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TRANSPORT OF NOBLE GASES IN GRAPHITES

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ABSTRACT

A model was derived for the diffusion of gases in porous media in the absence of temperature and pressure gradients, in which portions of the medium are visualized as a collection of uniformly distributed "dust" particles (giant molecules) which are constrained to be stationary. Thus, it was possible to derive all the desired results from rigorous diffusion equations for multi-component mixtures. The results apply over the entire pressure range from the Knudsen region to the normal diffusion region. This model permits a satisfactory derivation of the fact that, at all pressures, the flux ratio of two counter-diffusion gases is $(m_2/m_1)^{1/2}$ in porous media under steady state and uniform-pressure conditions.

The effect of non-zero pressure gradients on the diffusion equations is to introduce into the fundamental kinetic theory equations both a pressure diffusion term and an external force term. Somewhat surprisingly, there is a considerable cancellation of terms, and the final diffusion equation has the same form as in the uniform pressure case. No additional parameters beyond those necessary to define a diffusing system at uniform pressure are thus required to compute the diffusion rates when pressure gradients are present. A complete solution requires also a forced flow equation giving J (the net flux) as a function of the pressure gradient. A forced flow equation is derived on the basis of the dusty-gas model, but one parameter must be made disposable in order to compensate for the fact that the model permits only a diffusive mechanism for flow, never a viscous mechanism. A series of experiments with one gas mixture is discussed as well as the possibility of extending the model to include the effects of temperature gradients.

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INTRODUCTION

Studies on the counter diffusion of argon and helium in graphites² have continued with respect to both theory and experimentation. The theoretical studies have advanced from isothermal uniform-pressure conditions to isothermal conditions where the pressure is non-uniform and, more recently, to conditions where the temperature is non-uniform. The experimental work has progressed at a somewhat slower pace than in the past as the experiments are being carried out with low permeability graphites which are slightly more difficult to handle than the highly permeable materials used in the initial experiments. The current experimental work concerns isothermal cases of diffusion in the presence of total-pressure gradients in regions where Knudsen and Poiseuille effects control the forced-flow parts of the problem, while Knudsen and normal effects control the diffusion parts of the problem. These experiments could be of considerable significance since they could lead to modifications of the most recent theory advanced for these combined effects.

Theoretical treatments of superposed flow problems within the Knudsen region are quite simple because, in this region, forced and diffusive phenomena are the same. In the normal region, the superposed theory for capillaries is well understood, and the theory for porous media has been appreciably advanced. The intermediate case, which is very applicable to nuclear reactor problems, remains as the most difficult of all. A good deal of the difficulties stem from the fact that the overall superposed problem must be approached from five different standpoints, two with respect to geometry and three with respect to flow behavior. The

flow phenomena, which have been mentioned before, are: Poiseuille (forced-viscous) flow, Knudsen (forced and/or diffusive) flow, and normal diffusion; the geometrical models are the "bundle of identical capillaries"^{3,4} and a recently devised "dusty-gas" model.⁵ The immediate problem of designing reactor components precludes the luxury of restricting the present studies to a simple geometry-flow mechanism pair. Indeed, in view of a desire for utilization of earlier results to maximum advantage, one must be able to pass freely back and forth between the two geometries and various flow mechanisms in such a way that these different concepts complement, rather than contradict, one another.

FORCED FLOW WITHOUT SEPARATION

To fix ideas, one may give consideration to the forced-flow part of the problem first - in particular to the differences between the viscous flow and diffusive phenomena which are observed when a single gas (or gas mixture which is not allowed to separate) is forced through a porous medium under a total-pressure gradient. Isothermal experiments of this type are generally predicated, both in theory and practice, on the first assumption that flow will be controlled by the viscous mechanism. Thus, Poiseuille's model for a single capillary will be followed. This is a continuum theory, wholly unrelated to the diffusive mechanism, but related to momentum transport via shearing forces. For a capillary, one writes

$$\frac{dp}{dz} = \frac{1}{r} \frac{\partial}{\partial r} \left(\eta r \frac{dv_z}{dr} \right) \quad (1)$$

for linear flow along z (cm). The viscosity of the gas is η (poise); dp/dz (dynes/cm³) is the pressure gradient along z ; dv_z/dr (sec⁻¹) is the rate of change of the mass average velocity along z with respect to the radial direction r (cm). Two integrations of Eq. (1) give the relationship

$$v_z(r) - v_o = \left(\frac{r^2 - r_o^2}{4\eta} \right) \left(\frac{dp}{dz} \right). \quad (2a)$$

The average v with respect to r is:

$$v = v_o - \left(\frac{r_o^2}{8\eta} \right) \left(\frac{dp}{dz} \right). \quad (2b)$$

The constant v_o (cm/sec) at r_o (the capillary wall) turns out to be very important for the case of superposed flow since v_o is utilized to allow for the mass average velocity resulting from diffusive flow when $dp/dz = 0$. It is not at all necessary to take v_o as representative of viscous slip at this point because the latter may be developed in different fashions. Also, the viscous slip depends on dp/dz which is not apparent from Eq. (2b).

With the $v_o = 0$ in Eq. (2b), it is quite easy to write down the analogous equation for porous media by replacing the $r_o^2/8\eta$ term by B where v is now referred to the gross area and length of the medium. For porous media,

$$v = - \frac{B}{\eta} \frac{dp}{dz}. \quad (3a)$$

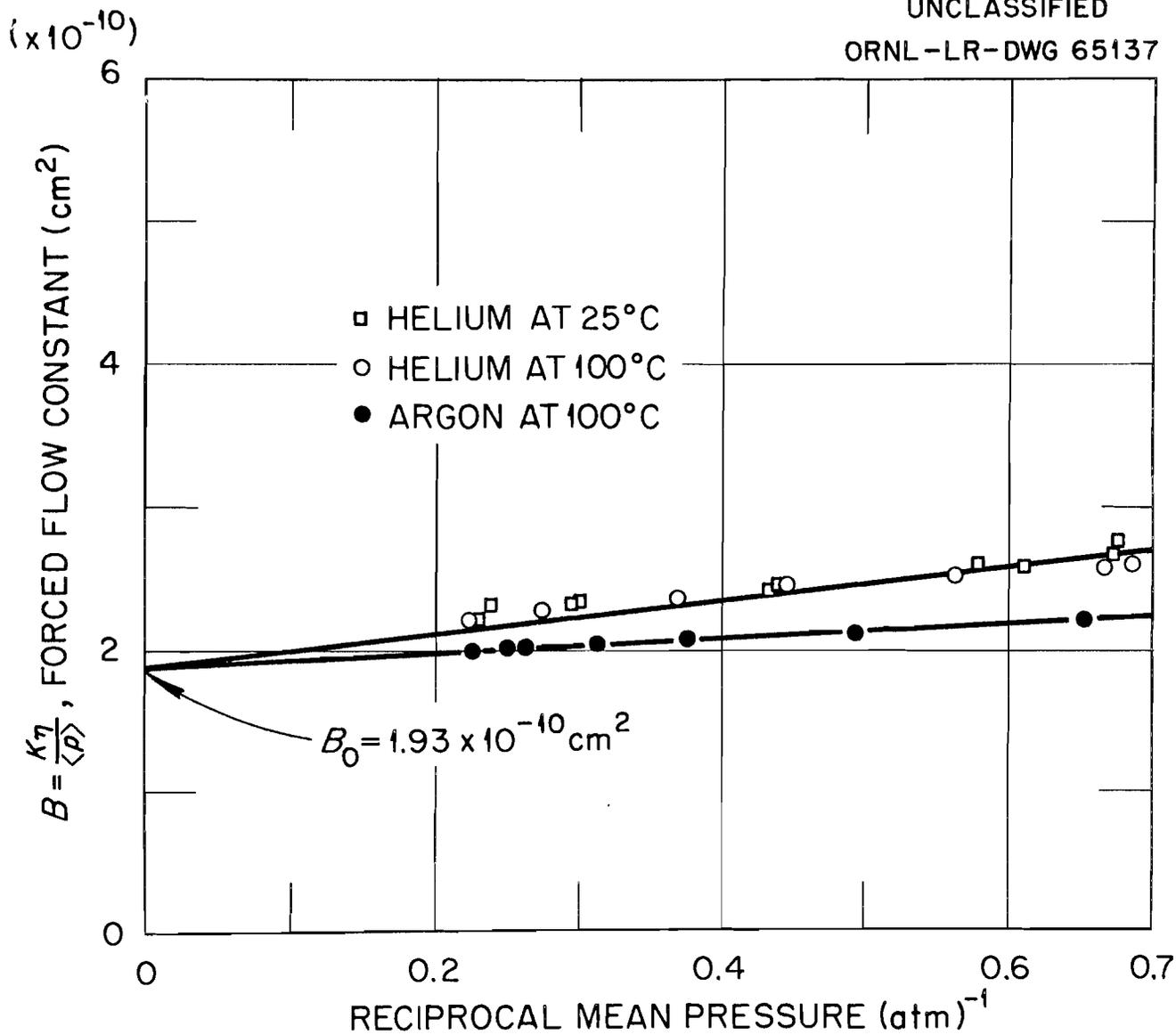
The constant B (cm^2) is $(\epsilon/q)(r_o^2/8\eta)$ where ϵ is the open porosity of the medium and q is the square of the ratio of the average capillary length to the medium length. A bundle of capillaries, all of radius r_o , is envisioned at this point.

In these experiments, the mass average velocity, v , is identical to the particle velocity, $u = J_f/n$, where J_f (atoms/ cm^2sec) is the forced flux, n (atoms/ cm^3) is the gas density given by gas law as p/kT . An expression for isothermal flow may be developed from Eq. (3a) by substitution of $J_f kT/p$ for v and integrating over the length, L (cm). The result is

$$J_f kT = \frac{B \langle p \rangle \Delta p}{\eta L}, \quad (3b)$$

where $\langle p \rangle$ is $1/2 [p(0) + p(L)]$ and Δp is $p(0) - p(L)$.

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High Pressure Permeability Data for Graphite Specimen I.

Fig. 1.

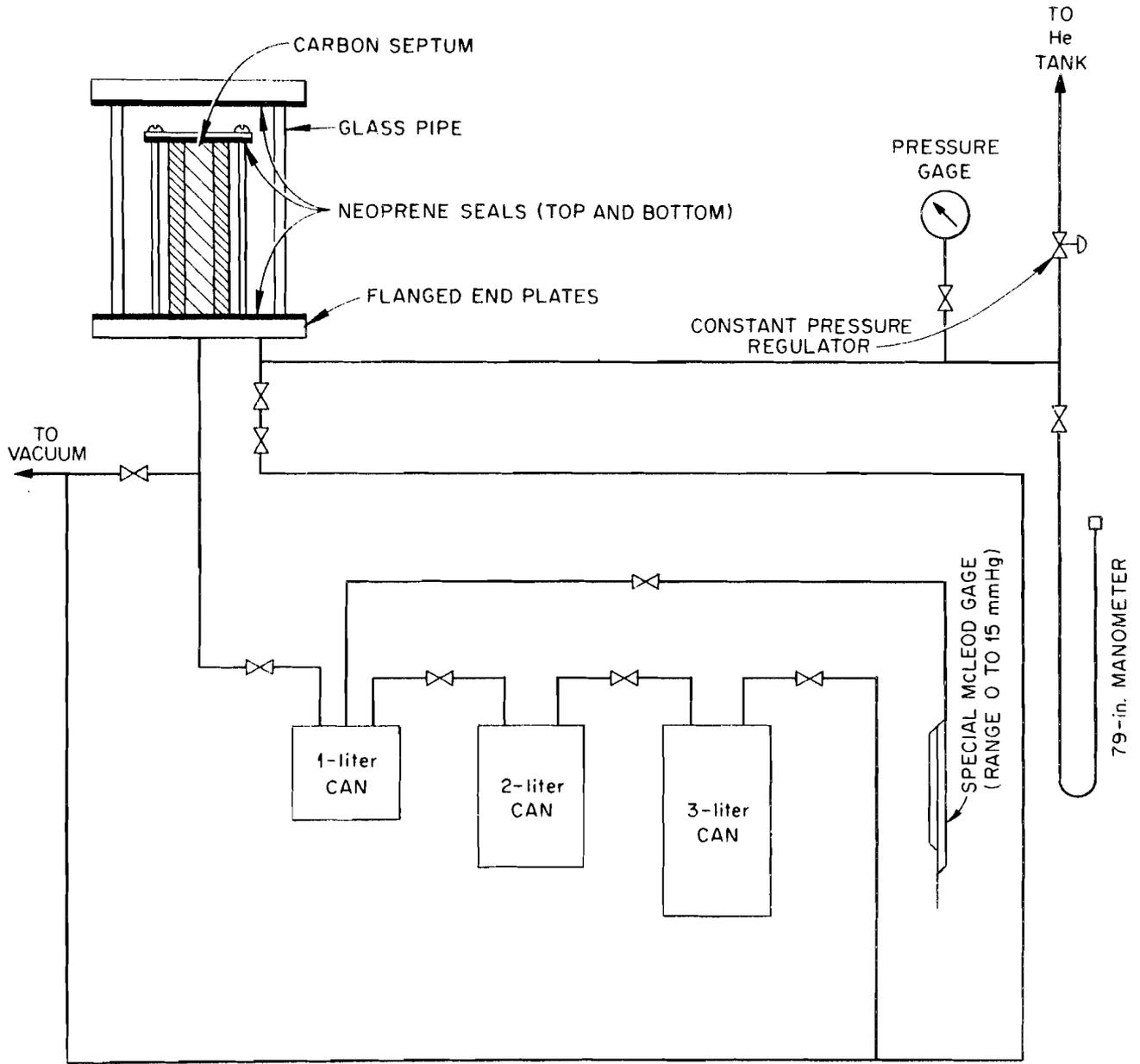


Diagram of Pressure Rise Apparatus for Forced Flow Measurements with Low Permeability Materials.

Fig. 2.

Plots of the experimentally determined B versus $\langle p \rangle^{-1}$ for highly permeable graphites result in nearly horizontal lines (zero slope) as indicated on Fig. 1. Thus Eq. (3b) gives a fair estimate of forced flow behavior of permeable graphites.

Forced-flow experiments with high permeability graphites are carried out with the diffusion apparatus (Fig. 5) with the inlet on one side, and the outlet on the other side, closed. For low permeability graphites, the apparatus indicated on Fig. 2 is utilized because the flow rates are relatively low and important sub-atmospheric experiments can be performed with ease.

Plot of B versus $\langle p \rangle^{-1}$ for low permeability graphites result in curves with considerable slope as shown in Fig. 3. However, the curves are linear, thus $B = B_0 (1 + a/\langle p \rangle)$ and Eq. (3b) may be written as

$$J_f kT = \left(\frac{B_0 \langle p \rangle}{\eta} + \frac{B_0 a}{\eta} \right) \frac{\Delta p}{L} = K \frac{\Delta p}{L}, \quad (4a)$$

where K (cm^2/sec) is a new constant (actually a coefficient) which exhibits a linear relationship with $\langle p \rangle$ as shown in Fig. 4. The K's of Fig. 4 are merely the B's of Fig. 3 multiplied by $\langle p \rangle/\eta$. It turns out that $aB_0/\eta = 4/3 \bar{c} K_0$, where \bar{c} is the mean thermal speed $(8kT/\pi m)^{1/2}$. The parameter K_0 is given by $(\epsilon/q) r_h \phi$; where r_h is the mean hydraulic radius, $\phi = 3\pi/16[(2 - \phi)/\phi]$, ϕ is the fraction of diffusive wall collisions, $1 - \phi$ is the fraction of specular reflections. For a single capillary, $4/3 \bar{c} K_0$ becomes $\pi r_0 \bar{c}/8$, when $\phi = 1$.

For porous media,

$$J_f kT = \left(\frac{B_0 \langle p \rangle}{\eta} + \frac{4}{3} K_0 \bar{c} \right) \frac{\Delta p}{L}. \quad (4b)$$

The $B_0 \langle p \rangle/\eta$ term gives the viscous flux, the $4/3 K_0 \bar{c}$ gives the "diffusive flux", and the sum of the two gives the total flux measured.

A very important piece of information over and above an accurate description of forced flow behavior can be gained through the experimental determination of B_o and K_o . These parameters may be written in terms of r_h , the hydraulic radius, and k_o , a shape factor, as

$$B_o = (\epsilon/q)(m^2/k_o) \quad \text{and} \quad K_o = (\epsilon/q)(\phi)(r_h),$$

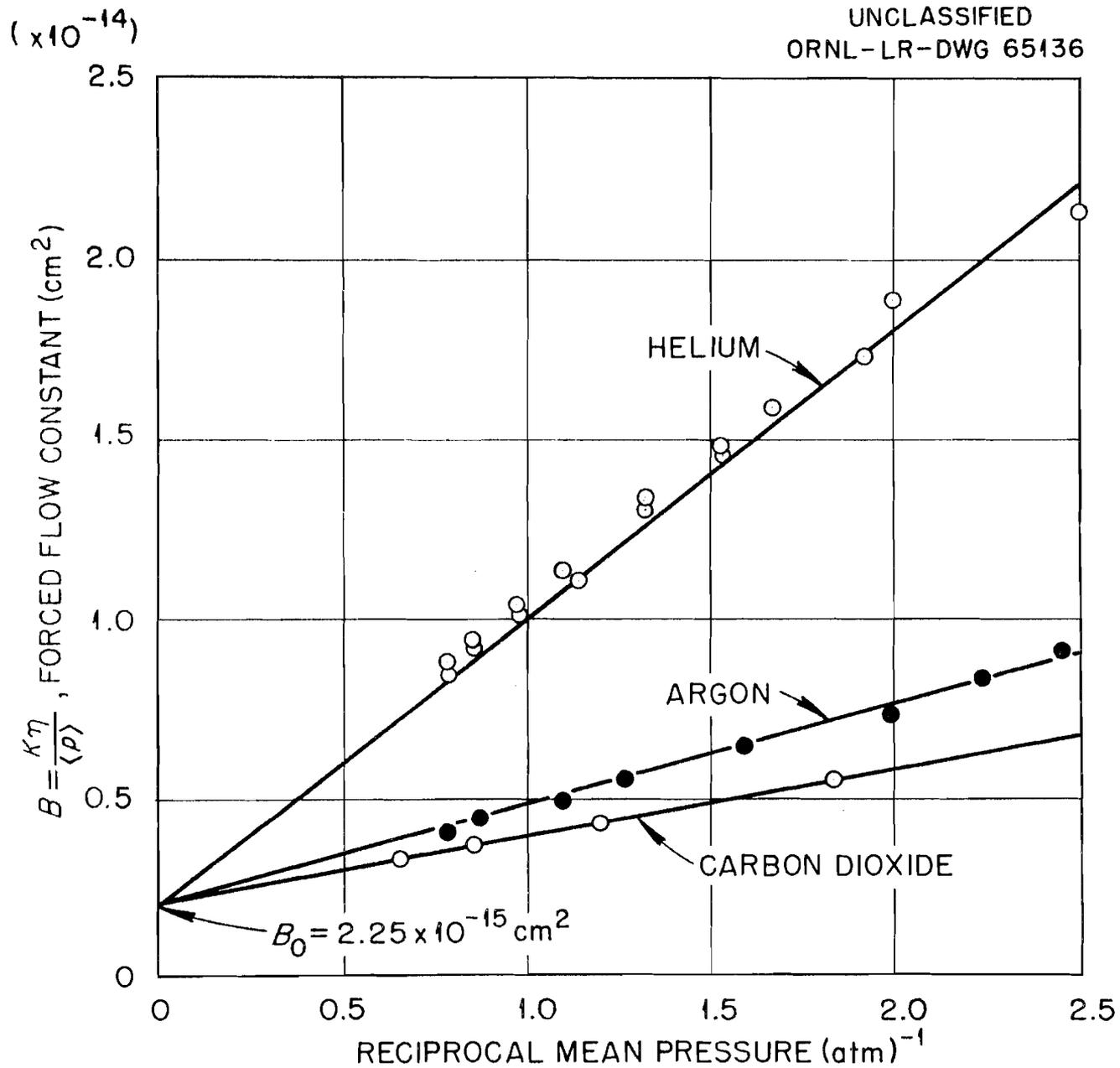
which may be combined to give⁴:

$$\frac{\epsilon}{q} = \frac{(K_o)^2}{(k_o)(B_o)(\phi)^2} \quad (5)$$

According to Eq. (5), ϵ/q (the porosity-tortuosity ratio) can be obtained through permeability data alone if ϕ and k_o are known. It shall be shown later that the D_{12} (cm²/sec) values obtained experimentally (with a given graphite) should be equivalent to the mutual diffusion coefficients, \bar{D}_{12} (cm²/sec), multiplied by the same ϵ/q determined through permeability measurements (with the same piece of graphite). Since \bar{D}_{12} for most of the gas pairs of interest are known, and, furthermore, since the $(4/3)(K_o)(\bar{c})$ term turns out to be the Knudsen diffusion coefficient, all the experimental information required to solve the diffusion and the diffusion plus forced-flow problems might be given, at least approximately, by a series of forced-flow experiments with one gas.

NORMAL DIFFUSION

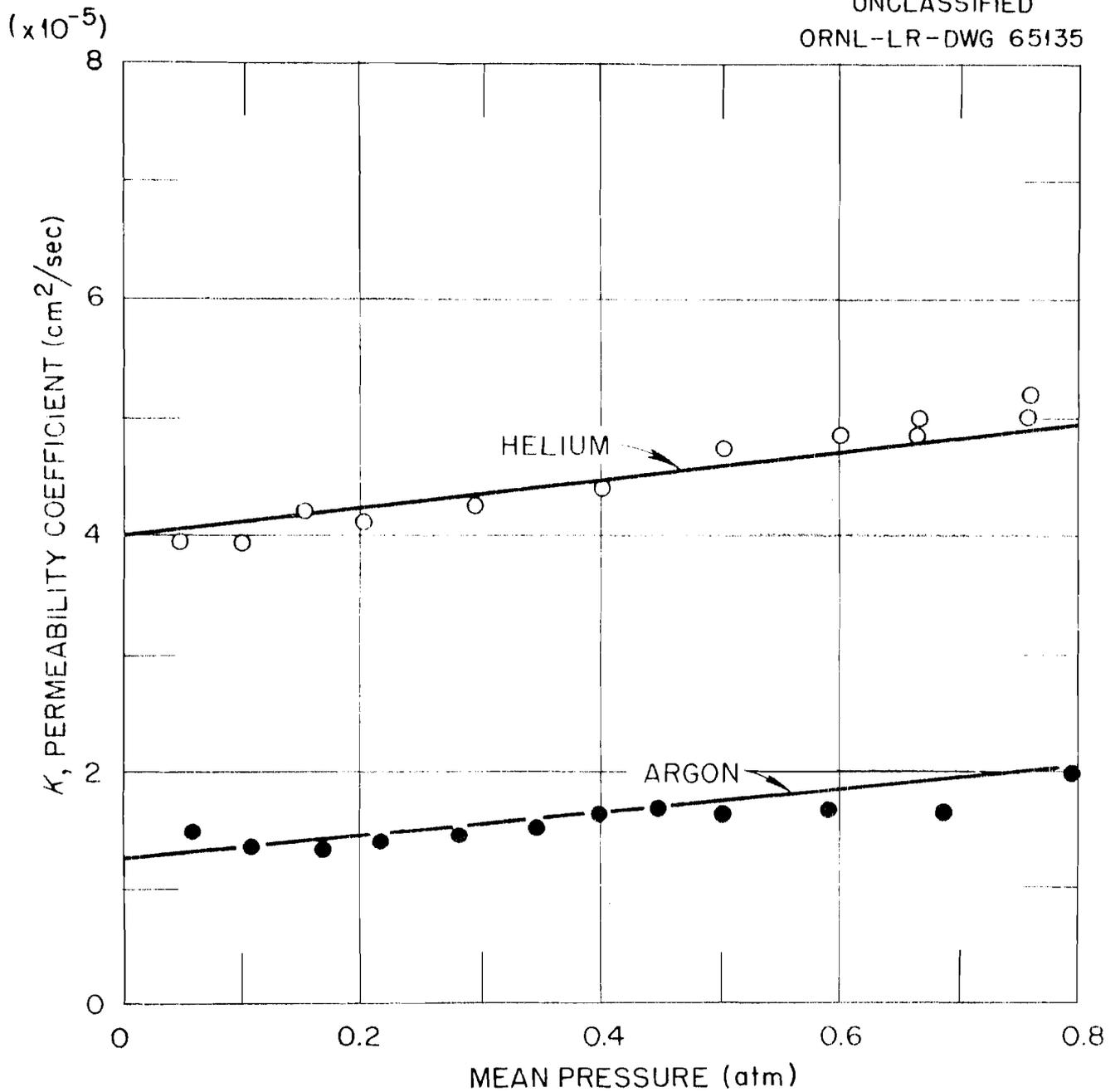
The selection of suitable flux equations which describe steady-state flow in porous media is an important facet of these studies; therefore, it is pertinent to review the basic relationships⁶ from which our working equations are derived. This review may be conveniently restricted to binary gas systems (gas 1 and 2) in the normal region without great losses of generality. All the analytical results (viscosity effects excluded) which have been utilized in this work are directly



High Pressure Forced Flow Data for Graphite Specimen IV at 25°C.

Fig. 3.

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Low Pressure Forced Flow Data for Graphite Specimen IV at 25°C Based on the Intercepts at $p=0$, $K_0 = 2.39 \times 10^{-10} \text{ cm}^2/\text{sec}$.

Fig. 4.

related to the basic definition of the mass flux j_i (grams/cm²sec, $i = 1$ or 2) in terms of the diffusion velocity, \bar{V}_i (cm/sec). For gas 1,

$$j_1 = n_1 m_1 \bar{V}_1. \quad (6a)$$

The expression for j_2 is given as above with the subscripts interchanged. This relationship is not too useful as it stands because \bar{V}_1 is not the J_1/n_1 measured in the laboratory; rather, it is a velocity referred to v (See Eq. 1) such that $\bar{V}_1 = J_1/n_1 - v$ and the same for \bar{V}_2 . This definition of mass flux, j_i , is based on the requirement that the changes in momenta associated with diffusive fluxes are zero. In other words, the sum of $j_1 + j_2$ or $d_1 + d_2$ must be zero at steady state.

$$n_1 m_1 \bar{V}_1 + n_2 m_2 \bar{V}_2 = 0 = m_1 J_1 + m_2 J_2 - \rho v, \quad (7)$$

where $\rho = n_1 m_1 + n_2 m_2$. This reveals that $J_1/J_2 = -m_2/m_1$ when $v = 0$ which is the theoretical result of $dp/dz = 0$ in large tubes when $v_0 = 0$ (See Eq. 2b). Also, for binary systems, one may express j_i in terms of the binary diffusion coefficient, \bar{D}_{ij} , and a driving force, d_j (cm⁻¹), as

$$j_1 = (n^2/\rho) m_1 m_2 \bar{D}_{12} d_2. \quad (6b)$$

The diffusion coefficient varies with $x_i = n_i/n$ when more than two gases are considered. In the present case, $\bar{D}_{12} = \bar{D}_{21}$; thus, $d_1 + d_2 = 0$. The Maxwell diffusion equation develops from Eqs. (6a) and (6b) when one solves for \bar{V}_1 and \bar{V}_2 then writes the difference such that

$$\bar{V}_2 - \bar{V}_1 = J_2/n_2 - J_1/n_1 = (n^2/n_1 n_2) \bar{D}_{12} d_1, \quad (8a)$$

which gives

$$(n^2 \bar{D}_{12})^{-1} (J_2 n_1 - J_1 n_2) = d_1. \quad (8b)$$

For linear flow, in general⁶,

$$d_i = \frac{d}{dz} \left(\frac{n_i}{n} \right) + \left(\frac{n_i}{n} - \frac{n_i m_i}{\rho} \right) \frac{d \ln p}{dz} - \frac{n_i m_i}{p \rho} \left(\frac{p}{m_i} F_i - \sum_{k=1}^v n_k F_k \right). \quad (9a)$$

For linear flow in binary systems,

$$d_1 = \left[\frac{1}{n} \frac{dn_1}{dz} \right] - \left[\frac{n_1 m_1}{n \rho} \frac{dn}{dz} \right] - \left[\frac{n_1 F_1}{nkT} - \frac{n_1 m_1}{n \rho} \left(\frac{n_1 F_1 + n_2 F_2}{kT} \right) \right]. \quad (9b)$$

The driving force is given here as the sum of a concentration term, a pressure diffusion term, and a special kind of external force term. The original Maxwell equation was intended for situations where $dn/dz = 0$ and the external forces F_1 and F_2 were absent in Eq. (9b). Thus, originally, $d_1 = dx_1/dz$. The last two terms result from rigorous treatments by Chapman and Enskog where non-zero F_1 , F_2 , and dn/dz were considered.

NORMAL DIFFUSION WITH PRESSURE GRADIENTS

The force terms involving the F_1 and F_2 (dynes/particle or atom) have been of considerable significance in these studies. The forces are especially restricted to those which might alter the details of the intermolecular collisions controlling the diffusion behavior. For example, gravitational forces, $F_i = m_i (dv/dt)$, which should not affect the collision process directly, cancel out to give a zero force term. The fluxes associated with the viscous mechanism were considered, then avoided, by taking $\bar{v}_1 - \bar{v}_2$ in Eq.(8a). The variations in density and/or pressure are already allowed for in Eq. (9b). Additional details concerning viscous mechanisms should not be inserted into the external force group of d_1 . Further discussion of this group will be given in the next section.

As an introduction, let us consider normal diffusion in large tubes wherein $F_1 = F_2 = 0$ and very small dn/dz give large changes in J . This means that the pressure diffusion term in Eq. (9b) is negligible.

Based on the above assumptions regarding d_1 , a convenient diffusion-flux equation for the individual components may be developed by substituting $J - J_1$ for J_2 , x_1 for n_1/n , $1 - x_1$ for x_2 , and dx_1/dz for d_1 in Eq. (8b), and then rearranging. The equation is

$$J_1 = -n\bar{D}_{12} dx_1/dz + x_1 J. \quad (10)$$

A similar non-independent equation may be written for J_2 . An integral form of Eq. (10) is

$$\exp \frac{JL}{n\bar{D}_{12}} = \frac{1 - (J/J_1)x_1(L)}{1 - (J/J_1)x_1(0)}, \quad (11)$$

which applies to many steady-state flow situations (even when $dp/dz \neq 0$), and in particular, to the Wicke⁷ method of performing diffusion experiments which is utilized in our present studies. When $dp/dz = 0$, the ratio J/J_1 may be replaced by $1 - m_1/m_2$, and Eq. (11) reduces to a relationship in J alone. However, this condition is difficult to accomplish in the laboratory. When it is, the J_1/J_2 ratio tends toward $1 - (m_1/m_2)^{1/2}$ at lower pressures. Nevertheless, Eq. (11) still holds for capillaries and permeable porous media.

A complete solution to the problem involves the reduction of Eq. (11) to a relationship incorporating a single flux - preferably J_1 when $dp/dz \neq 0$. This means that J must be estimated via forced flow information which, in turn, means that v must be considered. The equation relating the overall particle velocity $u = J/n$ to the mass average velocity v may be developed through our previous assumptions on d_1 by substituting the J_1 and J_2 relationships given by Eq. (10) in the right hand side of Eq. (7). The latter reduces to

$$u = \bar{D}_{12} \frac{d(\ln p)}{dz} + v \quad (12)$$

At $dp/dz = 0$, $v_o = 0$ for large capillaries, but $u_o \neq 0$. Actually,

$$u_o = \bar{D}_{12} \frac{d \ln p_o}{dz}.$$

Thus,

$$u = u_o + \bar{D}_{12} \left[\frac{d \ln (p/p_o)}{dz} \right] - (r_o^2/8\eta) \frac{dp}{dz}. \quad (13)$$

The usual experimental or computational procedure is to consider a series of fluxes with different dp/dz values at the same boundary concentration. Since the \bar{D}_{12} term is smaller than the viscous term in Eq. (13), one may write

$$u \sim u_o - (r_o^2/8\eta) dp/dz. \quad (14a)$$

The integral form of Eq. (14a) in terms of the total flux is

$$J \sim J_o - (r_o^2 \langle n \rangle / 8 \langle \eta \rangle) (\Delta P/L), \quad (14b)$$

where ΔP is applied so as to enhance the flow of the heavy gas. A combination of Eq. (11) and Eq. (14b) constitute a complete solution for the superposed problem in the normal region (for theoretical capillary behavior) in terms of the variables ΔP and x_1 . The flow parameters required are \bar{D}_{12} and $\langle \eta \rangle$, which are characteristic of the binary gas system; the required capillary characteristics are the length and the diameter.

For porous media in the Knudsen region it is clear that $J_1/J_2 = - (m_2/m_1)^{1/2}$ when $dp/dz = 0$. It turns out that this same condition holds, even in the normal region. Regardless of this, the results cited for capillaries hold also for porous media, using \bar{D}_{12}^8 and $\langle B \rangle$ in place of \bar{D}_{12} and $(r_o^2/8 \langle \eta \rangle)$, respectively. Experimental verification of the applicability of Eqs. (11) and (14b) has been recently published by the authors^{9, 10} and Hugo and Wicke¹¹.

COMBINED NORMAL-KNUDSEN DIFFUSION

A Dusty Gas Model

Extension of capillary theory to cover diffusion in porous media creates a major discrepancy in theory as the experimental results are contradictory in regard

to the J_1/J_2 condition at uniform pressure. Although the theory predicts a non-zero J_0 , it also predicts a v_0 of zero; whereas, actually, $v_0 = - [(m_1 m_2)^{1/2} / \rho] J_0$. One might attempt to show the $(m_2/m_1)^{1/2}$ condition by assuming that viscous forces are absent when $dp/dz = 0$ and that the second term in Eq. (4b) is a true diffusive term, with a partial pressure gradient given by $(4/3 K_0 \bar{c}_1)^{-1} (J_1)$. Since $dp_1 = - dp_2$, $J_1/J_2 = - (\bar{c}_1/\bar{c}_2) = - (m_2/m_1)^{1/2}$. On the basis of single gas experiments alone, however, the assumed diffusion term is only a sufficient (not necessary) condition for its final form (with dp/dz) in the forced flow equation. It is of greater significance to note that the primary diffusive parts of the problem have been disregarded completely, e. g., Eq. (10). One should be reluctant to offer this argument as a proof of the J_1/J_2 condition; however, the fact that the $4/3 K_0 \bar{c}_1$ term shows the same temperature and pressure dependencies as a nD_{ij} term strongly suggest that the $(m_2/m_1)^{1/2}$ condition arises as the result of a diffusive flow. If this is so, the diffusion equations applicable to capillaries are incomplete for cases where porous media are involved; for one should be able to derive the $(m_2/m_1)^{1/2}$ condition from the complete diffusion equations (which cannot be done via previous relationships) without having to resort to pieces of the forced flow equations.

Since additional diffusion information is required, it is only logical to turn to multicomponent forms of Eq. (8b). This suggests that one might visualize the pore surfaces, which are associated with the gas-wall collision mechanism, as being a collection of solid dust particles suspended directly in the path of the flowing gases⁵. The dust may be treated formally as an additional gas component subject to very special conditions. It should be pointed out that Waldmann¹² has given extensive treatments to such systems wherein the dust is free to move. In

the present case, the dusty-gas is composed of large spherical particles constrained to remain stationary ($J_d = 0$) and uniformly distributed ($dn_d/dz = 0$). Accordingly, the dust cannot exert a partial pressure, so the total pressure and all related quantities are fictitious and are denoted with a prime. For example,

$$\rho' \equiv \sum_{j=1}^{\nu} n_j m_j = n_d m_d + \sum_{i \neq d}^{\nu} n_i m_i$$

where, in this case, i refers to real gases and ν is the total number of components.

The fraction of medium considered as dust is very small compared to the medium as a whole; thus, the original pore geometry as well as relationships like

$$D_{12} = \epsilon/q \bar{D}_{12}$$

are retained. The present treatment is merely an extension of the old capillary model as far as pore geometry is concerned. The size of the dust particles are assumed large in comparison to real gases so that the reduced mass, μ , and collision diameter, σ_{12} , in the usual expression¹³ for nD_{ij} become m_i and r_d , respectively. This is consistent with the $4/3 K_O \bar{c}_i$ term. It is not necessary, but it is convenient, to assume uniformity of particle sizes.

The multicomponent forms of Eq. (8b) for one dimensional flow of ν components are

$$\sum_{i \neq j}^{\nu} i \frac{1}{n_i^2 (D'_{ij})} (n_j J_i - n_i J_j) = d_j, \quad (15)$$

which are called the Stefan-Maxwell equations. There are $\nu - 1$ independent equations in this set. According to Bird¹⁴, Stefan assumed that the Maxwell equations could be used for $\nu > 2$ conditions without changing the binary coefficients to multicomponent coefficients. The validity of this very important and convenient decision was demonstrated sometime later by Curtiss and Hirschfelder¹⁵.

External Force-Pressure Gradient Relationships

The results based on Eq. (15) are not restricted to uniform pressure conditions, but may include situations where forced flow and pressure gradients are present¹⁶. It will be necessary to discuss additional features of the dusty gas which take these situations into account. The additional features involve: the mode of suspension, the driving force gradient, and the external force terms.

The details of suspension are precise in that the only forces allowed to operate on the dust particles are assumed to be diffusive forces. If a pressure gradient exists in a gas-dust system, the dp/dz exerted externally on the gases is transmitted to the dust in the direction of the forced flow. This force is counter balanced by an equivalent external force which keeps the particles stationary. The total clamping force may or may not be the constraining force on the particles; however, the mode of suspension is such that only diffusive forces can be applied externally. The external forces which act on the dust in both directions are

$$n_d F_d = \frac{dp}{dz}, \quad (16)$$

where F_d is the external force exerted on each dust particle. The F_d does not depend directly on J , only on the dp/dz . Although the dp/dz may introduce a viscous component, $(B_0 n/\eta)(dp/dz)$, which will drastically alter the J_1/J_2 , this should not affect F_d . Furthermore, we pretend that the dust does not alter the parabolic velocity profile associated with viscous effects. Since the wall slip effects are now counted as dust effects, the v_0 remains as $-[(m_1 m_2)^{1/2}/\rho]J_0$ because of the dust. Equations (15) and (16) afford a complete solution to the diffusion part of the problem.

By substituting Eq. (16) in Eq. (9b), one finds that the external force part (the last part) of d_d is

$$- \left[\frac{n_d F_d}{n' kT} - \frac{n_d m_d}{n' \rho'} \left(\frac{n_d F_d}{kT} \right) \right] \Rightarrow \left[\frac{1}{n'} \left(\frac{dn}{dz} \right) - \frac{n_d m_d}{n' \rho'} \left(\frac{dn}{dz} \right) \right],$$

and that the external force parts of the d_i , where i now denotes all the real gases, are, e. g.,

$$- \left[0 - \frac{n_i m_i}{n' \rho'} \left(\frac{n_d F_d}{kT} \right) \right] = - \left[0 - \frac{n_i m_i}{n' \rho'} \left(\frac{dn}{dz} \right) \right]$$

because all the F_i are zero. When all terms in d_j are considered, one finds that a surprising amount of cancellation occurs such that:

$$\sum_j d_j = d_d + \sum_{\substack{i \\ i \neq d}} d_i = -\frac{1}{n'} \frac{dn}{dz} + \frac{1}{n'} \sum_{\substack{i \\ i \neq d}} \frac{dn_i}{dz} = 0.$$

One may conclude here that the F_d definition, Eq. (16), is compatible with the diffusion relationships because $\sum_j d_j = 0$.

The $j = d$ equation of the set given by Eq. (15), with $d_d = - (1/n') (dn/dz)$

and $J_d = 0$, gives

$$\sum_{\substack{i \\ i \neq d}} \frac{(n_d)(J_i)}{(n')(D'_{id})} = -\frac{dn}{dz}. \quad (17)$$

If D_{iK} is defined by

$$D_{iK} = \frac{n' D'_{id}}{n_d} = \frac{n D_{id}}{n_d},$$

Equation (17) may be written for two real gases as either

$$\frac{J_1}{D_{1K}} + \frac{J_2}{D_{2K}} = -\frac{1}{kT} \frac{dp}{dz}, \quad (18a)$$

or

$$J - \left[1 - \left(\frac{m_1}{m_2} \right)^{1/2} \right] J_1 = -\frac{D_{2K}}{kT} \frac{dp}{dz}, \quad (18b)$$

where both forms give the $J_1/J_2 = - (m_2/m_1)^{1/2}$ condition when $dp/dz = 0$. According to the equation, the J_1/J_2 condition is independent of pressure, temperature, and the values of D_{1d} relative to D_{12} . These results follow experimental observations.

The Diffusion Equations

The diffusive-flux equation like Eq. (10) for two gases may be developed by taking $j = 1$, in Eq. (15), with $d_1 = (1/n')(dn_1/dz)$:

$$\frac{1}{n'(D'_{12})} (n_1 J_2 - n_2 J_1) + \frac{1}{n'(D'_{1d})} (n_1 J_d - n_d J_1) = \frac{dn_1}{dz} .$$

Substituting $J_d = 0$, $J_2 = J - J_1$, and $n' = n_1 + n_2 + n_d = n + n_d$, one obtains after rearrangement

$$J_1 = - D_1 \frac{dn_1}{dz} + \delta_1 x_1 J \tag{19}$$

where

$$(D_1)^{-1} = (D_{12})^{-1} + (D_{1K})^{-1},$$

and

$$(\delta_1)^{-1} = 1 + (D_{12}/D_{1K}).$$

The same set of equations apply for J_2 , but one must be careful to interchange all subscripts. An important trick in getting rid of the prime quantities is to remember that $n'D'_{ij} = nD_{ij}$. As p increases, D_{12} decreases inversely with p , while D_{1K} remains constant. Therefore, Eq. (19) takes the form given by Eq. (10) at high pressures because $D_1 \rightarrow D_{12}$ (and $\delta \rightarrow 1$ as $p^{-1} \rightarrow 0$). At low pressures, $D_1 \rightarrow D_{1K}$ and $\delta \rightarrow 0$, the $x_1 J$ term vanishes and, only the well known Knudsen diffusion equation remains. Equation (19) would have been exactly the same had the development been restricted to $dp/dz = 0$ conditions. Thus, the effects of pressure gradients are introduced via integration.

To prepare Eq. (19) for integration, it is convenient to use the relationship

$$\frac{dn_1}{dz} = n \frac{dx_1}{dz} + x_1 \frac{dn}{dz},$$

which substituted into Eq. (19) leads to

$$\frac{dx_1}{dz} + \left(\frac{1}{n} \frac{dn}{dz} - \frac{J}{nD_{12}} \right) x_1 + \frac{J}{nD_1} = 0. \quad (19a)$$

It is necessary to specify n as a function of z somewhere in the integration process. We have assumed a linear relationship since the Δn 's of interest will be small in high permeability materials. Also, they will tend toward linearity in low permeability regions because of the Knudsen characteristics. Thus,

$$n(z) = n(0) + (\Delta n)(z/L) \quad (20)$$

where

$$\Delta n = n(L) - n(0).$$

The integrated form of Eq. (19a) is

$$\exp \left(\frac{JL}{nD_{12}} \right) = \frac{nD_{12} J_1 \left(\frac{1}{D_{1K}} + \frac{\Delta n}{JL} \right) + n(L) [(J_1 - Jx_1(L)]}{nD_{12} J_1 \left(\frac{1}{D_{1K}} + \frac{\Delta n}{JL} \right) + n(0) [(J_1 - Jx_1(0)]}. \quad (21)$$

When $dp/dz = 0$, $n(0) = n(L)$ and the above may be written as:

$$J = \frac{nD_{12}}{L} \ln \left[\frac{1 - \delta_1 \beta x_1(L)}{1 - \delta_1 \beta x_1(0)} \right], \quad (22)$$

where $\beta = (J/J_1)_0 = 1 - (m_1/m_2)^{1/2}$.

One may note that the uniform pressure equation with $\delta = 1$ is merely Eq. (11). Equations (21) and (22) constitute a complete solution to the diffusion problem at all pressures if all the J 's and coefficients are known.

The Forced Flow Equation

As mentioned before, it is most convenient to use the diffusion equations with an auxiliary relationship which will enable one to predict J on the basis of:

(a) permeability information and (b) Δn or Δp . This will eliminate one of the fluxes in Eq. (21). The only forced-flow information carried by Eq. (21) is the reasonable assumption that $n(z)$ or $p(z)$ should be linear; no other forced-flow information was required. The effects of the forced-flow problem on the diffusion problem were buried in J , since the diffusion equations do not require a knowledge of viscosity, etc. This is one of the beauties of the dusty-gas diffusion model which is absent in the forced-flow problem.

The development of Eq. (14b) for capillaries indicated that the forced-flow problem is indeed a difficult one; for one is now concerned with v which varies from point to point at steady state and is related to J through a variable $\langle \eta \rangle$. Attempts to use the same approach used for Eq. (14b) were immediately abandoned because of the complexity of the resulting equations. Our alternate procedure is therefore somewhat empirical, but it appears to yield useful results.

A glance at Eqs. (17), (18a), and (18b) will reveal that at least the Knudsen part of the forced-flow equation is available through the $j = d$ equations of the model. With this as a basis, one may define $1 - \zeta_1$ and ζ_1 as the fractions of Knudsen and viscous forced-flow components, respectively. As $p^{-1} \rightarrow 0$, $\zeta_1 \rightarrow 1$; flow is entirely viscous. As $p \rightarrow 0$, $\zeta_1 \rightarrow 0$; flow is entirely Knudsen.

$$\zeta_1 = \frac{B_o p / \eta}{K} \qquad 1 - \zeta_1 = \frac{D_{1k}}{K}$$

where $K = B_o p / \eta + D_{1k}$

For a single gas experiment Eq. (17) gives

$$J_1 = - (D_{1k} / kT) (dp/dz), \qquad (23a)$$

but J_1 in the above equation is only the diffusive part of the total forced J .

When $J_1 = (1 - \zeta_1)(J) = (D_{1k}/K)J$ is substituted in Eq. (17), the usual permeability

relationship, Eq. (4a), is recovered. For an experiment with two gases, the Knudsen part is given by Eq. (18b). The left hand side of Eq. (18b) is treated as a single flux for convenience. Thus, in close analogy to cases involving a single gas,

$$\zeta_{21} = \frac{B_o P / \eta}{C_2} \quad 1 - \zeta_{21} = \frac{D_{2K}}{C_2} \quad (23b)$$

where $C_2 = B_o P / \eta + D_{2K}$. The $J - \beta J_1$ in Eq. (18) is actually $(1 - \zeta_{21})(J - \beta J_1)$ when viscous effects are present. This results in a tentative expression for the forced flow experiment which is

$$J = \beta J_1 - (D_{2K} + B_o P / \eta) \frac{dn}{dz}, \quad (24a)$$

or

$$J = \beta J_1 - \frac{C_2}{kT} \frac{dp}{dz}. \quad (24b)$$

At present, we denote C_2 as a disposable parameter to be determined through experiment.

EXPERIMENTAL WORK

Two sets of diffusion experiments have been completed during the last year. The experiments involved the counter-diffusion of helium and argon in two graphites which may be classified as moderately low permeability materials. Insofar as possible, the total pressure of the gases was maintained uniform. A diagram of the experimental set-up is presented in Fig. 5. As opposed to our earlier experiments with high permeability graphites, appreciable Knudsen effects were observed, not only in the permeability results, but also in the diffusion results. The diffusion results with these two specimens offered the first opportunity to verify the validity of the diffusion equations presented in the previous section for the intermediate region. Experimental verification of the dusty-gas model constituted one of the major objectives for the experimental work performed during the previous year.

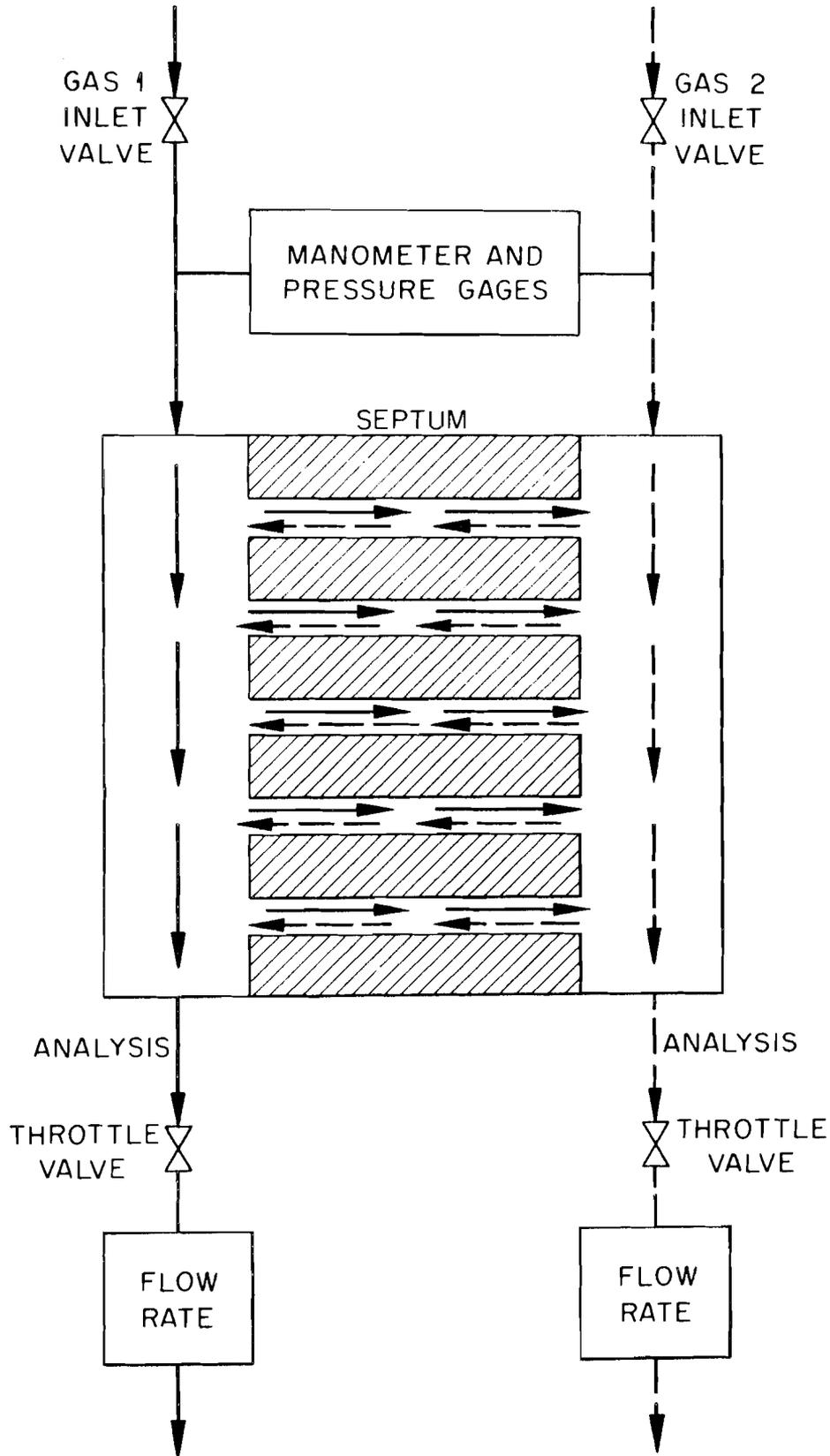


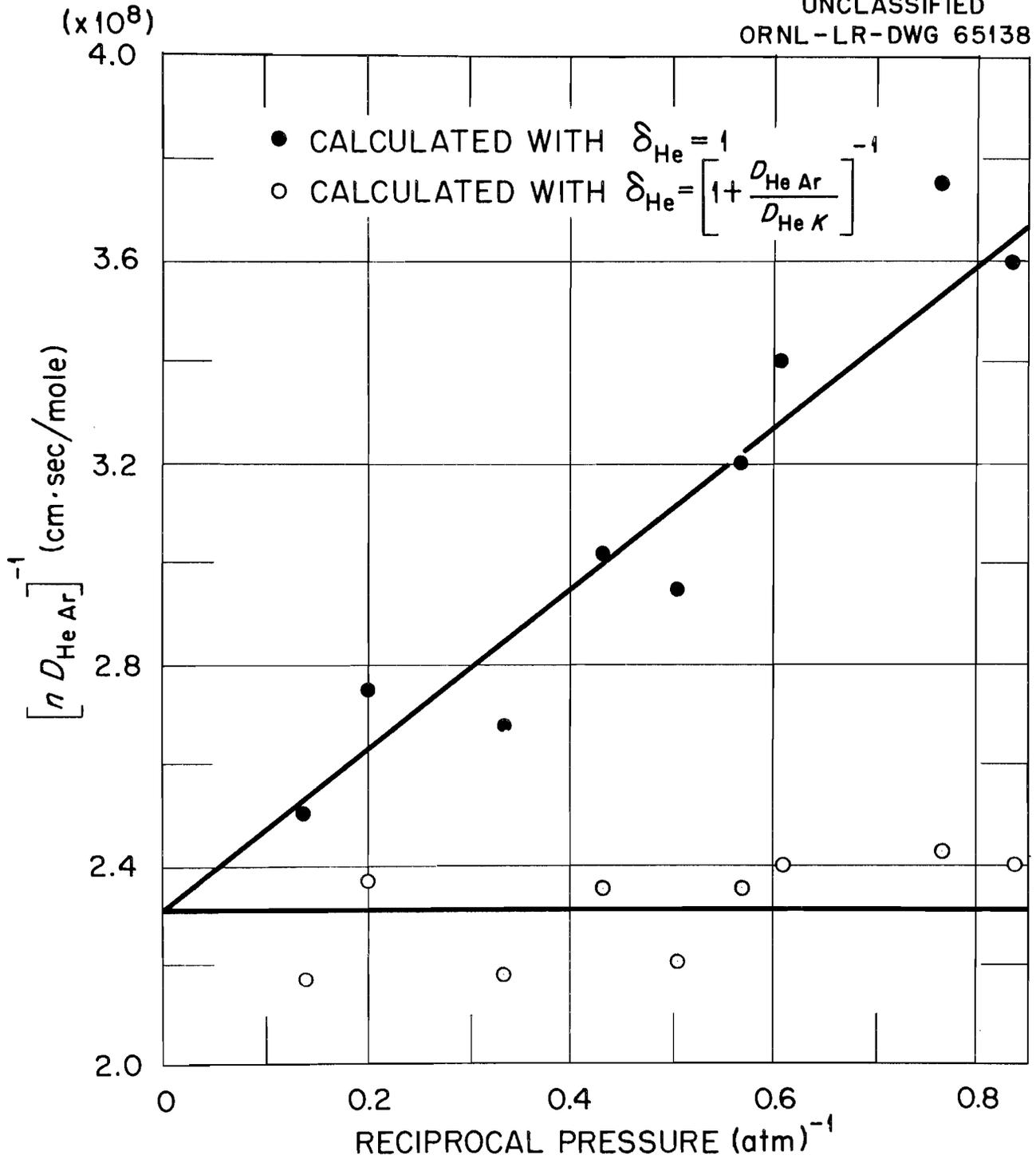
Diagram of Steady-State Counter-Diffusion Experiment.

Fig. 5.

Another important, but rather long range objective, exists with respect to the applicability of the dust-gas model to graphites wherein the permeability coefficient varies markedly along the flow path. The two low-permeability specimens were selected with this objective in mind. Both specimens originated from the same source, which was a piece of thin wall graphite pipe, both surfaces of which were subjected to a permeability reduction treatment. One piece of the pipe was mounted as a specimen in the "as received" condition (denoted Specimen IV, see Figs. 3 and 4). Approximately 10 mils were machined from both surfaces of an adjacent piece of the pipe prior to mounting as a specimen (denoted as Specimen III, see Fig. 6).

The results of the permeability experiments reveal that the removal of the coating increases the permeability constant by a factor of 6. From all outward appearances, however, the diffusion results look very much the same with the expected exception that the diffusion rates were much higher in the uncoated specimens than in the "as received" specimen. The dusty-gas model was followed in both cases in the same way. For this reason we have selected the results for the uncoated (relatively uniform) material for the present discussion.

The counter-diffusion results for Specimen III are shown in Fig. 6. All of these results were obtained through experiments conducted at 25°C at several uniform pressures which range from approximately 1.2 to 6.5 atm. A glance at Eq. (22), which is applicable to these experiments, reveals that a single diffusion experiment would have been sufficient to evaluate nD_{HeAr} since D_{HeK} and D_{ArK} had been determined previously via forced flow experiments. A single diffusion experiment, however, would not have been sufficient to verify Eq. (22) over a range of pressures. Having obtained flux data at several pressures, the problem



Results of Counter Diffusion Experiments at 25°C with Graphite Specimen III. The Flow Parameters for this Graphite are:
 $n D_{\text{He Ar}} = 4.33 \times 10^{-9}$ moles/cm·sec, $D_{\text{He K}} = 3.2 \times 10^{-4}$ cm²/sec.

Fig. 6.

arises as to the acquisition of an average nD_{HeAr} , but this becomes a simple matter if the procedure indicated on Fig. 6 is followed.

This procedure involves the computation of an apparent nD_{HeAr} from the flux and concentration data according to Eq. (22) under the incorrect assumption that δ_{He} is unity (as a first approximation). One then plots the reciprocal apparent nD_{HeAr} versus the reciprocal pressure (closed points, Fig. 6). It may be shown that plots of this type should result in a straight line. The value desired is the intercept since the apparent value becomes a true value at high pressures. The applicability of the selected intercept may be verified by recalculating nD_{HeAr} via Eq. (22) with the correct δ_1 , which varied with pressure. A plot of the true nD_{HeAr} values should result in a horizontal line because the true value is independent of pressure. Experimental values were computed in this manner and are shown as open points on Fig. 6.

A comparison of the closed and open points on Fig. 6 at low pressures (high reciprocal pressures) demonstrates the importance of the Knudsen effects in the over-all diffusion mechanism. The apparent nD_{HeAr} values, for which Knudsen effects are ignored, differ considerably from those in which Knudsen effects are considered.

Our current experimental program involves an extension of the Specimen III data to conditions where pressure gradients exist. The objective of these experiments is to determine the correct pressure dependence of C_2 as given by Eq. (24b) and, in particular, whether or not the intercept of C_2 versus $\langle p \rangle$ is actually D_{2K} as given by Eq. (24a). In addition, the effect of graphite non-uniformity is under study. This work is to be based on comparisons of the results of Specimens III and IV.

DIFFUSION IN THE PRESENCE OF PRESSURE AND TEMPERATURE GRADIENTS

Thermal Diffusion in the Normal Region

Considerable thought has been given to the possibility of extending our present theoretical treatment and experimental program to include cases where, not only pressure gradients, but also temperature gradients are present. All of the effort expended thus far has been toward the theoretical aspects of the problem. As in the previous treatments, we have encountered the most fortunate circumstance whereby the solutions to the more difficult parts of the problem are available in the form of classical theory. Once again the desired results appear in the Stefan-Maxwell equations with the driving force terms as given by the Chapman-Enskog theory.

The applicable equations are the same as those discussed before with an additional term added to the driving force. This added term involves the thermal diffusion coefficient. As opposed to the usual binary-diffusion coefficient, D_{ij} , the thermal diffusion coefficient, D_{ij}^T , depends in a complicated way on the mole fraction of the gases. Perhaps for this reason information regarding this coefficient is available only for binary gas mixtures. This, of course, precludes an extension of our present model to include temperature gradients, because thermal diffusion coefficients for a three component mixture would be required. Nevertheless, there are a few situations of applied interest which are adequately described by binary-diffusion equations.

For ease of discussion, it is convenient to write down the applicable binary-diffusion equations⁶.

$$\frac{1}{n^2 D_{12}} (n_2 J_1 - n_1 J_2) = d_2 - \frac{d \ln T}{dz} \left[\frac{n_1 n_2}{n^2 D_{12}} \left(\frac{D_1^T}{n_1 m_1} - \frac{D_2^T}{n_2 m_2} \right) \right]$$

The same equation may be written for component 2 with the subscript interchanged, but this will not be an independent equation. Considerable care must be taken with respect to signs, as the heaviest molecules present must tend to move toward low temperature regions. The usual convention in a 1-2 system is to assign the subscript 1 to the heavy gas and use the signs as given in these equations.

Again, $D_{12} = D_{21}$ and $d_2 = -d_1$. Thus by Eq. (7), $D_1^T = -D_2^T$ and Eq. (25) may be written in the alternate forms:

$$\frac{1}{n^2 D_{12}} (n_2 J_1 - n_1 J_2) = - \left[d_1 + \left(\frac{D_1^T \rho}{n^2 D_{12} m_1 m_2} \right) \frac{d \ln T}{dz} \right] \quad (26a)$$

or

$$(\bar{v}_1 - v) - (\bar{v}_2 - v) = - \frac{n^2 D_{12}}{n_1 n_2} \left(d_1 + k_T \frac{d \ln T}{dz} \right) \quad (26b)$$

The usual procedure for acquiring information about D_1^T and/or k_T for various binary mixtures is to conduct an equilibrium experiment in large closed tubes wherein the concentrations and temperatures at the ends of the tubes are measured. It is found that the concentration of the heaviest gas is highest at the coldest end of the tube. The total pressure is uniform because the tubes are large and closed. The experiment is described by the integral form of Eq. (26b) with

$$\bar{v}_1 - \bar{v}_2 = 0.$$

Thermal Transpiration

An analogous situation exists with respect to single gas - porous media systems, where portions of the medium are treated formally as a second gas component (dust). The tendencies for equilibrium separation are the same as in the previous case; however, the dust is fixed and cannot move and as a consequence

of this, more real gas (light) particles tend to be present at the hot end than at the cold end (at equilibrium). As before, the ratio of the amount of heavy particles to light particles tends to be highest at the coldest end of the tube.

These thermal separation tendencies are always opposed by forced flow tendencies (in the normal region) and diffusive flow tendencies (in the Knudsen region). For a given medium, subjected to a temperature gradient, one would expect that the single-gas pressure would be uniform throughout the medium at high pressures. On the other hand, a pressure difference across the tubes appears (p_A at the hot end $>$ p_B at cold end) as the Knudsen limit is approached. This difference would be zero at zero pressure; thus, one would expect a maximum pressure difference at some low pressure. This process was observed by Graham as early as 1846. In 1879 an extensive investigation of this effect was carried out by Reynolds¹⁷ (for whom the famous group $Re = Dv\rho/\eta$ was named) using Stucco and Meerscham as porous media. Reynolds was responsible for the term: thermal transpiration. Similar experiments were performed by Knudsen¹⁸. The relationship deduced for regions corresponding to

$\delta_1 \rightarrow 0$ on the dusty-gas model was

$$p_A/p_B = (T_A/T_B)^{1/2} \quad (27)$$

A derivation of this formula for large tubes is given by Kennard¹⁹, who utilizes classical capillary arguments. An encouraging development with respect to the dusty-gas model is that the same result may be obtained from Eq. (26b) and Eq. (16) with the additional information that $k_T = 1/2 (x_{\text{real gas}})$. The latter information comes from the realization that when $\delta_1 \rightarrow 0$, the gas is under conditions which correspond to those of a Lorentzian gas. At present, it appears that one should be

able to develop an expression which will describe the thermal transpiration behavior over the entire region from $p_A = p_B (T_A/T_B)^{1/2}$ at $\delta_i \rightarrow 0$ to $p_A = p_B$ at $\delta_i \rightarrow 1$.

Figure Captions

1. High Pressure Permeability Data for Graphite Specimen I.
2. Diagram of Pressure Rise Apparatus for Forced-Flow Measurements with Low Permeability Materials.
3. High Pressure Forced-Flow Data for Graphite Specimen IV at 25°C.
4. Low Pressure Forced-Flow Data for Graphite Specimen IV at 25°C Based on the Intercepts at $p = 0$, $K_0 = 2.39 \times 10^{-10}$ cm.
5. Diagram of Steady-State Counter Diffusion Experiment.
6. Results of Counter Diffusion Experiments at 25°C with Graphite Specimen III.
The Flow Parameters for this Graphite are: $nD_{\text{HeAr}} = 4.33 \times 10^{-9}$ moles/cm-sec;
 $D_{\text{HeK}} = 3.2 \times 10^{-4}$ cm²/sec.

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The omega function is a reduced collision integral which varies primarily with temperature.
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