#### THE VISCOSITY OF COMPRESSED GASES

By James H. Boyd, Jr.†

DEPARTMENT OF CHEMICAL ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY

(Received April 7, 1930)

### ABSTRACT

New data and a new theory for the viscosity of compressed gases are presented. Data for nitrogen, hydrogen and a mixture of these gases are given, in the calculation of which, the "end effects" are not neglected as has been done in the past. Previous viscosity data are of doubtful validity owing to neglect of this factor. The theory is based on an analogy between the kinetic pressure and viscosity of a gas and is derived using an equation of state of the Lorentz type. Allowance is made for the difference between the viscosity and compressibility covolumes. The theory is substantiated experimentally and further confirmed by the recalculation of other data on the variation of Reynolds' criterion with the pressure, which is here shown to be constant. The mixture data offer a direct opportunity of comparing the Lorentz and linear rules for the calculation of the covolume of a mixture from the covolumes of the components and such comparison indicates that the Lorentz rule is not to be preferred. The substantiation of the new theory is the first direct proof of the validity of the separate treatment of the kinetic and cohesive pressures in the equation of state.

### I. INTRODUCTION

THE viscosity coefficient of a gas is defined as the time rate of the net transfer of momentum across an imaginary, plane unit-surface in the interior of a flowing gas when there is a unit velocity gradient normal to the plane surface and normal also to the direction of gas flow. The statement is often encountered that the viscosity of gases is independent of the pressure. At atmospheric pressure and less this is substantially true and is confirmed experimentally but for high pressures theory predicts and experiment concurs in giving greater values of the gas viscosity.

A number of theories of the viscosity at high gas densities have been advanced and Meyer,<sup>1</sup> Brillouin<sup>2</sup> and Batschinski<sup>3</sup> have attempted solutions of this problem. Far more significant are the investigations of Jäger,<sup>4</sup> H. B. Phillips<sup>5</sup> and Dubief<sup>6</sup> who employed equations of state of the van der Waal type in their derivations. H. B. Phillips' paper is of particular interest in view of certain generalizations made concerning the effect of intermolcular forces on gas properties.

† Research Assistant, Research Laboratory of applied chemistry.

<sup>1</sup> Meyer, Kinetic Theory of Gases, 2 Ed., Eng. Trans., Longmans, Green and Co., 1899.

<sup>2</sup> Brillouin, Lecon sur la Viscosite, II, p. 132, Villiers, Paris, 1907.

<sup>3</sup> Batschinski, see Bingham, Fluidity and Plasticity, pp. 142-152, McGraw Hill, New York, 1922.

<sup>4</sup> Jäger, Wien. Sitz. Ber. 150, 2A, 15 (1896); 108, 2A, 447 (1899).

<sup>5</sup> H. B. Phillips, J. Math. and Phys., M. I. T. 1, 42 (1921).

<sup>6</sup> Dubief, J. de Phys. et Rad. 7, 402 (1926); Compte Rendus 180, 1164 (1925); 182, 688 (1926).

In the experimental field Warburg and von Babo<sup>7</sup> and P. Phillips<sup>8</sup> determined the viscosity of gaseous carbon dioxide at pressures exceeding one hundred atmospheres and for several temperatures. Wildhagen,<sup>9</sup> in his study of the flow of compressed air, measured the viscosity of air at room temperature for pressures up to two hundred atmospheres. All of the writers cited used some form of the transpiration method. In all of these investigations end effects were neglected.

The transpiration method of determining viscosity coefficients is that most readily adapted to use at high pressures. This method is based on Poiseuille's law for isothermal viscous flow which may be expressed

$$\Delta p = \frac{k_c M}{\rho} \mu \tag{1}$$

where  $\Delta p$  is the pressure drop in centimeters of mercury at 0°C, occasioned by the flow of M grams per second of an incompressible fluid of viscosity  $\mu$ and density  $\rho$  through a tube of circular section whose dimensions determine the value of  $k_c$ . The density and viscosity are in c.g.s. units and  $k_c$  equals  $8L/13.596 \ g\pi r^{4*}$  where L and r are the length and radius respectively in centimeters of the tube and g is the gravitational acceleration. When Eq. (1) is integrated assuming the ideal gas laws and an isothermal expansion there results

$$p_1^2 - p_2^2 = 2RTk_c M\mu \tag{2}$$

Here  $p_1$  and  $p_2$  are the upstream and downstream pressures respectively, R the gas constant and T the absolute temperature.

Neither of these equations may be applied directly to experimental data as they neglect "end effects" which are caused by losses in the kinetic energy of the fluid due to changes in the cross-section of the path of flow. As a result the observed pressure difference is greater than it would be were there no such loss. Accordingly Eqs. (1) and (2) should be modified as otherwise the calculated values of the viscosity coefficients would be high. End effects are discussed by Brillouin,<sup>10</sup> Fisher,<sup>11</sup> Rapp,<sup>12</sup> Bingham,<sup>13</sup> Benton,<sup>14</sup> Walker, Lewis and McAdams,<sup>15</sup> and by Trautz and Weizel.<sup>16</sup> The majority of these writers agree, on reducing their results, that the proper form for the end correction is

- <sup>9</sup> Wildhagen, Z. Angew. Math. u. Mech. 3, 181 (1923).
- \* The coefficient of slip is negligible and has been omitted here.
- <sup>10</sup> Brillouin, reference 2, pp. 117-124.
- <sup>11</sup> Fisher, Phys. Rev. 32, 216 (1911).
- <sup>12</sup> Rapp, Phys. Rev. 2, 263 (1913).
- <sup>13</sup> Bingham, Fluidity and Plasticity, p. 17.
- 14 Benton, J. Ind. Eng. Chem. 11, 623 (1919).
- <sup>15</sup> Walker, Lewis and McAdams, Principles of Chemical Engineering, p. 90, 2nd Ed., McGraw Hill, New York, 1927.
  - 16 Trautz and Weizel, Ann. d. Physik 48, 799 (1915).

<sup>&</sup>lt;sup>7</sup> Warburg and von Babo, Ann. d. Physik 17, 390 (1882).

<sup>&</sup>lt;sup>8</sup> P. Phillips, Proc. Roy. Soc. Lon. 87a, 48 (1912).

$$\Delta p_e = \frac{k_e M^2}{\rho} \tag{3}$$

where  $\Delta p_e$  is the end effect pressure drop and  $k_e$  is the end effect constant. Eqs. (1) and (2) accordingly become

$$\Delta p = \frac{k_c M \mu}{\rho} + \frac{k_c M^2}{\rho} \tag{4}$$

$$p_1^2 - p_2^2 = 2RT(k_c M\mu + k_e M^2)$$
(5)

It is of interest to consider the effect of a change in density of a given gas on the magnitude of the end correction when the latter is negligible at atmospheric pressure. Assume that the pressure drop due to the viscous action of the gas is relatively small and constant and that the viscosity is independent of the density. Eq. (4) is sufficient for this estimate since at the higher pressures the gas density is substantially constant throughout the apparatus. For these conditions  $M/\rho$  is constant and therefore the end correction,  $k_e M^2/\rho$ , is linear in density. For density variations of several hundred-fold the end correction may well be of the order of ten to twenty percent. This approximation shows that all previous high pressure investigations are of questionable quantitative significance in view of the neglect of end effects.

### II. THE EXPERIMENTAL METHOD

The transpiration method was used in this investigation and consisted in measuring the pressure drop occasioned by the isothermal flow of a gas of known density at a measured rate through a metal capillary whose constants,  $k_c$  and  $k_e$ , were determined by direct calibration. This necessitated relatively large amounts of the gases and so precluded the use of highly purified materials. Hydrogen and nitrogen of the highest commercial purity obtainable were used in these experiments.

The capillary used in these experiments was a steel tube about a meter long and roughly 0.025 cm in internal diameter. It was immersed in a stirred water bath thermostat whose temperature was read from calibrated thermometers fully immersed. The temperature variation seldom exceeded 0.2°C and generally was within 0.1°C which was adequate for these experiments. The calibration of the capillary for  $k_c$  and  $k_e$  will be described later. A metal capillary was used to insure isothermal flow.

The pressure-drop measurements were made with a new type of high pressure manometer. In principle, the instrument consisted of a mercury filled manometer whose arms were of widely different diameters thus giving practically the entire pressure differential in the smaller arm. The change of the mercury level in the smaller arm was detected by successively making and breaking an electrical circuit by means of a platinum tipped screw rod which was insulated from the body of this apparatus. The relative travel of the rod was determined by measuring the distance between its upper end and

a fixed reference plane by means of a micrometer depth gauge. A galvanometer indicated the completion of the circuit through which a feeble current flowed whose source was a thermocouple immersed in ice and water. This very feeble current was desirable to minimize arcing on breaking the circuit. The pressure differential was calculated from the difference between the flow and zero or no-flow readings. In this calculation corrections were made for the drop in mercury level in the larger arm, the gas density, and the temperature variation of the mercury density.

The gas density was computed from the temperature and pressure of the gas flowing. Pressures were measured with a dead weight piston gauge of the type developed by Keyes<sup>17</sup> and his coworkers. The gas temperature was taken to be that of the bath and the density was calculated from these data using Bartlett's<sup>18</sup> compressibility factors. No attempt was made to

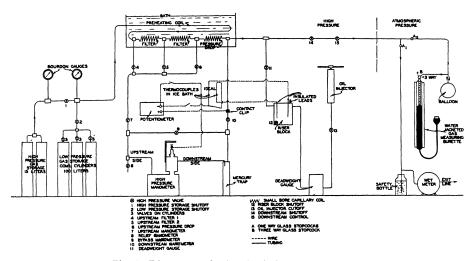


Fig. 1. Diagrammatic sketch of viscosity apparatus.

correct the gas density for the water vapor present since its concentration was very low as has been shown by Bartlett.<sup>19</sup>

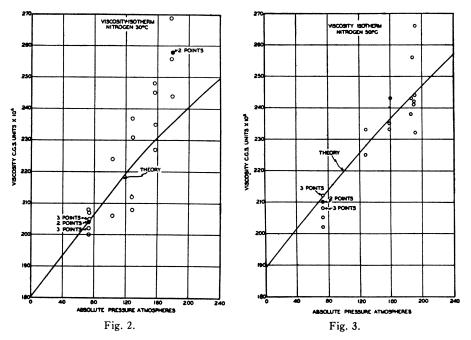
The transpiration rate was determined by expanding the compressed gas and passing it into an exhausted rubber balloon for an observed time interval measured with a calibrated, split-second stop watch. The gas was then drawn into a water jacketed burette and measured at known temperature and pressure. From these data and the gas composition the transpiration rate was calculated.

The gas mixture was made up in a small holder, allowed to stand for several hours, compressed and then analyzed. The same method of compression was used for the pure gases to obtain pressures exceeding 150 atmospheres.

- <sup>17</sup> Keyes, and Dewey, J. Opt. Soc. Am. and Rev. Sci. Instr. 14, 491 (1927).
- <sup>18</sup> Bartlett, J.A.C.S. 49, 687 (1927); 49, 1955 (1927).
- <sup>19</sup> Bartlett, Cupples and Tremearne, J.A.C.S. 50, 1275 (1928).

The apparatus is shown diagrammatically in Fig. 1. The gas flowed from the storage cylinders through a preheating coil of relatively large capillary tubing and then through two fine steel capillaries employed as dust filters before entering the pressure drop capillary. These capillaries were all immersed in the bath. On leaving the pressure-drop capillary the gas passed through a needle control valve and was reduced to atmospheric pressure. Care was taken that steady viscous flow was maintained during experiments.

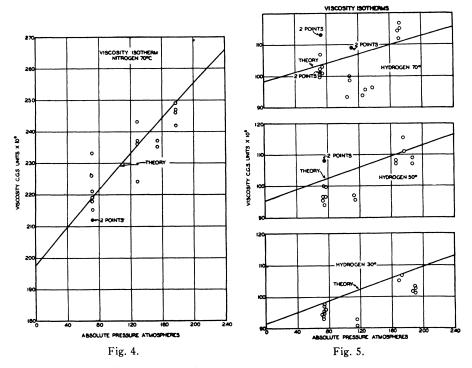
The capillary constant  $k_c$  was determined by low pressure transpiration experiments which were calculated by Eq. (5) inspection of which shows that  $(p_1^2 - p_2^2)/M$  is linear in M. Actually Eq. (5) ignores the effect of the acceleration of the gas in the capillary but since the data plotted by the



above method were linear the value of  $k_c$  was readily calculated on obtaining the intercept by extrapolation to zero gas flow. A very satisfactory check was given by an alternative method based on the determination of the volume of the capillary. This latter procedure required the weight, length and average external diameter of the tubing and further necessitated the determination of the density of the steel in the tubing. From these data  $k_c$ was calculated. The excellent agreement of the results obtained by these two separate methods gave great confidence in the validity of the transpiration method for this calibration. The distention of the capillary by changes in temperature and pressure which, if appreciable, would affect the value of the constant, was found to be negligible for the ranges of temperature and pressure employed here. A supplementary transpiration calibration for  $k_c$ 

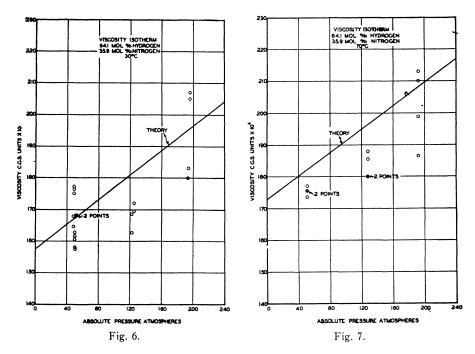
was required because of a very slight rusting of the interior walls of the capillary. This rusting was due to the condensation of small amounts of water vapor from the compressed gas which occurred on increasing the pressure in the capillary above that in the supply cylinder from which the gas was drawn. This was avoided in subsequent experiments by performing them in the order of their descending pressures. After establishing this procedure check transpiration calibration experiments showed the value of  $k_c$  to be unchanged.

The constant  $k_c$  was determined by means of high pressure transpiration experiments which were calculated with Eq. (4) which is linear in  $\Delta p \cdot \rho/M$ versus M. The slope of such a plot gave the value of  $k_c$ . Here the use of



Eq. (4) simplified the calculations and was valid because at high pressures the gas density was substantially constant throughout the apparatus. This constancy of the density required that the linear velocity of flow in the capillary also be constant, and thus the acceleration effect previously mentioned was eliminated in the high pressure experiments. Experiments with nitrogen were made proving that the constant is independent of the temperature and pressure ranges covered here. Further experiments with hydrogen checked the value so determined and showed it to be independent of the gas employed. The magnitude of  $k_e$  exceeds that predicted from theory but this is believed due to a divergence between the actual experimental conditions and those postulated in the theoretical derivations. In any case this does not invalidate the results reported here.

In the high pressure experiments the system was brought under pressure by permitting the gas to flow through the capillaries to the *downstream* side of the differential manometer, under the mercury seal and into the upstream side. When the pressure was equalized throughout the system the by-pass valve and then the upstream valve were opened. The zero reading was then made after which the screw rod was run up the riser well to a point above the approximate mercury level expected in the experiment. Gas flow at the desired rate was obtained with the downstream control valve. The by-pass valve was then closed and twenty minutes allowed to insure a steady flow



before manometer readings were taken. In each case the mercury approached its equilibrium position from below thus tending to introduce a compensation of errors. The gas was then passed into the balloon during an observed time interval after which manometer readings were again made and the average of the initial and final readings was taken for computation. The pressure was next measured by means of the dead weight piston gauge. The bath temperatures were noted during each experiment. The volume of the gas in the balloon was then determined at atmospheric pressure and room temperature. These data permitted the calculation of the viscosity coefficients.

# III. EXFERIMENTAL RESULTS

Viscosity coefficients for nitrogen and hydrogen were obtained at  $30^{\circ}$ ,  $50^{\circ}$  and  $70^{\circ}$ C for pressures from 75 to 180 atmospheres. Similar data were obtained for a mixture containing 64.1 mol percent of hydrogen and 35.9

	30°C	50	)°C	70	)°C
Absolut	e Viscosity	Absolute	Viscosity	Absolute	Viscosity
Pressure		Pressure	c.g.s. units	Pressure	c.g.s. units
Atm.	$ imes 10^6$	Atm.	×10 <sup>6</sup>	Atm.	×10 <sup>6</sup>
178.8	258	191.0	232	176.9	246
178.8	244	191.0	266	176.9	242
177.6	258	189.8	242	176.9	247
177.6	256	189.8	244	176.9	249
176.9	269	188.0	241	154.1	237
176.9	276	188.0	256	154.1	235
156.8	235	185.5	238	127.5	224
156.8	227	185.5	243	127.5	236
156.2	245	158.7	243	126.7	243
156.2	248	158.5	235	126.7	237
128.4	231	158.5	233	71.5	219
128.4	237	128.4	225	71.5	221
128.4	208	128.4	233	71.5	215
128.4	212	73.2	208	71.5	212
103.6	224	73.2	212	71.5	218
103.6	206	73.0	210	71.5	212
74.3	207	72.9	212	70.4	226
74.1	205	72.7	205	70.4	233
73.7	202	72.7	208		
73.5	200	72.4	208		
73.5	202	72.4	210		
73.5	204	72.1	212		
73.5	205	72.1	203		
73.5	205				
73.3	204				
73.0	208				
73.0	202				

TABLE I. Viscosity data, nitrogen.

TABLE II. Viscosity data, hydrogen.

30	°C	50	°C	70	°C
Absolute	Viscosity	Absolute	Viscosity	Absolute	Viscosity
Pressure	c.g.s. unit	Pressure	c.g.s. units	Pressure	c.g.s. units
Atm.	$ imes 10^6$	Atm.	$ imes 10^6$	Atm.	×10 <sup>6</sup>
191.7	102.5	186.8	107.0	173.4	115.0
191.7	101.2	186.8	109.0	172.8	116.8
189.8	103.4	176.1	111.0	172.1	112.7
188.0	101.6	175.5	115.6	171.7	115.8
172.8	106.2	165.7	107.7	138.5	98.4
169.1	105.2	164.8	107.8	128.7	96.7
116.3	92.8	113.8	95.7	125.6	94.8
115.9	90.8	113.2	96.8	112.5	109.0
104.0	98.7	76.9	99.7	112.1	109.0
103.3	102.0	76.7	96.7	108.7	100.0
74.7	95.8	75.7	108.0	107.6	98.8
74.2	97.7	75.7	108.0	105.8	93.5
74.0	95.6	75.0	94.2	74.7	103.0
73.6	94.8	75.0	100.0	74.6	101.0
73.6	97.6	73.5	96.6	73.7	113.7
73.6	94.6	73.4	95.5	73.5	113.7
73.5	93.0			72.7	101.3
73.3	94.7			72.7	101.4
				72.0	102.4
				71.7	107.0
				71.5	101.6
				71.2	99.5

30°	С	70°	С
Absolute	Viscosity	Absolute	Viscosity
Pressure	c.g.s. units	Pressure	c.g.s. units
Atm.	×10 <sup>6</sup>	Atm.	×10 <sup>6</sup>
195.9	205	192.4	187
195.9	207	192.4	199
194.4	183	192.1	210
194.4	180	192.1	213
124.9	172	128.4	188
124.9	170	128.4	180
122.2	163	127.8	186
122.2	168	127.8	180
50.4	168	51.0	176
50.4	168	51.0	173
50.2	163	50.7	175
50.2	161	50.7	177
50.1	158		
50.1	158		
49.2	177		
49.2	160		
48.7	175		
48.7	176		
48.0	164		
48.0	168		

TABLE III. Viscosity data. 64.1% Hydrogen—35.9% Nitrogen

mol percent of nitrogen at  $30^{\circ}$  and  $70^{\circ}$ C for a somewhat greater pressure range.

The new viscosity data are presented in Tables I to III and are shown graphically in Figs. 2 to 7 inclusive.

# IV. A NEW VISCOSITY THEORY

In the theory of the equation of state it has been customary to regard the hydrostatic pressure as the net effect of a kinetic (distending) pressure and of a cohesive pressure. The kinetic pressure of a gas is defined as the time rate of the transfer of momentum across an imaginary plane unit surface in the interior of the gas. The viscosity coefficient is, by definition, the time rate of the *net* transfer of momentum in a flowing gas across a similar unit plane when there is a unit velocity gradient normal to the plane surface and normal also to the direction of gas flow. Thus the viscosity and kinetic pressure are similar phenomena whose origin is in the molecular motion and therefore it is logical that the kinetic pressure and the viscosity may be treated by the same analytical method.

Of the quantitative equations of state that of Beattie and Bridgeman<sup>20</sup> has had marked success in reproducing the observed pressures of a number of gases for wide ranges of temperature and pressure. Application of this equation to the computation<sup>21</sup> of the specific heat and Joule-Thomson coefficients of compressed air has shown good agreement between theory and experiment. The derivation of the equation is based on the two main assump-

<sup>&</sup>lt;sup>20</sup> Beattie and Bridgeman, Proc. Am. Acad. Sci. 63, 229 (1928).

<sup>&</sup>lt;sup>21</sup> Bridgeman, Phys. Rev. 34, 527 (1929).

tions that the kinetic and cohesive pressures may be treated separately and that the law of intermolecular force be such that it diminish rapidly with distance.

Their evaluation of the kinetic pressure is of interest here. The kinetic pressure of a perfect gas is calculated on the basis of a rectilinear free path, but the existence of intermolecular forces, as in a real gas, alters the linearity of the free path and increases the molecular migration in the gas interior. H. B. Phillips<sup>22</sup> on general considerations has pointed out this is so regardless of the nature and law of such forces and, further, that this is independent of the size of the molecules. Beattie and Bridgeman employ a slight modification of H. B. Phillips' method of calculating the kinetic pressure of a real gas and obtain

$$P_a = \bar{\rho}RT(1+r) = P_i(1+r) \tag{6}$$

where  $P_a$  and  $P_i$  are the pressures of the actual and ideal gases respectively,  $\bar{p}$  is the density, R the gas constant, T the absolute temperature, and r the fractional increase in the molecular migration relative to an ideal gas owing to the intermolecular forces. Further, r is a function of the density and covolume

$$r = B_0 \bar{\rho} (1 - b\bar{\rho}) \tag{7}$$

where  $B_o$  is the covolume in liters per mol, b a characteristic constant of the gas and the density is in mols per liter. These authors also correct the kinetic pressure to allow for the change in the time of molecular encounter with temperature and the complete expression for the kinetic pressure now is

$$P_a = P_i(1+r)(1-\epsilon) \tag{8}$$

where  $\epsilon$  is the encounter factor and equals  $c\bar{\rho}/T^3$ , c being another characteristic constant of the gas. Eq. (8) is of the form first derived by Lorentz in his calculation of the kinetic pressure.

In adapting this equation to viscosity theory the viscosity coefficients are substituted for the kinetic pressure terms. It is well known that for isothermal pressure changes at low densities the viscosity of a gas is independent of the density. Thus the viscosity of a real gas at low densities is substantially that of a perfect gas,  $\mu_0$ . For high densities the viscosity coefficient of a real gas,  $\mu$ , corresponds to  $P_a$ . In the equation of state the covolume,  $B_o$ , is obtained from compressibility data. Among others, Jeans<sup>23</sup> and Keyes<sup>24</sup> have remarked that the compressibility covolume differs from that obtained from viscosity data. Therefore it is consistent and desirable in a viscosity theory to use the viscosity covolume,  $B_o'$  and further the relative density effect on the viscosity covolume should be the same as for the compressibility covolume and in addition the time of encounter factor

<sup>22</sup> H. B. Phillips, reference 5.

<sup>23</sup> Jeans, The Dynamical Theory of Gases, pp. 282, 326, 4 Ed., University Press, Cambridge, 1925.

should be identical for both the kinetic pressure and viscosity. The viscosity equation is then

$$\mu = \mu_0 (1 + r)(1 - \epsilon).$$
(9)

The constants b and c are the same as before and are derived from comprescibility data. The term  $B_0'$  is evaluated from the relation given by Keyes<sup>25</sup> which on reducing to units employed here is

$$B_{0}' = \left(\frac{3.159 \times 10^{-7} (M_{w}^{1/2})}{D}\right)^{3/2} \tag{10}$$

where  $M_w$  is the molecular weight and D is a constant in Sutherland's equation

$$\mu_0 = \frac{DT^{1/2}}{1 + C/T} \,. \tag{11}$$

The relation cited for the calculation of the viscosity covolume requires that the covolume be independent of the temperature which is true for gases obeying Sutherland's Law.

So far the theory has been implicitly limited to pure gases but as Beattie and Bridgeman's equation of state has been found valid<sup>26</sup> for mixtures the viscosity theory is readily extended to this case also, provided that  $\mu_0$ for the mixture be known. The constants  $B_0'$ , b and c for the mixture are calculated from those for the components by the rule of linear combination, where

$$B_{0'mix} = \Sigma(B_{01}' X_{1})$$
  

$$b_{mix} = \Sigma(b_{1} X_{1})$$
  

$$c_{mix} = \Sigma(c_{1} X_{1}),$$
(12)

and  $X_1$  is the mol fraction of component (1) in the mixture. The viscosity theory is now complete.

The theory derived here is based on the analogous treatment of the kinetic pressure and viscosity of a real gas and uses a viscosity covolume instead of a compressibility covolume which, it is assumed, density changes affect in exactly the same way. The viscosity covolume, <u>Bo</u>', is calculated from the constants in Sutherland's equation and so it is assumed to be independent of the temperature. The time of encounter factor should be the same in the two cases. By a suitable combination of the constants of the components the theory is applicable to mixtures.

# V. DISCUSSION OF RESULTS

Examination of the tabulated results shows that the data prove beyond question that, at high densities, the viscosity of a gas is not independent of

24 Keyes, Z. Phys. Chem. Cohen Fest Band, 709 (1927).

<sup>&</sup>lt;sup>25</sup> Keyes, Chem. Rev. 6, 210 (1929).

<sup>26</sup> Beattie, J. Am. Chem. Soc. 51, 19 (1929).

the density. The maximum relative increase in the viscosity observed for nitrogen is 25 percent, for hydrogen is 10 percent and for the mixture is 20 percent. The increase in viscosity is not as great as might have been expected on the basis of previous work which however is believed to be of gravely questionable validity in view of the neglect of end effects.

The absolute accuracy of the calculated coefficients is not all that could be desired. Errors in the computed values of the viscosity and in the constants,  $k_{e}$  and  $k_{e}$ , are due to errors of observation and the presence of impurities in the gases used. This latter factor is significant in the case of hydrogen as its viscosity at low pressures and its density are both extremely sensitive to traces of impurities. This source of error is not significant for nitrogen and the mixture. The method of calculation is of itself not conducive to accuracy since it involves the taking of differences and so the error in the calculated viscosities is generally greater than that of the observations.

TABLE IV.	Comparison of	theory with	experiment for	nitrogen.
$B_0$ compressibilit	y = 0.05046 Be	attie and B	ridgeman	
$B_0'$ viscosity = 0.0	Ď421*		0	

$B_0'$	viscosity	=0.042
--------	-----------	--------

		30°C		
Pressure	No. of		Viscosity (	Coefficients
Atm.	Experi-		c.g.s. ur	$its \times 10^6$
	mental	Observed	Viscosity	Compr.
	Points	Mean	Covolume	Covolume
1		181*		
73	11	204	204	212
103.6	2	215	214	220
128.4	4	222	222	237
156.8	4 4	240	229	248
176.9	6	260	235	257
		50°C		
1		189.5*		
73	10	209	212	220
128.4	2	229	228	244
158.5	2 3 8	237	236	256
188	8	246	244	267
		70°C		
1		198*		
71.5	8	219.5	219	224
126.7	4	235	236	242
154.1	2	236	243	252
176.9	4	246	249	259

\* Calculated from Sutherland's constants derived by least squares by Dr. F. G. Keves after a critical survey of the literature and transmitted to the author in a private communication. The values of these constants were

	С	$D \times 10^{5}$
Nitrogen	101.3	1.386
Hydrogen	35.8	0.588

The new data afford a test of the theory derived above which is graphically shown in Figs. 2 to 7. The time of encounter factor was neglected in all calculations as for the least favorable case, lowest temperature and highest density, the correction is less than one percent for nitrogen and is much less for hydrogen. Numerical comparison of the mean observed and calculated viscosity coefficients for nitrogen are given in Table IV. Both viscosity and compressibility covolumes were used in computing the viscosities.

In general there is excellent agreement between experiment and theory when the viscosity covolume is used, but with the compressibility covolume there is a progressively greater difference between the observed and calculated values. The evidence is decidedly in favor of the new theory using the viscosity covolume and the three discrepancies between theory and fact are all attributed to experimental error. In the 30° isotherm two thirds of the maximum pressure is attained without introducing a trend in the comparison and the disagreement is attributed to experimental error. The discrepancy in the 70° isotherm occurs at a point where but two experimental values were available so the disagreement here is not regarded as serious.

A numerical comparison for the hydrogen data is not given as the graphical comparison shows reasonably good agreement in view of the sensitivity of the hydrogen density and low pressure viscosity to traces of impurities. The hydrogen data are of a confirmatory nature.

The mixture data are of especial interest in that they are believed to be the first data of this nature and they afford the opportunity of a direct comparison of the linear and Lorentz<sup>27</sup> rules for the calculation of the covolume of a mixture from those of the components. This comparison is particularly significant in view of the appreciable difference in magnitude of the covolumes of the components. The Lorentz rule of combination for a binary mixture is

$$B'_{0\ mix} = B'_{01}X^2 + B'_{012}(1 - X_1)X_1 + B'_{02}(1 - X_1)^2$$
(13)

where  $X_1$  is the mol fraction of component one and

$$B_{012}' = \left[\frac{1}{2}(B_{01}')^{1/3} + \frac{1}{2}(B_{02}')^{1/3}\right]^3 \tag{14}$$

The calculated and observed values are given in Table V. A slight but not significant trend in favor of the Lorentz rule is shown. The highly desirable

TABLE V.	Comparison of the Lorentz and linear rules for mixtures.
	64.1% Hydrogen-35.9% Nitrogen
	30°C

Pressure	No. of	V	iscosity Coeffici c.g.s. units×1	ents 06
Atm.	Exper. Points	Mean Obs.	Calc. Lorentz	Calc. Linear
1		158*		
49.4	8	166.4	167.0	167.3
123.5	4	168.1	181.5	182.0
195.	4	193.1	195.5	196.0
		70°C		
1		173*		
51	4	175.3	181.8	182.0
128	4	183.5	196.7	197.3
192	$\overline{4}$	202	207.9	208.5

\* By interpolation from data of Kleint, Landolt-Bornstein-Roth Tabellen, 5 Ed., Berlin 1923.

27 Lorentz, Wied. Ann. 12, 127, 660 (1881).

simplicity of the linear rule leads to its recommendation here. A plot of the theoretical (using the linear rule) and observed values gives good agreement as shown in Fig. 7.

Further confirmation of the theory is obtained by a recalculation of Wildhagen's<sup>28</sup> data which purport to show a variation of Reynolds' criterion with the pressure. This quantity is defined by the equation

$$M/r\mu = \text{constant} \tag{15}$$

and the variation claimed above is in contradiction with a vast amount of experimental evidence which has shown that the value of the criterion is independent of the fluid employed.

Viscosities were computed with the new viscosity theory and values of Reynolds' criterion recalculated for Wildhagen's data. The results are given in Table VI and yield a constant for Reynold's criterion which is strong evidence in support of the new viscosity theory. The chief source of error in

TABLE VI. Recalculations of Wildhagen's values for Reynold's criterion for compressed air.

Pressure Atm.	40	80	120	160	200
	Value	s of viscosity coe	fficients $\times 10^6$		
Wildhagen			-		
(Mean of $A$ and $B$ )	195	224	235	268	321
Calculated from					
Viscosity Theory	192	205	218	230	242
· · · · · · · · · · · · · · · · · · ·		Reynold's crit	erion		
Wildhagen					
(Mean of $A$ and $B$ )	2000	1835	1910	1763	1526
Calculated from					
Viscosity Theory	2030	2010	2060	2050	2025
	2030	2010	2000	2050	202

Wildhagen's results lies in the neglect of end effects and may attain the order of thirty percent at high densities. The magnitude of the end effects in the cases of Warburg and von Babo<sup>29</sup> and of P. Phillips<sup>30</sup> is not easy to estimate but is believed to be of the order of at least ten per cent on the basis of previous considerations.

The author wishes to acknowledge his appreciation of the financial aid given him by the Research Laboratory of Applied Chemistry and the committee on Graduate Courses and Scholarships of the Massachusetts Institute of Technology. He is particularly grateful to Dr. T. E. Warren for his assistance and to Dr. J. A. Beattie for his many helpful suggestions. Further, the author wishes to thank Drs. W. K. Lewis, F. G. Keyes and P. K. Frolich for their advice and criticism.

<sup>28</sup> Wildhagen, reference 9.

<sup>30</sup> P. Phillips, reference &

<sup>&</sup>lt;sup>29</sup> Warburg and von Babo, reference 7.