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ABSTRACT

The theory and experimental techniques used for analyzing mixtures of H_2-N_2 and D_2-N_2 over the entire range of compositions are given. A gas-blending apparatus used for preparing the calibration mixtures is also described. It is shown that the optical interferometer is a reliable gas-analytical tool capable of yielding accurate results in binary mixtures, and that the deviations from linearity of the index of refraction vs composition data can be adequately explained from molar refraction theory and the predicted deviations from ideal gas-mixing behavior. The index of refraction for deuterium for white light is slightly smaller than that of hydrogen: 1.80×10^{-6} index-of-refraction units.

GAS ANALYSIS BY OPTICAL INTERFEROMETRY[*]

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INTRODUCTION

This paper reports the results of a rather extensive calibration of an optical interferometer used as a tool for gas analysis. The work was done in connection with an experimental program in which liquid-vapor equilibrium data were obtained for the systems hydrogen-nitrogen[11] and deuterium-nitrogen,[12] and it was desired to have gas-analysis equipment for fast, accurate routine analysis. The accuracy to which sample compositions were desired was better than 0.1% for the vapor samples and better than 0.05% for the liquid samples.

After a preliminary investigation of other analytical methods such as Orsat techniques, velocity of sound, effusion, and thermal conductivity, it was established that the above lacked either accuracy or reliability; however, the possibility of using an optical interferometer was apparent once the known indices of refraction of the pure components were compared against the sensitivity limits stated by the manufacturer (Carl Zeiss, Jena).

It was also known that the relation between the index of refraction of a gas mixture and the composition is approximately linear, although it was not known if the linearity could be assumed to hold within 0.03%, since all previous data on mixtures are of lower accuracy and very few extend over the entire range of composition.

Edwards determined the sensitivity of his apparatus by filling both chambers with dry, CO_2-free air, and obtaining the interferometer reading while pressures

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were different in the two chambers.[4] This reading, together with the known index of refraction of air, gave him the desired value of interferometer sensitivity. He then prepared a CO_2-air mixture containing 2.52% CO_2 and found that the calculated index of refraction agreed with that found experimentally.

Mohr analyzed flue gases containing from 4% to 14% CO_2 for CO_2 and O_2, calibrating his interferometer by standard gas-absorption techniques.[13] He declared his accuracy to be ± 0.5% and the index of refraction to be linear in this range.

Cuthbertson and Cuthbertson measured the indices of refraction of mixtures of O_2 and O_3, analyzing their mixtures either by the volume increase upon decomposition or by chemical absorption.[3] The scatter in their data ran from 1% to 3%, and the range of compositions investigated was limited to about 7% O_3.

The best values for the dependence of index of refraction on composition are those of Valentiner and Zimmer.[18] They measured the index of refraction of synthetic gas mixtures, which they made by measuring accurately the amounts of pure components and mixing them inside their blending apparatus. Their data extend over the entire composition range, with an average deviation of about 0.5%. They found a small deviation from linearity for the system H_2-CO_2, which was almost completely masked by the scatter. Their data for the ternary system He-Ne-H_2 are linear, thus contradicting an earlier result of Ramsay and Trovers that had indicated deviations of the order of 3% for 50% mixtures of He-H_2.[16]

Therefore, the assumption of linearity of variation in index of refraction with composition is seen to require a more careful investigation if uniform accuracies of the order of 0.03% are required. Actually, as a result of this study, it has been shown that for the systems investigated small deviations from linearity do occur but can be predicted from the deviations from ideal-gas behavior of the gas mixture.

EXPERIMENTAL PROCEDURE

Operating Procedure

The experimental procedure recommended by the manufacturers was modified to allow the use of relatively small gas samples and application of vacuum techniques. The interferometer was connected to the vacuum-system manifold and reference gas cylinders as shown in Fig. 1.

The absolute calibration of the interferometer was obtained with monochromatic light of 5461Å. The calibration consists of obtaining the micrometer readings that correspond to the successive bands that pass through the ocular as the micrometer screw is rotated, and is usually expressed in the form of a calibration table in which values of the band number, h, are listed versus the corresponding values of $R-R_0$, where R_0 is the reading corresponding to the zero-order band--obtained with white light when both gas chambers are evacuated. These readings correspond to equal increments in thickness of the compensating glass plate, and correspondingly to equal increments in index of refraction difference between the unknown and reference substances. Although the band-number calibration thus obtained holds only for a particular wavelength of light, it can be used with white light if only a measure of equal increments in refractive-index difference is required. (See Band Shift, below)

The procedure for making a measurement is as follows. The system is first evacuated until the thermocouple gauges Nos. 9 and 10 show a pressure smaller than 5μ, at which point the gas sample may be introduced into the system. The hydrogen content of the sample determines the reference gas and chamber to be used. Take the case of a sample that is know to contain about 50% H_2, and is to be read against nitrogen gas as reference. The sample is introduced into chamber L, for a gas of low index of refraction, while the reference nitrogen is introduced into chamber H, for a gas of high index of refraction. If the amount of sample is not sufficient to bring up the pressure in L to atmospheric pressure, additional gas may be pumped out from the line by manipulating stopcocks Nos. 2 and 3 and the mercury level in L. The pressure in the gas cell is shown by the height of the mercury column over the mercury seals No. 11. When the gas cell is at atmospheric pressure, and enough gas is left in L for the purging procedure that is to be described, stopcock No. 3 is closed and the line is evacuated for admission of the reference gas into chamber H. Chamber H is filled by closing stopcock No. 1 and opening valve No. 7 by the reference nitrogen cylinder.

When both chambers have been filled with gas, a waiting period of about
1 minute is allowed for the gases to reach approximately the same temperature
in the gas cells. The pressure is then raised in chamber L by admitting mer-
cury, until the gas bubbles out through the mercury seal. The pressure in L
is now above atmospheric; the mercury seal is lowered until the gas inside
the chamber is directly connected with the atmosphere through the long glass
capillary (about 1 mm in diameter), which minimizes the diffusion of air into
the interferometer tubes. The same procedure is repeated for the gas in
chamber H, and a period of 2 minutes is allowed for temperature equilibration
before the interfermometer is read.

The interferometer reading is obtained by lining up all the clearly visible
bands of the upper spectra with the most prominent band of the reference
spectrum, denoted band 4 in Fig. 2. For each of the successive bands in the
upper spectra there is a corresponding reading which is identified by the sub-
scripts 1, 2, 3, or 4, according to the relative intensity of the lines, 4 corres-
ponding to the blackest line, 1 to the most colored, 2 and 3 for intermediate
degrees of blackness. The reading of any individual band is accomplished by
rotating the micrometer screw (always in the same direction, to minimize the
possible effects of backlash in the mechanism).

The above procedure is carried out for two reasons: to compensate for
possible errors in the absolute calibration of the interferometer, and to obtain
a set of independent readings of the same quantity, readings which are later
brought to a common basis in the calculations. The distribution of color in the
different bands of the upper spectrum is valuable in the identification of the zero-
order band, as described later under band shift.

After a preliminary set of readings is taken, the mercury is allowed to rise
in chamber H, thus purging the gas in the gas cell with the gas contained in H.
A new reading is taken on the zero-order band. The same procedure is followed
with the gas contained in reservoir L. This purging procedure allows for the
detection of any lack of homogeneity of the gases in the chambers due to in-
complete evacuation, slow leak, diffusion, or--in the case of the calibration
blends--lack of homogeneity due to incomplete mixing in the blending apparatus.

While the reference and unknown gases are being purged, the necessary
pressure and temperature readings are made.

After the readings are taken, the mercury seals are raised until the tips of
the capillary tubes are under mercury, and stopcocks Nos. 1, 3, and 4 are

opened so as to pump out all the gas in the system. After the pressure has decreased to below 100 microns a new reading is taken, to establish the reading corresponding to the zero-order band when both chambers are evacuated. This zero reading is fairly constant, although it seems to be somewhat dependent on room temperature.

Band Shift

The use of white light allows for the easy identification of the zero-order interference band, whereas this identification is impossible to make with monochromatic light. For this reason white light is used almost universally when the interferometer is used for analytical purposes. However, owing to the difference in the dispersive powers of the glass in the compensating plate and the substances in the sample reservoirs, the distribution of energy in the upper spectra shifts gradually with increasing difference in index of refraction, changing the chromaticity of the different bands until the zero-order band no longer corresponds to the two dips in light intensity that appear black but may be displaced from it by one or more bands; i.e., the zero-order interference fringe is now colored.

The position of the zero-order band was determined during the calibrations of the interferometer with gas blends of known composition, by purging the blend with reference gas while following the position of one of the bands by rotating the micrometer screw. For the above example, where the unknown sample was in chamber L, the procedure would be as follows. Stopcocks 1, 3, and 4 are closed after the introduction of the gases in the chambers. Valve No. 7 is opened until the reference gas pressure, indicated in the compound gauge, is slightly above atmospheric. Valve No. 6 is closed and cock No. 3 opened. Valve No. 7 is opened. Then valve No. 6 is opened slightly while the movement of the bands in the interferometer field is followed. The band shift is established by the change in the relative color intensity of the band; thus, for the above example, if the blackest band is followed, it will gradually become more colored, and when both chambers are filled with essentially the same gas-- reference nitrogen--the band will be found to lie one band to the left of the blackest band, which for this case is known to be the zero-order interference band. Figure 2 shows the pattern of relative color intensity of the different bands versus composition and interferometer reading, and was used to determine the position of the zero-order band for unknown samples. Similar plots were

obtained for the hydrogen-nitrogen samples read versus reference nitrogen and for the deuterium-nitrogen mixtures. This method of obtaining and plotting the band shift is very similar to the one recommended by Karagunis et al.,[7] and allows for the identification of the zero order band regardless of how colored it may be.

Pressure and Temperature Measurement

Barometric pressure was read on a Fortin-type U.S. Signal Corps barometer, and tabulated corrections provided by the manufacturer were made for temperature and local gravity. The error in the pressure measurement is of the order of ± 0.1 mm of mercury.

Temperature was measured by means of a copper-constantan thermocouple, 5 feet of which were wound around the gas cells inside the interferometer case with the assembly insulated with 2 inches of fiberglass insulation. The latter made for very slow changes in the temperature of the gas cells, while the winding of the thermocouple wire around them minimized the effects of thermal conduction along the thermocouple wire. The thermocouple was read with a type K-2 Leeds and Northrup potentiometer, and was calibrated at the sodium sulfate point and against a Bureau of Standards certified thermometer. The error in temperature measurement was smaller than 0.01° C.

Purity of the Gases Used

The purification of the gases used was accomplished by passing the raw commercial gas at high pressure and at a slow rate through a bed of activated charcoal held at a low enough temperature to remove most of the higher-boiling impurities from the raw gas; thus, for nitrogen purification, the bed was held at dry-ice temperature, while for hydrogen and deuterium purification, the bed was cooled with liquid nitrogen.

This method of purification seemed to be quite effective, as evidenced by the following mass spectrographic analysis of typical samples of purified gases. (It should be noted that the amounts of impurities recorded below are the maximum limits of impurities in the sample, assuming that the mass spectrograph has zero background.)

Gas	H_2 (%)	D_2 (%)	N_2 (%)
A	- - -	- - -	0.022
O_2	0.004	0.004	0.004
N_2	0.009	0.01	99.974
H_2	99.977	0.37	- - -
D_2	0.009	99.63	- - -
	100.00	100.00	100.00

THEORY

This section describes the equations used for data reduction in routine analysis as well as the equations relating the deviations in linearity of the index of refraction vs composition curves to the nonideal mixing behaviour of real gases.

Equations Used for Data Reduction

The Lorentz-Lorentz molar refraction is known to give, to a good approximation, the changes in index of refraction with pressure, temperature, and composition, and was used to reduce all the interferometer readings to standard conditions. It is defined by

$$N = \frac{n^2 - 1}{n^2 + 1} \frac{M}{\rho} \tag{1}$$

where N is the molar refraction,

   n is the index of refraction,

   M is the molecular weight,

   ρ is the density.

The density can be expressed in terms of the ideal gas density given by

$$\rho = \frac{P}{rT} M , \tag{2}$$

where P = pressure,

   T = absolute temperature,

   r = gas constant, expressed in appropriate units,

to obtain

$$N = \frac{n^2 - 1}{n^2 + 2} \quad \frac{rT}{P} \quad , \tag{3}$$

which can be simplified by the introduction of

$$e = n - 1 . \tag{4}$$

Since e is a very small quantity compared with unity ($e = 299.8 \times 10^{-6}$ for nitrogen), its square can be neglected, so that we obtain

$$N \cong \frac{2}{3} \quad e \; \frac{rT}{P} \quad , \tag{5}$$

or

$$e \cong \frac{3}{2} \quad \frac{NP}{rT} \quad . \tag{6}$$

The interferometer, however, measures

$$h = a(e_r - e_g) , \tag{7}$$

where

a = interferometer sensitivity,

h = band number,

$e_r = n-1$ for the reference gas,

$e_g = n-1$ for the unknown gas,

whereas we are interested in the values of

$$h_0 = a [(e_0)_r - (e_0)_g] , \tag{8}$$

where the subscript 0 refers to some standard reference state like $0^\circ C$, 760 mm of mercury. The values of h can be transformed into values of h_0 by

$$[(e_0)_r - (e_0)_g] = e_r \; \frac{T_r}{273} \cdot \frac{760}{P_r} - e_g \; \frac{T_g}{273} \cdot \frac{760}{P_g} \quad , \tag{9}$$

and

for the particular case in which $P_r = P_g = P$; $T_r = T_g = T$, Eq. (9) can be simplified to

$$[(e_0)_r - (e_0)_g] = \frac{760}{273} (T/P) (e_r - e_g)$$

$$= 2.7822 (T/P) (e_r - e_g)$$

$$= 2.7822 (T/P) \frac{h}{a} .$$ (10)

Therefore one obtains

$$h_0 = 2.7822 (T/P) h .$$ (11)

This last equation expresses the functional relationship between the values of h, P, T, and h_0 and was used to bring all data to the same standard conditions.

For $P_r \neq P_g$ but $T_r = T_g = T$, then

$$h_0 = 2.7822 (T/P) h + (1 - P_r/P_g) (e_0)_r a.$$ (12)

Thus, if the pressures in the two gas chambers are not identical, an appreciable correction has to be applied, which involves the absolute values of interferometer sensitivity and index of refraction of the reference gas.

Equation (12) can be used, however, to determine either the absolute sensitivity or the absolute value of e_0 for a gas, if the other value is known. Thus, for determining the value of the sensitivity both chambers are filled with a gas of known index of refraction the pressure in both chambers is determined, and since $h_0 = 0$,

$$a - 2.7822 \, Th/(P_r - P_g) (e_0)_r.$$ (13)

For the purposes of routine analysis, the calibration consists of obtaining the emperical relationship between composition of the sample and band number.

Index of Refraction of Real Gas Mixtures

In the discussion of the experimental results obtained, it will be pointed out that the results can be expressed in terms of a straight line, within the limits of experimental error.

The equation of that line is of the type

$$x_c = s h_0 + b.$$ (14)

It is interesting to note that the value of the coefficient s is not a constant for a given gas mixture, thus, it was 0.0068616 for the H_2 - N_2 data read versus reference hydrogen, and 0.0068476 for the data read versus reference nitrogen, showing a discrepancy of 0.204% in the absolute values of the slopes.

This discrepancy can be partially explained by assuming slightly different lengths for the two gas chambers, but the difference between the two tubes required to account for the discrepancy would be 0.5 mm. An alternate explanation for the difference between the two slopes is the possibility that the lines of index of refraction versus composition may have a small degree of curvature due to deviations from ideal gas-mixing behavior.

It is fortunate that for this case the second virial coefficients of the pure components and the interaction coefficient have been experimentally determined, thus making it possible to calculate the density of the mixtures as a function of composition, values which can be substituted into the molar-refraction equations to obtain correct values of index of refraction of the mixture.

Molar refraction theory predicts that the molar refraction of a mixture is a linear combination of the molar refractions of the pure components. For a binary mixture it is

$$N_M = N_1 x_1 + N_2 x_2 , \tag{15}$$

where N_M is the molar refraction of the mixture and N_1 and N_2 are molar refractions of the pure components. For a gas mixture one has

$$e_M \frac{M_M}{\rho_M} = e_1 \frac{M_1}{\rho_1} x_1 + e_2 \frac{M_2}{\rho_2} x_2 . \tag{16}$$

If the components are ideal gases and mix without interaction, Eq. (2) can be substituted above to obtain

$$(e_M)_I = e_1 x_1 + e_2 x_2 , \tag{17}$$

where the subscript I applies to ideal mixtures. Combining Eqs. (16) and (17), we have

$$e_M - (e_M)_I = e_1 x_1 \left[\frac{\rho_M}{M_M} \cdot \frac{M_1}{\rho_1} - 1 \right] + e_2 x_2 \left[\frac{\rho_M}{M_M} \cdot \frac{M_2}{\rho_2} - 1 \right] , \tag{18}$$

An expression that can be simplified by making the substitution

$$\frac{p}{M} = \frac{1}{V} \, . \tag{19}$$

where V is the molar volume, to obtain

$$\left[e_M - (e_M)_I \right] = e_1 x \left[\frac{V_1}{V_M} - 1 \right] + e_2 x_2 \left[\frac{V_2}{V_M} - 1 \right] . \tag{20}$$

The values of the molar volume of the mixture can be calculated from the virial equation

$$\frac{PV}{RT} = 1 + \frac{B}{V} \, , \tag{21}$$

where the second virial coefficient is given by

$$B_M = B_1 x_1^2 + 2 B_{12} x_1 x_2 + B_2 x_2^2 \, . \tag{22}$$

The following values have been given in the literature for the second virial coefficients in the system $H_2 - N_2$:

Reference	B_{H_2}	B_{N_2}	B_{12}
Keyes[8]	+ 14.54	- 2.78	
Hildebrand[5]	+ 14.5	- 6.2	+ 13.7
calculated from data in Perry[15]	+ 13.7	- 10.5	
Lunbeck and Roerboom[10]	+ 13.70	- 4.71	+ 13.5 + 11.5
Theoretical[10]			+ 11.5
Values used in the calculations	$+ 14.1_1$	$- 6.0_5$	$+ 13.3_3$

The values of V obtained from Eq. (21) were combined with these values of e obtained from the International Critical Tables,[6] at

$$\lambda = 5461 \text{ Å} \, ,$$

H_2: $e = n-1 = 139.65 \cdot 10^{-6}$,

N_2: $e = n-1 = 299.77 \cdot 10^{-6}$,

$e_{N_2} - e_{H_2}$ $= 160.12 \cdot 10^{-6}$,

to obtain the values of $e_M - (e_M)_I$.

Thus, additivity in the molar refraction, when combined with the proper density values for the mixtures, predicts a small deviation from linearity for the index of refraction. The maximum deviation, of $8.3 \cdot 10^{-8}$ index-of-refraction unit, occurs at 45% H_2, and should be large enough to be reflected in a difference in the slopes of the lines expressing composition versus refractive index. This is indicated in Fig. 3, which shows the over-all pattern of index of refraction versus composition, in which the deviations from linearity are greatly exaggerated.

RESULTS

The results of calibrating the interferometer with gas blends of known compositions are partially illustrated in Figs. 2 and 4, while the complete set of data is tabulated in the original reports.[11, 12] Figure 2 presents the general trend of interferometer readings versus gas composition, and was used mostly in the determination of band shift and as a help in selecting the zero-order interference fringe. It may be observed that the line presented in Fig. 2 has a slight curvature, which is due almost entirely to the lack of linearity between interferometer readings and band numbers.

If a plot were made of composition versus band numbers, it would appear as a straight line having the following equations:

H_2-N_2 mixtures read versus reference hydrogen,
$$x_c = 0.99774 - 0.0068616 \, h_0 ; \qquad (23)$$
H_2-N_2 mixtures read versus reference nitrogen,
$$x_c = 0.0068476 \, h_0 - 0.00014 ; \qquad (24)$$
D_2-N_2 mixtures read versus reference hydrogen,
$$x_c = 0.986567 - 0.0067845 \, h_0 ; \qquad (25)$$
D_2-N_2 mixtures read versus reference nitrogen,
$$x_c = 0.0067705 \, h_0 - 0.000135 . \qquad (26)$$

In the above equations x_c is the mol fraction of hydrogen--or deuterium--calculated from the measured value of h_0. The values of $x - x_c$ -- that is, mol fraction of hydrogen in the synthetic mixture as obtained in the blending apparatus minus mol fraction calculated from the above expressions--are illustrated in Fig. 4 for hydrogen-nitrogen mixtures read versus reference hydrogen.

In Fig. 4 distinction is made between the points obtained before the blending technique was perfected and the values obtained later. While only two of the later values show deviations larger than 0.001, most of the earlier blends fall outside this range. The scatter of the points shown in Fig. 4 is due to the errors in making the blend in the blending apparatus and the errors in reading the interferometer, so that it is actually difficult to assign a definite value to either one of the two sources; however, the scatter for most of the "good" points is less than 0.0005.

Index of Refraction of Deuterium
and Internal Consistency of the Data

From Eqs. (23) and (25) and the value of sensitivity of the interferometer-- band numbers per unit index of refraction difference--one can obtain the difference in index of refraction between pure hydrogen and pure deuterium. The index of refraction of deuterium for white light is slightly smaller than that of hydrogen: 1.80×10^{-6} index-of-refraction units.

Equations (23) through (26) were calculated for best fit to the experimental data; however, the following internal-consistency test can be made. If the coefficients for the H_2-N_2 data are corrected for the difference in index of refraction between hydrogen and deuterium, one can obtain the corresponding coefficients for the D_2-N_2 system. This test was made with the following results:

for blends read versus reference nitrogen,

coefficient of h_0 for best fit to D_2-N_2 blends = 0.0067705,

coefficient of h_0 from H_2-N_2 data, corrected = 0.0067709,

and for blends read versus reference hydrogen,

coefficient for best fit to the D_2-N_2 blends = 0.0067845,

coefficient of h_0 from H_2-N_2 data, corrected = 0.0067847.

Comparison of Calculated and Experimental Values of Index of Refraction

As indicated above, the nonideal gas mixing of real gases leads to a small deviation from linearity in the index of refraction vs composition curves. It is desirable to compare the calculated and experimental values of index of refraction.

At this point, however, the information available is not sufficient to show if the deviations from linearity predicted from molar refraction agrees with the experimental data, since the absolute sensitivity of the interferometer is not know with sufficient accuracy to convert e values in h values. Alternatively, if the point of intersection of the lines of slopes s_1 and s_2 (Fig. 4) were known, the calculated and experimental values could be brought to the same basis. However, since the maximum deviation from linearity occurs at 45% H_2 and the fit of Eqs. (23) and (24) to the data is good at this concentration, it was decided to assume that the lines intersect at x = 0.45. This is the only assumption that was necessary for the following calculations. From this assumption and from the slopes given in Eqs. (23) and (24), it is possible to calculate the value of $h_2 - h_1$, from which the values of interferometer sensitivity a and average slope s follow. Thus, the value of s was found to be 0.0068553, with a corresponding value of interferometer sensitivity of 0.91102 band numbers per index-of-refraction difference x 10^6. Once s is know, values of h corresponding to the different concentrations of the synthetic mixtures can be calculated and compared with the experimental findings, giving Fig. 5, which shows values of $h_M - (h_M)_I$ for the experimental blends, and the values of $h_M - (h_M)_I$ obtained from the values of $e_M - (e_M)_I$ and the interferometer sensitivity. The agreement between the two sets of values is quite good.

It may be concluded that, at least for the H_2-N_2 system, the assumption of additivity of molar refraction is a very good approximation to fact, and that the probably deviation corresponds to an error of less than 0.01% in composition.

Sources of Error

The assumption of ideal-gas behavior, as applied in Eqs. (1) through (13), introduces some error in the values of h_0; however, for the gases used (H_2 and N_2) and the usual range of temperature and pressures (15° to 30°C, 740 to 750 mm Hg), the degree of error introduced is well below the limit of accuracy of the interferometer with 50-cm-long gas chambers.

The tolerances of error in the measurements of temperature and pressure are not very stringent provided the gases in the two chambers are at exactly the same pressure and temperature (see Eq. (12)). For H_2-N_2 mixtures, with 50-cm-long gas chambers, it is necessary to measure concentrations below 60% H_2 against nitrogen gas as reference, and mixtures containing more

than 40% H_2 against hydrogen gas as reference, thus obtaining a certain amount of overlapping in the region near 50%.

For mixtures containing 60% H_2 read versus reference nitrogen, the value of h_0 is about 89, and the errors in temperature and pressure corresponding to an error of 0.01% in composition are $0.045^{\circ}C$ and 0.12 mm of mercury. For lower values of h_0 the allowable tolerances are correspondingly increased as evidenced in Eq. (11). Thus, the errors in the measurement of pressure and temperature are almost negligible compared with the lack of reproducibility in the interferometer readings, which at best is about 0.5 unit in drum reading or about 0.02% in composition.

The interferometer is very satisfactory as an analytical instrument, however, and allows for fast accurate analysis of gas mixtures.

The time required for analysis is of the order of 80 min per sample, but most of that time is actually involved in pumping out the lines and involves no loss of operator time.

ACKNOWLEDGMENT

APPENDIX

The Gas-Blending Apparatus

An apparatus capable of preparing synthetic gas mixtures of any composition with a high degree of accuracy was necessary for the calibration of the analytical techniques. A number of alternative designs for such a piece of equipment have been reported in the literature, especially in the last few years, in connection with methods for calibrating infrared and mass spectrometers.

An early example of blending apparatus was that of Valentiner and Zimmer,[18] which was used in connection with the calibration of an optical interferometer. Their design is fairly complex, not well adapted to vacuum techniques, and has some dead volume in the bores of stopcocks. The average scatter of their calibration data was about 0.5%, which probably originated in the blending apparatus.

Taylor and Young[17] and Busey et al.[1] describe mixing apparatuses that are better adapted to making blends of liquids of high vapor pressure or of easily condensable vapors than of the permanent gases.

Langer measures the gases independently in the same gas buret, and transfers them to a sample reservoir.[9] A small uncertainty in the composition of the blend results from the gas trapped in a fritted glass section, gas which cannot be removed when a second constituent is added to the mixture. He compares the a priori composition of a nine-component blend with the mass spectroscopic analysis of the same blend. The maximum deviation between the two sets of compositions is 0.79%, the minimum 0.01%, but it is difficult to ascertain whether the error originates in the blending apparatus or in the subsequent analysis.

Opler and Smith describe a fairly simple blending apparatus, in which the gases are measured in two separate reservoirs and then blended.[14] The same stopcocks are used for admission of the pure gases and removing the finished blend, however, and the small amount of pure constituent trapped in the bore introduces some uncertainty in the final composition. They do not quote any limits of accuracy. None of the above seemed suitable for this investigation, because it was desired to have a blending apparatus with an a priori accuracy of about 0.01%, and capable of maintaining this accuracy over the composition range of 4% to 96% of any component. Further, it was to be well adapted for making binary mixtures, although it was expected that a few multicomponent mixtures might be made in it.

The apparatus devised is shown diagramatically in Fig. 6. It was permanently mounted in an aluminum frame with "3-M" Bedding Compound.*
The apparatus has two calibrated burets in which the pure components are measured. Each buret acts as one leg of a mercury manometer, the other leg being open to the atmosphere. After the pressures and the volumes of the individual gases are determined, the burets are interconnected for blending.

The diameters of the tubes in the different sections of the burets were chosen so as to minimize the percentage error in the PV product. This point can be clarified further as follows: if a standard reading error of 0.1 mm is assumed, the diameter of the tubing is selected so that the percentage error in reading the volume is about the same as the percentage error in reading the pressure, taking into consideration the additional source of error introduced by the capillary correction. This point is discussed in greater detail by Cook.[2]

A more detailed description of the blending apparatus follows, together with the experimental procedure used in making a blend.

Calibration

The volume calibration of the burets was obtained by weighing the mercury drained from the appropriate sections. To avoid gas bubbles, the apparatus was filled with mercury after the burets had been evacuated to less than 10 microns. There is a small volume uncertainty due to small amounts of stopcock grease from stopcocks A and B that may extrude and adhere to the top sections of the burets; for this reason the above stopcocks were lubricated with a minimal amount of grease. Successive volume calibrations were internally consistent, and the volume uncertainty was below what would produce an error in composition of 0.01%.

Blending

The apparatus is connected to the vaccum-system manifold and pumped out before admission of the gases to be blended. The gas that is to be present in highest concentration in the final mixture is the one admitted to buret No. 1.

The mercury level in No. 1 is adjusted in the calibrated section above stopcock D, and the first gas is admitted. The pressure of the gas is adjusted to be very close to atmospheric. Stopcock A is closed and the system evacuated

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*Manufactured by Minnesota Mining and Manufacturing Co.

for admission of the second constituent into buret No. 2. The mercury level
in No. 2 is adjusted to obtain the proper volume ratio between the two gases.
After the pressure in the system is below 5 microns, as shown by a vacuum
thermocouple gauge in the vacuum-system manifold, the second gas may be
admitted to buret No. 2. Stopcock B is now closed and the system is evacuated.

Once the pressure in the system is below 5 microns, stopcocks E and H
are opened, letting the mercury rise in the intermediate tube until it is above
stopcock C, which is now closed. The mercury level is allowed to rise until
it reaches point K.

At this point the blending apparatus is charged and ready for the determination
of the pressure and volume of the gases in the burets. This reading is accomp-
lished by connecting each of the burets to the manometer tube, by opening stop-
cocks G and D or F. For certain volume and pressure ratios it is possible to
open the three stopcocks simultaneously and adjust the amount of mercury in
the system so that the mercury meniscus in each of the burets is in a calibrated
section. For the apparatus described presently, mixtures containing about 6%,
17%, 41%, and 52% of either component could be read in this fashion. For other
mixtures, the determination could not be carried out simultaneously.

The blending apparatus is disconnected from the vacuum system and
immersed in a well-stirred water bath. The water bath was designed specifically
for this purpose and was provided with long plate-glass windows, to allow
accurate reading of the mercury levels.

The mercury levels and the position of the fiduciary mark (Fig. 6) are
read with a cathetometer to the nearest 0.1 mm; the apparatus was always
carefully leveled before a set of readings was taken.

The atmospheric pressure and temperature of the water bath are recorded
and the blending apparatus is ready to be connected to the vacuum system for
transfer of the blend to the apparatus to be calibrated.

Once the blending apparatus is connected, stopcocks G and either D or F
are closed, stopcocks A and B are opened, and the gas is transferred back and
forth between burets Nos. 1 and 2 for mixing.

The amount of time devoted to this particular operation is quite important.
It was found that as much as 40 minutes was required for proper mixing and
that using shorter mixing times resulted in inconsistent results. This is
probably the main drawback of this piece of equipment; however, it can be

improved appreciably by the inclusion of another bulb, of about 100 cc capacity, below the calibrated section of buret No. 1, to allow complete transfer of the gases from one buret to the other and to increase the amount of mixing in any given transfer. After the gases are properly blended, the mercury level in the central tube is lowered below the mercury cutoff, and the blend is introduced into the vacuum-system manifold by opening stopcock C.

From the values of pressure and volume of the gases the value of the PV product was calculated, by use of the ideal-gas law. The temperature of the water bath was noted to ascertain the mercury-density correction factor, but was not used to reduce the PV product to a standard temperature, since both gases are at the same temperature and the percent correction would be the same for both gases. The number of mols of each gas was computed from the PV product and the value of the actual molar volume of the gas.

For the gases used in this work--hydrogen and nitrogen--the above calculation procedure is justified, since the deviations from ideal gas behavior would introduce errors smaller than 0.01% in the final molar composition of the blend.

The pressure readings were corrected for the capillarity effects of the tubes of the burets. The diameter of the manometer tube, 18 mm i.d., was chosen to eliminate the need for any correction.

The hollow bore of stopcocks A and B was partially filled with sealing wax, to eliminate the dead volume and the possibility of having an unmixed pocket of gas. For the same reason the mercury level in the central tube is raised to point K.
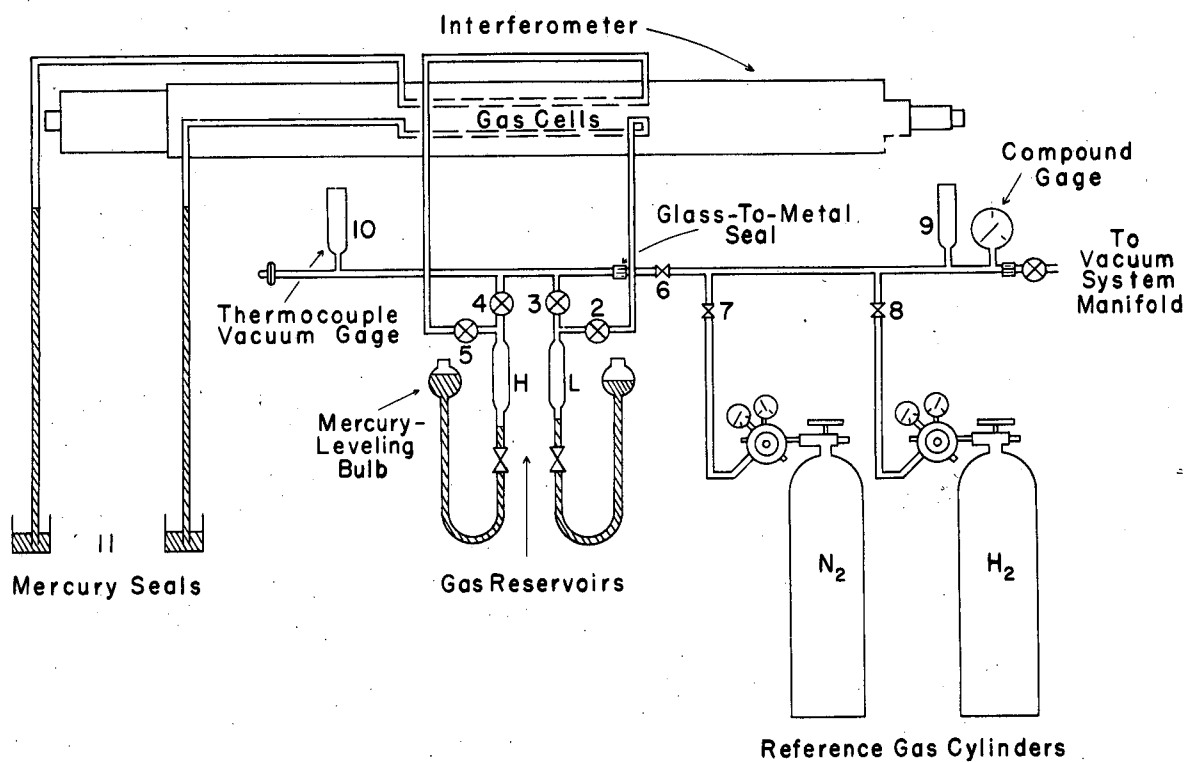
This particular design of blending apparatus, in which the gases are measured in two independent burets, performed very satisfactorily after the effect of mixing time was ascertained and allowed for. It is believed that the average error in the composition of a blend was of the order of 0.01%, as evidenced by the data obtained in the calibration of the interferometer.

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Figure Captions

Fig. 1. Optical interferometer, flow diagram.

Fig. 2. Band shift for hydrogen-nitrogen mixtures read versus reference hydrogen.

Fig. 3. Index of refraction versus composition, diagrammatic.

Fig. 4. Values of $x-x_c$ versus composition for hydrogen-nitrogen mixtures read versus reference hydrogen.

Fig. 5. Comparison of theoretical and experimental values of $h-(h_M)_I$.
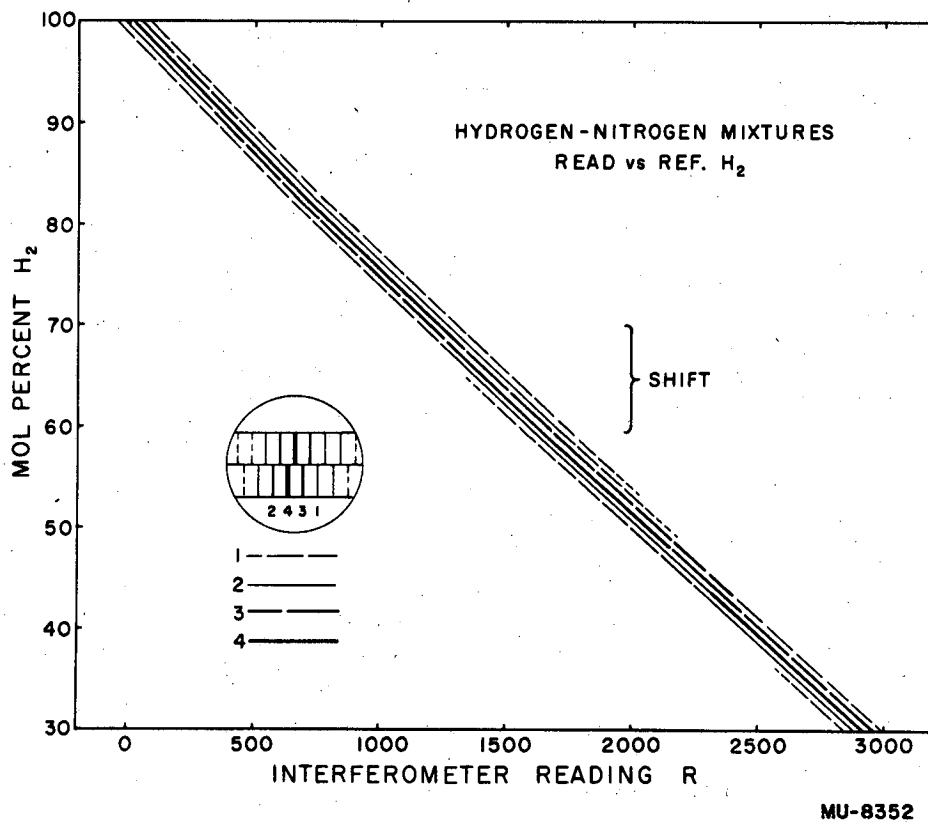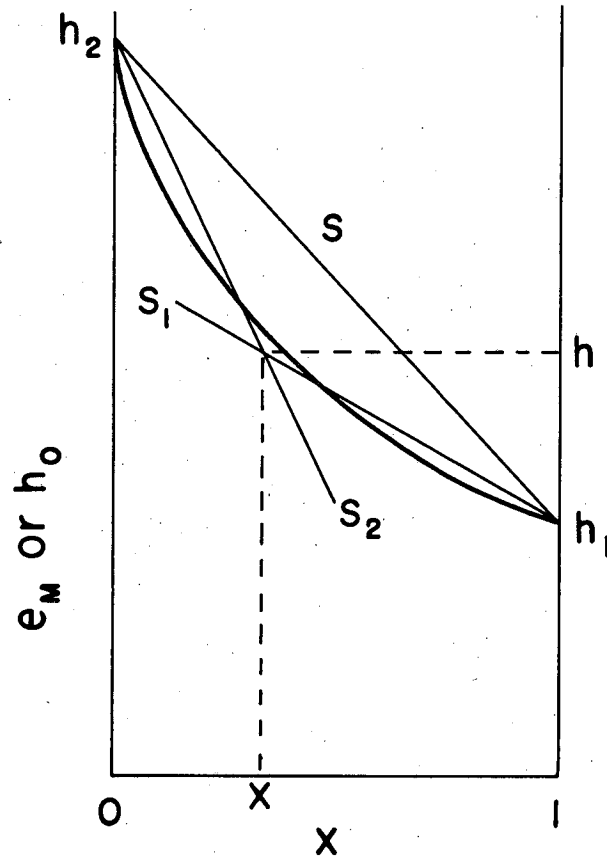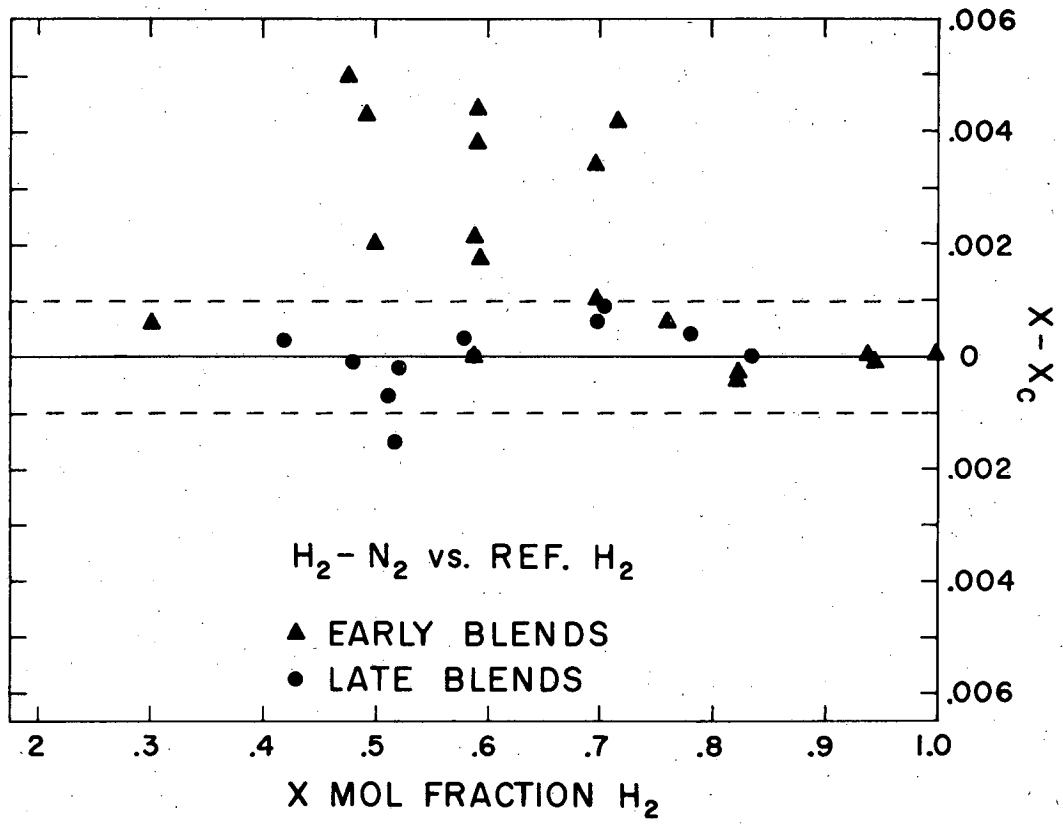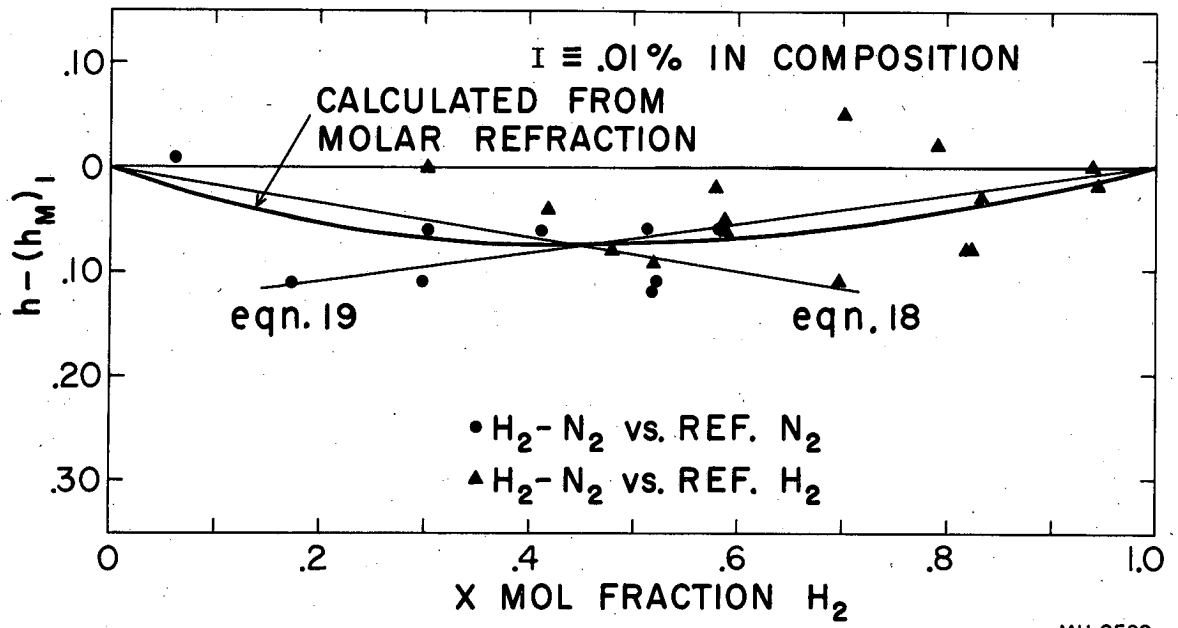
Fig. 6. Gas-blending apparatus.

Fig. 1.

Fig. 2.

MU-9593

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.