Calculation and Comparison of Adsorption Curves of Three ISO-Variables A CSE Study of Lean Coal from China

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Abstract: A series of isothermal adsorption experimental data of MZQ coal sample in Shanxi province of China has been transformed to fit a temperature pressure-adsorption equation with high accuracy. Besides isothermal adsorption curve, isobaric adsorption curve and isosteric adsorption curve have been created and presented. The Clausius-Clapeyron equations have been used to illustrate that gas isosteric adsorption is an exothermic process. The calculation procedure of unit isosteric adsorption enthalpy has been present. The increase of adsorption amount causes the unit isosteric adsorption enthalpy exponentially decreased, so the unit isosteric desorption enthalpy exponentially decreased.
Key words: temperature-pressure-adsorption equation; Clausius-Clapeyron equation; isobaric adsorption; isosteric adsorption.

I. INTRODUCTION

The adsorption of coalbed methane is of great significance for the prediction of coalbed methane reserves, coal and gas outburst, and the extraction and utilization of gas. The adsorption of coalbed methane is a typical physical adsorption, like the equation describing the state of the substance, involving three variables of the gas adsorption volume (adsorption capacity), adsorption temperature, and adsorption pressure [1-3]. Due to the research of adsorption theory from shallow to deep, especially the limitation of adsorption experimental instruments and conditions, the experimental method of fixing one variable and measuring the correlation between the other two variables is often adopted [4-7]. The high-pressure constant temperature adsorption experiment of coal is the most used method. So (1) can the interpretation temperature be obtained from a series of high-pressure constant temperature adsorption experimental data; (2) can the correlation between pressure and adsorption capacity during constant temperature adsorption be displayed and compared with the experime value of the original series of high pressure constant temperature; (3) can the correlation between temperature and adsorption capacity during constant pressure adsorption be displayed; (4) can the correlation between temperature and pressure during constant adsorption be displayed; (5) can the data measuring adsorption be used to calculate the equivalent adsorption function of Clausius-Clapeyron's equation, and draw some thermodynamic conclusions? This paper intends to use a series of isothermal and high-pressure adsorption experimental data from Maozequ Coal Mine in Shanxi Province, China, to conduct some research and give answers to the above five questions.

II. EQUATIONS AND DATA

A. The Langmuir adsorption equation

The Langmuir adsorption equation can be represented as:

$$V = \frac{abP}{1+bP} \qquad (1)$$

Equation (1) is the theoretic treatment of isothermal adsorption, without containing the adsorption temperature as a variable.

B. Temperature-pressure-absorbing equation (TPAE) [8-10]

Using the temperature and pressure as independent variables and adsorption amount as dependent variable, the TPAE can be expressed as

$$V = \frac{1}{\sqrt{MT}}\left[A + BP^{\beta}T^{1.5}\exp\left(\frac{\Delta}{T}\right) \right] \qquad (2)$$

Equation (2) is a theoretical derivation of statistical thermodynamics, which contains all three variables of adsorption.

C. The Clausius-Clapeyron equations

The indefinite integral formula of the Clausius-Clapeyron equation for calculating the molar enthalpy of adsorption is:

$$ln\, P = \frac{\Delta_g^l H_m}{R}\frac{1}{T} + C \qquad (3)$$

According to equation (3), a straight line should be drawn with *lnP* to *1/T*. The sign of the slope can be used to determine the thermodynamic properties of adsorption, exothermic or endothermic. If the slope of the straight line is negative, it can be determined that the molar adsorption enthalpy is less than 0, which means that adsorption is an exothermic process, and temperature has a negative effect on the exothermic process, and vice versa. The value of the slope of straight line can be used to calculate the molar adsorption enthalpy. The definite integral expression of the Clausius-Clapeyron equation of adsorption is

$$-\Delta_g^l H_m = \frac{RT_2T_1}{(T_2-T_1)} ln \frac{P_2}{P_1} \qquad (4)$$

At the isosteric adsorption, if $P_2 > P_1$, then temperature T_2 must be larger than the original T_1. Therefore, if the right side of Equation 4 is positive, the adsorption enthalpy must be negative, which means the adsorption is an exothermic process, temperature has a negative effect on the adsorption amounts. The physical significance of Equation 4 is that to maintain the same adsorption capacity, the pressure must be increased when the temperature rises. Therefore, $P_2 > P_1$ and $T_2 > T_1$ can be used to verify the adsorption is an exothermic process.

D. Sample

A lean coal from Maozequ (MZQ) coal mine in Shanxi Province, China is used. The data and parameters of MZQ coal samples are listed in Table 1.

Table 1: The Date and Parameters of MZQ Coal Sample [1]

Parameter	Data
$R_{0,\,max}$/%	1.76
Vitrinite/%	61.5
Inertinite/%	33.3
Exinite/%	1.4
Mineral/%	3.9
Ash/%	13.9
Moisture/%	10.3

The MZQ coal under different testing temperatures is listed in Table 2. The temperature range is 30~100°C and pressure is 0~30 MPa.

Table 2: The Langmuir Volume and The reciprocal of Langmuir Pressure of MZQ Coal [1]

Testing temperature/°C	a/cm^3g^{-1}	b/MPa^{-1}
30	27.17	0.289
50	22.78	0.281
70	19.92	0.252
85	20.33	0.185
100	10.73	0.424

III. RESULT AND DISCUSSION

The details regarding the regression of TPAE from series Longmuir adsorption has been presented early [9]. The four parameters of TPAE regressed from Table 2 parameters of lean coal are listed in Table 3.

Table 3: The TPAE Parameters Regretted from ISO Thermal Adsorption Measurements of MZQ Coal

Parameter	Value
A	0.168
B	0.0007334
□/K	1557
□	0.3236

The TPAE is a three-dimensional (temperature-pressure-adsorption) curved surface as shown in Figure 1. The 5 rows' points are corresponding 5 Langmuir's temperatures of MZQ coal.

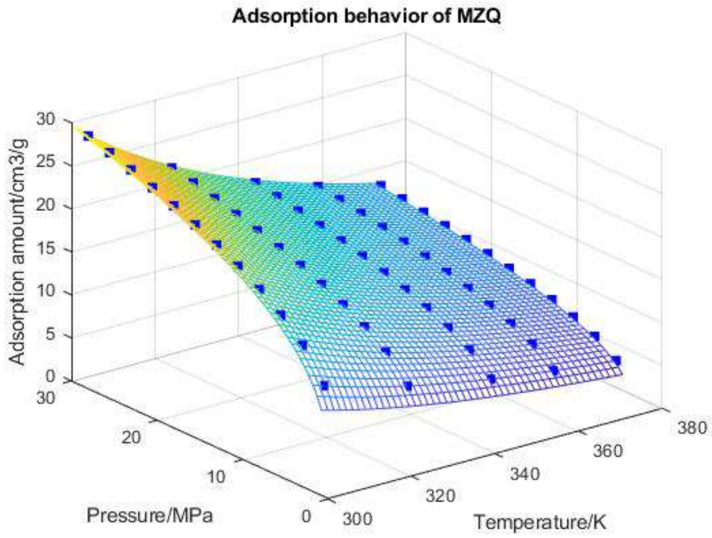

Figure 1: The measured adsorption values and TPAE surface of MZQ coal

Figure 1 proves that a series of high-pressure constant temperature adsorption experimental data can be mathematically presented in a three-dimensional (temperature-pressure-adsorption) curved surface.

A. Isothermal adsorption

Both Equation 1 and Equation 2 can be used by fixed the temperature T values to measure the relationship between adsorption quantity and pressure. After introducing one pressure value, the adsorption amount can be calculated. By repeating these steps, the 30°C and 50°C isothermal adsorptions of MZQ coal are generated and presented in Figure 2.

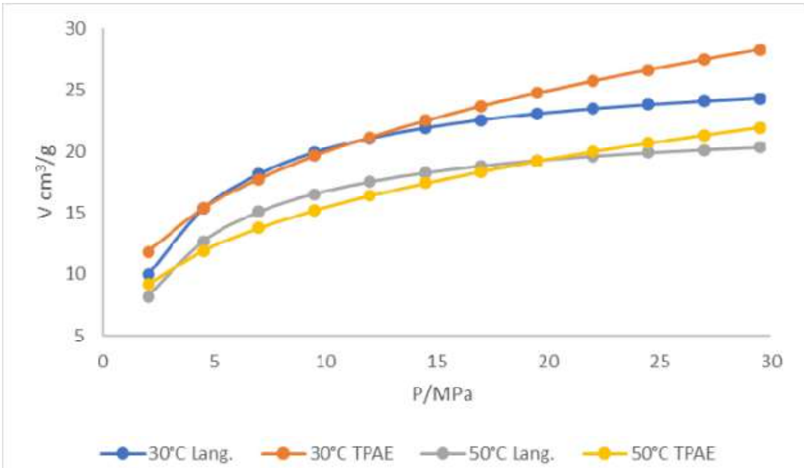

Figure 2: The comparison between Langmuir and TPAE isothermal adsorption of MZQ coal

The isothermal adsorptions calculated based on Equation 1 are defined as "Lang.", and the isothermal adsorptions calculated based on Equation 2 are defined as "TPAE". From the curves in Figure 2, it is easy to see that, for both Langmuir equation and PTAE, the adsorption amount decreased with the temperature increasing, which phenomenon proves that the adsorption temperature haves a negative effect. A comparison of the two calculation methods (Langmuir and TPAE) shows that there was no significant difference in the adsorption capacity obtained at the same temperature and pressure. Drawing a horizontal line from left to right in Figure 2, it will cross the isothermal adsorption curve of lower temperature first, then cross the isothermal adsorption curve of higher temperature second. In this way, it is proved that the adsorption is an exothermic process because of $T_2 > T_1$ so$P_2 > P_1$.

B. Isobaric adsorption

Equation 2 can be used by fixed the pressure P values to measure the relationship between adsorption quantity and temperature. After introducing one temperature value, the adsorption amount can be calculated. By repeating this step, the 5MPa, 10MPa, and 15MPa isobaric adsorption of MZQ coal are generated and presented in Figure 3. From the curves in Figure 3, it is easy to see that the adsorption amount decreased with the temperature increasing, which phenomenon proves that the adsorption temperature haves a negative effect. Drawing a horizontal line from left to right in Figure 3, it will cross the isobaric adsorption curve of lower pressure first, then cross the isobaric adsorption curve of higher pressure second. In this way, it is proved that the adsorption is an exothermic process because of $T_2 > T_1$ so $P_2 > P_1$.

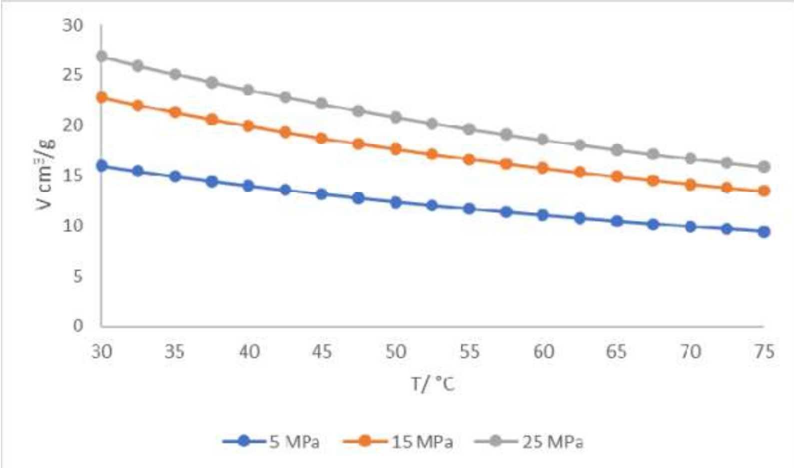

Figure 3: The isobaric adsorption of MZQ coal

C. Isosteric adsorption [10-13]

Equation 2 can be used by fixed the adsorption amount to measure the relationship between adsorption pressure and temperature. After introducing one temperature value, the adsorption pressure can be calculated. By repeating this step, the 10 cm^3/g, 15 cm^3/g, and 20 cm^3/g isobaric adsorption of MZQ coal are generated and presented in Figure 4.

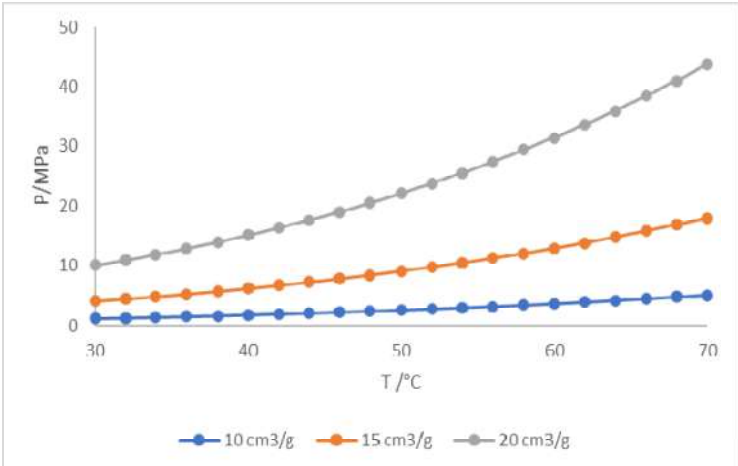

Figure 4: The isosteric adsorption of MZQ coal

From Figure 4, the isosteric adsorption curve is always an ascending curve. It is proved that the adsorption is an exothermic process because of $T_2 > T_1$ so $P_2 > P_1$.

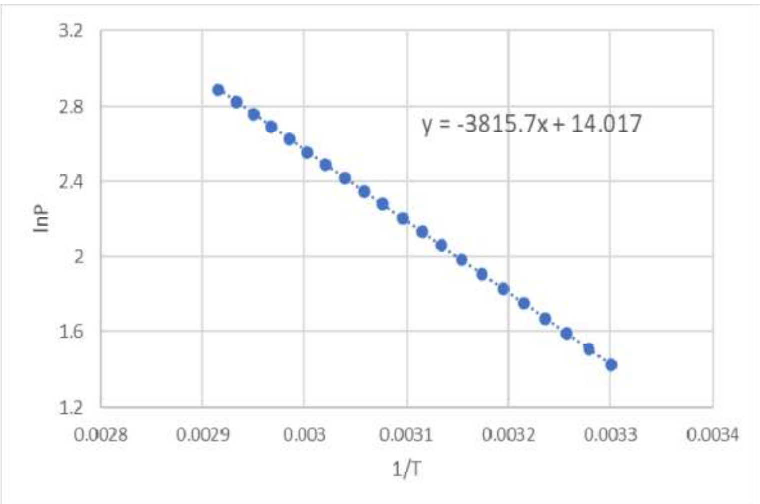

Figure 5: The illustration of 15 cm^3/g adsorption of MZQ coal.

Fixed the adsorption amount at 15.0 cm^3/g, and then based the Clausius-Clapeyron equation of adsorption created the lnP vs 1/T plot as Figure 5.

The lnP vs 1/T plot is a straight line. The slope of straight line can be used to calculate the molar adsorption enthalpy. From Figure 5, the lnP vs 1/T straight line has a negative slope, which indicates that the gas adsorption is an exothermic process.

D. The calculation of unit isosteric adsorption enthalpy

The study of thermodynamics is the direction and limits of the reaction. Intensive quantity and extensive quantity are two basic conceptions that run through chemical thermodynamics. The enthalpy of adsorption is an extensive quantity, which is related to the amount of adsorbed. To avoid unnecessary confusion, this paper defines "unit isosteric adsorption enthalpy" as: the enthalpy value of each adsorbed unit amount under exact fixed adsorbed amount. Using the slope of the straight line in Figure 5 to illustrate how to calculate the unit isosteric enthalpy of adsorption of MZQ coal under 15 cm^3/g adsorption.

(1) Multiply the slope by the gas constant R=0.008314KJ/ (mol · K) to get the total adsorption enthalpy under the corresponding adsorption volume, KJ/mol;
(2) Divide the total adsorption enthalpy by the adsorption amount (15.0cm^3/g) to obtain the unit isosteric adsorption enthalpy $KJ \cdot mol^{-1} \cdot cm^{-3} \cdot g$.

E. The applications of unit isosteric adsorption enthalpy

Be careful, for different adsorption amount, the different unit isosteric adsorption enthalpy can be gotten. Meanwhile, the increase of adsorption amount causes the unit isosteric adsorption enthalpy exponentially decreased, so the unit isosteric desorption enthalpy exponentially decreased. This phenomenon indicates not only that the surface of the coal seam is not smooth, and the energy of the surface is uneven, but also how the outside energy is accumulated in the coal gradually.

The adsorption is an exothermic process. Based on the thermodynamic principle, exothermic processes can happen spontaneously. If someone wants to judge which coals, normal coal, or deformed coal, should adsorb first, it is necessary to calculate separately the total adsorption amount of these two kinds of coal under the stratification, and then calculate the unit isosteric adsorption enthalpy of each coal. From the perspective of energy, normal coal can release more energy at the same temperature and pressure so normal coal should have the highest priority to carry out adsorption.

The reverse process of an exothermic is an endothermic process. The endothermic processes can't happen spontaneously, desorption must be conducted with outside energy. If someone wants to determine which coals, normal coal, or deformed coal, should desorb first, it is necessary to calculate separately the total desorption amount of these two kinds of coal under the stratification, then calculate the unit isosteric desorption enthalpy of each coal. From the perspective of energy, deformed coal needs less outside energy at the same temperature and pressure to desorb, so deformed coal should have the highest priority to carry out desorption.

IV. CONCLUSION

A series of isothermal adsorption experimental data of MZQ coal sample in Shanxi province of China has been transformed to fit a temperature pressure-adsorption equation with high accuracy. Besides isothermal adsorption curve, isobaric adsorption curve and isosteric adsorption curve have been created and presented for the first time. The Clausius-Clapeyron indefinite integral equation and definite integral equation have been used to illustrate that gas isosteric adsorption is an exothermic process. The calculation procedure of unit isosteric adsorption enthalpy has been present. The increase of adsorption amount causes the unit isosteric adsorption enthalpy exponentially decreased, so the unit isosteric desorption enthalpy exponentially decreased.

Symbol Description

a: Langmuir volume, cm^3/g
b: The reciprocal of the Langmuir pressure, MPa^{-1}
A: Geometric shape constant of microporous medium
B: Adsorption flow coefficient of the adsorption site
C: The indefinite integral constant
M: The molecular weight of methane, 16
P: The adsorption pressure, MPa
R: Gas state constant, J/(mol·K)
T: The adsorption temperature, K
V: The adsorption amount, cm^3/g
$\Delta_g^l H_m$: The adsorption enthalpy, KJ/mol
The parameter measuring the relative influence of adsorption pressure, dimensionless.
The energy difference between the lowest potential energy and the activation energy of an adsorbed molecule, which mainly measures the relative influence of adsorption temperature, K

Subscript

g: Gas phase
l: Liquid phase
m: mole

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