Density measurements on mixtures in the supercritical region by a single-sinker densimeter
—— IMPACTS Project

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Global warming

全球气候变暖

According to **Climate Change 2013 - The Physical Science Basis** by IPCC:

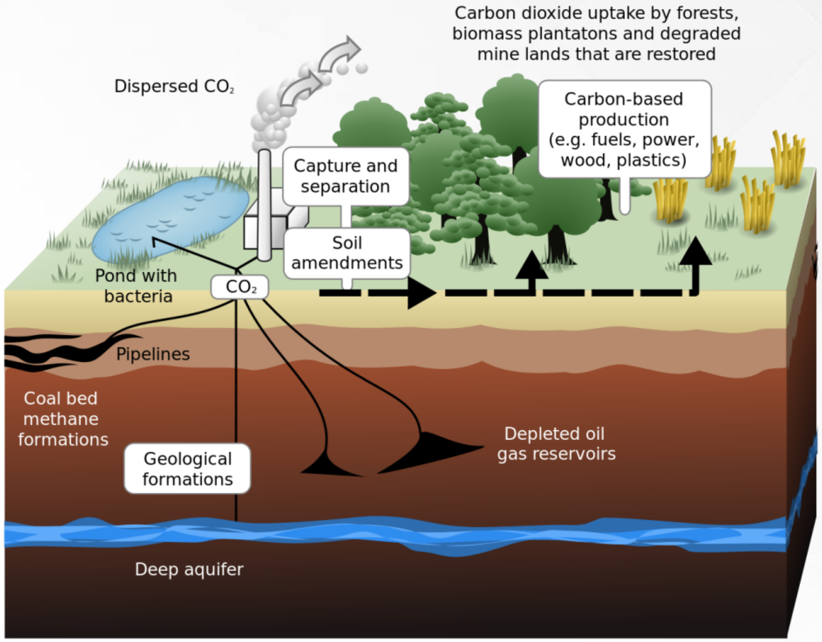
- The globally averaged surface temperature was estimated to increase 0.85 °C over the period 1880–2012.
- A total increase of 0.78 °C between the average of the 1850–1900 period and the 2003–2012 period is estimated.
- In 2011 the concentrations of CO_2 was 391 ppm, exceeding the pre−industrial levels by about 40%.

CCS as an important solution

二氧化碳捕获与封存

Carbon capture and storage (CCS) is considered to be one of the most important strategies in mitigating global carbon emissions.

- The substances involved in CCS are CO_2, Ar, N_2, O_2, H_2O, SO_x, NO_x and other trace substances.
- The design of CCS systems requires knowledge of volumetric and phase equilibrium properties of their mixtures.
- There are still large knowledge gaps with regard to volumetric properties of their mixtures. Our work in IMPACTS focuses on CO_2, N_2, and Ar.



Picture downloaded from:
http://web.ornl.gov/info/ornlreview/v33_2_00/research.htm

Review on CO_2/N_2 and CO_2/Ar

二元混合物CO_2/N_2 and CO_2/Ar 综述

Table: Review of volumetric measurements on CO_2/N_2 and CO_2/Ar

T/K	p/MPa	Mole fraction of CO_2	Uncertainty* T; p; ρ; ρ combined (Coverage factor)	Author	Year
$x\mathrm{CO_2} + (1-x)\mathrm{Ar}$					
323.15	5.0–101.3	0.12 – 0.83	n/a; n/a; n/a; (n/a)	Abraham and Bennett	1960
288.15	2.40 – 14.34	0.70 – 0.94	0.01 K ; 0.1 MPa; n/a; (n/a)	Sarashina *et al.*	1971
373.15 – 573.15	0.3 – 59.3	0.18 – 0.80	n/a; n/a; n/a; (n/a)	Schönmann	1971
313.15 – 353.15	5.8 – 58.8	0.20 – 0.71	n/a; n/a; n/a; (n/a)	Kosov and Brovanov	1975
313.15	0.3 – 20.9	0.35 – 0.81	n/a; n/a; n/a; (n/a)	Altunin and Koposhilov	1976
303.15 – 373.15	0.2 – 24.7	0.35 – 0.81	n/a; n/a; n/a; (n/a)	Altunin and Koposhilo	1977
303.15 – 383.15	1.0 – 20.0	0.8306, 0.9692	0.05 K; ± 0.03%; 0.2 kg/m^3; (n/a)	Mantovani *et al.*	2012
$x\mathrm{CO_2} + (1-x)\mathrm{N_2}$					
273.15 – 473.15	5.0 – 50.6	0.24 – 0.47	n/a; n/a; 0.5%; (n/a)	Kritschewsky and Markov	1940
298.15	0.0 – 0.1	0.48	0.01 K; n/a; 0.002%; (n/a)	Edwards and Roseveare	1942
298.15 – 398.15	3.0 – 50.0	0.2513, 0.5048	n/a; n/a; 0.05%; (n/a)	Haney and Bliss	1944
303.15	0.0 – 0.1	0.49 – 0.50	n/a; n/a; n/a; (n/a)	Gorski and Miller	1953
253.15 – 288.15	2.4 – 14.5	0.46 – 0.94	0.01 K; 0.1 MPa; n/a; (n/a)	Arai *et al.*	1971
323.15 – 343.15	0.3 – 20.4	0.21 – 0.76	n/a; n/a; n/a; (n/a)	Altunin and Chin	1972
313.15 – 353.15	5.9 – 58.8	0.23 – 0.67	n/a; n/a; n/a; (n/a)	Kosov and Brovanov	1975
273.15 – 473.15	0.3 – 9.9	0.18 – 0.98	n/a; n/a; n/a; (n/a)	Rivkin	1975
243.15 – 333.15	2.7 – 19.6	0.90 – 0.95	0.02 K; 0.01 MPa; n/a; (n/a)	Kaminishi	1978
250 – 329	2.2 – 33.0	0.98	0.03 K; 0.01%; 0.02%; (n/a)	Ely *et al.*	1987

Review on CO_2/N_2 and CO_2/Ar

二元混合物CO_2/N_2 and CO_2/Ar 综述

T/K	p/MPa	Mole fraction of CO_2	Uncertainty* T; p; ρ; ρ combined (Coverage factor)	Author	Year
$xCO_2 + (1-x)N_2$					
323.15, 348.15	49.0 – 273.7	0.25, 0.5, 0.74	0.1 K; 0.25 MPa; 0.5% – 1%; (n/a)	Hacura *et al.*	1988
300, 320	0.1 – 10.6	0.10 – 0.90	0.005 K; 0.005% – 0.015%; n/a; (n/a)	Brugge *et al.*	1989
303.15 – 333.15	0.75 – 5.99	0.9998	0.01K; 0.1%; n/a; (n/a)	McElroy *et al.*	1989
205 – 320	0.1 – 48.4	0.44696	0.01K; 0.005% – 0.015% *p*; n/a; (n/a)	Esper *et al.*	1989
250 – 329	up to 33.0	0.982	0.008 K; 0.01%; 0.1% – 0.15%; (n/a)	Ely *et al.*	1989
208 – 400	0.0 – 48.4	0.44	0.01 K; 0.1%; 0.1%; (n/a)	Bailey *et al.*	1989
293.2	0.6 – 5.1	0.27 – 0.70	n/a; 0.01%; n/a; (n/a)	Jiang *et al.*	1990
274 – 349	0.2 – 26.1	0.10 – 0.31	n/a; n/a; n/a; (n/a)	Jaeschke and Humphreys	1991
473.15	100.0	0.10 – 0.90	0.01 K; 0.01 MPa; n/a; (n/a)	Seitz *et al.*	1994
205 – 300	1.1 – 77.5	0.3991, 0.4459, 0.5037	0.01 K; 0.01 MPa; 0.1%; (n/a)	Duarte–Garza *et al.*	1995
225 – 450	0.2 – 69.1	0.10 – 0.90	0.01 K; 0.01 MPa; 0.1%; (n/a)	Duarte–Garza *et al.*	1995
673.15	19.9 – 99.9	0.1 – 0.9	0.05 K; 0.02 MPa; 1 kg/m^3; (n/a)	Seitz and Blencoe [	1996
323.15 – 573.15	9.9 – 99.9	0.1 – 0.9	0.05 K; 0.02 MPa; 1 kg/m^3; (n/a)	Seitz *et al.*	1996
225 – 450	up to 69.1	0.10 – 0.90	0.005 K; 0.006 MPa; 0.1%; (k = 2)	Brugge *et al.*	1997
250 – 400	up to 19.9	0.1, 0.15	0.0039 K; 0.015%; 0.02% – 0.15%; (n/a)	Mondéjar *et al.*	2011
303.15 – 383.15	1.0 – 20.0	0.9021, 0.9585	0.05 K; ± 0.03%; 0.2 kg/m^3; (n/a)	Mantovani *et al.*	2012
250 – 400	up to 19.9	0.20, 0.50	0.0039 K; 0.015%; 0.02% – 0.15%; (k = 2)	Mondéjar *et al.*	2012

Data for mixtures with CO_2 concentration lower than 10% were not found in literature

Our measurements

我们的测量

CO_2/N_2	CO_2/Ar	$CO_2/N_2/Ar$
5% CO_2 + 95% N_2 1% CO_2 + 99% N_2	5% CO_2 + 95% Ar 1% CO_2 + 99% Ar	90% CO_2 + 5% N_2 + 5% Ar 95% CO_2 + 4% N_2 + 1% Ar
CO_2 concentrations lower than 10% were not found in literature	CO_2 concentrations lower than 10% were not found in literature	These ternaries were not measured before. They are more close to real mixtures in CCS.

$25\ ^\circ\mathrm{C} \le T \le 150\ ^\circ\mathrm{C}$ $8\ \mathrm{MPa} \le p \le 30\ \mathrm{MPa}$

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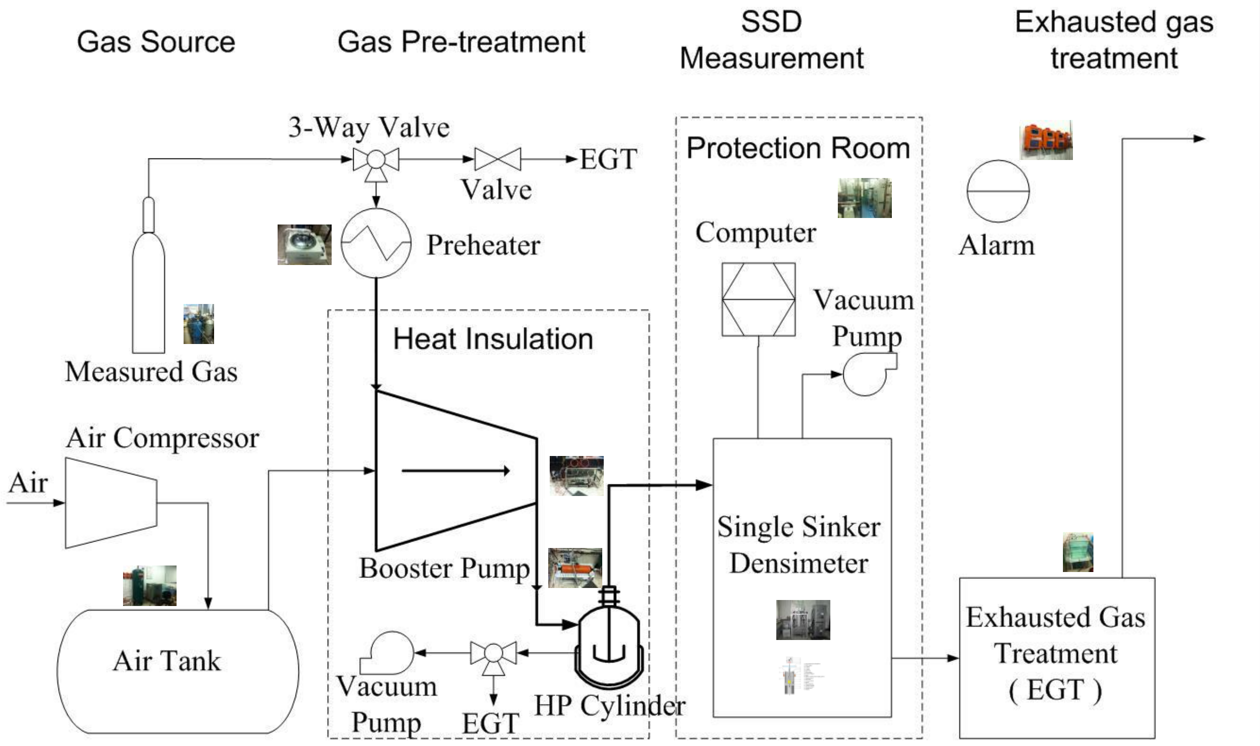
Density measuring system

测量系统简介



Technical specifications

重要测量参数

Temperature (Range: 0 ~ 150° C)

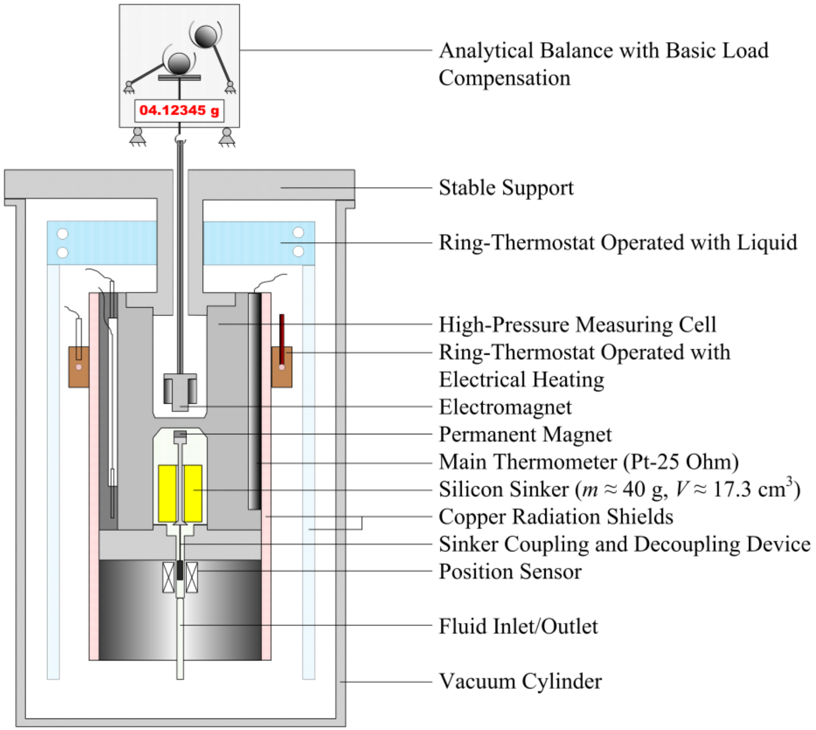
- measured with Pt-25 Ohm resistance thermometer and ASL F700 resistance bridge referenced to a 100 Ohm resistor.
- Combined Uncertainty: 35.1 mK (*k*=2)

Pressure (Range: 0 ~ 35 MPa)

- measured with Paroscientific Digiquartz Model 9000-6k-101;
- Combined Uncertainty: 3.39 kPa (*k*=2)

Sinker weighing

- Weighings via magnetic suspension coupling; balance – Mettler Toledo XP 205 – has uncertainty of 0.002% (*k* = 2) of reading.
- Density measurement uncertainty: 0.033 % (k=2)



(method according to *Brachthäuser et al., 1993*)

Examples of single-sinker densimeters

单浮体密度计综述

	Range & Uncertainty (k=2)			
Group	**Temperature**	**Pressure**	**Density**	**Measured examples**
Hall	193.15 – 523.15 K 5.0 mK	Up to 200 Mpa 0.01% of 40 or 200 Mpa	0 to 2000 kg/m^3 0.1%	CO_2, C_2H_6, N_2, CH_4, Natural gases
Chamorro	250 – 400 K 3.9 mK	Up to 20 Mpa 0.007 – 0.015% of 20Mpa	0 to 2000 kg/m^3 0.020 – 0.155%	CH_4 + N_2, CO_2 + N_2,CH_4 + CO_2, CO + N_2
Kuramoto	293.15 – 473.15 K 3.0mK (–)	Designed up to 20 Mpa –	– 6.7 – 11.7 ppm (–)	iso-Octane, n-Nonane, n-Tridecane, Water, 2,4-Dichlorotoluene, 3,4-Dichlorotoluene, Bromobenzene
Wagner	235 – 520 K 8.0 mK	Up to 30 Mpa 0.006% or 50 Pa	2 to 2000 kg/m^3 0.015%	cyclohexane, toluene, and ethanol , n-heptane, n-nonane, 2, 4-dichlorotoluene, and bromobenzene, ethylene, ethane, and sulphur hexafluoride, Ar, N_2, CH_4, CO_2
Span I	90 K – 290 K 15.0 mK	0.05 MPa – 12 MPa 0.01 %	10 to 1,000 kg/m^3 0.01% (for liquids)	Designed to measure LNG
Span II	235 K – 475 K 15.0 mK	Up to 20 MPa 0.01 %	2 to 2000 kg/m3 0.02%	Currently in use for gas phase density measurements of CCS mixtures
Our group	273.15 - 423.15 K 35.1 mK	0 – 35 MPa 3.39 kPa	2 to 2000 kg/m^3 0.033 %	CO_2 + N_2, CO_2 + Ar, CO_2 + N_2 + Ar, CO_2 + CH_4

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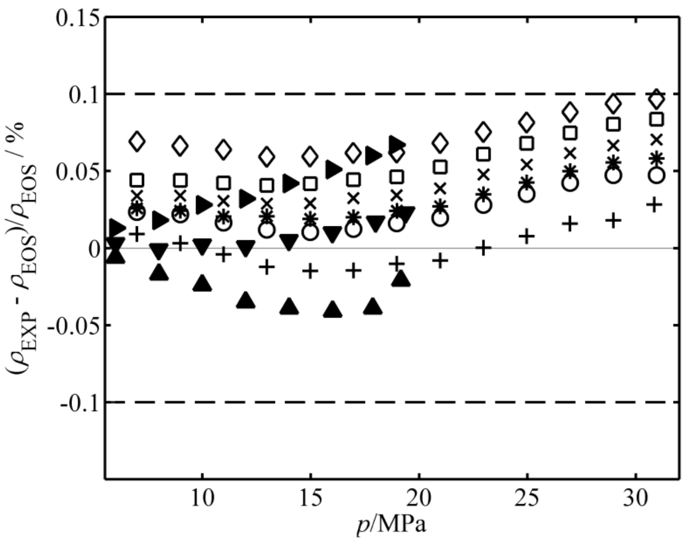
Measurements on CO_2/N_2

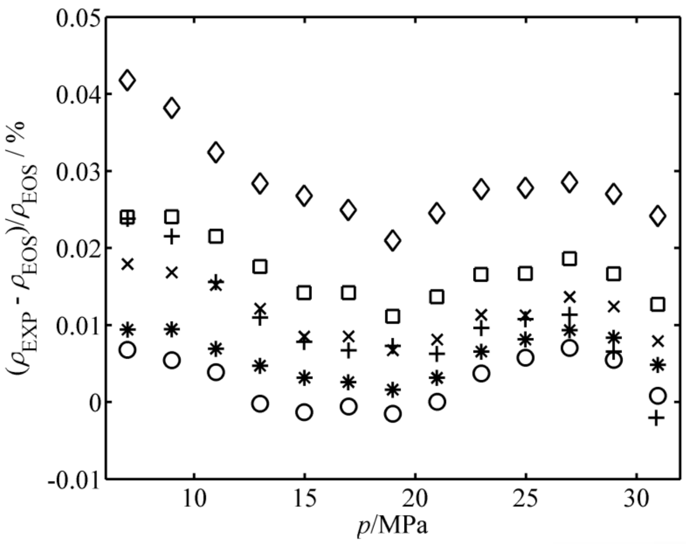
CO_2/N_2的测量结果

Relative deviations from experiment to GERG-2004 EOS

+ 25 ° C; ○ 50 ° C; ⁎ 75 ° C; × 100 ° C; □ 125 ° C; ◇ 150 ° C.



($0.95\ N_2 + 0.05\ CO_2$)

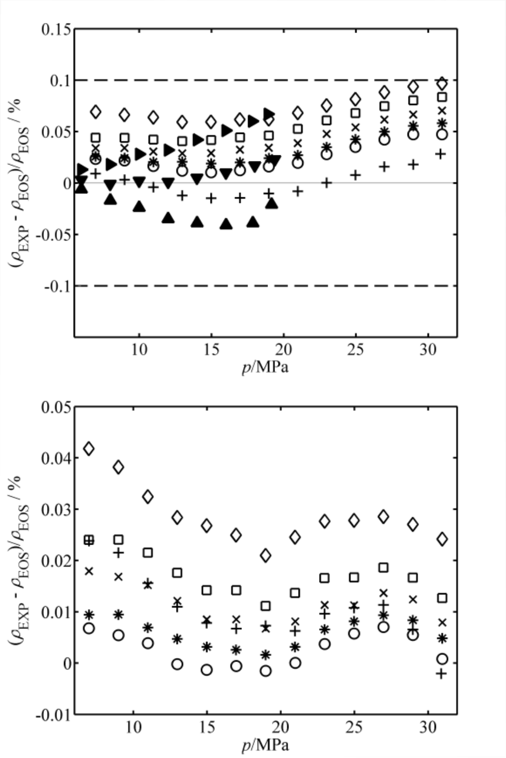


($0.99\ N_2 + 0.01\ CO_2$)

Results on CO_2/N_2 measurement

GERG-2004 EOS 对CO_2/N_2 的预测能力评估

- For (0.05 CO_2 + 0.95 N_2), the experiments agree well with GERG EOS within ±0.1%.
- The way relative deviations change with temperature and pressure agrees well with that of measurement results on (0.10 CO2 + 0.90 N2) by Mondéjar [1].
- For (0.01 CO_2 + 0.99 N_2), the experiment results agree well with GERG EOS within ±0.04%.
- Conclusion: Measurement results agree well with GERG EOS within the uncertainty of the equation.



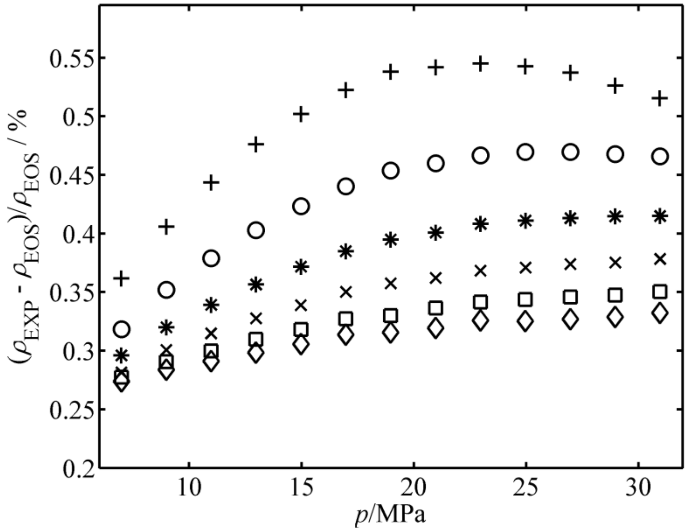
[1] M.E. Mondéjar, M.C. Martín, R. Span, C.R. Chamorro, New (p,ρ,T) data for carbon dioxide – Nitrogen mixtures from (250 to 400)K at pressures up to 20MPa, The Journal of Chemical Thermodynamics, 43 (2011) 1950-1953.

Measurements on CO_2/Ar

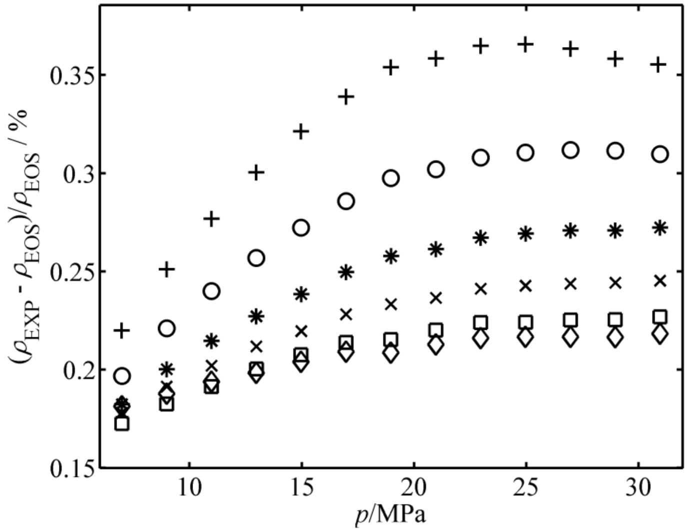
测量二元混合物CO_2/Ar

Relative deviations from experiment to GERG-2004 EOS

+ 25 ° C; ○ 50 ° C; ⁎ 75 ° C; × 100 ° C; □ 125 ° C; ◇ 150 ° C.



(0.95 Ar + 0.05 CO_2)



(0.99 Ar + 0.01 CO_2)

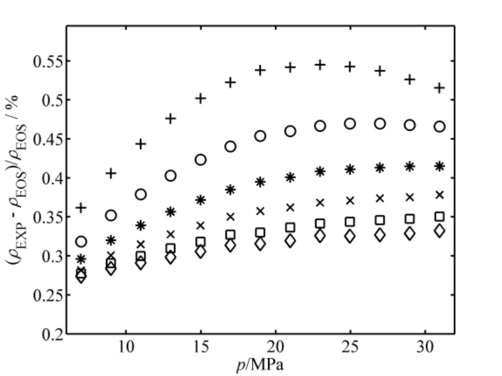
Results on GERG in predicting CO_2/Ar

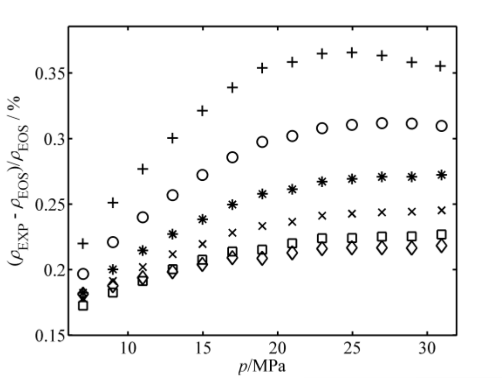
GERG-2004 EOS 对CO_2/Ar 的预测能力评估

- On both (0.05 CO_2 + 0.95 Ar) and (0.01 CO_2 + 0.99 Ar), the experimental results agree with GERG-2004 EOS within the uncertainty of the EOS (±0.5%), except at 298.15 K from 17 MPa to 29 MPa on (0.05 CO_2 + 0.95 Ar).

- Compared to CO_2−N_2, the deviation is higher, because less measurements had been made on CO_2−Ar, and no departure function for CO_2−Ar was built in GERG-2004 EOS

- Conclusion: the new experiment data could be used to develop a specific departure function for CO_2−Ar



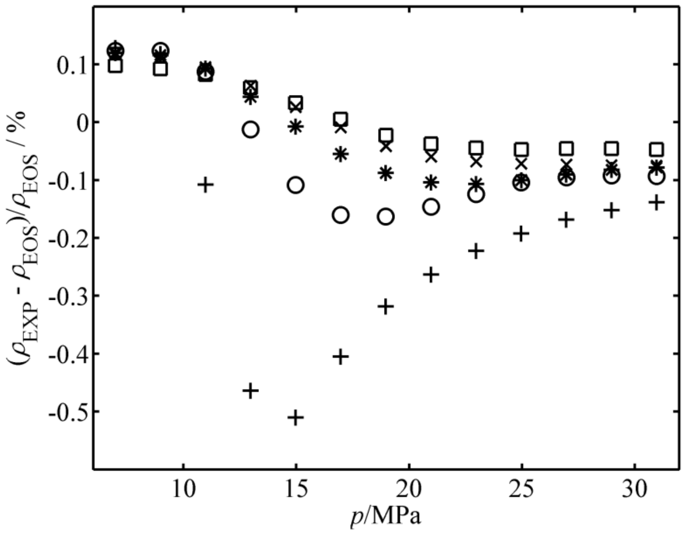


Measurements on $CO_2/Ar/N_2$

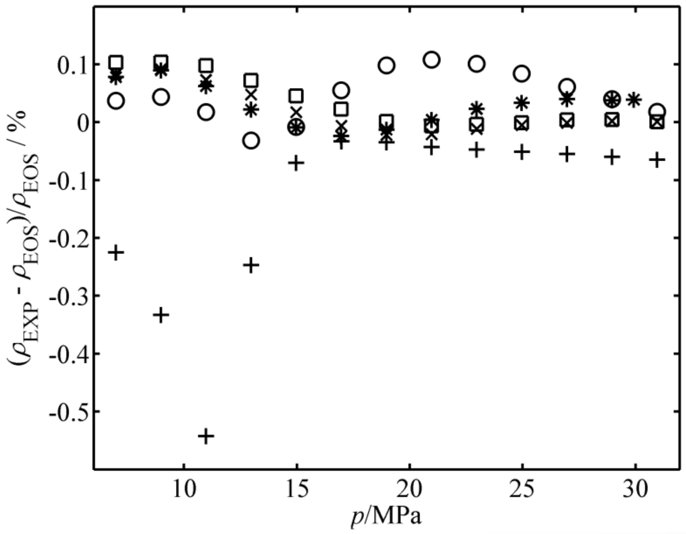
测量二元混合物$CO_2/Ar/N_2$

Relative deviations from experiment to GERG-2004 EOS

+ 50 ° C; ○ 75 ° C; ⁎ 100 ° C; × 125 ° C; □ 150 ° C;



(0.05 N_2 + 0.05 Ar + 0.90 CO_2)

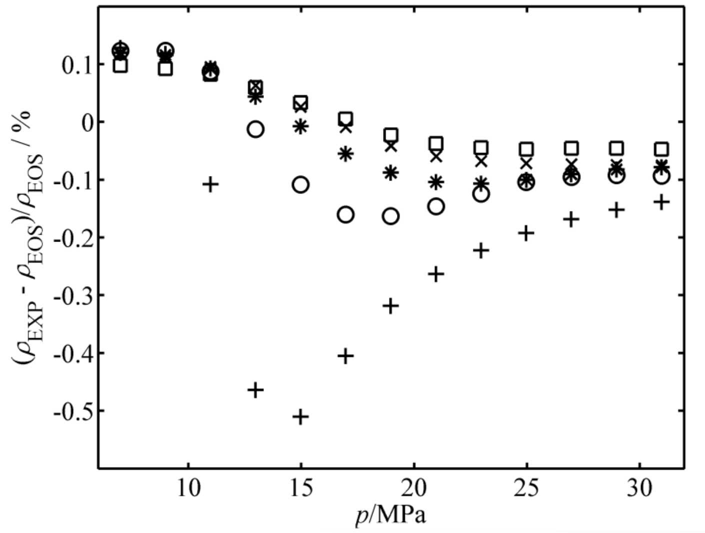


(0.04 N_2 + 0.01 Ar + 0.95 CO_2)

$(0.05\ N_2 + 0.05\ Ar + 0.90\ CO_2)$

GERG-2004 EOS 对CO_2/Ar/N_2 的预测能力评估

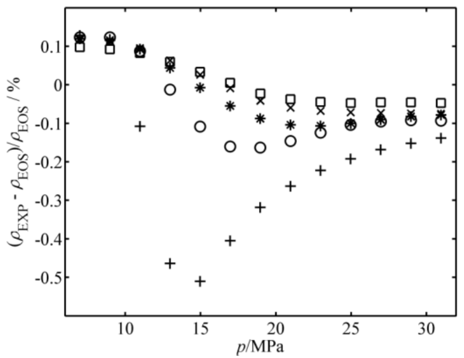
- Except for (50 °C, 12~24 MPa), experimental results agree well with GERG−2004 EOS within ± 0.2%.
- At (50 °C, 14.6 MPa), the maximal negative deviation is observed. However, this point is not the closest one among all the measurements to critical point.
- So why is this point special?

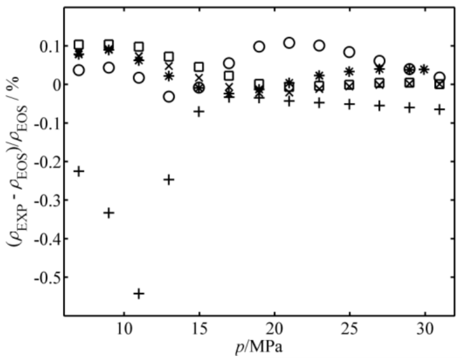


$(0.05\ N_2 + 0.05\ Ar + 0.90\ CO_2)$

GERG-2004 EOS 对CO_2/Ar/N_2 的预测能力评估

T/ °C	50	75	100
p/MPa where the maximal deviation is discovered	14.6	18.4	22.7
p/MPa on Widom line[1]	13.1	17.6	22.5
p/MPa on maximal locus of $(\partial\rho/\partial T)_p$	13.8	19.1	25.0





Result:

- Maximal deviation happen around Widom line.
- Similar result was obtained in $(0.04\ N_2 + 0.01\ Ar + 0.95\ CO_2)$

Conclusion :

- Either GERG EOS has higher uncertainty near Widom line, or there are some serious unknown phenomena occur near Widom line.

[1]Widom line: maximal locus of isobaric heat capacity, c_p. Widom line and maximal locus of $(\partial\rho/\partial T)_p$ are estimated by GERG-2004 EOS.

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