

# THE ISOKINETIC EFFECT AS RELATED TO THE ACTIVATION ENERGY FOR THE GASES DIFFUSION IN COAL AT AMBIENT TEMPERATURES

## Part I. Fick's diffusion parameter estimated from kinetic curves

A. Mianowski<sup>1</sup> and Aleksandra Marecka<sup>2\*</sup>

<sup>1</sup>Silesian Technical University, Department of Inorganic Chemistry and Technology, B. Krzywoustego Street 6, 44-100 Gliwice, Poland

<sup>2</sup>AGH – University of Science and Technology, Faculty of Fuels and Energy, Mickiewicza Av. 30, 30-059 Cracow, Poland

The present paper contains theoretical analysis and a thorough discussion of the applicability of Fick's approach to modelling CO<sub>2</sub> and CH<sub>4</sub> diffusion in heterogeneous coal, especially with regard to the estimation of a single diffusion coefficient from the dependence defined by a number series. The computations were performed for high rank coal depending on the grain size of coal samples and within a narrow range of temperature – 293 and 303 K.

The results of the model's application to the experimental data show that the method of estimation of the diffusion coefficient is very important. Our results also show that the diffusion coefficient changes are closely related with the one-parameter analysis of coal grain size distribution.

It was shown that for the investigated grain size distribution the diffusion coefficient as expressed by Fick's law may only be determined as a value which is directly proportional to the diffusion parameter. Hence, the estimation of  $D/r^2$  is recommended.

**Keywords:** coal, diffusion coefficient, Fick's II law, gases, sorption

## Introduction

Gas sorption measurements on coal at ambient temperatures are of great importance both to science and technology. This subject becomes especially interesting with regard to the concept of CO<sub>2</sub> sequestration in underground geological formations, in unmineable coal seams [1–4] among others, and safety considerations (sudden outbursts of methane) [5, 6]. Recent works [7–9] have also shown that, in extreme cases, as a result of oxidation progressing processes of coal seams and coal dumps or these coals used as gas collectors (in the storing process), certain amounts of molecular hydrogen (H<sub>2</sub>) may be emitted.

Many ways of calculating the kinetic parameters for the description of sorption kinetics in porous sorbents, under precisely defined experimental conditions, have been proposed in literature. However, they all involve strong preliminary approximations.

In literature, only limited information concerning the modelling of the sorption kinetics of various gases on coal is available, which is not the case with the activated carbon.

Models based solely on the diffusion model or on the non-Fickian kinetics model (Langmuir type relationship) have been most often used. Nevertheless, they are too complex to be solved for different porous

solid bodies. For this reason, the linear driving forces (LDF) approximation has been applied [10–12]. The disadvantage of the latter approximation is that it can be only used in convenient conditions in which it is valid, i.e. for the near-equilibrium ones (a large diffusion parameter  $D/r^2$  [11]). Generally, the LDF model should be applied carefully for coal sorbents, i.e. for slow processes (low diffusion parameter value).

In the case of activated carbon, it is assumed that the rates of sorption and desorption in a graphitic channel of a given width follow the Langmuir's kinetics (Eqs (3) and (4) in Ref. [13]). The kinetics equation is of the first-order (symbol F1).

In most cases, however, e.g. for ambient temperatures and pressure and in the case of coal, the diffusion model based on Fick's II law is adopted, and some simplifications are introduced in order to determine the diffusion coefficient ( $D$ ) [10, 14–20]. In the study [19], the kinetic constant ( $k$ ) was estimated from the model F2. In the continuation of the studies [19] in the present paper, this problem is discussed in greater detail. However, particular attention is paid to the correctness of the kinetic model F2, because when using simple methods of the parameters estimation basing on Fick's II law, the obtained results are not satisfactory enough. This analysis is recognized as an important consideration for activation energy, discussed in further study.

\* Author for correspondence: marecka@agh.edu.pl

In earlier years, measurements of sorption and diffusion of gases in high rank coal under isothermal-isobaric conditions were initiated. The aim of the present study was to determine Fick's diffusion coefficient ( $D$ ). The study is an attempt to show the final analysis of experiments and a complementary study of a mathematical description of the set of empirical data for the pressure range under examination, in view of the solutions of Fick's law known from the literature.

**Experimental**

*Materials and methods*

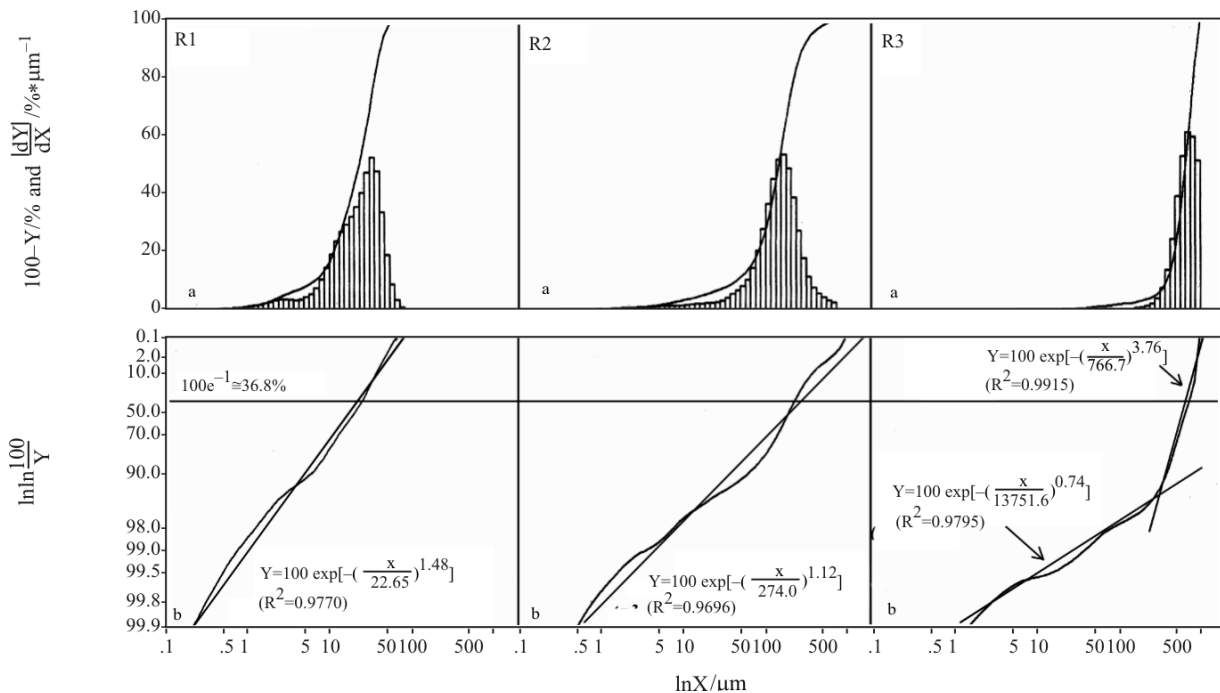
The sorption experiments have been conducted on coal type 42 (anthracite in Polish classification) and index 100B (in international classification) with some characteristics as follows:  $C^{daf}=92.13\%$ ;  $W^a=0.8\%$ ;  $A^d=9.2\%$ ;  $V^{daf}=9.5\%$ . The investigations were carried out in pressures range up to 0.1 MPa. The diffusion of carbon dioxide and of methane was measured using volumetric method.

The samples with four grain sizes, between below 0.032 and 1.5 mm, were selected for further measurements by the conventional grinding method. Coal samples of 100 g were preground using a rotating pulveriser and then ground in a ball mill at the atmospheric pressure and at ambient temperature in air. Particle size is recognized as an important consideration for estimation of the diffusion coefficients. Hence, three grain fractions obtained in the

grinding processes were subjected to grain analysis in Laser-Particle-Sizer (Analysette 22, Fritsch GmbH) which enables to determine the grain size distribution only up to the maximal diameter of grains below 1 mm.

From this analysis the mean diameter has been determined as the arithmetic mean and the harmonic mean, which is directly proportional to the kinetic external surface area ( $S_{kinetic}$ ) of a model system of spheres (of  $1\text{ g cm}^{-3}$  density). A graphic presentation of the grain size distributions R1 to R3 is shown in Fig. 1. The drawn straight lines are the linearization of the grain distributions RRSB [21, 22], and the total results are presented in Table 1. From Fig. 1 it follows that fraction R1 is the most homogeneous when taking into consideration the relation of the coal mass fraction – slope of the RRSB function  $\gamma=1.48$ . However, the narrow fraction R3 (0.49–0.75 mm) contains only 40% of the required size fraction of rather great uniformity ( $\gamma=3.76$ , thus grain size distribution is similar to geometric-arithmetic distribution [23]). The rest of the section is of low uniformity (Fig. 1). This analysis indicates that the real fraction R1 can be described analytically. However, Fig. 1 presents evidence that we are unable to prepare isomorphous grain mixtures for the investigations. Hence, it has been demonstrated that the use of the average granulation parameters is not recommended.

This study is related to the paper [19]. However, the focus is on the practical aspect of the problem of estimating a single rate constant from the dependence described by a number series. Accordingly, the kinetic curves of sorption processes have been analysed



**Fig. 1** Grain size distribution of the examined coals a – cartesian coordinates, b – RRSB distribution function

**Table 1** Characteristics of coal grain size

	Dimension by mechanical separation/mm	Dimension according to laser analysis/mm	Mean radius, r/mm	Mean radius according to laser analysis, r/mm	$S_{BET}^*/m^2 g^{-1}$	$S_{kinetic}$ according to laser analysis/ $cm^2 g^{-1}$
R1	<0.032	85.00% < 0.0337	0.008	0.0105	2.44	0.73
R2	0.10–0.30	60.02% 0.10–0.30	0.1	0.1155	0.24	0.12
R3	0.49–0.75	40.06% 0.49–0.75	0.31	0.3415	0.13	0.03
R4	1.00–1.50	not measured	1.25	not measured	0.11	not measured

\*obtained from low-temperature sorption of krypton [19], expressed in  $m^2 g^{-1}$ , as opposed to the external kinetic surface which is expressed in  $cm^2 g^{-1}$ . Ranges essentially differing between the fractions are rejected

at the temperatures of 293 and 303 K, for two gases and for four grain fractions of coal samples, i.e. 2·3·4=24 experimental data, altogether.

**Calculation technique**

The problem considered in this work is the elaboration of a method of estimating the kinetic parameter for an isomorphous spherical sorbent in accordance with Fick’s II law, starting from the following differential form of the diffusion equation that takes into account the sorption process (Fick’s II law presented in [17, 18]):

$$\frac{\partial c}{\partial \tau} = D \nabla^2 c \tag{1}$$

Depending on the adopted initial and boundary conditions, there are many forms of solving Eq. (1) (e.g. [24–29]). Generally, in the case of a spherical sorbent, a radial diffusion direction towards the grain intrinsic is assumed. Thus, the solution:

$$y = a/a_m = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-n^2 \pi^2 D \tau / r^2}}{n^2} \tag{2}$$

is obtained, in which the diffusion coefficient ( $D$ ) is occasionally assumed to be the effective diffusion coefficient ( $D_{eff}$ ) [17, 18, 30].

The solution of Eq. (1) for short times (very fast processes) is the approximation:

$$y = \frac{6}{r} \sqrt{\frac{D \tau}{\pi}} \tag{3}$$

For  $y > 0.5$ , we apply Eq. (2) for  $n=1$ , and for  $y < 0.25$ , Eq. (3) [15, 19, 24] is applied. As a result, it is possible that the diffusion coefficient may vary in the range of the considered intervals. However, it is also certainly influenced by the rate of the series convergence, and consequently, it depends on the number of terms in a number series.

When trying to define the aim of the study more accurately, one would expect the adaptation of the solution of the Eq. (2) for high rank coal. Finally, the se-

lection of the method of calculating the diffusion coefficient at different temperatures will influence the estimation of activation energy expressed by the analogue of the Arrhenius law.

The application of the solution of Eq. (2) to estimate the diffusion coefficient for coal – gas systems has become a problem. There are some methods which, at certain approximation may be used to simplify the formal difficulties.

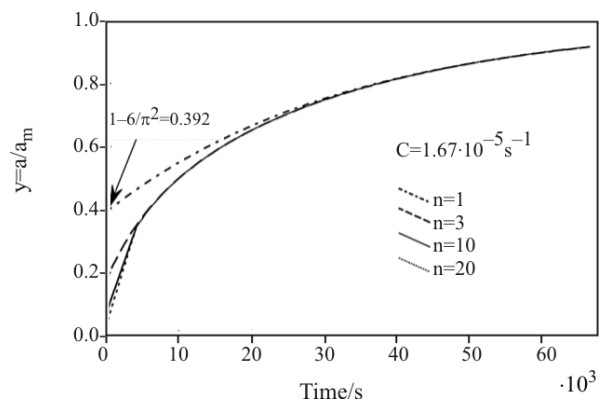
The most important ones are:

- linearization of Eq. (2) for  $n=1$  (first term of the number series) is more accurate only for  $0.86 \leq y \leq 1$  (than  $y > 0.5$ , Fig. 2);
- application of the formula given by Timofiejew [24] for the half-time of the sorption process ( $\tau_{0.5}$ ), i.e. while  $y=0.5$

$$D = 0.308 \frac{r^2}{\pi^2 \tau_{0.5}} \tag{4}$$

- a method frequently used by Ciembroniewicz [20], which relies on the transformation of the relation  $D\tau/r^2$  vs.  $\tau$
- linearization of the relation  $y$  vs.  $\sqrt{\tau}$  for the initial part of the kinetic curve ( $y^2$  vs.  $\tau$  being much better), only for very fast processes (better in form Eq. (3)) [15, 24]

$$y^2 = \frac{36 D \tau}{\pi r^2} \tag{5}$$



**Fig. 2** Simulated progress of the Eq. (2) for varying number of the series terms;  $1 \leq n \leq 20$

- introduction of a new variable to Eq. (2) [30]:

$$K = \frac{\pi^2 D}{r^2} \tau \quad (6)$$

in which the left hand side could be formulated by an algebraic expression containing the fractional uptake  $y=a/a_m$  [30].

### Discussion of the solution of Eq. (2)

In agreement with the trends of formulating the kinetic equations containing time in the first power, for the sake of simplicity we introduce the following denotations into the solution of Eq. (2):

$$t = e^{-\tau}, \text{ for } \tau=0; t=1 \text{ for } \tau=\infty \text{ and } t \rightarrow 0 \quad (7)$$

and

$$C = \frac{\pi^2 D}{r^2} \quad (8)$$

Thus, we obtain:

$$y = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{t^{Cn^2}}{n^2} \quad (9)$$

where  $t$  changes along with the time  $\tau$  in the interval  $1 \leq t \leq 0$ .

It should be noted that the relation between Eqs (6) and (8) is very simple:

$$K = C\tau \quad (10)$$

For  $t=1$  and  $\tau=0$  we get  $y=0$  on the left hand side, whereas on the right hand side we get:

$$0 = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \quad (11)$$

In Eq. (2), the number series is a special case of Riemann's  $\xi$  function for the exponent 2 [19]:

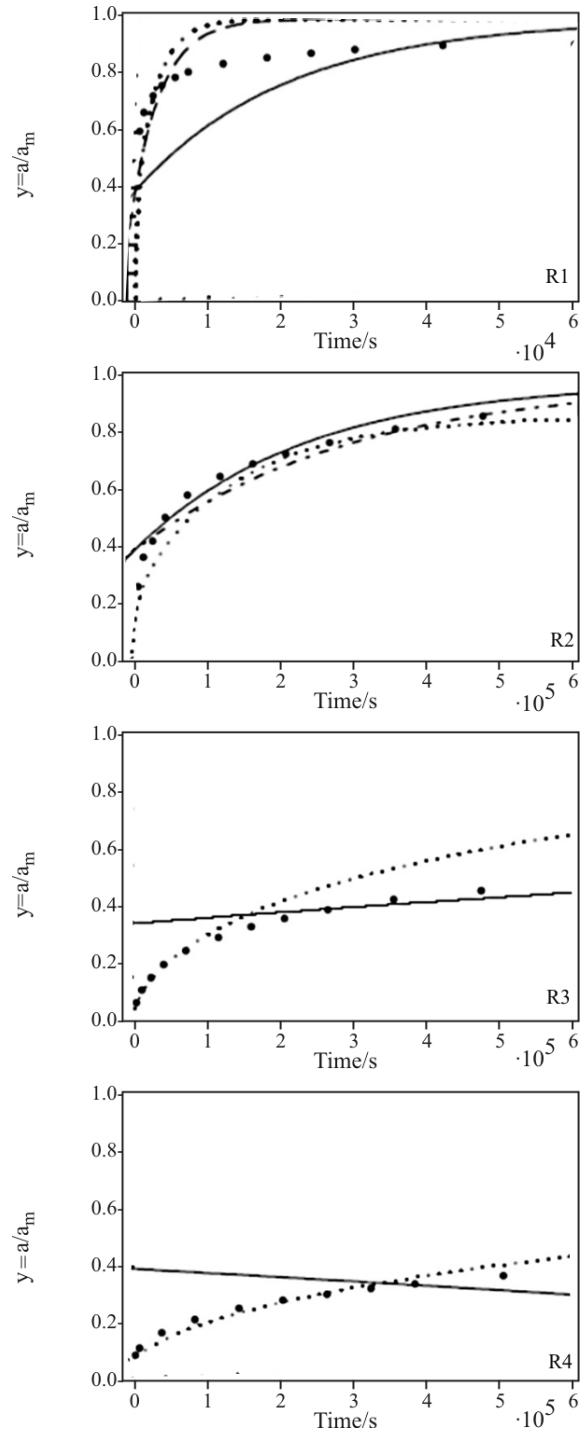
$$\xi(2) = \sum_{n=1}^{\infty} \frac{1}{n^2} = \pi^2/6 = 1.6449 \quad (12)$$

Thus, only in this case in Eq. (2) will there be agreement between the left and the right hand sides of the equation. Otherwise, when stopping the number series (9), e.g. after the first three terms ( $n=3$ ), we obtain the following relation:

$$0 < 1 - \frac{6}{\pi^2} 1.361 = 0.1725 \quad (13)$$

The use of Eq. (2) or Eq. (9) is difficult on account of slow convergence of the number series in the initial measurement range, i.e. for a time close to zero. Figure 2 illustrates the situation under consideration clearly.

An analysis of the problem has shown that the estimation of the complex parameter  $C$  (Eq. (8)) should be realized in parallel, in three ways (Eqs (14) to (16)):



**Fig. 3** The model fitting and the experimental data of  $\text{CH}_4$  sorption kinetics on coal (for four typical cases); ● – experimental; — — linear correlation without an intercept (M. REG.); - - - -  $n=1$  (NON. REG.); ···· -  $n=10$  (NON. REG.)

- the series is stopped at the term  $n=1$ , and linear correlation without an intercept (M. REG.) is applied:

$$-\ln \frac{\pi^2}{6}(1-y) = C\tau \quad (14)$$

- the procedure of non-linear regression (NON. REG.) for  $n=1$  is applied:

$$\frac{\pi^2}{6}(1-y) = e^{-C\tau} \quad (15)$$

- the procedure of non-linear regression for a greater number of terms,  $n \gg \gg 1$ , is applied:

$$\frac{\pi^2}{6}(1-y) = \sum_{n=1}^{\infty} \frac{e^{-n^2 C\tau}}{n^2} \quad (16)$$

For the experimental data set under consideration, it was determined using the trial and error method, that  $n=10$  is sufficient. However, in some cases satisfactory accuracy is obtained even for  $n=3$  or 4.

The three adopted calculation procedures (14)–(16), together with Fig. 3, account for the necessity of such a solution of the problem.

For very fast sorption processes, the experimental data are instantaneously grouped in the neighbourhood of the asymptotic part of the kinetic curve. On the other hand, for slow sorption processes the experimental points are grouped near the initial region of the kinetic curve. In this case, the number of the accepted terms of the series (Eq. 2), which is convergent at the initial stage of the progress of the sorption process, becomes very important.

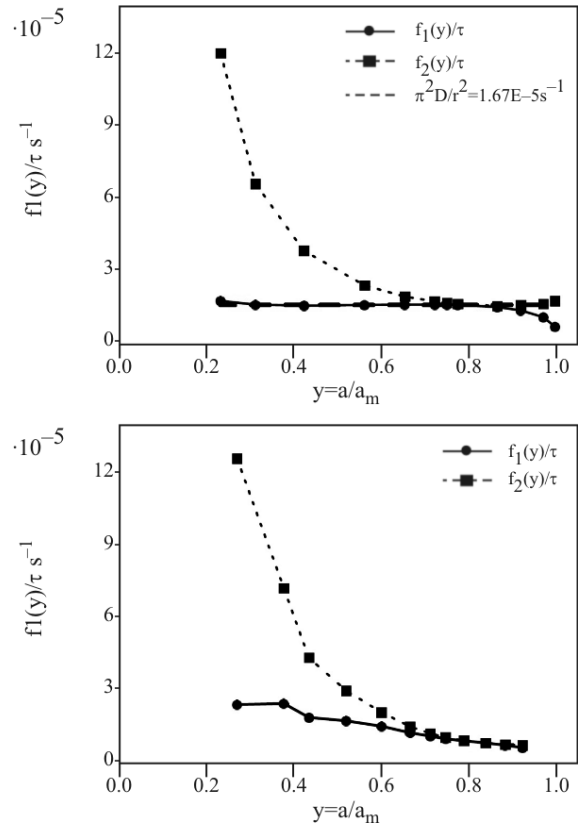
*Comparison with another simplified method*

Another mathematical approach, which adapts the algorithm found in the study [30], and is explained in the greater detail below may be used to provide additional evidence that a mathematical description of coal–gas systems using Fick’s II law is very difficult. This approach is based on Eq. (2), in a form that guarantees minimal error of estimation with minimal values of the target function as a measure of the quality of fitting the experimental data. Finally, for Eq. (8) we obtain:

$$C\tau = \frac{\pi^2 D}{r^2} \tau = 0.286 \cdot 8.151^y \cdot y^{1.453} \quad 0.0025 \leq y \leq 0.8 \quad (17)$$

$$C\tau = \frac{\pi^2 D}{r^2} \tau = \frac{0.285 - 0.284y}{1 - 1.927y + 0.927y^2} \quad 0.8 \leq y \leq 0.9 \quad (18)$$

Equations (17) and (18) are used in the following way: the right hand sides of both equations, which depend only on  $y = a/a_m$ , are calculated and the obtained values are divided by the time, with  $\tau \neq 0$ . The ob-



**Fig. 4** Graphical interpretation of formulae (17) and (18), a – model prediction, b – experimental data in the system: coal (R2) – CH<sub>4</sub> at T=303 K;  $f_1(y)$  and  $f_2(y)$  – right hand sides of Eq. (17) or Eq. (18)

tained values are then plotted vs.  $y$  in the adopted relevance interval. In the case when Eq. (2) is satisfied, we can separate straight lines, parallel to the coordinate axis  $y$ , for the value  $C = \pi^2 D/r^2 = \text{constant}$ .

Figure 4a presents as an example the respective dependence for  $C = \pi^2 D/r^2 = 1.67 \cdot 10^{-5} \text{ s}^{-1}$  (see Fig. 2). Figure 4b shows those results of our study which can be regarded as the closest to the model. This figure confirms the earlier observations that it is not possible to describe the kinetic curve by Eq. (2) in the whole range of the measured times.

**Results and discussion**

Taking into consideration the results of the kinetic analysis, it should be noted that only the single parameter ( $C$ ) was estimated by means of the three dependences. Equations (14) and (15) may be recognized as theoretically equivalent, whereas the formulae (15) and (16) may not be recognized as such. The parameter ( $C$ ) determined from Eq. (14) was introduced as an initial parameter in the non-linear regression (NON REG.), i.e. in Eq. (15), and the parameter determined from Eq. (15) was then put into Eq. (16).

**Table 2** Estimated values of the parameter  $C$  for gases sorption on coal ( $T=293$  K)

	$-\ln \frac{\pi^2}{6}(1-y)=C\tau$				$\frac{\pi^2}{6}(1-y)=e^{-C\tau}$			$\frac{\pi^2}{6}(1-y)=\sum_{n=1}^{n=10} \frac{e^{-n^2 C\tau}}{n^2}$		
	$C \cdot 10^5 / s^{-1}$	$R^2_0$	$F$	<i>s.l.</i>	$C \cdot 10^5 / s^{-1}$	$R^2$	ratio	$C \cdot 10^5 / s^{-1}$	$R^2$	ratio
carbon dioxide										
R1	45.35	0.7116	59.22	0.0 <sup>(5)</sup>	281.05	0.7283	341.37	362.23	0.5133	179.93
R2	5.68	0.9263	301.68	0.0 <sup>(5)</sup>	6.29	0.7619	571.95	11.91	0.6194	348.83
R3	1.31	0.8920	198.25	0.0 <sup>(5)</sup>	1.28	0.6961	485.04	1.55	0.9730	5714.98
R4	0.17	0.3859	15.08	0.001	0.15	0.1782	570.88	0.25	0.9476	9311.34
methane										
R1	2.39	0.794	42.44	0.0001	8.15	0.207	67.71	12.47	0	41.36
R2	0.29	0.942	178.65	0.0 <sup>(4)</sup>	0.30	0.818	64.82	0.48	0.891	115.99
R3	0.02	0.035	0.40	0.1330		not determined		0.15	0	14.81
R4	-0.06	0.117	2.90	0.1024		not determined		0.06	0	11.28

*s.l.* – significance level, e.g. 0.0<sup>(4)</sup>=0.0000

The kinetics data in Table 2 indicate that the values of the determined constant ( $C$ ) depend on the accepted calculation technique, including the impossibility of its determination. It is also surprising that the probability variation of the determined constant on the significance level (in statistical symbols) ranges from 0.0<sup>(4)</sup> to a practically zero level. The relationships obtained for carbon dioxide are more adequate than those obtained for methane. In the case of CH<sub>4</sub> and the specific surface area R4 –  $S_{BET}=0.11$  m<sup>2</sup> g<sup>-1</sup>, the result was absurd (for the Eq. (14)).

This occurred regardless of whether the applied temperature was 293 or 303 K.

According to predictions and literature, Eq. (14) offers a better description of the final part of the kinetic curve. The obtained results cannot be used to describe the kinetic curve in its initial range, since there

is disagreement between the initial parameters, which follows from the fact that for  $\tau=0$  and  $n=1$  (Fig. 2):

$$y=1-\frac{6}{\pi^2} \cong 0.392 > 0 \quad (19)$$

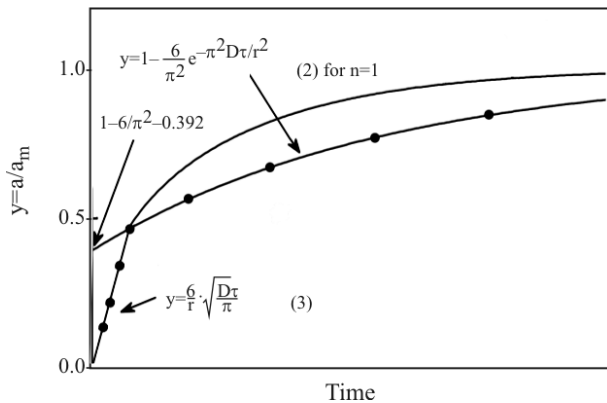
Consequently, the initial range, which is better described by Eq. (16), and occasionally by Eq. (15), cannot be used for estimation, as it does not yield any solutions.

A hypothesis can be suggested that the complex kinetic parameter ( $C$ ) (Eq. (8)), which is directly proportional to the diffusion coefficient ( $D$ ), for the examined system: coal (type 42) – CO<sub>2</sub> and CH<sub>4</sub>, varies with the progress of the sorption process, i.e. it becomes reduced. This decrease may be continuous or stepwise, the latter being true for the finest grain size (R1 –  $S_{BET}=2.44$  m<sup>2</sup> g<sup>-1</sup>). The changes observed for carbon dioxide (Table 2), on the other hand, are continuous.

As it is easy to demonstrate, the present study belongs to the category of chemometric analyses, applied to kinetic experimental data. As follows from the data in Table 2, some cases belong to the range of problems for which the determination coefficient:

$$R^2 \cong 0 \quad (20)$$

but, nevertheless, the objective of the study, i.e. the estimation of Fick's diffusion coefficient is attained.



**Fig. 5** Comparison experimental and predicted data for the imposed number of terms of the number series; ● – experimental

### Conclusions

- The kinetics data in Table 2 present the final results of the estimation procedures, indicating essential

differences in the values of parameter  $C$ , determined from Eq. (8), whereas Fig. 3, shows an example of the physical interpretation of the obtained results. For a large specific surface area (for  $R1 - S_{\text{BET}} = 2.44 \text{ m}^2 \text{ g}^{-1}$ ), the initial sorption range of experimental data enables the determination of the classic diffusion coefficient from Fick's II law (Eqs (15) and (16)), and this parameter then undergoes variation, i.e. it diminishes and at that point may be estimated from Fick's simplified law, stopping the series (2) at the first term ( $n=1$ , in Eq. (9) with the limiting conditions (7)).

- As the specific surface area,  $S_{\text{BET}}$ , approaches to zero, very distinct differences resulting from the mathematical form adopted for the estimation of the complex constant (parameter  $C$ ), may be observed, leading even to absurd solutions ( $C < 0$ ).
- The course of the kinetic curve, shown in Fig. 5, indicates a stepwise decrease of the diffusion coefficient, and, accordingly, the applied relation given in [25] can be presented as the inequality:

$$D_{\text{short times}} \neq D_{\text{long times}}$$

The results of this study confirm the existence of a strong relation between Fick's second law and the kinetic model F2 proposed in the study [19].

- Finally, the selection of the method of calculating the diffusion coefficient at two temperatures is recommended for the analysis of activation energy expressed by analogue of the Arrhenius law.

In our calculation procedure, the estimation of the diffusion coefficient  $D$  is neglected. This problem has been formulated in view of the necessity of analyzing the constant  $C$ , because for such materials as coal we cannot provide an evaluation of one-parameter analysis of the coal grain size distribution. Thus, the mentioned law will formally refer to a complex expression containing the diffusion parameter  $D/r^2$  (with dimension  $\text{s}^{-1}$ ), and may consequently be expressed as Eq. (8). Hence, in case of a more complicated problem of one-parameter distribution, even for the narrow fraction R3, it is better to use the constant  $C = \pi^2 D/r^2$ . In the final evaluations the interrelation of the kinetic-diffusion parameters was taken into consideration.

## Nomenclature

$a$	Amount adsorbed after time $\tau$ , $\text{mmol g}^{-1}$
$a_m$	Maximal amount adsorbed at equilibrium state, $\text{mmol g}^{-1}$
$A^d$	Ash content, mass% dry coal
$c$	Concentration of sorbate in non-adsorbed state, $\text{mmol cm}^{-3}$
$C$	Complex kinetic parameter in Eq. (8), $\text{s}^{-1}$

$C^{\text{daf}}$	Carbon content, mass% daf
$D$	Fickian diffusivity, $\text{cm}^2 \text{ s}^{-1}$
$D_{\text{eff}}$	Effective diffusion coefficient, $\text{cm}^2 \text{ s}^{-1}$
$f_1(y), f_2(y)$	Right hand sides of Eq. (17) or Eq. (18), Fig. 4
F	Statistical test
F1, F2	Mechanism symbol according to first and second kinetic order, respectively
$K$	Complex variable introduced in Ref. [30]
M. REG.	Multiple regression
$n$	Integer, $n \geq 1$ , number of terms of the series (2)
NON. REG.	Non-linear regression
ratio	Correlation ratio in procedure of non-linear regression, analogue of F test
$r$	Grain radius, cm
$R^2$	Determination coefficient, $0 \leq R^2 \leq 1$
$R_0^2$	Determination coefficient for one parameter straight line (without intercept in the equation), $0 \leq R_0^2 \leq 1$
RRSB	Rosin-Rammer-Benett-Sperling function of grains size distribution
$t$	Additional variable in Eq. (7)
$T$	Absolute temperature, K
s.l.	Significance level
$S_{\text{BET}}$	Specific surface area, $\text{m}^2 \text{ g}^{-1}$
$S_{\text{kinetic}}$	External surface area, $\text{cm}^2 \text{ g}^{-1}$
$V^{\text{daf}}$	Volatile matter, mass% daf
$W^a$	Moisture, mass% analytical
$y = a/a_m$	Fractional uptake, $0 \leq y \leq 1$
$Y$	part by mass of grains larger than size $X/\mu \text{ m}$ , %, Fig. 1

## Subscripts

$a$	Analytical state
$d$	Dry coal basis
$\text{daf}$	Dry ash-free

## Greek symbols

$\gamma$	Slope of the RRSB function in linear form (i.e. in the functional scales)
$\tau$	Time, s
$\tau_{0.5}$	Half-time of the sorption process for $y=0.5$ , s
$\nabla^2$	Laplacian for $x, y, z$ coordinates, $\left( \frac{\partial^2 c}{\partial x^2}; \frac{\partial^2 c}{\partial y^2}; \frac{\partial^2 c}{\partial z^2} \right)$

## References

- 1 S. Holloway, Energy Convers. Mgmt., 38 (1997) S193.
- 2 P. Freund and W. G. Ormerod, Energy Convers. Mgmt., 38 (1997) S199.
- 3 A. Marecka, Konferencja Naukowo-Techniczna 'Koksownictwo 2005' SITPH, Polanica-Zdrój, (2005) (in Polish).
- 4 F. X. Han, J. S. Lindner and C. Wang, Naturwissenschaften, 94 (2007) 170.
- 5 T. C. Ruppel, C. T. Grein and D. Bienstock, Fuel, 51 (1972) 297.

- 6 A. Marecka, Materiały Seminarium 'Węgiel kamienny-własności, akumulacja, uwalnianie i pozyskiwanie gazów kopalnianych', Cracow 1994, p. 17 (in Polish).
- 7 S. L. Grossman, I. Wegener, W. Wanzl, S. Davidi and H. Cohen, *Fuel*, 73 (1994) 762.
- 8 S. L. Grossman, S. Davidi and H. Cohen, *Fuel*, 74 (1995) 1772.
- 9 S. Czajkowska, A. Marzec and A. Mianowski, *Karbo*, (2004) 122 (in Polish).
- 10 J. Cranck, *The Mathematics of Diffusion*, Clarendon Press, Oxford 1975.
- 11 M. L. Sykes, H. K. Chagger and K. M. Thomas, Proc. of the Conf. on Carbon 92, Deutsche Keramische Gesellschaft, Essen, Germany 1992, p. 263.
- 12 T. A. Braymer, C. G. Coe, T. S. Farris, T. R. Gaffney, J. M. Schork and J. N. Armor, *Carbon*, 32 (1994) 445.
- 13 D. D. Do and K. A. Wang, *Carbon*, 36 (1998) 1539.
- 14 J. Cranck and G. S. Park, *Trans. Faraday Soc.*, 45 (1949) 240.
- 15 R. M. Barrer in R. F. Gould, *Intracrystalline diffusion*, American Chemical Society, Washington DC 1971.
- 16 D. M. Smith and F. L. Williams, *Soc. Petrol Engng. J.*, 63 (1984) 529.
- 17 A. Ciembroniewicz and A. Marecka, *Arch. Min. Sci.*, 37 (1992) 99.
- 18 A. Ciembroniewicz and A. Marecka, *Fuel*, 72 (1993) 405.
- 19 A. Marecka A and A. Mianowski, *Fuel*, 77 (1998) 1691.
- 20 A. Ciembroniewicz, *Zeszyty Naukowe AGH*, 1499, Cracow 1993, (in Polish) and references therein.
- 21 A. Mianowski, *Int. J. Miner. Process.*, 24 (1988) 11.
- 22 J. Pysiak, *J. Thermal Anal.*, 43 (1995) 9.
- 23 A. Mianowski, *Problematyka przygotowania wsadu węglowego w produkcji koksu wielkopiecowego*, Z. N. Pol. Śl., 886 (Chemia 115) Gliwice 1986 (in Polish).
- 24 D. P. Timofiejew, *Kinetika adsorpcji*, Ed. Izd. AN. SSSR, Moscow 1962, (in Russian).
- 25 Z. J. Grzywina and A. M. Simon, *Pol. J. Chem.*, 68 (1994) 831.
- 26 T. Ozawa, *J. Thermal Anal.*, 5 (1973) 563.
- 27 T. Ozawa, *J. Thermal Anal.*, 31 (1986) 547.
- 28 T. Schwarz, G. Steiner and J. Koppelman, *J. Thermal Anal.*, 35 (1989) 481.
- 29 P. Staszczuk, M. Płando-Czyż, M. Błachnio and V. V. Kutarov, *J. Therm. Anal. Cal.*, 86 (2006) 261.
- 30 A. P. Terzyk and P. A. Gauden, *Sep. Sci. Technol.*, 36 (2001) 513.

---

Received: February 14, 2008

Accepted: May 29, 2008

OnlineFirst: October 12, 2008

---

DOI: 10.1007/s10973-008-9058-3