TABLE II

HYDROLYSIS OF INDIUM TRIIODIDE SOLUTIONS AT 25°

Moles of InI₃ per liter	pH	Degree of hydrolysis x	Hydrolysis constant $K_h \times 10^5$
0.002500	3.37	0.170	8.7
.005000	3.28	.105	6.2
.01000	3.18	.066	4.7
.02000	3.09	.041	3.5
.04000	3.02	.024	2.4
.06000	2.96	.018	2.0
.08000	2.92	.0150	1.8
.1000	2.88	.0130	1.7
.1500	2.81	.0103	1.6
.2000	2.75	.0089	1.6
.2500	2.70	.0080	1.6
.3000	2.64	.0076	1.7

culated[2,7] for both the bromide and iodide solutions. These are summarized in Tables I and II. If the results for the four most dilute solutions be

(7) Britton, "Hydrogen Ions," D. Van Nostrand Company, Inc., New York, N. Y., 1929, pp. 168–170.

neglected in each case,[2] the remaining values for K_h are then reasonably constant with means of 1.4×10^{-5} and 1.8×10^{-5} for the bromide and iodide respectively.

Comparison of these averages with the mean value of 1.2×10^{-5} reported for solutions of indium trichloride[2] indicates that the extent of hydrolysis is only slightly increased in the series chloride to bromide to iodide.

Summary

1. Variations of pH with concentration at 25° are given for pure indium tribromide and triiodide solutions.

2. Calculation of hydrolysis constants on the assumption that the hydrolysis products are [In(H₂O)₅(OH)]⁺⁺ and H₃O⁺ yields average values of 1.4×10^{-5} and 1.8×10^{-5} for the bromide and iodide solutions, respectively.

Ionic Competition in Base-Exchange Reactions[1]

BY R. H. BRAY

A knowledge of the equilibria between exchangeable cations and electrolytes in colloidal systems has assumed new importance in recent years. The properties of clays in many of their ceramic uses, particularly castings, the weathering of minerals, the physical properties of soils, the softening of water and the recent application of new cation-exchange resins to numerous purposes are regulated by cation-exchange equilibria.

Exchange Equilibria in Soils

The equilibria between the exchangeable cations on the soil clays and electrolytes in the soil water influence many important processes concerned with soil leaching and plant nutrition. The most important of these equilibria are those which involve relatively small amounts of electrolyte and relatively large amounts of cation-exchange material. However, cation-exchange studies usually have concerned themselves with the range within which clay and electrolyte are present in equivalent amounts or almost so.

A second aspect, little studied, is the influence of a mixed cation composition on the release or

adsorption of an individual cation, as for example where exchangeable calcium, magnesium, potassium, and hydrogen are present on the exchange complex and a mixture of potassium and sodium chlorides is added to the system.

A third aspect, likewise little studied, is the influence of relatively large amounts of exchangeable cations on the release of relatively small amounts of complementary ions and vice versa, as for example where 0.1 m. e. of exchangeable potassium occurs in a soil containing 10 m. e. of calcium, 5 of magnesium, and 5 of hydrogen as complementary exchangeable cations.
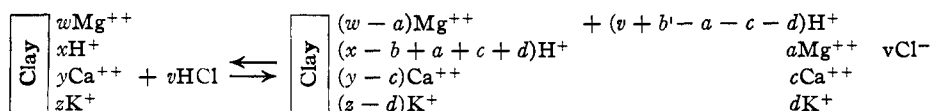
These aspects of cation-exchange may be summed up as follows. (a) The ratio of exchangeable cation to electrolyte is wide. (b) The ratio between complementary ions is wide. (c) The number of different kinds of ions present is large. The purpose of the present study is to present experimental cation-exchange data obtained under the above conditions and to evaluate the data in terms of exchange adsorption isotherms.

General Considerations

The exchangeable cation composition of a clay system containing a relatively small amount of

electrolyte largely controls the cation composition of the electrolyte present in solution. As the electrolyte content is increased this influence decreases until, with large amounts of electrolyte present, the composition of the cations added largely controls the composition of the exchangeable cations.

$$\text{Clay} \begin{bmatrix} w\text{Mg}^{++} \\ x\text{H}^{+} \\ y\text{Ca}^{++} \\ z\text{K}^{+} \end{bmatrix} + v\text{HCl} \xrightarrow{\longleftarrow} \text{Clay} \begin{bmatrix} (w-a)\text{Mg}^{++} \\ (x-b+a+c+d)\text{H}^{+} \\ (y-c)\text{Ca}^{++} \\ (z-d)\text{K}^{+} \end{bmatrix} \begin{array}{l} + (v+b'-a-c-d)\text{H}^{+} \\ a\text{Mg}^{++} \quad v\text{Cl}^{-} \\ c\text{Ca}^{++} \\ d\text{K}^{+} \end{array}$$

The equilibrium between the exchangeable cations and the cations of the electrolyte is influenced not only by the amounts of each cation present but by their properties as exchangeable cations occurring at the surface of the particular type of cation-exchange material or materials which may be present. The cations are not adsorbed equally (exchange adsorption) when present in equal amounts. This unequal adsorption has been studied by numerous investigators. Jenny[2] gives the adsorption series for Putnam clay for the mono-valent cations as follows

$$\text{LiCl} \leqq \text{NaCl} < \text{KCl} < \text{RbCl} < \text{CsCl} < \text{HCl}$$

In the soil–water system occurring naturally in the soils of a humid region the electrolyte content is generally small. The cation composition of the electrolytes present will be, under such conditions, controlled largely by the exchangeable cation composition with little influence from the original cations of the electrolytes introduced into the soil water by the weathering of soil minerals, rainfall, nitrification, and other biological activities.

The proportion of the cations in the intermicellar soil water will differ from the proportions of the cations on the exchange complex. In as far as one exchangeable cation has a greater "ease of release" than another it will be present in the intermicellar water in larger proportions relative to the amount of each present.

The composition of the intermicellar soil water (the so-called soil solution in early soils investigations) is influenced, therefore, not only by the amounts of the exchangeable cations but also by their relative ease of release.

The experimental procedure used in the following study had as its object the study of the above relationships, i. e., the equilibria between mixtures of different exchangeable bases such as occur in soils and small amounts of electrolytes in

(2) Hans Jenny, J. Phys. Chem., 40, 501–517 (1936).

solution, in order to obtain a better understanding of some of the processes involved in plant nutrition and soil weathering and leaching.

The immediate objective was to study the influence of mixed exchangeable cations on the cation composition of the intermicellar water in a soil–water system according to the scheme

By limiting the amount of the replacing cations added and using an electrolyte which does not produce any secondary reactions, free competition (exchange competition) should occur between the cations on the clay for a place in the solution in which both the amount present and the relative ease of release should play significant roles. The results should be applicable to cation–exchange systems where small amounts of electrolytes such as nitrates and chlorides are present as in soil–water systems.

Experimental

In the present study 300 g. of air-dried soil, whose cation composition was known, was shaken for ten minutes at approximately 25° in 1000 ml. of 0.005 N hydrochloric acid. This is equivalent to 1.66 milligram-equivalents (m. e.) of H^{+} per 100 g. of soil. The soil was allowed to settle for one-half hour and the supernatant solution was decanted through a filter. Potassium, calcium and magnesium were determined in the filtrate. The base-exchange materials in the soils used were approximately one-third organic and two-thirds inorganic. The inorganic materials were mainly the montmorillonite (beidellite)-illite associations as found in Illinois soils and shales.[3]

The exchangeable bases and the base-exchange capacity were determined by leaching with neutral, normal ammonium acetate. The bases were determined in the filtrate and the ammonium-saturated soil was washed free of ammonium acetate with neutral absolute methyl alcohol. The ammonium ion was replaced by leaching with 0.1 N hydrochloric acid and determined.

Discussion of Results

Table I gives the exchangeable cation composition of the soils used and the milligram-equivalents (m. e.) of potassium, magnesium, and calcium released by the addition of 1.66 m. e. of H^{+} as hydrochloric acid to each 100 g. of soil. This is one-sixth of the cation capacity of the soil possessing the lowest capacity. In every soil the amount of release was in the order potassium, magnesium, calcium. The order of magnitude

(3) R. E. Grim, R. H. Bray and W. F. Bradley, Am. Mineral., 22, 813–829 (1937).

in which they occur naturally in the soils used is also potassium, magnesium, calcium. However, Table II shows that the percentage of each base released is in the order calcium, magnesium, potassium. The results show that the amount of a given cation which is released is determined not only by the relative amount present but also by the properties of the individual ions when they occur as exchangeable cations on a given cation-exchange surface.

TABLE I

DETERMINATION OF CATION RELEASE ON ILLINOIS SURFACE SOILS

Soil num-ber	Original replaceable cations, m. e.				Base exchange capacity, m. e.	Cations release,[a] m. e.			
	K	Mg	Ca	H		K	Mg	Ca	Total
S6754	0.16	1.2	10.5	0	11.3	0.037	0.10	1.31	1.45
S6758	.26	6.3	23.4	7.9	37.9	.028	.56	1.05	1.64
S6759	.36	10.7	31.8	0	37.1	.032	...	....	....
S6760	.17	4.6	22.2	0	26.0	.027	.40	1.08	1.51
S6761	.16	4.8	15.9	3.4	24.3	.022	.43	0.95	1.40
S6762	.12	2.2	5.6	2.0	9.9	.036	.63	1.08	1.75
S6763	.05	1.0	1.3	7.6	10.0	.035	.49	0.58	1.11
S6767	.20	3.9	10.7	5.1	19.9	.029	.47	.95	1.45
S6769	.16	1.8	4.6	9.5	16.1	.065	.42	.62	1.11
S6765	.17	1.3	2.7	6.7	10.9	.082			
S6757	.23	12.1	26.7	0	37.6	.020			

[a] Cations released upon the addition of 1.66 m. e. of H^+ (as HCl) to 100 g. of soil; m. e. = milliequivalents (per 100 g. of soil).

TABLE II

CALCULATION OF THE CONSTANTS FOR RELATIVE "EASE OF RELEASE" (ILLINOIS SURFACE SOILS)

Soil number	Per cent. release.			% K released % Ca released or f_K	% Mg released % Ca released or f_{Mg}
	K	Mg	Ca		
S6754	23.2	8.3	12.5	1.84	(0.66)
S6758	10.7	8.9	4.5	2.38	1.98
S6759	8.9	....	....	....	....
S6760	15.9	8.7	4.9	3.18	1.77
S6761	13.7	9.0	6.0	2.28	1.50
S6762	30.0	28.6	19.0	1.56	1.48
S6763	70.0	49.0	44.6	1.57	1.10
S6767	14.5	12.2	8.9	1.63	1.37
S6769	40.6	23.3	13.5	3.00	1.72
S6765	48.2	....	....	....	....
S6757	8.7	....	....	....	....
Average				2.20	1.60

$f_K = 2.2$; $f_{Mg} = 1.6$; $f_{Ca} = 1.0$; $f_H = 0.35$ (calculated from Jenny's data for Putnam clay).

The Calculation of the "Relative Ease of Release"

The relative properties of the cations, as replaceable ions, which have brought about the above reversal in order are not fully understood. Valence and ion size appear to be concerned in this phenomenon. Relative "ease of release" is a term used to describe it. In the equations developed below it is considered a constant for a given ion on a given clay material similar in nature to the clays used in this experiment and for the conditions represented in the experiment. The calculation of this constant (f) is shown in Table II where the constant for calcium (f_{Ca}) is taken as 1.0 and the relative constants for potassium and magnesium are calculated by dividing the percentage release of each by the percentage release of calcium.

It is evident that the technique used is successful in showing the "relative ease of release" of the ions where mixtures of different kinds of ions are present in different proportions as represented by the soils used. This technique permits one to study the influence of both (a) the amount of each cation present and (b) the "relative ease of release" on the composition of the extractable soil water within a range in which the results secured can be applied to soil water extracts containing small amounts of electrolytes.

Development of Base Exchange Equations

It can be assumed that the ratio of a given cation to the total cations released when a small amount of electrolyte is added, is proportional to (1) the relative amount present in the exchangeable form and (2) the "relative ease of release." The following equation expresses this proportionality

$$K_{p1} = \frac{Kf_K}{Kf_K + Caf_{Ca} + Mgf_{Mg} + Hf_H}$$

or

$$K_{p1} = Kf_K/Cf_b \tag{1}$$

where K_{p1} = ratio of potassium released to the total cations released from the colloid, where the release is small relative to the cation-exchange capacity, Ca, H, K, etc. = m. e. of exchangeable cations, f_K, f_{Ca}, etc. = constants for "relative ease of release" of the respective cations, C = cation-exchange capacity, and

$$f_b = \frac{Kf_K + Caf_{Ca} + Mgf_{Mg} + Hf_H + \ldots + Rf_R}{C}$$

or average f for the exchangeable cations. Equation 1 may be modified for systems where small amounts of exchangeable cations and large amounts of electrolyte are present.

$$K_{p2} = K\frac{1}{f_K}\bigg/ Cf_{br} \tag{2}$$

where K_{p2} = ratio of potassium retained to the total cations retained on the colloid where the retention is small and

$$f_{br} = \frac{K\frac{1}{f_K} + Ca\frac{1}{f_{Ca}} + Mg\frac{1}{f_{Mg}} + H\frac{1}{f_H} + \ldots + R\frac{1}{f_R}}{C}$$

Equation 2 as written assumes the same f values as in Eq. 1. This assumption may not hold and different f values may be necessary for these two equations.

Equations 1 and 2 are concerned only with the release or retention of the original exchangeable cations. Similar equations give the distribution of the cations of the added electrolyte.

$$K_{p_3} = K_a\frac{1}{f_K}\Big/ A f_{ar} \qquad (3)$$

Where K_{p_3} = ratio of potassium adsorbed to the total cations adsorbed from solution, where a large amount of electrolyte is added, K_a, Ca_a, etc. = m. é. of each cation added, A = total m. e. cations added and

$$f_{ar} = \frac{K_a\frac{1}{f_K} + Ca_a\frac{1}{f_{Ca}} + Mg_a\frac{1}{f_{Mg}} + H_a\frac{1}{f_H} + \ldots + R_a\frac{1}{f_R}}{A}$$

Also

$$K_{p_4} = K_a f_K / A f_a \qquad (4)$$

where K_{p_4} = ratio of the added potassium not adsorbed to the total cations not adsorbed where a small amount of electrolyte is added and

$$f_a = \frac{K_a f_K + Ca_a f_{Ca} + Mg_a f_{Mg} + H_a f_H + \ldots + R_a f_R}{A}$$

The above equations permit the calculation of the *ratio* of a given ion released or adsorbed to the total cations adsorbed or released. The *amount* of a given cation adsorbed or released can be calculated as follows

$$K_{S_1} = \frac{K f_K}{C f_b} E \qquad (5)$$

where K_{S_1} = amount in m. e. of potassium released where E is small relative to C, and E = total release of cations from the colloid in m. e. Also

$$K_{S_2} = \frac{K\frac{1}{f_K}}{C f_{br}} [C - E] \qquad (6)$$

where K_{S_2} = amount in m. e. of potassium retained by the colloid where E is large and approaches C in value and

$$K_{S_3} = \frac{K_a\frac{1}{f_K}}{A f_{ar}} E \qquad (7)$$

where K_{S_3} = amount in m. e. of potassium adsorbed from solution by the colloid where per cent. adsorption of A is small and

$$K_{S_4} = \frac{K_a f_K}{A f_a} [A - E] \qquad (8)$$

where K_{S_4} = m. e. of potassium retained by the solution (not adsorbed) where the per cent. adsorption of A is large.

The above equations will be approximately correct only where either the release or retention is small. That is, the influence of the "relative ease of release" (f) or the "relative tightness of retention" $(1)/(f)$ in the above equations on the exchange competition approaches zero (a) as a complete release is approached by large electrolyte additions (Eq. 5 and 8) or (b) complete retention is approached by very small electrolyte additions (Eq. 6 and 7).

If it is assumed that the influence of f on the ratio released (exchange competition) decreases in proportion to the progress of the release, the following approximate correction to the above equations can be made.

$$K_{C_1} = \left[\frac{K f_K}{C f_b} + \left[\frac{K}{C} - \frac{K f_K}{C f_b}\right]\frac{E}{C}\right] E \qquad (9)$$

where K_{C_1} = K_{S_1} corrected for increasing release or retention and

$$K_{C_2} = \left[\frac{K\frac{1}{f_K}}{C f_{br}} + \left[\frac{K}{C} - \frac{K\frac{1}{f_K}}{C f_{br}}\right]\frac{C - E}{C}\right][C - E] \qquad (10)$$

$$K_{C_3} = \left[\frac{K_a\frac{1}{f_K}}{A f_{ar}} + \left[\frac{K_a}{A} - \frac{K_a\frac{1}{f_K}}{A f_{ar}}\right]\frac{E}{C}\right] E \qquad (11)$$

$$K_{C_4} = \left[\frac{K_a f_K}{A f_a} + \left[\frac{K_a}{A} - \frac{K_a f_K}{A f_a}\right]\frac{A - E}{A}\right][A - E] \qquad (12)$$

where K_{C_1}, K_{C_3} and K_{C_4} are K_{S_1}, K_{S_3} and K_{S_4}, respectively, corrected for increasing release or retention.

In the above equations the value E, the total release (or adsorption) of the cations, varies with the amount of electrolyte added. Where a very small amount of electrolyte is added to a large amount of a clay, high in cation-exchange capacity, practically all of the cation is adsorbed and the amount of the exchangeable cations released (E) can be assumed as equivalent to the amount of electrolyte (A) added. The amount of release (E) depends on the number and kind of the exchangeable cations present and the number and kind of cations added to a given cation-exchange material where the anion added produces no secondary reactions. If, for example, one m. e. of potassium, as potassium chloride, is added to a suspension of clay possessing one m. e. capacity and saturated with calcium, the proportion of potassium to calcium on the colloid at equilibrium is 1/2.2 where f_{Ca} = 1 and f_K = 2.2. Doubling

the amount of potassium chloride added gives 1/2.2·2/1 for the proportion of potassium to calcium on the colloid or Af_{Ca}/f_K where A equals the m. e. of cation added.

The total number of parts on the colloid is $Af_{Ca} + Cf_K$ where C is the m. e. of exchangeable calcium originally present or the cation-exchange capacity. The proportion of potassium on the colloid is, then, $Af_{Ca}/(Af_{Ca} + Cf_K)$, where C is equal to or less than A. This multiplied by the cation-exchange capacity gives the amount (E) of potassium on the colloid or the calcium release

$$\frac{Af_{Ca}}{Af_{Ca} + Cf_K} C = E$$

This may be simplified to

$$E_1 = \frac{AC}{A(f_a/f_b) + C} \qquad (13)$$

where E_1 = total m. e. of cations released or adsorbed when A is equal to or smaller than C, f_a, f_b = average f for A and C, respectively, A = m. e. of cations added and C = m. e. cation exchange capacity. Also

$$E_2 = \frac{AC}{A + C(f_a/f_b)} \qquad (14)$$

where E_2 = total m. e. of cations released or adsorbed where A is equal to or greater than C.

Either E_1 or E_2 is substituted for E in Eq. 5 to 12 depending upon the relative values for A and C.

Jenny[2] has developed an equation (his Eq. 11) which calculates the cations adsorbed or released (W) when one kind of cation is on the colloid and another kind of cation is added to the system so that at most two kinds of cations are present. It is as follows

$$w = \frac{+(s+N) \pm \sqrt{(s+N)^2 - 4sN(1 - (v_w/v_b))}}{2(1 - (v_w/v_b))} \qquad (15)$$

where N = amount of electrolyte added initially; w = number of cations adsorbed or released at equilibrium; s = saturation capacity, and v_w, v_b = oscillation spaces of the adsorbed ions.

After the writer's equations were developed and the f values calculated, an inspection of Jenny's equation showed that v_w/v_b as used by Jenny was equivalent to $(f_w/f_b)^2$ where f_w is the writer's value for f for the added cation and f_b is the value for the exchangeable cation. On the other hand, an equation used later by Jenny and Ayers[4] derived from Jenny's Eq. 11, gave v_w/v_b equivalent to f_w/f_b.

(4) Hans Jenny and A. D. Ayers, Soil Sci., 48, 443–459 (1939).

If $(f_a/f_b)^2$ is substituted for Jenny's v_w/v_b in Eq. 11[2] where f_a is the average value for the added cations and f_b is the average value for the exchangeable cations as already described, Jenny's Eq. 11 can be used for mixed cation systems where more than two kinds of cations are present, serving the same purpose as the writer's Eq. 13 and 14, i. e., the calculation of E, the total m. e. of cations released. With this substitution, Jenny's Eq. 11 may also be substituted for E in Eq. 5 to 12 where the release of each individual ion in mixed systems is calculated.

The Applications of the Equations to Experimental Data

Equations 5 and 9 have been applied to the data in Tables I and II. Table III shows the calculation of the cation release using Eq. 5. Since A is not large, the correction in Eq. 9 changes the values very slightly and they are therefore not included in Table III. Agreements between calculated and observed values are good

TABLE III

CALCULATION OF CATION RELEASE (ILLINOIS SURFACE SOILS)

Soil number	Found[a]				Calculated[b]			
	K	Mg	Ca	Sum	K	Mg	Ca	Sum
S6754	0.037	0.10	1.31	1.45	0.045	0.25	1.29	1.58
S6758	.028	.56	1.05	1.64	.026	.47	1.02	1.52
S6759	.032	...	....	....	.030	...	....	....
S6760	.027	.40	1.08	1.51	.021	.40	1.20	1.62
S6761	.022	.43	0.95	1.41	.023	.52	1.00	1.54
S6762	.036	.63	1.08	1.75	.043	.57	0.87	1.48
S6763	.035	.49	0.58	1.11	.031	.45	.34	0.82
S6767	.029	.47	.95	1.45	.038	.55	.89	1.48
S6769	.065	.42	.62	1.11	.052	.42	.64	1.11
S6765	.082	...	....	....	.080	...	....	....
S6757	.020	...	....	....	.018	...	....	....

[a] Cations released upon the addition of 1.66 m. e. of H^+ (as hydrochloric acid) to 100 g. of soil. [b] Calculated by means of the equation

$$K_{S1} = \frac{Kf_K}{Kf_K + Caf_{Ca} + Mgf_{Mg} + Hf_H} E_1$$

Where K_{S1} = potassium released; K, Ca, etc. = replaceable cations; f_K, f_{Ca}, etc. = constant for relative "ease of release"; E_1 = total cations released.

in most cases. In Table III average values for f were used and it is recognized that part of the lack of agreement found may be due to the fact that the nature of the base-exchange materials will vary somewhat from soil to soil. The significant fact demonstrated is that average f values may be used for a wide variety of Illinois surface soils to obtain an estimation of the proportions of the cations occurring in the intermicellar soil water. The exchangeable bases as determined by

TABLE IV

CALCULATION OF IONIC EXCHANGE (%)[a]

M. e. of cation added to one of clay	—NH₄-Clay + NaCl— Experimental	E[b]	W[b]	—NH₄-Clay + KCl— Experimental	E	W	—NH₄-Clay + HCl— Experimental	E	W	—H-Clay + KCl— Experimental	E	W
0.5	21	24	21	33	33	30	50	46	48	9	12	11
1.0	32	31	32	51	50	50	85	86	85	14	14	15
2.0	45	47	44	67	67	65	91	93	97	22	24	21
4.0	54	64	57	75	80	80	91	96	99	34	39	29

[a] Data from papers by Jenny [*J. Phys. Chem.*, **40**, 510 (1936)] and Gieseking and Jenny [*Soil Sci.*, **42**, 374 (1936)].
[b] E calculated with Eq. 13 and 14; W calculated with Jenny's Eq. 11.

leaching with a neutral salt are shown by these data to be the same bases which are in equilibrium with electrolytes in the soil water after a very short shaking period. In the writer's opinion, bases which are technically in the exchangeable condition but which do not take part in such an immediate equilibrium should not be defined as readily exchangeable and should be determined separately from those which do. Potassium is a good example of an element which occurs both in a "readily exchangeable" condition and in a "difficultly exchangeable" condition.[5] The latter form takes no part in soil solution equilibria until it has been released to the readily exchangeable form from the soil colloid, probably through hydrolysis or replacement with hydrogen ions. Evidence for a very slow equilibrium between the "difficultly" and "readily" exchangeable potassium has been found.[5] It is essential to emphasize that methods which remove bases that take no part in the clay-soil water equilibria discussed above, do not give exchangeable base values which can be substituted in the above equations. It is therefore suggested that the exchangeable bases in such soils as have been studied be defined as those bases taking part in the equilibria described by the base-exchange equations. The equations are not applicable where the anions present produce secondary reactions such as precipitation or the formation of undissociated molecules.

Jenny[2] and Gieseking and Jenny[6] report numerous experiments with two ion systems where C is held constant and A is varied. Their calculated and observed values are generally in good agreement. Table IV gives their observed values and calculated values using Jenny's Eq. 11 and the writer's Eq. 13 and 14. With four m. e. of sodium chloride to one of ammonium clay the writer's equation does not give as good agreement

as does Jenny's, but for the hydrogen system the writer's equation gives the better agreement; otherwise there is not much difference between the values calculated by the two equations.

Jenny discusses the application of his equation to experimental data and concludes "that the equation developed is able to describe very satisfactorily the position and trend of the curves over a considerable range of electrolyte concentration." He ascribes deviation to variations in the structure of the colloidal particles (his equation is less satisfactory for zeolites and permutites) and to large differences in the properties of the ions.

The equations used in Table IV give only the total release (or total adsorption) not the release of a particular ion in mixed systems. They do not give a picture of the exchange competition between a variety of ions for places in the intermicellar water (or for places on the exchange surface). Published exchange data where mixed ions (more than two kinds) have been used, which can be used to test Eq. 1 to 12 are not readily obtainable. However, Vanselow[7] added varying ratios of sodium and potassium chlorides to soils and bentonites saturated with either one of the two ions. For example he added 14.3 m. e. of sodium chloride and 85.7 m. e. of potassium chloride to 42.9 m. e. of a sodium saturated bentonite. In this case the release of sodium from the colloid is calculated with Eq. 14 and the amount of sodium adsorbed from the added sodium chloride with Eq. 7. The sodium in solution at equilibrium is the sum of the sodium added and the sodium released, minus the sodium adsorbed.

These equations have been applied to Vanselow's data for bentonite 7 and the observed and calculated values are given in Table V. Very satisfactory agreement is obtained between calculated and observed values. It is noticeable that Vanselow recovers more than the added 100 m. e. in most cases. The calculated values indi-

(5) R. H. Bray and E. E. DeTurk, *Soil Sci. Soc. Proceedings.* **3**, 101–106 (1938).
(6) J. E. Gieseking and Hans Jenny, *ibid.*. **42**, 273–280 (1936).
(7) A. P. Vanselow, *Soil Sci.*, **33**, 95–113 (1932).

cate that it is the sodium ion which is contributing mostly to this higher than theoretical recovery. This would be expected if some hydrolysis occurred under the conditions of the experiment.

TABLE V

EXPERIMENTAL DATA FOR BENTONITE 7[a] AND THE CALCULATION OF THE COMPOSITION OF THE LEACHATE AFTER EQUILIBRIUM

All concentrations expressed as milligram equivalents per liter. Na$^+$ and K$^+$ added as the chlorides. Na = sodium saturated clay. K = potassium saturated clay. $f_{Na} = 6.2$, $f_K = 2.3$ for bentonite 7.

Initial concentrations				Analytical results		Calculated results[b]	
Na$^+$	K$^+$	Na	K	Na$^+$	K$^+$	Na$^+$	K$^+$
100.0	0	0	25.0	86.3	14.9	85.1	14.9
100.0	0	0	42.9	81.1	20.6	80.2	19.8
85.7	14.3	0	42.9	71.9	29.2	70.5	29.5
71.4	28.6	0	42.9	61.8	39.5	60.0	40.0
14.3	85.7	42.9	0	48.4	53.1	47.0	53.0
80.0	20.0	20.0	0	87.4	13.5	86.7	13.3
28.6	71.4	42.9	0	60.0	42.1	56.9	43.1
30.0	70.0	50.0	0	64.8	37.9	61.3	38.7
0	100.0	42.9	0	37.0	64.7	37.0	63.0
0	100.0	25.0	0	22.7	78.3	22.8	77.2

[a] A. P. Vanselow, *Soil Sci.*, **33**, 101–103 (1932).

[b] K added as chloride + K released from colloid − K adsorbed = K$^+$ in solution or KCl added + E_2 (by Eq. 14) − K_{c_3} (by Eq. 11) = K$^+$ in solution.

Limitations in the Use of the Cation-Exchange Equations

The Calculation of E.—Equations 13 and 14 and Jenny's Eq. 11 have been applied to such
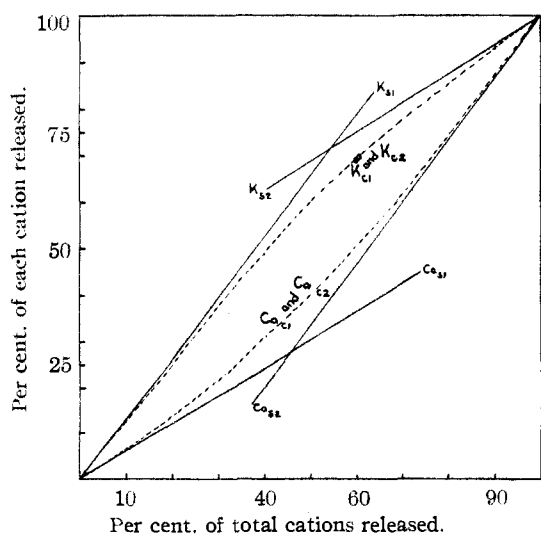

Fig. 1.—Exchange isotherms for equivalent amounts of exchangeable ions, showing the effect of the f value on the relative release:

$$\boxed{\text{CLAY}}\begin{array}{l} K = 1\,\text{m. e.} \\ Ca = 1\,\text{m. e.} \end{array} + X\text{m. e. RCl} \quad \begin{array}{l} f_K = 2.2 \\ f_{Ca} = 1.0 \end{array}$$

systems as 1 m. e. of NH$_4$-Clay plus 0.05 m. e. of hydrochloric acid and 1 m. e. of H-Clay plus 0.05 m. e. of ammonium chloride. Where wide f ratios ($f_{NH_4} = 2.2$ and $f_H = 0.35$) and wide ratios of exchange capacity to electrolyte are present, as represented by these two systems, the calculated adsorption or release with Jenny's equations is not in good agreement with the writer's. Jenny's equation favors a greater retention of hydrogen on the colloid in both cases. More study of such systems (also where C is small and A is large) is needed to show where each equation best fits the observed facts.

The Calculation of the Release or Adsorption of a Single Cation.—Limitations in the use of Eq. 1 to 12 inclusive are best brought out by applying them to different systems. Figure 1 shows the application of Eq. 5, 6, and 9 to a clay system 50% saturated with calcium and 50% with potassium to which varying amounts of electrolyte are added. The curves were obtained by substituting values for E and plotting the calculated percentage release of each base against the total percentages of bases released. Such a system is relatively simple. Fairly accurate results should be obtained with Eq. 5 or 6 where the release is relatively small but Eq. 9 is needed in the middle range of release to correct for the increasing release. Although no data are available for such a system, the excellent agreement obtained with Vanselow's data (Table V) would lead one to expect similar good agreement with this system.

Vanselow's data were obtained with two kinds of ions added as electrolytes instead of two kinds of ions present on the exchange complex. Figure 2 shows the plotting of one of Vanselow's systems where the electrolyte is held constant with the amount of clay varying and where the adsorption of potassium from solution is plotted against total adsorption. For any one system Vanselow has only one amount of colloid, 42.9 m. e., and his observed value falls on the curve obtained with Eq. 11. The straight line curves were obtained with Eq. 7 and 8. The equations appear to fit Vanselow's conditions almost exactly but his conditions do not cover the whole range possible, *i. e.*, the range of small release or retention where either small or large amounts of electrolyte are added or where a wide ratio between the competing ions occurs.

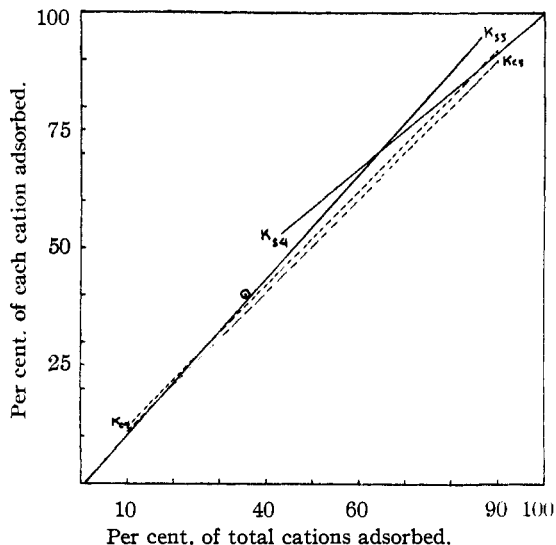The corrected equations, 9, 10, 11, and 12,

Fig. 2.—Exchange isotherms for a system containing a constant amount of mixed electrolytes to which varying amounts of clay are added:

CLAY $\begin{array}{c} X\text{m. e.} \\ \text{Na} \\ \text{bentonite} \end{array}$ $+ \begin{array}{c} 85.7 \text{ m. e. K}^+ \\ 14.3 \text{ m. e. Na}^+ \end{array}$ } as Cl

$f_K = 2.3$ } for bentonite 7 (Vanselow)
$f_{Na} = 6.2$

⊙ = value where Na bentonite = 42.9 m. e.

fit the systems studied very well. However, the corrected equations can be shown to be inaccurate in the middle range of release where the competing ions are present in a wide ratio as, for example,
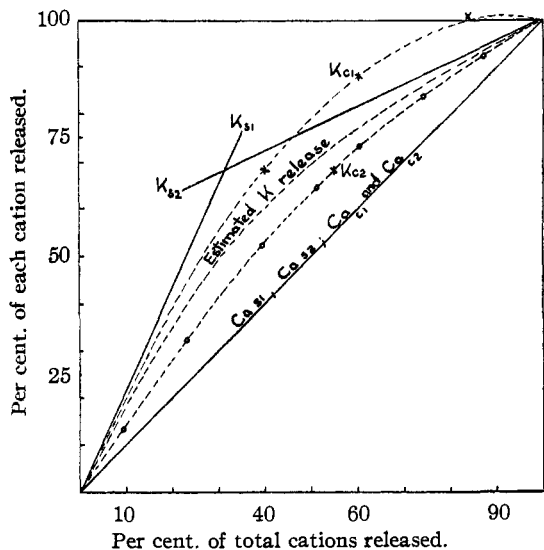

Fig. 3.—Exchange isotherms for a system containing a wide ratio of exchangeable ions.

CLAY $\begin{array}{c} K = 0.1 \text{ m. e.} \\ Ca = 9.9 \text{ m. e.} \end{array}$ $+ X\text{m. e. RCl} \begin{array}{c} f_K = 2.2 \\ f_{Ca} = 1.0 \end{array}$

where 9.9 m. e. of calcium and 0.1 m. e. of potassium are competing either for adsorption or release. This system is represented in Fig. 3 where Eq. 5, 6, 9, and 10 are used to calculate the release. The corrected equations do not stay within the bounds imposed by Eq. 5 and 6 over the whole range. The only practical way of approximately applying corrected equations to such systems appears to be to plot both corrected curves and either use each curve over the range where it is most nearly accurate, i. e., small release for 9, and small retention for 10, or plot a curve by inspection between the two curves as has been done in Fig. 3.

Figure 4 illustrates the release of the ions from a mixed cation composition and shows that the shape of the corrected curve for any ion depends on the f values of the other ions present.
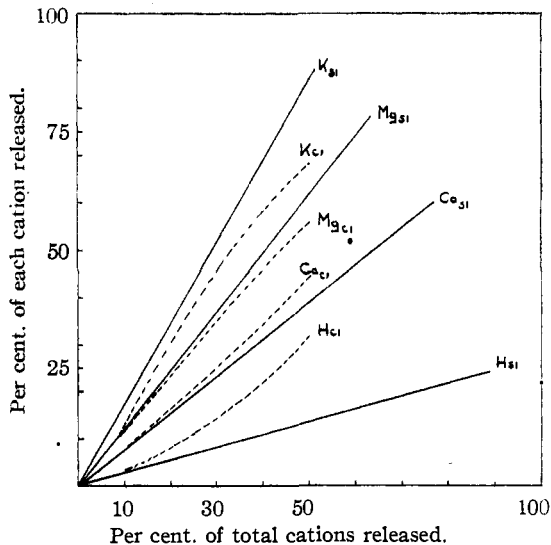
Fig. 4.—Exchange isotherms for a system containing a mixture of cations:

CLAY $\begin{array}{c} K = 1 \text{ m. e.} \\ Mg = 1 \text{ m. e.} \\ Ca = 1 \text{ m. e.} \\ H = 1 \text{ m. e.} \end{array}$ $+ X\text{m. e. RCl}$ $\begin{array}{c} f_K = 2.2 \\ f_{Mg} = 1.6 \\ f_{Ca} = 1.0 \\ f_H = .35 \end{array}$

Ionic Exchange-Competition

Under conditions where f values have been established for both the given cation-exchange material and the conditions of the experiment the equations can be used to evaluate the exchange-competition between the cations concerned. The evaluation of this exchange-competition in systems with mixed exchangeable cation compositions should help to predict the effect of an added electrolyte or electrolytes on the dispersion of clay

systems where a mixed exchangeable cation composition occurs.

The relative base composition of the intermicellar soil water, from which plant roots not directly in contact with soil colloids obtain mineral nutrients may be approximately calculated. The influence on the composition of the intermicellar water of both the amount of a given base present and the amounts of the other cations present is clearly brought out by the equations and should serve as an aid in furthering our knowledge of soil-plant relationships.

The equations permit the setting up of certain rules which will hold for the above conditions. These rules, which express the less obvious relationships in the equations governing exchange competition, may be stated as follows:

(1) Where a cation of a higher f value is replaced by one with a lower f value, the proportionate release of the other cations present on the colloid will be increased.

(2) Where a cation with a lower f value is replaced by one with a higher f value, the proportionate release of the other cations present on the colloid will be decreased.

(3) The higher the average f value for the colloid as a whole, the greater the buffering ability, i. e., the greater the adsorption of an added cation.

(4) Substituting a cation of a higher f value for one with a lower f value in the electrolyte increases the adsorption of the accompanying electrolyte cations.

(5) Substituting a cation of a lower f value for one with a higher f value in the electrolyte decreases the adsorption of the accompanying electrolyte cations.

(6) The higher the average f value for the electrolytes added, the less the replacing ability.

(7) The smaller the amount of electrolyte added, the greater the relative influence of the "ease of release" or f value on the amount of a given cation released.

According to rule 1, the substitution of calcium for hydrogen on a clay colloid, as is accomplished by liming, will decrease the relative release of the other ions and, theoretically, make them less available to plant roots, as far as the factors involved are concerned. Correspondingly, rule 2 predicts that the substitution of hydrogen for calcium on a clay colloid will increase the relative release of the other exchangeable cations as far as the factors involved are concerned.

Both of these predictions are directly opposite to the conclusions of Jenny and Ayers.[4] They found that the substitution of calcium for hydrogen increased the potassium release when carbon dioxide was bubbled through the suspension and concluded that liming made potassium more "available." This is contrary to the predictions made above and also to the predictions made by Jenny's equation. This does not point to any discrepancy in the equations. Rather it illustrates that the equations do not include the effects of secondary reactions which may reverse the expected trend. It is unsafe to predict what the final over-all effect will be under soil conditions where factors outside the ones included in the laboratory experiment are present.

Jenny and Ayers also place great stress on the degree of saturation, i. e., $K/C \times 100$ where $K =$ m. e. of potassium present and $C =$ m. e. cation exchange capacity, and consider that it will "assume a dominant role because it controls the exchangeability." This is not shown by the base-exchange equations given above which show "exchangeability" to be a function of many variables and that K and C can dominate only when they are the only variables. Table I shows that under most conditions the other variables have "controlled the exchangeability" in that more potassium is released from some soils containing less potassium and lower degrees of potassium-saturation than from others higher in potassium and with higher degrees of saturation with potassium.

Rule 6 applies especially to conditions where it is desired to remove a given exchangeable cation almost quantitatively with a single equilibrium extraction as is done in the rapid soil tests. The equations permit one to calculate the efficiencies of the acid or salt extracting solutions or their mixtures now being used or whose use is contemplated where the anions are the anions of a strong acid such as Cl or ClO$_4$. Theoretically, sodium acetate should be almost as efficient in replacing the exchangeable cations as sodium chloride or sodium perchlorate. This has not been found to be the case.[8] The relative efficiency of sodium acetate in replacement is much lower than can be attributed to the decreased activity of the sodium ion present as sodium acetate.

A reaction not accounted for in the equations is the effect of acid on the clay colloids. Acid

(8) R. H. Bray, Soil Sci. Soc. Proc., 1, 225–231 (1937).

conditions cause the release of a certain amount of aluminum from the silicate lattice which apparently stays on the exchange surface and is released through exchange reactions.[9] It is found in the filtrate of those soils which are acid enough to prevent its precipitation. In soil studies it is usually measured as part of the acidity of the solution where phenolphthalein is used as an indicator. Therefore, although the equations should permit one to calculate the pH or H-ion concentration of the supernatant solution in equilibrium studies, the pH will usually be found to be higher than calculated since part of the release calculated as hydrogen is present as aluminum.

It would be difficult to evaluate the probable use of the above equations in studies concerned with such problems as the investigation of exchange diffusion as postulated by Winters[10] or the special case of exchange diffusion called contact exchange by Jenny.[11] While it is theoretically possible to consider such a process as occurring in the absence of electrolytes, under soil conditions it becomes impossible to consider it separately from the processes involved in the reactions covered by the above equations because both exchangeable ions and electrolytes occur in the micellar water.

Either a direct exchange (contact exchange) or an indirect exchange (exchange through medium of an electrolyte) must be supported by a continuous renewal of the ions at the contacting

surfaces, a renewal which must come as a result of exchange diffusion or of diffusion as an electrolyte or, as is probable in the soil, of a combination of both processes. Without this renewal "contact exchange" could supply very few ions to the plant roots which contact only a very small part of the colloid surfaces in the soil.

Summary

The immediate equilibria between mixtures of exchangeable cations as they occur naturally in clays and small amounts of an added cation have been studied.

Cation-exchange equations have been developed from the data obtained which enable calculation of the release (or adsorption) of an individual cation in the presence of one or more complementary cations on the colloid when one or more cations are added as highly ionized electrolytes.

The relative "ease of release" for univalent and bivalent exchangeable cations is in the order Na > K > Mg > Ca > H as shown by their f values in the above-mentioned equations.

The exchangeable bases as usually determined by leaching with a neutral salt solution are shown to be those which are in equilibrium with added electrolytes after a short shaking period and are defined as readily exchangeable bases.

The secondary effect of the aluminum of the silicate lattice on the pH of the supernatant solution in acid clay studies is discussed in relation to the application of base-exchange equations.

(9) H. Paver and C. E. Marshall, *J. Soc. Chem. Ind.*, **53**, 750 (1934).
(10) Eric Winters, Doctor's Thesis, University of Illinois, 1938.
(11) H. Jenny and R. Overstreet, *Soil Sci.*, **47**, 257–272 (1938).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF POMONA COLLEGE]

The Configuration of Complex Kojates Formed with Some Transition Elements as Determined by Magnetic Susceptibility Measurements

BY JACK W. WILEY, GEORGE N. TYSON, JR., AND JACK S. STELLER

Organo-metallic compounds have been widely investigated in recent years.[1] In this work it has been found possible to synthesize complex kojates containing the divalent form of the transition elements manganese, iron, cobalt, nickel and copper, in the quadricovalent state, with kojic acid. The magnetic susceptibilities of these complexes have been measured and, on the basis of these results, the most probable configurations

have been assigned to the molecules. Kojic acid readily forms complexes with divalent ions other than those reported in this work, such as zinc and cadmium.

Experimental

Synthesis.—Sugar free kojic acid (2-hydroxymethyl-5-hydroxy-γ-pyrone) was neutralized with sodium hydroxide and adjusted to a pH of approximately 9. J. T. Baker and Co. C. P. metal acetate salts were used as the source of the metal ion, except the ferrous ion was obtained from

(1) Baudisch and Welo, *Chem. Rev.*, **15**, 1 (1934).