THE HEAT OF VAPORIZATION OF OXYGEN,
NITROGEN AND AIR.

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IN a recent determination of the heat of vaporization of air¹ it was observed that the results varied in a fairly definite way with the change of composition of the liquid. It seemed desirable to determine this constant for each of the constituents in order that a comparison could be made of the heat required to vaporize corresponding amounts of oxygen and nitrogen when separate and when mixed as liquid air.

The apparatus used was described in the former paper and the only changes found desirable were to use manganin wire instead of german silver, as the latter becomes very brittle after several immersions in liquid air, and to use a chronograph to record the times when meter readings were taken. The gases were liquefied by using liquid air as a cooling agent and subjecting the cold gas to considerable pressure. The apparatus used is shown in Fig. 1. Compressed gas from the cylinder *C* passed through an iron tube filled with caustic potash and then through a coil of fine copper tubing into a receptacle *R*. A gauge *G* indicates the drop

Fig. 1.

in pressure due to condensation, and when the pressure became constant the coil and receptacle were known to be filled with liquid. On closing stopcock *S*₁ and opening *S*₂ the liquid could be removed without wasting gas from the cylinder. This operation was repeated

¹ PHYSICAL REVIEW, Sept., 1902.

until the pressure in *C* became so low that further liquefaction was impossible. Oxygen liquefied very rapidly at pressures between 40 and 200 pounds per square inch but higher pressures are needed for nitrogen. A more economical method would be to use much greater pressures with small cylinders which could be entirely immersed in liquid air.

The oxygen was secured by electrolysis of water and after passing through caustic potash was found by analysis to be 98.8 to 99.9 per cent. pure. Atmospheric nitrogen was separated from oxygen by drawing air through iron tubes filled with copper turnings and heated above a red heat. The tubes used were two inches in diameter and about twenty inches long joined so as to make a rectangular coil giving approximately seventeen feet of copper packing. About 200 liters of nitrogen per hour was developed containing less than .5 per cent. oxygen. After filling the receiving reservoir, coal gas was passed through the hot coil, reducing the copper oxide, thus keeping up the activity of the copper.

The rate of vaporization was very constant when using the pure liquids even when considerable heat was developed by the coil, but when using liquid air there was a tendency to superheating and the meter readings were less regular. It is probable that the gas given off somewhat explosively when the current was used contained a larger quantity of nitrogen than that given off just before or just after this occurrence. Both of these facts tend to make it more difficult to get concordant results with liquid air than with the pure liquids.

A sample set of data for each gas may be of some interest.

Liquid Oxygen. December 19, 1902.

Duration of run,	828	sec.
Loss rate (no current) 1 liter in	76	sec.
Total amount of gas registered by meter,	45	liters.
Net amount due to energy from current,	34.1	liters.
Mean temperature of gas at meter,	16.3°	C.
Mean value of current,	1.22	amperes.
Mean potential difference at terminals of heating coil,	10.97	volts.
Barometric pressure,	74	cm. Hg.
Density of oxygen at 0° —76 cm. Hg,	1.429	gm. per liter.
Variation of voltage during run,	.02	volt.
Heat of vaporization,	59.5	(minimum).

Second run,	63.0 (maximum).
Mean of all six runs,	61.0
Thermodynamic computation,	60.8

The variation in the determinations of the temperature coefficient of vapor pressure is from 70 to 80, a much higher percentage than in the results of the heat of vaporization.

Nitrogen. March 27, 1903.

Duration of run,	309.6	sec.
Time to lose 1 liter (no current),	135.0	sec.
Total register by meter,	30.0	liters.
Net vaporization due to current,	27.71	liters.
Average current,	1.54	amperes.
Average voltage,	13.61	volts
Average temperature,	21.5°	C.
Barometer,	73.7	cm. Hg.
Density of nitrogen (grams per liter),	1.427	
Heat of vaporization,	49.73	calories per gram.

Another run required 308.2 seconds to vaporize 30 liters as against 309.6 above. The mean value found from a series of similar observations was 49.83; the greatest variation from the mean was .11. The result agrees very well with that computed from the vapor tension, which gives 49.25.

The composition of the vapor given off was found by pyrogallol absorption. The following convenient method was used to determine the corresponding liquid composition. The analysis of the liquid and vapor phases have been given by Baly and by Linde who allowed small portions of the liquid to vaporize completely in order to determine the liquid phase. If however readings of the meter are taken at small intervals from the start until *all* the liquid is vaporized and the vapor given off at each meter reading is analyzed a curve may be plotted using percentages of oxygen as ordinates and total amount of gas developed as abscissæ. The area of this curve gives the total oxygen content of the original liquid. The amount of oxygen in the liquid at any point is the area between the curve, the x axis, the ordinate at that point and the final ordinate. The composition of the liquid may thus be determined without in any way disturbing the process of vaporization. The results are given in the curves (Fig. 2). A comparison between the observed results and those computed assuming that the heat used for each component is

Per Cent. O.	Heat of Vaporization Observed.	Heat of Vaporization Computed.
48	50.6	54
66.5	57.9	56.8
90	59	59.8

TABLE I.

Curves I and II.

Per Cent. O Vapor.	Liters Evaporated.	Per Cent. O Liquid Computed.	Per Cent. O Vapor.	Liters Evaporated.	Per Cent. O Liquid Computed.
16.8	0	44.3	79	472	91.8
18.9	100	50	91.4	520	96.3
25	216	59	95.5	543	97.8
31.5	278	65.3	98	560.5	98.9
44.5	347	73.8		580.1(final).	
61	419	83.5			

TABLE II.

Curves III and IV.

Per Cent. O Vapor.	Per Cent. O Liquid.	Per Cent. Total Gas.	Abs. T. [Baly].
16.8	44.3	0	80.7
17.5	47.3	10	81.0
19.5	51.0	20	81.3
22.2	55.1	30	81.7
26.1	61.5	40	82.4
33.3	66.6	50	83.5
44.6	73.8	60	85.1
58.0	81.5	70	86.7
77.0	91.0	80	88.8
91.9	96.2	90	90.2
		100	90.6

TABLE III.¹*Curve IV.*

T. Ab. T.C.	Per Cent. O Vapor.	T. Ab. T.C.	Per Cent. O Vapor.
80-193	12	86-187	52.3
81-192	17.6	87-186	60.3
82-191	24	88-185	69.5
83-190	30	89-184	79.2
84-189	36.8	90-183	89.6
85-188	44.4	91-182	

Boiling point of O 90.6°A. — 182.4°C.

“ “ “ N 77.5° — 195.5°C.

¹ Baly, Phil. Mag., 49, 217. Also Traver's Study of Gases.

Fig. 2.

Fig. 3.

Fig. 4.

the same as would be required to vaporize the same amount from the pure liquids is shown below. The agreement is not very exact but is as close as could be expected owing to the difficulties noted above.

Fig. 5.

For convenience in reference curves are added showing the variation in temperature with percentage of entire liquid evaporated. The values of the temperatures for various compositions of the vapor phase were taken from Baly.¹

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¹ Phil. Mag. (49), p. 417, 1900.