59. *The Dielectric Polarisation of Gaseous Sulphur Dioxide.*

By R. J. W. Le Fèvre, I. G. Ross, and B. M. Smythe.

Two sets of measurements for the above property, over the temperature range 290—440° K., have been obtained independently and with non-identical apparatus. The two apparatus both possess the simplicity of, but incorporate improvements upon, the oscillator–wavemeter combination used before by Le Fèvre and Russell.

The total polarisation of sulphur dioxide is represented in c.c. by ${}_{T}P = 10{\cdot}91 + 16164/T$, whence the dipole moment is 1·619 D., and the atomic polarisation *ca.* 1·4 c.c. (or 15% of the electronic polarisation).

The work now to be described was undertaken for two reasons : (*a*) because sulphur dioxide, being one of the simplest substances having a negative Kerr constant, seemed an attractive case upon which to test various extant " rules " for the variation of apparent dipole moment with state (cf. Le Fèvre and Russell, *Trans. Faraday Soc.*, 1947, **43**, 374, and following paper), and (*b*) because a need was felt, during day-to-day observations of dielectric constant (ε) on gases, for a reference compound having a higher value of ε than that of carbon dioxide, the material previously used (*idem, loc. cit.*). The remainder of this communication deals with point (*b*).

Sulphur dioxide, being readily available and easy to handle and purify, was an obvious choice as the desired secondary standard. Its earlier examination by Jona (*Physikal. Z.*, 1919, **20**, 14) and Zahn (*Physical Rev.*, 1926, **27**, 455) suggested that it would have advantages over carbon dioxide in that, for it, $\varepsilon - 1$ is about nine times as great, at room temperature. Consequently the change of capacity (*i.e.*, the quantity actually measured) following the introduction of sulphur dioxide between the plates of a condenser would be ten times that produced by carbon dioxide under equivalent conditions. As calibrating materials, therefore, these two gases should lead to accuracies, other things being equal, in much the same ratio.

Our plan, accordingly, has been to make a careful comparison of sulphur dioxide with carbon dioxide, using for the latter the dielectric constant of 1·000905 at 25° and 760 mm. (corresponding to a temperature-invariant polarisation of 7·341 c.c.) adopted by Le Fèvre and Russell (*loc. cit.*).

Apparatus.

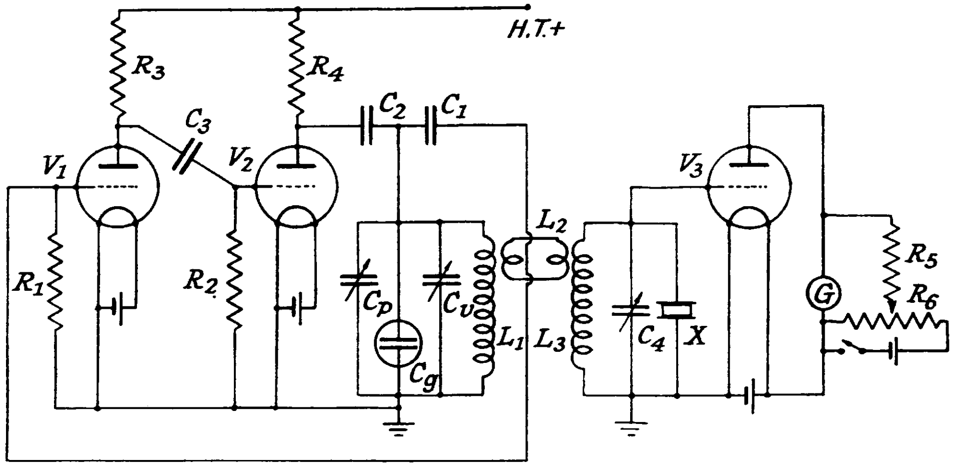
Le Fèvre and Russell (*loc. cit.*) had incorporated the replaceable capacity (gas cell) into the circuit of a dynatron oscillator, the signal from which was picked up in an adjacent wavemeter. Very little of their original apparatus, however, being available in Sydney, it became necessary to rebuild *de novo*. Certain facts then emerged which caused us to discard the dynatron. Since this generator is still recommended in the second edition of " Dipole Moments " (Methuen, 1948) we wish to state briefly our reasons for the change. (*a*) The secondary emission from the plates of modern valves is less easy to induce than was the case with those commercially obtainable eleven years ago; we observed this empirically ourselves and later learned that changes in manufacture and design have been deliberately directed to this end (private communication from Messrs. Amalgamated Wireless, Australia Ltd.). (*b*) Supposedly identical valves can have secondary-emission characteristics which vary over wide limits. " Samples which are closely uniform when used as amplifiers display marked disparity in dynatron characteristics. The dynatron effect is more or less accidental, and consistency is not always sought for " (Scroggie, *Wireless Eng. and Expt. Wireless*, 1933, **10**, 527). (*c*) We found unexpectedly that the available inductance : capacity ratios were limited by the fact that oscillations ceased when $-L/CR$ was made less than $(R_n)_{\text{minimum}}$ (R = resistance in the tank circuit, R_n = effective negative resistance of the valve, cf. Brunetti, *Proc. Inst. Radio Eng.*, 1937, **25**, 1595) ; the last point was a serious drawback since any factor tending to diminish the capacity of the gas cell would obviously react similarly upon the accuracy of our readings.

An experimental survey of other possible arrangements was therefore undertaken. These included variants of the heterodyne-beat method involving either audible or cathode-ray-tube reading-points. Several designs of oscillators were tried, mutually in pairs, or singly against the 50-c./s. mains or the carrier wave of a local Sydney broadcasting station. Finally we convinced ourselves that, except through a great increase of complexity (compare the circuit diagram of Stranathan, *Rev. Sci. Instr.*, 1934, **5**, 334) and of associated maintenance troubles, no significant improvement would be secured over the very simple equipment used by Le Fèvre and Russell. The problem was thus reduced to choosing a variable oscillator to replace the dynatron.

Eventually we adopted (*a*) a push-pull circuit of the Franklin type, and (*b*) a transconductance generator, both using power supplies drawn entirely from batteries. These, each with an attendant wavemeter containing a quartz resonator, have formed the basis of two apparatus, built and operated separately and independently (by I. G. R. and B. M. S. respectively). They will now be described *seriatim*.

Franklin Oscillator–Wavemeter Combination (*see Fig.* 1).—The lay-out comprises a Franklin oscillator *A* (cf. Witt and Franklin, B.P. 369,575) coupled to a wavemeter *B*. The specifications of the circuit components are as follows. Valves V_1, V_2, V_3 : Radiotron 1H4-G. Capacitors : C_g, gas cell (described below); C_v, coarse variable condenser (second-grade Sullivan, maximum capacitance 200 pF.); C_p, precision variable condenser (see below); C_1 and C_2 should be equal and as small as possible, compatibly with adequate signal strength—7pF. was found to be satisfactory; C_3, 0·001 μF.; C_4, split-stator variable condenser, maximum capacitance 150 pF. Resistors : R_1, R_2, R_3, R_4, all 50,000 ohms; R_5, 20,000 ohms;

FIG. 1.



(A) (B)

R_6, 1000-ohms potentiometer. Inductances : L_1, 90 turns 20 S.W.G. cotton-covered copper wire wound on a hexagonal bakelite former, 1¼″ diameter, the whole coated with paraffin wax; L_3, 120 turns on a similar former; L_2, coupling coil, consisting of a single turn of stiff tinned copper wire, and located immediately above L_1, L_3, whose centres are 4½″ apart. *X*, quartz resonator crystal, frequency 1000 kc./s. (supplied in mount by Amalgamated Wireless, Australia, Ltd.); *G*, Cambridge galvanometer, sensitivity 1100 mm./microamp. at 1 m. The two circuits are built on separate steel chassis. C_g, C_v, and C_p are connected to the chassis by short lengths of coaxial cable.

Gas Cell.—The gas cell C_g resembles that described by Le Fèvre and Russell. Three coaxial rhodium-plated brass cylinders (16 gauge) are separated by small rectangular quartz spacers, 12 in all, the inner and outer cylinders (each 10 cm. long and earthed) being connected by a ring fitting tightly between them; the H.T. lead is led out, from the middle cylinder (9 cm. long), through a hole in the ring *via* a glass bush. The cell is sealed into an annular " Pyrex " glass cylindrical vessel, provided with a gas inlet. The leads are of 26 S.W.G. platinum wire, and penetrate the top of the vessel to the lower ends of mercury-filled glass tubes, into which dip the connections to the oscillator. The empty capacity is roughly 200 pF. The high-tension electrode is shielded by a brass foil wrapping (earthed).

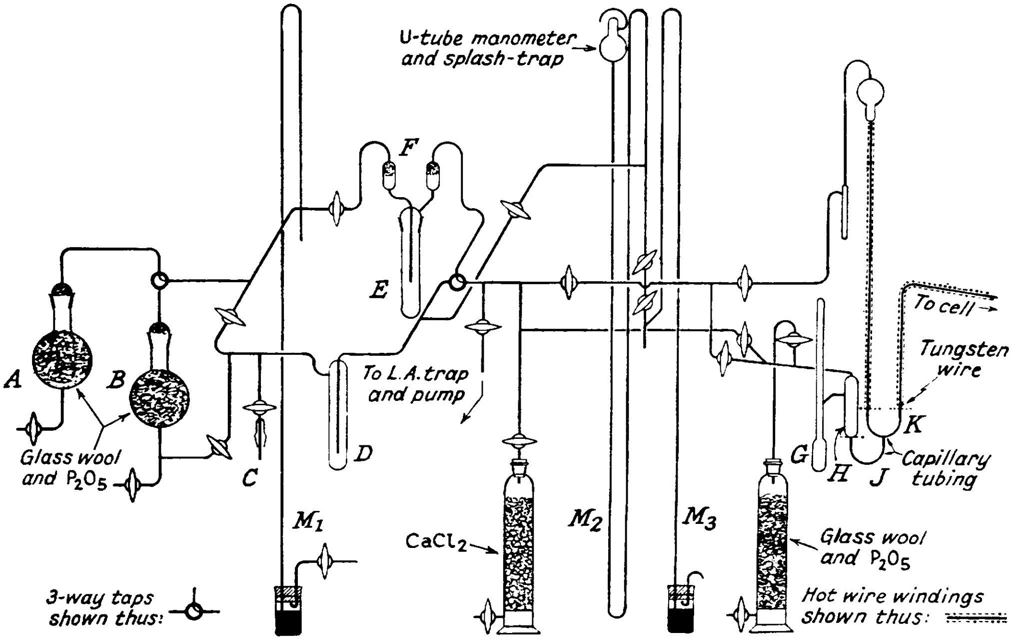
The cell is located by a brass-rod scaffolding in an oil-thermostat. The temperature is read from a calibrated thermometer placed in a symmetrical position to the cell with respect to the heaters and stirrer. The electrical components, including batteries and excepting only the gas cell and precision condenser, are enclosed in a large heavily-lagged box, lined with sheet zinc (earthed) for shielding. No thermostatic control has been found necessary.

Precision Variable Condenser.—The design of the precision condenser is substantially the same as that shown in Fig. 4. The steps have diameters of 3 cm. and 2·45 cm., the cylinder around them is 20 cm. long and of 2·375 cm. inner radius. The working range is 8 pF. traversed in 160 turns; each division (1/100th turn) then corresponds to 0·0005 pF. The limit of reading (set by the response of *G*) is one-half of such a division. The total capacity is about 35 pF.

Performance of Oscillator.—The frequency stability of the oscillator was beyond expectations. After it had run continuously for a fortnight, it was determined that, with C_g at room temperature, under conditions in which a change of frequency of ½ c./s. could be detected, no change was observed during ½ hour.

Performance of this kind is remarkable. It would be of interest to obtain an explicit expression for the frequency in terms of all the circuit components, so that the probable influence of the more likely sources of frequency drift could be accounted for. However, the theoretical and practical aspects of this particular oscillator have been virtually neglected in the literature. An attempt to apply Kirchhoff's laws to the equivalent circuit of the oscillator, along the lines followed by Llewellyn (*Proc. Inst. Radio Eng.*, 1931, **19**, 2063) for several simpler oscillators leads to excessively involved expressions, which, in any event, must be regarded as only approximate in view of his tacit neglect of phase changes in the process of amplification (cf. Jen, *ibid.*, p. 2109). None the less, it seems clear that the chief reason for the observed stability is the small coupling, provided by the condensers C_1, C_2, between the tank and the rest of the circuit. The whole can be regarded as an LC circuit, the capacitative arm, C, of which is shunted by (*a*) one of the coupling condensers, C_1 or C_2, and (*b*) the other coupling condenser (C_1 and C_2 may be considered as approximately equal) in series with an impedance, Z, representing the remainder of the circuit. Then, to the extent that C_1 or C_2 is negligible compared with C (or $C + C_{1 \text{ or } 2}$) it is justifiable to take the impedance of this arm as that of C alone, *viz.*, $1/j\omega c$, which is not influenced by changes of Z.

FIG. 2.



Resonance Curve.—The form of the resonance curve is not that shown in the paper of Le Fèvre and Russell (*loc. cit.*). Because the coupling of the circuits exceeds the critical value, the curve has two humps, with two major crevasses (on either of which readings can be taken), and upwards of 30 minor crevasses, all excessively sharp and narrow, and too sensitive for use; these may be due to the excitation of subsidiary modes of vibration of the crystal.

The maximum anode current in the wavemeter is about 60 microamps. Since the galvanometer used gives its full deflection with about 1 microamp., a balacing e.m.f. is applied. The arrangement shown in Fig. 1 is one which, unlike a simple series arrangement of cell and rheostat, gives a uniform increase in back current as the knob of the potentiometer R_6 is turned.

Coaxial Cable Effect.—It has been mentioned that the condensers C_g, C_p, C_v are connected to the chassis by coaxial cables. The important observation was made that the lengths of these cables influence strongly the amplitude of the resonance curve, as measured in the wavemeter circuit. In particular, if the length of cable connecting the cell (which constitutes the major part of the total capacity of the tank) to the rest of the circuit is doubled, the amplitude of the resonance curve is decreased by 30%. The effect of changing the lengths of cable to the smaller capacitances C_p and C_v is much less; while the connection of, say, one metre of unterminated cable in parallel with the other capacitances has no significant effect on the amplitude.

These considerations have a bearing on the design of the whole apparatus: to obtain maximum sensitivity it is necessary that the oscillator should be located as near as possible to the cell C_g.

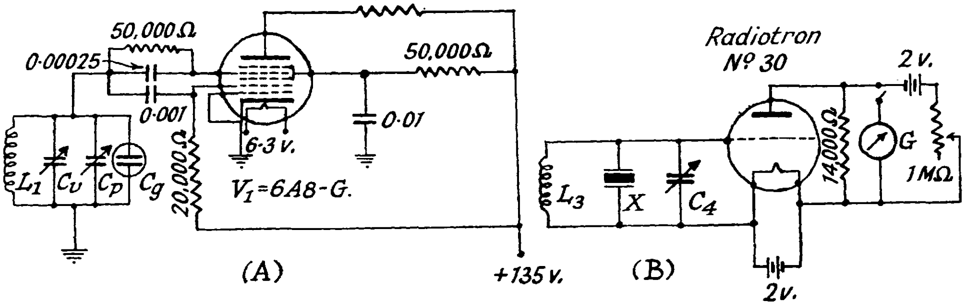
It is not known whether they have been noted with other oscillators. Their explanation is difficult. The most obvious suggestion is that power dissipation in the cable causes the drop in signal strength; for as the capacitance across the end of the cable is increased, so also the admittance of the cable + capacitance as a whole increases, and consequently also the power dissipated. It is uncertain just how the amplitude of oscillations depends on the effective resistance of the tuned circuit, although this is clearly a participating factor.

Significant losses in short lengths of high-quality cable are, however, unheard of. The cable used is A.W.A. Telcon h.f. cable, solid copper core (0·035″ diam.), with braided outer conductor (0·25″ diam.). The dielectric is a polythene–polyvinyl ester mixture, $\varepsilon = 2{\cdot}3$, resistivity 10^{17} ohm/cm., power factor 0·0003. The characteristic impedance, Z_0, is 70 ohms (modulus)—the calculated value is $75 + 1{\cdot}6j$ ohms —and the capacitance 21·5 pF./ft. The attenuation is 0·41 decibels/100 feet at 1 mc./s. (*i.e.*, for a correctly terminated line). Several different specimens of cable were used, and the connectors frequently refitted. The lengths of cable used (not more than 60 cm.) are no significant submultiple of a wavelength at 1 mc./s.

Using the appropriate exact transmission-line formulæ (Race and Larrick, *Trans. Amer. Inst. Elect. Eng.*, 1942, **51**, 526), the impedance of a cable of these specifications, 100 cm. in length, terminated by a capacitance of 500 pF., is found to be $1{\cdot}8 - 277j$ ohms, the real (resistive) part of which seems far too small to account for the effect described.

Gas-handling Apparatus.—The final form of the gas-handling apparatus is shown diagrammatically in Fig. 2. The bulbs, *A* and *B*, contain phosphoric oxide dispersed on glass wool, to serve for the preliminary drying of the gases. The connection of the traps (*E*, *D*) is such as to permit repeated cyclic distillation of gases. Of these traps, *E* is removable, and can thus be partly filled with drying agents, distillation over phosphoric oxide having been found the most effective method of drying. The bulbs, *F*, containing plugs of glass wool, serve to prevent phosphoric oxide being carried through the rest of the system when the liquid in the trap bumps while boiling. When blocked, the traps are cut out and replaced after washing.

FIG. 3.



The various connections to manometers enable a check to be kept on the pressures in all parts of the apparatus while distillation is in progress—a necessary precaution when icing of the downpipes of the traps occurs, with possible building up of back-pressures during distillation. M_2 is a U-tube manometer for working at positive pressures, and is equipped with a splash-trap.

The system to the right of M_3 is the device used by Groves and Sugden (*J.*, 1934, 1094; 1939, 1144, 1147). (Although not needed for sulphur dioxide, it was introduced during construction to allow higher-boiling liquids to be examined later, if desired.) The two gases are from cylinders. As a routine, they are dried (P_2O_5) and redistilled before admission to the cell.

Reading Procedure.—The oscillator and thermostat are allowed to run for about ½ hour to attain equilibrium. Two points on opposite sides of the bottom of the crevasse, about 14 condenser turns apart, and for which the galvanometer deflection is about 1 cm. per condenser scale-division, are used as reference points. Apart from the fact that during the taking of readings the heaters and stirrer in the thermostat are best switched off—since they cause slight instability—the sequence of operations is similar to that noted later (p. 280). Each set of readings takes approximately 12 minutes to perform.

Negative Transconductance Oscillator–Wavemeter Combination (*see Fig.* 3).—The oscillator (*A*) is built around a 6A8G Radiatron pentode, the three condensers C_v, C_p, and C_g being in parallel with the inductance L_1 (a ceramic grooved coil, 2″ in diameter, wound with 54 turns of No. 20-gauge bare tinned wire). The variable condenser C_v is a short-wave radio commercial type of *ca.* 100 pF., used to set the frequency of the oscillator approximately to that of the quartz (so that the plate current of the wavemeter is on the crevasse, and fine tuning then possible with the precision condenser C_p). C_v remains unaltered during a series of measurements. Resistors and other capacities are specified on Fig. 3. The wavemeter (*B*) is mounted on the same chassis as the oscillator, and the whole, with associated power supplies, housed in an insulated box to maintain fairly constant ambient temperatures around the components and to prevent radiation from the heated thermostat standing alongside.

Gas Cell.—This is simpler than that used by I.G.R., consisting of two brass tubes 9·5 cm. long, the inner of which (diameter, 5·1 cm.) is mounted concentrically with the outer (diameter 5·4 cm.). Six "Pyrex"-bead spaces, inserted under slight tension, prevent movement of the two cylinders. The assembly is sealed into an annular "Pyrex" envelope with the same kind of electrical connections as for the cell previously described. The outside cylinder is earthed. The empty capacity of this cell is approx. 80 pF.

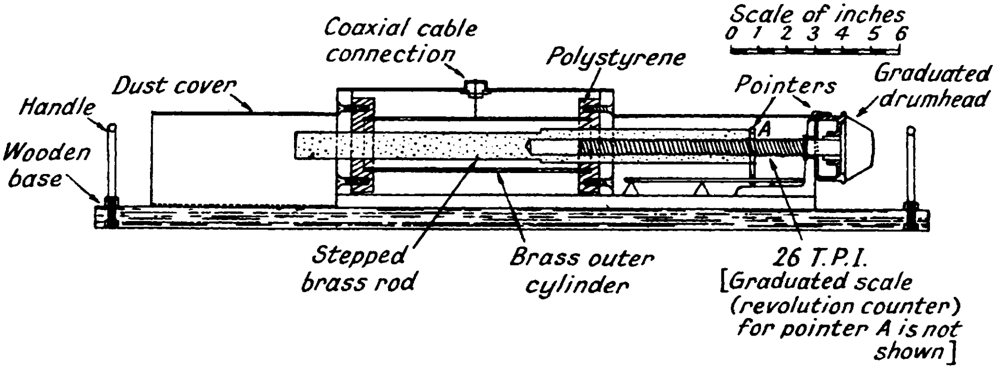
The cell-mounting, thermostat, and gas supply arrangements are substantially the same as those of I.G.R. above.

The Precision Condenser, C_p.—Details of this are shown as Fig. 4. It, as also that of I.G.R., utilises a "stepped-rod" on the principle described by Watson, Rao, and Ramaswamy (*Proc. Roy. Soc.*, 1934, **143**, 558), but with an altered design to provide a more rigid method of support of the high-potential component. Two polystyrene rings are grooved tightly to hold the brass cylinder, A (internal diameter 4·7 cm., length 20 cm.), and screwed to the ½″ steel end-plates. Insulation by polystyrene is as efficient as the method used by Watson and obviously permits robust overall construction. The stepped brass rod (diameters, 3·0 and 2·68 cm.) is precision-turned to slide through two graphite-lubricated bearings (B) on the steel end-plates. The steel screw on which the stepped rod rotates has a pitch of 26 turns per in. and is ground true with the threaded sleeve of the rod. The total capacity of the condenser is *ca.* 30—40 pF. and the variable range 4 pF.

A moving pointer slides against a linear scale, indicating numbers of turns, while the rotating head (marked in hundredths) gives fractions of turns; readings are always taken in the same direction to avoid errors due to backlash. Each condenser shows satisfactory " straight-line " properties, confirmed by the fact that readings of capacity differences for a particular pressure of carbon dioxide at the same temperature are the same at any point on the scale. In practice most readings are taken over the middle of the scale because of possible end-effects.

FIG. 4.

Precision variable condenser.



Operation.—Routine procedure is as follows. The thermostat is set at the desired temperature and left for 12 hours during which the room reaches steady conditions (some radiation from the thermostat cannot be prevented). The oscillator etc. is then started and allowed to run for 5 hours at the frequency of the quartz. Meanwhile sulphur dioxide is collected in the apparatus. A series of readings at varying pressures (generally 12—16 pressures at a particular temperature, requiring some 2—3 hours) may now be taken. With the cell evacuated, the precision condenser is adjusted until zero current flows through the galvanometer. A second reading is obtained such that some 6—8 turns of the condenser are needed to pass from the first point on the current–capacity crevasse to that which is exactly opposite. This range provides the greatest sensitivity and stability. Next, the vapour is introduced into the cell, after 3 minutes the pressure is recorded, and capacity readings are taken as before. The cell is lastly evacuated, and after 3 minutes a final set of readings made. These timings are important if the mean of the two vacuum readings is to be the " true " vacuum reading corresponding to the vapour reading. This is so, since a slow drift in frequency cannot be entirely avoided. Providing, however, this is regular over 9 minutes (the period between two vacuum readings) it need not impair the measurements.

RESULTS.

The results are recorded as described by Le Fèvre and Russell (*loc. cit.*; see p. 378 for a sample set). The method used in a relative one, requiring preknowledge only of the polarisation of the standard gas (carbon dioxide in the present work). In what follows δC is the difference between drum and scale readings of the precision variable condenser when the cell is filled to a measured pressure, and the mean of the two " vacuum " readings taken before and after that particular " vapour " reading; p is the pressure in cm.

Values of $\delta C/p$ for each temperature are first plotted against pressure. A curved graph at this stage would suggest deviations from ideality of the gas, and/or to surface adsorption (Zahn, *Physical Rev.*, 1926, **27**, 329); however, in the case of carbon dioxide no such deviation occurs. We therefore take as the limiting value of $\delta C/p$ at zero pressure the arithmetic mean of the observed $\delta C/p$ readings.

Evidently the compressibility of carbon dioxide may be ignored. The measurement of pressure is actually used as an indirect measurement of the density of the gas, the underlying assumption being that δC (which is proportional to the change in dielectric constant) should be proportional to the number of molecules present per c.c., *i.e.*, to the density. For an ideal gas the density is proportional to the pressure, and $\delta C = k.p$. For a real gas we must substitute for p, the observed pressure, the " ideal pressure," p_i, that it would exert if Boyle's law were observed, *i.e.*, $\delta C = k.p_i = kp/(1 - Ap)$, where A is the compressibility; hence $\delta C/p = k/(1 - Ap)$.

This is a non-linear relation. Yet in the case of carbon dioxide, a linear graph, parallel to the p axis, is obtained. One can conclude therefore that for this substance compressibility considerations are unimportant. Direct experiments (Cawood and Patterson, *J.*, 1932, 2180; cf. Moles, Toral, and Escribano, *Trans. Faraday Soc.*, 1939, **35**, 1439) have shown very low A values, *e.g.*, 0·0053 at 21°, 0·0048 at 31° (where p is measured in *metres* of mercury). From these, even at room temperatures, the correction to $\delta C/p$ would amount only to $+\frac{1}{4}\%$ at 50 cm.

With sulphur dioxide below 100° the graphs *are* curved. They were accordingly extrapolated graphically to zero pressure, when, as may be seen from the equation above, $p = p_c$ and $\delta C/p = \delta C/p_c$. (For sulphur dioxide the compressibilities are 0·0165 at 30°, 0·0132 at 50°, corresponding in the first instance to a correction of $+8\%$ at 50 cm.) This extrapolation covers effects due to association of the molecules, which for sulphur dioxide is responsible for part of the compressibility. Gazulla and Perez (*Z. physikal. Chem.*, 1944, **193**, *A*, 162) find, from measurements of thermal conductivity, the equilibrium constant for the dissociation of the double molecule $(SO_2)_2$ to be given by $\log K_p = -8200/4{\cdot}573T + 8{\cdot}70$. At 40° and 1 atmosphere the partial pressure of $(SO_2)_2$ is thus only 1·14 cm., or 1·5% of the total pressure. This contribution tends, of course, to zero at $p \longrightarrow 0$.

Table I refers to carbon dioxide. To the "observed" figures in the third column the linear relation between $x' = (\delta C/p)_{p \rightarrow 0}$ and $1/T$ is fitted by the method of least squares. For the apparatus of I. G. R. we have $x' = 0{\cdot}3308 + 2083{\cdot}6/T$, while for that of B. M. S., $x' = 0{\cdot}0413 + 1408{\cdot}1/T$. The fourth column contains x' appropriately recalculated for each temperature. Also recorded are the pressure ranges, over which the readings were taken, and the number of observations made at each temperature.

TABLE I.

T (°K.).	Apparatus.	x'.	$x'_{calc.}$.	p range in cm.	No. of observations.
291·4	I. G. R.	7·47	7·48	15—69	9
317·8	,,	6·91	6·89	20—66	16
349·0	,,	6·38	6·30	20—93	13
375·1	,,	5·75	5·89	21—67	10
437·5	,,	5·14	5·10	21—66	18
289·3	B. M. S.	4·92	4·91	20—71	9
314·5	,,	4·51	4·52	23—73	12
351·2	,,	4·07	4·06	39—71	9
357·3	,,	3·99	3·98	22—76	14
373·0	,,	3·77	3·82	21—61	5
401·5	,,	3·60	3·55	39—70	10
429·0	,,	3·31	3·32	56—74	9
456·5	,,	3·13	3·14	37—75	10

TABLE II.

Polarisation of sulphur dioxide.

T(° K.).	Apparatus.	x.	P.	$P_{calc.}$.	$P_{calc.}$.	p range in cm.	No. of observations.
297·2	I. G. R.	65·2	65·99	65·86	65·30	13—66	15
340·1	,,	50·7	58·36	58·99	58·43	23—53	8
349·0	,,	4·86	57·32	57·76	57·22	20—65	10
351·0	,,	4·80	56·92	57·50	56·96	20—65	17
381·4	,,	4·19	53·74	53·82	53·29	20—67	11
408·5	,,	3·73	51·04	51·00	50·48	20—65	11
(437·0	,,	3·17	46·27	58·41	47·89	20—66	15)
296·2	B. M. S.	42·5	65·10	65·26	65·48	19—66	9
306·2	,,	40·0	63·22	63·48	63·70	19—69	11
307·3	,,	39·9	63·39	63·29	63·51	20—62	6
343·5	,,	32·9	58·27	57·75	57·96	30—63	7
382·5	,,	26·9	53·10	52·95	53·16	20—71	8
406·5	,,	24·0	50·27	50·46	50·67	21—65	13
440·5	,,	20·9	47·34	47·39	47·60	24—70	12
444·0	,,	20·6	47·02	47·10	47·31	24—71	18

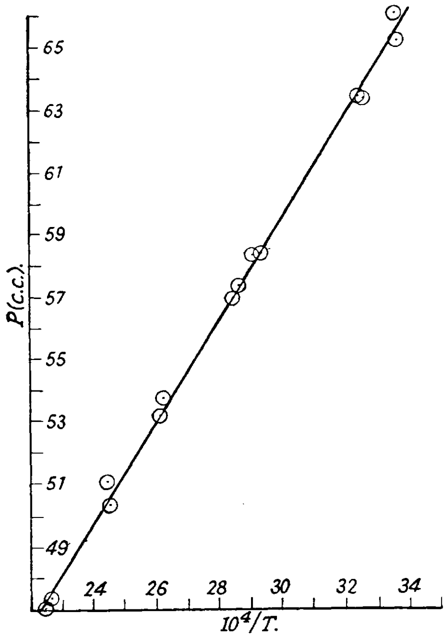
To evaluate the polarisation of sulphur dioxide, from parallel sets of measurements on this gas, we note that at zero pressure (where $\varepsilon + 2 = 3$) the Clausius–Mosotti expression becomes

$P = K(\delta C/p)_{p\to 0}(pv)_{p\to 0}$, where v is the volume occupied by one mole of gas. But in this limit $(pv)_{p\to 0} = p_c v_c$ (in the nomenclature above) $= v$, the molar volume of a perfect gas at one atmosphere. This is a general relation for all gases, K being a constant throughout. Therefore, if we put $(\delta C/p)_{p\to 0}$ for carbon dioxide $= x'$, and for sulphur dioxide $= x$, then $P_{SO_2} = P_{CO_2} \cdot x/x' = 7{\cdot}341\ x/x'$ c.c. (using the polarisation of carbon dioxide given at the beginning of this paper).

The values thus determined for P_{SO_2} are plotted against $1/T$, and straight lines again fitted by the method of least squares. The results are shown in Table II.

Fig. 5 shows the observed polarisations (column 4 of Table II) superimposed on the graph of $P = 10{\cdot}91 + 16164/T$ (column 6 of Table II). Column 5 of Table II gives the polarisations calculated from each set of data separately by the equations: $P = 11{\cdot}31 + 16213/T$ (I. G. R.) and $P = 10{\cdot}72 + 16155/T$ (B. M. S.). The incomplete agreement seems to be connected more with the shape and layout of components than with the manner in which the apparatus is operated. Relative performance may be examined by the scatter of $\delta C/p$ for a particular gas at a given temperature. In the above determinations the estimated order of accuracy is about $\pm 1\%$ for carbon dioxide. For sulphur dioxide, with $\delta C/p$ about nine times as great, the corresponding figure is *ca.* $\pm 0{\cdot}2\%$, not $\pm 0{\cdot}1\%$ as might be expected. The loss of accuracy is due probably to slight imperfections in the precision condensers, which necessarily have a very slight longitudinal play (to enable screw action to take place at all), quite apart from any deviations from linearity in capacitance, and to actual mechanical changes occasioned by rotating their drumheads upwards of 50 times between vacuum and gas readings.

FIG. 5.



The expressions just written for P should be compared with $10{\cdot}64 + 16100/T$, computed by us from data recorded by Zahn (*Physical Rev.*, 1926, **27**, 455). Earlier papers by Badeker, Klemenčic, and Verain (references and summaries in "International Critical Tables," Vol. VI, p. 74) give dielectric-constant estimations at too few set temperatures and pressures to permite valuation of the constants A and B in the Debye equation. Jona (*Physikal Z.*, 1919, **20**, 14), however, reports fuller figures; from these we calculate [using $(\varepsilon - 1)/(\varepsilon + 2)$, and least squares]: $P = 20218/T - 0{\cdot}194$. A negative A term is, of course, impossible and must be attributed to experimental errors, which A reflects sensitively.

The Dipole Moment of Sulphur Dioxide.—This, from $\mu = 0{\cdot}01273B^{\frac{1}{2}}$, is, for the various B values already given, 1·619 D. ($B = 16164$), 1·620 D. ($B = 16213$), 1·618 D. ($B = 16155$), and 1·615 D. ($B = 16100$; Zahn), 1·81 D. ($B = 20218$; Jona).

The Faraday Society Table of dipole moments (Appendix to *Trans.*, 1934, **30**) shows, under sulphur dioxide, a reference to Braunmühl, whose paper does not however include this substance. It further quoted Jona's result as $\mu = 1{\cdot}76$ D., but this appears to have been obtained using $P = V(\varepsilon - 1)/3$. We have given special consideration to the experiments of Jona, since, in contrast with the estimates (1·615—1·619) by Zahn and us, his datum resembles the higher group (1·7—1·9 D.) drawn from observations of electrostriction (Frivold, *Physikal. Z.*, 1921, **22**, 603; Kliefoth, *Z. Physik*, 1926, **39**, 402). This phenomenon, however, does not yet rest upon a proven theoretical basis, and the measurements involved (changes in volume of *ca.* 3×10^{-4} c.c.) are very delicate. Frivold, in three determinations between 292·0° and 292·8°, found $\mu = 1{\cdot}74$, 1·90, and 1·86 D. High field strengths, E, being employed, Kliefoth questioned the sufficiency of the simple (Gans) relation, used by Frivold, namely: $\delta v/v_0 = E^2(\varepsilon - 1)/8\pi p$, and considered the effect of higher powers of E. It is significant that his estimate for μ_{SO_2} is 1·7 D.—*i.e.*, lower than Frivold's.

Jona was among the first to use a heterodyne-beat H.F. method but during the 30 years since his publication there has been great improvement in radio components and practice. His figure, moreover, may be offset by lower ones, calculable by the refractivity method from the single $(\varepsilon - 1)$ measurements of other earlier workers: 1·61 D. from Klemenčic (*Sitzungsber. Akad. Wiss. Wien*, 1885, II, **91**, 712); 1·60 D. from Bādeker (*Z. physikal. Chem.*, 1901, **36**, 305); 1·59 D. from Verain (*Ann. Physique*, 1914, **1**, 255).

For the above reasons, and noting the near agreement between Zahn and ourselves, we record the dipole moment of sulphur dioxide as 1·619 D.

Atomic Polarisation of Sulphur Dioxide.—The refractive index of this gas has been measured by, *inter alia*, Cuthbertson and Cuthbertson (*Proc. Roy. Soc.*, 1909, *A*, **83**, 171) and Huxley and Lowery (*ibid.*, 1943, *A*, **182**, 207). The last-named authors have reviewed the subject and reported an extended study of the dispersion. From their Sellmeier formula: $(n - 1)_0 = 5{\cdot}220 \times 10^{27}/(8178 \times 10^{27} - \nu^2)$ we estimate n^2_∞ to be 1·001277, and (V_0 being 22·4141, *vide* International Critical Tables, Vol. 3, p. 3) R_∞ to be 9·54 c.c. A corresponding computation from the Cuthbertson data yields 9·58 c.c. These are close to the $[R_L]_D$ of 9·49 c.c. found by Nasini (*Gazzetta*, 1883, **13**, 296). The A value (cf. p. 282) cannot be more certain than $10{\cdot}9 \pm 0{\cdot}6$, so that ${}_AP = 1{\cdot}4 \pm 0{\cdot}6$ c.c., *i.e.*, from 1 to 3% of the total polarisation at room temperatures or 8—21% of ${}_EP$ (for comparison, the analogous % for carbon dioxide is 12; Watson and Ramaswamy, *Proc. Roy. Soc.*, 1936, *A*, **156**, 144). We have attempted its *a priori* calculation, following Coop and Sutton (*J.*, 1938, 1280). Wagner (*Z. physikal. Chem.*, 1943, *A*, **193**, 55), from Raman spectra, gives the O–S–O angle as 135° and the O–O force constant as $1{\cdot}217 \times 10^5$ dynes/cm. If $r_{S-O} = 1{\cdot}43 \times 10^{-8}$ cm. (Schomaker and Stevenson, *J. Amer. Chem. Soc.*, 1940, **62**, 1270), $f_{\text{bending}} = V_0 = 2{\cdot}49 \times 10^{-11}$ ergs/radian; or, with $r_{S-O} = 1{\cdot}37 \times 10^{-8}$ cm. (Sponer, "Molekülspektren," Springer, 1935), $V_0 = 2{\cdot}28 \times 10^{-11}$ ergs/radian (we note that the corresponding figure for ozone is $2{\cdot}34 \times 10^{-11}$, *i.e.*, of the same order; Simpson, *Trans. Faraday Soc.*, 1945, **41**, 215). For the apical angle quoted, μ_{S-O} is 2·12 D.; for one of *ca.* 120° (as earlier reported by Dadieu and Kohlrausch, *Physikal. Z.*, 1932, **33**, 165) it is 1·62 D. Coop and Sutton (*loc. cit.*; cf. Bloom and Sutton, *J.*, 1941, 727) give ${}_AP = 4\pi n \mathbf{N}\mu_1^2/9V_0$, where n is the number of angular co-ordinates necessary to express completely the possible independent modes of bending of the opposing dipoles, each of magnitude μ_1. Sutton's actual cases (*e.g.*, *p*-benzoquinone) all had high degrees of symmetry. Dekker (*Rec. Trav. chim.*, 1945, **64**, 126) has applied Sutton's equation to triangular molecules by using $\mu_1 \sin(\alpha/2)$ instead of μ_1 (2α = angle between valency bonds). For sulphur dioxide he estimates ${}_AP$ as 0·07 c.c. This seems unnecessarily small, for from the figures given above we find the lowest ${}_AP$ to be 0·13 c.c., and the highest 0·28 c.c. Nevertheless, the observed quantity is much larger. The computation is sensitive to 2α. Thus, using the lower r_{S-O} and V_O values, for 2α = 120°, 135°, 140°, 150°, 155°, and 160°, atomic polarisations follow of respectively 0·15, 0·28, 0·37, 0·68, 1·00, and 1·56 c.c.

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