to have any influence upon the rate of transformation of imino nitrogen into ammonia nitrogen.

SAPPORO, JAPAN.

[CONTRIBUTION FROM THE BUREAU OF STANDARDS.]

GAS INTERFEROMETER CALIBRATION.[1]

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The Rayleigh-Zeiss gas interferometer has found numerous applications in high precision gas analysis. However, it requires preliminary calibration and its accuracy is limited by the accuracy of the calibration even though the precision of reading be considerably greater. This interferometer and its uses have been described in detail by Haber and Lowe,[2] L. Stuckert,[3] L. H. Adams,[4] and others.

This type of gas interferometer measures the difference in refractivity of two samples of gas contained in two gas chambers which in the laboratory type of apparatus are 100 cm. long. Light from an illuminated slit passes through both chambers, after which the two beams combine to produce interference fringes which are observed through an eye piece. The optical path of the two beams can be brought to equality by tilting a glass compensator plate which is placed in the path of one of the beams. If the temperature, pressure, or composition of the gas in one of the chambers is changed, the optical paths are different and the interference fringes are shifted. The fringes are brought back to their original position by tilting the compensator plate. The angle through which the compensator plate has been tilted, which is measured by means of a drum attached to the micrometer screw, is a measure of the change in refractive index of the two gases.

The customary method of calibration is to place a standard gas in one chamber and to determine the number of scale divisions the fringes are shifted when the second chamber contains the standard gas plus various known percentages of the gas for which the instrument is being calibrated; the gases in the two chambers are kept at the same temperature and pressure. The results are, of course, no more accurate than the method of analysis of the mixtures, although the precision of reading may be considerably greater.

L. H. Adams[5] has shown how the sensitivity of the interferometer (water or gas) can be calculated from certain dimensions and constants

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[1] Published with the permission of the Director, National Bureau of Standards.

[2] Haber and Lowe, *Z. angew. Chem.*, **23**, 1393 (1910).

[3] Stuckert, *Z. elektrochem.*, **16**, 37 (1910).

[4] L. H. Adams, THIS JOURNAL, **37**, 1181 (1915).

[5] *Loc. cit.*

of the interferometer parts. This is a rather involved procedure, however, and one practicable only in well-equipped physical laboratories.

The method here proposed requires no special apparatus and only a knowledge of the refractive indices of the gases which are to be used. The calibration is accomplished by filling both chambers of the interferometer with dry air free from carbon dioxide and determining the scale reading when the pressure in one chamber is reduced by known amounts. The pressure can be most accurately determined by use of a water gage; a drying tube should, however, be inserted between the gage and the gas chamber to prevent diffusion of water vapor into the chamber. For the portable instrument which is less sensitive than the laboratory type, a mercury gage is sufficiently sensitive. The scale limit of the laboratory type interferometer is reached when the pressure difference has reached about 100 mm. of mercury. The theoretical considerations on which the method is based are as follows:

The refractivity (R) of a gas may be defined as the function $(n - 1)$, in which n is the refractive index of the gas. The refractivity of a gas is proportional to its density,[1] or

$$n - 1/d = \text{constant}.$$

From this relation, the refractivity of a gas can be calculated for different temperatures and pressures by application of the gas laws.

The interferometer serves to measure the difference in refractivity of the gases in the two chambers. Hence the interferometer scale may be calibrated in terms of refractivity differences. To do this it is necessary to know the scale reading corresponding to a given difference in refractivity. This is determined by filling both chambers of the interferometer with dry air at a definite temperature and pressure and then progressively varying the pressure on one chamber and noting the scale reading corresponding to each pressure. The difference in refractivity given by each scale reading (observed reading minus "zero" reading) is then calculated from the following formula:

$$\Delta R = \frac{273 \times 0.0002926\ (p_1 - p_2)}{760\ T} \tag{1}$$

The pressures in the two chambers are p_1 and p_2 and the temperature T remains constant. The refractive index[2] (n_D) of air at 0°, 760 mm. pressure is taken as 1.0002926.

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[1] Mathews, *J. Franklin Inst.*, 177, 673 (1914), discusses the various formulas proposed to show the relation between refractive index and density. The Lorenz-Lorentz formula $(n^2 - 1/n^2 + 2)$ and the Gladstone-Dale formula $(n - 1)$ are equivalent for gases at pressures up to a few atmospheres. Gale (*Phys. Rev.*, 14, 1 (1902)) concludes from his results that if there is any variation from the formula $n - 1/d = k$ for air up to 20 atmospheres it is less than 1 part per thousand.

[2] Jones and Partington, *Phil. Mag.*, **29**, 28 (1915).

The relation between scale reading and refractivity differences for part of the range of one of these instruments (100 cm. gas chambers) is shown in Fig. 1. By means of such a refractivity curve the calibration of the instrument can be calculated for any gas, as follows:

If R_1 is the refractivity of the standard gas at 0° and 760 mm. and R_2 is the refractivity under the same conditions of the second gas for which the calibration is sought, the difference in refractivity for any percentage of the latter is given by the following equation in which a is the percentage of the second gas present in the mixture:

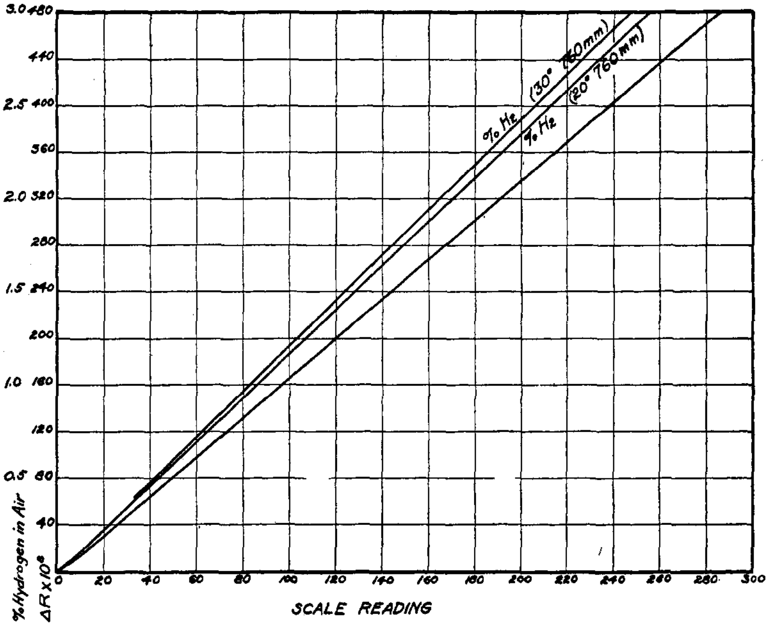

Fig. 1.—Calibration curves for gas interferometer.

$$\Delta R = \frac{273}{T}\frac{p}{760} \cdot \frac{a}{100} \cdot (R_1 - R_2) \qquad (2)$$

The validity of this equation depends upon the fact that the refractivity of a mixture of gases is equal to the sum of the refractivities of each constituent times the percentage of it present in the mixture. It has been shown[1] that although this does not hold strictly, it is a very close approximation. For example the refractivity of air calculated according to this mixture rule from the refractivity values given by Jones and Partington[2] for oxygen, nitrogen and argon and the percentage composition of

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[1] Ramsey and Travers, *Proc. Roy. Soc. London*, **62**, 225 (1897–98); Cunaeus, *Z. physik. Chem.*, **36**, 232 (1901).

[2] *Loc. cit.*

air as given by Sir William Ramsay is as follows: $(0.0002711 \times 0.2094) + (0.0002976 \times 0.7812) + (0.0002802 \times 0.0094) = 0.0002919$. This is only 0.24% lower than the observed value 0.0002926.

Since the refractivity of a gas is proportional to its density, it is necessary to consider the deviation from Boyle's law in the case of gases at pressures much different from the normal pressure (760 mm.). For example in a mixture of air with 1% of carbon dioxide, the partial pressure of the carbon dioxide will be 7.6 mm. under standard conditions, but its density, and therefore its refractivity, will be approximately 0.67% lower than the value calculated by means of Boyle's law, because of the fact that it is too compressible to correspond to an "ideal gas." The values for the "ideal refractivity" calculated by Jones and Partington[1] by means of Berthelot's equation of state can be conveniently used in this connection.

It should be noted from the form of Equations 1 and 2 that the readings are influenced by the temperature and pressure even though the gases in both chambers are under like conditions. This effect is the smallest when the refractivities of the two gases are most nearly alike.

From these relations of scale reading and refractivity and of percentage composition and refractivity, it is evident that the relation of scale reading to percentage composition can be computed. The curve marked hydrogen in Fig. 1 gives the scale readings for different percentages of hydrogen in air using air as the comparison gas.

To check this method of calibration by analysis a mixture of air and carbon dioxide was made up and stored in a 14-liter mercury-sealed gas holder. Volumetric analysis of this mixture showed the presence of 2.52% CO_2 (±0 .05%). Two different interferometers calibrated by the method described each indicated the presence of 2.52% of carbon dioxide in this mixture showing agreement well within the limits of error of the volumetric analysis. If the interferometer calibration had not been corrected for the deviation of carbon dioxide from Boyle's law, it would have indicated 2.47% CO_2, a difference which is, however, negligible for a great many purposes.

No general statement can be made as to the accuracy of the method proposed, for this depends upon the gases in question; however, the accuracy is usually greater than is possible by volumetric-gas analytical methods, especially in the case of small percentages. The greatest advantage of the method is the speed and ease with which results for the entire range of the instrument can be obtained. This advantage is especially great in case the calibration curves are not straight lines, for in such cases a series of mixtures of known composition must be prepared if employing the usual calibration procedure.

WASHINGTON, D. C.

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[1] *Loc. cit.*