

The Application of Temperature-Pressure-Adsorption Equation in the Adsorption Thermodynamic of Coal Seam

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To cite this article:

Li Dong, Zhang Xuemei, Hao Jingyuan, Ma Qinghua. The Application of Temperature-Pressure-Adsorption Equation in the Adsorption Thermodynamic of Coal Seam. *American Journal of Chemical Engineering*. Vol. 9, No. 6, 2021, pp. 141-146.

doi: 10.11648/j.ajche.20210906.12

Received: October 28, 2021; Accepted: November 15, 2021; Published: November 23, 2021

Abstract: In order to study the adsorption thermodynamics of coal seam, a series of isothermal adsorption experimental data, in 30°C to 100°C temperature range, 0.0MPa to 32.0MPa pressure range, 0.0 cm³/g to 35 cm³/g adsorbed amounts range, of long flame coal, fat coal, lean coal and meager coal are transformed into the isosteric adsorption data through a temperature-Pressure-Adsorption equation. Both the small percentage values of the relative average error and the agreement between the measured points and the TPAE surfaces have proved the TPAE can accurately represent the series of isothermal adsorption experiments. The enthalpy of the gas adsorption process is calculated by the indefinite integral of Clausius-Clapeyron equation. The concept and calculation method of unit isosteric adsorption enthalpy (IAE) is presented. The adsorption process of the coal is an exothermic process because the lnP vs 1/T plot is a straight line with a negative slope. The phenomenon of unit IAE being decreased with the increasing of adsorption amount indicates that the energy in-homogeneity on the coal surface. Since the adsorption process of the coal is an exothermic process, adsorption always occurs first at higher energy and more active positions in order to release more energy and to make the system more stable. The higher rank coal has a larger unit IAE, and there must be a larger adsorption capacity.

Keywords: Clausius-Clapeyron Equation, Temperature-Pressure-Adsorption Equation, Isosteric Adsorption Enthalpy, Unit IAE, Coal Rank

1. Introduction

The study of adsorption on coal seam or shale surface is very important for determining gas content, evaluating adsorption capacity, and searching a reasonable engineering development scheme [1-5]. The discussion of isosteric enthalpy of adsorption is also an area of concern [6-9] regarding the thermodynamic interaction between the adsorption medium surface and gas. The most commonly used adsorption is series isothermal adsorptions. Those series isothermal adsorption data is reported according to the Langmuir Equation. Therefore, there are some questions about not only how to transform isothermal adsorption into isosteric adsorption, but also how to calculate and use the isosteric adsorption enthalpy IAE. This paper just wants to

answer those questions.

2. 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 according to the second law of thermodynamics:

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

In formula, $\Delta_{\alpha}^{\beta} H_m$ is the mole enthalpy. If the process enthalpy is positive, the process is an endothermic process, and the temperature has a positive effect on the process. If the process enthalpy is negative, the process is an exothermic

process, and the temperature has a negative effect. The subscript m indicates Mole. Subscript α indicates the initial state; superscribe β indicates the final state. All thermodynamic variables (such as volume, enthalpy, entropy.....) of a process are calculated by subtracting the initial state from the final state. The indefinite integral of the Clausius-Clapeyron equation for the adsorption procedure is:

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

In formula, $\Delta_g H_m$ is the mole enthalpy. As described above, subscript g indicates the initial state; superscribe l indicates the final state. The process of matter transforming from initial gas into final liquid is an adsorption process. According to Equation (2), if a straight line could be drawn between $1/T$ and $\ln P$, based on the slop of the straight line, the energy transform direction, temperature effect, and enthalpy amounts, can be arrived. For example, if the straight line had a negative slope, the adsorption process is an exothermic process, and the temperature has a negative effect. Since the temperature increase is disadvantage for the exothermic process, so under the same conditions (adsorption gas, pressure, coal sample), the adsorption amount will decrease with the adsorption temperature increasing.

If the surface position energy of the adsorption medium is in-homogeneous, then the adsorption should first occur at a higher energy (greater activity) position, because more energy can be released, so that the energy between the adsorbent and the adsorbed is lower and more stable.

The amount of adsorption enthalpy can be calculated, which will be illustrated later.

3. Temperature-Pressure-Adsorption Equation

The adsorption amount of solid is the function of both temperature and gas pressure. At constant temperature, the curve reflecting the relationship between the adsorption amount and the equilibrium pressure is called the adsorption isotherm, which is easily experiment conducted in the laboratory. The data of adsorption isotherm is commonly

treated using the Langmuir adsorption isothermal equation. Obviously, the Langmuir adsorption isothermal equation is not convenient to be used in the isosteric adsorption. There must be a bridge to cross the isothermal adsorption and the isosteric adsorption. That bridge is the temperature–pressure–adsorption equation (TPAE). TPAE is three variables (temperature, pressure, and adsorption volume) equation that is designed to study the real (isothermal, isosteric, or isobaric) adsorption [10–17].

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

In Equation (3), the temperature and pressure are the independent variables, and the adsorption amount V is the dependent variable. To understand the interrelationship between temperature and pressure, the temperature T of adsorption and the adsorption quantity V are taken as the independent variables, and the pressure P is the dependent variable as:

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

4. Isothermal Adsorption Data of Coal

Some scholars measured long flame coal of Shanxi Yangquan mine, lean coal of Shanxi Maozequ mine, fat coal of Shanxi Nanyu mine, and meager coal of Shaanxi Xiangshan mine. Those isothermal experiments are conducted with the temperature between 30°C and 100°C and with upper limit pressure of 30MPa. The Langmuir adsorption isothermal equation is presented as:

$$V = \frac{abP}{1+bP} \quad (5)$$

In the formula, a is the Langmuir volume, $\text{cm}^3 \cdot \text{g}^{-1}$, b is the reciprocal of the Langmuir pressure, MPa^{-1} . The units of volume and pressure are the most common units used in the industrial scale. The data of adsorption isotherm of all four coal samples is treated and reported through the Langmuir adsorption isothermal equation, and presented in Table 1.

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

coal	30°C		50°C		70°C		85°C		100°C	
	a	b	a	b	a	b	a	b	a	b
Long flame	15.51	0.1094	13.29	0.0909	9.62	0.0995	10.63	0.0722	9.62	0.069
fat	18.50	0.1942	15.45	0.2169	12.84	0.2146	10.26	0.2415	5.63	0.8065
lean	20.60	0.289	17.25	0.2809	15.12	0.2513	15.41	0.1845	8.13	0.4237
meager	26.89	0.2865	23.10	0.2725	18.58	0.2825	15.15	0.3106	8.13	0.8475

5. Results and Discussion

5.1. TPAE's Parameter Regression

Using the Langmuir parameters in the Table 1 and submitting into Equation (5), the adsorption amount at the

specified temperature and certain pressure is calculated. According to the original author, there were 15 pressure points per temperature up to 30.0MPa. Therefore, each coal sample should have 75 adsorption amount for five testing temperatures. Those 75 adsorption amount points calculated by using the Langmuir parameters are defined as “measured points”, and to be used for the regression to determine the

four parameters A, B, Δ and β of TPAE [16]. Table 2 presents these four regressed parameters of four coal seams. It should be noticed that the TPAE with corresponding four regressed parameters only suitable for specified coal at certain temperature range (30°C to 100°C) and certain pressure range (up to 30.0MPa).

5.2. TPAE's Verification

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 (30°C to 100°C) and certain pressure range (up to 30.0MPa). Figure 1 and Figure 2 are the "measured points" and TPAE surfaces of the four coal seams used.

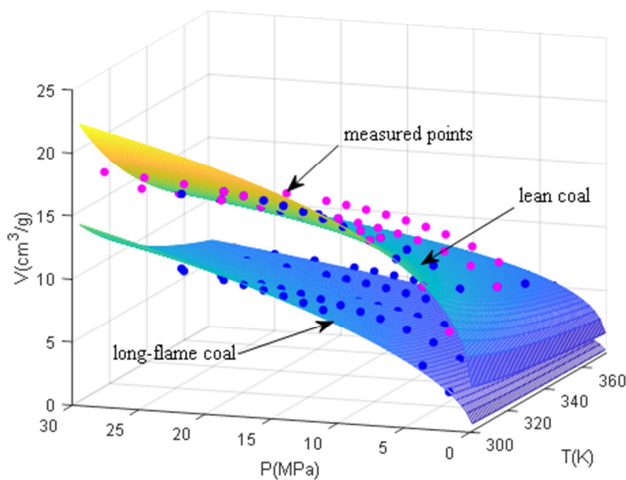


Figure 1. Measured point and TPAE regression surface of lean coal and long-flame coal.

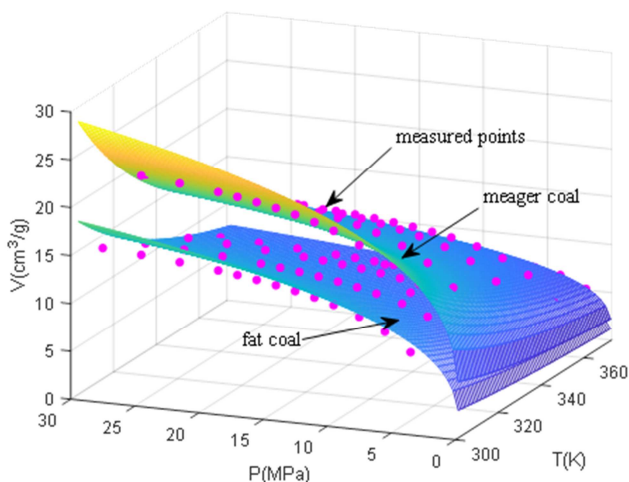


Figure 2. Measured point and TPAE regression surface of fat coal and meager coal.

At the same time, TPAE can be used to calculate the 75 adsorption amount at the exactly the same temperatures and pressures. The values calculated by using the TPAE are defined as "calculated points". The corresponding mean relative error $\bar{\delta}$ between the "measured points" and the "calculated points" is then calculated and listed in Table 2 too.

Table 2. Regressed TPAE parameters based on the Langmuir parameters in Table 1.

coal	Long flame	fat	lean	meager
A	0.168	0.168	0.168	0.168
B	0.00019	0.000298	0.000587	0.000341
β	0.5797	0.3316	0.328	0.2832
Δ	1488	1684	1540	1829
$\bar{\delta}$ /%	5.47	8.60	9.00	9.10

Both the small percentage values of the relative average error listed in Table 2 and the agreement between the measured points and the TPAE surface in Figure 1 and Figure 2 prove the TPAE can accurately represent the series of isothermal adsorption experiments.

5.3. $\ln P$ Drawing with $1/T$

The equation (4) can be used to calculate the isosteric adsorption enthalpy. For example, the adsorption amount is set up as a constant of $5.0\text{cm}^3/\text{g}$, follow the steps of:

1. assumes a thermodynamic temperature T , and substitute into the equation (4);
2. calculate the natural logarithm of adsorption pressure $\ln P$;
3. repeat the above two steps to create a series of the natural logarithm of adsorption pressure $\ln P$ at the corresponding temperature T .

According to the Clausius-Clapeyron Equation (2), the plot of $1/T \sim \ln P$ can be produced. Figure 3 shows the interrelationship between adsorption pressure and adsorption temperature of the four coal at an adsorption amount of $5.0\text{cm}^3/\text{g}$.

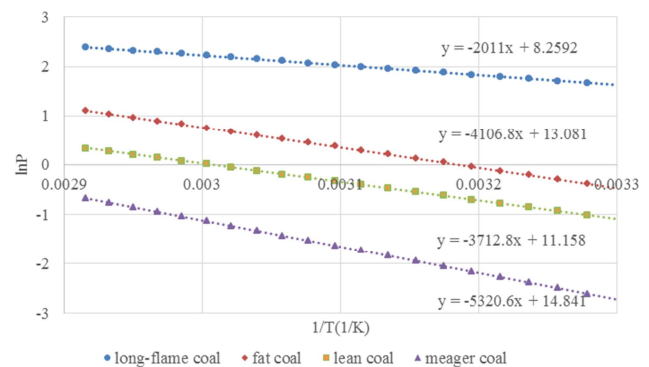


Figure 3. $1/T \sim \ln P$ of the four coal at an adsorption amount of $5.0\text{cm}^3/\text{g}$.

As can be seen from Figure 3, at the adsorption amount of $5.0\text{cm}^3/\text{g}$, the four coal $\ln P$ and $1/T$ map four lines with different negative slopes. That is to say, all isosteric adsorption enthalpy (IAE) of the four coal are negative. In other words, the adsorption is exothermic process. The slopes of the four trend lines for the four coal lines in Figure 3 are listed in Table 3.

Table 3. Slopes of the four coal $\ln P \sim 1/T$ at an adsorption amount of $5.0\text{cm}^3/\text{g}$.

coal	Long flame	fat	lean	meager
slope	-2011	-4107	-3713	-5321

5.4. Isostatic Adsorption Enthalpy IAE

An IAE and an unit IAE can be obtained using the slope in Table 3 as:

The slope in Table 3 time by the gas constant

$R=0.008314\text{KJ}/(\text{mol K})$, results an IAE, KJ/mol;

The IAE was divided by the isosteric amount (here it is $5.0\text{cm}^3/\text{g}$), an unit IAE would be obtained, $\text{KJ mol}^{-1} \text{cm}^{-3} \text{g}$.

The results are listed in Table 4.

Table 4. An unit IAE of the four coal at an adsorption amount of $5.0\text{cm}^3/\text{g}$.

Adsorption amount/ cm^3g^{-1}	an unit IAE/ $\text{KJ}\cdot\text{mol}^{-1}\cdot\text{cm}^{-3}\cdot\text{g}$			
	Meager coal	Lean coal	Fat coal	Long flame coal
5	-8.85	-6.17	-6.83	-3.34

The intensive quantity and the extensive quantity are two basic conceptions that run through chemical thermodynamics. Because the enthalpy is an extensive quantity, both the IAE and the unit IAE must be the extensive quantity. The physical significance of unit IAE in the Table 4 is "the enthalpy per unit amount ($1.0\text{cm}^3/\text{g}$) at an isosteric amount of adsorption $5.0\text{cm}^3/\text{g}$ ". Therefore, the IAE can be used to compare the enthalpy different for different rank of coal at the same adsorption amounts; the unit IAE can be used to compare the enthalpy different for the same coal at the different adsorption

amounts.

Previous studies have shown that at the same temperature and pressure, high rank coal can adsorb more methane than lower rank coal adsorb. According to the data in Table 4, the highest rank coal, meager coal, has the largest unit IAE. Which means the largest amount of heat is released; but the lowest rank coal, long flame coal, has the smallest unit IAE.

Figure 4 shows the relationship between the maximum reflectance ($R_{o,max}$) of the four coal groups and its corresponding unit IAE.

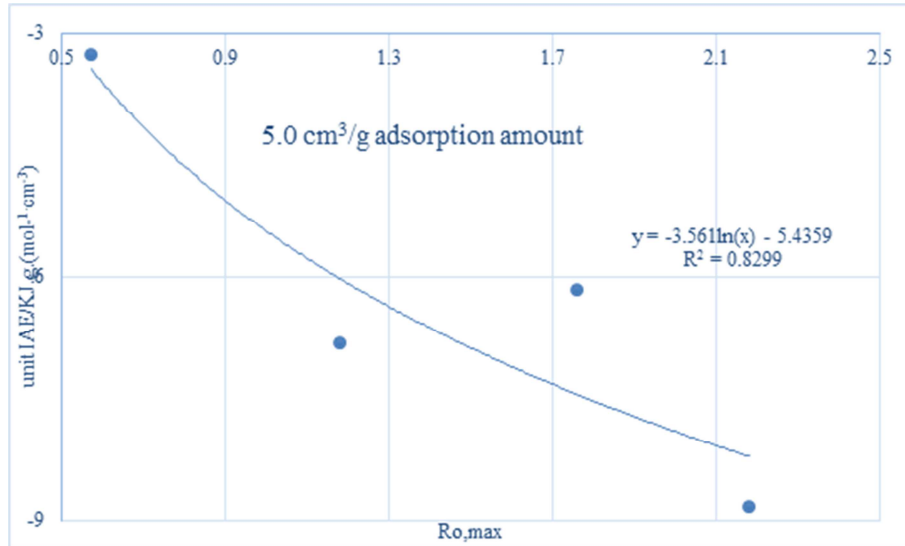


Figure 4. Relationship between the maximum reflectance ($R_{o,max}$) and unit IAE.

5.5. Unit IAE of the Same Coal

The unit IAE of four coal under different adsorption quantities are listed in Table 5.

Table 5. Unit IAE under different adsorption quantities.

Adsorption amount/ cm^3g^{-1}	Meager coal	Lean coal	Fat coal	Long flame coal
5	-8.85	-6.17	-6.83	-3.27
10	-4.42	-3.09	-3.41	-1.63
15	-2.95	-2.06	-2.28	-1.09
20	-2.21	-1.54	-1.71	-0.82
25	-1.77	-1.23	-1.37	-0.65

The data in Table 5 show that the unit IAE of four coal under different adsorption quantities is always negative. That is, whether small amount or large amount, methane adsorbs on the coal layer is an exothermic process. 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.

Figure 5 shows the relationship between unit IAE and the adsorption amount of the long flame coal.

The mathematical relationship between unit IAE and the adsorption amount of the long flame coal shows the logarithmic form as:

$$\text{unit IAE} = c \cdot \ln(\text{adsorption amount}) + d \quad (6)$$

The other three coal species shows the same logarithmic relations. All results are listed in Table 6.

Table 6. Logarithmic parameters of four coal.

coal	$R_{o,max}/\%$	c	d	R^2
meager	2.18	4.4083	-15.356	0.95
lean	1.76	3.0767	-10.717	0.95
fat	1.18	3.4023	-11.851	0.95
Long flame	0.57	1.6295	-5.676	0.95

From the data analysis in Table 6, the two parameter values will vary with the coal rank change. As the coal rank increases, the absolute value of both parameter c and d increase.

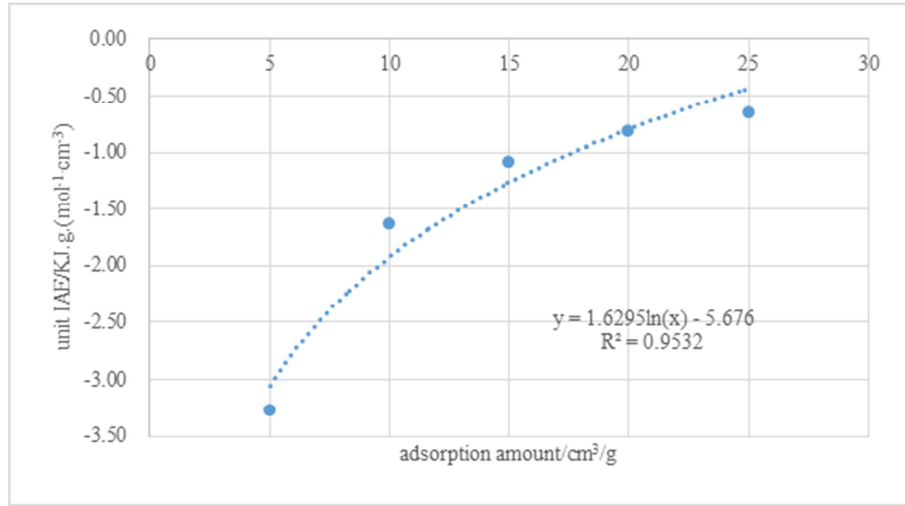


Figure 5. Relationship between unit IAE and the adsorption amount of the long flame coal.

6. Conclusion

According to the indefinite integral of the Clausius-Clapeyron equation, for adsorption, the $\ln P \sim 1/T$ produces a straight line with a negative slope. The negative slope indicates that the adsorption is an exothermic process.

Temperature-Pressure-Adsorption equation (TPAE) can be used to convert a series of isothermal adsorption data into isosteric adsorption data, which can be used to calculate the IAE and unit IAE.

The IAE can be used to compare the enthalpy different for different rank of coal at the same adsorption amounts; the unit IAE can be used to compare the enthalpy different for the same coal at the different adsorption amounts. The unit IAE for the same coal at the different adsorption amounts not only shows that the energy on the surface of the adsorption medium is not homogeneous, but also shows that adsorption always occurs first at positions with higher energy and greater activity.

Under the same adsorption amount, with the rise of the coal rank, the absolute value of the unit IAE increases, that is, more heat is released.

Symbol Description

A	—	Micropore geometry form constant, dimensionless
B	—	Absorption flow coefficient, dimensionless
C	—	Definite integral constant
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)
$R_{o, max}$	—	Maximum reflectivity of Vitrinite;
T	—	Absorption temperature, K;
V	—	Adsorption quantity, cm³/g;
a	—	Langmuir volume, cm³·g⁻¹
b	—	The reciprocal of the Langmuir pressure, MPa⁻¹
c	—	The parameter in Equation 6
d	—	The parameter in Equation 6

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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