

KINETICS AND THERMODYNAMICS OF ION EXCHANGE:  
SILVER AND CALCIUM IONS ON DOWEX RESIN

by  
Win-Chun Jao

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Howard D. Mettee January 21, 1986  
Advisor Date

Sally M. Hatchkins February 5, 1986  
Dean of "the Graduate School Date

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## ABSTRACT

### KINETICS AND THERMODYNAMICS OF ION EXCHANGE: SILVER AND CALCIUM IONS ON DOWEX RESIN

Win-Chun Jao

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Activation energies have been measured for a variety of ion exchange systems showing zero and first order kinetics in film-controlled exchanges. Previous work has focussed on particle-controlled diffusion processes, where the polymer matrix affects the **activation** parameters. In the present experiments, the film is predominantly water so that the controlling medium is **more** completely defined. First order kinetics is observed whenever the ion initially in solution is **more** attracted to the **resin** than the initially resin-bound ion. Zero order kinetics occurs in the opposite circumstance.

The results show that  $\text{Ag}^+$  and  $\text{Ca}^{2+}$  replacing  $\text{Na}^+$ , in **Na-Dowex** are **first** order.  $\text{Na}^+$  with **Ag-Dowex**, and  $\text{Mg}^{2+}$  with **Ca-Dowex**, are found to be **zero** order. The activation energies found for the  $\text{Ag}^+ + \text{Na-Dowex}$  exchange is 22 kJ/mol and that for the reciprocal  $\text{Na}^+ + \text{Ag-Dowex}$  exchange is 38 kJ/mol. The corresponding values for the  $\text{Ca}^{2+} + \text{Na-Dowex}$  exchange and the  $\text{Mg}^{2+} + \text{Ca-Dowex}$  exchange are 24 and 18 kJ/mol, respectively.

The difference in activation energies of 16 kJ/mol between the reciprocal  $\text{Ag}^+ + \text{Na-Dowex}$  and  $\text{Na}^+ + \text{Ag-Dowex}$  exchanges is larger than the expected enthalpy difference for the reaction (apx. 5kJ/mole or less), which may be related to the difference in ionic binding strength of the  $\text{M}^+$   $\text{SO}_3\text{R}^-$  bonds in the matrix. This is consistent with the relative water solubilities of  $\text{Ag}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$ .

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## LIST OF SYMBOLS

SYMBOL	DEFINITION	UNITS
$K_e$	Equilibrium constant	
(aq)	Aqueous state	
$K_A^B$	Selectivity coefficient for the ion $B^+$ relative to A	
$\gamma$	Activity coefficient	
$K_a$	True thermodynamic equilibrium constant	
$K_C$	Selectivity coefficient	
$a$	Ionic activity	$\text{mol/cm}^2 \text{ sec}$
$J$	Flux	
$D$	Diffusion coefficient of ion in solution	$\text{cm}^2/\text{sec}$
$C$	Concentration of ion in solution	$\text{mol/L}$
$Z$	Direction	
$t$	Time	min
$F$	Fractional attainment of equilibrium	
$r_0$	Bead radius	cm
$\delta$	Film thickness	cm
$\bar{C}$	Concentration of ion in resin	$\text{mol/L}$
$\bar{D}$	Diffusion coefficient of ion in resin	$\text{cm}^2/\text{sec}$
$n$	Dummy-index for the series	
$\sum$	Summation	
$k$	Rate constant	$\text{sec}^{-1}$
$E_{act}$	Activation energy	$\text{kJ/mol}$
$T$	Absolute temperature	$^{\circ}\text{K}$
$R$	Gas constant (8.3143)	$\text{J/}^{\circ}\text{K mol}^{-1}$
$\Delta H_R$	Enthalpy of the overall reaction	$\text{kJ/mol}$

SYMBOL	DEFINITION	UNITS
$\Delta H^\ddagger$	Activation enthalpy	kJ/mol
$\Delta G^\ddagger$	Activation free energy	kJ/mol
$h$	Planck's constant ( $6.634 \times 10^{-34}$ )	J·sec
$\alpha$	Distribution coefficient	
$D'$	Diffusion coefficient in the particle matrix	cm <sup>2</sup> /sec
$\Delta S^\ddagger$	Activation entropy	kJ/mol
meq/mL	Milliequivalent per milliliter	
mm	Millimeter	
pH	Negative log of hydrogen ion concentration ( $H_3O^+$ )	
g	Gram	
µg/L	Microgram per liter	
AA	Atomic Absorption Spectrophotometer	
$\bar{d}$	Average diameter	mm
ppm	Parts per million	
M	Molarity	mole/liter
$k_f$	Forward reaction rate constant	sec <sup>-1</sup>
$k_r$	Reverse reaction rate constant	sec <sup>-1</sup>
$k_{exp}$	Experimental rate constant	sec <sup>-1</sup>
exp	Exponential	--
$\pi$	Pi (3.1416)	
ln	Natural logarithm	



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## CHAPTER I

### INTRODUCTION

#### General

A growing concern about the energetics of ion-solvent interactions has been noted recently.<sup>1,2</sup> A major portion of the extensive fundamental work in ion-exchange studies has been devoted to room temperature **thermodynamics** or kinetics. Relatively little consideration has been given to the temperature dependence of these ion-exchange processes. **Ion-exchange** presents **itself** as an interesting method to investigate the energetics of the **two** relevant transport processes—either film or particle diffusion—which are currently accepted as the major controlling factors in the **process**,

Helfferich<sup>3,4</sup> has presented a rigorous **summary** of the mathematical treatment of the theory of ion-exchange **equilibria** and kinetics,

According to this and earlier treatments, the rate of ion-exchange is controlled by diffusion through either the resin bead (particle-diffusion control), or through the **adherent** solvent **film**(**film-diffusion** control). Different equations result for the rate-determining steps in very dilute solution ( $\leq 1 \times 10^{-4}$  N), where the rate seemed to conform with the behavior expected from a film-controlled, **Ficksian** diffusion mechanism. Solution concentration and resin **basi-**

city in particular, also proved to affect the equilibrium performance of the resins. Other parameters whose effects are **commonly** investigated are pH, composition, and in a few instances temperature.

### Ion-Exchange Resins

Granular ion-exchange resins were first described in 1935 by Adans and **Holmes**.<sup>5</sup> They discovered that synthetic organic polymers, more commonly referred to as resins, are capable of exchanging ions. The chemical behavior of such an ion-exchange resin is determined by the nature of the functional groups attached to the hydrocarbon skeleton. There are two **major** classes of ion-exchange **polymers**: cation exchangers, which carry exchangeable cations; and anion exchangers, which carry exchangeable anions.

Dowex 50 is an important cation-exchange resin,<sup>6</sup> prepared by the copolymerization of styrene and **divinylbenzene** (used as the crosslinking agent), and the copolymer is reacted with concentrated sulfuric acid. The reaction is shown in Figure 1. Because of its ease of availability and frequent use in earlier studies, Dowex 50 was chosen for the present work.

### Thermodynamic Equilibrium of Ion-exchange Reactions

When an ion-exchanger is placed in an aqueous solution containing a different ion from that initially bound to the resin, an exchange of ions occurs until equilibrium is attained. The equilibrium **constant of the**

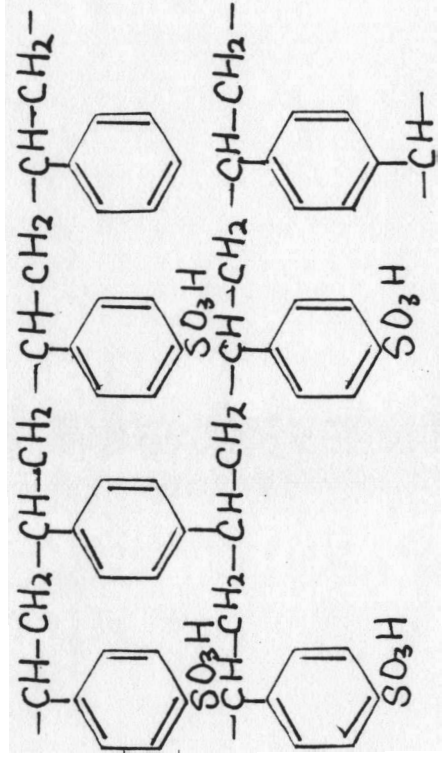
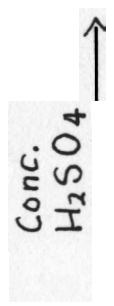
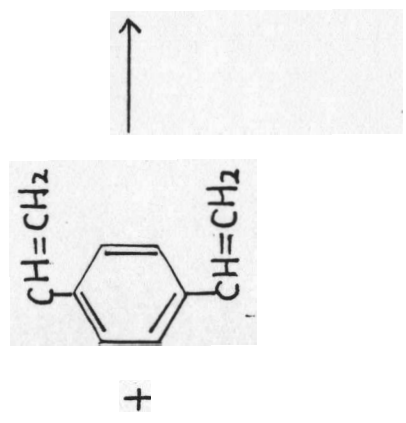
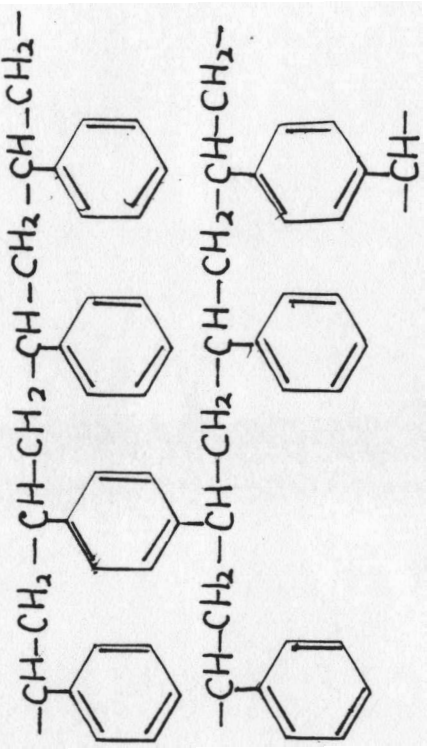
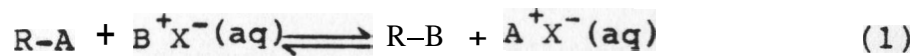


Fig. 1. Strong-acid polystyrene-type cation exchange resin (Dowex 50) synthesis.

exchange reaction



can be represented by the equation

$$K_e = \frac{[R-B] [A^+(aq)]}{[R-A] [B^+(aq)]} \quad (2)$$

where A, B are the exchanging ions, R is the exchanger matrix. The position of equilibrium depends upon the relative proportions of the R-A and B<sup>+</sup>(aq) and chemical nature of A<sup>+</sup> ion and B<sup>+</sup> ion. In general an ion-exchange resin will show a preference for one ion over another. This is the phenomenon of "selectivity". In fact, the value of K<sub>e</sub> is often referred to as the selectivity coefficient and is further defined by the expression

$$K_A^B = \frac{[B^+] [A^+]}{[A^+] [B^+]} \quad (3)$$

where [A<sup>+</sup>], [B<sup>+</sup>] are the concentrations of ions in the resin.

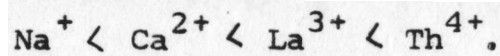
and [A<sup>+</sup>], [B<sup>+</sup>] are the concentrations of ions in the external solution.

The value of K<sub>A</sub><sup>B</sup> indicates quantitatively the preference the resin has for the ion B<sup>+</sup> relative to A<sup>+</sup>, and is usually measured in solutions equimolar in A<sup>+</sup> and B<sup>+</sup>. If K<sub>A</sub><sup>B</sup> > 1, the resin prefers B<sup>+</sup> compared to A<sup>+</sup>, if K<sub>A</sub><sup>B</sup> = 1 the resin has no preference, and if K<sub>A</sub><sup>B</sup> < 1 the resin takes up A<sup>+</sup> more strongly than B<sup>+</sup>.

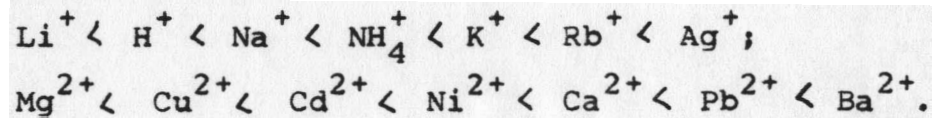
The selectivity coefficient is not a constant but is influenced by various factors,<sup>7</sup> which are listed below,

1. The particle size, degree of crosslinking, capacity, and the nature of the functional group.
2. The radius and charge of the exchangeable ions.
3. The total concentration (ionic strength) of the solution ions, including those capable and incapable of exchange. In addition, the type and quantity of other solvents or compounds in the solution.

At low concentrations of aqueous solutions at room temperature, nearly all ion exchangers give preference to polyvalent ions over monovalent species. Thus for example, the increasing order of preference is given as<sup>7</sup>



For some monovalent and divalent cations the corresponding orders are<sup>3</sup>



which suggests an increasing preference for the larger ions of the same charge.

These electrolytes form non-ideal solutions, and it is necessary to introduce activity coefficients ( $\gamma$ ) to represent the real thermodynamic properties of the solutions. A more sophisticated form of the law of mass action for the exchange is

$$K_a = \frac{(\bar{B}^+) \bar{r}_B (A^+) r_A}{(\bar{A}^+) \bar{r}_A (B^+) r_B} = K_C \frac{\bar{r}_B r_A}{\bar{r}_A r_B} \quad (4)$$

$\bar{r}_A$   $\bar{r}_B$  are the activity coefficients of ions in the resin phase and



$r_A r_B$  in the solution,  $K_a$  is the true thermodynamic equilibrium constant,  $K_C$  is the selectivity coefficient, derived directly from experiment.

### The Donnan Membrane Theory

When an ion exchange particle is **immersed** in a solution of electrolyte, the equilibrium concentration of free electrolyte inside the particle is found to be less than that outside. This imbalance in the concentration at equilibrium can be explained by the "Donnan membrane theory".<sup>8</sup> The "ionic activity product" of an electrolyte can be calculated by applying the Donnan equilibrium theory.

$$(\bar{a}_{A^+} \bar{a}_{X^-})_{\text{resin}} = (a_{A^+} a_{X^-})_{\text{solution}} \quad (5)$$

$X^-$  being a permanent counterion, or coion

and

$$\frac{\bar{a}_{A^+} \bar{a}_{X^-}}{\bar{a}_{B^+} \bar{a}_{X^-}} = \frac{a_{A^+} a_{X^-}}{a_{B^+} a_{X^-}} \quad (6)$$

Introducing concentrations and activity coefficients in place of activities, the selectivity coefficient is given by

$$K_C = \frac{(\bar{r}_{B^+}) (\bar{r}_{A^+})}{(\bar{r}_{A^+}) (\bar{r}_{B^+})} = \frac{\bar{r}_A r_B}{\bar{r}_B r_A} \quad (7)$$

An important point is that activity coefficients of most salts do not differ from concentrations in dilute solutions, but considerable differences develop at high concentrations as may occur within the bead.

## The Kinetics of Ion Exchange

Ion-exchanger beads containing  $A^+$  ions are placed in a well stirred solution of an electrolyte which contains counter ions  $B^+$ ,  $B^+$  migrate into the beads, and ions  $A^+$  migrate out of the beads into the solution. This cotransport phenomena is purely a diffusion controlled process, as the bulk of the early work shows. (See Figure 2) The exchange of  $B^+$  for  $A^+$  in the bead is not usually controlled by chemical switching of ions at the ionic sites within the particle matrix. This is thought to occur instantaneously in most cases,

Boyd, Adamson and Myers<sup>9</sup> first applied the Nernst-film model (Figure 3), instead of using the bulk hydrodynamic view which was common at that time. It is supposed that convective transfer increases gradually from the particle surface to the bulk solution through a nearly stagnant film, with a definite boundary separating it completely from the bulk, mixed solution.

On the-basis of the film theory, the ion-exchange reactions are controlled by either of two diffusion processes—through the film, or through the particle itself.

Mass diffusion is governed by the Fick's First Law,

$$J = -D \frac{dC}{dz} \quad (8)$$

where  $D$  is the diffusion coefficient, and  $\frac{dC}{dz}$  is the gradient

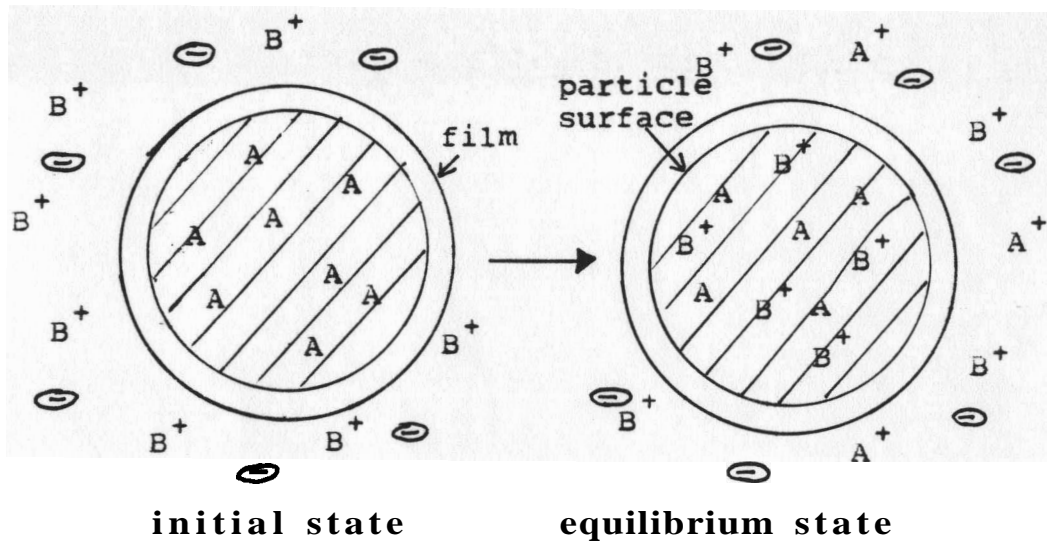


Fig. 2.  $A^+$ ,  $B^+$  exchanged counterions,  $\ominus$  coions. Ion exchange in a solution.

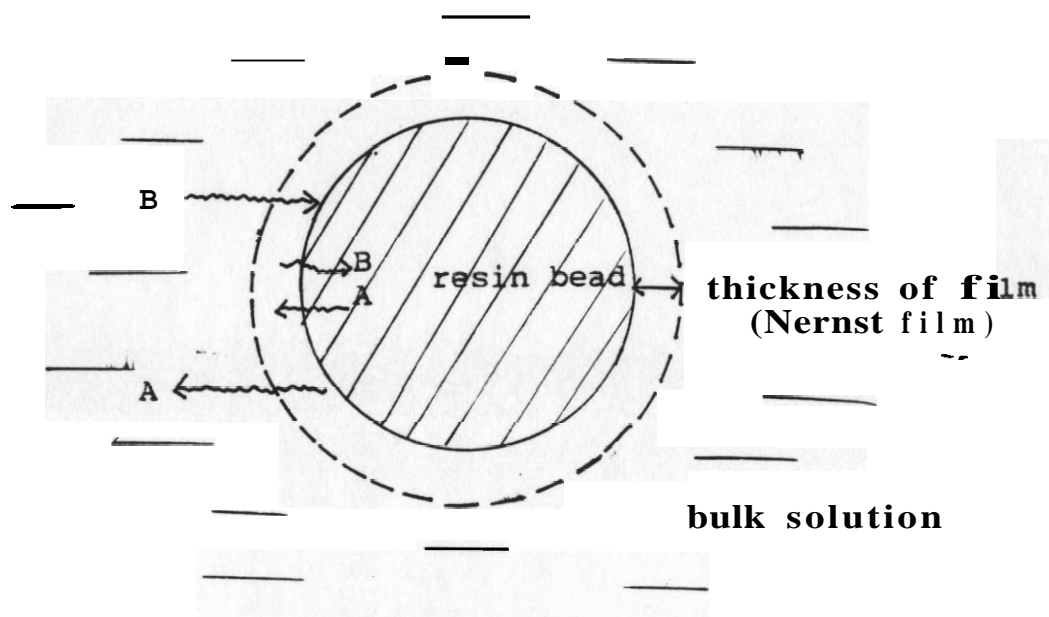


Fig. 3. Film diffusion and particle diffusion in ion-exchange kinetics.

of concentration of the solute in the direction  $Z$ , and  $J$  is the **flux**. But the present problem involves **nonsteady** conditions of diffusion, and therefore the derived equation, **the Fick's Second Law**, must be employed.

$$\frac{dC(t,Z)}{dt} = D \left( \frac{d^2C(t,Z)}{dZ^2} \right) \quad (9)$$

This equation gives the concentration of species C at any point in the system ( $Z$ ) at any time ( $t$ ), and it clearly depends on how fast the gradient itself is changing. (The net effect is that nature **"smooths"** peaks in distributions.)

Much of our present information concerning the rate of exchange of ions between beads and solutions comes from the work of Boyd and Soldano.<sup>10,11,12,13</sup> These workers first distinguished two rate controlling **steps**: film diffusion or particle diffusion.

In film diffusion, ions are transported across a concentration gradient between the bulk aqueous solution and the surface of an ion-exchange particle. In particle diffusion, there is no gradient in the bulk solution and the film layer, and the **movement** of ions is along a gradient within the particle itself. Both of these cases are shown in Figure 4. Following the consequences of **Fick's** laws, with boundary conditions applied for film diffusion the "fractional attainment of equilibrium",  $F$ , at any time,  $t$ , is

$$F(t) = 1 - \exp\left(\frac{-3DC_0^2}{r_0^2 \delta C}\right) \quad (11)$$

where  $r_0$  = bead radius;  $\delta$  = film thickness;  $C$  = concentration of ion in solution;  $\bar{C}$  = concentration of ion in the resin;  $D$  = interdiffusion coefficient of the ion in solution,

Exponential rate laws of the form  $F(t) = 1 - \exp(-kt)$ , as in (11), are thus obtained in this case.

For particle diffusion control, the fractional attainment of equilibrium is given by the familiar relation

$$F(t) = 1 - \left(\frac{6}{\pi^2}\right) \sum_{n=1}^{\infty} \left(\frac{1}{n^2}\right) \exp\left(-\frac{\bar{D}t\pi^2 n^2}{r_0^2}\right) \quad (12)$$

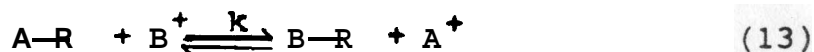
where  $\bar{D}$  = interdiffusion coefficient of ion in resin;  $n$  = a dummy index for the series.

Particle diffusion rates are less dependent on the external aqueous solution and appear to depend on the nature and ionic composition of the exchanger.

These two mechanisms of diffusion control of ion exchange can be recognized by plotting  $F(t)$  vs.  $t$ , as shown in Figure 5, given by Boyd, Adamson, and Myers.<sup>9</sup>

### Activation Energy

For a general ion-exchange reaction



the rate is indicated

$$-\frac{d[A^+]}{dt} = k[B^+][R-A] \quad (14)$$

The order of the reaction is strictly second-order, but for a fixed amount of resin (with excess A), it is pseudo-first-

order in  $B^+$ . The Arrhenius activation energy,  $E_{act}$ , is determined by the temperature dependence of the rate constant,  $k$ , and is given by<sup>14</sup>

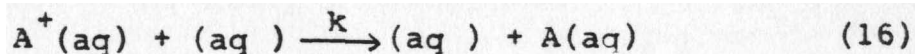
$$\frac{d \ln k}{d (1/T)} = - \frac{E_{act}}{R} \quad (15)$$

The temperature dependence of an equilibrium constant of an ion-exchange process gives different information from that of the kinetic one (Figure 6), namely the enthalpy of the overall exchange reaction,  $\Delta H_R$ . With film diffusion control, the apparent activation energy is only that of the film-phase diffusion, whereas for particle diffusion control, the apparent activation energy includes both a film and a particle diffusion component.

It can be shown that the activation enthalpy,  $\Delta H^\ddagger$ , in homogeneous diffusion is practically equal to activation energy,  $E_{act}$ , so  $\Delta H^\ddagger$  can be calculated with equation 15.<sup>14</sup>

### Diffusion Considered as a Rate Process

The connection between a \*\*chemical<sup>w</sup> rate constant and a diffusion coefficient has been made by treating ion jumping from site to site within the solvent as a **symmetrical reaction**.<sup>15</sup>



$$k = \left(\frac{kT}{h}\right) \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) \text{ (Eyring rate equation)} \quad (17)$$

$$D = \frac{1}{2} l^2 k \quad \text{(Diffusion process)} \quad (18)$$

Thus the diffusion coefficient is directly proportional to the rate constant, and  $l$  is the site to site

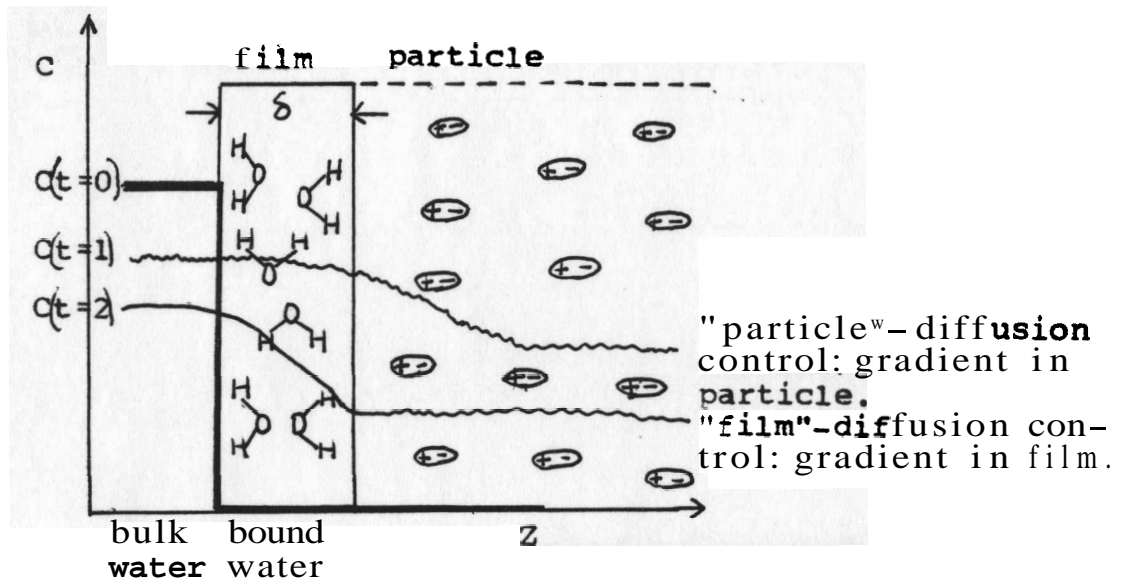


Fig. 4. Schematic concentration gradient as a function of particle distance of the ion exchanger, initially and at a later time.

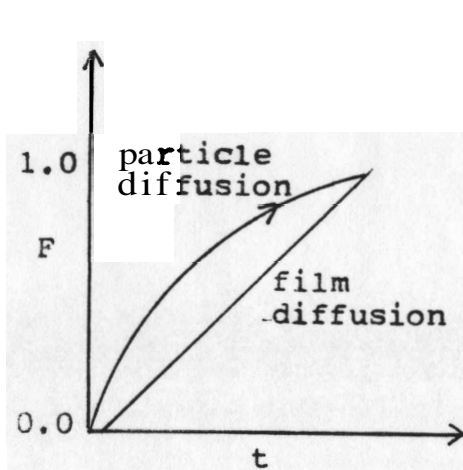


Fig. 5. Fractional attainment of equilibrium as a function of time for particle and film-diffusion control exchange. 11

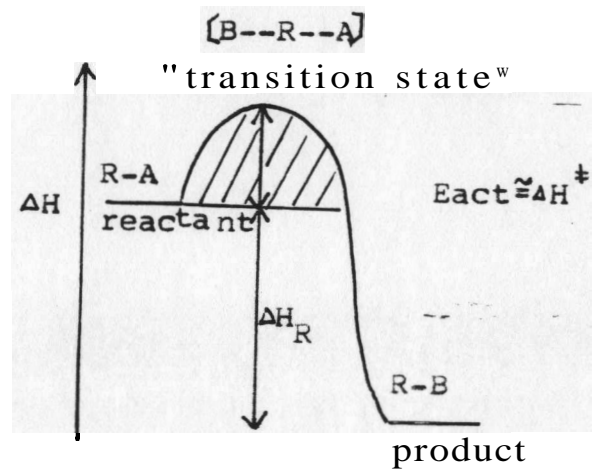


Fig. 6. Activation enthalpy of ion-exchange reaction.

**distance.**

For our small temperature range, over which  $l$  and  $\Delta S^\ddagger$  can be regarded as **constant,**

$$\frac{d \ln D}{d (1/T)} = \frac{d \ln k}{d (1/T)} = - \frac{\Delta H^\ddagger}{R} \quad (19)$$

### Statement of the Problem

The goal of this work is to contribute to the understanding of the energetics of ion-solvent interactions, **as** measured by the ion-exchange process. In our systems, this work will **include** the energy **of** all the interactions between the ions and the surrounding **solvent, and** between the ions and various cation substituted Dowex **resins.**

Atomic absorption permits the analysis of very dilute **solution** systems, in which film diffusion usually controls the exchange. Thus, ion-solvent interactions are not **influenced** by ion-ion interactions of more concentrated systems. **In** this paper, the ionic activity coefficients **are** near unity in solution and the enthalpy values **for** ion-exchange<sup>e</sup> processes are expected to be **small** in the temperature range studied. There are no comparable activation **energy values** in the literature from kinetic studies of **film-controlled** diffusion. However, particle-controlled **data** indicates appreciable activation energies, which in this case apply at least **partly** to the particle **network.**



## CHAPTER II

### REVIEW OF THE LITERATURE

#### Theory of Thermodynamics

A **thermodynamic** relation states that in a reversible process taking place at constant temperature and pressure, the free energy change is equal to the net work done by the system. In our systems, this work will include the energy of all the interactions between the ions and the surrounding **solvent**,<sup>16</sup> and between the ions and the **Dowex resin**.

An early example of an approximate model for **ion-solvent** interactions is that suggested by Born in 1920. The **Born model** views the free energy of ion-solvent interactions as equal to the work of transferring a charged sphere from **vacuum** into a **continuum**. Then, the free energy of ion-solvent interaction is viewed as a function of the reciprocal of the ionic radius, and it results from the transfer of ions from a vacuum to the solvent.

The "**ion-dipole model**" of ion-solvent interactions extends the early Born model by considering that the ion sees the solvent as consisting of discrete water dipoles oriented around it. The interaction between the ion and its nearest neighbors creates the primary solvent sheath. The heat of ion-solvent interactions can then be separated into the steps of cavity formation, formation of primary solvated

ion, Born charging, and several other smaller terms,

A still better approximation is to view the solvent as a quadrupole. Then one can not only explain why oppositely charged ions of equal radius have differing heats of hydration, but also predict quantitatively the way these differences vary with ion radius,

Contemporary ion-solvent interaction theory<sup>16</sup> slightly **modifies** this quadrupole view of the solvent by adding an induced dipolar interaction between the ion and immediate solvent shell. This term accounts for the **polarizability** of the solvent. Table 1 shows how these various terms contribute to the heats of the ion-solvent interaction.<sup>16</sup>

TABLE 1

COMPARISON OF TERMS IN ION-SOLVENT ENTHALPIES (kJ/MOLE)

Ion	Born Charging	Ion-Dipole	Ion-Quadrupole	Ion-Induced Dipole	Total <sup>‡</sup>	Experimental
Li <sup>+</sup>	-207	-546	+290	-261	-640	-543
Na <sup>+</sup>	-188	-394	+178	-137	-457	-428
K <sup>+</sup>	-170	-291	+113	-80	-346	-348
Rb <sup>+</sup>	-164	-262	+97	-61	-307	-323

<sup>‡</sup>Totals all include +84 kJ to create the solvent cavity.

In work done with Dowex 50 resins, Bonner<sup>17, 18</sup> and Kraus<sup>19</sup> noted that the values of heat for the ion exchange process are often small in the temperature range near 25°C. Measurement of the selectivity coefficient,  $K_C$ , as a

function of temperature permits evaluation of an apparent enthalpy change for ion-exchange process through the relationship

$$\frac{d \ln Kc}{d (1/T)} = - \frac{\Delta \bar{H}}{R} \quad (20)$$

The enthalpy change  $\Delta \bar{H}$  refers to the molar heat of exchange of the ions between an ideal aqueous solution and an ideal resin.

Since our solutions are all dilute (<.001M) the ionic activity coefficients are near unity. The corresponding coefficients in the Dowex are not known, so that it is sufficient here to regard them as unity, consistent with standard practice. Table 2 lists the  $\Delta H$ 's found by Bonner and Pruett, and Bonner and Smith, in this way.

TABLE 2

$\Delta \bar{H}$ 's FOR  $M^+$  (aq) + X-DOWEX EXCHANGERS

System	$\Delta \bar{H}$ (kJ/mol)	
	16% DVB	8% DVB
Cu <sup>2+</sup> /H-D	+2.5	
Mg <sup>2+</sup> /H-D	+2.5	+1.0
Cu <sup>2+</sup> /Zn-D	0.0	
Ca <sup>2+</sup> /Cu-D	-0.5	
Cu <sup>2+</sup> /Mg-D	-0.8	
Pb <sup>2+</sup> /Ca-D	-1.1	-0.5
Na <sup>+</sup> /H-D	-2.8	

It seems fair to conclude that the  $\Delta H$ 's are generally **small**, **close** to  $\pm 1$  kJ/mol in Dowex with 8% DVB, **particulary** when the change in **formal** charge on the ions is zero.

### Theory of Kinetics

The kinetics of the exchange will **be** governed by either film or particle diffusion depending on which is rate controlling. **The** over-all transport of mass can be **divided** into three steps.

Diffusion through a surface film (mostly water in our **case**). The fractional attainment of equilibrium,  $F$ , can be written as <sup>9</sup>

$$\ln (1-F) = - \frac{3Dt}{r_0 \delta \alpha} \quad (21)$$

where  $D$  is the diffusion constant in the **film**,  $\delta$  is the film thickness,  $r_0$  **is** the radius of particle, and  $\alpha$  is the **dis-**tribution coefficient of the ion between the two phases.

For diffusion through the adsorbent particle, it is assumed **that** the initial concentration of adsorbate in solution remains constant. The fractional attainment of equilibrium,  $F$ , can be written as <sup>9</sup>

$$F = 6/r_0 \sqrt{D't/\alpha} \quad --(22)$$

where  $D'$  is the internal diffusion coefficient in the particle matrix.

If film diffusion is rate controlling, the  $\ln (1-F)$  will **vary** inversely with the particle size,  $r_0$ , the film thickness,  $\delta$ , and with the distribution **coefficient**,  $\alpha$ .

If particle diffusion is rate controlling,  $F$  should

proceed linearly with  $t^{1/2}$  and the slope should vary inversely with  $r_0$ , and directly as  $(D_0/\alpha)^{1/2}$

The derivation of the diffusion coefficients **from** kinetic data either requires **assumptions** about the film layer thickness ( $\delta$ ), or they apply to a particular particle matrix.

### "Energy Component" Analysis and Interpretation

Trends of heats of solution of different ions in water are adequately reproduced by "**cluster formation enthalpies**", which are based on the **modified quadrupole** theory. These calculated energies have been partitioned<sup>2</sup> into components representing (i) solute-first solvent shell, (ii) solute-bulk solvent, (iii) first shell-first shell, (iv) first shell-bulk, and (v) bulk-bulk interactions. Comparison of these components with the **corresponding** results obtained for liquid water provides detailed insight into the nature of solvent reorganization in the surrounding media, complementing the structural information provided by hydrogen bonding analysis. A most interesting feature revealed by these calculations is the formation of a first **solvation** shell, whose solvent molecules exhibit **mutual** repulsion. **This is, a** tightly **bound** shell, consisting of 4 or 5 water molecules depending on the **ion**, — travels with the ion from site to site through the bulk solvent.

The activation energy for "**self**" diffusion, using radioactively labelled isotopes of a number of ions related to this study have been determined, which, however, apply

to "particle"-controlled diffusion. Table 3 lists these values.

TABLE 3

ACTIVATION ENERGIES AND DIFFUSION  
COEFFICIENTS FOR SELF-DIFFUSION IN TWO DOWEX MATRICES<sup>13</sup>

Ion	Dowex 50W-X16 <sub>2</sub>		Dowex 50W-X8 <sub>2</sub>	
	Eact(kJ/mol)	D(cm <sup>2</sup> /sec)X10 <sup>6</sup>	Eact(kJ/mol)	D(cm <sup>2</sup> /sec)X10 <sup>6</sup>
Na <sup>+</sup>	35	0.24	27	0.94
Ag <sup>+</sup>	28	0.28	25	0.64
Zn <sup>2+</sup>	36	0.012	31	0.063
Sr <sup>2+</sup>	46	0.003	35	0.034

The results imply higher activation energies for those ions more resistant to flow, and both parameters increase with the extent of cross-linking in the matrix, **These values show trends, therefore,** which are consistent with a particle-controlled diffusion process. Beyond **this, the divalent** ions show about a 25% increased activation energy over the monovalent ions.

## CHAPTER III

### EXPERIMENTAL

#### Materials and Apparatus

The **Dowex 50W-X8** in the  $\text{Na}^+$ -form was purchased from **Dow Chemical Company**, Midland, **Michigan**. **Sodium**, silver, calcium, and magnesium standard solutions (1000 ppm  $\pm$  1%) were certified Atomic Absorption Standards from Fisher **Scientific**. Calcium chloride (anhydrous) was analytical grade, Baker Analyzed Reagent, and the silver nitrate was laboratory grade. The acid used to adjust the pH of solution was ACS reagent grade nitric acid (70.5%).

The instrument used for analysis of the absorbance of metal ion solutions was a Instrumentation Laboratory **AA/AE**, Model Video 11, Atomic Absorption Spectrophotometer.

The Heating Bath and Circulator, used for sample of solutions the temperature **control**, was manufactured by Haake Inc., Saddle Brook, N.J. This cell was equipped with a water jacket whose temperature was controlled to  $\pm 0.1^\circ$  by thermometer (Figure 7).

#### Chemistry of Dowex 50W-X8

**Dowex 50W-X8**, is a strong acid cation exchanger that consists of a sulphonated polystyrene-vinylbenzene copolymer containing exchangeable  $\text{Na}^+$  ions (Figure 8). The properties of **Dowex 50W-X8 are:** total exchange capacity

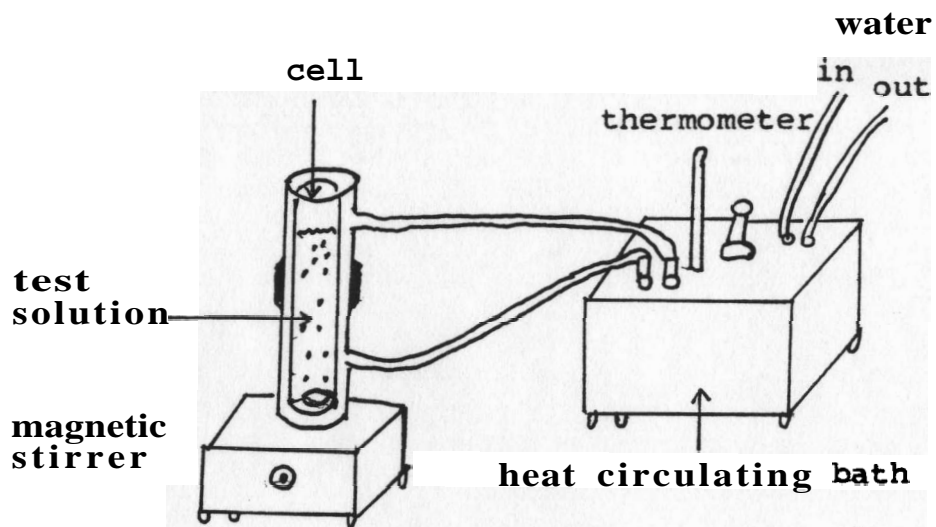


Fig. 7. The apparatus for temperature control of the ion exchange cell.

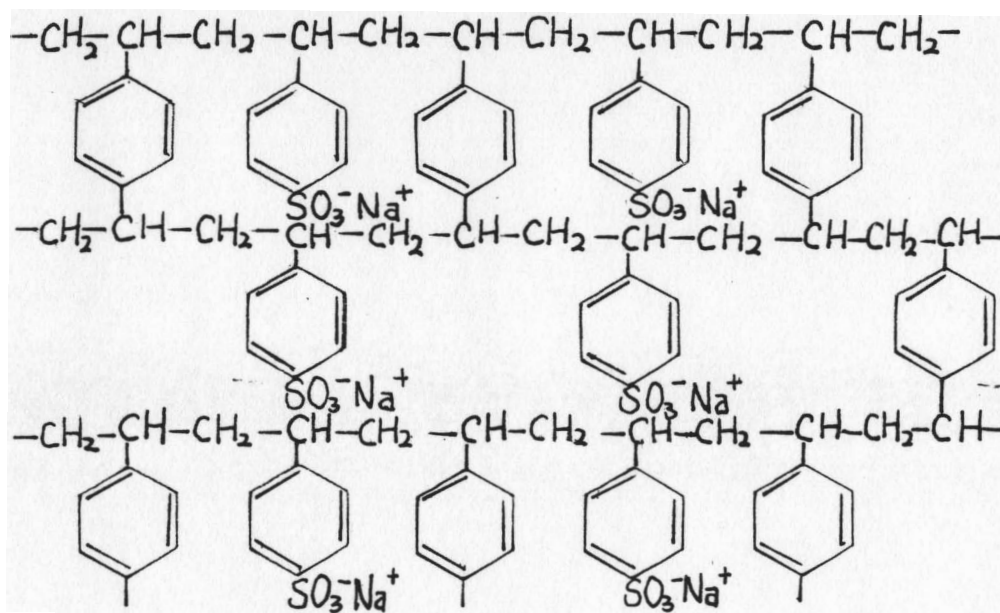


Fig. 8. The structure of the Dowex 50W resins. sodium form.



6.27 meg/ml, mesh size 20-50, and a stated moisture content 43%.  
 Table 4 compares U.S. mesh values and particle diameters.

TABLE 4

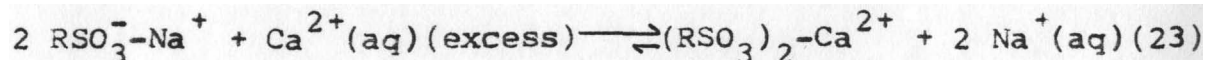
PARTICLE SIZE IN US MESH AND MM

US mesh	diameter(mm)
16-20	1.20-0.85
20-50	0.85-0.29
50-100	0.29-0.15
100-200	0.15-0.08
200-400	0.08-0.04

The outstanding advantages of the Dowex 50W-X8 resin are its thermal stability up to 200°C, the pH-independence of total exchange capacity, and its stability with washing of salt forms.

Dowex 50W-X8 Treatment

Dowex 50W-X8 resin (sodium form) (3g) was transformed into the Ca-form by treatment with 500ml 0.5N CaCl<sub>2</sub> solution in beaker stirred for 20 hours. Subsequently, it was washed to remove occluded Ca<sup>2+</sup> with deionized-distilled water several times, suction-filtered, and dried in air over 2 days. The reaction is (where R represents the polystyrene backbone)



The synthesis of Ag-Dowex was performed in an identical manner, except that the solution used was  $\text{AgNO}_3(\text{aq})$ , and the Na-Dowex was first washed to **remove** possible traces of  $\text{Cl}^-$ .

Procedure for Sodium-Silver Ion-Exchangers

"**Standard silver solutions**" were prepared in the range from 0 to 1000  $\mu\text{g/L}$ . The standard curve for silver was constructed using the IL Video 11 AA/AE Spectrophotometer. The optimized instrumental parameters for all runs are shown in Table 5.

TABLE 5

Ag INSTRUMENTAL PARAMETERS

Mode	AA (Single beam)	--
Statistics	5	
Integration	Automatic	
Integration time	1 second	
Light source	Ag Hollow cathode	
Flame description	Air-acetylene, oxidizing (Fuel lean, blue)	
Lamp current	3 mA	
Voltage	530	
Wavelength	328.1 nm	
Band pass	1 nm	--
Acetylene pressure	15 psig	
Oxidant flow	12 scfh	
Aspiration rate	5 mL/min	
Fuel flow	3-5 scfh	

A 50 mL volume, initially 1000  $\mu\text{g/L}$   $\text{Ag}^+$  (standard), was placed in the temperature controlled cell. The jacketed cell was placed over a magnetic stirrer and 0.1 g of Na-

Dowex resin (air-dried) was added. "Instantaneous"  $\text{Ag}^+$  were measured every 3 min, over a 25-30 min period, by aspirating a small volume of solution into the AA flame for about 5 seconds. The aliquot was taken from the top portion of solution to prevent Dowex particles from being drawn into the pneumatic tubing. (The stirred particles occupied the lower 20% of the cell,) Temperatures of ion-exchange systems were set at  $25^\circ\text{C}$ ,  $32^\circ\text{C}$ ,  $39^\circ\text{C}$ , and in an ice-water bath, 0.10 g of Dowex resin was used in all cases, except at  $0^\circ\text{C}$  where 0.20 g was found more practical. Other solutions of  $\text{Na}^+$ , using Ag-Dowex, the complementary system, were treated similarly except that in these cases the increase in  $\{\text{Ag}^+\}$  was followed as a function of time.

#### Procedure for Sodium-Calcium Ion-Exchanges

The same general procedure as that described for the sodium-silver ion exchanges, except that the  $\{\text{Ca}^{2+}\}$  was monitored using a calcium hollow cathode lamp in the AA, and different monochromator settings were used.

In these experiments, both the  $\text{Ca}^{2+}$  loss due to absorption into Na-Dowex, and the  $\text{Ca}^{2+}$  release from Ca-Dowex due to its replacement by  $2\text{Na}^+$ , was followed.

#### The pH-Dependence of Sodium-Calcium Ion-Exchange

Standard Calcium solutions were made in the range from 0 to 800  $\mu\text{g/L}$ . All solutions were acidified with 1.5 ml Baker concentrated nitric acid (70.5 per cent), giving a

**pH $\approx$ 1.** The sodium-calcium ion-exchange **was** performed at room temperature.

### The Dependence on the Amount of Dowex

The effect of the amount of **Na-Dowex**, in a 200  $\mu\text{g/L}$  standard calcium solution, was studied using weights of Na-Dowex of 0.076 g, 0.114 g, 0.152 g, and 0.228 g. In these cases, the **{Ca $^{2+}$ }** **decrease** was measured over time.

### The Diameter and Density of Dowex Exchange Particles

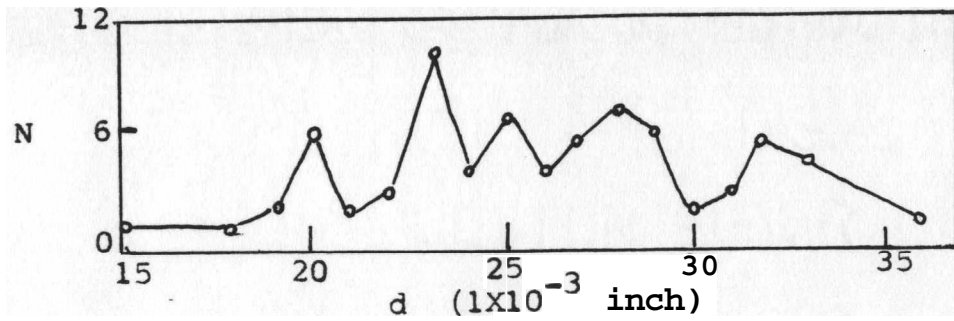
Ion exchange beads are marketed in particle **size** ranges. To determine the range of particle sizes of air dried exchangers, a micrometer was used to measure the diameters of about 80 beads of the Na-, Ag-, and **Ca-Dowex** exchangers. The density of dry ion exchange resins **was** measured by using a calculated, 10 mL pycnometer.

### Characterizing the Particles

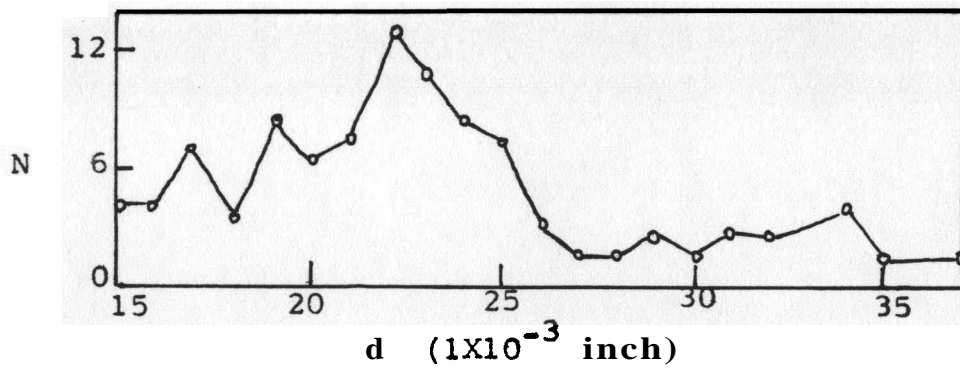
#### The **Dowex 50W-X8** Particle Radius and Density

The number of particles having a given diameter for the Na-, Ca-, and Ag-Dowex particles are presented in Figures 9-11,

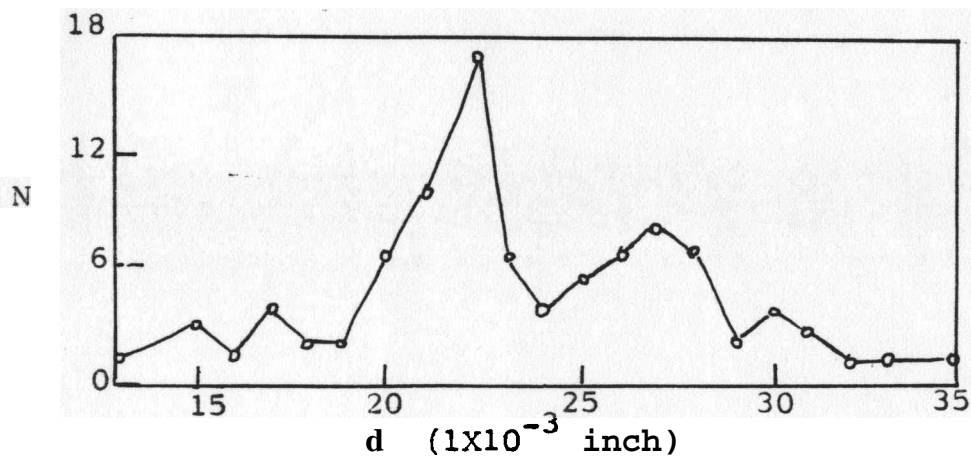
The average diameter ( $\bar{d}$ ) and radius ( $r_0$ ) of the beads were calculated, and the results were given in Table 6.



**Fig. 9.** Distribution of the particle diameters of air dried Na-Dowex, where N is the number of Dowex particles.



**Fig. 10.** Distribution of the particle diameters of air dried Ca-Dowex.



**Fig. 11.** Distribution of the particle diameters of air dried Ag-Dowex.

TABLE 6  
AVERAGE DIAMETER OF DOWEX 50W-X8

Dowex 50W-X8	$\bar{d} \times 10^{-3}$ inch	$r_o$ (cm)
Na-Dowex	26.6 $\pm$ 4.8	0.033
Ca-Dowex	22.5 $\pm$ 3.6	0.029
Ag-Dowex	23.5 $\pm$ 4.2	0.030

The densities of the air dried M-Dowex particles was determined by the water displacement method from the pycnometer, and these results are seen in Table 7.

TABLE 7  
DENSITY OF DOWEX 50W-X8

Dowex 50W-X8	D in g/mL
Na-Dowex	1.45
Ca-Dowex	1.50
Ag-Dowex	1.99

#### The Degree of Cross-linking

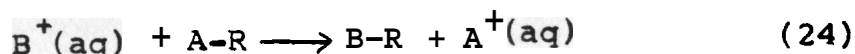
The degree of cross-linking is characterized by a value "X% cross-linked", which expresses the amount of cross-linking agent used to produce the particular resin, In our Dowex, the degree of cross-linking is recognized from the

designation Dowex 50W-X8, which means that styrene was copolymerized with 8% divinylbenzene.

Other types of Dowex commonly contain 4, 12, 16 or 24% "cross-linking" and this in turn affects the permeability of the particles to the flow of solvent and charged ions. Thus one cannot expect all Dowex 50W's to behave similarly in these respects.

#### Fractional Attainment of Equilibrium (F) for Ion Exchange

For the process

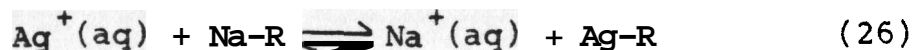


the equilibrium expression is traditionally written as the selectivity constant, ignoring the activity coefficients of the ions in both the solution and the resin,

$$K_A^B = \frac{\{B^+\}}{\{A^+\}} \cdot \frac{\{A^+\}}{\{B^+\}} \quad (25)$$

where the  $\{\}$  refer to effective resin concentrations.

In our case, the exchange reaction



is used as an example of how to calculate F, the fractional attainment of equilibrium. It is convenient to summarize the moles and concentrations as shown in Table 8,

TABLE 8

## ION-EXCHANGE SYSTEM PARAMETERS

	Initial	Equilibrium
Solution volume, $V_s$ (L)	0.050	0.045
Particle volume, $V_p$ (L)	$6.5 \times 10^{-5}$	$6.5 \times 10^{-5}$
Exchange capacity (meq/g)	6.3	6.3
$[Ag^+(aq)]$ (M)	$1.0 \times 10^{-5}$	
* $[Na^+-R]$ (M)	4.0	4.0
$[Na^+(aq)]$ (M)	0	$(1.0 \times 10^{-5} - X)$
* $[Ag^+-R]$ (M)	0	$(1.0 \times 10^{-5} - X)(V_s/V_p)$
$n_{Ag^+(aq)}$ (moles)	$5.0 \times 10^{-7}$	
$n_{Na^+-R}$ (moles)	$2.6 \times 10^{-4}$	

\* ( I refer to  $[M^+]$  in the resin, not the molar concentration of the resin.

It is clear that  $Na^+$  is 500 X more abundant in the resin than  $Ag^+$  in solution in this system, so that even if all the  $Ag^+(aq)$  were absorbed into the resin. the  $[Na^+-R]$  would hardly be affected. It is also clear that the ion initially in the resin is nearly  $10^6$  X more concentrated than the ion in solution. Using the selectivity constant of Kitchener

$$K = \frac{[Ag^+][Na^+]}{[Na^+][Ag^+]} = 9 \quad (27)$$

$$\frac{[(1 \times 10^{-5} - X)(770)] [(1.0 \times 10^{-5} - X)]}{[4][X]} = 9 \quad (28)$$



As  $X \ll 1 \times 10^{-5}$ , it may be eliminated from those terms, and  $X$  is solved for

$$X = 8.6 \times 10^{-10} \text{ M} \quad (29)$$

Thus, 99.99% of the  $\text{Ag}^+$  originally present in the aqueous phase is absorbed by the particle at equilibrium. As a practical matter, the fractional attainment of equilibrium,  $F$ , becomes the fractional loss of  $\text{Ag}^+$  from solution.

$$F(t) = \frac{(\text{Ag}^+)_o - (\text{Ag}^+)_t}{(\text{Ag}^+)_o - (\text{Ag}^+)_e} \approx 1 - \frac{(\text{Ag}^+)_t}{(\text{Ag}^+)_o} \quad (30)$$

Likewise, for particles initially loaded with a large excess of  $\text{Ag}^+$ , and exchanging a very small fraction of these for  $\text{Na}^+$ ,

$$F(t) \approx \frac{(\text{Na}^+)_t}{(\text{Na}^+)_o} \quad (31)$$

## CHAPTER IV

### RESULTS AND DISCUSSION

#### Fractional Attainment of Equilibrium (F)

Since the first treatment of kinetics of ion exchange adsorption by Boyd, Adamson and Myers,<sup>9</sup> the concept has generally been recognized that two diffusion mechanisms can occur, other factors being equal, in the region of low bulk solution concentrations, the rate is determined by the diffusion of ions through the liquid film surrounding the exchange particle. At high bulk concentrations, diffusion of the ions through the exchange particle itself is the rate-controlling step. A few examples of selectivity coefficients are given in Table 9. It is necessary to refer to such coefficients in evaluating the experimental results.

TABLE 9

SELECTIVITY COEFFICIENTS  $K_B^A$  FOR THE EXCHANGE OF VARIOUS CATIONS FOR  $Na^+(B)$  IN DOWEX 50 WITH 8% DVB

Ion(A)	$K_B^{A(20)}$	$K_B^{A(3)}$	$K_B^{A(7)}$
Na <sup>+</sup>	1.00	1.00	1.00
Ag <sup>+</sup>	9.00	4.30	3.90
Ca <sup>2+</sup>	21.00	2.60	
Mg <sup>2+</sup>		1.70	

In order to establish which mechanism operates in the present, highly dilute systems, it was necessary to determine the fractional attainment of equilibrium,  $F$  as a function of time,  $t$ . These are shown in Figures 12 to 16 for various combinations of metal ions in solution and in the **Dowex** particles. A comparison of the literature values of  $K$  (Table 9), and the experimental ( $F, t$ ) plots as given in Figure 12 to 16, leads to the following cases:

1.  $Ag^+$  and  $Ca^{2+}$  with Na-Dowex(50W-X8)

$Ag^+$  and  $Ca^{2+}$  replacing  $Na^+$  in Na-Dowex are shown in Figures 12 and 13. The nearly linear initial behavior observed indicates the rate-determining step is at first film-controlled diffusion. A dropping off at later periods implies a switch to particle-control. The selectivity coefficient  $K_{Na}^M > 1$  means the Na-Dowex absorbs  $Ag^+$  or  $Ca^{2+}$  more strongly than  $Na^+$ .

2.  $Na^+$  with Ag- and Ca-Dowex(50W-X8)

The inverse selectivity coefficient  $K_M^{Na} < 1$  means the Dowex resin absorbs  $Na^+$  less strongly than either  $Ag^+$  or  $Ca^{2+}$  ions. Despite this difference, Ag-Dowex, replaced by  $Na^+$ , as shown Figure 14 seems to conform to a film-controlled diffusion process, while Ca-Dowex replaced by  $Na^+$  (Figure 15) indicates a particle-controlled diffusion. This latter is shown by a rapid growth curve, followed by a slower exchange. The general conclusion that film-controlled diffusion occurs for these dilute systems is violated only when there is a much stronger attraction of the resin for the departing ion compared to the incoming ion (ie.  $Na^+$  and  $Ca^{2+}$ -Dowex).

F for Ag<sup>+</sup> / Na-Dowex

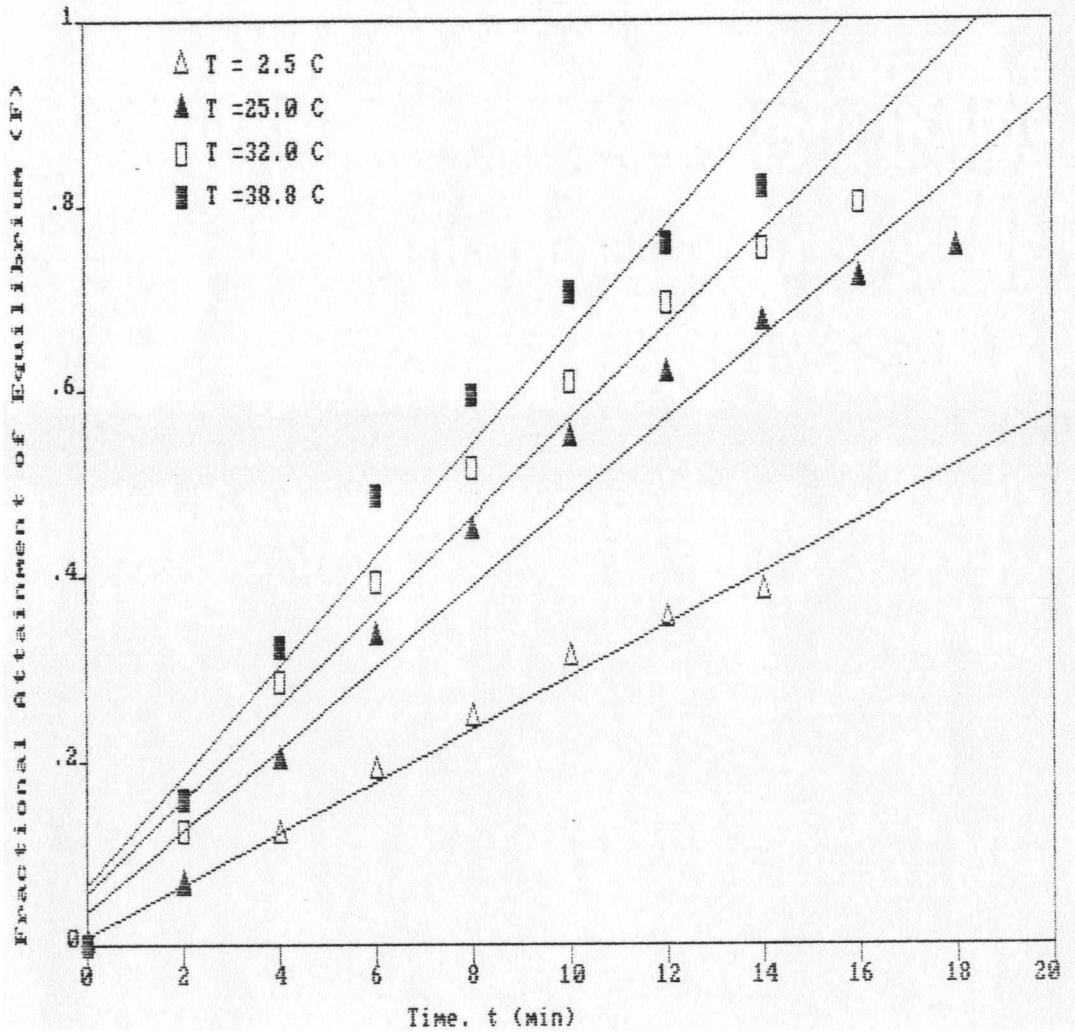


Fig. 12, Fractional attainment of equilibrium vs. time at four temperatures using 50mL of 1 ppm Ag<sup>+</sup>(aq) and 0.1g Na-Dowex.

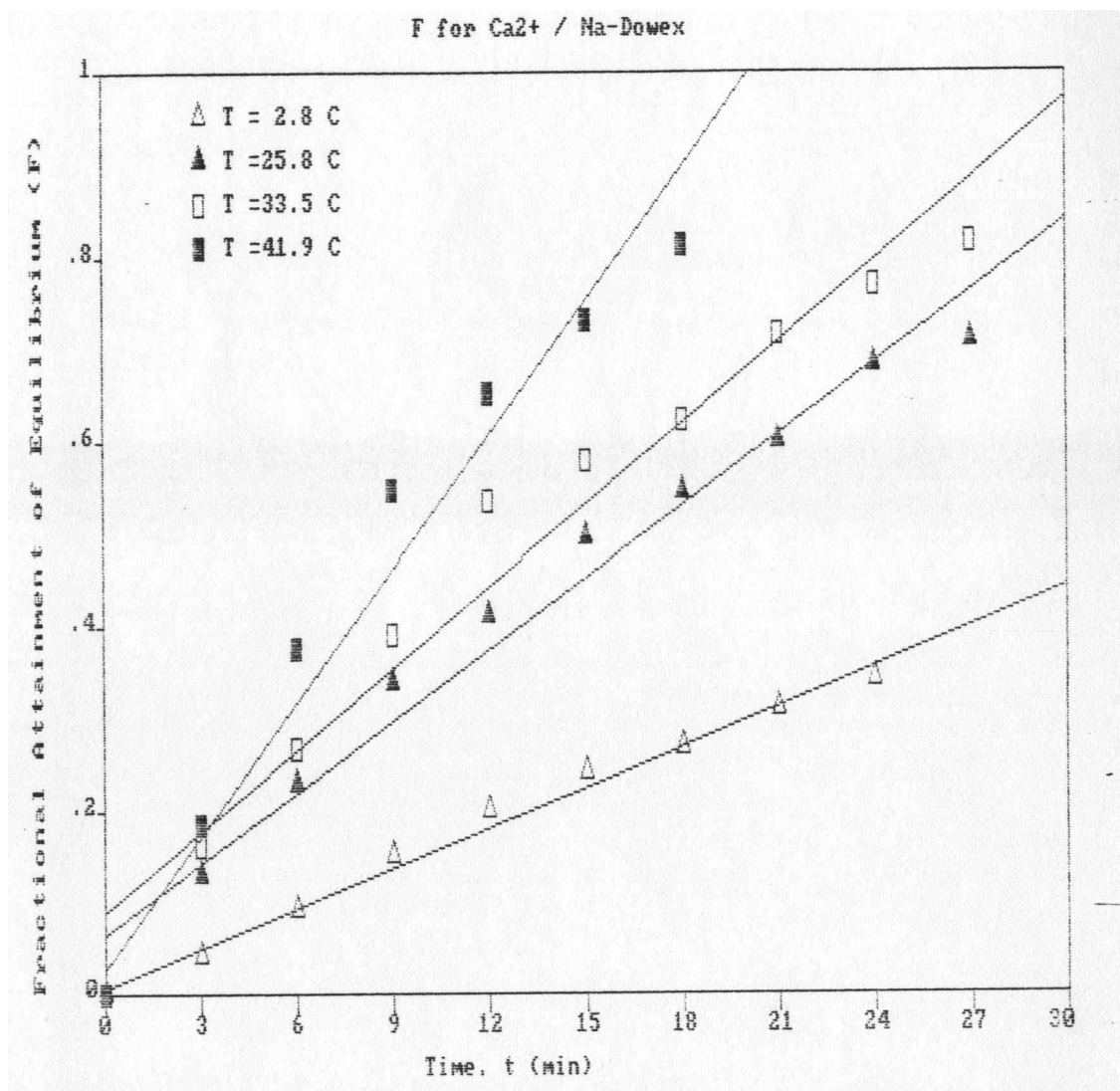
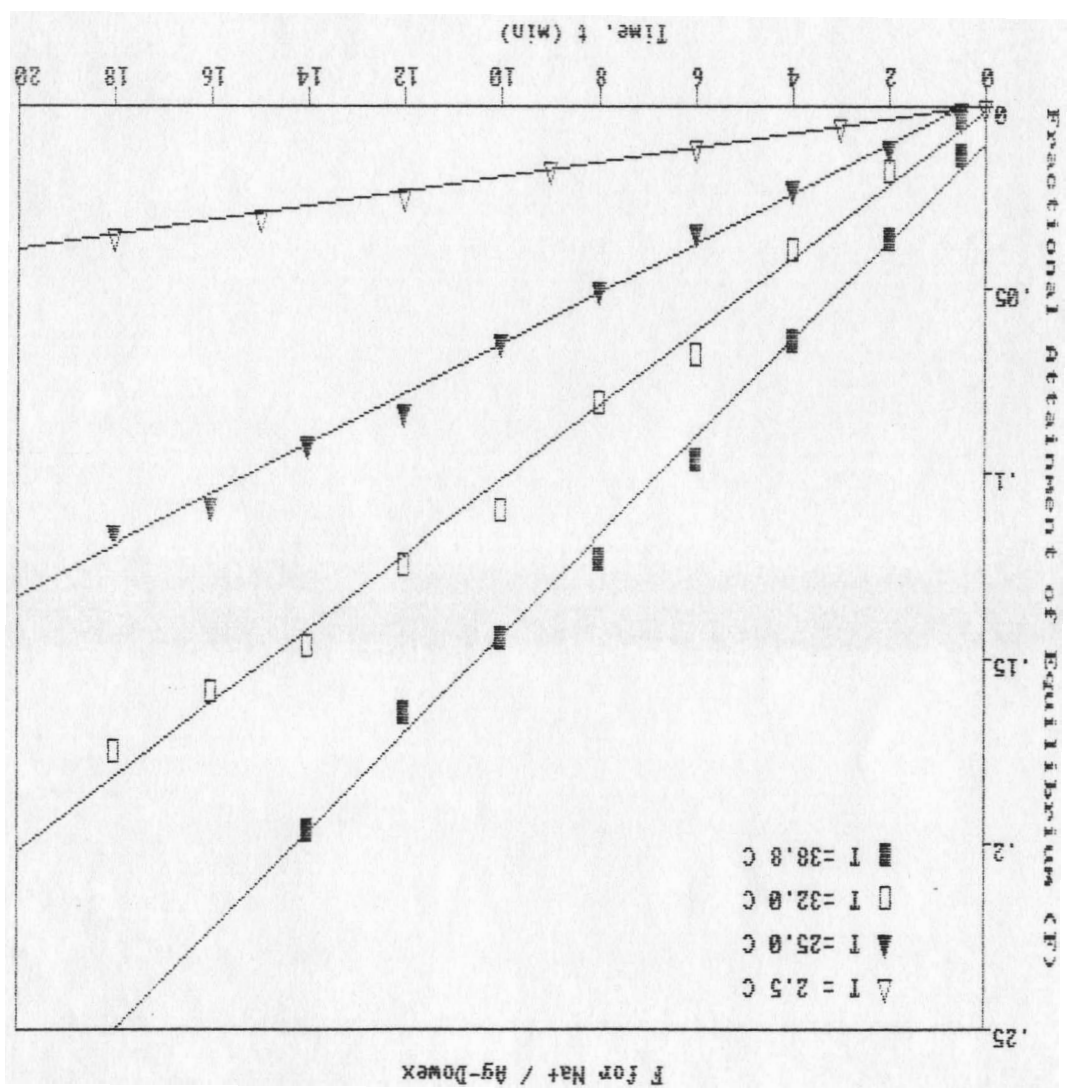


Fig. 13. Fractional attainment of equilibrium vs. time at four temperatures using 50mL of 0.5 ppm Ca<sup>2+</sup>(aq) and 0.1g Na-Dowex.

Fig. 14. Fractional attainment of equilibrium vs. time at four temperatures using 50ml of 1 ppm  $\text{Na}^+(\text{aq})$  and 0.02g Ag-Dowex.



F for Na<sup>+</sup> / Ca-Dowex

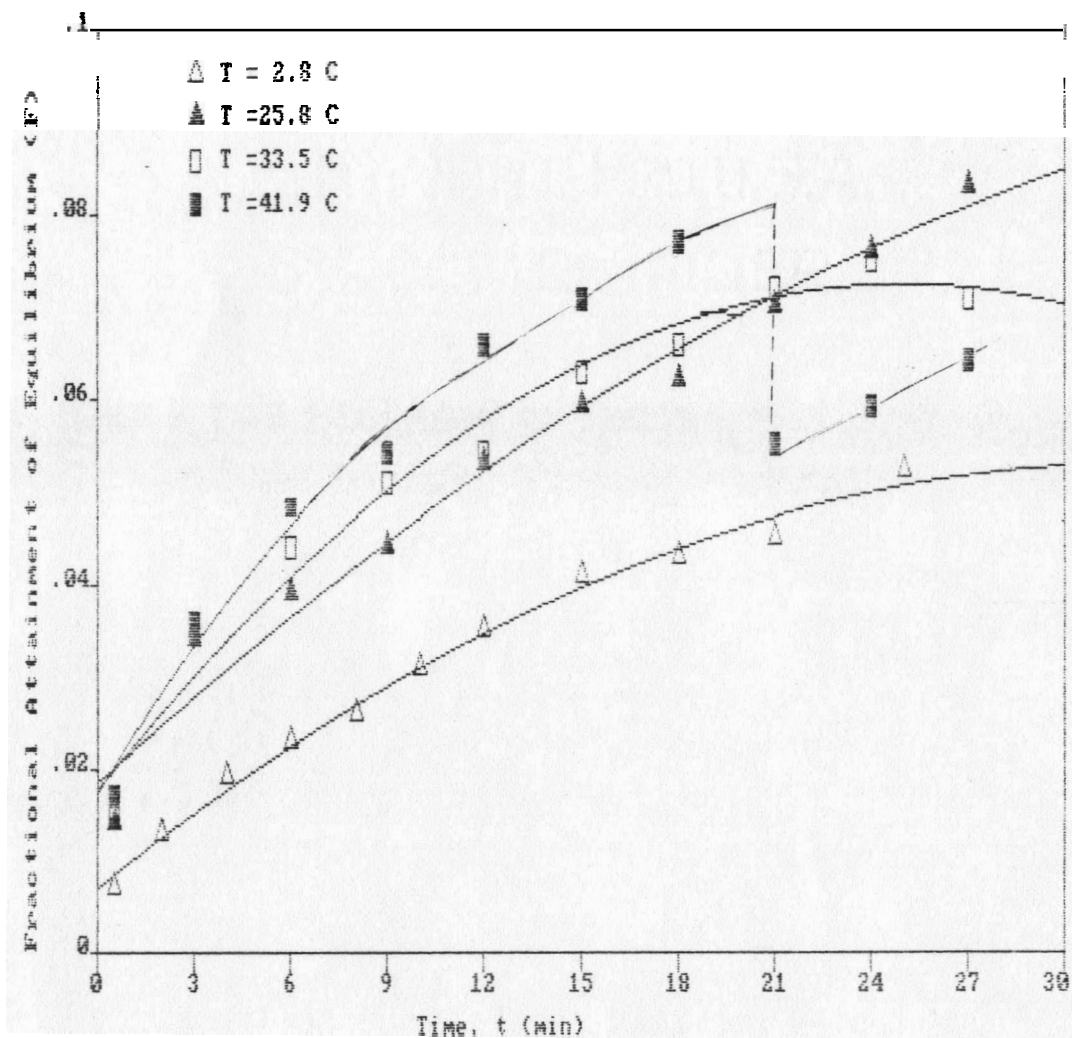


Fig. 15. Fractional attainment of equilibrium vs. time at four temperatures using 50mL of 1 ppm Na<sup>+</sup>(aq) and 0.1g Ca-Dowex.

F for Mg<sup>2+</sup> / Ca-Dowex

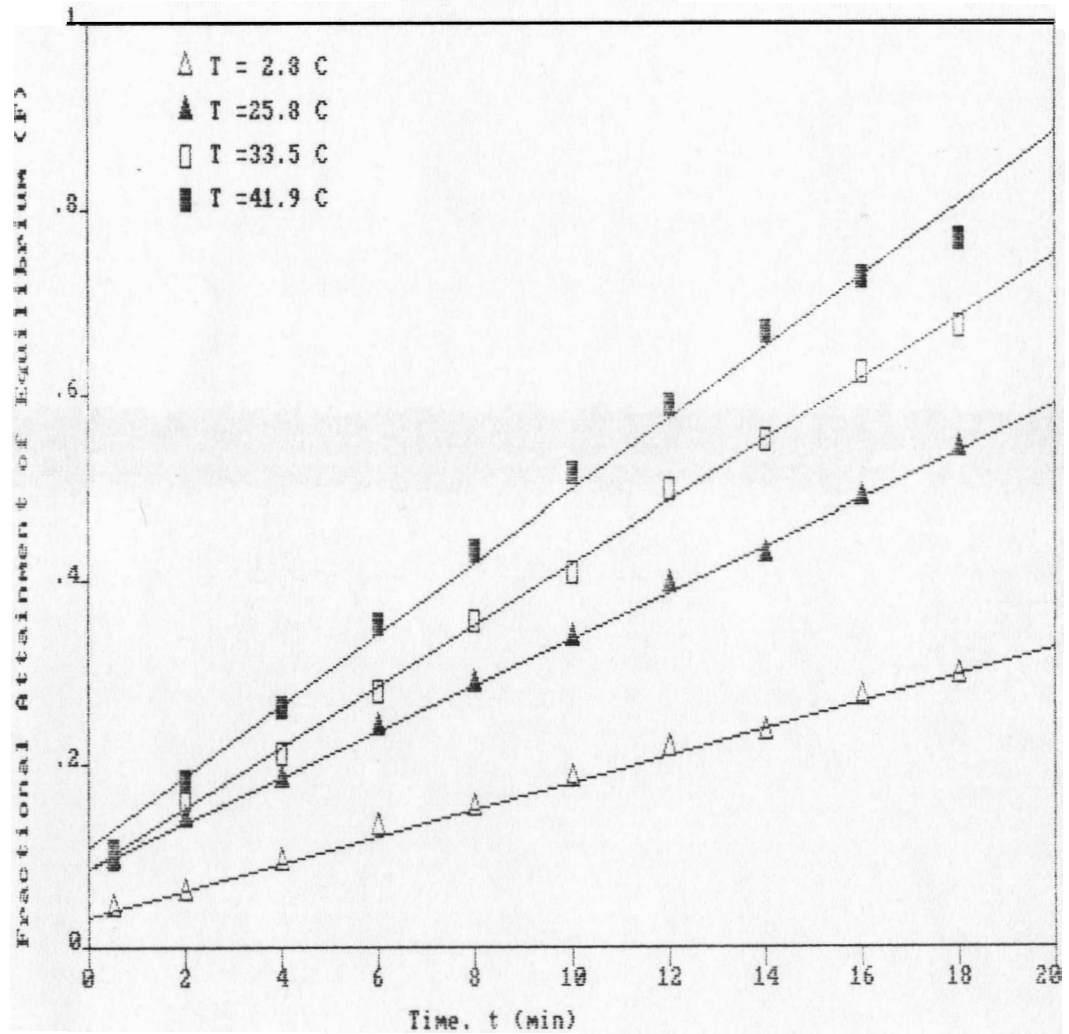


Fig. 16, Fractional attainment of equilibrium vs. time at four temperatures using 50mL of 0.5 ppm Mg<sup>2+</sup>(aq) and 0.1g Ca-Dowex.

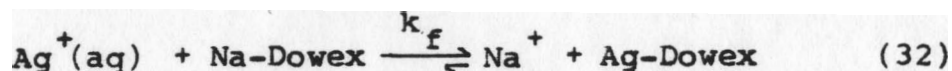


3. Mg<sup>2+</sup> with Ca-Dowex(50W-X8)

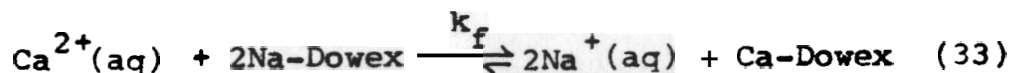
Figure 16 indicates a return to film-controlled diffusion, where Mg<sup>2+</sup> replaced Ca<sup>2+</sup>,

Pseudo-First-Order Kinetics of Ion Exchange

The rate constant data presented in Table 10 and 11 were obtained for the exchange reactions below,



and



The rate of disappearance of metal ions can be described by

$$-\frac{d(\text{Ag}^+)}{dt} = k_f \{ \text{Ag}^+ \} \{ \text{Na-Dowex} \} \quad (34)$$

and

$$-\frac{d(\text{Ca}^{2+})}{dt} = k_f \{ \text{Ca}^{2+} \} \{ 2\text{Na-Dowex} \} \quad (35)$$

These equations (for film-diffusion) may be simplified by noting that the {M-Dowex} is effectively constant, where M is present in 1000 fold excess over the solution ion.

Then

$$-\frac{d(\text{Ag}^+)}{dt} = k_{\text{exp}} \{ \text{Ag}^+ \} \quad (36)$$

and

$$-\frac{d(\text{Ca}^{2+})}{dt} = k_{\text{exp}} \{ \text{Ca}^{2+} \} \quad (37)$$

The rate constants,  $k_{\text{exp}}$ , can be calculated from the equations

$$k_{\text{exp}} = -d \ln (\text{Ag}^+)/dt \quad (38)$$

and

$$k_{\text{exp}} = -d \ln (\text{Ca}^{2+})/dt \quad (39)$$

The  $\ln$  of the concentrations are plotted as a function of time at the various temperatures (Figures 17 and 18), and show the expected first order behavior.

TABLE 10

RATE DATA FOR  $\text{Ag}^+$  EXCHANGE WITH Na-DOWEX

Temp., $^{\circ}\text{C}$	Rate constant, $k_{\text{exp}}$ , $\text{sec}^{-1}$
2.5	0.0351 $\pm$ 0.002
25.0	0.0828 $\pm$ 0.003
32.0	0.1019 $\pm$ 0.005
38.8	0.1179 $\pm$ 0.006

TABLE 11

RATE DATA FOR  $\text{Ca}^{2+}$  EXCHANGE WITH Na-DOWEX

Temp., $^{\circ}\text{C}$	Rate constant, $k_{\text{exp}}$ , $\text{sec}^{-1}$
2.8	0.0238 $\pm$ 0.001
25.8	0.0481 $\pm$ 0.002
33.5	0.0637 $\pm$ 0.003
41.9	0.0860 $\pm$ 0.005

Values for the apparent activation energy of diffusion,  $E_{\text{act}}$  were computed using the usual Arrhenius

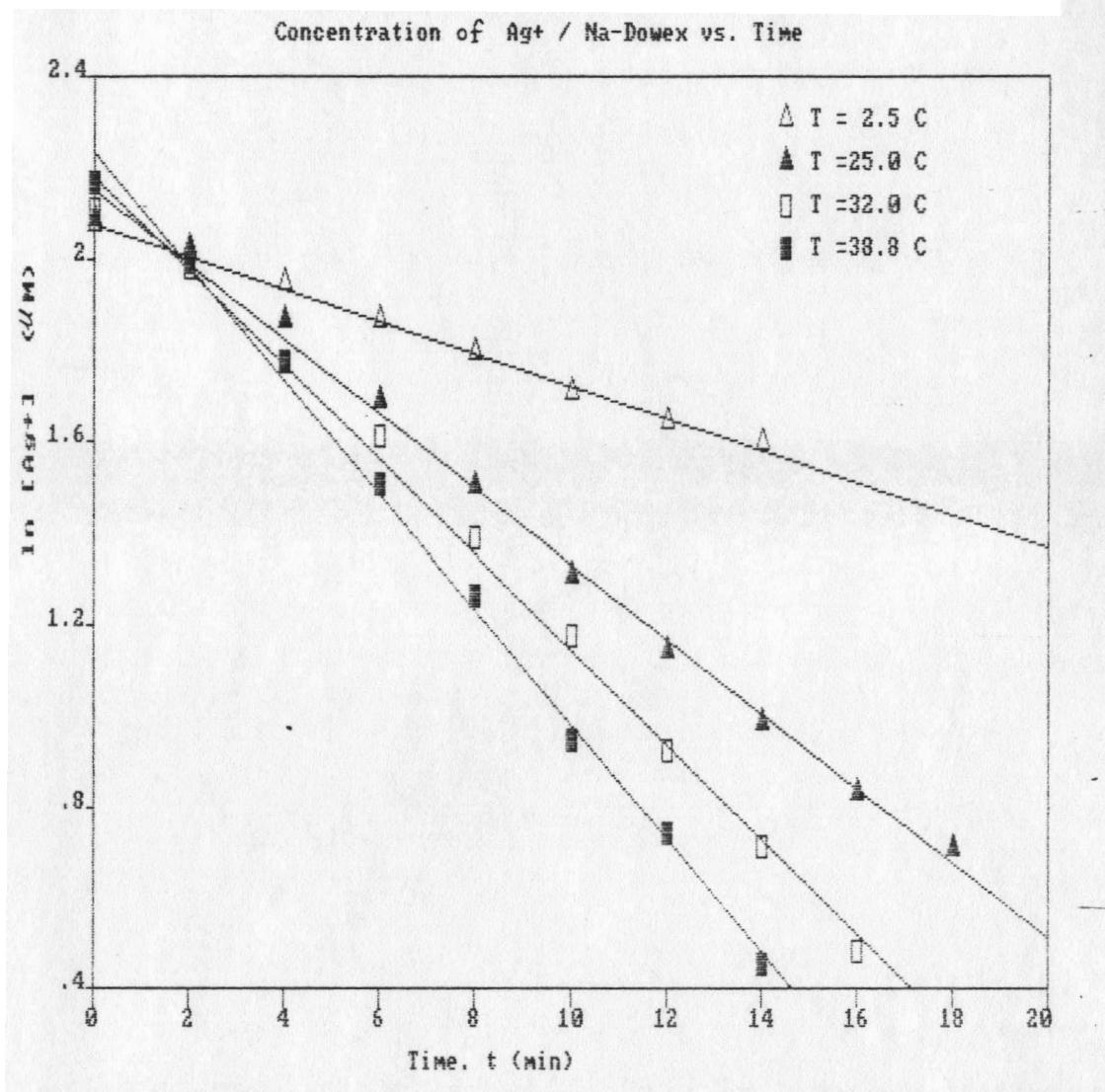


Fig. 17. Concentration of  $\text{Ag}^+$  vs. time in  $\text{Ag}^+$ /Na-Dowex system showing first order loss of  $\text{Ag}^+(\text{aq})$  from solution, at four temperatures.

Concentration of  $\text{Ca}^{2+}$  / Na-Dowex vs. Time

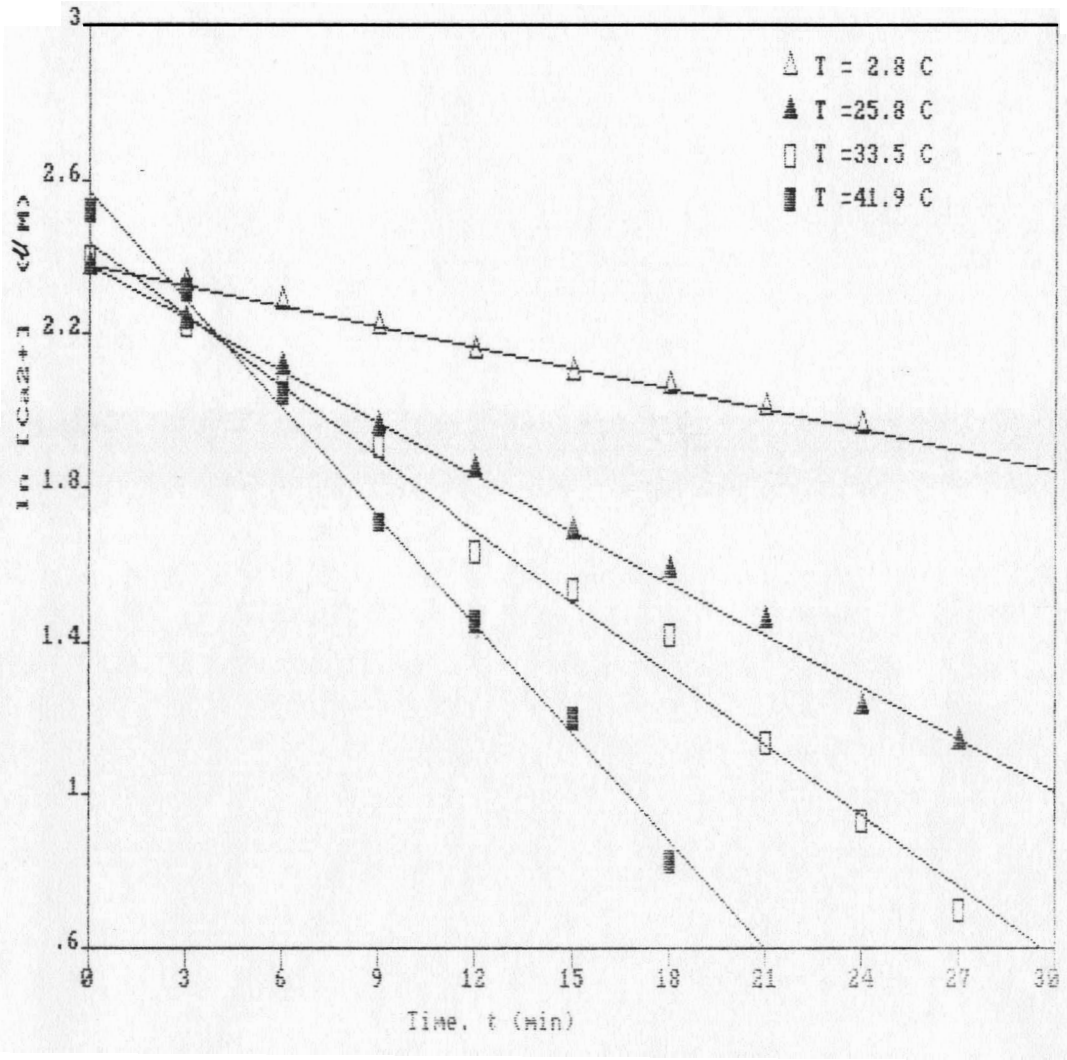


Fig. 18. Concentration of  $\text{Ca}^{2+}$  vs. time-in  $\text{Ca}^{2+}$ /Na-Dowex system showing first order loss of  $\text{Ca}^{2+}(\text{aq})$  from solution, at four temperatures.

formula

$$\frac{d(\ln k_{\text{exp}})}{d(1/T)} = - \frac{E_{\text{act}}}{R} \quad (40)$$

The plots of  $\ln k_{\text{exp}}$  vs.  $1/T$  for these two ion-exchange reactions were given in Figures 19 and 20. Table 12 collects the corresponding information.

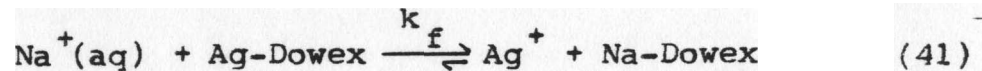
TABLE 12

ACTIVATION ENERGIES FOR FIRST-ORDER  $M^+$  EXCHANGE WITH Na-DOWEX

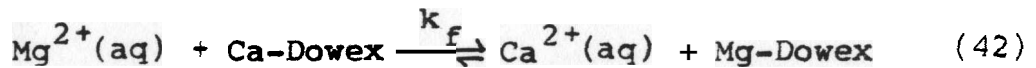
Counter ion	$E_{\text{act}}$ (kJ/mol)
$\text{Ag}^+$	$21.6 \pm 2.9$
$\text{Ca}^{2+}$	$24.0 \pm 3.0$

### Zero-Order Kinetics of Ion Exchange

The rate constant data presented in Table 13 and 14 -- were obtained for the exchange reactions.



and



The rate of appearance of metal ions can be described by

$$\frac{d[\text{Ag}^+]}{dt} = k_f [\text{Na}^+] [\text{Ag-Dowex}] \quad (43)$$

and

$$\frac{d[\text{Ca}^{2+}]}{dt} = k_f [\text{Mg}^{2+}] [\text{Ca-Dowex}] \quad (44)$$

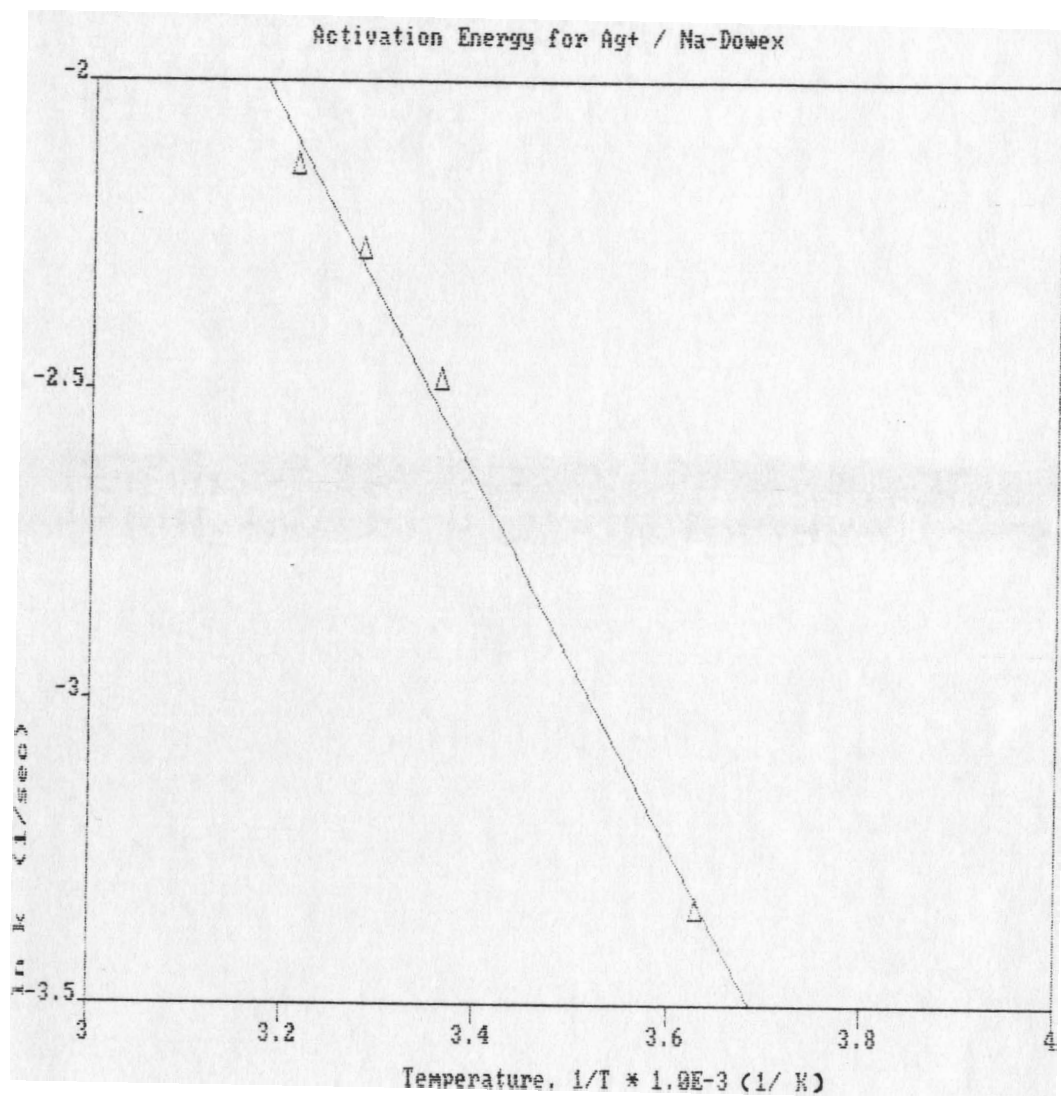


Fig. 19. Arrhenius plot for Ag<sup>+</sup>/Na-Dowex giving an activation energy of  $21.6 \pm 2.9$  kJ/mol.

Activation Energy for Ca<sup>2+</sup> / Na-Dowex

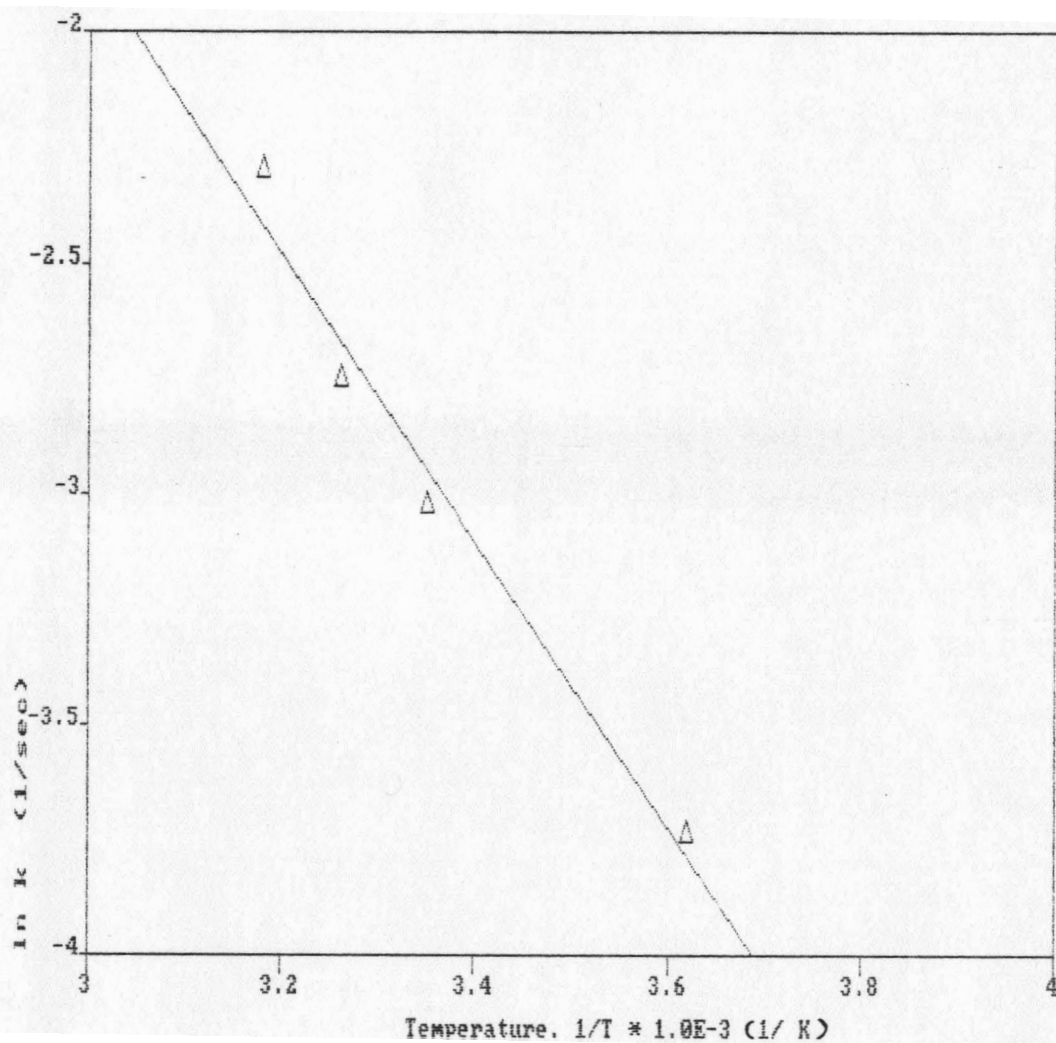


Fig. 20. Arrhenius plot for Ca<sup>2+</sup>/Na-Dowex giving an activation energy of  $24.0 \pm 3.0$  kJ/mol.

The equation (for film-diffusion control) found in these cases is

$$\frac{d(M^+)}{dt} = k_{\text{exp}} \quad (45)$$

where  $M^+$  is either  $\text{Ag}^+$  or  $\text{Ca}^{2+}$ , and the character is **zero** order.

The rate constants,  $k_{\text{exp}}$ , can be calculated from the equation

$$k_{\text{exp}} = \Delta[M^+]/\Delta t \quad (46)$$

The concentrations are plotted as a function of time at the various temperatures in Figures 21 and 22 and the data collected in Tables 13 and 14.

TABLE 13

RATE DATA FOR  $\text{Na}^+$  EXCHANGE WITH  $\text{Ag}$ -DOWEX

Temp., °C	Rate constant, $k_{\text{exp}}$ , M/sec
2.5	0.088
25.0	0.297
32.0	0.463
38.8	0.625

TABLE 14

RATE DATA FOR  $\text{Mg}^{2+}$  EXCHANGE WITH  $\text{Ca}$ -DOWEX

Temp., °C	Rate constant, $k_{\text{exp}}$ , M/sec
2.8	0.0164
25.8	0.0272
33.5	0.0339
41.9	0.0422



Concentration of Na<sup>+</sup> / Ag-Dowex vs. Time

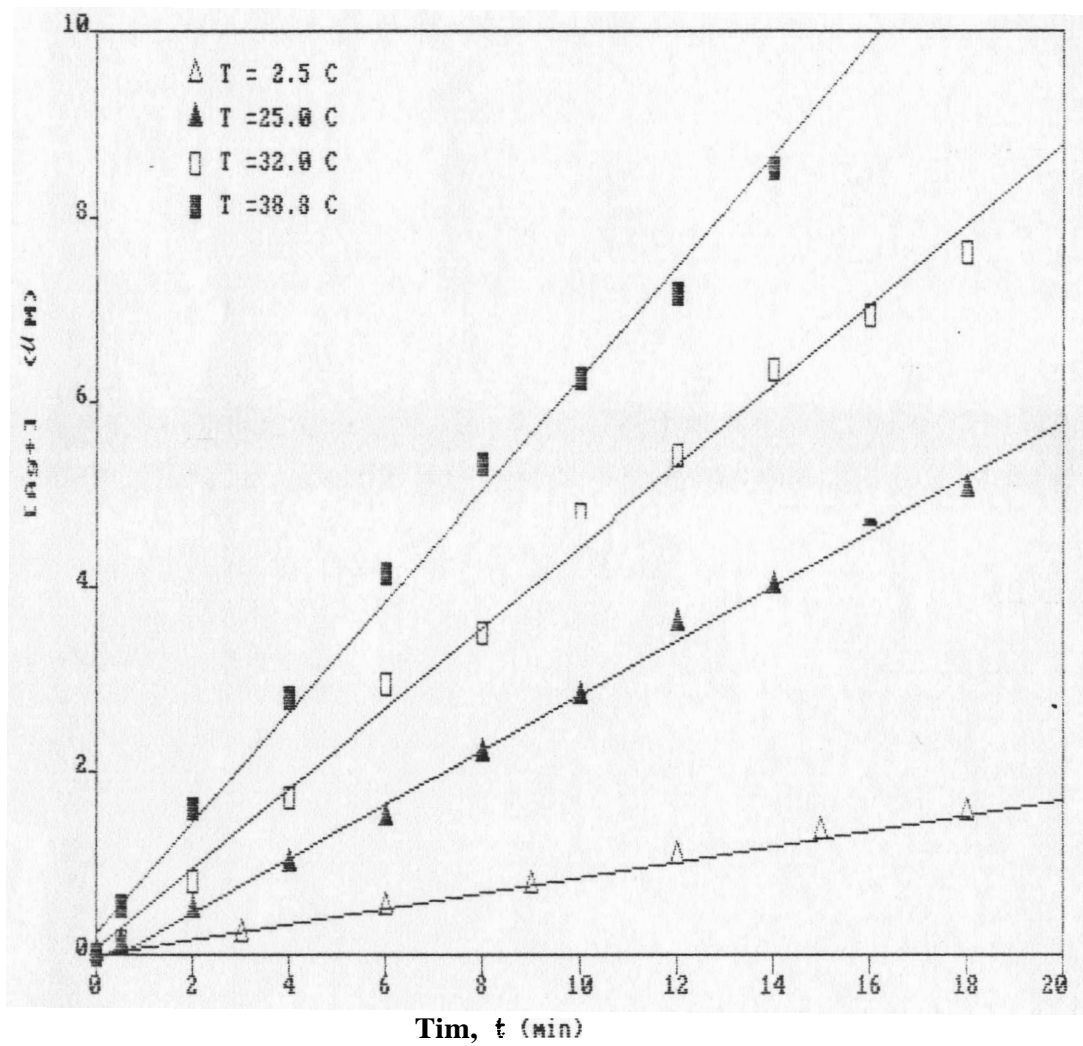


Fig. 21. Concentration of Ag<sup>+</sup> vs. time in Na<sup>+</sup>/Ag-Dowex system showing zero order release of Ag<sup>+</sup>(aq) from the Dowex, at four temperatures.

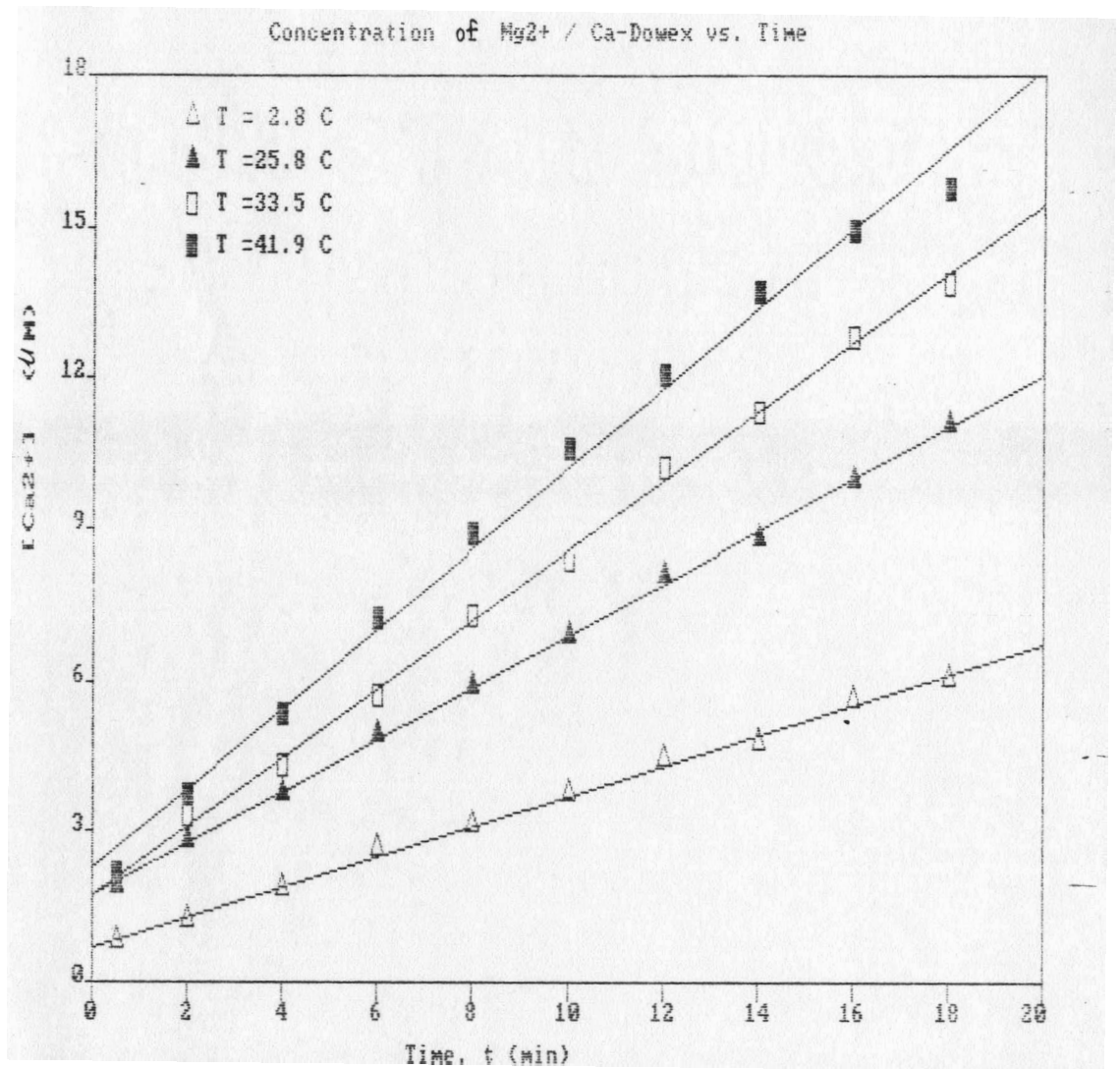


Fig. 22. Concentration of  $Ca^{2+}$  vs. time in  $Mg^{2+}$ /Ca-Dowex system showing zero order release of  $Ca^{2+}(aq)$  from the Dowex, at four temperatures.

Values for the apparent activation energy of these rate constants were **computed** as **before**. The **Arrhenius** plots are given in Figures 23 and 24, and the resultant data are presented in Table 15

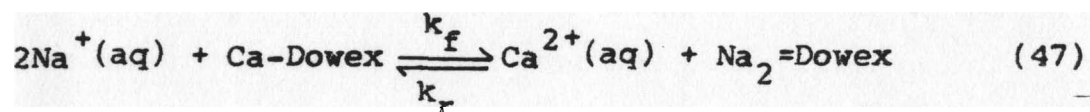
TABLE 15

ACTIVATION ENERGIES FOR ZERO-ORDER ION EXCHANGE FOR METAL IN DOWEX RESINS

Ion exchanger	Counter ion	$E_{act}$ (kJ/mol)
Ag-Dowex	Na <sup>+</sup>	38.5 ± 4.2
Ca-Dowex	Mg <sup>2+</sup>	18.1 ± 1.7

Fractional Order Kinetics of Ion Exchange

The sodium-Calcium exchange reaction can be written as



The rate of appearance of calcium can be represented here

$$\frac{d[\text{Ca}^{2+}]}{dt} = k_f [\text{Na}^+]^2 [\text{Ca-Dowex}] - k_r [\text{Ca}^{2+}] [\text{Na}_2=\text{Dowex}] \quad (48)$$

As shown in Figures 25 and 26, the relative concentrations of calcium vs. time, at different temperatures, is estimated to be between -1/2 and -1 order. It is noteworthy that this unusual kinetic description fits the only case found to be particle-controlled in its **diffusion mechanism**.

Activation Energy for Na<sup>+</sup> / Ag-Dowex

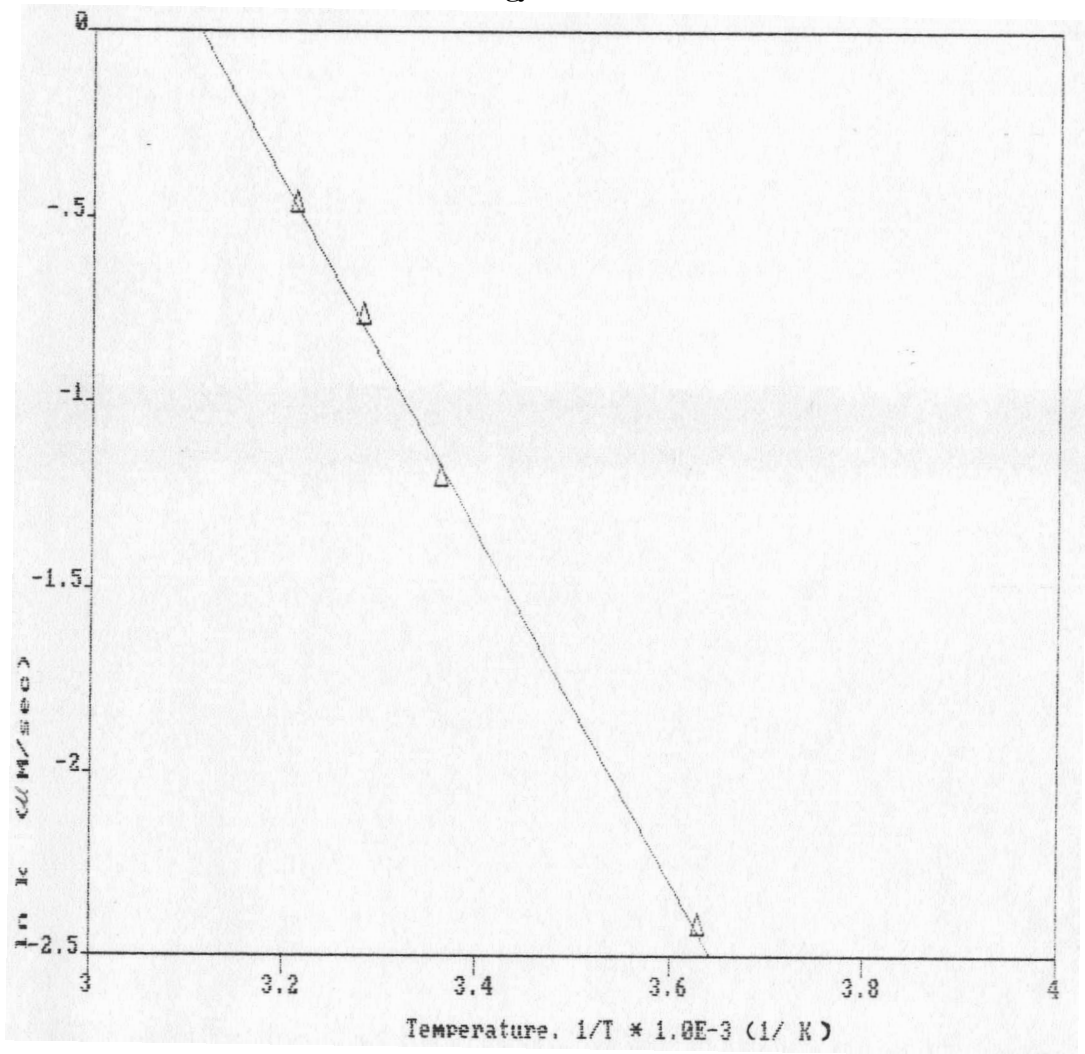


Fig. 23. Arrhenius plot for Na<sup>+</sup>/Ag-Dowex giving an activation energy of  $38.5 \pm 4.2$  kJ/mol.

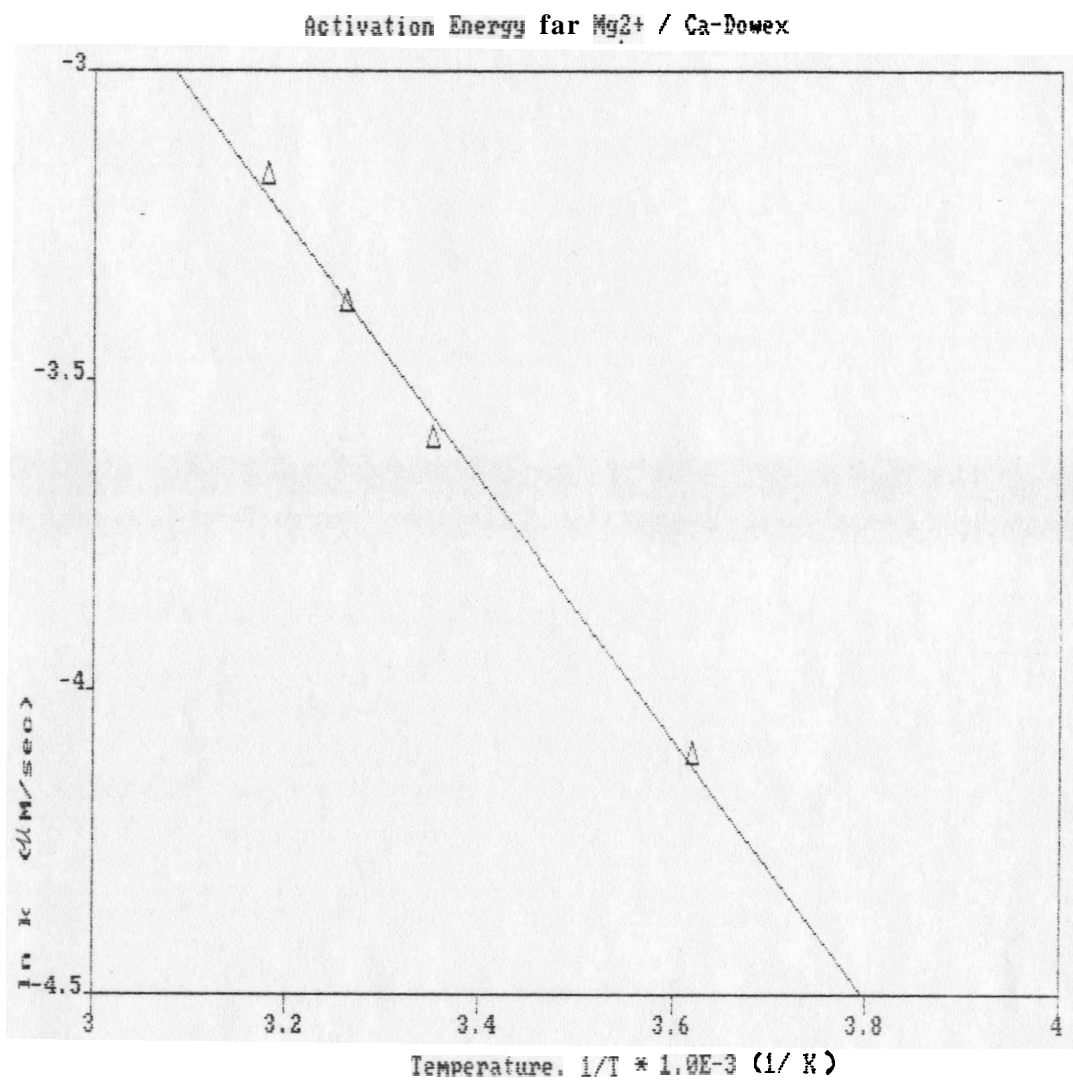


Fig. 24. Arrhenius plot for Mg<sup>2+</sup>/Ca-Dowex giving an activation energy of 18.1 ± 1.7 kJ/mol.

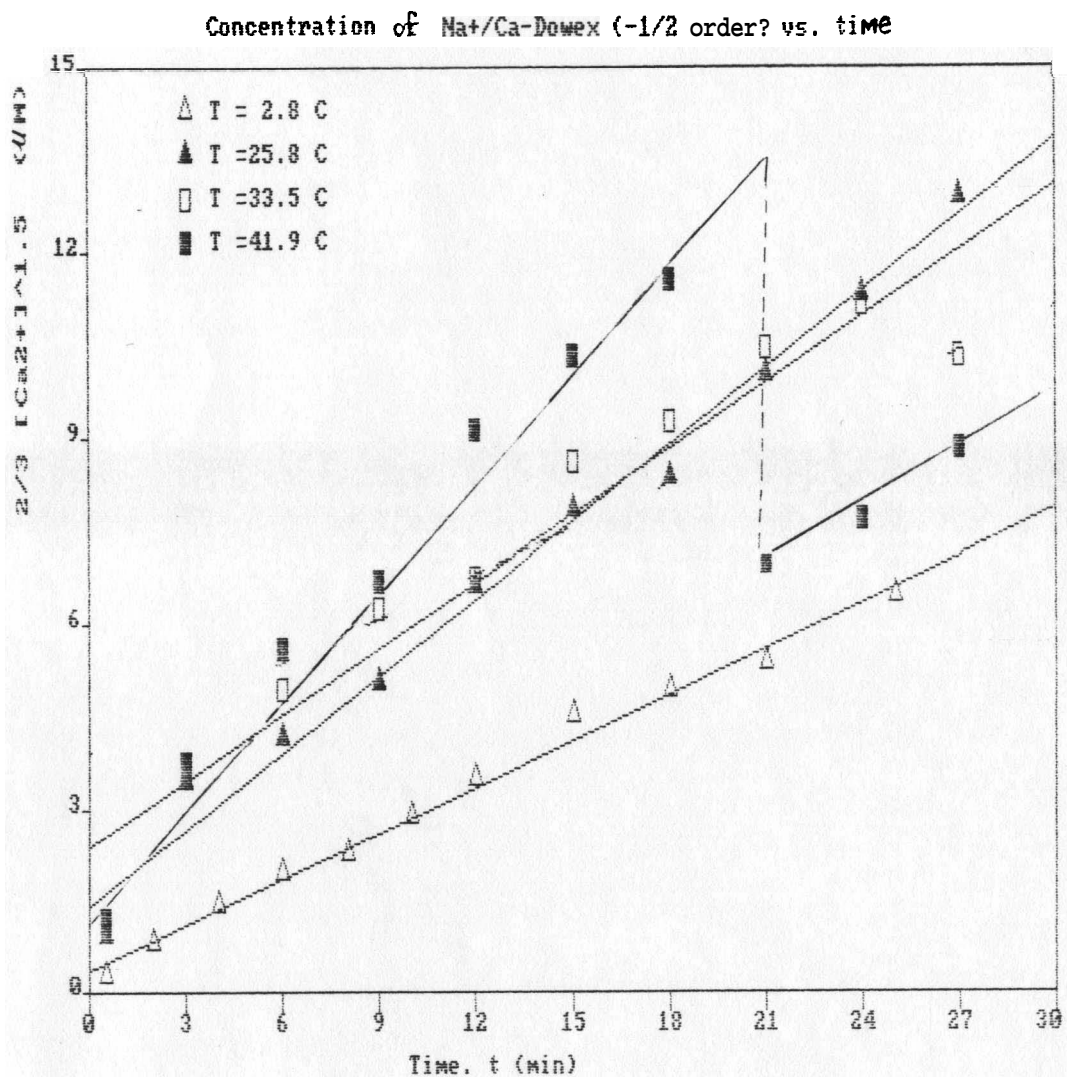


Fig. 25. Concentration of  $Ca^{2+}$  vs. time in  $Na^+$ /Ca-Dowex system estimating -1/2 order release of  $Ca^{2+}(aq)$  from the Dowex, at four temperatures.

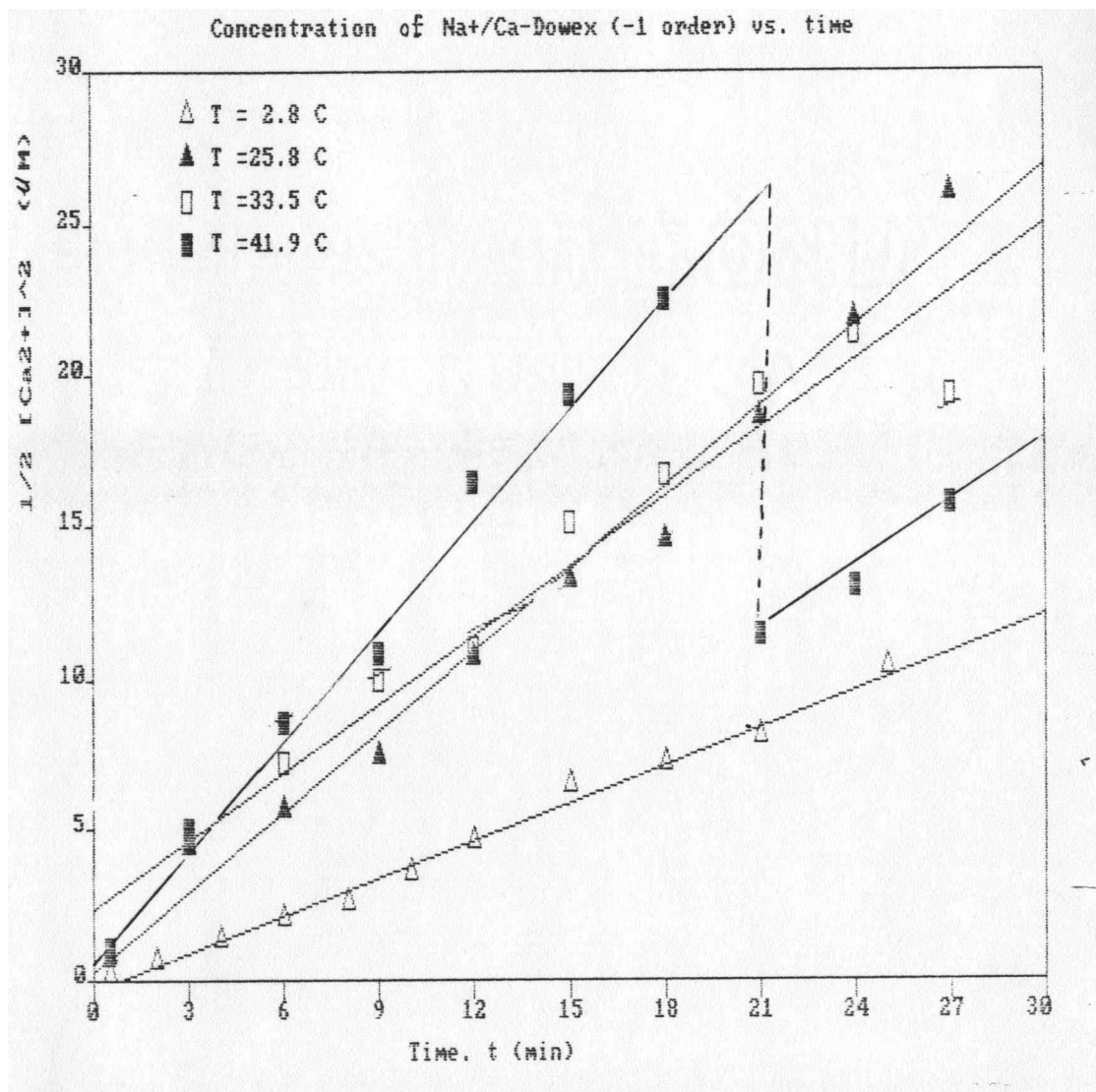


Fig. 26. Concentration of  $\sim a^*$  vs. time in Na<sup>+</sup>/Ca-Dowex system estimating -1 order release of Ca<sup>2+</sup>(aq) from the Dowex, at four temperatures.

### pH Independence of Calcium Ion Exchange

It might be expected that the  $-SO_3^-$  groups in Dowex-SOW could be protonated with  $H^+$  in competition with  $M^+$  in aqueous solvents. Thus a pH dependence is possible. However, under our conditions, moderate variation of the pH did not change the values of rate constant for the  $Ca^{2+}/Na$ -Dowex exchange significantly. (Table 16 and Figure 27)

TABLE 16

pH INDEPENDENCE OF CALCIUM ION EXCHANGE  
AT ROOM TEMPERATURE IN Na-DOWEX RESIN

	Rate constant, $k$ , $sec^{-1}$
0.5	$0.046 \pm 0.002$
7.0	$0.048 \pm 0.002$

### The Effect of The Amount of Dowex on The Ion-Exchange Kinetics

Ion-exchange rate constants for the  $Ca^{2+}$  plus Na-Dowex system were investigated over the mass range 0.076 to 0.228g Dowex. A comparison of these quantities is shown in Table 17 and Figure 28. The rate constants are found to be directly proportional to the amount of Dowex resin. This makes possible a comparison of rate data obtained with different amounts of Dowex by simple normalization to a common amount. It also shows that the rate of adsorption of the  $Ca^{2+}$  is proportional to the surface area presented



pH Independence of  $\text{Ca}^{2+}$  / Na-Dowex

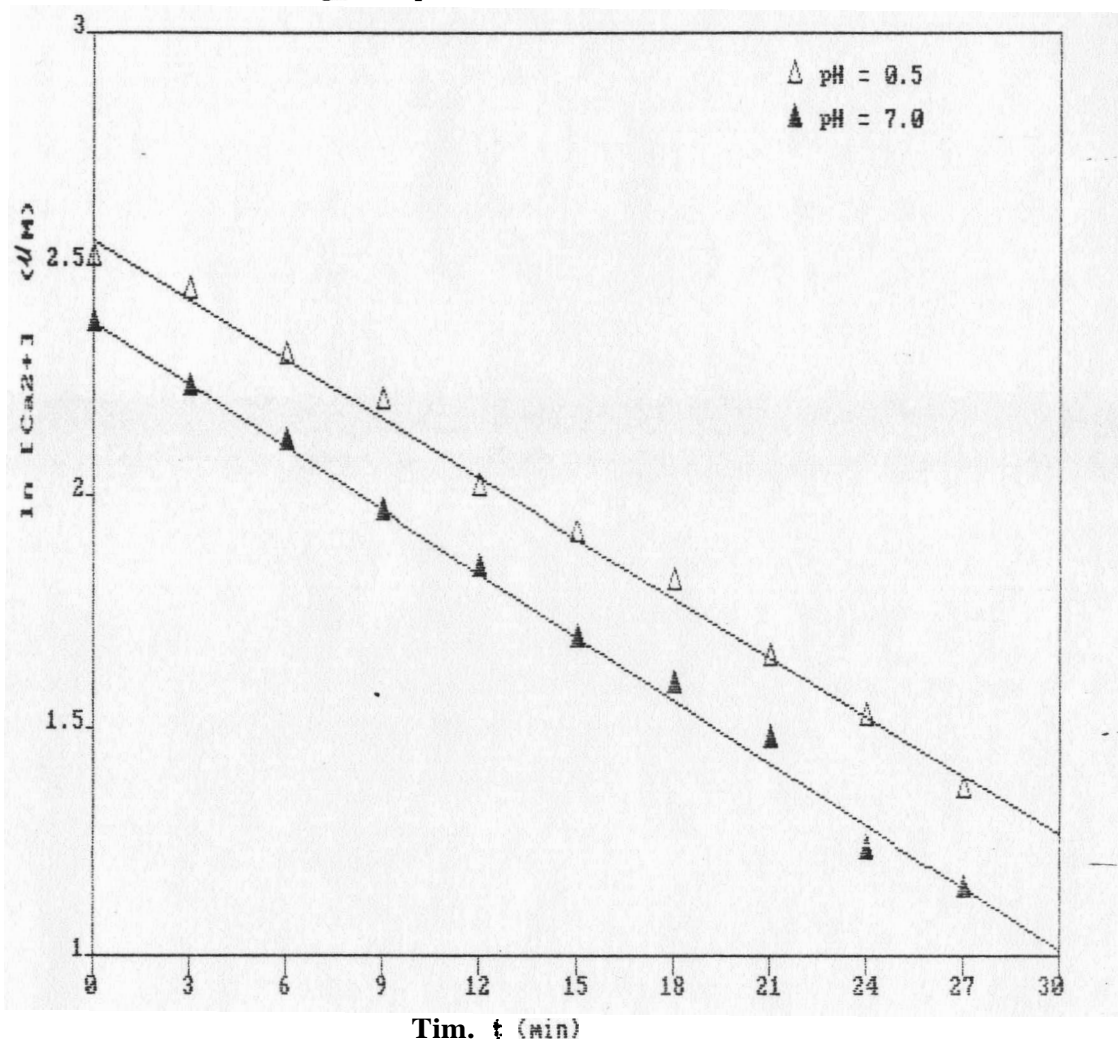


Fig. 27. Concentration of  $\text{Ca}^{2+}$  vs. time in  $\text{Ca}^{2+}$ /Na-Dowex system showing the pH independence at room temperature.

Ca<sup>2+</sup>(aq) Decay with Various Amounts of Na-Dowex

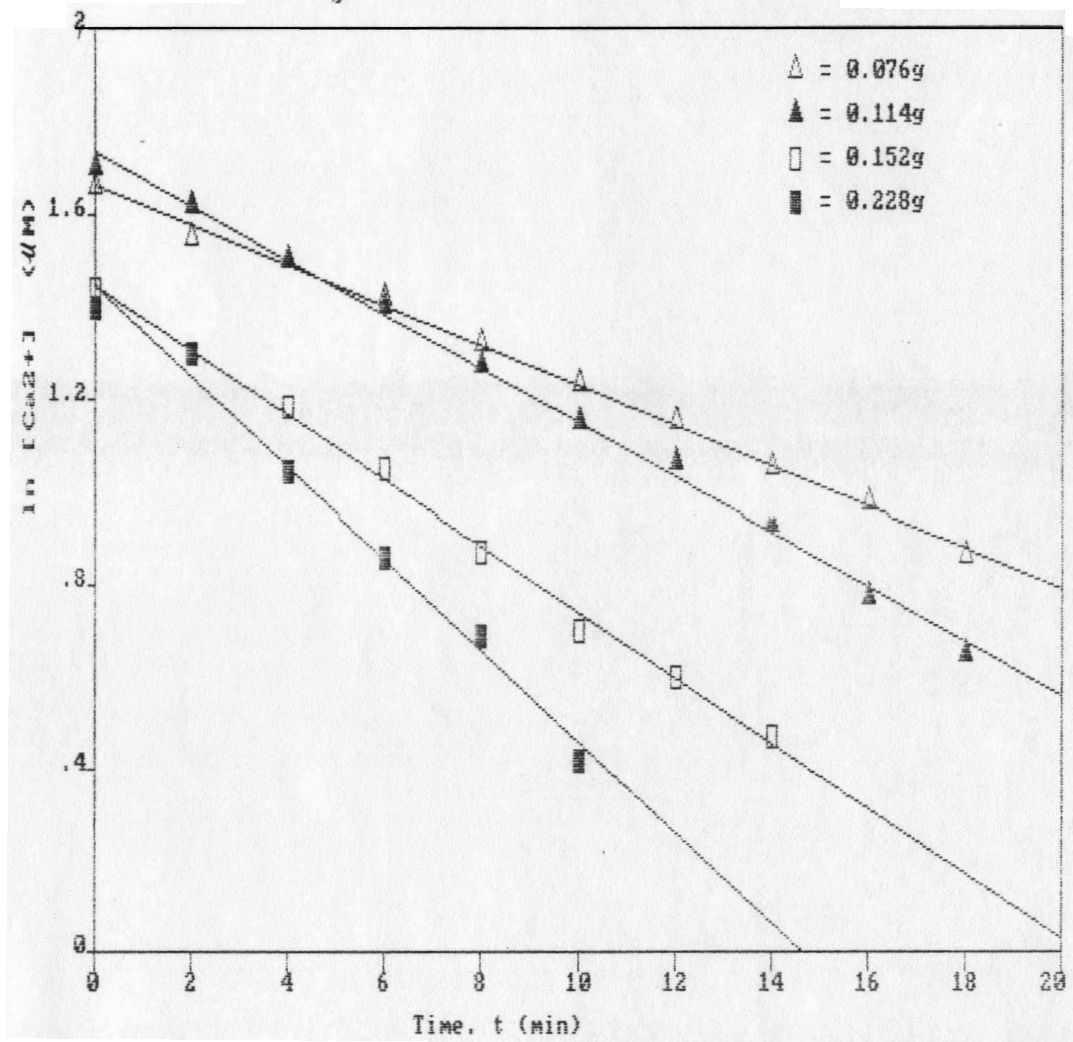


Fig. 28. Concentration of Ca<sup>2+</sup> vs. time in Ca<sup>2+</sup>/Na-Dowex system showing proportion to the amount of Dowex resin at room temperature.

by the Dowex particles to the solution, which is consistent with a film-diffusion controlled process,

TABLE 17

THE EFFECT OF THE MASS OF DOWEX ON THE  
 $\text{Ca}^{2+}$  PLUS Na-DOWEX ION EXCHANGE AT  $26^{\circ}\text{C}$

Weight, g	$k, \text{sec}^{-1}$	$k^{\circ}(\text{for } 0.1\text{g})(\text{sec}^{-1})$
0.076	0.037	0.049
0.114	0.055	0.048
0.152	0.071	0.047
0.228	0.110	0.048

Table 18 summarizes the kinetic data for all the processes considered in comparison with what is available in the literature. It is apparent that no direct comparisons are possible, mainly because the activation energies previously measured apply to particle-controlled diffusion processes,

TABLE 18

## SUMMARY OF ION EXCHANGE ACTIVATION ENERGY DATA

Resin type	Exchange reaction	Control mechanism	Kinetic order	E <sub>act</sub> (ΔH <sup>‡</sup> ) kJ/mol	
				This work	Boyd and Soldano <sup>4</sup>
Dowex 50W-X8	$\text{Ag}^+ + \text{Na-D} \longrightarrow$	film	(1st order)	21.6 ± 2.9	
	$\text{Ca}^{2+} + \text{Na-D} \longrightarrow$	film	(1st order)	24.0 ± 3.0	
Dowex 50W-X8	$\text{Na}^+ + \text{Ag-D} \longrightarrow$	film	(0 order)	<b>38.5 ± 4.2</b>	
	$\text{Mg}^{2+} + \text{Ca-D} \longrightarrow$	film	(0 order)	<b>18.1 ± 1.7</b>	
Dowex 50-X8.6	$\text{Na}^+ + \text{Na-D} \longrightarrow$	particle			27.2
	$\text{K}^+ + \text{K-D} \longrightarrow$	particle			21.8
	$\text{Ag}^+ + \text{Ag-D} \longrightarrow$	particle			<b>24.7</b>
Dowex 50-X8	$\text{Zn}^{2+} + \text{Zn-D} \longrightarrow$	particle			<b>30.7</b>
	$\text{Sr}^{2+} + \text{Sr-D} \longrightarrow$	particle			34.7

\* indicates radioactive tracer.

## CHAPTER V

### CONCLUSIONS

The present work has shown that atomic absorption spectroscopy is a suitable technique for studying ion exchange kinetics in dilute solutions. Past studies have been confined to those cases of high ionic strengths and particle-controlled diffusion cases, which are complicated by inter-ionic effects as well as ion-matrix effects.

With the exception of the  $\text{Na}^+ + \text{Ca-Dowex}$  experiment, which appeared negative order in  $\text{Ca}^{2+}$ , our systems were predominantly film-controlled, and either zero or first order in their behavior. Generally, when the Dowex resin was more attracted to the solution ion compared to the matrix ion, a first order loss of the solution ion was observed. But when the matrix bound ion was more attracted than the solution ion, zero order exchange took place.

Finally, when the disparity in attractiveness was greatest, with the most strongly bound ion initially in the matrix, negative order kinetics was observed, indicating the possible significance of a back reaction.

The activation energies measured in this work apply to more idealized film-controlled diffusion, where the film is almost exclusively water. Previous workers have limited their studies to particle-controlled cases, at high ionic strengths, where activation data are contributed to by more

factors.

Although no direct comparison with earlier data can be made, it should be noted that there is really no large difference in the activation energies between the two. Perhaps this is due to the essentially aqueous nature of both the film and the channels within the polymer matrix.

Unexpectedly, however, the difference between the activation energies for the  $\text{Ag}^+ + \text{Na-Dowex}$  exchange ( $22 \pm 3$  kJ/mol) and the reciprocal  $\text{Na}^+ + \text{Ag-Dowex}$  exchange ( $38 \pm 4$  kJ/mol) is much greater than the expected enthalpy difference for the exchange (1 kJ/mol).

Since the transition state for both exchanges involves the codiffusion of  $\text{Ag}^+$  and  $\text{Na}^+$  through an essentially aqueous film, the implication is that the enthalpy difference should be close to 16 kJ/mol. This could be related to the much lower solubility of  $\text{Ag}_2\text{SO}_4$ , compared to  $\text{Na}_2\text{SO}_4$ , if the  $\text{Ag}^+ \text{SO}_4^{2-}$  interaction resembles that in the Dowex matrix. This enthalpy should be measured under our conditions.

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