University of Missouri-Columbia
Department of Chemistry
Organic Cume, December 8, 2007
Dr. Rainer Glaser

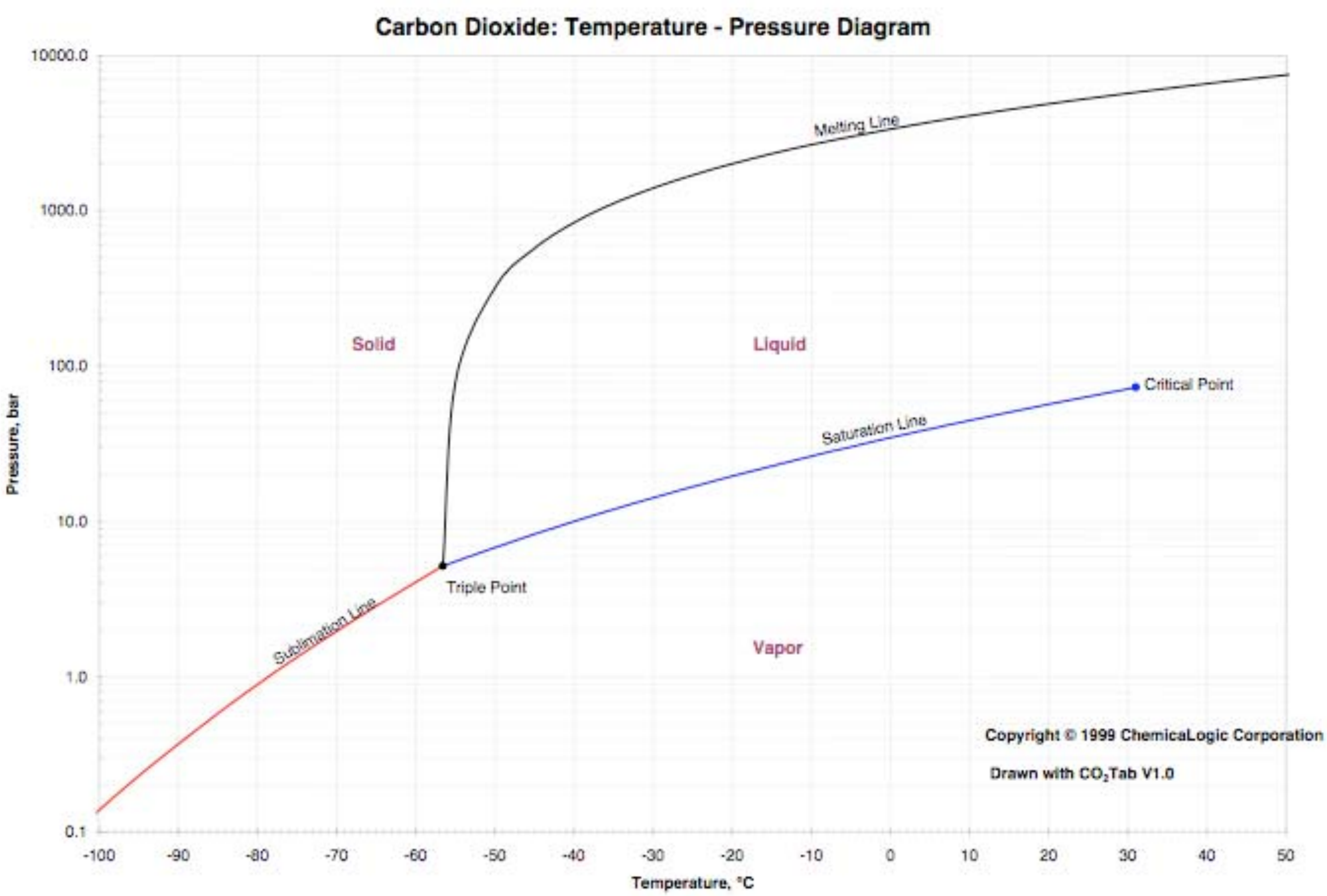
CO_2 Enhanced Oil Recovery

Or

How to Get Filthy Rich in the Oil Industry

Leading Reference

Effects of Viscous and Capillary Forces on CO_2 Enhanced Oil Recovery under Reservoir Conditions. Nobakht, M.; Moghadam, S.; Gu, Y. *Energy & Fuels* **2007**, *21*, 3469-3476.



Question 1. Molecular Properties & Intermolecular Bonding. (20 points)

The majority of the discussions in this exercise have to do with intermolecular bonding of H_2O, CO_2, CH_4 (natural gas) and $C_{15}H_{32}$ (our crude oil model). (20 points)

(a) Provide approximate melting points and boiling points for X and specify the strongest kind of interaction (and only the strongest) in pure bulk X. (10 points)

X	m.p.	b.p.	Strongest Intermolecular Interaction
H_2O			
CO_2			
CH_4			
$C_{15}H_{32}$			

(b) Mark (Yes / No) to indicate whether molecule X possesses a significant permanent electrical dipole moment and/or a significant electrical quadrupole moment. In the last column, list all Y that form stable mixtures with X (*i.e.* in X = H_2O row you are asked to indicate whether water forms stable mixtures with Y = CO_2, CH_4 and $C_{15}H_{32}$). (10 points)

X	Permanent Dipole?	Quadrupole Moment?	X Forms stable mixtures with Y
H_2O			
CO_2			
CH_4			
$C_{15}H_{32}$			

Question 2. Primary, Secondary, and Tertiary Oil Recovery.

Tertiary oil recovery is commonly called "enhanced oil recovery" (EOR) and CO_2-based EOR methods are discussed in the leading reference. (30 points)

(a) Describe the major methods used for **primary & secondary oil recovery**. (6 points)

Primary Oil Recovery:
Secondary Oil Recovery:

(b) Provide rough estimates for the effectiveness of primary, secondary and tertiary oil recovery. Specify the effectiveness by provision of the amount of **recovered oil as percentage of original oil** in place (OOIP). [Only very approximate numbers are expected; *i.e.* ±5-10%.] (6 points)

Primary:	Secondary:	Tertiary:

(c) Describe the **fundamental problem** that is being addressed by all of the tertiary recovery methods. Which property of crude oil limits the effectiveness of crude oil recovery? How do tertiary recovery methods aim to alter / change / improve this property? (6 points)

(d) The CO_2-EOR experiments described in the leading reference all were carried out at **T = 27 °C**. Did the authors provide any reason(s) for this choice? Does this particular choice of temperature matter? Why not perform the experiments at room temperature, at 0 °C, or at 100 °C? (4 points)

(e) The authors of the leading reference specified pressure with the unit "**MPa**." What does "MPa" stand for? How does one convert between the units "MPa" and "atmosphere (atm)"? (4 points)

(f) The CO_2-EOR experiments described in the leading reference all were carried out at pressures in the range **2 – 12 MPa**. Considering the phase diagram provided on the front page: Is CO_2 a gas or a liquid under those pressure and temperature conditions? (4 points)

Question 3. CO_2 Sources. (20 points)

(a) What is the primary source of commercial CO_2? [You are not being asked about vendors of dry ice, for example. The question is how "the chemical CO_2" is produced, mined, manufactured,… or whatever. If there are any "natural sources" that are tapped for commercial purposes, then state how these natural sources have formed.] (6 points)

(b) A project in Kansas funded by the U.S. Department of Energy seeks to demonstrate that CO_2-EOR can be feasible in Kansas. This project uses waste heat from a 15-megawatt natural-gas-fired turbine generator to provide thermal energy for a 25 million gallon-per-year corn ethanol plant. The project then recovers some of the CO_2 that is a byproduct of the fermentation process involved in corn ethanol production and uses this CO_2 for EOR flooding in the Hall-Gurney field in central Kansas.

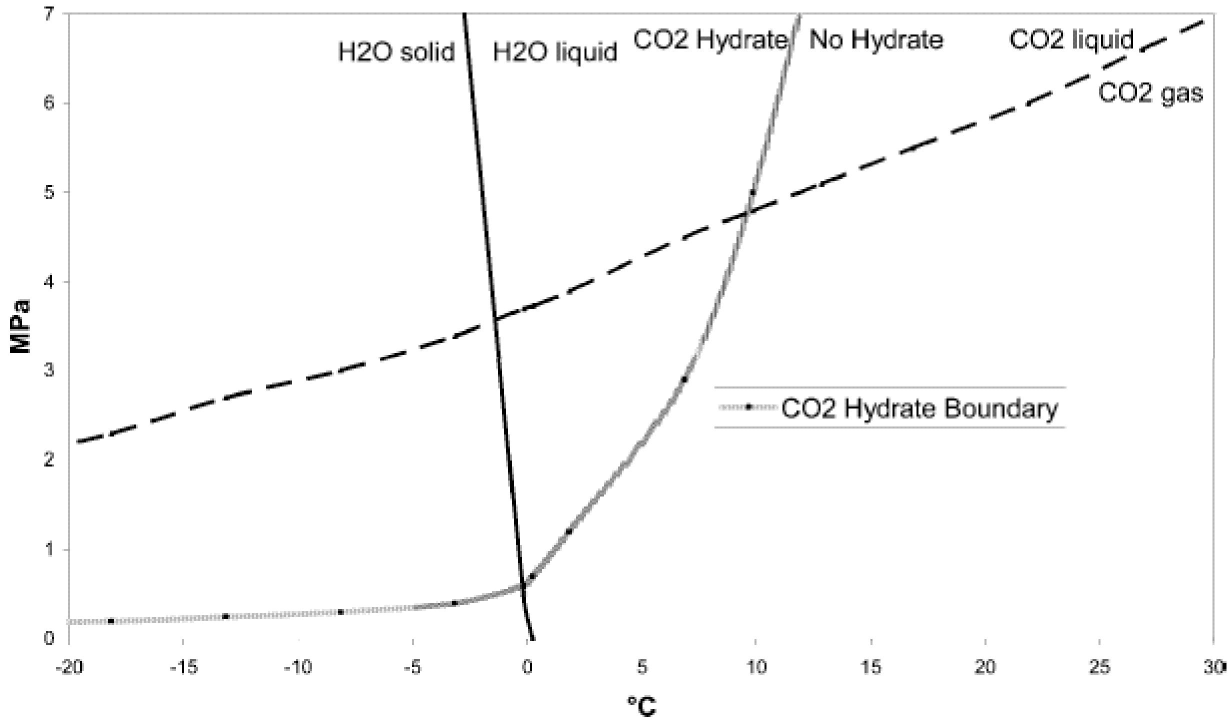
Chemical reaction formula for CO_2 preparation in the natural-gas-fired turbine? (3 points)
Chemical reaction formula for CO_2 preparation via fermentation in corn ethanol production? (3 p.)
Why is CO_2 generation by fermentation more economical than CO_2 generation from the natural-gas-fired turbine? (8 points)

Question 4. CO_2 Sinks & Sequestration. (30 points)

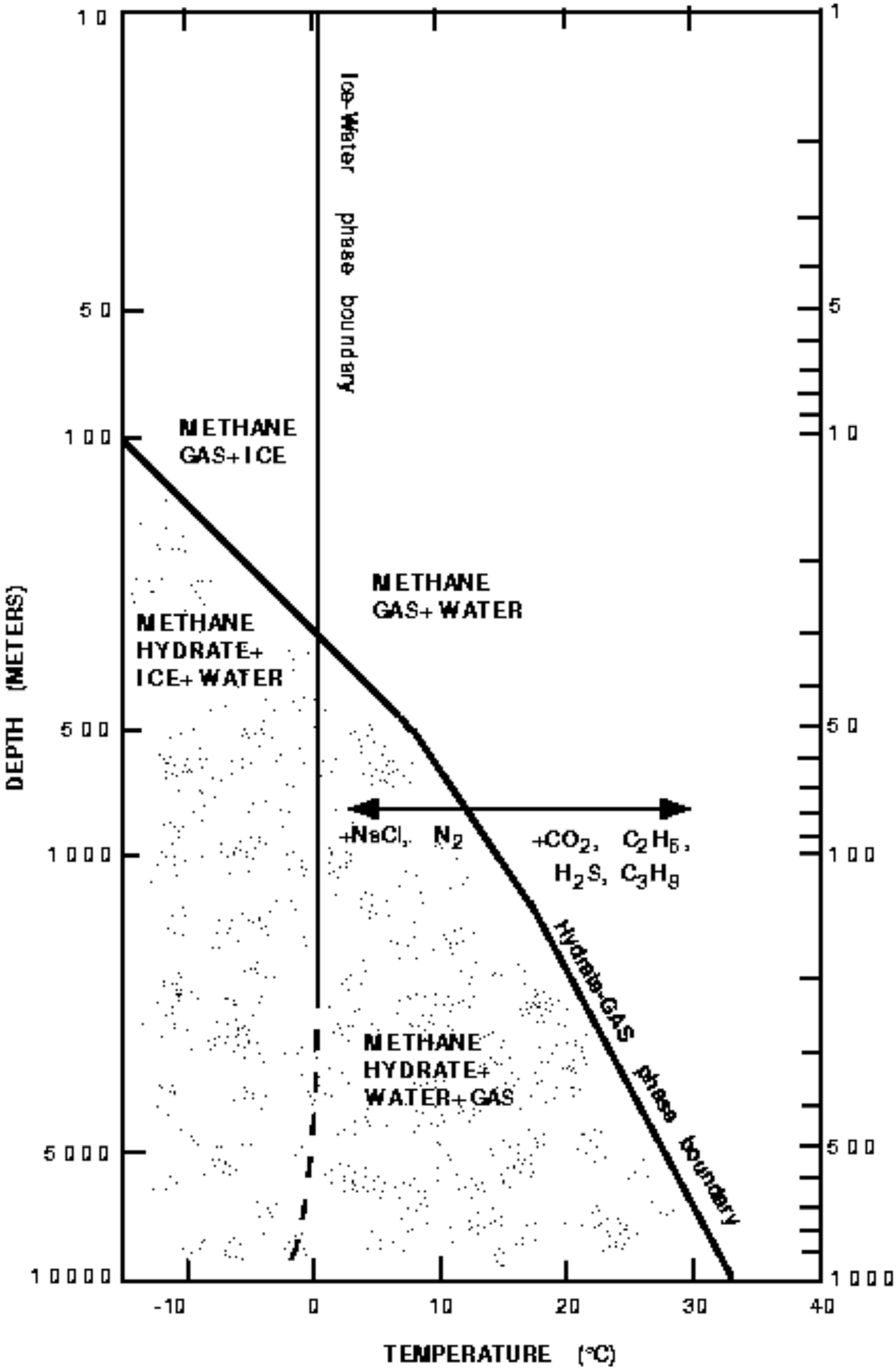
(a) What happens to the CO_2 used in CO_2-EOR? **Is CO_2 recovered after EOR?** If CO_2 is recovered, how is the CO_2 recovered and how effective is the recovery process? If CO_2 is not actively recovered, what happens to the CO_2 over short (1-10 years) and longer time spans (10–1000 years)? (8 points)

(b) Limestone is a natural CO_2 sink. Limestone is formed by heating CaO or $Ca(OH)_2$ in the presence of CO_2 to several hundred degrees Celsius (but < 850 °C). When heated above 850 °C (and at normal pressure) limestone again releases CO_2. Explain the thermodynamics of this solid-gas equilibrium reaction. [No need to address kinetics; all processes are fast above 800 °C]. What effect(s) dominate(s) the equilibrium below / above 850 °C? [Words suggested for use in discussion: temperature dependence; equilibrium constant; reaction enthalpy, entropy, free enthalpy; lattice energy,…] (10 p.)

(c) **CO_2-Hydrates** provide a natural CO_2 sink and these interesting aggregates are relatively little known. Methane-hydrates are more well-known because they have been discussed as a possible source of natural gas by controlled methane release. The uncontrolled release of methane from CH_4-hydrates has been a source of concern with regard to global warming. -- Is CO_2-hydrate stability a significant concern in CO_2-sequestration? Consider the phase diagrams provided below and on the next page and argue whether CO_2 sequestration via CO_2-hydrates is feasible and safe. (12 points)



Source: *Energy & Fuels* **2007**, *21*, 3285.



10
50
100
500
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5000
10000
1
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100
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-10
0
10
20
30
40
Ice-Water phase boundary
METHANE GAS+ICE
METHANE GAS+WATER
METHANE HYDRATE+ ICE+WATER
+NaCl, N2
+CO2, C2H6, H2S, C3H8
Hydrate-GAS phase boundary
METHANE HYDRATE+ WATER+GAS
DEPTH (METERS)
PRESSURE (ATM)
TEMPERATURE (°C)