RESULTS AND DISCUSSION

The experiments were carried out with cerium phosphate /CeP/ and arsenate /CeAs/ samples characterized in the previous paper[2].

The ions were selected concerning their places in the periodic table of the elements.

In Fig.1. the results obtained the HCl solutions at various concentrations, and in Fig.2. the results obtained in NH_4Cl solution at various concentrations are shown. Comparing the Pauling's ionic radii values with the crystal lattice size it was found that it has no influence on the ion exchange process[2]; this fact may be verified by the equilibrium data too.

As it can be seen in the figures a change in the ion concentration has no influence on the position of the equilibrium, there is practically no difference between the times to reach the equilibrium at various ion concentrations /10^{-1}M and 5×10^{-3}M/.

The same statement is valid for the solution concentrations too.

In all cases it was found that the exchange process is very fast. At the given conditions of the experiments the equilibrium was attained within two hours /maximum/ in a single-step process. These data may be useful for the further experiments concerning the ion-exchange properties of cerium phosphate and arsenate, and for their possible practical application.

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ANALYSIS OF KINETIC MODELS FOR HETEROGENEOUS ISOTOPE EXCHANGE

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A model was set up for the solid/liquid phase isotope exchange kinetics on the basis of the Freundlich-type energetic non-uniformity. The superposition of a great number of first order rate equations was analysed by a computer programme.

In recent years many authors reported linear ln /1-F/ vs ln t relationship for solid/liquid type isotope exchange[1-4]. Though these findings were overwhelmingly ascribed to the energetic non-uniformity of the solid surface, no attempts were made to prove directly whether the superposition of numerous first order exchange processes, each of them taking place simultaneously on an energetically uniform part of the solid surface, may yield a linear ln /1-F/ vs ln t plot at all.

The aim of this paper is to show that when assuming a continuum of surface sites of different activation energy and using the Freundlich-type energetic non-uniformity, a considerable part of the ln /1-F/ vs ln t plots is linear. Attempts were also made to explain the physical meaning of the slope of the linear sections.

The analysed kinetic model was assumed having the characteristics as folows:

a/ A monolayer of the exchangeable element is formed on a chemically indifferent metal /e.g. noble metal/, the surface of which is a continuum of surface sites of different desorption energy. There are no gaps in the energy-distribution function which is in our case the Freundlich-type energetic non-uniformity:

$$E_i^+ = E_o^+ - \Omega \quad \ln /1-F/ \qquad /1/$$

where E_i^+ is the activation energy for the i-th monoenergetic cell, E_o^+ and Ω are constants of energy dimension.

b/ The exchange proceeds on the energetically uniform sites according to a first order rate equation:

$$\ln /1-F/_i = - k_i .t \qquad /2/$$

c/ The exchange process is not controlled by liquid phase diffusion.

So as to obtain the rate constants for the monoenergetic cells, the surface of the solid phase was divided into n imaginary monoenergetic cells of the same size. The activation energy to each of these cells was ascribed according to eq.1:

$$E_i^+ = E_o^+ - \Omega \ . \ \ln /1-F/ = E_o^+ - \Omega \ . \ \ln /1 - \frac{i}{n}/ \qquad /1a/$$

The first order rate constant for the i-th monoenergetic cell was then obtained by transforming activation energy into rate constant by the use of the Arrhenius equation:

$$k_i = k_o \ /1 - \frac{i}{n} /^{\frac{\Omega}{RT}} \qquad /3/$$

The computer programme consisted in the solution of the sum of a great number of eq.2:

$$\ln /1-F/ = \ln \sum \frac{1}{n} /1-F/_i = \ln \sum \frac{1}{n} e^{-k_i t} =$$

$$= \ln \sum_{i=o}^{i=n-1} \frac{1}{n} e^{-k_o /1- \frac{i}{n}/^{\frac{\Omega}{RT}} .t} \qquad /4/$$

followed by plotting ln /1-F/ against ln t.

RESULTS

Figs.1-3 show plots of ln /1-F/ vs ln t for different n,k_o and $\frac{\Omega}{RT}$ values[x]. From the curves the following conclusions can be drawn:

a/ When summing a great number of first order rate equations, the plot of ln /1-F/ against ln t thus obtained has a linear part. The lenght of this latter increases both with n, i.e. number of the first rate equations, and with $\frac{\Omega}{RT}$ as well.

b/ At constant n the increase of k_o results in the parallel shift to the left, while when $\frac{\Omega}{RT}$ is increased the slope of the linear parts will be decreased:

$$\frac{d \ln /1-F/}{d \ln t} = \gamma = \frac{RT}{\Omega} \qquad /5/$$

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[x] The interval encircled in Figs.1-3 by a dotted line represents the fraction exchange - time interval investigable by the usual experimental technique. The mark ├─┤ shows parts of the ln /1-F/ vs ln t plots the linearity of which is better than 1 %.

c/ The linear sections of the plots seen in Figs.1-3 can be described by eq. 6:

$$\ln /1-F/ = -\frac{RT}{\Omega} \ln t + \text{const.} \qquad /6/$$

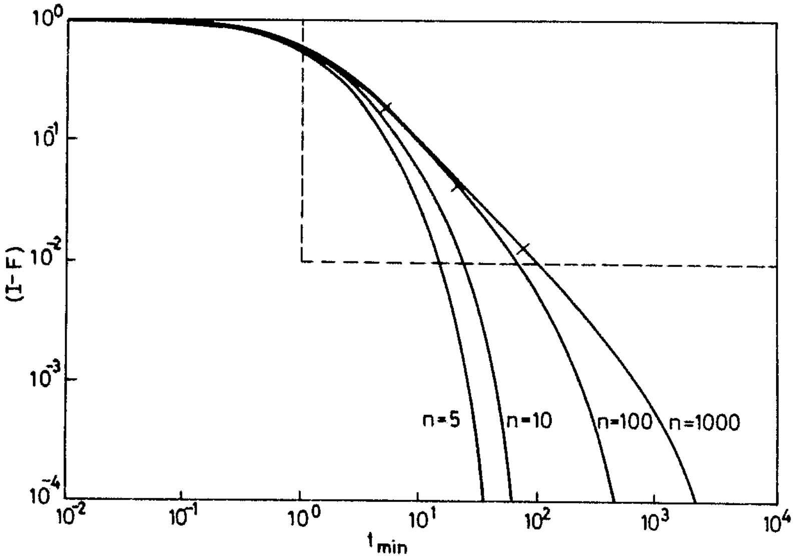

Fig.1. Plot of $\ln /1-F/$ vs $\ln t$; $k_o = 1$, $\frac{\Omega}{RT} = 1$

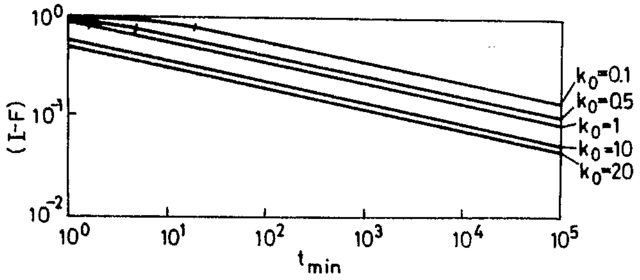

Fig.2. Plot of $\ln /1-F/$ vs $\ln t$; $n = 100$, $\frac{\Omega}{RT} = 5$

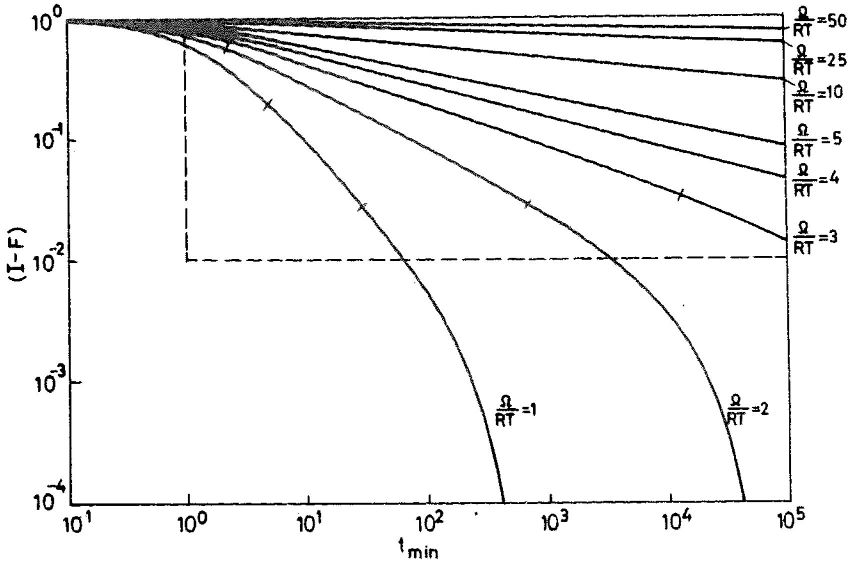

Fig.3. Plot of $\ln /1-F/$ vs $\ln t$; $n = 100$, $k_o = 1$

DISCUSSION

To give the physical meaning of Ω, which is a proportionality factor of energy dimension in eq.1, it is to be considered that among the monoenergetic cells numbered n there will be one, for which $/1 - \frac{i}{n}/ \cong 0{,}37 \simeq \frac{1}{e}$. Let us denote this cell as i_e and use eq.3 for this single cell, then we obtain:

$$k_{i_e} = k_o e^{-\frac{\Omega}{RT}} \qquad /7/$$

i.e. Ω is the activation energy of the i_e-th cell which is to be found at the 63 % of the total number of the monoenergetic cells. Comparing eqs.6 and 7 it can be stated that the slope of the linear parts of the $\ln /1-F/$ vs $\ln t$ plots is equal to RT divided by the activation energy of the i_e-th cell. It can be further shown that $\frac{RT}{\Omega}$ is proportional to the difference between the first order rate constants of the first and second monoenergetic cells[5].

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CALCULATION OF THE FRACTION OF EXCHANGE FOR HETEROGENEOUS UNSTABLE SYSTEMS

I. DISSOLUTION OF THE SOLID PHASE

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In the present work modified equations, for the calculation of the fraction of exchange for heterogeneous unstable systems, are derived. The inactive solid phase is dissolving during the experiment.

INTRODUCTION

The results of heterogeneous exchange were generally expressed in terms of fraction of exchange "F".

The equations of Wahl and Bonner[1] and that of Zimens[2], relating the progress of solid-liquid exchange reactions with time, are only applicable if the composition of the system /i.e. the concentration of the liquid n^L and the concentration of the solid phase n^S/ remains constant during the experiment. Consequently the activity of the liquid phase for samples labelled before precipitation /A_∞ - value/ remains unchanged.

However if the composition of the system changes the simple formula /1/ produces erroneous results for the fraction of exchange. In order to obtain the correct value for the fraction