Research Article

Adsorption Equilibrium and Thermodynamic Analysis of CO₂ and CH₄ on Qinshui Basin Anthracite

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Adsorption isotherms of CH₄ and CO₂ on Qinshui Basin anthracite were obtained at the temperatures of 283 K, 303 K, and 323 K using the gravimetric method. The feasibility of the displacement of CH₄ by injecting CO₂ on this anthracite was verified by calculating the selectivity factor of CO₂ over CH₄ (α_{CO₂/CH₄}), adsorption affinities, and thermodynamic properties of CH₄ and CO₂. Results show that the values of α_{CO₂/CH₄} are more than 4.0. Henry’s constant (K_H) of CH₄ is smaller than that of CO₂, indicating CH₄ has a weaker affinity with coal surface. As temperature improves, K_H of CO₂ and CH₄ decrease. Gibbs free energy change (ΔG) and surface potential (Ω) of CO₂ are more negative than those of CH₄, indicating CO₂ adsorption on anthracite is more spontaneous and favorable. The absolute values of Ω and ΔG of CH₄ and CO₂ increase with pressure rises. Isosteric heat of adsorption (Q_{st}) of CH₄ is lower than that of CO₂. With increasing loading, Q_{st} and entropy loss (ΔS) of CH₄ decrease, while Q_{st} and ΔS of CO₂ increase. The higher ΔS of CO₂ reveals that the adsorbed CO₂ molecules constitute a more stable rearrangement than CH₄ molecules. High temperature reduces ΔS of CH₄ and CO₂.

1. Introduction

In the last few decades, coalbed methane has gradually grown in significance as an alternative to conventional natural gas resource due to its low pollution, abundant reserves, and wide distribution [1]. Meanwhile, coalbed methane is deemed as a dangerous gas for the underground coal mining activity, as the release of CH₄ during coal mining process can potentially result in the risk of gas explosion and coal and gas outburst [2]. The effective exploitation and disposition of coalbed methane is essential for the safe mining of coal. With the worsening of the global greenhouse effect, the sequestration of anthropogenic CO₂ into deep geological formations, such as deep unmineable coal seams, saline aquifers, depleted oil and gas reservoirs, and shale gas sediments, has received lots of attention [3–6]. Based on the higher adsorption affinity of CO₂ over CH₄ on coal surface, injected CO₂ can competitively displace the preadsorbed CH₄ out of micropores and subsequently stay in the fracture and coal matrix [4], which is a promising technology that has the benefits of enhanced coal methane recovery and CO₂ sequestration in a geological time scale.

The underlying principle of the technology of enhanced coal methane recovery by CO₂ injection (CO₂-ECBM) is
the competitive adsorption between injected CO₂ and preadsorbed CH₄. More than 80% of coalbed methane is stored in the form of adsorbed gas [7]. Investigation about the adsorption performances of CH₄ and CO₂ on coal could provide useful information to understand the adsorption mechanisms of CH₄ and CO₂ and verify the feasibility of the technology of CO₂-ECBM. To date, many studies have addressed the adsorption behaviors of CH₄ and CO₂ on different rank coals by the means of laboratory experiment and numerical simulation analysis [2, 8–17]. Their results indicate that the adsorption amount and adsorption rate of CO₂ on coal are larger than those of CH₄ [2, 13, 16]. The adsorption abilities of CH₄ and CO₂ on coal are tightly related to the reservoir condition (pressure, temperature, and effective stress) and the physical-chemical property of coal (mineral composition, total organic carbon content, ash content, pore structure, surface functional group, and moisture content) [8–12, 14, 16, 17]. Various adsorption models including the Langmuir model, Brunauer-Emmett-Teller (BET) model, and pore-filling model are capable of dealing with the adsorption data of CH₄ and CO₂ on coal [2, 14, 15, 17, 18]. The values of selectivity factor of CO₂ over CH₄, which is a key indicator to assess the displacement efficiency of CO₂, are all higher than one on different rank coals [8, 13, 15–18].

Adsorption processes are often accompanied by heat generation and changes in the entropy and enthalpy of the adsorption system. Research about the interaction between coal matrix surface and adsorbate molecule from the thermo-dynamic point of view is conducive to comprehending the intrinsic adsorption mechanisms of CH₄ and CO₂ on coal. The adsorption thermodynamic properties viz., isosteric heat of adsorption (Qₛᵗ), surface potential (Ω), Gibbs free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS), have specific physical meaning to illustrate the adsorption phenomenon. At present, the thermodynamics of adsorption of CH₄ and CO₂ on porous materials, such as shale, carbon molecular sieves, activated carbon fiber, and zeolite 13X, have been analyzed [19–22]. Duan et al. [19] investigated the thermodynamics of CH₄ and CO₂ on Sichuan Basin marine shale. They found that the absolute values of entropy loss, Gibbs free energy change, and surface potential of CO₂ are bigger than those of CH₄, and CO₂ molecules constitute a more stable and ordered arrangement on matrix surface. Song et al. [20] conducted the thermodynamic analysis of CH₄ and CO₂ on three carbon molecular sieves. Their results indicated that with increasing surface coverage, the absolute value of entropy change rises, while the absolute value of Gibbs free energy reduces. Zhou et al. [21] discussed the thermodynamic characteristic of CO₂ on activated carbon fiber and suggested that the Gibbs free energy change of CO₂ increases smoothly over the whole pressure range, whereas the entropy loss decreases continuously. Mofarahi and Bakhtyari [22] estimated the thermodynamic parameters of CH₄ on zeolite 13X. They observed that adsorption loading has no influence on the isosteric adsorption heat of CH₄ at lower degree of coverage, and the absolute values of Gibbs free energy and surface potential increase with enhancing equilibrium pressure.

There are also some studies on the thermodynamic behaviors of CH₄ and CO₂ on coal [13, 14, 23, 24]. Busch and Gensterblum [14] revealed that the isosteric adsorption heats of CH₄ and CO₂ on coal both gradually reduce with the increase of moisture content. Zhou et al. [23] discovered that the change of Gibbs free energy after CO₂ adsorption on coal is higher than that after CH₄ adsorption, and the initial isosteric adsorption heats of CO₂ and CH₄ are 48.2 and 33.4 kJ/mol, respectively. Dong et al. [24] performed a molecular simulation study about the adsorption of CH₄ and CO₂ on middle-rank coal, and reported that with the increase of sorption loading, Qₛᵗ of CO₂ and CH₄ reduce at first, and then slowly rise. In addition, Qₛᵗ of CH₄ is lower than that of CO₂ at the same adsorbed density. You et al. [13] researched the adsorption behaviors of CH₄, CO₂, and their mixtures on bituminous coal by the means of numerical simulation. Their results showed that Qₛᵗ of CH₄ and CO₂ both decrease with increasing adsorption amount, and this decline is due to the presence of heteroatom functional groups. Apparently, the thermodynamic characteristics of CH₄ and CO₂ on coal, especially the surface potential and entropy change, require further study. Therefore, it is of fundamental importance to perform the detailed thermodynamic analysis of CO₂ and CH₄ on coal.

In this paper, the adsorption isotherms of CH₄ and CO₂ on anthracite were measured using the accurate gravimetric method at the temperatures of 283 K, 303 K, and 323 K and pressures up to 1.80 MPa. The Langmuir-Freundlich model was adopted to fit the adsorption data. The selectivity factor of CO₂ over CH₄ on anthracite was predicted based on the single component adsorption isotherm using ideal adsorbed solution theory. Henry’s constant was estimated and used to analyze the affinity between adsorbate and coal matrix surface. Adsorption thermodynamic parameters of CH₄ and CO₂ on coal were calculated and discussed. This research will lay the foundation for the better understanding of the adsorption mechanisms of CH₄ and CO₂ on coal and provide guide for the future application of the technology of CO₂-ECBM.

2. Material and Method
2.1. Material Preparation and Characterization

2.1.1. Material Preparation. The Qinshui (QS) anthracite adopted in this study was sampled from the southern district of Qinshui Basin of China at the depth of 350 m. Before measurement and characterization, the bulk coal was crushed and sieved into 0.85 to 0.425 mm particles.

2.1.2. Characterization of Coal Sample

(1) Mesopore and Macropore Morphology Analysis. The mesopore and macropore structures of this anthracite were analyzed with an ASAP 2020M system (Micromeritics Instruments, USA), using a low-pressure N₂ adsorption at 77 K. The BET surface area (S_BET), macropore volume (V_mac), mesopore volume (V_mes), micropore volume (V микр), total volume (V), and pore size distribution (PSD) were obtained based on N₂ adsorption isotherm data.
The desorption and adsorption isotherm data of N₂ at 77 K are shown in Figure 1(a). The PSD of QS sample determined by N₂ adsorption is depicted in Figure 1(b). The estimated mesopore and macropore parameters are listed in Table 1.

The hysteresis loop between adsorption and desorption curves belongs to type H₂ based on the definition of International Union of Pure and Applied Chemistry (IUPAC). The type of this hysteresis loop indicates that the pore of QS anthracite is slit shape. The PSD shown in Figure 1(b) indicates that QS anthracite has continuous wide meso/macro-pore size distribution from 13 nm to 60 nm. In addition, it can be found from Table 1 that QS anthracite has a lot of mesopores (pore size of 2-50 nm) whose volume ($V_{\text{mes}}$) is much larger than the volume of macropore ($V_{\text{mac}}$ of pore size larger than 50 nm).

(2) Micropore Morphology Analysis. The micropore structure of QS sample was also obtained using ASAP 2020M system by CO₂ adsorption at 273.15 K. The micropore surface area ($S_{\text{DR}}$) and micropore volume ($V_{\text{DR}}$) were calculated by the Dubinin-Radushkevich (DR) model based on CO₂ adsorption data. The micropore size distribution was determined by the nonlocal density functional theory (NLDFT) model.

The adsorption isotherm of CO₂ at 273.15 K is shown in Figure 2(a). The estimated micropore parameters are listed in Table 1. The micropore size distribution of QS sample
determined by CO₂ adsorption is depicted in Figure 2(b). We can find that QS anthracite has a broad micropore distribution with major peak at around 0.55 nm.

It is noticeable that the value of $S_{DR}$ of 58.59 m²/g is much higher than that of $S_{BET}$ of 0.62 m²/g. Meanwhile, the value of $V_{DR}$ of 0.023 cm³/g is bigger than those of $V_m$ of 0.0018 cm³/g and $V_{mac}$ of 0.0005 cm³/g. Therefore, the surface and pore volume of QS anthracite are mainly contributed by micropore, and micropore will provide a large number of adsorption sites for the adsorption of CH₄ and CO₂ on this anthracite.

(3) Ultimate and Proximate Analyses. Ultimate and proximate analyses were used to characterize coal chemical composition. Ultimate analysis was performed by Flash EA2000 elemental analyzer, Thermo Fisher Scientific. The results of ultimate and proximate analyses of this anthracite are given in Table 2. It is clear that carbon, hydrogen, oxygen, and nitrogen are the main elements in coal reservoir, accounting for more than 95% of the total element content.

2.2. Adsorption Isotherm Measurement and Simulation. A high-resolution intelligent gravimetric analyzer (IGA-100B, U.K.) was employed to measure the adsorption isotherms of CH₄ and CO₂ at pressure up to 1.80 MPa and at temperatures of 283 K, 303 K, and 323 K.

Adsorption isotherm can offer useful information about the surface property of porous material and the interaction between adsorbent and adsorbate [25]. Meanwhile, adsorption isotherm simulation is of great importance for the prediction of adsorption capacity and the interpretation of adsorption mechanism. In this study, the Langmuir-Freundlich (L-F) model was applied to simulate the adsorption data of CH₄ and CO₂. The L-F model is described in the following form [26]:

$$q = \frac{q_m b P}{1 + b P},$$  

where $q$ is the adsorption amount at pressure $P$; $q_m$ is the saturation adsorption capacity of adsorption sites; $b$ is the affinity coefficient of adsorption sites; and $c$ is equal to $1/n$, where $n$ is the deviation from an ideal homogenous surface.

2.3. Ideal Adsorbed Solution Theory. The adsorption of binary gas mixtures can be directly predicted from pure component adsorption data using ideal adsorbed solution theory (IAST) proposed by Myers and Prausnitz [27]. Many studies have confirmed the effectiveness of IAST to predict the adsorption of mixture gases on a variety of porous materials [28–30].

![Figure 3: Adsorption isotherms of CO₂ and CH₄ at different temperatures on anthracite.](image)
The spreading pressure $\pi$ and the reduced spreading pressure $\pi^*$ are defined by [31]:

$$\pi = \frac{RT}{A} \int_0^{\rho_0} \frac{q}{P} dP,$$

(4)

$$\pi^* = \frac{AN\pi}{RT} = \int_0^{\rho_0} \frac{q}{P} dP,$$

(5)

where $T$ is the temperature, $R$ is the universal gas constant, and $A$ is the surface area of adsorbent per unit mass.

Substituting Equation (1) into Equation (5), it can be found that

$$\pi^* = \frac{1}{c_1} qm \ln \left(1 + b_1 (\frac{P}{P_1})^{c_1} \right).$$

(6)

When the adsorption of binary mixture gases reaches equilibrium, the reduced spreading pressures of component 1 and component 2 are equal:

$$\pi_1^* = \pi_2^*,$$

$$\pi_1^* = \frac{1}{c_1} qm_1 \ln \left(1 + b_1 \left(\frac{P}{P_1}\right)^{c_1} \right),$$

(7)

$$\pi_2^* = \frac{1}{c_2} qm_2 \ln \left(1 + b_2 \left(\frac{P}{P_2}\right)^{c_2} \right),$$

where $\pi_1^*$ and $\pi_2^*$ are the reduced spreading pressures of component 1 and component 2, respectively; $c_1$ and $c_2$ are the L-F coefficients of component 1 and component 2, respectively; $qm_1$ and $qm_2$ are the saturation adsorption capacities of component 1 and component 2, respectively; $b_1$ and $b_2$ are the affinity coefficients of component 1 and component 2, respectively.

Combining Equations (3–7) and (8) leads to:

$$\frac{1}{c_1} qm_1 \ln \left(1 + b_1 \left(P \frac{y_1}{x_1}\right)^{c_1} \right) - \frac{1}{c_2} qm_2 \ln \left(1 + b_2 \left(\frac{P(1-y_1)}{1-x_1}\right)^{c_2} \right) = 0.$$  

(8)

For the given $P_1$ and $y_1$, the value of $x_1$ can be obtained by Equation (8).

The selectivity factor $a$ can be decided by:

$$a = \frac{x_1/y_1}{x_2/y_2},$$

(9)

where $y_2$ and $x_2$ are the mole fractions of component 2 in the bulk gas phase and adsorbed phase, respectively.

2.4. Henry’s Law Constant. Henry’s constant ($K_{H}$) can be applied to calculate the affinity between adsorbent surface and adsorbate molecule. Molecule-surface forces predominate at low pressure, and Henry’s constant is directly related to the interaction of matrix surface with adsorbate molecule [33]. A larger $K_{H}$ reflects the stronger affinity between adsorption pair.

In order to calculate $K_{H}$, the relationship between adsorption amount and equilibrium pressure can be expressed by a virial equation [34]:

$$\ln \left(\frac{q}{P}\right) = A_0 + A_1 q + A_2 q^2 + \cdots,$$

(10)

where $A_0$, $A_1$, and $A_2$ are the virial coefficients. The first virial coefficient $A_0$ is related to Henry’s constant, as $K_{H} = \exp (A_0)$. At the low-pressure range, $q$ is small, and the high-order terms in Equation (10) can be neglected. Thus, Equation (10) can be written as follows:

$$\ln \left(\frac{q}{P}\right) = -A_0 - A_1 q.$$  

(11)

By fitting the linear region of $\ln (P/q)$ vs. the loading $q$, $A_0$ and $K_{H}$ can be obtained.

**Table 3: Physical and chemical characteristics of CO$_2$ and CH$_4$ molecules.**

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>CO$_2$</th>
<th>CH$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic diameter (nm)</td>
<td>0.33</td>
<td>0.38</td>
</tr>
<tr>
<td>Shape</td>
<td>Linear</td>
<td>Tetrahedron</td>
</tr>
<tr>
<td>Quadrupole moment (10$^{-26}$ esu-cm$^2$)</td>
<td>4.30</td>
<td>0.0</td>
</tr>
<tr>
<td>Dipole moment (10$^{-26}$ esu-cm$^2$)</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Polarizability (10$^{-25}$ cm$^3$)</td>
<td>29.1</td>
<td>25.9</td>
</tr>
<tr>
<td>Boiling point (K)</td>
<td>216.55</td>
<td>111.65</td>
</tr>
</tbody>
</table>
2.5. Thermodynamics of Adsorption. The thermodynamic parameters in this paper are calculated using the following equations [19, 22, 35, 36]:

\[ Q_{st} = RT^2 \frac{\partial \ln P}{\partial T} \frac{\partial}{\partial q}, \]

\[ \ln P = - \frac{Q_{st}}{RT} + C, \]

\[ \Omega = -RT \int_0^P q \, d(\ln P), \]

\[ \Delta G = \frac{\Omega}{q} = -RT \int_0^P q \, d(\ln P), \]

\[ \Delta H = -Q_{st}, \]

\[ \Delta S = \frac{\Delta H - \Delta G}{T}, \]

where \( C \) is the integration constant.

3. Results and Discussion

3.1. Adsorption Isotherms of CO\textsubscript{2} and CH\textsubscript{4} on Anthracite. The adsorption isotherms of CO\textsubscript{2} and CH\textsubscript{4} at three temperatures are shown in Figure 3. We can find that the adsorption amounts of CO\textsubscript{2} and CH\textsubscript{4} increase monotonically with increasing equilibrium pressure. For the adsorption of CO\textsubscript{2} on coal, the adsorption rate is faster at low-pressure range. As pressure enhances, CO\textsubscript{2} adsorption rate gradually decreases. For the adsorption of CH\textsubscript{4} on coal, the adsorption rate is almost the same over the whole pressure range. The adsorption amounts of both gases at three temperatures are as follows: 283 K > 303 K > 323 K. High temperature will be detrimental to gas adsorption on anthracite, especially for the adsorption of CO\textsubscript{2}. This is mainly because increasing temperature will give the adsorbate molecules more energy to overcome the van der Waals force and electrostatic interaction and stay in the gas phase [21]. On the shale organic nanochannels, the effect of temperature on CH\textsubscript{4} adsorption is more remarkable [37]. Meanwhile, the adsorption isotherms of both gases belong to type I according to the IUPAC classification, which indicates that the adsorbent sample is typically microporous material conforming to the result of the characterization of pore structure of this anthracite.

At the same condition, the adsorption quantity of CO\textsubscript{2} on anthracite is much higher than that of CH\textsubscript{4}. The ratios of adsorption amount of CO\textsubscript{2} relative to CH\textsubscript{4} (\( q_{CO2}/q_{CH4} \)) at three temperatures are displayed in Figure 4. We can find that the values of \( q_{CO2}/q_{CH4} \) range from 1.8 to 6.1, and these values are in coincidence with previous reports [1, 9, 10, 12, 38]. More than 1.8 of the value of \( q_{CO2}/q_{CH4} \) verifies the possibility of the displacement of adsorbed CH\textsubscript{4} by injecting CO\textsubscript{2}. With elevating equilibrium pressure, \( q_{CO2}/q_{CH4} \) declines. It seems that the continuous decrease of the adsorption rate of CO\textsubscript{2} and the minor change of the adsorption rate of CH\textsubscript{4} can account for the downward trend of \( q_{CO2}/q_{CH4} \). At
pressure lower than 0.2 MPa, $q_{CO_2}/q_{CH_4}$ is the biggest at 323 K, while at 303 K $q_{CO_2}/q_{CH_4}$ is the smallest. When the pressure is higher than 0.2 MPa, low temperature is beneficial to obtaining bigger $q_{CO_2}/q_{CH_4}$.

The larger adsorption capacity of CO₂ than CH₄ on coal is attributed to the different characteristics of CH₄ and CO₂. Table 3 summarizes the physical and chemical properties of CO₂ and CH₄ molecules. The smaller kinetic diameter and the linear shape of CO₂ molecule allow CO₂ to diffuse into the more restricted inner pore spaces where the entry of CH₄ is not permitted. Relevant research has shown that CO₂ molecule can diffuse into an additional 40% of the organic pore structure compared with CH₄ molecule [39]. Besides, CH₄ is nonpolar, while CO₂ has a permanent quadrupole moment. This quadrupole moment can lead to the intensive electrostatic interaction between CO₂ molecule and porous adsorbent surface [20] and thereby the larger adsorption quantity. Meanwhile, the boiling point of CH₄ is lower than that of CO₂. The fluid with higher boiling point is easily adsorbed to porous material, as the fluid with higher boiling point has the larger intermolecular attraction and is liable to liquefaction [40].

3.2. Simulation of Adsorption Isotherms of CO₂ and CH₄ The simulated results of the adsorption curves of CH₄ and CO₂ using the L-F model are presented in Figures 5(a) and 5(b), respectively. It is obvious that the simulated results agree well with the experimental results, revealing that the adopted L-F model is able to describe the adsorption curves of CH₄ and CO₂ on anthracite.

Table 4 lists the parameters of CH₄ and CO₂ in the L-F model. As given in Table 4, $q_m$ for CO₂ and CH₄ both decrease with increasing temperature, implying that low temperature helps to achieve higher coalbed methane content.
Figure 7: Comparison of predicted adsorption selectivity of CO₂ over CH₄ at three temperatures for the adsorption of different CO₂/CH₄ mixture gases: (a) \( y_{CO₂} = 0.1 \), (b) \( y_{CO₂} = 0.5 \), and (c) \( y_{CO₂} = 0.9 \).

Table 5: Comparison of \( \alpha_{CO₂/CH₄} \) on different coals and shales.

<table>
<thead>
<tr>
<th>Coal</th>
<th>Pressure ( P ) (MPa)</th>
<th>Temperature ( T ) (K)</th>
<th>( \alpha_{CO₂/CH₄} )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracite</td>
<td>0-1.80</td>
<td>283-323</td>
<td>4.00-5.30</td>
<td>This study</td>
</tr>
<tr>
<td>Lignite</td>
<td>0-1.80</td>
<td>288-328</td>
<td>4.84-5.27</td>
<td>Liu [18]</td>
</tr>
<tr>
<td>Bituminous</td>
<td>0-1.80</td>
<td>288-328</td>
<td>4.43-4.95</td>
<td>Liu [18]</td>
</tr>
<tr>
<td>Anthracite</td>
<td>0-1.80</td>
<td>288-328</td>
<td>5.03-7.97</td>
<td>Liu [18]</td>
</tr>
<tr>
<td>Bituminous coal model</td>
<td>3.04-32.25</td>
<td>295.70-370.20</td>
<td>2.00-9.00</td>
<td>Zhang et al. [8]</td>
</tr>
<tr>
<td>Coal molecular model</td>
<td>3.04-14.82</td>
<td>295.70-325.70</td>
<td>1.25-5.00</td>
<td>Brochard et al. [42]</td>
</tr>
<tr>
<td>Bituminous coal model</td>
<td>0-15</td>
<td>300-340</td>
<td>3.20-6.80</td>
<td>You et al. [13]</td>
</tr>
<tr>
<td>Coal surface model</td>
<td>0-10</td>
<td>298</td>
<td>2.20-14.50</td>
<td>Liu et al. [15]</td>
</tr>
<tr>
<td>Sichuan Basin shale</td>
<td>0-2</td>
<td>278-318</td>
<td>2.72-7.87</td>
<td>Duan [43]</td>
</tr>
<tr>
<td>Barnett shale</td>
<td>0-27.50</td>
<td>313</td>
<td>2.42</td>
<td>Duan [43]</td>
</tr>
<tr>
<td>Marcellus shale</td>
<td>0-27.50</td>
<td>313</td>
<td>4.76</td>
<td>Duan [43]</td>
</tr>
</tbody>
</table>
and sequestrate large amounts of CO₂. Meanwhile, the values of b of both gases also decrease with the improvement of temperature. In addition, the values of Ω for the adsorption of CH₄ and CO₂ all deviate from the unity, which reveals that the anthracite is heterogeneous sedimentary rock. For the naturally occurring carbonaceous organic-rich materials, such as coal and shale, the most prominent feature of these solid surfaces is its inhomogeneity [41]. On the one hand, the inhomogeneity comes from lattice defects, vacancies, and dislocations in crystals. On the other hand, the presence of chemical impurities can also cause the inhomogeneity of solid surface.

3.3. Adsorption Selectivity of CO₂ over CH₄ on Anthracite. The predicted adsorption selectivity factors of CO₂ over CH₄ (α_{CO₂/CH₄}) on anthracite are illustrated in Figure 6. For an equimolar CO₂/CH₄ mixture system, α_{CO₂/CH₄} > 1 infers that CO₂ is preferentially adsorbed in the binary mixture [37]. High selectivity implies the enrichment in the adsorbed phase of CO₂ over CH₄ compared with the ratio in gas phase [8]. It is noticeable that mole fraction of CO₂ (y_CO₂) in mixture gases has significant influence on α_{CO₂/CH₄}. Meanwhile, the variation trends of α_{CO₂/CH₄} at three temperatures are different.

At 283 K, with the increase of pressure, α_{CO₂/CH₄} quickly increases to the maximum and then slowly declines. In the low-pressure range, α_{CO₂/CH₄} improves with the increase of CO₂ mole fraction in mixture gases. In the high-pressure range, α_{CO₂/CH₄} decreases with increasing CO₂ mole fraction in mixture gases. At 303 K, the change pattern of α_{CO₂/CH₄} is similar to that of α_{CO₂/CH₄} at 283 K. The difference is that the inflection point of variation curve of α_{CO₂/CH₄} at 303 K is delayed at 303 K. It should be noted that at 323 K, the change pattern of α_{CO₂/CH₄} is different from those of α_{CO₂/CH₄} at 283 K and 303 K. At 323 K, α_{CO₂/CH₄} continuously reduces as pressure increases. Meanwhile, the lower CO₂ mole fraction in mixture gases is helpful to obtain bigger α_{CO₂/CH₄} at 323 K. Zhang et al. [8] and You et al. [13] also observed that the adsorption selectivity of CO₂ over CH₄ declines gradually with the increase of the bulk CO₂ mole fraction.

The comparison of α_{CO₂/CH₄} at different temperatures for the adsorption of different CO₂/CH₄ mixture gases (y_CO₂ = 0.1, y_CO₂ = 0.5, and y_CO₂ = 0.9) are depicted in Figure 7. It can be found that α_{CO₂/CH₄} at 283 K is higher than that at 303 K for the adsorption of three selected CO₂/CH₄ mixture gases. When equilibrium pressure is bigger than 0.20 MPa, α_{CO₂/CH₄} at 283 K is the highest for the adsorption of mixture gases of 10:90/CO₂:CH₄. For the adsorption of mixture gases of 50:50/CO₂:CH₄, α_{CO₂/CH₄} at 283 K is the highest when equilibrium pressure is bigger than 0.10 MPa. For the adsorption of mixture gases of 90:10/CO₂:CH₄, α_{CO₂/CH₄} at 283 K is the highest when equilibrium pressure is bigger than 0.05 MPa. Generally, the technology of CO₂-ECBM is applied in deep unmineable coal seams with reservoir pressure higher than 0.5 MPa. Therefore, low temperature is beneficial for injected CO₂ to displace preadsorbed CH₄.

As shown in Figure 7, the values of α_{CO₂/CH₄} are more than 4.0, revealing that the adsorbed CH₄ on coal surface can be directly displaced by injected CO₂. The higher the α_{CO₂/CH₄} is, the higher the displacement efficiency of CO₂ is. Hence, the further application of the technology of CO₂-ECBM in this anthracite seam is feasible.

Comparison of α_{CO₂/CH₄} on different coals and shales is listed in Table 5. It is clear that the values of α_{CO₂/CH₄} in studied anthracite are within the range of the values of α_{CO₂/CH₄} in other coals reported by previous researchers [8, 13, 15, 18, 42]. This confirms that using the IAST model to calculate the values of α_{CO₂/CH₄} is reliable. In addition, the values of α_{CO₂/CH₄} on coals are comparable to those of α_{CO₂/CH₄} on shales, which shows that the technology of enhanced shale gas recovery by CO₂ injection is also feasible.

3.4. Henry’s Law Constants of CO₂ and CH₄ on Anthracite. The calculated results of Henry’s constant for CH₄ and CO₂ on anthracite are given in Table 6. K_H for CO₂ and CH₄ both decrease with increasing experiment temperature. High temperature can reduce the adsorption affinity of two gases on anthracite surface. Accordingly, the adsorption capacity decreases with temperature increases as shown in Figure 3. Under same condition, K_H of CH₄ is much smaller than that of CO₂, and CO₂ has stronger adsorption affinity with anthracite. The permanent quadrupole moment of CO₂ molecule, which causes stronger electrostatic interaction between CO₂ and adsorbent, brings about greater affinity of CO₂ on porous material surface [21]. As a result, the adsorption amount of CO₂ is much higher than that of CH₄ on anthracite.

3.5. Thermodynamic Analysis of Adsorption of CO₂ and CH₄ on Anthracite

3.5.1. Surface Potential. The minimum isothermal work, which is necessary to load the adsorbent to a given level, is defined as surface potential Ω [36]. The calculated results of surface potential for CH₄ and CO₂ as a function of pressure are illustrated in Figures 8(a) and 8(b), respectively. At all experiment temperatures, the absolute values of Ω of CO₂ and CH₄ rise monotonically with increasing system pressure. This is mainly because higher isotherm work is needed to fill more adsorbate molecules into cavity pores than at the initial stage of adsorption [19]. This phenomenon is also found for gas adsorption on other porous materials, such as zeolite 13X, shale, and chabazite zeolite [19, 22, 36]. Meanwhile, with the elevation of temperature, the decrease of Ω in the negative value takes place. Surface potential is a criterion of
necessary work to achieve the equilibrium of system. Thus, a lower equilibrium capacity leads to smaller (less negative) surface potential [33], and high temperature can reduce the absolute values of $\Omega$ of CO$_2$ and CH$_4$. It should be noted that under the same condition, the absolute value of $\Omega$ of CO$_2$ is much bigger than that of CH$_4$, revealing that CO$_2$ adsorption on anthracite is more favorable.

3.5.2. Gibbs Free Energy Change. Gibbs free energy refers to the increment of free energy of system with increasing adsorbent unit area at constant temperature and pressure [23]. The calculated results of Gibbs free energy change $\Delta G$ of CO$_2$ and CH$_4$ on anthracite are displayed in Figures 9(a) and 9(b), respectively. We can note that the values of $\Delta G$ of both gases are negative, implying that the adsorption processes of both gases on anthracite are spontaneous. The absolute values of $\Delta G$ of both gas rise gradually with the increase of pressure, which indicates that the degree of spontaneity of gas adsorption is larger at high pressure. Therefore, the adsorptions of CO$_2$ and CH$_4$ are more likely to occur under high pressure condition. The absolute value of $\Delta G$ of CO$_2$ is apparently bigger than that of $\Delta G$ of CH$_4$, and the degree of spontaneity of CO$_2$ adsorption is greater. According to the minimum energy principle, any interface has the tendency to spontaneously reduce the energy of interface. The solid interface is difficult to shrink due to the immobility of molecule or atom on interface. Thus, the surface free energy can only be reduced by adsorbing other molecule. The greater free energy change

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**Figure 8:** Surface potentials of CO$_2$ (a) and CH$_4$ (b) on anthracite at different temperatures.

**Figure 9:** Gibbs free energy changes of CO$_2$ (a) and CH$_4$ (b) on anthracite at different temperatures.
3.5.3. Isosteric Heat of Adsorption. The heat effect of adsorption can be quantified by isosteric heat of adsorption $Q_{st}$ ($-\Delta H$, enthalpy change). Adsorption heat can result in the change in temperature [19]. This temperature variation will cause the localized changes in the kinetic and equilibrium properties, which ultimately influences the adsorption behavior and displacement efficiency [44]. When the adsorbent surface is energetically homogeneous and the lateral adsorbate-adsorbate interaction can be neglected, $Q_{st}$ is independent of adsorbate loading. When the adsorbent is energetically heterogeneous, $Q_{st}$ becomes a function of adsorbate loading [45]. The degree of adsorbent heterogeneity has a strong effect on $Q_{st}$. The means of indirect estimation from temperature-dependent adsorption equilibrium data or direct measurement by dosing calorimetry can be adopted to acquire $Q_{st}$ [44]. In this paper, the values of $Q_{st}$ for CO$_2$ and CH$_4$ were obtained by the indirect estimation approach based on the adsorption isotherm data at three temperatures.

The calculated results of $Q_{st}$ for CO$_2$ and CH$_4$ are plotted in Figure 10. The values of $\Delta H$ ($-Q_{st}$) for both gas are negative, indicating that the adsorption processes of CO$_2$ and CH$_4$ on anthracite are exothermic. Therefore, low temperature can enhance the adsorption amounts of CO$_2$ and CH$_4$. In addition, $Q_{st}$ for CO$_2$ and CH$_4$ are not constant with the increase of adsorption amount, confirming that the studied anthracite is inherently heterogeneous. As the adsorption quantity enhances, $Q_{st}$ of CO$_2$ increases consistently, whereas $Q_{st}$ of CH$_4$ declines monotonously.

At the initial stage of adsorption, the available sorption sites are abundant and the lateral adsorbate-adsorbate inter-

![Figure 10: Isosteric heat of adsorption of CO$_2$ and CH$_4$ on anthracite.](image)

action energy is lower. As adsorption loading increases, more and more cavities are occupied by adsorbate. Thus, the decrease in $Q_{st}$ with adsorption loading takes place [46]. For the adsorption of CH$_4$ on anthracite, the continuous reduction of $Q_{st}$ suggests that the interaction energy among CH$_4$ molecules is much weaker at higher surface coverage. With the increase of pressure (i.e., loading), more CH$_4$ molecules are in a free state within the pore structure of anthracite. For the adsorption of CH$_4$ on shale, the isosteric heat of adsorption also reduces with adsorption loading increases [19].

For CO$_2$ adsorption on anthracite, the intermolecular force among CO$_2$ molecules is gradually strengthened in the cavity pores with enhancing pressure. Compared with CH$_4$ molecule, CO$_2$ molecule with higher boiling point has the larger intermolecular attraction and is liable to liquefaction. At higher surface coverage, the stronger lateral interaction between CO$_2$ molecules results in the increase of $Q_{st}$. Similar changing trend of $Q_{st}$ was reported by Zhou et al. for CO$_2$ adsorption on coal matrix [23].

Meanwhile, the value of $Q_{st}$ of CH$_4$ is lower than that of CO$_2$. He et al. [47] have found that the hindering effect of spherical molecules caused by pore wall is smaller than that of nonspherical molecules for the same size. Contrary to regular tetrahedral CH$_4$ molecule, the diffusion of claviform CO$_2$ molecule into micropores is more influenced by inner pore walls, thereby releasing more energy and heat. During the displacement coalbed methane process, the release of heat from CO$_2$ adsorption will improve the temperature of coal reservoir. The rising temperature is beneficial to CH$_4$ desorption and the enhancement of coalbed methane recovery. Nevertheless, the increase of temperature is harmful for the sequestration of injected CO$_2$.

3.5.4. Entropy Change. Entropy is the measurement of disorder or patterns in which the thermodynamic system is rearranged [22]. The entropy change $\Delta S$ is a net of balance between rotation, vibration, and translation freedoms of adsorbate molecule within matrix [33]. Research about the behavior of entropy change as a function of adsorption loading helps to understand the packing manner of adsorbed molecules. The calculated results of $\Delta S$ of CO$_2$ and CH$_4$ on anthracite are shown in Figures 11(a) and 11(b), respectively. It can be seen that the values of $\Delta S$ of CO$_2$ and CH$_4$ are negative, which elucidates that the adsorption of CO$_2$ and CH$_4$ on coal surface are from a random phase to an order phase. The adsorption progress involves the reduction in the degree of freedom and the formation of a more stable rearrangement in adsorbent surface.

Relevant literature has observed that for the adsorption of CH$_4$ molecule, the entropy loss is between -82 and -87 J/mol/K at temperature ranging from 273 to 423 K [48]. For CH$_4$ adsorption on this anthracite, the value of $\Delta S$ is from -4.96 to -14.51 J/mol/K over the temperature range of 283-323 K, which is very bigger than -82 J/mol/K. The smaller entropy loss of CH$_4$ on anthracite implies that injected CH$_4$ is not completely adsorbed on coal matrix but free gas stayed in the inner pores. As illustrated in
Figure 11(b), the entropy loss of CH$_4$ reduces as adsorption amount increases. Therefore, more injected CH$_4$ molecules are trapped in the coal pore volume rather than adsorbed on matrix surface with increasing surface coverage, and the degree of orderliness the system becomes lower.

As illustrated in Figure 11(a), for CO$_2$ adsorption on anthracite, the entropy loss enhances with increasing surface coverage, inferring that the orderliness degree of the whole system becomes bigger. The increase in entropy loss is mainly because the free space in the cavity reduces, and the freedom of the adsorbate molecule becomes severely limited [21]. Hence, the adsorbed CO$_2$ is in a more stable state at higher surface coverage. The value of $\Delta S$ of CO$_2$ is from -12.97 to -45.76 J/mol/K at temperature ranging from 283 to 323 K. The value of $\Delta S$ of CO$_2$ on anthracite is smaller than those of $\Delta S$ of CO$_2$ on 5A and 13X zeolites [33], which indicates that the orderliness of adsorbed CO$_2$ on 5A and 13X zeolites is higher than that on anthracite.

It is obvious that the entropy loss of CH$_4$ on anthracite is lower than that of CO$_2$ at the same condition. Barrer [49] has found that the interaction between permanent quadrupole moment of molecule and electrostatic field can result in a more efficient packing. If the molecule packing is more effective, the larger adsorption heat will be released [33]. Due to the existence of quadrupole moment, the packing manner of CO$_2$ molecule on anthracite is more efficient, and $Q_{st}$ of CO$_2$ is greater as shown in Figure 10. Meanwhile, the bigger entropy loss of CO$_2$ reveals that the adsorbed CO$_2$ molecules form a more stable configuration, which is also one reason why the sorption amount of CO$_2$ on coal is larger than that of CH$_4$. In addition, the entropy losses of both gases decline slightly with the increase of temperature. High temperature will not conducive to forming a more ordered and stable configuration for adsorbed CH$_4$ and CO$_2$, and thus, the sorption quantities of both gases decrease as temperature rises.

4. Conclusions

In this paper, the adsorption isotherms of CH$_4$ and CO$_2$ on Qinshui Basin anthracite were obtained at the temperatures of 283 K, 303 K, and 323 K. The adsorption selectivity factor of CO$_2$ over CH$_4$ on anthracite was predicted. The affinities and thermodynamic properties of CH$_4$ and CO$_2$ on anthracite were investigated. The main conclusions are as follows:

(1) The sorption ability of CO$_2$ on anthracite is much larger than that of CH$_4$. At the temperatures of 283 K and 303 K, $\alpha_{CO2/CH4}$ quickly increases to the maximum and then slowly declines with the increase of pressure. At 323 K, $\alpha_{CO2/CH4}$ monotonously reduces as pressure enhances. CO$_2$ mole fraction in mixture gases has obvious effect on $\alpha_{CO2/CH4}$. The values of $\alpha_{CO2/CH4}$ are more than 4.0, revealing that the technology of CO$_2$-ECBM is feasible. In actual coal reservoir, low temperature is helpful for injected CO$_2$ to displace preadsorbed CH$_4$. Henry’s constant of CH$_4$ is smaller than that of CO$_2$, and CH$_4$ has a weaker adsorption affinity with matrix surface.

(2) The values of $\Omega$ of both gases are more negative with the increase of pressure. The absolute value of $\Omega$ of CO$_2$ is much bigger than that of CH$_4$, revealing that CO$_2$ adsorption is more favorable. As pressure increases, the absolute values of $\Delta G$ of CO$_2$ and CH$_4$ rise. The larger absolute value of $\Delta G$ of CO$_2$ indicates that the degree of spontaneity of CO$_2$ adsorption is higher.

(3) As adsorption loading enhances, $Q_{st}$ of CO$_2$ increases, while $Q_{st}$ of CH$_4$ declines. The value of $Q_{st}$ of CO$_2$ is larger than that of CH$_4$. With increasing surface coverage, the entropy loss of CH$_4$ decreases.
while the entropy loss of CO$_2$ enlarges. Improving temperature will reduce the entropy losses of both gases. The higher entropy loss of CO$_2$ suggests that the adsorbed CO$_2$ molecules constitute a more ordered configuration than adsorbed CH$_4$ molecules.

Data Availability

The data used to support the findings of this study are available from the corresponding authors upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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