The Mathematical Analysis of Temperature-Pressure-Adsorption Data of Deep Shale Gas

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Abstract: Coal is a porous medium and natural adsorbent with well-developed void system. Coal bed gas is usually defined as a hydrocarbon gas, which is adsorbed mainly on the surface of coal matrix particles, free in coal pores or dissolved in coal seam water. The adsorption amount of solid to gas is a function of temperature and gas pressure. Adsorption of gas content in shale is not only an important parameter for shale gas geological reserves and recoverable reserves, but also a key indicator for designing the production process. As the buried depth increases, the temperature and pressure of the reservoir also increase. Therefore, it is necessary to establish an equation to organically link the independent variables and dependent variables such as temperature, pressure, shale, methane adsorption amount to predict adsorptive gas content in shale. Temperature-pressure-adsorption equation (TPAE) has been used to treat the series isothermal adsorption data of 4 kinds of shale rock published by Li Wuguang. In the test temperature and pressure range, TPAE can not only simplify Langmuir parameters, but also picture the quantitative relationship around the temperature-pressure-adsorption. If known TPAE parameters, and the changing temperature and pressure, the partial differential of temperature results in the negative effects of temperature. Furthermore, both the partial differential of pressure and total differential can be exactly calculated. This method using temperature pressure adsorption equation provides a new idea for predicting the adsorption capacity of shale gas. It can make more accurate calculation for shale gas content under variable temperature and pressure.

Keywords: Shale, Temperature Pressure Adsor- Ption Equation (TPAE), Relative Error, Partial Differential of Temperature, Partial Differential of Pressure, Total Differential

1. Introduction

Reservoir forming characteristics of shale gas and coal gas are self generating and self storing. Although the occurrence state of shale gas exists adsorptive state and free state, the adsorptive gas quantity for coalbed rock is about 5 times of shale. Adsorptive gas content in shale is not only an important parameter for shale gas geological reserves and recoverable reserves, but also a key indicator for designing the production process [1-5]. As the buried depth increases, the temperature and pressure of the reservoir also increase. Therefore, it is necessary to establish an equations to organically link the independent variables and dependent variables such as temperature, pressure, shale, methane adsorption amount. The adsorption amount of solid to gas is a function about temperature and gas pressure. In order to find out the objective law easily, among the three dependent variables-adsorption, temperature and pressure, generally one variable is fixed to determine the relationship between the other two variables. This relationship can only be expressed by curves. At constant pressure, the curve that reflects the relationship between the adsorption capacity and temperature is called Adsorption isobar line; at constant adsorption, the curve that reflects the relationship between the equilibrium pressure and the temperature of the adsorption is called the adsorption isometric line; At constant temperature, the curve that reflects the relationship between the adsorption capacity and the equilibrium pressure is called the adsorption isotherm. the consistently used Langmuir equation is the isothermal adsorption equation as known [6, 7].

The form of Langmuir equation is as follows:

$$V = \frac{V_L p}{p_L + P} \qquad (1)$$

In this equation,

V_L is the Langmuir's volumecm^{3}g^{-1};

P_L is the Langmuir's pressure MPa;

P is the pressure MPa;

V is the adsorption capacity cm^{3}g^{-1}.

In the past, a series of isothermal adsorption experiments were used to study coal petrography [8-10], including high temperature at 100°C [11], multiple adsorption [12], adsorption and desorption [13]. The obtained isothermal adsorption data is processed with the Langmuir isothermal adsorption equation. Recently more and more researchers are aware that adsorption at different temperature and pressure is very important for the engineering design of unconventional oil and gas.

2. The Mathematical Form and Verification of the 'Temperature Pressure Adsorption Equation'

2.1. Mathematical Form

Temperature-pressure-adsorption equation TPAE is used [14-20], while the gas molecules adsorb on porous media surface and flow in molecular pore, to solve the influence on gas passing rate caused by adsorption conditions (temperature, pressure and adsorption medium performance).

The equation can be expressed as

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

In the equation,

V is the unit pressure, the gas passing rate on unit area (adsorption amount);

A is a fixed geometric shape constant of microporous porous medium;

B is the adsorption flow coefficient, which is related to the site of the adsorption site;

Δ is the energy difference between the lowest potential energy and the activation energy of an adsorbate molecule in the adsorbate flow;

M is a molecular weight, and the molecular weight of methane is 16;

T is the absolute temperature (Calvin);

P is pressure, such as MPa;

β is a constant in the Freundlich adsorption isotherm equation.

Theoretically, it requires at least two data sets, one is variable temperature and the other is variable pressure, to determine four constants A, B, Δ and β in equation (2).

2.2. Comparison Between TPAE Equation and Langmuir Isothermal Adsorption Equation

(I) The Langmuir isothermal adsorption equation is used

to deal with the data of isothermal adsorption, therefore the effect of temperature is obtained by comparing the size of the Langmuir parameters at different temperatures. In addition to pressure, TPAE also contains temperature as its independent variable. Thus, the influence of temperature can be obtained by partial derivation of temperature. The influence of pressure can be obtained by partial derivation of pressure, and the combined effect of temperature and pressure can be obtained by calculating the total differential of TPAE.

(II) The Langmuir isothermal adsorption equation is used to deal with the data of isothermal adsorption, however, if there are n temperatures, 2n of Langmuir parameters exist which including n Langmuir temperatures and n Langmuir pressures. For the same n temperatures, only 4 parameters are required by using TPAE equation.

(III) The Langmuir isothermal adsorption equation is used to deal with the data of isothermal adsorption, The continuity of the pressure is shown as a curve at the measured temperature. In other words, the continuity of its temperature does not exist. However, TPAE is a continuous surface in the range of temperature and pressure in which can be measured.

3. The Source of Adsorption Experimental Data

The adsorption data were collected from reference [1], including shale core performance and Langmuir adsorption volume and Langmuir pressure at 4 different depths in a shale gas reservoir.

Table 1. Shale Core properties of 4 different depths [1].

Shale sample	TOC/%	R$_0$/%	porosity/%	permeability/ (10^{-3}μm^2)
T-1	3.42	2.71	1.5	0.0065
T-2	1.75	0.94	2.1	0.0037
R-1	2.26	2.01	0.9	0.0025
R-2	2.28	1.45	1.2	0.0026

Table 2. The Langmuir adsorption volume and Langmuir pressure of shale core at 4 different depths and different temperatures [1].

Shale sample	temperature°C	a/(m^3/t)	b/MPa^{-1}
T-1	30	3.36	0.467
	40	3.18	0.472
	50	3.05	0.481
	60	2.92	0.498
T-2	30	2.03	0.302
	40	1.98	0.308
	50	1.94	0.315
	60	1.83	0.324
R-1	30	2.81	0.407
	40	2.73	0.427
	50	2.69	0.442
	60	2.63	0.461
R-2	30	2.62	0.444
	40	2.58	0.457
	50	2.40	0.465
	60	2.39	0.472

According to the adsorption volume of a series of temperature and pressure in Table 2, the TPAE parameters-A, B, Δ, β of the TPAE of 4 different depth shale cores are calculated by nonlinear regression. However, in references [1], only the Langmuir isothermal adsorption parameters of shale series are mentioned. The test temperature and the amount of adsorption under different pressures are calculated with the shale Langmuir parameters published in the literature review, and as 'Langmuir measured values'. From the view of references [1], all shale isothermal adsorption experiments were carried out at 4 different temperatures between 30°C and 60°C. At the same time, the test pressure of each temperature is less than 12 MPa. Thus, each temperature for each shale is calculated from 0.5 MPa to 11 MPa, with a total of 12 pressure points. Each kind of shale has 48 'Langmuir measured values'. The TPAE parameters are obtained by the regression of these 'Langmuir measured values'. The results are listed in Table 3.

Table 3. *TPAE parameters of 4 shale cores with different depths under testing temperature and pressure.*

Shale sample	A	B
T-1	0.05	0.001487
T-2	0.05	0.001137
R-1	0.05	0.001500
R-2	0.05	0.001660
Shale sample	β	Δ
T-1	0.3680	722
T-2	0.4629	560
R-1	0.3895	602
R-2	0.3771	607

4. Results and Discussion

4.1. Verification for TPAE

If 12 pressure points are calculated at each temperature for each shale, each shale has 48 "Langmuir measured values". With the 4 parameters of the homologous shale samples listed in Table 3, The shale adsorption capacity can be calculated under the same 48 "Langmuir measured values" at the same temperature and pressure, which is defined as TPAE's adsorption capacity.

The relative error is defined as:

$$\overline{\delta} = \frac{|V_R - V_C|}{V_R} x100\% \qquad (3)$$

here,

$\overline{\delta}$ is the average relative error;

V_R is the regressed adsorption volume calculating from the Langmuir equation;

V_C is the calculated adsorption volume calculating from the TPAE;

According to the relative error of 4 kinds of shale, TPAE can be verified. The results of these calculations are listed in Table 4.

Table 4. *Relative error of 4 different shale.*

Comparison sample	T-1	T-2	R-1	R-2
Minimum relative error/%	0.40	0.14	0.57	0.25
Maximum relative error/%	18.90	19.40	21.19	20.57
Mean relative error/%	7.70	7.60	7.73	7.74

Though the data from table 4, it can be determined that TPAE is suitable for shale series isothermal adsorption experimental data processing. TPAE is a surface equation which contains two dimensional variables of temperature and pressure. ture 1 shows the visibility of TPAE equation. The surface in Figure 1 is calculated according to the TPAE parameter of T1 shale in Table 3. The points in Figure 1 represent the values calculated according to the Langmuir's volume and the Langmuir's pressure of the T1 shale in Table 2.
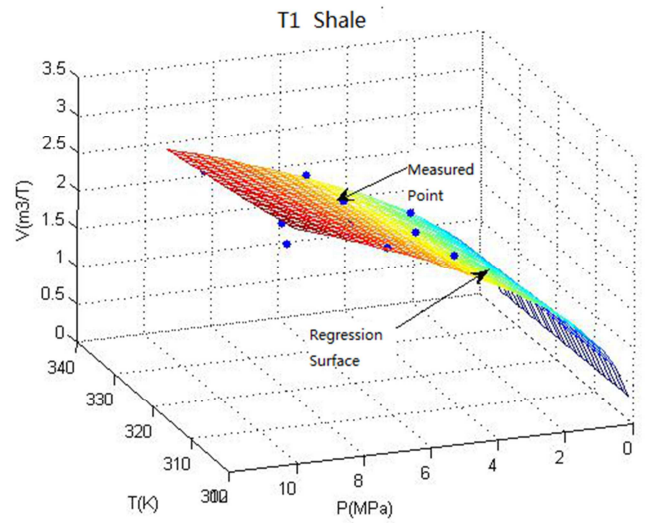

Figure 1. *Visibility of TPAE equation according to the TPAE parameter of T1 shale in Table 3.*

From Figure 1, it is shown that the TPAE surface fits the Langmuir calculated adsorption value, which also shows that TPAE equation is suitable to deal with the experimental data on isothermal adsorption of shale series.

4.2. Partial Derivative and Partial Differential of TPAE

If the A value is relatively small, TPAE (2) can be simplified to:

$$V = \frac{B}{\sqrt{M}} T \exp(\frac{\Delta}{T}) P^{\beta} \qquad (4)$$

(I)   The influence of temperature under constant pressure condition

The equation (4) means that the adsorpted volume still is a function of two variables, T temperature and P pressure. Therefore, it can be operated the derivation as:

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \qquad (5)$$

here:

$\left(\dfrac{\partial V}{\partial P}\right)_T$ is the derivative of V with respect to P, treating T

as a constant, is called the partial derivative with respect to P;

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as a constant, is called the partial derivative with respect to T;

$$(\frac{\partial V}{\partial T})_P = \frac{B}{\sqrt{M}} P^{\beta} \exp(\frac{\Delta}{T})\left(1 - \frac{\Delta}{T}\right) \qquad (6)$$

According to the equation (6), under the condition of constant pressure and variable temperature, the changing direction of adsorption amount $(\dfrac{\partial V}{\partial T})_P$ depends on negative

and positive for $\left(1 - \dfrac{\Delta}{T}\right)$. If $\left(1 - \dfrac{\Delta}{T}\right)$ is less than zero, that is Δ

$>$T, the right side of equation (6) is less than zero, The change of adsorption capacity under isobaric conditions is negatively affected by temperature change. Vice verse.

The 4 kinds of shale involved in this paper, all satisfy $\Delta >$ T, as shown in Figure 2, the temperature derivatives are less than zero.
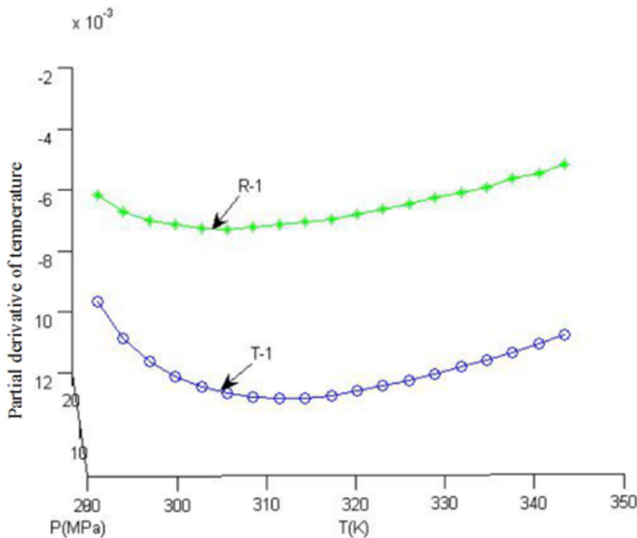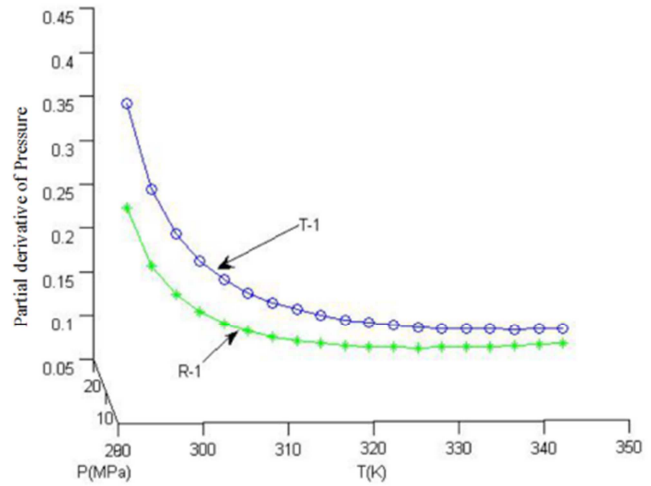

Figure 2. Temperature deviation of T-1 and R-1 shale.

Note that the temperature deviation is less than zero, and there is an extreme value. Comparing the Δ value in Table 3, there exists relatively large Δ value, although the temperature derivative curve changes greatly, but it is below the temperature derivative curve of relatively small Δ value.

(II) The influence of pressure under constant temperature condition

Under isothermal condition, The influence of adsorption capacity on the pressure equals to that equation (4) only partial to the pressure. the result is as followed,

$$(\frac{\partial V}{\partial P})_T = \frac{B}{\sqrt{M}} T \exp(\frac{\Delta}{T})\beta P^{\beta-1} \qquad (7)$$

Because the right side of equation (7) is always positive, not negative, as shown in figure (III)Therefore, under the isothermal condition, the adsorption pressure always have a

positive influence on the adsorption capacity of coal $(\dfrac{\partial V}{\partial P})_T$.

Note: the pressure deviation is greater than zero, and it is monotonous.

Figure 3. Pressure deflector of T-1 and R-1 shale.

Comparing the β value in Table 3 , there exists relatively large β value, although the pressure derivative curve changes greatly, but it is below the temperature derivative curve of relatively small β value.

(III) The common influence of temperature and pressure

Refer to the common influence of temperature and pressure on the adsorption capacity, the equation (4) is mathematically total differential. The equation (8) can be obtained as followed:

$$dV = \frac{B}{\sqrt{M}} T \exp(\frac{\Delta}{T})\beta P^{\beta-1} dP + \frac{B}{\sqrt{M}} P^{\beta} \exp(\frac{\Delta}{T})\left(1 - \frac{\Delta}{T}\right) dT \quad (8)$$

If all the parameters involved in equation (6), (7) and (8) are all known, and the changing amount of temperature and pressure is selected, Then partial derivative of adsorption on temperature, partial derivative of adsorption on pressure, total differential of adsorption capacity on temperature and pressure can be calculated. The equation (5) shows that the influence of pressure still exists when the adsorption capacity is partial to the temperature under constant pressure condition. The influence of pressure on the adsorption capacity does not disappear under constant pressure condition. In the same way, the equation (8) shows that the influence of temperature still exists when the adsorption capacity is partial to pressure under constant temperature condition. The influence of temperature on the adsorption capacity does not disappear under constant temperature condition. Meanwhile, on the surface, adsorption the variable quantity of adsorption capacity in equation (8) is a function of temperature and pressure. Input the actual

temperature gradient and ground pressure gradient obtained from the gas well exploration into the equation, variable quantity of adsorption capacity in equation (8) is a function of buried depth.
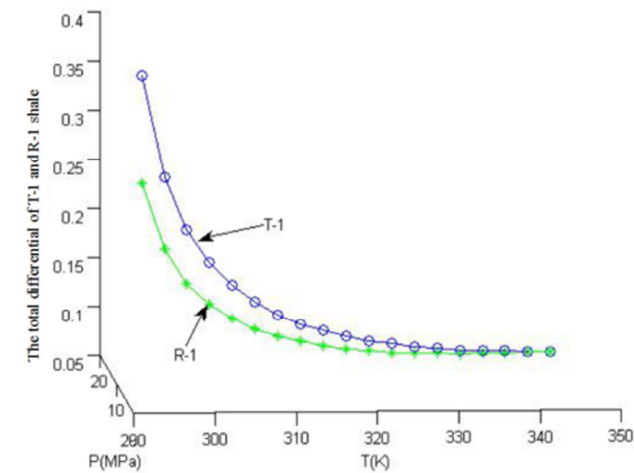

***Figure 4.** The total differential of T-1 and R-1 shale.*

TOC effects

TOC means the total organic carbon. In general, the higher TOC value, the larger adsorption amounts. The four kinds of shale rock properties and their corresponding TPAE parameters are listed in Table 5.

***Table 5.** The four kinds of shale rock properties and their corresponding TPAE parameters.*

	TOC	R_O	B	Δ	β
T-1	3.42	2.71	0.001487	722	0.36795
T-2	1.75	0.94	0.001137	560	0.46293
R-1	2.26	2.01	0.0015	602	0.38953
R-2	2.28	1.45	0.00166	607	0.3771

From the only four sets of data, the relationship between TOC and R_O can be verified on the following figure R_O means the thermal maturity of the sample.
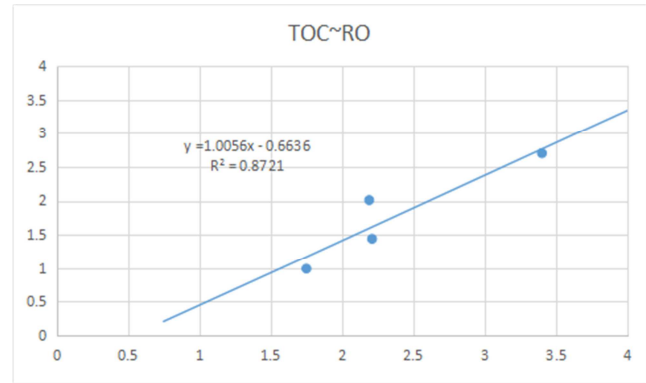

***Figure 5.** The relationship between TOC and R_O.*

If there are good relationship, TOC and R_O are no two independent variables. This pair of variables has one independent variable, but another one is dependent. The higher of TOC, the larger R_O value.

TOC and Δ

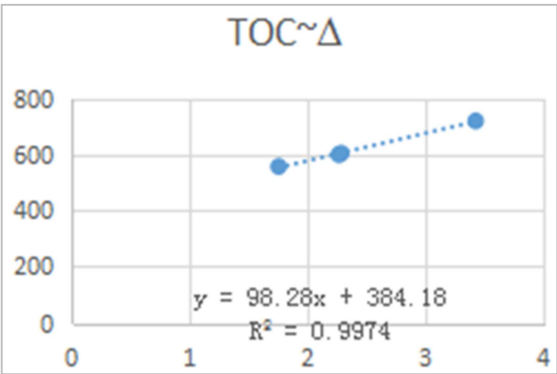Δ is a parameter in the TPAE, which relates to the temperature effects.

***Figure 6.** The relationship between TOC and Δ.*

The higher of TOC, the larger Δ value, the more serious of temperature negative effect.

TOC and β

β is a parameter in the TPAE, which relates to the pressure effect.
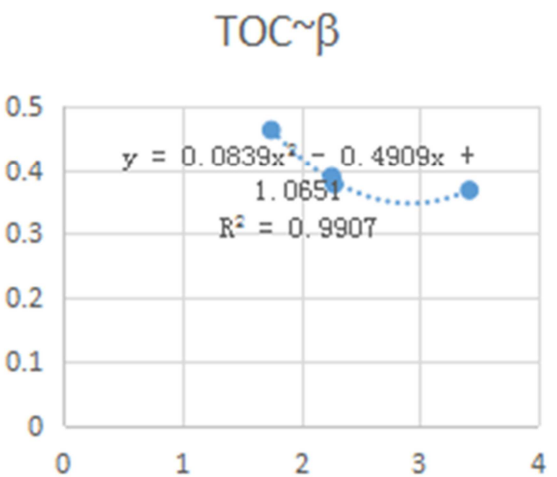

***Figure 7.** The relationship between TOC and β.*

Larger TOC value indicates smaller β value and less serious of pressure positive effect at the same time.

5. Conclusion

TPAE equation can also be used to deal with the series isothermal adsorption experimental data of shale. Within the tested temperature and pressure range, TPAE can simplify each shale's 4 test temperature, 8 Langmuir's parameters to 4 parameters of each shale, and express the quantitative relationship between the three by using the Temperature Pressure Adsorption surface. It can be seen from the relative figure that TPAE surface of the T-1 shale is in good agreement with the adsorption values calculated from the Langmuir volume and the Langmuir pressure. For any kind of shale if TPAE parameters are known and variable quantity of

temperature and pressure is chosen, then partial derivative of adsorption on temperature, partial derivative of adsorption on pressure, total differential of adsorption capacity on temperature and pressure can be calculated accurately.

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Biography

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