

**607. *The Normal Density of Propane and Its Expansion  
Coefficients between 0° and 20°.***

By D. S. MASSIE \* and R. WHYTLAW-GRAY.

By the use of a buoyancy microbalance a comparison has been made of the balancing pressures of oxygen and propane at the same density as in previous measurements but at a temperature of 5° instead of 20·76°.

By combining the new with the earlier data the normal density of propane and its compressibility at 0° between 0 and 1 atmosphere has been calculated as well as the two coefficients of expansion between the above temperatures.

In a previous investigation (this vol., p. 1746) the pressures at which oxygen and propane have equal densities were determined at two different oxygen pressures by use of a silica-fibre buoyancy microbalance. From these two pressure ratios the limiting ratio at zero pressure and hence the relative molecular weights of the two gases were obtained. Since, however, the measurements were made at a temperature of 20·76° it was not possible from the results to calculate with any certainty the normal density of propane, *i.e.*, the weight of a litre of this gas under standard conditions. To do this it is only necessary to measure one pressure ratio again at a temperature not far removed from 0°.

Thus in the limiting pressure equation (Cawood and Patterson, *Phil. Trans.*, 1936, *A*, 236, 77),

$$P_1/P_2 = \frac{M_2}{M_1} \cdot \frac{1 - A_1 P_1}{1 - A_2 P_2} \quad \dots \quad (1)$$

in which in this case  $P_1/P_2$  represents the pressure ratio, at 0°, of oxygen and propane,  $M_1$  and  $M_2$  their respective molecular weights, and  $A_1$  and  $A_2$  their compressibility coefficients per

\* Seconded from I.C.I. Ltd., Butterwick Research Laboratories, The Frythe, Welwyn, Herts.

atmosphere at 0°.  $A_2$  can be calculated, for  $A_1$ , the compressibility of oxygen, is known;  $P_1/P_2$  is measured; and  $M_2/M_1$  is equal to the limiting pressure ratio previously measured and is independent of temperature since in the limit both gases have the same coefficient of expansion.

Now, knowing  $A_2$  and the normal density of oxygen, *i.e.*, 1.42894 g./l., we can easily calculate the corresponding value for propane at 0°.

Experimentally the  $P_{O_2}/P_{C_3H_8}$  ratio required was measured after the water tank in which the microbalance was immersed had been cooled to a temperature not far removed from 5°. It would have been preferable to have made the comparison closer to the ice point but this was not possible with the means at our disposal. The microbalance tank was connected through a rotary water pump with a larger tank containing an electric refrigerator unit, and the cooled water was circulated continuously from the refrigerator to the microbalance tank and back in a closed circuit. After some 24 hours it was found that a steady state had been attained and the temperature then remained remarkably constant.

The following series of measurements was obtained. The pressure measurements were corrected to a balancing temperature of 5.00° and each measurement given in the table is the mean of five readings.

	Mean corrected pressure, mm. mercury at 0°.		Ratio.
	Oxygen	Propane	
		473.545	1.39433
660.280			1.39436
		473.536	1.39436
660.280			1.39426
		473.570	1.39442
660.357			1.39445
		473.562	1.39444
	660.354		
Mean values	660.313	473.554	1.39438 ± 0.00002

Now the value of the ratio at the same density, determined previously at a temperature of 20.76°, is  $1.39268 \pm 0.00002$  and, assuming a linear variation over 5°, we get the value 1.39492 for the ratio at 0° at oxygen and propane pressures of 648.365 and 464.804 mm., respectively. Previous results show that the limiting ratio is  $1.37807 \pm 0.00006$ . Using the expression given above and assuming  $A$  for oxygen at 0° to be 0.00094, we find

$$A \text{ for propane} = 0.02105$$

and  $1 + \lambda = 1.02150$

Again, when the normal density of oxygen is taken as 1.42894, the limiting density expression leads to

$$\frac{D_{O_2}^{lim}}{D_{C_3H_8}^{lim}} = \frac{D_{O_2}(1 - A_{O_2})}{D_{C_3H_8}(1 - A_{C_3H_8})} \dots \dots \dots (2)$$

where  $D_{O_2}$  and  $D_{C_3H_8}$  are the normal, and  $D_{O_2}^{lim}$  and  $D_{C_3H_8}^{lim}$  the limiting, densities of the two gases, and

$$D_{O_2}^{lim}/D_{C_3H_8}^{lim} = 1/(\text{limiting pressure ratio}) = 1/1.37807$$

whence the normal density of propane is 2.00963 which is probably more accurate than the earlier value, found by Timmermans (*J. Chim. physique*, 1920, 18, 133; 1934, 31, 165), of 2.01987 which with  $1 + \lambda$  calculated by Batuceas (*i.e.*, 1.0220) leads to 12.04 for the atomic weight of carbon—a quite impossible value.

*Coefficients of Expansion.*—(a) *At constant volume.* If we could assume that, during the long period of many months between the earlier and the present measurements, the zero point of the balance had remained perfectly constant we could calculate directly from the pressure readings at the two temperatures the coefficients both for oxygen and propane, but from past experience we have found that small fluctuations undoubtedly occur owing, possibly, to

adsorption of "Apiezon" grease vapour in a high vacuum or to slight changes (caused by vibration) in the position of the balance in its case.

On account of this uncertainty it is sounder to use the pressure ratios, which alter only very slightly with pressure, rather than the individual pressures, and to assume a value for oxygen. Thus, if the coefficient is calculated from the two balancing pressures of oxygen at 0° and 20·76° we find 0·003685; this is almost certainly too high, for by interpolation of the data of Holborn and Otto (*Z. Physik*, 1922, **10**, 367) we find the coefficient between our temperature limits and at the same initial pressure to be 0·003672. On the basis of the latter value and our ratios, the coefficient for propane can be calculated as follows from the expression

$$(P_{O_2}/P_{C_3H_8})^{0^\circ} \cdot (1 + \beta_{O_2}t)/(1 + \beta_{C_3H_8}t) = (P_{O_2}/P_{C_3H_8})^{20\cdot76^\circ}$$

$$\text{or} \quad R_1/R_2 = (1 + \beta_{C_3H_8}t)/(1 + \beta_{O_2}t)$$

where  $\beta$  is the coefficient of expansion of the gases at constant volume, and  $R_1$  and  $R_2$  are the pressure ratios at 0° and 20·76°.

Thence we find  $\beta_{C_3H_8}^{0-20\cdot76^\circ} = 0\cdot003755$  at an initial pressure of 465 mm. If we assume that the change of  $\beta$  with pressure is linear and that 0·003661 is the coefficient for a perfect gas, the value at an initial pressure of 1 atmosphere is  $\beta_{C_3H_8}^{0-20\cdot76^\circ} = 0\cdot003815$ . Alternatively, the value of the pressure ratio at 0° for a propane pressure of 760 mm. can be calculated and the corresponding pressure of oxygen obtained. By use of the appropriate coefficient, this oxygen pressure can then be converted into the pressure at 20·76°, and the propane pressure at the higher temperature calculated from the ratio. The expansion coefficient of propane can then be deduced directly from the two pressures at equal densities, *i.e.*, at constant volume.

To make the calculation, equation (1) must be used in the form in which the ratio  $P_{C_3H_8}/P_{O_2}$  is a strictly linear function of the propane pressure and not as written where  $P_{O_2}/P_{C_3H_8}$  is linear with respect to  $P_{O_2}$ . This is easily done by taking reciprocals of the ratios, thus:

$$\frac{P_{C_3H_8}}{P_{O_2}} = \frac{1}{R_{lim}} \cdot \frac{(1 - A_{C_3H_8}P_{C_3H_8})}{(1 - A_{O_2}P_{O_2})} = \frac{1}{R}$$

whence for  $P_{C_3H_8} = 760$ ,  $P_{O_2} = 1068\cdot44$  mm.

Now at this pressure the coefficient for oxygen (0—20·76°) interpolated from Holborn and Otto's measurements is 0·003678, so that at 20·76° the oxygen pressure becomes

$$1068\cdot44[1 + (0\cdot003678 \times 20\cdot76)] = 1150\cdot02 \text{ mm.}$$

Putting this value into equation (1) used in its original form we find for the ratio 1·40214 and for the corresponding propane pressure 820·19 mm. Whence  $\beta_{C_3H_8}^{0-20\cdot76^\circ} = (820\cdot19 - 760\cdot00)/(760 \times 20\cdot76) = 0\cdot003815$  at an initial pressure of 1 atmosphere, which is identical with the value obtained by direct linear extrapolation of the coefficient to 1 atmosphere from a pressure of 465 mm.

(b) *At constant pressure.* The coefficient ( $\alpha$ ) of expansion at constant pressure can be calculated from the ratio of the densities of oxygen and propane at 0° and 20·76°. Thus if the normal densities are  $O_2 = 1\cdot42894$  and  $C_3H_8 = 2\cdot00963$  the ratio at 20·76° becomes

$$(D_{C_3H_8}/D_{O_2})^{20\cdot76^\circ} = (D_{C_3H_8}/D_{O_2})^{0^\circ} \cdot (1 + \alpha_{O_2}t)/(1 + \alpha_{C_3H_8}t)$$

where  $\alpha_{O_2}$  and  $\alpha_{C_3H_8}$  are the coefficients of the two gases at an initial pressure of 1 atmosphere.

However,  $(D_{C_3H_8}/D_{O_2})^{20\cdot76^\circ} = (M_{C_3H_8}/M_{O_2}) \cdot (1 - A_{O_2}P)/(1 - A_{C_3H_8}P)$  where  $P = 1$  and  $M_{C_3H_8}/M_{O_2} = \text{limiting ratio} = 1\cdot37807$ .

For  $A_{O_2}$  we use 0·00066, a value found by us recently at 22·05°, and for  $A_{C_3H_8}$  the value 0·016832 obtained at 20·76° (this vol., p. 1752). Further  $\alpha_{O_2} = 0\cdot003676$  (from Holborn and Otto's data). Thus we obtain

$$(\alpha_{C_3H_8})_{0-20\cdot76^\circ} = 0\cdot003884 \text{ at 1 atmosphere.}$$

Summarising the results, we have

Normal density of propane at 0°, 760 mm., sea level, lat. 45°.....	= 2·00963 ± 0·00013
Compressibility $A$ at 0° per atm. ....	= 0·02105 ± 0·00006
Coefficients of expansion between 0° and 20·76° .....	$\beta = 0\cdot00381(5)$
	$\alpha = 0\cdot00388(4)$

On account of the small temperature range (5—20·76°) and the extrapolation involved in the method of calculation, no great accuracy is claimed for the coefficients of expansion, though

[1949]

*The Thermal Decomposition of Acetic Acid.*

2877

they are probably reliable to the third significant figure. The method provides an interesting alternative to standard methods for measuring expansion coefficients and could be developed to give results of the same degree of accuracy.

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