# The Viscosity of Dissociated and Undissociated Gases for Temperatures up to 10,000° K.

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Considerable interest is being expressed in the development of relationships for the prediction of the transport properties of gases at high temperatures for use in design calculations by aerodynamicists. Vasilesco (*18*) and Bonilla, Wang, and Weiner (*8*) have measured viscosities at atmospheric pressure for several substances for temperatures up to 1,800°C. with viscometers of the transpiration type. However, accurate viscosity values are often required in missile applications for higher temperatures at which no experimental values are currently available.

Amdur and coworkers (*1* to *5*, *7*) have experimentally measured intermolecular potentials for several substances at high temperatures through molecular beam measurements. Mason and coworkers (*6*, *17*, *19*) have utilized these potentials to calculate collision integrals for a number of substances in their molecular and atomic states for temperatures in the range $1{,}000 < T < 10{,}000$°K. The established collision integrals for this temperature range can be used in conjunction with the dissociation equilibrium constants available in the literature and theoretical relationships for the transport properties of mixtures to establish the viscosity, thermal conductivity, and self-diffusivity of the substance as functions of temperature and pressure. These calculations neglect the effects of ionization which may be prevalent at temperatures above 5,000°K. These theoretical considerations have been utilized in the present study for the development of a generalized method for the prediction of the viscosity of any substance in its molecular or atomic state for temperatures as high as 10,000°K.

## GENERALIZED RELATIONSHIP FOR UNDISSOCIATED GASES

Stiel and Thodos (*16*) have developed a generalized relationship for the prediction of atmospheric viscosity values of nonpolar substances which do not exhibit significant quantum effects for temperatures up to 2,000°K. Through a dimensional analysis approach, they have shown that for these substances the product $\mu^*\xi$ is a unique function of the reduced temperature. Therefore, viscosity values for the inert and diatomic gases in their undissociated states were obtained from the work of Mason et al. (*6*, *17*, *19*), and the resulting values of the viscosity parameter $\mu^*\xi$ were plotted against reduced temperature as shown in Figure 1. The viscosity behavior of these undissociated gases, with the exception of neon and oxygen, in this temperature range is represented with fair accuracy by a single relationship. The deviation of neon cannot be explained by a consideration of quantum effects, since it has been shown by de Boer and Bird (*10*) and by Buckingham (*9*) that these effects are insignificant at these high temperatures, as confirmed by the general agreement of helium and hydrogen. Hartunian and Marrone (*11*) have recently obtained high-temperature viscosity values for oxygen through shock-tube measurements which are consistently higher than those calculated by Yun, Weissman, and Mason (*19*). Since the accuracy of the calculated viscosity values is within only about 10%, the agreement of Figure 1 is considered to be satisfactory. Experimental points of Vasilesco (*18*) and Bonilla, Wang and Weiner (*8*) are also included in Figure 1 and are in general agreement with the resulting curve.

## GENERALIZED RELATIONSHIP FOR COMPLETELY DISSOCIATED GASES

To calculate the viscosity parameter $\xi$ and the reduced temperature of a completely dissociated gas, a hypothetical critical temperature and pressure have to be determined for the atomic species. The method of estimating hypothetical critical constants must be different for substances which exhibit excessive quantum effects than for those which do not.

The only free radical which has excessive quantum effects is monatomic hydrogen. Hirschfelder, Curtiss, and Bird (*12*) point out that "if two hydrogen atoms in 1s states collide with a small amount of kinetic energy, there

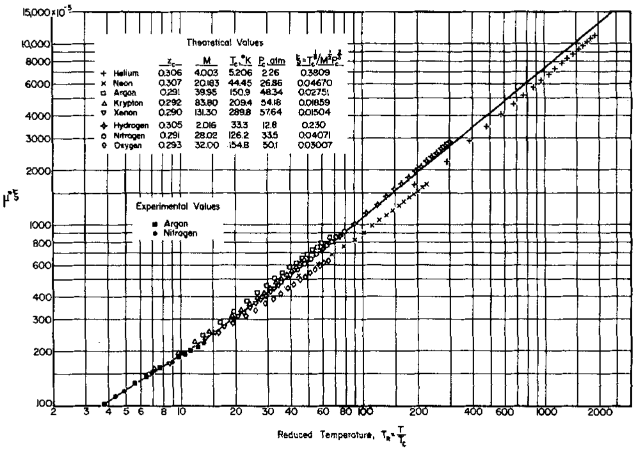

Fig. 1. Relationship between $\mu^*\xi$ and $T_R$ for the inert and diatomic gases in their undissociated states.

is a chance of one in four that they will follow a $^1\Sigma$ energy curve which corresponds to the normal $H_2$ molecule, and there is a chance of three in four that they will follow the $^3\Sigma$ curve which corresponds to the lowest repulsive state of hydrogen. According to this postulation, the following force constants result: $\epsilon/\kappa = 40.45$°K. and $\sigma = 3.125$Å. However, more realistic approximations were made by Margenau (*13, 14*) who used direct first-order perturbation and dispersion energy calculations for the case of a hydrogen atom interacting with a hydrogen molecule. From his data, the following average force constants result for this case:

$$\left(\frac{\epsilon_{12}}{\kappa}\right)_{avg} = 32.27\text{°K.} \quad \text{and} \quad (\sigma_{12})_{avg} = 2.75\text{Å.}$$

From the values of the force constants reported for molecular hydrogen (*12*), $(\epsilon/\kappa)_{22} = 37.3$°K. and $\sigma_{22} = 2.928$Å. From the semiempirical combining rules, $\epsilon_{12} = \sqrt{\epsilon_{11}\,\epsilon_{22}}$ and $\sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22})$, the following force constants for atomic hydrogen were obtained:

$$\left(\frac{\epsilon}{\kappa}\right)_{11} = 27.92\text{°K.} \quad \text{and} \quad \sigma_{11} = 2.572\text{Å.}$$

These values were used to calculate the quantum mechanical parameter for atomic hydrogen, $\Lambda^* = 3.211$. The quantities $T_c^*$ and $P_c^*$ were obtained for atomic hydrogen from plots of $\Lambda^*$ against these quantities presented elsewhere (*12*). From these quantities, the following required values for atomic hydrogen were obtained:

$$T_c = 7.26\text{°K.} \quad \text{and} \quad \xi = 0.9422.$$

Since the atomic species which do not exhibit excessive quantum effects resemble the inert gases in nature, their hypothetical critical temperatures and pressures were determined from the critical constants of the inert gases. For neon, argon, krypton, and xenon, the quantity $\xi$ was plotted against the corresponding atomic weight, $M$, on log-log coordinates as shown in Figure 2. In this figure more stress has been placed on the gases which display lesser quantum effects. The linear relationship of Figure 2 can be expressed analytically as

$$\xi = \frac{0.217}{M^{0.556}} \tag{1}$$

This equation permits the establishment of $\xi$ for a completely dissociated species from its atomic weight.

To establish hypothetical critical temperatures for the atomic substances, the critical temperatures of the inert gases were plotted against their corresponding critical pressures as shown in Figure 3. A single curve was obtained which can be expressed analytically as

$$T_c^{0.15} = 1.238 + 0.0183\,P_c \tag{2}$$

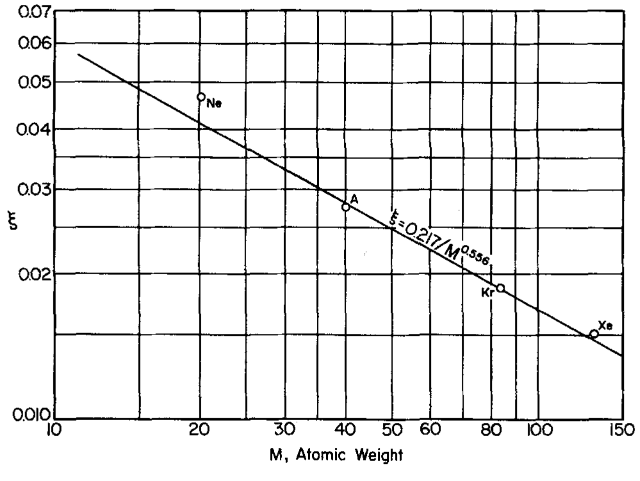

Fig. 2. Relationship between ξ and atomic weight for the inert gases.

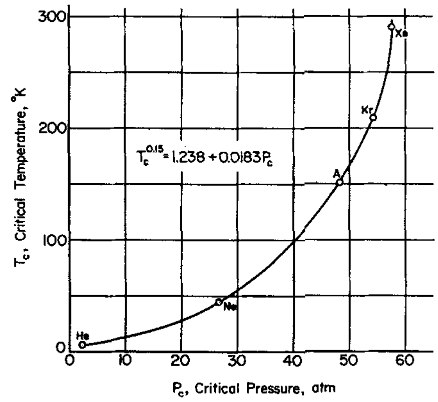

Fig. 3. Relationship between critical temperature and critical pressure for the inert gases.

From Equations (1) and (2), the critical temperatures of atomic species can be calculated.

In this manner, the hypothetical critical temperature and viscosity parameter $\xi$ of atomic nitrogen and oxygen were determined:

| | $T_c$, °K. | $\xi$ |
|---|---|---|
| Nitrogen, N | 75.0 | 0.0500 |
| Oxygen, O | 80.0 | 0.0465 |

By the use of the calculated hypothetical critical temperatures and viscosity parameters, values of $\mu^*\xi$ were calculated from the reported viscosities of atomic nitrogen, oxygen, and hydrogen (*17, 19*) and were plotted against the corresponding reduced temperatures, as shown in Figure 4. It can be seen from this figure that essentially the same relationship resulted for these three substances and is virtually identical with that presented in Figure 1 for the undissociated gases. This behavior results from the fact that both the molecular and atomic species follow the same type of force law.

## CALCULATION OF VISCOSITIES OF PARTIALLY DISSOCIATED SUBSTANCES

To calculate viscosity values of dissociated gases at high temperatures, the equilibrium composition of the molecular and atomic mixture must be known. For the dissociation reaction of a diatomic gas

$$\frac{1}{2}A_2 \rightleftarrows A \tag{3}$$

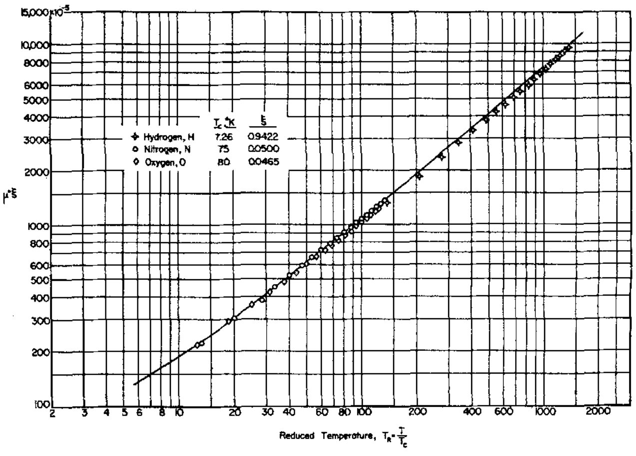

Fig. 4. Relationship between $\mu^*\xi$ and $T_R$ for completely dissociated substances.

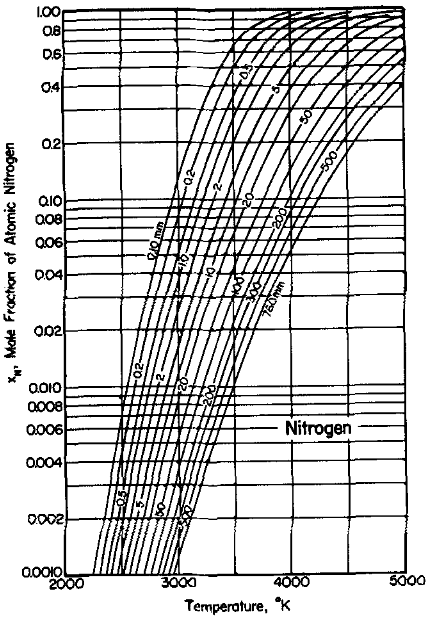

Fig. 5. Isobaric relationships between $x_N$ and temperature for nitrogen at high temperatures.

the equilibrium mole fraction of the atomic species can be calculated from the expression

$$x_A = \frac{2}{1 + \sqrt{\frac{4\pi}{K^2} + 1}} \qquad (4)$$

where $K = p_A/\sqrt{p_{A2}}$ is the equilibrium constant for the dissociation reaction. From the values reported by Rossini et al. (*15*), the equilibrium mole fractions of atomic hydrogen, nitrogen, and oxygen were calculated from Equation (4) for isobars from 0.1 to 760 mm. of mercury and temperatures up to 5,000°K. For nitrogen, the relationships between the equilibrium composition and temperature for constant pressures are presented in Figure 5.

Once the equilibrium composition is established, the viscosity of a partially dissociated gas can be calculated from the corresponding values of $\xi'$ and $T_c'$ for the mixture by the use of the curve of Figure 1. For substances which exhibit quantum effects, the following equations can be used to establish these parameters:

$$\xi' = \frac{(w_A T_{cA} + w_{A2} T_{cA_2})^{1/6}}{(w_A M_A + w_{A2} M_{A2})^{1/2} (w_A P_{cA} + w_{A2} P_{cA_2})^{2/3}} \qquad (5)$$

$$T_c' = w_A T_{cA} + w_{A2} T_{cA_2} \qquad (6)$$

where $w_A$ and $w_{A2}$ represent the weight fraction of the dissociated and undissociated species, respectively.

For hydrogen, viscosities calculated in this manner were compared with the corresponding values determined by Vanderslice et al. (*17*). Typical results for temperatures from 1,000° to 10,000°K. are presented.

| Composition, mole fraction H | $H_2$ | Deviation, % |
|---|---|---|
| 0.20 | 0.80 | 7.60 |
| 0.40 | 0.60 | 7.97 |
| 0.60 | 0.40 | 8.83 |
| 0.80 | 0.20 | 1.12 |

The relatively large deviations for this substance are due to the maxima exhibited for the viscosity values calculated by Vanderslice et al. (*17*), which any approximate method that uses parameters obtained from those of the pure molecular and atomic substances cannot take into account.

For substances which do not exhibit appreciable quantum effects, the following equations can be used to calculate the critical temperatures and $\xi$ values of the partially dissociated gases:

$$\xi' = w_A \xi_A + w_{A2} \xi_{A2} \qquad (7)$$

$$T_c' = w_A T_{cA} + w_{A2} T_{cA2} \qquad (8)$$

Viscosity values for partially dissociated nitrogen and oxygen were calculated from values of the parameters obtained in this manner and were compared with the corresponding values reported by Yun et al. (*19*) for temperatures from 1,000° to 10,000°K.

| N | $N_2$ | Deviation, % |
|---|---|---|
| 0.20 | 0.80 | 0.39 |
| 0.40 | 0.60 | 1.27 |
| 0.60 | 0.40 | 2.17 |
| 0.80 | 0.20 | 2.49 |

| O | $O_2$ | Deviation, % |
|---|---|---|
| 0.20 | 0.80 | −6.60 |
| 0.40 | 0.60 | −2.24 |
| 0.60 | 0.40 | 1.50 |
| 0.80 | 0.20 | 2.40 |

Thus, it can be seen that the method developed in this study is capable of producing reasonably accurate viscosity values for gases at high temperatures.

## NOTATION

$h$ = Planck constant, $6.6254 \times 10^{-27}$ erg-sec.
$K$ = equilibrium constant for dissociation reaction, $p_A/\sqrt{p_{A2}}$, atm.$^{1/2}$
$m$ = mass of molecule or atom, g.
$M$ = molecular or atomic weight
$p_i$ = partial pressure of species $i$
$P_c$ = critical pressure, atm.
$P_c^*$ = normalized critical pressure, $P_c/\frac{\epsilon}{\sigma^3}$
$T$ = temperature, °K.
$T_c$ = critical temperature, °K.
$T_c'$ = pseudocritical temperature, °K.
$T_c^*$ = normalized critical temperature, $T_c/\frac{\epsilon}{\kappa}$
$T_R$ = reduced temperature, $T/T_c$
$w_i$ = weight fraction of species $i$
$x_i$ = mole fraction of species $i$

### Greek Letters

$\epsilon$ = maximum energy of attraction between two particles, ergs
$\kappa$ = Boltzmann constant, $1.3805 \times 10^{-16}$ ergs/°K.
$\Lambda^*$ = quantum mechanical parameter, $h/\sigma\sqrt{m\epsilon}$
$\mu^*$ = viscosity of gas at atmospheric pressure, centipoises
$\xi$ = viscosity parameter, $T_c^{1/6}/M^{1/2}P_c^{2/3}$
$\xi'$ = pseudoviscosity parameter
$\pi$ = pressure, atm.
$\sigma$ = collision diameter, A.

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# Filtration Behavior of a Mixture of Two Slurries

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## HYDRAULIC PRESSURE AND POROSITY VARIATION

It has long been known that filter cakes are not deposited with uniform porosity. The layers near the medium are compact and dry, and the surface is wet and soupy, indications that the porosity is a minimum at the medium and increases as the cake surface is approached. It has also been known that the hydraulic pressure variation is not linear with distance. In the past ten years attention has been increasingly focused on these effects in relation to various models and theories proposed with respect to the internal nature of filter cakes. Basically, as a fluid flows through a compressible solid, a frictional drag develops which causes nonuniform compaction. The porosity $\epsilon_x$ and filtration resistance $\alpha_x$ vary throughout filter cakes, and average values deduced from overall measurements have limited worth. As in the cases of heat exchangers and absorption towers, it is necessary to study local conditions if the fundamental theory is to be elucidated. The Ruth compression-permeability cell (9), combined with apparatus for determining hydraulic pressure distribution described in this paper, affords a basic tool for obtaining data similar to temperature distribution curves in heat transfer apparatus.

When a liquid flows frictionally past the particles in a filter bed, the drag exerted on each particle is communicated to the next particle, and a cumulative effect causes the last layers to be more compact than the first. By means of a force balance (2), the sum of the hydraulic pressure $p_x$ and the solid compressive pressure $p_s$ may be shown to equal the applied filtration pressure in accord with

$$p_x + p_s = p \qquad (1)$$

One of the most important postulates of filtration states that the porosity and filtration resistances, determined under a given mechanical loading $p_s$ in a compression-permeability cell, are the same as the porosity and resistance at a point where the cake compressive pressure equals the mechanical loading in the cell.

Whereas $p_s$ is measured directly in the compression-permeability cell, it can be calculated only indirectly in the filter cake by means of Equation (1) with the directly measurable quantities $p$ and $p_x$. The compression permeability cell essentially consists of a cake contained between two rigid porous plates. After application of any desired cake pressure $p_s$ to the movable upper plate, the solid is allowed to reach an equilibrium porosity; liquid is then permitted to flow through the bed under a low head so that the permeability or filtration resistance can be determined. At some point in the solid, the liquid pressure has dropped from the applied pressure $p$ to a local value of $p_x$.

In accordance with the force-balance equation, the cake pressure $p_s$ may be calculated by means of $p_s = p - p_x$. At this point $\alpha_x$ and $\epsilon_x$ are assumed to be the same in the filter cake and compression-permeability cell. When porosity is measured in a cell, a definite period of time ranging from a few minutes to several hours (5 to 20 min. being common) is required to reach equilibrium. If the filtration is performed under the conditions of rapid cake buildup, sudden change of pressure or rate, or oscillation