[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

Heterogeneous Ion Exchange in a Flowing System

BY HENRY C. THOMAS

A description of the performance of a mass of zeolite exchanging ions with a solution in which it is immersed may become possible if the form of the law governing the exchange is known. (In what follows we will understand by the term *zeolite* any solid substance, carbonaceous, resinous, or mineral, capable of exchanging ions with a solution.) We suppose that the ion exchange is governed by a law of the concentration product type. Others have investigated the applicability of such a law. du Domaine, Swain, and Hougen[1] have studied the exchange of sodium for calcium ion on this basis. In order to obtain results immediately applicable to the problem of water softening, they introduce certain approximations in the mathematical development. It has seemed worth while to reconsider the problem for such cases as may be susceptible of treatment without approximation. By this means we make available at least a part of the theory necessary for a fundamental study of the mechanism of the exchange processes.

The Differential Equation for the Flow Process.—Insofar as the rate of ion exchange can be characterized by a law explicit in the concentrations only of ions in solution and of exchangeable atoms or ions in the zeolite, the performance of a column of zeolite can be described as follows: Let the initial exchangeable cation concentration of the solution be c_0. Let $c(l, t)$ and $p(l, t)$ be the concentrations of this cation in the solution and in the zeolite, respectively, at time t after the entrance of the solution into the column and at distance l from the input end of the column. Suppose that the net rate of exchange of the cation into the zeolite is given by

$$\frac{\partial p}{\partial t} = F(c, p) \qquad (1)$$

Such a rate law is to be expected if the exchange processes are slow compared to any diffusion processes in the solution or in the zeolite particles. At least during the early stages of the "breakthrough" period, when the zeolite first approaches saturation, this type of law might be expected to hold. Various forms for F may be written down according to various theories of interaction between zeolite and solute. For an exchange between univalent ions the simplest reasonable law is given by

$$\frac{\partial p}{\partial t} = k_1(a - p)c - k_2p(c_0 - c) \qquad (2)$$

in which are presupposed two opposing second order reactions with velocity constants k_1 and k_2. In (2) a has been written for the initial exchange capacity of the zeolite. In what follows p and a will be considered as measured in milliequivalents per gram of zeolite and c and c_0 in milliequivalents per milliliter of solution.

To obtain the fundamental equation for the process, we need first the condition for the conservation of exchanging cation. We may define certain necessary quantities as follows:

v_0 = fractional free space in the zeolite column
M = over-all density of zeolite as packed in the column
R = $\delta V/v_0\delta t$ = linear rate of flow of the solution. The discussion will be restricted to constant flow rate.

The conservation condition demands that

$$c\delta V = \left(c + \frac{\partial c}{\partial l}\mathrm{d}l\right)\delta V + \frac{\partial c}{\partial t}v_0\mathrm{d}l\delta t + \frac{\partial p}{\partial t}M\mathrm{d}l\delta t$$

or

$$R\frac{\partial c}{\partial l} + \frac{\partial c}{\partial t} + m\frac{\partial p}{\partial t} = 0 \qquad (3)$$

in which m has been put for M/v_0. The first order equations (1) and (3) may conveniently be combined to give a single second order equation by putting

$$\left.\begin{aligned} x &= l/R \\ y &= \frac{1}{m}\left(x - \frac{l}{R}\right) \end{aligned}\right\} \qquad (4)$$

Thus we obtain

$$\frac{\partial p}{\partial y} = mF(c, p) \qquad (5)$$

and

$$\frac{\partial c}{\partial x} = -\frac{\partial p}{\partial y} \qquad (6)$$

Equation (6) shows that there exists a function of x and y, $f(x, y)$, such that

$$\mathrm{d}f = c\mathrm{d}y - p\mathrm{d}x$$

with

$$\left.\begin{aligned} c &= \frac{\partial f}{\partial y} \\ p &= -\frac{\partial f}{\partial x} \end{aligned}\right\} \qquad (7)$$

From (5), (6) and (7) we get then the fundamental equation for the flow process:

$$\frac{\partial^2 f}{\partial x\partial y} + mF\left(\frac{\partial f}{\partial y}, -\frac{\partial f}{\partial x}\right) = 0 \qquad (8)$$

Given the form of the rate law F the solution of (8) with appropriate initial conditions will constitute the solution of the problem.

It is unfortunate that equation (8) for any but first order chemical rate laws is only a quasilinear differential equation, that is, linear only in the highest order derivative. While the existence of solutions has been proved for the general equation (8),[2] unless some trick is found which will

---

(1) du Domaine, Swain and Hougen, *Ind. Eng. Chem.*, **35**, 546 (1943).

(2) Courant and Hilbert, "Methoden der mathematischen Physik," Vol. II, p. 317 ff.

linearize the equation, such solutions may be obtainable only through excessively laborious iteration procedures. In the case of the opposing second order reactions represented by (2) such a trick has been found.

The Solution for Second Order Kinetics.—Under (2) equation (8) becomes

$$\frac{\partial^2 f}{\partial x \partial y} + A\frac{\partial f}{\partial x} + B\frac{\partial f}{\partial y} + C\frac{\partial f}{\partial x}\frac{\partial f}{\partial y} = 0 \tag{9}$$

in which have been written for convenience

$$\begin{aligned} A &= mk_2c_0 \\ B &= mk_1a \\ C &= m(k_1 - k_2) \end{aligned} \tag{10}$$

If now we make the logarithmic substitution

$$Cf = \ln\{e^{-(Bx + Ay)}\Phi(x, y)\} \tag{11}$$

we obtain the linear equation

$$\frac{\partial^2 \Phi}{\partial x \partial y} - AB\Phi = 0 \tag{12}$$

Equation (12), the simplest hyperbolic differential equation, is one familiar to the mathematicians; general methods for the solution of initial value problems involving such equations have long been known. The method of Riemann[3] is well suited to the needs of this problem. In the application of this integration procedure we need the values of Φ and its derivatives along an initial value curve, say $g(\xi,\eta) = 0$, in the $x - y$ plane. The solution for $\Phi(x,y)$ may be shown to depend only on Φ and its derivatives on that part of g cut out by the characteristics of the hyperbolic differential equation. In the case of the equation (12) the characteristics are simply the straight lines parallel to the axes through the point of interest (x,y). In the problem at hand the initial values of Φ are specified along a pair of characteristics (the axes). We have a "characteristic initial value" problem. In such a case the further specification of the derivatives would be redundant.

First, we have to show how the boundary values of Φ are given by the specification of initial concentrations. Recalling the substitutions (7) and (11) we find

$$\left.\begin{aligned} c &= \frac{1}{C}\left(\frac{\partial \ln \Phi}{\partial y} - A\right) \\ &\text{and} \\ p &= -\frac{1}{C}\left(\frac{\partial \ln \Phi}{\partial x} - B\right) \end{aligned}\right\} \tag{13}$$

It is obvious that an arbitrary constant added to $\ln \Phi$ is trivial (*i. e.*, will not affect c and p). Most simply we choose $\Phi(0,0) = 1$. The initial values along one axis are obtained when we notice that at the input end of the column, *i. e.*, for $x = 0$, $y \geq 0$, we must have $c = c_0$

$$\left.\begin{aligned} &\frac{\partial \ln \Phi(0, y)}{\partial y} = \alpha \\ &\text{whence} \\ &\Phi(0, y) = e^{\alpha y} \end{aligned}\right\} \tag{14}$$

with $\alpha = mk_1c_0$. We shall also write $\beta = mk_2a$, so that $\alpha\beta = AB$. At the head of the advancing column of solution, specified by $t = l/R$, *i. e.*, for $y = 0$, $x \geq 0$, we have $p = 0$

$$\left.\begin{aligned} \frac{\partial \ln \Phi(x, 0)}{\partial x} &= B \\ \Phi(x, 0) &= e^{Bx} \end{aligned}\right\} \tag{15}$$

The application of the Riemann procedure now leads directly to the solution of (12) under the initial conditions (14) and (15). Because of the symmetry of the differential equation the required Riemann function is $I_0(2\sqrt{AB(x - \xi)(y - \eta)})$, in which ξ and η are the variables of integration around the boundary of the region determined by the characteristics and the axes. I_0 is the zeroth order Bessel function for purely imaginary argument. The solution for Φ is

$$\Phi(x, y) = I_0(2\sqrt{ABxy}) + \int_0^x Be^{B\xi}I_0(2\sqrt{ABy(x - \xi)})\mathrm{d}\xi + \int_0^y \alpha e^{\alpha\eta}I_0(2\sqrt{\alpha\beta x(y - \eta)})\mathrm{d}\eta \tag{16}$$

Properties of the Integrals.—For the following treatment of the integrals in (16) I am much indebted to Professor Lars Onsager. Writing

$$\varphi(u, v) = e^u \int_0^u e^{-t}I_0(2\sqrt{vt})\mathrm{d}t$$

the solution for Φ is seen to be

$$\Phi(x, y) = I_0(2\sqrt{ABxy}) + \varphi(Bx, Ay) + \varphi(\alpha y, \beta x) \tag{16'}$$

Now after expanding the Bessel function in power series, rearranging the absolutely and uniformly convergent series, and integrating term-wise by parts, one finds

$$\varphi(u, v) = e^{u+v} - \sum_{0 \leq m \leq n}^{\infty} \frac{u^m v^n}{m!\,n!} = \sum_{0 \leq n < m}^{\infty} \frac{u^m v^n}{m!\,n!}$$

Since

$$I_0(2\sqrt{uv}) = \sum_0^{\infty} \frac{(uv)^n}{n!\,n!} \equiv \sum_{0 \leq n = m}^{\infty} \frac{u^m v^n}{m!\,n!}$$

we have the important relation

$$\varphi(u, v) + \varphi(v, u) = e^{u+v} - I_0(2\sqrt{uv}) \tag{17}$$

On differentiation of the double series for φ one finds

$$\frac{\partial \varphi(u, v)}{\partial u} = \varphi(u, v) + I_0(2\sqrt{uv}) \tag{18}$$

Making use of (17) and (18) we find at once

$$\frac{\partial \varphi(u, v)}{\partial v} = \varphi(u, v) - \frac{\partial}{\partial v}I_0(2\sqrt{uv}) \tag{19}$$

It is also convenient to notice that the limiting values of the integral are

$$\left.\begin{aligned} \varphi(0, v) &= 0 \\ \varphi(u, 0) &= e^u - 1 \end{aligned}\right\} \tag{20}$$

By means of these relations (16) is readily proved to be the solution of (12) satisfying the initial conditions. The solution for Φ is thus unique.[4]

---

(3) *Ibid.*, pp. 311-317.

(4) *Ibid.*, p. 321.

The Concentrations.—By means of the formulas developed in the preceding section the calculation of c and p from (13) is easily carried out. The results are

$$\frac{c}{c_0} = \frac{I_0(2\sqrt{ABxy}) + \varphi(\alpha y, \beta x)}{I_0(2\sqrt{ABxy}) + \varphi(Bx, Ay) + \varphi(\alpha y, \beta x)} \qquad (21)$$

and

$$\frac{p}{a} = \frac{\varphi(\alpha y, \beta x)}{I_0(2\sqrt{ABxy}) + \varphi(Bx, Ay) + \varphi(\alpha y, \beta x)} \qquad (22)$$

It is instructive to rephrase the quantities involved in these formulas and write them explicitly in the velocity constants. This will show more clearly the physical quantities of significance in determining the performance of the zeolite. We put

$$\left.\begin{aligned} r &= c_0(t - l/R) = c_0my \\ &\text{and} \\ s &= Mla/Rv_0 = amx \end{aligned}\right\} \qquad (23)$$

When r and s are multiplied by the volume rate of flow, Rv_0, we get

Rv_0r = total milliequivalents of cations passed, and
Rv_0s = total milliequivalents of exchangeable cation per unit cross section of preceding zeolite.

In these terms the expression for the concentration of exchanging cation becomes

$$\frac{c}{c_0} = \frac{I_0(2\sqrt{k_1k_2rs}) + \varphi(k_1r, k_2s)}{I_0(2\sqrt{k_1k_2rs}) + \varphi(k_1s, k_2r) + \varphi(k_1r, k_2s)} \qquad (21')$$

The application of these formulas to experimental results is entirely feasible. Extensive tables of the Bessel functions are available.[5] The computation of the integrals may be carried out by appropriate series expansions. Since the parameters of the integrals involve the unknown velocity constants k_1 and k_2, these quantities will probably best be obtained by fitting (21) to "break-through" data on a column run under known conditions. Preliminary experiments by Mr. Allen L. Solomon of this Laboratory indicate that the exchange reactions may be too rapid for an accurate determination of the constants by simply shaking the zeolite with solution.

It is hoped that the application and testing of the theory here presented may be made the subject of a further communication.

NOTE ADDED IN PROOF.—Very recently Nachod and Wood[6] have shown that the velocities of exchange of calcium for hydrogen or sodium follow a second order rate law. On the basis of their results the development of the present paper becomes the proper foundation for the description of the performance of packed ion exchange columns used in water softening.

In conclusion the author wishes to express his thanks to Professor Lars Onsager for his interest in this problem and for many most helpful conversations on the subject.

Summary

A mathematical description is given of the performance of a cation exchange column for the case in which the rate of the exchange is determined by a second order law. The effect of the reverse reaction is included without approximation.

---

[5] E. Anding, "Bessel'schen Funktionen Imaginären Argumentes," Leipzig, 1911.

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

NEW HAVEN, CONN. RECEIVED MARCH 1, 1944

[CONTRIBUTION FROM THE ALUMINUM RESEARCH LABORATORIES, ALUMINUM COMPANY OF AMERICA]

Aluminum Phosphide—Preparation and Composition[1]

BY WAYNE E. WHITE AND A. H. BUSHEY

Chemical literature records claims for the existence of five different binary compounds of aluminum and phosphorus. Wöhler[1a] first reported combination of the two elements and later A. Rossel and L. Franck[2] obtained a product reported to be Al_3P_5, by passing phosphorus vapor over heated aluminum. L. Franck[3] reported Al_3P_7,[4] Al_5P_3, Al_3P, and AlP as products which he obtained by slight variations in the general procedure of reacting aluminum with phosphorus vapor. In some cases air was entirely eliminated from the glass reaction chamber by means of hydrogen; in other cases air was swept out with a stream of phosphorus vapor alone before the aluminum was heated. Unsuccessful attempts were made to secure effective reaction in sealed tubes. In all preparations the reacted masses were taken to high temperatures to volatilize any unreacted phosphorus.

Unaware of earlier work except that of Granger[5] who concluded that aluminum phosphide was unstable and could not be prepared, Fonzes-Diacon[6] believed himself to be the first to make this compound. While mistaken in regard to discovery, he was original in his method of preparation. He mixed aluminum powder and red phosphorus in equal weights and ignited the mixture with a

---

[1] Original manuscript received October 21, 1943.

[1a] F. Wöhler, *Pogg. Ann.*, **11**, 160 (1827).

[2] A. Rossel and L. Franck, *Ber.*, **27**, 53 (1894).

[3] L. Franck, *Chem. Ztg.*, **22**, 237-240 (1898).

[4] Inspection of the analytical data supplied by Franck reveals that this product was 67% aluminum and 33% phosphorus. This composition corresponds to the formula Al_7P_3 rather than Al_3P_7 as reported.

[5] Granger, Doctorate Thesis, Paris, 1898.

[6] Fonzes-Diacon, *Compt. rend.*, **130**, 1315 (1900).