

STUDY OF A MODEL OF HETEROGENEOUS ISOTOPE EXCHANGE KINETICS BY COMPUTER*

By

G. TÓTH and F. GALINA

Department of Chemical Technology, Technical University Budapest

Received June 18, 1975

Presented by Ass. Prof. Dr. I. Szebényi

In connection with the kinetics of isotope exchange taking place on a solid/liquid interface, several authors [1–6] have described the relationship $(1 - F)$ vs. t , linearizable in the log-log system. Exchange kinetics deviating from the first order have been attributed to the energetic inhomogeneity of the solid surface, and it was assumed that the linear relationship $\log(1 - F)$ vs. $\log t$ is the result of the superposition of several simultaneous first-order processes. No direct proof confirming this assumption is, however, at disposal. Such proof would need the knowledge of the energetic distribution function, namely activation energy vs. number of surface sites. In possession of this function, on the one hand, the question could be decided what $(1 - F)$ vs. t relationship results from the superposition of the elementary first-order processes for the given distribution function, and on the other hand, the activation energy of isotope exchange could be calculated from the relationship describing the time dependence of the exchange fraction.

On principle, the energetic distribution function can be calculated from differential heats of adsorption. However, functions obtained in this manner would be distorted, owing to the attraction or repulsion forces exerted onto each other by the adsorbed particles, since differential heats of adsorption can only be measured at varying coverage. In addition, even distribution functions calculated from such differential heats of adsorption are rather rare.

Consequently, the energetic distribution function characterizing some given solid surface can be determined indirectly only: some distribution function is assigned arbitrarily to the surface, the surface is imaginarily divided into monoenergetic compartments, activation energies and first-order rate constants, resp., are assigned to the individual compartments on the basis of the chosen distribution function, and the relationship $(1 - F)$ vs. t resulting from the superposition of all first-order processes is studied. In case that this relationship — in agreement with many experimental data — can be linearized in the log-log system, this may be considered as a proof that the arbitrarily

* Dedicated to Prof. G. Schay on the occasion of his 75th birthday.

chosen energetic distribution function does in fact characterize the solid surface in question. The problem essentially consists in computerized evaluation of the equation

$$(1 - F) = \sum_{i=1}^{i=n} \frac{1}{n} (1 - F)_i = \sum_{i=1}^{i=n} \frac{1}{n} e^{-k_i t}, \quad (1)$$

In the present paper we wish to report some results of this type.

Characterization of the studied model of isotope exchange kinetics

The model on which our computations were based is characterized by the following features:

(i) Only the external surface layer of the solid phase participates in the exchange process.

(ii) The energetic inhomogeneity of the solid surface, i.e. activation energy change in dependence on the number of surface sites is of the Freundlich type:

$$E_i^{\ddagger} = E_0^{\ddagger} - \Omega \cdot \ln(1 - F)_i. \quad (2)$$

(iii) On compartments imaginarily formed from surface sites with identical or closely similar activation energies, the exchange process can be described by a first-order rate equation:

$$(1 - F) = e^{-k_i t} = e^{-A \cdot e^{-E_i^{\ddagger}/RT} \cdot t} \quad (3)$$

(iv) The exchange process is not diffusion-controlled.

(v) In the moment $t = 0$, only the surface of the solid phase contains the radioactive tracer, i.e. when $t = 0$, $(1 - F) = 1$.

To set up the system of equations (1), we imaginarily divided the surface into n monoenergetic compartments equal in size, and arranged them in the order of increasing activation energy (i.e. decreasing rate constant):

No. of compartment i	$1, 2, 3, \dots, n$
Activation energy E_i^{\ddagger}	$E_1^{\ddagger}, E_2^{\ddagger}, E_3^{\ddagger}, \dots, E_n^{\ddagger}$
Rate constant k_i	$k_1, k_2, k_3, \dots, k_n$

Activation energies were assigned to the individual monoenergetic compartments by means of Eq. (2a):

$$E_i^{\ddagger} = E_0^{\ddagger} - \Omega \ln \left(1 - \frac{i}{n} \right) \quad (2a)$$

where n is the number of compartments and i their serial number. Some examples for the relationship $(E_i^{\ddagger} - E_0^{\ddagger})$ vs. $(1 - F)$ calculated according to Eq. (2) are shown in Fig. 1.

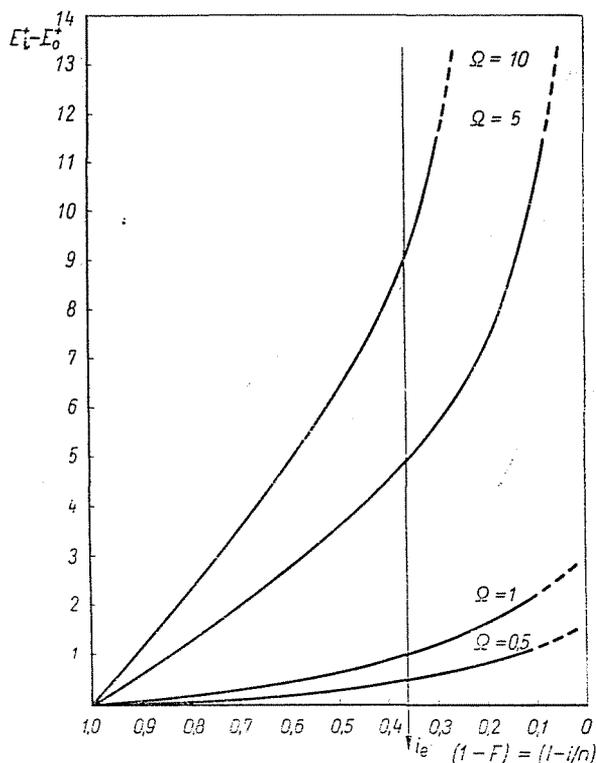


Fig. 1. Relationship $E_i^+ - E_0^+$ vs. $(1 - F)$ calculated according to Eq. (2) for $\Omega = 10, 5, 1$ and 0.5

In connection with the constants E_0^+ and Ω in Eq. (2) we wish to note here that they are energy-type quantities whose physical meaning will be discussed later.

The relationship between the activation energy E_i^+ belonging to the individual compartments and the rate constant k_i , according to the Arrhenius equation, is

$$k_i = A \cdot e^{-E_i^+/RT} \delta \quad (4)$$

The distribution function of the rate constants is obtained from Eqs (2a) and (1):

$$k_i = k_0 \left(1 - \frac{i}{n}\right)^{\Omega/RT} = A \cdot e^{-E_0^+/RT} \cdot \left(1 - \frac{i}{n}\right)^{\Omega/RT} \quad (5)$$

Examples for this relationship are shown in Fig. 2.

While k_0 is the rate constant belonging to the monoenergetic compartment with the serial number $i = 0$, Ω is the activation energy difference

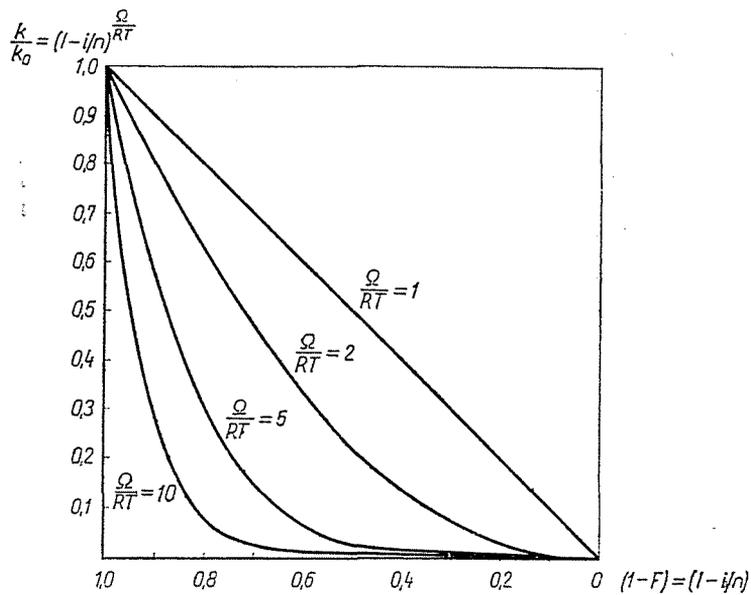


Fig. 2. Relationship k_i vs. $(1-F)$ calculated according to Eq. (5)

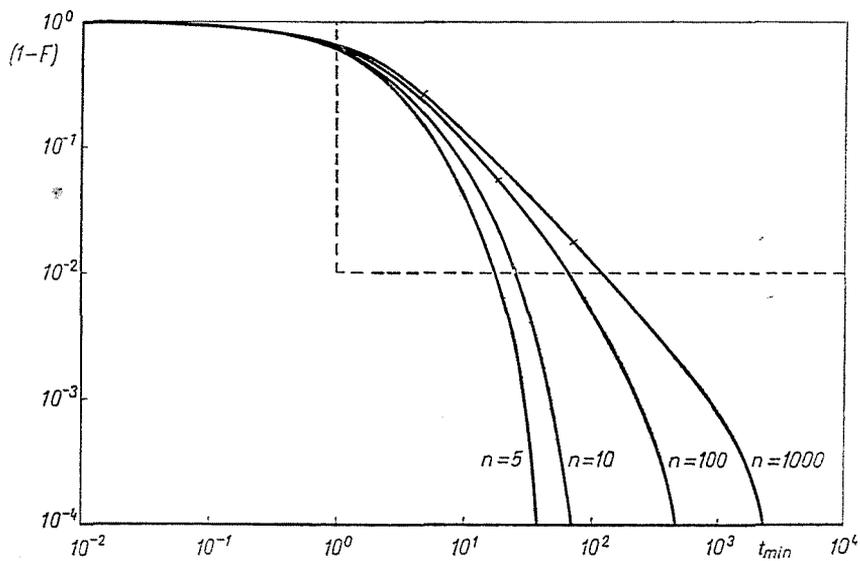


Fig. 3. Relationship $\log(1-F)$ vs. $\log t$ for $k_0 = 1$, $\Omega/RT = 1$ and different values of n

between the compartments $i = 0$ and $i = 0.632 n$. This can readily be understood by considering that there must exist one compartment for which

$$\frac{1}{1 - \frac{1}{n}} \approx 2.71 \approx e \quad (6)$$

is a good approach. The rate constant belonging to this compartment i_e is, according to Eq. (5),

$$k_{i_e} = A \cdot e^{-E_i^+/RT} \cdot e^{\Omega/RT} = A \cdot e^{-(E_i^+ - \Omega)/RT} \quad (7)$$

For the case when $E_0^+ = 0$, Ω directly yields the activation energy belonging to the compartment i_e :

$$k_{i_e} = A \cdot e^{-\Omega/RT} \quad (7a)$$

By substituting the k_i values into Eq. (3), we arrive to the system of equations

$$(1 - F) = \frac{1}{n} \sum (1 - F)_i = \frac{1}{n} \sum_{i=0}^{i=n-1} e^{-k_i t} = \sum_{i=0}^{i=n-1} e^{-k_0 \cdot (1 - \frac{i}{n}) \Omega/RT} \quad (3a)$$

The results of the computerized solution of this system of equations are given in the followings.*

Results

The relationship $\ln(1 - F)$ vs. $\ln t$ has been calculated by utilizing Eq. (3a) in the following manner: two of the three variables n , k_0 and Ω/RT were kept constant and the third was varied. The results obtained with $k_0 = 1$ and $\Omega/RT = 1$ at a varying number of components are presented in Fig. 3. The exchange time/exchange fraction region belonging to exchange times exceeding 1 minute and exchange fraction $(1 - F)$ exceeding 0.01, i.e. the region that can usually be investigated by normal measuring techniques is marked with dash lines. The portions of the curves where linearity is better than 1% are marked by———.

* In Eq. (3a), summation was carried out from $i = 0$ to $i = n - 1$. Hence the rate constant of the first compartment is equal to k_0 . Had the summation been performed from $i = 1$ to $i = n$, the rate constant of the last component would have been $k_n = k_0 \cdot \left(1 - \frac{n}{n}\right) = 0$ and therefore the value $\ln(1 - F)$ belonging to the exchange time t would have exceeded the true value by $\ln \frac{1}{n}$.

Fig. 4 presents the curves for $n = 100$ and $k_0 = 1$, with Ω/RT values varying, while Fig. 5 shows $\log(1 - F)$ vs. $\log t$ curves for $n = 100$, $\Omega/RT = 5$ and varying values of k_0 .

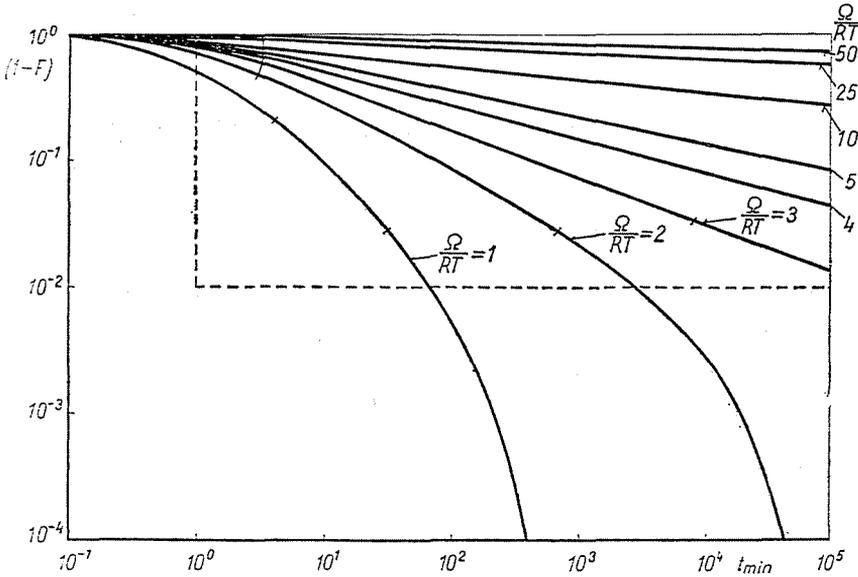


Fig. 4. Relationship $\log(1 - F)$ vs. $\log t$ for 100 components ($n = 100$), $k_0 = 1$, and different values of Ω/RT

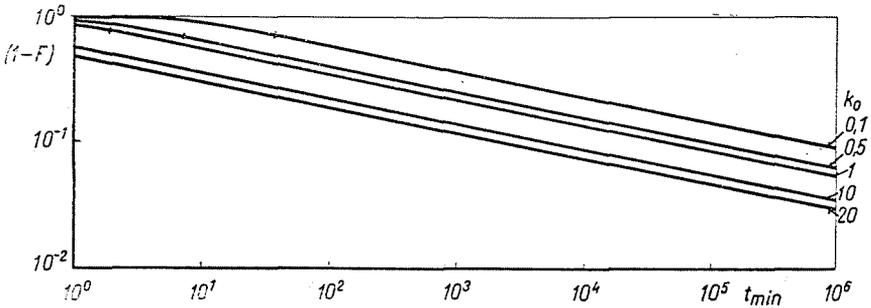


Fig. 5. Relationship $\log(1 - F)$ vs. $\log t$ for 100 components ($n = 100$, $\Omega/RT = 1$, and different values of k_0)

Discussion

The curves in Fig. 3 demonstrate that the relationship $\log(1 - F)$ vs. $\log t$, calculated on the basis of Eq. (3a), contains a linear portion already with $n = 100$ and $\Omega/RT = 1$. With increasing n , the length of the linear portion increases.

The curves in Fig. 4 show that the slope of the linear portions is identical with RT/Ω . Some data are listed in Table I.

Table I

$\frac{d \ln(1-F)}{d \ln t} = \gamma$	$\frac{\Omega}{RT}$	$(-\gamma) \cdot \frac{\Omega}{RT}$
-0.02	50	1.00
-0.04	25	1.00
-0.10	10	1.00
-0.20	5	1.00
-0.25	4	1.00
-0.33	3	1.00

According to the data in Table I, the straight portions of the $\log(1-F)$ vs. $\log t$ functions can be described by the equation

$$\ln(1-F) = -\frac{RT}{\Omega} \ln t + \ln(1-F)_{t=1}, \quad (8)$$

that is, the slope of the straight portions is unequivocally related to the constant Ω in Eq. (2), the Freundlich equation describing energetic inhomogeneity.

Since $\ln(1-F)_{t=1}$, i.e. the exchange fraction corresponding to unit time can be expressed with the aid of k_0 and $\frac{RT}{\Omega}$ *:

$$\ln(1-F)_{t=1} = -\frac{RT}{\Omega} \ln k_0, \quad (9)$$

the following equation is obtained from Eqs (8) and (9) for the time dependence of the exchange fraction:

$$\ln(1-F) = -\frac{RT}{\Omega} \ln k_0 + \ln t. \quad (10)$$

This equation only contains, besides RT , the constants k_0 and Ω of Eq. (5).**

* It may be seen from Fig. 5 that in the case of $k_0 < 1$, extrapolation of the straight portions of the functions $\ln(1-F)$ vs. $\ln t$ to $t=1$ yields $\ln(1-F)_{t=1}$ values exceeding zero and $(1-F)_{t=1}$ values exceeding 1. We wish to note that $(1-F)$ values exceeding 1 cannot be interpreted in the original sense, since it follows from the definition of the exchange fraction that its value changes between 0 and 1. None the less, $\ln(1-F)_{t=1}$ values obtained by extrapolation to $t=1$ are suitable for the calculation of $\ln k_0$ in this case too.

** A deviation was observed from Eq. (10) in the value of about $\ln(1-F) = 0.04$, insofar as the straight portions extrapolated to $t=1$ yielded, for large values of Ω/RT and $k_0 = 1$, $\ln(1-F) = -0.04$ instead of zero. This deviation is attributable to the limited digit range of the applied computer.

We wish to point out another relationship existing between $\frac{RT}{\Omega}$, k_1 and k_0 , obtained by expanding in series the right-hand-side of the relationship valid, according to Eq. (5), for the first monoenergetic compartment:

$$k_1 = k_0 \left(1 - \frac{1}{n}\right)^{\Omega/RT}. \quad (5a)$$

This will result in the relationship

$$\frac{RT}{\Omega} = \frac{k_0}{(k_0 - k_1)n} \quad (11)$$

demonstrating that the slope of the linear portions of the function $\ln(1 - F)$ vs. $\ln t$ is directly proportional to k_0 , and inversely proportional to the difference between the rate constants belonging to the first two compartments and to the number of components.

Eq. (10) allows to calculate, from the experimentally determined relationship $(1 - F)$ vs. t , either Ω or k_0 values. We wish to note that in the present work, we did not take into account the effect of the concentration of the exchanged components on exchange rate. This problem shall be considered in subsequent work, as well as the question whether a linear relationship between $\ln(1 - F)$ and $\ln t$ can come about in the case of other (e.g. Temkin-type) energetic inhomogeneity.

Summary

A model for the kinetics of heterogeneous isotope exchange was established by dividing the solid surface imaginarily into monoenergetic compartments of equal size, and assigning rate constants to the individual compartments according to the Freundlich type energetic inhomogeneity.

The function resulting from the superposition of the numerous first-order rate equations was evaluated by computer. It was found that the obtained function $(1 - F)$ vs. t is linearizable in the log-log system.

We established a relationship between the slopes and axis intercepts of the linear portions and the constants in the Freundlich equation describing energetic inhomogeneity.

References

1. HAISSINSKY, M., COTTIN, M., VARJABEDIAN, B.: *J. Chim. Phys.* **45** (1948) 212.
2. FARKAS, J., Gy. NAGY, L., VARSÁNYI, Gy.: *Period. Polytechn. Chem. Eng.*, **13**, (1969) 297.
3. MILLER, J.: *Isotopenpraxis*, **6**, (1970), 345.
4. ATKINSON, R. J., POSNER, A. M., QUIRK, J. P.: *J. Inorg. Nucl. Chem.*, **34** (1972). 2201.
5. TÓTH, G.: *Radiochim. Acta*, **19** (1973) 62.
6. TÓTH, G.: *Radiochim. Acta*, **17** (1972) 12.

Dr. Géza TÓTH }
Ferenc GALINA } H-1521 Budapest