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KINETICS OF THE REACTION OF MnO_4^- WITH AN ORGANIC EXCHANGER

Kinetic data of the uptake of permanganate ion on Dowex 21 K on the OH^- form are obtained at different temperatures, particle diameters and concentrations.

The results follow the equation used by Wen and Nativ et al. and may support the idea that the rate controlling step of the exchange reaction is a diffusion process in the particle which has been modified by a fast chemical reaction with MnO_4^- .

1 — INTRODUCTION

This work is part of a research project aiming at finding inorganic forms of anion organic exchanger with selectivity for alkaline and earth-alkaline ions. When a strong basic resin in the OH^- form was converted into the permanganate form, some peculiar properties of this new exchanger were detected which, to our knowledge, have not yet been reported.

The MnO_4^- ion exchange in resin seems to be an irreversible reaction. This ion is so strongly sorbed into the resin that its elution is practically impossible.

Besides, some selectivity for caesium [1] was detected in this form when we investigated the distribution coefficients in the resin using caesium, potassium and sodium solutions in tracer concentrations.

This result is an interesting one and may be very useful in analytical separations as well as in some other fields.

The main objective of this paper is to study the permanganate ion exchange reaction with the resin and to examine critically some criteria which have been laid down about rate controlling mechanism. Therefore a careful investigation was carried out to find the dependence of the rate of exchange on solution concentration of permanganate, particle size and temperature.

2 — EXPERIMENTAL

The resin used was a strong basic Dowex 21 K in the OH^- form, obtained from the original Cl^- form, immediately before each experiment.

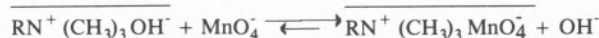
The kinetic measurements were taken under limited bath technique.

Forty milliliters of the potassium permanganate solution (0.03 to 0.002 M) were poured into a reaction vessel, thermostated by water circulation system.

The resin in a weighed amount (60 ± 2 mg dry resin) was added to the vessel already at the desired temperature (273 K, 295 K, 313 K, ± 0.1 K) under constant stirring.

Radiometer equipment, connected to a register, has been used to record pH, which ranged from 6.5 to 11.5. It is supposed that this change in pH is due to

the ion exchange reaction that can be written as follows:



The barred symbols indicate the resin phase.

The maximum capacity of ion exchange resin was obtained by a dynamic method using a small glass column in which an accurately weighed amount of Dowex 21 K had been introduced. Standard solutions were let to flow slowly through the resin for 24 hours until saturation. The exchange capacities determined for SO_4^{2-} and MnO_4^- were 3.1 meq and 2.5 meq per gramme of dry resin respectively.

By standard sieving, two different fractions of particles were obtained with the mean radius 0.013 cm and 0.024 cm.

To decrease the effect of the initial change in swelling, wet resin was always used, but all the data are referred to dry resin.

3 — DISCUSSION

EXCHANGE MECHANISM

Two diffusional models were tried to get the best fit to our experimental data. Both of them are based in the assumption that the particle diffusion is the controlling step of the exchange reaction, but they differ conceptually because only one of them considers the solid particle as an homogeneous medium. Assuming that the composition of the exchanger remained virtually unaltered during the reaction, BOYD *et al.*[2] have derived the following equation

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 Bt) \quad (1)$$

where F is the fractional attainment of equilibrium at time t , $B = \frac{\pi^2 \bar{D}}{r^2}$ and \bar{D} is the diffusion coefficient of the exchange ion inside the resin and r is the radius of spherical particle.

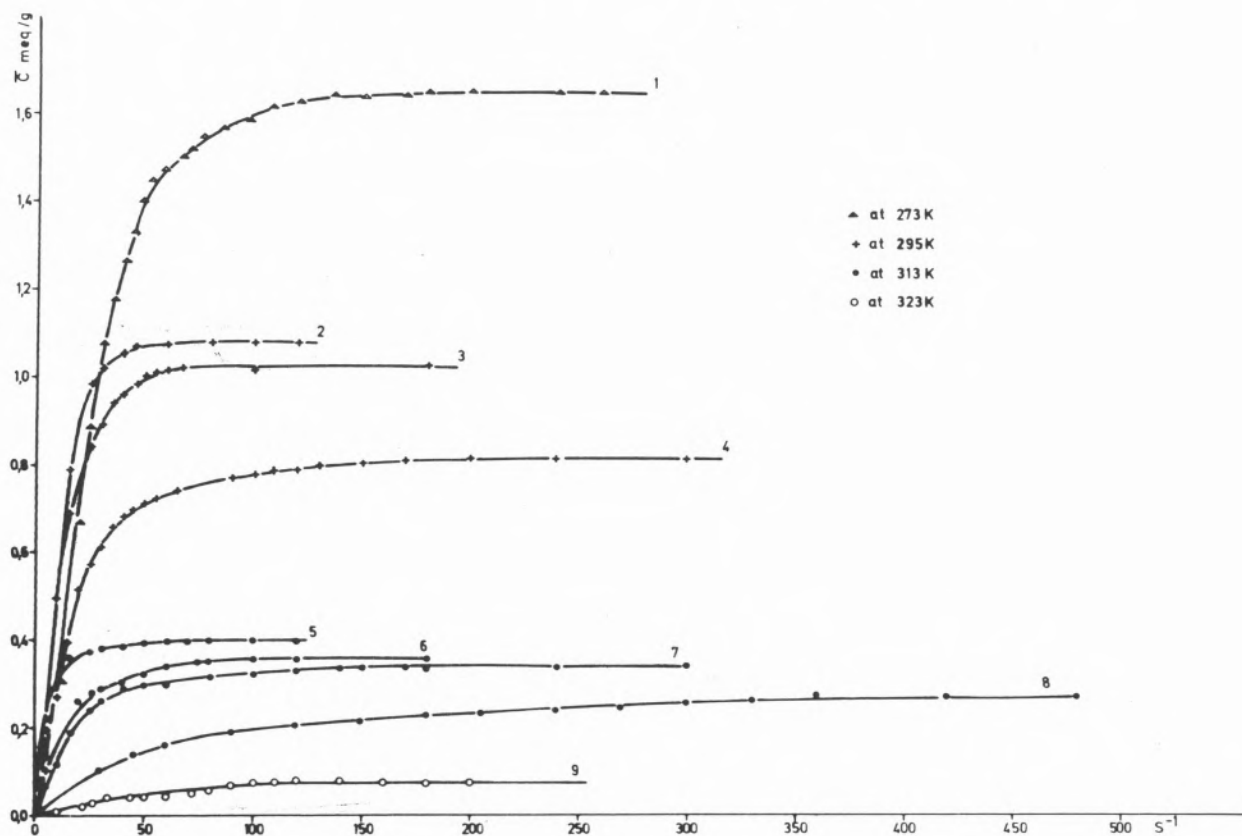


Fig. 1

Rate of uptake of permanganate ion in Dowex 21 ($r = 0.013$ cm) Numbers are concentrations: 1 - 0.032 M; 2, 5, 9 - 0.02 M; 3, 6 - 0.016 M; 4, 7 - 0.01 M and 8 - 0.0030 M

The plots of Bt against t should be linear and pass through the origin if particle diffusion is rate controlling (REICHENBERG test [3]).

WEN [4] and NATIV [5], assuming that on ion-exchange processes a fast reaction takes place in the solid, producing a sharp moving boundary between the reacted shell and the unreacted core, and based on the concept of pseudo-steady state, deduced the following equation

$$t = \frac{C_{\text{So}} R^2}{6 C_{\text{Ao}} \bar{D}} [1 - 3(1-F)^{2/3} + 2(1-F)] \quad (2)$$

being C_{Ao} the initial concentration of the solution, C_{So} the concentration of solid reactant, F the fractional conversion at time t , and \bar{D} the effective diffusivity of the counter-ion through the porous reacted layer.

RESULTS

Some typical results are expressed in fig. 1, where plots represent the uptake of MnO_4^- , \bar{C} (meq/g), vs. t . One can also see the large influence of ion concentration and temperature on the reaction rate. Towards the end of the reaction the exchange becomes so slow that it can be considered virtually in equilibrium, which is reached earlier with the more concentrated solutions. Note that the maximum value of conversion $F = \frac{\bar{C}_t}{C_{\text{tot}}}$ in terms of total capacity (measured in column) does not exceed 70%.

The virtual equilibrium, for the sake of comparison, was assumed to lay at the point at which \bar{C} remains unchanged for a period of not less than 5 min. In fig. 2, the values of \bar{C}_{eq} thus obtained are plotted against initial solution concentrations, C_0 .

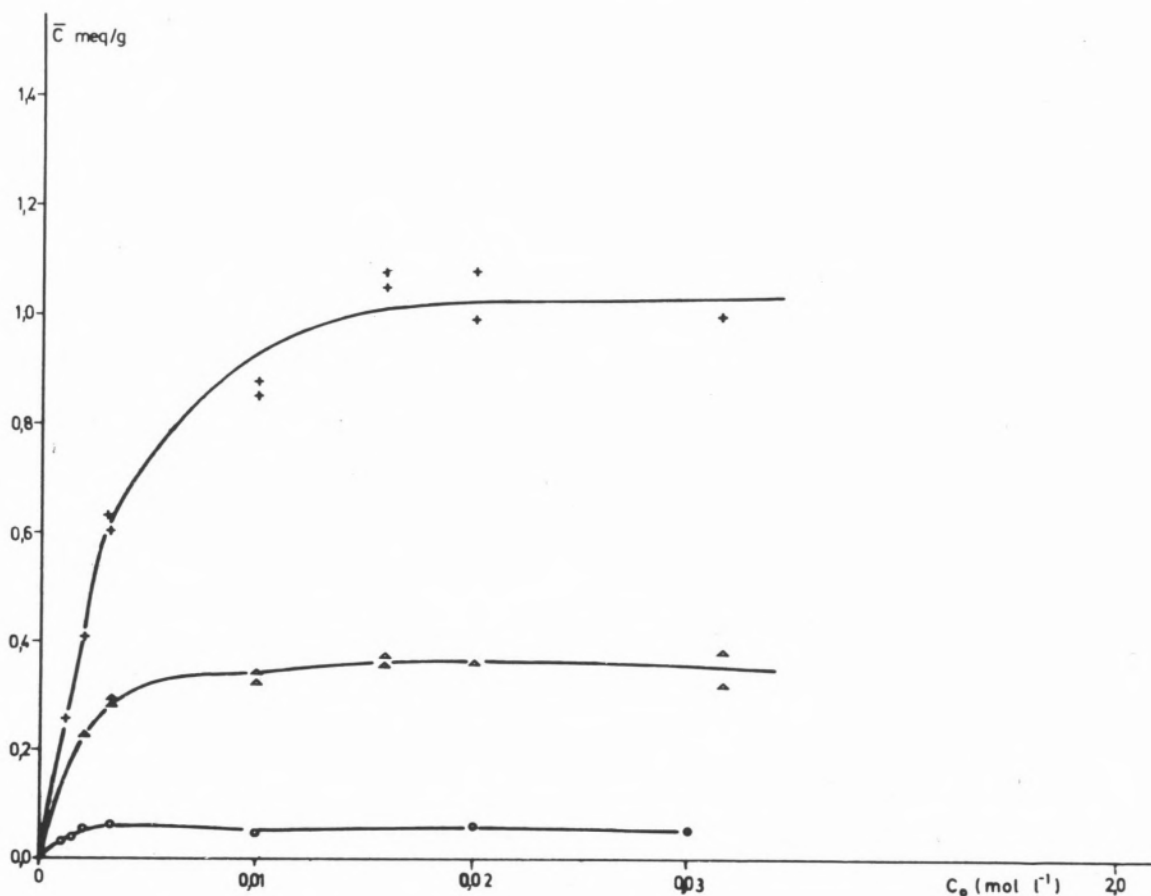


Fig. 2

Influence of temperature on the uptake +295 K; \triangle 313 K; \circ 323 K C_0 Initial concentration

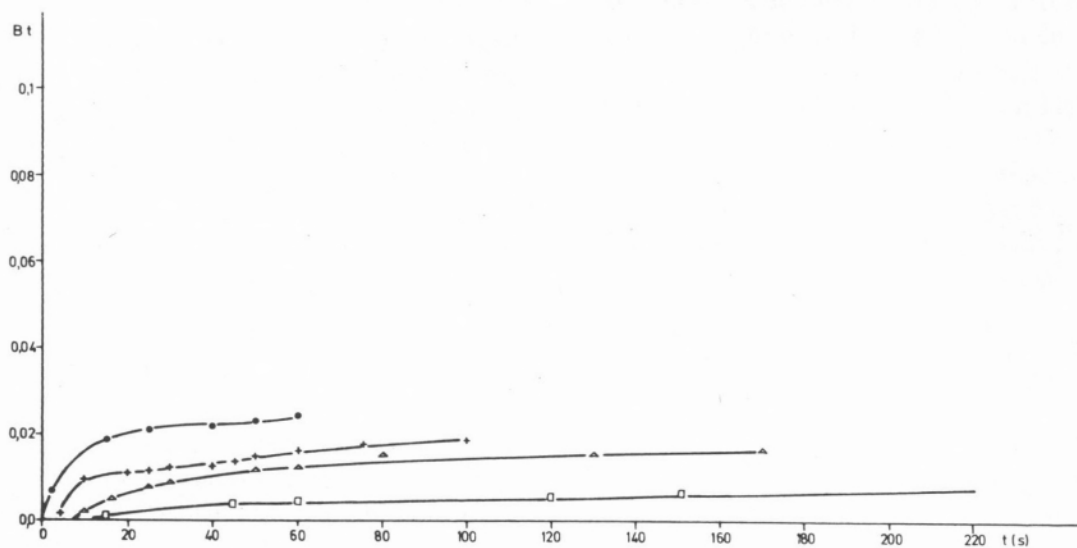


Fig. 3

Bt vs t plots calculated by the conversion F Initial concentrations \bullet 0.032 M ; $+$ 0.016 M ; \triangle 0.01 M ; \square 0.0032 M

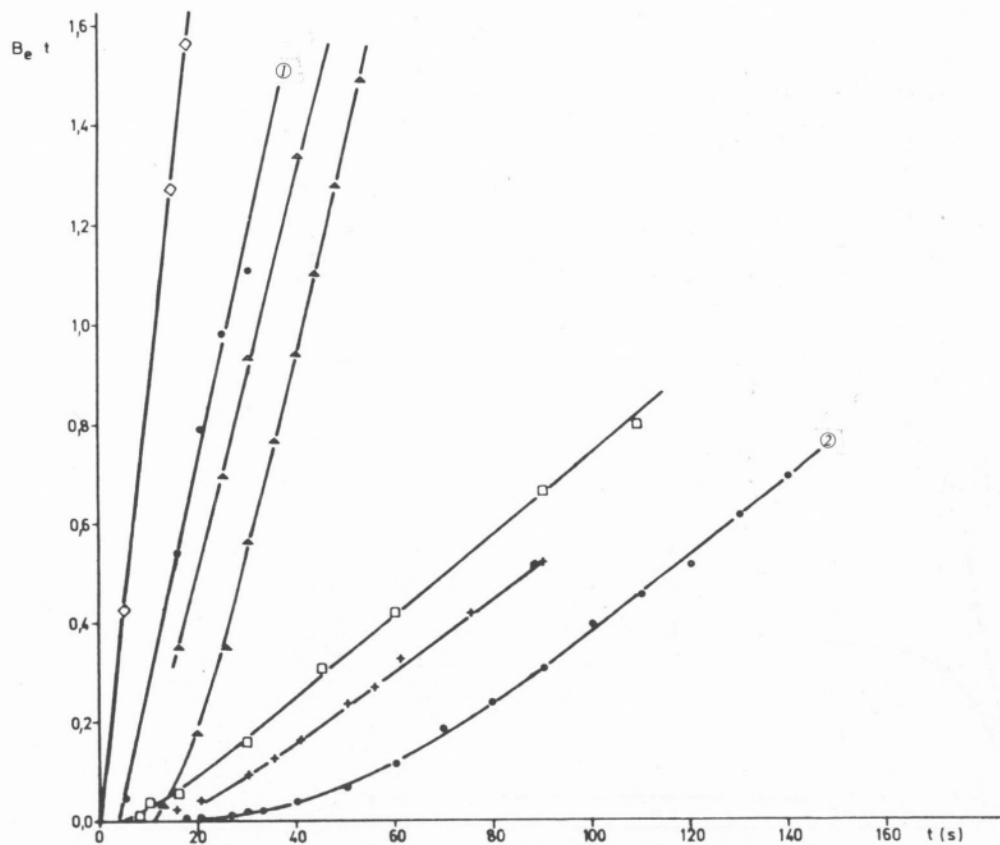


Fig. 4

$B_e t$ vs t plots for different initial concentrations and temperature \diamond 0.032 M ; \bullet 0.016 M \odot ; \triangle 0.01 M ; \square 0.003 M ; $+$ 0.002 M ; at 313 K \blacktriangle 0.016 M ; \bullet 0.003 M at 273 K $\textcircled{1}$

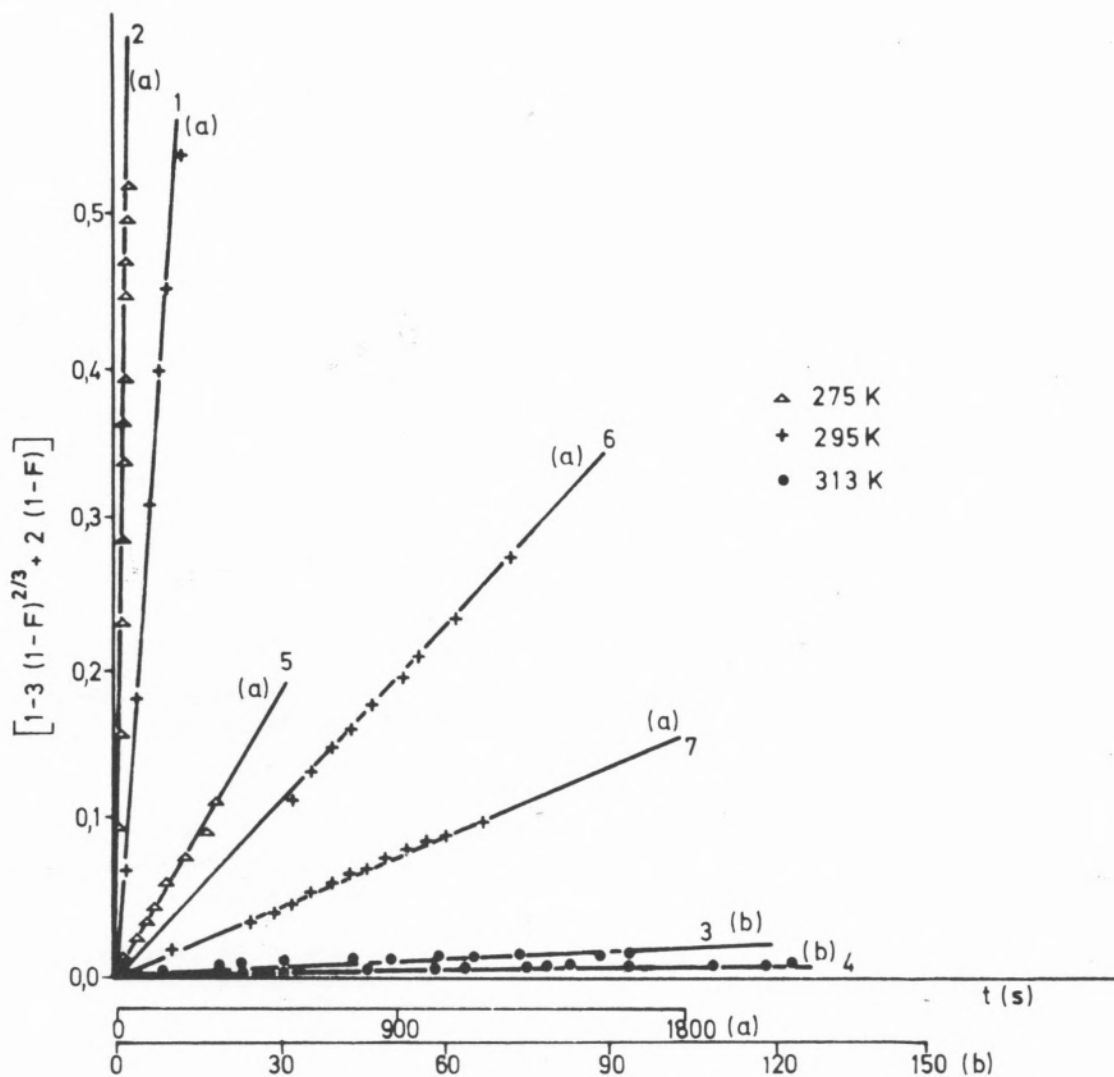


Fig. 5

Test of mathematical model for some typical kinetics data Initial concentrations: (1 - 0.03 M); (2,3 - 0.02 M); (4 - 0.01 M); (5,6 - 0.003 M); 7 - 0.002 M)

It is found that for a given temperature C_{eq} levels off, which means that it is in practice possible to consider such limiting value as a virtual pseudo-equilibrium capacity $\bar{C}_{eq,max}$.

Considering that these quantities correspond to the 100 per cent exchange, different conversion values were evaluated, $F_{(e)} = \frac{\bar{C}_t}{\bar{C}_{eq,max}}$.

According to BARRET [6] the applicability of the BOYD equation (2) and the Reichenberg test depends very much upon whether the F values are calculated considering total exchange or in terms of the exchange at equilibrium from kinetic data.

Our results were fitted to Boyd's model using both values of conversion, F and $F_{(e)}$, to calculate Bt and $B_{(e)}t$ from Reichenberg's table [3].

Figs. 3 and 4 illustrate the difficulties referred to by BARRET [6], and can not explicitly prove that the rate controlling step is particle diffusion.

In fact, although the fitting looks better in fig. 4, where some linearity is observed when more concentrated solutions of counter-ions are approached, the extrapolations are far from the origin, giving some evidence that the mechanism is not so simple as particle diffusion model would predict.

Table 1
Effective Diffusion Coefficients
 D ($\text{cm}^2 \text{s}^{-1}$)

[Mn O ₄] (M/l)	r (cm)	TEMPERATURE (K)			
		273	295	313	232
0,032-0,01	0,013	$6,4 \times 10^{-6}$	$6,2 \times 10^{-6}$	$5,2 \times 10^{-7}$	$6,9 \times 10^{-9}$
0,032-0,01	0,024		$6,7 \times 10^{-6}$		

The applicability of equation (2) to our results can be seen in fig. 5, where values of $[1 - 3(1 - F)^{2/3} + 2(1 - F)]$ are plotted against t . Straight lines passing through the origin may support the model developed by Wen and Nativ, which assumes that the rate controlling step is the diffusion through the external shell of the particle, where a fast and irreversible reaction has previously taken place.

The effective diffusion coefficients, \bar{D} , evaluated by linear regression, are summarized in Table 1.

The values of \bar{D} appear to be independent of the solution concentrations in the range 0.032 to 0.01 M. The diffusion coefficients are seen to be markedly influenced by the temperature, decreasing with increasing temperature. The depressing effect of temperature on the diffusion coefficients is more apparent the higher the temperature.

The decreasing of \bar{D} with increasing temperature is an unusual result, which does not seem to have been reported so far.

However in studies on ion-exchange processes [7] and corrosion of certain metals [8] a decrease in uptake or rate with increasing temperature has been found.

Our results may give some support to the idea that pore-blocking or some equivalent process occurring during the reaction, deeply enhanced by temperature, modifies the porosity of the reactive layer and therefore the effective diffusion coefficients.

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RESUMO

Cinética da reacção do ião MnO_4^- com um permutador orgânico aniónico.

Neste trabalho estuda-se a fixação do ião permanganato na resina aniónica Dowex 21 K na forma OH sob condições diversas de concentração, temperatura e diâmetro de partícula sólida, e apresenta-se a discussão do ajuste dos resultados obtidos a dois modelos matemáticos difusionais.