MEASUREMENTS ON DIELECTRIC CONSTANTS AND DIPOLE MOMENTS OF GASES BY MEANS OF MICROWAVES AT 9400 MEGACYCLES

Thesis

submitted to the
Electrical Engineering Department
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by

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the degree of

ELECTRICAL ENGINEER .

S u m m a r y

The dielectric constants and dipole moments of several gases (i.e. oxygen, dry air, water vapor, ozone, difluorodichloromethane and monochlorotrifluoromethane) have been determined by a microwave method, using comparison to a gas of known dielectric constant. Accuracy of about 2 % has been obtained for the dielectric constant and 6 % for the dipole moment. The method is discussed from theoretical and practical points of view, possible improvements are pointed out and its general suitability for measurements of this kind is investigated.

I Introduction

The measurements described here were carried out in continuation of the experiments made by M.E. Hines, R.H.MacNeal, and A.F.Fairbanks. The purpose of these investigations was to get an accurate and easy way to measure the dielectric constant of various gases. The chemistry departement of the California Institute of Technology was especially interested in getting the value of the dipole moment of ozone in order to have another clue to the still uncertain structure of ozone.

With his original set Hines tried to make absolute measurements; he had considerable difficulties with temperature effects, so that the accuracy of his results was not as expected. MacNeal and Fairbanks changed the equipment to allow relative measurements only, but these with increased accuracy. They extended the set for tests on ozone and got rather accurate values in their measurements and comparison of oxygen, dry air and ozone. However their set proved not to be sufficient for measurements on other than room temperature. I took over their equipment at this point with the intention to make it suitable for use on an extended temperature range.

The investigations described here were carried out from October 1947 to December 1948 during three terms and part of the summervacations. Actually most of the time required was used for mechanical work (improvements on the equipment).

I should like to express my thanks to all of those who were helpful to me in any way in my work especially to Dr. W.H.Pickering and Dr. R.H.MacNeal and particularly to Dr.O.Wulf for his fruitful suggestions and his help as to the chemical aspect of the procedure.

II THEORETICAL CONSIDERATIONS

a) POLARISATION, DIELECTRIC CONSTANT, ABSORPTION, DIPOLE MOMENT

In our method we determine the dipole moment by measurements of the dielectric constant at various temperatures. This is done at a frequency of 9400 megacycles, using the change of frequency in a cavity caused by the dielectric constant of the gas in the cavity.

There are essentially three kinds of polarisability:

$$P_{total} = p_e + p_m + p_d \qquad (1)$$

The first effect is due to the displacement of the nucleus respective to the electron shell in an atom. It is independent of temperature and state of aggregation. Second there is polarisation due to changes in interatomic distances within a molecule; this effect is generally very small. The third influence is dipole orientation which part can be rather large. It is not observed in solid state and to its full extent only in gases or very dilute solutions. Dipole polarisation varies with temperature as the random motion of the molecules tries to counteract any orientation.

Atoms and molecules have various possibilities of oscillations if they are excited by electromagnetic fields. In the vicinity of such resonance frequencies the dielectric constant shows the following general behavior:

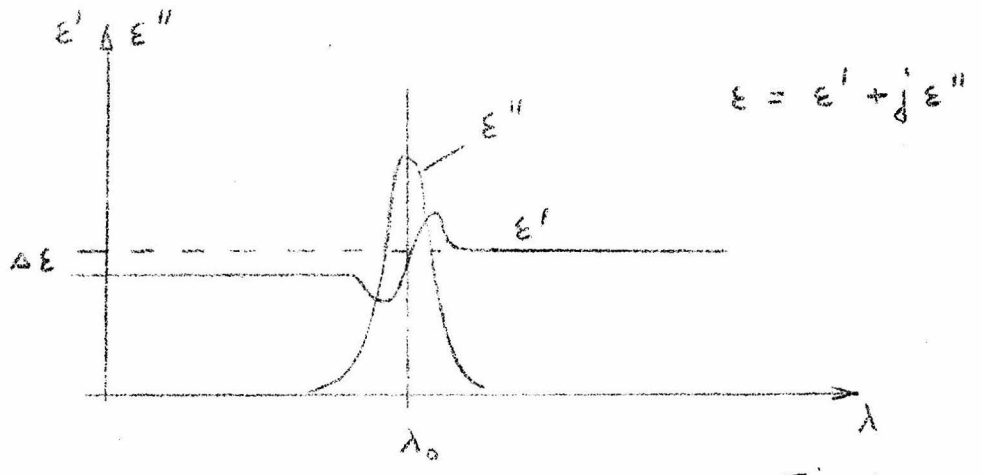


Fig. 1

At infinite frequency all materials are transparent ($\varepsilon = 1$) as there is no particle which would follow the oscillation. going to lower frequencies in passing over a resonance frequency there is a final increase $\Delta\varepsilon$ in dielectric constant. As part of the energy of the passing waves is lost at the resonance frequency, we call these regions "absorption bands" too. There are the following groups of absorption bands: resonances of inner electrons (ultra violet and X-ray range); resonances approximately in the visible range (outer electrons); intermolecular vibrations ($f = 10^{12} \ldots 10^{13}$ cps). Dipole rotation does not give rise to a true resonance (the disturbing forces of temperature collisions cannot be looked at like an elastic force) but there is absorption due to the time lag of the dipole movement which gives a complex dielectric constant.

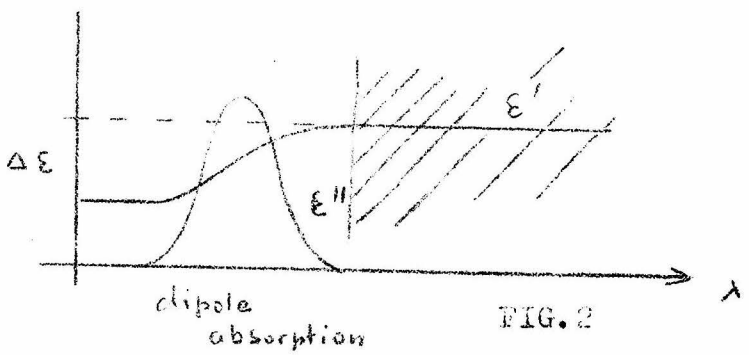


FIG. 2

Generally the critical frequency for dipole inertia fails at wavelengths of millimeters and fractions thereof, but with heavy molecules it may be in the centimeter range. If we want to get the dipole moment by means of measuring the dielectric constant we have to make our experiments in the shaded area of fig. 2.

Suppose this condition fulfilled (i.e. inertia of dipoles negligible) we know that the dipole polarisation is inversely proportional to temperature (Curies law). In concentrated solutions the effect of the neighbouring molecules has to be considered *). As we use only gases

*) Onsager Journ. Ass. Chem. Soc. 36
Debye Ann. Phys. 1937

at low pressures we have not to consider this point and we may use the Debye formula:

$$P = \frac{4\pi}{3} N_0 \left(\alpha + \frac{\mu^2}{3kT}\right) \qquad (2)$$

μ = el. dipole moment
$k = 1.37 \times 10^{-16}$ $(erg\ cm^3)^{\frac{1}{2}}$ erg/°K
I = polarization
M = gram mol
$N_0 = MN/d$ = Avogadro number
d = density
$N = 27 \times 10^{18}/cm^3$ = Loschmidt numb.

and applying the Clausius-Mosotti relation

$$P = \frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{d} \qquad (3)$$

we get:

$$\frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{d} = \frac{4\pi}{3} N_0 \left(\alpha + \mu^2/3kT\right) \qquad (4)$$

The dielectric constants with which we are concerned are in the order of 1.001 - 1.005, so we can simplify (with less than ½ % error)

$$\delta = \varepsilon - 1 = 4\pi N \left(\alpha + \mu^2/3kT\right) \qquad (5)$$

If we have two values of δ at different temperatures, we get μ in the following manner:

$$\delta_1 = 4\pi N \left(\alpha + \mu^2/3kT_1\right)$$
$$\delta_2 = 4\pi N \left(\alpha + \mu^2/3kT_2\right)$$

$$\delta_1 - \delta_2 = \Delta\delta = 4\pi N \mu^2/3k \left(1/T_1 - 1/T_2\right) = 4\pi N \frac{\mu^2}{3k} \frac{\Delta T}{T_1 T_2}$$

$$\mu = \left(\Delta\delta \frac{T_1 T_2}{\Delta T}\right)^{\frac{1}{2}} (3k/4\pi N)^{\frac{1}{2}} \qquad (6)$$

b) SATURATION, INERTIA, MOLECULAR MOBILITY.

If very high field strengths are used, some saturation-effect of polarization should turn up, as in an extreme case all dipoles would be oriented approximately parallel and no further increase in dipolar polarization would be possible. Let us check if such an effect would be possible in our case. The highest field strength that can occur in any case would be the break-down fieldstrength of the tested gas. With air this is around 2o ooo V/cm. The energy content of 1 cm^3 is, expressed in terms of field and dielectric constant:

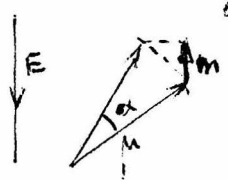
$$w = \varepsilon E^2/2$$

and the increase due to the effect of dipoles:

$$\Delta w = \Delta d E^2/2$$

On the other hand we have for the energy due to the displacement of the dipole charges:

$$\Delta w = N \bar{l} q E = N m E$$



q = unit charge
$\bar{l}$ = statistical effective dipole length in field direction

Let us take the following average relation between μ and m:

$$m = \alpha \mu \, 2^{\frac{1}{3}}$$

Combining the above equations:

$$\alpha = \frac{\Delta d \, E}{N \mu 1.4} \qquad (7)$$

Taking the following values $\Delta d = .005$ $\quad E = 20000/300$ cgs
$N = 27\ 10^{18}$ $\quad \mu = 10^{-18}$

we get

$$\alpha \approx 1/100 \approx \tfrac{1}{2}^{\circ}$$

For this small angle we can certainly not detect deviation from linearity even at the breakdown fieldstrength which we shall never reach in our set.

But there is another point to consider, which proves to be more dangerous, the inertia of the molecules. We make a very rough estimate: let us assume 1 mW to be dissipated in the used cavity (of 50 cm^3) which is $1/\ 50 \cdot 10^{10} \cdot 10^3 = 10^{-14}$ Joule/cycle = n. Assuming all energy to be found at a particular instant in the E-field, we get with a Q of 50 000 (Q = stored energy/dissipated energyper cycle):

$$n = \frac{\varepsilon E^2}{2Q^2} \qquad E = Q\ (2n/\varepsilon)^{\frac{1}{2}}$$

E approx. 10^4 V/cm

The force on unit charge is

$$f_1 = \frac{10000}{300}\ 4.8 \cdot 10^{-10} \approx 1.5 \cdot 10^{-8} \quad dyn \qquad (8)$$

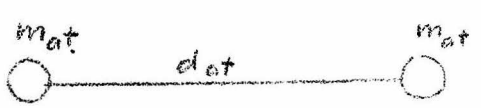
Now we want to compare this force with the force needed for acceleration. We reduce the mass of the molecule to the centers of charge by multiplying with the square of the ratio of the radii.

$$m' = m_{at} \left(\frac{d_{at}}{d_{ch}}\right)^2$$

m' = reduced mass
m_{at} = mass of atomar group connected with one charge
d_{at} = distance of the ceters of mass
d_{ch} = distance of the centers of charge

acceleration force:

$$f_2 = d_{ch}\ w^2\ m' \qquad (9)$$



Taking $\mu = .5 \cdot 10^{-18} = d_{ch} \cdot q$, $q = 4.8 \cdot 10^{-10}$ $\therefore d = 10^{-9}$
unit mass= $1.7\ 10^{-24}$, angle of oscillation $\approx 1/100$
$d_{at} \approx 3 \cdot 10^{-8}$

gives for ozone f_2 around 10^{-10} dyn
for the Freons f_2 around 10^{-8} dyn

Thus we see that for ozone $f_2 \ll f_1$ and probably we have nothing to fear from inertia, but for the heavier Freons the forces are of the same order of magnitude and we might expect some trouble. (Of course these very rough approximations could easily be wrong by a factor of 10,

Not only inertia counteracts any forced motion of the molecules but also temperature agitation, resulting in an energy loss (this is an effect apart from the temperature influence on dipole orientation). We have seen that the angel of rotation is very small, so for an estimate we assume linear motion and use the mobility K for ions which is in the order of $1\ \frac{cm}{s}/\frac{V}{cm}$.

$$\left.\begin{array}{rl} K &= \bar{v}/E \\ \text{accelerating force} &= E\,q \\ \text{"resistive" force} &= R\,\bar{v} \end{array}\right\} \quad R = e/K \quad (VAs^2/cm^2) \qquad (10)$$

Using the same values as on p.8 our velocity is $d_{at}w/100$ and we get:

$$\frac{R\bar{v}}{qE} = \frac{d_{at}\,w}{100\,KE} \approx 6\cdot10^{-4} \qquad (11)$$

This result demonstrates, that resistance (somewhat like viscous resistance) against movement of the molecules is negligible against the thermal disturbing force of dipole orientation.

Conclusively we see that neither mobility nor saturation effects will occur in our experiment. But inertia could have some influence although we expect it only for heavy molecules and scarcely for ozone.

c) EFFECT OF PARAMAGNETISM

As mentioned above we are going to determine the difference in resonance frequency of a cavity filled first with a standard gas and then with the test gas. As we have both electric and magnetic field in a cavity, the Maxwell field theory proves that we actually determine the velocity of propagation $v = c/(\varepsilon\mu)^{\frac{1}{2}}$ of el.magn. waves in the gas

(or the index of refraction) and not the dielectric constant. In a diamagnetic substance the deviation of μ from 1 is negligible but as oxygen is paramagnetic, we have to investigate this case too. Curie *) gives the following value for the magnetic susceptibility of oxygen:

$$\chi \cong .\ 11\ 10^{-6} \quad \text{at room temperature}$$

$$\mu = B/H = 1 + 4\pi\chi$$

Thus

$$\mu_{O_2} = 1.0000014$$
$$\varepsilon_{O_2} = 1.00053$$

The effect of paramagnetism will therefore be about 1/3 % of the influence of dielectric polarizability, so we shall neglect its influence and assume $\mu = 1$ for all gases in our tests. In this case $\varepsilon = n^2$ (n = index of refraction), which holds in the transparent regions of frequency.

*) ref. Landolt Börnstein, Physikalisch Chemische Tabellen HW 1204

III DESCRIPTION OF THE METHOD

a) DETERMINATION OF THE DIELECTRIC CONSTANT

Two cavities are fed by a klystron (723) the repeller voltage of which is modulated to sweep the frequency over a certain range in which the resonances of the two cavities lay. The output of the two cavities, rectified by crystal diodes, is amplified and superposed with opposite sign in a mixer stage. The result is observed with an oscilloscope. The idea is, to tune the cavities to the same frequency by adjusting the two resonance peaks on the scope to coincidence.

FIG.3

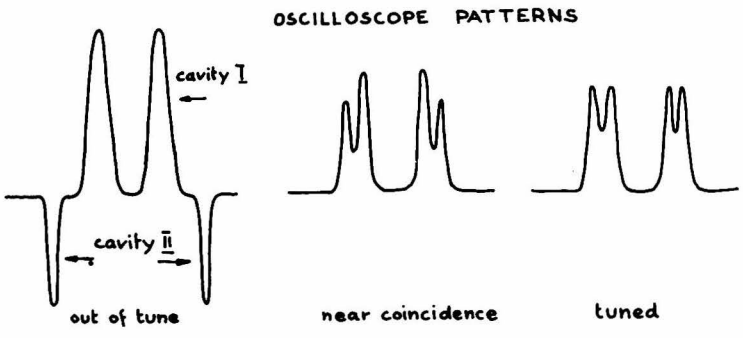
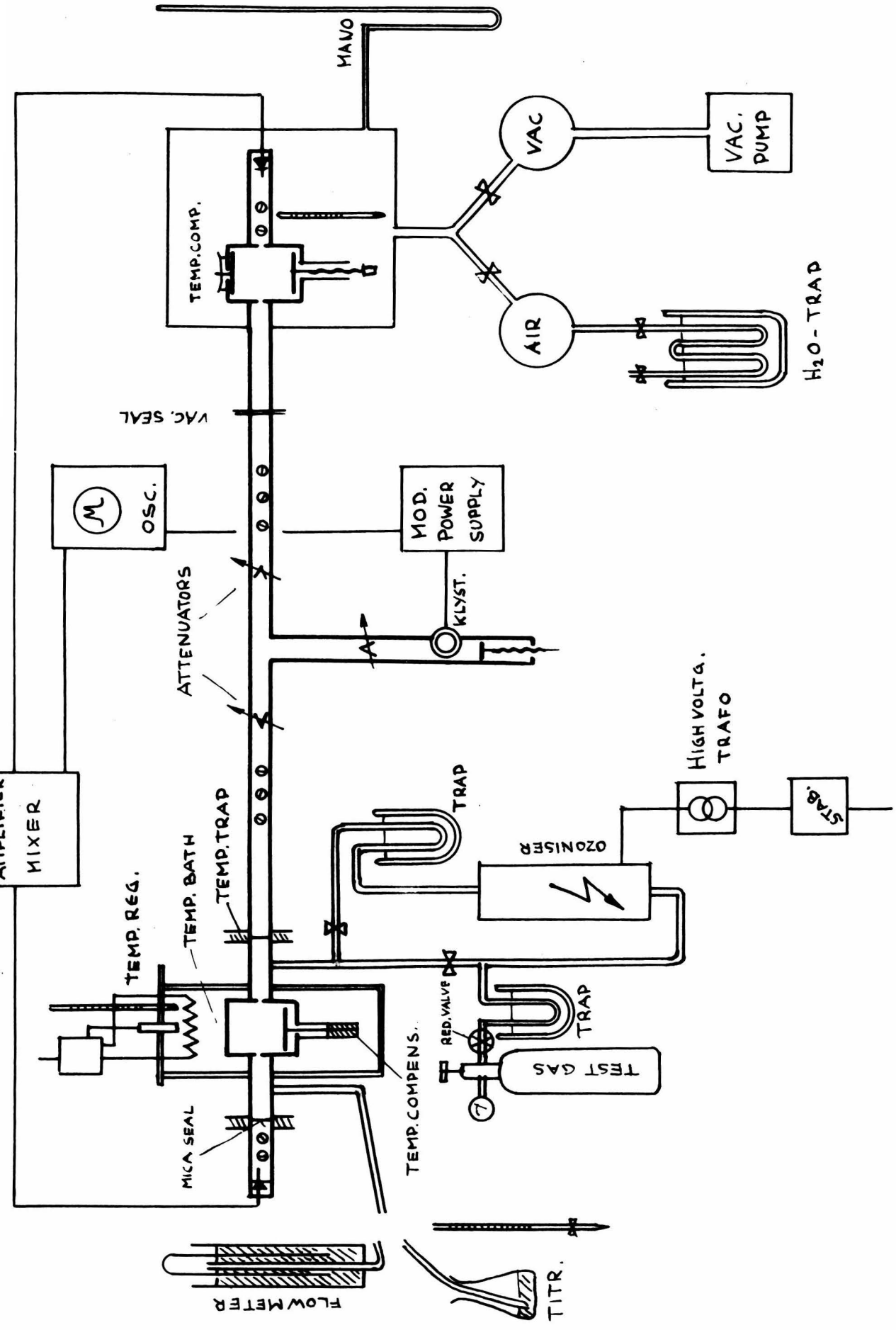


FIG. 4


MANO
VAC
VAC. PUMP
TEMP.COMP.
AIR
H2O-TRAP
VAC. SEAL
OSC.
MOD. POWER SUPPLY
KLYST.
ATTENUATORS
MIXER
HIGH VOLTG. TRAFO
TRAP
OZONISER
TEMP. REG.
TEMP. BATH
TEMP. TRAP
RED. VALVE
TRAP
TEST GAS
MICA SEAL
TEMP. COMPENS.
FLOW METER
TITR.

EP. 2-49

Measurements were made in the following manner: both cavities were filled with the standard gas and tuned, first by adjusting the leggth of the cavities by a micrometer, then by varying the gas pressure in the bell jar. Then cavity I was filled with the test gas (or its mixture with the standard gas) and the pressure in cavity II readjusted to coincidence of the resonance frequencies. From the difference in pressure (about one mm Hg change in pressure could be detected) the variation in dielectric constant of the standard gas was calculated:

$$f = C_c/(\varepsilon\mu)^{\frac{1}{2}} \qquad C_c = \text{factor of cavity} \tag{12}$$

$$\frac{df}{d\varepsilon} = -\tfrac{1}{2}\, C_c/(\mu\,\varepsilon^3)^{\frac{1}{2}}$$

$$\mu = \text{const.} = 1$$

$$\varepsilon \approx 1$$

$$\delta = \varepsilon - 1$$

$$df = k\, d\varepsilon = k\, d\delta \tag{13}$$

In the range of pressures and temperatures with which we are concerned, the following formula holds:

$$\delta = \delta_0 \frac{p}{p_0}\frac{T_0}{T} = \text{const. } p/T \tag{14}$$

Let us use these indices:

1 test cavity (I) filled with gas A
2 comparison cav. (II) filled with S (δ_0 at p_0) } matched
3 test cavity filled with B
4 comp. Cavity filled with S } matched

$$\delta_3 - \delta_1 = \delta_4 - \delta_2$$

$$\delta_3 = \delta_{B_0}\frac{T_0}{p_0}\frac{p_3}{T_3}$$

$$\delta_{B_0}\frac{T_0}{p_0}\frac{p_3}{T_3} - \frac{\delta_{A_0}}{p_0}\frac{T_0 p_1}{T_1} = \frac{\delta_{s_0} T_0}{p_0}\left(\frac{p_4}{T_4} - \frac{p_2}{T_2}\right)$$

$$\delta_{B_0} \frac{p_3}{T_3} = \delta_{A_0} \frac{p_1}{T_1} + \delta_{S_0}\left(\frac{p_4}{T_4} - \frac{p_2}{T_2}\right)$$

$$\delta_{B_0} = \frac{T_3}{p_3}\left\{\frac{\delta_{A_0} p_1}{T_1} - \frac{\delta_{S_0} p_2}{T_2} + \frac{\delta_{S_0} p_4}{T_4}\right\} \qquad (15)$$

For the case, where we have a mixture of the test gas and a standard gas in cavity I, we write tho following relations in order to extract the desired dielectric constant:

$$v\,\delta_{I\,II} = v_I\,\delta_I + v_{II}\,\delta_{II}$$

the respective volumes: $v_I + v_{II} = v$

$$\delta_{I\,II} = \delta_I + \frac{v_{II}}{v}\left(\delta_{II} - \delta_I\right)$$

$$\delta_{II} = \frac{1}{\nu_{II}}\left(\delta_{I\,II} - \delta_I\right) + \delta_I \qquad (16)$$

$$\nu_{II} = \frac{v_{II}}{v}$$

In the actual case: $\delta_{I\,II} \equiv \delta_3 \quad \delta_I \equiv \delta_1$

and remembering that $\delta_I, \delta_{II}, \delta_{I\,II}$ are measured at T_3, p_3

we get

$$\delta_{II_0} = \frac{\delta_{A_0}}{\nu}\left[(\nu - 1) + \frac{T_3 p_1}{T_1 p_3}\right] + \frac{\delta_{S_0}}{\nu}\left[\frac{T_3 p_4}{T_4 p_3} - \frac{T_3 p_2}{T_2 p_3}\right] \qquad (17)$$

In our experiments we shall generally deal with a simpler case, where $T_1 = T_3$; this yields to a simplification of (17):

$T_1 = T_3$ and $T_2 = T_4$

$$\delta_{\overline{\overline{\Pi}}_0} = \frac{1}{\nu}\left\{\delta_{A_0}\left[(\nu-1)+\frac{p_1}{p_3}\right]+\frac{T_3\,\delta_{s_0}}{T_2\,p_3}(p_4-p_2)\right\} \qquad (18)$$

and if in addition $p_1 = p_3$:

$$\delta_{\overline{\overline{\Pi}}_0} = \frac{1}{p_3}\left\{\delta_{A_0}p_3 + \delta_{s_0}\,\frac{(p_4-p_2)T_1}{T_2\,\nu}\right\} \qquad (19)$$

If convenient we might also take the same gas for A and S, so that we can write (19) as:

$$\delta_{\overline{\overline{\Pi}}_0} = \frac{\delta_{s_0}}{p_1}\left\{p_1+\frac{(p_4-p_2)T_1}{T_2\,\nu}\right\} = \delta_{s_0}\left\{1+\frac{(p_4-p_2)T_1}{\nu\,p_1\,T_2}\right\} \qquad (20)$$

If the temperature differences are only small, we can, instead of using the more complicated formula with different temperatures, take constant temperature and make the correction by calculating a pressure p' instead of p. For a positive temperature difference we make a negative pressure correction of the same percentage:

T_r = refer temperature T_x= measured temp.
p_x= measured pressure p_c = corrected pr.

$$T_x = T_r\,(1+\alpha)$$

$$T_r p_x/T_x = p_x/(1+\alpha) \approx p_x(1-\alpha) = p_c$$

Formulas (18),(19) and (20) give us the dielectric constant if the test gas is inserted only in mixture with a known gas. If however the whole cavity is filled by the test gas, formula (15) can be simplified for analogous conditions as for (18) and (19) and we have:

$$\delta_{B_0} = \frac{1}{p_3}\left\{\frac{\delta_{A_0}}{\cancel{p_3}}\, p_1 + \delta_{S_0}\,\frac{T_3}{T_2}\,(p_4 - p_2)\right. \qquad (21)$$

$T_1 = T_3 \qquad T_2 = T_4$

$$\delta_{B_0} = \delta_{A_0} + \delta_{S_0}\,\frac{T_3}{T_2}\,\frac{p_4 - p_2}{p_1} \qquad (22)$$

$T_1 = T_3 \qquad T_2 = T_4 \qquad p_1 = p_3$

b) STANDARDS USED

Applying a comparison method, we need a standard gas with known dielectric constant, preferably without dipole moment. Oxygen and dry air served this purpose. Values given in the literature differ by several percents. Although Hines' value for dry air was suspected not to be accurate enough I used this one, as at first it was the only value available for a frequency of 9400 Mc. ($\varepsilon_{\text{dry air}} = 1.000580$). Comparing air and oxygen I derived ε_{ox} from MacNeals and my own measurements which differed less than ½% ($\varepsilon_{ox} = 1.000533 \pm 2\cdot10^{-6}$).

Later, almost at the end of my investigations, a paper of Crain *) (University of Texas) was published and these values seemed to be pretty reliable. In consequence I recalculated all the runs with Crains values:

dry air : $\delta = 0.000572$

oxygen : $\delta = 0.000530$

at 0°C and 760 mm Hg.

c) CONSIDERATIONS ON THE NECESSARY PURITY OF THE GASES

We start with the requirement, that the error introduced by impurities of the gases should not exceed a few tenths of a percent. The following holds for a mixture of gases:

*) Crain, Phys. Rev. sept.15 1948 p.691

$$\delta_1(1-c_2) + \delta_2 c_2 = \delta_{12}$$

$$\frac{\delta_{12} - \delta_1}{\delta_1} = \frac{1}{1000} \qquad c_1 , c_2 = \text{volume \% of component}$$

$$\frac{\delta_2 - \delta_1}{\delta_1} c_2 = \frac{1}{1000} \qquad \text{for .1 \% accuracy}$$

$$c_2 \leq \frac{\delta_1}{(\delta_2 - \delta_1)1000} \tag{23}$$

one source of error is water vapor with a dielectric constant of approximately 1.010 at 20°C (red. to 0°C 760 mm) *)

$$c_2 \leq \frac{\delta_1}{\Delta\delta \cdot 1000} = \frac{1}{20000} = 5 \cdot 10^{-5} \qquad \delta_1 = .0005 \quad \Delta\delta = .01$$

(requiring the error of each individual component not to exceed .1 %) Water vapor is separated by using dry ice traps. The vapor pressure at -78°C of water is .00056 mm. This is about $8 \cdot 10^{-7}$ of the pressure used in the test cavity. The same holds for the cavity in the bell jar, as the trap is at athmospheric pressure. Thus these traps are sufficient.

If there is any vacuum leakage in our equipment, impurification by air becomes important. The most important component of air beeing watervapor and assuming a maximum absolute humidity of 3 % :

$$c_2 \leq \frac{.0005 \quad 100}{.01 \quad 3 \quad 1000} = 1{,}6 \cdot 10^{-3} \qquad \text{of the total volume}$$

This proved to be the most difficult condition to fulfill with our experimental setup. Vacuum leakage in the structure of waveguides and bell jar was often the cause of intolerable frequency shifts, especially at low pressures in cavity II as expected. However in a more permanent set this condition would not be hard to fulfill.

*)the diel. constant of watervapor at this temperature is almost entirely due to dipolar polarization.

As to carbon dioxyde its content should not exceed .15%, if we apply (23) to its diel. constant, or should not deviate by more than that amount from its normal percentage if air is used as reference. As normal CO_2 content of air is .03 %, there is no error to be expected from it.

Using O_2 as standard, its N_2 content must be less than 1 %. The purity of the O_2 tanks is guaranteed to contain less than .3 % N_2 (.5 % total impurities).

d) TITRATION

To determine the content of ozone in the ozone-oxygen mixture, we determine the rate of flow through the test cavity and the amount of ozone leaving (resp. entering) the cavity per time unit.

Titration is done in the following way: ozone is bubbled through a solution of potassium iodine. Two flasks in series were tried, but a single one proved to be sufficient as no detectable amount of O_3 went through the second one. This is the reaction which takes place:

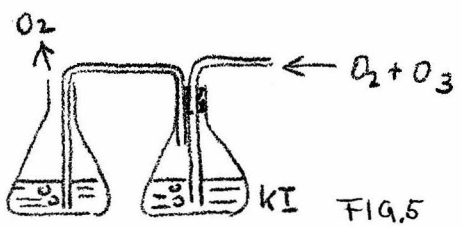


FIG.5

$$2\,KI + H_2O + O_3 \longrightarrow I_2 + 2\,KOH + O_2 \qquad (24)$$

A few drops of acetic acid were added to keep the sol. on the acid side and several ccm of starch solution as an indicator for free iodine.

For titration sodiumthiosulfate was used in approx. o.1 N solution (titration until solution colorless). The concentrations of the solutions were chosen in a manner to have ample KI in 50 cm^3 for ozone bubbling through at a rate of around 2 cm^3/sec. and to use approximately 10 cm^3 of sodiumthiosulfate for the titration (.1 % accuracy).

Titration:

$$I_2 + 2\ S_2O_3^{=} \longrightarrow 2\ I^- + S_4O_6^{=} \qquad (25)$$

Accordingly the ozone content is calculated from the following equations:

$$n(O_3) = \tfrac{1}{2}\, n(\text{thio}) = \tfrac{1}{2}\, N(\text{thio}).V(\text{thio})$$

$$V(O_3) = \frac{n(O_3)\ V_o\ p_o\ T}{p\ T_o} = \frac{n(O_3)\ T\ 22410\cdot 760}{p\ 273} \qquad (26)$$

$22410\cdot 760/273 = K$

V = volume
N = normality
V_o = 22.41 l
p = pressure
t = bubbling time
r = rate of flow = $V(fl)/\tau$
V(fl) = volume of flowmeter
τ = time required to fill flowmeter

$$V(mix) = r\ t$$

$$\%\ O_3 = \frac{N(\text{thio})\ V(\text{thio})\ T\ K}{2\ p\ r\ t}$$

$$\%\ O_3 = \frac{N(\text{thio})}{2\cdot V(fl)\cdot t} \cdot K \cdot \frac{V(\text{thio})\cdot T\cdot \tau}{p} \qquad (27)$$

e) TEMPERATURE EFFECTS

The considerations in III a) were based on the assumptions that the resonance frequencies of the evacuated cavities do not vary with the temperature. We shall see now that the effect of thermal expansion is quite considerable.

The resonant wavelength of a cylindrical cavity obeies the following relations:

$$\lambda_k = 2/(1/l^2 + \mathfrak{L}/r^2)^{\frac{1}{2}} \qquad (28)$$

l = length, r = radius of cavity

$$4/\lambda_k^2 = 1/l^2 + c/r^2 = (r^2 + cl^2)/\, l^2 r^2$$

γ & γ_e being the coefficients of thermal expansion for radial resp. longitudinal expansion, we write:

$$l = l_0(1 + \gamma_l t) \qquad r = r_0(1 + \gamma t)$$

Now let us calculate the change in frequency due to expansion:

$$\Delta\lambda_k = \frac{\partial\lambda_k}{\partial l}\Delta l + \frac{\partial\lambda_k}{\partial r}\Delta r$$

$$\lambda_k = \frac{2lr}{\sqrt{r^2 + cl^2}}$$

$$\frac{\partial\lambda}{\partial l} = \frac{(r^2+cl^2)^{1/2} r - lr\frac{cl}{(r^2+cl^2)^{1/2}}}{r^2 + cl^2} = 2\frac{r^3}{(r^2+cl^2)^{3/2}}$$

$$\frac{\partial\lambda}{\partial l} = \frac{\lambda_k^3}{4l^3}$$

$$\frac{\partial\lambda}{\partial r} = \frac{2cl^3}{(r^2+cl^2)^{3/2}} = \frac{c}{4r^3}\lambda_k^3$$

$$\Delta\lambda = \frac{\lambda_k^3}{4}\left(\frac{1}{l^3} + \frac{c}{r^3}\right)$$

$$\frac{d\lambda}{dt} = \frac{\lambda_k^3}{4}\left(\frac{\gamma_l}{l^2} + c\frac{\gamma}{r^2}\right) \qquad (29)$$

if we set $\gamma_l = \gamma$ we get

$$\frac{\frac{d\lambda}{\lambda}}{dt} = \left(\frac{\lambda_k}{2}\right)^2 \gamma\left(\frac{1}{l^2} + \frac{c}{r^2}\right) \qquad (29a)$$

in our case with γ(brass) = .000019
l = 26 mm
r = 25 mm
c = 1.48 for the TE 011 mode

$$\frac{\frac{d\lambda}{\lambda}}{dt} = .000019 \ /^{\circ}C$$

We made the splitting in γ & γ_ℓ in order to have a possibility to compensate the expansion effect. So we set now

$$\frac{\partial\lambda/\lambda}{dt} = 0 = (\frac{\lambda}{2})^2(\gamma_\ell/l^2 + \gamma_c/r^2)$$

$$\therefore \quad \underline{\gamma_\ell = -c\gamma\frac{l^2}{r^2}} \qquad (30)$$

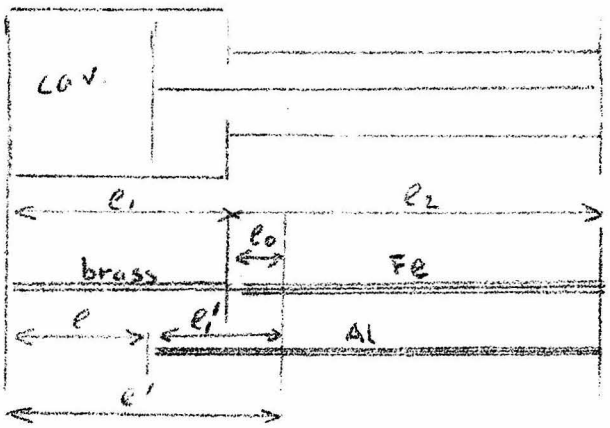
(we have neglected higher orders of γ and the fact that γ is not exactly contant, so strictly speaking this derivation holds only for one point)

Taking γ(brass) = .000019 , we get $\gamma_\ell = -.000030$

We cannot expect the temperature to be more accurate than $\frac{1}{2}$ °C with our experimental set, so an uncompensated cavity would cause an error of 10 parts in 10^{-6} which is not tolerable (from both cavities together about 4% error in ε)

We used therefore a compensation method to reduce the error substantially. The compensation for the first cavity consisted of an arrangement similar to the one used in compensated clocks.

FIG. 6



Def. $\Delta\ell_1' \Big|_{\Delta\ell} = \Delta\ell_1 \Big|_{\text{brass}}$

From this definition and the expansion coefficient for iron being .0000093 we get for $l_1 = 50$ mm $l_1' = 40$ mm and as $l = 26.5$ mm ... $l' = 66.5$ mm $l_0 = 16.5$ mm
We calculate the necessary l_2 to meet eq.(30):

$$\gamma(Fe)\, l(Fe) - \gamma(Al)\,(l(Fe)-l_0) = -\gamma_e l$$

$$l(Fe) = l_2$$

$$l_2 = (\gamma_e \cdot l + \gamma_{Al}\, l_0)/(\gamma_{Al} - \gamma_{Fe}) \cong 70 \text{ mm}$$

For the second cavity, not having available enough space for this kind of compensation, we used the following system:

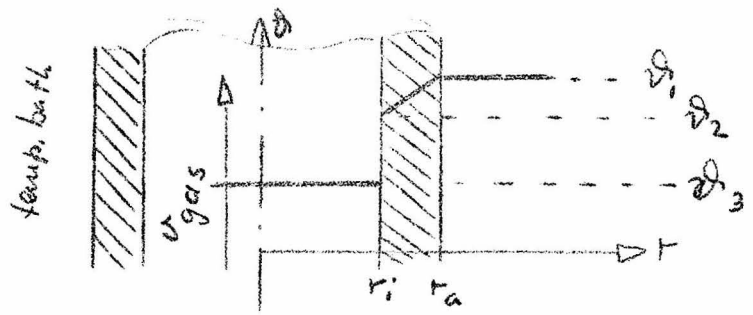
FIG.7

The action of the principle is evident and we do not reproduce the calculations for this case.

Another important question is, if the gas, particularly in the test cavity where we have continuous flow, accepts accurately enough the temperature of the cavity. Again we shall tolerate an error of .1 % for ξ or about .3 °C. We require this temperature being reached before the gas enters the cavity. Let us calculate the necessary length of glass tubing immerged in the temperature bath.

Assuming turbulent flow in the tubes, we make the following simplified assumptions for the temperature potential:

FIG. 8



We assume only radial flux of heat and the following specifications:

$$v = 4 \text{ cm/s}$$

$$|\vartheta_1 - \vartheta_3|_{a.t} \approx 0.1\,^{\circ}C \quad ; \quad |\vartheta_1 - \vartheta_3|_{m} \approx 100\,^{\circ}C$$

radial flux of heat = Q

$$q = Q/t$$

heat conduction in glass:

$$dq = 2\pi \lambda_g \frac{d\ell}{\ln \frac{d_a}{d_i}} (\vartheta_1 - \vartheta_2) \quad x) \qquad (31)$$

$$\lambda_g = 0{,}5 \div 0{,}8 \quad \text{kcal/m h °}$$

Convection:

$$\alpha = 3{,}65 \frac{\lambda}{d} \quad \text{kcal/m}^2\text{ h °} \qquad (32)$$

$$\lambda_{O_2} = .021 \quad \text{kcal/m° h}$$

$$dq = \alpha (\vartheta_2 - \vartheta_3) \pi \, d_i \, d\ell$$

$$dq = 11.5 \, \lambda_o (\vartheta_2 - \vartheta_3) \, d\ell \qquad (33)$$

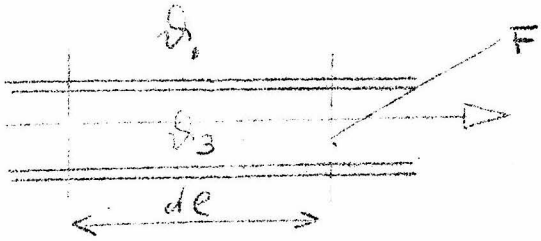
(this is for laminar flow, turbulence gives better conditions)

eliminating ϑ_2:

$$dq \underbrace{\left(\frac{\ln {}^{d_a}/_{d_i}}{2\pi \lambda_g} + \frac{1}{11.5 \lambda_o} \right)}_{K_1} = \Delta\vartheta \, d\ell \qquad (34)$$

$$\Delta\vartheta = \vartheta_3 - \vartheta_1$$

x) "Hütte" p. 447



$$d\Delta\vartheta = -d\vartheta_3$$

$$dq = q \cdot c \cdot d\vartheta_3$$

$$q = v \cdot F \cdot \gamma = v \frac{\pi}{4} d^2 \gamma$$

$$\frac{dq}{d\ell} = \frac{d\vartheta_3}{d\ell} \quad \underbrace{v \frac{c d_i^2 \pi \gamma}{4}}_{K_2} = -\frac{d\Delta\vartheta}{d\ell} K_2 \qquad (35)$$

combining (34) and (35):

$$\frac{dq}{dl} + K_1 K_2 \frac{d^2 q}{d\ell^2} = 0$$

$$\frac{\Delta\vartheta}{K_1} + K_2 \frac{d\Delta\vartheta}{d\ell} = 0 \qquad (36)$$

The solution of this equation is:

$$\Delta\vartheta = \vartheta e^{-\frac{\ell}{K_1 K_2}} \qquad (37)$$

$$\Delta\vartheta \Big|_{\ell=0} = \vartheta$$

$$\ell = K_1 K_2 \ln \frac{\vartheta}{\Delta\vartheta} \qquad (38)$$

Let us take the following numerical values:

glass tube 6/8 mm

$\vartheta / \Delta\vartheta = 1000$

$c_p = .24$ kcal/kg °

$\therefore$ $K_1 = 4.2$ m h °/kcal

$K_2 = 12.6\ 10^{-4}$ kcal/h °

$l \approx 4$ cm

(this calculation shows that, due to the small c_p of gases, the temperature drop is located nearly only in the sheet of convection)

IV TECHNICAL DESCRIPTION OF THE EQUIPMENT

a) MICROWAVE EQUIPMENT

The two cavities are connected to a klystron by a shunt T-section. Attenuators in all three branches reduce coupling between branches and source (a reflex klystron is influenced considerably by a varying load as this one) The branches are matched by tuning screws, they are terminated by cavities which have both an output coupling to a crystal detector. Coupling holes in the cavities are made as small as possible in order to get a high Q. (d = 3 mm). The cavities are cylindrical and oscillate in the TE 011 mode.

Let us assume that we are able to detect a frequency-deviation of 1/10 of the half bandwidth. The cavities have a calculated unloaded Q of approximately 30 000 (silverplated).

$Q = f/2\Delta f = \varepsilon \alpha / d\varepsilon$ $\quad \frac{1}{\alpha}$ = half bandwidth/detectable deviation

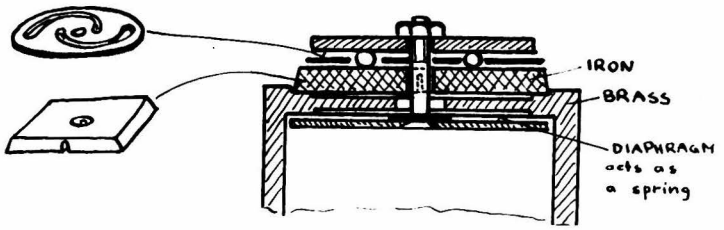
$$d\varepsilon = \varepsilon \alpha / Q = 3\ 10^{-6} \quad \text{if} \quad \alpha = 1/10 \quad \varepsilon \approx 1 \qquad (39)$$

which is around 1 % of δ in our case Actually the Q was

probably worse, but the experiments proved that with proper precautions an α of 1/100 would be possible.

One of the cavities was mounted in a bell jar, the connecting waveguide is sealed off at a choke flange by a polystyrene sheet. The length of the cavity can be varied by a micrometer screw for coarse frequency adjustment. On the opposite side of the cavity a temperature compensation was added:

Fig.9

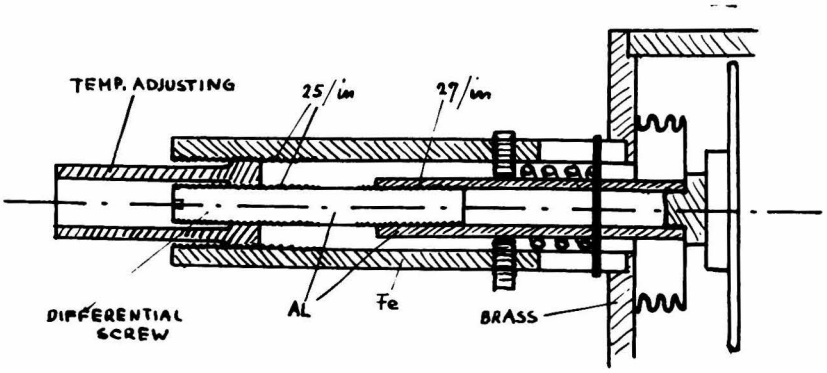


Moreover the empty space of the bell jar was filled up to some extent with iron bars to give the whole thing a large heat capacity to minimize temperature variation resulting from evacuating and refilling the jar.

Two 1-gal. bottles are connected to the bell jar, one of them filled with the standard gas, the other evacuated. This allows easy adjustment of the pressure.

The other cavity is submerged in oil. A thermostat and an electrical heating element allowed to keep the temperature constant within $\frac{1}{2}^{\circ}$C. This cavity had the following design:

Fig.10

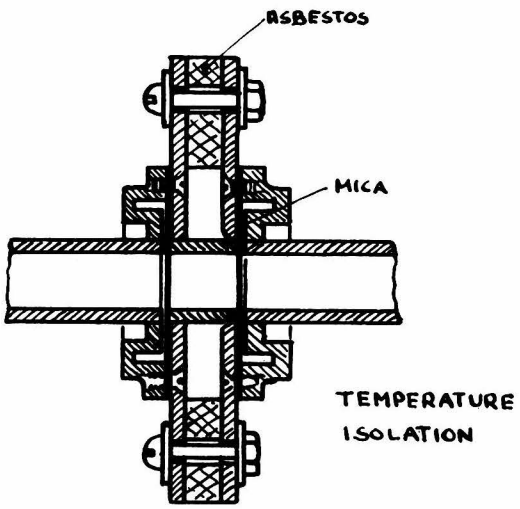


The performance of the compensation was checked and adjusted. It was possible to keep the frequency variation within $2{,}10^{-6}/^{\circ}$C.

To prevent corrosion by the ozone, the inside was coated with a very thin layer of tygoøn. It was necessary to isolate the waveguidees at the entrance to the temperature bath against heat fbw. Otherwise on the hot runs too much heat was conducted to the outside, which was harmful to the crystal set. On the cold runs condenswater drops and ice inside the waveguides disturbed the experiment. The cooling was done with ice water and with dry ice in a alcohol bath.

Mica sheets were used in connection with the temperature isolation to seal the cavity off against the rest of the plumbing.

Fig.11

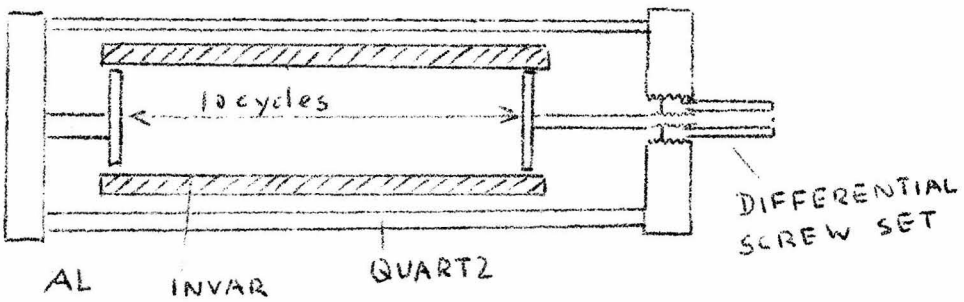


This cavity was the weak point in the set, as it was scarcely possible to find a sealing compound which is not attacked either by hot ozone or hot oil. The cavity could not be soldered off for the sake of the tygoon coating. A water-bath could not be used either as the high dipolar moment of water would destroy the measurements if only very minor leakages would occur. Finally at the high temperatures only air circulation was used for heating, which is of course less accurate than a liquid bath. Very small amounts of impurities which had leaked into the cavity accelerated the decomposition of ozone. I made one preliminary test with gold coating which looked satisfactory and it seems to me that the only possibility is, to goldplate the entire system as far as in contact with the test gas,

using no plastics coating and soldering off the cavity.

Hines' idea of absolute measurement should be tried again. It seems to me that with proper design sufficient temperature constancy could be obtained, for instance using a long"invar" cavity mounted in a good thermostat. We could use the following design:

FIG.12



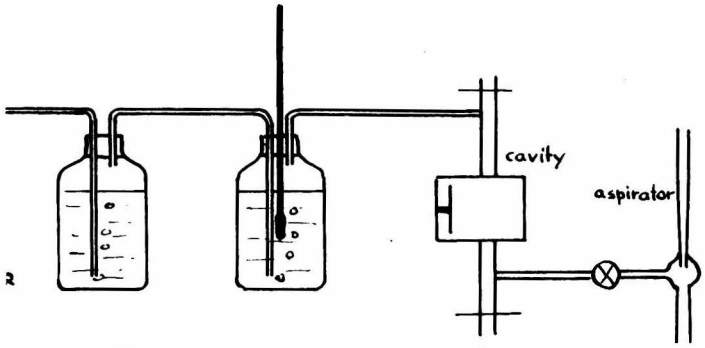
b) OXYGEN-OZONE, WATER VAPOR -EQUIPMENT

This eqipment is essentially the same as has been described by R.H. MacNeal in his report and I confine myself in describing some improvements. A precision-reducing valve was used to regulate the flow of oxygen. In addition the high voltage transformer was fed by a constant voltage set, both measures taken as the ozone-content proved to vary more than permissible.

A flowmeter was designed which permitted to keep the pressure constant and the same as during the titration period. Air was used in most cases as a standard gas, it was taken out of the room and dried through two dry ice traps.

For the runs with watervapor the following arrangement provided the necessary saturated air or oxygen.

FIG.13



No change of H_2O content was noticed if one of the two

bottles was removed at a flow rate of 2 cm^3/ sec. The temperature of the water in the bubbling bottles determines the content of watervapor in the gas.

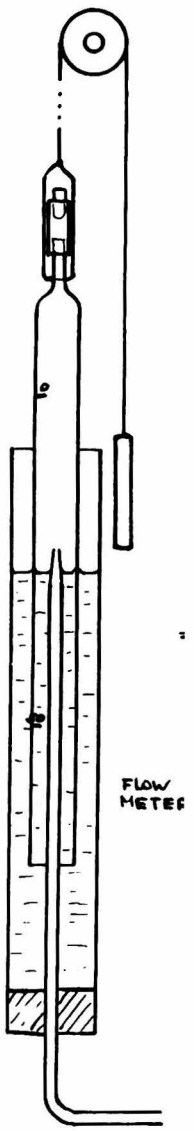


FIG. 14

c) POWER SUPPLY AND MODULATOR

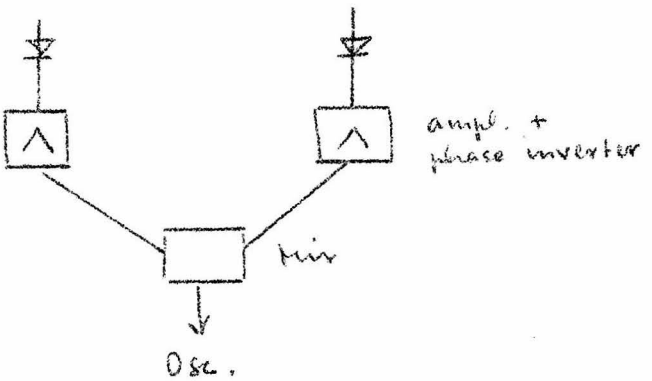
Nothing in particular has to be said on the power supply of the mixer-amplifier. Power supply and modulator for the klystron were designed by Hines. He converted a 60 cycle sinusoidal voltage in a square wave and after that into a triangular waveform. I suppose that this was intended for a different kind of indication, as there is no reason for such a procedure with our case of coincidence tuning, on the contrary. Sinusoidal modulation of the repeller voltage, parallel with sychronous sinusoidal oscilloscope deflection would give better results and a simpler modulator. In an improved set this would have to be considered, and as we shall see later, a higher modulation frequency should be used.

d) DETECTION AND INDICATOR CIRCUIT

The output of the cavities is rectified by 1 N 23 crystals. Two coaxial cables connected the crystals with the mixer-amplifier, essentially the one decribed in the paper of Fairbanks and MacNeal. A penthode in one channel

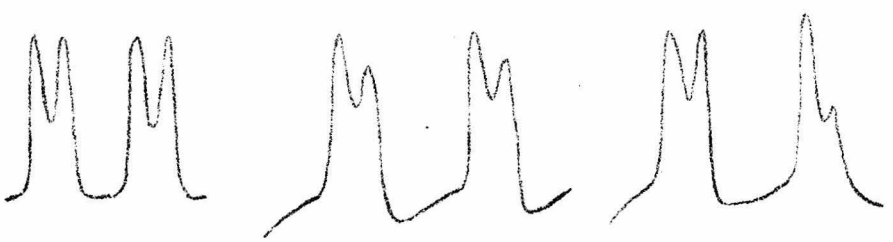
double
a triode in the other one produce opposite phase of the two components which are superposed in a mixerstage.

FIG.15



The frequency response of the amplifier had to be improved on the low frequency range. Actually a new amplifier would have been necessary, but because of shortage of time I tried to improve the existing one as ~~much good~~ as possible. If low frequency and phase response are insufficient, the following effect occurs:

FIG.15



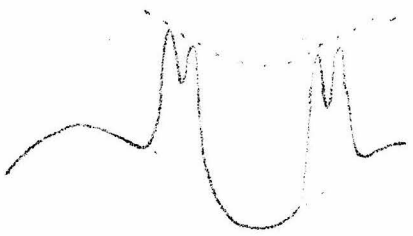
The four peaks which are produced during one sweep as a result of the superposition of the two resonance curves cannot be adjusted to equal amplitude as in a). We may either adjust according to b) which would be correct in this case but can be done much less accurate or like c) which can be done accurately but yields wrong results from the following reason: With the change in temperature and with the alternatively different gases in the cavities the Q will change considerably. So the relative slope of the cavity output envelope varies. Thus the small deviation from exact tuning which results if we tune according to c) is not constant and introduces an error of uncertain value

but at least a few times larger than the error due to unavoidable inaccuracies. Only if at all measurements the Q is approximately equal the requirements on the amplifier are less rigid.

In connection with this we may remark that the tuning can be done much easier and more accurately if the cavities have differnt Q's, so that the responses do not cancel entirely on the screen but give patterns like Fig.3. For equal Q it was very hard to determine the point of exact cancellation, whereas the two peaks of superposed unequal Q-curves can be matched even with considerable noise background.

As a result of the experiments with the set I would propose the following improvements+ The use of a sweep frequency of around 500 or 1000 cps; this would allow to cut off hum. It is nearly impossible to avoid some pickup of hdm, especially with the high gains necessary (loose coupling to the cavities), but as the sweep frequency is 60 cps too, this hum appears synchronously superposed on the screen and reduces accuracy of adjustment.

FIG.16



It is however possible to build a good amplifier for the band from 300 to 15000 cycles without much trouble and without clumsy condensers and danger of motorboating. There is no danger that a frequency of 1000 c would not allow proper building up of the oscillation in the cavities: even with a Q of 100 000 the build up time would be only about 10 microseconds which does not affect the slope of the Q-curve on the scope. Second: I would build two exactly alike amplifier channels and invert one of the crystals in the set. This would simplify the set and make it more symmetrical. Calibrated input potentiometers would make it easy to measure the variation of the Q of the cavities and thus to determine the absorption of the gases.

If we need the equipment only to measure the dielectric constant, nonlinear distortions in the amplifier are unimportant, however for measurements on the Q linearity should be pretty good.

V MEASUREMENTS AND RESULTS

a) GENERAL PROCEDURE

The system was tuned up and the cavities roughly matched by the micrometer of cavity II. The cooling system for the ozoniser refilled with ice and the H_2O traps with dry ice. Then the actual procedure (for ozone runs) was the following:

1 reading roomtemperature and atmospheric pressure

2 evacuating bell jar and refilling with standard gas

3 continuous flow of standard gas in cavity I

4 matching of the frequency with pressure in cavity II

5 reading pressure II, temperatures I & II, time

6 ozonizer on, pump for cooling water circulation in ozonizer on.

7 await stable conditions (ozone content), meanwhile prepare bottle for titration

8 matching roughly

9 measure flow

10 accurate tuning

11 read pressure II, temperature I & II, time

12 bubbling through KI-solution (1 or two minutes)

13 retuning if necessary

14 read pressure II, temp.I & II, time

15 flow measurement (to interpolate flow at time of titration)

16 ozonizer and pump off, evacuating II

17 short flushing of I with slightly increased flow rate

18 await stable conditions, meanwhile titrate last sample

19 as 4 a.s.o.

There were always slight shifts in frequency with time and between corresponding measurements a minimum of a few minutes was necessary (for flushing cavity, flow meas. and titration). So each point of the measurements was obtained by a chain of at least 3 + 5 complete "cycles" 4 to 19.

The runs air -- oxygen
oxygen or air --water vapor
air -- freon were made analogous with omission of titration and flow measurements. Vapor content was calculated from water temperature. From each run an average value of the dielectric constant was determined with the interpolated data. If the sucessive values in a run were much different, the run was repeated until reproducable measurements were obtained. A large number of measurements could not be used because of too much frequency shift, impurities in the test cavity, vacuum leakage large decomposition rate of ozone and various other difficulties.

b) OXYGEN - AIR

these values are calculated on the based $\delta_{air} = .000580$

T_1 °C	T_2 °C	p_4-p_2 mm Hg	δ red. to 0° 760 mm	
23.5	23.5	68 ± 6	.000534 1%	baro 737
49.8	25.1	58 ± 4	.000533 1%	

T_1	T_2	$p_4 - p_2$	δ		
69.8	27.5	54 ± 2	.000534	.5 %	
109.5	26.2	45 ± 10	.000535	2 %	
79.8	25.4	51 ± 3	.000533	.5 %	9 - 7 - 48
90.5	25.6	47 ± 2	.000536	.5 %	

the values are plotted on Fig.17

The difference between air and oxygen is somewhat larger than the one determined by Crain but within the error of 1%

$$\Delta \delta = .000046 \pm 5 \cdot 10^{-6}$$

c) DRY AIR -- OXYGEN, SATURATED WITH WATER VAPOR

These measurements were only made as a check on the method

T_1 °C	T_{water} °C	partial vap. press. mm Hg	ν vol.%	T_2 °C	$p_4 - p_2$ mm Hg	δ red. to 0°, 760mm		
49.6	27.0	26.74	3.52	27.8	367 ± 2	.00924	1%	BARO
49.4	27.2	27.06	3.56	27.8	346 2	890	1	738/735
79.8	24.5	23.06	3.06	25.4	260 2	842	1	9-2-48/
90.1	25.2	24.04	3,19	25.8	262 2	836	1	9-7-48
109.5	25.2	24.04	3.19	26.2	225 5	759	3	

from (6) we get

$$\mu = 1.87 \pm 0.05 \quad (\text{erg cm}^3)^{\frac{1}{2}}$$

The actual value, determined at low frequencies is 1.84 (Sänger).

(see graph Fig.18)

δ

FIG. 18

POLARISATION vs TEMPERATURE

9400 Mc

values red. to 0°C 760mm Hg

.008

.007

.006

.005

.004

.003

.002

.001

0.000

Water vapor

$\mu = 1.87 \pm 0.05 \cdot 10^{-18}$ cgs

T^{-1}

0 1 2 3 $\times 10^{-3}$

δ	Δδ
.00058	$5 \cdot 10^{-5}$
57	4
56	3
55	2
54	1
.00053	0

FIG. 17

dry air

$\mu = 0$

oxygen

1 2 3 $\times 10^{-3}$ T^{-1}

c) OXYGEN --OXYGEN + OZONE

The ozone runs caused most of the troubles of the experiments. At the beginning the values obtained were never reproducable. but the diffigulties were finally overcome and an unavoidable rate of decomposition was determined by a set of titrations at several temperatures at the input and output to the cavity (decomposition could certainly be avoided by a completely new design of the cavity using the experiences made with these measurements). For the calculations I assumed that the process of decomposition itself does not affect the dielectric constant. The difference in ozone content between input and output was the same for both directions of flow also the tuning compared with cavity II. So I assumed that most of the decomposition takes place in the cavity itself where the gas stays for some time; for calculation I took the averaged content of input and output.

Typical run for the determination of the decomposition rate:

Date : 11 - 5 - 48
room : baro 739 mm, t = 21.5 °C
cavity temp. = 22.0 °C
N(thio) = .0981
bubbling for titration : 60 sec
V(fl) = 100 cm³

	time min.	flow τ sec.	titration V_1 cm³	V_2 cm³	V(thio) cm³	% O_3
1 entering	1654	105,3	0040	0430	3.90	8.33
2 leaving	1700	105.0	0430	0800	3.71	7.90
3 entering	1706	105.2	0802	1195	3.93	8.37
4 leaving	1712	105.9	1197	1573	3.76	8.03
5 entering	1718	105.5	1573	1971	3.98	8.50
6 leaving	1724	105.3	1977	2353	3.76	8.02

ENTERING $\overline{8.40}$
LEAVING $\overline{7.98}$) 7%

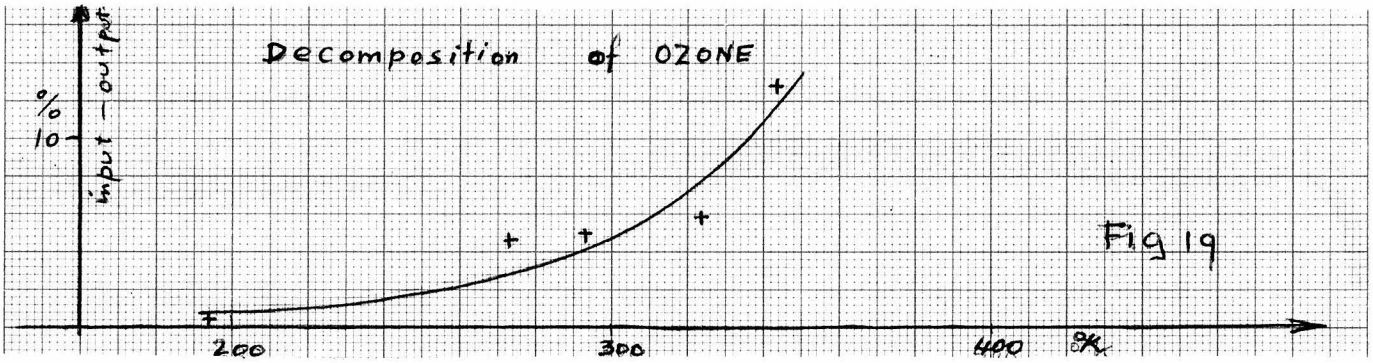


Fig 19

Typical ozone run:

Date: 11 - 4 - 48
baro 738 mm
N(thio) .0981
titration 60 sec
V(fl) 100 ccm

t_1 °C	τ sec	titration ccm	t_{room} °C	v% oz %	t_2 °C	mano readg. P_{II} mm	Δp mm	δ red. 0°760	time min
44.0					21.8	568 389	179		1607
44.0	92.6	0214 0624	21.2	7.70	21.8	623 326	297		17
44.0	92.2	4.10			21.8	624 825	299	116 .001782	19
44.0					21.8	570 387	183		32
43.8	59.5	0625 1250			21.8	626 323	303		41
43.7	59.7	6.25	21.2	7.57	21.8	627 322	305	119 1838	43
43.6					21.7	571 386	185		43
43.6	60.0	1252 1877			21.7	626 323	303		55
43.4	60.3	6.25	21.0	7.63	21.7	626 323	303	118 1812	1705
43.4					21.6	570 386	184		08
									18

graphical interpolation:

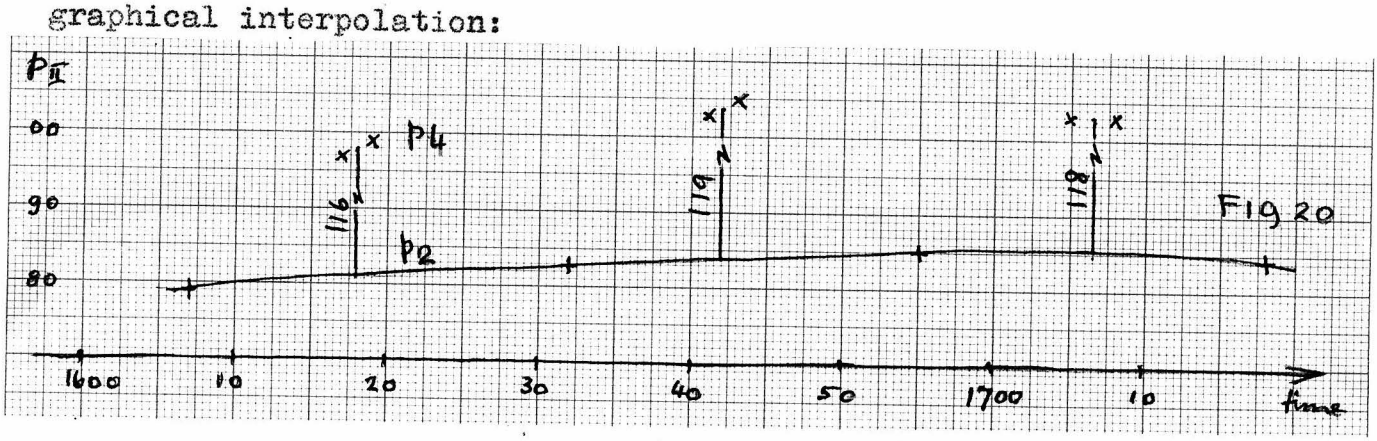


Fig 20

average δ = 0.00178 ± 3 if we make a correction of 2.5 % for ozone decomposition

Using the method of graphical interpolation, i.e. plotting of the frequency shift, relatively accurate values could be obtained even with considerable frequency shift. (The example on p.36 is a rather stable one)

The following table gives a summary of such runs which were used for the determination of the dipole moment.

date	baro	T_1 °K	%ozone	p_4-p_2	t_2	δ red. corr.		corr. decomp.
10-14	738	194.5	7.35	256	23.8	.002297	±25	0
11-19	739	194.5	8.24	269	23.6	2190	30	½ %
11-24	738	194.5	6.84	230	22.0	2225	40	0
10-21	739	273	8.12	156	23.0	1855	20	2.5 %
11-17	740	273	8.29	156	21.4	1840	30	2.5
11-2	740	296	8.10	144	22.9	1870	30	2.5
9-13	735	303	6.78	110	25.6	1830	70	
10-29	738	303	8.29	141	22.8	1840	20	2.5
11-4	738	317	7.63	118	21.7	1780	30	2.5
11-15	740	342	7.80	116	21.7	1740	70	6.5

these results are plotted in Fig. 21 p.38

from (6) we get the value for the dipole moment:

$$\mu = .52 \pm .03 \cdot 10^{-18} \quad \text{cgs} \quad (\text{erg}^{\frac{1}{2}}\text{cm}^{3/2})$$

d) OXYGEN - FREON

There are no special difficulties with the freons, they are easy to handle and not corrosive. The dielectric constant is too large so that the available pressure range in cavity II with air is not sufficient for measuring the difference between freon and air. There are several ways to use the method also for these cases:

1 use of a standard gas with larger diel. const.
2 design of cavity II for overpressure too
3 invert the procedure in the following way:

a freon in I, freon in II
b oxygen in I, freon in II

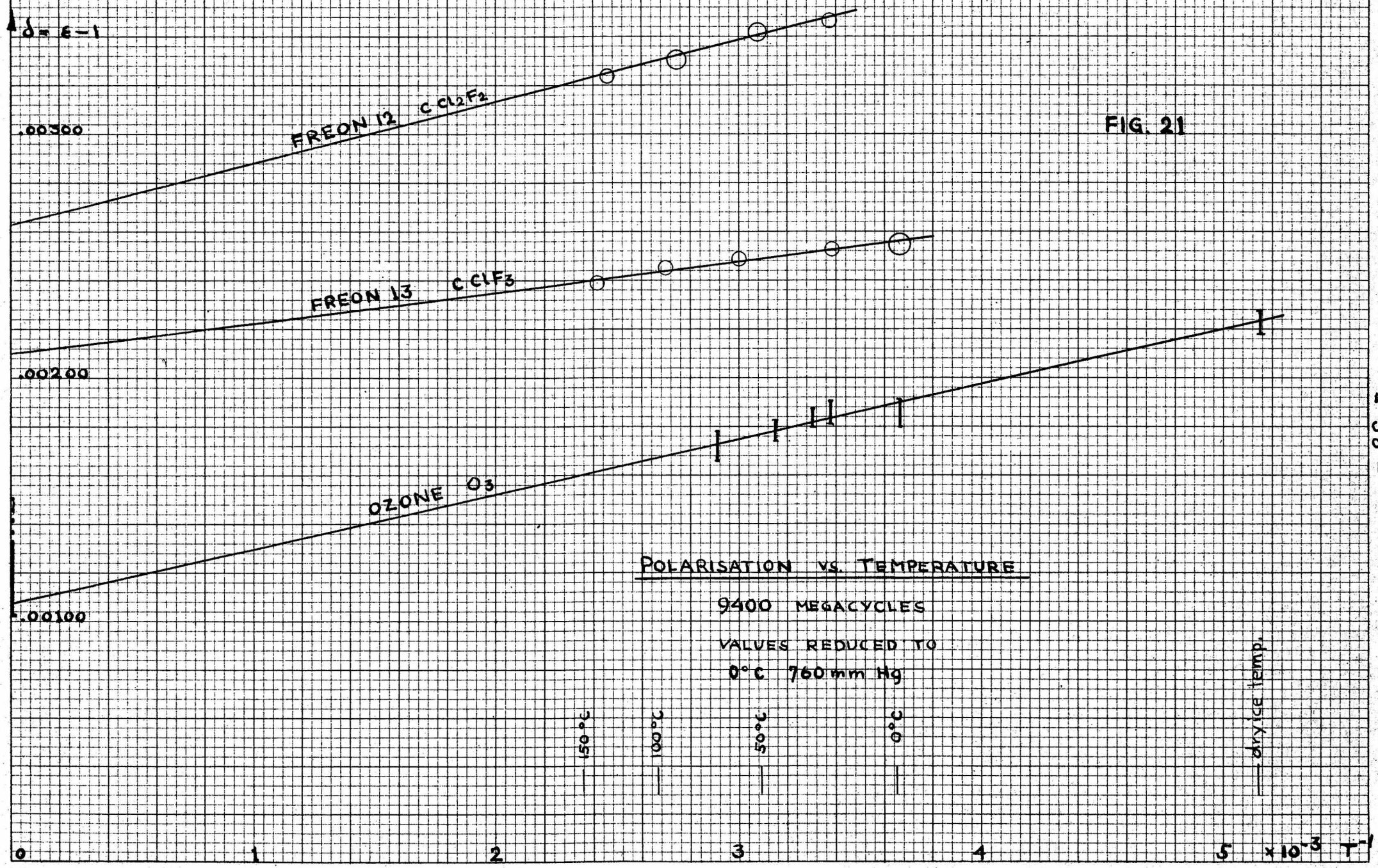

δ = ε − 1
.00300
.00200
.00100
FREON 12 C Cl2F2
FREON 13 C ClF3
OZONE O3
POLARISATION vs. TEMPERATURE
9400 MEGACYCLES
VALUES REDUCED TO
0° C 760 mm Hg
-50°C
-100°C
-50°C
0°C
dry ice temp.
0
1
2
3
4
5
×10⁻³ T⁻¹

FIG. 21

We used the third alternative, i.e. pressure cavity always filled with freon, test cavity alternatively with freon and oxygen. At first the dielectric constant of freon at one point was determined and then the calculation is the same as in the other runs except for a small correction due to the temperature dependability of the freon polarizability. With freon 13 at around 0°C with freon 12 already at room temperature a strange effect occurred: there were two pressures where an equilibrium was possible; at a certain point (around atmospheric pressure 0...25°C) increasing and decreasing the pressure in the freon filled cavity II shifted the frequency in the same direction. I did not have enough time to follow up this phenomenon which would have been interesding, so I used the one value which fitted into the measurements at higher temperatures.

R e s u l t s for Freon 12, $Cl_2C F_2$, dichlorodifluoromethane: (averaged values of individual runs)

date	baro corr.	T_1 °K	t_2 °C	$p_4 - p_2$ mm	δ red
12- 9	744	330	24	565	.00348
12- 9	744	364	24	496	334
12-10	744	406	24	417	323
12-14	747	297	24.2	633	346
12-14	747	324	25.2	572	341
12-14	747	365	25.8	491	330

see FIG. 21

The resulting dipole moment of

$$\mu = 0.55 \pm .03 \cdot 10^{-18} \text{ c.g.s.}$$

compares pretty good with the measurements of Smyth & McAlpine *) But we saw in II b) that we should not rely too much on this result, because of the effect of inertia. The dipole moment should at least be checked at another frequency which has not necessarily to lay very much off from the used one (10 or 1 cm waves would be intersting).

*) Smyth and McAlpine give a value of .51 in
Journ. Chem. Phys. 60 (1933) 1
see also Tables of el. dipole moments, techn. report II lab. for insulation research M.I.T. april 47

R e s u l t s for Freon 13, Cl C F$_3$, momochlorotrifluoromethane:

date	baro corr. mm	T_1 °K	t_2 °C	$p_4 - p_2$ mm	δ red
12- 6	744	297	22.5	644	.00350
12- 7	745	335	22.5	509	249
12- 7	746	370	22	450	245
12- 7	746	413	22	392	240
12- 7	746	415	22	390	239
12- 8	746	273	21	637	254

see fig. 21

we calculate a dipole moment of

$$\mu = 0.39 \pm .025 \cdot 10^{-18} \text{ c.g.s.}$$

The same remark as for the Freon 12 applies here too. The result is insofar interesding as we would expect a higher dipole moment for the less symmetrical Freon 13 - molecule.

f) REMARKS TO THE OZONE RUN

As a check for the determination of the dipole moment the value of for $T = \infty$ may be used (no dipole movement). Though it is not possible to predicht the accurate value, if not all the resonance frequencies from ∞ to $\lambda = 3$ cm are known, we can all the same give a lower limit and in the case of ozone the proper value is not expected to differ very much from this limit (see IIa)). Measurements on the index of refraction *) in the visible spectrum let us extrapolate to an -value of around 1.00102 . Fig. 21 shows that the difference of this value from our measurements is within the limits of error.

*) Landolt & Börnstein, Phys. Chem. Tab.
International Critical Tables

g) SUMMARY OF RESULTS

gas	temp. range investigated °K	ε 0°C 760mm	$\mu \cdot 10^{18}$ cgs	ε_∞ extrapol. red. to 0 760
H_2O	320 ÷ 390	1.0108 ± 2	1.87 ± 5	
O_3	194 ÷ 360	1.00190 2	0.52 3	1.00108 ± 10
$ClCF_3$	273 ÷ 420	1.00257 2	.39 2.5	1.00210 10
Cl_2CF_2	300 ÷ 410	1.00355 2	0.55 3	1.00263 10

[ε_∞ for ∞ temperature or otherwise eliminated movement of dipoles. All errors given in units of the last given decimal]

VI CONCLUSIONS

As a whole the method gave some interesting results and proved to be very convenient for measurements of this kind. However the desired accuracy has not been entirely obtained. I am convinced that a completely new design could improve the accuracy of the method by a factor of 10 or more. The proposed improvements would be:

1 higher scanning frequency and improved amplifier with proper amplitude and phase response.

2 better vacuum techniques, eventually design of cavity II for over and underpressure.

3 improved design of the cavities: use of INVAR steel or probably the best thing to do would be to use quartz for the construction of the cavity and metallize it in vacuum.

4 use gold plating for all parts which come into contact with the test gas. The drop in Q against silver plating can be tolerated.

5 use vacuum sealing also for the test cavity and design this cavity for use in bell jar as well

as for continuous flow.

6 calibrated input of mixer amplifier to be able to make absorption measurements.

7 eventually design of a cavity for absolute measurements as mentioned in IV c)

8 study the possibility of using the method over an extended frequency range.

As to the method in general I would make the following remarks: The method is a very nice idea, as the high Q of microwave elements can be used to determine small frequency shifts in a very convenient manner. However as we saw, we get into trouble with absorption bands if we measure heavier molecules. But just these are the ones which are most interesding at present. If we want only to determine the dipole moment, it would probably be better to go back to lower frequencies. Beat methodøs in connection with crystal oscillators could yield as good results as this method does. Temperature and vacuum troubles would be about the same as we had.

But if we could extend the microwave method from a single frequecy to a considerable band or at least to a number of discrete frequencies, this would be an ideal method for absorption and refraction measurements.

5 - 30 - 49

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VII REFERENCES

Lewis & Smyth, Journ. Am. Chem. Soc. 61 (1939) p 3063

Watson, Rao, Ramaswamy, Proc. Roy. Soc. London A143 (1934) p.558

Smyth & McAlpine, Journ. Chem. Phys. 1 (1933) p.190

Tables of Electric Dipole Moments, techn, report II lab. for insulation research M.I.T. 1947 april

Landolt & Börnstein Phys. Chem. Tabellen

Potapenko & Wheeler, Rev.Mod.Phys. 20 (1948) p.143

Crain, Phys.Rev. (1948) sept 15 p.691

Smyth & McAlpine, Journ.Chem.Phys. 60 (1933) 1

International Critical Tables 7:10

Contents