TABLE I

EMPIRICAL CONSTANTS, MOLAR POLARIZATIONS, MOLAR REFRACTIONS AND ELECTRIC MOMENTS OF SOME HETEROCYCLIC COMPOUNDS IN BENZENE SOLUTION

Compd.	ϵ_1	a	v_1	b	P_2	MR_D	μ Obsd.	μ Calcd.[a]
2-*t*-Butylthiophene	2.2716	1.093	1.14270	−0.147	60.32	42.96	0.93	0.60
2,5-Di-*t*-butylthiophene	2.2732	0.245	1.14484	−0.098	68.30	62.21	0.55	0.35
2-Iodothiophene	2.2710	2.080	1.14400	−1.585	61.15	35.02	1.13	1.48
2-Bromothiophene	2.2720	2.967	1.14500	−1.193	71.46	32.04	1.39	1.67
3-Mercaptothiophene	2.2721	1.916	1.14472	−0.502	56.09	32.58	1.07	1.08
2-Methylfuran	2.2717	0.418	1.14467	−0.039	33.21	23.33	0.70	0.71
2-Furoamide (dioxane)	2.2100	18.88	0.97284	−0.274	298.0	27.02	3.64	3.55
2-Furoic acid (dioxane)	2.2085	7.220	0.97286	−0.280	131.9	24.81	2.29	1.96

[a] Calculated by use of group moments and angles for benzene derivatives.

3-Mercaptothiophene.—A sample of 3-mercaptothiophene was the gift of Prof. R. D. Schuetz. The material was fractionated just before use, b.p. 70° (21 mm.), n^{25}_{D} 1.6188, d^{25}_{4} 1.2510.

2-*t*-Butylthiophene and 2,5-Di-*t*-butylthiophene.—Samples of these compounds were provided by the Socony-Vacuum Oil Co., Paulsboro, N.J. and were used after two fractionations; 2-*t*-butylthiophene, b.p. 163° (751 mm.), n^{25}_{D} 1.4932, d^{25}_{4} 0.9491; 2,5-di-*t*-butylthiophene, b.p. 212° (745 mm.), n^{25}_{D} 1.4908, d^{25}_{4} 0.9137.

2-Furoic Acid and 2-Furoamide.—Eastman Kodak Co. materials were recrystallized several times before use; m.p. 134° (2-furoic acid) and 142° (2-furoamide).

Apparatus and Technique.—Dielectric constants of six solutions, ranging in mole fraction solute from 0.001 to 0.02, were measured at 25° by the heterodyne-beat method. The apparatus and technique have been described.[6] Dipole moments were computed from the molar polarizations P_2 of the solutes (at infinite dilution) obtained by the method of Halverstadt and Kumler.[7] The slopes a and b, and intercepts ϵ_1 and v_1, obtained from plots of the observed dielectric constants and molar volumes *versus* mole fraction solute, are shown in Table I along with the molar polarizations of solute P_2, the observed molar refractions MR_D (calculated values are shown for furoic acid and furoamide), and the dipole moments μ. The probable error in the electric moment values is about ±0.1 *D* for all compounds except 2,5-di-*t*-butylthiophene to which a probable error of ±0.2 is assigned.

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(7) I. F. Halverstadt and W. D. Kumler, THIS JOURNAL, **64**, 2988 (1942).

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Studies in Low Concentration Chemistry. XI. The Adsorption of Sulfate and Scandium Ions

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Theories of the adsorption of trace-concentration ions from aqueous solution onto polar and non-polar materials are of considerable variety and in a few cases somewhat contradictory.[1,2] In the case of ion adsorption by a polar substance, there are numerous indications that the forces of attraction are electrostatic. The degree of adsorption may be influenced by solubility relationships, lattice structure relationships, size, polarizability and the valence of the adsorbate ion as well as the degree of crystalline perfection of the adsorbent and the charge upon it.[1–8] Although less work has been done on the adsorption of ions onto non-polar materials, some theories have been advanced. The mechanism of adsorption of acids onto charcoal is considered by Kolthoff[9] to be a capillary effect caused by a reduction of interfacial tension; other investigators[10] postulate a reaction with basic oxides; still others[11] consider it to be some sort of attractive force common to all acids.

In this investigation, radiotracer studies were made of the adsorption of sulfate and scandium ions from low concentration solutions onto charcoal and various insoluble compounds. These studies included: (a) qualitative investigations on the adsorbent characteristics of numerous insoluble substances, (b) investigations of adsorption rates, (c) investigations of the effects of *p*H and acid used to adjust the *p*H upon adsorption onto charcoal, and (d) investigations of adsorption-concentration relationships.

Experimental

Materials.—Sulfur-35 as carrier-free sulfate in dilute hydrochloric acid was obtained from Oak Ridge National Laboratory. Isotopic dilutions were made with reagent grade sodium sulfate to prepare solutions of known concentrations. High specific activity scandium-46 with a known quantity of inactive scandium in dilute hydrochloric acid was obtained from the same source. Isotopic dilutions were made with scandium perchlorate which had been prepared from 99.8% scandium oxide as obtained from Research Chemicals, Inc., Burbank, California.

Neutral Norit-A Decolorizing Carbon and a number of reagent grade insoluble salts were employed as adsorbents. The chromates, sulfides, oxalates, halides were prepared by precipitation, filtration and aging for at least a day. Standard solutions were prepared from reagent grade chemicals.

Apparatus.—All sulfate adsorption experiments were carried out in 15-ml. weighing bottles stoppered with ground glass caps. Agitation of samples was effected by placing the weighing bottles on a mechanical shaker. Scandium adsorption determinations were performed in a similar manner except that 25-ml. polyethylene bottles were used for containers to avoid adsorption of the scandium by the glassware. All *p*H measurements were made with a Beckman model H-2 *p*H meter equipped with micro electrodes.

Samples for the determination of radioactivity were

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(1) A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 124–135.

(2) E. Broda, "Advances in Radiochemistry," Cambridge University Press, New York, N. Y., 1950, pp. 9–14.

(3) I. M. Kolthoff, *Analyst*, **77**, 1000 (1952).

(4) L. Imre, *Z. angew. Chem.*, **43**, 857 (1930).

(5) J. F. King and P. R. Pine, *J. Phys. Chem.*, **37**, 851 (1933).

(6) J. F. King and U. T. Greene, *ibid.*, **37**, 1047 (1933).

(7) K. Fajans and T. Erdey-Gruiz, *Z. physik. Chem.*, **A158**, 97 (1931).

(8) H. Horowitz and F. Paneth, *ibid.*, **89**, 513 (1915).

(9) I. M. Kolthoff, *Rec. trav. chim.*, **46**, 549 (1927).

(10) A. King, *J. Chem. Soc.*, 889 (1935).

(11) K. D. Jain and J. B. Jha, *J. Indian Chem. Soc.*, **18**, 321 (1941).

taken with a Misco 0.1-ml. micropipet and a Misco pipet filler. The liquid was deposited and dried on a copper planchet. All samples were counted with a Tracerlab Model SC-33 1000 Scaler attached to a Nuclear Model D-34 G-M Tube shielded by a Tracerlab Model SC-9 Sample Changer.

Results

Preliminary Experiments on Sulfate Ion.—A number of insoluble salts were tested qualitatively to ascertain if they would adsorb appreciable amounts of sulfate ion from solutions 10^{-7} *M*. In each case 1 g. of adsorbent was equilibrated with 5 ml. of sulfate solution and allowed to stand for 2 hr. Adsorbents taking up greater than 90% of the sulfate were barium chromate, lead(II) chromate, lead(II) oxide, lead(II) sulfide, silver sulfide, mercury(II) sulfide, zinc sulfide and mercury(II) oxalate. Adsorbents taking up between 10 and 90% of the sulfate were tin(IV) chromate, barium oxalate, tin(IV) sulfide, copper(II) sulfide, zinc oxide, copper(II) chromate and titanium dioxide. Adsorbents showing essentially no adsorption were silver chloride, silver bromide, silver iodide, silver chromate, silver oxide, silver oxalate, lead(II) bromide, lead(II) iodide, lead oxalate, mercury(II) bromide, mercury(II) iodide, mercury(II) oxide, mercury(II) chromate, zinc chromate, copper(II) oxalate, copper(II) oxide, silicon dioxide and tin(IV) oxide.

Studies of the rate at which 10^{-7} *M* sulfate is adsorbed by various insoluble salts showed that in most cases equilibrium is established in less than 15 min. Two adsorbents, barium chromate and zinc sulfide, showed a continued increase in adsorption for times up to 300 min. One adsorbent, silver sulfide, showed a decrease in the initial adsorption upon longer periods of agitation. Most adsorbents show a decrease in adsorption of 10^{-7} *M* sulfate as the *p*H value increases. Adsorption could not be induced on a poor adsorbent, silver chloride, by varying the *p*H value of the solution. It was possible to induce adsorption of 10^{-8} *M* sulfate onto silver chloride by addition of silver nitrate to the solution, but such experiments were unsuccessful with higher concentrations of sulfate.

Investigations of adsorption–concentration relationships for sulfate adsorption on numerous insoluble substances which reach equilibrium rapidly indicated a simple Henry's law relationship for sulfate solutions of concentrations 10^{-6}, 10^{-7} and 10^{-8} *M*. This means that in this concentration region the number of sulfate ions adsorbed per mg. of adsorbent is proportional to the concentration. At and above 10^{-5} *M* sulfate, this law was not adhered to, but a modified form of it could be used, namely, the Freundlich equation.

Sulfate Adsorption onto Charcoal.—Figure 1 shows the adsorption of sulfate ions onto charcoal as a function of *p*H using different acids for adjustment of the *p*H value. Each experiment in these determinations was performed by the addition of 400 mg. of charcoal to a 5-ml. portion of 10^{-7} *M* sulfate solution. Each solution was adjusted to the desired *p*H value by the addition of the designated acid and the corresponding loss of sulfate ions was determined at equilibrium. In all cases, the total anion concentration was 0.01 *M*. In more detailed investigations, the adsorption of sulfate ions in the presence of hydrochloric acid was found to obey Henry's law for all sulfate concentrations from 10^{-3} down to 10^{-8} *M*.

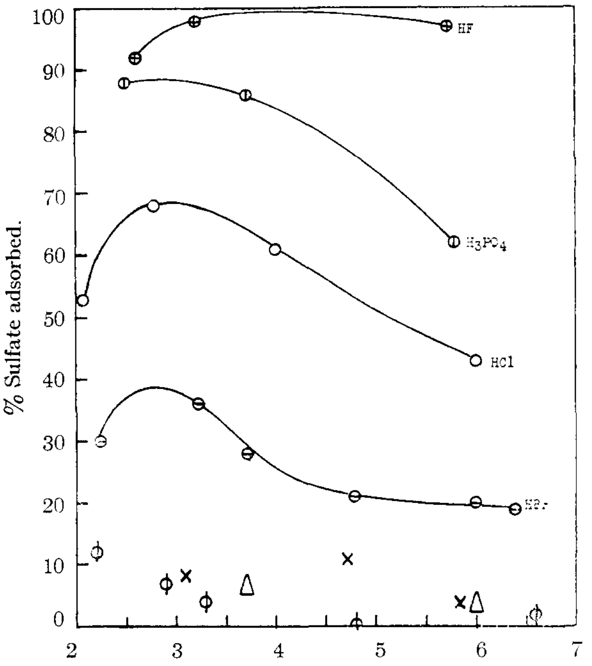

Fig. 1.—The adsorption of sulfate ions on charcoal in the presence of various acids: Δ = $HClO_4$; X = HI; ϕ = CCl_3CO_2H; other acids as labeled above.

Scandium Adsorption onto Charcoal.—Figure 2 shows the adsorption of scandium from a 10^{-6} *M* solution onto charcoal in the presence of hydrochloric and perchloric acids. It can be seen that the relationship of scandium absorption to acid concentration is log–log in character.

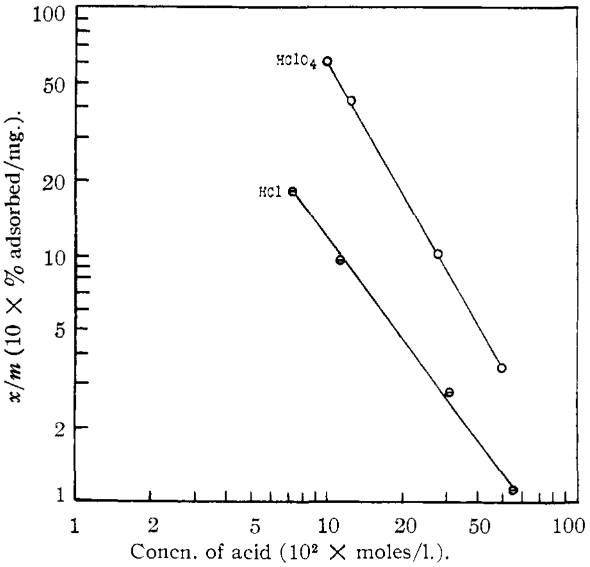

Fig. 2.—The adsorption of scandium ions on charcoal as a function of acid concentration.

The adsorption of scandium from solutions of various concentrations onto charcoal in the presence of 0.1 *M* perchloric acid was studied and found to show a deviation from Henry's law at concentrations of 10^{-4}, 10^{-5}, 10^{-6} and below. The procedure followed in these determinations was to place weighed amounts of charcoal into 10-ml. aliquots of radioactively labeled scandium solution of a known concentration in 0.1 *M* perchloric acid. After equilibrium had been established, the aliquots were sampled, and the percentage loss of solution activity per mg. of charcoal was plotted against the percentage of activity remaining in solution. The results are illustrated in Fig. 3. Unlike the case with sulfate ions, the curves for different concentrations of scandium are not identical, allowing a determination of the concentration of an unknown labeled scandium solution to be made by absorption methods. Several unknowns were made up by other persons and excellent results were obtained in determining their concentrations.

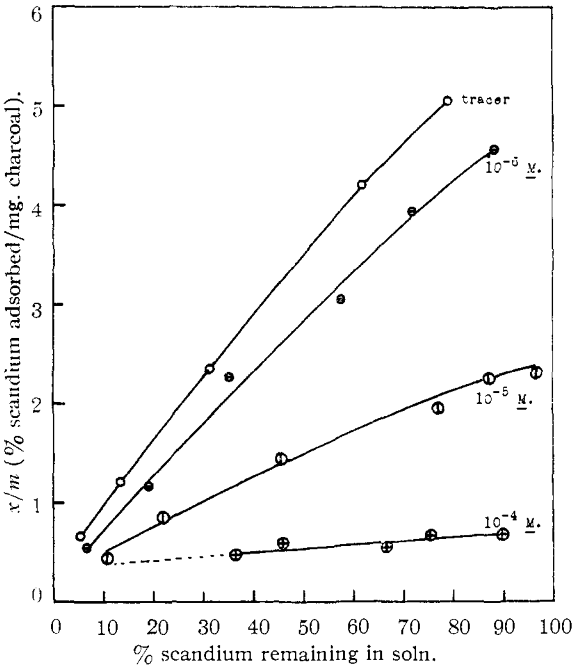

Fig. 3.—The adsorption of various concentrations of scandium ions on charcoal in the presence of 0.1000 *N* perchloric acid.

Discussion

The adsorbent properties of the various insoluble compounds with respect to tracer quantities of sulfate ion appear to be dependent upon conditions similar to those which influence the adsorption of tracer cations.[1-8,12] Considerations much like those discussed by Hahn allow some systematics to be introduced into the behavior of the insoluble compounds employed as adsorbents. In most cases, the sulfate ions attained adsorption equilibrium quite rapidly, giving curves similar to those shown by Hahn[13] and Kolthoff.[14] Cases in which there is a continuous increase in the adsorption of sulfate ions with long periods of equilibration probably indicate that the sulfate ions are isomorphously replacing the adsorbent anions. This process is described by Kolthoff,[15] who predicted the observed behavior for the adsorption of ions onto barium sulfate.

The rapid rise in adsorption followed by a slow decrease with time as seen in the case of silver sulfide is probably due to aging and a consequent reduction of available surface area.

The decrease in adsorption of sulfate ions as the *p*H of the solution is increased could indirectly indicate that hydrogen ions are adsorbing on the surface of the adsorbent and then that the sulfates are held in a second layer. Analogous behavior has been reported for cases of tracer cation adsorption.[12]

The observed adsorption–concentration relationship (Henry's law) for adsorption of low concentration sulfate ions onto charcoal and numerous insoluble compounds is similar to the adsorption of gases at low pressures.[16] Behavior resembling this has been observed in several previous instances involving the adsorption of cations on crystalline materials.[17] Ostwald[18] and Broece[19] have shown a similar relationship for the adsorption of certain acids in moderate concentrations onto both charcoal and crystalline materials.

The data of Fig. 1 are extremely interesting and may be interpreted consistently if the assumption is made that the sulfate ions are attaching to hydrogen ions which form the primary layer on the surface of the adsorbent. The order in which the acids inhibit the adsorption of sulfate ions is the same as the order of the heats of hydration or of the entropies of solution of the acid anions.[20] The order of inhibition of adsorption of the low concentration sulfate ion also seems to follow the order of adsorbability of the various acids.[9] Thus it appears that competitive adsorption may be invoked as an explanation for the behavior of the sulfate. In the case of an acid like HF, since the anion hydration energy is quite high, the fluoride ion remains in solution rather than adsorbing out on the charcoal. This allows the sulfate ions to adsorb. However, in the case of acids like HI, the energy of hydration of the anion is small and the energy release realized on adsorption can compete successfully. Thus the surface of the adsorbent is covered with iodide ions which prevent the adsorption of sulfate ions. The maximum in some of the curves may be related to the sulfate–bisulfate equilibrium.

The variation in adsorption of tracer scandium ions as the acid concentration is altered, as illustrated in Fig. 2, could be assigned to the adsorption of a hydroxy form of scandium. This belief is

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(12) O. Hahn, "Applied Radiochemistry," Cornell University Press, Ithaca, N. Y., 1936, pp. 138–164.

(13) O. Hahn, ref. 12, p. 158, Fig. 40a.

(14) I. M. Kolthoff, *Analyst*, **77**, 1003 (1952), Fig. 2A and 2B.

(15) I. M. Kolthoff, *ibid.*, **77**, 1006 (1952), Fig. 5C and 5D.

(16) W. K. Lewis, L. Squires and G. Broughton, "Colloidal and Amorphous Materials," The Macmillan Co., New York, N. Y., 1943, pp. 69–95.

(17) J. Kurbatov, J. Kulp and E. Mack, THIS JOURNAL, **67**, 1923 (1945); V. Khlopin and V. Kuxnetsova, *Acta Physicochem. U.R.S.S.*, **11**, 661 (1939).

(18) W. Ostwald, *Kolloid-Z.*, **88**, 144 (1939).

(19) S. Broece, *ibid.*, **91**, 20 (1940).

(20) For values see J. A. A. Ketelaar, "Chemical Constitution," Elsevier Publishing Co., New York, N. Y., 1953, p. 102; O. K. Rice "Electronic Structure and Chemical Binding," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 402–408.

suggested on the basis that it is compatible with ideas on the radiocolloidal properties of scandium in low concentrations[21] and that the observed log-log relationship can be arrived at by a theoretical treatment of a reaction of the type

$$Sc^{+3} + nH_2O \rightleftarrows Sc(OH)_n^{3-n} + nH^+$$

and the assumption of the adsorption of the hydroxy form of the scandium. An alternate explanation is competition between scandium(III) ions and the hydrogen ion for sites on the adsorbent.

Figure 3 shows adsorption–concentration relationships for scandium on charcoal in the presence of 0.1 *N* perchloric acid. The value of these observations is that they indicate a useful approach for obtaining the concentrations of unknown solutions of tracer scandium. The deviations from Henry's law in this case might be assigned to the adsorption of hydroxy forms of scandium, or since the acid anion affects adsorption, it might be referred to competitive complex formation.

Acknowledgment.—The authors wish to express their appreciation to the U. S. Atomic Energy Commission for the grant of funds which made this work possible.

[21] G. K. Schweitzer and W. M. Jackson, *J. Chem. Educ.*, **29**, 513 (1952).

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A Comparative Study of Methyl Compounds of the Elements

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Thirty-four elements, representing all the active major groups of the periodic table, are known to form methyl compounds of the type, $E(CH_3)_n$.[1] Most of these have covalently bound methyl groups in which there are no unshared electrons or unoccupied low energy orbitals. The methyl compounds as a group thus present a unique opportunity for observing, with a minimum of ambiguity, the relationships among physical and chemical properties and atomic charges associated with bond polarities.

Partial charges on the atoms of all known (and a few other) methyl element compounds have been estimated by methods recently described.[2] The net charges on methyl (the sum of charges on carbon and hydrogen), together with an outline of some properties of the methyl compounds, are presented in Table I. The order is of decreasing negative and increasing positive net charge on methyl. This is equivalent to the order of progressive change in polarity of the C–E bonds.

TABLE I

POLARITY AND PROPERTIES OF METHYL COMPOUNDS

Element	Net charge on CH_3	Physical state[a]	Spontaneous reactivity[b] with O_2	CO_2	H_2O
Cs	−1.000	S, NV	r	r	r
Rb	−1.000	S, NV	r	r	r
K	−1.000	S, NV	r	r	r
Na	−1.000	S, NV	r	r	r
Li	−1.000	S, NV	r	r	r
Ba	−0.479				
Sr	− .452	(known only in complex soln.)			
Ca	− .416				
Mg	− .325	S, V	r	r	r
Be	− .250	S, V	r	r	r
Al	− .170	L	r	r	r
Cd	− .131	L	r	n	s
Zn	− .095	L	r	n	s
B	− .067	G	r	n	n
Si	− .067	L	n	n	n
In	− .065	S, V	s	n	s
Sn	− .032	L	n	n	n
Ga	− .031	L	r	n	s
P	− .023	L	r	n	n
Sb	− .019	L	r	n	n
Hg	− .016	L	n	n	n
H	− .012	G	n	n	n
Tl	− .002	S, V	r	n	s
Ge	− .001	L	n	n	n
Te	.002	L	s	n	n
Pb	.004	L	n	n	n
C	.010	G	n	n	n
Bi	.013	L	s	n	s
As	.023	L	s	n	n
I	.046	L	n	n	n
S	.053	L	n	n	n
N	.062	G	n	n	n
Se	.067	L	n	n	n
O	.151	G	n	n	n
Br	.170	G	n	n	n
Cl	.235	G	n	n	n
F	.357	G	n	n	n

[a] S = solid, L = liquid, G = gas, V = volatile, NV = non-volatile. [b] r = rapid, s = slow, n = very slow or none.

Physical State.—All methyl compounds of the elements in which the net negative charge on methyl exceeds −0.25 are solids. Where the change is −1.00, and possibly even where it would exceed −0.40, the solids are non-volatile, nonfusible and generally insoluble, appearing to be polymeric. Evidence of association diminishes with decreasing negative charge on methyl. All the rest are volatile and most beyond Mg and Be are liquids or gases. In no compound with charge on methyl less than −0.17 is there evidence of vapor phase association.

Oxidation.—Oxidation by oxygen appears to be related to atomic charges and also to availability of low energy orbitals. All methyl compounds having net negative charges on methyl greater than about −0.07, and also, presumably, an unoccupied low energy orbital, are spontaneously inflammable in air. When the orbital is available (as in B, Al, Ga, In, Tl, P, As, Sb, Bi), apparently whether or not it contains electrons, even smaller net negative charges on methyl appear sufficient for easy oxidation, although not always spontaneous inflammation. When the orbital is not available (as in Si, Ge, Sn, Pb), the compound appears relatively stable toward oxidation. Incidentally, the Group V alternations previously explained[3] are to be

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[1] See N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, New York, N. Y., 1950, for references to the original literature.

[2] R. T. Sanderson, *J. Chem. Educ.*, **32**, 140 (1955).

[3] R. T. Sanderson, THIS JOURNAL, **74**, 4792 (1952).