Joule–Thomson Effect on a CCS- Relevant (CO₂ + N₂) System

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ABSTRACT: The Joule–Thomson effect is a key chemical thermodynamic property that is encountered in several industrial applications for CO₂ capture and storage (CCS). An apparatus was designed and built for determining the Joule–Thomson effect. The accuracy of the device was verified by comparing the experimental data with the literature on nitrogen and carbon dioxide. New Joule–Thomson coefficient (μJT) measurements for three binary mixtures of (CO₂ + N₂) with molar compositions xN₂ = (0.05, 0.10, 0.50) were performed in the temperature range between 298.15 and 423.15 K and at pressures up to 14 MPa. Three equations of state (GERG-2008 equation, AGA8-92DC, and the Peng–Robinson) were used to calculate the μJT compared with the corresponding experimental data. All of the equations studied here except PR have shown good prediction of μJT for (CO₂ + N₂) mixtures. The relative deviations with respect to experimental data for all (CO₂ + N₂) mixtures from the GERG-2008 were within the ±2.5% band, and the AGA8-DC92 EoSs were within ±3%. The Joule–Thomson inversion curve (JTIC) has also been modeled by the aforementioned EoSs, and a comparison was made between the calculated JTICs and the available literature data. The GERG-2008 and AGA8-92DC EoSs show good agreement in predicting the JTIC for pure CO₂ and N₂. The PR equation only matches well with the JTIC for pure N₂ while it gives a poor prediction for pure CO₂. For the (CO₂ + N₂) mixtures, the three equations all give similar results throughout the full span of JTICs. The temperature and pressure of the transportation and compression conditions in CCS are far lower than the corresponding predicted mixtures, the three equations all give similar results throughout the full span of JTICs. The temperature and pressure of the transportation and compression conditions in CCS are far lower than the corresponding predicted JTICs.

1. INTRODUCTION

The greenhouse gas (GHG) emissions identified as the culprit causing climate change have received worldwide attention. CO₂ emissions are much higher than the limit recommended by scientists compared to other greenhouse gases.¹ Carbon capture and storage (CCS) is arising as key technology that can effectively slow down the substantial increase in greenhouse gases.² The captured CO₂ transportation and storage are vital in the CCS process.³,⁴ The CO₂ pipeline transportation is the most widely used transportation mode.⁵ The pressure loss along the pipeline is inevitable; thus, the Joule–Thomson effect is a key issue in pipeline transportation.⁶ The Joule–Thomson effect could be a contributing factor leading to a phase transition in the CO₂ steam transportation. Once there are leakages in the pipeline, the temperature decrease caused by carbon dioxide flash and throttling expansion will cause brittle fracture of the pipeline due to supercooling. Another important aspect of the Joule–Thomson cooling in CCS is the geological storage process in which the impure CO₂ stream would be injected into depleted hydrocarbon reservoirs or saline aquifers.⁸ The injection efficiency and formation permeability could be influenced by formation of hydrates due to significant Joule–Thomson cooling of the CO₂ stream.⁹

The Joule–Thomson effect has been important thermodynamics in the study of the CCS applications.

Nitrogen is considered to be one of the most common impurities present with the captured carbon dioxide in the CCS process, which can greatly affect the thermodynamic properties of the CO₂ stream and the efficiency of pipeline transportation.¹⁰ The research on the (CO₂ + N₂) mixtures mainly focuses on the thermodynamic properties relevant to CCS, such as density,¹¹–¹³ vapor–liquid equilibrium,¹⁴,¹⁵ viscosity,¹⁶ etc. However, the work on the Joule–Thomson effect of (CO₂ + N₂) mixtures has not been reported.

At present, most of the research studies on the Joule–Thomson effect focus on pure substances such as N₂, CO₂, H₂, Ar, He, CH₄, C₂H₄, etc.¹⁷–²⁷ Also, there are also a small number of binary and ternary mixtures’ Joule–Thomson effect reports.²⁸–³³ For binary systems, only (CO₂ + CH₄)³² and (CO₂ + Ar)³³ systems that contain the components relevant to
Equation 4 or 5 must be zero when we predict the Joule–Thomson inversion curve, and the common form can be obtained as eq 642

$$
T \left( \frac{\partial P}{\partial T} \right)_V + V \left( \frac{\partial P}{\partial V} \right)_T = 0
$$

The Joule–Thomson inversion curve (JTIC) is connected by the points in the $P$–$T$ region, where the $\mu_{JT}$ is equal to 0. Also, the points in the curve divide the Joule–Thomson cooling region ($\mu_{JT} > 0$) and Joule–Thomson heating region ($\mu_{JT} < 0$).43

In this work, three equations of state including classical typical cubic state equation (PR EoS)44 and multiparametric equations (GERG-200845 and AGA8-92DC46 EoSs) were used to predict the $\mu_{JT}$ and JTICs. The detailed information of the three equations of state is given in the Supporting information.

3. EXPERIMENTAL SECTION

3.1. Chemicals. Carbon dioxide (purity $\geq 99.999\%$, cylinder number 12797179) and hydrogen (purity $\geq 99.999\%$, cylinder number 182084292) were purchased from Guangdong Huate Gas Co., Ltd. in Foshan, China. Also, critical parameters of the pure compositions were obtained from the NIST database47 for CO2 and N2. Three (CO2 + N2) binary mixtures were also supplied by Guangdong Huate Gas Co., Ltd., China. The molar composition (0.95 CO2 + 0.05 N2, cylinder number 206801101), (0.90 CO2 + 0.10 N2, cylinder number 206801059), and (0.50 CO2 + 0.50 N2, cylinder number 204114127) mixtures were prepared following the method of GB/T 5274-200848 (Chinese National Standards) and used without further purification.

3.2. Apparatus and Procedure. The $\mu_{JT}$ measurement device is schematically shown in Figure 1. The whole apparatus was divided into the following three parts: gas supply part, experimental section, and circulating pressurization part. The

Figure 1. Schematic diagram of the $\mu_{JT}$ measurement apparatus: 1, gas cylinder; 2, three-way valve; 3, needle valve; 4, mass flowmeter; 5, needle valve; 6, numerical control thermometer; 7, temperature sensor; 8, needle valve; 9, pressure sensor; 10, Joule–Thomson valve; 11, temperature sensor; 12, pressure sensor; 13, three-way valve; 14, gas boost pump; 15, air supply compressor; 16, needle valve; 17, three-way valve; and 18, 19; gas storage.
gas supply part provides gaseous mixtures from a specific cylinder with a volume of 40 L to a mass flowmeter monitoring the mass flow rate of gases. The gases then flow into a thermostatic heater, which could control the gas temperature. High-precision temperature sensors are set to monitor the temperature of gases. Temperature sensors have a temperature range of $-173.15$ to $523.15$ K with a precision of $\pm 0.1$ K. When the gas temperature is constant, we could regulate the throttle valve to control the Joule–Thomson effect. The throttle valve is made of the splicing of large diameter pipelines and small diameter pipelines. To create a thermal insulation environment, a thick thermal insulation material should be attached to the throttle valve. Meanwhile, high-precision sensors were installed before and after throttling the experimental part. Each pressure sensor has a precision of $\pm 0.01$ MPa and a maximum range of up to 40 MPa. The entire pipeline is designed as a closed circuit and is circulated and supplied by a pneumatic compressor. The pneumatic booster pump is powered by an air compressor, which can provide a maximum boost of $0.7$ MPa. The pneumatic booster pump has a maximum pressure of $25$ MPa. A gas storage tank composed of two industrial gas cylinders is used to store mixed gas. Each cylinder has a volume of $40$ L and pressures up to $15$ MPa.

The operation process for the $\mu_{JT}$ measurements is as follows: open the screws of cylinders #1, #18, and #19 to supply gases. We can adjust the flow of the gases by regulating needle valves #3 and #5. We must set the numerical control constant temperature heater in advance according to the experimental requirements. The temperature sensors $#7$ ($T_1$) and $#11$ ($T_2$) were set to monitor the temperature before and after the experimental throttling process. When the pressure and temperature reach the desired value, we could regulate the needle valve $#8$ and read the pressure value on pressure sensor $#9$ ($P_1$). The values on temperature sensor $#10$ ($T_2$) and pressure sensor $#12$ ($P_2$) represent the temperature and pressure after throttling, respectively. In the experiment, to ensure that the experimental gas can be recycled, we need to turn on the pneumatic booster pump #14. Before starting the booster pump, we need to turn on the air compressor #15 to provide power.

Also, $\mu_{JT}$ can be calculated as

$$\mu_{JT} = \frac{\Delta T}{\Delta P} = \frac{T_2 - T_1}{P_2 - P_1}$$

(7)

The uncertainty calculation method followed GUM.\textsuperscript{19} Temperature standard uncertainty $u_T$ is given by the manufacturer of $\pm 0.029$ K. Taking into account the temperature calibration and drift, oscillation, etc., the expanded uncertainty in temperature $U(T)$ is about $0.080$ K ($k = 2$). Also, the pressure standard uncertainty $u_p$ is $\pm 0.0029$ MPa. Also, considering the drift of calibration pressure, the expanded uncertainty in pressure $U(P)$ is about $0.0070$ MPa ($k = 2$). The standard uncertainties of $\mu_{JT}$ are further obtained based on the experimental variance of $\mu_{JT}$ in repeated measurements. The standard uncertainty $u_\mu$ is $0.008$ K MPa$^{-1}$ for $\text{CO}_2$ and $0.005$ K MPa$^{-1}$ for $\text{N}_2$. Also, the absolute expanded uncertainties $U(\mu_{JT})$ ($k = 2$) for all ($\text{CO}_2 + \text{N}_2$) mixtures are about $0.0017−0.0029$ K MPa$^{-1}$.

4. RESULTS AND DISCUSSION

4.1. Experiment System Verification. Within the scope of verifying the new self-built $\mu_{JT}$ measurement device, experiments on pure $\text{CO}_2$ and pure $\text{N}_2$ were carried out. We measured the $\mu_{JT}$ for pure $\text{CO}_2$ in the range $303.15−423.15$ K and pressures up to $14$ MPa. At the same time, similar tests were carried out on $\text{N}_2$ at $293.15−423.15$ K and pressures between $0.1$ and $14$ MPa. The data for pure substances are compared with the existing relevant literature data\textsuperscript{21,50} and shown in Figure 2a,b. AAD is the average absolute deviation defined by eq 8; AA$\%$D is the average absolute percentage deviation defined by eq 9. The AAD and AA$\%$D for pure $\text{CO}_2$ and $\text{N}_2$ on $\mu_{JT}$ of experimental data from this work along with other literature data are shown in Tables 1 and 2.

$$\text{AAD} = \frac{1}{N} \sum_{i=1}^{N} |\mu_{JT}^\text{exp} - \mu_{JT}^\text{lit}|$$

(8)

$$\text{AA}\%\text{D} = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{\mu_{JT}^\text{exp} - \mu_{JT}^\text{lit}}{\mu_{JT}^\text{lit}} \right|$$

(9)

As can be seen in Table 1, the experimental data for $\text{CO}_2$ show desirable agreement with the experimental data reported by Roebuck et al. and Wang et al. The high AA$\%$D between this work and Roebuck et al. data occurring in $\mu_{JT}$ is $1.5−2\%$, while it is $4−5\%$ with Wang et al. data at $303.15$ and $323.15$ K. The data in the critical region have a higher deviation due to the drastic change in thermophysical properties. With an increase in temperature, the AA$\%$D and AAD become smaller, which is
also in line with the law reported by Wang et al. According to Wang, the deviations in the supercritical state and liquid state are larger than that of the gas state, and the deviation between average absolute errors between Wang and Roebuck is 4.93%.\(^5\) As shown in Table 2, the AAD between the \(N_2-\mu_{JT}\) data measured in this work and the existing one is small, about 0.1 K·MPa\(^{-1}\) in a wide range of temperature. The AA\%D increased with increasing temperature, from 0.33% at 298.15 K to 1.58% at 423.15 K. It also can be seen from Figure 2 that our results are in good agreement with the \(N_2-\mu_{JT}\) and \(CO_2-\mu_{JT}\) data. Thus, the device we built highly meets the accuracy for experimental measurements.

### 4.2. Joule–Thomson Coefficients of the \(CO_2 + N_2\) Mixtures

The \(\mu_{JT}\) measurements of three \((CO_2 + N_2)\) binary mixtures with the compositions \((x_{N_2} = 0.05, 0.10, \text{and } 0.50)\) were based on the existing reported literature studies.\(^1\)\(^,\)\(^3\)\(^,\)\(^-\)\(^5\) Measurements were performed at six temperatures of 298.15, 323.15, 348.15, 373.15, 398.15, and 423.15 K and pressures from 0.1 to 14 MPa, and the results are shown in Figure 3.

Figure 3a–c shows a uniform law, that is, increasing the temperature decreases the \(\mu_{JT}\) of mixtures and increasing the pressure also decreases the \(\mu_{JT}\) of mixtures. In the region of high temperatures and high pressures, the cooling effect of gas throttling expansion will be weakened, which is similar to the existing literature.\(^5\) In Figure 4a–d, the effect of nitrogen

### Table 1. Average Absolute Deviation (AAD) and Average Absolute of Percentage Deviation (AA\%D) between the \(\mu_{JT}\) Values Measured for Pure \(CO_2\) in This Work and the Literature Data\(^2\)\(^,\)\(^5\)

| \(T/K\) | AA\%D | AAD/K·MPa\(^{-1}\) | AA\%D | AAD/K·MPa\(^{-1}\) |
|----------|--------|------------------|--------|------------------|
| 303.15   | 2.01   | 0.12             | 4.28   | 0.07             |
| 323.15   | 1.48   | 0.08             | 5.87   | 0.26             |
| 373.15   | 0.67   | 0.03             | 1.26   | 0.07             |
| 398.15   | 0.70   | 0.03             | 2.43   | 0.12             |
| 423.15   | 0.72   | 0.03             | 2.13   | 0.09             |

### Table 2. Average Absolute Deviation (AAD) and Average Absolute of Percentage Deviation (AA\%D) between the \(\mu_{JT}\) Values Measured for Pure \(N_2\) in This Work and the Literature Data\(^1\)

| \(T/K\) | AA\%D | AAD/K·MPa\(^{-1}\) |
|----------|--------|------------------|
| 298.15   | 0.33   | 0.01             |
| 323.15   | 0.75   | 0.01             |
| 348.15   | 0.87   | 0.01             |
| 373.15   | 0.78   | 0.01             |
| 398.15   | 1.32   | 0.01             |
| 423.15   | 1.58   | 0.01             |

Figure 3. \(P-T-\mu_{JT}\) plots for \((1-x)CO_2 + xN_2\) binary mixtures \(CO_2\) with mole fractions: (a) \(x = 0.05\), (b) \(x = 0.10\), and (c) \(x = 0.50\) at six temperatures: 298.15–423.15 K and pressure up to 14 MPa.
concentration in mixtures on $\mu_{JT}$ and temperature decrease ($\Delta T$) can be seen at 298.15 and 323.15 K. Figure 4a shows the comparison on $\mu_{JT}$ between pure CO$_2$ and binary mixtures with different contents of nitrogen at 298.15 K. It is clear that the Joule–Thomson coefficients of pure CO$_2$ decrease significantly above 7.3 MPa, while the decrease of the mixture of $x_{N_2} = 0.05$ and 0.1 M concentrations are slower than that of pure CO$_2$. Figure 4b shows the effect of different concentrations on temperature decrease ($\Delta T$) at the same initial temperature (298.15 K), which follows the same trend as that in Figure 4a. In Figure 4b, the Joule–Thomson cooling effect of pure CO$_2$ below 7.3 MPa is stronger than that of (CO$_2$ + N$_2$) mixtures, while the temperatures after throttling ($T_2$) of mixtures above 7.3 MPa are lower than that of pure CO$_2$. Moreover, the Joule–Thomson cooling effect of (0.5 CO$_2$ + 0.5 N$_2$) is stronger than the mixtures with ($x_{N_2} = 0.05$, 0.10) and pure CO$_2$. The main reason for this phenomenon is that the addition of N$_2$ changes the critical point and the two-phase zone. Figure 4c,d, respectively, depicts the $\mu_{JT}$ and $\Delta T$ comparison of pure CO$_2$ and (CO$_2$ + N$_2$) mixtures at 323.15 K. Figure 4c,d shows a similar trend that the Joule–Thomson cooling effect of pure CO$_2$ is more significant than that of the equimolar mixture are also greater than those of pure CO$_2$ when the pressure above 12 MPa.

4.3. Modeling. The experimental $\mu_{JT}$ data for mixtures were compared to the corresponding $\mu_{JT}$ calculated from the GERG-2008 EoS, the AGA8-DC92 EoS, and the PR EoS using REFPROP software. These three equations are very representative. The GERG-2008 EOS, based on a multifluid mixture model explicit in the reduced Helmholtz energy, has 21 considered components, has a wider range of temperature and pressure, and contains department functions and mixing parameters that were fitted by experimental data. Also, the GERG-2008 EOS plays an important role in the field of CCS engineering application. The AGA8-DC92 equation is a high-precision extended virial equation of state proposed by the International Organization for Standardization (ISO) based on the calculation of natural gas compressibility factor and is commonly used in the property calculation of the (CO$_2$ + N$_2$) binary system. The PR equation is selected to test the prediction ability of the classical cubic equation for $\mu_{JT}$. The relative deviations (AA%) of experimental $\mu_{JT}$ data from values calculated from the above three EoSs are calculated using eq 10.
\[ \mu_{JT}^{\text{cal}} = \sum \mu_{JT} \] (10)

Figure 5. Relative deviations in \( \mu_{JT} \) of experimental \( \mu_{JT} \) data for three (CO\(_2\) + N\(_2\)) mixtures from \( \mu_{JT} \) values calculated from the GERG-2008 equation of state vs pressure for (a) binary (0.95 CO\(_2\) + 0.05 N\(_2\)), (b) (0.90 CO\(_2\) + 0.10 N\(_2\)), and (c) (0.50 CO\(_2\) + 0.50 N\(_2\)) mixtures.

Figure 6. Relative deviations in \( \mu_{JT} \) of experimental \( \mu_{JT} \) data for three (CO\(_2\) + N\(_2\)) mixtures from \( \mu_{JT} \) values calculated from the AGA8-92DC equation of state vs pressure for (a) binary (0.95 CO\(_2\) + 0.05 N\(_2\)), (b) (0.90 CO\(_2\) + 0.10 N\(_2\)), and (c) (0.50 CO\(_2\) + 0.50 N\(_2\)) mixtures.

Figure 7. Relative deviations in \( \mu_{JT} \) of experimental \( \mu_{JT} \) data for three (CO\(_2\) + N\(_2\)) mixtures from \( \mu_{JT} \) values calculated from the PR equation of state vs pressure for (a) binary (0.95 CO\(_2\) + 0.05 N\(_2\)), (b) (0.90 CO\(_2\) + 0.10 N\(_2\)), and (c) (0.50 CO\(_2\) + 0.50 N\(_2\)) mixtures.

\[ AA\% \, D = \frac{100}{N} \sum_{i=1}^{N} \left( \frac{\mu_{JT}^{\exp} - \mu_{JT}^{\text{cal}}}{\mu_{JT}^{\exp}} \right) \] (10)

Figure 5a shows the relative deviations between the GERG-2008 EoS and experimental data for the (0.95 CO\(_2\) + 0.05 N\(_2\)) mixture, Figure 5b for the (0.90 CO\(_2\) + 0.10 N\(_2\)) mixture, and Figure 5c for the (0.50 CO\(_2\) + 0.50 N\(_2\)) mixture over the whole temperature and pressure range measured. It is clear that the
deviations increase with increasing concentration of N₂. For the GERG-2008 EoS, the deviations at high temperatures are smaller than those at low temperatures. The deviation of the (0.95 CO₂ + 0.05 N₂) mixture from the experimental value is within 1%, the (0.90 CO₂ + 0.10 N₂) mixture is within 1.5%, and the (0.50 CO₂ + 0.50 N₂) mixture is within 2.5%. Figure 6a–c shows the relative deviations between the AGA8-92DC EoS and experimental data for the three mixtures. The prediction ability of AGA8-92DC EoS on μJT behaves well but worse in the range of high temperatures. The overall deviation of the three mixtures is within 3%. The relative deviations between the PR EoS and experimental data for the above three mixtures are shown in Figure 7a–c.

In conclusion, the GERG-2008 equation has the best prediction on the μJT for the (CO₂ + N₂) mixture, and the fitting data can also meet the experimental data better in the critical region. AGA8-92DC is second only to GERG-2008 and also shows good performance in predicting. The PR EoS gives poor prediction on the μJT value for (CO₂ + N₂) mixtures.

The Joule–Thomson inversion curve (JTIC) is connected by the points where the Joule–Thomson coefficients are equal to zero, which divide the working range of cooling and heating of substances. The area inside the curve where the μJT > 0 belongs to the cooling area, while the area outside the curve is completely opposite. The μJT < 0 belongs to the heating area of the JTIC. Since most of the points on the curve are in the extremely harsh temperature and pressure range that is difficult
to reach, it is currently popular to evaluate the JTIC using the equations of state. The calculation of the JTIC is also a huge test for the equations of state because the calculation of the JTIC is more complicated and contains pressure derivatives.\footnote{54}

In this work, the above three equations are used to calculate the JTICs for (CO$_2$ + N$_2$) mixtures. We first select CO$_2$ and N$_2$ as test cases to calculate the JTICs using the above equations, and the results are shown in Figure 8a,b. The comparison between literature values\textsuperscript{\textendash}\textsuperscript{20\textendash}22 and calculated JTIC for carbon dioxide is shown in Figure 8a. The Span and Wagner equation of state\textsuperscript{55} is considered to be the reference equation for estimating the physical properties of pure CO$_2$ and is also used to evaluate the JTIC. As can be seen from Figure 8a, GERG-2008 EoS and AGA8-92DC EoS are in good agreement with the Span and Wagner equation of state, but the PR EoS is slightly different from it. The GERG-2008 and AGA8-92DC EoSs predict well with the experimental values of Price et al.\textsuperscript{22} and de Groot et al.,\textsuperscript{20} while it shows some difference with the Roebeck et al.\textsuperscript{31} in the low-temperature branch. The GERG-2008 and AGA8-92DC EoSs provide more reliable predictions on pure CO$_2$ than the PR. Also, JTIC for pure N$_2$ using the same EoSs is depicted in Figure 8b. Based on the obtained results, GERG-2008, AGA8-92DC, and PR EoSs provide nearly the same results for nitrogen JTIC. The predictions of these three EoSs are of high satisfaction with the experimental data,\textsuperscript{17,19} except that the maximum inversion pressure and its corresponding temperature are slightly different. The calculations of $\mu_{JT}$ and JTIC from the three equations show that the order of good prediction is GERG-2008 $>$ AGA8-2008 $>$ PR equation. The comparison is in accordance with the previous study,\textsuperscript{55} indicating that GERG-2008 has a clear advantage over cubic EoSs in the calculation of Joule–Thomson coefficients. Some researchers\textsuperscript{35,36} also confirmed that the multiparameter equations are superior to the cubic equations on the Joule–Thomson effect. Figure 9 shows the calculated JTIC from the above three EoSs for (0.95 CO$_2$ + 0.05 N$_2$). In Figure 9, the GERG-2008 and AGA8-92DC equations show similar results on the low-temperature branch, and they show some similarity with the PR equation. On the high-temperature branch, the GERG-2008 and PR equations almost coincide, but the AGA8-92DC equation is quite different from them. The Joule–Thomson inversion curves of mixture (0.90 CO$_2$ + 0.10 N$_2$) calculated by the same equations are shown in Figure 10. As illustrated in Figure 10, three equations meet consistently on the low-temperature branch, while they show some differences on the high-temperature branch. Figure 11 shows the calculated Joule–Thomson inversion curves from these three EoSs for (0.50 CO$_2$ + 0.50 N$_2$). Three predicted curves show desirable agreement at low temperatures. The AGA8-92DC and PR

![Figure 10](https://example.com/figure10.png) Predicted Joule–Thomson inversion curves for (0.90 CO$_2$ + 0.10 N$_2$) using GERG-2008, AGA8-92DC, and PR equations of state.

![Figure 11](https://example.com/figure11.png) Predicted Joule–Thomson inversion curves for (0.50 CO$_2$ + 0.50 N$_2$) using GERG-2008, AGA8-92DC, and PR equations of state.
The maximum inversion pressure ($P_{\text{inv,max}}$), corresponding temperature ($T_{\text{inv,i}}$), and maximum inversion temperature ($T_{\text{inv,max}}$) are very significant parameters for JTICs. When the pressure or temperature of the actual working condition is greater than $P_{\text{inv,max}}$ or $T_{\text{inv,max}}$, it will produce a heating effect. The $P_{\text{inv,max}}$, $T_{\text{inv,i}}$, and $T_{\text{inv,max}}$ for pure substances and three (CO$_2$ + N$_2$) mixtures were calculated by the aforementioned EoSs and are shown in Table 3. As we can see from Table 3, the calculated $P_{\text{inv,max}}$, $T_{\text{inv,i}}$, and $T_{\text{inv,max}}$ for pure CO$_2$ and N$_2$ from three EoSs were very similar. For the (CO$_2$ + N$_2$) mixtures, the obtained $P_{\text{inv,max}}$ and $T_{\text{inv,i}}$ were similar, except for (0.5 CO$_2$ + 0.5 N$_2$); the $T_{\text{inv,max}}$ of the PR equation is slightly smaller than the other two equations. Compared with pure CO$_2$, the $P_{\text{inv,max}}$ and $T_{\text{inv,max}}$ of the (CO$_2$ + N$_2$) mixtures decrease with the increasing nitrogen concentration. The reported pressure range of CO$_2$ pipeline transport in the CCS process is between 7.5 and 20 MPa, and the temperature range is between 218.15 and 303.15 K. CO$_2$ storage is carried out at temperatures from 277.15 to 423.15 K and pressures between 0.1 and 50 MPa. As can be seen from Table 3, the temperature and pressure of the transportation and compression conditions are far less than the corresponding $P_{\text{inv,max}}$ and $T_{\text{inv,max}}$ for (0.95 CO$_2$ + 0.05 N$_2$) and (0.90 CO$_2$ + 0.10 N$_2$). In the actual CCS throttling processes, the (CO$_2$ + N$_2$) mixtures will produce a cooling effect.

## 5. CONCLUSIONS

A set of reliable experimental apparatus was built to specifically investigate the Joule–Thomson effect. $\mu_{\text{JT}}$ experimental data for pure carbon dioxide in the temperature range of 303.15–423.15 K and at pressure up to 14 MPa are compared with Roebuck’s data, and the relative deviation is within $1.36\%$. For pure nitrogen, the relative deviation between the $\mu_{\text{JT}}$ experimental data and the existing literature data is within 0.94% at six isotherms between 298.15 and 423.15 K at pressure 0.1–14 MPa. The results indicate that the apparatus can better meet the accuracy for measurement and industrial needs.

New $\mu_{\text{JT}}$ measurements for three binary mixtures of (CO$_2$ + N$_2$) with molar compositions $x_{\text{N}_2} = (0.05, 0.10, 0.50)$ were performed in the new experimental apparatus at the temperature range between 298.15 and 423.15 K and at pressures up to 14 MPa. The experimental data for the three (CO$_2$ + N$_2$) mixtures are in agreement with the reported literature: as the temperature and pressure increase, the $\mu_{\text{JT}}$ values decrease. Adding nitrogen will change the phase equilibrium and thus the critical parameters, compared with pure carbon dioxide. Compared to the throttling process of pure CO$_2$, the nitrogen-containing CO$_2$ streams first enter the two-phase zone. At 298.15 K, when the pressure is above the critical pressure (near 7.3 MPa), the throttling effect becomes more significant, and the throttling temperature decreases in the presence of mixed gases of N$_2$, compared with pure CO$_2$.

The new experimental data were compared with the corresponding $\mu_{\text{JT}}$ calculated from GERG-2008, AGA-8-DC92, and PR EoSs. The relative deviations of the experimental data for all (CO$_2$ + N$_2$) mixtures from the GERG-2008 were within the $\pm 2.5\%$ band and from the AGA-8-DC92 EoS were within $\pm 3\%$. The PR EoS shows a bad prediction of $\mu_{\text{JT}}$ for (CO$_2$ + N$_2$) mixtures, and the relative deviation is as high as $10\%$. The poor $\mu_{\text{JT}}$ description of the PR equation is mainly due to its simple form. Therefore, it can be concluded that experimental data agree well with the values estimated by GERG-2008 and AGA-8-92DC but not PR EoS.

The aforementioned equations were also tested to predict the Joule–Thomson inversion curves for pure and binary systems. The obtained results compared with reported literature depicted that the GERG-2008 and AGA-8-92DC EoSs show good agreement in predicting the JTIC for pure CO$_2$ and N$_2$. The PR equation only matches well with the JTIC for pure N$_2$, while it gives a poor prediction for pure CO$_2$. For the three (CO$_2$ + N$_2$) mixtures, the three equations all give similar results throughout the full span of JTICs, while the $P_{\text{inv,max}}$ values from AGA8-92DC and PR are slightly larger than that from GERG-2008. The GERG-2008 and AGA-92DC EoSs are more reliable and satisfactory than the PR EoS on the prediction of JTICs. The calculated $P_{\text{inv,max}}$ and $T_{\text{inv,max}}$ show that the (CO$_2$ + N$_2$) mixtures will produce a throttling cooling effect under transportation and compression conditions in CCS processes. In this work, the experimental data on $\mu_{\text{JT}}$ for the (CO$_2$ + N$_2$) mixtures could offer some information for actual CCS applications and fill the blank of the corresponding thermodynamic database.

## ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00554.

Critical parameters of the components of the studied (CO$_2$ + N$_2$) mixtures in this work (Table S1) and mixing parameters for the three equations (Table S2) (PDF)

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9865

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Notes
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■ LIST OF SYMBOLS

| Symbols | Definition |
|---------|------------|
| \( \mu_{JT} \) | Joule–Thomson coefﬁcient, K·MPa\(^{-1} \) |
| \( C_p \) | speciﬁc isobaric heat capacity, J·kg\(^{-1}\)·K\(^{-1} \) |
| \( H \) | molar enthalpy, J·mol\(^{-1} \) |
| \( P \) | pressure, MPa |
| \( P_{\text{inv,max}} \) | maximum inversion pressure, MPa |
| \( T_{\text{inv,i}} \) | maximum inversion pressure corresponding temperature, K |
| \( T_{\text{inv,max}} \) | the corresponding temperature, K |
| \( \rho \) | density, kmol·m\(^{-3} \) |
| \( R \) | molar gas constant, J·kg\(^{-1}\)·K\(^{-1} \) |
| \( T \) | temperature, K |
| \( V \) | volume, m\(^3\) |

Superscripts
1 | before throttling |
2 | after throttling |
exp | experimental data |
lit | literature data |

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