portant, however, since ammonium is readily removed and rubidium and cesium are so rarely met with in weighable quantities.   The interference from sodium is more serious and restricts the method to the examination of samples or residues weighing not more than twenty milligrams in cases where the sodium content is entirely unknown.   Where the sodium content is approximately known, larger samples may, in many cases, be used.   The other common metals usually associated with potassium apparently do not interfere even when present in larger amounts than shown in the typical experiments recorded in the table.   This method is more particularly suitable for the rapid estimation of potassium in small residues of alkali and alkaline earth salts and is convenient where a series of determinations is to be made.

Summary

There has been described a rapid method for the colorimetric estimation of potassium depending upon its precipitation as potassium picrate by an alcoholic solution of picric acid with the subsequent solution of the separated precipitate in water, yielding a highly-colored solution suitable for colorimetric comparison with standard solutions prepared in a like manner from known amounts of potassium.

PRINCETON, NEW JERSEY

ELECTRIC MOMENT AND MOLECULAR STRUCTURE.
II.   TERTIARY BUTYL AND TRIPHENYLMETHYL CHLORIDES AND ALCOHOLS

BY C. P. SMYTH AND R. W. DORNTE

In an earlier paper[1] it has been shown that the relation between electric moment and chemical behavior is usually slight, but it has seemed desirable to pursue the investigation further for the case of a few closely related groups of markedly different chemical behavior.   For this purpose, the n-butyl, $tert.$-butyl, and triphenylmethyl groups seemed particularly suitable. The n-butyl alcohol[2] and chloride[3] having already been investigated, the corresponding $tert.$-butyl and triphenylmethyl compounds were measured. While the determinations were being made, Parts[4] published values for the moments of the primary, secondary and tertiary butyl halides, which will be used in the subsequent discussion.   It was hoped that the polariza-

[1] Smyth, THIS JOURNAL, 51, 2380 (1929).

[2] Miles, Phys. Rev., 34, 964 (1929); Smyth and Stoops, THIS JOURNAL, 51, 3312 (1929).

[3] Smyth and Rogers, ibid., 52, 2227 (1930).

[4] Parts, Z. physik. Chem., [B] 7, 327 (1930).

tion–concentration curves obtained in the measurements would give qualitative information concerning the effects of the shapes of the groups upon the action of the molecular fields of force.

Preparation of Materials

Heptane and benzene were obtained as in previous work.[3]

Tert.-butyl Chloride.—The material was prepared by Mr. George Rigby working with Professor James F. Norris at the Massachusetts Institute of Technology. It was made from a good grade of *tert.*-butyl alcohol by the action of concentrated hydrochloric acid, washed with a dilute solution of sodium bicarbonate and then with water, distilled and fractionated twice. The part boiling at 50.7° was shaken with anhydrous potassium carbonate for six hours and fractionated twice. After standing for twelve hours with phosphorus pentoxide, it was distilled, treated again with phosphorus pentoxide and redistilled; b. p. 50.7° with a maximum range of 0.05°; n_D^{20} 1.38528.

Tert.-butyl Alcohol.—Material given us by Dr. H. B. Glass of Johns Hopkins University was redistilled, as it had stood for some time; b. p. 82.6–82.8°; n_D^{20} 1.38777.

Triphenylchloromethane.—Material obtained from the Eastman Kodak Company was twice recrystallized from carefully dried benzene and washed thoroughly with ether; m. p. 111°.

Triphenylcarbinol.—Material prepared by Dr. R. H. Smith working with Professor Donald H. Andrews of Johns Hopkins University was loaned to us; m. p. 162°.

Method of Determination

The dielectric constants, ϵ, and densities, d, were measured with the apparatus used in previous work,[5] the former being determined at a wave length of 600 meters. The determinations were made at fixed temperatures with 10° intervals in the case of the *tert.*-butyl chloride and 20° intervals for the other substances. The polarizations, P_2, of the polar components of the solutions were calculated by means of the equations

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \frac{c_1 M_1 + c_2 M_2}{d} \text{ and } P_2 = \frac{P_{12} - P_1}{c_2} + P_1$$

in which P_{12} is the polarization of the mixture, and c_1 and c_2, M_1 and M_2 and P_1 and P_2 are, respectively, the mole fractions, molecular weights and polarizations of the individual components. The values of P_2 have been plotted against those of c_2 (see Fig. 1 and Fig. 2) and extrapolated to $c_2 = 0$ to obtain the values of P designated as P_∞. The values of P_∞ when plotted against $1/T$ should give a straight line, as required by the Debye equation, $P = a + b/T$, in which $a = P_E + P_A$, the sum of the electronic polarization, P_E, and the atomic, P_A, and $b = 4\pi N\mu^2/9k$, N being the Avogadro number, 6.061×10^{23}, μ, the electric moment, and k, the molecular gas constant, 1.372×10^{-16}. In the case of *tert.*-butyl chloride, the intercept and slope of this straight line give values of a and b, from which the moment is calculated. However, the solutions of *tert.*-butyl alcohol in heptane, like those of the normal alcohol previously investigated,[2] are so strongly affected by association that the values obtained for P_∞ are not those for

[5] Smyth, Morgan and Boyce, This Journal, **50**, 1536 (1928); Smyth and Morgan, *ibid.*, **50**, 1547 (1928); Dornte and Smyth, *ibid.*, **52**, 3546 (1930).

molecules oriented at random and actually increase sharply with rising temperature instead of decreasing.   As these values could not be used to determine the moment, the alcohol was also run in benzene solution, in which the effect of association was reduced.   Because of their low solubility in heptane, the triphenylmethyl compounds also were measured in benzene solution.   Unfortunately, the shorter temperature range within which benzene is liquid renders the location of the $P_\infty - 1/T$ curves inaccurate for these solutions.   It has seemed best, therefore, to disregard P_A
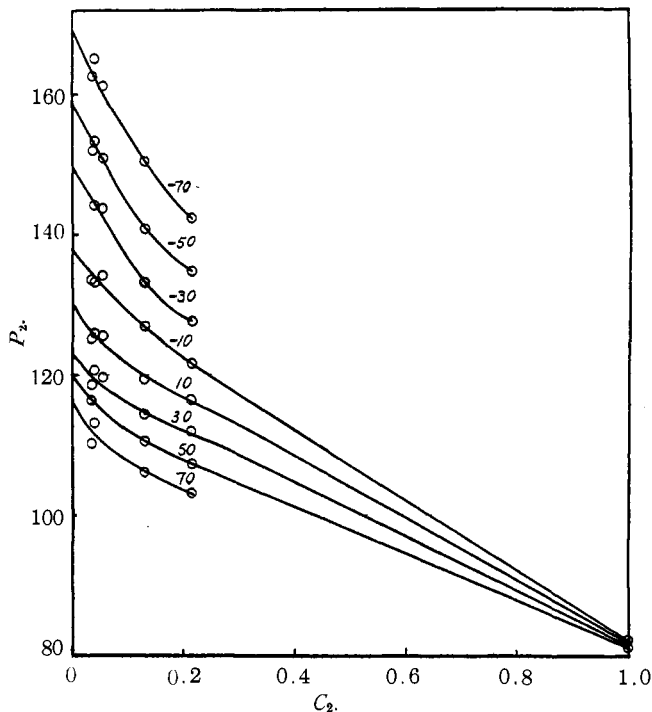

Fig. 1.—Polarizations (P_2) of *tert.*-butyl chloride in solution in heptane.

for these substances and use for P_E the molar refraction for the sodium D line, MR_D, which is slightly higher than P_E, a fact which partially compensates for the neglect of P_A.   In the alcohol values, at any rate, the error caused by the effect of molecular association is greater than the small error due to neglect of P_A.   Instead of using the constant $(P_\infty - a)T = b$ for the calculation of the moment as in the case of *tert.*-butyl chloride, we obtain an approximately constant value for the quantity $(P_\infty - MR_D)T$, calculate the moment from the value at each temperature by means of the relation $\mu = 0.0127 \times 10^{-18} \sqrt{(P_\infty - MR_D)T}$, which follows from the preceding equation, and take the mean of the values obtained.

The experimental results and the values calculated from them are shown in Tables I and II. For the sake of brevity, half of the values obtained for *tert.*-butyl chloride are omitted, the data being given at 20° intervals only.
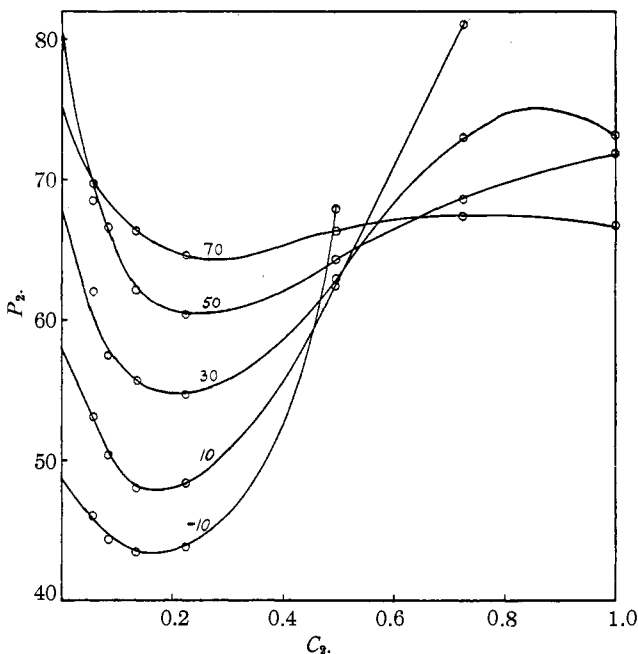

Fig. 2.—Polarizations (P_2) of *tert.*-butyl alcohol in solution in heptane.

Table III gives what appear to be the best values of the moments. The values for MR_D given in Table II are calculated from our measurements of the refractive indices of the pure liquids or of the substances in solution. The value of P_E for *tert.*-butyl chloride was obtained by extrapolation to infinite wave length.

TABLE I

DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS AND POLARIZATIONS OF POLAR COMPONENTS

Heptane–*Tert.*-butyl Chloride

Mole fr. of (CH₃)₃CCl = t, °C.	0	0.0389	0.0543	0.1309	0.2156	1.000
−70	2.048	2.289	2.381	2.892	3.559	
−50	2.020	2.231	2.314	2.754	3.335	
−30	1.992	2.179	2.258	2.641	3.141	
−10	1.966	2.129	2.199	2.5′	2.981	11.72
10	1.939	2.084	2.144	2.447	2.849	10.34
30	1.910	2.042	2.095	2.366	2.720	9.23
50	1.879	2.000	2.053	2.292	2.598	
70	1.848	1.960	2.007	2.219	2.487	

TABLE I   (*Continued*)

Mole fr. of (CH₃)₃CCl = t, °C.	0	0.0389	0.0543	0.1309	0.2156	1.000
−70	0.7585	0.7632	0.7652	0.7759	0.7886	
−50	.7421	.7470	.7485	.7592	.7713	
−30	.7259	.7305	.7322	.7423	.7539	
−10	.7095	.7140	.7155	.7250	.7363	0.8796
10	.6926	.6968	.6984	.7076	.7183	.8556
30	.6756	.6798	.6814	.6897	.7002	.8316
50	.6581	.6621	.6636	.6715	.6816	
70	.6398	.6439	.6453	.6527	.6620	

	$P\infty$			$P_2((CH_3)_3CCl)$		
−70	168.9	165.5	161.3	150.5	142.3	
−50	159.0	153.4	151.0	140.7	134.7	
−30	149.2	144.3	144.1	133.2	127.6	
−10	137.8	133.3	134.3	127.0	121.7	82.19
10	130.1	126.0	125.7	119.4	117.1	81.85
30	123.3	121.6	120.0	114.5	112.2	81.54
50	120.9	117.3	118.1	110.6	107.5	
70	117.3	113.9	114.5	106.2	103.2	

Heptane-*Tert.*-butyl Alcohol

Mole fr. of (CH₃)₃COH = t, °C.	0.0585	0.0853	0.1344	0.2259	0.4957	0.7265	1.000
−50	2.056	2.067					
−30	2.037	2.058	2.084	2.167			
−10	2.018	2.037	2.076	2.168	3.316		
0					3.117	7.33	
10	2.004	2.027	2.069	2.178	3.026	6.21	
30	1.991	2.016	2.072	2.197	2.958	4.91	10.92
50	1.972	2.007	2.066	2.204	2.920	4.28	8.49
70	1.934	1.981	2.045	2.193	2.889	3.99	6.89

				d			
−50	0.7456	0.7470					
−30	.7293	.7305	0.7336	0.7401			
−10	.7125	.7139	.7169	.7234	0.7455		
0					.7370	0.7635	
10	.6954	.6969	.6997	.7062	.7279	.7541	
30	.6781	.6794	.6820	.6882	.7096	.7348	0.7775
50	.6599	.6611	.6635	.6694	.6903	.7146	.7563
70	.6417	.6422	.6441	.6494	.6694	.6932	.7343

				P			
−50	37.7	36.1					
−30	42.1	42.1	39.4	40.4			
−10	46.2	44.3	43.5	43.8	67.9		
10	53.1	50.4	48.0	48.4	62.4	81.0	
30	62.0	57.5	55.4	54.7	62.9	73.0	73.2
50	69.7	66.6	62.1	60.4	64.3	68.6	69.9
70	68.5	70.5	66.3	64.6	66.3	67.4	66.8

TABLE I (*Concluded*)
Benzene-*Tert.*-butyl Alcohol

Mole fr. of $(CH_3)_3COH =$ t, °C.	0	0.0133	0.0264	0.0477	0.1159
			ϵ		
10	2.301	2.355	2.403	2.439	2.681
30	2.263	2.314	2.356	2.392	2.646
50	2.17	2.259	2.297	2.341	2.588
70	2.176	2.208	2.239	2.280	2.514
			d		
10	0.8891	0.8876	0.8857	0.8796	0.8752
30	.8676	.8658	.8640	.8579	.8532
50	.8460	.8439	.8421	.8360	.8313
70	.8239	.8219	.8201	.8145	.8083
	P_∞		$P_2((CH_3)_3COH)$		
10	90.0	84.4	82.6	71.0	72.0
30	92.4	88.2	82.3	71.5	74.9
50	80.4	75.5	74.7	70.7	75.3
70	69.5	65.8	66.9	65.1	73.8

Benzene-Triphenylchloromethane

Benzene-Triphenylcarbinol

Mole fr. of $(C_6H_5)_3CCl =$ t, °C.	0.0122	0.0282	0.0605	0.0969	Mole fr. of $(C_6H_5)_3COH =$	0.0103	0.0214	0.0375
			ϵ				ϵ	
10	2.385	2.488	2.692	2.902		2.352	2.401	2.473
30	2.338	2.430	2.622	2.811		2.307	2.356	2.421
50	2.289	2.378	2.553	2.728		2.259	2.306	2.368
70	2.238	2.323	2.481	2.648		2.208	2.254	2.310
			d				d	
10	0.8990	0.9113	0.9342	0.9575		0.8962	0.9037	0.9141
30	.8777	.8903	.9135	.9372		.8749	.8825	.8933
50	.8561	.8691	.8929	.9170		.8534	.8615	.8722
70	.8343	.8475	.8719	.8966		.8310	.8395	.8508
	P_∞		$P_2((C_6H_5)_3CCl)$		P_∞		$P_2((C_6H_5)_3COH)$	
10	167.3	166.4	164.4	162.9	160.1	139.6	137.3	134.6	133.5
30	163.5	163.2	159.0	159.2	155.9	136.0	133.1	134.2	131.1
50	157.3	156.7	155.9	155.2	152.4	132.8	125.5	129.6	128.3
70	152.3	(146.9)	151.3	150.1	148.7	127.4	(117)	123.6	122.7

TABLE II
VALUES OF $(P_\infty - a)T$, $(P_\infty - MR_D)T$ AND THE MOMENT
$(CH_3)_3CCl$

T, °A.	$(P_\infty - a)T$	T, °A.	$(P_\infty - a)T$	
203	27850	283	27850	$a = 31.7$
223	28400	303	27750	$b = 28200$
243	28500	323	28800	$\mu = 2.14 \times 10^{-18}$
263	27900	343	29300	$P_E = 25.3$
				$P_A = a - P_E = 6.4$

	$(CH_3)_3COH(MR_D = 22)$		$(C_6H_5)_3CCl(MR_D = 84.0)$		$(C_6H_5)_3COH(MR_D = 80.9)$	
	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$
283	19860	1.79	23570	1.95	16670	2.12
303	21280	1.86	24090	1.97	16760	2.13
323	18800	1.74	23680	1.95	16830	2.14
343	16210	1.62	23430	1.94	16020	2.04

<div align="center">

TABLE III

MOMENTS $\times 10^{18}$

</div>

n-C_4H_9Cl	1.90	n-C_4H_9OH	1.65
$(CH_3)_3CCl$	2.14	$(CH_3)_3COH$	1.65
$(C_6H_5)_3CCl$	1.95	$(C_6H_5)_3COH$	2.11

<div align="center">

Discussion of Results

</div>

The variation of P_2 for *tert.*-butyl chloride with temperature and concentration is very similar to that of the normal chloride. A 70° rise in temperature lowers the polarization of the pure liquid by only 1.2 in the case of both substances. The values of P_2 for the tertiary chloride are somewhat higher than those for the normal because of the higher moment and the P_2–c_2 curves (Fig. 1) are similar in shape to those for the normal,[3] but slightly steeper, the difference being that which the slightly higher moment should cause. In the study of the alkyl halides just referred to, it was found that there was a slight decrease in the slope of the P_2–c_2 curves in going from ethyl to n-butyl to n-heptyl bromide, although the moments of the three substances were the same. This decrease was presumably due to the decrease in the effects of the molecular dipoles upon one another because of the increased screening effects of the larger alkyl groups. It had been thought that the branching of the carbon chain might give increased screening effect, but there is no evidence of such increase in the P_2–c_2 curves for *tert.*-butyl chloride.

The behavior of the alcohols resembles that of the chlorides in that the P_2–c_2 curves for the *tert.*-butyl compound in heptane (Fig. 2) are like those for the n-butyl,[2] showing the same peculiar maximum, which flattens with rising temperature, but a more pronounced minimum, also flattening with rising temperature. Intermolecular action is so strong that the apparent values obtained for P_∞ below 50°, not given in Table II, increase with rising temperature instead of decreasing as required by the Debye equation. At 50 and 70° the values of P_∞ agree satisfactorily with those obtained from the benzene solutions, which, as in the case of the benzene solutions of the normal alcohol, conform approximately to the Debye equation. The polarization of the tertiary alcohol at 20°, 75.4, is close to that of the normal compound, 77.3, at the same temperature, but the decrease for the tertiary compound with rising temperature is greater. The small differences in behavior must be due to the difference in the shapes of the carbon chains in the two molecules as the moments are the same. The general similarity in behavior is in accord with the conclusion of Stewart from the x-ray diffractions[6] that when the hydroxyl group is on the first or second carbon of the chain, the molecular arrangement is the same in different alcohols and different from what it is if the hydroxyl group is

[6] Stewart and Skinner, *Phys. Rev.*, **31**, 1 (1928); Stewart, *Chem. Rev.*, **6**, 483 (1929); Stewart, *Phys. Rev.*, **35**, 726 (1930).

elsewhere. This is borne out by the measurements of Smyth and Stoops,[7] which showed that ethyl, n-butyl, and n-octyl alcohols were similar in behavior while 2-methylheptanol-3 gave P_2-c_2 curves very different in form. The mere assumption that the molecules lie end to end with the OH groups paired when the OH is on the first or second carbon and side by side when it is otherwise located is sufficient to explain the x-ray diffractions but insufficient to explain the dielectric behavior. The complex and unsatisfactory situation in regard to the latter has been discussed in other papers.[8]

The limited solubility of the triphenylmethyl compounds has made it impossible to run P_2-c_2 curves over a sufficient range to warrant their reproduction. However, the values in Table I show that the rates of change of the polarizations of triphenylchloromethane and triphenylcarbinol with concentration are lower than those of the tert.-butyl and n-butyl compounds, the intermolecular action being less. In other words, the screening effect of the large phenyl groups reduces the action of the molecular dipoles upon one another.

In Table III, 1.90×10^{-18} is given for the moment of n-butyl chloride as the weighted mean of the value 1.88×10^{-18} determined by Smyth and Rogers[3] and 1.97×10^{-18} obtained by Parts,[4] greater weight being attached to the former value because it was obtained from measurements over a wide range of temperature in which P_A was determined. The value for tert.-butyl chloride, 2.14×10^{-18}, is in excellent agreement with the value 2.15×10^{-18} found by Parts. The value 1.65×10^{-18} assigned to n-butyl alcohol is the result of the accurate measurements of Miles upon the vapor.[2] It is lower than the value 1.74×10^{-18} obtained from the measurements in benzene previously referred to, which is almost identical with the mean of the values given for the tertiary alcohol in Table II. Because of the agreement of this mean value, 1.75×10^{-18}, with the apparently too high value found for the normal alcohol in solution, and because of the tendency of the values to decrease with increasing temperature, which suggests the possible presence of a small error due to association at the lower temperatures, the value 1.65 is assigned to tert.-butyl alcohol. The values for the triphenylmethyl compounds are the means of the values at the different temperatures in Table II, which are in satisfactory agreement with one another.

The difference between the moments of n-butyl chloride and tert.-butyl chloride is interesting in view of the theory of induced moments which has been applied[1,3,8] to the alkyl halides. It was shown that the principal doublet in the molecule of a normal alkyl halide exerted an inductive effect upon the carbon chain sufficient to cause a small but appreciable moment in the second carbon of the chain, the moment of the ethyl halide being,

[7] Smyth and Stoops, THIS JOURNAL, **51**, 3330 (1929).

[8] Smyth and Stoops, Refs. 2 and 7; Smyth, *Chem. Rev.*, **6**, 549 (1929).

as a result, higher than that of the methyl, As lengthening of the chain beyond ethyl did not increase the moment of the molecule, it was concluded that the inductive effect of the principal halide doublet was not sufficient to produce a detectable moment at a distance greater than that of the second carbon atom.   In n-butyl chloride, then, only the first and second carbons have sufficient moments induced in them to contribute appreciably to the total moment of the molecule, but, in *tert.*-butyl chloride, there are three carbons approximately at the distance of the second carbon in the normal compound.   The small moments induced in each of these three carbons should contribute appreciably to the total moment, which should thus be greater than that of n-butyl chloride.   The same should, of course, hold for the bromides and iodides, and this is evident in the values found by Parts, the moments of the tertiary compounds being considerably higher than those of the normal.   In the *sec.*-butyl halides, the two carbons next to the first should be affected by the principal doublet so that the total moment should be larger than that of the n-butyl halide and smaller than that of the tertiary.   The actual values found by Parts for the *sec.*-butyl halides are between those for the normal and those for the tertiary.   In the isobutyl halides the branching of the chain is two carbons away from the principal doublet, so that only two carbons are appreciably affected by the principal doublet just as in the case of the normal compounds.   The identical values found by Parts for the n-butyl and the isobutyl compounds are, therefore, to be expected.   This view of the effect of induction receives support from the moments found for the heptyl halides by Errera and Sherrill.[9]   When the halogen in a heptyl halide is moved from the end of the chain to the second carbon, to which two other carbons are, of course, attached, the moment rises because both of these carbons are now affected by induction.   However, moving the halogen farther along the chain to give the 3- or 4-halogenated heptane produces no more effect because the carbons beyond the first two from the halogen in each direction are not affected sufficiently to contribute to the moment.

   The absence of an appreciable difference between the moments of n-butyl and *tert.*-butyl alcohols is consistent with the moments of the other alcohols, as there is no significant difference between the values of methyl and ethyl alcohol or of the higher normal alcohols.   The moment of the alcohol molecule is the resultant of the moment in the neighborhood of the C–O bond and that in the neighborhood of the H–O bond and this resultant makes a considerable angle with the general direction of the carbon chain,[10] which may account for the absence of inductive effect along the chain. In any event, in the absence of a difference between methyl and ethyl alco-

   [9] Errera and Sherrill, Leipziger Vorträge, 41 (1929);   THIS JOURNAL, **52,** 1993 (1930).
   [10] See Eucken and Meyer, *Physik. Z.*, **30,** 397 (1928).

hols, one would not expect the attachment of an increased number of carbons to the first to make much difference in the moment.

The moments found for the triphenylmethyl compounds are difficult to explain. The difference between *n*-butyl chloride and triphenylchloromethane is too small to be significant. The three benzene carbons attached to the first carbon of the latter compound appear to be less affected by the principal doublet than the three aliphatic carbons in *tert.*-butyl chloride. This is in harmony with the fact that the moment of chlorobenzene, $1.52 \times 10^{-18,5}$ is lower than those of the higher normal alkyl chlorides. However, this does not account for the high moment of triphenylcarbinol. This might be explained by supposing that the electropositive character of the triphenylmethyl group increases the moment at the C–O bond and thereby increases the total resultant moment. If, however, this is true, why is not the moment at the C–Cl bond increased so as to give triphenylchloromethane a moment higher than that of *tert.*-butyl chloride? The question may be complicated by the existence of the supposed benzenoid and quinonoid structures in the triphenylmethyl compounds, but this tautomerism does not appear to offer any satisfactory explanation of the observed differences.

As before,[1] we thus see very little relation between electric moment and chemical activity. The chemical behavior of *n*-butyl and *tert.*-butyl compounds, which should depend to a considerable extent upon the nature of the group bond, is markedly different in the two classes of compounds, but the moments of the two alcohols are the same and it is probable that the moments associated with the group bonds in the chlorides are the same, the differences in total moment being due to differences within the groups. The very different triphenylmethyl radical gives no indication of a very different moment associated with the group bond in the chloride, although the high moment of the triphenylcarbinol suggests a difference in the alcohol. The moments of the normal and tertiary butyl compounds can evidently be explained in terms of spatial considerations and induction. It must be remembered that we do not know the cause of the small moment of toluene or of the differences between the moments of the monohalogenated benzenes and the alkyl halides, although they seem quite natural and to be expected. It is not surprising, therefore, that the differences between the triphenylmethyl and the alkyl compounds do not as yet lend themselves to explanation. It may be concluded, however, that the triphenylmethyl compounds show no radical differences in moment corresponding to their different chemical behavior.

Summary

The dielectric constants and densities of solutions of *tert.*-butyl and triphenylmethyl chlorides and alcohols in heptane or benzene have been determined over varying ranges of temperature, and the data have been

used to calculate the polarizations of the substances and the electric moments of their molecules.

The polarizations show that the branched carbon chain of the *tert.*-butyl group has no measurably greater screening effect upon the force field of the dipole than the straight chain of the *n*-butyl group, while the larger triphenylmethyl group has a greater screening effect.

A theory of induced moments has been applied to explain the values here obtained, together with those of other investigators of alkyl halides. The moments of the molecules increase from the normal to the secondary to the tertiary compound because of the increase in the number of carbon atoms subjected to the inductive influence of the principal dipole, while the moment of the iso compound is the same as that of the normal if the branch in the chain is at least two carbons away from the halogen because only these two carbons are measurably affected by the principal dipole.

As previously observed, the moments do not show differences corresponding to the differences in chemical behavior.

PRINCETON, NEW JERSEY

DIFFERENTIAL POTENTIOMETRIC TITRATION.
IV. (a) AN ADAPTATION OF THE METHOD TO THE USE OF HYDROGEN ELECTRODES.
(b) A TEST OF STANDARDS FOR PRECISE ACIDIMETRY

BY DUNCAN A. MACINNES AND IRVING A. COWPERTHWAITE

In the third paper of this series[1] an improved apparatus for differential potentiometric titrations, involving a simple gas lift pump, was described, and data were given showing the usefulness of the method for measurements of high precision. We are, however, in this Laboratory, much interested in solutions of acids. Until recently our measurements on conductances, transference numbers, etc., have been hampered by the lack of precise (0.01% or better) methods for acidimetry. This has been especially true with regard to solutions of weak acids. Our attempts to use the quinhydrone electrode for acidimetry were not successful. This was probably due to the rapid oxidation of this substance as soon as the solutions approach the neutral point. An effort was also made to get the desired accuracy by means of indicators, using color standards, without greater success. Either of these methods might, with further investigation, have been developed to give adequate precision. It was, however,

[1] The papers already published in this series are (a) MacInnes and Jones, THIS JOURNAL, **48**, 2831 (1926); (b) MacInnes, Z. physik. Chem. (Cohen Festband), 217 (1927); (c) MacInnes and Dole, THIS JOURNAL, **51**, 1119 (1929).