

DYNAMICS OF MASS TRANSFER IN CAPILLARY
POROUS BODIES DURING
CHEMICAL CONVERSION

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The author analyzes the physicochemical mechanism of mass transfer from a heated capillary porous body during its thermal decomposition. The penetration parameters of chemical conversion fronts are determined, also a relation is established between the basic mass transfer coefficients and the heating rate.

When certain capillary porous bodies are heated to rather high temperatures, there occur chemical reactions (thermal decomposition) accompanied by liberation or absorption of heat. The rate of a chemical reaction can be expressed in terms of a power law:

$$W = kC_A^{m_A} C_B^{m_B}, \dots, \quad (1)$$

with C_A, C_B, \dots denoting the concentrations of substances A, B, \dots , which participate in the reaction, with the rate constant k depending on the temperature, and m_A, m_B, \dots denoting the orders of the reactions relative to the respective substances. It is usually assumed that chemical conversion occurs simultaneously over the entire specimen volume. Under actual conditions, however, it occurs first at the body surface and then, with time, the conversion zone gradually extends deeper into the body.

For thermophysical engineering calculations it is important to know the rate at which the zone of chemical conversion extends into the body and how the physicochemical properties of the material as well as its structure depend on the heating rate. The mass transfer process during chemical conversion due to heating will be called here the dynamics of mass transfer in capillary porous bodies.

Under the simplest assumption that chemical conversion occurs only at its front and that no reaction takes place before and behind the front, the mechanism of mass transfer dynamics will be analogous to the freezing mechanism in wet soil – known in thermophysics as the Stefan problem.

In the Stefan problem the phase transformation front (ice formation front) moves deeper into the body. Its velocity is determined by the law according to which the distance ξ of the phase transformation front from the body surface increases with time, i.e., by the shape of the $\xi = f(\tau)$ curve. In problems with phase transformation (freezing of water or melting of ice) one usually assumes that the distance ξ is a power function of time τ :

$$\xi = \beta\tau^n, \quad (2)$$

with β denoting the coefficient of penetration of a phase transformation front. The penetration velocity of a phase transformation front is

$$\frac{d\xi}{d\tau} = \beta n\tau^{n-1}. \quad (3)$$

When $n = 1$, then β is equal to the penetration velocity of a phase transformation front.

The relative quantity of liquid transformed into ice (in %) is

$$M_{\phi} = \frac{\beta}{R_0} \tau^n. \quad (4)$$

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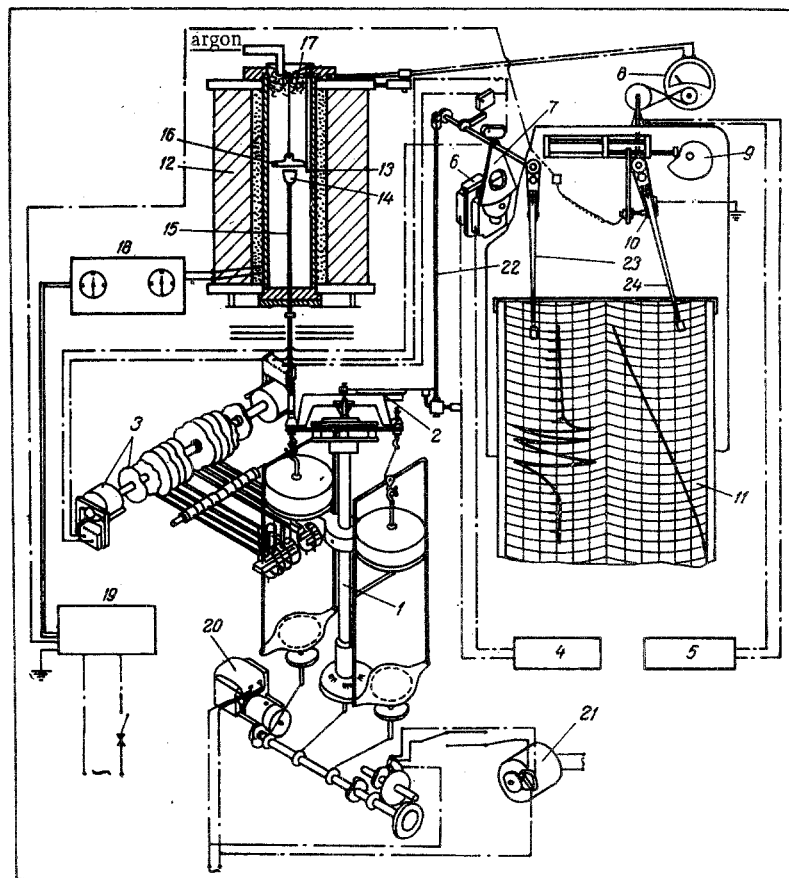


Fig. 1. Schematic diagram of the test apparatus; 1) analytical balance, 2) capacitive probe, 3) mechanism for compensating the loss of weight, 4 and 5) electronic amplifiers, 6) reversible motor, 7) gear sector, 8) capacitive millivoltmeter, 9) cam, 10) contactor of the regulating circuit, 11) temperature and weight-loss charts, 12) electrical furnace with a platinum/rhodium coil, 13) platinum-platinum/rhodium thermocouple, 14) crucible with test specimen, 15) rod of refractory material, 16) suspended lid, 17) glass wool, 18) autotransformer with voltage-tap changer, 19) electronic relay for furnace protection, 20) mechanism for recording the time, 21) synchronous motor, 22) rigid feedback coupling, 23) weight-loss recorder, 24) temperature recorder.

Here R_v denotes the ratio of volume to surface, i.e., the characteristic dimension of the body.

In the reverse problem (melting of a body) or in the problem of liquid evaporating from a capillary porous body, when liquid is removed as the evaporation front penetrates into the body (the Stefan problem), the quantity M_{ϕ} may represent the relative loss of weight due to evaporation of the liquid.

The law (2) describing the penetration of a phase transformation front does, therefore, determine the mass transfer dynamics in terms of Eq. (4). The latter applies, however, only to the simplified mechanism of phase transformation, i.e., to the "pure" Stefan problem.

We will assume that at the phase transformation front occurs not the complete but only a partial transition of a substance from one phase to another (e.g., transition of a liquid to vapor). Simultaneously with the penetration of the phase transformation front into a body at a velocity $d\xi/dt$ there occurs behind this front a phase transformation of the part of the substance which has not been transformed during the front passage through it. The mechanism of phase transformation can be described as follows: there exists a zone of phase transformation bounded on one side by the body surface and on the other side by the phase transformation front. The latter penetrates into the body according to the law $\xi = \beta\tau^n$ and behind it there

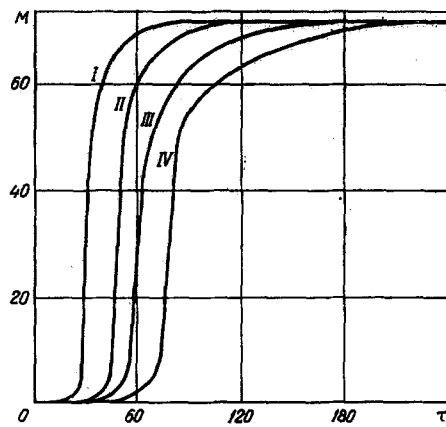


Fig. 2. Curves of the relative weight loss M (%) as a function of time τ (min); heating rate $11.2^\circ\text{C}/\text{min}$ (I), $8.32^\circ\text{C}/\text{min}$ (II), $4.17^\circ\text{C}/\text{min}$ (III), $3.67^\circ\text{C}/\text{min}$ (IV).

also occurs a phase transformation of a part of the substance. While (4) applies only within certain time intervals ($0 < \tau < \tau_{\text{end}}$), where τ_{end} is determined from the relation $\xi_{\text{end}} = R = \beta\tau_{\text{end}}^n$ (ξ_{end} denoting the maximum possible distance from the phase transformation front to the body surface, equal to half the body thickness R):

$$\tau_{\text{end}} = \sqrt[n]{\frac{R}{\beta}}, \quad (5)$$

in our case the equation of mass transfer should represent the dynamics of mass transfer over the entire period of thermal heating ($0 < \tau < \infty$). Based on the mechanism of zone penetration, the equation of mass transfer dynamics will then become

$$M_\Phi = \frac{A_\Phi \tau^n}{B_\Phi + \tau^n}, \quad (6)^*$$

with constants A_Φ and B_Φ determined from tests. In this case, as $\tau \rightarrow \infty$, we have $M_\Phi \rightarrow A_\Phi$, i.e., $(M_\Phi)_{\text{max}} = A_\Phi$. When the substance has transformed completely, A_Φ should be equal to 100% or $A_\Phi = 1$, depending on whether the relative mass transfer is measured in percent or in fractions of unity.

It is easy to show the relation between constant B_Φ and coefficient β . During the initial period, phase transformation proceeds essentially by a penetration of the phase transformation front, i.e., with phase transitions within the phase transformation zone disregarded ($B_\Phi \gg \tau^n$), Eq. (6) yields

$$M_\Phi = \frac{A_\Phi}{B_\Phi} \tau^n, \quad (7)$$

and (7) with (4) yield

$$\beta = R_v \frac{A_\Phi}{B_\Phi} = \frac{R_v (M_\Phi)_{\text{max}}}{B_\Phi}. \quad (8)$$

Consequently, the coefficient of penetration of a phase transformation front is inversely proportional to B_Φ .

We will accept this mechanism of phase transformation in a wet body for analyzing the chemical conversion in a capillary porous body during its heating. The equation of mass transfer dynamics during chemical conversion will now become

$$M = \frac{A\tau^n}{B + \tau^n}, \quad (9)$$

or

$$\frac{M}{M_{\text{max}}} = \frac{\tau^n}{B + \tau^n}, \quad (10)$$

with constants A and B determined from tests.

During the heating of a body, then, chemical conversion occurs within a certain zone; the chemical conversion zone. It is bounded by the body surface and by the chemical conversion front, the latter penetrating into the body according to the law $\xi = \beta\tau^n$. Throughout the entire heating period there occur, simultaneously with the penetration of the chemical conversion front, chemical reactions throughout the zone.

*The validity of Eq. (6) will be demonstrated in a separate article.

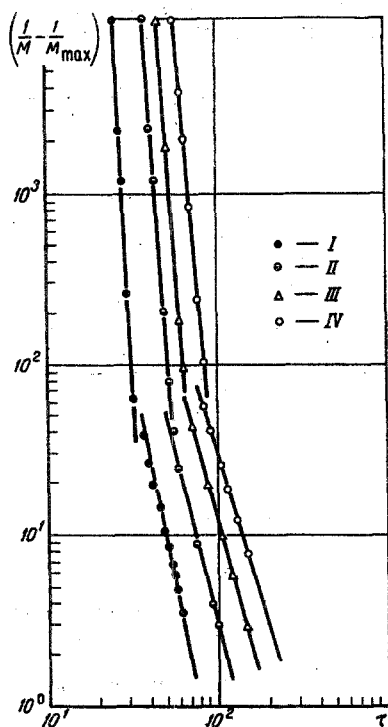


Fig. 3. Curves of $(1/M - 1/M_{\max}) = f(\tau)$; heating rate 11.2°C/min (I), 8.32°C/min (II), 4.17°C/min (III), 3.67°C/min (IV). Time τ (min).

When this zone extends to the center of the body, then conversion will occur throughout the body and the process will begin to slow down to a gradual end. During extended heating ($\tau \rightarrow \infty$) at the temperature reached by the body, therefore, conversion of the substance proceeds incompletely ($A < 100\%$). For a continuation of the process, it is necessary to raise the temperature.

The constant coefficient B and the constant exponent n in (10) can be determined from a test curve $M = f(\tau)$. Equation (10) can be rewritten as

$$\lg \left(\frac{1}{M} - \frac{1}{M_{\max}} \right) = \lg \frac{B}{M_{\max}} - n \lg \tau. \quad (11)$$

Consequently, the slope of the $\log(1/M - 1/M_{\max}) = f(\log \tau)$ curve is equal to the exponent n and its intercept on the axis of ordinates is equal to $\log B/M_{\max}$.

Constant B can be determined from the value of τ_{\max} . Indeed, the mass transfer rate is

$$\frac{dM}{d\tau} = \frac{ABn\tau^{n-1}}{(B + \tau^n)^2}. \quad (12)$$

Equating the second derivative $d^2M/d\tau^2$ to zero, we find

$$B = \frac{n+1}{n-1} \tau_{\max}^n. \quad (13)$$

Formula (13) was also used for calculating B .

The dynamics of mass transfer in capillary porous bodies was studied with the aid of a Stanton balance (built for use in a high-temperature furnace) and by continuously recording the weight-loss curves during the heating of a specimen. The Stanton apparatus, shown schematically in Fig. 1, consisted of two basic components: an analytical balance 1 with a mechanism for automatically recording the changes of weight, and an electrical-resistance furnace 12 with a programmed temperature recorder. The sensitivity of the analytical balance was 0.0005 g and its maximum weight capacity was 50 g. The vertical electrical resistance furnace 12 was cylindrical in shape, with a platinum/rhodium coil $D = 37.5$ mm in diameter and $H = 360$ mm high. The programmed temperature recorder made it possible to heat a specimen inside linearly at various rates. The heating mode was established by an appropriate setting of the cam profile 9, the cam being driven by a synchronous motor

The test specimen was placed in a crucible on a special refractory base directly coupled to the rear arm of the balance beam, and thus inserted into the furnace from underneath into a position on level with the junction of the thermocouple for measuring the furnace wall temperature. The bottom opening in the furnace was then covered with ceramic rings leaving a small clearance for the base rod. On top the furnace was carefully insulated with a set of lids hanging down and asbestos fibers. The crucible with a specimen had been balanced into an equilibrium position before the furnace was turned on, and the subsequent departure from this equilibrium position during heating was recorded on a strip chart.

In order to eliminate in our analysis any weight change due to oxidation of the original substance, or due to solid and gaseous products of reactions, as well as thermal side effects, the specimen was heated in an atmosphere of an inert gas (argon).

Curves representing the mass transfer dynamics in a capillary porous body (relative weight loss as a function of time) are shown in Fig. 2 for four different modes characterized by heating rates $b = 11.2$, 8.32, 4.17, and 3.67°C/min respectively.

The relative weight loss of material during heating will be denoted by M :

$$M = \frac{\Delta G}{G_0} \cdot 100, \quad (14)$$

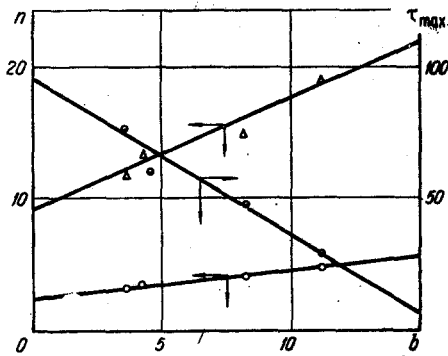


Fig. 4. Exponent n and time τ_{\max} (min) as functions of the heating rate b ($^{\circ}\text{C}/\text{min}$).

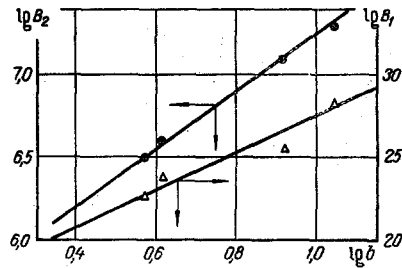


Fig. 5. Curves of $\log B = f(\log b)$.

with ΔG denoting the actual loss of material and G_0 denoting the initial weight.

It is evident here that the $M = f(\tau)$ curves are S-shaped. Therefore, the mass transfer rate $dM/d\tau$ has a maximum and these curves have knees. The time which corresponds to such an extremum will be denoted by τ_{\max} , inasmuch as the rate is now $(dM/d\tau)_{\max}$. It has been found that these extrema occur at $\tau_{\max}^I = 30$ min, $\tau_{\max}^{II} = 48$ min, $\tau_{\max}^{III} = 58.5$ min, and $\tau_{\max}^{IV} = 78$ min respectively, the superscripts here corresponding to the different heating rates. The quantity A has been defined as the asymptote of the $M = f(\tau)$ curves. According to the graph, $A = M_{\max} = 72\%$ in all four heating modes.

Curves of $(1/M - 1/M_{\max}) = f(\tau)$ are shown in Fig. 3 for these four heating modes. It is evident here that the test points lie on straight lines and, therefore, the validity of Eq. (9) has been confirmed experimentally. The graphs in Fig. 3 also clearly indicate, however, that the slope changes abruptly. This means that the exponent n changed during the heating process. When the body was heated at the rate $b = 11.2^{\circ}\text{C}/\text{min}$, for example, the exponent was $n = 19.1$ during the first 30 min ($\tau \leq 30$ min) and $n = 4.8$ after the first 30 min ($\tau > 30$ min). A similar pattern was noted in other heating modes (Fig. 3). One may assert, on this basis, that during the initial heating period ($0 < \tau < 30$ min), with the body temperature rising from 20 to 350°C , there occurred predominantly one chemical reaction of decomposition and then, at the body temperature rising from 350 to 750°C ($30 \text{ min} < \tau < \infty$), the decomposition was basically due to another chemical reaction. This transition from one chemical conversion to another is characterized by a break point on the curve or an abrupt change of the exponent n . It is quite natural that exponent n fundamentally characterizes the nature and the mechanism of conversion of a given substance but also that its magnitude depends on the heating rate b .

This is explained by the faster rise of the body temperature during heating at a higher rate.

Curves of $n = f(b)$ are shown in Fig. 4. It is evident here that exponents n_1 and n_2 are, to the first approximation, linear functions of the heating rate:

$$n_1 = 9.2 + 0.86b; \quad n_2 = 2.45 + 0.215b. \quad (15)$$

The empirical formulas (15) are equations of the straight lines in Fig. 4. It appears that the exponent is approximately four times higher for the first period of the reaction than for the second period (high temperature): $n_1/n_2 \approx 4$. At $b = 0$ the value of the exponent characterizes the rate of the chemical reaction, inasmuch as it characterizes the mass transfer rate at an infinitesimally low heating rate.

The constant B in (13), which characterizes the penetration velocity of a chemical conversion front, is a function of n and τ_{\max} , which in turn are functions of the heating rate. In Fig. 4 is also shown the $\tau_{\max} = f(b)$ curve, which indicates that, to the first approximation, τ_{\max} is a linear function of b :

$$\tau_{\max} = 96 + 6b. \quad (16)$$

Consequently, the maximum mass transfer rate for the given material is characterized by the time $(\tau_{\max})_0 = 96$ min. Inasmuch as τ_{\max} and n are functions of the heating rate, coefficient B will be a function of it too. Curves of $\log B_1 = f_1(\log b)$ and $\log B_2 = f_2(\log b)$ are shown in Fig. 5. It is evident here that the test points fit closely on straight lines which can be described by the following equations:

$$B_1 = 4 \cdot 10^{26} b^{11.2}; B_2 = 0.41 \cdot 10^{26} b^{1.65}. \quad (17)$$

Thus, B_1 is larger than B_2 by a few orders of magnitude (B_1 is of the order of 10^{23} - 10^{28} , while B_2 is of the order of 10^6). The relation between coefficients B and the heating rate can then be represented by empirical equations of the general form

$$B = B_0 b^p, \quad (18)$$

where constants B_0 and p are determined from tests. For our material $B_{01} = 4 \cdot 10^{26}$ and $B_{02} = 0.41 \cdot 10^6$.

The coefficient of penetration of chemical conversion front is

$$\beta = R_v \frac{M_{\max}}{B}. \quad (19)$$

In our case

$$\beta_1 = R_v \cdot 18 \cdot 10^{-26} b^{-11.2}; \beta_2 = R_v \cdot 176.5 \cdot 10^{-6} b^{-1.65} \quad (R_v \approx 0.125 - 0.214 \text{ cm}). \quad (20)$$

Thus, while a capillary porous body is heated, thermal decomposition is accompanied by chemical reaction: one occurs during the first period at temperatures up to 350°C and another occurs during the second period at temperatures from 350 to 750°C. In both cases the chemical conversion front penetrates into the body according to a power law, with the chemical reactions proceeding within a continuously expanding conversion zone. On the basis of the values of B_0 and n_0 or $(\tau_{\max})_0$, one can, to the first approximation, estimate physicochemically the thermal properties of a test material.

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