



## Application of temperature-pressure-adsorption equation in calculating the adsorption enthalpy of coal seam

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### Abstract:

A series of isothermal adsorption experimental data of long flame coal, fat coal, lean coal and lean coal in Ordos Basin are used to verify a temperature-pressure-adsorption equation, and the functional relationship between adsorption equilibrium pressure and temperature was discussed. The enthalpy of the gas adsorption process is calculated by the Clausius-Clapperon equation. The concept and calculation method of unit isosteric adsorption enthalpy is presented. The adsorption process of the coal is an exothermic process because its negative enthalpy. The unit isosteric adsorption enthalpy decreases with the increase of adsorption capacity because of the energy inhomogeneity on the coal surface. Because of the exothermic adsorption process, so the adsorption occurs at a higher energy site first in order to release more energy. The higher rank coal has a larger unit isosteric adsorption enthalpy, and there must be a larger adsorption capacity. The adsorption capacity of high rank coal decreases rapidly with the increase of adsorption temperature, but the low rank coal decreases less.

**Keywords:** Clausius-Clapeyron equation; Temperature-pressure-adsorption equation; Isotheric enthalpy of adsorption; Unit isotheric enthalpy of adsorption; Gas adsorption; Coal rank

The study of surface and adsorption of coal or shale is very important for the determination of gas saturation, the evaluation of adsorption capacity and the search of reasonable engineering development plan [1-5]. It is also an interesting field to discuss the thermodynamic relationship between the surface of the adsorbing medium and the adsorbed gas by using the equivalent adsorption enthalpy [6-10]. In this paper, the temperature-pressure-adsorption equation is used to regress the temperature-adsorption data of four coal samples from Yangpo Spring Mine, Yangpo Spring Mine, Nanyu Mine, Maozequ Mine and Xiangshan Mine in eastern Ordos Basin. The relationship between adsorption equilibrium pressure and temperature was calculated by using the derived equation of equal adsorption, the calculation method of equal adsorption enthalpy was discussed, and the influence of coal grade on equal adsorption enthalpy was studied.

## 1 Clausius-Clapeyron equation

Clapeyron equation is the second law of thermodynamics. It describes the relationship between equilibrium pressure  $P$  and equilibrium temperature  $T$  when pure matter is in two-phase equilibrium.

$$dP / dT = \Delta_{\alpha}^{\beta} H_m / (T_{\alpha}^{\beta} V_m) \quad (1)$$

In the formula,  $\Delta_{\alpha}^{\beta} H_m$  is the molar enthalpy of change. If the enthalpy of the molar process is positive, the process is endothermic, and the temperature has a positive effect on the endothermic process. If the enthalpy of molar process is negative, the process is exothermic, and the temperature has a negative effect on the exothermic process. Subscript  $m$  denotes mole. Subscript  $\alpha$  denote the initial state; superscript  $\beta$  denote the final state. Thermodynamic variables (such as volume, enthalpy, entropy, etc.) in the calculation process are subtracted

from the final state by the initial state. The indefinite integral formula of Clausius-Clapeyron equation for adsorption process is as follows:

$$\ln P = \frac{\Delta_g^l H_m}{RT} + C \quad (2)$$

According to equation 2, drawing  $1/T$  with  $\ln P$  should be a straight line. If  $\ln P$  plots a negative slope line for  $1/T$ , the molar enthalpy of adsorption can be determined as  $\Delta_g^l H_m < 0$ , that is, adsorption is an exothermic process. For exothermic processes, it can be inferred that:

- (1) Under the same conditions (adsorption gas, pressure), the adsorption capacity of the same coal sample will decrease with the increase of adsorption temperature.
- (2) If the energy on the surface of the adsorbent is not uniform, the adsorption should first occur at the higher energy (higher activity) position, because this can release more energy, so that the energy between the adsorbent and the adsorbent is lower and more stable.
- (3) At the same adsorption gas, pressure and temperature, coal samples with higher energy (i.e., higher activity) should have larger adsorption capacity.

## 2 Temperature-Pressure-Adsorption Equation

The adsorption capacity of solid to gas is a function of temperature and gas pressure. At constant temperature, the curve reflecting the relationship between adsorption capacity and equilibrium pressure is called adsorption isotherm. Langmuir adsorption isotherm equation is the most commonly used one. Temperature-Pressure-Adsorption Equation (TPAE) is a four-parameter equation that organically links temperature, pressure and adsorption volume to study how the adsorption amount of coal or shale changes under the simultaneous action of adsorption temperature and pressure.

$$V = (MT)^{-0.5} \left[ A - BT^{1.5} P^\beta \exp(\Delta / T) \right] \quad (3)$$

In the formula:

A: Geometric shape constant of adsorption medium, dimensionless;

B: Adsorption flow coefficient, dimensionless;

M: Molecular weight, methane molecular weight 16;

P: Pressure during testing, Mpa;

T: Thermodynamic temperature, K;

V: Adsorption capacity, m<sup>3</sup>/T;

B : The parameters affected by pressure are dimensionless;

$\Delta$  : The parameter of temperature effect, K.

In equation 3, temperature and pressure are independent variables, and adsorption V is dependent variable. In order to study the relationship between temperature and pressure, the temperature T and adsorption V in equation 3 are taken as independent variables and the pressure P as dependent variables.

$$\ln P = 1/\beta \ln[(V(MT)^{0.5} - A)/(BT^{1.5} \exp(\Delta/T))] \quad (4)$$

It is also determined that when calculating the adsorption enthalpy of the same amount, the measured data (series of isothermal adsorption, variable temperature and pressure adsorption) must be calculated by regression of equation (3), and verified.

### 3 Isothermal adsorption experimental data of coal and rock

Some scholars have used four series of isothermal adsorption tests of coal samples (gas coal ( $R_{\max}= 0.88$ ), coking coal ( $R_{\max}= 1.44$ ), lean coal ( $R_{\max}= 2.06$ ) and anthracite ( $R_{\max}= 3.56$ ) (temperature between 30°C and 100°C, upper limit pressure of 30 MPa) [11]. The temperature adsorption data reported in Langmuir parameter form in Table 1 are Langmuir volume, cm<sup>3</sup>.g<sup>-1</sup>, B the reciprocal of Langmuir pressure and MPa<sup>-1</sup>.

**Table 1 Measuring Conditions of Coal Samples and Parameters of Langmuir Volume and Langmuir**

	Equation				
Coal	20°C	30°C	40°C	50°C	

Samples	a	b	a	b	a	b	a	b
Gas Coal	27.95	0.162	25.89	0.156	25.66	0.147	25.47	0.129
Coking Coal	28.93	0.342	28.82	0.291	29.06	0.246	28.34	0.221
Meagre Coal	45.27	0.383	41.47	0.351	40.04	0.317	40.38	0.257
Anthracite	57.53	0.319	54.93	0.256	56.84	0.210	57.93	0.169

## 4 Results and Discussion

### 4.1 Parametric Regression of TPAE

Langmuir isothermal adsorption equation was used to calculate the regression sample group. According to the original diagram, 10 pressure points are measured at each temperature until the upper limit pressure is 10 MPa [16]. Each coal sample should have 40 regression samples at five test temperatures. Linear regression was used to calculate 40 regression samples of each coal sample to determine TPAE, four parameters A, B, and beta of equation (3). Then the corresponding average relative error is calculated. The four TPAE parameters of the four coals and the corresponding average relative errors are listed in Table 2.

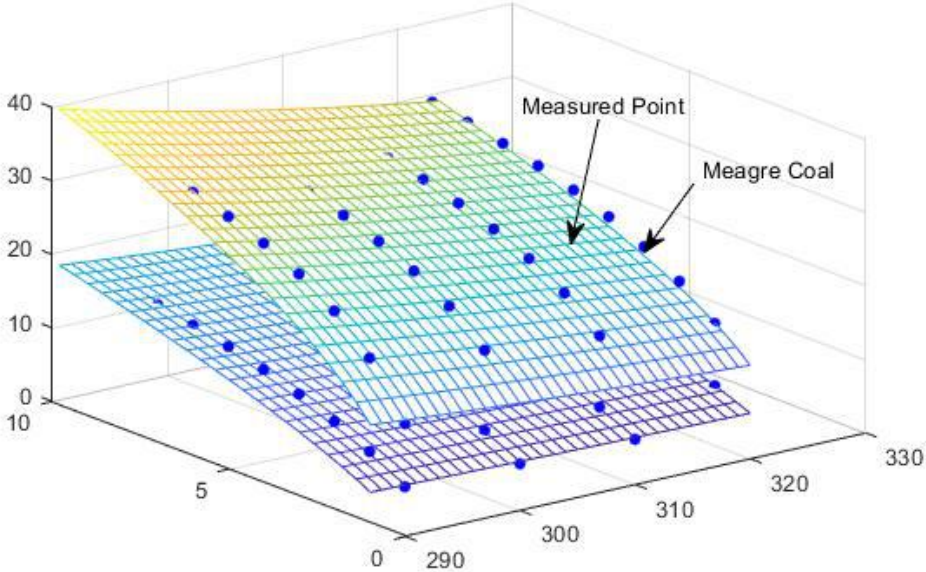
**Table 2: TPAE parameters are obtained by regression based on Langmuir volume and Langmuir equation parameters in Table 1**

Coal Samples	Gas Coal	Coking Coal	Meagre Coal	Anthracite
A	0.168	0.168	0.168	0.168
B	0.00189	0.00361	0.00323	0.00288
$\beta$	0.657	0.522	0.4819	0.5574
$\Delta$	994	983	1173	1222
$\bar{\delta}/\%$	4.60	5.16	5.20	5.52

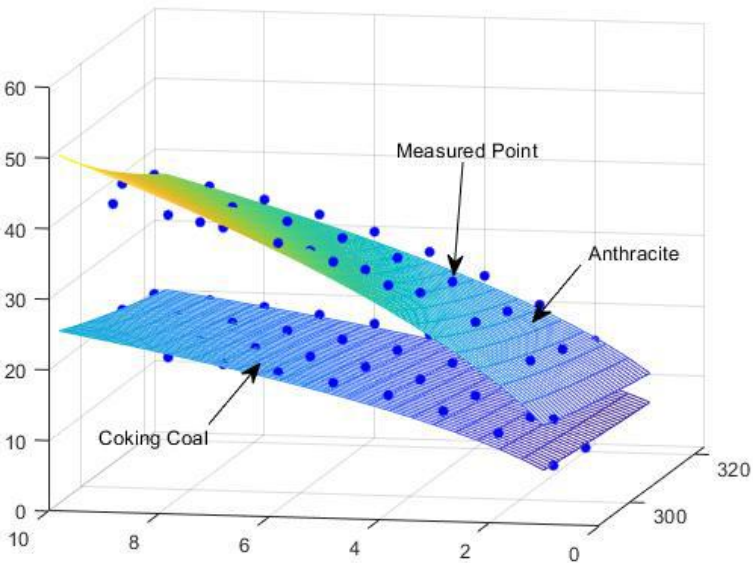
$\bar{\delta}$  is the relative average error percentage between 40 pairs of regression sample groups and

calculated sample groups.

In addition to calculating the relative average error, it can also be used as a graphical method to show the consistency of TPAE with experimental data (using the calculated value of Landscape parameter as the "measured point" and TPAE equation as the temperature-pressure-adsorption surface)[11]. Fig. 1 and Fig. 2 are the "measured points" and TPAE surfaces of the four coal samples used.



**Fig. 1 Measured points of gas coal and lean coal and TPAE regression surface**



**Fig. 2 The measured points of coking coal and anthracite and TPAE regression surface**

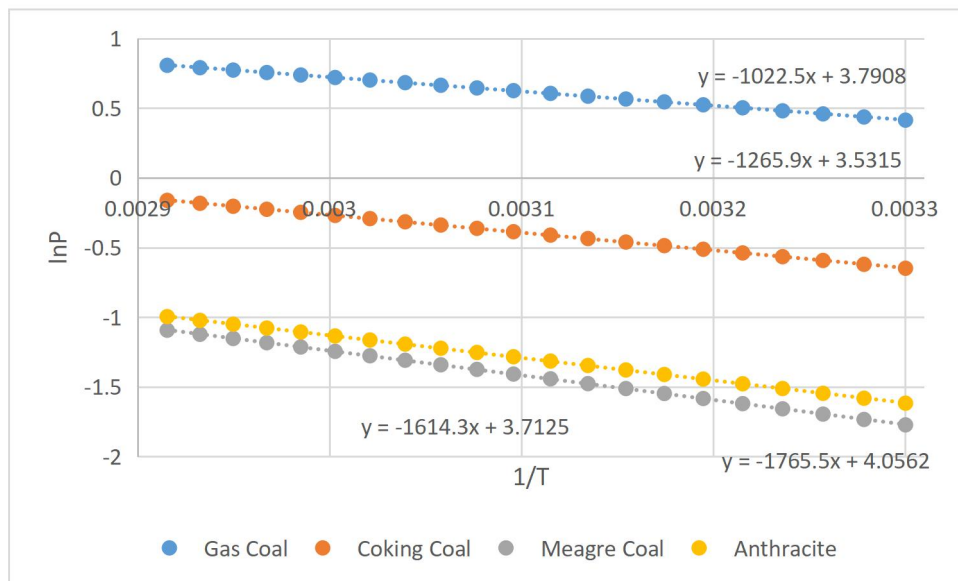
The temperature-pressure-adsorption equation, TPAE, can accurately represent the series of isothermal adsorption experiments from the relative average error of Table 2 and the coincidence between the points of Fig. 1 and Fig. 2 and the surface.

#### 4.2 lnP and 1/T mapping

The adsorption isotherm describes the functional relationship between equilibrium pressure and temperature when the adsorption capacity is constant. If the adsorption capacity in equation (4) is constant to 5.0 cm<sup>3</sup>/g, the following specific steps should be taken:

- ① Suppose a thermodynamic temperature T is substituted into the equation (4);
- ② At this thermodynamic temperature T, the adsorption capacity is 5.0cm<sup>3</sup>/g, and the corresponding pressure is required.
- ③ Repeat ① and ② to get a series of pressure P at a series of temperature T when the adsorption capacity is 5.0 cm<sup>3</sup>/g[12-14].

According to Clausius-Clapeyron equation (equation 2) and drawing 1/T of lnP, the relationship between adsorption pressure and temperature of four coal samples at different adsorption amounts can be obtained. Fig.3 shows the relationship between adsorption pressure and adsorption temperature for four kinds of coal with adsorption capacity of 5.0 cm<sup>3</sup>/g.[12]



**Fig. 3 The relationship between lnP and 1/T of four coals when the adsorption capacity is 5.0 cm<sup>3</sup>/g**

Fig. 3 shows that when the adsorption capacity is 5.0 cm<sup>3</sup>/g, four straight lines with different negative slopes can be drawn from lnP and 1/T of the four coals. That is to say, the adsorption enthalpy of four kinds of coal is negative (adsorption exothermic). The slopes of the four trend lines of the four coals in Figure 3 are listed in Table 3, respectively.

**Table 3 lnP and 1/T slope of four coal samples at adsorption capacity of 5.0 cm<sup>3</sup>/g**

Coal Samples	Gas Coal	Coking Coal	Meagre Coal	Anthracite
Slope	-1023	-1266	-1766	-1614

### 4.3 Unit Equivalent Adsorption Enthalpy

Fig. 3 shows the slope of four trend lines of four kinds of coal when the adsorption capacity is 5.0 cm<sup>3</sup>/g. After calculating the slope in Table 3 as the isosteric enthalpy of adsorption, the unit isosteric enthalpy of adsorption is calculated as follows:

(1) The slope of coal sample in Table 3 is multiplied by the gas constant  $R=0.008314\text{KJ}/(\text{mol}\cdot\text{K})$  to obtain the equivalent adsorption enthalpy, KJ/mol, at the corresponding adsorption capacity.

(2) The equivalent adsorption enthalpy  $\text{KJ}\cdot\text{mol}^{-1}\cdot\text{cm}^{-3}\cdot\text{g}$  was obtained by dividing the adsorption enthalpy by the adsorption amount[15].

The results are listed in table 4.

**Table 4 Unit equivalent adsorption enthalpy of four coal samples at adsorption capacity of 5.0 cm<sup>3</sup>/g**

Unit Equivalent Adsorption Enthalpy/ $\text{KJ}\cdot\text{mol}^{-1}\cdot\text{cm}^{-3}\cdot\text{g}$				
Adsorption/ $\text{cm}^3\text{g}^{-1}$	Gas Coal	Coking Coal	Meagre Coal	Anthracite
5	-1.701	-2.105	-2.937	-2.684

Because the enthalpy of adsorption is a broad measure of thermodynamics, the equivalent enthalpy of adsorption and the unit enthalpy of adsorption are also broad measures of thermodynamics, i.e. related to the quantity discussed. The physical meaning of the enthalpy

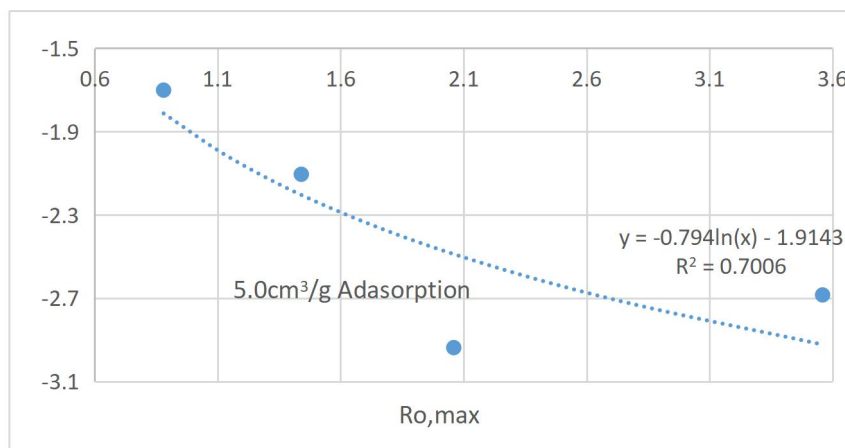


per unit of adsorption is "the enthalpy per unit of adsorption (1.0 cm<sup>3</sup>/g) when the adsorption is a quantitative one (e.g. 5.0 cm<sup>3</sup>/g). In order to study the effect of coal rank on the adsorption enthalpy, it is necessary to compare the adsorption enthalpy per unit under the same adsorption capacity of different coal types. In order to study the effect of different adsorption capacity on the adsorption enthalpy of the same coal sample, it is necessary to compare the adsorption enthalpy per unit of the same coal sample under different adsorption capacity.

Previous studies have shown that under the same adsorption temperature and pressure, the adsorption capacity increases with the increase of coal rank. According to the data in Table 4, it can be seen that with the increase of coal grade, the absolute value of the unit adsorption enthalpy increases, that is, more heat is released.

#### 4.4 Coal Class and Unit Equivalent Adsorption Enthalpy

The relationship between coal rank and unit adsorption enthalpy can be studied by mapping the maximum reflectance of vitrinite (R<sub>o, max</sub>) of four coals and their corresponding unit adsorption enthalpy. Fig. 5 shows the relationship between different coal ranks and the unit adsorption enthalpy under the condition that the adsorption capacity is 5.0 cm<sup>3</sup>/g.



**Fig. 4 Relation between coal rank (different R<sub>o, max</sub>) and unit adsorption enthalpy of four kinds of coal samples**

Obviously only four sets of vitrinite maximum reflectance and unit adsorption enthalpy data of four kinds of coal show that the logarithmic form is not convincing. But it should be seen that under the same adsorption capacity, with the increase of coal rank, the absolute value of the unit adsorption enthalpy increases, that is, the trend of releasing more heat.

#### 4.5 Unit Equivalent Adsorption Enthalpy of the Same Coal Sample with Different Adsorption Quantities

The unit adsorption enthalpy and adsorption capacity of four kinds of coal under different adsorption capacity are listed in Table 5[16].

**Table 5 Unit equal adsorption enthalpy of four coal samples at different adsorption amounts**

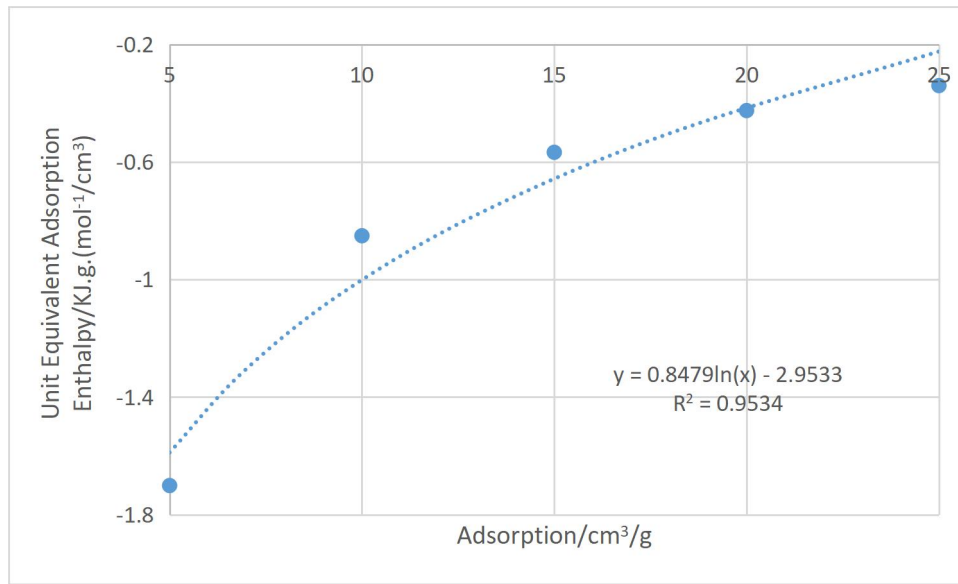
Adsorption/cm <sup>3</sup> ·g <sup>-1</sup>	Gas Coal	Coking Coal	Meagre Coal	Anthracite
5	-1.701	-2.105	-2.937	-2.684
10	-0.851	-1.053	-1.469	-1.342
15	-0.567	-0.702	-0.979	-0.895
20	-0.425	-0.526	-0.734	-0.671
25	-0.340	-0.421	-0.587	-0.537

The data in Table 5 show that the enthalpy per unit adsorption is always negative at different adsorption volumes. That is to say, the adsorption process of methane on coal seam is exothermic whether it is a small amount of adsorption or a large amount of adsorption. At the same time, the absolute value of the adsorption enthalpy decreases with the increase of the adsorption capacity.

(1) The surface of adsorption medium (coal seam cracks and micropore) is not smooth, and the surface energy is not uniform.

(2) Adsorption always takes place at the position of higher energy and higher activity, and then at the position of lower energy and lower activity.

Only logarithmic trend curve fitting is made for the data of long flame coal. Fig. 6 gives the logarithmic fitting equation and fitting error  $R^2$ .



**Fig. 5 Interrelation between unit adsorption enthalpy and adsorption capacity of gas-coal**

The mathematical relationship between unit adsorption enthalpy and adsorption capacity of long flame coal shows logarithmic form.

$$\text{Unit Equivalent Adsorption Enthalpy} = a \ln(\text{Adsorption}) + b \quad (5)$$

The mathematical relationship between the unit adsorption enthalpy and the adsorption capacity of the other three coals shows a logarithmic relationship.

**Table 6 Two parameter values and fitting errors in logarithmic equation of four kinds of coal**

Coal Samples	R <sub>o,max</sub> /%	a	b	R <sup>2</sup>
Gas Coal	0.88	0.8497	-2.953	0.95
Gas Coal	1.44	1.0491	-3.654	0.95
Gas Coal	2.06	1.4639	-5.098	0.95
Gas Coal	3.56	1.3374	-4.6589	0.95

From the data analysis in Table 6, the two parameters in the logarithmic equation of the unit equivalent adsorption enthalpy and adsorption amount of four kinds of coal will change with the change of coal rank. With the increase of coal rank, parameter a increases gradually, and the absolute value of parameter B (because parameter B is negative) also increases gradually.

## 5 Conclusion

(1) For adsorption, the change of molar volume from the initial state to the stop state is negative. According to the indefinite integral formula of Clausius-Clapeyron equation,  $\ln P$  has a negative slope on  $1/T$  straight line, i.e. exothermic process.

(2) Temperature-Pressure-Adsorption Equation (TPAE) can be used to process a series of isothermal adsorption data. When temperature  $T$  and adsorption capacity  $V$  are taken as independent variables and pressure  $P$  as dependent variables, the equivalent adsorption can be studied and the equivalent adsorption enthalpy can be calculated.

(3) Comparing the change of the equal adsorption enthalpy of the same coal sample under several different adsorption volumes, the average equal adsorption enthalpy must be calculated first. The average equivalent adsorption enthalpy decreases with the increase of adsorption capacity, which not only indicates that the surface energy of the adsorption medium is not uniform, but also indicates that the adsorption always takes place at the location of higher energy and higher activity.

(4) On the premise of the same adsorption capacity, the relationship between different coal ranks and the unit adsorption enthalpy can be compared. At the same adsorption capacity, with the increase of coal grade, the absolute value of adsorption enthalpy per unit of equal amount increases, that is, more heat is released.

## Symbolic Description

$A$	—	Microporous geometric shape constants, dimensionless
$B$	—	Adsorption flow coefficient, dimensionless;
$M$	—	The molecular weight of methane is 16.
$\Delta_{\alpha}^{\beta} H_m$	—	Enthalpy, KJ/mol
$P$	—	Adsorption pressure, MPa;

$R$	—	Gas state constant; J/(mol·K)
$R_{o, max}$	—	Maximum reflectance of vitrinite;
$T$	—	Adsorption temperature, K;
$V$	—	Adsorption capacity, cm <sup>3</sup> /g;
$\beta$	—	The parameters affected by pressure are dimensionless.
$\Delta$	—	The energy difference between the lowest potential energy and activation energy of an adsorbed molecule, K;
$\bar{\delta}$	—	Average relative error, 100%

#### Subscript

$g$	—	Gas phase
$l$	—	liquid phase
$m$	—	Mole
$\alpha$	—	Initial state
$\beta$	—	Final state
$o, max$	—	Maximum reflectivity

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