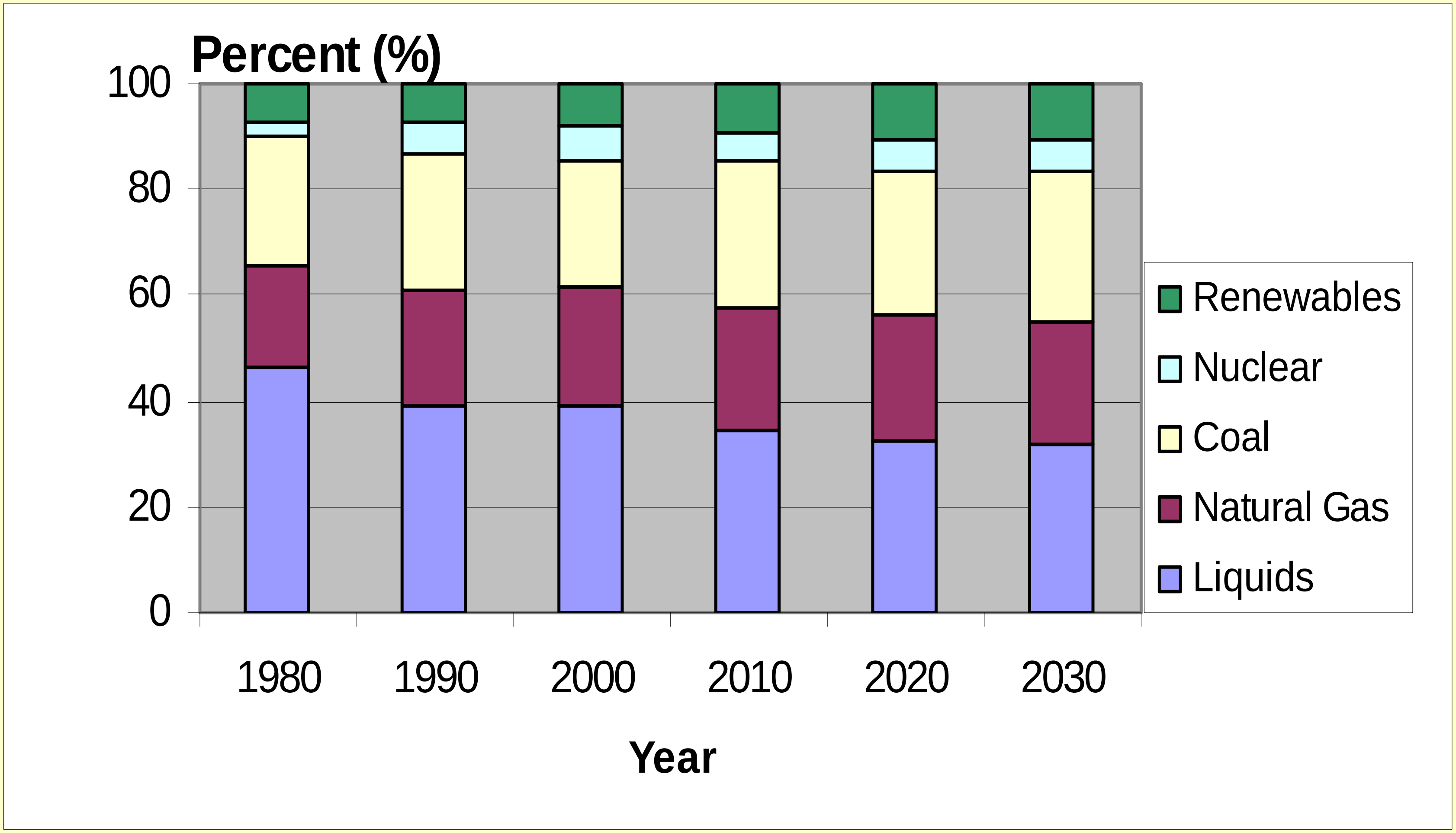
Ocean 39,820 GtC

0.2

Sediments 150 GtC

Units = Gt C/year, IPCC (2005), Modified from DataNet Presentation (Lucia et al.)

World Energy Consumptions



12% Renewables → Needs CO_2 Sequestration.

- Modified from Report #:DOE/EIA-0484(2009)

CO_2 Emissions

- **CO_2 concentration in the atmosphere increases gradually:**
  - **280 to 350 ppm of CO_2 from pre-industry level to current level.**
  - **60% of total greenhouse emissions come from CO_2.**
- **Goal**
  - **Sequester 1 GtC/year in 2023 and 4 GtC/year in 2050.**

http://www.netl.doe.gov/technologies/carbon_seq/refshelf/project%20portfolio/2007/2007Roadmap.pdf

Gupta and Coyle (2003)

Costs for Carbon Capture and Storage (CCS)

Cost Breakdown:

Capture: \$40/ton CO_2 1)
Transport: \$8/ton CO_2 2)
Storage: \$11/ton CO_2 3)

1) Average of three types of Power Plants in IPCC report (2005)
2) Highest value in 250 Km pipe in IPCC report (2005)
3) Average of geologic and ocean storage in IPCC report (2005)

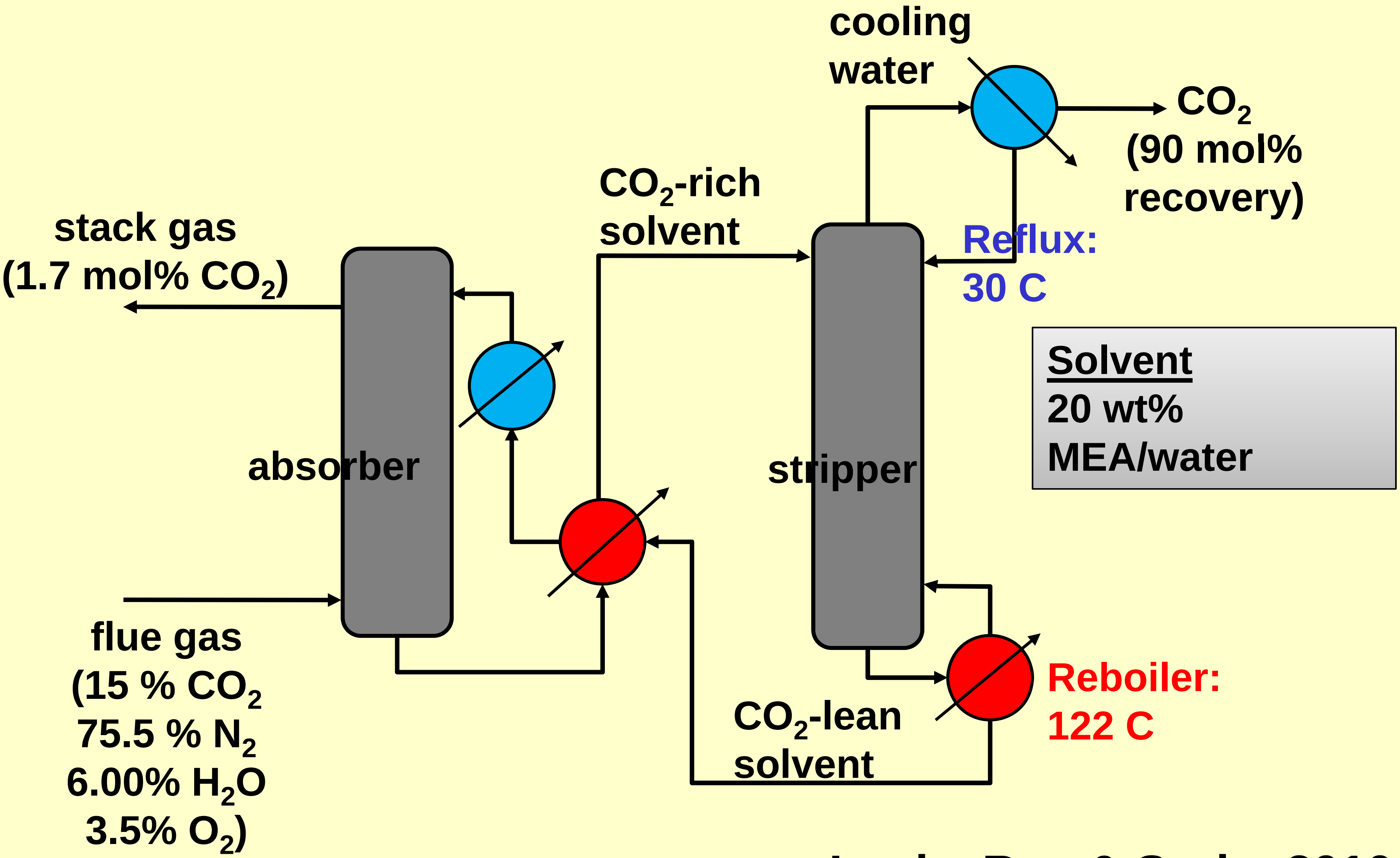
Various Methods for CO_2 Capture

Solvent-based Method: MEA, Ammonia, Methanol (Rectisol), Dimethyl ether (Selexol)

Hydrate-aided Separation: Water (with or without Promoters)

Others: Membrane, Chemical Looping Method, Sublimation, etc.

Energy-Efficient MEA Process for CO_2 Capture



cooling water

CO_2 (90 mol% recovery)

CO_2-rich solvent

stack gas (1.7 mol% CO_2)

Reflux: 30 C

absorber

stripper

Solvent

20 wt% MEA/water

flue gas (15 % CO_2
75.5 % N_2
6.00% H_2O
3.5% O_2)

CO_2-lean solvent

Reboiler: 122 C

Lucia, Roy & Sorin, 2010

VLE for CO_2-MEA-H_2O

Simultaneous Phase and Chemical Equilibrium

- complicated by presence of ions (H^+, HCO_3^-, CO_3^{2-})
  - $CO_2 + H_2O = H_2CO_3$
  - $H_2CO_3 = HCO_3^- + H^+$
  - $HCO_3^- = CO_3^{2-} + H^+$

- many researchers use
  - electrolyte NRTL for liquid
  - ideal gas or RK for vapor

Difficulties are experienced with current phase models

- need experimental data to regress parameters
- sometimes hard to use
- simulations often don’t match operating data

Data-Driven VLE for CO_2-MEA-H_2O

Experimental data:

- provides partial pressure of CO_2 over MEA-water solution
- can be readily interfaced with simulation models
- VLE easily computed by interpolation

All results in this work for 20 wt% MEA in water:

- found non-pinched minimum designs (distance method)
- 9 – 18% more energy savings

Lucia, Roy & Sorin, 2010

CO_2 Capture via Clathrate Hydrates

Post-Combustion Capture:

- Dominant components: CO_2 (less than 20%) & N_2
- P difference for hydrates: CO_2 29 bar and N_2 339 bar at 280 K
- Case-I (10% CO_2)

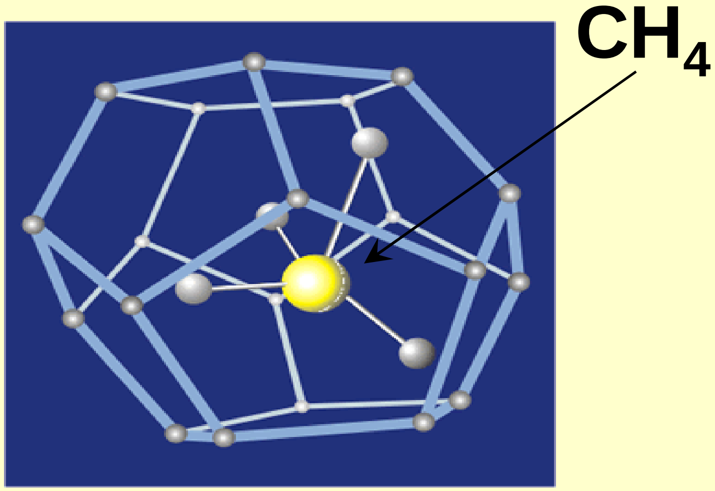
Pre-Combustion Capture:

- Dominant components: CO_2 (20-40%) & H_2
- Pressure difference: CO_2 29 bar and H_2 3000 bar at 280 K
- Case-II (40% CO_2)
- Micro-DSC incorporated Conceptual Design (Cyclopentane as a promoter)

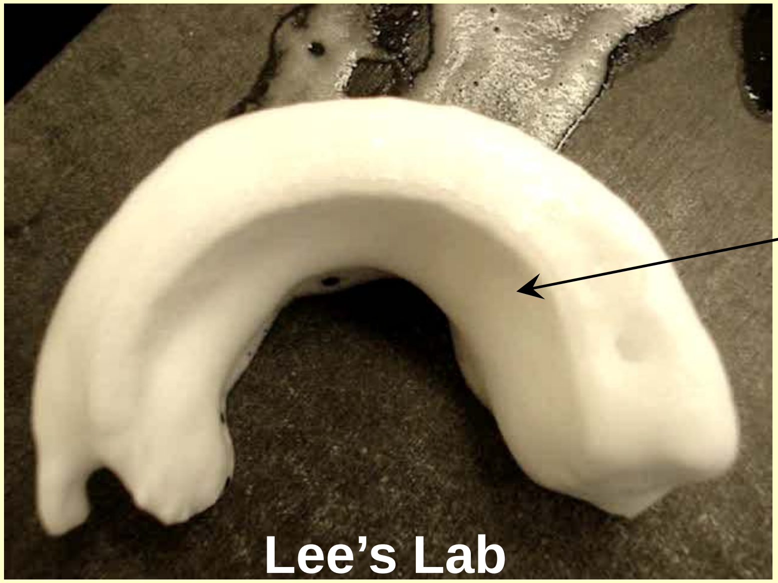
What Are Clathrate Hydrates?

- Non stoichiometric crystalline compounds:

  water + light gases (methane, ethane, propane, hydrogen, CO_2…)
- Formed under high P and low temp.
- General formula:
  - *Gas ·nH_2O* (n varies from 5 to 8)



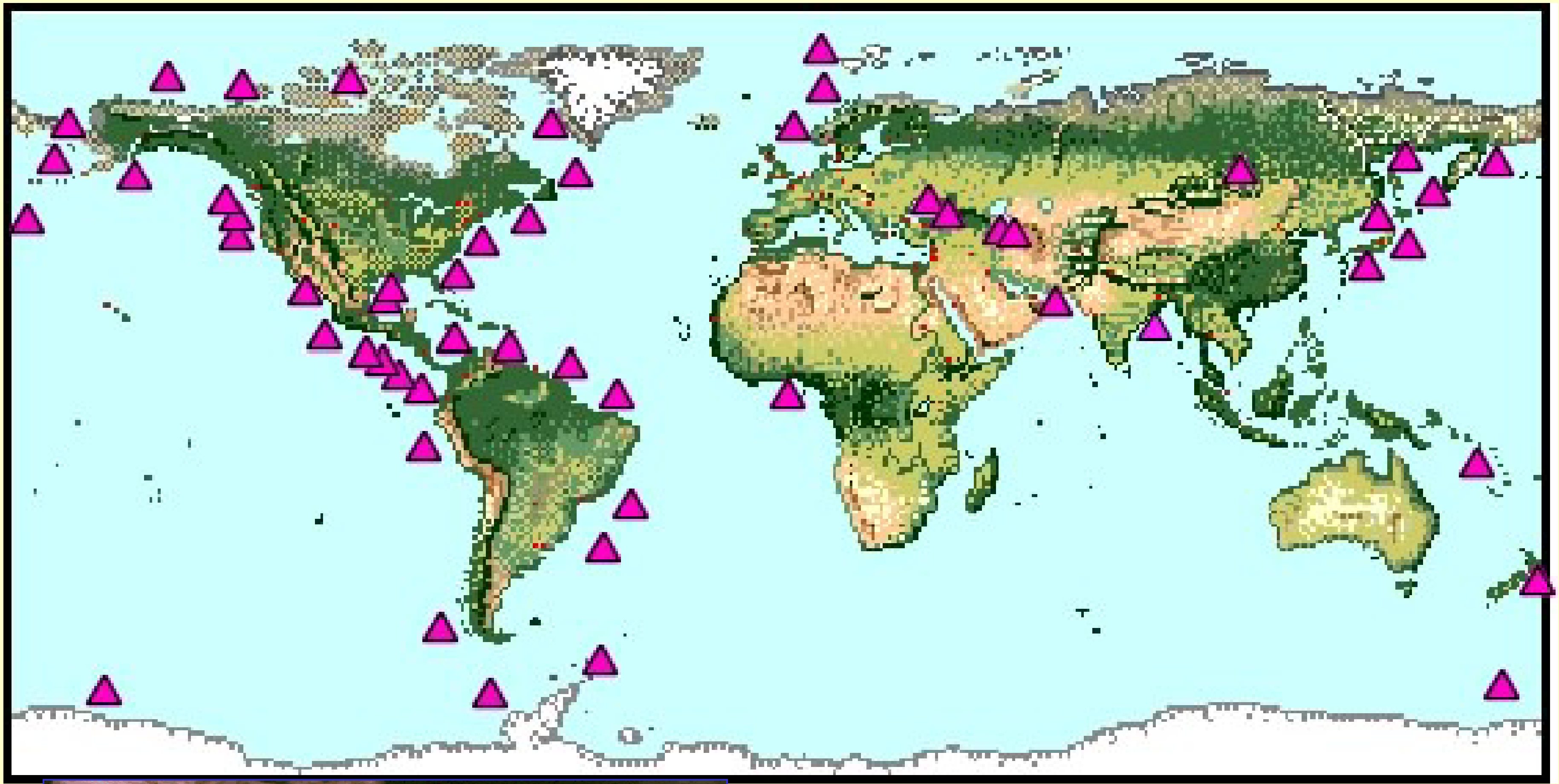
Methane Hydrate (DOE)



Lee's Lab

CO_2 Hydrates

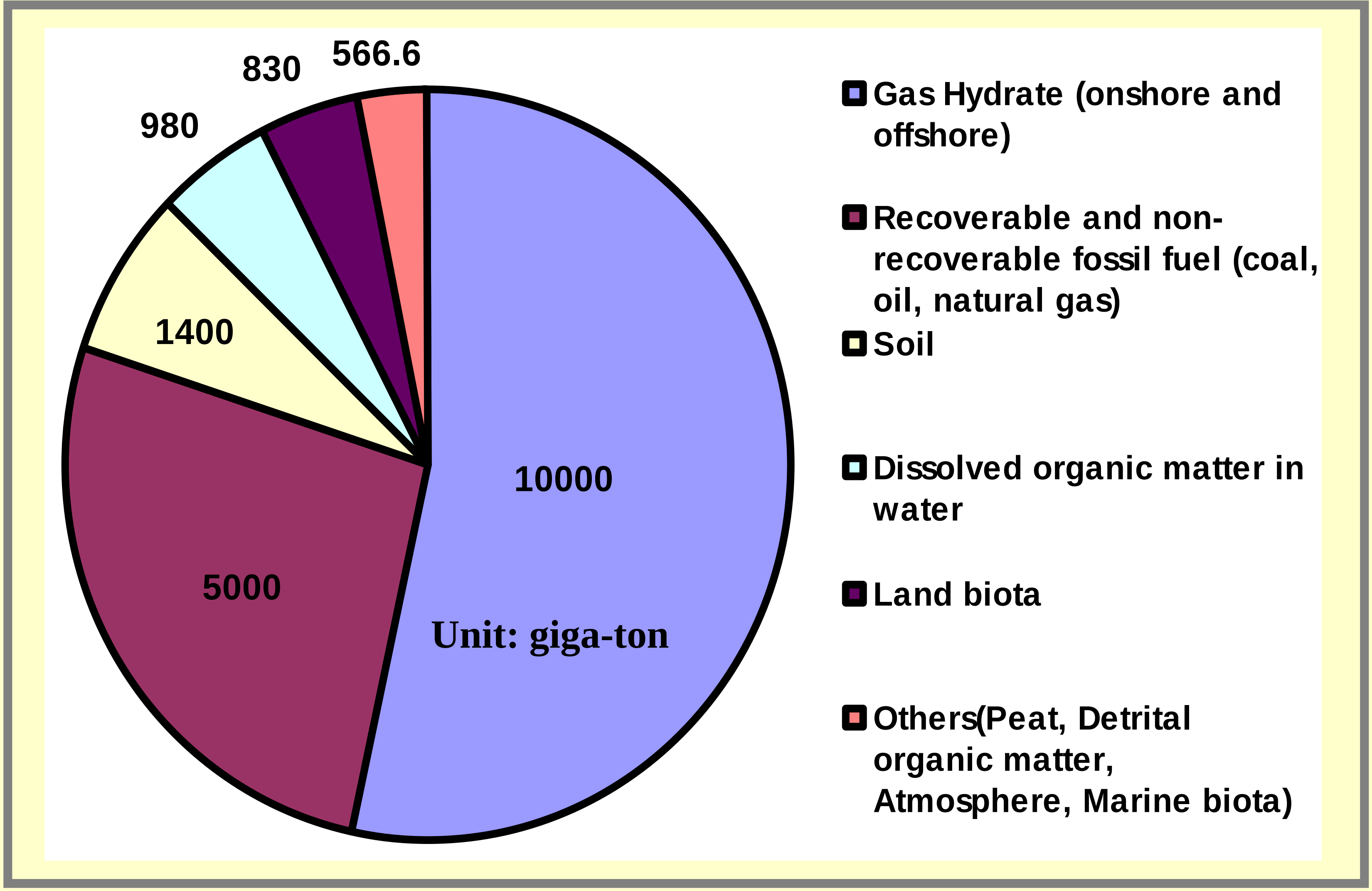
Natural Gas Hydrate in the World



Natural gas: CH_4 (95%), C_2H_6 (2.5%), C_3H_8 (1.5%), N_2 (1.0%)

Picture taken by USGS

Potentially Abundant Source for Natural Gas: Distribution of Organic Carbon in Earth



- 200,000 trillion cubic feet (Collett,1999)
- 10^{16} m^3 (Kvenvolden, 1988, 1994)

High Storage Capacity of CH_4 Hydrate

- Storage capacity: 170 vol of CH_4 / 1vol of Hyd.
- Formula: $CH_4 \cdot 5.75H_2O$
- Unit Molar Mass: 17.7 Kg/kmol
- Density: 913 Kg/m^3
- Mole number of CH_4 in 1 m^3 hydrate:

  $(913 \div 17.7) \times (1 \div 6.75) = 7.64$ Kmol/m3

Assume ideal gas and STP (0^oC and 1atm)

$PV = nRT \rightarrow V = nRT/P = 7.64 \times 0.082 \times 273/1 = 171 m^3$

Methane Hydrate (burning ICE)

Lee’s Lab

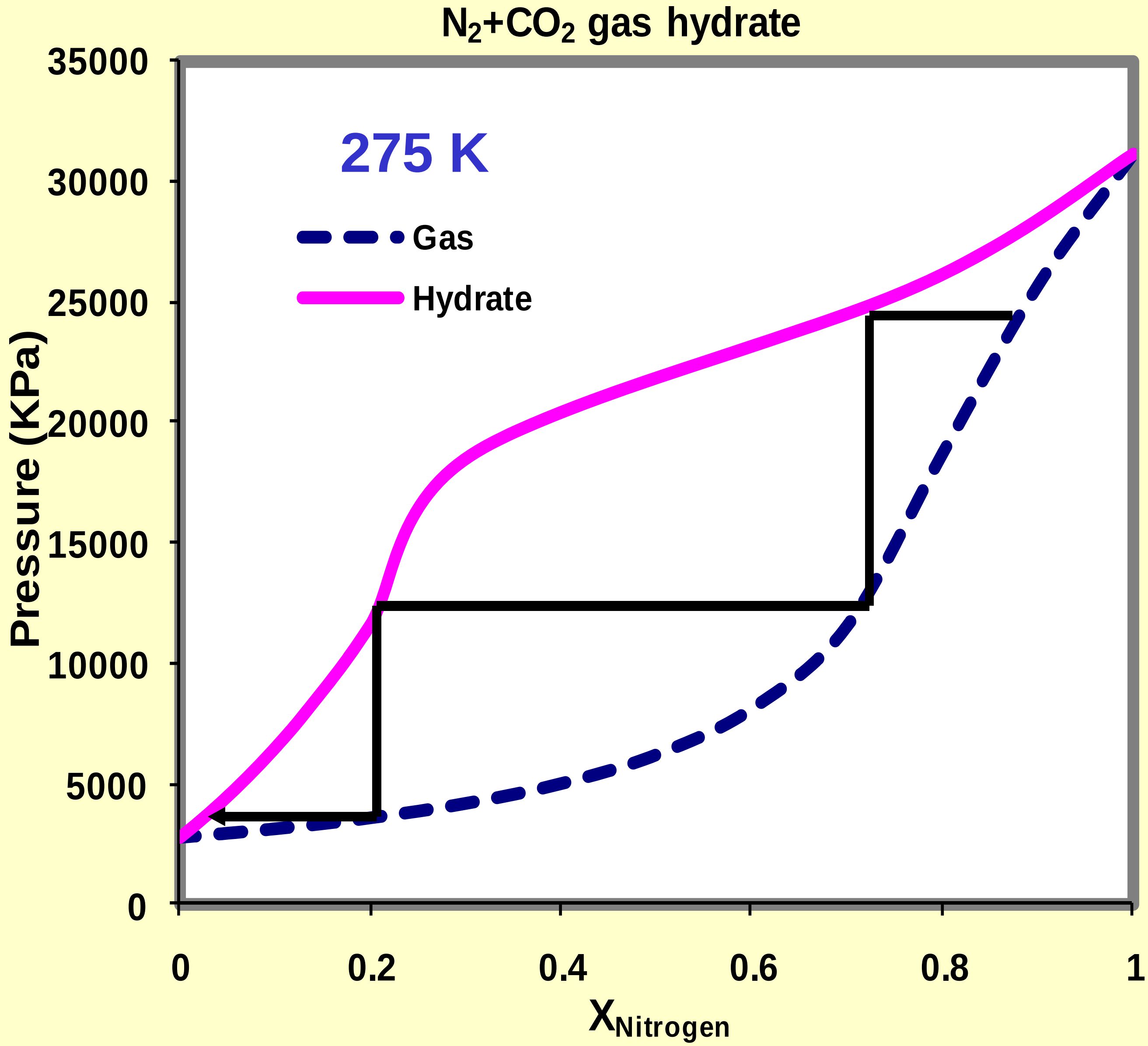
Pictures taken by AIST, Japan

Hydrate Plugs

- **Plugging of natural gas and oil pipelines**
- **Flow Assurance: major challenge**
- **Not ice but hydrates (Hammerschmidt, 1934)**

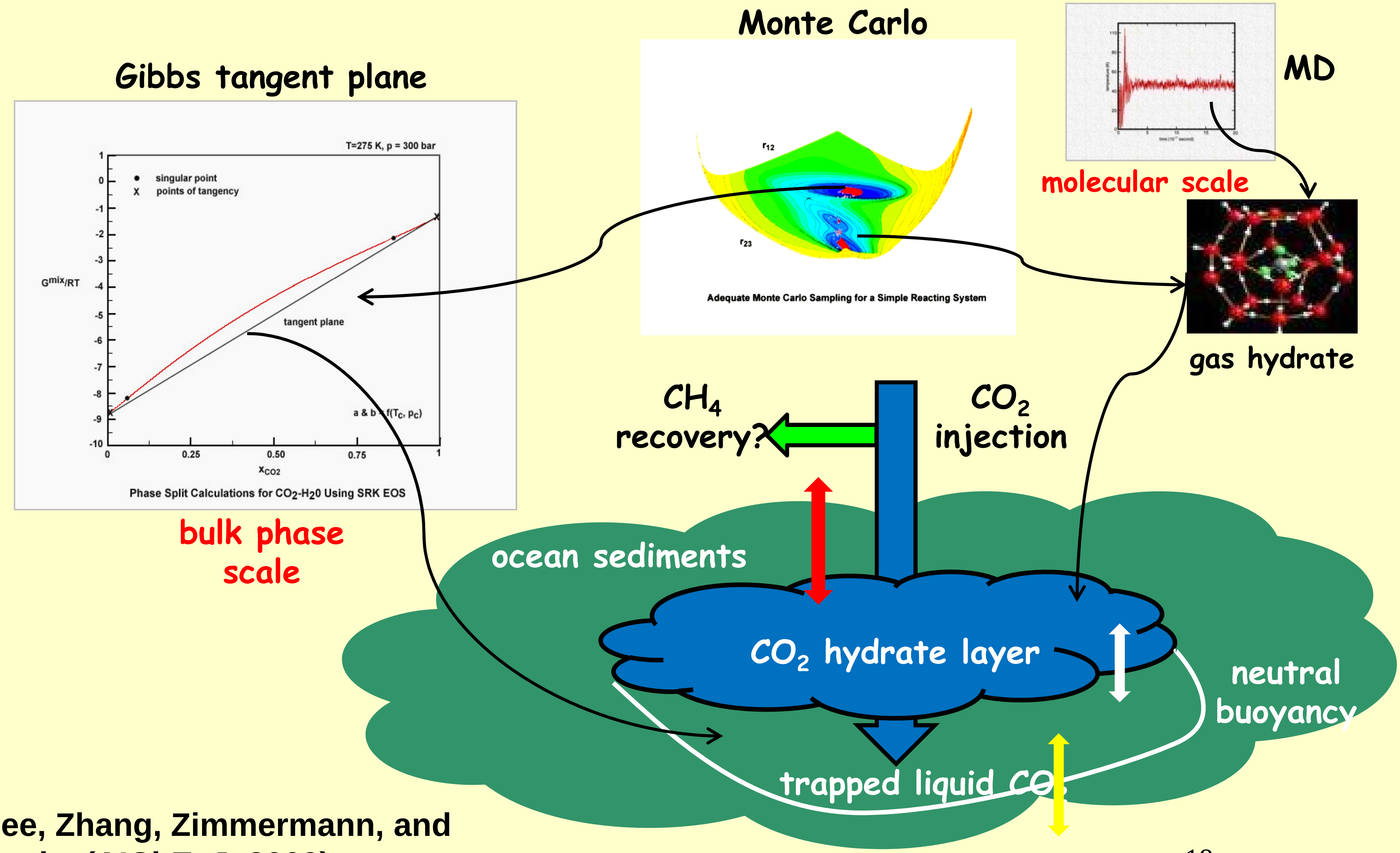
www.hydrafact.com/Gas_Hydrates.html

N_2+CO_2 Separation via Clathrate Hydrates



Determined by the Lee and Holder Model (AIChE J, 2002)

CO_2 Storage in Deep Ocean Sediments



Gibbs tangent plane

bulk phase scale

Monte Carlo

MD

molecular scale

gas hydrate

CH_4 recovery?

CO_2 injection

ocean sediments

CO_2 hydrate layer

neutral buoyancy

trapped liquid CO_2

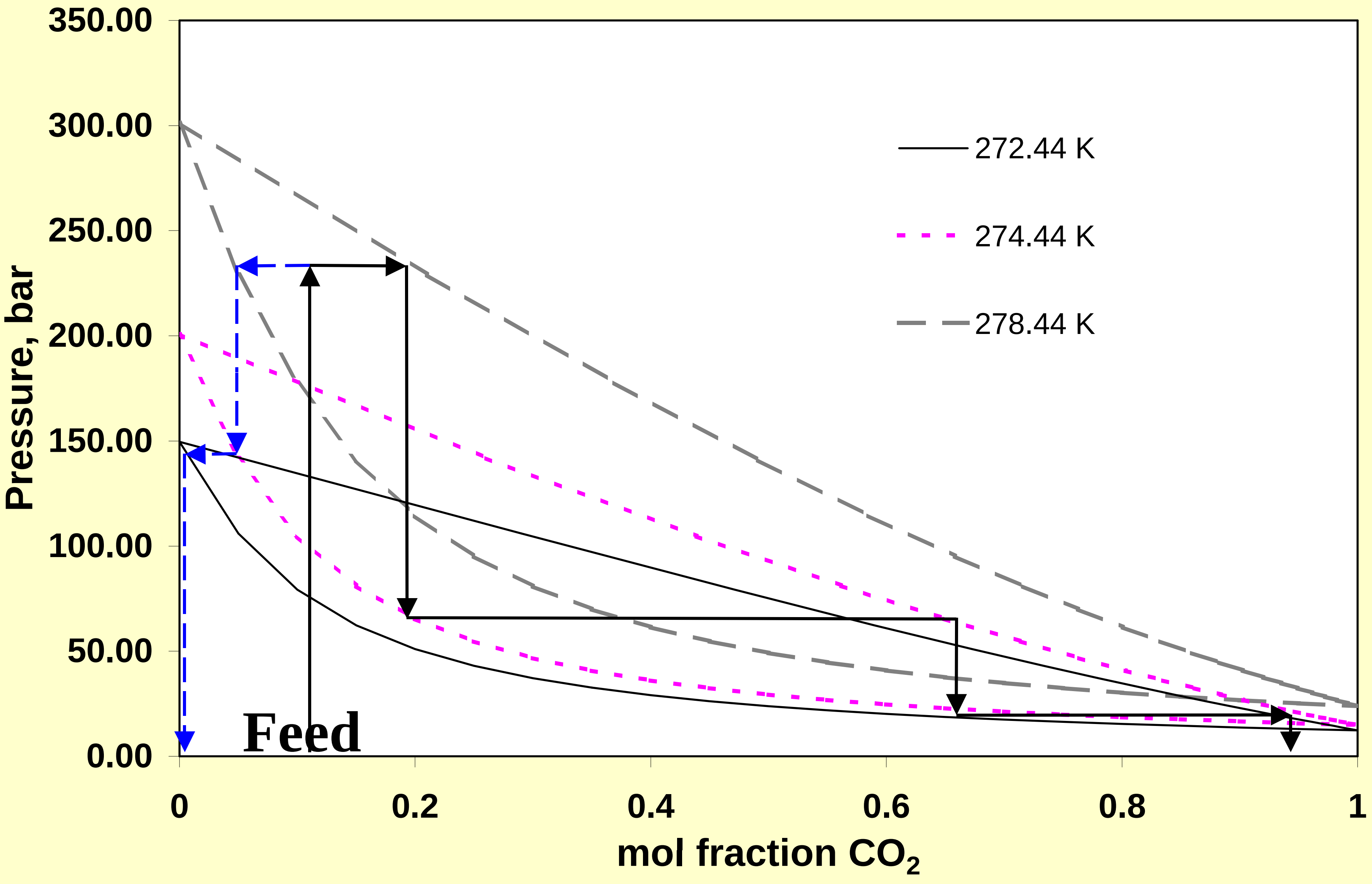
reservoir scales

Lee, Zhang, Zimmermann, and Lucia (AIChE J, 2009)

Summary for Hydrate Applications

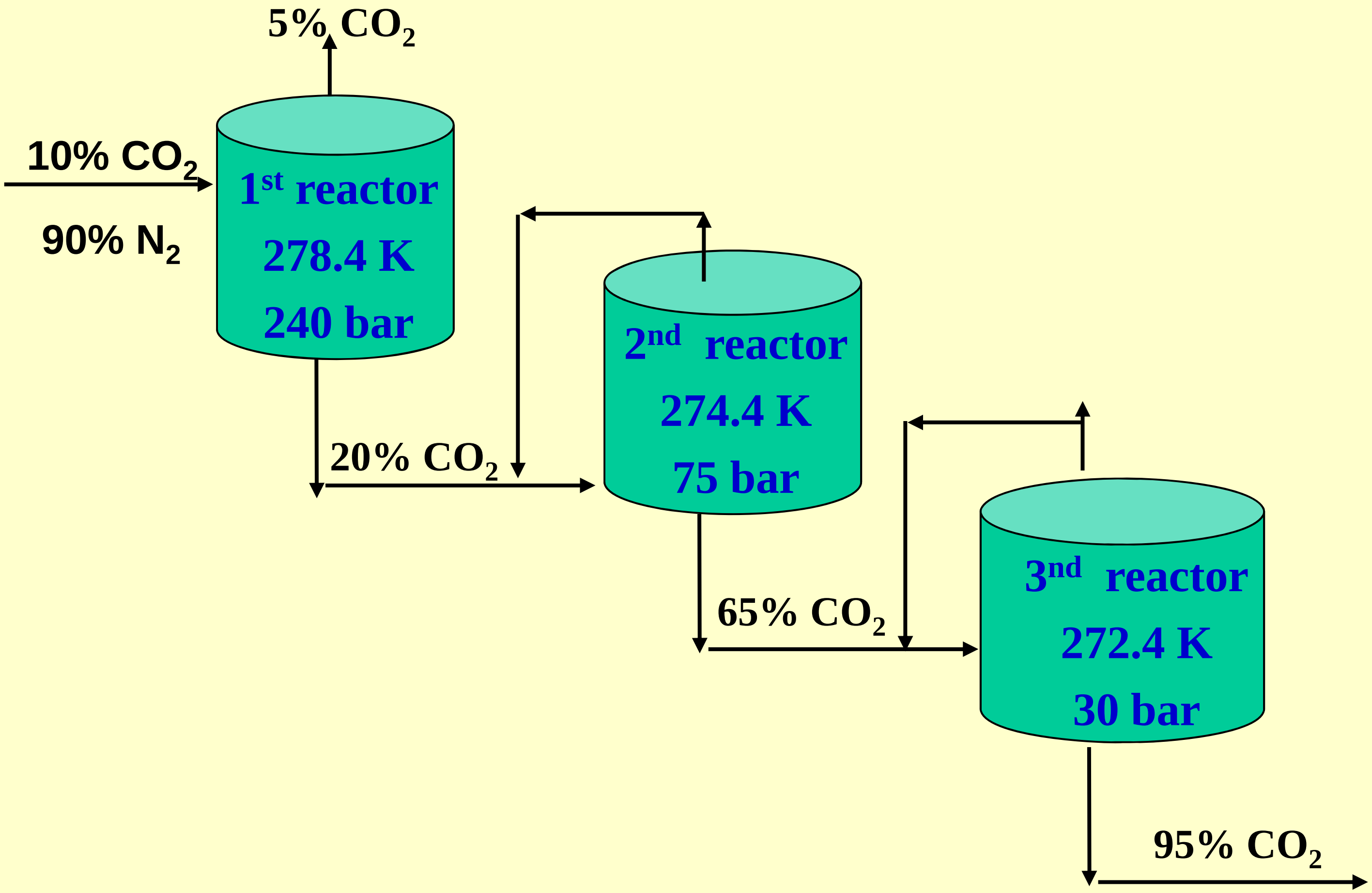
- **Energy source**
- **Gas storage**
- **Flow assurance**
- **Separation of gas mixtures**
- **CO_2 storage in the ocean sediments**

Case-1: $CO_2 + N_2$ Separation



Determined by using the Lee and Holder Model (AIChE J., 2002)

Case-1: Flow Diagram (CO_2 Hydrate Side)



5% CO_2

10% CO_2

90% N_2

1st reactor

278.4 K

240 bar

20% CO_2

2nd reactor

274.4 K

75 bar

65% CO_2

3nd reactor

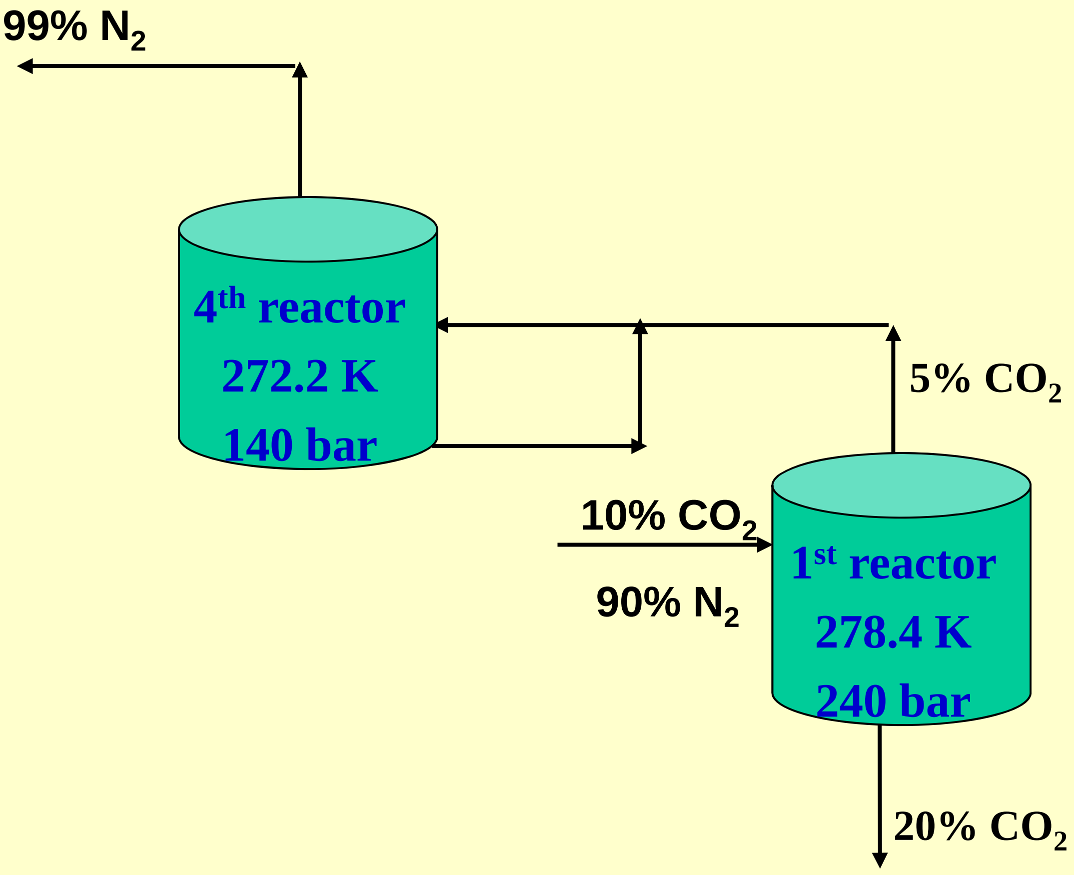
272.4 K

30 bar

95% CO_2

Separation factor: 1st - 4.75, 2nd - 7.42, 3rd - 10.23

Case-1: Flow Diagram (N_2 Gas Side)



$99\%\ N_2$

4^{th} reactor

272.2 K

140 bar

$5\%\ CO_2$

$10\%\ CO_2$

$90\%\ N_2$

1^{st} reactor

278.4 K

240 bar

$20\%\ CO_2$

Case-1: Remarks

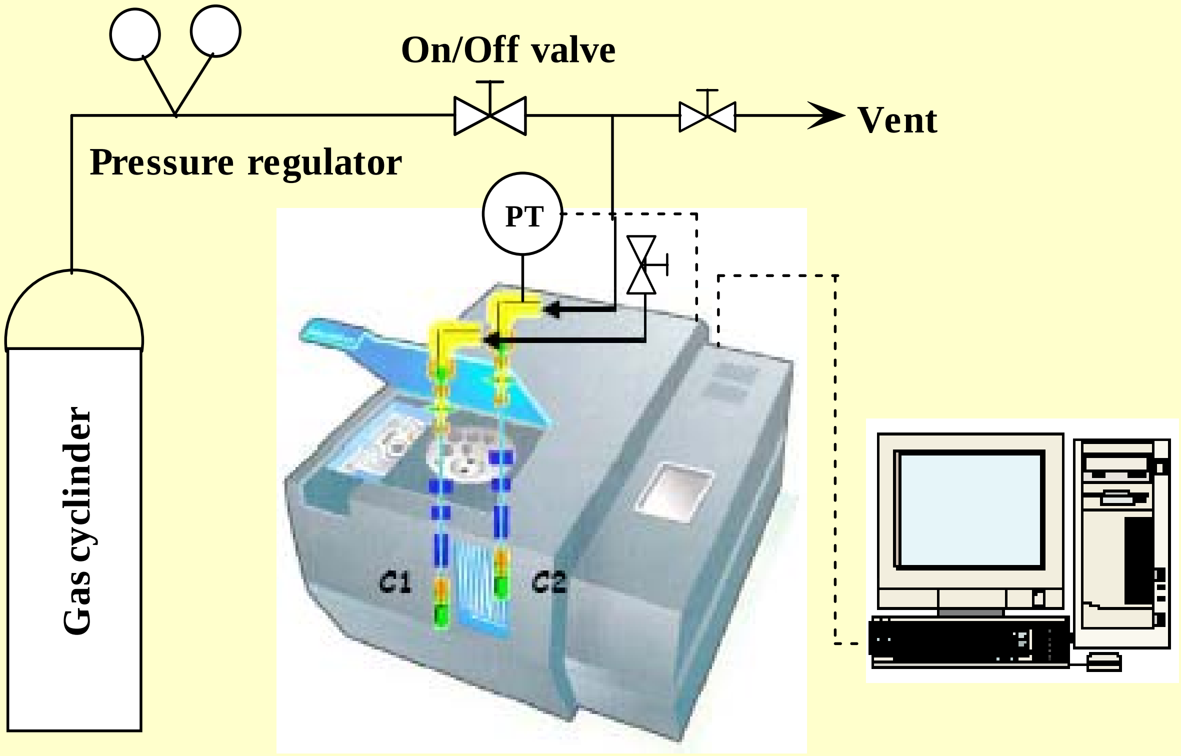
- **Separation factor (SF) is not so high (around or less 10)**
- **High compression cost for high pressure (above 10MPa)**
- **To reduce operating P, promoters (THF1)-2), TBAB3), CP4) etc) can be used → but SF will be decreasing5).**

1) **Kang and Lee, ES&T 34, 4397–4400 (2000).**
2) **Kang et al., Fluid Phase Equilibria 185, 101–109 (2000)**
3) **http://www.aseanenvironment.info/Abstract/43005208.pdf**
4) **Zhang and Lee, J. Chem Eng. Data,54 (2), pp 659–661 (2009,)**
5) **Linga et al., CES, 62, 4268 – 4276 (2007).**

Case-2: CO_2+ H_2 Separation with CP

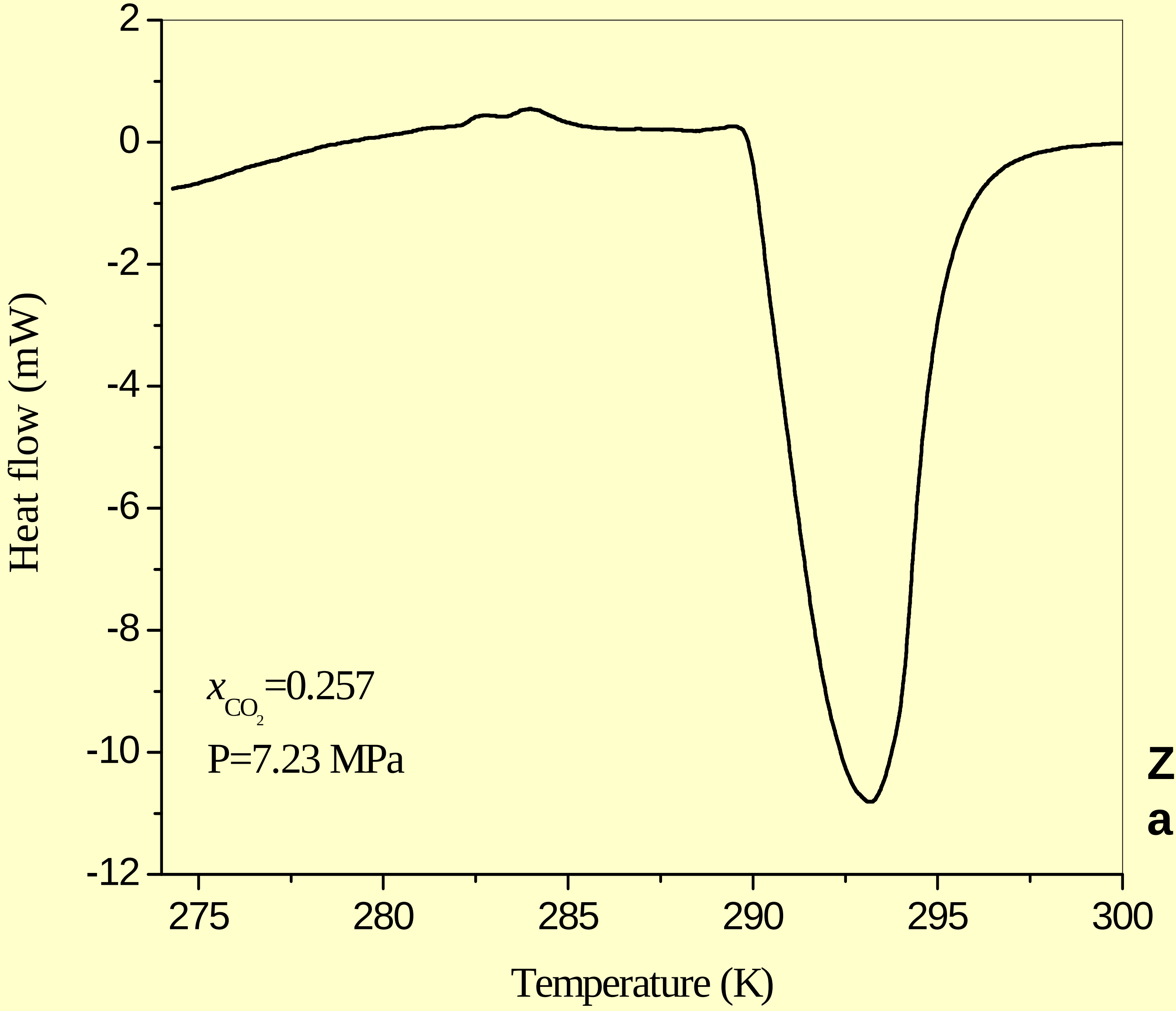
- CP is immiscible with water (while THF miscible) → equilibrium does not change with concentrations.
- CP equilibrium temp: 7C, THF: 4 C at 20 wt%.
- No phase equilibrium data of CO_2 + H_2 + CP ternary hydrate systems
- μ-DSC experiment incorporated design

Fast Equilibrium Determination High-pressure Micro-DSC



- **Sample volume: 10 – 30 μL.**
- **Up to 500 bar and down to –45 C.**
- **1 - 2 hrs for one equilibrium point.**

Typical Thermograph in a Micro-DSC



Zhang et al.,CES, 2009

Statistical Thermodynamic Model

$$\Delta\mu_W^H = \Delta\mu_W \qquad (1)$$

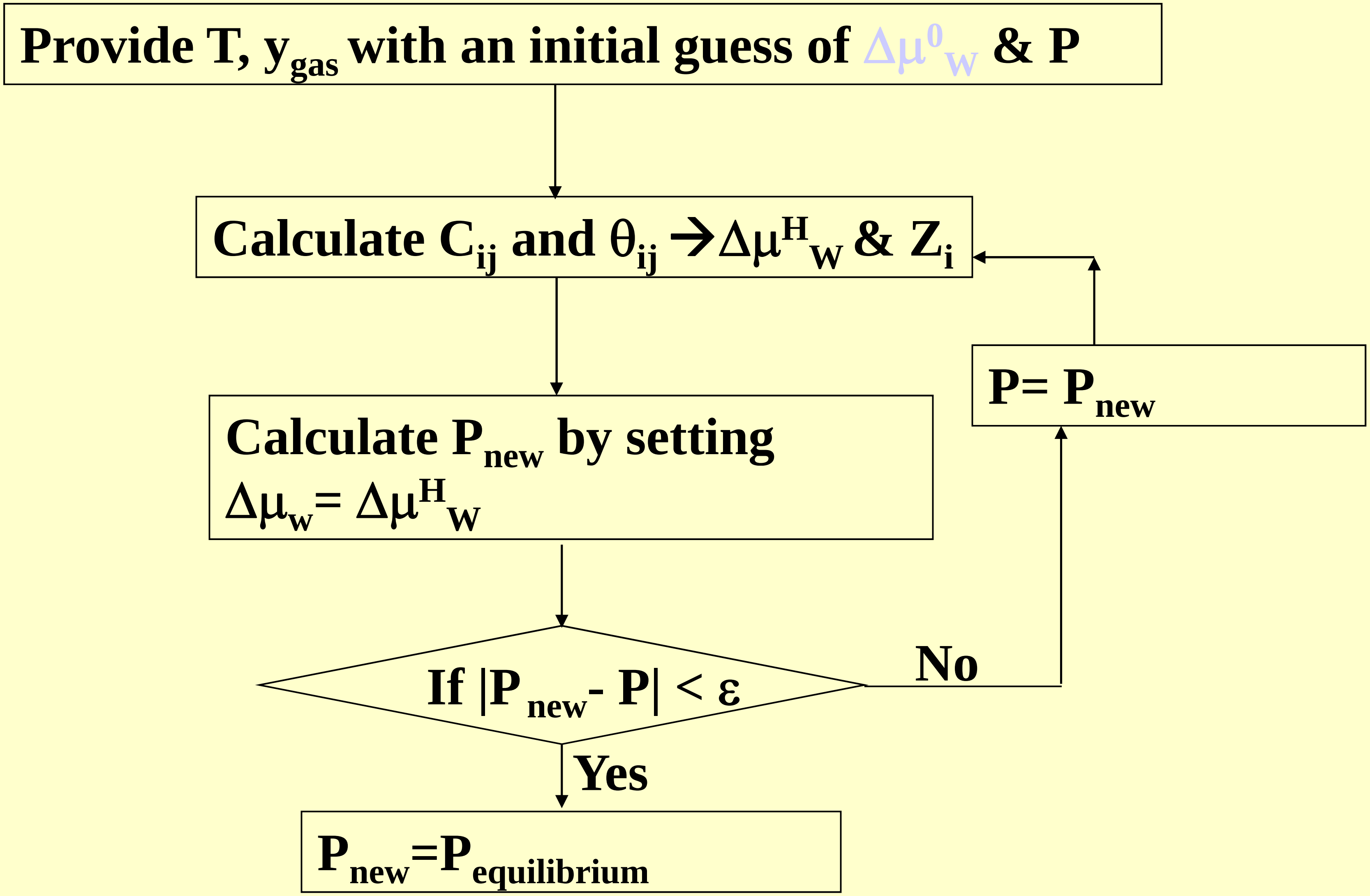
$$\Delta\mu_W^H = -RT\sum_{i=1}^{2}\nu_i \ln(1-\sum\theta_{ij}) \qquad (2)$$

$$\theta_{ij} = c_{ij}f_j/(1+\sum_j c_{ij}f_j) \qquad (3)$$

$$c_{ij} = \frac{4\pi}{kT}\int_0^a exp(-\frac{W(R)}{kT})R^2dR \qquad (4)$$

$$(\frac{\Delta\mu_W}{RT_F}) - (\frac{\Delta\mu_W^0}{RT_0}) = -\int_{T_0}^{T_F}(\frac{\Delta h'_W}{RT^2})dT + \int_0^P(\frac{\Delta V'_W}{RT_F})dP - ln(\gamma_W X_W) \quad (5)$$

Equilibrium Prediction for Ternary Hydrates



Provide T, y_{gas} with an initial guess of $\Delta\mu^{0}_{W}$ & P

Calculate C_{ij} and θ_{ij} $\rightarrow \Delta\mu^{H}_{W}$ & Z_i

Calculate P_{new} by setting
$\Delta\mu_{w} = \Delta\mu^{H}_{W}$

If $|P_{new} - P| < \varepsilon$

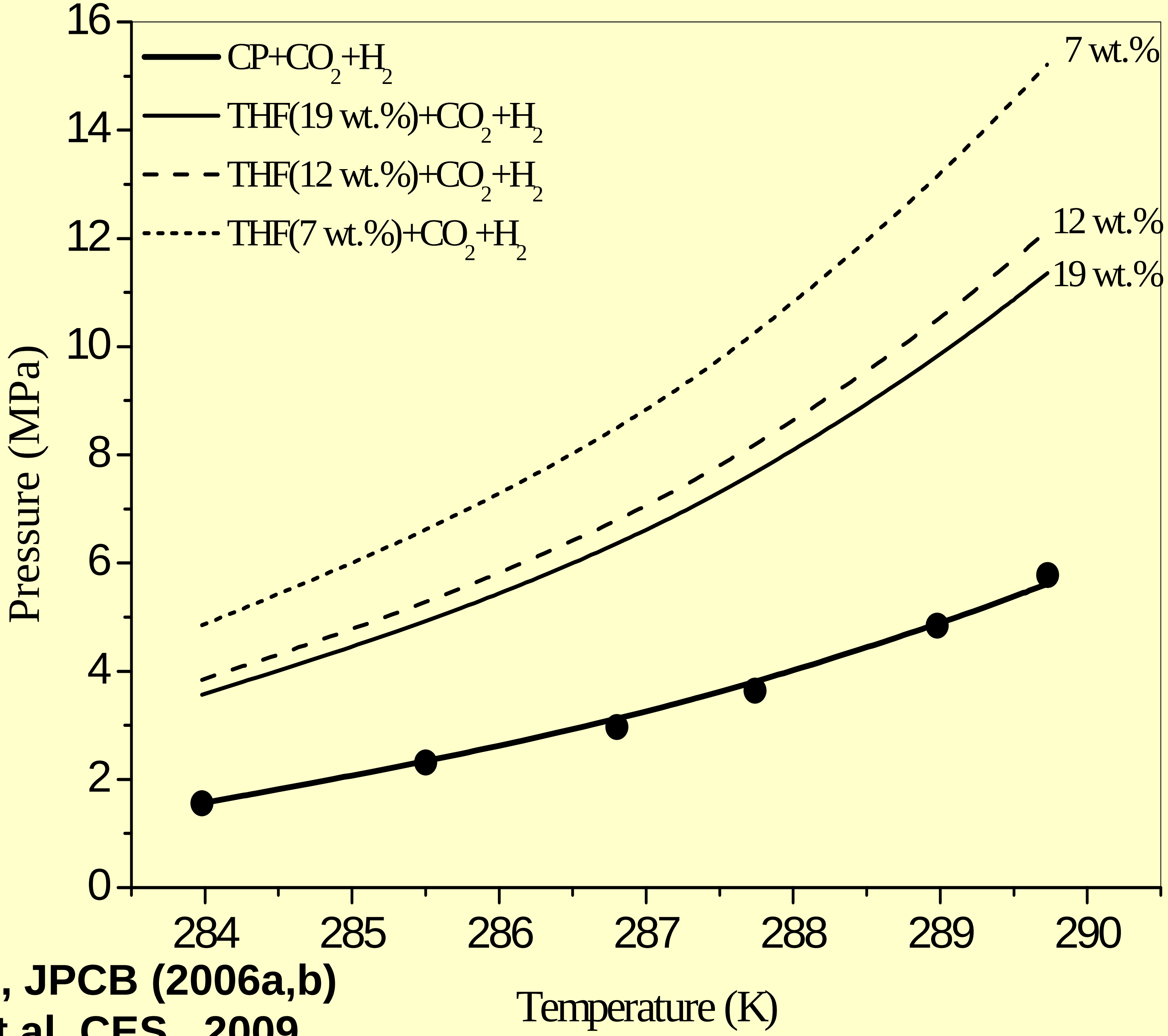
No

$P = P_{new}$

Yes

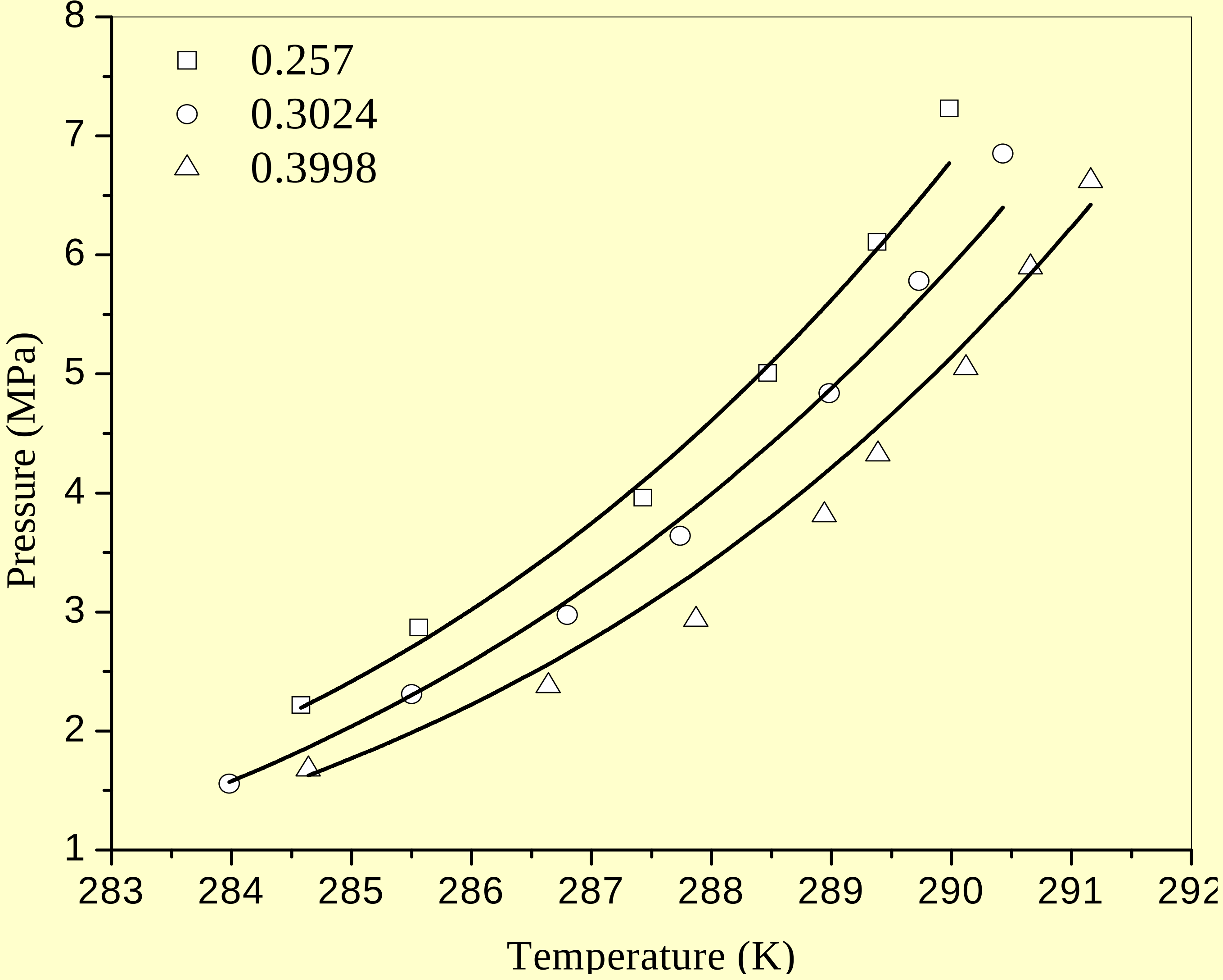
$P_{new} = P_{equilibrium}$

H_2-CP-CO_2 .vs H_2-THF-CO_2



Lee et al, JPCB (2006a,b)
Zhang et al.,CES, 2009

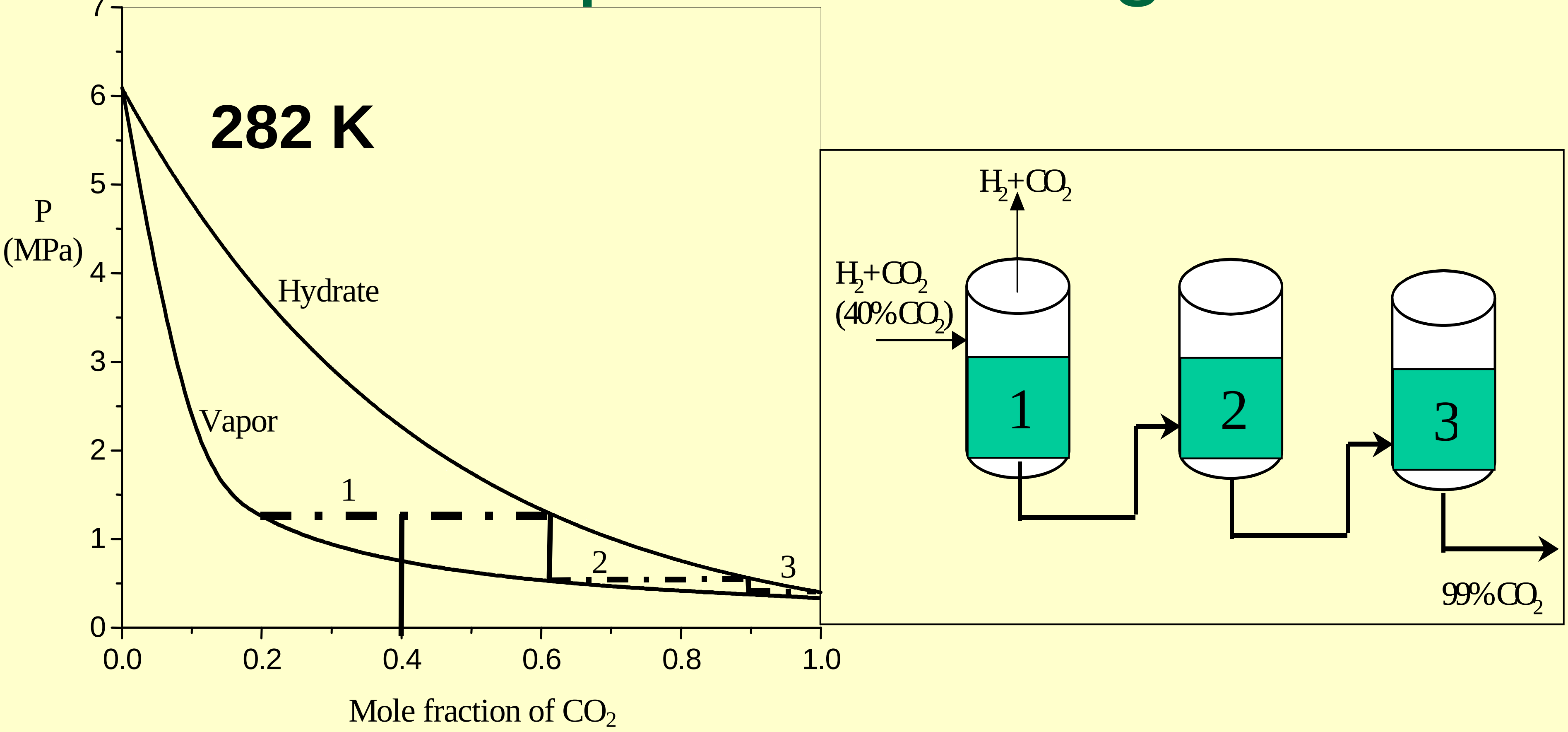
HL_1L_2V Phase Equilibrium



$$\boxed{ADD\,\% = \frac{\sum_{1\;\,30}^{n}\left(\left(P_{i,exp.} - P_{i,cal.}\right)\times 100 \Big/ P_{i,exp.}\right)}{n}}$$

$$\xrightarrow{\textbf{Minimize}} \boldsymbol{\Delta\mu^{0}_{W} = 1{,}060\ \text{J/mol}}$$

Conceptual Design



- **Three equilibrium stages enough for enriching CO_2 in the hydrate phase.**
- **Further H_2 purification needed in the H_2+CO_2 mixture.**

Concluding Remarks

- **Thermodynamically feasible for CO_2 separation from the pre/post-combustion streams in power plants.**
- **Low formation/dissociation temp Diff < 40 C.**
- **Thermodynamic promoter, CP, can greatly reduce equilibrium pressure. CP is a kinetic promoter as well for CO_2 hydrates (Zhang and Lee, 2009).**
- **Need to enhance the formation rate and to achieve flow assurance.**
- **Combined Micro-DSC experiments and theoretical modeling provide a new avenue for conceptual design.**

Acknowledgement: This work is gratefully supported by NSF (no. CBET-0854210).