DENSITY AND DIFFUSION MEASUREMENT BY DISPLACEMENT INTERFEROMETRY IN EXTREME CASES[1]

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1. *Behavior of Hydrogen.* The method described in the preceding paper[2] was applied for the case of a gas of small density (H_2); but the results came out much too large and the diffusion coefficients correspondingly too small. Nevertheless the data in successive repetitions of the diffusion experiments agreed very well with each other. In Figure 1, I give two examples among many, in which the ordinates s are the fringe displacements ($\Delta x = 21.5 \times 10^{-6}\Delta s$, Δx being the slide micrometer displacement corresponding to Δs) observed at the times in minutes given by the abscissas. One of the diffusions is prolonged for nearly an hour. The presence of H_2 in the open tube (68.4 cm. long) is still apparent after several hours.

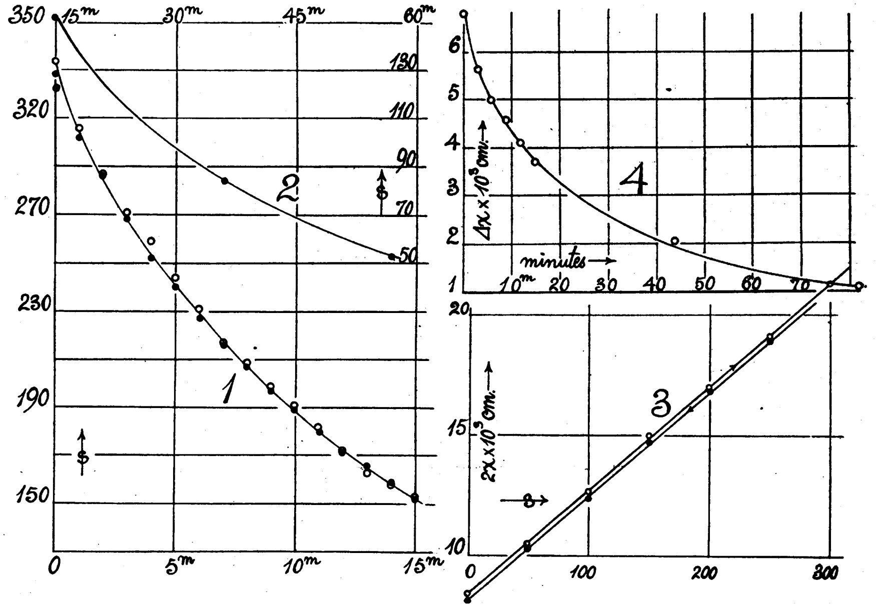
Careful consideration of the various sources of error involved in these gas density measurements, led to the conclusion that part of the pressure in the U-gauge is taken up by the surface tension of the mercury and does not appear in the mercury depression $\Delta h = \Delta x \cos \theta$, $\theta = 46.8°$, registered by the interferometer. In fact computing backward from the known density of hydrogen, the values of Δx are on the average 0.00077 cm. too small, which is equivalent to an error in pressure of $\Delta h = 0.00054$ cm. of mercury about.

Fearing that there might be some irregularity in the relation of measurements made in terms of fringe displacements (s ocular scale parts) and in terms of displacements of the slide micrometer of the interferometer (x cm.), a comparison, Figure 3, was made throughout a much broader interval than was used. The relation, however, is linear with the same slope in the ascending series and in the descending series. Nevertheless, there is a lag, unexplained, between the two. Consequently, subsequent measurements were made in terms of x only, the slide micrometer being previously set in place and the fringes used only to determine the zero or fiducial position.

2. *Fresh Mercury.* As the mercury of the U-gauge had become old and tarnished, these discrepancies were ascribed to it and a new charge of fresher distilled mercury was therefore introduced into the gauge, and other minor improvements added. Using the same vertical quill tube (length 68.4 cm., diameter 0.3 cm.), the mean of five experiments gave practically the same large density ($\rho_0 = 181 \times 10^{-6}$, as compared with $\rho_0 = 188 \times 10^{-6}$, above) as before. Thus the value of Δx was again

deficient by 7.1×10^{-4} cm., implying that a pressure of 5×10^{-4} cm. of mercury is borne by the capillary forces and not registered in depression of the surface of the U-gauge. The loss of pressure owing to the diffusion of hydrogen out of the tube, now measured by the slide micrometer only ($\Delta h = \Delta x \cos 45°$ cm. of mercury), is shown in Figure 4, throughout about 80 minutes.

If the discrepancy in question is in the gauge, then by using longer tubes so as to reduce the percentage effect of the error, the density of hydrogen obtained should approach the normal value. A variety of experiments made, fully bore this out. Thus in case of a tube of eighth inch gas pipe (diameter 1.6 cm.) 158 cm. long, the density obtained was $\rho_0 = 130 \times 10^{-6}$. Half-inch gas pipe, 70 cm. long, reproduced the former larger value.



It follows therefore that for pressures below 5×10^{-4} cm. of mercury, little can be done but to add to the micrometer displacement, Δx, the capillary error δx. The equations for the density at $t°$ should therefore read (ρ_t to be corrected for vapor pressure)

$$\rho_t = \rho_a - C(\Delta x + \delta x) - \rho_w$$

where ρ_w is the density of water vapor at $t°$, if present, ρ_a the density of air and $C = \rho_m \cos \theta / H$ for the tube length H and interferometer angle θ, ρ_m being the density of mercury. In the last example, if $\delta x = 6 \times 10^{-4}$ cm. be taken

$$\rho_t = 0.001192 - 0.0608(0.0173 + 0.0006) - 0.000017 = 83 \times 10^{-6}$$

whence $\rho_0 = 89.7$ happens to be exactly the density of hydrogen. This would fall off about 2.5% on correcting for vapor pressure.

Coefficient of Expansion of a Gas. The occurrence of a static corrective δx referred temporarily to the surface tension of mercury is surprising. It was therefore determined to test the matter further by measuring the density of air heated to 100°, or in other words, to find the coefficient of expansion. Here, for example, with an eighth inch gas pipe 70 cm. long, surrounded by a steam jacket while the outside air temperature was 27°, the slide micrometer showed $\Delta x = 0.0015$ cm. Using as above $\delta x = 0.0006$ for the static error $\Delta\rho = 0.137\ (\Delta x + \delta x) = 288 \times 10^{-6}$; $\Delta\rho/\Delta t = 3.95 \times 10^{-6}$ and $(\Delta\rho/\rho_0)/\Delta t = 0.0037$, a close approach to the coefficient of expansion, where Δx alone would have given a value of 40% too low.

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[1] Advance note, from a Report to the Carnegie Institution of Washington, D. C.

[2] These PROCEEDINGS, **10,** 1924, p. 153–5.

IONIC MOBILITIES IN GASEOUS MIXTURES

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Since 1909 there have been two rival theories[1,5,6] of the nature of the normal gas ions purporting to describe their behavior. One theory assumes the ion to be a cluster of neutral molecules about a charged molecule, and constitutes the so-called "cluster" ion theory. On this theory the mobility is decreased below that to be expected for a charged molecule which does not exert forces on the surrounding molecules, because of the decreased mean free path of the large cluster ion. The alternative, or "small ion" theory assumes that the ion is but a single charged molecule whose average free path is decreased by its attractive forces on the surrounding neutral molecules. Many attempts have been made by means of experiments to decide between them with but little success. In 1916[2] one of the writers performed what he considered a crucial experiment which, while it gave results that appeared to favor the small ion theory was not the experimentum crucis anticipated. With the hope of getting further evidence on this question, the writers set themselves the task of determining ionic mobilities in mixtures of ammonia gas and air.

The mobility of the positive ion in NH_3 is given as about 0.6 cm./sec. per volt/cm. while that in air is 1.8 cm./sec. The assumption that this difference in mobility is due to a clustering effect would lead one to expect