small amount of the 8.0 d. iodine activity, suggesting possibly the occurrence of an interhalide complex anion. The completeness of the separations is indicated by peak to trough ratios ranging from 100 to 600.

Group VIIB Separations.—The three transition elements Mn, Tc and Re are known to form oxygenated anions of the type XO_4^- when present in their respective heptavalent oxidation states. The separation of these anions by use of an ion-exchange column should be possible, therefore, provided they are stable in the systems employed. Such proved not to be the case with permanganate which was found to react with the exchanger. Pertechnetate, although unstable in acid solution, is stable in alkaline solutions, and, if a strong base exchanger is used, it can be separated from perrhenate ion. The fractionation of trace amounts of technetium from microgram amounts of rhenium was conducted using a 0.72 sq. cm. × 51 cm. cylindrical bed of 100/120 mesh Dowex-2 initially in the sulfate form. The mixture of 90 h. Re^{186} and 6.0 h. Tc^{99m}, placed at the top of the bed as NH_4ReO_4 and NH_4TcO_4 in solution, was prepared by dissolving slow neutron irradiated molybdenum metal known to contain 2–3 p. p. m. rhenium impurity in concentrated sulfuric acid and distilling. The distillate containing the Tc and Re (and perhaps other volatile activities from impurities) was diluted, the mixed rhenium and technetium sulfides precipitated and then dissolved in ammoniacal hydrogen peroxide to give perrhenate and pertechnetate, respectively. The separation by elution was conducted at a flow rate of 1.7 ml./min. at room temperature with a solution 0.1 *M* in $(NH_4)_2SO_4$ and NH_4SCN adjusted to a *p*H of 8.3–8.5 with NaOH. The identity of the activity in the first peak (Fig, 1b) which appeared immediately as would be expected with cations was not established. When the second activity peak (identified as rhenium) had dropped by a factor of *ca.* 20 the concentration of eluant was increased to 1.0 *M*, maintaining the *p*H constant, in order to bring out the technetium which was shown to be well over 99% pure by its decay with a 6.0 h. period over ten half-lives. The reversal of the order of elution of Re and Tc with regard to atomic weight may be of interest.

Finally, it may be remarked that anion exchange columns filled with the new strong-base exchangers have been found to be somewhat less efficient than the nuclear sulfonic acid type cation exchangers, all other variables such as particle size, flow rate, temperature, etc., being the same. In the foregoing halide separations approximately 200–250 theoretical plates were shown, whereas with cations roughly twice as many stages are usually found with beds of the same depth. This difference may result in part, if not entirely, from the approximately twofold lower exchange capacity of the anion exchangers.

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Kinetic Analysis of Consecutive Irreversible Second Order Reactions[1]

BY DEXTER FRENCH

The kinetic analysis of consecutive reactions[2] of the type $A + B \rightarrow C;\ C + B \rightarrow D$ has not been generally feasible because of the difficulty of devising analytical expressions for the concentrations of *A*, *B*, etc., as functions of *t*. In practice this difficulty has usually been circumvented by adjustment of the reaction conditions so that the reaction is kinetically first order, for example by use of a large excess of the reactant *B*. However, in those cases in which the progress of the reaction is followed by measuring the concentration of *B* it is clearly undesirable to drown out its kinetic order by the use of a large excess.

A practical method for the determination of the kinetic constants for consecutive second order reactions has occurred to us, and while the principle is extremely simple it does not seem to have been used before. Let *a*, *b* and *c* represent the concentrations of *A*, *B* and *C*, respectively. If one sets up the differential rate equations

$$\mathrm{d}a/\mathrm{d}t = -k_1ab \qquad (1)$$

$$\mathrm{d}b/\mathrm{d}t = -k_1ab - k_2cb \qquad (2)$$

$$\mathrm{d}c/\mathrm{d}t = k_1ab - k_2cb \qquad (3)$$

it is apparent that these may be readily converted to equations of first order type by introduction of the parameter $\theta = \int_0^t b\mathrm{d}t$. Since $\mathrm{d}\theta = b\mathrm{d}t$

$$\mathrm{d}a/\mathrm{d}\theta = -k_1a \qquad (4)$$

$$\mathrm{d}b/\mathrm{d}\theta = -k_1a - k_2c \qquad (5)$$

$$\mathrm{d}c/\mathrm{d}\theta = k_1a - k_2c \qquad (6)$$

Equations 4 through 6 constitute a readily integrable set with the solutions

$$a = a_0e^{-k_1\theta} \qquad (7)$$

and, assuming $c_0 = 0$

$$b = b_0 - a_0\ [2 - 2e^{-k_1\theta} - k_1(e^{-k_2\theta} - e^{-k_1\theta})/(k_1 - k_2)] \qquad (8)$$

$$c = k_1a_0(e^{-k_1\theta} - e^{-k_2\theta})/(k_2 - k_1) \qquad (9)$$

The relationship between θ and *t* is readily established by plotting *b* against *t* and integrating graphically. The data giving *b* as a function of *t* are then converted to the θ basis and subsequently handled as a first order process.

Swain[3] has given a method of treatment for consecutive first order reactions which involves matching experimental points at selected stages of the reaction (15, 35 and 70% of completion) against standard curves calculated for various ratios of k_2/k_1 at these stages. We have found it more convenient to determine the values of k_1 and k_2 by a curve matching technique as follows: introduce the new variables $x = k_1\theta$ and $y = k_2/k_1$. Equation 8 now becomes

$$b = b_0 - a_0[2 - 2e^{-x} - (e^{-x} - e^{-xy})/(y - 1)] \qquad (10)$$

By plotting $(b_0 - b)/a_0$ against log *x* for various values of *y*, one obtains a family of S-shaped curves. The experimental curve relating $(b_0 - b)/a_0$ to log θ is then compared with the calculated *y*-family and an approximate value for *y* may be estimated. It is then possible to construct new curves for values of *y* in this neighborhood and thereby fit the experimental curve as closely as the data allow. The value of k_1 may be deduced from the lateral displacement of log θ against the log *x* scale which gives the best fit

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[1] Journal Paper No. J-1779 of the Iowa Agricultural Experiment Station, Ames, Iowa; Proj. 1116.

[2] Chien, THIS JOURNAL, 70, 2256 (1948).

[3] Swain, *ibid.*, 66, 1696 (1944).

on the curves, particularly at the low θ values. The numerical value of k_2 is then simply k_1y.

The principles of this method of kinetic treatment may be readily extended and applied to more complex systems; an example of such an extension is the approximate analysis of the periodate oxidation of the Schardinger dextrins which will be reported in another paper.[4]

[4] French and McIntire, THIS JOURNAL, 72, in press (1950).

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Ion Charge and Exchange Rates with Ion-exchange Polymers

BY G. E. BOYD, A. W. ADAMSON AND L. S. MYERS, JR.

At this time it is possible to report certain early observations on the influence of cationic charge on exchange rates with a synthetic ion-exchange polymer.[1] The uptake of ions bearing one, two and three charges, respectively, from dilute hydrochloric acid solutions was measured as a function of time using a flow technique[2] and radioactive isotopes as tracers: 14.8 h. Na^{24}, 1.62×10^5 y. U^{233} and 275 d. Ce^{144}. Since the exchanger had been equilibrated with a solution of the same macro-composition as that which subsequently contained radio-tracer, negligible changes took place in the composition of the exchanger and in the ionic strength of the external solution. Accordingly, the rate process observed was that which occurs at equilibrium. The exchange velocity diminished rapidly as the ionic charge increased (Fig. 1). As a consequence of the existence of several kinetic mechanisms, considerable overlap was found. As previously,[2] three rate processes could be distinguished: (a) a first order film diffusion process (F) for systems in which the exchanging ion showed a large equilibrium distribution coefficient, K_d, in favor of the exchanger; (b) a particle diffusion mechanism (P); and (c) an "intermediate" rate process (I) which resulted from the coupling of F and P. The rate constants for the systems of Fig. 1 are summarized in Table I.

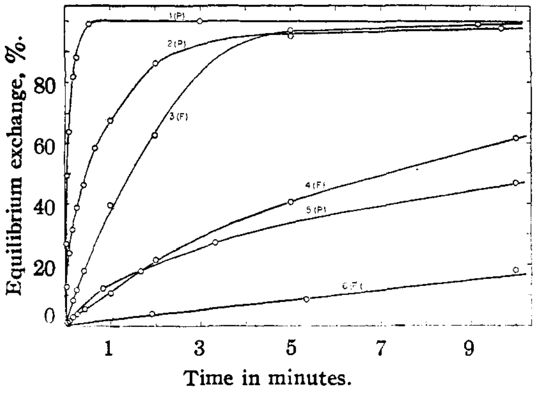

Fig. 1.—Effect of ion charge on cation exchange rates: (P) particle diffusion and (F) film diffusion mechanism: curve 1, Na^+ from 0.1 N HCl; curve 2, UO_2^{++} from 0.3 N HCl; curve 3, Na^+ from 0.001 N HCl; curve 4, UO_2^{++} from 0.033 N HCl; curve 5, Ce^{+++} from 0.5 N HCl; curve 6, Ce^{+++} from 0.1 N HCl.

TABLE I

RATE CONSTANTS FOR THE EXCHANGE OF VARIOUS IONS IN DILUTE HYDROCHLORIC ACID SOLUTIONS AT 25° (AVERAGE PARTICLE RADIUS = 0.0178 CM.)

System	Equilibrium distribution coefficient, K_d	Rate constant Observed	Rate constant Adjusted to $K_d = 10^4$	Mechanism
Na^+ from 0.001 N HCl	1810	9.3×10^{-3} sec.$^{-1}$	16.8×10^{-4}	Film diffusion[a]
UO_2^{++} from 0.003 N HCl	4660	2.0×10^{-3}	9.3×10^{-4}	Film diffusion[a]
Ce^{+++} from 0.1 N HCl	52,500	1.4×10^{-4}	7.1×10^{-4}	Film diffusion[a]
Na^+ from 0.1 N HCl	25	3.7×10^{-6} cm.^{2} sec.$^{-1}$		Particle diffusion
UO_2^{++} from 0.3 N HCl	55	3.6×10^{-7}		Particle diffusion
Ce^{+++} from 0.5 N HCl	3890	9.4×10^{-9}		Particle diffusion

[a] Film diffusion data corrected to a constant flow rate of 10 ml./cm.^{2}/sec.

The differences in the film diffusion rate constants depend in part on K_d according to the equation[2]: $k(\text{sec.}^{-1}) = 3D^1/rK_d\delta$ where r is the particle radius, and δ the "film thickness." The variation which persists after correcting to a common K_d (see column 4, Table I) results from the differing coefficients, D^1, for the ions in the film.

Diffusion through the cation exchange polymer must be governed by other factors. Not only do the ions move more slowly than in aqueous solutions, but there is also a much more pronounced dependence on charge. The internal diffusion coefficients,[2] D^i, appear to be independent of K_d and external flow rate, and to depend only on the nature and composition of the exchanger, on the temperature and perhaps on the ionic strength of the external solution. Independently of the nature of the polymer or of the character

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[1] Amberlite IR-1, Rohm and Haas Company, Philadelphia, Pa. This material is presumed to have been a cross-linked phenol-formaldehyde polymer containing structurally bound methylene sulfonic acid groups solely responsible for the exchange capacity at low pH values.

[2] G. E. Boyd, A. W. Adamson and L. S. Myers, Jr., THIS JOURNAL, 69, 2836 (1947).