Effects of Temperature and Gas Mixing on Formation Pressure, CO_2 Sequestration and Methane Production in Underground Coalbeds*

James G. Blencoe
Aqueous Chemistry and Geochemistry Group
Chemical Sciences Division
Oak Ridge National Laboratory
Oak Ridge, TN

Simon L. Marshall and Michael T. Naney
Electrochemical Systems, Inc.
Oak Ridge, TN

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Personnel

James G. Blencoe is a research geochemist with more than 30 years of experience investigating the thermodynamics and phase relations of geologic materials (rock-forming minerals, silicate melts, and mixed-volatile fluids). He is currently the lead investigator on a DOE/BES-funded project to determine the densities, excess molar volumes and vapor-liquid equilibria of binary and ternary CO_2-CH_4-N_2-NaCl-H_2O mixtures at 300-400°C, 50-1000 bars.

Simon L. Marshall is an applied mathematician with extensive experience in the mathematical modeling of physical and chemical systems, including: development of activity-coefficient models and equations of state for multi-component aqueous mixtures at high temperatures and pressures, preparation of computer codes for numerical solution of compressible fluid-flow problems, and theoretical analysis and calculation of lattice potentials and cohesive energies for ionic crystals.

Michael T. Naney is an experimental petrologist with special expertise in the design, construction and operation of equipment for making precise and accurate measurements of the thermophysical properties and phase relations of geologic materials at elevated temperatures and pressures.

Recent Publications

Blencoe, J. G., Seitz, J. C., and Anovitz, L. M., 1999, The CO_2-H_2O system. II. Calculated thermodynamic mixing properties for 400°C, 0-400 MPa. *Geochim. Cosmochim. Acta*, 63, 2393-2408.

Blencoe, J. G., Naney, M. T., and Anovitz, L. M., 2001, The CO_2-H_2O system: III. A new experimental method for determining liquid-vapor equilibria at high subcritical temperatures. *Amer. Mineral.*, 86, 1100-1111.

Blencoe, J. G., Anovitz, L. M., and Singh, J., 2000, A semi-empirical excess pressure equation for CO_2-H_2O fluids at 400°C, 0-400 MPa. *Proceedings of the 13th International Conference on the Properties of Water and Steam*, 126-133.

Seitz, J. C., and Blencoe, J. G., 1999, The CO_2-H_2O system. I. Experimental determination of volumetric properties at 400°C, 10-100 MPa. *Geochim. Cosmochim. Acta*, 63, 1559-1569.

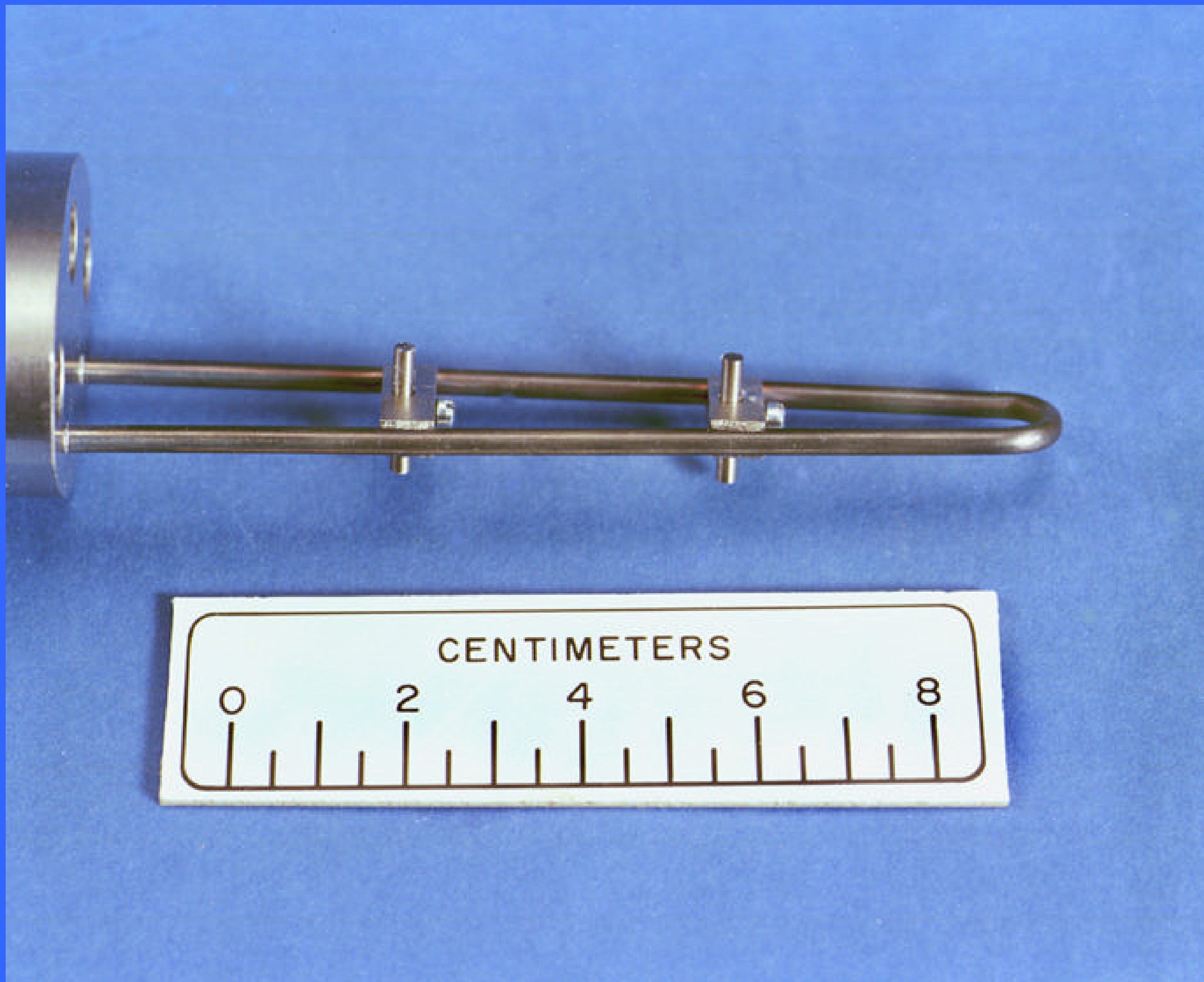
Recent Publications (Cont'd)

Blencoe, J. G., Drummond, S. E., Seitz, J. C., and Nesbitt, B. E., 1996, A vibrating-tube densimeter for fluids at high pressures and temperatures. *Int. Jour. Thermophysics*, 17, 179-190.

Seitz, J. C., and Blencoe, J. G., 1996, Volumetric properties for {(1-x)CO_2 + xCH_4}, {1-x)CO_2 + xN_2}, and {1-x)CH_4 + xN_2} at the pressures (19.94, 29.94, 39.94, 59.93, 79.93, and 99.93) MPa and the temperature 673.15 K. *J. Chem. Thermodynamics*, 28, 1996, 1207-1213.

Seitz, J. C., Blencoe, J. G., and Bodnar, R. J., 1996, Volumetric properties of {(1-x)CO_2 + xCH_4}, {(1-x)CO_2 + N_2}, and {(1-x)CH_4 + N_2} at the temperatures (323.15, 373.15, 473.15, 573.15) K and pressures (9.84, 19.84, 29.84, 39.84, 59.83, 79.83, 99.83) MPa. *J. Chem. Thermodynamics*, 28, 521-538.

Seitz, J. C., Blencoe, J. G., and Bodnar, R. J., 1996, Volumetric properties of {x_1CO_2 + x_2CH_4 + (1-x_1-x_2N_2} at the temperatures (323.15, 373.15, 473.15, 573.15) K and pressures (19.84, 39.84, 59.83, 99.83) MPa. *J. Chem. Thermodynamics*, 28, 539-550.


CENTIMETERS
0 2 4 6 8

Key Issues

At the elevated temperatures and pressures encountered in deep, unmineable coalbeds:

- The densities and viscosities of binary and ternary CO_2-CH_4-N_2 gas mixtures*
- Coal swelling/shrinkage in “brine”-mixed gas (CO_2-CH_4 ± N_2) pressure media
- Geochemical reactions induced by CO_2 injection (change in “brine” pH, dissolution of heavy metals, etc.)
- Rates and magnitudes of gas (CO_2-CH_4 ± N_2) sorption/desorption onto/from “dry” and “moist” coal samples

*Principal focus of the new research

Approach

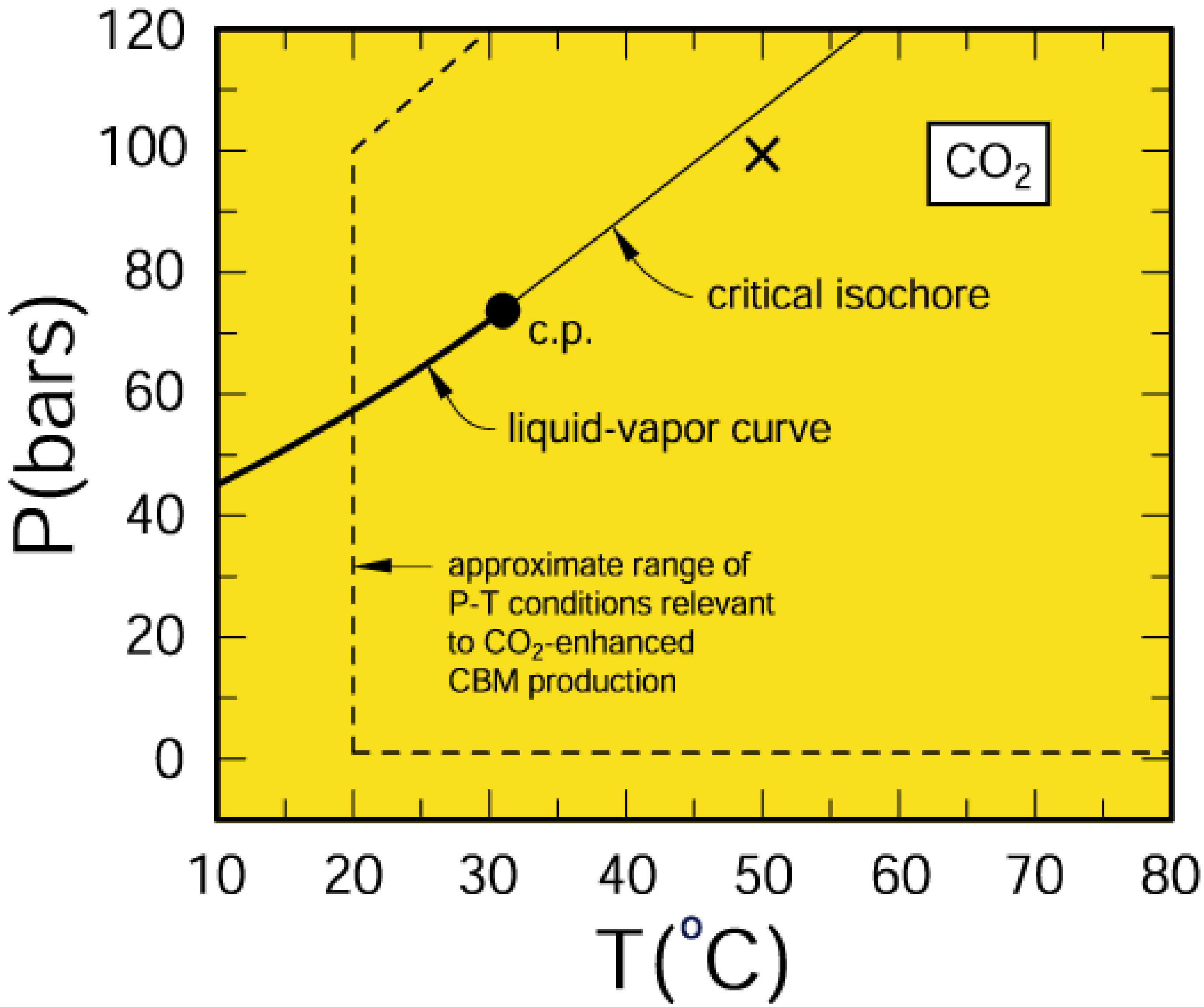
- Experiments will be performed at 25-200°C, 1-300 bars, using a custom designed stirred-autoclave apparatus with a 1.8 liter internal volume.
- Aliquots of CO_2-CH_4 ± N_2 gas will be loaded into, and extracted from, the autoclave through multiple injection and sampling ports <u>during experimentation</u>.
- Coal swelling/shrinkage in “brine”-mixed (CO_2-CH_4 ± N_2) gas pressure media can be observed and measured optically through sapphire windows in the autoclave.
- The density data obtained for binary and ternary CO_2-CH_4-N_2 gases will be used to develop volumetric equations of state for the mixtures.

Justification

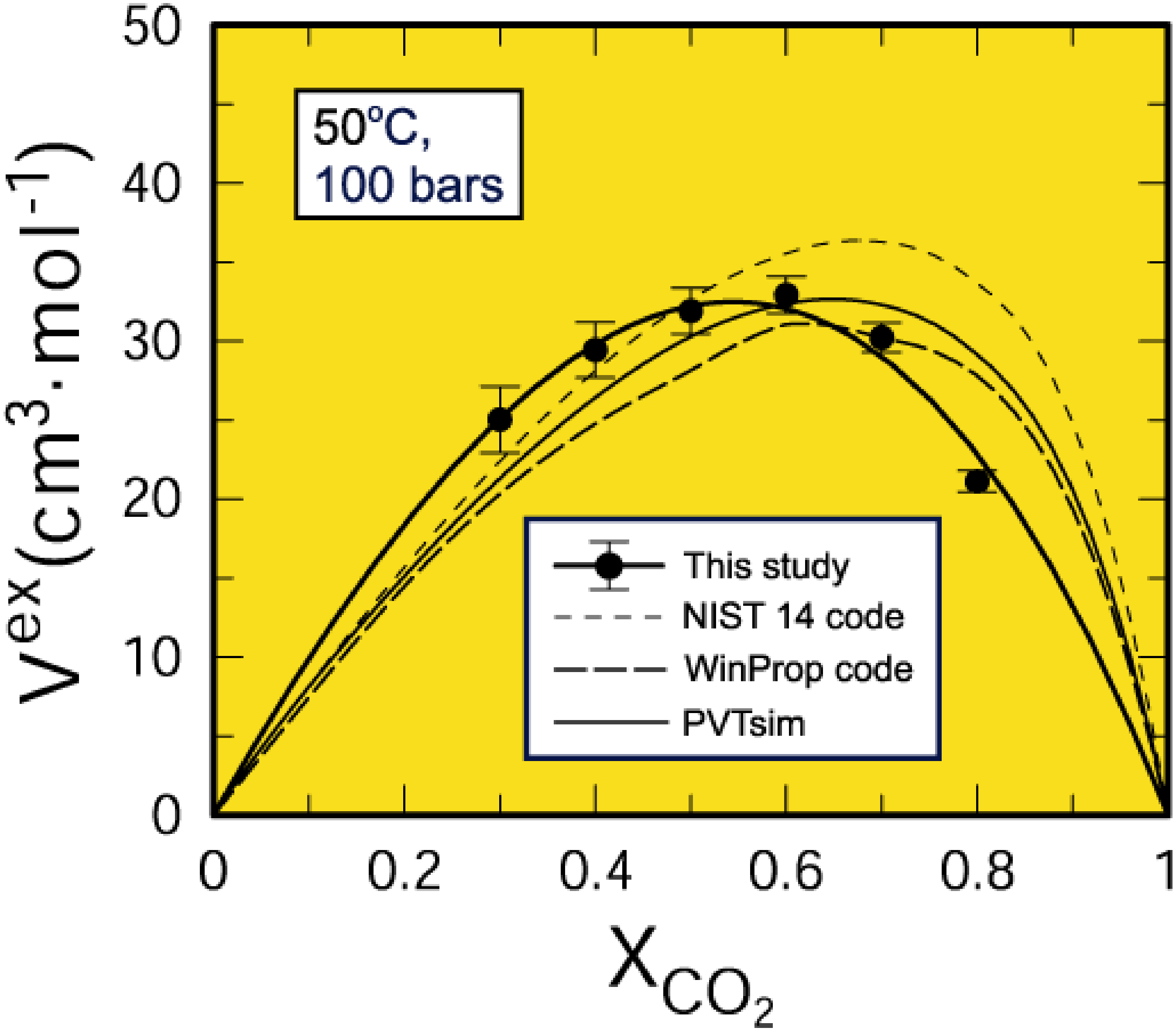
- The densities of CO_2-CH_4-N_2 gas mixtures at elevated temperatures and pressures are <u>not</u> accurately predicted by commercial computer codes.
- To our knowledge, the viscosities of CO_2-CH_4-N_2 gases have not been measured at temperatures and pressures relevant to CO_2-enhanced CBM production.
- We are unaware of any attempts to precisely and accurately measure coal swelling/shrinkage in “brine”-mixed (CO_2-CH_4 ± N_2) gas pressure media.
- Additional technical information is needed on the geochemical reactions that will occur when CO_2 is injected into deep, unmineable coalbeds.

Justification (Cont’d)

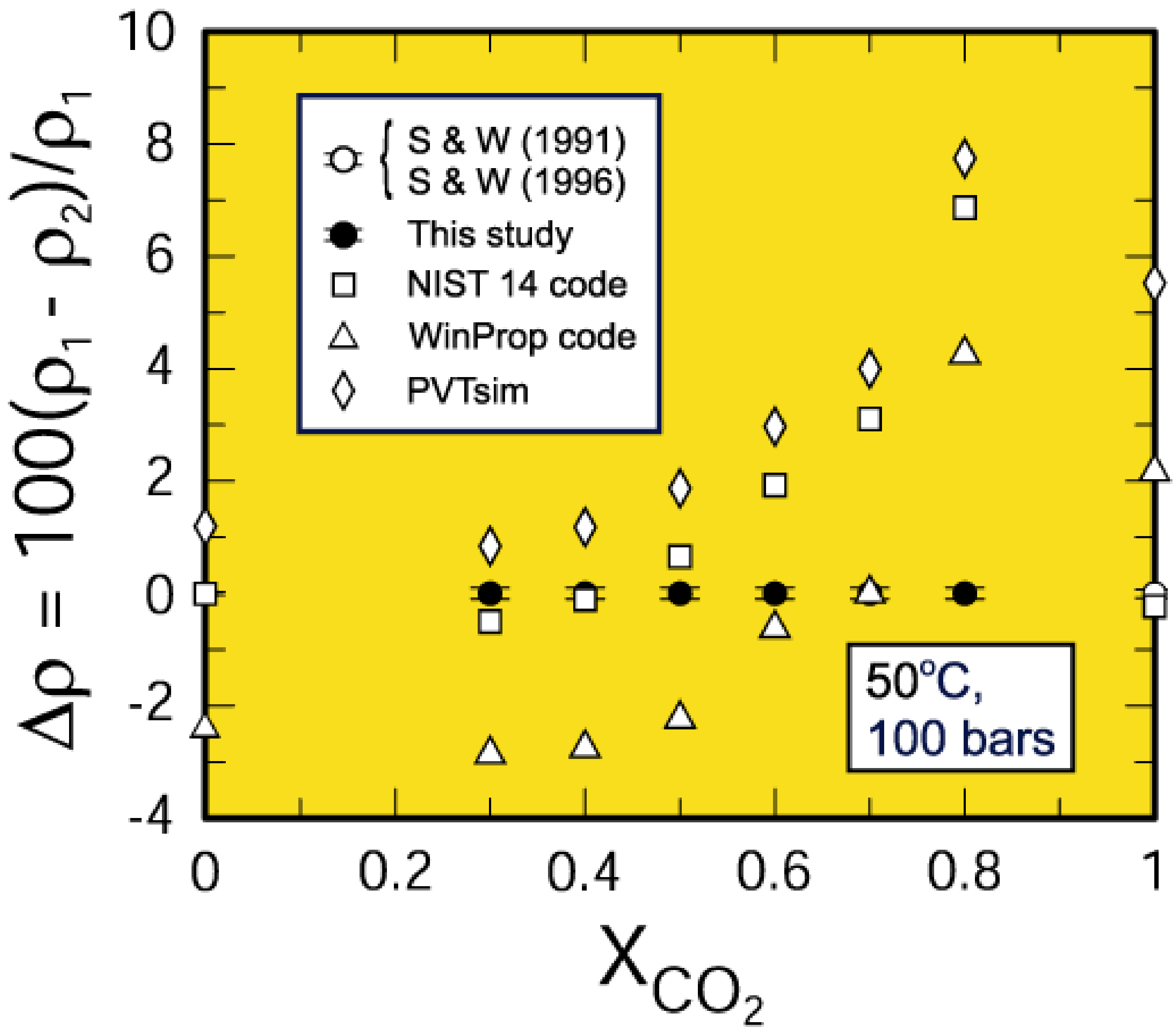
- CO_2-CH_4-N_2 mixing is strongly nonideal at *P-T* conditions near the critical point of CO_2. Depending on ambient temperature and pressure, gas mixing could produce pressure surges during injection of CO_2 into deep unmineable coalbeds.
- Nonideal CO_2-CH_4-N_2 mixing will also have significant effects on measured, mixed-gas sorption isotherms for coal, because CO_2-CH_4-N_2 sorption/desorption on coal surfaces will depend on the activities of the gas species, rather than their mole fractions.



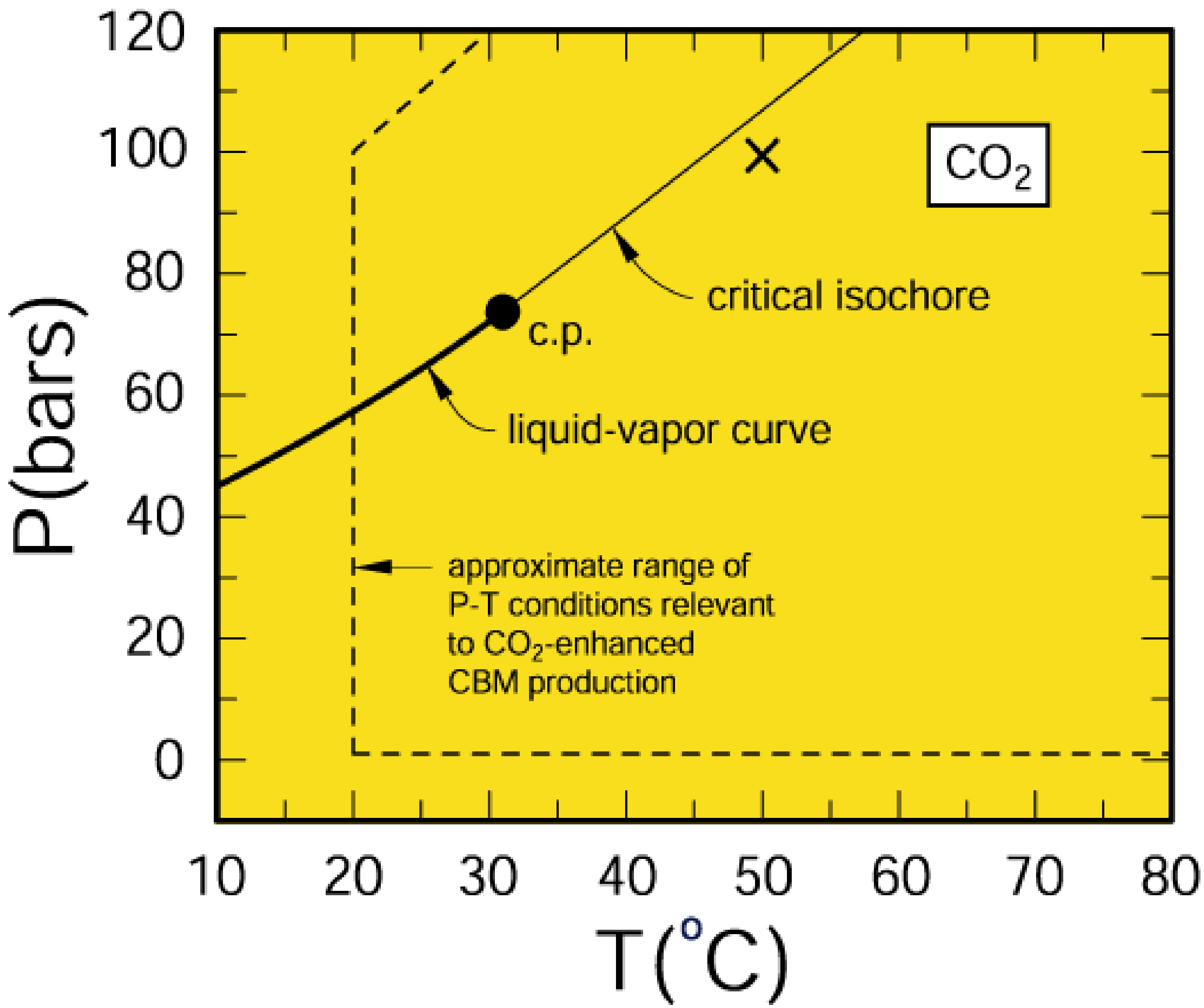
P(bars)
120
100
80
60
40
20
0
10
20
30
40
50
60
70
80
T(°C)
CO2
critical isochore
c.p.
liquid-vapor curve
approximate range of
P-T conditions relevant
to CO2-enhanced
CBM production



50°C,
100 bars
This study
NIST 14 code
WinProp code
PVTsim
$V^{ex}(cm^3 \cdot mol^{-1})$
X_{CO_2}
0
10
20
30
40
50
0
0.2
0.4
0.6
0.8
1



10
8
6
4
2
0
-2
-4
Δρ = 100(ρ1 - ρ2)/ρ1
S & W (1991)
S & W (1996)
This study
NIST 14 code
WinProp code
PVTsim
50°C,
100 bars
0
0.2
0.4
0.6
0.8
1
XCO2



120
100
80
60
40
20
0
P(bars)
10
20
30
40
50
60
70
80
T(°C)
CO2
c.p.
critical isochore
liquid-vapor curve
approximate range of
P-T conditions relevant
to CO2-enhanced
CBM production