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Citation: *The Journal of Chemical Physics* **17**, 1076 (1949); doi: 10.1063/1.1747115

View online: <http://dx.doi.org/10.1063/1.1747115>

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The Theory of Flame Propagation*

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(Received March 16, 1949)

The characteristics of steady-state one-dimensional flames are expressed in terms of a set of first-order ordinary differential equations suitable for solution by differential analyzers or high speed digital computing devices. Arbitrary systems of chemical kinetics and reaction rates can be investigated. The effect of ambient temperature, pressure, heat transfer from the flame to the flame holder, diffusion of free radicals, thermal conductivity, etc., are easily estimated. The equations which we use are the ordinary hydrodynamic equations of change generalized to include the effect of the chemical reactions. In these the usual expressions for reaction rates are introduced, that is, the rate at which the

composition would change in a closed vessel under the local conditions of temperature and density. Equations expressing the diffusion velocities in terms of the composition gradients are given. The flame holder has been idealized in the form of a porous plug through which the fuel can pass freely from left to right, but a semipermeable membrane prevents the product gases moving in the opposite direction. It is found that heat transfer to this flame holder is required to stabilize the position of the flame. The conditions obtained at the hot boundary are expressed parametrically in terms of the roots of a secular equation.

THE hydrodynamic equations are generalized to include diffusion and chemical kinetics. These equations must govern all flame phenomena including steady-state flames, ignition, and detonation. In this paper, we give detailed consideration to the equations describing the steady-state propagation of one-dimensional flames. These equations are reduced to a form suitable for solution by high speed digital computing devices. Because of diffusion, heat transfer, and the finite rate of chemical reactions, it is difficult to define the initial conditions of a flame. On this account it is necessary to introduce a mathematical idealization of a flame holder. The amount of heat absorbed by the flame holder determines the quenching distance and probably affects the stability. At the hot boundary there is a mathematical indeterminacy which can be removed by the use of L'Hospital's rule. The flame velocity is a characteristic of the equations solved in conjunction with the specified boundary conditions.

The following relations must be solved simultaneously: (1) Equation of state, (2) equation of motion, (3) equation for the conservation of energy, (4) one equation of continuity for each chemical component. The chemical kinetics appear only in the equations of continuity. In the general case, except for the equation of state, these relations are partial differential equations involving three space coordinates and time. The general equations are given in the Appendix A.

In this paper we consider the simpler case of a steady-state one-dimensional flame. Under these conditions all time derivatives vanish and since only one space coordinate is important, the equations become ordinary differential equations. The velocity of the gas on the cold side of the flame is the flame velocity. The physical conditions at the hot and cold boundaries can be satisfied only with a single flame velocity or a single mass rate flow. By imposing these requirements on the solution of the set of equations, one obtains a theoretical value of

the flame velocity. Because the flame velocities are always small compared to the velocity of sound, the pressure drop across a flame is negligibly small.¹ For this reason we can assume that the pressure remains constant, ignore the equation of motion and simplify the remaining equations.

1. THE EQUATIONS OF CONTINUITY

The velocity with which component i is flowing is $v + V_i$, where v is the mass average rate of flow and V_i is diffusion velocity of i . From the definition of v it is clear that

$$\sum_i n_i m_i V_i = 0, \quad (1)$$

where n_i is the concentration of component i (moles per cm³) and m_i is the molecular weight. We let K_i be the rate of production by chemical reaction of molecules of i (moles/cm³ sec.). This is the same rate of the chemical reaction which would apply in a static reaction vessel under the local conditions of temperature and composition. The form of the dependence of K_i on temperature and composition depends upon the assumed kinetics of the reactions involved. This point will be discussed further in Section 4. In terms of these quantities the equations of continuity can be written

$$(d/dx)[n_i(v + V_i)] = K_i. \quad (2)$$

One rather simple result can be obtained immediately. Since mass is neither created nor destroyed by the chemical reactions, the K_i satisfy the relation

$$\sum_i m_i K_i = 0. \quad (3)$$

Multiplying each Eq. (2) by m_i , adding, and making use of Eqs. (1) and (3), we find

$$(d/dx)(\rho v) = 0, \quad (4)$$

* This work was carried out under Navy Bureau of Ordnance Contract NOrd 9938.

¹ See Appendix B.

where ρ is the gas density defined by

$$\rho = \sum_i n_i m_i. \quad (5)$$

This is the over-all equation of continuity and integrates immediately to give

$$\rho v = M \text{ (a constant)}. \quad (6)$$

The constant of integration, M , is the mass rate of flow (g/cm² sec.). The solution of the set of flame equations will satisfy the physically required boundary conditions for only one value of M .

2. THE ENERGY BALANCE EQUATION

Let H_i be the enthalpy (internal energy plus RT) per mole of component i ; let q be the total heat flux due to both thermal conductivity and to the transport of energy by diffusion; and let p be the pressure. The energy balance equation can then be written,²

$$\frac{d}{dx} \left[\left(\sum_i n_i v H_i \right) - p v \right] + \frac{dq}{dx} + p \frac{dv}{dx} = 0. \quad (7)$$

Since we assume that the pressure variation is negligible, this equation is integrable. The constant of integration is evaluated from the conditions at the hot boundary of flame ($x = +\infty$), where q is zero. Letting the subscript m refer to conditions at the hot boundary, and replacing v by M/ρ , we obtain

$$\frac{q}{M} = \left[\sum_i \frac{n_i H_i}{\rho} \right]_m - \left[\sum_i \frac{n_i H_i}{\rho} \right]. \quad (8)$$

But q can also be expressed in terms of the heat flux due to thermal conductivity and that due to the energy transport by diffusion.

$$q = -\lambda \frac{dT}{dx} + \sum_i n_i H_i V_i. \quad (9)$$

Eliminating q from Eq. (8) we have the energy balance equation,

$$\frac{\lambda}{M} \frac{dT}{dx} = \sum_i \frac{n_i H_i}{\rho} \left(1 - \frac{V_i}{M} \right) - \left[\sum_i \frac{n_i H_i}{\rho} \right]_m. \quad (10)$$

3. THE DIFFUSION VELOCITIES

The problem is not completely formulated until an expression for the diffusion velocities is given. In a previous paper,³ we obtained an expression for the diffusion velocities,

$$V_i = -\frac{n^2}{\rho n_i} \sum_j m_j D_{ij} \frac{d}{dx} \left(\frac{n_j}{n} \right), \quad (11)$$

² Here we ignore a small viscosity term which remains even in the one-dimensional case. See Appendix A.

³ C. F. Curtiss and J. O. Hirschfelder, J. Chem. Phys. 17, 550 (1949).

where (assuming the equation of state for a perfect gas)

$$n = \sum_i n_i = p/RT \quad (12)$$

is the total number of moles per cm.³ The D_{ij} are not the usual diffusion constants for binary mixtures, \mathfrak{D}_{ij} , but they can be written in terms of the \mathfrak{D}_{ij} and the composition.

The expression (11) for the diffusion velocities is too complicated for the present application. Instead we use the approximate form³

$$V_i = -\frac{n}{n_i} D_i \frac{d}{dx} \left(\frac{n_i}{n} \right), \quad (13)$$

where the D_i are given by

$$D_i = \left(1 - \frac{n_i m_i}{\rho} \right) / \sum_{j \neq i} \frac{n_j}{n \mathfrak{D}_{ij}}. \quad (14)$$

Equation (13) is exact in the case of binary mixtures and gives the correct diffusion velocity of any component of a general mixture which is present as a trace. In other cases it is still a good approximation. Inasmuch as it is the diffusion of active particles, such as atoms and free radicals, which are present in small quantities, that is important in the mechanism of flame propagation it seems reasonable to use the approximate form of the diffusion equation.⁴

4. THE WORKING EQUATIONS

At this point we have derived all of the basic relations: a set of continuity equations, the energy balance equation, and a set of diffusion velocity equations. From these equations one obtains the composition, temperature, and rate of diffusion of each component as a function of distance throughout the flame. These equations can be written in a somewhat simpler form by the introduction of new variables. As the composition variables we use the mole fraction of each component

$$y_i = n_i/n. \quad (15)$$

It is convenient to express the diffusion velocities in terms of a quantity I_i which is the rate of flow of component i in moles divided by the total mass rate of flow,

$$I_i = n_i(v + V_i)/M. \quad (16)$$

This gives

$$V_i = (M I_i / n y_i) - v. \quad (17)$$

In terms of the new variables the equations of continuity, Eqs. 2, become

$$M(d/dx) I_i = K_i. \quad (18)$$

⁴ Because of the conditions imposed upon the V_i by Eq. (1) one should be careful not to use the entire possible set of D_i , i.e., the last one is left as undetermined so that Eq. (1) may be satisfied automatically. This does not cause any difficulties in the subsequent development.

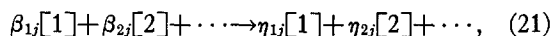
The diffusion velocity equations, Eqs. (13), become

$$\frac{dy_i}{dx} = \frac{M}{nD_i} \left[\frac{ny_i}{\rho} - I_i \right]. \quad (19)$$

The energy balance equation, Eq. (10), becomes

$$-\frac{\lambda}{M} \frac{dT}{dx} = \sum_i H_i I_i - \left[\sum_i \frac{n}{\rho} H_i y_i \right]_m. \quad (20)$$

The function K_i appearing in Eq. (18) is the rate of production of molecules of component i due to chemical reaction. The mechanism of the reactions occurring in the flame can be described in terms of a set of chemical reactions describing the actual processes. Each of these can be written in the form



the β_{ij} and η_{ij} being integers and the $[i]$ indicating species i . In general, a particular species will occur only on one side of the equation so that many of the β_{ij} and η_{ij} are zero. The rate of such a reaction can be written in the form

$$k_j(T) n_1^{\beta_{1j}} n_2^{\beta_{2j}} \cdots \quad (22)$$

But since $n = p/RT$ is a function only of T we can also write the rate in the form

$$f_j(T) y_1^{\beta_{1j}} y_2^{\beta_{2j}} \cdots, \quad (23)$$

where

$$f_j(T) = k_j(T) n^{\sum \beta_{ij}}. \quad (24)$$

The rate at which species i is produced (or reacts) due to this particular reaction is

$$(\eta_{ij} - \beta_{ij}) f_j(T) y_1^{\beta_{1j}} y_2^{\beta_{2j}} \cdots, \quad (25)$$

and consequently the total rate of production of component i by chemical reaction is

$$K_i = \sum_j (\eta_{ij} - \beta_{ij}) f_j(T) y_1^{\beta_{1j}} y_2^{\beta_{2j}} \cdots \quad (26)$$

If the system consists of g different atomic species then there are g linear relations among the K_i which lead to g linear relations among I_i . These relations are due to the fact that the total amount of each element present is conserved in a chemical reaction. Let ν_{ik} be the number of atoms of species k in a molecule of i . Then from Eq. (21) and the conservation of atomic species, k , we have for the reaction, j ,

$$\sum_i \nu_{ik} \beta_{ij} = \sum_i \nu_{ik} \eta_{ij}. \quad (27)$$

Thus multiplying each of Eqs. (26) by ν_{ik} and summing over i , one finds⁵

$$\sum_i \nu_{ik} K_i = 0. \quad (28)$$

Then if we multiply Eq. (18) by ν_{ik} , sum over i , and

integrate, we obtain the g relations

$$\sum_i \nu_{ik} I_i = \alpha_k, \quad k = 1, 2, \cdots, g, \quad (29)$$

where the α_k are integration constants to be fixed by the initial composition of the gas. These relations may be used to reduce the number of I_i variables appearing in any specific problem.

The quantities, f_j , H_i , D_i , λ , and $n = p/RT$, are taken to be known functions of T . Then since ρ is given by Eq. (5) as

$$\rho = n \sum_i m_i y_i, \quad (30)$$

the Eqs. (18), (19), and (20) are sufficient (except for boundary conditions, to be discussed in Section 5) to determine all the y_i , I_i , and T as functions of x . However, it is convenient to reduce the number of equations by one by taking T rather than x as the independent variable. In this way we obtain the working equation:

$$\frac{d}{dT} I_i = \frac{\lambda K_i}{M^2 \left[\sum_i H_i I_i - \left(\sum_i \frac{n}{\rho} H_i y_i \right)_m \right]}, \quad (31)$$

and

$$\frac{dy_i}{dT} = \frac{\lambda \left(\frac{n}{\rho} y_i - I_i \right)}{n D_i \left[\sum_i H_i I_i - \left(\sum_i \frac{n}{\rho} H_i y_i \right)_m \right]}. \quad (32)$$

The characteristics of one-dimensional steady-state flames are determined by the integration of Eqs. (31) and (32) simultaneously. The integrations are started at the hot boundary. The initial conditions are discussed in the following section. The value of M is obtained by requiring that the solution satisfy the physical conditions imposed at the cold boundary. In numerical solutions, one obtains M by a successive trial and error procedure.

5. THE BOUNDARY CONDITIONS

We first discuss the boundary conditions in terms of the original problem, i.e., taking x to be the independent variable. From these conditions we obtain the boundary conditions on the equations in which T is the independent variable. At the hot boundary, indicated by a subscript m , all of the fuel has burned and an equilibrium has been established between the fuel and its combustion products. As x approaches infinity, T , y_i , and I_i approach the finite values T_m , $(y_i)_m$, and $(I_i)_m$ asymptotically. Hence,

$$(dT/dx)_m = 0, \quad (33) \quad (dy_i/dx)_m = 0, \quad (34)$$

and

$$(dI_i/dx)_m = 0, \quad (35)$$

⁵ The relation (3) is of course contained in this set.

and since the diffusion velocity is zero,

$$I_{im} = \left(\frac{n}{\rho} y_i \right)_m. \quad (36)$$

These conditions are sufficient to describe a solution to the set of equations. However, one further condition (at the cold boundary) is physically specified. It is this condition which leads to the fact that a satisfactory solution is obtained for only one value of the parameter M .

Conditions at the cold boundary are somewhat more difficult to describe since it is not physically reasonable to separate the flame from the "flame holder" from which it originates. However, the existence of a flame holder is certainly not compatible with a one-dimensional treatment. Thus it is necessary to introduce a somewhat artificial concept to replace the physical flame holder. We first notice two important properties of the flame equations: first, since the reaction rate expressions give a finite rate at the initial temperature, it is necessary to start the solution at a finite value of x ; and secondly, since the reaction rate is finite, the concentration gradients are finite and molecules of the product tend to diffuse back past this initial point. These two properties are physically rather unimportant, yet they introduce a mathematical problem which must be considered in describing the cold boundary condition. We picture the flame holder as consisting of a semi-permeable membrane; a membrane permeable to the molecules of the fuel gas and inert constituents, but completely impermeable to the product molecules. In this way product molecules are prevented from diffusing back past the initial point. Let the subscript "0" refer to conditions within the mixing chamber or immediately before the membrane, and the subscript "c" to indicate conditions just outside the plug where the flame front really begins. The rate of flow of each component, $n_i(v+V_i)$, is the same on both sides of the membrane. But before the membrane the composition is constant so that the diffusion velocities are zero. Hence,

$$[n_i(v+V_i)]_c = (n_i v)_0, \quad (37)$$

or from the definitions, Eqs. (15) and (16),

$$(I_i)_c = \left(\frac{n}{\rho} y_i \right)_0. \quad (38)$$

It should be noticed from Eq. (16) that

$$\left(\frac{n}{\rho} y_i \right)_c = \left(\frac{n}{\rho} y_i \right)_0 \left/ \left[1 - \frac{V_i \rho}{M} \right] \right., \quad (39)$$

so that the gas on the flame side of the membrane does not have the exact composition of the fuel mixture. The slight jump in the composition variables is due to the semipermeable nature of the membrane. However, the diffusion velocities near the membrane are small com-

pared to the gas velocity so that $V_i \rho / M \ll 1$ and the jumps in the y_i are extremely small.

The flame holder has one further property. It acts as a heat sink. From Eq. (9) we see that the heat flux through the initial point ($-q_0$) is

$$-q_0 = [\lambda(dT/dx)]_0. \quad (40)$$

The value of ($-q_0$) is taken to be a property of the flame holder. The maximum flame temperature, T_m , is then determined from the conservation of energy equation, Eq. (20), where T is set equal to T_0 .

$$-q_0 = \left(\lambda \frac{dT}{dx} \right)_0 = M \left[\left(\sum_i \frac{n}{\rho} H_i y_i \right)_0 - \left(\sum_i \frac{n}{\rho} H_i y_i \right)_m \right]. \quad (41)$$

The composition variables, $(y_i)_0$, and the temperature T_0 are the initial conditions specified by the nature of the problem. The composition at the hot boundary is that characteristic of chemical equilibrium at the temperature T_m . Hence Eq. (41) is an equation for T_m in terms of the $(y_i)_0$, T_0 , and the heat lost to the flame holder ($-q_0$).

Let us consider Eqs. (31) and (32) in which T is the independent variable. The cold boundary condition, Eq. (38), remains unchanged in form. But for the hot boundary conditions in place of Eqs. (33), (34), and (35) we must obtain expressions for all of the dy_i/dT and all of the dI_i/dT . We notice that at T_m all of the K_i are zero since chemical equilibrium has been established. It is then clear that the left sides of both Eqs. (31) and (32) are indeterminate. Thus we must apply L'Hospital's rule, and find that at $T = T_m$,

$$\frac{d}{dT}(I_i) = \frac{1}{M^2 z} \left[A_i + \sum_k J_{ik} \frac{dy_k}{dT} \right], \quad (42)$$

where

$$A_i = \lambda \sum_j (\eta_{ij} - \beta_{ij}) \frac{df_j}{dT} y_1^{\beta_{1j}} y_2^{\beta_{2j}} \dots, \quad (43)$$

$$J_{ik} = \lambda \sum_j (\eta_{ij} - \beta_{ij}) f_j \frac{\beta_{kj}}{y_k} y_1^{\beta_{1j}} y_2^{\beta_{2j}} \dots, \quad (44)$$

and

$$z = \frac{d}{dT} \left[\sum_i H_i I_i - \left(\sum_i \frac{n}{\rho} H_i y_i \right)_m \right], \quad (45)$$

or

$$z = \sum_i \left[I_i \frac{dH_i}{dT} + H_i \frac{d}{dT}(I_i) \right]. \quad (46)$$

It is convenient to consider z to be another variable and to consider the differential equation, Eq. (46), to be an additional equation. We thus obtain a parametric solution. Applying L'Hospital's rule to Eq. (32) we find that

at the hot boundary,

$$\frac{dy_i}{dT} = \frac{\lambda RT}{p D_i z} \left[\frac{d}{dT} \left(\frac{n}{\rho} y_i \right) - \frac{d}{dT} (I_i) \right]. \quad (47)$$

The derivative of I_i can be eliminated between Eqs. (42) and (47). The resulting equation is linear in the dy_j/dT ,

$$\sum_i \left[\left(\frac{n}{\rho} - z b_i \right) M^2 z \delta_{ij} - J_{ij} - \left(\frac{n}{\rho} \right)^2 m_j y_i M^2 z \right] \frac{dy_j}{dT} = A_i, \quad (48)$$

where

$$b_i = \frac{p}{RT} \frac{D_i}{\lambda}. \quad (49)$$

In a similar way we find from Eqs. (42) and (46)

$$\sum_j L_j \frac{dy_j}{dT} = M^2 z^2 - N_0 M^2 z - Q_0, \quad (50)$$

where

$$L_j = \sum_i H_i J_{ij}, \quad (51)$$

$$N_0 = \sum_i (n/\rho) y_i (dH_i/dT), \quad (52)$$

and

$$Q_0 = \sum_i A_i H_i. \quad (53)$$

Equations (48) and (50) form a set which is just sufficient to determine all of the dy_j/dT and z . However, from the definition of the y_j we know that

$$\sum_i (dy_i/dT) = 0. \quad (54)$$

Equation (48) is consistent with Eq. (54).⁶ It is convenient to eliminate one dy_j/dT from Eq. (48) and consider one less equation in the set. A solution may then be made for the remaining dy_j/dT . Let us eliminate dy_1/dT from the set through the relation

$$dy_1/dT = - \sum_{j>1} (dy_j/dT). \quad (54')$$

Thus, from Eq. (48),

$$\sum_{j>1} \left[\left(\frac{n}{\rho} - z b_i \right) M^2 z (\delta_{ij} - \delta_{i1}) - J_{ij} + J_{i1} - \left(\frac{n}{\rho} \right)^2 (m_j - m_1) y_i M^2 z \right] \frac{dy_j}{dT} = A_i. \quad (55)$$

Similarly, from Eq. (50) we obtain

$$\sum_{j>1} (L_j - L_1) dy_j/dT = M^2 z^2 - N_0 M^2 z - Q_0. \quad (56)$$

⁶ Provided the D_i form a constant set. See reference 3.

We use all but one of the set of Eqs. (55) (ignoring $i=1$) and Eq. (56) to determine the dy_j/dT ($j \neq 1$) and z . The equations are linear in the dy_j/dT and hence z can be obtained as the solution of the secular equation

$$|S_{ij}| = 0, \quad (57)$$

where

$$S_{11} = Q_0 + N_0 M^2 - z^2 M^2, \quad (58)$$

$$S_{1j} = L_j - L_1, \quad j = 2, 3, 4 \dots, \quad (59)$$

$$S_{i1} = A_i, \quad i = 2, 3, 4 \dots, \quad (60)$$

and

$$S_{ij} = (J_{ij} - J_{i1})$$

$$+ \left[\frac{n}{\rho} \frac{n}{\rho} - (m_j - m_1) y_i - \delta_{ij} \right] M^2 z + b_i \delta_{ij} z^2 M^2, \quad (61)$$

$$i = 2, 3, 4 \dots,$$

$$j = 2, 3, 4 \dots$$

Having obtained z , we can obtain the dy_j/dT ($j \neq 1$) from Eq. (55) (using $i = 2, 3, 4 \dots$). Then dy_1/dT is obtained from Eq. (54) and all of the dI_i/dT from Eq. (42). In this way we obtain the boundary conditions to be applied in solving the flame equations, Eqs. (31) and (32).

The authors wish to thank W. P. Spaulding, M. L. Henkel and Harry Hummel for help in developing the present theory. At the present time W. P. Spaulding, M. L. Henkel, R. Vandervort, and P. Knaplund are trying to obtain numerical solutions for a few specific examples.

APPENDIX A

In this appendix we give the general hydrodynamic equations of change. The set of flame equations discussed in this paper is a special case of the more general case corresponding to one-dimensional steady-state flow. The equations are:

1. The equations of continuity,

$$(\partial n_i / \partial t) + \nabla \cdot [n_i (v + V_i)] = K_i.$$

2. The equation of conservation of energy,

$$\frac{\partial}{\partial t} \sum_i n_i E_i + \nabla \cdot \left[\sum_i n_i H_i (v + V_i) - \lambda \nabla T \right] = v \cdot \nabla p - \frac{2}{3} \eta (\nabla \cdot v)^2 + 2 \eta \Phi : \nabla v.$$

Here E_i is the internal energy per mole of component i , η is the coefficient of viscosity, Φ is the symmetric tensor,

$$(\Phi_{ij}) = \frac{1}{2} \frac{\partial v_i}{\partial x_j} + \frac{1}{2} \frac{\partial v_j}{\partial x_i},$$

and the $:$ indicates the product of two tensors defined by

$$w : y = \sum_{ij} W_{ij} Y_{ij}.$$

3. The equation of motion,

$$\rho \frac{\partial v}{\partial t} + \rho v \cdot \nabla v = - \nabla \cdot p - \frac{2}{3} \eta (\nabla \cdot v) + 2 \nabla \cdot \eta \Phi.$$

APPENDIX B

In the one-dimensional steady-state case, ignoring viscosity, the equation of continuity becomes

$$\rho v dv/dx = - dp/dx.$$

In this case $\rho v = M$ is a constant and we have, after integration,

$$\rho v^2 = -p + \text{constant}.$$

Indicating the cold side of the flame by subscript "0" and hot side by "m" we have

$$\rho_m v_m^2 - \rho_0 v_0^2 = p_0 - p_m.$$

The velocity of sound in a gas is

$$c = (\gamma p / \rho)^{1/2}.$$

Using this to eliminate the ρ_0 and ρ_m we find

$$\frac{p_m}{p_0} = \frac{1 + \gamma(v_0^2/c_0^2)}{1 + \gamma(v_m^2/c_m^2)}.$$

The ratio of specific heats, γ , is only slightly larger than unity and in the case of ordinary flames the ratio v/c is small. Hence, p_m/p_0 never varies much from unity and we can ignore variations in the pressure throughout the flame.

To amplify this point, let us consider a typical case. A flame velocity of the order of 30 cm/sec. is usual. This is the velocity of the cold gas relative to the flame front. Since the temperature rises by a factor of about 10, the velocity of the hot gases relative to the flame front is about 300 cm/sec. The velocity of sound in gases at ordinary temperatures is about 3×10^4 cm/sec. The velocity of sound goes up as the square root of T and thus in the hot gases c is about 9×10^4 cm/sec. Taking $\gamma = 1.3$ these figures result in

$$p_m/p_0 = 1 + 1.69 \times 10^{-6} - 1.88 \times 10^{-6} = 1 - 1.71 \times 10^{-5}.$$

Thus the pressure drop through a flame at 1 atmos. pressure is about 0.01 mm of mercury.

It should be pointed out that although variations in the pressure are unimportant in this problem, in the case of a real three-dimensional flame the small variations may be important in determining the geometrical shape of the flame front.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 17, NUMBER 11 NOVEMBER, 1949

Self-Diffusion in Argon*

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(Received March 9, 1949)

The self-diffusion coefficient of argon was measured at five different temperatures between -183°C and 53.5°C by observing the diffusion of radioactive A^{41} into normal argon. The decrease in the observed diffusion coefficient caused by the larger mass of A^{41} was deduced and found to be 0.6 percent. The experimental values are compared with several theoretical calculations. In particular, it is shown that use for argon of an inverse power model ($V \propto r^{-\nu}$), with different values of ν ascribed to different temperature ranges, is not permissible since widely different values of ν at the same temperature can be obtained from different experimental data. The experimental figures agree very well with numerical calculations by Hirschfelder, Bird, and Spotz based on an interaction potential of the form $4E[-(r_0/r)^6 + (r_0/r)^{12}]$.

THE rate at which different gases intermingle is usually described by a diffusion coefficient which in general depends on the intermolecular force fields of the diffusing molecules. Enskog and Chapman have derived expressions which relate the value of the diffusion coefficient to these interaction potentials. A knowledge of the values of the coefficients thus enables something to be said about the forces between the diffusing molecules. For this purpose the case of self-diffusion—i.e., all molecules involved being the same—is much the most satisfactory to consider. Only a single type of interaction has to be considered; there is no variation of the coefficient with relative concentration; and the potential function involved, that between like molecules; is usually of greater interest, being also involved in the equation of state and in the coefficients of viscosity and thermal conductivity.

Of course, there is really no such thing as a self-diffusion coefficient for a gas. By definition a self-diffusion coefficient describes the interdiffusion of identical

molecules; but since the molecules are identical there is no way of following the course of the diffusion, and therefore no process actually takes place. Now suppose that the molecules of one of the gases differ only very slightly from those of the other gas—a good example would be molecules having the nucleus of one atom in a metastable state only a little above the ground state. The progress of these molecules through normal molecules could be followed, and if the mass of the molecule containing the metastable nucleus were increased only a very small amount, the diffusion coefficient thus measured could be identified with the self-diffusion coefficient calculated classically on the assumption that the origin of each molecule could be determined at any time.

This paper describes measurements at several temperatures of the diffusion of radioactive A^{41} through ordinary argon, which is more than 99 percent A^{40} . The difference in mass between these two molecules is of course quite appreciable, but the next section shows how the "true" self-diffusion coefficient of either isotope may be deduced from results in a case where the diffusing molecules differ only in mass.

* Part of a dissertation presented to the faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy.

** Assisted in part by the ONR under Contract N6ori-44.