Journal of Thermal Analysis, Vol. 31 (1986) 805–812

KINETICS OF EVOLUTION OF INDIVIDUAL GASES IN THE COURSE OF SHALE THERMAL DECOMPOSITION

II. Kinetic parameters

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(Received July 2, 1985)

Kinetic parameters describing the evolution of C_nH_m, CH_4, CO and H_2 in the course of shale thermal decomposition were calculated by the Allakhverdov–Nirsha method allowing for sum of square difference behaviour in the kinetic parameters. The mean kinetic parameters were determined for each gas according to the parameters which were determined for the different seams of commercial deposits. The calculated results agreed well with the experiments.

In part I of this series [1], experimental data on the thermal decomposition of shale were presented. In this article we concentrate mainly on determination of the kinetic constants of the investigated processes.

Numerous kinetic equations have been suggested for the description of experimental kinetic curves. However, it has been clearly shown in a number of works (e.g. [2–4]) that all the kinetic parameters are formal and that this situation can not be improved by mathematical operations. Thus, the criterion for the choice of the kinetic equation is not so much the physical and chemical sense of the equation as the convenience of its application to describe the experimental data.

The Erofeev equation (also sometimes called the Erofeev–Avrami equation [5] and the usual three-parameter equation) (based on the Arrhenius model) can be applied best to describe the experimental data. True, the Erofeev equation is usually used to describe isothermal processes. We have shown both experimentally and theoretically [6, 7] that the kinetic parameters of this equation depend on the temperature under non-isothermal conditions. Thus, it becomes unsuitable for use, and accordingly in the present work the data were evaluated with the Arrhenius model:

$$\frac{d\alpha}{dt} = K_0 \exp(-E/RT)(I-\alpha)^n \qquad (1)$$

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where α is the fraction reacted; t is time; T is temperature; R is the molar gas constant; K_0 is the preexponential factor; E is the activation energy; and n is the reaction order.

The process of evolution of each gas was considered as one chemical reaction and the kinetic parameters were determined for it. Thus, the reactions which gave the small peak at $T \approx 775$ K in the course of H_2 evolution and the peak at $T \approx 730$ K in the course of CH_4 evolution were not considered separately. It was also assumed that the kinetic parameters n, E and K_0 did not depend on temperature. Such an assumption is correct in the sufficiently wide temperature range of ~500 K [8].

Results and discussion

A number of methods permit the determination of the kinetic parameters of Eq. (1), with different degrees of accuracy [9, 10]. From our point of view, one of the most interesting of them at present is the Allakhverdov–Nirsha method [11]. This can be considered, in a sense, as a successful modification of the well-known Doyle method [12]. It seems to us that it is necessary to dwell briefly upon the method of calculations and the changes which we made.

The reaction order n was determined from the equation

$$(1-\alpha_m)y = n^{\frac{1}{1-n}} \tag{2}$$

Activation energy was determined from Eq. (3):

$$E = nR\vartheta \tag{3}$$

where

$$\vartheta = \frac{T_m^2\left(\frac{d\alpha}{dT}\right)_m}{1-\alpha_m} \tag{4}$$

The index m means that the corresponding variable was taken at the moment of the reaction rate maximum. It was supposed in the first step that $y = 1$, and the reaction order and activation energy were determined from (2)–(4). In the second and following steps of the calculation y was calculated from Eq. (5):

$$y = \sum_{i=1}^{\infty} (-1)^{i-1}(i!)\chi^{i-1} \tag{5}$$

where

$$x = \frac{RT_m}{E} \tag{6}$$

E and n were calculated *for every y*. The calculations ended when $|n_j - n_{j-1}| \leqslant 10^{-4}$, where j is the calculation step.

Next were determined

$$K_m = \left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_m \cdot q \cdot (1-\alpha)^{-1} \tag{7}$$

and

$$K_0 = \frac{K_m}{\exp\left(-\dfrac{E}{RT_m}\right)} \tag{8}$$

where $q = \dfrac{\mathrm{d}T}{\mathrm{d}t}$ is the heating rate.

It can be seen that the main idea of this method is to calculate the kinetic constants using one point, the reaction rate maximum, and three experimental values connected with this point: T_m, α_m and $\left(\dfrac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_m$. The heating rate q was considered as an experimental condition. This method is good and does not need a long computation time. However, it gives a good result only if the experimental values of T_m, α_m and $\left(\dfrac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_m$ are determined very accurately. Using this method, we found that the difference between two curves $\alpha_e(T)$ and $\alpha_c(T)$ was sometimes rather large (here $\alpha_e(T)$ is the experimental curve, and $\alpha_c(T)$ is the calculated curve). This induced us to consider the influence of the errors in the experimental values of T_m, α_m and $\left(\dfrac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_m$ on the kinetic calculation results. The difference between $\alpha_e(T)$ and $\alpha_c(T)$ was described by the sum of square differences

$$S^2 = \frac{1}{N-1}\sum_{l=1}^{N} [\alpha_e(T_l) - \alpha_c(T_l)]^2$$

where N is the number of points in the experimental curve $\alpha_e(T)$. We used $N = 20$. In fact, in this case it is necessary to study the surface structure of the function $S'^2 = S'^2\left(T_m, \alpha_m, \left(\dfrac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_m\right)$ in four-dimensional space. The results of such an investigation will be reported in the near future; in this work we estimate only the influence of the most frequent errors.

It is well known that errors in temperature determination are widespread in thermal analysis. Errors in α_m and $\left(\dfrac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_m$ determination are less probable, but they do appear from time to time. Accordingly, we decided to estimate the influence of all these errors, but separately (the simplest case). The calculation results are presented in Figs 1–3. One of the CO formation experimental curves was used for calculations. In our case the minimum value of the sum of square differences $S^2 = 4.36 \cdot 10^{-5}$ was reached when $\alpha_m = 0.63$, $T_m = 1052$ K, and $\left(\frac{d\alpha}{dT}\right)_m = 7.10^{-3}\ \mathrm{K}^{-1}$. It should be noted that any experimental curve can be described well enough by a calculated curve only if $S^2 \leqslant 2.10^{-4}$. It is easy to see

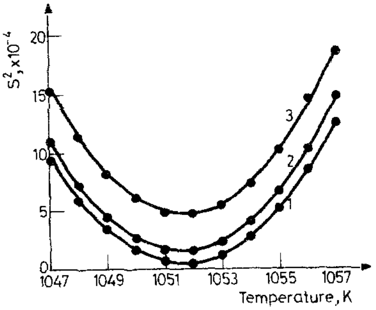

Fig. 1 Dependence of sum of square differences on the reaction rate maximum temperature.

(1) $\alpha_m = 0.63, \left(\frac{d\alpha}{dT}\right)_m = 7 \cdot 10^{-3}\ \mathrm{deg}^{-1}$

(2) $\alpha_m = 0.65, \left(\frac{d\alpha}{dT}\right)_m = 7.10^{-3}\ \mathrm{deg}^{-1}$

(3) $\alpha_m = 0.65, \left(\frac{d\alpha}{dT}\right)_m = 7.5 \cdot 10^{-3}\ \mathrm{deg}^{-1}$

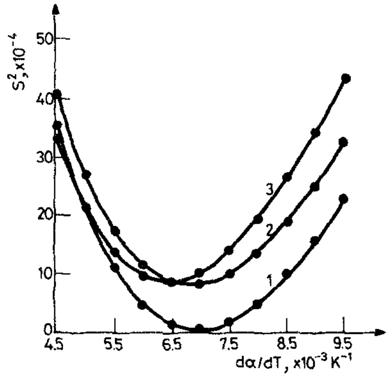

Fig. 2 Dependence of sum of square differences on the reaction rate maximum value

(1) $\alpha_m = 0.63$, $T_m = 1052$ K
(2) $\alpha_m = 0.63$, $T_m = 1056$ K
(3) $\alpha_m = 0.65$, $T_m = 1056$ K

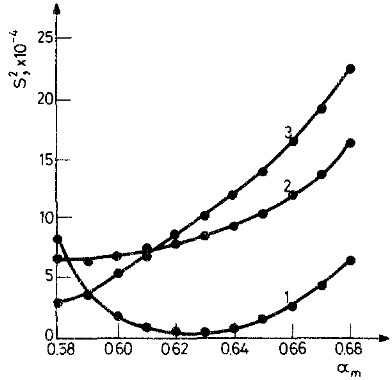

Fig. 3 Dependence of sum of square differences on the fraction reacted at the reaction rate maximum temperature.

(1) $T_m = 1052$ K, $\left(\frac{d\alpha}{dT}\right)_m = 7 \cdot 10^{-3}$ deg^{-1}

(2) $T_m = 1056$ K, $\left(\frac{d\alpha}{dT}\right)_m = 7 \cdot 10^{-3}$ deg^{-1}

(3) $T_m = 1056$ K, $\left(\frac{d\alpha}{dT}\right)_m = 7.5 \cdot 10^{-3}$ deg^{-1}

(curve 1, Fig. 1) that even a 3 degree error in T_m determination (this is not rare in thermal analysis) increases the sum of square differences by a factor of 8–12 times and makes impossible a correct description of the experimental curve. If a small error is made in α_m determination, then the tolerated error in temperature decreases to 1–2 degree (curve 2, Fig. 1). If even small errors are made in $\left(\frac{d\alpha}{dT}\right)_m$ and α_m determination (curve 3, Fig. 1), it becomes impossible to describe the experimental curve with sufficient accuracy. The results of analogous calculations are presented in Figs 2 and 3, where $\left(\frac{d\alpha}{dT}\right)_m$ or α_m is a variable. It can be seen from the pesented data that the results are very sensitive to the experimental errors and the range of tolerated errors is very small: $\Delta T_m < 3$ degree, $\Delta\alpha_m < 0.025$, and $\Delta\left(\frac{d\alpha}{dT}\right)_m < 0.05 \cdot 10^{-3}$ degree^{-1}. If errors exist in several values at the same time, it is practically impossible to obtain a satisfactory description of the experiment. It is clear from the above that if one-point methods are used for determination of the kinetic parameters, it is necessary to examine whether the experimentally determined extremum points are true (if only by elimination of further points). In the contrary case, considerable errors are possible. All of the above statements relate not only to the Allakhverdov–Nirsha method, but to any modification of methods using extremum points (e.g. [12, 13]).

The experimental kinetic curves $\alpha = \alpha(T)$ are presented in Figs 4–7. It should be remembered that each of them is the statistical mean curve for the seam, as the samples of different fractions were used for the kinetic investigations. It is clear that the curves have some differences and so the kinetic constants were determined separately for each of the curves and the statistical mean constants were then calculated. It was assumed that the normal (Gaussian) distribution law is correct for the density of probability distribution of the results. It was also assumed that the random error is equal to the standard deviation σ. As the results of calculations, the following kinetic constants and intervals were determined (Table 1).

Table 1 Kinetic constants

Gas	n	E, kJ mole^{-1}	K_0, s
C_nH_m	0.61±0.08	168.9±0.9	$(2.4\pm0.3)\cdot10^9$
CH_4	2.70±0.09	152.9±0.7	$(1.39\pm0.09)\cdot10^8$
CO	0.46±0.08	131.0±0.8	$(7.07\pm0.08)\cdot10^3$
H_2	0.85±0.04	97.0±0.9	$(0.80\pm0.09)\cdot10^3$

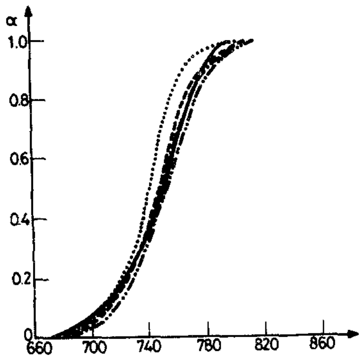

Fig. 4 Kinetic curves for C_nH_m evolution.

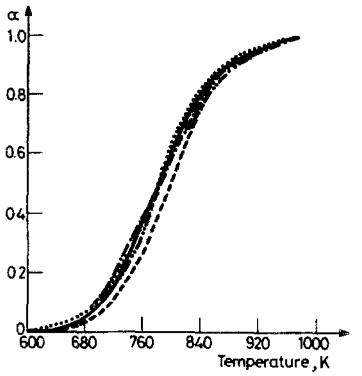

Fig. 5 Kinetic curves for CH_4 evolution

– – – seam B, –.– seam E, –. .– seam I, – . . . . – seam III, ——— Calculated curve

The curves calculated according to the determined kinetic parameters are presented as full lines in Figs 4–7. It can be seen that the coincidence with experiment is quite satisfactory.

The presented results show that, in spite of differences in deposits, in seam types and in fractions, the separate gas formation kinetics in the course of shale thermal decomposition can be described by the common kinetic constants, different for every gas.

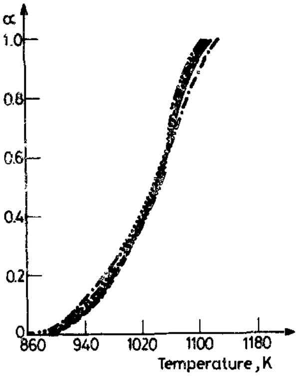

Fig. 6 Kinetic curves for CO evolution.

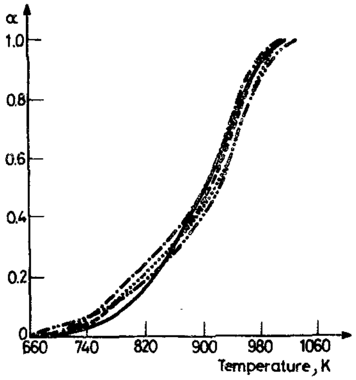

Fig. 7 Kinetic curves for H_2 evolution

– – – seam B, –.– seam E, –. .– seam I, – . . . . – seam III, ——— calculated curve

Conclusions

We would like to draw attention to the fact that, on increase of the heating rate, the initial temperature, the final temperature and the reaction rate maximum temperature all moving towads higher values. The temperature range of the reaction becomes wider. This fact has been found experimentally by many scientists [9] and corroborated by theory [14]. In the numerous works by Chukhanov (e.g. [15]) it was shown that it is possible to vary the formation of products by changing the heating rate. This testifies both to the different shifts of reactions to the high-temperature ranges and to the appearance of other reactions. We know of no analogous investigation on the kinetics of separate gas evolution at this high heating rate for Pribaltic shale. Thus, no comparison can be made with the data presented here. The kinetic constants obtained should therefore be used for the high-rate processes with care, as changes in mechanism and consequently in the kinetics of the reactions when the heating rate is increased by several orders can not be excluded.

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Zusammenfassung — Die Ergebnisse der Berechnung kinetischer Parameter, die die Freisetzung von C_nH_m, CH_4, CO und H_2 im Verlaufe der thermischen Zersetzung von Schiefern beschreiben, werden mitgeteilt. Die Berechnungen wurden nach der Methode von Allakhverdov und Nirsha ausgeführt. Die Mittelwerte der kinetischen Parameter wurden für jedes Gas bestimmt und mit den für Material aus Flözen verschiedener industriell ausgebeuteter Lagerstätten ermittelten Parametern verglichen. Es wird gezeigt, daß die Berechnung mit den experimentellen Werten gut übereinstimmende Ergebnisse liefert.

Резюме — Представлены результаты расчетов кинетических параметров, описывающих выход C_nH_m, CH_4, CO, H_2 при термическом разложении сланца. Расчеты проводились методом Аллахвердова–Нирша с учетом поведения суммы квадратов отклонений в пространстве кинетических параметров. Для каждого газа определены средние кинетические параметры на основе параметров, определенных для различных пластов промышленных месторождений. Показано, что результаты хорошо согласуются с экспериментом.