125. *Formation and Structure of Some Organic Molecular Compounds. Part III. The Dielectric Polarisation of Some Solid Crystalline Molecular Compounds.*

By H. Kronberger and J. Weiss.

The mean dielectric constants of a number of polynitro-molecular compounds, of quinhydrone, and of their respective components in the solid state have been measured in the Hertzian region by an immersion method. This furnishes new evidence in favour of the ionic character of these molecular compounds which is also supported by the discussion of some of the other physical properties in the solid state.

In Parts I and II (J., **1942**, 245; **1943**; 462) it was suggested that the bonding in molecular compounds of molecules with systems of conjugated double bonds (*e.g.*, polynitro-compounds, quinones, etc.) is ionic or at least partly ionic in character. This was supported by the experimental evidence then available (*e.g.*, dipole moments, electrical conductivity) for certain molecular compounds in solution, but the fact that all such compounds in solution are to some extent dissociated into their components, together with their comparatively low solubilities, made it desirable to investigate some properties of the solid molecular compounds.

The *X*-ray work by Hertel *et al.* is compatible with the ionic structure, as was shown in Part I (*loc. cit.*), although it is, of course, practically impossible to deduce anything definite about the character of the bond in these complicated molecules from a determination of the crystal structures alone. Powell and Huse's work (J., **1943**, 153, 435) is not conclusive, particularly as they investigated only two compounds (which are not representative) and in both cases the donor molecule had an electronegative iodine atom as a substituent. Powell (Report on the Conference of the *X*-Ray Analysis Group of the Institute of Physics, *Nature*, 1944, **153**, 533) also has now concluded that some of the interatomic distances recorded are too small to be accounted for by van der Waals forces.

The m. p.'s of molecular compounds with large, polarisable molecules cannot be expected to behave in the same way as those of simple ionic crystals, although the m. p.'s of the molecular compounds are often higher than those of their components. Even simple metal halides with layer lattices often show comparatively low m. p.'s. According to Hund (*Z. Physik*, 1925, **34**, 833), this is due to the fact that in these cases the process of melting only means a destruction of the lattice into polar molecules without a separation into the ions. A similar state of affairs presumably exists in the case of some molecular compounds.

In the absence of any quantitative measurements on the hardness of molecular compounds, nothing can be said about this at present although it is clear, particularly from the extensive work of Reis and Zimmermann (*Z. physikal. Chem.*, 1922, **102**, 298), that in organic substances no simple relation exists between hardness and ionic structure. On the other hand, Kochendörfer (*Z. Krist.*, 1934, *A*, **97**, 263, 280; *Z. Physik*, 1937, **108**, 264) has recently found that the mechanical behaviour (*e.g.*, slip-hardening) of some organic crystals (*e.g.*, naphthalene) is quite similar to that of simple ionic crystals or metals.

The characteristic properties of ionic crystals are revealed by certain optical measurements (*e.g.*, absorption in the infra-red) and by their dielectric properties (cf. Born and Göppert-Mayer, " Handbuch der Physik," 2nd edn., XXIV/2), but very little information is yet available about the dielectric constants of organic crystals.

We now report some of the dielectric properties of a number of molecular compounds and of their components. We have actually measured the (mean) dielectric constants of these substances in the form of crystalline powders. The measurements were carried out by an immersion method which was originally proposed by Starke (*Ann. Physik*, 1897, **60**, 629, 641) and later used by Eucken and Büchner (*Z. physikal. Chem.*, 1934, *B*, **27**, 321) and by Højendahl (*K. Danske Videnske Selskab.*, 1938, **16**, No. 2) for the determination of dielectric constants of inorganic salts. However, the metal–glass cells described by these authors were found very unsatisfactory for our purpose and we have developed two new types of all-glass cells with burnt-on platinum electrodes. One of the cells could be used for very small amounts of substance (0·05—0·1 g.). Special care was taken to ensure a random distribution of the small crystals between the electrodes of the condenser cells. The (mean) dielectric constants determined in this way with different samples in different immersion liquids and in the two different cells were reproducible within ±0·5%. The measurements were carried out at a temperature of 17° ± 1·0° and at radio frequencies (about 800 kc./sec.), a double heterodyne method being used.

In Table I the (mean) dielectric constants (ε) of the substances investigated are given. The densities of the solids (*d*) were taken from the literature or determined by a flotation method (see Experimental). The molecular polarisations of the molecular compounds, $P^{(AB)}$, and of the components, $P^{(A)}$ and $P^{(B)}$, were calculated according to the formulæ of Lorentz–Lorenz and of Drude, (1) and (2), respectively :

$$P_{(L)} = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{d} = \frac{4}{3}\pi N \gamma_{(L)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$P_{(D)} = \frac{\varepsilon - 1}{3} \cdot \frac{M}{d} = \frac{4}{3}\pi N \gamma_{(D)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

M being the molecular weight, **N** Avogadro's number, and γ the total polarisability per molecule.

The formula (1) was derived for isotropic media or for complete random distribution, but modern theory generally favours (2), which, according to Mott and Gurney (" Electronic Processes in Ionic Crystals," Oxford Univ. Press, 1940), even in simple ionic crystals gives a much better account of the facts if the electronic

TABLE I.

Dielectric Constants and Corresponding Molecular Polarisations.

Substance.	*M.*	*d.**	ε.	$P_{(L)}$.	$P_{(D)}$.
Anthracene	178	1·245 [1]	3·46	64·1	116·7
Benzidine	184	1·39	3·61	61·6	115·3
3 : 4-Benzpyrene	252	1·351	3·52	85·1	156·7
Chrysene	228	1·27 [2]	3·32	78·1	138·6
Coronene	300	1·37	3·38	96·9	173·7
Quinol	110	1·33 [3]	3·58	38·0	71·2
20-Methylcholanthrene	268	1·277 [4]	3·53	96·1	177·0
Naphthalene	128	1·158 [1]	3·07	45·2	76·2
Phenanthrene	178	1·175	3·01	60·7	101·3
p-Phenylenediamine	108	1·205	3·95	44·4	88·0
Picric acid	229	1·764 [5]	3·59	60·1	112
Pyrene	202	1·27	3·21	67·5	117·3
Benzoquinone	108	1·31 [3]	3·12	34·1	58·1
s-Trinitrobenzene	213	1·687	3·00	50·4	84·0

	Molecular compound.	*M.*	*d.*	ε.	$P_{(L)}$.	$P_{(D)}$.
(A)	Anthracene–picric acid	407	~1·50	3·29	117	207
(B)	Anthracene–*s*-trinitrobenzene	391	1·40	3·25	119·6	209·7
(C)	Benzidine–*s*-trinitrobenzene	397	1·45	3·47	121·2	225·3
(D)	3 : 4-Benzpyrene–*s*-trinitrobenzene	465	1·475	3·20	133·3	231·3
(E)	Chrysene–*s*-trinitrobenzene	441	1·420	3·12	128·6	219·7
(F)	*Coronene–*s*-trinitrobenzene*	513	1·455	3·40	156·7	282·0
(G)	20-Methylcholanthrene–*s*-trinitrobenzene	481	1·446	3·32	145·0	257·0
(H)	Phenanthrene–*s*-trinitrobenzene	391	1·432	3·04	111·0	186·3
(I)	*p*-Phenylenediamine–*s*-trinitrobenzene	321	1·425	3·91	110·7	218·3
(J)	*Pyrene–*s*-trinitrobenzene*	415	1·50	3·20	117·0	202·7
(K)	Quinhydrone	218	1·401 [6]	4·12	79·3	162·0

* The densities were determined by the authors unless otherwise stated.

[1] Neuhaus, *Ber.*, 1934, **67**, 1627. [2] Iball, *Proc. Roy. Soc.*, 1934, *A*, **146**, 140. [3] Caspari, *ibid.*, 1932, *A*, **136**, 82. [4] Iball, *Z. Krist.*, 1936, **94**, 7. [5] Rudolfi, *Z. physikal. Chem.*, 1909, **66**, 705. [6] Siegmund, *Monatsh.*, 1909, **29**, 1091.

structures overlap each other, and this certainly holds for the ions present in the molecular compounds. Recently the matter has been discussed by Darwin (*Proc. Roy. Soc.*, 1943, *A*, **182**, 152), who concludes that Drude's formula gives a far better approximation also for an assembly of ionised molecules.

Table II shows that there are sometimes considerable differences between the molecular compounds and the sum of the polarisations of their respective components.

TABLE II.

Deviations from Additivity.

Comparison of the polarisations of the molecular compounds, $P^{(AB)}$, with the sum of the polarisations, $P^{(A)} + P^{(B)}$, of the components.

Molecular compound (see Table I).	$\{P^{(A)} + P^{(B)}\}_L$.	$P_{(L)}^{(AB)}$	$\Delta P_{(L)}$.	Deviation, %.	$\{P^{(A)} + P^{(B)}\}_D$.	$P_{(D)}^{(AB)}$	$\Delta P_{(D)}$.	Deviation, %.
(A)	124·2	117·0	−7·4	−5·9	229·0	207·0	−22·0	−10·0
(B)	114·5	119·6	5·1	4·5	200·7	209·7	9·0	4·5
(C)	112·0	121·2	9·2	8·2	199·3	225·3	26	13
(D)	135·5	133·3	−2·2	−1·6	240·7	231·3	− 9	− 5
(E)	128·5	128·6	0·1	0·1	222·6	219·7	− 2·9	− 1·3
(F)	147·3	156·7	9·4	6·8	257·7	282·0	24·3	9·9
(G)	146·5	145·0	−1·5	−1·0	261	257	− 4·0	− 2·0
(H)	111·1	111·0	−0·1	−0·1	185·3	186·3	1·0	0·5
(I)	94·8	110·7	15·9	16·8	172·0	218·3	46·3	27·0
(J)	117·9	117·0	−0·9	−0·8	201·0	202·7	1·7	1·0
(K)	72·3	79·3	7·0	9·7	129·3	162·0	32·7	25·3

DISCUSSION.

In the case of van der Waals forces one should get at least an approximate additivity of the molecular polarisations. If, on the other hand, the formation of the molecular compound is accompanied by electronic changes, *e.g.*, by an electron transfer of the type

$$\underset{\text{(donor)}}{\mathrm{A}} + \underset{\text{(acceptor)}}{\mathrm{B}} \rightleftarrows (\mathrm{A}^+\mathrm{B}^-) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

deviations from additivity must be expected. Table II shows that the deviations can be positive or negative in character. The approximate additivity observed in a few cases may then be regarded as more or less accidental (the positive and negative effects cancelling each other). These effects can be easily interpreted from a theoretical point of view. The measurements were carried out at radio-frequencies and sufficiently far from the m. p.'s for orientation (or rotation) effects to be neglected. In this case a lattice of ions is distorted in two different ways in an electric field : (i) Distortion of the electronic clouds of the ions by the external field, which is practically independent of the lattice—this gives rise to the electronic polarisation (P_E). (ii) Displacement of the positive and negative ions (in opposite directions) in the quasi-static external field and also a change of the total electric moment in the field of the ions of the lattice. Actually, every possible interionic or intramolecular vibration between the ions, atoms, and radicals gives rise to a corresponding term in the polarisation of the heavy particles, $P_{(IAR)}$. Thus :

$$P_{(IAR)} = P_I + P_A + P_R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

(cf. Errera, " Polarisation diélectrique," Paris, 1928; Fuchs and Wolf, " Dielektrische Polarisation," Leipzig, 1935).

The dielectric constant measured at radio-frequencies gives the total polarisation (P) according to

$$P = P_E + P_{(IAR)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The electronic polarisation (P_E) can be measured optically by means of the refractive index (in the near infrared), since the displacement of the electrons follows the rapidly varying field of the electromagnetic light waves. In the absence of vibrating ions, atoms, or radicals the last term in equation (5) disappears, and the dielectric constant in the Hertzian region should become identical with the one deduced from the refractive index (n) according to Maxwell's equation ($\varepsilon_0 = n^2$).

Intermolecular changes accompanying the formation of the molecular compounds are without appreciable influence on the electronic polarisation. However, any changes in the structure of the electronic clouds of the constituents must be of considerable importance. Whereas the two components enter as uncharged molecules, they are transformed into ions in the molecular compound. The fields of the positive and negative charges now present have a profound effect on the electronic clouds of these highly polarisable molecules. It is clear that the introduction of a positive charge will result in a " hardening " of the electron cloud which expresses itself in a decrease of the electronic polarisation and (electronic) polarisability (α), whereas a negative charge will cause a " softening " of the electron cloud of the molecule in which it is present.

The general effect of electric fields on the polarisability has been discussed by Hellmann (" Einführung in die Quantenchemie," Vienna, 1937, p. 172), who has also given an approximate expression (valid only for homogeneous fields). He has shown that the effective polarisability ($\alpha_{\text{eff.}}$) in the presence of a strong field depends on the polarisability (α) in the " unstrained " state and on the field strength. It is clear that $\alpha_{\text{eff.}} < \alpha$ for positive charges, whereas $\alpha_{\text{eff.}} > \alpha$ for negative charges. This effect has also been discussed by Born and Heisenberg (*Z. Physik*, 1924, **23**, 388) and by Smyth (" Dielectric Constant and Molecular Structure," The Chemical Catalog Co. Inc., 1931).

A second-order effect of a similar type is also known from the work of Fajans, Joos, and others (cf. Hellmann, *loc. cit.*), who found that the refraction of ions, *e.g.*, in ionic crystals, is not constant but changes on the formation of the crystal or of a polar molecule. It has been shown particularly by Neugebauer (*Z. Physik*, 1935, **94**, 655) that this is due to the influence of the field of the positive ion on the electronic cloud of the negative ion and *vice versa*. However, this effect is small compared with that in the case of the molecular-compound formation, where there is no field at all present at first and the change is from neutral to charged. In the case of the molecular compounds this will be only a second-order term somewhat decreasing the primary effect (as the positive charge of the cation is partly neutralised by the electron cloud of the anion and *vice versa*).

For the difference in the electronic polarisability (ΔP_E) on account of molecular-compound formation according to equation (3) one finds

$$\Delta P_E = P_E{}^{(AB)} - (P_E{}^{(A)} + P_E{}^{(B)}) = (P_E{}^{(A^+)} + P_E{}^{(B^-)}) - (P_E{}^{(A)} + P_E{}^{(B)}) \quad . \quad . \quad . \quad . \quad (6)$$

or

$$\Delta P_E = -\,\Delta P_E{}^{(A)} + \Delta P_E{}^{(B)} = -\,(P_E{}^{(A)} - P_E{}^{(A^+)}) + (P_E{}^{(B^-)} - P_E{}^{(B)}) \quad . \quad . \quad . \quad (6a)$$

where $P_E{}^{(A+)}$ and $P_E{}^{(B-)}$ denote the effective polarisations under the influence of the electric fields concerned. It is clear that $P_E{}^{(A+)} < P_E{}^{(A)}$ (" hardening ") and $P_E{}^{(B-)} > P_E{}^{(B)}$ (" softening ").

In the term $P_{(IAR)}$ (due to the heavier particles) it is useful to distinguish between intra- and inter-molecular (or interionic) changes of the polarisations due to the formation of the molecular compound. It is clear that here the main contribution will be due to the ionic polarisation, $P_I{}^{(AB)}$, of the ions formed, and that any intermolecular changes will be small compared with this term. We may, therefore, write as a first approximation for the difference of the vibrational polarisation terms, $\Delta P_{(IAR)}$, in molecular-compound formation

$$\Delta P_{(IAR)} = P_{(IAR)}{}^{(AB)} - [P_{(IAR)}{}^{(A)} + P_{(IAR)}{}^{(B)}] \approx P_I{}^{(AB)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

if we neglect the small differences in the intramolecular terms.

From equations (6) and (7) one obtains for the change of the total molecular polarisation on molecular-compound formation :

$$\Delta P = \Delta P_E + \Delta P_{(IAR)} \cong -\,\Delta P_E{}^{(A)} + \Delta P_E{}^{(B)} + P_I{}^{(AB)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The value of ΔP can be positive or negative, which is borne out by the experiments (Table II). Larger negative deviations are to be expected if the original donor molecule is comparatively small and more polarisable than the acceptor molecule.

The situation is essentially the same if only a partial electron transfer takes place, because it is not the true charge (e) which matters but the change of the electric moment (μ) formed from two adjacent ions in the mutual dielectric displacement (x) of the ions against each other (*i.e.*, $d\mu/dx = e_{eff.}$). It has already been pointed out that the electronic polarisations can be deduced independently from the refractive indices (n). A knowledge of the refractive indices of the molecular compounds would also allow one to determine directly the part (f_i) of the total polarisation which depends on the ionic vibrations and is given by the expression of Errera and Brasseur (*Physikal. Z.*, 1933, **34**, 368) :

$$f_i = (\varepsilon - n^2)/(\varepsilon - 1) \qquad \ldots\ldots\ldots\ldots \qquad (9)$$

which is free from any assumptions about the internal field.

The measurements of refractive indices were tedious. Eventually we tried a modification of Wood's method (*Phil. Mag.*, 1901, **1**, 624), briefly described in the Experimental. Although the measurements were satisfactorily reproducible, we often obtained only one or two of the refractive indices, which is probably due to a preferred orientation of the crystallites in the solid prisms. We hope to return to this in a later publication.

Another method for investigating the structure of crystalline molecular compounds would be to measure the change in the diamagnetic anisotropy occurring on the formation of the molecular compound. If one of the non-localised π-electrons is transferred, this should sometimes result in a decrease of the diamagnetic susceptibility. This was pointed out to one of us (J. W.) by Dr. Kathleen Lonsdale.

That the diamagnetic susceptibility of a molecular compound might sometimes be smaller than that of the sum of its components follows also from the above discussion for those cases where a decrease of the electronic polarisation has been observed, on the basis of the work of Kirkwood (*Physikal. Z.*, 1932, **33**, 57; see also Muller, *Proc. Roy. Soc.*, 1936, *A*, **154**, 624), who has established a relationship between polarisability and diamagnetic susceptibility. Some indication of these effects can be got from measurements by Krishnan and Banerjee (*Phil. Trans.*, 1935, **234**, 265) and Banerjee (*Z. Krist.*, 1939, *A*, **100**, 316), which are given in Table III

TABLE III.

Substance.	Mean (g.-molecular) diamagnetic susceptibility, $-\chi \times 10^6$.	Deviation, %.	Substance.	Mean (g.-molecular) diamagnetic susceptibility, $-\chi \times 10^6$.	Deviation, %.
p-Benzoquinone ...	27·0		Perylene	95·5	
Quinol	64·0		*s*-Trinitrobenzene	55·7	
	Sum : 91·0			Sum : 151·2	
Quinhydrone	92·0 $\}\Delta = 1{\cdot}0$	1·1	Perylene–*s*-trinitrobenzene	142·2 $\}\Delta = -9{\cdot}0$	−6·3

and show a small (positive) deviation in the case of quinhydrone (as might be expected from our own results) but a larger negative deviation in the case of the more polarisable perylene in the perylene–*s*-trinitro-molecular compound.

EXPERIMENTAL.

Preparation of Substances.—The component substances were ordinary purified specimens. Coronene was recrystallised several times from boiling benzene. Benzpyrene and methylcholanthrene were kindly supplied by Prof. J. W. Cook. Except (F) and (J), which are new, the molecular compounds (all 1 : 1) were prepared according to the following references, the letters referring to Table I : (A) Behrend, *Z. physikal. Chem.*, 1894, **15**, 186. (B) Sudborough, J., 1916, **109**, 1344. (C) Noelting and Sommerhof, *Ber.*, 1906, **39**, 77. (D) Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1938, **60**, 1665. (E) Sudborough (*loc. cit.*). (F) *Coronene–s-trinitrobenzene*, from boiling benzene, decomposes before melting (Found : N, 7·9. $C_{24}H_{12},C_6H_3O_6N_3$ requires N, 8·1%). (G) Fieser and Hershberg, *loc. cit.*, p. 945. (H) Sudborough (*loc. cit.*). (I) Noelting and Sommerhof (*loc. cit.*). (J) *Pyrene–s-trinitrobenzene*, from benzene, m. p. 248° (Found : N, 10·2. $C_{16}H_{10},C_6H_3O_6N_3$ requires N, 10·0%). (K) Cf. Siegmund, *Monatsh.*, 1909, **29**, 1091.

Measuring Cells.—The dielectric constants were measured by the change of capacity which the substances under investigation produced in the condenser-cell. The substances were available in the form of fine crystalline powders; this necessitated the use of an immersion method. The first experiments, carried out with a cell according to Eucken (*loc. cit.*), proved unsatisfactory because (i) it was difficult to obtain for the leads an absolutely tight insulating seal which was not attacked by the organic solvents used, and (ii) the brass container had a large heat capacity and a comparatively large coefficient of expansion.

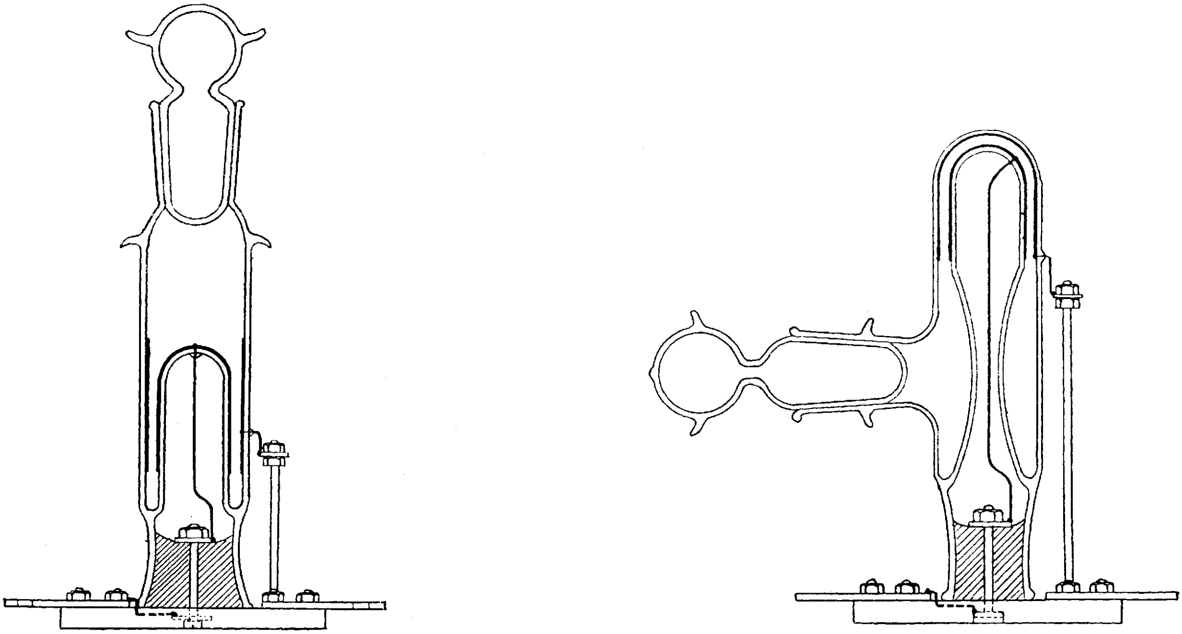
A new type of cell was therefore developed : two forms of it are shown in Figs. 1*a* and 1*b*. The vessels were made of Hysil glass and parts of the inner walls were platinised, forming the electrodes. The outer electrode was kept at A.C.–earth potential. The leads were brought out through seals in the glass and terminated on two brass plates on the base. Cell 1*a* had the advantage that any small air bubble accidentally present in the liquid was well outside the electrodes when the cell was in either the upright or the inverted position. Cell 1*b* was designed for substances of which only small quantities (less that 0·1 g.) were available. The vessels were mounted on a special type of holder which enabled the cells to be turned upside-down into accurately reproducible positions. Since the total capacity of cell and holder was slightly different for either position, due to the difference in the geometrical configuration of the conductors, an adjustable, earthed, brass strip was arranged to act as an automatic trimmer, so that the total capacity was independent of the position of the cell. The leads from the holder to the oscillator were stout, bare, copper wires of about 4 mm. thickness. The connection was rigid and kept as far away from earth as possible.

Circuit (Fig. 2).—A double-heterodyne method was used for measuring the change of capacity of the cell. D_1 and D_2 were two Dynatron oscillators working at about 800 kc./sec. The wave form was checked on a cathode ray oscillograph and found to be practically free from harmonics. C was a cumulative grid detector coupled extremely loosely to the oscillators, in order to prevent any reaction between the latter. With the coupling used, any small change, or further reduction of the coupling had no effect on the oscillators. T was a General Radio Company's Audio Oscillator, Type 813A, 1002 c./sec. ± 0·1%. In order to measure with sufficient accuracy the small changes of the capacity of the cell C_1, the following method was adopted : C_2 was a precision variable air condenser (linear capacity) ranging from 55 $\mu\mu$ F. to 2039 $\mu\mu$ F. (General Radio Company). The scale was divided into 100 parts, tenths being read by means of a vernier.

This condenser was connected in series with a small, fixed, mica condenser (C_3). By suitably choosing the value of this condenser, the measuring condenser could be made to cover the entire variation of the capacity of the cell. All the condensers were carefully shielded; hand capacity was completely absent. The changes in the measuring cell were compensated by adjustment of the precision condenser C_2.

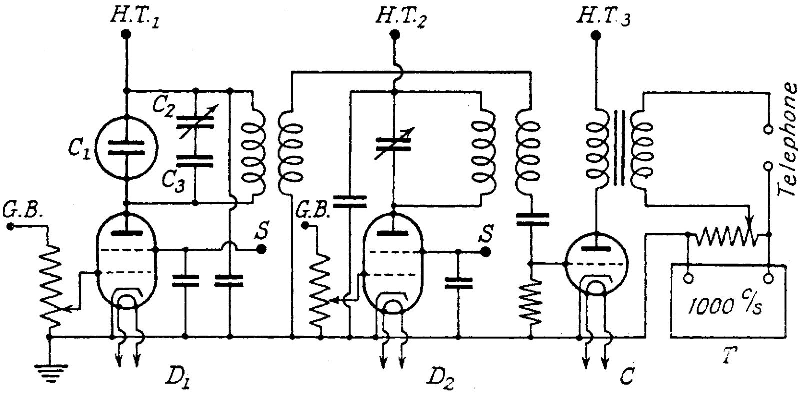
FIG. 1*a*. FIG. 1*b*.

Condenser cells.



(*a*) (*b*)

FIG. 2.



Analysis shows that any two changes $\Delta_1 C_1$ and $\Delta_2 C_1$ in the capacity of the cell and the corresponding two changes $\Delta_1 C_2$ and $\Delta_2 C_2$ in the measuring condenser are connected by the relation

$$\Delta_1 C_1/\Delta_2 C_1 = \Delta_1 C_2[(C_2 + C_3) + \Delta_2 C_2]/\Delta_2 C_2[(C_2 + C_3) + \Delta_1 C_2] \quad . \; . \; . \; . \; . \; . \; . \quad (10)$$

The dielectric constant ε_1 of an unknown liquid is then given by

$$(\varepsilon_1 - 1) = \Delta_1 C_1(\varepsilon_2 - 1)/\Delta_2 C_1 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (11)$$

where $\Delta_2 C_1$ is the change of capacity produced by a substance of known dielectric constant ε_2. The conductivities of the solid substances and of their solutions in the immersion liquids were found to be so low that no correction had to be applied for damping. The rest of the circuit is of conventional design, care being taken to have all connections rigid. A drift of frequency due to heating of various circuit elements was eliminated by carefully heat-insulating the components involved. It was possible to keep the frequency stable to 50 cycles for long periods; the frequencies were checked, however, during and after each measurement by using one empty cell as a dummy condenser.

Procedure.—The three oscillators were switched on and left for about 1 hour before any measurements were taken. With the cell on the holder, the measuring condenser was set to a convenient value (nearly at maximum capacity) and this was taken as " zero ". The same " zero " was used for all the experiments. The second oscillator was then adjusted until the lower heterodyne note appeared and produced slow beats (5/sec.) with the tuning-fork oscillator. In order to calibrate the instrument, *i.e.*, to determine the constant ($C_2 + C_3$) in the above expression, two measurements were carried out with pure benzene and ethyl ether. The correctness of the value of the constant was checked on chloroform. The values of the dielectric constants used were those given by Hartshorn and Oliver (*Proc. Roy. Soc.*, 1929, *A*, **123**, 664) and Højendahl (*Z. physikal. Chem.*, 1932, *B*, **20**, 54).

In order to carry out measurements with solids, the crystalline substance was filled into the cell, so that the space between the two electrodes was approximately filled. The immersion liquids were then added. Light petroleum, ether, benzene, and nitrotoluene were found suitable, and the value obtained for the dielectric constant of any particular substance was independent of the immersion liquid. Great care had to be taken that no air was trapped by the particles or absorbed on their surface. The composition of the immersion liquid was now adjusted until its dielectric constant was the same as that of the solid. This was done by tilting the cell on the holder through 180° so that the solid dropped out of the space between the electrodes. If this did not produce any change in the frequency, the dielectric constants of the solid and of the immersion liquid were taken to be equal. At the balance position, the cell was tilted a few more times in order to ensure that a random distribution of the crystals was measured.

Measurement of Refractive Indices.—Wood's (*loc. cit.*) method was used but a simpler and more rigid type of prism was developed. It consisted of a strip of plate glass, 1 mm. thick and 1·5 cm. wide, bent to form a prism, the refracting angle lying between 3° and 6°. The substance was melted in near the refracting edge, the prism placed on a spectrometer table, and the refractive index determined in the usual way. When measuring the refracting angle, use was made of the reflections from both surfaces, in order to check the parallelism of the plate glass. Only that part of the prisms near the refracting edge was used, the rest being screened off by paper. For each substance, two measurements were made in one prism, the substance being remelted after the first measurement. The procedure was then repeated, for the same substances, with another prism of different refracting angle.

Determination of Densities.—A flotation method was used. The substances were kept under a vacuum for an appreciable time, and the immersion of the solids also took place under a vacuum.

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