405. *Dielectric Polarisation and Molecular-compound Formation in Solution. Parts I and II.*

By D. P. EARP and S. GLASSTONE.

Part I. The Structures of the Compounds of Ethers with Some Halogeno-methanes and -ethanes.

Two views are generally held concerning the structure of the compounds formed between apparently saturated organic molecules. According to the older theory, it is supposed that the different molecules are held together by physical forces, presumably of a van der Waals or dipole-association type; in recent years there has been a growing opinion that in some cases, at least, of molecular-compound formation the constituent molecules are held together by a definite co-ordinate link (cf. Lowry, *Chem. and Ind.*, 1924, **43**, 418; Bennett and Willis, J., 1929, 256; Moore, Shepherd, and Goodall, *ibid.*, 1931, 1447). One method for distinguishing between the two possibilities, suggested by Bamberger and Dimroth (*Annalen*, 1924, **438**, 67), has been recently applied by Hammick and Sixsmith (this vol., p. 580) to the compound formed between a nitro-derivative and a hydrocarbon: the results of the investigation appear to provide clear proof that in the particular case studied true chemical combination occurs. Another method, now to be described, is based on the measurements of dielectric polarisation; it is reasonable to suppose that, if compound formation involved dipole association, the polarisation of a mixture of the two components would be less than the sum of the separate values, whereas the introduction of a co-ordinate link, resulting from chemical union, should result in a definite exaltation of the polarisation. There seemed some evidence from published data that such increases do in fact occur where compound formation appears probable (Ebert, *Naturwiss.*, 1925, **13**, 68; Hassel and Uhl, *Z. physikal. Chem.*, 1930, *B*, **8**, 187; Jenkins, *Nature*, 1934, **134**, 217).

The systems chosen for examination in this work were those consisting of an ether and a tri- or a tetra-halogenated methane; it is well known that ethyl ether and chloroform form solid compounds (see Wyatt, *Trans. Faraday Soc.*, 1929, **25**, 49), and measurements of the vapour pressure, viscosity, and heat evolution of the two liquid components indicate that the compound formation occurs in the liquid phase. The dielectric constants of ether–chloroform mixtures also show marked abnormalities (Philip, *Z. physikal. Chem.*, 1897, **24**, 18; Schultze, *Z. Elektrochem.*, 1912, **18**, 77; Sayce and Briscoe, J., 1926, 2623), and hence it seemed that the polarisations might reveal results of interest (cf. Hassel and Uhl, *loc. cit.*). Carbon tetrachloride also forms solid compounds with ether (Wyatt, *Trans. Faraday Soc.*, 1929, **25**, 43), and although the deviations from ideal behaviour in the liquid phase are not very marked, mixtures of this type appeared to be worthy of investigation. In the course of the present work the following systems have been studied: ethyl ether with chloroform, bromoform, iodoform, ααα-trichloroethane, carbon tetrachloride and tetrabromide, and penta- and hexa-chloroethanes; *iso*propyl ether with chloroform, bromoform, and carbon tetrachloride and tetrabromide; and ββ′-dichlorodiethyl ether with chloroform.

In the preliminary experiments, mixtures of ether and chloroform were prepared in *cyclo*hexane, and the dielectric polarisations determined; deviations were observed from strict additivity, but these were too small to be reliable for the calculation of a mass-action constant. After the method had been abandoned, analogous experiments with *n*-butyl alcohol and hydrogen chloride in benzene solution were reported by Williams (*J. Franklin Inst.*, 1935, **219**, 47), who found the same difficulty in interpreting the results. By the use of binary mixtures only, as described below, it has been possible to obtain evidence as to the structures of various molecular compounds in solution, to estimate the amounts of compound formed in various mixtures, and to calculate mass-action constants.

EXPERIMENTAL.

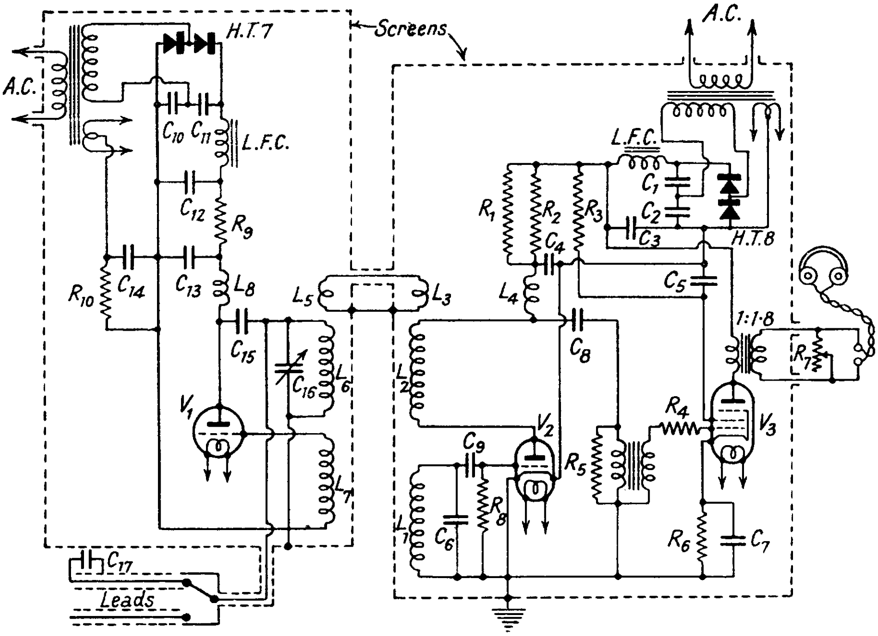
Dielectric Constants.—These were measured by the heterodyne method, with the apparatus shown in Fig. 1, which differs from most others in that it is operated entirely from the *A.C.* electric mains. Provided the current were switched on about one hour before measurements were made, no difficulty was experienced in obtaining reproducible results; any variation in the voltage of the mains affects both fixed and variable oscillators to the same extent.

R_1 and R_2 were 20,000, R_3 15,000, R_4 and R_5 50,000, R_6 300, R_7 1000 (max.), R_8 250,000, R_9 10,000, and R_{10} 600 ohm resistances; C_1, C_2, C_3, C_{10}, and C_{11} were 4μF, C_4, C_5, C_{13}, and C_{14} 2μF, C_7 and C_8 1μF, C_9 0·0001μF, C_{12} 8μF (electrolytic), C_{15} 0·002 μF, condensers; L_1 and L_7 were 35-turn, L_3 and L_5 single-turn, L_2 40-turn and L_6 33-turn, inductances; L_4 and L_8 were high-frequency chokes. The valves used were Mullard AC104 (V_1), Osram MH4 (V_2) and Mazda AC/Pen. (V_3).

The condenser cell (C_{17}) for the test liquid was similar either to that described by Hartshorn and Oliver (*Proc. Roy. Soc.*, 1929, *A*, **123**, 664) or to those used by Sugden (J., 1933, 768), according to the dielectric constant of the liquid; the results obtained from both types were almost identical. Mixtures containing carbon tetrabromide or bromoform were found to attack nickel, " staybrite " steel, and silver; for such liquids a vessel of the Hartshorn and Oliver type with rhodium-plated condenser plates was used. The standard variable condenser (C_{16}) had a maximum capacity of 360 μμF; it was made by Gambrell Bros., and calibrated at the National Physical Laboratory. The leads making connexion between the dielectric cell (C_{17}) and the variable oscillator were enclosed in earthed brass tubes, in order to eliminate capacity changes caused by the presence of the operator, and compensation for the capacity of these leads was obtained by the use of a second set of similar enclosed leads (Fig. 1). Allowance for the effect of residual capacities was made by using pure benzene, $\varepsilon = 2{\cdot}282$ at 20° (Hartshorn and Oliver, *loc. cit.*), as a standard. The actual manipulation of the apparatus followed conventional lines and need not be described.

All measurements were made at 20°, a Dewar vessel containing water being used as a thermostat. The dielectric cell was completely surrounded by an earthed copper jacket; experiments showed that capacity effects due to the thermostat could be eliminated in this manner.

FIG. 1.



Density and Refractive Index.—Densities were determined by means of U-shaped pyknometers, the ends being closed with ground glass caps. Refractive indices were measured in a Pülfrich refractometer at 20°.

Materials.—*Ethyl ether.* This was washed thoroughly with dilute caustic soda solution, then with water several times, dried over calcium chloride, and finally over sodium wire; it was distilled from sodium as required; b. p. 34·6°.

Chloroform. Refluxed for several hours with, and distilled from, phosphoric oxide; b. p. 61·1—61·2°.

Bromoform. Washed thoroughly with water, dried with calcium chloride, and fractionated in a vacuum; b. p. 46°/15 mm.

Iodoform. Recrystallised from alcohol, m. p. 119° (decomp.).

Carbon tetrachloride. Pure commercial specimen dried over calcium chloride and distilled; centre fraction, b. p. 76·5°.

Carbon tetrabromide. Pure crystals (B.D.H.).

iso*Propyl ether.* Kept over sodium, distilled, and redistilled after again standing over sodium; b. p. 69·1°.

ββ'-*Dichlorodiethyl ether.*—Dried over sodium, distilled, and redistilled; b. p. 177—178°.

Ethylene dibromide. Dried over phosphoric oxide, and fractionated; b. p. 131·6°.

Hexachloroethane. Recrystallised from alcohol–ether.

Pentachloroethane. Dried over phosphoric oxide; constant-boiling fraction, b. p. 161—162°, used.

ααα-Trichloroethane. This was prepared by Regnault's method (*Annalen*, 1840, **33**, 317), careful fractionation being necessary; b. p. 74·5—75·0°.

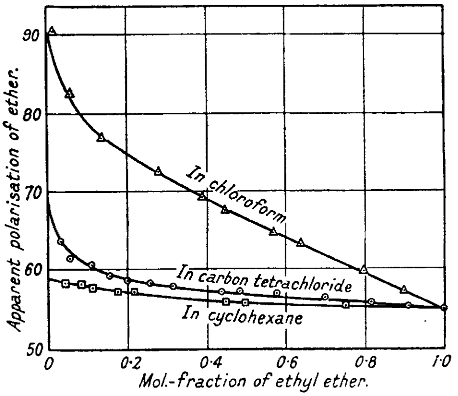
cyclo*Hexane*.—A large quantity of commercial material was dried over sodium and fractionated, b. p. 80·8—81·0°; this was not quite pure, but portions of the same specimen were used throughout the work.

In addition to the mixtures already mentioned (p. 1710), measurements were also made of each of the individual substances in the non-polar liquid *cyclo*hexane; mixtures of chloroform and ethylene dibromide were also studied for reasons which will appear later.

Results.

From the measurements of dielectric constants and densities, the total polarisations of the mixtures (P_{12}) were calculated; from these the molar polarisation of one component (P_2) was determined in the usual manner by the equation $P_{12} = f_1P_1 + f_2P_2$, the polarisation of the other component (P_1) being assumed to be equal to that in the pure liquid state and to remain constant throughout. When the molar polarisation of the one component, *e.g.*, ethyl ether, in a mixture, *e.g.*, with chloroform, was plotted against its mol.-fraction, and the curve compared with the corresponding values in *cyclo*hexane, an interesting result was observed (see Fig. 2). The polarisation of the ether in the chloroform mixtures is not only greater than in *cyclo*hexane, but there is, further, a more rapid increase at high dilutions; a similar effect is shown by the molar polarisations of chloroform in ether solutions. It is of interest that in the measurements of Krchma and Williams (*J. Amer. Chem. Soc.*, 1927, **49**, 2408) on ether in carbon tetrachloride there is evidence of an increase of the molar polarisation of ether at small concentrations, which has been confirmed by the present authors; the aforementioned workers neglected the high value, as it was attributed to experimental error (private communication from Professor Williams), but in the view of the other results now reported there is little doubt that it has an important significance.

FIG. 2.



A reasonable explanation for the marked increase of polarisation, above the normal value, in dilute solutions of ethers and halogenated paraffins is that the compound formation, which undoubtedly occurs in the liquid mixtures, involves the formation of a new co-ordinate link joining the two molecules; this will result in an increase of the molar polarisation of each component determined separately in the manner described. For a mixture of two substances A and B, forming a compound represented by A→B, the polarisation of the compound A, calculated from the total polarisation of the mixture, the value for B being assumed to remain constant, will include the contribution of the co-ordinate linkage according to the extent of compound formation. It is evident, from the law of mass action, that as the dilution of A is increased, the proportion present in the form of compound must increase, so that the calculated molar polarisation consequently increases, the effect being especially rapid as infinite dilution of A is approached. The extrapolated value for the polarisation of A at infinite dilution represents the actual value in the compound, including the new linkage, thus A→. If to this is added the assumed constant polarisation of B, the sum is the value for A→B, *i.e.*, the molar polarisation of the molecular compound. Similarly, the same polarisation for the compound should be obtained by determining the extrapolated value for B at infinite dilution, which gives →B, and adding the assumed constant polarisation of A. For example, the extrapolated polarisation of ether at infinite dilution in chloroform (Fig. 2) is 90·0, the constant value of 44·9 being assumed for chloroform, giving a total of 134·9; if the ether value is taken as constant at 54·7, then the extrapolated molar polarisation of chloroform is 78·5, the sum being 133·2 for the equimolecular compound. Provided the dielectric constant of the two components be similar, as in the case considered, it has been found generally that the two values for the polarisation of the compound are quite close: when the dielectric constants are markedly different, *e.g.*, for ββ′-dichlorodiethyl ether ($\varepsilon = 21{\cdot}17$) and chloroform ($\varepsilon = 4{\cdot}816$), the results differ in a manner to be expected (see below).

It should be mentioned that no abnormality was observed in the electron polarisations of the constituents of any of the mixtures, so the whole of the deviations observed must probably be included in the orientation polarisation. This is in harmony with the view that the deviations are to be attributed to compound formation, since a new linkage would contribute a negligible amount to the molecular refractivity.

Calculations of Mass-action Constants.—In order to develop further the arguments presented, an attempt has been made to calculate the mass-action constants for the various equilibria $A + B \rightleftharpoons AB$, on the assumption that the compound consists of only 1 mol. of each component. Since the total mol.-fractions of A and B present in the mixture as made up, *viz.*, f_A and f_B, and the molar polarisations of A, B, and AB (*i.e.*, P_A, P_B, and P_{AB}, respectively) are known, it should be a simple matter to calculate the mol.-fraction of compound (x) from the measured polarisation P, by means of the relationship

$$P = P_A(f_A - x)/(1 - x) + P_B(f_B - x)/(1 - x) + P_{AB}x/(1 - x),$$

additivity of polarisations in solution being assumed, as usual.

In applying this method of calculation, however, it is necessary to use values for P_A, P_B, and P_{AB} applicable to media of the *same dielectric constant* as that in which P was measured. Several relationships between polarisation and dielectric constant have been proposed (Müller, *Physikal. Z.*, 1933, **34**, 689; *Trans. Faraday Soc.*, 1934, **30**, 729; Jenkins, *ibid.*, p. 739; *Nature*, 1934, **133**, 106; Sugden, *ibid.*, p. 415), but none of these proved quite satisfactory for the mixtures studied in the present work; it was found, however, that when the molar polarisation was plotted against $[(\varepsilon - 1)/(\varepsilon + 2)]^2$ a much closer approximation to a straight line was obtained in the majority of cases. Graphs of this kind were, therefore, used for the purpose of interpolating and extrapolating values of the polarisations for any required dielectric constant. The data for the P_A and P_B graphs were obtained from measurements of A and B respectively, in *cyclo*hexane or in benzene, whereas those for P_{AB} were derived by drawing a straight line through two points representing the values obtained in the manner already described. In most cases the latter procedure was not possible, since the dielectric constants for the two liquids were so close together; a constant value for P_{AB} was then assumed throughout, the error involved in this assumption being small. Since the mol.-fraction of the compound is now known, the mass-action constant can be calculated as $x(1 - x)/(f_A - x)(f_B - x)$, the activities being expressed as actual mol.-fractions. The results of the measurements and calculations are given below; the minimum data only, sufficient to check the figures, are quoted. The following tables are for mixtures with *cyclo*hexane or, in a few instances where this appeared to give abnormal results, with benzene; f_2 and P_2 refer to the other constituent of the mixture, and ε and $d_{4°}^{20°}$ are the dielectric constant and density at 20°.

(I) *Ethyl ether and* cyclo*hexane.*

f_2.	ε.	$d_{4°}^{20°}$.	P_2.
0·00000	2·033	0·7784	—
0·04720	2·109	0·7751	58·11
0·08854	2·178	0·7720	58·17
0·12325	2·246	0·7691	57·53
0·17310	2·317	0·7664	57·17
0·21749	2·398	0·7631	57·30
0·50429	3·035	0·7475	55·40
0·74972	3·634	0·7314	55·29
1·00000	4·335	0·7135	54·65

(II*a*) iso*Propyl ether and* cyclo*hexane.*

f_2.	ε.	$d_{4°}^{20°}$.	P_2.
0·00000	2·032	0·7784	—
0·06900	2·147	0·7728	69·60
0·08219	2·176	0·7720	71·02
0·19207	2·373	0·7644	71·35
0·20642	2·408	0·7638	71·60
0·35236	2·692	0·7551	71·73
0·52276	3·027	0·7459	71·38
0·69424	3·372	0·7375	71·12
1·00000	3·976	0·7239	70·25

(II*b*) iso*Propyl ether and benzene.*

f_2.	ε.	$d_{4°}^{20°}$.	P_2.
0·00000	2·282	0·8763	—
0·05982	2·412	0·8629	73·95
0·17152	2·631	0·8405	72·28
0·30333	2·881	0·8168	71·55
0·47866	3·179	0·7893	70·91
0·69922	3·522	0·7587	70·40
1·00000	3·976	0·7239	70·25

(III) *Dichlorodiethyl ether and* cyclo*hexane.*

f_2.	ε.	$d_{4°}^{20°}$.	P_2.
0·00000	2·032	0·7784	—
0·07225	2·510	0·8096	161·0
0·17213	3·421	0·8540	153·4
0·31667	5·148	0·9187	145·3
0·48756	7·916	0·9953	133·1
0·64967	10·95	1·0673	120·7
0·81778	15·45	1·1407	111·2
1·00000	21·17	1·2194	102·1

(IV) *Chloroform and* cyclo*hexane.*

f_2.	ϵ.	$d_{4°}^{20°}$.	P_2.
0·00000	2·032	0·7784	—
0·08127	2·163	0·8208	51·36
0·11979	2·225	0·8415	50·81
0·13658	2·255	0·8506	50·76
0·18364	2·324	0·8770	49·14
0·19226	2·338	0·8816	49·04
0·56846	3·270	1·1285	47·36
0·78515	3·959	1·2960	46·50
1·00000	4·816	1·4890	44·89

(V) *Bromoform and* cyclo*hexane.*

f_2.	ϵ.	$d_{4°}^{20°}$.	P_2.
0·00000	2·032	0·7784	—
0·05026	2·103	0·8645	50·08
0·17145	2·287	1·0788	49·81
0·38967	2·680	1·4925	49·15
0·68373	3·367	2·1151	48·16
1·00000	4·385	2·8904	46·36

(VI) *Iodoform and benzene.*

f_2.	ϵ.	$d_{4°}^{20°}$.	P_2.
0·000000	2·282	0·8760	—
0·007485	2·297	0·9015	60·1
0·010653	2·302	0·9123	59·4
0·017516	2·318	0·9355	60·7

(VII) *Carbon tetrachloride and* cyclo*hexane.*

f_2.	ϵ.	$d_{4°}^{20°}$.	P_2.
0·00000	2·032	0·7784	—
0·27294	2·084	0·9819	28·48
0·53458	2·137	1·1892	28·40
0·77419	2·194	1·3918	28·42
1·00000	2·242	1·5940	28·28

(VIII) *Carbon tetrabromide and* cyclo*hexane.*

f_2.	ϵ.	$d_{4°}^{20°}$.	P_2.
0·00000	2·032	0·7784	—
0·02573	2·051	0·8378	41·4
0·05026	2·069	0·8945	41·6
0·07225	2·087	0·9458	41·9

(IX*a*) *Pentachloroethane and* cyclo*hexane.*

f_2.	ϵ.	$d_{4°}^{20°}$.	P_2.
0·00000	2·032	0·7784	—
0·06664	2·105	0·8440	54·88
0·14615	2·223	0·9214	56·47
0·22539	2·334	0·9973	56·60
0·35410	2·513	1·1183	57·20
0·58643	2·951	1·3282	58·04
0·80917	3·376	1·5207	58·11
1·00000	3·833	1·6792	58·52

(IX*b*) *Pentachloroethane and benzene.*

f_2.	ϵ.	$d_{4°}^{20°}$.	P_2.
0·00000	2·282	0·8760	—
0·05873	2·370	0·9386	57·84
0·14082	2·496	1·0221	58·15
0·24753	2·660	1·1239	58·22
0·46450	2·973	1·3104	58·35
1·00000	3·833	1·6792	58·52

(X) *ααα-Trichloroethane and* cyclo*hexane.*

f_2.	ϵ.	$d_{4°}^{20°}$.	P_2.
0·00000	2·032	0·7784	—
0·06838	2·250	0·8124	86·35
0·12759	2·464	0·8425	86·65
0·25053	2·947	0·9060	84·51
1·00000	7·518	1·3288	68·81

(XI) *Hexachloroethane and* cyclo*hexane.*

f_2.	ϵ.	$d_{4°}^{20°}$.	P_2.
0·00000	2·032	0·7784	—
0·03749	2·045	0·8238	40·6
0·05131	2·050	0·8405	40·8
0·06955	2·059	0·8623	40·7

The results for the mixtures of an ether and a halogenated paraffin are given in the following tables, where again only the minimum data are quoted. The mol.-fraction of the ether in each case is represented by f_A; P_A and P_B are the molar polarisations of ether and of halogen derivative, respectively. K is the mass-action constant, calculated as already described; the values of P_{AB} used in the calculations are quoted in each case.

(XII) *Ethyl ether and chloroform* (P_{AB} = 134).

f_A.	ϵ.	$d_{4°}^{20°}$.	P_A.	P_B.	K.
0·00000	4·813	1·4890	—	44·89	—
0·01685	4·919	1·4722	90·2	45·53	0·66
0·05387	5·093	1·4387	82·5	46·52	0·66
0·13528	5·376	1·3660	76·8	48·41	0·52
0·27792	5·732	1·2446	72·3	51·79	0·50
0·39321	5·835	1·1511	69·22	54·46	0·44
0·44819	5·835	1·1080	67·81	55·87	0·43
0·57176	5·693	1·0130	64·83	59·97	0·40
0·64215	5·577	0·9597	63·46	61·0	0·41
0·79885	5·124	0·8478	59·77	65·8	0·44
0·90082	4·742	0·7782	57·33	69·6	0·40
0·96063	4·502	0·7393	55·64	72·8	0·58
1·00000	4·335	0·7134	54·65	—	—

(XIII) *Ethyl ether and bromoform* (P_{AB} = 124).

f_A.	ϵ.	$d_{4°}^{20°}$.	P_A.	P_B.	K.
0·00000	4·385	2·8904	—	46·36	—
0·03311	4·495	2·8059	76·0	47·09	0·65
0·10146	4·750	2·6443	75·3	48·69	0·61
0·19056	5·016	2·4376	72·56	50·58	0·56
0·44145	5·441	1·8730	66·83	55·93	0·44
0·66627	5·301	1·3881	61·94	60·91	0·43
0·85888	4·826	0·9904	57·81	65·54	0·47
0·95559	4·474	0·7994	55·51	66·87	0·47
1·00000	4·335	0·7135	54·65	—	—

(XIV) *Ethyl ether and iodoform.*

f_A.	ϵ.	$d^{20°}_{4°}$.	P_A.	P_B.	K.
0·970884	4·396	0·8070	54·87	61·8	—
0·979193	4·383	0·7803	54·83	63·3	—
0·983600	4·369	0·7657	54·79	63·2	—
0·987624	4·362	0·7532	54·75	62·1	—
0·991497	4·355	0·7408	54·73	63·4	—
1·00000	4·335	0·7135	54·65	—	—

(XV) *Ethyl ether and ααα-trichloroethane* (P_{AB} = 134).

0·00000	7·518	1·3288	—	68·81	—
0·49056	6·071	1·0302	58·22	72·12	0·044
0·60925	5·701	0·9557	57·84	73·77	0·044
0·73730	5·273	0·8763	57·02	75·44	0·045
0·86276	4·826	0·7986	55·94	76·91	0·049
0·93111	4·560	0·7559	55·31	77·81	0·048
1·00000	4·335	0·7135	54·65	—	—

(XVI) *Ethyl ether and pentachloroethane* (P_{AB} = 136·5).

0·00000	3·833	1·6792	—	58·52	—
0·09078	4·120	1·6102	77·91	60·94	0·45
0·19518	4·398	1·5282	73·86	63·18	0·37
0·30591	4·652	1·4360	71·04	65·73	0·36
0·45035	4·883	1·3075	67·46	69·00	0·35
0·63244	4·980	1·1280	62·87	72·65	0·35
0·76321	4·868	0·9880	59·88	75·37	0·38
0·86063	4·697	0·8781	57·70	77·29	0·40
0·93847	4·503	0·7871	55·94	78·02	0·45
1·00000	4·335	0·7135	54·65	—	—

(XVII) iso*Propyl ether and chloroform* (P_{AB} = 157).

0·00000	4·916	1·4890	—	44·89	—
0·03961	5·020	1·4399	102·5	46·26	0·95
0·10017	5·361	1·3709	104·4	48·69	0·95
0·17349	5·657	1·2932	101·6	51·44	0·78
0·28517	5·945	1·1881	97·74	55·86	0·65
0·43925	6·001	1·0619	92·52	62·34	0·60
0·65894	5·449	0·9088	84·49	72·40	0·58
0·82041	4·787	0·8147	78·01	80·33	0·62
0·90944	4·385	0·7678	74·21	84·65	0·64
1·00000	3·976	0·7239	70·25	—	—

(XVIII) iso*Propyl ether and bromoform* (P_{AB} = 139).

0·00000	4·385	2·8904	—	46·36	—
0·06527	4·646	2·6781	98·41	48·33	0·81
0·12234	4·863	2·5079	97·32	50·12	0·72
0·22803	5·133	2·2165	93·43	53·31	0·56
0·36445	5·370	1·8784	90·54	57·99	0·53
0·46743	5·379	1·6490	87·53	61·53	0·49
0·61709	5·215	1·3484	83·41	67·58	0·49
0·77011	4·816	1·0755	78·60	74·14	0·53
0·88658	4·441	0·8891	74·85	82·22	0·61
1·00000	3·976	0·7239	70·25	—	—

(XIX) *Dichlorodiethyl ether and chloroform* (P_{AB} = 161—202).

0·00000	4·816	1·4890	—	44·89	—
0·05181	5·716	1·4713	145·5	47·16	1·18
0·11160	6·792	1·4514	139·0	49·52	0·78
0·19333	8·386	1·4235	131·1	52·07	0·48
0·36146	11·75	1·3742	122·0	56·19	0·27
0·47960	13·32	1·3411	114·7	56·54	0·21
0·62776	15·75	1·3027	109·8	57·80	0·11
0·77905	17·99	1·2667	105·9	58·49	0·10
0·88257	19·39	1·2441	103·8	58·20	0·09
1·00000	21·17	1·2194	102·1	—	—

f_A.	ε.	$d_{4°}^{20°}$.	P_A.	P_B.	K.
(XX) *Ethyl ether and carbon tetrachloride* (P_{AB} = 94·7).					
0·00000	2·242	1·5940	—	28·28	—
0·03862	2·323	1·5581	63·53	—	—
0·06053	2·364	1·5386	61·45	—	0·105
0·11003	2·463	1·4940	60·83	—	0·095
0·15809	2·550	1·4510	59·32	—	0·062
0·20399	2·639	1·4101	58·81	—	0·057
0·26413	2·761	1·3571	58·33	—	0·057
0·32161	2·879	1·3058	57·97	—	0·056
0·44406	3·134	1·1966	57·26	—	0·052
0·48548	3·232	1·1598	57·29	—	0·058
0·58144	3·453	1·0746	57·02	—	0·069
0·70024	3·705	0·9712	56·19	—	0·056
0·81740	3·985	0·8701	55·82	—	0·068
0·90979	4·179	0·7902	55·32	—	0·085
1·00000	4·335	0·7135	54·65	—	—
(XXI) *Ethyl ether and hexachloroethane* (P_{AB} = 104).					
0·83599	3·998	0·9390	55·98	48·39	0·107
0·86405	4·048	0·9025	55·58	47·47	0·095
0·95206	4·241	0·7814	55·00	48·57	0·089
1·00000	4·335	0·7135	54·65	—	—
(XXII) iso*Propyl ether and carbon tetrachloride* (P_{AB} = 105).					
0·00000	2·242	1·5940	—	28·28	—
0·06916	2·394	1·5105	75·67	28·69	0·051
0·15477	2·585	1·4136	75·44	29·23	0·052
0·26390	2·793	1·2996	74·01	29·63	0·060
0·40649	3·059	1·1638	72·97	30·15	0·067
0·50208	3·243	1·0804	72·80	30·85	0·061
0·65893	3·495	0·9547	71·80	31·26	0·077
0·80056	3·700	0·8526	70·98	31·21	0·093
0·91995	3·877	0·7735	70·53	32·78	0·067
1·00000	3·976	0·7239	70·25	—	—
(XXIII) *Ethyl ether and carbon tetrabromide* (P_{AB} = 106).					
0·74603	4·248	1·3694	56·81	47·93	0·12
0·80214	4·321	1·2250	56·60	49·48	0·14
0·83651	4·274	1·1366	56·05	46·62	0·07
0·87170	4·335	1·0454	55·63	48·26	0·09
0·91577	4·355	0·9310	55·43	51·19	0·16
1·00000	4·335	0·7135	54·65	—	—
(XXIV) iso*Propyl ether and carbon tetrabromide* (P_{AB} = 121).					
0·71116	3·928	1·3069	72·62	47·44	0·104
0·75699	3·952	1·2083	72·27	47·89	0·105
0·81613	3·976	1·0847	71·82	48·53	0·103
0·87130	3·976	0·9723	71·24	48·35	0·095
0·92647	3·984	0·8635	70·86	49·36	0·108
1·00000	3·976	0·7239	70·25	—	—

DISCUSSION.

In view of the approximations involved in the calculations, and the use of concentrations expressed in mol.-fractions to represent activities, the general agreement between the values of K for any given mixture may be taken as supporting the arguments on which the calculations are based.* If any ratio other than equimolecular for the composition of the compound be assumed, then the K values show a marked drift. An examination of the mass-action constants, or better the curves representing the amount of compound formed in

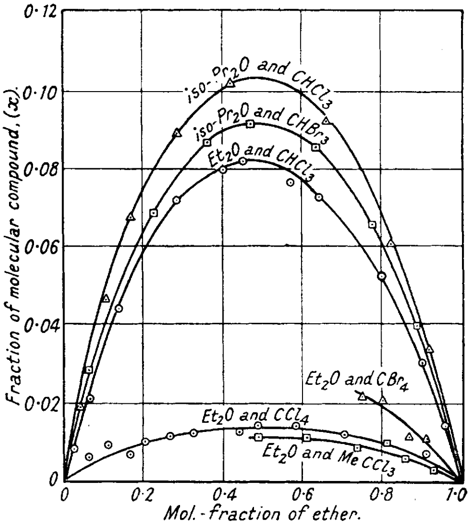
---

* A consideration of the errors involved shows that the chief source of the errors in K probably lies in the values of P_A, P_B, and P_{AB} used in calculating x; where the dielectric constants of the mixtures do not vary appreciably over the range of concentrations studied, the errors are not considerable, except for solutions containing a large excess of one or other component. When the dielectric constants differ, however, as with dichlorodiethyl ether and chloroform (see also Part II), the deviations may be much more serious, owing to the uncertainty in correcting for the dielectric-constant effect. Possible errors in the extrapolation necessary to give P_{AB} (p. 1712) can be shown to have no serious influence on the general nature of the results obtained.

any given mixture (Fig. 3), shows that in the ether–chloroform series the tendency for compound formation to occur is in the order *iso*propyl ether > ethyl ether > ββ′-dichlorodiethyl ether, and in the series ethyl ether–trihalogenomethane, the tendency is chloroform $\geqslant$ bromoform > iodoform. The order for chloroform and bromoform is in agreement with that deduced from a study of vapour pressures of their mixtures with ether (Weissenberger, Schuster, and Liebacher, *Monatsh.*, 1926, **46**, 295). Owing to the limited solubility of iodoform, only a few measurements were possible with it, and no value of K could be determined; the molar polarisations, however, when compared with those in benzene, show that compound formation with ether occurs to only a small extent.

If the molecular compounds involve a co-ordinate link, as suggested above, then it is probable that the oxygen atom of the ether acts as donor : this view is in harmony with the fact that the presence in the ether of electron-repelling groups, *e.g.*, in *iso*propyl ether, causes the tendency for compound formation to be increased, whereas electron-attracting groups, *e.g.*, in ββ′-dichlorodiethyl ether,* result in a decreased formation of compound as compared with ethyl ether. Since the tetrahalogenomethanes also form compounds with ether, and since a hydrogen atom attached to carbon shows little tendency to co-ordinate (cf. Sidgwick, " Covalent Link in Chemistry," 1933, p. 161), it was at first supposed that the halogen atom acted as the electron acceptor of the ether–CHX_3 compounds, but this view had to be abandoned. If co-ordination occurs through the halogen atom, then : (i) the tendency for compound formation should be in the order I > Br > Cl, as with the CX_4 compounds (see p. 1718); (ii) the extent of compound formation with a given ether should be almost the same for CHX_3 and for CX_4; (iii) ααα-trichloroethane should form a compound as readily as chloroform. Actually, the iodoform–ether compound is much less stable than that with chloroform, and the latter is considerably more stable than those formed between ether and ααα-trichloroethane or carbon tetrachloride. The conclusion appears inevitable, therefore, that co-ordination occurs through hydrogen joined to carbon, the process being facilitated by the attachment of negative (halogen) groups to the latter; this would account for the observed order of stability of the compounds with ether, *viz.*, $CHCl_3 > CHBr_3 > CHI_3$. There is reason to believe that when any highly negative groups, *e.g.*, phenyl or nitrophenyl, are joined to carbon in this manner co-ordination through a hydrogen atom is facilitated; this point will be considered in a later investigation.

FIG. 3.



The experimental results recorded above demonstrate that pentachloroethane shows as much tendency as chloroform to combine with ether, whereas the hexachloro-compound behaves in a manner similar to carbon tetrachloride. It is probable that even with the CHX_3 and C_2HX_5 compounds there is some co-ordination through the halogen atom, although the extent is relatively small; since such co-ordination occurs more readily with bromine than with chlorine, it may account for the fact that the compound of bromoform with ether is formed nearly as readily as that of chloroform, whereas a difference, such as that observed with *iso*propyl ether, would have been expected if co-ordination took place only through the hydrogen atom.

---

* The variation in the values of K for the dichlorodiethyl ether and chloroform mixtures is due to the marked difference in dielectric constant of the two components, and consequent uncertainty in the quantities P_A, P_B, and P_{AB}. The approximately constant K values in the lower portion of Table XIX are probably the most reliable; the same effect is observed with mixtures of acetone or quinoline with chloroform (see Part II, p. 1720).

Using the "classical" method of representing co-ordinated hydrogen, the compound of an ether with CHX_3 may be written $R_2O{\rightarrow}H{\cdot}CX_3$. According to modern views, however (see Sidgwick, *Ann. Reports*, 1934, **31**, 40), the compound formation may be regarded as being due to resonance between two states having similar energies, thus :

$$\underbrace{R_2O\ \ H{-}CX_3}_{} \rightleftarrows \underbrace{R_2\overset{+}{O}{-}H\ \ \overset{-}{C}X_3}_{}$$

The difference in these two states results merely from the movement of two pairs of electrons, there being no movement of atoms (*idem, ibid.*, 1933, **30**, 112). Owing to the mutual attraction of the oppositely charged portions in the excited state, no electrical conductivity is to be anticipated, and in fact none was found in mixtures of chloroform and ether.

From the molar polarisations of the compounds, determined in the manner already described, and the measured electron polarisations, their dipole moments have been calculated; some of the results (expressed in Debye units) are : $Et_2O,CHCl_3$ 2·06; $Et_2O,CHBr_3$ 1·84; $Pr^{\beta}_2O,CHCl_3$ 2·27; $Pr^{\beta}_2O,CHBr_3$ 1·98. From these values and the known moments of the constituents, an approximate idea of the contribution of the new linkage in the compound can be obtained; by making some allowance for the direction of this bond, its moment can be shown to be of the order of 0·5 *D*. This value is very much smaller than that to be expected from a complete co-ordinate link, as for example between aluminium or boron halides and ethers, etc. (cf. Nespital, *Z. physikal. Chem.*, 1932, *B*, **16**, 153), but the discrepancy is not surprising in view of the probable nature of the actual linkage resulting from resonance; the electronic shift is by no means as complete as in the case quoted, or even in the formation of sulphoxides (cf. Hampson, Farmer, and Sutton, *Proc. Roy. Soc.*, 1933, **143**, *A*, 147). Further confirmation of the "incomplete" or "partial" nature of the hydrogen bond is obtainable from calorimetric measurements : when 1 g.-mol. each of chloroform and ether are mixed, 1,200 cals. are evolved (Macleod and Wilson, *Trans. Faraday Soc.*, 1935, **31**, 596), and since from the present work it appears that 0·168 g.-mol. of compound is formed in such a mixture, the heat of formation of the new oxygen–hydrogen bond is about 7,000 cals., as compared with about 110,000 cals. for the normal linkage. Macleod and Wilson (*loc. cit.*) calculated the heat of formation of the ether–chloroform compound as 6,000 cals., in good agreement with the result quoted. It may be noted that, from measurements of the heat absorbed on dissolving various primary alcohols in hydrocarbons, von Elbe (*J. Chem. Physics*, 1934, **2**, 73) concluded that the heat of formation of the hydrogen bond, with oxygen, in the associated forms of the alcohols, was about 11,000 cals.

The tetrahalogeno-methanes show less tendency to form compounds with ethers than do the corresponding trihalogeno-derivatives; nevertheless, the polarisation measurements indicate that molecular compounds are formed in solution and that they probably involve a chemical, rather than a physical, type of union. The ease of compound formation is greater for carbon tetrabromide than for the tetrachloride, this being opposite to the order for the trihalogenomethanes. Apart from formulæ including singlet linkages, which involve the attachment of five groups to, or the presence of a "lone" electron on, the carbon atom, the only reasonable "classical" structure of the molecular compounds is $R_2O{\rightarrow}X{-}CX_3$. Such a formula makes the halogen bicovalent, and requires it to have a valency group of ten electrons : a similar condition is supposed to apply in the polyhalides and in other compounds (Sidgwick, "Electronic Theory of Valency," 1929, p. 293). The tendency to form polyhalides increases in the order $Cl < Br < I$, which is the same, at least as far as chlorine and bromine are concerned, as that for the carbon tetrahalides to form compounds with ethers. Carbon tetraiodide is unstable and could not be studied in this work.

The dipole moment of the new bond in the R_2O,CX_4 compounds, as with the R_2O,CHX_3 compounds, is only about 0·5 *D*—the moment of, *e.g.*, $(C_2H_5)_2O,CCl_4$ is 1·47—and so the linkage cannot be a complete one. This linkage may, like the hydrogen bond, result from a combination of two resonating states, but any definite formulation must, for the present, be regarded as speculative.

Hexachloroethane behaves in a manner analogous to carbon tetrachloride, giving a mass-action constant of the same order of magnitude for its combination with ethyl ether; the compounds formed may be formulated in a similar way for both cases.

A fundamental assumption, made as the basis of the calculations in this paper, is that dielectric polarisations are strictly additive: this assumption is invariably made in the determination of dipole moments from measurements in solution, and there is little reason to doubt its general validity, but certain aspects of the matter require further consideration. In many of the mixtures studied, both constituents are polar, but this does not appear to affect the additivity to any serious extent, provided allowances be made for variations in the dielectric constants of the different mixtures. In order to test this point, measurements were made of a series of mixtures of ethylene dibromide and chloroform, which have similar dielectric constants ($\varepsilon = 4\cdot827$ and $\varepsilon = 4\cdot816$, respectively); the results are given below. The total polarisation of the dibromide (P) at the mol.-fraction (f) was calculated by means of the usual additivity equation, the polarisation of the chloroform being taken as constant (44·89).

Ethylene dibromide and chloroform.

f.	ϵ.	$d^{20^\circ}_{4^\circ}$.	P.	f.	ϵ.	$d^{20^\circ}_{4^\circ}$.	P.
0·00000	4·816	1·4890	—	0·53730	4·819	1·8786	47·98
0·07600	4·812	1·5466	47·68	0·65005	4·824	1·9551	48·10
0·18289	4·804	1·6264	47·39	0·79133	4·827	2·0481	48·19
0·30811	4·808	1·7175	47·50	0·91637	4·827	2·1367	48·06
0·41438	4·812	1·7933	47·84	1·00000	4·827	2·1805	48·30

It is seen that the polarisation of ethylene dibromide remains almost constant, and has the same value as in heptane (*viz.*, 48; Smyth and Kamerling, *J. Amer. Chem. Soc.*, 1931, **53**, 2988).

Further evidence that the polarity of the solvent does not seriously affect the additivity relationship, provided there be no chemical interaction between solvent and solute, can be obtained from various recorded measurements of polarisation and dipole moments (Graffunder and Heymann, *Z. Physik*, 1931, **72**, 744; Hassel and Uhl, *loc. cit.*; Wyman, *J. Amer. Chem. Soc.*, 1931, **53**, 3292: Åkerlöf, *ibid.*, 1932, **54**, 4125; Fairbrother, J., 1933, 1541; Higasi, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1934, **24**, 57; Jenkins, *loc. cit.*).

Association, of either a dipolar or a chemical type, may introduce errors, particularly if the extent of the association of a given substance varies appreciably with the nature of the medium. The substances used in the present work show little tendency to form polymerides, as may be seen from measurements of the polarisations in *cyclo*hexane or in benzene. It appears, therefore, that the assumption of additivity of polarisation is not liable to be a serious source of error.

SUMMARY.

(1) Measurements have been made of the dielectric polarisations of mixtures of ethyl, *iso*propyl, and $\beta\beta'$-dichlorodiethyl ethers with a number of halogen derivatives of methane and ethane, in which molecular-compound formation is expected to take place.

(2) From the molar polarisations of the separate constituents, it is concluded that compound formation in the cases considered involves the introduction of a new co-ordinate linkage which contributes to the dipole moment.

(3) A method for calculating the proportion of compound present in any mixture has been developed and used to determine mass-action constants; from the results it appears that, in the compounds of the type R_2O,CHX_3, co-ordination occurs between the oxygen atom and the hydrogen attached to carbon. Formulæ for the various compounds are proposed, based on the concept of wave-mechanical resonance; the " partial " nature of the new linkage can be explained in this manner.

(4) In a number of instances the total polarisation has been found to be a linear function of $[(\varepsilon - 1)/(\varepsilon + 2)]^2$, and it is concluded that if no chemical interaction occurs, polarisations are additive, even in mixtures of two polar substances, provided allowance be made for variation of dielectric constant.

Part II. The Structures of the Compounds of Acetone, Quinoline, and Dioxan with some Halogenomethanes.

In continuation of the foregoing work, similar studies were made with mixtures of (*a*) acetone and (*b*) quinoline with bromoform, chloroform, and carbon tetrachloride, and of 1 : 4-dioxan with the last two. Acetone was chosen because, like ethyl ether, it gives solid compounds with chloroform and carbon tetrachloride (see Wyatt, *Trans. Faraday Soc.*, 1928, **24**, 429; 1929, **25**, 49), and liquid mixtures with chloroform show abnormal behaviour. Quinoline gives a well-defined, pale-coloured compound, $3C_9H_7N,CHI_3$, with iodoform (Rhoussopoulos, *Ber.*, 1883, **16**, 202), in which it seemed possible that co-ordination occurred between the three nitrogen atoms and the iodine atoms (cf. Bennett and Willis, J., 1929, 256); co-ordination of this type would, of course, be different from that found with the ethers and the trihalogeno-methanes. Dioxan has no dipole moment, and its oxygen atoms might be expected to act as electron donors; it appeared, therefore, that measurements of mixtures with acceptor molecules would prove of interest.

EXPERIMENTAL.

The measurements of dielectric constants, densities, and refractive indices were carried out as already described.

Materials.—Acetone. The liquid was refluxed for several days with alkaline permanganate, distilled, dried over anhydrous potassium carbonate, and fractionated; b. p. 56·5°.

Quinoline. This was kept over caustic potash for some days, and then repeatedly distilled until colourless; b. p. 238°.

1 : 4-*Dioxan.* This was kept over sodium wire for a few days, and then carefully fractionated; b. p. 101·2—101·4°.

Results.

The results of measurements of mixtures of acetone, quinoline, and dioxan with *cyclo*hexane are given below, the symbols having the same significance as on p. 1713.

(I) *Acetone and* cyclo*hexane.*

f_2.	ϵ.	$d_{4^\circ}^{20^\circ}$.	P_2.
0·00000	2·032	0·7784	—
0·04599	2·397	0·7769	163·6
0·12911	3·128	0·7752	148·2
0·33234	5·529	0·7734	121·0
0·55818	9·333	0·7745	96·41
0·82135	15·56	0·7812	75·00
1 00000	21·17	0·7907	63·91

(II) *Quinoline and* cyclo*hexane.*

f_2.	ϵ.	$d_{4^\circ}^{20^\circ}$.	P_2.
0·00000	2·032	0·7784	—
0·11034	2·669	0·8146	131·2
0·23971	3·583	0·8577	125·8
0·39563	4·746	0·9089	115·1
0·62017	6·541	0·9807	102·5
0·76571	7·709	1·0253	96·14
1·00000	9·293	1·0933	86·68

(III) 1 : 4-*Dioxan and* cyclo*hexane.*

f_2.	ϵ.	$d_{4^\circ}^{20^\circ}$.	P_2.
0·00000	2·032	0·7784	—
0·26904	2·066	0·8287	25·01
0·52820	2·109	0·8891	24·83
0·73594	2·154	0·9465	24·79
1·00000	2·229	1·0335	24·76

The data for the other mixtures, in which compound formation was expected, are given in the subsequent tables; f_A and P_A represent the mol.-fractions and determined molar polarisations, respectively, of acetone, quinoline, and dioxan, and P_B refers to the other component. The symbols ϵ, d, P_{AB}, and K have the same meaning as before; the significance of K_2 and K_3 is explained later (p. 1721).

(IV) *Acetone and chloroform* (P_{AB} = 127—201).

f_A.	ϵ.	d.	P_A.	P_B.	K.	K_2.
0·00000	4·813	1·4890	—	44·89	—	—
0·03432	5·615	1·4677	147·1	47·88	—	—
0·07148	6·448	1·4441	134·9	50·38	1·00	0·45
0·17734	8·732	1·3757	112·2	55·32	0·95	0·48
0·31636	11·28	1·2831	93·6	58·86	0·54	0·42
0·53306	14·49	1·1327	78·14	61·17	0·37	0·42
0·72434	17·17	0·9958	70·57	62·44	0·31	0·67
0·85192	18·96	0·9019	67·06	63·0	0·26	1·02
0·94718	20·17	0·8307	64·85	62·2	0·41	5·48
0·97295	20·52	0·8115	64·30	62·9	0·31	7·89
1·00000	21·17	0·7907	63·91	—	—	—

(V) *Acetone and bromoform.*

f_A.	ε.	*d*.	P_A.	P_B.	f_A.	ε.	*d*.	P_A.	P_B.
1·00000	21·17	0·7907	63·91	—	0·12255	6·519	2·6600	126·1	52·84
0·95086	20·30	0·9138	64·97	66·65	0·05189	5·321	2·7988	144·3	50·47
0·26782	8·802	2·4050	99·0	58·91	0·00000	4·385	2·8904	—	46·36

(VI) *Acetone and carbon tetrachloride.*

0·00000	2·242	1·5940	—	28·28	0·57880	10·66	1·1858	88·83	62·51
0·04186	2·675	1·5686	170·3	32·94	0·75685	14·46	1·0304	76·21	66·6
0·09496	3·265	1·5352	157·7	38·12	0·89866	18·06	0·8952	68·44	68·5
0·20665	4·650	1·4624	134·9	46·77	0·97431	20·30	0·8178	64·98	68·9
0·35814	7·069	1·3565	114·0	56·20	1·00000	21·17	0·7907	63·91	—

(VII) *Quinoline and chloroform* (P_{AB} = 143—181).

f_A.	ε.	*d*.	P_A.	P_B.	*K*.	K_3.
0·00000	4·815	1·4890	—	44·89	—	—
0·03406	5·293	1·4716	131·7	46·52	2·86	13,000
0·09184	6·023	1·4420	124·3	48·74	1·33	300
0·19265	7·054	1·3939	113·6	51·36	0·84	21·3
0·31852	7·972	1·3367	104·9	53·48	0·53	2·99
0·49000	8·722	1·2661	97·34	55·18	0·36	0·61
0·65313	9·090	1·2052	92·65	56·18	0·34	0·29
0·82762	9·217	1·1459	89·04	56·28	0·20	0·10
0·93982	9·274	1·1113	87·41	56·27	0·15	0·06
1·00000	9·293	1·0933	86·68	—	—	—

(VIII) *Quinoline and bromoform.*

f_A.	ε.	*d*.	P_A.	P_B.	f_A.	ε.	*d*.	P_A.	P_B.
0·00000	4·385	2·8904	—	46·36	0·51647	8·121	1·8330	96·98	57·36
0·03334	4·792	2·8052	130·9	48·12	0·66448	8·571	1·5867	92·47	57·79
0·09453	5·407	2·6650	125·3	50·40	0·80604	8·859	1·3679	89·10	56·36
0·20107	6·384	2·4337	114·8	53·44	0·93979	9·054	1·1761	87·03	56·51
0·34593	7·738	2·1442	104·8	56·75	1·00000	9·293	1·0933	86·68	—

(IX) *Quinoline and carbon tetrachloride.*

0·00000	2·242	1·5942	—	28·28	0·53670	6·308	1·3108	103·2	—
0·03217	2·473	1·5765	142·8	—	0·67462	7·218	1·2429	96·67	—
0·12050	3·121	1·5282	132·9	—	0·83162	8·277	1·1646	90·47	—
0·24647	4·124	1·4607	122·9	—	0·95452	8·911	1·1132	87·49	—
0·38850	5·207	1·3863	111·8	—	1·00000	9·293	1·0933	86·68	—

(X) *Dioxan and chloroform.*

0·00000	4·816	1·4890	—	44·89	0·56717	3·208	1·2257	27·72	48·76
0·07138	4·502	1·4565	24·50	44·88	0·72172	2·877	1·1554	27·00	50·61
0·15588	4·215	1·4174	24·91	45·00	0·82232	2·632	1·1102	26·51	52·61
0·28102	3·829	1·3593	26·40	45·25	0·93494	2·378	1·0615	25·45	54·73
0·41580	3·518	1·2960	27·00	46·47	1·00000	2·229	1·0335	24·76	—

(XI) *Dioxan and carbon tetrachloride.*

0·00000	2·242	1·5940	—	28·28	0·62730	2·267	1·2622	25·42	29·37
0·08885	2·252	1·5509	26·24	28·42	0·77369	2·257	1·1751	25·19	29·65
0·18113	2·261	1·5032	26·42	28·64	0·86195	2·246	1·1203	24·99	29·71
0·29901	2·268	1·4442	26·01	28·80	0·93764	2·237	1·0728	24·87	29·81
0·46980	2·270	1·3520	25·65	29·07	1·00000	2·229	1·0335	24·76	—

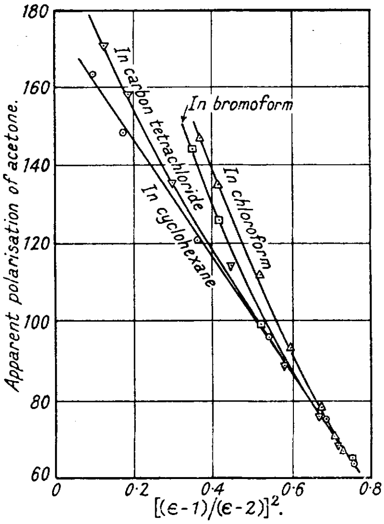
When the polarisations of acetone and quinoline were plotted against the respective mol.-fractions, as in Fig. 1 (Part I), the polarisations appeared to be less in chloroform and bromoform solution than in *cyclo*hexane; this discrepancy is undoubtedly due to the difference in the dielectric constants of the media, for when the polarisations of acetone are plotted against the corresponding value of $[(\varepsilon - 1)/(\varepsilon + 2)]^2$, as in Fig. 4, the increase of polarisation due to compound formation is evident (see also Kubo, *Bull. Inst. Phys. Chem. Res. Japan*, 1934, **13**, 1221). Owing to the large range of the dielectric constant, the uncertainties, particularly in connexion with the calculated polarisations of the molecular compounds, are considerable, and consequently the values of *K* are not very constant. The calculation was only attempted for mixtures of acetone and of quinoline with chloroform, and even in these cases the agreement is not very good; the figures in the column headed *K* are based on the assumption that an equimolecular compound is formed, K_2 on the assumption that the compound $COMe_2,2CHCl_3$,(P_{AB} = 190—246) is present exclusively, and K_3 that the compound $3C_9H_7N,CHCl_3$(P_{AB} = 316—453), analogous to the solid compound obtained with iodoform, is the product. It appears possible from the values of K_2 that the compound of acetone with 2 mols. of chloroform is formed in excess of the latter, but the compound with 3 mols. of quinoline is certainly not present to any appreciable extent in solution.

The best method for comparing the relative extents of compound formation was to plot the polarisations against the function of the dielectric constant, as in Fig. 4. With both acetone and quinoline the order of compound stability is chloroform > bromoform ⋙ carbon tetrachloride, so the two substances behave in a manner similar to ether.

DISCUSSION.

In the acetone molecule the oxygen atom presumably acts as donor, whereas the nitrogen atom has this function in quinoline; co-ordination evidently occurs through the hydrogen atom of CHX_3, as with the ether compounds, the extent of compound formation being greater with chloroform than with bromoform. The solubility of iodoform is so low in both acetone and quinoline that the measurements were of little value : it is evident that the corresponding compounds must be very unstable. From the quinoline solutions the compound $3C_9H_7N,CHI_3$ crystallised out very rapidly, and in view of the fact that there appears to be no evidence for the existence of this and analogous compounds in solution, the substance was analysed and its composition confirmed. It is evident from the results of this work that the separation of a solid compound from a liquid mixture cannot be regarded as evidence of the existence of that compound in solution; further, the formula of a solid molecular compound cannot always be used to throw light on its structure. The formula of the quinoline–iodoform compound would suggest co-ordination through the halogen atom, but this probably occurs only to a small extent. It appears that the substance $3C_9H_7N,CHI_3$ is to be regarded as a "lattice compound"; the large dimensions of the three iodine atoms cause the space in the solid to be divided up in such a manner that three quinoline molecules can fit into it so as to form a unit, without any transfer of electrons necessarily taking place from one molecule to the other. Bennett and Willis (*loc. cit.*) and Moore, Shepherd, and Goodall (J., **1931**, **1447**) have emphasised the fact that colour intensification is generally an indication of chemical union between two molecules; it is of interest that the compound $3C_9H_7N,CHI_3$ is less highly coloured than iodoform itself.

FIG. 4.



The acetone and quinoline compounds with chloroform, bromoform, and carbon tetrachloride may be formulated as the combination of two resonance states, in a manner similar to that described in Part I. Calculations show that in each case the moment to be attributed to the linkage, O→H for acetone, and N→H for quinoline, is about 0·5 *D*, so the linkages are similar to one another and to that formed by the oxygen atom of ether. It is of interest that the heat of formation of the N→H linkage in the molecular compounds formed between quinoline or *p*-toluidine and a phenolic compound is also of the order of 6,000 cals. (Glass and Madgin, J., 1934, 260, 1292), compared with 90,000 cals. of the ordinary N — H bond. It appears probable that a partial linkage, resulting from resonance, occurs in the well-known molecular compounds of nitro-derivatives and hydrocarbons; the heats of formation are of the order of 5,000 cals., or less (cf. Briegleb *et al.*, *Z. physikal. Chem.*, 1932, *B*, **19**, 255; 1934, *B*, **26**, 63), and in the case of trinitrobenzene it appears from measurements in benzene solution (cf. Jenkins, *Nature*, 1934, **134**, 217; Briegleb and Kambeitz, *Z. physikal. Chem.*, 1934, *B*, **27**, 11) that a linkage, having a moment of the order of 0·5 *D*, occurs in the molecular compound formed.

The results with dioxan were not as definite as was hoped. The polarisations of chloroform and carbon tetrachloride at infinite dilution in dioxan are 57·0 and 29·9 respectively, as compared with the values of 53·0 and 28·5 in *cyclo*hexane. The differences can hardly be attributed to differences in dielectric constant, which are very small, and so it may be attributed to the formation of a new linkage in compounds of the type $C_4H_8O_2,CHX_3$ and $C_4H_8O_2,CX_4$.

The polarisations of dioxan in chloroform and carbon tetrachloride increase at first with decreasing concentration, in harmony with the view that the afore-mentioned compounds are present, but as infinite dilution is approached, the values decrease again and finally become quite normal. A reasonable explanation of this behaviour is that in excess of CHX_3 or of CX_4 both oxygen atoms of the dioxan donate electrons to separate molecules of the former, giving $C_4H_8O_2,2CHX_3$ and $C_4H_8O_2,2CX_4$; the new linkages thus formed have dipole moments of the same magnitude acting in opposite directions, so that they tend to cancel. The CHX_3 molecular compounds can, of course, be readily formulated as the combination of two resonance states, as in the cases already considered.

SUMMARY.

(1) The study reported in Part I has been extended to mixtures of acetone, quinoline, or 1 : 4-dioxan with some halogenomethanes. Compound formation is shown to occur in a manner analogous to that found with ethers, a new linkage being formed between the constituent molecules.

(2) Dipole-moment and thermal data indicate that the linkage, generally involving coordinated hydrogen atom, is of a " partial " nature, in harmony with the proposed structures based on resonance. It appears that the same type of linkage occurs in compounds between nitrogenous bases and phenols, and between certain nitro-compounds and hydrocarbons.

(3) The danger of inferring the structure or presence in solution of a particular molecular compound from the formula in the solid state is emphasised, and the importance of colour is mentioned.

The authors' thanks are due to the Department of Scientific and Industrial Research for a maintenance grant to one of them (D. P. E.); to Dr. G. D. Reynolds for help in the design and construction of the apparatus; and to Messrs. Bowker and Sons, Ltd., Sheffield, for rhodium plating the test-condenser parts.

THE UNIVERSITY, SHEFFIELD. [*Received, September* 30*th*, 1935.]