XCIII.—*The Densities of Liquid Nitrogen and Liquid Oxygen and their Mixtures.*

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DETERMINATIONS of the densities of liquid nitrogen and liquid oxygen have been made by a number of investigators (Baly and Donnan, Trans., 1902, 81, 907), but in all cases the measurement of the temperature was not very accurate, so that some uncertainty attaches to the values given. Now in certain cases it is convenient to measure the volume of a large quantity of gas by determining the volume of liquid formed from it at some known temperature, and this is particularly the case when dealing with the analysis of a mixture of gases of which the greater portion consists of nitrogen and oxygen (Inglis, *J. Soc. Chem. Ind.*, 1906, 25, 149). The following

experiments were therefore undertaken to determine the densities of liquid nitrogen, liquid oxygen, and a few of their mixtures at two fixed temperatures.

Temperatures in the neighbourhood of -190° C. are most conveniently and accurately measured by determining the vapour pressure of pure oxygen at the temperature in question and making use of the vapour pressure curve of oxygen as determined by Travers (*Phil. Trans.*, 1902, A, 152). This method was used in these experiments and measurements of the densities were made at temperatures at which the vapour pressure of pure oxygen was (a) 100 mm., (b) 200 mm. On the hydrogen scale, these vapour pressures correspond to temperatures 74.70° and 79.07° Abs. respectively or to -198.33° and -193.96° .

The oxygen used in the experiments was prepared by heating potassium permanganate and was passed through soda-lime and phosphorus pentoxide tubes. The nitrogen was prepared by heating a mixture of solutions of ammonium sulphate and potassium nitrite. The crude nitrogen obtained in this way was fractionated at a low temperature and was also passed through a tube containing red-hot copper.

In order to determine the density of the liquefied gas, a known volume of liquid was allowed to evaporate into a space of known volume (273.3 c.c.) and the pressure at a known temperature was then measured. This space was almost completely (270.9 c.c.) surrounded by a water-jacket so that the temperature of the gas could be measured rapidly and accurately. The portion of the space not jacketed (2.4 c.c.) was so small that no sensible error was introduced in considering its temperature the same as that of the jacketed portion, for the difference in temperature never exceeded 5° C. After the volume of the gas had been determined, the whole of it was transferred to a gas holder, and from this a sample was taken for analysis. The analysis was carried out by removing the oxygen (by means of phosphorus) from a known volume of the gas and measuring the residual nitrogen. The error of an analysis carried out in this way did not exceed 0.1 per cent.

The density bulb itself was blown on one end of a piece of capillary tubing which was graduated for 30 mm. above the bulb. The bulb and capillary were calibrated in the usual way with mercury. Taking the density of mercury as 13.603 at 0° (this being the apparent density using brass weights), the volume of the bulb to zero graduation was found to be 0.27880 c.c. at 17.5° , and the volume of each 10 mm. of the capillary was 0.00266 c.c. at the same temperature. These volumes can be corrected for the contraction that takes place on cooling to -197° by making use of Baly's value (*Phil. Mag.*, 1900, [v], 49, 518) for the mean coefficient of contraction of glass between

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15° and -190°. This correction leads to the values 0.27747 and 0.00265 at -197°. The correction necessary for a change of temperature of less than 10° is too small to be considered, so that the volume of the bulb may be considered constant between the two temperatures used in the experiments.

In carrying out an experiment, the density bulb, together with a bulb containing liquid oxygen and connected to a manometer, was surrounded with liquid air boiling under diminished pressure, and by adjustment of this pressure the temperature was reduced to that required for the experiment. The gas was then admitted to the density bulb, and when the meniscus appeared on the graduated part of the capillary tube the supply of gas was cut off and the temperature kept constant until the meniscus remained at a constant level. This volume of liquid was evaporated off and measured as already described. The results are given in Tables I and II.

TABLE I.

Temp. 74.70° abs. Oxygen, vap. press. 100 mm.

Nitrogen per cent. by vol. found.	Volume of liquid in c.c. found.	Volume of gas in c.c. found.	Volume of liquid from 200 c.c. of gas.		
			Calculated.	Smoothed.	Difference.
0.0	0.28332	242.1	0.2340	—	—
0.0	0.28580	243.3	0.2338	0.2338	—
0.0	0.27919	238.9	0.2337	—	—
1.8	0.28429	241.8	0.2352	0.2351	+ 0.0001
4.5	0.28205	238.3	0.2367	0.2368	- 0.0001
9.8	0.28354	236.4	0.2399	0.2399	—
13.9	0.27959	230.6	0.2425	0.2426	- 0.0001
26.4	0.28369	226.4	0.2506	0.2508	- 0.0002
37.8	0.28301	218.9	0.2585	0.2586	- 0.0001
49.1	0.28197	211.8	0.2663	0.2663	—
55.8	0.27983	206.6	0.2709	0.2710	- 0.0001
59.3	0.28200	206.1	0.2736	0.2736	—
65.6	0.28343	204.0	0.2779	0.2779	—
69.2	0.28162	200.7	0.2807	0.2804	+ 0.0003
72.4	0.28144	199.2	0.2826	0.2826	—
86.8	0.28324	193.8	0.2923	0.2930	- 0.0007
88.0	0.28436	193.3	0.2942	0.2940	+ 0.0002
98.8	0.28065	186.1	0.3016	0.3020	- 0.0004
100.0	0.28182	185.9	0.3032	—	—
100.0	0.28214	186.3	0.3028	0.3030	± 0.0002

TABLE II.

Temp. 79·07° abs. Oxygen, vap. press. 200 mm.

Nitrogen per cent. by vol. found.	Volume of liquid in c.c. found.	Volume of gas in c.c. found.	Volume of liquid from 200 c.c. of gas.		
			Calculated.	Smoothed.	Difference.
0·0	0·28206	237·3	0·2377	0·2376	+ 0·0001
0·0	0·28070	236·3	0·2376	0·2376	—
23·6	0·28232	223·8	0·2523	0·2523	—
47·5	0·28264	209·6	0·2697	0·2696	+ 0·0001
73·2	0·28383	196·2	0·2892	0·2891	+ 0·0001
100·0	0·28343	182·3	0·3109	0·3110	- 0·0001
100·0	0·28293	181·9	0·3111	0·3110	+ 0·0001

If two liquefied gases mix without change of volume, the volume of liquid formed from a fixed volume of gas has a linear relation to the composition of the gas. In the tables, therefore, the volume of liquid formed from 200 c.c. gas (N.T.P.) is given, and if these values are plotted against the molecular percentage of nitrogen (see figure) it is found that the deviation from a straight line is only slight. Thus, in Table I, if there were no contraction, the volume of liquid corresponding to 49·1 per cent. of nitrogen would be 0·2678 instead of 0·2663, the contraction being therefore only 0·6 per cent. For the percentage 47·5 in Table II, the value would be 0·2726 if there were no contraction; the observed value being 0·2697, the contraction is slightly over 1 per cent. As one would naturally expect, the contraction is greater at the higher temperature, but it is somewhat surprising that there is any contraction at all at so low a temperature.

The densities of the pure liquids may be calculated from the figures given in the tables, and the values found are given in Table III.

TABLE III.

Temperature.	Density of nitrogen.		Density of oxygen.	
	I. and C.	B. and D.	I. and C.	B. and D.
74·70° abs.	0·8297	0·8218	1·223	1·217
79·07 abs.	0·8084	0·8010	1·203	1·196

These values may be compared with those found by Baly and Donnan (*loc. cit.*), which are also given in the tables, and it is to be noticed that there are considerable differences which are probably due to uncertainty in the temperature measurements of these investigators.

In a paper published by one of us (Inglis, *Phil. Mag.*, 1906, [vi], 11, 640) on the isothermal distillation of nitrogen and oxygen, it was shown that the partial pressure of nitrogen above a mixture of nitrogen and oxygen

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was approximately proportional to the concentration of nitrogen in the liquid, but that a similar relation in the case of oxygen did not hold. Owing to the densities of mixtures of nitrogen and oxygen not having been determined, the concentrations had to be calculated from Baly

and Donnan's results on the assumption that no contraction took place on mixing the two liquids. The results which have now been obtained enable us to calculate the concentrations more accurately, and the figures so obtained are given in Tables IV and V, the concentrations being given in grams per 100 c.c.

TABLE IV

Temp. 74.70° abs. Oxygen, vap. press. 100 mm.

<i>Nitrogen.</i>			<i>Oxygen.</i>		
Concen- tration. <i>C.</i>	Partial pressure, mm. <i>P.</i>	<i>C/P.</i>	Concen- tration. <i>C.</i>	Partial pressure, mm. <i>P.</i>	<i>C/P.</i>
0.0	—	—	122.3	100.0	1.223
5.6	34.5	0.1624	114.0	95.5	1.194
7.7	47.5	0.1620	111.1	93.5	1.188
11.9	72.7	0.1636	105.1	90.0	1.168
17.1	104.5	0.1634	97.6	85.5	1.141
21.3	129.5	0.1649	91.3	81.0	1.127
25.7	155.7	0.1651	85.0	77.0	1.104
30.2	182.5	0.1656	78.3	72.5	1.080
32.8	197.9	0.1659	74.5	69.9	1.065
36.5	218.6	0.1668	69.1	66.4	1.041
40.2	242.0	0.1662	63.7	61.7	1.032
42.5	255.4	0.1665	60.3	59.6	1.012
45.8	274.6	0.1666	55.5	55.9	0.992
48.9	293.3	0.1667	50.9	53.4	0.953
52.2	314.3	0.1662	45.9	48.7	0.943
53.0	318.8	0.1661	44.9	47.7	0.941
57.4	347.9	0.1650	38.2	42.1	0.907
61.6	374.6	0.1644	32.1	36.6	0.876
66.1	405.0	0.1633	25.3	30.5	0.831
69.2	427.2	0.1621	20.7	25.8	0.801
72.6	450.7	0.1610	15.7	20.3	0.774
75.9	475.8	0.1595	10.7	14.2	0.757
79.2	500.8	0.1580	5.8	8.2	0.709
82.6	528.5	0.1564	(0.5)	(0.5)	(1.0)
83.0	(531.0)	(0.1563)	0.0	—	—

TABLE V.

Temp. 79.07° abs. Oxygen, vap. press. 200 mm.

<i>Nitrogen.</i>			<i>Oxygen.</i>		
Concen- tration. <i>C.</i>	Partial pressure, mm. <i>P.</i>	<i>C/P.</i>	Concen- tration. <i>C.</i>	Partial pressure, mm. <i>P.</i>	<i>C/P.</i>
0.0	0.0	—	120.3	200.0	0.601
3.6	37.0	0.0964	115.3	194.5	0.593
11.0	114.3	0.0965	104.6	181.2	0.577
19.8	205.8	0.0964	91.9	165.7	0.555
27.8	284.8	0.0975	82.0	150.7	0.544
38.5	402.2	0.0957	64.3	127.8	0.503
47.1	495.5	0.0951	51.5	108.5	0.474
54.3	577.6	0.0941	40.5	89.4	0.453
63.4	634.7	0.0926	26.9	65.3	0.412
70.2	773.6	0.0907	16.6	42.4	0.391
75.3	845.6	0.0890	8.7	24.4	0.355
80.8	931.0	0.0868	0.0	0.0	—

These figures show only slight differences when compared with those obtained on the assumption that there is no contraction on mixing the

liquefied gases, and they indicate conclusively that the law governing the relation of the partial pressure to the concentration is simpler in the case of nitrogen than in the case of oxygen. For moderate concentrations of nitrogen, the relation is that known as Henry's law, thus showing that liquid nitrogen has the normal molecular weight. For moderate concentrations of oxygen there is a deviation from this law, and this deviation indicates that liquid oxygen has a higher molecular weight than oxygen vapour. The association factor so indicated is about 1.09.

In conclusion, we wish to thank Sir William Ramsay for the kind interest he took in this work.

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