31. *Studies on Hydrogen Cyanide. Part XIII. The Dielectric Constant of Anhydrous Hydrogen Cyanide.*

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The dielectric constant of anhydrous liquid hydrogen cyanide has been measured, together with its variation with temperature. Both the dielectric constant and the temperature coefficient are abnormally high, and are interpreted in terms of the formation of transitory linear polymers of high dipole moment whose mean length is shortened by thermal agitation with increasing temperature. The effect is probably characteristic of this type of association.

As an ionising solvent (J. E. Coates and Taylor, J., 1936, 1245, 1495) liquid hydrogen cyanide is exceptional in the magnitude of its dielectric constant, which is the largest yet recorded for any liquid. The lack of agreement between the earlier measurements of the dielectric constant by Fredenhagen and Dahmlos (*Z. anorg. Chem.*, 1929, **179**, 77), Bredig (*Z. angew. Chem.*, 1923, **36**, 456) and Schlundt (*J. Physical Chem.*, 1901, **5**, 191) showed the need for a redetermination of this constant.

Probably the most satisfactory way of measuring the dielectric constant of highly polar liquids is Wyman's modification (*Physical Rev.*, 1930, **35**, 623) of Drude's method. This makes use of the dependence of the natural frequency of a resonator upon the dielectric constant and magnetic permeability of the medium surrounding it. Since the magnetic permeability of most liquids does not differ appreciably from unity, the natural frequency of any given resonator immersed in various liquids is a function in most cases of their dielectric constants only. Hence, if f_1 and f_2 are the natural frequencies of a resonator immersed in media of known and unknown dielectric constants, respectively, ϵ_1 and ϵ_2, then $\epsilon_2 = \epsilon_1(f_1^2/f_2^2)$. As shown by Wyman (*loc. cit.*), errors occur if the medium has appreciable conductance, but are negligible in the case of water at frequencies of the order of 10—100 megacycles/sec. For hydrogen cyanide at the same frequencies, with its lower conductance and higher dielectric constant, errors due to this cause would be even smaller. A practical advantage of the method over alternative procedures involving the direct measurement of capacity is the greater ease and accuracy with which frequency is measured. A further point is the elimination of the generally uncertain corrections for lead reactance which are necessary when the usual condenser cell methods are used.

EXPERIMENTAL.

Resonators.—These (*A*, *B*, *C*, *D*) were four flattened three-turn coils of thick brass wire (0·3 cm. diameter) designed to have as large a self-capacitance as possible, and to have a small electrostatic field. Resonators *A* and *D* were rhodium plated. Fig. 1 is a full-scale illustration of the smallest resonator *A* and shows the general form of the coils. They were robust, and their natural frequencies remained unchanged throughout the work, the natural air frequencies ranging from 228·4 to 396·2 megacycles/sec. Such high frequencies were not measured directly, the resonators being calibrated with conductivity water in which the frequencies were about nine times smaller. Hence the dielectric constant of hydrogen cyanide was derived from the water values, which were measured to an accuracy of 0·2% by Wyman (*loc. cit.*) and Drake, Pierce, and Dow (*ibid.*, p. 613). The resonator in use was suspended by a thin silk thread in the liquid, which was contained in a long vertical glass tube. The latter was fitted with a stirrer and a thermometer (graduated in 0·1°) which had been calibrated at the National Physical Laboratory. This assembly was immersed in a large unsilvered Dewar vessel containing light petroleum, cooled when required by the addition of solid carbon dioxide. The apparatus was placed about 20—30 cm. from the inductance of a 10-watt oscillator which covered a frequency range of 10—150 megacycles/sec.

Procedure.—This consisted in swinging the oscillator tuning condenser backwards and forwards and noting the vernier reading at which the anode current meter indicated maximum absorption of radiation by the resonator. The oscillator was then immediately calibrated by beating with the harmonics of a 1·750 megacycles/sec. quartz crystal oscillator of low power and very low temperature coefficient (AT-cut). By an interpolation, the frequency at which maximum absorption occurred could be determined with an accuracy of about 0·1%. During measurement, care was taken not to allow the resonator to remain in the state of resonance for more than a second, in order to eliminate the possibility of error due to heating of the liquid in contact with it. Measurements with this apparatus were made at three regions of temperature. In Table I, f_a is the resonant frequency in air, *T* the temperature, and ϵ the measured dielectric constant of hydrogen cyanide.

TABLE I.

Resonator.	f_a(Mc./s.).	*T*.	ϵ.	Resonator.	f_a(Mc./s.).	*T*.	ϵ.
A	396·2	17·1°	119·5	C	272·3	$16{\cdot}6_5$°	120·6
		−12·1	200·6	D	228·4	17·7	118·8
		−13·3	205·6			− 2·2	164·7
B	317·1	$17{\cdot}5_5$	118·9			−13·3	205·0

A difficulty of this method of measurement is that of temperature control, particularly at the lower temperatures. To measure more accurately the variation of dielectric constant with temperature another method was used. This consisted in measuring the capacity of a condenser filled with hydrogen cyanide at various thermostatically controlled temperatures. In principle the method was the same as that described by Sugden (J., 1933, 768), any novel features being described below.

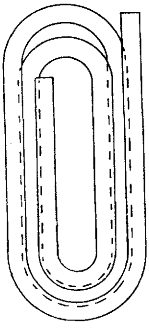


FIG. 1.

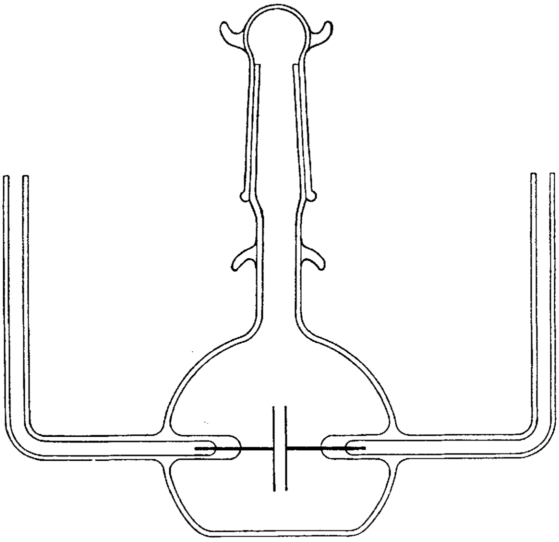
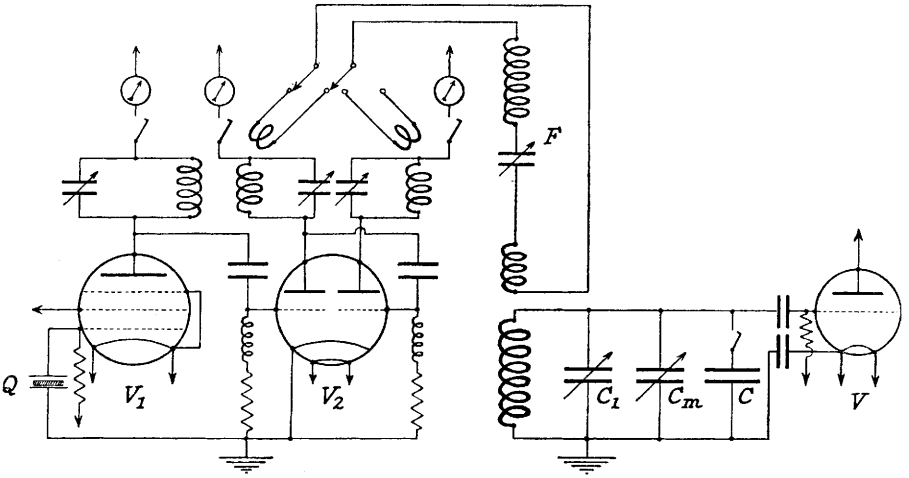


FIG. 2.

Condenser Method.—The condenser (Fig. 2) was made of Jena 16^{III} glass to avoid risk of polymerisation of the hydrogen cyanide by alkali in ordinary soft glass. It was fitted with robust bright platinum electrodes, the electrode leads being well separated to reduce inter-lead capacity. The air capacity was 1·65 μμF., and the volume about 120 c.c. The condenser was held by an ebonite clamp in a paraffin thermostat, totally enclosed by a four-inch thickness of cork slab, and controlled down to −30° to within ±0·01°. Cooling was effected by a ¾ H.P. refrigerator unit. The temperature of the thermostat was measured by a thermometer calibrated at the N.P.L., read by a periscope.

Electrical Apparatus.—This had a few new features. The condenser containing the hydrogen cyanide could be connected in parallel with an accurately calibrated, variable condenser which formed part of a resonant circuit loosely coupled to an oscillator. Its capacity was measured in the usual way by observing the change in capacity of the measuring condenser necessary to restore the circuit to resonance when the liquid dielectric condenser was switched in parallel. The apparatus was designed with the object of minimising the errors of measurement associated with this method. These are caused by: (1) Variation of frequency of the oscillator, (2) variation of the inductance of the resonant circuit, and the capacity of its various leads, (3) the inductance of the leads in the resonant circuit and measuring condenser, (4) the conductance of the dielectric in the cell, (5) the earth capacity of the cell, (6) variation of the temperature of the cell. The circuit is shown in Fig. 3. The first source of error was eliminated by the use of an oscillator controlled by a quartz crystal of low temperature coefficient, followed by a frequency multiplier. A quartz oscillator has the advantage of very good frequency stability, and the circuit was designed to give a number of harmonics any one of which may be amplified, filtered out, and fed into the resonant circuit. The frequency of the crystal was 79·56 kc./sec., thus the second harmonic had a pulsatance of 10^6. A voltage stabiliser was used in the power supply to keep the oscillator output reasonably constant. The resonant circuit was mounted firmly, connections being made by thick copper wires or tubes supported by porcelain insulators in order to reduce error (2) and also to avoid errors due to resistance of leads. Error (3) was minimised by mounting the measuring condenser as close as was practicable to the thermostat tank containing the cell, so that the leads to the latter from the measuring condenser were as short as posible. The cell was put in circuit by dipping a short length of 36 S.W.G. copper wire into the mercury in the " live " arm of the cell (see Sugden, *loc. cit.*). The attainment of resonance was detected by means of a valve voltmeter connected to a 2-valve D.C. amplifier: this method was highly sensitive. Error (4) was minimised by purifying the dielectric liquid until its conductance was very small, and by using a cell of as small a capacity as was consistent with accurate capacity measurements. The cell was firmly clamped in the thermostat in an accurately reproducible position, thus ensuring that the earth capacity of the cell, error (5), depended only on the cell dielectric. The measuring condenser C_m was a dual-range logarithmic-law type of maximum capacity 1000 $\mu\mu$F. supplied by Messrs. H. W. Sullivan. A logarithmic-law condenser was chosen in preference to one obeying a linear capacity law, since both large and small capacities may be determined with equal accuracy by choosing a suitable part of the condenser scale for the determination. The condenser was calibrated by the National Physical Laboratory at every 5° on both ranges, and at the same time the inductance was determined at various points on both ranges. Hand capacity effects were completely absent. The condenser C_1 served to adjust the position of resonance to a suitable point on the scale of C_m, and also served a purpose mentioned later.

FIG. 3.



Q, 79·56 kc./sec. quartz, crystal (AT cut).
F, Harmonic filter.
C_1, 50—1000 $\mu\mu$F. variable condenser.
C_m, Sullivan 100—1000 $\mu\mu$F. dual range measuring condenser.
C, Dielectric constant cell.
V, Mullard PM2DX.
V_1, Mullard PM24M.
V_2, Raytheon type 53.

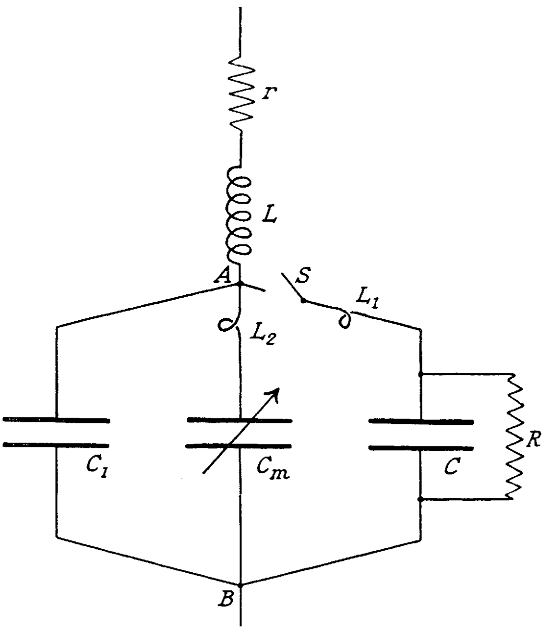


FIG. 4.

The cell was calibrated, and the earth capacity correction determined, by the method used by Lattey and Gatty (*Phil. Mag.*, 1929, **7**, 985) and Lattey and Davies (*ibid.*, 1931, **12**, 1111). The calibration data were: (1) the data of Table I; (2) chlorobenzene, $\epsilon_{25} = 5{\cdot}612$; (3) benzonitrile, $\epsilon_{25} = 25{\cdot}19$; (4) nitrobenzene, $\epsilon_{25} = 34{\cdot}75$; (5) water, $\epsilon_{25} = 78{\cdot}54$. The dielectric constants of (2), (3), and (4) were accurately determined by Sugden (*loc. cit.*) and that of water by Drake, Pierce, and Dow, and by Wyman (*locc. cit.*). The corrections due to dielectric leakage and to lead inductance were evaluated by the method given by Sugden, with two modifications. In the series resonant circuit (Fig. 4), L and r are respectively the inductance and resistance of the resonance coil, which is tuned by three condensers; C represents the capacity of the experimental cell, and L_1 the inductance of its leads between the points A and B, which were the terminals of the measuring condenser. The shunt resistance due to the conductance of the dielectric is represented by R; L_2 and C_m represent the inductance and capacity of the measuring condenser, and C_1 the effective capacity of the loading condenser. The switch S being opened, the circuit is retuned to resonance by altering C_m to a new value C'_m, where $C'_m = C_m + C_{\text{obs.}}$, and $C_{\text{obs.}}$ is the observed capacity of the experimental cell. L'_2 represents the inductance of the measuring condenser at the setting C'_m. Sugden connects $C_{\text{obs.}}$ with the true capacity C by the equation:

$$C_{\text{obs.}} = C\{1 + \delta_1(1 - a) + \delta_2 - (\delta'_3C'_m - \delta_3C_m + a\delta_1C_m + a\delta_1C_1)/C\},$$

where $\delta_1 = 1/(R^2C^2\omega^2)$; $\delta_2 = L_1C\omega^2$; $\delta_3 = L_2C_m\omega^2$; $\delta'_3 = L'_2C'_m\omega^2$; $a = C(C_0 - C)/C_0^2$; $C_0 = C_1 + C_m + C$; $\omega =$ angular frequency.

The inductance of the measuring condenser varied with its setting, to the extent of about 30% on one range and about 5% on the other. Sugden found a variation of about 10% for his condenser, and assumed L_2 to be constant in deriving his final equation connecting C and $C_{\text{obs.}}$. Calculation showed that L_2 was responsible for a large fraction of the total correction, and it was therefore decided to take this variation into account. This leads to an equation slightly different from Sugden's, *viz.*,

$$C = (C_{\text{obs.}} + C'_m\delta'_3 - C_m\delta_3)/(1 + \delta_1 C/C_0 + \delta_2)$$

From the form of the above equation it is evident that, by choosing suitable values for the frequency ω and the total capacity of the circuit C_0, the errors due to the inductance of the leads and the conductance of the dielectric may be made to cancel, so that $C_{\text{true}} = C_{\text{obs.}}$. This occurs when

$$\omega^{-4} = R^2C_0\{L'_2(C_m + C)^2 - L_2C^2_m - L_1C^2\}$$

For example, when the experimental cell contained water at 25°, its capacity was about 140 $\mu\mu$F. and its resistance about 72,500 ohms. If C_m is set to about 370 $\mu\mu$F., when its inductance is 185 e.m.u., then C'_m must be 510 $\mu\mu$F. and its inductance is 182 e.m.u. L_1 was constant for all experiments and was found from many observations on the same cell at frequencies from 11 to 44 × 10^6 radians per second to be 780 e.m.u. Inserting these values in the above equation, we have $\omega^{-4} = C_0 \times 3{\cdot}54 \times 10^{-8}$, which is balanced when $\omega = 2{\cdot}5 \times 10^6$ and $C_0 = 724$ $\mu\mu$F. The fifth harmonic of the crystal oscillator was therefore used, and C_1 was adjusted so that $C_0 = 724$ $\mu\mu$F.; the errors then cancel and any uncertainty in the evaluation of the residuals has negligible effect.

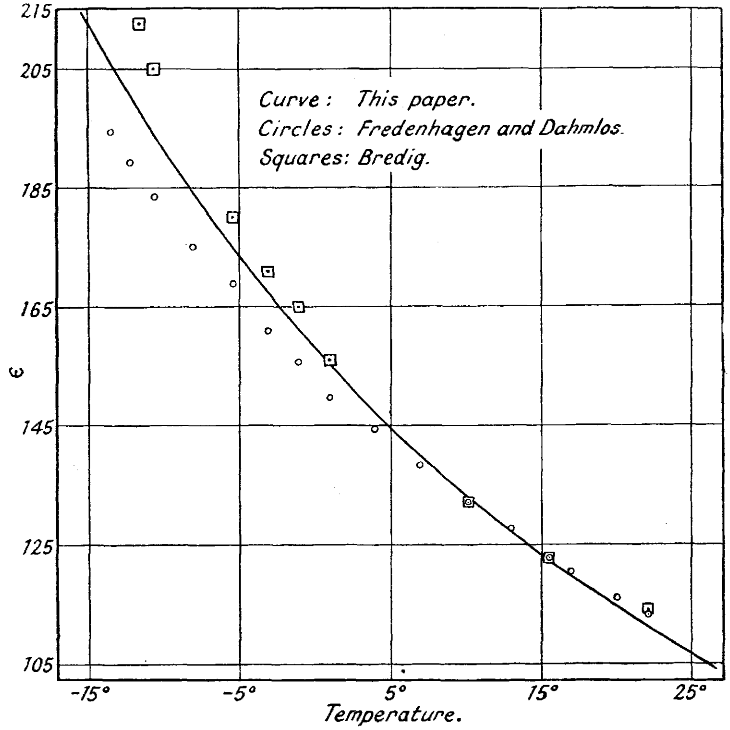


FIG. 5.

Purification of Liquids.—Chlorobenzene was repeatedly fractionated over phosphoric oxide until the main fraction boiled within 0·1°. Finally it was fractionated alone; $D^{25°}_{4°}$ 1·1010.

Benzonitrile was purified according to Sugden's method (*loc. cit.*), and had a specific conductance $\kappa_{25} = 7 \times 10^{-8}$ mho; $D^{25°}_{4°} = 1{\cdot}0004$.

Nitrobenzene.—Two specimens were prepared by different methods, A by steam distillation of a commercial sample, drying and fractional freezing over phosphoric oxide, followed by drying some weeks over phosphoric oxide; and B by nitrating A.R. benzene with the theoretical quantity of nitric acid and drying it over phosphoric oxide as above. Both specimens were distilled several times in a vacuum over phosphoric oxide and finally twice alone in a vacuum (without ebullition). The specific conductances were 8 × 10^{-9} (A) and 4 × 10^{-9} (B) mho at 25°. Neither specimen wetted the surface of the glass flask containing it; $D^{25°}_{4°}$ (A) = 1·1983.

Water. "Equilibrium" water was used.

Hydrogen cyanide. This was prepared by Coates and Taylor's method (*loc. cit.*) and had a specific conductance at 180° of less than 3×10^{-7} mho; f. p. −13·27° (Giauque and Ruehrwein, *J. Amer. Chem. Soc.*, 1939, **61**, 2626, found −13·24°).

Results.—The temperature variation of the dielectric constant of hydrogen cyanide was found to follow the equations:

(1) Between the f. p. and +18°, $\log_{10} \epsilon_t = 2{\cdot}199 - 0{\cdot}0079t + 5 \times 10^{-5}t^2$.
(2) Between +18° and the b. p., $\log_{10} \epsilon_t = 2{\cdot}1869 - 0{\cdot}00633t$.

Table II gives at various temperatures the smoothed values of the dielectric constant, which are probably correct to 0·5%. Fig. 5 shows that these values agree moderately well with those of Bredig (*loc. cit.*) and of Fredenhagen and Dahmlos (*loc. cit.*) in the higher temperature range, but they deviate markedly from the earlier values (especially those of the latter) at lower temperatures. There is no doubt that the technique of their electrical measurements falls short of that employed in the work here reported (particularly with respect to the neglect of residuals).

TABLE II.

Temp.	−15°*	−13·3°†	−10°	−5°	0°	5°	10°	15°	18°	20°	25°	25·7° ‡
ϵ	213·2	205·5	191·9	173·7	158·1	144·8	133·3	123·5	118·3	114·9	106·8	105·7

* Supercooled. † F. p. ‡ B. p.

Discussion.—The very high dielectric constant of liquid hydrogen cyanide has been explained in terms of hydrogen-bond formation which in this case results in *linear polymerisation*, and the existence in the liquid at any instant of a number of molecular units whose dipole moment is about 2—4 times that of the single molecules (Pauling, "The Nature of the Chemical Bond," 2nd Edn., 1940, p. 294; Kumler, *J. Amer. Chem. Soc.*, 1935, **57**, 600). The dipole moment of hydrogen cyanide, measured in the gas phase, is 2·93D. (Smyth and McAlpine, *ibid.*, 1934, **56**, 1679), hence molecular units with a dipole moment of between 6 and 12 are to be expected in the liquid. A slight degree of association has been observed in the gas phase by vapour-density measurements (Giauque and Ruehrwein, *loc. cit.*). In the liquid a greater degree of order is to be expected, particularly at low temperatures. Hence the normal influence of temperatures on dielectric constant would in this case be greatly amplified. In Table III the approximate temperature coefficients of the logarithms of the dielectric constants of a number of liquids are compared. The normal figure is about −0·0020 to −0·0025, whereas the value found for hydrogen cyanide is −0·0079, nearly four times as great. A similar effect is shown—though to a less extent—by hydrogen fluoride, with an intermediate coefficient of −0·0045, and some degree of linear association is very probable in this case also.

TABLE III.

Substance.	$-d \log_{10} \epsilon/dT$.	Reference.
Hydrogen cyanide ...	0·0079	
Hydrogen fluoride ...	0·0045	Fredenhagen and Dahmlos, *Z. anorg. Chem.*, 1929, **178**, 272.
Hydrogen chloride ...	0·0027	Glockler and Peck, *J. Chem. Physics*, 1936, **4**, 658.
Water	0·0020	Wyman (*loc. cit.*); Drake, Pierce, and Dow (*loc. cit.*).
Methyl alcohol	0·0023	Åkerlöf, *J. Amer. Chem. Soc.*, 1932, **54**, 4125.
Ethyl alcohol	0·0026	,, ,, ,, ,,
Ethylene glycol	0·0022	,, ,, ,, ,,
Glycerol	0·0021	,, ,, ,, ,,
Acetone	0·0020	,, ,, ,, ,,
Ammonia	0·0028	Bryan, *Physical Rev.*, 1923, **22**, 399.
Pyridine	0·0012	Cauwood and Turner, J., 1915, **107**, 276.
Nitrobenzene	0·0023	Abegg and Seitz, *Z. physikal. Chem.*, 1899, **29**, 242; Jezewski, *J. Phys. Radium*, 1922, **3**, 293.
Methyl cyanide	0·0025	Walden, *Z. physikal. Chem.*, 1910, **70**, 569; 1903, **46**, 103; Grimm and Patrick, *J. Amer. Chem. Soc.*, 1923, **45**, 2794.

Other liquids known to be associated by hydrogen bonding, *e.g.*, water, the alcohols, and ammonia, have coefficients of the same order as those of nitrobenzene and methyl cyanide, which cannot very well form hydrogen bonds. Hydroxylic and amine association is, so to speak, of the three-dimensional rather than of the linear type, and the increased association at low temperatures does not necessarily increase the mean dipole moment of the associated units.

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