Note

Theoretical aspects of the application of head-space analysis to the investigation of reaction kinetics in solutions

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The monographs on head-space analysis[1,2] contain no information concerning its application to kinetic investigations, although it has been suggested that head-space analysis may be used for the determination of rate constants and reaction order[1]. However, in a recent review of modern trends in the development of head-space analysis[3], particular attention has been paid to the study of reaction systems.

A number of papers deal with the problem of the kinetics of emission of harmful volatile impurities from polymer materials. However, either simply the time dependence of the amount of volatile components evolved is recorded or only particular cases are considered in which the progress of evolution of volatile substances may be approximated by a simple exponential function.

If the term "head-space analysis" is interpreted in a broad sense[4], its should encompass also the procedure of gas chromatography with flow stop and reversal, which has been applied to the study of reactions on the surface of solid catalysts (see, *e.g.*, ref. 5). However, the investigation of the possible applications of head-space analysis to the study of the kinetics of volatile product formation in solutions is only just beginning. The first paper in this field[6] was based on the periodical sampling of vapour from the reaction mixture and empirical detector calibration according to the volatile products in the vapours above solutions of known concentrations. Nevertheless, only one example of the determination of rate constants by this method is known[7] (oxidation of mercaptans with aqueous dimethyl sulphoxide).

Preliminary communications[8,9] have been concerned with the relationships concerning discrete and continuous gas extraction of volatile products of slow liquid-phase first-order reactions in heterogeneous systems with high mass exchange rates. In this paper the consideration of the possibility of using head-space analysis for obtaining kinetic information is continued, including cases in which the attainment of the phase equilibrium is hindered and methods of calculating the rate constants.

Symbols
    $C_L(t)$ and $C_G(t)$ are the concentrations (mass-volume concentrations) of the volatile product in a liquid, L, and in a gas, G, at the time t.
    τ is the time interval (min) between the replacements of the gas phase contacting the reaction mixture.

$K = C_L/C_G$ is the partition coefficient.

$K^{(q)} = C_{Lq}/C_{Gq}$ is the concentration ratio of the reaction product in the liquid and the gas phase in the qth stage of extraction.

$B_{\tau q} = C_{G(q+1)}/C_{Gq}$ is the "dynamic buffer coefficient"[10].

V_L and V_G are the volumes of the liquid and the gas phases, respectively; $r = V_G/V_L$.

$B^{(q)} = K^{(q)}/(r + K^{(q)})$ is the buffer coefficient[10].

K_1 is the rate constant for the process of transformation of the reagent into the volatile product; $E = \exp(-K_1\tau)$.

ω is the carrier gas flow-rate (ml/min).

$V_0 = \omega t$ is the gas volume passing during time t.

C_0 is the concentration (g/ml) of the non-volatile reagent in the liquid phase before the reaction start; $a = \omega/(KV_L)$; $b = C_0^0 K_1/K$; $\rho = a/K_1$.

Repeated gas extraction of reaction mixtures

Let us consider consecutive extraction stages of the volatile product of first-order reactions in the liquid phase by identical volumes of a pure inert gas. For the first extraction ($q = 1$) the material balance equations in the above system of designations are given by

$$(K^{(1)} + r)C_{G1} = C_0^0(1 - E) \tag{1}$$

and for the following extractions ($q = 2, \ldots, n$) by:

$$(K^{(q)} + r)C_{Gq} = C_0^0 E^{q-1}(1 - E) + K^{(q-1)}C_{G(q-1)} \tag{2}$$

Here the establishment of the phase equilibrium in the system is not assumed, and if the value characterizing the contribution of the volatile component in the gas phase is introduced

$$1 - B^{(q)} = r/(r + K^{(q)}) \tag{3}$$

we obtain the expressions for the concentrations of this component after the first and the subsequent extraction stages:

$$C_{G1} = \frac{C_0^0}{r}(1 - E)(1 - B^{(1)}) \tag{4}$$

$$C_{Gq} = \frac{C_0^0}{r}(1 - E)(1 - B^{(q)})\{E^{q-1} + B^{(q-1)}[E^{q-2} + B^{(q-2)}(\ldots)]\} \tag{5}$$

$$(q = 2, \ldots, n)$$

As already mentioned[11], it is not desirable to carry out a great number of gas extractions because of the possibility of a "memory" effect of the instrumentation and the great expenditure of time. Restricting ourselves to the minimum number of extractions required for calculations, we will assume the simplest proportional

dependence between the contributions of the volatile component in the gas phase in consecutive extractions

$$1 - B^{(q)} = \alpha(1 - B^{(q+1)}) \tag{6}$$

where α is a constant characterizing the deviation of component partition between the phases from the equilibrium partition $(0 \leqslant \alpha \leqslant 1)$. Then the values of the dynamic buffer coefficients determined directly are:

$$B_{\tau 1} = C_{G2}/C_{G1} = (E + B^{(1)})/\alpha \tag{7}$$

$$B_{\tau 2} = C_{G3}/C_{G2} = \left(\frac{E^2}{E + B^{(1)}} + B^{(2)} \right) \bigg/ \alpha \tag{8}$$

$$B_{\tau 3} = C_{G4}/C_{G3} = \left(\frac{E^3}{E^2 + B^{(2)}(E + B^{(1)})} + B^{(3)} \right) \bigg/ \alpha \tag{9}$$

In order to determine the kinetic parameters by the iterative method, it is convenient to rewrite eqns. 7–9 in the forms

$$\alpha = (E + B^{(1)})/B_{\tau 1} \tag{10}$$

$$B^{(1)} = 1 - \alpha + \alpha^2 B_{\tau 2} - E^2/B_{\tau 1} \tag{11}$$

$$E = \sqrt[3]{B_{\tau 1} B_{\tau 2} [1 - B^{(1)} - \alpha^2(1 - \alpha B_{\tau 3})]} \tag{12}$$

and to assume as zero (initial) approximation that these values are equal to 0.5.

An indispensable condition of a relatively precise measurement of rate constants K_1 for a limited number of consecutive extractions is the optimum choice of duration of each extraction stage, τ. Since $E = \exp(-K_1 \tau)$, the errors in K_1 and E are related to each other by:

$$\frac{|\Delta K_1|}{K_1} = \frac{1}{|\ln E|} \cdot \frac{|\Delta E|}{E} \tag{13}$$

Hence, the precision of determination of the rate constants K_1 attainable with the experimental error, ΔE, depends on the value of E and consequently on the ratio of K_1 to τ. Thus, if $\Delta E/E \approx 0.02$ and the required precision of the determination of K_1 is $\pm 10\%$, the value of E should be equal to $\exp(-0.02/0.1) = 0.82$. This value implies that at $K_1 \approx 0.1$ the duration of each extraction stage should be approximately 2 min, at $K_1 \approx 0.01$ it should be 20 min, etc. Arbitrary choice of the time τ can lead to excessive error or can even make the calculation of the parameters impossible[8–10]. Since it is difficult to reduce manually the duration of the gas phase replacement to a few seconds, the measurements of constants for rates higher than 0.1 min^{-1} would require special automatic instrumentation. Moreover, the measurement of constants

for slow reactions ($K_1 < 10^{-3}$ min^{-1}) can be carried out only during several hours and even longer.

If the reaction rate in the liquid phase is relatively slow (in order that the phase equilibrium may be considered to be virtually established at any moment of time) then $\alpha \approx 0$ and in this case, which has been considered previously[8], equations of the type 4 and 5 can be written in the form:

$$B_{\tau n} = B + E \left[\sum_{q=0}^{n-1} (B/E) \right]^{-1} \tag{14}$$

Since at $n \to \infty$ the sum contained in this equation acquires the value of ∞ at $(B/E) \geqslant 1$ and at $(B/B) < 1$ becomes equal to $[1 - (B/E)]^{-1}$, it is evident that with increasing extraction number the value of the dynamic buffer coefficient, $B_{\tau n}$) decreases, tending in the limit to the larger of the numbers B or E.

In order to determine parameters E and B, only the data on the first three extractions, *i.e.*, the values of $B_{\tau 1}$ and $B_{\tau 2}$ may be used. Indeed, eqns. 7 and 8 become

$$B_{\tau 1} = B + E \tag{15}$$

$$B_{\tau 2} = B + E^2/(B + E) \tag{16}$$

and

$$\left.\begin{array}{l} E/B_{\tau 1} \\ \text{and} \\ B/B_{\tau 1} \end{array}\right\} = 0.5 \pm \sqrt{(B_{\tau 2}/B_{\tau 1}) - 0.75} \tag{17}$$

The values of E, *i.e.*, the desired reaction rate K_1 proper, and B, *i.e.*, the partition coefficient K, may be found if $1 > B_{\tau 2}/B_{\tau 1} \geqslant 0.75$. However, it is impossible to determine which of the roots in eqn. 17 refers to E and which refers to B without supplementary information. This information may be provided by repeated experiments at a different extraction time, τ, other conditions being equal (when the value of E will vary) or at a different ratio of the phase volumes, r (when the value of B will vary).

Continuous gas extraction of the reaction mixtures

The change in the concentration of the volatile product of chemical liquid-phase reaction which is entrained by an inert gas passing above the liquid (or through it) is described by a linear non-homogeneous differential equation[8]:

$$\frac{dC_G}{dt} = -aC_G + be^{-K_1 t} \tag{18}$$

As a result of the differentiation of eqn. 18 over t and exclusion of b we have:

$$\frac{d^2 C_G}{dt^2} + (a + K_1) \frac{dC_G}{dt} + (aK_1)C_G = 0 \tag{19}$$

It is known that to solve eqn. 19 it is necessary to find the roots of the supplementary quadratic equation:

$$\lambda^2 + (a + K_1)\lambda + (aK_1) = 0 \tag{20}$$

The roots of eqn. 20 are evidently $-a$ and $-K_1$. If a and K_1 are real values and $a \neq K_1$

$$C_G(t) = C_1 e^{-at} + C_2 e^{-K_1 t} \tag{21}$$

where C_1 and C_2 are integration constants. In the case when $a = K_1$, we have:

$$C_G(t) = (C_1 t + C_2)e^{-at} \tag{22}$$

In combination with the initial condition $C_G(0) = 0$, eqns. 21 and 22 become, respectively:

$$C_G(t) = \frac{b}{K_1 - a}(e^{-at} - e^{-K_1 t}) \tag{23}$$

$$C_G(t) = bte^{-at} \tag{24}$$

The form of the corresponding functions is shown in Fig.1. Both curves exhibit a maximum at t_m and an inflexion at $t_b = 2t_m$. The values of t_m and t_b may prove to be useful for increasing the precision of the time-scale and for the establishment of the initial moment of time, $t = 0$ (moment of the start of chemical interaction). For example, it is important in the case when the moment of introduction of the reagent into the chromatographic system does not coincide with that of the beginning of its interaction with the other reactants or with the catalyst. Moreover, since at $a \neq K_1$ we have $t_m = \ln\rho/K_1 (\rho - 1)$ and at $a = K_1$ we have $t_m = 1/a$, it is evident that if one of the constants, a or K_1, is known, it is possible to calculate the other constant by using the value of t_m.

It follows from ref. 12 that eqns. 23 and 24 are the solutions of the homogeneous difference second-order equation
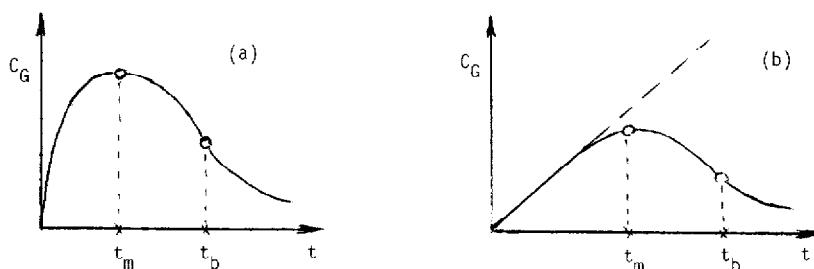
$$C_G(t + 2) + pC_G(t + 1) + qC_G(t) = 0 \tag{25}$$

Fig. 1. Dependence of $C_G(t)$ according to eqns. 23 (a) and 24 (b).

with the initial condition $C_G(0) = 0$. Moreover:

$$\left.\begin{aligned}-p &= \exp(-K_1) + \exp(-a) \\ q &= 1/\exp(K_1 + a)\end{aligned}\right\} \tag{26}$$

The coefficients p and q can be calculated from the experimental data for $C_G(t)$ by the least-square method (as linear regression coefficients). As the sum and the products of the values $\exp(-K_1)$ and $\exp(-a)$ are known, the constants K_1 and a can easily be determined. For the experimental data $C_G(0) = 0$, $C_G(\Delta t)$, $C_G(2\Delta t)$, ... with equal intervals between the measurements of $\Delta t \neq 1$, eqn. 25 becomes:

$$C_G(t + 2\Delta t) + pC_G(t + \Delta t) + qC_G(t) = 0 \tag{27}$$

Now the values of p and q are expressed by equations similar to eqn. 26:

$$\left.\begin{aligned}-p &= \exp(-K_1\Delta t) + \exp(-a\Delta t) \\ q &= 1/\exp[(K_1 + a)\Delta t]\end{aligned}\right\} \tag{28}$$

In practice the value of C_G is usually replaced by that of $H(t)$ proportional to it: this is the height or the surface area of the chromatographic peak representing the product content in the gas phase at the time t.

The first two points should be borne in mind. First, if it is not known which of the parameters, K_1 or a, is larger, eqns. 25 and 28 cannot be uniquely identified with the roots of K_1 and a. In these cases it is necessary to use additional information from experiments carried out under different conditions (temperature, gas flow-rate, etc.). Secondly, the "restoration" of the parameters K_1 and a in eqns. 23 and 24 is possible only if the experimental data for $H(t)$ are sufficiently precise[12].

In order to establish the effect of random errors in chromatographic measurements (peak heights or areas), a computer simulation of experiments was carried out. It consisted of two stages: (1) On the basis of the initial values of b, K_1 and a, the value of $H(t)$ was calculated according to eqn. 23 and using the random number generator a random error was introduced into this value. This error corresponded to the standard deviation of 2% consistent with the possibilities provided by the gas chromatograph. (2) The values of $H(t)$ obtained in this manner were used to "restore" the desired parameters K_1 and a by the above procedure. Among cases with $\rho > 1$, such cases were considered in which t_m ranged from 5 to 10 min. It is in this range of t_m that the results of this restoration are most uncertain *a priori*.

Table I gives the results of the application of this method of determining the parameters K_1 and a from the data on $H(t)$ with a relative error of 2%. Each ine of the table contains the results of the treatment of 6–12 computer simulations. In each simulation, up to 22 points were taken into account. It is seen that at $\rho = 2$ the restoration of the values of both parameters was observed for all Δt intervals, whereas at $\rho \geqslant 10$ it was usually possible to obtain a reliable value only for the smaller parameter. In order to explain this fact, let us analyze the equation of errors for the value of $H_m = H(t = t_m)$ determined by the relation

$$H_m = CK_1\rho^{1/(1-\rho)}$$

TABLE I

VALUES OF THE PARAMETERS K_1 AND a FROM THE RESULTS OF 6–12 COMPUTER SIMULATIONS

Initial data					Results of calculations	
$K_1 \cdot 10^{-3}$ (min^{-1})	a (min^{-1})	ρ	t_m (min)	t (min)	$K_1 \cdot 10^{-3}$ (min^{-1})	a (min^{-1})
5	0.5	100	9	10	4.93	—
				5	4.82	—
				2	3.7	0.61
10	1.0	100	5	10	9.97	—
				5	9.92	—
				2	9.2	—
10	0.5	50	8	10	9.9	—
				5	9.8	—
				2	8.3	0.56
50	0.5	10	5	10	49.9	—
				5	49.5	—
				2	49.4	0.57
50	0.2	4	9	10	49.9	0.20
				5	49.3	0.22
				2	52	0.21
100	0.2	2	7	10	98	0.21
				5	99	0.22
				2	97	0.24

where C is a constant

$$\frac{\Delta H_m}{H_m} = \frac{\Delta K_1}{K_1} + \varphi(\rho)\frac{\Delta \rho}{\rho} \tag{29}$$

where $\varphi(\rho) = (1 - \rho)^{-2}(1 - \rho + \rho\ln\rho) \in [0 + 1]$

In the cases considered here $\Delta H_m/H_m = 0.02$ and evidently:

$$\frac{\Delta \rho}{\rho} = \frac{\Delta K_1}{K_1} = \frac{\Delta a}{a} \leqslant \frac{1}{\varphi(\rho)}\left(\frac{\Delta H_m}{H_m} + \frac{\Delta \rho}{\rho}\right) \tag{30}$$

The relative error in the larger constant a is determined from eqn. 30: since $1/\varphi(\rho)$ greatly increases with ρ, the value of $(\Delta a/a)$ also increases with ρ. As a result of this increase, the smaller of the roots $\exp(-K_1)$ and $\exp(-a)$ becomes (as a rule at $\rho \geqslant 10$) negative and it is impossible to restore the values of both parameters from the data for $H(t)$ by the non-iterative method.

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