

# Critical comments on the measurement of equilibrium data by chromatographic method\*

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The method for evaluating thermodynamic data from the temperature dependence of retention time of the chromatographic elution curves in a system gas (vapour)—solid phase is analyzed. The applicability limits of the chromatographic method have been assigned and it is shown how under rather non-equilibrium conditions the first statistical moment of a chromatographic elution curve depends on the diffusion coefficient of the investigated component of adsorbent, grain size of adsorbent, and resolution power of the measuring system.

Обсуждается метод оценки термодинамических данных, полученных на основе температурной зависимости времен задержки проявительных хроматографических кривых в системе газ (пар)—твердая фаза. Приводится интервал применимости хроматографического метода и показывается, каким образом в условиях, сильно удаленных от равновесных, зависит первый статистический момент проявительной хроматографической кривой от коэффициента диффузии исследуемого компонента в адсорбенте, далее от величины зерен адсорбента и от разрешающей способности измерительной системы.

The methods of gas chromatography are currently used for the measurement of thermodynamic quantities in the gas—liquid systems [1]. A great many papers are concerned with the measurement of the Henry constants and adsorption heats in gas—solid phase systems. In this respect, the studies of *Kiselev* and co-workers [2] are the most renowned. On the other side, it is pointed out that considerable differences between the values of equilibrium quantities obtained chromatographically and those obtained by other methods occur in some cases [3]. These discrepancies are supposed to be connected with the kinetic effects arising in chromatographic column. For instance, *Kiselev* claims [4] that the condition of a good agreement between the heats measured calorimetrically and those obtained chromatographically necessitates the existence of sufficiently narrow and symmetrical peaks. It is worth noticing that the difference between the dynamical and statistical capacity of adsorption bed which is well known in the dynamics of adsorption beds corresponds to this variance.

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Recently, a basic contribution to the theory of chromatography and measurement of physical constants by chromatographic techniques was represented by the so-called moment method. A survey of some applications of the moment method has been given in a review [5]. From the results obtained independently by several authors it follows that the first statistical moment of elution curve or frontal chromatographic curve depends, in general, only on the structural and equilibrium characteristics of the system and is independent of kinetic quantities.

Therefore, there is a question as to the responsibility for this inconsistency of theoretical conclusions with experimental results consisting in the fact that the corresponding values of the Henry constants obtained by chromatographic measurements are smaller than those obtained by static measurements [6] provided the chromatographic measurements have been performed with a system in a rather non-equilibrium state.

This study is an attempt to present a semiquantitative interpretation of the above-mentioned phenomenon on the basis of an approximate solution of the problem of adsorbate diffusion into adsorption grains.

### Theoretical and discussion

In a recent paper [7] the relationships between the moments of chromatographic curves and the moments of the kinetic curves measured on a sample of packing of chromatographic column were derived for linear adsorption isotherm. (In this case the kinetic curve represents a time function  $\gamma(t)$  of the relative saturation of adsorption grains at a step change in the concentration of adsorbate on the external surface of adsorption grains [8].) For instance, for the second statistical moment of a chromatographic curve we obtain the expression

$$\mu_2 = 2\mu'_1 \lambda_1, \quad (1)$$

where  $\mu'_1$  is the first normal statistical moment of elution curve giving the position of the centre of gravity of the chromatographic peak,  $\mu_2$  is the second central moment of elution curve characterizing the width of this curve, and  $\lambda_1$  is the first statistical moment of kinetic curve. For some types of adsorbent, e.g. zeolite, the first statistical moment of chromatographic curve may be written in the form

$$\mu'_1 = (\mu'_1)_V + (\mu'_1)_S + (\mu'_1)_A, \quad (2)$$

where  $(\mu'_1)_V$  is the mean residence time of a molecule of adsorbate in the dead volume of column,  $(\mu'_1)_S$  is the mean residence time of a molecule of adsorbate on the external surface of the microcrystals of zeolite. This surface is not always negligible [9]. The symbol  $(\mu'_1)_A$  stands for the mean residence time of a molecule in the volume of microcrystals which may be expressed by the following relationship

$$(\mu'_1)_A = \frac{z}{u} K_\gamma \frac{1 - \alpha}{\alpha} \quad (3)$$

where  $z$  is the length of column,  $u$  is the linear velocity of carrier gas,  $\alpha$  is the so-called external porosity of bed, i.e. the fraction of the total volume of bed corresponding to the volume outside microcrystals, and  $K_\gamma$  is a constant characterizing the equilibrium gas—solid phase provided the adsorption isotherm is linear.

Let us assume that we have performed a kinetic experiment, i.e. we have found the corresponding kinetic curve characterized by the quantity  $\lambda_1$  and on the other

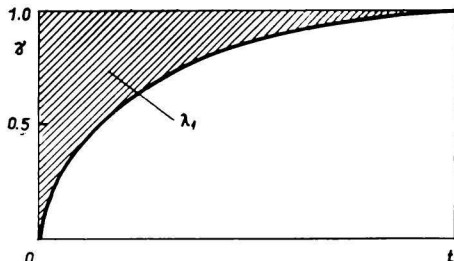


Fig. 1. Kinetic curve in  $\gamma$  vs.  $t$  coordinates. The hatched area represents the value of the first statistical moment of kinetic curve  $\lambda_1$ .

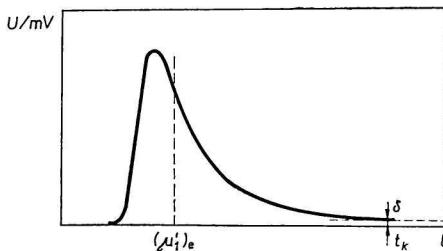


Fig. Elution chromatographic curve in  $U$  (deflection of recorder) —  $t$  coordinates.

$(\mu'_1)_e$  is the first statistical moment of elution curve found experimentally,  $\delta$  is the noise level, and  $t_k$  is the longest period of time after which it is still possible to separate the signal from the noise.

side, we have carried out the corresponding chromatographic experiment (Fig. 1 and 2). The quantity  $\lambda_1$  is given by the area limited by the curve  $\gamma(t)$ , axis of ordinates, and straight line  $\gamma = 1$ . The chromatographic experiment is characterized by the first statistical moment found experimentally  $(\mu'_1)_e$  (the experimental character of this values is denoted by index e) as well as the period of time  $t_k$  corresponding to the maximum time after which the contribution of signal from the base-line noise can be separated. In principle, the value of this quantity is given at the respective sensitivity by the noise level  $\delta$ . The least value of signal  $U(t)_{\min}$  which we are able to distinguish is given by the relation  $U(t)_{\min} > \delta$ .

Let us suppose that the scales of kinetic and chromatographic experiments are quite different so that it holds

$$\lambda_1 \gg t_k. \quad (4)$$

Because of this condition it seems logical that all processes occurring in the column can manifest themselves in a chromatographic signal only provided they are in operation in the time interval  $\langle 0, t_k \rangle$ . From this reasoning it follows that the shape of the concentration profile penetrating into microcrystals must be taken into account until the time  $t = t_k$ . If we solve the diffusion into the particles by using the form of the solution with moving boundary of zero concentration which is consistent with reality (see e.g. [10]) at the time  $t = t_k$ , we get a core inside the particle which is practically free of adsorbate and may be regarded as inert from the aspect of adsorption chromatography (Fig. 3). By modifying this problem for the diffusion into a spherical particle we obtain the following expression for the position of the boundary between zero concentration and non-zero concentration at the time  $t = t_k$

$$q(t_k) = R - \sqrt{\frac{D_{\text{eff}} t_k}{12}}, \quad (5)$$

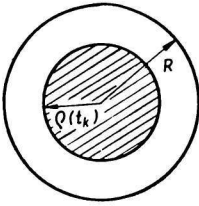


Fig. 3. Schematic picture of a spherical particle of sorbent with the radius  $R$  when the concentration profile penetrates inwardly.

$\rho(t_k)$  denotes the position of the boundary between zero and non-zero concentration at the time  $t = t_k$ .

where  $\rho(t_k)$  stands for the distance between this boundary and the centre of particle. By using this relation we may express the degree of accessibility  $\xi$  of the particles of adsorbent. Then  $[(\mu'_1)_a]_e$  assumes the form

$$[(\mu'_1)_a]_e = \frac{z}{u} K_\alpha \frac{1 - \alpha}{\alpha} \xi, \quad (6)$$

where in case of spherical particles  $\xi$  is given by the expression

$$\xi = 1 - \left( \frac{\rho(t_k)}{R} \right)^3 \quad (7)$$

For microcrystals having the shape of spherical particles eqn (6) may be rewritten by using expressions (5) and (7) and it appears that

$$[(\mu'_1)_a]_e = \frac{z}{u} K_\alpha \frac{1 - \alpha}{\alpha} \left\{ 1 - \left[ 1 - \sqrt{\frac{D_{\text{eff}} t_k}{12R^2}} \right]^3 \right\}. \quad (8)$$

In an analogous way we can obtain the following expression for the particles of adsorbent in the form of infinite plate

$$[(\mu'_1)_a]_e = \frac{z}{u} K_\alpha \frac{1 - \alpha}{\alpha} \sqrt{\frac{D_{\text{eff}} t_k}{12R^2}}. \quad (9)$$

This expression is easier to discuss. It is obvious that the greater the coefficient of diffusion and the smaller the size of microcrystals (for plate  $R$  is the half-width while for spherical particle  $R$  is the radius), the greater is the contribution of the moment  $[(\mu'_1)_a]_e$  found experimentally. Moreover, from the above expression it is also apparent how difficult the interpretation of chromatographic data is in these cases. The adsorption heats found chromatographically are evaluated from the temperature dependence of the first statistical moment of chromatographic peak. It ensues from eqn (9) that not only the temperature dependence of  $K_\alpha$  but also the temperature dependence of the diffusion coefficient  $D_{\text{eff}}$  is involved in the temperature dependence of  $[(\mu'_1)_a]_e$ . The above expressions are valid for the periods of time  $t_k < t_0$ , where  $t_0$  is the time at which  $\rho(t_0) = 0$ . Hence it holds

$$\sqrt{\frac{D_{\text{eff}} t_0}{12}} = R \quad (10)$$

and explicitly

$$t_0 = \frac{12R^2}{D_{\text{eff}}}. \quad (11)$$

In this range, *i.e.* for

$$t_k < \frac{12R^2}{D_{\text{eff}}} \quad (12)$$

the moment  $[(\mu'_1)_a]_e$  also depends on the resolution power of measuring system because  $t_k$  is some function of the level  $\delta$ . Therefore it may be written

$$t_k = f(\delta). \quad (13)$$

On the basis of this reasoning we cannot recommend to use the chromatographic measurements performed under rather non-equilibrium conditions for the evaluation of equilibrium data. On the other side, we may assume that the conditions for the evaluation of equilibrium constants are fulfilled provided  $t_k > t_0$  because in this case  $\xi = 1$  and  $[(\mu'_1)_a]_e$  is equal to the theoretical value.

In conclusion we should like to point out that the chromatographic measurements even under such non-equilibrium conditions when the term  $(\mu'_1)_a$  in the equation expressing  $(\mu'_1)_e$  quite vanishes are of some importance because they enable us to obtain some information on the adsorption taking place on the surface of microcrystals which is otherwise hardly available.

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