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Research Article

THE ADSORPTION THERMODYNAMICS AND ITS APPLICATION

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Abstract

A series of isothermal adsorption experimental data of Xiayukou#11 coal sample in Shaanxi Hanchengmine is transformed to fit a temperature-pressure-adsorption equation. In 20℃ to 50℃ temperature range, 0.0MPa to 14.0MPa pressure range, 0.0 cm^3/g to 65 cm^3/g adsorbed amounts range, all three kinds of Isobaric Adsorption, Isothermic Adsorption, and Isosteric Adsorption have been created and presented in figures. The Clausius-Clapeyron indefinite integral equation and definite integral equation have been used to illustrate that the gas isosteric adsorption is an exothermic process if the lnP vs 1/T plot of gas adsorption is a straight line with a negative slope, or if $P_2 > P_1$, then $T_2 > T_1$. The phenomenon of unit IAE being decreased with the increasing of adsorption amount indicates that the surface of the coal seam is not smooth, and the energy of the surface is uneven; and adsorption always occurs first at higher energy and more active positions.

Keywords: Clausius-Clapeyron equation; temperature-pressure-adsorption equation; Isobaric Adsorption; IsostericAdsorption; unit IAE.

INTRODUCTION

According to the second law of thermodynamics, there is an equation to describe the relationship of Gibbs function G, entropy S, and enthalpy H. The formula is

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

Since adsorption is a spontaneous process, the Gibbs function change Δ G <0. During the adsorption process, the gas molecules are adsorbed from three-dimensional space to the two-dimensional surface, the degree of freedom is reduced, and the translation of the molecules is limited, so the adsorption process is an entropy reduction process, namely entropy change ΔS<0. Therefore, the only possible outcome is that the enthalpy change ΔH of the adsorption process should be negative, that is, ΔH <0. The released heat of adsorption can be directly measured in the laboratory by a calorimeter. Can the adsorption enthalpy change be calculated from experiments and how? What information can it be revealed from the adsorption enthalpy change? Furthermore, it is well known that the amount of adsorption of solid is a function of temperature and gas pressure, which means that there are three variables (temperature, pressure, and adsorption amount) in any adsorption. In practice, one variable is often fixed, then the relationship between the other two variables is determined, which can be represented by two-dimensional curves. Therefore, three kinds of curves are available by combination, ①Isobaric Adsorption curve, reflecting the relationship between adsorption quantity and temperature at constant pressure;② Isothermic Adsorption curve, reflecting the relationship between adsorption quantity and equilibrium pressureat constant temperature;③ Isosteric Adsorption curve, reflecting the relationship between the equilibrium pressure and the temperature at a constant adsorption amount. All but the Adsorption isotherms are often seen in the papers and books [1-8], the Isobaric Adsorption curves and Isosteric adsorption cavers are rarely seen in the literature.

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This paper just want to use one coal adsorption as an example and to solve those questions.

Isothermal adsorption data and Temperature-Pressure-Adsorption Equation

The isothermal experiments of Xiayukou#11 coal of Shaanxi Hanchengmine has been conducted within the temperature range between 20℃ and 50℃ and pressure range between 0 MPa and 8.0MPa. The data has been treated and reported according to the Langmuir adsorption isothermal equation, and listed in the table 1. The Langmuir equation is presented as:

$$V = \frac{abP}{1+bP} \tag{2}$$

Table 1. Measured conditions of coal samples and Langmuir parameters [1]

20℃		30℃		40℃		50℃	
a	b	a	b	a	b	a	b
63.1	0.62	52.3	0.65	35.8	0.74	26.5	0.77

Since there are three variables (temperature, pressure, and adsorption amount) involved in any adsorption, isothermal experimental data of Xiayukou#11 must be transformed into the Temperature-Pressure-Adsorption Equation (TPAE)[9-14], which is presented as:

$$V = \frac{1}{\sqrt{MT}}\left[A + BP^{\beta}T^{1.5}\exp\left(\frac{\Delta}{T}\right)\right] \tag{3}$$

In Equation (3), looks like Langmuir equation, the adsorption amount V still is the dependent variable, the temperature and pressure are the independent variables. Using the Langmuir parameters in the Table 1 and submitting into Equation (2), it is very easy to calculate the adsorption amount at the specified temperature and certain pressure. There are 14 pressure points for each temperature up to 14.0MPa. Therefore, Xiayukou#11 should have 56 adsorption amount for four testing temperatures. Those 56 adsorption amount are defined as "measured points", and used for the regression to determine the four parameters A, B, Δ and β of TPAE [13]. Table 2 presents these four regressed parameters of Xiayukou#11.

Table 2. Four regressed parameters of Xiayukou#11 coal

A	B	□	□	$\bar{\delta}$/%
0.168	0.0000167	0.2755	2964	6.05

It should be noticed that the TPAE with corresponding four regressed parameters only suitable for specified coal at certain temperature range (20□ to 50□) and certain pressure range (0.0MPa to 14.0MPa).

With the four parameters A, B, Δ and β , TPAE can be used to create a three dimensional curvature surface in the certain temperature range (20□ to 50□) and certain pressure range (up to 14.0MPa). Figure 1 is the "measured points" and Xiayukou#11 surface.

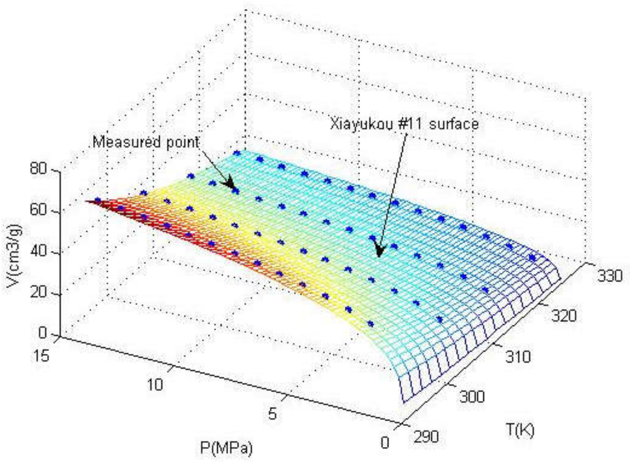

Figure 1. Measured point and TPAE surface of Xiayukou#11 coal of Shaanxi Hanchengmine

At the same time, TPAE can be used to calculate the 56adsorption amount at the exactly the same temperatures and pressures as the Langmuir equation. The corresponding mean relative error $\bar{\delta}$ between the Langmuir equation and the TPAE is then calculated and listed in Table 2 too. From both the figure 1 and the mean relative error $\bar{\delta}$, it is confidently to conclude that the series adsorption isotherms and TPAE can be interconvertible.

The Clausius-Clapeyron equation

The Clapeyron equation is used to describe the equilibrium pressure P and equilibrium temperature T on a two-phase equilibrium of pure matter. For gas adsorption, the indefinite integral of the Clausius-Clapeyron equation is presented as:

$$\ln P = \frac{\Delta_g^l H_m}{R}\frac{1}{T} + C \tag{4}$$

According to the indefinite integral of the Clausius-Clapeyron equation, the ln P vs 1/T plot of gas adsorption should be a straight line with a negative slope. From the slope of the straight line, the mole enthalpy of adsorption can be calculated. The definite integral of the Clausius-Clapeyron equation for gas adsorption is presented as:

$$\ln\frac{P_2}{P_1} = \frac{\Delta_g^l H_m}{R}\left(\frac{T_1 - T_2}{T_1 T_2}\right) \tag{5}$$

Since the mole adsorption enthalpy is negative for an exothermic process, in order to let the definite integral of the Clausius-Clapeyron equation validate for an isosteric adsorption, when $P_2 > P_1$, then $T_2 > T_1$. This is one important conclusion deduced from the definite integral of the Clausius-Clapeyron equation.

Applications

The experimental conditions for Xiayukou#11 coal of Shaanxi Hanchengmine have been defined in 20□ to 50□ temperature range and 0.0MPa to 14.0MPa pressure range. The adsorbed amounts are in the range of 0.0 cm^3/g to 65 cm^3/g. All three kinds of limitation will be forced in the following discussions.

Isobaric Adsorption

Since the isobaric adsorption measures the relationship between adsorption quantity and temperatureat constant pressure, the equation (3) can be used by fixed the pressure P values. After introducing one temperature value, the adsorption amount can be calculated. By repeating this step, the 1MPa, 7.5MPa, and 14MPa isobaric adsorption of Xiayukou#11 coal are generated and presented in Figure 2.

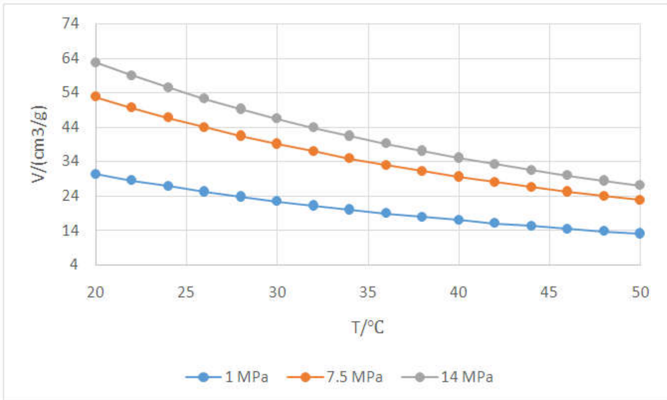

Figure 2. The isobaric adsorption of Xiayukou#11 coal

From the curves in Figure 2, it is easy to see that the adsorption amount decreased with the temperature increasing, which phenomenon proves that the adsorption is exothermic process because of temperature having a negative effect. If a horizontal line was extended at 34 cm^3/g from left to right, this line will meet up the 7.5 MPa isobaric adsorption curve first at temperature about 35□, then meet up the 14 MPa isobaric adsorption curve later at temperature about 42□. This approves the deduction from the definite integral of the Clausius-Clapeyron equation: when $P_2 > P_1$, then $T_2 > T_1$.

Isothermic Adsorption

Since the isothermic adsorption reflects the relationship between adsorption quantity and equilibrium pressureat constant temperature, the equation (3) can be used by fixed the temperature T values. After putting one pressure value, the adsorption amount can be calculated. By repeating this step, the 20□, 35□, and 50□isothermic adsorption curves of Xiayukou#11 coal are produced and presented in Figure 3.

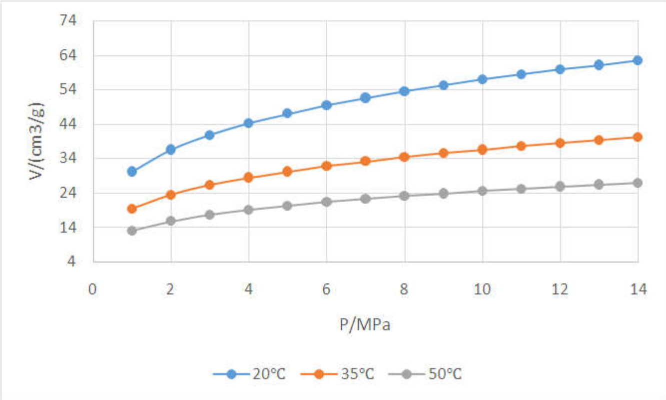

Figure 3. The isothermic adsorption of Xiayukou#11 coal

In Figure 3, if a vertical line was drawn from top to bottom at 6 MPa, it will meet up 20□ isothermic adsorption curve at adsorption amount about 50 cm^3/g first, then will meet up 35□ isothermic adsorption curve at adsorption amount about 32 cm^3/g. It approves that the temperature has a negative effect for an exothermic process. If a horizontal line was extended at 34 cm^3/g from left to right, this line will meet up the 20□ isothermic adsorption line at pressure of 1.5 MPa, then meet up the 35□ isothermic adsorption line at pressure about 8 MPa. This approves the deduction from the definite integral of the Clausius-Clapeyron equation: when $P_2 > P_1$, then $T_2 > T_1$ too.

Isosteric Adsorption

In order to understand the interrelationship between temperature and pressure, TPAE must be changed into the temperature T of adsorption and the adsorption quantity V as the independent variables, and the pressure P as the dependent variable:

$$\ln P = \frac{1}{\beta}\ln\left[\frac{V\sqrt{MT}-A}{BT^{1.5}\exp\left(\frac{\Delta}{T}\right)}\right] \tag{6}$$

The equation (6) can be used by fixed the adsorption amount V values. After putting one temperature value, the pressure can be calculated. By repeating this step, The 10 cm^3/g, 20 cm^3/g, and 30 cm^3/g isosteric adsorption curves of Xiayukou#11 coal are created and presented in Figure 4.

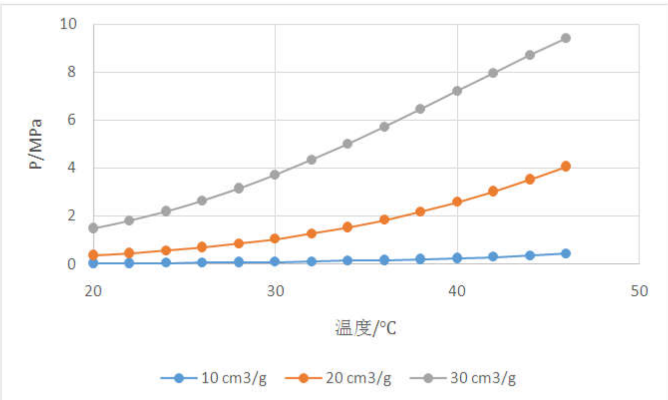

Figure 4. The isosteric adsorption of Xiayukou#11 coal

From the isosteric adsorption curves in Figure 4, it approves directly the deduction from the definite integral of the Clausius-Clapeyron equation: when $P_2 > P_1$, then $T_2 > T_1$.

The another application of adsorption thermodynamics is to calculate the adsorption enthalpy. Based on the equation 6, the lnP vs 1/T plotting of 30cm^3/gisosteric adsorption can be produced and presented in Figure 5.

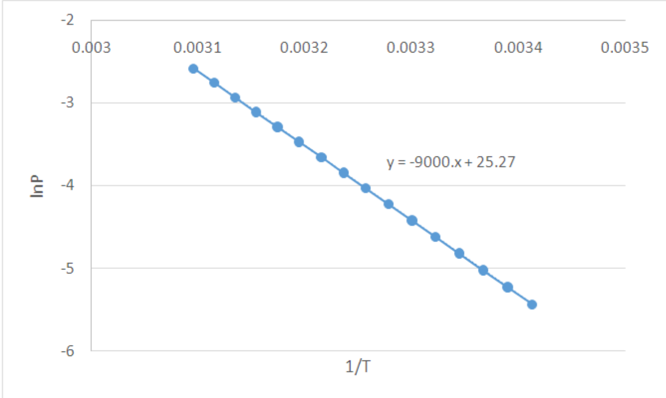

Figure 5. The 30cm^3/gisosteric adsorption lnP vs 1/T plotting of Xiayukou#11 coal

As can be seen from Figure 5, at the adsorption amount of 30.0cm^3/g, the lnP~1 / T forms a straight lines with a negative slope, -9000.6.That is to say, theisostericadsorption enthalpy (IAE) of Xiayukou #11 coal of Shaanxi Hanchengmine is negative.

The IAE and an unit IAE can be obtained as:

- The slope in lnP~1 / T plottimes by the gas constant R=0.008314KJ/ (mol K), results an IAE, KJ/mol;
- The IAE was divided by the isosteric amount (here it is 30.0cm^3/g), an unit IAE would be obtained, KJ mol^{-1} cm^{-3} g. Based on the procedure mentioned above, the IAE and an unit IAE at different adsorption amount can be obtained. Table 3 listed the unit IAE at different adsorption amount.

Table 3. The unit IAE at different adsorption amount of Xiayukou #11 coal

Adsorbed amount	Unit IAE	Adsorbed amount	Unit IAE
cm^3/g	KJ.mol/(cm^3.g)	cm^3/g	KJ.mol/(cm^3.g)
4.0	-18.71	28.0	-2.67
8.0	-9.35	30.0	-2.49
12.0	-6.24	32.0	-2.34
16.0	-4.68	36.0	-2.08
20.0	-3.74	40.0	-1.87
24.0	-3.12	44.0	-1.70

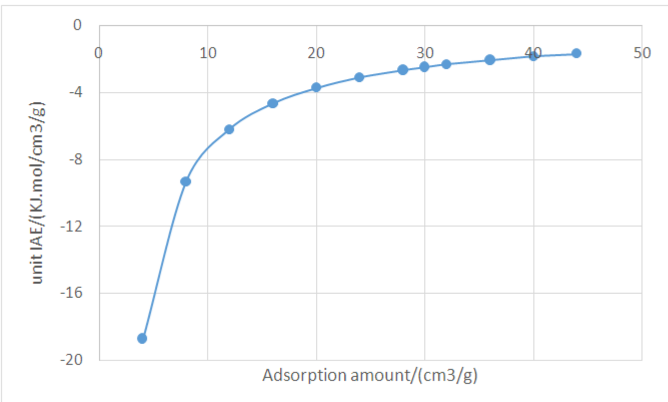

Figure 6. The relationship between unit IAE and the adsorption amount of Xiayukou #11 coal

Meanwhile, the unit IAE decreases with the increasing of adsorption amount. This phenomenon indicates:

The surface of the adsorption medium (coal seam) is not smooth, and the energy of the surface is uneven; and Adsorption always occurs first at higher energy and more active positions, and then in turn at lower energy and less activity.

Conclusion

The isothermal adsorption data of Xiayukou#11 coal of Shaanxi Hanchengmine has been used to regress the parameters of TPAE. It is proved that the series adsorption isotherms and TPAE are interconvertible. Using produced TPAE of Xiayukou#11 coal of Shaanxi Hanchengmine, in 20□ to 50□ temperature range, 0.0MPa to 14.0MPa pressure range, 0.0 cm^3/g to 65 cm^3/g adsorbed amounts range, all three kinds of Isobaric Adsorption curve, Isothermic Adsorption curve, and Isosteric Adsorption curve have been created and presented in figures. The Clausius-Clapeyron indefinite integral equation has been used to illustrate that if the lnP vs 1/T plot of gas adsorption was a straight line with a negative slope, then gas adsorption is an exothermic process. The Clausius-Clapeyron definite integral equation has been used to illustrate if gas adsorption was an exothermic process, for isosteric adsorption, when $P_2 > P_1$, then $T_2 > T_1$. The phenomenon of unit IAE being decreased with the increasing of adsorption amount indicates that the surface of the adsorption medium (coal seam) is not smooth, and the energy of the surface is uneven; and adsorption always occurs first at higher energy and more active positions.

Symbol Description

A	—	Micropore geometry form constant, dimensionless
B	—	Absorption flow coefficient, dimensionless
C	—	Integral constant
G	—	Gibbs function
H	—	Enthalpy
M	—	Adsorbed molecular weight, methane molecular weight is 16
$\Delta_{\alpha}^{\beta} H_m$	—	Enthalpy, KJ/mol
P	—	Adsorption pressure, MPa
R	—	Gas state constant ; J/(mol.K)
S	—	Entropy
T	—	Absorption temperature, K ;
V	—	Adsorption quantity, cm^3/g ;
a	—	Langmuir volume, $cm^3.g^{-1}$
b	—	the reciprocal of the Langmuir pressure, MPa^{-1}
β	—	Parameters of pressure influence, dimensionless
Δ	—	The energy difference between the lowest potential energy and the activation energy of an adsorbed molecule, K
$\bar{\delta}$	—	Average relative error, 100%
superscript, subscript		
g	—	Gas phase
l	—	liquid phase
m	—	Moore
α	—	The initial state
β	—	The final state

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