of the beaker and remaining on the filter paper with warm dil. nitric acid. After being made alkaline with ammonium hydroxide, the solution is evaporated to dryness and ignited to constant weight.

4. The method developed yields results deviating from the calculated values by from —0.03 to +0.04%, depending upon the amount being estimated, whereas a deviation of from —1.39 to —1.55% was obtained, using the method commonly employed.

PHILADELPHIA, PENNSYLVANIA

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THE ADEQUACY OF THE ASSUMPTION OF MOLECULAR AGGREGATION IN ACCOUNTING FOR CERTAIN OF THE PHYSICAL PROPERTIES OF GASEOUS NITROGEN

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Introduction

At the present time direct proof of molecular aggregation is not generally possible. Indeed, there exist no tests for conceived varieties of molecular species, particularly in the gaseous phase, when only small numbers of the polymerized molecules exist. It is of course well known that nitrogen dioxide polymerizes or associates chemically to a double species, N_2O_4, but in this instance a change in color attends the shift in species; moreover, the numbers of the doubled molecules are so considerable at a pressure of one atmosphere and less, that the departure from the perfect gas laws of either species is not sufficient to prevent detection of the polymerization by means of density measurements.

Acetic acid furnishes an example of a gas or vapor which presents no change in color on shift of species to double molecules, and here again the large changes in density at low pressures are satisfactorily explained on the assumption that a doubling of species exists. It is quite possible, perhaps even certain, that acetic acid vapor and other associating gases would show a change in the absorption spectrum in regions other than the visible, but investigations to determine this important fact are lacking as far as known.

The detection, in gases under considerable pressure, of small amounts of associated or aggregated molecules either double or of higher order, presents a problem of great difficulty when the attempt is made to detect the polymerized species by means of an examination of the pressure-volume-temperature data. Obviously even at atmospheric pressure, if the fraction of double molecules is small enough, the presence of the latter may be masked because of the normal departure of the simpler species from the perfect gas laws. Thus, Lewis[1] finds the assumption of association sufficient to explain the departure of the magnetic susceptibility of oxygen from Curie's law and assigns 0.0003 as the polymerized fraction at 0° and 1 atmosphere. The departure of oxygen from the perfect gas laws, however, is of the order of magnitude of 0.1% at N. T. P., so that the one double molecule in about 7000 calculated by Lewis would produce a change in density which the best gas-density determinations that have ever been made would scarcely detect.

In the case of gases under pressure, it is clear that the problem of estimating the amount of higher-order species of molecules through the pressure-volume-temperature data is beset with peculiar difficulties. To estimate accurately the degree of aggregation, there are lacking, first, certain knowledge of the equation of state of a single and invariable molecular species; second, the equation of state of a mixture of two or more different species; third, the general thermodynamic equations connecting the numbers of the different molecular species with the temperature and pressure at any pressure in the gaseous phase. For the latter, the only complete treatment developed is for perfect gases.

Investigations have been in progress for a number of years in this Laboratory dealing with these problems. Indeed, it is now believed that the assumption is warranted that for an *invariable molecular species* at not too small volumes, the equation of state[2] is

$$p = \frac{RT}{v - \beta e^{-\alpha/v}} - \frac{A}{(v + l)^2} \tag{1}$$

where β, A, α and l are constants. Moreover, measurements about to be published for mixtures of nitrogen and methane indicate that the same form of equation represents the observed pressures with good approximation.

The development of the application of thermodynamics to reversible chemical reactions in gases has progressed but little beyond the perfect gas stage. The progress which has been made, however, cannot wholly be taken advantage of because of the almost complete state of ignorance which surrounds the problem of the theory of the temperature dependence of the specific heats of gases. Until substantial progress has been made with the latter problem no final quantitative theory of the aggregation effect is generally possible.

The important question of whether the aggregated fraction can be assumed amenable to the same thermodynamical treatment that applies to a chemical reaction in the gaseous phase can probably be answered in the

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[1] Lewis, THIS JOURNAL, **46**, 2027 (1924).

[2] It is perhaps apropos to refer to the opinion of van Urk that Equation 1 is similar to that suggested by Goebel. This latter equation has the form $p = [RT/(v - b_0 + b_1p)] - [a/(v - c)^2]$, where b_0, b_1, a and c are constants. Clearly, Equation 1 requires the pressure to increase linearly with temperature at constant volume, whereas the equation of Goebel requires a curved isometric.

affirmative. There is, however, one element of difference which is important in the quantitative sense. The ordinary chemical reaction is accompanied by a very large heat effect whereas the heat effect due to aggregation appears to be relatively small. This condition accentuates the difficulties due to the present primitive state of the theory of gaseous specific heats, for the temperature coefficient of the aggregation would be a more important factor than for a chemical reaction where the magnitude of the heat effect is sufficient to make an exact knowledge of the specific heats of the reacting molecular species far less necessary.

The influence of pressure, at constant temperature, on gaseous chemical reactions is just beginning to receive quantitative development.[3] Since in the case of the simpler gases the aggregation effect seems to be only appreciable at higher pressures, the pressure effect on the aggregation reaction becomes important. It is necessary, in this connection, that the characteristic constants of the equation of state for the aggregated species should be known to calculate the pressure coefficient. It has been found impracticable to obtain these constants directly from pressure-volume-temperature data. In the case of molecules without permanent or natural electrical moments (assuming that simple ratios exist between the constants of the unaggregated and aggregated species), it is not difficult to find by trial the magnitude at least of the A and β constants. The assumed constants combined with the constants of the unaggregated species must give both the correct pressure effect for the aggregation and also the correct pressures when used in the equation of state.

To summarize the material available for estimating the extent and nature of the aggregation effect for at least the simpler types of molecules, we have: (1) the experimental fact that as higher temperatures are approached the constant-volume pressures are increasingly linear with the temperature; (2) an equation of state of considerable accuracy which at not too small volumes requires a linear increase of pressure with temperature at constant volume; (3) experimental proof that the equation of state for binary mixtures of nitrogen and methane,[4] two representative gases of the simpler kind, is of the same form as that which applies to the pure gases.[5]

The Equation of State for Slight Aggregation

The classical example of a simple association is that of nitrogen oxide-nitrogen tetroxide. If y is the associated fraction and the perfect gas

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[3] Gillespie, This Journal, **48**, 28 (1926).

[4] Burks, *Unpublished Thesis*, Mass. Inst. Tech.

[5] If aggregated molecules actually exist in a gas one may regard the gas as a mixture of simple and aggregated molecules, each species having its appropriate constants. Experimental proof that mixtures of nitrogen and methane are representable by Equation 1 makes it appear probable that the same rules of combination of constants (in the mixture's equations of state) hold also for aggregated and unaggregated species.

laws are assumed for both of the molecular species, the equation of state takes the form

$$p = (RT/v)\,(1 - y/2) \tag{2}$$

The isometric corresponding to this equation will evidently tend to linearity at high temperatures (assuming that nitrogen dioxide does not decompose) where the pressure is substantially $p = RT/v$. As the temperature falls, however, the pressures become increasingly less than those corresponding to the extrapolation of the linear high-temperature portion until substantially complete association is attained, when the pressure tends again to be linear with temperature and pressure given by the equation $p = (^1/_2\,RT)/v$.[5]

The constants of the equation of state for the two species in the example chosen are not known but if they were known the equation of state would be, from Equation 1,

$$p = \frac{RT(1 - y/2)}{v - \delta_y} - \frac{A_y}{(v + l_y)^2} \tag{3}$$

where δ_y is written for the quantity $\beta_y e^{-\frac{\alpha_y}{v}}$ corresponding to an associated fraction y and similarly for the remaining quantities A_y and l_y.[6]

Equation 3, while complicated, takes on a simple form where the associated fraction is small, particularly if the pressure is low (less than several atmospheres)—for the variation of the constants δ_y, A_y, l_y are then of higher order as compared with $R(1 - y/2)$. Equation 3 under these simplifying conditions becomes, where A_1, δ_1, l_1 pertain to the simple species,

$$p = \frac{RT\,(1 - y/2)}{v - \delta_1} - \frac{A_1}{(v + l_1)^2} \tag{4}$$

The fraction associated by the known perfect gas law thermodynamic development is

$$\frac{y}{(1 - y)^2} = gf(T)\,\frac{1}{v} \tag{5}$$

where g is a constant and $f(T)$ is $e^{\frac{2\Delta U}{RT}}$, provided differences in heat capacities of the two reacting species are neglected.

Equation 4 may be readily expanded in a series of reciprocal volumes resulting in the equation

$$pv = RT\left[1 + \left(\beta + \frac{A}{RT} - \frac{gf(T)}{2}\right)\frac{1}{v} + \left(\beta^2 - \alpha\beta + \frac{2Al}{RT} - \frac{gf(T)}{2}\,\beta\right)\frac{1}{v^2} + \ldots\right] \tag{6}$$

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[6] If, for example, the β constant for the unaggregated species is designated β_1 and the aggregated type molecules β_2, β_y might be given by the equation $\beta = \beta_1\,(1 - y) + \beta_2 y$. This proves to be the case in the nitrogen-methane mixtures. The A_y, judged by analogy with the nitrogen-methane mixtures, would be $A_y = [\sqrt{A_1}(1 - y) + \sqrt{A_2}\,y]^2$ while α_y and l_y would be of a form similar to that given for β_y. The fraction associated, y, is a function of both volume and temperature and it is therefore clear that A_y, δ_y and l_y are volume and temperature functions.

where $gf(T)$ $(1/v)$ has been substituted for y from Equation 5 on the assumption that y is small. If y should prove to be large, this approximation should, of course, be corrected by using in the B coefficient $gf(T)/(1-y)^2v$. For nitrogen the approximation $gf(T)$ $1/v$ appears to be sufficient to represent y although where larger values of y are needed Equation 5 must be employed.

The actual observations pertaining to a gas may be represented by a reciprocal volume series of the form

$$pv = RT\left(1 + B\frac{1}{v} + C\frac{1}{v^2} + \ldots\ldots\right) \tag{7}$$

The coefficient B may, therefore, be identified with $[\beta - A/RT - gf(T)/2]$ from Equation 6, which graphically is the slope of the pv isotherm at $p = 0$. The coefficient C, which is more complicated in form, need not be discussed explicitly since the values of C available are not known with sufficient accuracy at the present time to make profitable their use according to the methods to be developed in the present paper.

The quantity $f(T)$ in the form $e^{\frac{2\Delta U}{RT}}$ would become unity at $T = \infty$. On the other hand, $f(T)$ becomes increasingly large as T diminishes. The coefficient B, accepting $f(T)$ as of form $e^{\frac{2\Delta U}{RT}}$, is thus linear in reciprocal T at sufficiently high temperatures and increasingly concave to the axis of abscissas, $1/T$, at lower temperatures.

It is important to note that in the absence of double molecules, an association of three of the simpler molecules to triple molecules would leave the B coefficient simply $(\beta - A/RT)$, since z, the fraction of triple molecules, for small values of z, varies as the reciprocal volume squared, thus first appearing in the coefficient C.

In what follows it will be assumed that if aggregation to double molecules takes place in a gas, Equation 4 applies (aggregation small). The form of $f(T) - e^{\frac{2\Delta U}{RT}}$, similar in form to that pertaining to an ordinary chemical association of perfect gases wherein the heat capacities of the two species of molecules are supposed equal, will also be assumed to apply to the case of aggregation. These simplifying conditions form the basis for a preliminary treatment, having been found to be sufficient to indicate semiquantitatively the nature of the effects to which the assumption of aggregation leads.

The Experimental Data for Nitrogen

There now exists a considerable amount of pressure-volume-temperature data for nitrogen from temperatures of about —146° to 400°. The bulk of low-temperature data is due to A. Th. van Urk,[7] and recently Smith and

[7] Van Urk, *Thesis*, Leiden, **1924**; *Proc. 4th. Int. Congress Refrigeration*, **1**, 75 (1924).

Taylor[8] have published measurements of pressure and temperature for various constant volumes from 23 cc. per g. The data above 200° are due to Holborn and Otto,[9] as well as other data in the interval of 0° to 200°, and recently additional data below zero have been published by the latter.

With the exception of the data due to Smith and Taylor all the experimental material was obtained from measurements of pressure and volume at constant temperature. Holborn and Otto's results are correlated at each temperature by means of equations of the form of 7. Van Urk, however, gives no similar equations for his data below zero. The data have, therefore, been correlated by means of quadratic equations in reciprocal volume. In determining the coefficients, RT as well as B and C may be regarded as a coefficient to be determined from the data. On the other hand, since R is known, RT may be computed for each temperature and the quadratic equations reduced to linear equations in density. The constants for both procedures are given in Table I. The B coefficients determined by the method of computing RT appear to vary most regularly with temperature. The observational data are about equally well represented (1 part per 1000) by either formulation to volumes of 10 cc. per g.

TABLE I

DATA OF VAN URK FOR NITROGEN

I, coefficients of equation $pv = a + b(1/v) + c(1/v^2)$; II, coefficients of equation $pv = rT + b'(1/v) + c'(1/v^2)$; $r = 2.9286/799.55$; $M = 28.02$; $R = 82.058$; $T = 273.13 + t$.

	I			II		
t	a	$\frac{c}{a} \times 10^6$	B or $\frac{b}{a} \times 10^3$	rT	$\frac{c'}{rT} \times 10^6$	B' or $\frac{b'}{rT} \times 10^3$
− 23.62	0.91191	2.12494	0.65225	0.91392	3.3438	0.7599
− 50.26	.82466	5.86276	1.46130	.81634	2.6558	1.1025
− 81.10	.70870	5.16802	1.96441	.69972	2.4438	1.6007
−102.25	.62975	5.13793	2.49445	.62592	3.7626	2.3183
−121.19	.55298	4.07217	2.95527	.55653	5.1499	3.1045
−131.27	.51911	5.72218	3.59236	.51949	5.7616	3.6022
−141.53	.48267	6.64502	4.24466	.48203	6.5597	4.2251
−144.46	.47166	6.91246	4.44429	.47130	6.8385	4.4306
−146.32	.46534	7.06050	4.58300	.46448	7.0530	4.5750

The unit of pressure is the atmosphere of 76 cm. of mercury at 0°; the unit of volume is the volume of 1 g. of the gas at 0° and 1 atm. (799.55 cc. per gram).

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[8] Smith and Taylor, THIS JOURNAL, **45**, 2107 (1923). Van Urk has called attention in his dissertation to the fact that the pv isotherm for 0°, taken from Smith and Taylor's data, is about 0.5% lower than this isotherm, as measured by both van Urk and Holborn and Otto. Smith and Taylor have since found that an error of about this magnitude was made in computing the amount of nitrogen introduced into their piezometer [*ibid.*, **48**, 3122 (1926)].

[9] Holborn and Otto, *Z. Physik*, **10**, 367 (1922); **23**, 77 (1924); **30**, 320 (1924); **33**, 1 (1925).

In Table II will be found a list of the coefficients corresponding to temperatures from 400° to —146.32°. The numbers in the last column designate the reference to the literature from which the coefficients B were taken. The coefficients at round temperatures, —50°, —100°, —130°, are coefficients of p from empirical equations for pv of the form $a + b'p + c'p^2$ given by Holborn and Otto.

Table II

Equations for Isotherms

Pressure in atmospheres, volume in "Amagat Units" or the volume at 0° and 1 atm. taken as the volume unit.

Temp., °C.	a or RT	$B_{\text{obs.}} \times 10^3$	$B_{\text{calcd.}}$	$C \times 10^6$	Observer, Ref.
400	2.46523	+1.04694	1.1420	2.51379	*b*
300	2.09905	+0.91733	0.9562	2.01090	*b*
200	1.73285	+ .67840	.6897	2.39479	*b*
150	1.54975	+ .50839	.5080	2.48681	*b*
100	1.36664	+ .26641	.2763	2.87953	*b*
50	1.18352	− .01670	− .0301	2.74274	*b*
0	1.00046	− .45516	− .4561	3.03602	*b*
100	1.36661	+ .26609	+ .2763	2.87617	*a*
50	1.18351	− .02493	− .0301	2.76710	*a*
0	1.00046	− .43386	− .4561	2.64643	*a*
20	1.07370	− .24448	− .2673	2.32840	*c*
0	1.00041	− .40996	− .4561	2.06556	*c*
− 23.62	0.91392	− .7599	− .7229	3.3438	*d*
− 50.26	.81634	−1.1025	−1.1004	2.6558	*d*
− 81.10	.69972	−1.6007	−1.6961	2.4438	*d*
−102.25	.62592	−2.3183	−2.2704	3.7626	*d*
−121.19	.55653	−3.1045	−2.9936	5.1499	*d*
−131.27	.51949	−3.6022	−3.5168	5.7616	*d*
−141.53	.48203	−4.2251	−4.2162	6.5597	*d*
−144.46	.47130	−4.4306	−4.4574	6.8385	*d*
−146.32	.46448	−4.575	−4.6237	7.0530	*d*
− 50	....	−1.177	−1.0962	....	...
−100	....	−2.315	−2.2010	....	...
−130	....	−3.561	−3.4444	....	...

[a] Holborn and Otto, *Z. Physik*, **10**, 367 (1922).

[b] Holborn and Otto, *ibid.*, **23**, 77 (1924).

[c] Van Urk, *Thesis*, Leiden, **1924**.

[d] Van Urk data constants computed by Keyes and Taylor.

Fig. 1 gives a graphic representation of the data contained in Table II. In this representation B is plotted with $1/T$ as abscissas. It is evident that the general prediction based on B represented by $[\beta - A/RT - gf(T)/2]$ is fulfilled.

Discussion of the Relation between B and the Temperature

The quantity $f(T)$ is of a mathematical form which makes it impractical to attempt to determine the four constants β, A, g and ΔU directly by ordinary methods. The treatment of the constant-volume pressures and temperatures between 0° and 200° has shown that the magnitudes of the β and A constants of the equation of state are approximately $\beta = 1.7$ and $A = 1650$. By trial it was found that $\beta = 1.768$, $A = 1643$, $g = 0.016378$ (in cc. per g. units), and $\Delta U = 614$ cal. represent the B coefficients as well as may be expected in view of the simplicity of $f(T)$. Equation 5 in the form $\log y/(1 - y)^2$ is the most convenient to use in computations and follows.

$$\log_{10} \frac{y}{(1 - y)^2} = \frac{266.9}{T} - 1.7858 - \log_{10} v \text{ cc./g.} \qquad (8)$$

The constants g and ΔU were determined, as already stated, on the assumption that y as it enters the B coefficient was small enough to be assumed equivalent to $y/(1 - y)^2$. The value of y from $y/(1 - y)^2$ even at —150° (0.0032) is greater than y by only 1 part in 156.

In units based on the volume of 1 g. of nitrogen at zero taken as unity,[10] the pressure being in atmospheres, there results the following equation for B.

$$B = 0.002211 - \frac{0.702}{T} - \frac{2.0483 \times 10^{-5}}{2} e^{614/T} \qquad (9)$$

Col. 3 of Table II contains computed values of B in Amagat units. In Fig. 1, the full line through the observational data was computed from Equation 9 while the straight line above the data represents the first two terms of the right-hand member of Equation 9. The agreement of the computed and observed data is sufficient to indicate that the assumption of aggregation suffices to reproduce the general characteristics of the relation between B and the temperature.

The higher temperatures 400°, 300° and 200° indicate a trend away from the linear portion of the curve between 0° and 150° which is not reproduced by Equation 9. There is, of course, no difficulty in giving to $f(T)$ a form which will reproduce the curvature indicated by the observations at the higher temperatures. It appears best, however, to postpone such an attempt until an increased knowledge of aggregation in gases has either indicated or definitely excluded the possibility of such an effect accompanying aggregation. The simple form here used for $f(T)$ reduces substantially to unity at higher temperatures and A/RT vanishes leaving $(\beta - g)$, a constant independent of temperature, for the B coefficient.[11]

Fig. 1 has been used to insert the Holborn and Otto B coefficients for argon. It will be observed that the general trend of the data is identical with that of nitrogen, except that there is no tendency for the 300° and 400° B values to depart from the nearly linear course shown by the B values

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[10] The unit of volume in terms of the volume of a gram of gas in cc. at N. T. P. will be referred to hereafter as the "Amagat unit."

[11] Helium has a very small A/R value (in Amagat units about 0.014 as compared with 0.702 for nitrogen) and B would vary but little from constancy (10%) above zero.

from 0° to 200°. On the other hand the A/R value for argon is somewhat larger than for nitrogen and a higher temperature may be required to disclose a trend in the high-temperature B value similar to that of nitrogen. Hydrogen, helium and neon, all of which have small values of A/R,

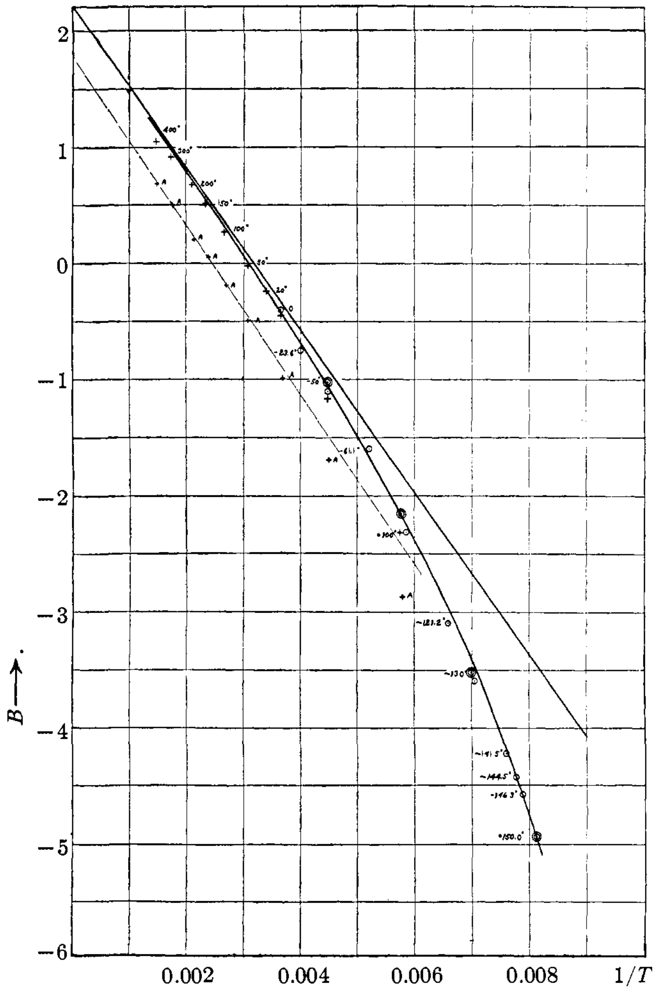

Fig. 1.—B coefficients for nitrogen. +, Holborn and Otto. ⊙, van Urk. ◎, Onnes.

show the high-temperature curvature effect that nitrogen does, but the detailed discussion of these substances will find more suitable place in another paper. For the present, it is clear that the general course of the dependence of the B coefficient on temperature has been accounted for on a rational basis and that further knowledge of the properties of aggregated molecules must be awaited before a finally satisfactory quantitative theory can be concluded.

The Comparison of the Observed and Computed Pressures

The usual procedure followed to obtain the approximate values of the equation of state constants A, β, α and l of Equation 1 has been to employ data pertaining to as high temperatures as possible, ignoring the slight actual curvature of the isometrics. By this compromise it is possible to represent the observational data with very satisfactory accuracy, provided the curvature is small. Some years ago, however,[12] the desirability of finding means of estimating the aggregation was suggested. The present paper indicates one method based on the B coefficients and Equations 4 and 5. An earlier paper[13] showed that the Joule-Thomson data in its relation to temperature at low pressures could be accounted for on the hypothesis of aggregation using Equations 4 and 5, thereby giving a means of estimating the amount of supposed aggregation. The long range of data for nitrogen offers an opportunity of testing how well the actual curvature of the isometrics of nitrogen are reproduced when the aggregation effect is included in the equation of state.

The values of β and A ($\beta = 1.768$; $A = 1643$ in cc. per g. atm. units) have already been determined from the B coefficients. Emphasis has already been put on the fact that these constants, in the absence of B coefficients of the highest accuracy, can be only approximate (unless by chance 1 or 2% of the true values). The values of α and l might be determined from the c coefficients but the relation of these data to the temperature is too erratic to be used for the purpose. The values of α and l were, therefore, assumed to complete the constants of Equation 1. This was made possible from equations of state of Form 1 which have been used to represent data for nitrogen wherein the curvature of the isometrics was neglected. The equation assumed to calculate the pressures is as follows.

$$p_{\text{atm.}} = \frac{2.9286\,T\left(1 - \frac{y}{2}\right)}{v - 1.768\,e^{-1.082/v}} - \frac{1643}{(v + 0.22)^2} \tag{10}$$

When aggregation is assumed absent this becomes

$$p_{1\ \text{atm.}} = \frac{2.9286\,T}{v - 1.768\,e^{-1.082/v}} - \frac{1643}{(v + 0.22)^2} \tag{11}$$

Equation 5[14] will be used for computing y and in Table III are listed the pressures computed by Equation 10 and observed for the constant volumes 26.651, 19.989, 13.326 and 10.661 cc. per gram, corresponding to

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[12] Keyes and Felsing, THIS JOURNAL, **41**, 589 (1919).

[13] Keyes, *ibid.*, **46**, 1584 (1924).

[14] It is convenient to make a plot of $y/(1 - y)^2$ and y which may be used to expedite computations of y from equations of this kind.

densities 75, 60, 40 and 30 in the Amagat volume units. These observed pressures were interpolated by means of the isothermal-density-series equations given by Holborn and Otto and similar equations relative to temperatures below zero for van Urk's data, using the coefficients given in Table I. The third horizontal row corresponding to each volume likewise contains the pressure diminution assumed to be due to aggregation, namely, $[2.9286T/(v - \delta)](y/2)$, and the last row the difference between the pressure given by Equation 11 and the observed pressure. The two latter quantities should be equal for exact agreement of the observed pressures and those given by Equation 10.

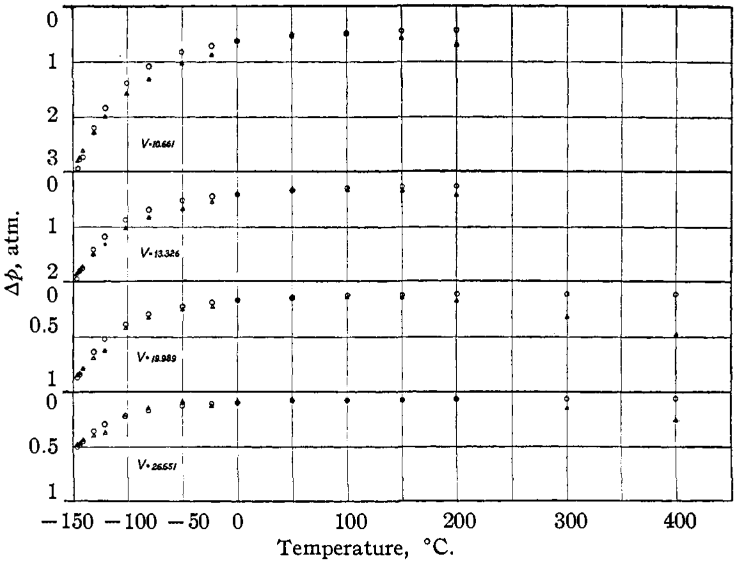

Fig. 2.—Deviations from linearity of nitrogen isometrics; ○, calculated; Δ, van Urk; Holborn and Otto.

Fig. 2 is a graphic representation of the departure of both these observed and computed pressure differences, indicating that the departure from linearity of each isometric is reproduced in its general features by Equation 10. The three highest temperatures indicate an increase of the pressure differences given by subtracting the observed pressures from Equation 11. This effect might be explained by failure of the equation used to calculate y (Equation 8). Nevertheless, it would seem to require for its explanation on the aggregation hypothesis an increase in y at higher temperatures. Further measurements at 200° and higher temperatures, together with a more exact knowledge of the relation of aggregation to temperature, may be expected to explain the failure of the isometrics to remain linear after attaining substantial linearity between 0° and 150°.

TABLE III

COMPARISON OF THE PRESSURES OF NITROGEN WITH THOSE COMPUTED BY EQUATION 11

Unit of pressure 76 cm. of Hg at 0°

	−146.32°	−144.46°	−141.53°	−131.27°	−121.19°	−102.25°	−81.1°	−50.26°
				v = 10.661 cc. per g.				
Press., Eq. 10	24.160	24.943	25.923	29.772	33.371	39.943	47.087	57.308
Press., obs.	24.290	24.958	26.029	29.697	33.231	39.761	46.868	57.110
Eq. 11 − Eq. 10	2.926	2.757	2.724	2.190	1.848	1.395	1.086	0.832
Eq. 11 − press. obs.	2.796	2.742	2.618	2.265	1.988	1.577	1.306	1.030
				v = 19.989 cc. per g.				
Press., Eq. 10	20.861	21.479	22.269	25.161	27.917	32.957	38.444	46.329
Press., obs.	20.953	21.457	22.277	25.075	27.782	32.829	38.301	46.186
Eq. 11 − Eq. 10	1.937	1.785	1.728	1.405	1.173	0.876	0.685	0.522
Eq. 11 − press. obs.	1.845	1.807	1.720	1.419	1.308	1.004	.828	.665
				v = 13.326 cc. per g.				
Press., Eq. 10	15.386	15.714	16.234	18.031	19.756	22.917	26.389	31.392
Press., obs.	15.412	15.721	16.234	17.971	19.649	22.887	26.355	31.368
Eq. 11 − Eq. 10	0.869	0.839	0.787	0.631	0.518	0.385	0.296	0.224
Eq. 11 − press. obs.	.843	.832	.787	.691	.625	.418	.330	.248
				v = 26.651 cc. per g.				
Press., Eq. 10	12.100	12.341	12.817	14.015	15.260	17.559	20.090	23.751
Press., obs.	12.130	12.351	12.723	13.975	15.719	17.566	20.107	23.785
Eq. 11 − Eq. 10	0.504	0.481	0.449	0.355	0.292	0.216	0.166	0.124
Eq. 11 − press. obs.	.474	.471	.443	.395	.373	.209	.149	.090
	−23.62°	0°	50°	100°	150°	200°	300°	400°
				v = 10.661 cc. per g.				
Press., Eq. 10	66.043	73.758	90.005	106.211	122.403	138.582	....	.....
Press., obs.	65.865	73.750	90.023	106.206	122.289	138.327	....	.....
Eq. 11 − Eq. 10	0.704	0.622	0.527	0.481	0.449	0.430	....	.....
Eq. 11 − press. obs.	.882	.630	.509	.494	.571	.693	....	.....
				v = 19.989 cc. per g.				
Press., Eq. 10	53.083	59.046	71.628	84.177	96.708	109.249	....	.....
Press., obs.	52.992	59.044	71.640	84.159	96.654	019.099	....	.....
Eq. 11 − Eq. 10	0.439	0.390	0.328	0.298	0.278	0.267	....	.....
Eq. 11 − press. obs.	..530	.392	.315	.316	.332	.417	....	.....
				v = 13.326 cc. per g.				
Press., Eq. 10	35.688	39.485	47.508	55.517	63.521	71.521	87.516	103.507
Press., obs.	35.649	39.490	47.517	55.500	63.497	71.460	87.313	103.135
Eq. 11 − Eq. 10	0.188	0.168	0.141	0.127	0.118	0.114	0.110	0.110
Eq. 11 − press. obs.	.227	.163	.132	.144	.142	.175	.313	.482
				v = 26.651 cc. per g.				
Press., Eq. 10	26.897	29.679	35.560	41.435	47.307	53.175	64.911	76.645
Press., obs.	26.874	29.695	35.571	41.433	47.306	53.156	64.822	76.447
Eq. 11 − Eq. 10	0.104	0.093	0.078	0.070	0.065	0.063	0.060	0.060
Eq. 11 − press. obs.	.127	.077	.067	.072	.066	.082	.149	.258

It is quite evident that very exact agreement between the observed and computed pressures may be obtained by modifying Equation 8. This has not been done in the present paper since it would contribute little or nothing to the examination of the usefulness or theory of the aggregation hypothesis, especially since the variation of the constants with association has been altogether neglected.

An equation reproducing the pressure observations of Holborn and Otto with substantial accuracy from 0° to 200° may be obtained by neglecting the slight curvature of the isometrics. Such an equation follows.

$$p = \frac{2.9286T}{v - 1.766\,e^{-1.065/v}} - \frac{1687.1}{(v + 0.136)^2} \qquad (12)$$

Table IV gives a survey of the agreement realized between the pressures computed by Equation 12 and the observed pressures.

TABLE IV

PRESSURES COMPUTED BY EQUATION 13 COMPARED TO HOLBORN AND OTTO OBSERVATIONS

Vol., cc./g.		0°	50°	100°	150°	200°
40	Obs.	19.84	23.68	27.50	31.32	35.14
	Calcd.	19.848	23.673	27.499	31.324	35.149
30	Obs.	26.40	31.62	36.76	41.94	47.10
	Calcd.	26.411	31.586	36.761	41.936	47.111
25	Obs.	31.63	37.99	44.21	50.55	56.76
	Calcd.	31.648	37.931	44.214	50.496	56.779
20	Obs.	39.46	47.49	55.47	63.50	71.43
	Calcd.	39.486	47.478	55.468	63.459	71.449
15	Obs.	52.49	63.52	74.47	85.43	96.34
	Calcd.	52.526	63.490	74.454	85.418	96.382
10	Obs.	78.63	96.16	*113.61*[a]	*130.92*[a]	*148.20*[a]
	Calcd.	78.640	96.151	*113.559*[a]	*130.966*[a]	*148.374*[a]

[a] Extrapolated by means of the empirical pv equations.

On the other hand, the pressures computed by Equation 12 at 300° and 400° are always higher than the observations of Holborn and Otto. For example, at 40 cc. per gram and 400° the calculated pressure is one part in 300 greater than the observed pressures, and at 300° one part in 510.

The Heat Capacity at Constant Volume

The heat capacity of a gas at constant volume would be dependent upon the temperature alone if Equation 1 were the true equation of state. The existing observational material indicates, however, that in general this property is a function of the density as well as of temperature. As higher temperatures are approached, the constant-volume heat capacity becomes an increasingly less pronounced function of the density, as would be inferred from the fact that $(\partial p/\partial T)_v$ tends to become constant at higher temperature.

Aggregation, if it exists in a gas, would be a very important factor in contributing a heat effect to the gas since heating at constant volume diminishes the aggregated fraction with attendant heat absorption. Moreover, this effect would be considerable for the heat of aggregation is enormous relative to the normal heat capacity of the molecules *per se*.

The calculation of this effect presents no difficulties, although for making numerical calculation there is a paucity of data which is much to be regretted. The use of Equation 2 in connection with the thermodynamical equation $(\partial C_v/\partial_v)_T = T(\partial^2 p/\partial T^2)_v$ leads easily to the following equation, assuming that y is sufficiently small to identify $y/(1 - y)^2$ with y.

$$C_v = \text{constant} + 2\,Ry(\Delta U/RT)^2 \tag{13}$$

When T is infinite $C_v = \text{constant} = C_{v_1}$ and the contribution to the specific heat at constant volume due to aggregation to double molecules would on this basis be

$$C_v - C_{v_1} = \Delta C_v = 2\,Ry(\Delta U/RT)^2 \tag{14}$$

The phenomenological equation for Cv per unit mass of substance would be, on the assumption to double molecules only,

$$C_v = C_{v_1}(1 - y) + C_{v_2}y + (-\Delta U)\,(\partial y/\partial T)_v \tag{15}$$

where Cv_1 is the heat capacity *per se* of the single molecules and C_{v_2} that of the double molecules, the fraction associated being y. Using Equation 5, there results

$$C_v = C_{v_1} + (C_{v_2} - C_{v_1})\,y + 2\,Ry\,\frac{1 + y}{1 - y}\left(\frac{\Delta U}{RT}\right)^2 \tag{16}$$

This equation is of course identical with Equation 14 for $y = 0$.

There are unfortunately no experimental data bearing on C_{v_2} for any substance. The assumption will be made, however, that C_{v_1} is equal to C_{v_2} for aggregation and Equation 16 becomes

$$C_v = C_{v_1} + 2\,Ry\,\frac{1 - y}{1 + y}\left(\frac{\Delta U}{RT}\right)^2 \tag{17}$$

There are no data available for the constant-volume heat capacity of pure nitrogen. Jakob, however, has computed the specific heat at constant volume for air, using the experimentally measured constant pressure-specific heat capacity of air to 200 atm. at 59° by Holborn and Jakob[15] and an empirical equation of state for air representing the measurements of Holborn and Otto[9] on the pressure-volume-temperature properties.

In addition to these computations further computations based on the interpretation of the Joule-Thomson measurements of Bradley and Hale,[16] Noell,[17] and Jakob,[18] were employed to compile a table of the most probable values of the heat capacities at constant pressure and at constant volume from temperatures of —79.3° to 250° and over a pressure range from 0 to about 200 atmospheres.

In the absence of specific-heat data on pure nitrogen it is of interest to employ Equation 17 to compute the heat capacities of air, using Equation 8 for the supposed aggregation of nitrogen. The "computed" heat capacities employ for C_{v_1} the heat capacity of air at zero pressure which is

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[15] Holborn and Jakob, *Z. Techn. Physik*, **4**, 465 (1923).

[16] Bradley and Hale, *Phys. Rev.*, **29**, 258 (1909).

[17] Noell, *Z. Ver. deut. Ing.*, **62**, 49 (1918).

[18] Jakob, *Fortschritte Arb. Ver. deut. Ing.*, No. 202, **1917**.

given by Jakob as 0.172 cal. per gram from —79.3° to 50°. Table V gives the calculated numbers together with the Jakob values corresponding to 0,° —50 and —79.3° at several pressures to 193.55 atmospheres. Col. 4, ΔC_v, gives the amount by which C_{v_1} increases as the pressure increases.

TABLE V

C_v AS FUNCTION OF THE PRESSURE

Temp., °C.	Pressure, atm.	y	ΔC_v, calcd.	C_v, calcd.	C_v, Jakob
0	1	0.00019	0.0000	0.172	0.172
	48.39	.0095	.0017	.174	.175
	96.78	.0185	.0032	.175	.178
	145.17	.027	.0046	.177	.179
	193.55	.051	.0082	.180	.181
−50	0.0	.0000	.0000	.172	.172
	48.39	.0195	.005	.177	.178
	96.78	.0390	.010	.182	.182
	145.17	.0542	.013	.185	.186
	193.55	.067	.016	.188	.188
−79.3	0.0	.0000	.0000	.172	.172
	48.39	.036	.012	.184	.185
	96.78	.070	.022	.194	.196
	145.17	.098	.029	.201	.206
	193.55	.117	.033	.205	.215

It is evident from Table V that the relation of C_v to both pressure and temperature is given by Equation 17 as accurately as could have been expected. Indeed, it is anticipated that extended data bearing on the heat capacities of gases at constant volume will provide excellent data with which to test the value of the aggregation hypothesis.

Concluding Comments

Notwithstanding the tolerable agreement between observational material and computation disclosed in the present paper, it is well to emphasize that the existence of definite molecular aggregates is scarcely proved. Indeed, the treatment of aggregation adopted may be regarded from a theoretical point of view as defective since there is doubt that the mass law holds for aggregation which, at least for substances of the class of nitrogen, must be regarded as of purely electrical origin. However, even were the mass law applicable, the dependence of the aggregation on temperature and volume as given by the perfect gas treatment would be deficient at the comparatively high pressures here considered.

Moreover, disregarding all these disabilities of the treatment, there remains from the strictly theoretical point of view the important omission to allow for the variation of the fundamental constants A, β, α and l of the equation of state due to aggregation. The theory of the origin of the cohesive forces is sufficient to lead to a plausible inference concerning the ratios of the A constants and possibly also the β constants for definitely associated double and single molecules.

In the main, reliance for further information regarding aggregation must be placed on comparison, in addition to p-v-T data, of the variation of viscosity, dielectric constant, refractive index, absorption of light, and the Kerr effect with both temperature and pressure. Specific-heat data at constant volume are also valuable for the purpose although the technique of the measurement of this quantity has not as yet been finally worked out.

Summary

1. The attempt has been made to use the hypothesis of molecular aggregation in connection with the equation of state $p = (RT/v - \delta) - A/(v + l)^2$ to explain the observed dependence of the coefficient of $1/v$ in the virial equation on the temperature as well as the curvature of the isometrics at low temperatures in the case of nitrogen.

2. The dependence of the supposed aggregation on volume and temperatures has been assumed to conform to the mass law—perfect gas treatment used in discussing chemical equilibria, assuming the heat capacities of the simple and aggregated species to be the same per unit mass.

3. The aggregation equation for nitrogen has been obtained from the coefficient [B coefficient] of $1/v$, and also the values of β and A of the equation of state (1). The dependence of the B coefficients on temperature is represented in its general characteristics. The temperature trend, however, of the B coefficients due to Holborn and Otto at 300° and 400° is not exactly reproduced and in fact appears difficult to account for unless aggregation is related to temperature and volume otherwise than as herein assumed.

4. A comparison has been made of the observed isometric pressures for nitrogen with those calculated by means of the aggregation equation (8) combined with an approximate equation of state for the unaggregated species. It is shown that the curvature of the isometrics is reproduced except at 300° and 400°.

5. The aggregation equation (8) for nitrogen has been used to compute the constant-volume heat capacities of air as a function of the pressure. Good agreement is found between the observed and computed values.

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