

COMPARISON OF THE LOPATIN METHODS AND THEIR CRITICAL EVALUATION

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ABSTRACT

There are significant differences among the results of the LOPATIN methods used for estimating the vitrinite reflectance. These differences made it justified to compare and to critically evaluate these methods. Four methods have been compared: two methods by LOPATIN published in 1971 and 1976, resp., and the methods of KARPOV and WAPLES. In addition to the differences caused by deviations of geosystems used for the correlation, the LOPATIN methods basically differ from each other in the character of the correlation relationship and in the reaction kinetic principles employed.

The author thinks that the linear relationship between the logarithm of the vitrinite reflectance and that of the time-temperature index is better founded. For describing the geosystem published by Dow, the reaction kinetic principle is more adequate that are characterized by the following features: the activation energy does not depend on the temperature and, as a result of this, the change of the reaction rate by 10 °C decreases with the increase of the temperature. This reaction kinetic principle is used by LOPATIN in his method published in 1976.

INTRODUCTION

It is a generally accepted and proved fact that the hydrocarbons of the earth's crust form from the organic matter of the sedimentary rocks, i. e. from the kerogen, decisively as a result of thermal effects.

The composition of products originating in the course of the thermal decomposition is closely connected to the maturity of kerogen. (The composition of the decomposition products are denoted by the terms crude oil, wet gas, dry gas). For the quantitative characterization of the kerogen maturity, generally the reflectance of the vitrinite forming a part of the organic matter of sedimentary rocks is used. That is why the values of the vitrinite reflectance measured and estimated by calculation methods supply useful informations for judging potential hydrocarbon prospects. The estimation of the vitrinite reflectance by calculation methods plays an important part in judging the hydrocarbon prospects in sedimentary basins known in a small degree and, by comparing the measured and estimated values, in the paleogeothermal reconstruction.

Similarly to the kerogen, the change of the properties of vitrinite (volatile matter content, reflectance) is a result of a thermal decomposition originating under the thermal influence. The thermal decomposition process of vitrinites was first studied on coals. HUCK, KARWEIL [1955] and KARWEIL [1956] have stated that the thermal decomposition of vitrinites can be described by reaction kinetic relationships and, consequently, not only the temperature but also the time plays a role. BOSTICK [1973] extended this statement to vitrinites in sedimentary rocks. The thermal decomposition consists of the joint effect of very complicated, serial and parallel reactions. The reaction kinetic relationships permit the description of this complicated process in a

formal kinetic way which is characteristic of the total process. with apparent constants (with apparent activation energy, frequency factor and reaction order).

Resulting from the formal kinetic description, the abovementioned apparent reaction kinetic constants can be determined by comparing them with the well-known geosystems (correlation).

Extrapolating the kinetic constants arising from the laboratory model experiments may give rise to significant errors because of the deviation of the time factor by several orders of magnitude [SNOWDON, 1979]. LOPATIN [1971] has published a simple calculation method for estimating the vitrinite reflectance which has been modified in 1976. KARPOV [1975] and WAPLES [1980] have published another calculation method the basic principle of which is similar to that of LOPATIN'S method. The deviations of the results obtained for the same geosystems with the methods of identical basic principle that has been demonstrated in this article, have made justified a critical evaluation of Lopatin's methods.

THE COMMON THEORETICAL BASES OF LOPATIN'S METHODS

In the sedimentary rocks, the thermal decomposition of the vitrinite takes place under non-isothermal conditions; the rate of reaction calculated by using Arrhenius' equation is the function of time, too:

$$k(t) = A \cdot e^{-\frac{E}{RT(t)}} \quad (1)$$

Where: k = rate of reaction, million years⁻¹,
 t = geological time, million years,
 A = frequency factor, million years⁻¹,
 E = activation energy,
 R = universal gas constant,
 T = absolute temperature, Kelvin.

LOPATIN'S methods decompose the non-isothermal transformation into a series of isothermal transformations and by the sum of the actual non-isothermal transformation as a total of these isothermal transformations. Within the temperature interval $T+\Delta T$, the rate of reaction is considered as constant, and, assuming the kinetically first-order reaction. by means of the so-called "cooking" time Δt_i , spent in the temperature interval $T+\Delta T$, the transformation is calculated using the following formula:

$$\ln \frac{c_{T_i}}{c_{T_i+\Delta T}} = k_i \cdot \Delta t_i \quad (2)$$

Where: $c_{T_i}/c_{T_i+\Delta T}$ = transformation module of vitrinite,
 k_i = rate of reaction belonging to the lower or upper temperature limit of the temperature interval $T_i+\Delta T$,
 Δt_i = time spent in the temperature interval $T_i+\Delta T$.

Instead of the absolute rate of reaction, the LOPATIN'S methods make use of the relative rate of reaction, i. e. the so-called temperature factor of the rate of reaction, γ_i , which is the quotient of the absolute rate of reaction, belonging to the interval $T_i+\Delta T$ (k_i) and to a so-called reference temperature (T_R) chosen arbitrarily (k_R):

$$\gamma_i \equiv \frac{k_i}{k_R} \quad (3)$$

Eqn. 2 can be written in the following modified version by introducing the relative rate of reaction:

$$\ln \frac{C_{T_i}}{C_{T_i+\Delta T}} = k_R \cdot \gamma_i \cdot \Delta t_i \quad (4)$$

By summarizing the elementary isothermal transformations calculated in this way, the transformation approximating the non-isothermal transformation, from the beginning of the sediment formation up to the present situation, can be produced:

$$\ln \frac{C_{T_0}}{C_T} \approx \sum_{T_0}^T \ln \frac{C_{T_i}}{C_{T_i+\Delta T}} = k_R \sum_{T_0}^T (\gamma_i \cdot \Delta t_i). \quad (5)$$

Where: T_0 = temperature pertaining to the beginning of the sediment formation,
 T = temperature pertaining to the present situation,
 C_{T_0}/C_T = ratio of the non-isothermal transformation.

The sum of the elementary transformations is the index of the maturity time temperature (TTI):

$$\text{TTI} \equiv \sum_{T_0}^T (\gamma_i \cdot \Delta t_i). \quad (6)$$

By introducing this definition, the non-isothermal transformation can be expressed as:

$$\ln \frac{C_{T_0}}{C_T} \approx k_R(\text{TTI}). \quad (7)$$

Based upon reaction kinetic considerations, the methods after LOPATIN first determine the temperature factors, γ_i , pertaining to the isothermal sections, thereafter, they fix the "cooking" time (Δt_i) belonging to the individual isothermal sections on geosystems of relatively well-known heat history. The products temperature factor/"cooking" time ($\gamma_i \Delta t_i$) proportional to the isothermal transformations are summarized and, by doing so, the time/temperature index (TTI) is obtained. This index is correlated with the vitrinite reflectance values measured in known geosystems. Thus, the relationship between the vitrinite reflectance (R) and the time/temperature index is obtained.

The basic conditions of a well applicable relationship of general validity, R/TTI, are as follows:

- 1) The temperature factors of the reaction rate should be appropriate; they should describe the thermal decomposition of the vitrinite.
- 2) The vitrinite reflectance values measured in the known geosystems should meet the measure of the actual transformation of the vitrinite.
- 3) The thermal history of the known geosystems should comply with the actual thermal history.

The differences among LOPATIN's methods are derived from the differences among the geosystems used for the correlation that are considered as known or that are really known. A further deviation is that various temperature factors are used. Last not least, there is a difference concerning the character of the relation R/TTI, the magnitude of the temperature intervals suitable for the isothermal transformations and the reference temperature.

This article encompasses the following problems of the differences among LOPATIN's methods:

- characteristics of the geosystems used for the correlation;
- character of the relationship, R/TTI ;
- magnitude of the temperature factor and of the temperature intervals corresponding to isothermal transformations as problems connecting with each other;
- reference temperature.

1) *Characteristics of the geosystems used for the correlations*

LOPATIN [1971]: Drilling Münsterland—1, vitrinite reflectance: 1—5%.

LOPATIN [1976]: 38 coal layers, in the Soviet Union, USA and FRG; vitrinite reflectance: 0.3—5.5%.

KARPOV [1975]: 111 measuring results from various parts of the Soviet Union: vitrinite reflectance: 0.3—4.3%.

WAPLES [1980]: 402 measuring data obtained from 31 well, (no region indicated); vitrinite reflectance: 0.4—6%.

In all probability, the correlation approaches the actual relation, all the more the higher is the difference as to the time and the temperature and the vitrinite reflectance range. Considering these facts, LOPATIN's method [1971] can be regarded as uncertain, although this publication includes this basic idea that can be judged as right from that time. At the same time, LOPATIN's correlation published in 1976 based on a significantly larger amount of facts is less known and less accepted, presumably because the researchers, such as WAPLES, dealing with this topic, have accepted the redoubling of the reaction rate per 10 °C, whereas LOPATIN has changed this view point.

2) *Character of the relationship, R/TTI*

LOPATIN [1971]: $R = 1.301 \lg(TTI) - 0.5282$.

LOPATIN [1976]: $\lg R = 0.4762 \lg(TTI) - 1.1638$.

KARPOV [1975]: $\lg R = 0.1974 \lg(TTI) - 0.9852$.

WAPLES [1980]: $\lg R = 0.2645 \lg(TTI) - 0.4841$.

With the exception of LOPATIN's calculation method published in 1971, a linear relationship between the logarithm of the vitrinite reflectance and that of the time/temperature index was established in the other methods.

3) *Magnitude of the temperature factor and of the temperature intervals corresponding to isothermal transformations*

In his paper published in 1976, LOPATIN considered the value of the activation energy as a constant (41.84 kJ/mol) independently of the temperature and he chose the magnitude of the temperature intervals of isothermal phases starting from 50 °C in a way so that the reaction rate should be doubled. In case of a constant activation energy, the value of the temperature/intervals necessary for the doubling of the reaction rate (ΔT_i) can be calculated using the following formula:

$$\Delta T_i = \frac{1.378 T_i}{10000 - 1,378 \cdot T_i} \quad (8)$$

Temperature limits suitable for the doubling of reaction rate at a constant activation energy (41.84 kJ/mole)

Temperature limits (°C)	
LOPATIN [1976]	According to Eqn. 8
50	50
65	65.8
80	81.6
100	99.8
120	120.0
145	142.5
170	167.2
200	196.2
230	228.6

Table 1 demonstrates the temperature limits calculated by Eqn. 8 and determined by LOPATIN [1976].

LOPATIN's method is equivalent to the method according to which, in case of a constant activation energy, the change of the reaction rate per 10 °C (r) is a function of the temperature. (1976) With the increase of the temperature, the change of the reaction rate diminishes in conformity with the following relationship:

$$\lg r_i = \frac{21850}{T_i(T_i + 10)} \quad (9)$$

Where:

$$r_i = \frac{k_{T_i+10}}{k_{T_i}}$$

The temperature factors can be obtained under the same conditions using the following formulae:

$$\lg \gamma_i = 2185 \cdot \frac{T_i - T_R}{T_i \cdot T_R} \quad (10)$$

Fig. 1 shows the change of the reaction rate *vs.* temperature (Eqn. 9) on the basis of Eqn. 9. According to GOLITSYN [1973], the change of the topochemical reaction rate per 10 °C encountered in the diffusion range amounts to values between 1.2 and 1.5. (In Fig. 1, values suggested by GOLITSYN are indicated.)

The majority of the authors, such as LOPATIN [1971], KARPOV [1975], WAPLES [1980] chose the magnitude of the temperature intervals corresponding to isothermal transformations as having a value of 10 °C in the whole temperature interval of the non-isothermal transformation. This seemingly arbitrary selection was accounted for by the fact that, according to VAN'T HOFF's rule, the chemical reaction rates taking place as a result of thermal effects are doubled per 10 °C:

$$r = \frac{k_{T_i+10}}{k_{T_i}} = z \quad (11)$$

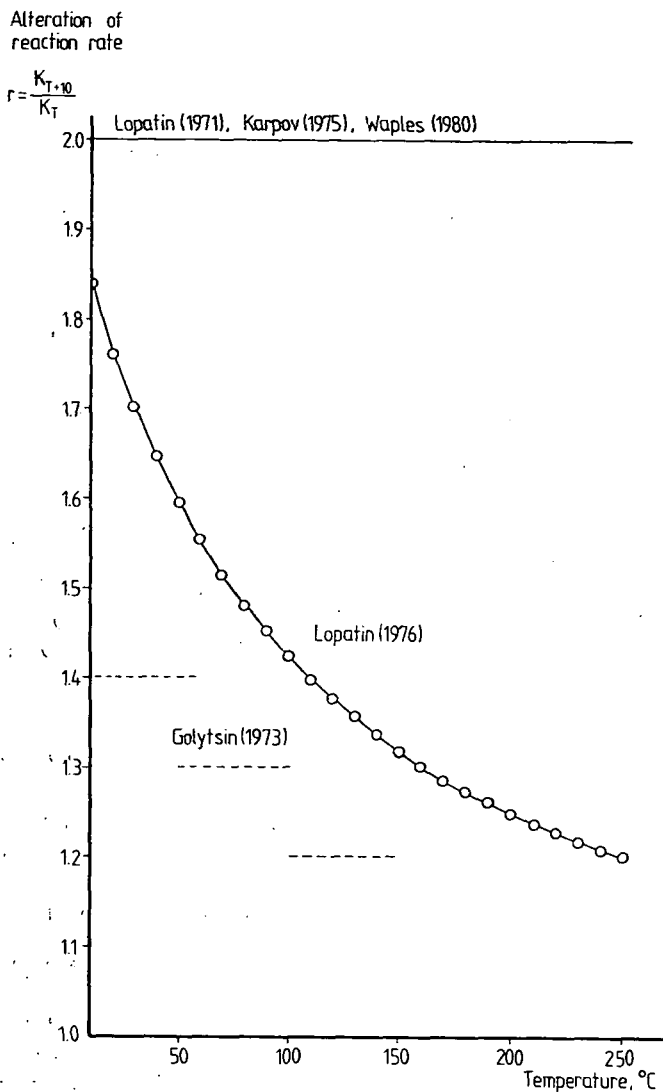


Fig. 1. Relationship between changes in the reaction rate by 10 °C and the temperature at a constant activation energy (41.84 kJ/mole)

Assuming the validity of VAN't HOFF's rule, the temperature factors belonging to the individual isothermal sections can be obtained using the following simple relationship:

$$\gamma_i = z^N \text{ or } \lg \gamma_i = N \lg z \quad (12)$$

Where:

$$N = \frac{T_i - T_R}{10} \quad (13)$$

Based upon the relationships to be demonstrated hereinafter, the condition of doubling the reaction rate per 10 °C results in the change of the activation energy with the increase of the temperature:

$$\lg r_i = \frac{1}{2.303 R} \left(\frac{E_{T_i}}{T_i} - \frac{E_{T_i+10}}{T_i+10} \right). \quad (14)$$

$$\lg r_i = \frac{1}{2.303 R} \left[\frac{T_i(E_{T_i} - E_{T_i+10}) + E_{T_i} \cdot 10}{T_i(T_i+10)} \right]. \quad (15)$$

Since $r=2$ and $\lg r > 0$, the difference of activation energy, resulting from Eqn. 15, $(E_T - E_{T+10})$ should be positive giving

$$E_{T_i} > E_{T_i+10}. \quad (16)$$

Thus, the doubling of the reaction rate per 10 °C involves the decrease of the activation energy.

Eqn. 14 should be considered as the equation describing the relationship activation energy/temperature corresponding to the doubling of the reaction rate per 10 °C. Accordingly, the function of activation energy *vs.* temperature can be expressed as:

$$E = - \frac{2.303 R \lg z}{10} \cdot T^2. \quad (17)$$

Starting from a specified temperature, T_0 , the change of the activation energy (ΔE) can be calculated using Eqn. 17:

$$\Delta E = \frac{2.303 R \lg z}{10} \cdot T_0^2 - \frac{2.303 R \lg z}{10} \cdot T^2. \quad (18)$$

Where: $\Delta E = E_T - E_{T_0}$ and $T > T_0$.

Fig. 2 shows the activation energy difference as a function of the temperature in case the reaction rate is doubled per 10 °C.

Therefore, LOPATIN's methods differ from each other in two alternative solutions:

- a) the change of the reaction rate per 10 °C does not depend on the temperature, the activation energy is not constant but it is a function of the temperature,
- b) the change of the reaction rate per 10 °C is not constant but it depends on the temperature, the activation energy is independent of the temperature.

4) Reference temperature

LOPATIN [1971]: 373 K (100 °C).

LOPATIN [1976]: 323 K (50 °C).

KARPOV [1975]: 283 K (10 °C).

WAPLES [1980]: 373 K (100 °C).

Even if the discrepancies of the geosystems used for the correlation are disregarded, it can be stated that there are two methods of LOPATIN's fundamental principle that are identical in all the parameters enumerated above. That is why the discrepancies arising from the differences of the geosystems cannot be determined by comparing the constants of the relationships $R(TTI)$.

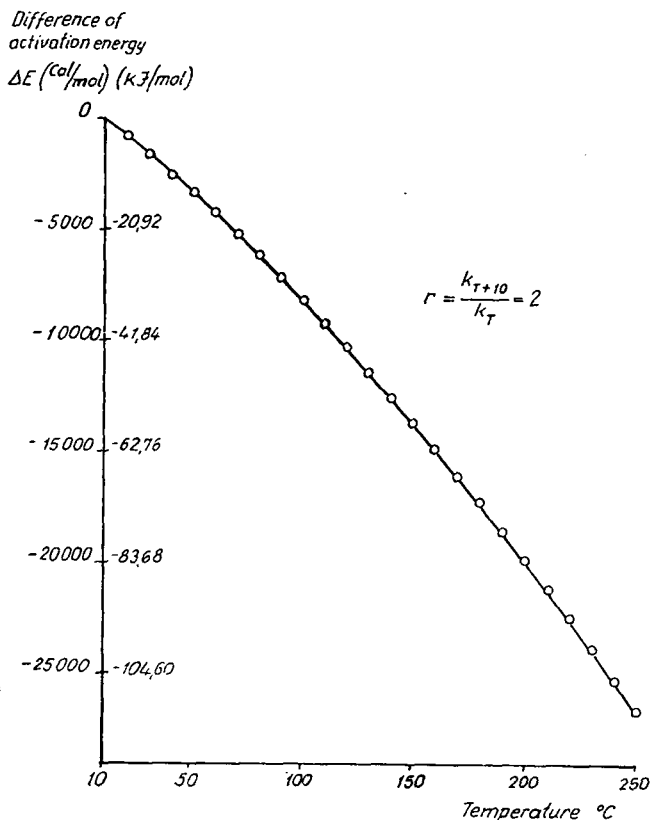


Fig. 2. Relationship between the activation energy difference and the temperature in case of the doubling of the reaction rate by 10 °C

A COMPARISON OF THE RESULTS OBTAINED BY LOPATIN'S METHODS ON THE SAME GEO-CONDITIONS

To perform the comparison, the identity of the following three geo-conditions, i. e. the heating rate, ξ , the sedimentation, as well as the temperature, T_i belonging to the beginning of the transformation, T_0 and to the end of the transformation must be ensured. These considerations can be accounted for in the following way:

Heating rate in the isothermal sections:

$$\xi \equiv \frac{\Delta T_i}{\Delta t_i} \quad (19)$$

Where: ξ = heating rate. (°C/million years);

ΔT_i = temperature range of the isothermal section which is (10 °C) identical in the whole temperature range of the non-isothermal transformation with LOPATIN's [1971], KARPOV's [1975] and WAPLES' [1980] methods; it is changing with LOPATIN's method [1976], with the increase of the temperature, it amounts to 15, 20, 25 and 30 °C;

Δt_i = time spent in the temperature interval, ΔT_i , of the isothermal sections, million years.

From Eqn. 19, Δt_i figuring in the time/temperature index can be expressed as:

$$\Delta t_i = \frac{\Delta T_i}{\xi_i} \quad (20)$$

If, in conformity with the identical geo-conditions, the heating rate is independent of the time (and of the temperature), then

$$\Delta t_i = \frac{\Delta T_i}{\xi} \quad (21)$$

If ΔT_i is constant (10 °C), then

$$\Delta t = \frac{10}{\xi} \quad (22)$$

For the whole time and temperature range of the non-isothermal transformation, it can be written

$$\sum \Delta t_i = t \text{ and } \sum \Delta T_i = \Delta T$$

Where:

$$\Delta T = T_i - T_o$$

In this case, according to Eqn. 21:

$$t = \frac{T_i - T_o}{\xi} \quad (23)$$

If the initial and final temperatures of the non-isothermal transformation, as a geo-condition, are constant and the heating rate is also constant, then the length of time of the transformation is constant, too. Therefore, all the parameters figuring in the calculation of the transformation are constant, they do not depend on the temperature provided the geo-conditions are identical. Presuming the heating rate and the subsidence rate, (λ), are constant, then in the total time and temperature range of the non-isothermal transformation, the geothermal gradients, G , should also be constant and independent of time and temperature since

$$\xi = G \cdot \lambda \quad (24)$$

Using LOPATIN's methods, the value of the vitrinite reflectance can be calculated by means of the following equations, provided there are identical geo-conditions:

$$\text{LOPATIN [1971]: } R = 1.301 \left(\lg \sum_{T_o}^{T_i} \gamma_i - \lg \xi \right) + 0.773 \quad (25)$$

$$\text{LOPATIN [1976]: } \lg R = 0.4762 \left(\lg \sum_{T_o}^{T_i} (\gamma_i \Delta T_i) - \lg \xi \right) - 1.1638 \quad (26)$$

$$\text{KARPOV [1975]: } \lg R = 0,1974 \left(\lg \sum_{T_o}^{T_i} \gamma_i - \lg \xi \right) - 0,7878 \quad (27)$$

$$\text{WAPLES [1980]: } \lg R = 0,2645 \left(\lg \sum_{T_0}^{T_i} \gamma_i - \lg \xi \right) - 0,2196 \quad (28)$$

The number of the vitrinite reflectance values belonging to various final temperature values as well as the possibility of the comparison is reduced to a great extent by the fact that LOPATIN's method [1976] and the other methods can be compared at a limited number of final temperature values (7 values) and there is a considerably large difference among the comparable temperature values ranging from 20 to 50 °C. That is why isometamorphic temperature values needed to attain the same vitrinite reflectance value seemed to be expedient to compare LOPATIN's methods at identical geoconditions. The vitrinite reflectance values serving as basis for the comparison were given by vitrinite reflectances authoritative from the view-point of hydrocarbon formation using Dow's values [1978]: 0.6; 1.0; 1.35; 2.0%.

To realize this method, it was necessary to determine the relationship between vitrinite reflectance and temperature, i. e. the function $R(T)$. The function $R(T)$ can be calculated by using the temperature factors in case of LOPATIN's [1971], KARPOV's [1975] and WAPLES' [1980] methods and b using the temperature function of the logarithm, of the sums of the products $\gamma_i \Delta T_i$ in case of LOPATIN's method [1976]. (The summation is done uniformly starting from 10 °C.)

$$\text{LOPATIN [1971] and WAPLES [1980]: } \lg \sum_{T_0}^{T_i} \gamma_i = 0.0302 \cdot T - 11.256 \quad (29)$$

$$\text{KARPOV [1975]: } \lg \sum_{T_0}^{T_i} \gamma_i = 0.0304 \cdot T - 8.350 \quad (30)$$

$$\text{LOPATIN [1976]: } \lg \sum_{T_0}^{T_i} (\gamma_i \Delta T_i) = -2563 \frac{1}{T} + 9.308 \quad (31)$$

In case of all methods with the exception of LOPATIN's method [1976], the logarithm of the sum of the temperature factor can be linearized by the temperature and, in case of LOPATIN's method, [1976] by the reciprocal value of the temperature, starting from 60 °C.

Using the above equations, the isometamorphic values necessary for attaining the various vitrinite reflectance values can be calculated by means of the following relationships:

$$\text{LOPATIN (1971): } T = 25.45 (R + 1.301 \lg \xi + 13.871) \quad (32)$$

$$\text{LOPATIN [1976]: } T = \frac{1221}{3.268 - \lg R - 0.4762 \lg \xi} \quad (33)$$

$$\text{KARPOV [1975]: } T = 166.7 (\lg R + 0.1974 \lg \xi + 2.436) \quad (34)$$

$$\text{WAPLES [1980]: } T = 125.2 (\lg R + 0.2645 \lg \xi + 3.197) \quad (35)$$

The temperature values determined by using the above relationships are shown in Table 2. The temperature values necessary to attain the identical vitrinite reflectance values are demonstrated as a function of the logarithm of the heating rate in Figs. 3, 4, 5 and 6.

TABLE 2

Isometamorphic temperature values calculated by LOPATIN's methods

ξ (°C/million years)	R %	Temperature (°C)			
		LOPATIN [1971]	LOPATIN [1976]	KARPOV [1975]	WAPLES [1980]
0.3	0.6	78	54	79	82
	1.0	88	74	116	110
	1.35	97	88	138	126
	2.0	114	107	166	148
1.0	0.6	95	77	96	99
	1.0	105	101	133	127
	1.35	114	116	155	144
	2.0	131	139	183	165
3.0	0.6	111	101	112	115
	1.0	121	129	149	143
	1.35	130	146	170	159
	2.0	147	173	199	181
15.0	0.6	134	144	135	138
	1.0	144	178	172	166
	1.35	153	201	193	183
	2.0	170	234	222	204

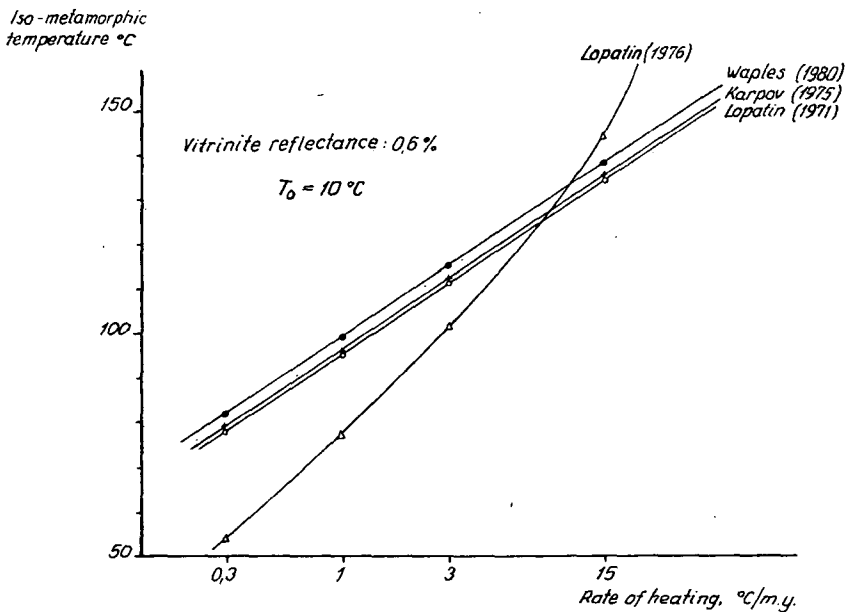


Fig. 3. Relationship between the isometamorphic temperature values belonging to the 0.6% vitrinite reflectance and the logarithm of the heating rate (at $T_0 = 283\text{ K}$, values calculated by using LOPATIN's methods)

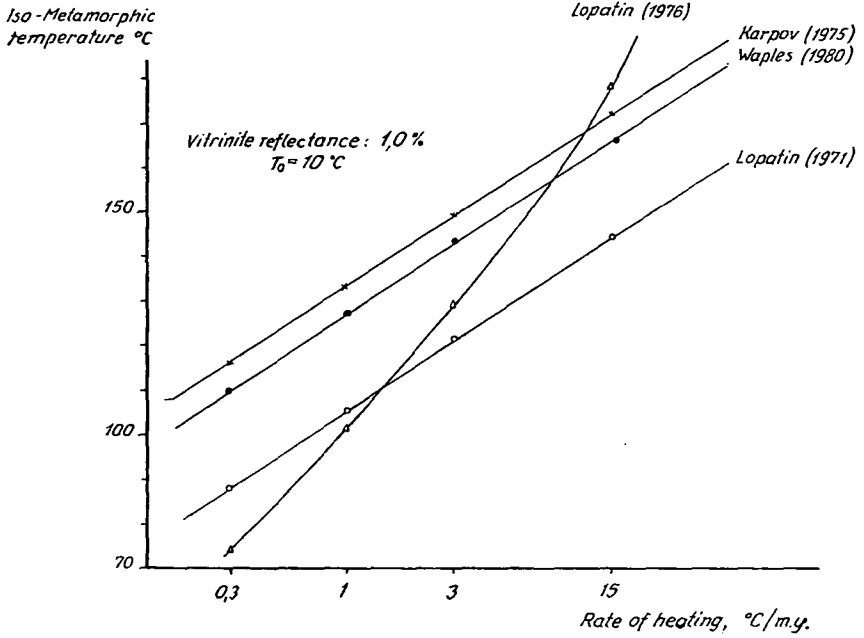


Fig. 4. Relationship between the isometamorphic temperature values belonging to the 1% vitrinite reflectance and the logarithm of the heating rate (at $T_0 = 283 \text{ K}$, values calculated by using LOPATIN's methods)

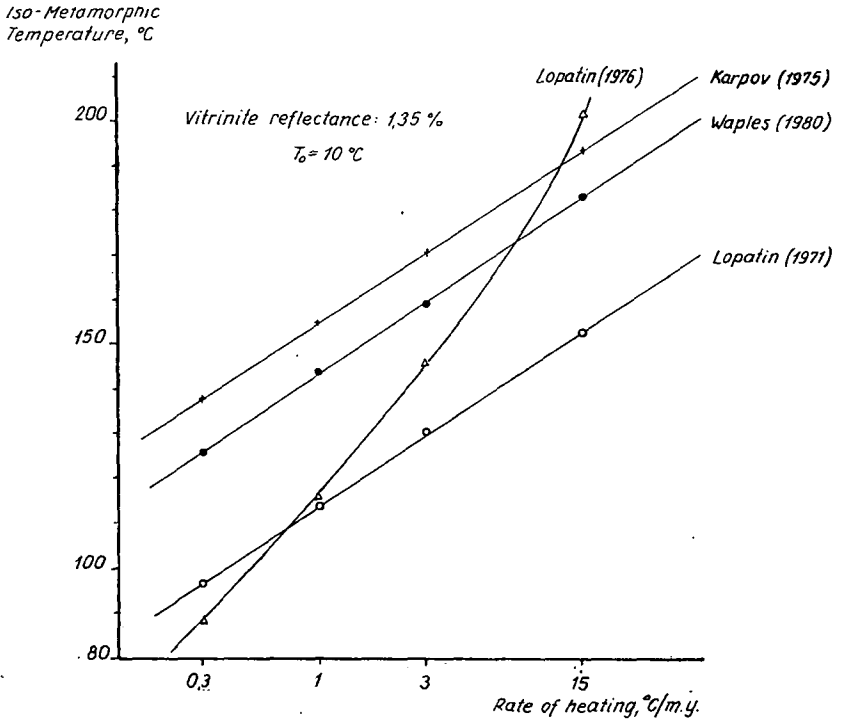


Fig. 5. Relationship between the isometamorphic temperature values belonging to the 1.35% vitrinite reflectance and the logarithm of the heating rate (at $T_0 = 283 \text{ K}$, values calculated by using LOPATIN's methods)

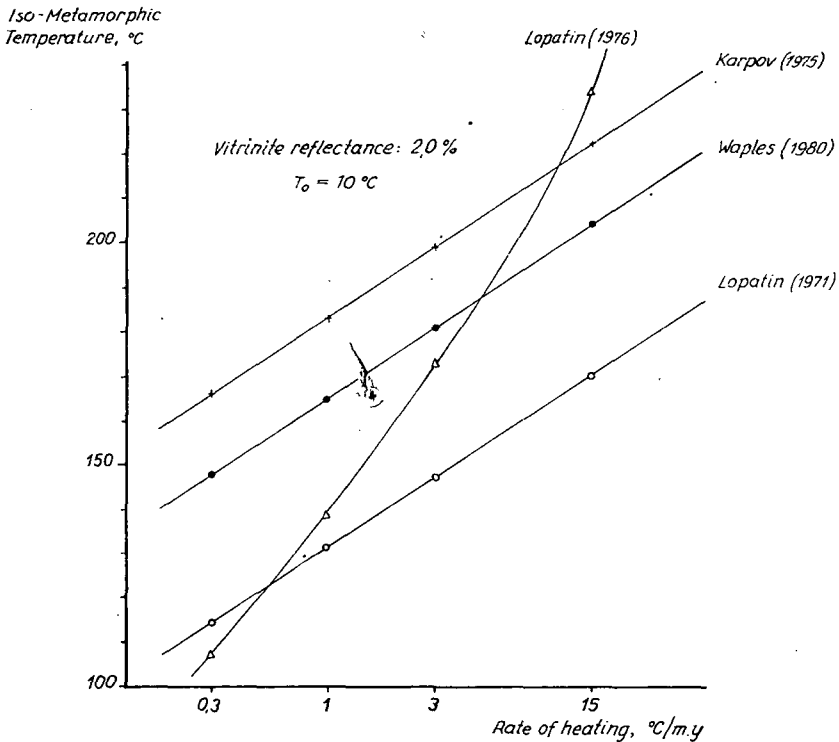


Fig. 6. Relationship between the isometamorphic temperature values belonging to the 2% vitrinite reflectance and the logarithm of the heating rate (at $T_0=283$ K, values calculated by using LOPATIN's method, 1976)

On the basis of the Figures, the following can be stated:

- 1) With methods [LOPATIN, 1971; KARPOV, 1975; WAPLES, 1980] using the doubling of the reaction rate by 10 °C and, consequently, the activation energy changing depending on temperature, the temperature values (isomorphic) needed to attain the identical vitrinite reflectance values are linear function of the logarithm of the heating rate. The slope of the linear functions suitable for the various methods is identical, the different temperature values are caused by the differences of the axial section of the linear relationship.
- 2) In case of LOPATIN's method [1976] which is different from the temperature and uses a constant activation energy, the reciprocal of the isometamorphic temperature values supplies a linear relationship with the logarithm of the heating rate, see Fig. 7.
- 3) The isometamorphic temperature values calculated by using the various methods at identical geoconditions show significant discrepancies. In case the vitrinite reflectance is equal to 0.6, the methods using the temperature-dependent activation energy result in nearly identical isometamorphic temperature values. With vitrinite reflectance values higher than 0.6, the differences grow considerably with the increase in vitrinite reflectance. At the same conditions (vitrinite reflectance, heating rate), the isometamorphic temperature values show an increase in the order of LOPATIN's [1971], WAPLES' [1980] and KARPOV's methods [1975].

Iso-Metamorphic
Temperature, °C

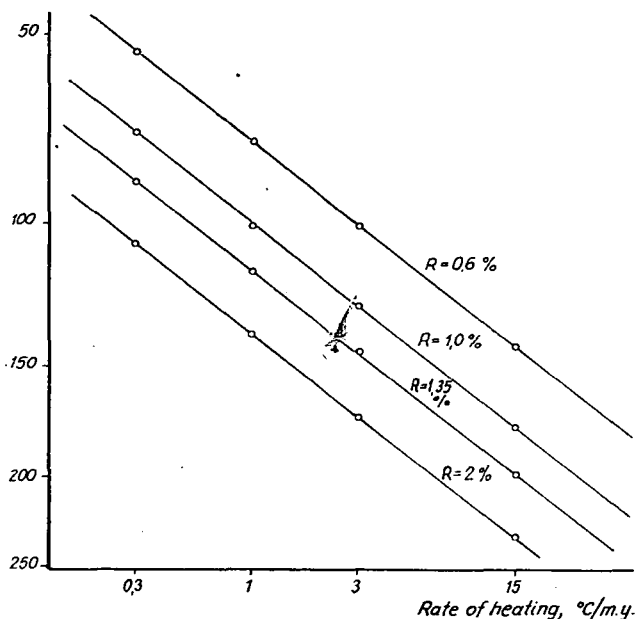


Fig. 7. Relationship between the reciprocal of the isometamorphic temperature values and the logarithm of the heating rate (at $T_0=283$ K, values calculated by using LOPATIN'S methods)

PROBLEMS CONNECTED TO THE CHARACTER OF THE RELATIONSHIP BETWEEN TIME-TEMPERATURE INDEX AND VITRINITE REFLECTANCE

The relationship between time-temperature index and vitrinite reflectance is expressed by $R = a \lg(\text{TTI}) + b$, or $\lg R = a \lg(\text{TTI}) + b$, where a and b are constant. The question arises which of the relationships is correct. To answer this question the relationship between the vitrinite reflectance and the concentration ratio (c_{T_0}/c_T) figuring in Eqn. 7, characteristic of the vitrinite transformation should be examined.

It can be assumed on good grounds that the concentration of the reactive groups of the vitrinite is proportional to the volatile matter content of the vitrinite (I):

$$C = f \cdot I \quad (36)$$

The concentration ratio is equal to the volatile matter content ratio:

$$\frac{C_{T_0}}{C_T} = \frac{I_{T_0}}{I_T} \quad (37)$$

The vitrinite reflectance-volatile matter content values that are related to each other published by KÖTTER [1960], can be correlated in the 0.18—3.0% vitrinite reflectance range and in the 0.055—0.6 volatile matter content rate by using the following linear relationship:

$$\lg I = -0.3696 R - 0.1512. \quad (38)$$

Where I : the volatile matter content of the vitrinite (g/g).

Fig. 8 shows the curve appropriate to the correlation equation. The values serving as a basis of the correlation equation were taken from KÖTTER's publication [1976] and the points indicated from the paper of TEICHMÜLLER [1971].

The prevailing surface value of the vitrinite reflectance belonging to the beginning of the sediment formation can be expressed as:

$$\lg I_{T_0} = -0.3696 R_{T_0} - 0.1512. \quad (39)$$

After Dow [1977], the surface value of the vitrinite reflectance falls between 0.18 and 0.20%; for this reason, a 0.19% value of the vitrinite reflectance was taken as a sur-

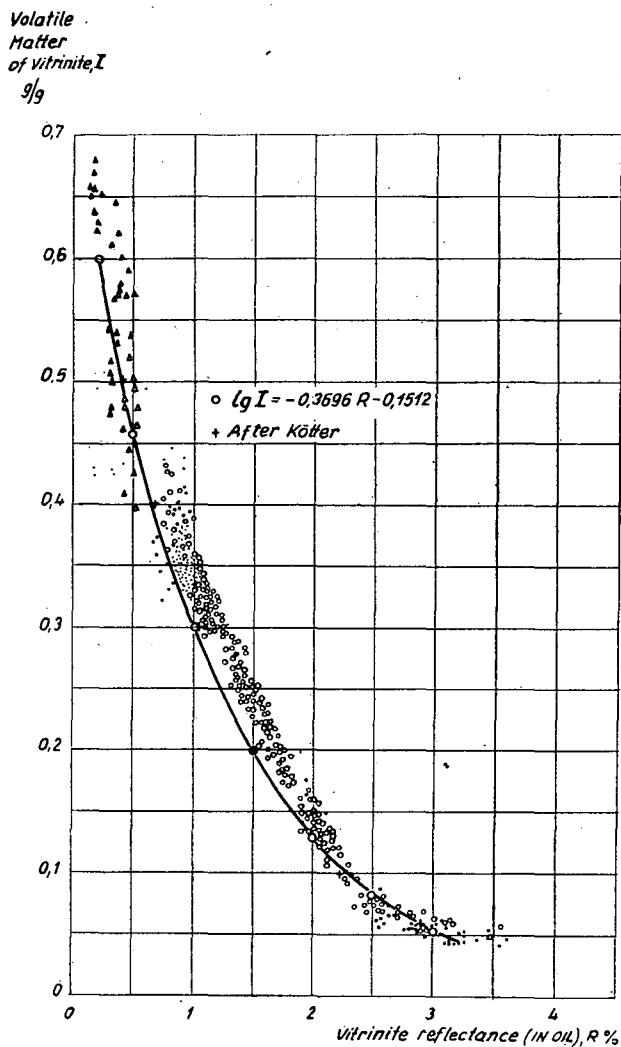


Fig. 8. Relationships between the vitrinite reflectance and the volatile matter content after KÖTTER (1960) and TEICHMÜLLER (1971) and a relationship suitable to the correlation equation determined for KÖTTER's data.

face value in the following expressions to which a 0.6 value of the volatile matter content belongs in accordance with Eqn. 38.

By using Eqns. 38 and 39, the relationship of the volatile matter content and the concentration ratio and the vitrinite reflectance may be written as:

$$\lg \frac{I_{T_0}}{I_T} = \lg \frac{C_{T_0}}{C_T} = 0.3696 (R_T - R_{T_0}). \quad (40)$$

Based upon Eqn. 7, a relation between the time-temperature index as well as the vitrinite reflectance can be obtained in the following way:

$$\ln \frac{C_{T_0}}{C_T} = 2.303 \lg \frac{C_{T_0}}{C_T} = 0.8512 \Delta R \quad (41)$$

where: $\Delta R \equiv R_T - R_{T_0}$ is an increment of the vitrinite reflectance.

$$0.8512 \Delta R = k_R(\text{TTI}) \quad (42)$$

$$\lg \Delta R = \lg(\text{TTI}) + \lg k_R + 0.070$$

In the vitrinite reflectance range of 0.6 to 2%, the following relation exists between the increment of the vitrinite reflectance and the vitrinite reflectance:

$$\lg \Delta R = 1.2506 \lg R - 0.1032 \quad (43)$$

Using the correlation Eqn. 43 in the context of Eqn. 42 gives:

$$\lg R = 0.800 \lg(\text{TTI}) + 0.800 \lg k_R + 0.1385 \quad (44)$$

Since the absolute reaction rate belonging to the reference temperature is constant if the identical methods are used, the following general formula holds true of the relationship between the time-temperature index and the vitrinite reflectance:

$$\lg R = a \lg(\text{TTI}) + b$$

This result also means that the relationship R (TTI) playing a role in LOPATIN'S method [1971] which establishes a linear relation between the vitrinite reflectance and the logarithm of the TTI values, cannot be considered as correct in the 0.6—2.0% vitrinite reflectance range.

It is expedient to investigate to what conclusions the formula of the relation R (TTI) leads, that can be considered as correct, at identical geoconditions.

Comparing Eqns. 26—28 and 29—31, it can be stated that the following relationships exist between the vitrinite reflectance and the temperature:

With KARPOV'S [1975] and WAPLES' [1980] methods:

$$\lg RY = (\text{constant})_1 \cdot T + (\text{constant})_2. \quad (45)$$

With LOPATIN'S method [1976]

$$\lg R = -(\text{constant})_1 \cdot \frac{1}{T} + (\text{constant})_2. \quad (46)$$

In Eqns. 45 and 46, $(\text{constant})_1$ is a constant independent of temperature and heating rate; whereas $(\text{constant})_2$ depends on the heating rate and independent of temperature. In case the heating rate can be considered as constant during the temperature

history, which is equivalent to that fact that, in the course of the temperature history, the surface temperature, the geothermal gradient and the subsidence rate were constant, then

$$T = T_0 + \frac{\xi}{\lambda} \cdot Z \quad (47)$$

elucidates that the general form of Eqn. 45 can be expressed as:

$$\lg R = (\text{constant}) \cdot Z + (\text{constant}). \quad (48)$$

and that of Eqn. 46:

$$\lg R = -(\text{constant}) f\left(\frac{1}{Z}\right) + (\text{constant}). \quad (49)$$

Where: Z = depth

$f\left(\frac{1}{Z}\right)$ = function of the reciprocal of the depth.

Therefore, Eqn. 48, in which the relationship between the logarithm of the vitrinite reflectance and the depth is linear, is characteristic of methods using the doubling of the reaction rate by 10 °C and changing the activation energy *vs.* temperature. This relationship is widely used in spite of the fact that its effectiveness is bound to various conditions, such as the doubling of the reaction rate by 10 °C, permanence of the geoconditions mentioned during the temperature history and the vitrinite reflectance range between 0.6 and 2.0%.

Eqn. 49 differs from the previous ones and it is a result of reaction kinetical considerations prevailing in LOPATIN's method [1976] which seems to be expedient to try in geosystems in the future.

PROBLEMS OF THE TEMPERATURE FACTOR

The problems of the temperature factor are solved by LOPATIN's methods basically in two ways. These two solutions and their consequences can be symbolized in the following way:

- 1) The change of the reaction rate by 10 °C is independent of the temperature it is constant, its value is 2 $\begin{matrix} \rightarrow \\ \leftarrow \end{matrix}$ the activation energy depends on the temperature, and decreases with its growth
- 2) The change of the reaction rate by 10 °C depends on the temperature and decreases with the growth of the temperature $\begin{matrix} \rightarrow \\ \leftarrow \end{matrix}$ the activation energy is independent of the temperature, it is constant

The consequence of solution 1) is that the following relationship exists between the vitrinite reflectance, the temperature and the heating rate in case there is a constant surface temperature and heating rate during the temperature history:

$$\lg R = (\text{constant}) \cdot T - (\text{constant}) \lg \xi + (\text{constant}). \quad (50)$$

The consequence of solution 2):

$$\lg R = -(\text{constant}) \cdot \frac{1}{T} - (\text{constant}) \lg \xi + (\text{constant}). \quad (51)$$

Starting from Eqns. 50 and 51, there is a possibility for comparing the consequences of the two above solutions with the behaviour of the geosystems. In case of solution 1), the relationship between the isometamorphic temperature and heating rate can be expressed as:

$$T = (\text{constant}) \lg \xi + (\text{constant}). \quad (52)$$

In case of solution 2):

$$\frac{1}{T} = -(\text{constant}) \lg \xi + (\text{constant}). \quad (54)$$

On the basis of Eqns. 50 and 51, the difference of temperature values belonging to the identical vitrinite reflectance values ($\Delta T_{R_1 R_2}$), in the case of solution 1) (constant heating rate) is given by

$$\Delta T_{R_1 R_2} = (\text{constant}). \quad (54)$$

In case of solution 2):

$$\Delta T_{R_1 R_2} = (\text{constant}) \cdot T_1 \cdot T_2. \quad (55)$$

Where: $\Delta T_{R_1 R_2} \equiv T_2 - T_1$, T_1 = isometamorphic temperature belonging to vitrinite reflectance R_1 and T_2 = that belonging to vitrinite reflectance R_2 .

From Eqn. 54 it can be seen that for solution 1) the difference of the isometamorphic temperature values do not depend on heating rate; in case of solution 2), resulting from Eqn. 55, it is dependent of the heating rate, since on the basis of Eqns. 52 and 53, it can be seen that the isometamorphic temperature is a function of the heating rate.

For comparing the conclusions and geosystems arising from the reaction kinetic considerations of LOPATIN's methods, the data published by Dow [1978] seem to be appropriate (see Table 3) because the present surface temperatures are identical, the sediment formation is continuous and the available data meet a rather wide interval of the heating rate. We cannot prove the constancy of the prevailing surface temperature and of the heating rate, the comparison, however, is not impeded by this circumstance since it results in an error of the same magnitude for all methods.

Fig. 9 demonstrates the difference of the isometamorphic temperature values belonging to vitrinite reflectance values of 0.6 and 1.35% ($\Delta T_{R_1 R_2}$) vs. the logarithm of the heating rate. This figure includes temperature differences, too, which were supplied by LOPATIN's various methods for these same vitrinite reflectance values. It can be stated that — according to data of the geosystems published by Dow — the difference of the isometamorphic temperature values is a function of the heating rate. Therefore, solution 2) of choosing the temperature factors stands nearer to the description of the behaviour of geosystems published by Dow; in this case, the process of the vitrinite transformation can be better approached by assuming an activation energy that does not depend on the temperature. In the geosystem published by Dow, the methods are more suitable for estimating vitrinite reflectance which select the temperature factors in a way so that their change by 10 °C should decrease with

Isometamorphic temperature values of the geosystem published by Dow (1978)

ξ (°C/million years)	Temperature (°C)		Temperature difference (°C) ΔT_{R1R2}
	$R = 0.6\%$	$R = 1.35\%$	
0.64	84	118	34
1.34	97	137	40
2.76	113	164	51
5.59	131	198	67
10.3	143	221	78
29.0	164	257	93

the increase in the temperature. Such a method is LOPATIN's calculation method published in 1976. The methods suitable to solution 1) [LOPATIN, 1971; KARPOV, 1975 and WAPLES, 1980] seem to be less appropriate for describing the behaviour of geosystems published by Dow. Checking of this statement appears to be expedient on several geosystems having similar series of data to that published by Dow.

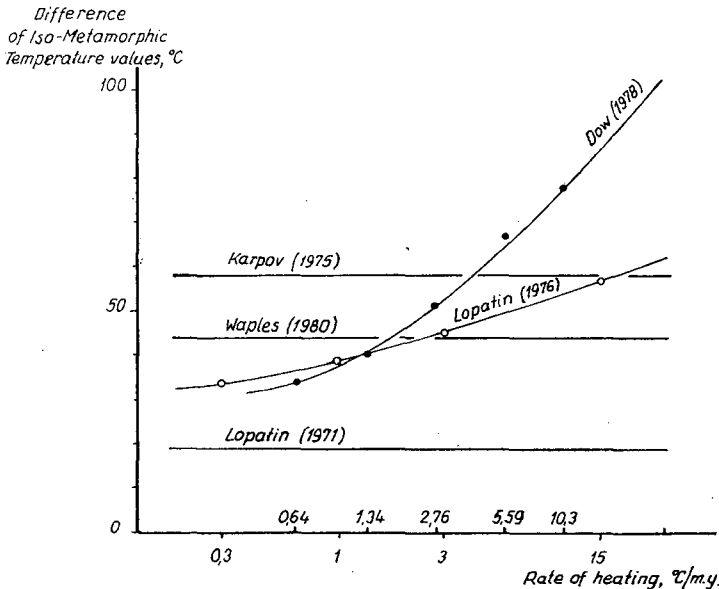


Fig. 9. Relationship between the difference of the isometamorphic temperature values belonging to the 0,6 and 1,35% reflectances and the logarithm of the heating rate

CONCLUSIONS

Based upon a comparison and critical evaluation of LOPATIN's methods, the following can be said:

- 1) The correct relationship between the vitrinite reflectance and the time-temperature index, in a vitrinite reflectance range of 0.6 to 2.0% that is important for hydrocarbon formation, is of the following type:

$$\lg R = (\text{constant}) \cdot \lg(\text{TTI}) + (\text{constant})$$

The relationships of this type correspond to LOPATIN's [1976], KARPOV's [1975] and WAPLES' methods [1980]. LOPATIN's method [1971] according to which there is a linear relationship between the vitrinite reflectance and the logarithm of the time-temperature index, is not acceptable. A farther modification of the latter method underlines this statement. The modified version is of identical type to the relationship published above.

- 2) Starting from the surface value of the vitrinite reflectance (0.19 %), there is a linear relation between the logarithm of the vitrinite reflectance increment and that of the time-temperature index throughout the full range of the vitrinite reflectance:

$$\lg \Delta R = (\text{constant}) \cdot \lg(\text{TTI}) + (\text{constant}).$$

- 3) The linear relationship between the logarithm of the vitrinite reflectance and that of the time-temperature index is valid from vitrinite reflectance values ranging from 0.6% to 2.0%. For the range important for hydrocarbon genesis (0.6—2.0%), the logarithm of the vitrinite reflectance increment and that of the vitrinite reflectance can be linearized by using the following relationship:

$$\lg \Delta R = 1.2506 \lg R - 0.1032.$$

- 4) For the description of the behaviour of the geosystem published by Dow, the temperature factors of LOPATIN's method [1976] are more suitable. The methods [LOPATIN, 1971; KARPOV, 1975 and WAPLES, 1980] assuming the constancy of the change of reaction rate, i. e. the doubling of it by 10 °C, and, as a result of this, the change of the activation energy *vs.* temperature, are less suitable for describing the actual behaviour of the geosystem published by Dow. The decrease of the constant activation energy independent of temperature, and, as a result of this, the decrease of the reaction rate change with the increase in temperature, as reaction kinetic considerations, are more appropriate to describe the geosystem published by Dow. The outcomes of this can be summarized in the following way for geoconditions that do not change with the time:

- 4.1. For the relationship between the vitrinite reflectance and the actual temperature:

$$\lg R = -(\text{constant}) \cdot \frac{1}{T} + (\text{constant}).$$

- 4.2. For the relationship between the vitrinite reflectance and the actual depth:

$$\lg R = -(\text{constant}) f\left(\frac{1}{Z}\right) + (\text{constant})$$

- 4.3. For the relationship between the temperature (isometamorphic temperature) necessary for reaching the identical vitrinite reflectance values and the heating rate:

$$\lg \xi = -(\text{constant}) \cdot \frac{1}{T} + (\text{constant})$$

As for the isometamorphic temperature, the relationship used by CONNAN (1974) which uses the geological time instead of the heating rate cannot be considered as correct. As a matter of fact, the relationship of the above form is not valid between

the geological time and the isometamorphic temperature but between the heating rate and the isometamorphic temperature.

The statements published in this paper relate to reaction kinetic considerations used in LOPATIN's methods as well as to the character of the correlation equation (relationship R (TTI) and to the limits of its validity, but they do not include the constants of the correlation equation which, because of the lack of knowledge about the absolute reaction rate belonging to the reference temperature, follow from the comparison with parameters measured deriving from the geosystems. The necessity of this correlation backs up the importance of the thermohistorical reconstruction of the geosystems serving as a basis for the comparison in creating generally applicable methods that can be used for vitrinite reflectance estimations.

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