

ON THE DENSITY AND SURFACE TENSION OF
LIQUID AIR.

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A SIMPLE lecture table experiment shows that the density of liquid air when allowed to boil freely increases rapidly. Therefore, determinations of its density by ordinary methods will give values too great. These values range from that of liquid air to approximately that of liquid oxygen, depending upon the activity of boiling and the time that has elapsed.

It was the first intention to confine this paper to the surface tension of liquid air, but it became evident that the surface tension too would change with age. By constructing a curve showing the variation of the surface tension with time for the liquid air contained in a given Dewar bulb exposed to constant radiation conditions we can approximate to its value when first made. However, in order to construct this curve, we must know the variation of the density with time under the same conditions. It is for this reason, therefore, that a few observations were made on the density and included in this paper.

THE DENSITY OF LIQUID AIR.

Various methods have been employed by investigators for determining the density of liquids at low temperatures. One method,¹ for an approximate determination, is to select some substance that will just float in the liquid and then compare the density of this with that of water. This method can not be used advantageously in determining the variation with age.

Weighing a sinker in the liquid was also used. This method, too, is only approximate since little or nothing is known concerning the cubical contraction of the sinker at those extremely low temperatures. It is a very convenient method, however, for de-

¹ H. Moissan and J. Dewar, *C. R.*, 125, pp. 505-511, 1897.

termining the variation of the density with time, and was therefore employed.

The liquid air was placed in a Dewar vacuum bulb of about three quarts capacity. The bulb was about half full to begin with. Two glass sinkers were used. The age of the liquid air at the time of weighing was noted. It was assumed that the coefficient of expansion of glass holds at the temperature of liquid air. Upon this assumption the formula¹ for the density becomes,

$$\text{Density} = \frac{V(W - W'')(\rho - \sigma) + (W - W')[V'\delta' - V(\delta - \sigma)]}{V'(W - W')}$$

in which,

V = volume at t° C.

V' = volume at -191° C.

W = weight of sinker in air.

W' = weight of sinker in water at t° .

W'' = weight of sinker in liquid air.

ρ = density of water.

δ = density of sinker at t° .

δ' = density of sinker at -191° .

σ = density of air at t° .

For the sake of comparison all of the data are given in the following table :

TABLE I.

Sinker.	No. 1.	No. 1.	No. 2.	No. 2.	No. 1.
July.	22d.	19th.	22d.	22d.	22d.
Age of Liquid Air.	30 min.	35 min.	40 min.	180 min.	190 min.
V	.724	.724	.5277	.5277	.724
V'	.7204	.7204	.5252	.5252	.7204
w	1.7986	1.7989	1.3036	1.3033	1.7986
w'	1.0769	1.0777	.7809	.7809	1.0769
w''	1.1068	1.0985	.7955	.7510	1.023
ρ	.998				
δ	2.4856	2.4856	2.4834	2.4839	2.4856
δ'	2.4908	2.4968	2.495	2.495	2.4968
σ	.0012				
Density.	.957	.9713	.9744	1.0594	1.075

¹ Stewart and Gee, Lab. Man., Vol. I., p. 139.

In Fig. 1 densities are plotted as ordinates, and time in minutes as abscissas. It is unfortunate that more values for the density were not obtained, though I think that those given will suffice. From the curve we infer that the density when first made is between .93 and .94. Olszewski¹ obtained 1.124 and .885 as the

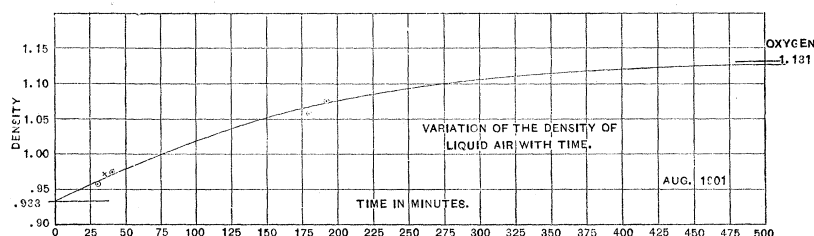


Fig. 1.

densities of liquid oxygen and liquid nitrogen respectively. These values give .932 as the density of liquid air. In 1895 Dewar² obtained for the above liquids 1.1375 and .85 respectively, and for liquid air .91. He weighed a large number of substances of known specific gravities in the liquids, making corrections for the contraction of the solids.

As time elapses the nitrogen boils away and the density approaches that of oxygen. The curve is asymptotic to an ordinate that represents the density of oxygen.³

THE SURFACE TENSION OF LIQUID AIR.

In the work on the surface tension of liquid air the same Dewar bulb was employed. Capillary tubes were first used in the usual manner. The angle of contact was taken as zero. There are several objections to their use, namely :

1. It is almost impossible to read the liquid surface, because of the slight agitation due to boiling.
2. Distortion due to the walls of the bulb.
3. The meniscus was continually changing its position due to evaporation, because its position above the liquid surface unduly exposed it.

¹ Wied. Ann., 31, p. 58, 1886.

² Proc. Roy. Inst., 15, p. 133.

³ J. Drugman and W. Ramsay, Chem. Soc., Journ., 77 and 78, pp. 1228-1233, Nov., 1900.

The following data were obtained with the five tubes employed :

TABLE II.
July 16th. Age of liquid air approx. 140 min. $\rho = 1.05$.

No. of Tube.	Diameter of Tube.	T in Dynes per cm.
1	.097 cm.	11.11
2	.066 "	12.18
3	.108 "	10.59
4	.0625 "	9.87
5	.1015 "	8.08
Average,		10.36

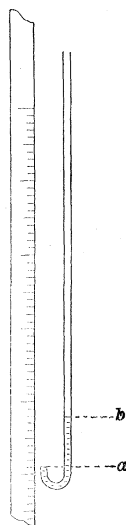


Fig. 2.

This result is somewhat less than that found by Forsch,¹ who gives for the surface tension by this method, after much of the nitrogen had evaporated, 12 dynes per cm.

In order to read the liquid level more accurately the capillary tube was slightly modified. The lower end of the tube was bent upward and cut off square at *a*, Fig. 2. The cathetometer was dispensed with and a thermometer stem used as a scale instead. This enabled the liquid level *a* to be accurately read (to within the errors of direct vision through the walls of the bulb). The meniscus at *b* was read three or four times and the mean taken. The values shown in table III were obtained :

One more modification was made, and that was to jacket the capillary tubes. This is shown in Fig. 3.

The opening *a* in the jacket enabled the same to be

TABLE III.
July 17th. Age of liquid air approx. 260 min. $\rho = 1.1$.

No. of Tube.	Diameter of Tube.	T in Dynes per cm.
1	.0847 cm.	12.53
2	.0487 "	10.14
3	.0485 "	12.72
4	.05 "	10.34
5	.05 "	9.32
6	.061 "	12.67
Average,		11.28

¹ Phys. Zeitschr., I., p. 177, Jan. 13, 1900.

filled by merely lowering the system into the liquid. The meniscus remained steady. Three tubes were employed. It was a little more difficult to cut the capillary tubes directly at the meniscus; however, this was overcome by reading the position of a file mark on the capillary tube.

From the data contained in the above three tables we see that the surface tension increases as the liquid air becomes poorer in nitrogen. However, little confidence can be put in the results, because of the crude methods employed.

A much more satisfactory method, one free from the above troublesome features, is the maximum weight method first suggested by Hall,¹ and later improved by Foley.² Mica frames, varying in length from 2 cm. to 6

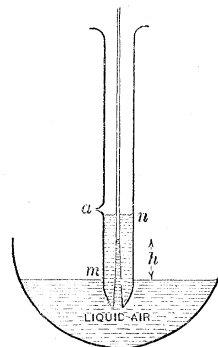


Fig. 3.

TABLE IV.

July 22d. Age of liquid air approx. 75 min. $\rho = 1$.

No. of Tube.	Diameter of Tube.	T in Dynes per cm.
1	.079 cm.	9.90
2	.091 "	10.91
3	.081 "	9.93
Average,		10.24

cm., were used. These frames were supported by a single silk fiber at least 60 cm. long, thus guarding against any temperature change in the balance arms. Fig. 4 shows the manner in which the frames were used. By means of a copper wire stirrup the frame mn was hung with its lower edge horizontal. The silk fiber that supported the stirrup and frame was so small that no appreciable amount of frozen moisture collected on it. The large Dewar bulb was used. The 6 cm. frames, because of their length, had to be lowered into the bulb endwise and hooked to the stirrup afterwards. The formula for these particular mica frames is,

¹ Phil. Mag., V., 36, p. 402, Nov., 1893.

² PHYS. REV., Vol. 3, No. 17, pp. 381-386, 1896.

$$T = g \left[\frac{W}{2(l-t)} + \frac{\rho l^2 t^2}{(l-t)^2} - \frac{lt}{4(l-t)^2} \sqrt{\rho^2 l^2 t^2 + 4w(l-t)\rho} \right],$$

in which

w = net maximum weight.

l = length of frame.

t = thickness of frame.

ρ = density of liquid.

g = force of gravity.

Observations with mica frames were made on three different days. The liquid air was run off in the morning. All measurements were made in the three-quart bulb. This bulb had no mercury in the vacuum chamber. Carbonic acid snow and frozen moisture

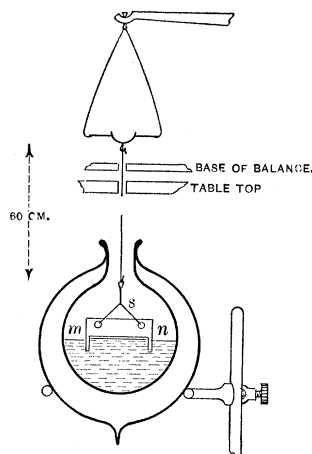


Fig. 4.

were removed by filtering the liquid through ordinary filter paper. The age of the liquid air includes the average age while it was being made, *i. e.*, if it took 30 minutes to run off a certain quantity of the liquid its age at the end of the 30 minutes was taken as 15 minutes.

Table V. contains the data obtained for one sample of liquid air for a number of mica frames. No difficulty at all was experienced in getting the values for w , in fact, by this method the data were as easily collected as when working with water.

TABLE V.

August 12th.

<i>w</i> in gms.	Length in cm.	<i>t</i> in cm.	ρ from Den- sity Curve.	Age in Minutes.	<i>T</i> in Dynes per cm.
.0454	2.02	.00283	1.026	115	10.78
.04825	1.952	.00263	1.038	135	11.91
.05068	1.974	.00276	1.045	145	12.38
.04875	1.974	.00276	1.09	240	12.59
.05248	2.02	.00283	1.099	265	12.45
.0518	1.952	.00263	1.104	280	12.79
.05228	1.952	.00263	1.108	295	12.91
.06964	2.572	.0026	1.116	320	13.05
.18516	6.65	.0035	1.124	352	13.34
.18284	6.65	.0035	1.1245	370	13.17
.18376	6.65	.0035	1.127	385	13.23
.07502	2.732	.00336	1.13	410	13.18
.07534	2.714	.00303	1.131	450	13.35

Table VI. represents three observations on a sample of liquid air that was originally placed in a small Dewar bulb containing mercury in the vacuum chamber. Cotton waste was placed in the mouth of the bulb, and the whole wrapped in a cloth. About four hours afterwards the liquid was filtered into the large bulb, and the following data taken :

TABLE VI.

August 13th.

<i>w</i>	<i>l</i>	<i>t</i>	ρ	Age.	<i>T</i>
.04796	2.02	.00283	1.037	133	11.42
.0491	1.974	.00276	1.047	150	11.98
.0497	1.952	.00263	1.053	160	12.07

In Table VII. is contained, with one exception, the data for one frame. This run was made especially with reference to the variation of the surface tension with time, and in many respects it is the most reliable of all. One half gallon of the liquid was filtered into the large bulb. When the last measurement was made the liquid was nearly all gone—scarcely enough to wet the lower edge of the frame.

The data contained in the above three tables are represented graphically in Fig. 5. In order that the values given in Table VI. come on the curve as located by the data in Tables V. and VII. the age had to be halved. This shows that the mercury mirror and the

TABLE VII.
August 15th.

w	l	t	ρ	Age.	T
.1526	6.646	.00243	.995	67	11.07
.15684	6.63	.004	1.024	112	11.28
.1666	"	"	1.065	182	12.00
.1739	"	"	1.083	222	12.53
.1777	"	"	1.095	257	12.96
.1806	"	"	1.103	274	13.01
.1821	"	"	1.108	294	13.12
.1838	"	"	1.114	312	13.24
.1846	"	"	1.118	324	13.30
.1847	"	"	1.122	340	13.31

other precautions taken to prevent evaporation add much to the life of the liquid.

The curve also shows that, for the large bulb, the surface tension tends toward a constant at an age of from 300 to 350 minutes.

The fact that the surface tension becomes constant is a further

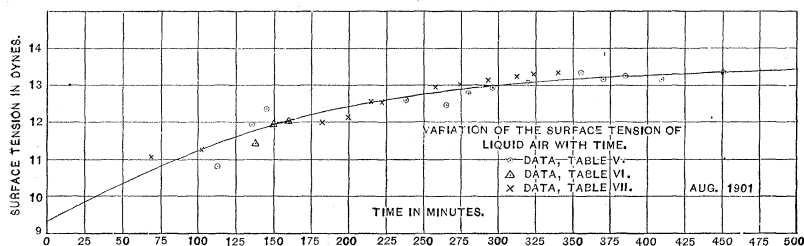


Fig. 5.

indication that the upper part of the density curve given in Fig. 1 is correct.

We would also infer from the curve that the surface tension of liquid air when first made is between 9 and 10 dynes per centimeter.

In conclusion I wish to thank Dr. E. L. Nichols for the courtesies of the department, also Dr. A. L. Foley for the die which he kindly sent me with which to cut the mica frames.

Since the above was put in type an article by L. Grunmach (Ann. d. Phys., No. 11, p. 559, 1901) on the "Surface Tension of Liquid Air" has come to my notice, in which he used the method of capillary ripples.

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