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SLOPES OF *pv* ISOTHERMS OF He, Ne, A, H_2, N_2, AND O_2 AT 0° C

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ABSTRACT

The change of *pv* (pressure times volume of a constant mass of gas) with pressure or density at constant temperature and low pressures is treated as a characteristic physical quantity. Various methods of determining this quantity from available experimental data for several gases, including He, Ne, A, H_2, N_2, and O_2, are examined with special reference to the reliability of the values at 0° C.

Reliable values for these quantities are important for many purposes, such as correcting temperatures measured by means of gas thermometers to the thermodynamic scale and in the derivation of the absolute temperature of the ice point, T_0.

CONTENTS

I. INTRODUCTION

In many fields of science it is frequently possible to calculate a desired result in several different ways, sometimes employing the results of more than one set of measurements. In many cases it is found that such calculations lead to somewhat different results, depending upon the assumptions and auxiliary numerical values used to obtain a derived result. If great exactness is desired it is obvious that careful consideration should be given to the reliability of (1) each set of experimental data, (2) each result derived therefrom, (3) the various methods of calculation, and (4) the assumptions employed. This appears to be especially applicable to the derivation of some of the so-called fundamental or basic physical constants, which cannot be obtained by direct measurement but must be obtained indirectly by calculation, using certain assumptions.

The numerical values of many basic physical constants which have been used for years are now in such an unsettled state that it is difficult for an unbiased person to decide which of the many published "recommended" or "accepted" values to use in his calculations. While this is particularly true in the case of the so-called atomic constants, it also appears to apply to what may be called thermodynamic constants, including the gas constant (R,k), the absolute temperature of certain "fixed points", such as the ice point, and the atomic or molecular weights of some of the simpler gases.

It is not the intention in this paper to derive additional "recommended" or "accepted" values for these constants but rather (1) to examine the reliability of some of the experimental data and methods used to obtain derived values for such constants, (2) to follow some of the recommended procedures which have proved useful in the appraisal of experimental data, and (3) to point out some of the apparent misinterpretations, inconsistencies, and discrepancies existing in the data on the properties of certain gases at pressures below 2 atmospheres.

II. AVAILABLE DATA

There are available in the literature very extensive data on the density or specific volume of different gases at various pressures and temperatures, often referred to as p,v,T data. Many of these published data are supposed to be the direct result of experiment and are frequently given in nonintegral multiples of some unit of density or specific volume, pressure, and temperature. Comparison of the experimental results of one observer with those of another observer, which are expressed in different nonintegral multiples of a different set of units, can be made accurately in general only by the expenditure of considerable arithmetical labor and by employing reliable methods of interpolation. Some data, which are given at integral temperatures and pressures, are supposed to be results obtained from experiments by some process of smoothing, the details of which are usually not specified. In some cases the results of a certain set of experiments, such as those obtained at a constant temperature, are given in the form of an empirical equation. In other cases a large group of experimental results covering a range of both temperature and pressure is embodied in a single equation, frequently called an equation of state. Many different forms of such equations with various degrees of complexity have been devised, but it is rather significant that there has been a pronounced decline in the number of such equations published in the last decade.

While it is possible to calculate from such equations not only the slopes of the pv isotherms but also many other important characteristics of gases, a serious difficulty arises if the demands as to accuracy are high and if careful consideration is given to the reliability of such derived results. In many instances the situation is so complex that it is exceedingly difficult, or next to impossible, to make even an educated guess as to the reliability of a derived result.

A superficial examination of the isothermal pv data discloses that the experimental results of the different observers in the range below 2 atmospheres generally differ markedly. Further investigation discloses that the results derived from a given set of experiments, including observations above this range and also at about 1-atmosphere pressure, differ appreciably, depending upon the interpretation of the experimental data and the methods employed to obtain a derived result.

There appear to be two schools of thought relative to the best method of determining numerical values for the slopes of the *pv* isotherms below 2 atmospheres. One group of experimenters, working in the field of atomic and molecular weights, use only data obtained at and below 1-atmosphere pressure in the reduction of their data, completely ignoring the existence of data at higher pressures. The propriety of this procedure has been questioned by Wild [1].[1] In obtaining probable values for certain atomic weights and also the gas constant, Birge [2] identifies himself with this school by ignoring data above 1 atmosphere.

Another group of experimenters, working in the field of gas thermometry, make similar reductions of their results obtained at pressures below 2 atmospheres, but use values for the isothermal slopes deduced from pressures considerably above this range. The Physikalisch-Technische Reichsanstalt and the Leiden Cryogenic Laboratory have published extensive data obtained in the interval 1 to 100 atmospheres. Since the major use they have made of these data is in the reduction of their gas thermometry results, their position on the subject may be inferred.

Since both groups have one point in common, namely, at 1 atmosphere, which has been used almost universally as a conventional reference point, it appeared to be worth-while to examine the course of the *pv* curve on both sides of this reference point, using some of the most precise data obtained by each group. It is generally assumed by both groups that the *pv* versus *p*, or the *pv* versus $1/v$ curves are straight lines below 2 atmospheres within the experimental errors of the measurements. For the purpose of this paper, the slopes of these curves are regarded as important quantities whose numerical values are needed to the highest accuracy attainable for calculating other important derived physical constants.

III. THEORETICAL PREDICTIONS

While the approach here is chiefly from the experimental side, it may be well to summarize briefly some of the predictions of theory, especially those relating to the form of equation which may be expected to represent experimental results satisfactorily. One important prediction is that at 0° C, at least, no chemical changes such as dissociation and association are to be expected in the case of the simpler monatomic and diatomic gases. Another is that the pressure, p, is a function only of the density, ρ, of a given kind of gas at a fixed temperature. Suppose it is assumed that the function is a power series

$$p=a_0+a_1\rho+a_2\rho^2+a_3\rho^3+\ .\ .\ .\ , \tag{3.1}$$

which is known to be capable of representing any curve if enough terms are employed. Suppose further that the constant coefficients, the a's, are determined from experimental data, using the method of

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[1] Figures in brackets indicate the literature references at the end of this paper.

least squares. Theory demands that $a_0=0$, but it practically never turns out to be zero identically in a least-squares treatment of the experimental data. It is very generally agreed that this may easily be ascribed to experimental errors and that the series may be written

$$pv=\frac{p}{\rho}=a_1+a_2\rho+a_3\rho^2+\ .\ .\ .\ , \tag{3.2}$$

where v is specific volume. It should be noted that pv has the physical dimensions of energy per unit mass, which makes it an important parameter from the standpoint of thermodynamics and statistical theory, which employ the well-known exact laws of conservation of mass and energy and permit the adding up of separate contributions to the total energy. Statistical theory predicts that at low pressures the foregoing series should be mathematically convergent, so that each succeeding term must be smaller than the preceding term.

All of these theoretical predictions appear to be amply supported by experiment. That the series is rapidly convergent is clearly indicated by the numerical values obtained from experiments which are considered later. For He, Ne, A, H_2, N_2 and O_2 at 0° C and one atmosphere, for example, the term $a_2\rho$ turns out to be less than 0.1 percent of a_1 in all cases, and the term $a_3\rho^2$ is at most of the order of a few parts in a million compared with a_1.

It is common practice to reduce pv measurements at pressures where high accuracy is attainable to low-pressure conditions in much the same way that accurate weighings are reduced to so-called vacuum conditions, that is, to what would have been obtained if the measurements had been made at very low pressures. The fact that accurate measurements cannot be made at low values of p and ρ appears in principle to be of no more practical importance than the fact that accurate weighings cannot be made in an absolute vacuum.

At very low pressures eq 3.2 reduces to a form which embodies the laws of ideal or perfect gases given in many textbooks, namely

$$pv=\frac{RT}{M}=a_1 \tag{3.3}$$

where v is the volume of 1 gram of gas, R is the universal gas constant, T is absolute temperature, and M is molecular weight, all three being determinable from combinations of experimental values for a_1.

Modern theories attribute the known deviations from the foregoing equation to the mutual interaction of the gaseous particles, sometimes referred to as Van der Waals' forces. It is generally agreed that the force of attraction between two such particles varies inversely as r^6, where r is the distance between centers. In some instances the force of repulsion is assumed to vary inversely as r^n, where n is about 9 to 12; in other instances an exponential relation is assumed. In any case, it seems clear that as the density is decreased indefinitely, the frequency of collisions, using the language of kinetic theory, must decrease. Since the average distance apart also decreases, the effects of Van der Waals' forces must also decrease, yielding values for a_1 at very low pressures which are independent of such effects, often called imperfections of the gases.

The situation at present, relative to the specific effects of such imperfections, appears to be that, while marked advances have been made, the theory is not yet far enough advanced to predict sufficiently accurate values for the constant a_2 and that better experimental values are needed in order to test adequately various hypotheses, and to aid in the development of reliable theories.

IV. METHODS OF CALCULATION

An accurate value for a_2, which has a different value for every temperature, has been the major goal of many experimental investigations. Some of the methods used to calculate a_2 from a given set of measurements, particularly at higher pressures, are open to several serious objections, because these methods introduce inaccuracies in a_2 which appear to exceed the inaccuracies inherent in the measurements themselves. High accuracy in calculations of this kind, as in the measurements, can be obtained only by exercising eternal vigilance in a multiplicity of small details. Many of these details appear worthy of brief mention here, since they are frequently ignored by many workers in this field.

It seems to be generally agreed that least-squares methods yield the "best" results and at the same time furnish an impersonal method of calculating mathematical probable errors which may be attached to published data. There are in the present application what may be termed "chemical errors," introduced by the presence of impurities in the gases, and also "physical errors," introduced in the calibration of weights and of the instruments used to measure pressure in terms of the fundamental standards of mass, length, and time, as well as many other possible physical sources of error. The true probable error should include all three kinds of errors, but the chemical and physical errors generally cannot be evaluated adequately from published information. Only by comparison of results from several independent investigations which differ by more than the sum of their mathematical probable errors can evidence be obtained of the magnitude of the systematic errors.

Least-squares methods have been followed here, but as pointed out by Birge [2] some judgment must be used in particular applications. For example, many of the results from the atomic-weight group give densities at only three pressures. If three terms in eq 3.2 are used, the fit is exact. If only two terms are used and each measurement is given equal weight, the usual solution yields the best simultaneous set of values for a_1 and a_2 From the standpoint of atomic weights, the emphasis is on obtaining a_1, but the immediate emphasis here is on obtaining the best value of a_2 from the measurements.

Considerable arithmetical labor may be saved by choosing one point as a reference and eliminating a_1. While, in principle, any point might be chosen, 1 atmosphere and 0° C has been used for convenience and designated by the subscript zero throughout this paper, unless otherwise specifically stated. Thus, writing the equation for any corresponding values of p and ρ

$$pv = a_1 + a_2\rho$$

and for the reference point

$$p_0v_0 = a_1 + a_2\rho_0.$$

Elimination of a_1 gives

$$pv-p_0v_0=a_2\rho-a_2\rho_0 \text{ or } \frac{pv-p_0v_0}{\rho-\rho_0}=a_2.$$

The mean value of a_2 obtained by this method of calculation is the same as the one obtained by the previous method, if each point is again given equal weight.

Thus far no attention has been given to the question of dimensions and units. It is obvious that $a_2\rho$ must have the same dimensions as *pv;* hence the numerical value of a_2 depends upon the units used. The very large number of different units used to express p, v, and ρ make interconversions for different combinations of units very difficult and troublesome at times. Such difficulties may be easily eliminated by writing the equation in the equivalent forms

$$pv=p_0v_0\left[1+a_2'\left(\frac{\rho}{\rho_0}-1\right)\right] \text{ or } \frac{\frac{pv}{p_0v_0}-1}{\frac{\rho}{\rho_0}-1}=a_2',$$

in which a_2' is obviously dimensionless and independent of the units used for p, v, and ρ.

In many cases the density is not measured. The mass of gas is held constant and only the volume is measured, so that ρ/ρ_0 must be replaced by v_0/v. Similarly for convenience, ρ/ρ_0 is very frequently replaced by p/p_0, which involves an approximation good to better than 0.1 percent in most cases considered here below 2 atmospheres, which is better than a_2 is known in general. Another alteration sometimes made is the use of an exponential equation. Since $e^x=1+x+x^2/2+\text{-----}$, with $x=a_2'\ [(\rho/\rho_0)-1]$, which is here always less than 0.001 below 2 atmospheres, $x^2/2$ and higher-power terms are less than 1 in 10^6. None of the measurements of p or v appears to be reliable to better than this amount.

These several alterations are referred to later, so that the various forms are assembled here as

$$pv=p_0v_0\left[1+\alpha_1\left(\frac{v_0}{v}-1\right)\right] \text{ or } \frac{\frac{pv}{p_0v_0}-1}{\frac{v_0}{v}-1}=\alpha_1 \tag{4.1}$$

$$pv=p_0v_0e^{\alpha_2\left(\frac{v_0}{v}-1\right)} \qquad \text{or } \frac{\ln\frac{pv}{p_0v_0}}{\frac{v_0}{v}-1}=\alpha_2 \tag{4.2}$$

$$pv=p_0v_0\left[1+\alpha_3\left(\frac{p}{p_0}-1\right)\right] \text{ or } \frac{\frac{pv}{p_0v_0}-1}{\frac{p}{p_0}-1}=\alpha_3 \tag{4.3}$$

$$pv=p_0v_0e^{\alpha_4\left(\frac{p}{p_0}-1\right)} \qquad \text{or } \frac{\ln\frac{pv}{p_0v_0}}{\frac{p}{p_0}-1}=\alpha_4. \tag{4.4}$$

The symbol α, with a different subscript for each form of equation, is used to denote that they are not identical in value, but for practical purposes the α's are all the same as a_2' in the range below 2 atmospheres. In precise language, each α represents a number obtained from measurements at any equilibrium state (pv) and at the reference state (p_0v_0) on a constant mass of gas at a constant temperature. In this sense the α's differ from the constant coefficient a_2 in that they are variable coefficients analogous to the α in the familiar equation $l=l_0[1+\alpha(t-t_0)]$, in which l is length, t is temperature, and α is usually called the coefficient of linear expansion. Over a short interval, all α's may be considered as constants for practical purposes, but measurements made over a wide interval prove them to be variables in every case. The fact that eq 4.1 to 4.4 all reduce to $0/0=\alpha$ at the reference state is of no consequence, for differentiation of these equations shows that all α's represent the derivative at this point, and hence they replace in the more exact mathematical language what have previously been called the isothermal pv slopes.

The analogy between the pv coefficients and the coefficient of linear expansion appears to be very close in several respects. For example, judgment dictates that, with the precision attainable, a highly reliable value for the coefficient of expansion of steel or fused silica cannot be obtained by making measurements at two temperatures 1 degree apart. The pv coefficients are correspondingly small and judgment again dictates that reliable values cannot be expected from measurements with attainable precision at pressures 1 atmosphere or less apart. In both cases it appears that greater reliability may be obtained by representing α, obtained from measurements over a wide interval, by means of an adequate empirical equation and then calculating therefrom a value of α at the reference point, which very probably would have been obtained if more precise measurements could have been made in the immediate vicinity of the reference point.

V. UNCERTAINTIES

The major objective here is to obtain not only a value for a_2 or α at 1 atmosphere from different investigations but also an estimate of reliability. In most investigations there are only a few, usually three to eight, essentially different points which serve to define a curve. The calculated value for the slope of the curve at 1 atmosphere may be so materially affected by systematic errors and by the form of analytical relation assumed to represent the curve that the calculated probable error may have but little significance as a criterion of reliability, and may give a false sense of security in the particular application. In order to make some allowance, although arbitrary, for such effects, the estimated uncertainty has been taken as approximately three times the mathematical probable error, following in general the recommendations of Rossini and Deming [3].

There are only two types of application used here. When α is assumed to be constant over an interval within the indicated precision of the data, the uncertainty, u, in the mean value of α is taken as

$$u=2\left[\frac{\Sigma w\Delta^2}{(n-1)(\Sigma w)}\right]^{\frac{1}{2}}. \tag{5.1}$$

When a linear relation such as $\alpha = a + bx$ is assumed, the uncertainty in a or the value of α when $x=0$, obtained by the method of least squares, is taken as

$$u = \frac{2}{(n-2)^{\frac{1}{2}}} \left[\frac{(\Sigma w\Delta^2)(\Sigma wx^2)}{(\Sigma wx)^2 - (\Sigma w)(\Sigma wx^2)} \right]^{\frac{1}{2}}. \tag{5.2}$$

In both cases, n is the number of observations, w is the weight assigned, and Δ is the residual or difference between the observed and calculated value of α.

An estimate of the true but unknown uncertainty may be obtained by assigning errors to each element which enters into the final result. In most of the measurements it appears almost certain that the true errors in each element are less than 1 in 10^3. Hence, to an approximation good to better than 1 in 10^6, the error in pressure may be written

$$p' = p + \Delta p = p\left(1 + \frac{\Delta p}{p}\right) = pe^{\frac{\Delta p}{p}}, \tag{5.3}$$

where p' is the true value, p is the observed value, Δp is the true error, and $\Delta p/p$ is the fractional error in p. Similar relations may be written for volume, v, mass, m; and temperature, T; so that

$$\frac{p'v'}{p_0'v_0'} = \frac{pv}{p_0v_0}e^y, \tag{5.4}$$

where the combined fractional errors are

$$y = \frac{\Delta p}{p} - \frac{\Delta p_0}{p_0} + \frac{\Delta v}{v} - \frac{\Delta v_0}{v_0} + \frac{\Delta m}{m} + \frac{\Delta T}{T}, \tag{5.5}$$

which includes possible errors in the assumed constancy of mass and temperature. Thus the true error in α appears in the last terms of relations, such as

$$\frac{\ln \dfrac{p'v'}{p_0'v_0'}}{\dfrac{p'}{p_0'} - 1} = \frac{\ln \dfrac{pv}{p_0v_0}}{\dfrac{p}{p_0} - 1} + \frac{y}{\dfrac{p}{p_0} - 1} \text{ or } \alpha_4' = \alpha_4 + \frac{y}{\dfrac{p}{p_0} - 1} \tag{5.6}$$

$$\frac{\dfrac{p'v'}{p_0'v_0'} - 1}{\dfrac{p'}{p_0'} - 1} = \frac{\dfrac{pv}{p_0v_0} - 1}{\dfrac{p}{p_0} - 1} + \frac{\dfrac{pv}{p_0v_0}y}{\dfrac{p}{p_0} - 1} + \ldots \text{ or } \alpha_3' = \alpha_3 + \frac{\dfrac{pv}{p_0v_0}y}{\dfrac{p}{p_0} - 1} + \ldots \tag{5.7}$$

and corresponding relations for α_1 and α_2 with $[(v_0/v) - 1]$ in the denominator. The error in the denominator has been neglected for simplicity, since by hypothesis this affects α less than 1 in 10^3, while the last term may be many times this amount.

For oxygen and argon α is of the order of 10^{-3}. In order to obtain a value of α for oxygen or argon with a true uncertainty of less than 1 percent, the combined fractional errors, y, must be less than the following:

$\frac{p}{p_0}-1$	y
0.5	5×10^{-6}
1	10^{-5}
10	10^{-4}
100	10^{-3}

For the other gases included herein, α is about 4 to 6×10^{-4}, so that the corresponding requirements are only slightly higher.

The scatter of the computed values of α obtained from measurements at less than 2 atmospheres indicates random fractional errors of several units in 10^{-5}, even in the most precise measurements available, and very much larger errors in other cases, which it has not seemed worthwhile to consider in detail here. Since there is no positive assurance that the systematic errors may not be as large as or even larger than the apparent random errors, which already exceed the limits stated above, it is obvious that α cannot be obtained with a true uncertainty of less than 1 percent from available measurements at pressures less than 2 atmospheres.

With measurements over an interval of 10 atmospheres or more the requirements are obviously not so exacting. It appears that the combined fractional errors in some of the published measurements at high pressures may not exceed about 10^{-4} in several instances. One of the uncertainties in the values for α at 1 atmosphere obtained from measurements over a large pressure interval appears to be in the analytical relations used to represent α over such an interval. In several instances linear relations have been used, whereas the data clearly indicate that such a relation is inadequate. A constant error obviously introduces an erroneous apparent trend in the values of α. Hence, anomalous trends in the values of α may well be viewed with suspicion and interpreted as possible evidence of the presence of systematic errors. In some instances the variation of α with pressure is small, for example, a few units in 10^{-8} per atmosphere for helium. There appears to be little reason for doubting that the values of α for helium at 0° C and low pressures, obtained from measurements over a wide pressure interval, are much more reliable than the values obtained from any available measurements over a small pressure interval at low pressures.

In view of the fact that small errors of the order of 10^{-5} and less become significant in some instances, it may be pointed out that the method of calculation using ratios automatically eliminates the effect of some of the possible systematic errors of this magnitude. For example, where p and p_0 are both measured by means of a mercury manometer

$$\frac{p}{p_0}=\frac{\rho hg}{\rho_0 h_0 g}, \tag{5.8}$$

where ρ is the density of mercury, h is the height of mercury column, and g is the average gravitational acceleration at the place where p is measured. The absolute value of g is obviously eliminated, and the absolute values of density are not needed as long as the density is uniform and proper corrections for temperature and pressure are applied. Thus the uncertainty in the ratio p/p_0 reduces essentially to uncertainties in the measurements of h, except for capillary corrections and other small but sometimes appreciable corrections, such as for gas columns.

The case is different, however, when p_0 is measured with a mercury manometer and p is measured with a piston gage. In this case

$$\frac{p}{p_0}=\frac{mg/A}{\rho_0 h_0 g}, \tag{5.9}$$

where A is the effective area of the piston and m is the effective mass of the piston and weights applied. The absolute value of g is eliminated, but uncertainties in the absolute values of all the other factors are involved. Thus an important element is the calibration of the piston gage, which is usually done by comparison with a mercury manometer; but many of the details of such calibrations are frequently not published. The agreement of results from different laboratories in several instances supplies indirect evidence that uncertainties in such calibrations apparently do not exceed about 10^{-4}.

Pressures much above 1 atmosphere are frequently determined at the Leiden Laboratory by means of closed-end manometers, which are usually filled with hydrogen. In Leiden Comm. 227a (1933) it is stated that in order to obtain a precision of 10^{-4} several improvements in the calibration and temperature control of the closed-end manometers were necessary. In a footnote, 1.35 mm is given as the radius of the tube containing the mercury meniscus. Uncertainties are recognized in the capillary corrections, which are relatively large in a tube of this size. There are also uncertainties in the volume of the gas beneath a plane tangent to the mercury surface, since the meniscus may assume various heights and shapes for a given setting of the vertex.

Illustrations are given later of other uncertainties which, for one reason or another, have found their way into some of the published values for α at low pressures. Many of the calculations of pv/p_0v_0 and α have been carried to one place beyond those given in the original publications, in order to obtain adequate values of u in equations 5.1 and 5.2 and to minimize uncertainties in the calculations themselves.

VI. OXYGEN

While the Reichsanstalt measurements include a number of gases and appear to be in reasonably good agreement with measurements obtained in other laboratories, all the analytical relations published as representations of the measurements appear to be somewhat erroneous. Since the reason for this unfortunate state of affairs is the same for all the gases and has not been pointed out previously, the data on oxygen are discussed in some detail as an illustration.

Referring to the data given in any horizontal row in table 1, the measurements were obtained essentially as follows: A pressure (column 1) is measured by means of a piston gage; a valve is closed, confining an unmeasured mass of gas in a known volume (column 2); another valve is opened, permitting the same mass of gas to expand into another known volume (column 4); and the pressure (column 3) is measured at approximately 1 atmosphere with a mercury manometer. The data in column 5, which were calculated from the data in the previous four columns, were used by Holborn and Otto to derive the following equation:[2]

$$pv=1.00130-1.30143\times10^{-3}p+3.6898\times10^{-6}p^2, \qquad (6.1)$$

where p is in m Hg, and $v=1$ when $p=1$. This equation, transformed to the form used here with 0° C and 1 atmosphere as the reference state, becomes

$$\frac{pv}{p_0v_0}=1-98.451\times10^{-5}\left(\frac{p}{p_0}-1\right)+2.13056\times10^{-6}\left(\frac{p}{p_0}-1\right)^2. \qquad (6.2)$$

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[2] Attention is called to the fact that the values of c in the equations $pv=a+bp+cp^2$ for oxygen at 0°, 50°, and 100° C given in *Z. Physik* **10**, 371 (1922) are in error. Corrected values for c are given in a later summary, *Z. Physik* **33**, 6 (1925), which contains the equation quoted here.

TABLE 1.—*Data on oxygen at 0 °C and 1 to 100 atmospheres obtained by Holborn and Otto*

Columns 1, 2, 3, and 4, observed values quoted from Z. Physik **10**, 367 (1922).
Column 5, calculated from observed values.
Column 6, based on $\alpha = \frac{1}{v_0}\left(\frac{dpv}{dp}\right)_t = -9.5 \times 10^{-4}$.
Column 7, corrected to common reference state, p_0=760 mm Hg, from values in columns 5 and 6.
Column 8, values quoted from Handbuch der Experimental Physik, **8** pt. 2, p. 175, with 1 atmosphere as the reference state.
Column 9, obtained from data in column 1 by dividing by p_0=760 mm Hg.
Column 10, obtained by dividing data in column 9 by data in column 7.

p	v	p_0	v_0	Observed $\frac{pv}{p_0v_0}$	Correction to p_0=760	Corrected $\frac{pv}{p_0v_0}$	Corrected $\frac{pv}{p_0v_0}$	$\frac{p}{p_0}$	$\frac{v_0}{v}$	$\frac{10^4\left(1-\frac{pv}{p_0v_0}\right)}{\frac{v_0}{v}-1}$	Mean values $-10^4\,\alpha_1$	$\frac{10^4\left(1-\frac{pv}{p_0v_0}\right)}{\frac{p}{p_0}-1}$	Mean values $-10^4\,\alpha_3$
1	2	3	4	5	6	7	8	9	10	11	12	13	14
mm Hg	*ml*	*mm Hg*	*ml*										
18960.1	106.025	775.06	2651.28	0.978268	-19×10^{-6}	0.978249	0.97798	24.9475	25.5022	8.8772	8.9415	9.0828	9.1506
18995.0	106.024	776.63	2651.32	.978064	−21	.978043	.97778	24.9934	25.5545	8.9425		9.1513	
19055.5	106.023	780.60	2646.83	.977836	−26	.977810	.97754	25.0735	25.6425	9.0048		9.2176	
37788.1	106.016	811.42	5157.09	.957362	−64	.957298	.95706	49.7212	51.9392	8.3829	8.3858	8.7646	8.7680
37811.0	106.015	813.90	5144.74	.957306	−67	.957239	.95701	49.7513	51.9737	8.3888		8.7713	
56045.1	106.005	766.73	8246.73	.939593	−8	.939585	.93930	73.7436	78.4853	7.7970	7.7670	8.3053	8.2892
56098.2	106.006	766.79	8252.82	.939725	−9	.939716	.93943	73.8134	78.5486	7.7371		8.2729	
74849.0	105.998	798.74	10741.62	.924716	−48	.924668	.92442	98.4855	106.5090	7.1399	7.1331	7.7275	7.7220
75394.8	105.998	804.99	10741.04	.924277	−56	.924221	.92398	99.2037	107.3376	7.1263		7.7165	

In figure 1 the coordinates of the points for oxygen on curves 2 and 3 are:

2 3 3 2

Equation 6.1 was apparently derived so as to reduce to $pv=1$ when $p=1$ m Hg, but the data in column 5 are obviously not on this basis. As a matter of fact, each row of data in the first five columns applies to a particular mass of gas and the different rows are not on a comparable basis. Adding to the data in column 5 the corrections in column 6 yields the data in column 7, which are all on the same basis. The corrections are relatively small, since p_0 observed is not far from 760 mm. In other instances, p_0 observed ranged from less than 500 mm to over 900 mm, and the corrections are larger. Applications of these necessary corrections materially improve the general consistency of the Reichsanstalt measurements.

Holborn and Otto have evidently misinterpreted all their measurements as having 1 m Hg and 0° C, as the reference state, possibly because p in m Hg was used for convenience in the equations. Further evidence of this misinterpretation is supplied by the values in column 8, which are given by Otto in the Handbuch der Experimental Physik. Apparently these values were obtained from column 5, misinterpreted as on a 1 m Hg basis, and corrected to a 760 mm Hg basis. The effect of this misinterpretation is shown graphically in figure 1. The dashed line 1 at the top, representing eq 6.2, is obviously a very poor representation of the observed points and consequently yields an erroneous value of α at 1 atmosphere.

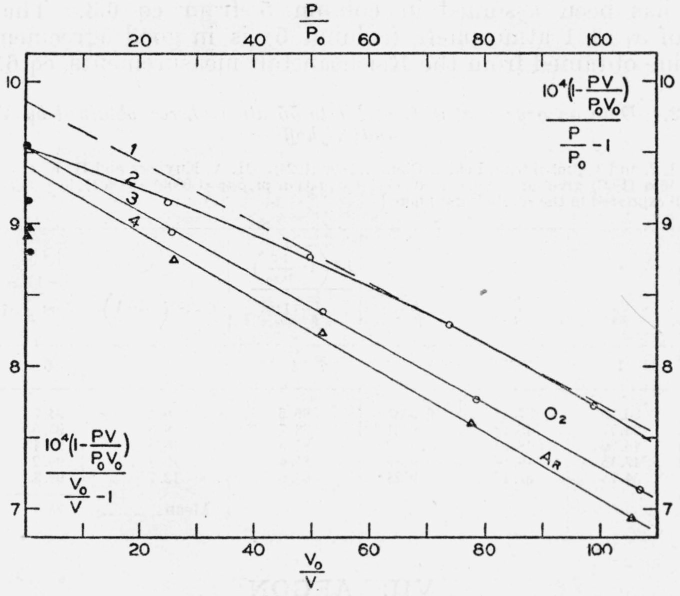

FIGURE 1.—*Data on oxygen (circles) and argon (triangles) at 0° C; Reichsanstalt data at 25 to 100 atmospheres; Baxter and Starkweather data below 1 atmosphere.*

Coordinates of lines 1 and 2 at top and right; coordinates of lines 3 and 4 at bottom and left. Line 1 represents eq 6.2; line 2 represents α_3 as a quadratic function of p/p_0. Line 3 represents eq 6.3 for oxygen. Line 4 represents eq 7.1 for argon.

Curve 2 in figure 1 indicates clearly that the observed values of α_3 given in table 1 cannot be represented adequately by a straight line. On the other hand, line 3 indicates that it represents reasonably well the observed values of α_1 in table 1. The weighted least-squares equation for line 3 is

$$\frac{pv}{p_0v_0}=1-(95.13\pm0.94)\times10^{-5}\left(\frac{v_0}{v}-1\right)+2.246\times10^{-6}\left(\frac{v_0}{v}-1\right)^2. \qquad (6.3)$$

The values of α_1 obtained from measurements below 1 atmosphere by Baxter and Starkweather, considered later, have been included in figure 1 to indicate that they appear inconsistent with the Reichsanstalt measurements, as might be expected from the previous discussion on uncertainties.

Measurements on oxygen obtained at the Leiden Laboratory are quoted in table 2. The values of α_1 in column 4 are insufficient to give an adequate determination of the variation of α_1 with density, which has been assumed in column 5 from eq 6.3. The mean value of α_1 at 1 atmosphere (column 6) is in good agreement with the value obtained from the Reichsanstalt measurements, eq 6.3.

TABLE 2.—*Data on oxygen at 0° C and 1 to 55 atmospheres obtained by Van Urk and Nijhoff*

[Columns 1, 2, and 3 quoted from Leiden Comm., 169c (1924). H. A. Kuypers and H. K. Onnes, Leiden Comm. 165a (1923) give for oxygen at 0° C the equation $pv/p_0v_0=1.00095-95.803\times10^{-5}\ (v_0/v)+2.0608\times10^{-6}(v_0/v)^2$ expressed in the symbols used here.]

$\frac{p}{p_0}$	$\frac{v_0}{v}$	$\frac{pv}{p_0v_0}$	$\frac{10^5\left(1-\frac{pv}{p_0v_0}\right)}{\frac{v_0}{v}-1}$	$0.2246\left(\frac{v_0}{v}-1\right)$	$-10^5\alpha_1$ at $\frac{v_0}{v}=1$
1	2	3	4	5	6
36.20	37.38	0.9685	86.6	8.1	94.7
38.77	40.13	.9661	86.7	8.8	95.5
46.90	48.91	.9590	85.6	10.8	96.4
47.15	49.17	.9589	85.4	10.8	96.2
54.75	57.45	.9528	83.6	12.7	96.3
				Mean	95.8

VII. ARGON

The Reichsanstalt measurements on argon are quoted in table 3, and values of α_1 are plotted in figure 1. It is apparent from line 4 that α_1 for argon is very similar to α_1 for oxygen (line 3). The equation for line 4, obtained graphically,[3] is

$$\frac{pv}{p_0v_0}=1-93.90\times10^{-5}\left(\frac{v_0}{v}-1\right)+0.235\times10^{-5}\left(\frac{v_0}{v}-1\right)^2, \qquad (7.1)$$

which yields $10^5\alpha=-93.9$ at 0° C and 1 atmosphere. The equation, given by Holborn and Otto [4] based on the same data, yields $10^5\alpha=-98.1$ at 1 atmosphere. The difference, about 4 percent, is about the same as that previously found for oxygen, and for the same reason.

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[3] Least-squares methods were not used in this case because the corrections to $p_0=760$ could not be applied, the details of the measurements not being given by Holborn and Schultze. The results (see fig. 1) parallel those for oxygen so closely that $10^5\ \alpha=-94\pm1$ at 1 atmosphere was taken as a reasonable estimate from a large-scale plot.

TABLE 3.—*Data on argon at 0° C and 1 to 100 atmospheres obtained by Holborn and Schultze*

[Columns 1 and 2 quoted from Ann. Physik **47**, 1089 (1915). The details of the measurements, such as quoted for oxygen, are not given. It is assumed here that the reference pressures, p_0, were sufficiently close to 760 mm Hg that corrections would amount to less than 1 in $10^5\,\alpha_1$. See notes on the measurements of Holborn and Schultze on helium for evidence in support of this assumption.]

p 1	$\frac{pv}{p_0v_0}$ 2	$\frac{10^5\left(1-\frac{pv}{p_0v_0}\right)}{\frac{v_0}{v}-1}$ 3	$0.235\left(\frac{v_0}{v}-1\right)$ 4	$-10^5\,\alpha_1$ at $\overset{v_0=1}{v\,\alpha}$ 5
*m*Hg				
19.230	0.97826	87.43	5.84	93.27
19.258	.97821	87.50	5.85	93.35
37.552	.95817	82.72	11.93	94.65
37.940	.95809	82.01	12.03	94.04
55.521	.94192	76.00	17.96	93.96
55.611	.94173	75.97	18.02	93.99
74.395	.92746	69.39	24.57	94.01
74.408	.92746	69.38	24.58	93.95
			Mean-------	93.90

Measurements obtained on argon at the Leiden Laboratory are quoted in the first part of table 4. The values of $10^5\,\alpha_1$, ranging from −72 to −75, were not plotted in figure 1 because they are grossly inconsistent with the Reichsanstalt data, as pointed out by Holborn and Schultze. A plausible clue to the reason for the large discrepancy is given by Wild [1] in a footnote, quoted as follows: "Professor Masson, of the University of Durham, informs me that Onnes' data on argon are in error, due to 'side trapping' of a small amount of gas in one limb of the piezometer, after measurement of its volume at one atmosphere."

By choosing one of the high-pressure measurements as the reference state and eliminating v_0 at 1 atmosphere, it may readily be shown that the data at 1 atmosphere are not consistent with the data at the higher pressures. The value of v_0 obtained by this process is greater by the factor 1.0035. The calculations made on this basis in the second part of table 4 lead to a value of $10^5\,\alpha=-93$ at 1 atmosphere, which is in fair agreement with that obtained from the Reichsanstalt measurements.

Attention is called to the fact that Onnes and Crommelin reported data for argon on 16 different isotherms, which are quoted in International Critical Tables, volume 3, page 4. All the data are based upon what appears to be an erroneous value for v_0.

TABLE 4.—*Data on argon at 0° C and 1 to 62 atmospheres obtained by Onnes and Crommelin*

Columns 1, 2, and 3 quoted from *Leiden Comm.* 118b (1910).
Column 4. These values of α_1 are inadequate to establish the change of α_1 with density.
Column 5. The value of 0.235 was assumed from the Reichsanstalt data on argon, eq 7.1, since the data in column 4 are insufficient to yield an adequate value for the change of α_1 with density.

$\frac{p}{p_0}$	$\frac{v_0}{v}$	$\frac{pv}{p_0v_0}$	$\frac{10^5\left(1-\frac{pv}{p_0v_0}\right)}{\frac{v_0}{v}-1}$	$0.235\left(\frac{v_0}{v}-1\right)$	$-10^5\alpha_1$ at $\frac{v_0}{v}=1$
1	2	3	4	5	6
20.576	20.877	0.98560	72.4	------------	--------
26.070	26.581	.98077	75.2	------------	--------
31.572	32.302	.97740	72.2	------------	--------
36.743	37.782	.97250	74.8	------------	--------
49.871	51.840	.96201	74.7	------------	--------
62.230	65.325	.95261	73.7	------------	--------
(REFERENCE VOLUME, v_0, INCREASED BY THE FACTOR 1.0035)					
20.576	20.950	0.98215	89.5	4.7	94.2
26.070	26.674	.97736	88.2	6.0	94.2
31.572	32.415	.97399	82.8	7.4	90.2
36.743	37.914	.96911	83.7	8.7	92.4
49.871	52.021	.95867	81.0	12.0	93.0
62.230	65.554	.94929	78.6	15.2	93.8
				Mean------	93.0

VIII. HYDROGEN

In the measurements at the Reichsanstalt and also the Leiden Laboratory, large corrections are required, since large portions of the gas were at about room temperature instead of the particular isotherm under investigation. In the measurements at the Van der Waals Laboratory of the University of Amsterdam by Michels and collaborators, there are no such corrections, since all the gas was at the same temperature, confined over mercury in a glass piezometer shaped somewhat like a McLeod gage, with a large lower bulb for determinations of v_0 at 1 atmosphere and a series of small upper bulbs with electric contacts sealed into the capillaries between the small bulbs. With the same pressure inside and outside the glass piezometer, the measurements were carried to much higher pressures. The precision of the measurements is much higher than in any other measurements available. The measurements obtained on hydrogen are quoted in table 5. With only six measurements of pv/p_0v_0, these were represented by a power series with five coefficients, only the first three coefficients being given in the publication cited, which yield $10^5\alpha=61.16$ at 0° C and 1 atmosphere. The reliability of this value is difficult to estimate under the circumstances.

Considerable effort has been devoted here to finding simple, yet adequate, interpolation equations in order that the advantages of least-squares methods may be fully utilized without undue labor, and as an aid in obtaining impersonal estimates of uncertainties in α at low pressures. Many people, including the author, rebel at using least-squares methods when more than about two unknown coefficients are involved, and especially when the number of observations approaches the number of unknown coefficients.

As an illustration of the characteristics of the four different α's defined by eq 4.1 to 4.4, calculated values over a wide interval are given in table 5 and are plotted as open circles in figure 2, the numbers 1 to 4 on the curves corresponding to α_1, α_2, α_3 and α_4 respectively. For curves 1 and 2, the abscissas are v_0/v, and for curves 3 and 4, the abscissas are p/p_0. Obviously, curves 1, 3, and 5 cannot be represented adequately by a linear equation; even a quadratic equation is insufficient. Curve 2 is apparently linear within the precision of the data and the equal weight, least-squares equation is

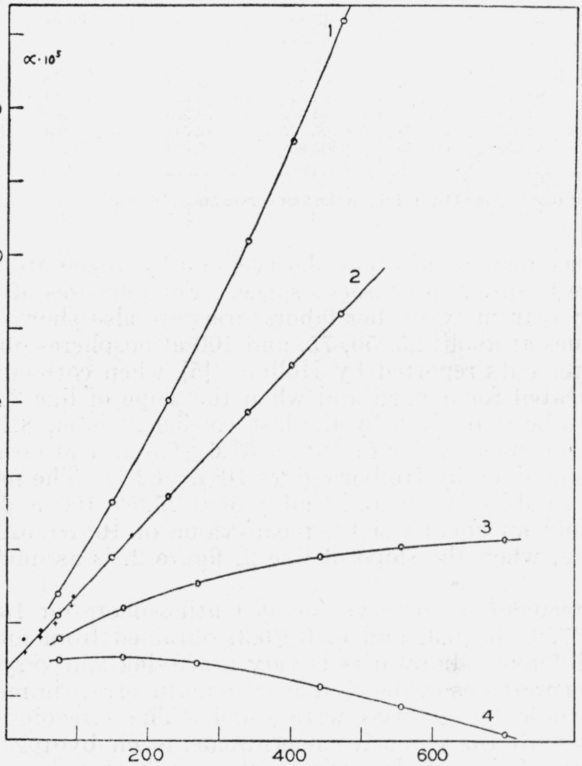

FIGURE 2.—*Data on hydrogen at 0° C.*

Curves 1, 2, 3, and 4 represent α_1, α_2, α_3, and α_4, respectively, calculated in table 5 from data of Michels, Nijhoff, and Gerber (open circles).

The abscissas for curves 1 and 2 are v_0/v; for curves 3 and 4 the abscissas are p/p_0. The data of Holborn are represented by crosses; data of Wiebe and Gaddy are represented by closed circles.

$$10^5 \ln \frac{pv}{p_0v_0} = (61.869 \pm 0.073)\left(\frac{v_0}{v}-1\right)+0.05175\left(\frac{v_0}{v}-1\right)^2. \qquad (8.1)$$

On a large-scale drawing, using a straightedge for curve 2 and a celluloid spline, held in place by lead weights for drawing curves 1, 3, and 4, it was apparent that all four curves tended to approach smoothly the same value of α at 1 atmosphere to about three significant figures.

TABLE 5.—*Data on hydrogen at 0° C and 1 to 700 atmospheres obtained by Michels, Nijhoff, and Gerber*

Columns 1 and 2 quoted from *Ann. physik* **12**, 562 (1932). Values in other columns were computed from these experimental values.

$\frac{p}{p_0}$ (1)	$\frac{v_0}{v}$ (2)	$\frac{pv}{p_0v_0}$ (3)	$\dfrac{10^5\left(\frac{pv}{p_0v_0}-1\right)}{\frac{v_0}{v}-1}$ $10^5\,\alpha_1$	$\dfrac{10^5 \ln \frac{pv}{p_0v_0}}{\frac{v_0}{v}-1}$ $10^5\,\alpha_2$	$\dfrac{10^5\left(\frac{pv}{p_0v_0}-1\right)}{\frac{p}{p_0}-1}$ $10^5\,\alpha_3$	$\dfrac{10^5 \ln \frac{pv}{p_0v_0}}{\frac{p}{p_0}-1}$ $10^5\,\alpha_4$
75.795	72.334	1.04785	67.08	65.51	63.97	62.48
164.193	148.221	1.10776	73.196	69.515	66.032	62.711
268.99	227.641	1.18164	80.144	73.642	67.779	62.278
442.27	338.39	1.30698	90.987	79.350	69.569	60.670
556.89	400.47	1.39059	97.777	82.541	70.264	59.315
701.34	468.89	1.49575	105.954	86.052	70.787	57.490

In figure 2 the coordinates of the points on the four curves are as follows:

3 and 4	1 and 2		1	2	3	4

The measurements of other observers on hydrogen are not given in detail here in order to conserve space. For purposes of comparison, values for α_2 from two other laboratories are also shown in figure 2. Mean values at about 25, 50, 75, and 100 atmospheres obtained from 11 measurements reported by Holborn [5], when corrected, as previously indicated for oxygen and when the slope of line 2, figure 2, is assumed to be that given by the last coefficient in eq 8.1, lead to an equal weight, mean value of $10^5\,\alpha=61.6\pm0.3$ at 1 atmosphere, while the equation given by Holborn gives $10^5\,\alpha=62.4$. The four measurements reported by Wiebe and Gaddy[6] at 25, 50, 100, and 200 atmospheres, yield an equal weight, mean value of $10^5\,\alpha=62.0\pm0.3$ at 1 atmosphere, when the slope of line 2, figure 2, is assumed as stated above.

The agreement of three values at 1 atmosphere for $10^5\,\alpha$, namely 61.87 ± 0.07, 61.6 ± 0.3, and 62.0 ± 0.3, obtained from measurements in three different laboratories is very gratifying and very significant, if it is interpreted as evidence that systematic errors in measurements made in these laboratories were small. The foregoing values are consistent with the extensive measurements on hydrogen at 20° C made at the Leiden Laboratory with a multiple-column, open-end, mercury manometer by Schalkwijk [7], when α_2 is calculated and compared with the measurements indicated by line 2, figure 2. The measurements reported by Nijhoff and Keesom [8] at 0° C, made with a closed-end mercury manometer, are less precise and lead to a value for α at 1 atmosphere, which is lower than those given above by a few percent.

IX. NITROGEN

Measurements on nitrogen obtained at the Van der Waals Laboratory of the University of Amsterdam are quoted in table 6. Michels, Wouters, and De Boer state that "series evaluation * * * carried out according to the method of mean squares" yielded the following equations:

$$10^5\frac{pv}{p_0v_0}=100045-46.020\frac{p}{p_0}+0.30048\left(\frac{p}{p_0}\right)^2-1.35\times10^{-7}\left(\frac{p}{p_0}\right)^4 \quad (9.1)$$

$$10^5\frac{pv}{p_0v_0}=100045-45.860\frac{v_0}{v}+0.30643\left(\frac{v_0}{v}\right)^2-1.84\times10^{-6}\left(\frac{v_0}{v}\right)^4, \quad (9.2)$$

which were obtained from their paper but are expressed in the symbols used here.

In order to test the effect on α at 1 atmosphere when a different form of equation was used and also to obtain an estimate of uncertainty, the following least-squares equation

$$10^5 \ln\frac{pv}{p_0v_0}=(-45.3166\pm 0.308)\left(\frac{v_0}{v}-1\right)+0.29868\left(\frac{v_0}{v}-1\right)^2 \quad (9.3)$$

was obtained from the same data, weighting each observation proportionally to $[(v_0/v)-1]$. As a check, the calculations were repeated, giving each observation equal weight, which yielded

$$10^5 \ln\frac{pv}{p_0v_0}=(-45.3236\pm 0.352)\left(\frac{v_0}{v}-1\right)+0.29885\left(\frac{v_0}{v}-1\right)^2. \quad (9.4)$$

Table 6.—*Data on nitrogen at 0° C and 1 to 52 atmospheres obtained by Michels, Wouters, and De Boer*

Columns 1, 2, 3, 4, and 5 quoted from Physica **1**, 587 (1934)

$\frac{p}{p_0}$	$\frac{v_0}{v}$	$\frac{pv}{p_0v_0}$	10^5 (observed-calculated)			
			Equation 9.1	Equation 9.2	Equation 9.3	Equation 9.4
1	2	3	4	5	6	7
19.0215	19.1606	0.99274	−4	−5	−4	−4
23.7629	23.9734	.99122	1	1	1	2
28.4968	28.7894	.98983	6	6	6	7
33.1101	33.4951	.98851	1	1	1	2
37.9526	38.4409	.98730	−1	−1	0	0
42.7435	43.3413	.98621	−6	−6	−5	−5
47.4376	48.1401	.98541	4	3	3	3
52.2160	53.0328	.98460	0	0	−3	−3

A comparison of the four equations is given in table 6, where the deviations of eq 9.1 and 9.2 have been copied from table 2 of the paper by Michels, Wouters, and De Boer. There is obviously very little difference between the various equations as far as representing the measurements is concerned, but there is considerable difference in the labor required to obtain four unknown coefficients in eq 9.1 and 9.2 and only two coefficients in 9.3 and 9.4 which were calculated with the equation in the linear form

$$\alpha_2=A+Bx \text{ or } \frac{\ln\frac{pv}{p_0v_0}}{\frac{v_0}{v}-1}=A+B\left(\frac{v_0}{v}-1\right). \quad (9.5)$$

Furthermore, calculation of the uncertainty in α at 1 atmosphere from equations such as 9.1 and 9.2 is complicated, while such a calculation is simple with eq 9.5. Differentiation of each equation gives for α at 1 atmosphere

$-10^5\alpha$	Equation
45.42	9.1
45.25	9.2
45.32 ± 0.31 [4]	9.3
45.32 ± 0.35 [4]	9.4

Michels, Wouters, and De Boer give some discussion of uncertainties in their measurements. The total volume, v_0, of the piezometer is given as about 1,500 cm^3, which means that the actual volumes of the gas at 0° C and 19 to 52 atmospheres were between about 75 to 30 cm^3.

In a joint publication from the Reichsanstalt and the University of Amsterdam, Otto, Michels, and Wouters [9] report measurements on nitrogen at 0° C and 45 to 227 atmospheres, in which the volume, v_0, of the piezometer is stated to be about 98 cm^3 and the volumes at high pressure to be between 2 and 0.43 cm^3. With nine different measurements of pv/p_0v_0, these authors represent their results at 0° C by means of two equations similar in form to eq 9.1 and 9.2 but with two more coefficients for sixth- and eighth-power terms, making a total of six coefficients. The authors do not state that the method of least squares was used in obtaining their equations, which, upon differentiation, yield two values for $-10^5\,\alpha$ at 1 atmosphere, namely, 45.31 and 44.70, corresponding to equations similar to eq 9.1 and 9.2, respectively.

Uncertainties in these two values are difficult to estimate under the circumstances, but it seems safe to infer from the evidence available that the true uncertainty in any value of α at 1 atmosphere, obtained from the same measurements by any accurate method of calculation, would exceed the true uncertainty in the value of α obtained from the measurements quoted in table 6. In other words, the values of α at 1 atmosphere obtained from the two investigations may be said to be in agreement, or at least not in conflict, within reasonable estimates of uncertainties. Apparently the same statement might be applied to the values of α for nitrogen at 0° C and 1 atmosphere obtained from many other investigations, some of which are listed by Otto, Michels, and Wouters [9], while Keesom and Tuyn [10][5] list from 15 different sources values of $-10^5\,\alpha$, which range from 37.2 (credited to Amagat) to 54.1 (credited to Bartlett).

No attempt can be made here to give an adequate discussion of calculations of the slopes of isotherms other than 0° C, but it may be of interest to outline briefly a possible procedure in examining the reliability of data available on nitrogen at 100° C. Suppose an equation similar to eq 9.4, but written in the more general form

$$\ln\frac{pv}{p_0v_0}=A+B\frac{v_0}{v}+C\left(\frac{v_0}{v}\right)^2+\;.\;.\;.\;.\;, \tag{9.6}$$

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[4] See eq 5.2 for the interpretation of $\pm u$, as used here. Readers accustomed to thinking in terms of least-squares probable error should mentally divide $\pm u$ by 3.

[5] This reference may be consulted for an extensive bibliography of p,v,T data on He, H_2, and N_2.

is assumed for the 100° C. isotherm, and that the coefficients A, B, and C are determined by least-squares methods, using the data given by Michels, Wouters, and De Boer, which include eight values [6] of pv/p_0v_0 at 100° C. for the same values of v_0/v quoted in table 6. Subtracting two such equations, one for 100° C. and one for 0° C., already obtained, yields

$$\ln \frac{(pv)_{100°}}{(pv)_{0°}} = (A_{100}-A_0)+(B_{100}-B_0)\frac{v_0}{v}+(C_{100}-C_0)\left(\frac{v_0}{v}\right)^2+\ . \ . \ . \ . \qquad (9.7)$$

It so happens that for nitrogen, C_{100} is very nearly equal to C_0, so that at constant volume $\ln p_{100°}/p_{0°}$ is very nearly linear in v_0/v over the range covered. Visual evidence of this is given in figure 3, where a linear scale of logarithms is used for the ordinates. The three points near the ordinate axis were obtained from the constant-volume gas-thermometer measurements of Beattie [11]. While measurements are reported at five different pressures, two intermediate points are not shown, for clarity. The other eight points were obtained from the essentially constant-volume gas-thermometer measurements of Michels, Wouters, and De Boer, and the line was drawn with a straightedge. The data from the two investigations appear to be mutually consistent to a few parts in 10^5, and consistent with an intersection with the ordinate axis between 1.3660 and 1.3661 on a large-scale plot.

It may be noted that

$$\ln \frac{(pv)_{100°}}{(pv)_{0°}} \doteq \ln \frac{T_{100}}{T_0} \doteq A_{100}-A_0 \text{ as } \frac{v_0}{v} \doteq 0$$

and

$$T_0 = \frac{100}{\frac{T_{100}}{T_0}-1},$$

by definition; hence

$$T_0 = \frac{100}{e^{(A_{100}-A_0)}-1}\ .$$

Thus a value for T_0, the ice point on the thermodynamic scale, may be obtained from the measurements of Michels, Wouters, and De Boer, but the calculated uncertainty in T_0 would obviously turn out to be relatively large.

A value of T_0 has been calculated by Beattie [11] based entirely on his measurements with nitrogen. He has also calculated values of T_0, using in principle three different values for the rate of change of $p_{100°}/p_{0°}$ obtained by various roundabout processes from measurements of Joule-Thomson coefficients, or of pv/p_0v_0 at higher pressures, which make the calculation of uncertainties very complicated. A more direct method of calculation of T_0 from the data on nitrogen appears

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[6] In obtaining the values of pv/p_0v_0 at 100° C., corrections were applied by Michels, Wouters, and De Boer for changes in volume of the glass piezometer with temperature and pressure, and for the fact that the temperature actually observed was 99.720° C. instead of 100° C. No mention is made of a correction for the vapor pressure of mercury, which is known to be about 0.0004 atmosphere at 100° C. The effect of such a correction if not already applied, would be to lower slightly the points shown in figure 3, a perceptible amount at $v_0/v=19$ on a large-scale plot, and barely perceptibly at $v_0/v=52$.

to be to combine the two sets of data shown in figure 3, using the observed ratios $p_{100°}/p_{0°}$. This may be done in several different ways.

One method is to use an adequate form of equation, preferably with a minimum of unknown coefficients, and a judicious assignment of weights to each observation. This method gives the high-pressure data the weight to which they appear entitled. Another method, which seems to lead to essentially the same final result and is sometimes preferable, because it is simpler, is to combine the data at low and high pressures to obtain a value for the rate of change of $p_{100°}/p_{0°}$ with either p/p_0 or v_0/v and to use this value to reduce each individual observed ratio $p_{100°}/p_{0°}$ near the ordinate axis and thus obtained a weighted mean value for $p_{100°}/p_{0°}=T_{100}/T_0$. In spite of the apparent advantages of these two methods of calculation, neither of them has ever been used to calculate T_0 or the uncertainty in T_0.

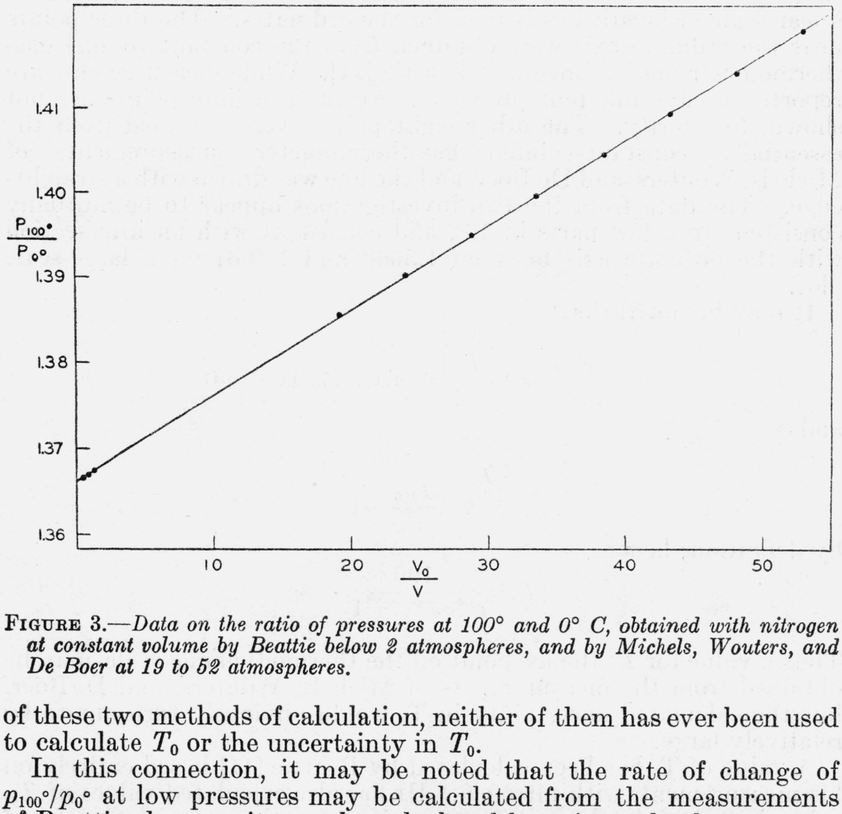

Figure 3.—*Data on the ratio of pressures at 100° and 0° C, obtained with nitrogen at constant volume by Beattie below 2 atmospheres, and by Michels, Wouters, and De Boer at 19 to 52 atmospheres.*

In this connection, it may be noted that the rate of change of $p_{100°}/p_{0°}$ at low pressures may be calculated from the measurements of Beattie alone, or it may be calculated by using only the measurements of Michels, Wouter, and De Boer and a method similar to the one outlined above. When consideration is given to the possible effects of constant or systematic errors in each investigation, it seems probable that a combination of both sets of data should yield a more reliable value for the rate of change of $p_{100°}/p_{0°}$, which is larger and hence of more importance for nitrogen than for some of the other thermometric gases. The result of such a combination leads to a relative value for the slopes at low pressures of the pv isotherms at 0 and 100 °C, or for practical purposes a value for $B_{100}-B_0$ in eq 9.7 or similar equations, and the uncertainty in the value for this difference may be calculated.

It is emphasized that this procedure seems preferable to the one usually followed, namely to obtain values for B_{100} and B_0 from the data on each isotherm separately, and then to obtain the difference. A value for $B_{100}-B_0$ may be calculated from measurements of the Joule-Thomson coefficient and the specific heat at constant pressure, but calculations of uncertainties are very complex, in fact impossible, since most of the primary Joule-Thomson data are reported in graphical form only. Apparently there are no Joule-Thomson measurements below 1 atmosphere pressure. Short extrapolations of pv data at constant volume or constant pressue appear to introduce no greater uncertainties in calculations of T_0 than the necessary extrapolations of Joule-Thomson data in order to apply them to gas-thermometer data at pressures below 1 atmosphere.

Another method of calculation, namely, a method of successive approximations, which may be used to advantage in the special case[7] when the data are given at constant volume or density, is to use eq 9.6 or 9.7 or an equivalent equation in the form

$$\ln\frac{(pv)_t}{(pv)_{0^\circ}}=\ln\frac{T}{T_0}+(B_t-B_0)\frac{v_0}{v}+(C_t-C_0)\left(\frac{v_0}{v}\right)^2+\;.\;.\;.\;, \qquad (9.8)$$

where $v_t=v0^\circ$ and v_0 is the reference volume at 0° C and 1 atmosphere. A value for T_0 may be assumed and any error in $t^\circ\ C$, observed or reported, may be neglected for the first approximation, yielding a value for $T/T_0=1+t/T_0$. Values for $(B_t=B_0)$ and $(C_t=C_0)$ may be obtained from data on $p_t/p_0{}^\circ$ at the higher pressures by graphical or least-squares methods, and these values used to correct low-pressure constant-volume gas-thermometer measurements to obtain a better value for T/T_0; and the process may be repeated, if necessary. The calculations may be made conveniently with eq 9.8 in the form

$$y=\frac{v}{v_0}\ln\frac{p_t}{p0^\circ}\,\frac{T_0}{T}=(B_t-B_0)+(C_t-C_0)\frac{v_0}{v}+\;.\;.\;.\;, \qquad (9.9)$$

since calculated values of y usually do not vary much over a moderate range of v_0/v. Values of y may be plotted on a sufficiently open scale to determine how many terms to use or to inspect the data for evidence of anomalous trends. Such trends may be caused by systematic

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[7] In the more general case, when the values of pv/p_0v_0 at 0° C and on the isotherm, T, are not given at constant volume or density and gas-thermometer data at low pressures are lacking, the following procedure may be used for a first approximation. In addition to assuming a value for T/T_0, a value at 0° C and $v_0/v=0$ may be assumed for $pv/p_0v_0=RT_0/p_0v_0$, designated by $1+\lambda$ in International Critical Tables, vol. 3. Each individual value for pv/p_0v_0 on any isotherm, T, may then be converted to

$$\frac{pv}{p_0v_0}\cdot\frac{p_0v_0}{RT_0}\cdot\frac{T_0}{T}=\frac{pv}{RT}.$$

Equation 9.6 may then be written in the form

$$\ln\frac{pv}{RT}=B\frac{v_0}{v}+C\left(\frac{v_0}{v}\right)^2+\;.\;.\;.\;,$$

or better still in the form

$$\alpha_0\equiv\frac{v}{v_0}\ln\frac{pv}{RT}=B+C\frac{v_0}{v}+\;.\;.\;.\;.$$

Thus values for α_0 may be plotted against v_0/v and approximate values for B and C may be obtained easily. A method similar to this has been applied to data on CO_2 over a wide range of pressures and in the critical region by the Demings, *Phys. Rev.* **56**, 108 (1939).

errors in the assumed values for T_0 and $t°$ C or elsewhere[8] in the measurements of pv/p_0v_0.

In applying this method of calculation to the particular case of the eight pairs of values of pv/p_0v_0 given by Michels, Wouters, and De Boer, each pair of values are at constant volume, giving one value for $p_{100°}/p_{0°}$ used in plotting figure 3. It may be noted that by assuming $T_0=273.16\pm0.02$ and neglecting any error in the reported values for $t=0$ °C and $t=100$ °C, gives $T_{100}/T_0=1.36609\pm0.00003$ as a point on the ordinate axis of figure 3, which may be used in the calculations to replace, in effect, the low-density gas-thermometer measurements of Beattie or of other observers. The true uncertainty in this value is probably less than the true uncertainty in any of the values of $p_{100°}/p_{0°}$ at higher densities. If the curve or the equation for the curve is not restricted at low densities, such as in least-squares calculations, using eq 9.7 and the eight higher points above, small errors, especially in the lower one or two points, may be so magnified as to lead to an intersection with the ordinate axis at 1.3663, which is far outside the limits of uncertainty assumed above, and the value for the slope of the curve at low densities, essentially $B_{100}-B_0$, is likewise more uncertain than when the equation for the curve is restricted at $v_0/v=0$.

A reliable value for the ratio T/T_0 is the goal sought in most measurements with a constant-volume gas thermometer. Several different tables of corrections to be applied to measurements made at different temperatures with nitrogen or other gases with different ice-point pressures have been published. Values for such corrections are obviously a great convenience in gas-thermometer calculations, but the reliability of some of the published values may be questioned, since many of the corrections depend upon values for $B_{100}-B_0$ and B_t-B_0 calculated from data on pv/p_0v_0 at high pressures on each isotherm separately, without restriction at low pressures in some instances, with $T_0=273.09$ or $T_0=273.20$ in other instances, and with many other uncertainties involved, some of which are mentioned in other sections of this paper.

X. HELIUM

Measurements on helium at 0 °C and up to 1,000 atmospheres obtained by Wiebe, Gaddy, and Heins are quoted in table 7. These authors reported the following least-squares equation:

$$\frac{pv}{p_0v_0}=1.00059+52.17\times10^{-5}\frac{p}{p_0}-3.876\times10^{-8}\left(\frac{p}{p_0}\right)^2. \qquad (10.1)$$

This equation is an illustration of many to be found in the literature that fail to represent the reference state of the gas, which should be taken as exact for purposes of calculation. It was mentioned previously, and is emphasized again, that the measurement of the volume, v_0, of the gas at 0 °C and 1 atmosphere takes the place of a measurement of the mass of the gas, so that v_0/v is, in a sense, a density, sometimes called Amagat density. Obviously, eq 10.1 and the

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[8] The data at 0° and 100° C given by Michels, Wouters, and De Boer, when treated as outlined, show an anomalous trend which appears to be too large to be caused by the vapor pressure of mercury at 100° C or by reasonable errors in the temperatures reported or in $T_0=273.16$. The value used for the coefficient of expansion of glass may be in error, or the cause may be a peculiar combination of errors in $p_{100°}$ and $p_{0°}$ at the lower densities, such as one measured after a compression and the other one measured after an expansion of the gas. Errors in the calibration of the piston gage are evidently not involved, since the ratio $p100°/p0°$ reduces to a ratio of weights applied.

observed values of pv/p_0v_0 quoted in table 7 apply to a constant mass of gas at a constant temperature, but in the least-squares solution to obtain eq 10.1 the mass of gas was obviously not restricted to constancy.

As an illustration of the effect on the coefficients and the deviations when this restriction is imposed and the same general form of equation is assumed, the equation

$$\frac{pv}{p_0v_0}=1+(53.033\pm0.58)\times10^{-5}\left(\frac{p}{p_0}-1\right)-4.802\times10^{-8}\left(\frac{p}{p_0}-1\right)^2 \qquad (10.2)$$

was obtained from the same data by least squares, giving equal weight to each observation. It may be noted from table 7 that the deviations from this equation are systematic, which suggests that another term is desirable. In fact, when the four different α's, eq 4.1 to 4.4, are computed from the measurements quoted in table 7 and plotted, a graph is obtained which is so similar to figure 2 in all respects, except for scale, that it is not reproduced here. For helium, as for hydrogen, α_2 appears to be linear in v_0/v over a wide range within the precision of the measurements. A least-squares equation for α_2 written as

$$\ln\frac{pv}{p_0v_0}=(53.212\pm0.44)\times10^{-5}\left(\frac{v_0}{v}-1\right)+8.000\times10^{-8}\left(\frac{v_0}{v}-1\right)^2 \qquad (10.3)$$

was obtained from the same measurements, weighting each observation proportional to $[(v_0/v)-1]$. It may be noted from table 7 that eq 10.3 is somewhat better than eq 10.1 or 10.2, according to the "Gauss" criterion sometimes used to express relative "closeness of fit" of different equations with a different number of coefficients. The random deviations from eq 10.3 suggest that no improvement may be expected from the use of additional terms. A graph, similar to figure 2, suggests that more terms must be used to represent α_1, α_3, or α_4 adequately.

TABLE 7.—*Data on helium at 0° C and 1 to 1,000 atmospheres obtained by Wiebe, Gaddy, and Heins*

$\frac{p}{p_0}$ (a)	$\frac{pv}{p_0v_0}$ (a)	$\frac{pv}{p_0v_0}$ calculated from equation—			$\Delta=(\text{obs.}-\text{calc.})\ 10^5$		
		eq 10.1	10.2	10.3	eq 10.1	eq 10.2	eq 10.3
1	1.0000	1.00101	1.00000	1.00000	+101	0	0
100	1.0523	1.05237	1.05203	1.05205	−7	+27	+25
200	1.1036	1.10338	1.10363	1.10359	+22	−3	+1
400	1.2026	1.20347	1.20395	1.20352	−87	−135	−92
600	1.3003	1.29967	1.30043	1.29948	+63	−13	+82
800	1.3924	1.39315	1.39308	1.39307	−75	−68	−67
1,000	1.4838	1.48353	1.48187	1.48336	+27	+193	+44
				$\left(\frac{\Sigma\Delta^2}{n-3}\right)^{\frac{1}{2}}$ ------	±85	--------	--------
				$\left(\frac{\Sigma\Delta^2}{n-2}\right)^{\frac{1}{2}}$ ------	--------	±123	±75

[a] Quoted from *J. Am. Chem. Soc.* **53,** 1721 (1931).

Measurements on helium at 0° C and up to 100 atmospheres obtained at the Reichsanstalt are quoted in table 8 and corrected, as previously explained in the section on oxygen. The data are insufficient to give an adequate value for the rate of change of α_3 with pressure, which has been assumed from eq 10.2 in obtaining the values of α at 1 atmosphere shown in the last column. The mean values of $10^5\,\alpha$, 52.5 and 53.0, are in good agreement with the corresponding values, 53.0 and 53.2, obtained in eq 10.2 and 10.3 from the measurements of Wiebe, Gaddy, and Heins.

Burnett [12] reported the results obtained in two concordant series of measurements with helium at 0° C, using two essentially identical metal containers, each with double walls, so that the pressures within and without the inner containers could be equalized. One container was evacuated and the other was filled with specially purified helium to a pressure of about 120 atmospheres. Opening an intercommunicating valve permitted equalization of pressure in the two inner containers. The valve was closed, one container was evacuated, and the process was repeated until the pressure was reduced to about 1 atmosphere after a series of six expansions. The unique feature claimed for the method is that the volumes of the two containers need not be measured and the two containers need not be exactly equal in volume. The calculations of the results, which appear to be straightforward, are too complex to reproduce here. Burnett gives an equation obtained by a "weighted least-squares method" which appears to amount to the following, in the symbols used here

$$\frac{pv}{p_0v_0}=1+52.430\times10^{-5}\frac{p}{p_0}. \tag{10.4}$$

This result, obtained with a radically different experimental procedure, appears to be in reasonably good agreement with the measurements of the Reichsanstalt and of Wiebe, Gaddy, and Heins.

TABLE 8.—*Data on helium at 0° C and 1 to 100 atmospheres obtained at the Physikalisch-Technische Reichsanstalt*

p	v	p_0	v_0	Observed $\frac{pv}{p_0v_0}$	Correction to p_0=760	Corrected $\frac{pv}{p_0v_0}$	$\frac{10^5\left(\frac{pv}{p_0v_0}-1\right)}{\frac{p}{p_0}-1}$	$10^5\,\alpha$[a] at $p=p_0$
Holborn and Schultze[b], Ann. Physik **47,** 1089 (1915)								
*mm*Hg	*ml*	*mm*Hg	*ml*					
19,229	110.797	779.54	2698.51	1.01279	1	1.01280	52.7	52.8
19,276	110.796	781.69	2697.70	1.01278	1	1.01279	52.5	52.6
37,794	110.789	789.02	5175.17	1.02543	2	1.02545	52.2	52.4
38,328	110.790	800.95	5168.76	1.02572	3	1.02575	52.1	52.3
							Mean	52.5
Holborn and Otto, Z. Physik **10,** 367 (1922)								
55,873	106.016	681.74	8367.9	1.03833	−5	1.03828	52.8	53.1
56,304	106.016	685.91	8379.2	1.03858	−5	1.03853	52.7	53.0
72,991	106.007	675.66	10907.8	1.04988	−6	1.04982	52.4	52.9
74,497	106.007	689.95	10888.7	1.01523	−5	1.05118	52.7	53.2
							Mean	53.0

[a] Obtained from the data in the previous column and an estimated rate of change of α_3 with pressure, 4.8×10^{-8}, obtained from data of Wiebe, Gaddy, and Heins (see eq 10.2).

[b] The data on p and pv/p_0v_0 are quoted from Ann Physik **47,** 1089 (1915), the data on v, p_0 and v_0 are quoted from Z Physik **10,** 367 (1922) for the same values of p and pv/p_0v_0, which appears to establish that these details were omitted in the paper by Holborn and Schultze.

The more recent measurements on helium at 0° C and up to 12 atmospheres obtained at the Leiden Laboratory are quoted in table 9. In spite of the special efforts to avoid errors, described in Leiden Comm 227a and 227b, it is evident that the results are seriously affected by systematic errors, and are not in as good accord with more precise measurements made in other laboratories as might be expected from the description and calculations given. Keesom and Van Santen represented the measurements quoted in table 9 by a weighted least-squares equation, which in the symbols used here, is

$$\frac{pv}{p_0v_0}=1+50.28\times10^{-5}\left(\frac{v_0}{v}-1\right), \qquad (10.5)$$

and the coefficient in this equation is stated to be accepted as "definitive" in connection with the present low-temperature scale used at the Leiden Laboratory. As mentioned previously, pressures were measured with a closed-end manometer, apparently filled with hydrogen. The so-called "normal volume," represented by v_0 here, is stated to be 548.861 cm^3 at 0° C, although actually measured "for practical reasons" at 18° C and corrected to 0° C. It is stated that a glass piezometer of 40-cm^3 capacity was immersed in an ice bath. A perusal of earlier communications, to which references are made, indicates that the 40-cm^3 piezometer when in the ice bath was probably connected by means of a flexible metal capillary to the top of a vertical glass tube (called the "stem of the piezometer" and stated to be 10.74 mm in diameter) maintained at 20° C in a stirred water bath. With mercury between the "stem" and the closed-end manometer, the helium in the piezometer and "stem" and the hydrogen in the closed end of the manometer were compressed to different pressures by means of auxiliary apparatus. At 6 atmospheres, more than half of the helium must have been at 20° C instead of 0° C. The exact manner of making the necessarily large correction does not appear to be given specifically in any of the communications examined, although similar measurements were made at 20° C, apparently for use in making such corrections. Uncertainties in the volume of the gas beneath a plane tangent to the mercury meniscus in the (10.74-mm diameter) "stem" were recognized, and mention is made of X-ray shadowgraphs taken of this meniscus.

TABLE 9.—*Data* [1] *on helium at 0° C and 1 to 12 atmospheres obtained by Keesom and Van Santen*

$\frac{p}{p_0}$	$\frac{v_0}{v}$	$\frac{pv}{p_0v_0}$	$\frac{10^5\left(\frac{pv}{p_0v_0}-1\right)}{\frac{v_0}{v}-1}$	Mean $10^5\,\alpha_1$
6.01487	6.00120	1.00228	45.6	46.0
6.02039	6.00632	1.00234	46.7	
6.05938	6.04541	1.00231	45.8	
6.75635	6.73732	1.00282	49.2	49.3
6.76536	6.74596	1.00288	50.1	
6.76787	6.74906	1,00279	48.5	
7.70765	7.67917	1.00359	53.8	52.7
7.71382	7.68803	1.00335	50.1	
7.69834	7.67063	1.00361	54.1	
9.94029	8.90267	1.00423	53.5	51.5
9.95584	8.92043	1.00397	50.1	
9.98098	8.94453	1.00405	51.0	
10.63712	10.58771	1.00467	48.7	50.3
10.64405	10.59301	1.00482	50.2	
10.65493	10.60214	1.00498	51.9	
11.48274	11.42075	1.00543	52.1	51.0
11.48867	11.42802	1.00531	50.9	
11.50026	11.44048	1.00523	50.1	
12.38806	12.32015	1.00551	48.7	49.1
12.43204	12.36263	1.00561	49.4	
12.45699	12.38790	1.00558	49.1	
12.46478	12.39543	1.00559	49.0	
			Mean	50.0 ±1.7

[1] Values in the first 3 columns are quoted from Leiden Comm. 227b (1933), regrouped according to values of p/p_0.

XI. NEON

Figure 4 illustrates an anomalous trend in α_2 obtained from measurements on neon reported by Michels and Gibson [13]. These measurements are among the earlier ones obtained in the Van der Waals laboratory by the method outlined in the section on hydrogen. The authors state their estimate of accuracy to be about 2 in 10^4, and the radii of the open circles have been chosen to indicate this uncertainty.

The Reichsanstalt measurements [14] on neon, designated by small black circles in figure 4, indicate the same normal trend in α_2 found for all the other gases considered. These measurements were corrected, as indicated previously in the section on oxygen. Glass containers were used in all of the Reichsanstalt measurements on gases previously discussed, with the same pressure inside and outside the glass, and small corrections were obviously applied for compression of the glass. In the measurements on neon, two different metal containers of the same diameter and wall thickness, but of different lengths, were used; and no corrections were made for the stretch of the containers with pressures up to 100 atmospheres inside and atmospheric pressure outside the containers. The metal containers were also used with nitrogen at temperatures up to 400° C, and measurements [15] were made at 0° C and also 100° C with the same pressure inside and outside the container, and also with atmospheric pressure outside. Apparently, the observed differences in volume were considered negligible for their purposes. The observed changes in volume are consistent with the value of 4.5×10^{-6} per atmosphere for

$(1/v)\ (dv/dp)$, calculated from the dimensions given and the elastic properties of the metal.

Attention is called to the lack of concordance in the values of v calculated from the relation $v=v_{0^\circ}\ [1+at+bt^2]$ given for the volume of the metal container and the value of v actually used in the calculations [15] for the different gases at temperatures above 0° C. The metal container, constructed by welding ends on a cylindrical tube, was apparently not annealed before the initial calibration was made by filling with toluene at 18° C. After the container was used in measurements with several different gases at several different temperatures up to 400° C, a subsequent calibration [14] with mercury disclosed that the container had shrunk more than 2 in 10^3. A change in volume of this order of magnitude would make a considerable change in all the α's at 1 atmosphere or the "B-values" calculated from the measurements at various temperatures with He, A, N_2, H_2, and a mixture of Ne and He. It seems probable that most of the shrinkage took place during the measurements at the higher temperatures with one of these gases, but the order of the measurements with the different gases is not definitely stated. There is a strong implication that measurements with nitrogen were made first, although the anomalous results, mentioned but not recorded, with hydrogen at 300° C are in the right direction to be caused by such shrinkage; but this may also be explained satisfactorily on metallurgical grounds. The seriousness of this unfortunate situation is that these are the only available measurements on some of the gases at temperatures up to 400° C, and it shakes the very foundations for several equations of state and many other conclusions based upon these measurements.

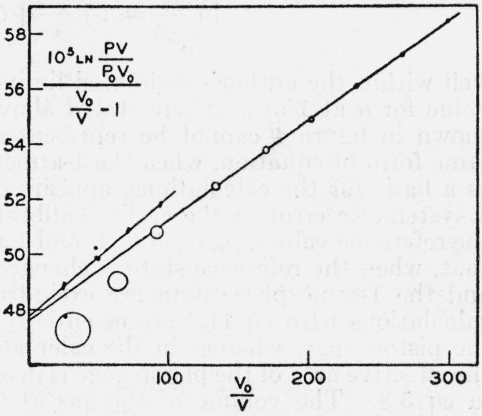

FIGURE 4.—*Data on neon at 0° C*

Reichsanstalt data, small closed circles; data of Michels and Gibson, open circles, with radii equivalent to uncertainty of 2 in 10^4 in pv/p_0v_0.

Uncertainties in the volume of the container at high temperatures in the measurements with neon [14] seem to be smaller than for the other gases, since rather convincing evidence is given that the container was adequately annealed by this time after numerous excursions to 400° C. Fortunately, the order is given in which the experiments on any one gas were made, and a good check with neon at 0° C is obtained before and after heating the container to 400° C. No corresponding check is supplied for the other gases. Using values of pv/p_0v_0 for nitrogen at 0° C up to 100 atmospheres, which were determined in glass containers and appear to be reliable to a few parts in 10^5, together with measurements on nitrogen at 0° C obtained with metal containers, leads to values for the volumes of the metal containers which are about 2 in 10^4 larger than the values obtained in calibrations with mercury. This result appears to be in harmony with the results found by Kaminsky and Blaisdell [16], who demonstrated that mercury does not fill the small crevices in metal surfaces which are filled by gases. When allowance is made for slightly greater volumes of the metal containers and also for their stretch, the value of α at 0° C and 1 atmosphere obtained from the Reichsanstalt measurements on neon, indicated in figure 4, is about $49 \pm 1 \times 10^{-5}$.

A similar value with about the same uncertainty may be obtained from the measurements of Michels and Gibson by eliminating the reference state, p_0v_0, at 0° C and 1 atmosphere and choosing one of the other states at higher pressures as a reference. When this is done, all the points indicated by the open circles in figure 4 are found to be represented by an equation of the form

$$\ln \frac{pv}{p_0v_0} = A + \frac{Bv_0}{v} + C\left(\frac{v_0}{v}\right)^2, \tag{11.1}$$

well within the author's estimated limits of 2 in 10^4 and leads to the value for α at 1 atmosphere stated above. The fact that the points shown in figure 4 cannot be represented within these limits by the same form of equation, when the 1-atmosphere reference state is used as a basis for the calculations, appears to be very strong evidence of a systematic error in the earlier calibration of the piston gage or in the reference values, p_0, v_0, at 0° C and 1 atmosphere. It may be noted that, when the reference state is changed to a state at high pressures and the 1-atmosphere data are excluded, all the ratios used in the calculations with eq 11.1 are essentially ratios of weights applied to the piston gage, whereas in the calculations of α_2 shown in figure 4, the effective area of the piston gage is involved, as previously indicated in eq 5.8. The volume of the gas at 0° C and 1 atmosphere was apparently not measured directly but was calculated from a measurement at about 25° C and 1 atmosphere and corrected to 0° C in a manner described in several later papers from the same laboratory.

XII. REICHSANSTALT MEASUREMENTS BELOW 2 ATMOSPHERES

The latest measurements, obtained at the Reichsanstalt by Heuse and Otto [17] at 0° C and at pressures below 2 atmospheres, yield the following values for $10^5\alpha$:

p_0[9] (mm Hg)	He	H_2	N_2
533.10	59	72	−25
727.17	38	46	−62
994.50	58	63	−55
$10^5\ \alpha$ from previous sections for comparison	53.0	61.9	−45.3

These measurements were made after many years of experience in such measurements, and after improvements in apparatus and technique had been developed. It is the purpose of this section to

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[9] Throughout this section, p_0 is used to designate a reference state, sometimes called the ice-point pressure in a gas thermometer, in order to conform to common practice in gas thermometry. It should not be confused with the 1-atmosphere reference pressure used in other sections.

investigate why these measurements yield such a wide scatter in α. There are reasons for expecting that the primary measurements of p and v at 0° C with the apparatus and method employed should have been capable of yielding a precision of the order of a few units in 10^6, which is comparable to about 1 percent in α, according to the analysis given in the section on uncertainties, when $[(p/p_0)-1]$ is about 0.3, as it is in all these measurements. The scatter, however, is many times this amount and appears to be systematic with the different gases at certain values of p_0.

The measurements were made at the same time and are reported in the same publication containing the latest determinations of pressure and volume coefficients of expansion of these gases in a gas thermometer over the fundamental interval, 0° to 100° C, which yield determinations of the thermodynamic temperature of the ice point, T_0. With each separate filling of the gas thermometer, measurements were made with a constant mass of gas in four different states, indicated in figure 5, where the point 0 is taken as the reference state for the group. Measurements at the states 1 and 0 yield a value for α or the slope of the 0° C isotherm. Similarly, measurements at the states 2 and 3 yield a value for the slope of the 100° C isotherm. Calculated values for the slope of the 100° C isotherm, for thermometer fillings to different p_0's, expressed in terms of $(10^5/v_0)(dpv/dp)$ are:

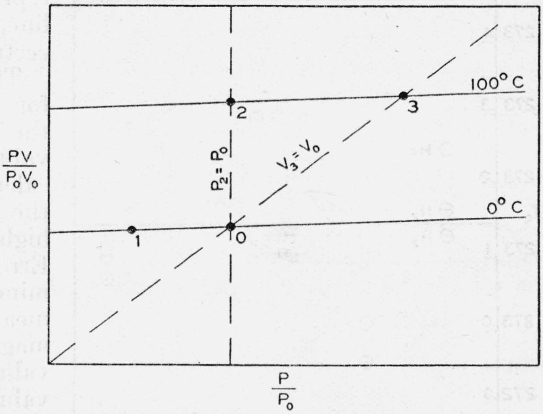

FIGURE 5.—*Diagram of a group of Reichsanstalt measurements with one filling of their gas thermometer.*

Measurements at states 0 and 2 were made at constant pressure and states 0 and 3 were measured at constant volume.

p_0 (mm Hg)	He	H$_2$	N$_2$
390.24	74	69	48
533.10	31	35	12
727.17	68	77	28
994.50	52	66	12
Mean	56	62	25

The scatter is greater than for the 0° C isotherm and departures from the mean appear to be systematic for all the gases at certain values of p_0.

In the Reichsanstalt calculations of T_0, the two isotherms were assumed to be straight lines, but the values used for the slopes were obtained from pv measurements up to 100 atmospheres. The assumption of straight lines and the measurements at the four states, indicated in figure 5, are obviously sufficient to determine intersections of the two isotherms with the ordinate axis, which supply a value for

$$\frac{(pv)_{100}}{(pv)_0}=\frac{T_{100}}{T_0} \text{ and a value for } T_0=\frac{100}{\dfrac{T_{100}}{T_0}-1}.$$

When T_0 is calculated from the measurements in this very direct manner, the results turn out as shown in table 10 and also in figure 6, which again supplies unmistakable evidence of systematic departures from the mean value, represented by the horizontal line, for all the gases at certain values of p_0.

The scatter of the values for T_0 is much greater than the scatter of the published values for T_0 obtained from calculations using values for the slopes determined from high-pressure measurements. Errors in the slopes determined by the low-pressure measurements are evidently magnified in the calculated values for T_0, since the same values for states 0, 2, and 3 in figure 6 are used in both methods of calculation. One method gets a value for T_0 from points 0 and 2, and another value from points 0 and 3, with "accepted" slopes, whereas the method used above requires all four points to get one value for T_0.

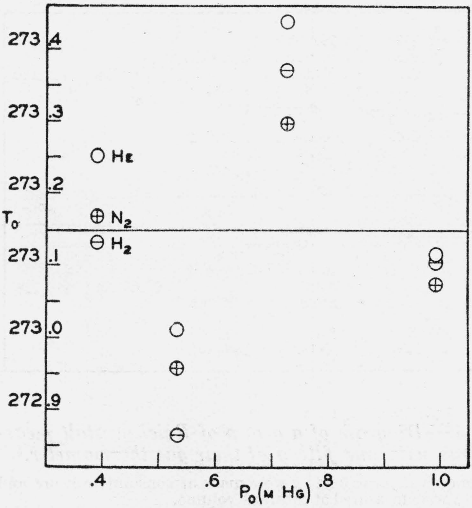

FIGURE 6.—*Values for the temperature of the ice point, T_0, on the thermodynamic scale calculated from the Reichsanstalt measurements on helium, hydrogen, and nitrogen quoted in table 10.*

Arguments might be advanced that the direct method of calculation used in table 10 is the proper one to use, that the low-pressure measurements are sufficient in themselves, should stand on their own feet, and high-pressure *pv* data should be ignored, as is done under similar circumstances when measurements of p and ρ are made for purposes of atomic-weight determinations [1]. Magnification of errors, especially systematic errors in the slopes determined over a short interval, however, appears to make the other method of calculation, using slopes determined over a wide interval, the more reliable one to use. On the other hand, it may be argued that the measurements at state 1 are ignored and given no weight in the Reichsanstalt calculations of T_0, while equal weight is given to measurements at all four states in the calculations in table 10.

TABLE 10.—*Calculations to T_0 from Reichsanstalt measurements*

Date 1929	State (see fig. 5)	t	p [a]	v [a]	pv	$\frac{pv}{p_0v_0}$	$\frac{(pv)_{p=0}}{p_0v_0}$	$\frac{T_{100}}{T_0}$	T_0
HELIUM									
		° C	m Hg	cm³	m Hg-cm³				
4/15	0	0	0.39024	----------	----------	1.000000	[b] 0.999727		
4/15	3	100	.53310	----------	----------	[a] 1.36611		1.365961	273.253
4/15	2	100	.39024	----------	----------	[a] 1.36597	1.365588		
4/13	1	0	.39024	425.624	166.0955	0.999889			
4/13	0	0	.53310	311.600	166.1140	1.000000	0.999586		
4/13	3	100	.72717	----------	----------	[a] 1.36602		1.366286	273.011
4/13	2	100	.53310	----------	----------	[a] 1.36594	1.365720		
4/12	1	0	.53310	428.199	228.2729	0.999903			
4/12	0	0	.72717	313.950	228.2950	1.000000	0.999636		
4/12	3	100	.99450	----------	----------	[a] 1.36611		1.365714	273.438
4/12	2	100	.72717	----------	----------	[a] 1.36587	1.365217		
4/10	1	0	.72717	426.301	309.9933	0.999797			
4/11	0	0	.99450	311.771	310.0563	1.000000	0.999245		
4/11	3	100	1.36280	----------	----------	[a] 1.36604		1.366146	273.115
4/11	2	100	0.99450	----------	----------	[a] 1.36579	1.365115		
HYDROGEN									
6/4	0	0	0.39024	----------	----------	1.000000	[b] 0.999680		
6/4	3	100	.53310	----------	----------	[a] 1.36617		1.366122	273.133
6/4	2	100	.39024	----------	----------	[a] 1.36604	1.365685		
6/3	1	0	.39024	425.383	166.0015	0.999865			
6/3	0	0	.53310	311.431	166.0239	1.000000	0.999496		
6/3	3	100	.72717	----------	----------	[a] 1.36613		1.366482	272.865
6/3	2	100	.53310	----------	----------	[a] 1.36604	1.365793		
6/1	1	0	.53310	426.572	227.4055	0.999881			
6/1	0	0	.72717	312.764	227.4326	1.000000	0.999554		
6/1	3	100	.99450	----------	----------	[a] 1.36620		1.365805	273.370
6/1	2	100	.72717	----------	----------	[a] 1.36593	1.365196		
5/30	1	0	.72717	426.938	310.4565	0.999777			
5/30	0	0	.99450	312.243	310.5257	1.000000	0.999171		
5/31	3	100	1.36280	----------	----------	[a] 1.36621		1.366159	273.105
5/31	2	100	0.99450	----------	----------	[a] 1.36589	1.365026		
NITROGEN									
4/4	0	0	0.39024	----------	----------	1.000000	[b] 1.000234		
4/4	3	100	.53310	----------	----------	[a] 1.36673		1.366074	273.169
4/4	2	100	.39024	----------	----------	[a] 1.36664	1.366394		
4/9	1	0	.39024	427.567	166.8537	1.000047			
4/9	0	0	.53310	312.973	166.8459	1.000000	1.000175		
4/9	3	100	.72717	----------	----------	[a] 1.36671		1.366356	272.959
4/9	2	100	.53310	----------	----------	[a] 1.36668	1.366595		
4/6	1	0	.53310	427.205	227.7430	1.000159			
4/5	0	0	.72717	313.141	227.7067	1.000000	1.000596		
4/5	3	100	.99450	----------	----------	[a] 1.36709		1.365904	273.296
4/5	2	100	.72717	----------	----------	[a] 1.36699	1.366718		
4/6	1	0	.72717	428.357	311.4884	1.000192			
4/8	0	0	.99450	313.151	311.4287	1.000000	1.000714		
4/8	3	100	1.36280	----------	----------	[a] 1.36740		1.366203	273.073
4/8	2	100	0.99450	----------	----------	[a] 1.36734	1.367178		

[a] Quoted values, all others are calculated values.

[b] Since measurements at state 1 were lacking, a value for the slope of the 0° isotherm was assumed in order to get at value for T_0 from this group.

A third method of calculation appears to have several advantages in this particular case, since it retains certain desirable features of each of the other methods and removes many of the systematic effects already mentioned by ignoring certain calibration measurements which are not described in detail, and uses instead measurements at state 1, thereby giving them considerable weight. In this method, the apparently more reliable values for the slopes supplied by high-pressure data are employed, as is done in the Reichsanstalt method, but are inserted into the calculations at an earlier stage in combination with measurements at states 1 and 0, figure 5. If such measurements yield an erroneous value for the slope at 0° C, and if the errors are random or accidental, the chances are even that the measurements at state 0 may be in error and hence may lead to two erroneous values [10] for T_0 in the Reichsanstalt method of calculation, which in effect gives this point double weight, because it is used in calculating a constant-volume and also a constant-pressure coefficient of expansion, and with accepted slopes, two separate values for T_0. On the other hand, if the measurements at states 1 and 0 appear to be systematically in error, it is obviously desirable to make the calculations so as to eliminate the effect of the systematic errors.

The unique feature of the latest Reichsanstalt measurements, which is supposed to make them more reliable than similar earlier measurements leading to $T_0=273.20$, was the use of a specially constructed mercury manometer, which was surrounded by ice. Several platinum wires were sealed into the glass walls at certain chosen heights and bent downward at the axis of a long vertical glass tube to serve as "prick points" at the center. Thus all of the pressure measurements were made with definite fixed heights of mercury columns, as indicated in table 10. The exact manner in which these heights were measured, once and for all, is not clearly described. It is mentioned, however, that the distances between prick points were measured at room temperature, although as used the manometer was at 0° C. It is mentioned further that only pressure ratios are important and that the above circumstance should introduce no appreciable error in the ratios of heights, which would appear to be true if there were no vertical temperature gradients during the measurements at room temperatures, if the sealing-in processes at several points had no effect, and if the coefficient of linear expansion of the glass was the same throughout. No information is supplied relative to possible refraction errors in sighting through possibly nonuniform glass walls to the prick points or onto the mercury surface brought into "optical contact" with the prick points in the calibration of the manometer. All of these and other uncertainties in the calibration of the manometer, which appear to be the source of the systematic effects previously mentioned, may be eliminated as outlined below.

Although Heuse and Otto apparently did not realize it, they had at their disposal in reality, almost every day they took observations extending over a period of several months, an independent and reasonably reliable partial calibration of their manometer with each filling of their gas thermometer. Instead of inserting accepted values for slopes into the calculations near the end as they did, everything

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[10] A possible illustration of this is in the case of N_2 at $p_0=390$ mm (see Heuse and Otto's table 7), where the reported values give for T_{100}/T_0, 1.36616 (constant pressure) and 1.36619 (constant volume), while the mean value for the 3 gases is 1.36609.

would have come out better if they had inserted the accepted slopes at 0° C into the manometer calibration at the beginning. Instead of using the measured heights in the calibration of the manometer to calculate 0° C slopes, which scatter widely and were not used in the calculations later on, the same calculations may be reversed, since measurements at states 1 and 0, together with accepted slopes for the different gases, lead directly to several calibrations of the manometer. Although such calibrations yield only pressure ratios, these are the important quantities anyway.

Equation 4.3, together with the assumption of constant slope over the small interval covered by these measurements, gives

$$\alpha=\frac{1}{v_0}\left(\frac{dpv}{dp}\right)_t=\frac{1}{v_0}\left(\frac{p_bv_b-p_av_a}{p_b-p_a}\right)_t, \tag{12.1}$$

where the subscripts refer to any two equilibrium states, a and b, of a given mass of gas at 0° C, and v_0 is the volume of the same mass of gas at 0° C and 1 atmosphere, which takes the place of a mass determination. All the values of α at 1 atmosphere, obtained in previous sections, are on this same basis and hence may be used to advantage in eq 12.1 or any transformation of it. This is emphasized because the later calculations are made to serve a double purpose, one of which is to obtain a test of the reliability of the values of α for the different gases.

In order to get eq 12.1 into a convenient form for the calculations at hand, the following steps are written out

$$p_bv_b-p_av_a=\alpha v_0(p_b-p_a)$$

$$p_b(v_b-\alpha v_0)=p_a(v_a-\alpha v_0)$$

$$\frac{p_b}{p_a}=\frac{v_a-\alpha v_0}{v_b-\alpha v_0}$$

$$\frac{p_b}{p_a}=1+\frac{v_a-v_b}{v_b-\alpha v_0}, \tag{12.2}$$

In the Reichsanstalt measurements, the quantity (v_a-v_b) was directly measured by weighing displaced mercury, which is one of the simplest and most accurate of laboratory measurements. The quantity v_b was obtained from similar measurements of the volume of the gas-thermometer bulb and the connecting glass tubing up to the lower mercury surface in the manometer. Using the measured volumes quoted in table 10, and values for v_0 to four figures, easily obtainable from the column headed pv, and the values of α previously obtained, the following results are given in detail as an illustration.

Date	Gas	$10^5\,\alpha$	αv_0	v_b	$v_b-\alpha v_0$	v_a-v_b	$\frac{p_b}{p_a}$
4/12	He	53.0	0.1592	313.950	313.7908	114.249	1.364093
6/1	H_2	61.9	.1852	312.764	312.5788	113.808	1.364094
4/5	N_2	−45.3	−.1357	313.141	313.2767	114.064	1.364100
Mean							1.364096

These results supply the best direct experimental evidence available that the values for the slopes of the 0° C isotherms below 2 atmospheres for these three gases are mutually consistent within reasonable uncertainties in these measurements. The maximum deviation from the mean ratio p_b/p_a is about 3 in 10^6, which appears to confirm the earlier statement that a precision of this order of magnitude should have been attainable in these measurements. To attain such a precision, of course, means that the two mercury surfaces in the manometer must be set in "optical contact" with the prick points with a precision of about 0.002 mm,[11] in the foregoing instances, since the recorded pressures quoted in table 10 are 533.10 and 727.17 mm Hg. But the ratio of these numbers obtained from measurements of heights in the initial calibration of the manometer is $p_b/p_a = 1.364041$. This value is different from the above mean by 40 in 10^6, which corresponds to a systematic error of about 30 percent in all the α's, 0.017 cm^3 in $v_a - v_b$, (0.23 g Hg) or 0.047 cm^3 in v_b (0.64 g Hg), all of which appear to be unreasonably large. It seems more likely that the height measurements in the initial calibration are responsible for the difference.

When the same calculations are carried out, using all the reported volume measurements, including oxygen ($10^5\ \alpha = -95.1$) and neon ($10^5\ \alpha = 49.0$), the results indicate a lower precision in several instances, as shown below.

Calibration based on measurements of heights

p_b	533.10	727.17	994.50	1362.80
p_a	390.24	533.10	727.17	994.50
p_b/p_a	1.366082	1.364041	1.367631	1.370035

Calibrations based on isothermal slopes and measurements of volume, reported in Heuse and Otto's table 2

He	1.366067	1.364093	1.367608	--------
H_2	1.366056	1.364094	1.367624	--------
N_2	1.366031	1.364100	1.367675	--------
O_2	1.366076	1.364081	1.367651	--------
Ne[a]	--------	--------	1.367650 [12]	--------
Mean	1.366057	1.364092	1.367642	--------

Calibration based on isothermal slope and measurements of volume, dated 2/6/1929 and reported in Heuse and Otto's table 1

He	1.366000	1.363969	1.367720	1.370275

There appears to be no convincing evidence in these results that the value used for α for any one gas is inconsistent with the values for the other gases. The scatter for the different gases at the third pressure ratio is about twice as large as at the other two ratios. One possible reason for this may be that a much longer piece of capillary tubing containing mercury at room temperature was used in the measurements of $v_a - v_b$ when the pressure exceeded 1 atmosphere. Furthermore, it may be noted from table 10 that the two states for He giving the lowest value (1.367608) were measured 1 day apart, and the two states for N_2 giving the highest value (1.367675) were measured 2 days apart, whereas the two states were measured on the same day for all the other gases at the corresponding ratio.

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[11] The author has had some experience which indicates that prick point settings on a mercury surface can be made to this precision without much difficulty.

[12] Calculated from volume measurements reported in Ann. Physik **6**, [4] 778 (1930).

In the calibration calculated from the measurements, dated February 6, 1929, the conditions were different. These measurements were obtained before the gas-thermometer bulb (v=297.134 cm^3) was sealed onto the capillary tubing. All these measurements were made with one He filling (v_0=70.38 cm^3) and the mercury displacements were smaller (14.528 to 36.709 cm^3). Heuse and Otto do not give the diameter of the manometer tubing, but state that a change of 0.1 mm in the height of the mercury meniscus corresponds to a change of 0.005 cm^3 in the volume of the gas beneath a fixed plane tangent to the mercury meniscus. All the differences from the means given above correspond to differences in the meniscus height in the two states of less than 0.2 mm, including the February 6, 1929, calibration. It seems likely that much of the scatter may be appropriately charged to differences in meniscus height rather than to corresponding errors up to 0.010 cm^3 (0.14 g Hg) in the volume measurements.

When the mean values for the pressure ratios determined with several gases are used in later calculations, most of the systematic effects previously mentioned are removed, the scatter is markedly reduced, and there is general improvement all along the line. For example, the constant-volume coefficients for N_2 are brought into much better agreement with the measurements reported by Beattie [11]. While the constant-volume coefficients, β_v, are changed, the constant-pressure coefficients, β_p, are unchanged. The improvement in the differences, $\beta_p-\beta_v$, which are related to the 100° C isotherm slopes, is illustrated below.

	As reported (height calibration)			Gas volume calibration	
p_0	$10^7\beta_p$	$10^7\beta_v$	$10^7(\beta_p-\beta_v)$	$10^7\beta_v$	$10^7(\beta_p-\beta_v)$
			HELIUM		
mm Hg					
390	36, 597	36, 611	14	36, 608	11
533	36, 594	36, 602	8	36, 607	13
727	36, 587	36, 611	24	36, 612	25
994	36, 579	36, 604	25	36, 604	25
			HYDROGEN		
390	36, 604	36, 617	13	36, 614	10
533	36, 604	36, 613	9	36, 618	14
727	36, 593	36, 620	27	36, 621	28
994	36, 589	36, 621	32	36, 621	32
			NITROGEN		
390	36, 664	36, 673	9	36, 670	6
533	36, 668	36, 671	3	36, 676	8
727	36, 699	36, 709	10	36, 710	11
994	36, 734	36, 740	6	36, 740	6

Calculations of a mean value for T_0 and an uncertainty in T_0 from these Reichsanstalt measurements on the basis of a different manometer calibration have not been carried out for several reasons. It requires a recalculation of all of the foregoing values to one more place. Uncertainties in the values of the difference between the 0 and 100 °C isotherm slopes are involved, as are questions of weighting. It appears, however, that the major change is a smoothing of the data and a reduction in the calculated uncertainty without much change in the mean value for T_0. On the basis of these 1929 measurements, Heuse and Otto reported a mean value of $10^8\beta=366{,}086$, which corresponds to $T_0=273.160$. Combining these with previous measurements, they reported a weighted mean of $10^8\beta=366{,}076$, which corresponds to $T_0=273.167$.

XIII. MEASUREMENTS BY BAXTER AND STARKWEATHER

It is the purpose of this section: (1) to demonstrate that the measurements of Baxter and Starkweather obtained at 0° C and 1 atmosphere or less are in substantial agreement, or at least do not seriously conflict, with the values of α already obtained from high-pressure measurements within the calculated uncertainties of the two sets of measurements; and (2) to illustrate that the calculated uncertainties in values for atomic weights and RT_0, based entirely on measurements at 0° C and 1 atmosphere or less, are larger than the calculated uncertainties based on both sets of measurements.

In the previous sections, the calculated uncertainties in α at 1 atmosphere were about 1 percent or less. It was pointed out in section V that 1 percent in α was comparable to about 5 in 10^6 in pv/p_0v_0 for these gases over a range of ½ atmosphere. As shown in table 11, the measurements of Baxter and Starkweather, which appear to be among the most precise measurements of this kind available, the calculated uncertainties in pv/p_0v_0 exceed the amount stated above and the calculated uncertainties in the α's range from 7 to 30 percent. In every case, however, the values of α obtained from high-pressure measurements are well within the calculated limits of uncertainty in the low-pressure measurements, as shown below.

$10^5\,\alpha$ from measurements at—			Differences in mean values (%)
Gas	High pressures	Low pressures	
O_2	−95.1±0.9	−93±7	−2
N_2	−45.3±0.3	−41±9	−12
Ne	49 ±1	59±16	−20
A	−94 ±1	−89±12	−5

The measurements of Baxter and Starkweather were apparently made by weighing all of these gases in glass "globes" of about 2-liter capacity, using the same manometer and technique throughout all these measurements. The constant sign of the differences between the mean values of α suggests the possibility of a systematic error in the measurements of density or pressure or both. According to the analysis given in section V, 2 percent in α for O_2 corresponds to about 0.004 mm Hg in p, or about 0.02 mg in the weighings of 2-liter globes. That the difference is this small is high tribute to the care and skill of the observers.

TABLE 11.—*Measurements of the density of gases at 0°C obtained by Baxter and Starkweather*

$\frac{p}{p_0}$	Pressure	Density	Uncertainty $\frac{10^6u}{\rho}$	No. obs.	$\frac{pv}{p_0v_0}$	$\frac{10^5\left(\frac{pv}{p_0v_0}\right)-1}{\frac{p}{p_0}-1}$ $10^5\alpha_2$	Uncertainty
			OXYGEN (PROC. NTL. ACAD. SCI. **12,** 703 (1926))				
	mm Hg[a]	g/liter					%
1	760	1.428962±10[b]	7	6	1.000000±00	------------	90
3/4	570	1.071485±29	27	20	1.000220±28	−88.0	13
1/2	380	0.714154±24	34	12	1.000458±35	−91.6	8
1/4	190	.356985±17	48	10	1.000716±48	−95.5	7
					Weighted[c] mean..	−93±7	
			NITROGEN (PROC. NTL. ACAD. SCI. **12,** 703 (1926))				
1	760	1.250361±29	23	18	1.000000±00	------------	----
2/3	506.667	0.833482±16	19	18	1.000110±30	−33.0	27
1/3	253.333	.416662±16	38	14	1.000290±44	−43.5	15
					Weighted[c] mean..	−41±9	
			NEON (PROC. NTL. ACAD. SCI. **14,** 57 (1928))				
1	760	0.899902±20	22	17	1.000000±00	------------	----
2/3	506.667	.600044±30	50	11	0.999818±55	54.6	30
1/3	253.333	.300090±26	87	12	0.999591±90	61.5	22
					Weighted[c] mean..	59±16	
			ARGON (PROC. NTL. ACAD. SCI. **14,** 57 (1928))				
1	760	1.783640±44	25	15	1.000000±00	------------	----
2/3	506.667	1.188739±45	38	7	1.000299±45	−89.7	15
1/3	253.333	0.594193±30	51	6	1.000594±72	−89.1	12
					Weighted[c] mean..	−89±12	

[a] At 0° C and g=980.616.

[b] In stating these uncertainties the decimal point has been disregarded for convenience. Thus 1.428962±10 is to be interpreted as 1.428962±0.000010.

[c] Weighting each α_2 inversely as the square of its uncertainty.

In figure 7, uncertainties in the measurements are indicated by arrows. If arrows indicating uncertainties in the values of α for O_2 and A had been shown in figure 1, the apparent inconsistency between low- and high-pressure measurements would be more readily understandable. It is evident from table 11, and also figure 7, that the uncertainties increase at the lower pressures and become magnified at $p=0$, where the highest accuracy is most desirable. The unbroken lines in figure 7 represent least-squares equations based entirely on the measurements of Baxter and Starkweather, "weighted according to their probable errors," as stated in the 34th annual report [18] of the committee on atomic weights. The broken lines represent the 0° C isothermal slopes or α's obtained in previous sections.[13]

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[13] The data on argon fall so close to the oxygen line in figure 7 that they were omitted to avoid confusion.

Mean values for ρ_0 and values for RT_0 and M may be calculated from the measurements quoted in table 11, as has been done by Baxter and Starkweather [18]. Similarly, values for ρ_0, RT_0 and M may be calculated by using the values of α previously obtained. The differences in the calculated uncertainties in the two cases may be of interest.

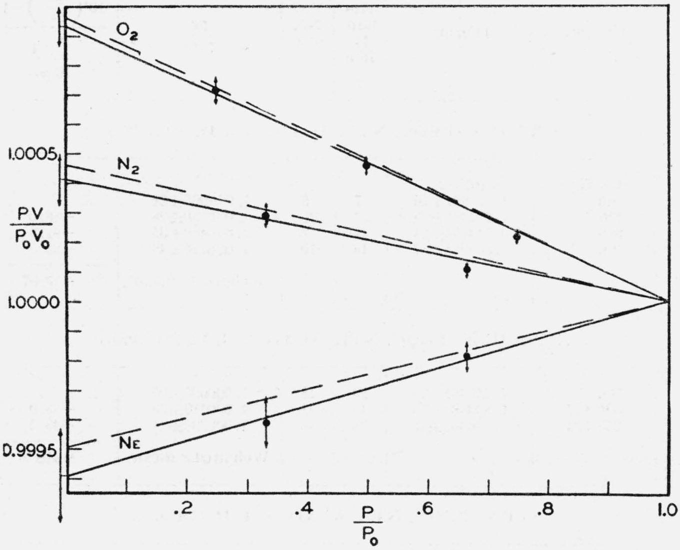

FIGURE 7.—*Data at 0° C by Baxter and Starkweather.*

Arrows indicate calculated uncertainties. Unbroken lines based on low-pressure measurements. Broken lines represent slopes calculated from high-pressure measurements.

Equations 3.3 and 4.3 combined with $p=0$, yield

$$pv=p_0v_0(1-\alpha)=\frac{RT_0}{M}, \tag{13.1}$$

which may be written, for these calculations, in the equivalent forms

$$RT_0=\frac{Mp_0(1-\alpha)}{\rho_0} \tag{13.2}$$

$$M=\frac{\rho_0RT_0}{p_0(1-\alpha)}. \tag{13.3}$$

Based entirely on the measurements of Baxter and Starkweather, the results turn out as follows:

$$RT_0=\frac{32(1.00093\pm7)}{1.428965\pm10}=22.4147\pm16$$

$$M(\mathrm{N_2})=\frac{(1.25037\pm2)(22.4147\pm16)}{1.00041\pm9}=28.0152\pm32$$

$$M(\mathrm{Ne})=\frac{(0.89990\pm2)(22.4147\pm16)}{0.99941\pm16}=20.1829\pm36$$

$$M(\mathrm{A})=\frac{(1.78364\pm4)(22.4147\pm16)}{1.00089\pm12}=39.9442\pm56$$

When the α's obtained from high-pressure measurements are used, the calculated uncertainties are reduced, as follows:

$$RT_0=\frac{32(1.000951\pm 9)}{1.428965\pm 10}=22.4151\pm 3$$

$$M(\mathrm{N_2})=\frac{(1.25039\pm 2)(22.4151\pm 3)}{1.000453\pm 3}=28.0149\pm 6$$

$$M(\mathrm{N}e)=\frac{(0.89990\pm 2)(22.4151\pm 3)}{0.99951\pm 1}=20.1812\pm 6$$

$$M(\mathrm{A})=\frac{(1.78364\pm 4)(22.4151\pm 3)}{1.00094\pm 1}=39.9430\pm 11$$

For comparison, the 1940 international atomic weights give 28.016 for N_2, 20.183 for Ne and 39.944 for A, the last two values apparently being based entirely on the measurements quoted in table 11. When consideration is given to the results of other observers and different values are used for ρ_0 and the estimated uncertainty in ρ_0, the results are slightly different,[14] of course, but the major uncertainty in all published atomic weight calculations of this kind is in the value of α determined by low-pressure measurements alone.

It should be noted from table 11 that the pressure unit is 760 mm Hg at 0° C and $g=980.616$. Expressing the above results for RT_0 in different units gives

22.4151 liter mole^{-1} atm ($g=980.616$)
22.4140 liter mole^{-1} atm ($g=980.665$)
22414.6 cm^3 mole^{-1} atm ($g=980.665$)
2271.16 joules mole^{-1}

XIV. CONCLUSION

As a result of many careful and painstaking investigations in recent years, the slopes of the *pv* isotherms at 0° C below 2 atmospheres for He, Ne, A, H_2, N_2, and O_2 appear to be known to about 1 percent, which is comparable to a few parts in a million in relative measurements of pressure and volume at this temperature and in this pressure range. Reliable values for the isothermal slopes are of importance in atomic-weight determinations, in gas thermometry, in certain theoretical calculations, in gas analyses (for example, in converting from volume percent to mole percent), and in many other applications where it is desired to avoid the approximations involved in the ideal gas laws.

Some of the summaries relative to these slopes, such as those given in International Critical Tables, in the Handbuch der Experimental Physik, and in the most recent summary by Keesom and Tuyn [10] give the impression that these slopes are very uncertain because of the wide scatter in the published values obtained by different observers. It is hoped that the foregoing discussion of the subject may supply the key to some of the reasons for such a wide spread in the published values.

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[14] Birge [2] used the same value of ρ_0 for O_2. He used "least-squares probable error" apparently in his ± terms. Putting these on the basis used here (see section V), his "adopted values" for ρ_0 and α lead to

$$RT_0=\frac{32\ (1.000927\pm 90)}{1.428965\pm 90}=22.4146\pm 24 \text{ liter mole}^{-1}\text{ atm } (g=980.616.)$$

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