TABLE III

REFRACTIVE INDEX FOR THE TETRAHYDROFURAN–WATER SYSTEM

THF, wt. %	Temperature, °C. 20	25	30	35
0.00	1.3330	1.3324	1.3320	1.3314
10.00	1.3433	1.3427	1.3419	1.3412
20.00	1.3537	1.3527	1.3519	1.3510
30.00	1.3637	1.3622	1.3611	1.3600
40.00	1.3724	1.3711	1.3695	1.3683
50.00	1.3801	1.3788	1.3769	1.3753
60.00	1.3872	1.3854	1.3837	1.3819
70.00	1.3934	1.3915	1.3896	1.3878
80.00	1.3987	1.3967	1.3949	1.3938
90.00	1.4033	1.4011	1.3989	1.3967
95.00	1.4050	1.4028	1.4008	1.3986
100.00	1.4068	1.4045	1.4022	1.4000

where d is the density and P is the weight % of tetrahydrofuran. Densities calculated using this equation agree with the experimental values within 2 parts in 10,000.

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The Heats of Neutralization of Acid Clays and Cation-exchange Resins[1]

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A note of considerable interest to soil scientists and others concerned with the chemical reactions of clays and other ion-exchange materials was recently published.[2] The author reported the heats evolved when acid bentonites prepared by electrodialysis and by passage through a column of H-sulfonic acid exchange resin were neutralized with NaOH. Also presented were potentiometric titration curves of clays prepared by the two procedures. Up to about 80% base saturation the freshly-columned clay gave a titration curve of strong acid character, similar to that of H-sulfonic acid exchange resins. At this point a sharp inflection was followed by a short region of buffering in the *p*H range 6–7, and then a second inflection. The heat of neutralization in the first portion of the titration curve was about −13.5 kcal. per mole, again indicating strong acid character.

In the case of electrodialyzed clay the initial strong acid portion of the potentiometric titration curve extended to only about 30% base saturation, while the region of buffering between *p*H 6 and 7 was pronounced. The heat of neutralization in the strong-acid portion of the curve was again about −13.5 kcal. per mole. This fell to around −5 kcal. in the *p*H range 6–7. Slabaugh has explained the heats and the course of the titration curves on the basis that two H-ion energy levels exist.

The present authors have made similar observations on a variety of clay and exchange resin systems, and have come to somewhat different conclusions. Clays of the montmorillonite type, of which Slabaugh's Wyoming bentonite is typical, are alumino silicates. It is well established that in slightly acid media such clay minerals decompose with the liberation of ionic aluminum.[3] Such ionic aluminum appears to be strongly adsorbed by the clay, with the result that acid clays prepared by electrodialysis, by dilute acid leaching, or by natural depletion of such cations as Ca and Mg in nature, contain both H and Al as exchangeable cations with the latter usually predominating.[3–5]

It is possible, however, as Slabaugh[2] has pointed out, to prepare acid clays which differ greatly from those obtained by more conventional means. Columning with H-exchange resin is one method by which this may be done. Rapid leaching with 1 *N* HCl also results in a clay with the electrochemical and thermochemical properties of columned clay. For the reasons outlined below, the present authors believe columned clay and 1 *N* HCl-leached clay to be H-clays, while electrodialyzed and dilute acid leached clays are H-Al-clays.

Figure 1 shows potentiometric titration curves of H- and Al-Amberlite IR-120, acid bentonite prepared by leaching with 0.1 *N* HCl, and acid bentonite prepared by leaching with 1 *N* HCl. Figure 2 compares the curve for acid bentonite prepared by leaching with 1 *N* HCl with those for bentonite leached first with 1 *N* HCl and then with $AlCl_3$, and bentonite leached with 1 *N* HCl and treated with an amount of $AlCl_3$ equivalent to one-half the exchange capacity. In all cases free electrolyte was removed by washing with water before the titrations were performed. The similarity between the curves for Al-resin, dilute acid-leached clay, and $AlCl_3$-leached clay is striking. Also very similar are the curves for H-resin and 1 *N* HCl-leached clay. The 1 *N* HCl-leached clay treated with $^1/_2$ symmetry concentration of $AlCl_3$ shows the features of both H- and Al-exchangers, with the H being neutralized first.

Heats of neutralization of several clay and exchange resin systems are presented in Table I. They were measured with an apparatus which has been described previously.[6] The heats reported in Table I are integral rather than the summation of differential heats as measured by Slabaugh,[2] and refer in all cases to the amount of NaOH consumed in the reaction. Heats of neutralization of H-exchange resins and of columned or 1 *N* HCl-leached bentonite were about −13.5 kcal., which is close to the heat of formation of water from the ions. Heats of neutralization of the Al-resin and

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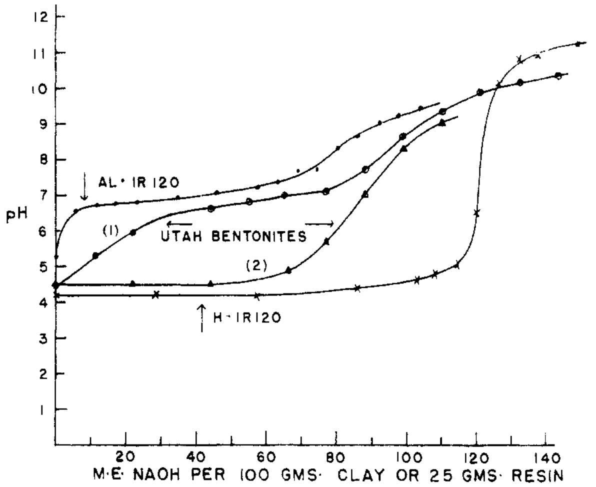

Fig. 1.—Potentiometric titration curves of H- and Al-Amberlite IR-120 and of acid Utah bentonites prepared by (1) leaching with 0.1 N HCl and (2) leaching with 1 *N* HCl.

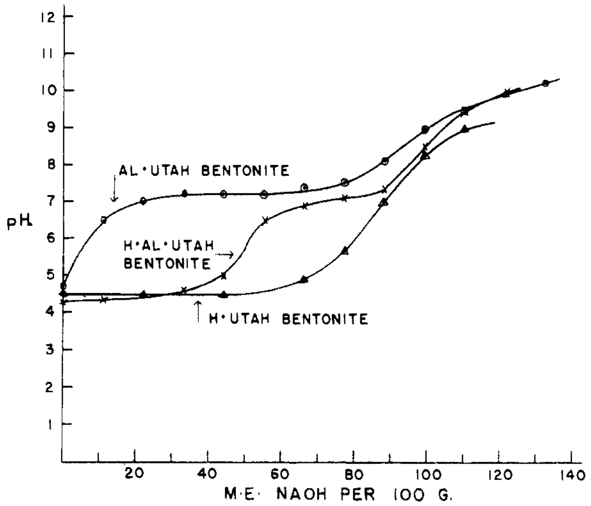

Fig. 2.—Potentiometric titration curves of H-Utah bentonite prepared by leaching with 1 *N* HCl, Al-Utah bentonite prepared by leaching first with 1 *N* HCl and then with $AlCl_3$, and of H-Al-Utah bentonite prepared by leaching with 1 *N* HCl and then treating with an amount of $AlCl_3$ equivalent to one-half the exchange capacity.

the $AlCl_3$-leached clay, as well as of the 0.05 *N* HCl-leached and of electrodialyzed clay, varied between −5.4 and −6.4 kcal. per mole of NaOH consumed.

TABLE I

HEATS OF NEUTRALIZATION (KCAL. PER EQUIVALENT) OF ACID CLAYS AND EXCHANGE RESINS

	Method of preparation				
Material	Electro-dialyzed	Leached with 0.05 *N* HCl	Leached with 1 *N* HCl	Col-umned	Leached with $AlCl_3$
Wyoming bentonite	−5.8	...	....	−13.4	
Utah bentonite	−6.4	−6.2	−13.5	−13.5	−5.4
IR-120	...	...	−13.6	....	−5.7

Exchangeable Al and exchangeable H can be replaced from clays and other cation exchangers by exhaustive leaching with neutral salt solutions.[3,4] The clays studied here were leached with *N* KCl and H and Al were determined in the leachate. For electrodialyzed bentonite, 0.05 or 0.1 *N* HCl-leached bentonite, and $AlCl_3$-leached bentonite, 95–100% of the titratable acidity in the KCl leachate was Al. For *N* HCl-leached bentonite and for columned bentonite, 90–100% of the titratable acidity was H. On storage of the latter two clays, a gradual increase in exchangeable Al and decrease in exchangeable H was observed.

The authors conclude from this that Slabaugh worked with H-Al clays, rather than with clays containing exchangeable H in different energy states.

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The Reactivity of Primary Alkyl Halides with Sodium Thiocyanate

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Many examples of the reactivity of the straight-chain alkyl halides in displacement reactions indicate a minimum in rate for the *n*-butyl derivative; further lengthening of the molecule increases the reaction rate.[1] Although the equilibrium counterpart of this interesting kinetic phenomenon has been investigated by Brown, Taylor and Sujishi,[2] no series of rate constants sufficiently accurate to establish its existence or magnitude can be found.

A convenient reagent for such a comparison is the nucleophilic thiocyanate ion.[3] The reaction of sodium thiocyanate with alkyl bromides, described in this paper, is easily followed at constant ionic strength and is homogeneous in alcoholic solution owing to the moderate solubility of sodium bromide.

$$RBr + NaSCN \longrightarrow RSCN + NaBr$$

Table I shows one of the runs made with *n*-hexyl bromide. All the results are summarized in Table

TABLE I

SAMPLE DATA FOR *n*-HEXYL BROMIDE[a]

t, min.	KIO_3, ml.	10^5 *k*, l./mole-sec.
0	20.89[b]	..
1355	19.20	1.18
3057	17.49	1.24
4317	16.60	1.22
5688	15.78	1.22
8826	14.39	1.22
11500	13.60	1.21
14184	13.09	1.17

[a] Initially 0.0960 *M*. [b] Corresponds to 0.2002 *M* NaSCN in sample.

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