pure calcium metagermanate. All of the germanium is present in the insoluble or filterable structure if the proportion of calcium hydroxide reaches or exceeds the amount present in the molecular ratio $2CaO:GeO_2$.

4.   The water of the hydrogel may be replaced by a number of other liquids such as methyl and ethyl alcohol or acetone and these non-aqueous liquids may in turn be replaced by ethyl ether or benzene, yielding a series of non-aqueous dispersoids which are permanent if protected from evaporation.

5.   Excess of lime water gives a very delicate and characteristic test for germanic oxide. A small fraction of a milligram of GeO_2 in 20 cc. of water may be recognized on account of the extraordinarily bulky nature of the hydrogel.

6.   Strontium germanate yields a dispersoid similar to the calcium salt but gels are not obtained at dilutions comparable to those used in the preparation of the calcium salt.

7.   Barium germanate is distinctly different from the calcium and strontium salts. This salt is very distinctly crystalline and appreciably soluble in water. Crystalline $BaGeO_3$ is formed in shining aggregates, probably octahedral. Under the polarizing prism it is shown to be isotropic.

PHILADELPHIA, PENNSYLVANIA

NOTE ON THE VACUUM CONTRACTION OF DENSITY BULBS[1]

BY MARCEL BECKERS[2]

Having undertaken the systematic study from a physicochemical point of view of the easily liquefied saturated hydrocarbons, we have been led to assemble at the start a considerable body of experimental material, in order to free ourselves from anxiety over apparatus problems during the measurements.

We had already calibrated a series of gas density bulbs for our measurements of the weight of a liter of n-butane,[3] but as regards contraction on evacuation, the values obtained differed in general by 25% from those calculated by the formula of E. Moles and R. Miravalles.[4]

[3] Beckers, *Bull. soc. chim. Belg.*, **36**, 559 (1927).

[4] Moles and Miravalles, *J. chim. phys.*, **21**, 1 (1924).

We have thought it worth while to reopen the question with new measurements. They have been carried out on bulbs numbered 3 to 10, previously calibrated, and on nine new ones, numbered 11 to 20. All the bulbs, whose capacity varied from 600 to 2000 cc., were constructed of Thuringian glass; although we do not know the age of this glass, only bulbs Nos. 6 and 7 devitrified in the flame, and we have not used them further in our work.

The uncertainty of the results obtained by the method of Travers being generally accepted, we have attempted to check them by a method different in principle, namely, the hydrostatic method. Six bulbs (Nos. 6, 15, 16 and 17; 12 and 13) have been measured in both ways. Due to the good agreement obtained, the other bulbs were studied by Travers' method alone.

To attain the desired accuracy, we have had continuously to overcome a number of experimental difficulties. The different investigators who have carried out measurements of this kind have also mentioned meeting obstacles, but unfortunately they have been reticent of details as to their mode of operation. Therefore, we think it worth while to describe our technique in detail, especially as such measurements are slow to make, and their accuracy depends on small factors.

Hydrostatic Method.—The technique adopted differs from that of Moles and Miravalles[4] as follows. The bulb, immersed in a water-bath, is weighed successively evacuated and filled with air. To effect this, the bulb was ballasted by a mass of iron, nickel plated and polished, whose weight was slightly greater than the buoyant force. The iron sinker was suspended by a sort of net made of three pliable brass wires, symmetrically placed in three meridians of the glass sphere, and joined together at the base where the weight was attached by a hook. The upper ends were fastened to another wire forming a concentric loop about one centimeter from the neck of the bulb. In this way, the weight is practically evenly distributed about the neck of the bulb; this region is particularly rigid, and one may assume that no sensible change is made in the amount of contraction by this method of procedure.

The calculation of the results requires knowledge of the weight of air included in the bulb. This quantity is determined by filling the bulb with dry air, freed from carbon dioxide by appropriate washing,[5] and by the knowledge of the interior volume. The pressure of the gas and the temperature of the room must also be noted.

One of the inconveniences of the hydrostatic method lies in the size of the corrections to be made for a variation in temperature of the water-bath, e. g., a variation of 0.14° with a volume of 1393 cc. leads to a correction of 0.034 g. In order to reduce these corrections as much as

⁵ E. Saerens, *Bull. soc. chim. Belg.*, **33**, 28 (1924).

possible, we arranged to have the temperature of the bath close to that of the room. It must also be noted that the total volume of the bulb, sinker, net, etc., must be taken into account in these calculations. This volume is determined by the loss in weight of the bulbs fitted with the same equipment as at the moment of construction of the counterpoises.

The bulb is completely immersed in the bath and the capillary above the stopcock is filled with distilled water before immersion.

The weighings were done on a balance sensitive to one milligram.

The suspension between water and air was made of a flexible copper wire 0.2 mm. in diameter; without taking special precautions, the measurements were easily reproducible to about one milligram.

One important source of error was due to bubbles of air which clung accidentally to the sides of the bulb; to prevent this the exterior surface was carefully freed from grease.

As an example of the calculation, the results on Bulb 15 are given.

Exterior volume of bulb, sinker, etc., 1385 cc.
Interior volume of bulb, 1161.4 cc.
Mean temperature of bath, 16.30°.
Change in density of water per 0.01° in the region of 16.30°, 155×10^{-8}.

Weighing (a)   Bulb filled with air, 68.437 g., bath at 16.31°
Correction for bath temp., $155 \times 10^{-8} \times 1 \times 1385 = 0.002$ g.
Corrected weight, 68.439 g.

Weighing (a′)   Bulb evacuated, 67.293 g., bath at 16.32°
Diff., (a) − (a′) = 68.439 − 67.293 = 1.146 g.
True weight of air from weight (a) =

$$1161.4 \times 1.293 \times \frac{273}{273 + 16.4} \times \frac{737.7}{760} = 1.375 \text{ g.}$$

Loss due to contraction = 1.375 − 1.146 = 0.229 g.
Value corr. for density of water at 16.3° = 0.2292 cc.[6]
Contraction, corrected to 760 mm. = 0.236 cc.

Later we found

Weighing (b)   Bulb filled with air, 68.455 g., bath at 16.32°
True weight of air =

$$1161.4 \times 1.293 \times \frac{273}{273 + 16.4} \times \frac{738.4}{760} = 1.376 \text{ g.}$$

Diff., (b) − (a′) = 68.445 − 67.293 = 1.152 g.
Loss due to contraction = 1.376 − 1.152 = 0.224 g.
Corrected to 760 mm. = 0.2305 cc.

Weighing (b′)   Bulb evacuated, 67.295 g., bath at 16.32°
Diff., (b) − (b′) = 68.445 − 67.295 = 1.150 g.
Loss due to contraction = 1.376 − 1.150 = 0.226 g.
Corrected to 760 mm. = 0.233 cc.

Mean contraction for the three measurements = 0.2332 cc.

For the six bulbs studied by this method the contraction has been determined by measurements (a), (a′), (b) and (b′), made in the same

[6] This correction is negligible.

way. From the four measurements we get three values for the contraction, differing in the most unfavorable case by only 2.5% from the mean (Table II). We may say here that the values deduced from (b) and (b') are in all cases the closest to those obtained by Travers' method.

Travers' Method.—In this method the bulb is placed in a strong and rigid vessel, and the space between the bulb and the wall of the vessel is filled with water. The vessel is provided with a passage for the inlet tube of the bulb, and also for a vertical capillary filled with water. On evacuating the bulb, the water descends in the capillary owing to the diminution in the volume occupied by the bulb. We have already[7] described the method of operation in our first experiments. We could not then obtain a steady meniscus; what is more, the readings on contraction did not agree with those on expansion. We thought that the precision of the thermostat might play a role in this discrepancy, so our first effort was to employ a more sensitive thermostat;[8] during the new measurements, the temperature variations from the mean were about $0.002°$. The dead space being 7 liters, and assuming a variation in the interior of the vessel of $0.001°$, the displacement possible in the capillary would be

$$7 \times 10^6 \times 2 \times 10^{-7} = 1.4 \text{ mm.}[8]$$

which is the order of precision desired in these measurements.

The cover of the vessel this time was curved and had a neck pointing up, larger on top than bottom. This was the manner of filling: the cover is fitted, in addition to the experimental bulb, with the calibrated capillary tube T, (see Fig. 1), and also a tube, H, with stopcock. The cylindrical vessel, placed in the thermostat, is filled with air-free distilled water to such a height that, on putting on the cover with bulb attached, the water does not quite reach the ground surface. Two weights, P, of 500 g. are tied to the stopcock in order to counterbalance approximately the buoyancy of the bulb. The cover is then closed tightly, taking care that the lubricant is evenly spread. Weights are placed on the cover so as to compensate largely for the buoyancy of the bulb.

First the bulb is evacuated[9] and then, by means of the tube, H, the space above the water in the cylinder. Due to the difference of pressure, air-free distilled water can then be slowly introduced through the capillary, T, until the space beneath the cover is almost filled. It is left under vacuum for a quarter of an hour, shaken lightly to detach bubbles from the bulb, then filled completely and the stopcock, L, closed. The distilled water used to fill the cylinder is stored in an auxiliary thermostat, maintained $0.2°$ higher than the thermostat used in the measurements, so as to compensate approxi-

[7] Ref. 3, p. 567.

[8] L. Maricq and M. Beckers, *Bull. soc. chim. Belg.*, **37**, 12 (1928).

[9] To prevent the plug leaving the barrel of the stopcock when the space above the water containing the bulb is evacuated.

mately for the lowering of temperature caused by evaporation *in vacuo.* After two hours the meniscus in the capillary is constant to about 1 mm.[3] After this lapse of time, all of the small bubbles in the apparatus are dissolved.

In our first experiments we did not succeed in preventing a rapid descent of water in the capillary. After various trials, we became sure that this difficulty was due to a slow rise of the cover as a result of the pressure of the water in the capillary, which was placed vertically. For, if the capillary has a length of 50 cm., the pressure is 50 g./cm.[2]. The cover having a surface of about 300 cm.[2], it would take 50 g. $\times$ 300 = 15 kg. to balance
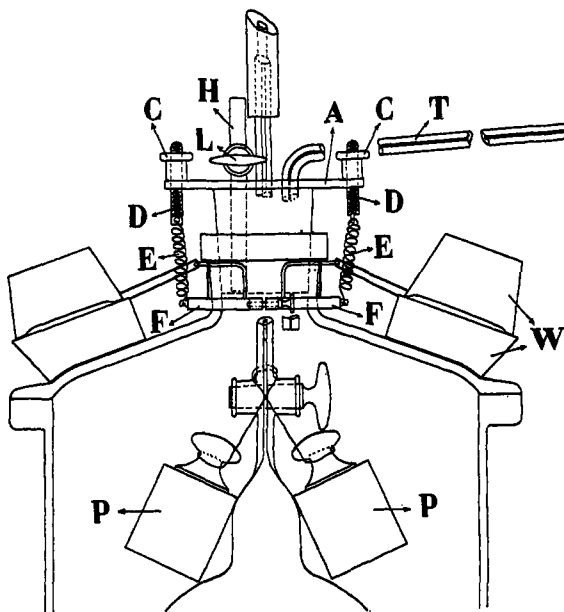

Fig. 1.

this force. Obviously it is necessary to avoid the slightest movement of the cover, for it would require a rise of only $^1/_{25}\,\mu$ to cause a displacement of 1 mm.[3] in the capillary. To lessen as much as possible the pressure produced by the water in the capillary, we bent the tube above the neck so as to render it nearly horizontal, thus reducing the pressure to a few cm. of water. In all our measurements the cover was held down by 10 kg. distributed equally over the surface.

From the time this artifice was used, we were able to hold the level constant in the capillary; but, in the first experiments, it slowly dropped during the measurements. Later we were able to complete a series of experiments during each of which the level remained constant within 1 or 2 mm.[3] from the beginning to the end of the measurement, *i. e.*, for several

hours. This difference of behavior can only be attributed to acquired skill in manipulating. For lubricating the ground joint we used anhydrous lanolin, which appeared to have the strongest adhesion.

To fasten the bulb and the other attachments to the cover, we tried two procedures. (1) A round disk of rubber with three holes was fixed in the neck and then covered with melted beeswax. In spite of all precautions, the wax cracked as it cooled, and even if one managed to cool it in one piece, it finally detached itself from the neck, as a result of the contraction on cooling. We had to abandon this method.

(2) A three-holed rubber stopper was solidly fixed in the cover as follows: a heavy metal plate, A, pierced also with three equally spaced holes, was placed above the stopper, B, and held tightly against it by three nuts, C, acting on threaded rods, D, flattened on one side. These screws are connected by means of springs, E, with a collar, F (in two pieces), which is rigidly attached to the neck of the cover by two screws. One could thus attain a progressive compression of the stopper, but, in spite of its strength, the stopper contracted slightly under an auxiliary pressure of 100 g. However, the level in the capillary came back very exactly as soon as this auxiliary pressure was removed. If any secondary action on the stopper is avoided, the level in the capillary remains very constant during a whole experiment, as we have already said. We may cite, by way of example, the results obtained with bulb No. 15; the level in the capillary decreased slightly during the experiment, and corresponding corrections have been made to the readings.

TABLE I

CONTRACTION AND EXPANSION DATA

Atmospheric pressure = 758.3 mm.

Contraction	0.2331	0.2343	0.2355	0.2343	0.2323	0.2331	Mean,	0.2338
Expansion	.2331	.2375	.2351	.2343	.2319	.2331	Mean,	.2341

Mean of the two series, 0.2340 cc. Contraction corrected to 760 mm., 0.2345 cc.

The mean of the values obtained on contraction and on expansion do not differ as a rule by more than 0.2%, although in a few cases they reach 0.4%.

Concordance of the Two Methods.—This is shown by the following figures for six bulbs.

TABLE II

CONCORDANCE OF TWO METHODS

Bulb	Vol., cc.	Contraction obs., cc. Hydrostatic	Travers	Mean contr., cc.	Dev. from mean, %
6	906	0.1412	0.1330	0.1371	2.9
15	1161	.2332	.2345	.2337	0.3
16	1176	.2593	.2661	.2627	1.3
17	1165	.304	.3121	.308	1.3
12	2159	.3738	.3922	.383	2.4
13	2146	.374	.3836	.3788	1.3

It follows that the mean value of the two methods does not differ from the values obtained from either by more than 2%. We may therefore be permitted to conclude that the values obtained by each method may be considered correct to within 2%.

The hydrostatic method seemed to offer chances for more important accidental errors than that of Travers, so that henceforth we will only consider the results obtained by this latter method.

There follows a table showing the contractions found by the method of Travers, and also the values of η and K in the formula proposed by Moles and Miravalles

$$\eta = \frac{KV}{w} 10^{-3} \text{ cc.}$$

where η is the compressibility of the bulb under one atm., reduced to one liter, V is the volume in cc., w is the weight of the glass (minus that of the stopcock), and K is a constant, equal to 15.5, according to the authors.

TABLE III

CONTRACTION DATA

Bulb	Vol., cc.	Wt. of glass (minus wt. of the stopcock), g.	Obs. contr. reduced to 760 mm.	η	$K = \eta \frac{w}{V}$
3	609	70	0.0867	0.1423	16.4
4	624	56	.1178	.1890	17.0
5	630	71	.0884	.1403	15.8
6	906	101	.1330	.1468	16.4
7	910	113.5	.1160	.1275	16.0
8	1158	110	.2210	.1909	18.1
9	1174	93	.2758	.2351	18.6
10	1264	106	.2852	.2255	18.9
11	2162	143.5	.5287	.2446	16.2
12	2159	186	.3922	.1817	15.6
13	2146	192.5	.3836	.1788	16.0
15	1161	103	.2345	.2019	17.9
16	1176	89	.2661	.2264	17.1
17	1165	80	.3121	.2678	18.4
18	778	133	.0743	.0955	16.3
19	794	142	.0735	.0980	17.6
20	785	142	.0714	.0909	16.4
				Mean	17.0

The mean value of K is 17.0, with a maximum experimental deviation of 11%, and a deviation of 10% from the value 15.5 proposed by Moles and Miravalles. We should point out that the mean value of K found for the three bulbs of two-liter capacity is 15.9. The low value for these three (11, 12, 13) is due to the necks of the bulbs being only one cm. long, while all the others were about 4 cm. long. If these latter had also been made with short necks, thus diminishing the weight of glass, K would have been lowered by 5 or 10%, and thus would have approached considerably nearer the value of Moles and Miravalles.

Our experiments lead us to the following conclusion. The contraction under vacuum of bulbs of capacity from 600 to 2200 cc., and whose wall thickness varies appreciably, can be represented to within a few per cent. by the empirical formula

$$\eta = K \times \frac{V}{w} \times 10^{-3}$$

in which K has a value of about 16.0, if, in establishing the weight, a deduction is made for the neck of the bulb.

Our results thus correspond with those of Moles and Miravalles and confirm these authors in the opinion they have expressed, thus: "From the preceding, it necessarily follows that the empirical formula we have established gives the values of the compressibility of density bulbs more exactly than those measured by the authors, by a single method, and without taking excessive precautions."

The values obtained for Bulbs 3 to 10 of the preceding determinations diverge markedly from those considered above. We have repeated the calculations of these results, and have recalibrated the capillaries used. This has led us to make only a few small corrections to the old numbers. We give in the following table the corrected old values, new values and the concordance between the two.

TABLE IV

VALUES FOR BULBS 3–10

Bulb	Atm. press. during expt., mm.	Old values		New values	Ratio, new : old values
		Contraction in cc. corr. to 760 mm.			
3	766	0.067		0.0867	1.30
4	751	.0845		.1178	1.395
5	738	.065		.0884	1.36
6	{ 745 / 770	.099 / .092 }	0.0955	.1330	1.39
7	{ 749 / 763	.0847 / .0855 }	0.085	.1160	1.36
8	763	.1555		.2210	1.42
9	766	.1885		.2758	1.46
10	{ 753 / 769	.2005 / .196 }	0.198	.2852	1.44

Leaving out Bulb 3, the mean value of the ratios in the last column is 1.403, and it would require a diminution of the contraction of Bulb 3 by only 0.004 cc. to bring this also to the 1.4 ratio.

The remarkable constancy of this ratio of new to old values, in spite of its great sensitivity to small variations of the value obtained for the contraction, leads logically to the admission of some systematic error in our first measurements. The thorough examination to which we have subjected them ourselves did not lead us to discover it.

It seems difficult to attribute this to the fact that in our older measure-

ments the water surrounding the bulb had not been freed from air. What-
ever the cause may be we must admit that our first experiments are in
error due to imperfection of the technique. It is to these same causes,
so it seems, that the erroneous values obtained in this field by most in-
vestigators are due.[10] Fortunately, they do not introduce any large error
into the gas density; in the case of butane, for instance, the density should
be corrected by about one part in 20,000.

Variation of the Contraction as a Function of the Pressure.—In
the determination of the density of a gas under reduced pressure ($^1/_3$ to
$^2/_3$ atm.) it is necessary to know the contraction of the bulb with the
same relative precision as under a pressure of one atmosphere. Until
now one has been forced to accept the hypothesis that the contraction was
a linear function of the pressure difference to which the bulb was sub-
jected.[11] We wished to make an experimental verification of this hy-
pothesis. Our measurements, by the Travers method, were carried out on
three bulbs, on two of which the contraction under $^1/_3$ atm. was measured,
and on the other at $^2/_3$ atm.

Our results are, in the three cases, completely in accord with the hy-
pothesis advanced. The table shows the results obtained on Bulb 13.

TABLE V

RESULTS ON BULB 13

Interior volume of the bulb, 2146 cc. Contraction reduced to 760 mm., 0.3836 cc.

Red. press., mm.	Values obtained in cc. On contraction	On expansion	Mean value	Calcd. value
479.4	0.2408	....	0.2408	0.2416
483.3	.2421	0.2443	.2432	.2436
479.9	.2411	.2411	.2411	.2419
477.6	.2399	.2399	.2399	.2407

To M. Timmermans, who has accepted the direction of our researches,
we would like to express here our sincere gratitude for his aid and his
willing support.

Summary

The contraction of density globes on evacuation has been investigated
in connection with a physicochemical examination of easily liquefied satu-
rated hydrocarbons. A hydrostatic method of measurement has been
applied to the problem, as well as the method of Travers; the results by
both methods are in good agreement.

The empirical equation proposed by Moles and Miravalles for the calcu-
lation of the compressibility of density globes is given additional con-
firmation by the results of the measurements.

Data have been obtained which lend support to the hypothesis that the

[10] Ref. 4, p. 8.
[11] G. Baume, *J. chim. phys.*, **6**, 18 (1908).

contraction of density globes is a linear function of the pressure difference
to which the bulb is submitted.

BRUSSELS, BELGIUM

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY]

THE DIELECTRIC POLARIZATION OF LIQUIDS. V. THE ATOMIC POLARIZATION

BY C. P. SMYTH

In previous communications[1] the total polarization, P, of a substance
has been divided into three parts, P_E, the electronic polarization, P_A, the
atomic polarization and P_M, the orientation polarization due to the
permanent moments of the molecules.   This series of papers is concerned
mainly with the conclusions to be derived from the values of P_M for liq-
uids, but, as P_M is commonly obtained from the total polarization, P,
by subtracting P_E and P_A, it is evident that no treatment of the problem
can be complete without consideration of the two latter quantities.   As
P_E is discussed in another paper,[2] the present treatment will be confined
to the significance of P_A, especially in its relation to molecular structure.

The polarization is commonly obtained from dielectric constants meas-
ured at frequencies up to 3,000,000 cycles or wave lengths down to 100
meters.   For much higher frequencies or shorter wave lengths, the orienta-
tion of the dipoles in an applied field often becomes less and P_M diminishes,
being negligible for frequencies in the infra-red region.   In the range of
visible light the frequency of the alternating field is so great that, for the
most part, the electrons only are affected by it, the polarization being P_E
alone. P_E is thus determined as the molar refraction for visible light.
In the absence of anomalous dispersion, the small variation of P_E with
wave length may be calculated by a simple dispersion formula such as that
of Cauchy or Sellmeier[3] and the value of P_E obtained for the comparatively
low frequencies, virtually infinite wave length, at which the dielectric
constant is measured.   However, the presence of oscillators with frequen-
cies in the infra-red region causes anomalous dispersion and, in consequence,
polarizations greater than the values obtained by extrapolation with the
simple formulas.   Actually these oscillators are displaced in the electric
field, forming electric doublets and thus contributing to the polarization
of the medium.   Although some of these oscillators may be electrons, the
majority are atoms, ions or radicals and, for this reason, their contribution

[1] (a) Smyth, Morgan and Boyce, THIS JOURNAL, **50**, 1536 (1928); (b) Smyth
and Morgan, *ibid.*, **50**, 1547 (1928); (c) Smyth and Stoops, *ibid.*, **50**, 1883 (1928).

[2] Smyth, Engel and Wilson, THIS JOURNAL, **51**, 1736 (1929).

[3] See Errera, "Polarisation Diélectrique," Les Presses Universitaires de France,
Paris, **1928**; also Smyth, *Phil. Mag.*, **45**, 849 (1923).