HC_y of 1.26 and 1.22 × 10^{-5} which are to be compared with literature values from conductance data of 1.26,[5] 1.34[6] and 1.32 × 10^{-5}.[7]

Similar measurements in the solvents methyl and ethyl alcohol and ethylene glycol, for the solvent salt lithium chloride are summarized in Table III. In these cases there are no literature values for comparison and the thermodynamic dissociation constant is based on the values for benzoic acid.

TABLE III

THE DISSOCIATION CONSTANT OF CYCLOHEXANECARBOXYLIC ACID IN ALCOHOLS

T, 25°; solvent salt, LiCl

Electrolyte mole/liter	CH_3OH $K_{A_xB_0}$[a]	CH_3OH 10^{10} K_c	CH_3OH K_c/K_a	C_2H_5OH $K_{A_xB_0}$[a]	C_2H_5OH 10^{10} K_c	C_2H_5OH K_c/K_a	$(CH_2OH)_2$ $K_{A_xB_0}$	$(CH_2OH)_2$ 10^{10} K_c
0		0.923			0.170			
0.10	0.220	8.32	9.0	0.195	7.61	44.8	0.213	94.0

[a] Reference acid, benzoic acid.

Justification for the assumption that the ratio of the dissociation constants is independent of the lithium chloride concentration is given in Table IV.

TABLE IV

$K_{A_xB_0}$ for HC_y/HB in the solvent ethanol

μ[a]	0.103	0.196	0.279	0.382	0.475
$K_{A_xB_0}$	.193	.195	.193	.195	.195

[a] Mainly LiCl.

Further evidence for the independence of the ratio of dissociation constants on electrolyte concentration in alcohols will be presented in another paper.

CHICAGO, ILLINOIS

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(5) J. S. Lumsden, *J. Chem. Soc.*, **87**, 90 (1905).

(6) N. Zelinsky and N. Izgaruisher, *J. Russ. Phys. Chem. Soc.*, **40**, 1379 (1908).

(7) C. H. Spiers and J. F. Thorpe, *J. Chem. Soc.*, **127**, 538 (1925).

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY, DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH]

Properties of Ion-Exchange Resins in Relation to their Structure. III. Kinetics of Exchange

BY D. REICHENBERG

RECEIVED MAY 28, 1952

A study has been made of the kinetics of sodium-hydrogen exchange on sulfonated cross-linked polystyrenes in bead form. Resins of 5 and 17% (nominal) divinylbenzene content were fractionated by wet elutriation and matched according to swollen particle diameter. The rates of exchange were measured by an "indicator" method. For both resins, the kinetics at high sodium ion concentrations in solution (>1 N) are clearly distinct from those at low concentrations (<0.05 N). At high concentrations, the rate is independent of the sodium ion concentration and inversely proportional to the square of the particle radius. At low concentrations, the rate is proportional to the sodium ion concentration and inversely proportional to the particle radius. These results support the view that at low concentrations, the rate is controlled by "film" diffusion, and at high concentrations by "particle" diffusion. Equations of the type derived by Boyd, Adamson and Myers on the basis of these mechanisms are obeyed. In further confirmation, when close fractions of the same mean particle diameter were compared it was found that the two resins exchange initially at the same rate *per particle* at low concentrations (film diffusion) but at markedly different rates at high concentrations (particle diffusion).

Although there had been previous experimental studies of the rates of ion-exchange reactions[1] the first serious attempt to elucidate the rate-controlling mechanism was made by Nachod and Wood.[2] They studied the rates of exchange of the pairs of ions hydrogen-calcium, calcium-hydrogen and sodium-calcium with a number of commercial cation-exchange resins in dilute (0.001 to 0.01 N) solutions. They concluded that the "rate of bringing dissolved ions up to and away from the surface of the exchange granules" (or what is now known as "film-diffusion") "is rate determining in the case of sulfonated coal between 27 and 60°." However, since other resins under identical agitation conditions showed widely different rates, other factors were considered to play some role. Anion-exchange (chloride-hydroxide) on weak base resins was found to be 1/400 to 1/4000 as fast, "suggesting a different reaction mechanism for this class of exchanger." In a later paper[3] they showed that in cation exchange in dilute solution the nature of the anion had no effect on the rate.

Kunin and Myers[4] studied the kinetics of anion-exchange on four weak-base resins using a number of anion-pairs and concluded that "diffusion" (or what is now called "particle diffusion") was the rate-controlling process in all cases.

A great clarification of the field was made by Boyd, Adamson and Myers.[5] Although a chemical process, film diffusion and particle diffusion had previously all been separately postulated as possible rate-determining mechanisms, they gave for the first time a clear analysis of the kinetics corresponding to each hypothesis. The equations that they derived were found to assume a particularly simple and readily verifiable form if the composition of the exchanger remained virtually unaltered by the exchange, *i.e.*, if the "in-going" ion was present in solution in minute concentration compared with that of the displaced ion. This necessitated radiotracer technique, an important point since in other studies (the present one included) in which radiotracer technique has not been used, it has been necessary to violate the above condition. In most other work, the resin is changed largely or entirely from one cationic form to the other. In these circumstances, while the equation derived by Boyd, Adamson and Myers for a particle diffusion

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(1) See reference (2).

(2) F. C. Nachod and W. Wood, THIS JOURNAL, **66**, 1380 (1944).

(3) F. C. Nachod and W. Wood, *ibid.*, **67**, 629 (1945).

(4) R. Kunin and R. J. Myers, *J. Phys. Colloid Chem.*, **51**, 1111 (1947).

(5) G. E. Boyd, A. W. Adamson and L. S. Myers, THIS JOURNAL, **69**, 2836 (1947).

controlled rate remains applicable, that for a film diffusion controlled rate becomes inapplicable.[6] Boyd, Adamson and Myers investigated the kinetics of the exchange for several ion-pairs with a phenolsulfonate resin and concluded that for very low concentrations (<0.003 N) in solution of the displaced ion, film diffusion was rate controlling, while at higher concentrations (>0.1 N) particle diffusion was rate controlling. From what has been said, it is clear that these conclusions cannot be applied directly to solutions in which the ingoing ion is no longer a microcomponent, even though the same resin were to be used. It is important also to remember that when Boyd, Adamson and Myers specified the concentration in solution, they referred to the *displaced* ion, while other authors refer to the *ingoing* ion.

Kressman and Kitchener[7] studied the kinetics of a number of exchanges on a phenolsulfonate resin. In their experiments, 2.5 mg. equiv. of resin in one ionic form was brought into contact for an appropriate time with 125 ml. of a solution containing an equivalent amount of the other ion, *i.e.*, the solution was always 0.02 N. Thus theirs was a "limited bath" method (unlike that of Boyd, Adamson and Myers, who used a "shallow bed," *i.e.*, "infinite bath," method) and the amount of ingoing ion in solution was insufficient to drive the exchange to completion. As a result, the appropriate equations for the case of particle diffusion took a rather complicated form and Kressman and Kitchener were obliged to use the simpler but very approximate "parabolic" equation of Barrer.[8] It is shown later in the present paper that where it is necessary to depart from the conditions laid down by Boyd, Adamson and Myers, it is best, particularly in the case of a "limited bath" method, to go to the other extreme, *i.e.*, to arrange matters so that the exchange proceeds nearly or entirely to completion. Kressman and Kitchener, working at the single concentration of 0.02 N, concluded that some of the exchanges (*e.g.*, potassium–ammonium) had a rate controlled by film diffusion while others (*e.g.*, tetramethylammonium–ammonium) had a rate controlled by particle diffusion. They found that for inorganic or small organic cations, the heat of activation under conditions of particle diffusion was 5 kcal./mole, *i.e.*, the same as for film diffusion. For larger organic cations, however, the heat of activation was somewhat greater, *e.g.*, 8 kcal./mole for the benzylphenyldimethylammonium–ammonium exchange.

When the present work was commenced, the aim was primarily to investigate the effect of resin structure (in particular, of the degree of cross-linking) upon rates of exchange with sulfonated cross-linked polystyrene resins. However, it was necessary first to elucidate for this type of resin the various mechanisms which might be rate-controlling and to define their regions of operation. Accordingly, the present work includes experiments on the effects of ingoing ion (sodium) concentration, temperature, particle size and rate of stirring as well as resin structure. It was also necessary (in view of what has been said above) to re-examine critically the various criteria which have been laid down as diagnostics of rate-controlling mechanisms. It may be stated here that examination of the effect of solution concentration has been found to be the best single criterion, though it appears to have been used hardly at all hitherto. It is simple and convenient to carry out and distinguishes sharply between a particle diffusion mechanism (exchange rate independent of concentration in solution) and a film diffusion or chemical mechanism (rate initially proportional to solution concentration). As Boyd, Adamson and Myers have pointed out, the *qualitative* effect of variation of the particle size is usually sufficient to confirm or eliminate a chemically controlled rate process.

Experimental

Resins.—The preparation of the resins examined, sulfonated cross-linked polystyrenes in bead form, has been described previously.[9] A commercial divinylbenzene mixture, containing 25–35% divinylbenzenes (mainly *m*-), about 65% ethylstyrenes and not more than 5% saturated material, was used. The proportion of DVB in this mixture was taken as 33%. Thus for the preparation of a resin containing nominally 17% DVB, 50 ml. of DVB mixture was mixed with 50 ml. of styrene. The monomers with catalyst (1% benzoyl peroxide) were added to an aqueous dispersion of "Promulsin" (a cellulosic derivative) and the whole mixture shaken mechanically. The concentration of "Promulsin" and the time of shaking determined the final size of the beads.

The suspension of monomer mixture in "Promulsin" was now copolymerized by heating at 80° for 18 hours. The "Promulsin" was then hydrolyzed by heating with 2 N H_2SO_4 at 70–80° for about 4 hours. The beads of copolymer were collected and washed with water. They were then sulfonated with concentrated sulfuric acid at 100° in the presence of 1% silver sulfate as catalyst. (The time of sulfonation was 24 hours in the case of the 5% DVB resin and 7 days for the 17% resin and in the case of the latter the beads were swollen with xylene before sulfonation.)

After the sulfonation, as much as possible of the sulfuric acid was drained off and the beads transferred to a dish which was left in a 75% relative humidity cabinet (over saturated sodium chloride solution). After this, the beads with the diluted acid (now about 30% H_2SO_4) were transferred to a large beaker and water added, a drop at a time, with stirring, until the acid strength was about 10%. After this, it could safely be diluted further. The beads were always kept wet throughout all the processes of cycling, particle-size fractionation and rate measurements. These precautions were necessary owing to the fact that the sulfonated beads of diameter greater than 500 μ were very susceptible to fracture and even breakage. Air-drying with subsequent dry-sieving[10] resulted in some fracture of the beads on rewetting, while wet-sieving caused considerable breakage. Also, the magnetic stirrer used in the previous work was found to grind the beads severely.

Particle Size Fractionation.—Owing to the fact that other methods damaged the beads, elutriation was chosen for fractionating the beads into different size ranges. There appeared to be very little literature on *wet* elutriation, possibly because it is applicable mainly to the same particle size ranges as are covered by standard-mesh sieves.

The resin, after cycling repeatedly with 2 N HCl and 2 N NaOH, was fractionated in two stages. In the first stage, a multi-tube elutriator was used, while in the second stage, fractions from the first stage were further fractionated in a single-tube elutriator.

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[6] Kressman and Kitchener (see ref. 7), although aware of this point, arrived at the same equation as Boyd, Adamson and Myers by another treatment. However, their treatment is considered fallacious, and the result differs from those obtained by the exact treatments of Adamson and Grossman and the present work—see below (equation 6).

[7] T. R. E. Kressman and J. A. Kitchener, *Faraday Soc. Discussions*, No. 7, 90 (1949).

[8] R. M. Barrer, *Trans. Faraday Soc.*, **45**, 1 (1949).

[9] K. W. Pepper, *J. Applied Chem. (London)*, **1**, 124 (1951).

[10] D. K. Hale and D. Reichenberg, *Faraday Soc. Discussions*, No. 7, 79 (1949).

For the multi-tube elutriator, 6 glass tubes (each of length 4 feet and of internal diameters 2.2, 2.9, 3.4, 4.1, 4.7 and 5.3 cm.) were arranged in series so that water from a constant-head tank, after passing through adjustable valves and a flowmeter, entered the bottom of the narrowest tube and left from the top of the widest. It then passed into a reservoir from which it was pumped back into the constant-head tank (the operation of the pump being controlled automatically by a float and micro-switch). A complete elutriation usually took a few days and from time to time during this period fresh resin was fed (in quantities up to 100 g.) through a side arm into the first tube. The range of flow rates used was 5 to 30 liters/hour. When the elutriation was complete, the resin fractions were drained from the bottom of each tube.

In the single-tube elutriator, water from a reservoir was pumped continually into a constant-level bottle, from which it flowed by gravity through an adjustable needle valve, an elutriation tube, a collecting tube and flowmeter back to the reservoir. The elutriation tube had an internal diameter of 2.1 cm. and a length of 28 cm. The collecting tube had a diameter of 4 cm. and a length of about 25 cm. and was fitted at the bottom with a glass stopcock of wide bore (6 mm.) by means of which the various resin fractions could be run off from time to time. It was found that satisfactory results could be obtained provided the elutriation tube was not "overloaded" with resin. An amount of resin of about 15 ml. settled volume was usually used. The flow rate was adjusted to a value that gave a collecting rate of about 2 beads per second. For beads of 500 μ diameter, this meant that a fraction of 1 ml. settled volume (or about $^1/_2$ ml. true volume) took about an hour to collect. In general, it was found that close fractionation was easier with resins of higher cross-linking (*i.e.*, a higher density of the swollen resin) and with larger particle sizes.

All the work described in the present paper was carried out on 3 samples:

Sample no.	Nominal % DVB in resin	Mean particle diameter, cm.	Standard deviation, cm.	Specific exchange capacity, mg. equiv. per g. dry resin	Capacity, mg. equiv. per ml. swollen resin
1	5	0.0544	0.0033	5.30	2.57
2	17	.0546	.0038	5.00	4.17
3	17	.0893	.0031	5.00	4.17

The mean diameters of the fractions were determined by measuring microscopically one diameter on each of 100 beads.

Before any set of rate measurements, the sample of resin to be used was examined microscopically for cracked or broken beads. In all cases, less than 1% of the beads were broken and less than 1% cracks could be detected. The beads were also examined after a series of rate measurements and if more than 10% of the beads were cracked or more than 2% broken, the set of rate measurements was rejected. In general, it was found that well over 50 individual rate experiments could be carried out before this amount of damage occurred.

Measurement of Rates of Exchange.—The indicator technique[10] was used. For each series of experiments, an amount of elutriated resin of a total capacity about $^1/_2$ mg. equiv. was introduced into a tube A, which was about 5 cm. long, about 7 mm. internal diameter and had a platinum gauze disc sealed in at the bottom and a B7 ground glass socket with hook fitted at the top. The resin was washed down until it all rested on the platinum gauze bed. Tube B, which consisted of a B7 ground glass cone with hook fitted at the bottom of a short tube containing another sealed-in platinum gauze disc, was then fitted on to tube A. The whole was connected to a vessel containing 2 *N* HCl and the resin thoroughly regenerated to the H^+ form. One-half hour was allowed for this purpose in the case of the 5% DVB resin and 1 hour for the 17% DVB resin. The tubes A and B (still fitted together) were then connected to a reservoir of conductivity-grade water and washed until the conductivity of the effluent was only 2–3 times as high as that of the water. The ion-exchange capacity of the sample was now determined by displacing all the exchangeable H^+ ion with 0.5 *N* NaCl solution into a conical flask and titrating with 0.01 *N* NaOH. The resin was again regenerated and washed. Tubes A and B were then drained, carefully separated without losing any resin and the resin in each tube (mainly, of course, in A) was washed into a jacketed vessel C using a total of 50 ml. of water from a buret. The vessel C had an internal diameter of 4.5 cm. and a height of 13 cm. (*i.e.*, a capacity of about 250 ml.) and water from a thermostat was continually circulated through the outer jacket. Dipping nearly to the bottom of C was a conventional-type paddle stirrer driven by an electric motor to which was also attached a tachometer. The vessel C was also provided with a thermometer. The resin and water in vessel C were left for 10–20 minutes to attain the required temperature. Meanwhile to a large boiling tube were added by pipet a known volume of NaCl solution of known concentration, a known volume of approximately 0.01 *N* NaOH (by buret), 2 ml. of 0.04% solution of the sodium salt of brom cresol green in water and an amount of water sufficient to bring the total volume of liquid in the tube to 100 ml. This tube was immersed in the same water thermostat from which liquid was circulated round vessel C. When all the reactants had reached the correct temperature, the motor and stirrer were adjusted to the correct speed. The boiling-tube was removed from the thermostat and its contents were immediately flung into the vessel C through a specially constructed funnel (with a 5″ mouth and a $^3/_4$″ aperture) while simultaneously a stop-watch was started. The time that elapsed before the indicator changed color (blue → yellow) was noted.

The tube A, now empty, was fitted to a special funnel D (with a B7 ground glass cone and hook at the bottom) and the resin was washed out of the vessel C and transferred quantitatively back into tube A. It was then regenerated back to the H^+ form and washed preparatory to another rate measurement.

As a check against possible losses of resin in transfer, etc., capacity measurements were made for every 6 rate measurements. In no case was a capacity difference of more than 1% noted.

Calculation of Results.—The indicator changed color when an amount of exchange had occurred equal to the total amount of hydroxyl ion originally in the solution. It is usual to express the amount of exchange as a fraction of the amount which occurs after infinite time, thus

$$F = \frac{Q_t}{Q_\infty} = \frac{\text{amount of exchange after time } t}{\text{amount of exchange after infinite time}}$$

In the present work, the results have all been calculated in terms of

$$X = \frac{\text{amount of exchange after time } t}{\text{total capacity of resin sample}}$$

For sodium ion concentrations of 1 *N* and above, *F* may be taken as equal to *X* to well within experimental error. For the results at 0.036 *N* and 0.018 *N*, *F* is greater than *X*, since Q_∞ is appreciably less than the capacity of the resin sample. (In the most extreme case, *X* was 0.83 of the value of *F*.) The values of *F* may be calculated since the relative affinity coefficients of sodium and hydrogen ions for these two resins are known.[11] However, the calculation is somewhat tedious (involving successive approximations) and it has been found possible to draw all the conclusions from the *X*–*t* data directly.

To obtain a curve of *X* against *t* for a given resin at a certain sodium ion concentration, the amount of NaOH used was varied and the amount of NaCl kept constant, *i.e.*, the sodium ion concentration was taken as equal to the initial sodium chloride concentration. This involves neglect of the NaOH which is present initially and disappears during the course of the experiment. Again, the error involved is negligible at high sodium ion concentrations and is small even at concentrations as low as 0.018 *N*.

Summarizing, although the system is, in principle, a "limited bath,"[7] with the concentrations (0.02 to 2 *N*), volume of solution (150 ml.) and amounts of resin (0.5 mg. equiv.) used in the present work, it was indistinguishable in practice from an "infinite bath" at high concentrations and differed only slightly even at the lowest concentrations used.

Results and Discussion

Most of the present work was carried out at 4 sodium ion concentrations, 1.82 and 0.91 *N* (re-

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[11] D. Reichenberg, K. W. Pepper and D. J. McCauley, *J. Chem. Soc.*, 493 (1951).

ferred to as "high" concentrations) and 0.0363 and 0.0182 N (referred to as "low" concentrations).

Preliminary experiments showed that variation of the rate of stirring from 500 to 2500 r.p.m. had no significant effect on the rate of exchange of sample 3 either at low or high concentrations. In subsequent work, therefore, the rate of stirring was fixed at 2000 r.p.m.

It has been shown in earlier work[10] that at low sodium ion concentrations the initial rate of exchange is proportional to the sodium ion concentration, while at high concentrations, it is independent of concentration over the whole of the exchange. This is illustrated in Fig. 1, where the reciprocal of the time for 0.420 conversion of the resin (17% DVB, 546μ diameter) is plotted against the sodium ion concentration.

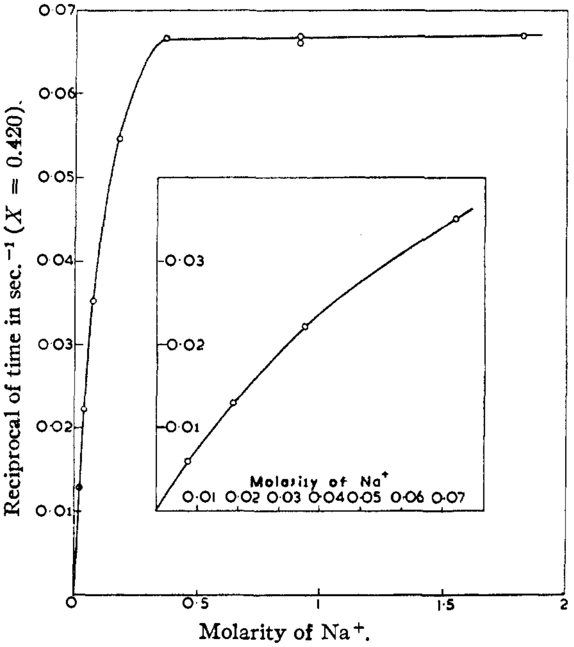

Fig. 1.—Influence of concentration on rate of exchange at 25° with 17% DVB resin of 546μ diameter.

It was also shown in the earlier work (and confirmed in the present work) that varying the particle size had a marked effect on the rate of exchange both at low and high concentrations. This clearly proves that a diffusion process of some kind is partly or completely responsible for controlling the rate of exchange.

Following Boyd, Adamson and Myers,[8] two kinds of diffusion processes were considered, "particle diffusion" and "film diffusion." It was argued that if the conditions were such that at equilibrium, the ingoing ion had nearly or entirely displaced the other ion from the resin, then particle diffusion would be characterized by an exchange rate that was independent of the concentration of the ingoing ion. Film diffusion, on the other hand, would be characterized by an exchange rate that was proportional, at least initially, to the concentration of ingoing ion. Hence, the provisional conclusion was drawn that at low sodium ion concentrations, sodium ion film diffusion was rate-controlling, while at high concentrations, particle diffusion might be rate-controlling.

These conclusions have received confirmation in the present work in respect of (a) the form of the kinetics; (b) the *quantitative* effect of particle diameter; (c) the effect of the degree of cross-linking of the resin. To assess these effects more clearly, particle diffusion and film diffusion are now considered in more detail.

The Kinetics of Particle Diffusion.—Assuming that all the resin particles were uniform spheres of radius r, Boyd, Adamson and Myers showed that, under conditions where particle diffusion was the sole rate-controlling process, the following expression should hold

$$F = \frac{Q_t}{Q_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-n^2Bt}}{n^2} \qquad \text{(1a)}$$

$$\text{where } B = \pi^2 D^i / r^2 \qquad \text{(1b)}$$

D^i being the effective diffusion coefficient of the two exchanging ions inside the resin particle.

The following points about the equation may be noted: (1) F is a calculable mathematical function of Bt and *vice versa*. Thus to check the equation with experimental data, it is most convenient if values of Bt are tabulated for each value of F. The values of Bt (obtained from the tables) may then be plotted against the experimental values of t and a straight line (of slope B) passing through the origin should be obtained provided the diffusion coefficient D^i does not vary with F over the range of X values involved.

(2) For a given value of t, F will be dependent only on D^i/r^2, *i.e.*, it will be independent of the concentration of ingoing ions. So, too, will Q_t since Q_∞ under the present experimental conditions is constant (at high Na$^+$ concentrations) and equal to the total exchange capacity of the resin. Thus not only will the "relative rate," dF/dt, be independent of the Na$^+$ concentration but the absolute rate dQ/dt will be also.

(3) B is inversely proportional to the square of the particle radius and since, for a given value of F, dF/dt and dQ/dt are proportional to B, the rate of exchange will be inversely proportional to the square of the particle radius for all values of F under conditions of particle diffusion.

Values of Bt have been calculated for suitable values of F and are tabulated in the Appendix. To test the conformity of the experimental results with equation (1), the value of Bt for each experimental point was obtained from the table and a curve was plotted of Bt against t.

Typical F-t curves at high Na$^+$ concentrations are shown in Figs. 2 and 3. These graphs show clearly the effects of the degree of cross-linking (Fig. 2) and of temperature and particle diameter (Fig. 3). They also show that at these high concentrations the sodium ion concentration has no effect on the rate of exchange. When the data of Fig. 3 are replotted with F replaced by the corresponding values of Bt, the curves shown in Fig. 4 are obtained. In all cases, at high concentrations, good straight lines passing through the origin are obtained. The same treatment has been applied to the results at low concentrations (using values of

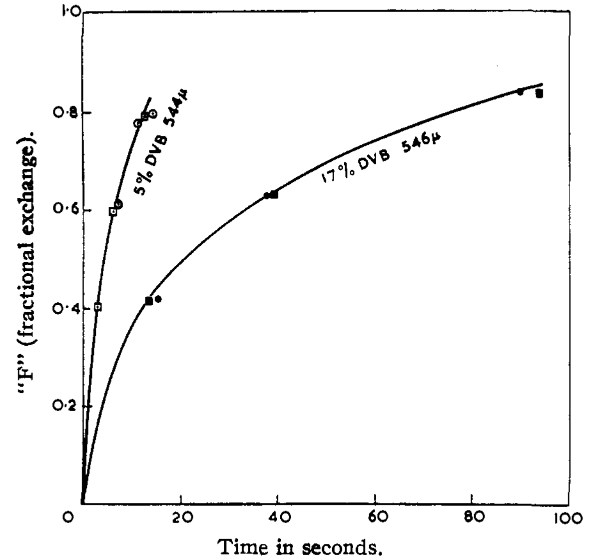

Fig. 2.—Influence of degree of crosslinking of resin on rate of exchange under conditions where particle diffusion is rate-controlling; particle diffusion. temp. 25°. 5%: ⊙. 0.91 *N;* □. 1.82 *N;* 17%: ●. 0.91 *N;* ■. 1.82 *N.*

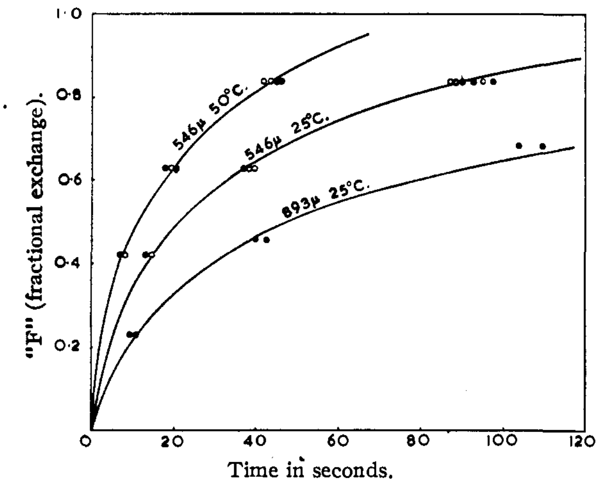

Fig. 3.—Influence of particle size and of temperature on rate of exchange under conditions where particle diffusion is rate-controlling; particle diffusion: 17% DVB resin: Na$^+$ concn.. O. 0.91 *N.* ● 1.82 *N.*

Bt based on the true *F* values) and it was found that, even allowing a considerable margin for experimental error, the *Bt–t* curves are definitely not linear. Hence, at high concentrations the *F–t* relationships correspond to the equation representing particle diffusion while at low concentrations, they do not.

The actual values of *B* derived (by the method of least squares) from the *Bt–t* plots are

Sample	DVB. %	Mean particle diameter. µ	*B*, sec.$^{-1}$ 25°	50°
1	5	544	0.10	0.23
2	17	546	.015	.031
3	17	893	.0061	. . .

From these results, it may be seen that the effect of increasing the mean particle diameter by a factor of 1.64 is to reduce the exchange rate constant *B* by a factor of 2.46. Now $(1.64)^2 \doteq 2.69$, so that to within 10% (which is considered to be about the over-all experimental error), the rate constant is inversely proportional to the square of the particle radius, in agreement with theory. (Boyd, Adamson and Myers obtained a similar result but in fact their data fit an inverse-cube law as closely as an inverse-square law.)

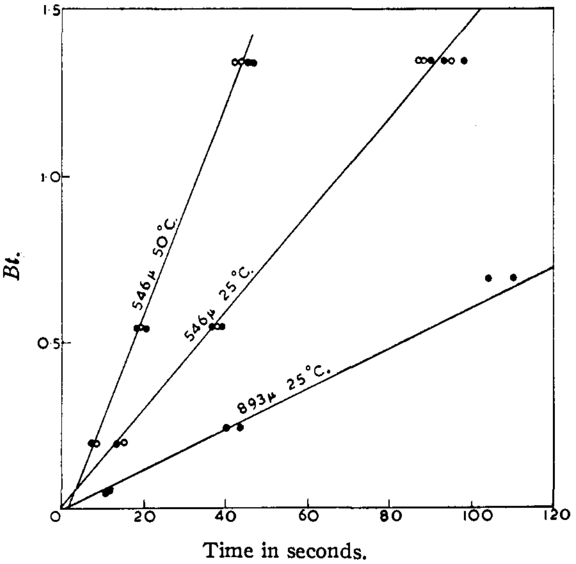

Fig. 4.—"*Bt*"–*t* plots. particle diffusion: 17% DVB resin; Na$^+$ concn.. O. 0.91 *N;* ●. 1.82 *N.*

From these values of *B*, and knowing the radii of the particles, we can calculate the values (given below) of the effective diffusion coefficient D^i controlling the rate of the Na–H exchange.

Nominal DVB. %	Mean particle diameter. µ	D^i, cm.^{2}/sec. 25°	50°	Heat of activation. kcal./g. mole
5	544	7.3×10^{-6}	1.7×10^{-5}	6.5 ± 0.6
17	546	1.1×10^{-6}	2.4×10^{-6}	5.8 ± .1
17	893	1.2×10^{-6}	....	

An error of 10% in the value of B_{50}/B_{25} will cause an error of 0.8 kcal./g. mole in the value of the heat of activation, ΔH. The value of ΔH for the 5% DVB resin may therefore be subject to an error of ±0.6 kcal./g. mole and it is quite probable that the heats of activation for the two resins are very similar at a value of 5.9 cal./g. mole. The heats of activation are, of course, independent of any measurement of the mean particle diameter.

From the results, it is clear that the 5% DVB resin exchanges 6.6 ± 0.3 times as rapidly as the 17% DVB resin at 25° and 7.1 ± 0.6 times as rapidly at 50°. If this more rapid diffusion were to be ascribed wholly to a lower heat of activation for the diffusion process, the heat of activation for the exchange process would have to be 1.1 kcal./g. mole less in the case of the 5% DVB resin than in the case of the 17% DVB resin. Consideration of the errors in the experimental heats of activation shows that while this possibility cannot be entirely ruled out, it appears unlikely.

Kinetics of Film Diffusion.—Boyd, Adamson and Myers derived the equation

$$\log_e (1 - F) = - RT \tag{2}$$

for an exchange rate controlled by film diffusion under conditions that the "ingoing" ion is a microcomponent of the system. Under the experimental conditions obtaining in the present work, the "ingoing" ion is a macrocomponent of the system and the derivation and resulting equation of Boyd, Adamson and Myers is no longer applicable. A more general treatment is now given.

The following assumptions are made: (1) The film thickness is small compared with the particle radius. Hence the film round a particle may be treated as if it were a slab of area $4\pi r^2$ and thickness Δr. Also, the total quantity of either sodium or hydrogen ions in the film at any instant is small compared with the exchange capacity of the particle.

(2) The same film thickness is operative for the diffusion of sodium ions "in" as for hydrogen ions "out." This assumption implies neglect of any effect due to the hydroxyl ions initially present.

(3) The rate is controlled *entirely* by film diffusion. Hence (a) concentration gradients inside the resin particle are negligible; (b) a "steady" state is set up after negligible time and exchange; (c) in this steady state, the rate of diffusion of sodium ions "in" across the film is exactly balanced at any instant by an equal rate of diffusion of hydrogen ions across the film in the opposite direction.

Let D^{H} and D^{Na} be the coefficients of diffusion of Na and H ions in the liquid. Let [Na] and [H] be the concentrations in the bulk of the solution and $[\mathrm{Na_S}]$ and $[\mathrm{H_S}]$ be the concentrations in the liquid immediately in contact with the resin surface. The rate of exchange in mg. equiv. per particle of resin is given by

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = 4\pi r^2 \frac{D^{\mathrm{Na}}}{\Delta r} \{[\mathrm{Na}] - [\mathrm{Na_S}]\} \tag{3a}$$

$$= 4\pi r^2 \frac{D^{\mathrm{H}}}{\Delta r} \{[\mathrm{H_S}] - [\mathrm{H}]\} \tag{3b}$$

Defining a quantity ϕ as the amount of exchange in mg. equiv. per ml. of swollen resin

$$\phi = \frac{Q}{\frac{4}{3}\pi r^3} = X \times (\text{capacity per ml. swollen resin}) \tag{4}$$

$$\frac{\mathrm{d}\phi}{\mathrm{d}t} = \frac{3}{r}\frac{D^{\mathrm{Na}}}{\Delta r} \{[\mathrm{Na}] - [\mathrm{Na_S}]\} \tag{5}$$

Now

$$\frac{X}{1 - X} = K_{\mathrm{H}}^{\mathrm{Na}} \times \frac{[\mathrm{Na_S}]}{[\mathrm{H_S}]}$$

where $K_{\mathrm{H}}^{\mathrm{Na}}$ is the relative affinity coefficient, defined more precisely elsewhere.[11] (Strictly speaking, the ratio of the activity coefficients in solution should be included but even in 0.1 N solution, this only makes a 2% difference in the value of $K_{\mathrm{H}}^{\mathrm{Na}}$.) It may be shown, from equations (3), (4) and (5), that

$$\frac{\mathrm{d}\phi}{\mathrm{d}t} = \frac{3}{r} \times \frac{D^{\mathrm{Na}}}{\Delta r} \times \left\{ \frac{[\mathrm{Na}] - \frac{1}{K_{\mathrm{H}}^{\mathrm{Na}}} \times \frac{X}{1 - X}[\mathrm{H}]}{1 + \frac{D^{\mathrm{Na}}}{D^{\mathrm{H}}} \times \frac{1}{K_{\mathrm{H}}^{\mathrm{Na}}} \times \frac{X}{1 - X}} \right\} \tag{6}$$

Essentially the same equation was derived by Adamson and Grossman.[12]

Owing to the simple relationship (equation (4)) existing between ϕ and X, equation (6) may be written in a form that expresses $\mathrm{d}X/\mathrm{d}t$ as a function of X. It would then be possible to integrate this equation numerically (since $K_{\mathrm{H}}^{\mathrm{Na}}$ is known for each value of X[11]) and to tabulate X as a function of t. The conformity of equation (6) with the experimental results could then be tested. However, the numerical integration is extremely tedious and in the present paper, a more concise (though necessarily less rigorous) confirmation will be obtained.

Consider the value of $\mathrm{d}\phi/\mathrm{d}t$ at low values of X. From equation (6)

$$\left(\frac{\mathrm{d}\phi}{\mathrm{d}t}\right)_{\text{initial}} = \frac{3}{r} \times \frac{D^{\mathrm{Na}}}{\Delta r} [\mathrm{Na}] \tag{7}$$

This equation has the following consequences: (1) It contains no quantity depending on the chemical nature or polymeric structure of the resin. Hence, for a given mean particle diameter, in solutions of the same concentration and under the same hydrodynamic conditions, the 5 and 17% DVB resins should have the same initial absolute rate of exchange per ml. of swollen resin. (2) $(\mathrm{d}\phi/\mathrm{d}t)_{\text{initial}}$ is proportional to [Na] (provided D^{Na} does not vary with concentration) and since, for a given resin, ϕ is proportional to X (equation (4)), the initial value of $\mathrm{d}X/\mathrm{d}t$ will be proportional to the Na concentration, as deduced previously; (3) $(\mathrm{d}\phi/\mathrm{d}t)_{\text{initial}}$ is inversely proportional to the mean particle radius r.

Typical X–t curves at low Na^+ concentrations are shown in Figs. 5 and 6. These graphs show that on an X–t basis, the 5% DVB resin exchanges more rapidly than the 17% DVB resin (Fig. 5). They also show the effect of concentration and of particle diameter (Fig. 6). ϕ may be readily calculated from the experimental X values since the capacity per ml. swollen resin is known for both resins, being 2.57 mg. equiv./ml. for the 5% DVB resin and 4.17 mg. equiv./ml. for the 17% DVB resin. When the data of Fig. 5 are replotted with X replaced by the corresponding values of ϕ, the curves shown in Fig. 7 are obtained. Initially, as predicted, $\mathrm{d}\phi/\mathrm{d}t$ is the same for the two resins provided that the swollen particle diameters are the same. After an appreciable amount of exchange has occurred, $\mathrm{d}\phi/\mathrm{d}t$ is *greater* in the case of the 17% DVB resin. (Similar behavior is exhibited in solutions of 0.018 N Na^+ concentration.) This latter fact may appear surprising at first sight but is predicted by equation (6). There are two separate factors contributing to this effect: (a) the fact that the capacity per ml. swollen resin is greater in the case of the 17% DVB resin; (b) the fact that the relative affinity coefficient, $K_{\mathrm{H}}^{\mathrm{Na}}$, is greater in the case of the 17% DVB resin for values of X from 0 to about 0.5.[11] (It may be remarked that the 5 and 17% DVB resins used in this work were the identical resins whose relative affinity characteristics have been described.) Equation (6) shows that if $K_{\mathrm{H}}^{\mathrm{Na}}$ is the same for both resins, then

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(12) A. W. Adamson and J. J. Grossman, *J. Chem. Phys.*, **17**, 1002 (1949).

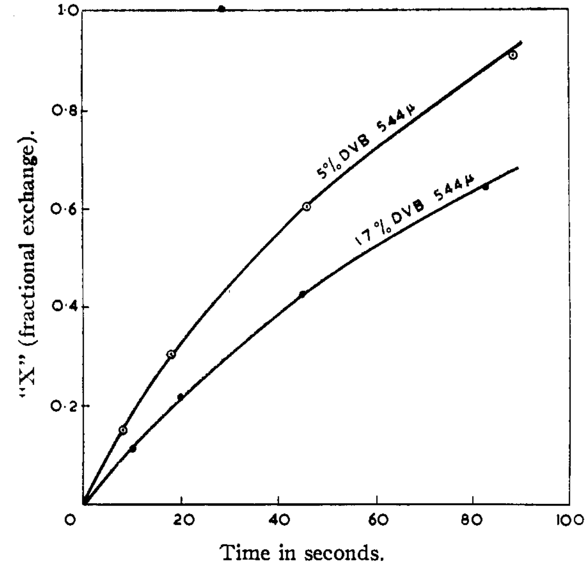

Fig. 5.—Influence of degree of crosslinking of resin on rate of exchange under conditions where film diffusion is rate-controlling. film diffusion: Na^+ concn., 0.036 *M;* temp. 25°.

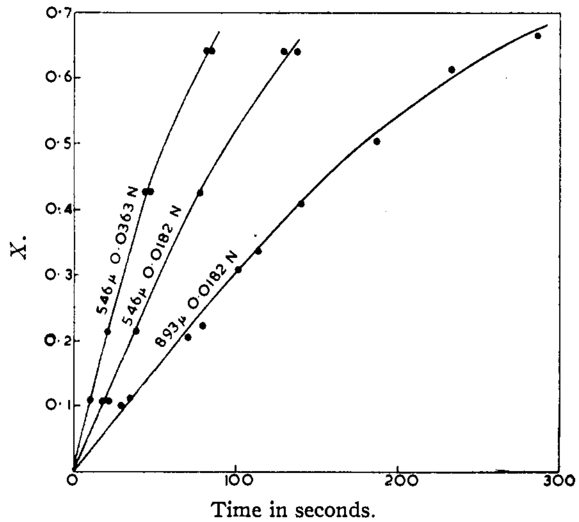

Fig. 6.—Influence of Na^+ concentration and of particle size under conditions where film diffusion is rate-controlling: film diffusion. 17% DVB resin at 25°.

for a given X, $d\phi/dt$ will be the same. Owing to (a), for a given X, ϕ will be greater for the 17% DVB resin. Since both dX/dt and $d\phi/dt$ decrease with increasing t, then for a given ϕ, $d\phi/dt$ will be greater for the 17% DVB resin. This effect is reinforced by (b), since equation (12) shows that for a given X, $d\phi/dt$ will be greater for the resin with the greater value of K_H^{Na}, *i.e.*, for the 17% DVB resin. It may be concluded that the rates of exchange in solutions of low Na^+ concentrations satisfy the criteria for film diffusion as the rate-controlling mechanism. By contrast, ϕ–t plots are shown in Fig. 8 of the data of Fig. 2 for solutions of high Na^+ concentrations. Here $d\phi/dt$ is greater for the 5% DVB resin over the whole of the exchange. This effect is the more striking as the ultimate value of ϕ is *lower* for the 5% DVB resin.

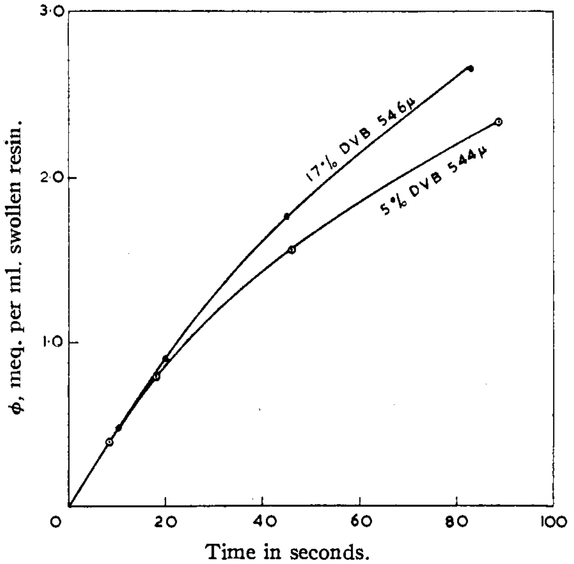

Fig. 7.—"ϕ"-t plots. film diffusion: Na^+ concn., 0.036 *N;* temp., 25°.

From the ϕ–t plots, we obtain the following initial values of $d\phi/dt$

DVB, %	Mean particle diameter, μ	Na^+ concn., N	Initial value of $d\phi/dt$, mg. equiv. ml./sec.	Calculated value of Δr, μ
5	544	0.0182	0.0235	5.1
		.0363	.0445	5.4
17	546	.0182	.0235	5.1
		.0363	.0445	5.4
17	893	.0182	.0140	5.3
		.0363	.0220	6.7

In calculating Δr, the effective film thickness, a value of 6.045×10^{-6} cm.²/sec. was used for D^{Na}, based on the value $D^{NaCl} = 15.25 \times 10^{-6}$ cm.²/sec.[13,14] and the assumption that D^{Na}/D^{NaCl} is equal to the transport number (about 0.4)[15] of

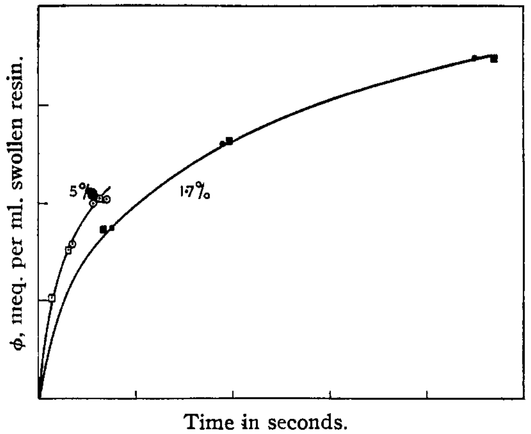

Fig. 8.—"ϕ"-t plots. particle diffusion: ϕ_∞ (5% resin) = 2.57 (mg. equivs. per ml.); ϕ_∞ (17% resin) = 4.13 (mg. equivs. per ml.).

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[13] H. S. Harned and C. L. Hildreth, THIS JOURNAL, **73**, 650 (1951).

[14] R. H. Stokes, *ibid.*, **72**, 763, 2243 (1950).

[15] H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, p. 158.

sodium in dilute sodium chloride solutions. The values of Δr so calculated are given in the final column. Good agreement is obtained except in the case of the 17% DVB resin of large particle size in 0.036 N solution. The anomalously high value of Δr obtained in this case is almost certainly due to particle diffusion playing a part in controlling the rate even though film diffusion still predominates. All the factors (large particle size, high cross-linking and higher Na^+ concentration) tend to promote particle diffusion. This suggestion receives additional support from the fact that, whereas with the samples of smaller particle size, doubling the sodium ion concentration caused a doubling of the initial value of $d\phi/dt$ (within experimental error), in the case of the last sample, there was an increase of only 57% when the Na^+ concentration was doubled.

The agreement (in solutions of 0.018 N Na^+ concentration) between the values of Δr for the two samples of 17% DVB resin of different particle size implies, of course, that under these conditions, the exchange rate is inversely proportional to the particle radius.[16]

The Nature of Particle Diffusion.—Boyd, Adamson and Myers[5] and Kressman and Kitchener,[7] noting that the heats of activation for the diffusion processes in the resin were much the same as for similar ions in water, suggested that diffusion in the resin might be regarded simply as diffusion in an aqueous medium. This view is now adopted and extended.

There is abundant evidence to show that anions play little or no part in the particle diffusion process. Kressman and Kitchener showed that using Chlorazol Sky Blue FFS or even finely divided phenolsulfonate resin as anions, much the same rate of $N(Et)_4$–NH_4 exchange was obtained as with the chlorides or bromides. The diffusion of ions within the resin must, therefore, be regarded as a "place-exchange" process. The energy of activation may be determined by (a) the electrostatic interaction of the cations with each other and with the anionic groups of the resin; (b) the energy of activation for the diffusion of the cations in the aqueous medium existing in the resin; (c) the activation energy associated with changes in the configuration of the cross-linked network whereby particular pores increase and decrease in size. That (b) is probably the most important factor is indicated by the closeness of the energy of activation for the particle diffusion process to that for diffusion in water. The rate of exchange at a given temperature will be determined not only by the activation energies of the various "steps" in the place-exchange process but also by their entropy changes. The results of the present work, though not conclusive, seem to indicate that any difference in the heats of activation is inadequate to account for the marked difference in the effective diffusion coefficients of the 5 and 17% DVB resins. This suggests that the difference lies primarily in a difference of the entropy of activation for the diffusion process. If, as indicated above, the most important stage of this process is simply the diffusion of ions in the aqueous medium in the resin, such an entropy difference is readily found. The resin of higher cross-linking has a smaller volume of diffusion medium (water) per unit volume of swollen resin. Using this hypothesis, one may, knowing the swellings of the resins, attempt to calculate theoretically the effect of cross-linking on the rate of exchange. Such calculations are complicated by the hydration of the ions, but if one assumes no hydration, *i.e.*, that all the water in the resin is available as diffusion medium, one calculates that the 5% DVB resin should exchange 1.46 times as rapidly as the 17% DVB resin. To account for the observed ratio of about 6.6, one must assume that the ions are hydrated to the extent of about 5 molecules of water per equivalent of resin. This is quite a reasonable figure.[17] However, more accurate data on the heats of activation are required before the theoretical interpretation can be extended.

Appendix

Boyd, Adamson and Myers[5] derived equation (1) and calculated F for a series of values of Bt.

However, it has been shown that the most useful form of tabulation is that of Bt for a series of suitable values of F. Since it is desirable that the errors in Bt should be less than correspond to a variation of 0.001 in the value of F, interpolation from the table given by Boyd, Adamson and Myers is unsuitable.

At sufficiently high values of F, only one term of the series represented by equation (1a) need be used.

Thus

$$F = 1 - \frac{6}{\pi^2}e^{-Bt}$$

or

$$Bt = -\log_e \frac{\pi^2}{6}(1 - F)$$

$$= -2.30258 \log_{10}(1 - F) - 0.49770 \qquad (8)$$

For any value of F, this equation gives too low a value of Bt, the error being zero when $F = 1$ and increasing to 0.49770 when $F = 0$.

For the lower range of values of F, equation (1a) may be transformed by noting that from Poisson's formula[18] one may obtain the result

$$\sum_{n=1}^{\infty} e^{-n^2(Bt)} = -\frac{1}{2} + \sqrt{\frac{\pi}{Bt}}\left[\frac{1}{2} + \sum_{n=1}^{\infty} e^{-\frac{\pi^2 n^2}{Bt}}\right]$$

Integrating with respect to (Bt) and rearranging

$$F = \frac{6}{\pi^{3/2}}\sqrt{Bt} - \frac{3}{\pi^2}(Bt) + \frac{6}{\pi^{3/2}}\int_0^{Bt} \frac{\sum_{n=1}^{\infty} e^{-\frac{\pi^2 n^2}{Bt}}}{\sqrt{Bt}}\, d(Bt) \qquad (9)$$

Only the first two terms need be considered

$$F = \frac{6}{\pi^{3/2}}\sqrt{Bt} - \frac{3}{\pi^2}(Bt) \qquad (10)$$

(Boyd, Adamson and Myers derived, for low values of F, the equation $F = \frac{6}{\pi^{3/2}}\sqrt{Bt}$ but only by making additional assumptions.) Equation (10) may be transformed so as to express Bt in terms of F, *i.e.*

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[16] Boyd, Adamson and Myers drew a similar conclusion from their data at low concentrations. However, there is an arithmetical error in the second line of their Table XI and their data, in fact, fit an inverse square law more closely.

[17] J. O'M. Bockris, *Quart. Revs.* (*London*), 3, 173 (1949).

[18] E. C. Titchmarsh, "Introduction to the Theory of Fourier Integrals," Clarendon Press, Oxford, 1937, p. 64.

$$Bt = 2\pi - \frac{\pi^2 F}{3} - 2\pi\left(1 - \frac{\pi F}{3}\right)^{1/2}$$

$$= 6.28318 - 3.2899F - 6.28318\,(1 - 1.0470F)^{1/2} \quad (11)$$

The last term in equation (9) is zero when $F = 0$ and increases as F increases. Hence, for any value of F, equation (11) gives too high a value of Bt, the error being zero when $F = 0$. Now, at a value of $F = 0.85$, equations (8) and (11) give values of Bt agreeing to within 0.005, corresponding to a variation of F at this point of less than 0.001. Hence equation (11) was used for values of F from 0 to 0.85 and equation (8) for values from 0.86 to 1. The results are shown in Table I. The errors in Bt are less than those corresponding to a variation of 0.001 in the value of F.

Table I

Table for Interpreting Experimental Results in Terms of the Particle Diffusion Equation

F	Bt	F	Bt	F	Bt	F	Bt
0	0	0.25	0.0623	0.50	0.301	0.75	0.905
0.01	0.00009	.26	.0678	.51	.316	.76	.944
.02	.00036	.27	.0736	.52	.332	.77	.985
.03	.00076	.28	.0797	.53	.348	.78	1.028
.04	.00141	.29	.0861	.54	.365	.79	1.073
.05	.00219	.30	.0928	.55	.382	.80	1.120
.06	.0032	.31	.0998	.56	.400	.81	1.171
.07	.0044	.32	.1070	.57	.419	.82	1.224
.08	.0057	.33	.1147	.58	.438	.83	1.280
.09	.0073	.34	.1226	.59	.458	.84	1.340
.10	.0091	.35	.1308	.60	.479	.85	1.404
.11	.0111	.36	.1391	.61	.500	.86	1.468
.12	.0132	.37	.1485	.62	.522	.87	1.543
.13	.0156	.38	.1577	.63	.545	.88	1.623
.14	.0183	.39	.167	.64	.569	.89	1.710
.15	.0210	.40	.177	.65	.594	.90	1.80
.16	.0241	.41	.188	.66	.620	.91	1.91
.17	.0274	.42	.199	.67	.647	.92	2.03
.18	.0309	.43	.210	.68	.675	.93	2.16
.19	.0346	.44	.222	.69	.703	.94	2.32
.20	.0386	.45	.234	.70	.734	.95	2.50
.21	.0428	.46	.246	.71	.765	.96	2.72
.22	.0473	.47	.259	.72	.798	.97	3.01
.23	.0520	.48	.273	.73	.832	.98	3.41
.24	.0570	.49	.287	.74	.868	.99	4.11

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On the Use of Structures as an Aid in Understanding Π-Electron Spectra

By William T. Simpson

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The possibility of obtaining symmetry species from known transformation properties of the squares of trial wave functions is investigated. Application to structures follows from the association of structures with wave functions squared. Observed electronic term values are arranged in a diagonal matrix which is then transformed into non-diagonal form. Base vectors in the transformed coördinate system are interpreted with respect to structures. It is pointed out that the energy matrix in non-diagonal form lends itself to various applications.

Introduction

The HLSP or valence bond method[1] provides a particular quantum mechanical basis for an understanding of the role played by *structures* (also called mesomeric forms, resonance forms, paper structures, etc.) but certain objections arise. In large molecules the wave functions which, according to the valence bond scheme, correspond to the principal or unexcited structures make only small contributions.[2] Moreover, the valence bond scheme as usually employed involves the neglect of quantities which are certainly large and does not ordinarily take into account the so-called σ-bonds. One wonders, in view of the practical uses to which structures can be put, if there is not some fundamental justification for an approach other than the valence bond method, which also involves the use of structures. In the next paragraphs several rather striking examples of the utility of structures will be cited.

It is found that the 2600 Å. band in benzene is in all probability $A_{1g} \rightarrow B_{2u}$[3] and this is exactly what one expects if the transition is considered to take place between ψ_g and ψ_e where

$$\psi_g = 2^{-1/2}(\psi_1 + \psi_2).\ \psi_e = 2^{-1/2}(\psi_1 - \psi_2)$$

and ψ_1^2 has the transformation properties of one Kekulé structure, ψ_2^2 of the other.[4] It is important to note that structures are taken as corresponding to ψ^2's.

The transition moment integral in the language of wave functions (squared) related to structures is

$$\int \psi_g \vec{q}\, \psi_e \, d\tau = \frac{1}{2}\left[\int \psi_1^2 \vec{q}\, d\tau - \int \psi_2^2 \vec{q}\, d\tau\right]$$

so that the electric moment implied by a distribution of charge transforming like one Kekulé structure must be different from that implied for the other in order than the transition be allowed. That the electric moments are in fact equal may be seen in pictorial fashion from the Kekulé structures

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(1) Recent treatments have been given by D. P. Craig, *Proc. Roy. Soc. (London)*, **A200**, 272 (1950), and M. Simonetta and V. Schomaker, *J. Chem. Phys.*, **19**, 649 (1951).

(2) A. Pullman, Doctoral Thesis, Univ. of Paris, 1946.

(3) See for example F. M. Garforth, *J. chim. phys.*, **45**, 6 (1948).

(4) This is demonstrated in Part 1.