

Pressure Dependence of the Diffusion Thermoeffect in Gases (Dufour Effect)*

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(Received 27 March 1967)

A modified Loschmidt apparatus for the measurement of the diffusion thermoeffect as a function of pressure is described. Measurements are reported for H_2 -Ar, H_2 -CO₂, and H_2 -CH₄ for pressures between 1 and 20 atm at room temperature. The experimental results have been explained semiquantitatively in terms of the pressure dependence of the relevant transport coefficients and their first composition derivatives. Terms arising because of the nonideality of the gases are also included in the phenomenological description. Relative values of diffusion coefficients for the three systems determined from the measurements are in good agreement with those determined by other methods, and the effect of pressure on the diffusion thermoeffect parallels the pressure dependence of the thermal diffusion factor as determined from gas-unmixing measurements. Suggestions are made for the future use of the method in determining other transport coefficients.

I. INTRODUCTION

The purpose of this paper is to report measurements on the effect of pressure on the diffusion thermoeffect in gases. The interpretation of the results is more complex than for the corresponding thermal diffusion effects. This is to be expected, since thermal conductivity is involved in the diffusion thermoeffect but not in thermal diffusion. We have studied H_2 -Ar and H_2 -CO₂ mixtures, for which the pressure dependence of thermal diffusion has already been measured, and H_2 -CH₄ mixtures, for which no such data are available.

In the diffusion thermoeffect, a composition gradient gives rise to a temperature gradient; that is, transient temperature differences develop in a diffusing mixture. These are not simply ordinary heat-of-mixing effects, but occur as well with ideal gases. The diffusion thermoeffect is the inverse of thermal diffusion, in which a temperature gradient causes the development of a composition gradient. The diffusion thermoeffect was discovered, but not understood, by Dufour in 1872, and was then apparently forgotten for nearly 70 years until its rediscovery by Clusius and Waldmann.¹

The analogous effect in liquids has been recognized as a possibility for some time, but its experimental detection was only recently accomplished.² The temperature differences in liquids are small and hard to observe, because of the slowness of diffusion in liquids and their large thermal conductivities and specific heats as compared to gases.

The Dufour effect in dense gases has never been

studied, although the effect of high pressures on thermal diffusion has been investigated a number of times.³⁻⁵ All measurements of the Dufour effect in gases have been at pressures of 1 atm and lower.^{4,6} The present apparatus can be operated over the range 0-50 atm, although the measurements reported here cover only the range 1-20 atm.

As a final remark, we note that the diffusion thermoeffect is of practical interest in connection with gas injection into boundary layers.⁷⁻⁹ It has also been cited¹⁰ as a source of error in measurements of the heat of mixing of gases.

II. EXPERIMENTAL

A. Apparatus and Procedure

The first measurements of the diffusion thermoeffect at other than atmospheric pressure were carried out by Waldmann⁶ using a steady-state flow method. These experiments left some questions open, especially those regarding pressure dependence, which are still not settled.¹⁰ We felt that a nonsteady-state method would yield more information, and constructed a diffusion apparatus of the Loschmidt type, similar to that used earlier by Waldmann¹¹ and by Miller.¹² Such an apparatus consists basically of a tube, closed at both ends, which can be divided into two equal parts. The temperature change is followed by a platinum wire acting as a resistance thermometer. Various possible apparatus

* K. E. Grew and T. L. Ibbs, *Thermal Diffusion in Gases* (Cambridge University Press, London, 1952).

† L. Waldmann, in *Handbuch der Physik*, S. Flügge, Ed. (Springer-Verlag, Berlin, 1958), Vol. XII.

‡ E. A. Mason, R. J. Munn, and F. J. Smith, *Advan. At. Mol. Phys.* **2**, 33 (1966).

§ L. Waldmann, *Z. Naturforsch.* **4a**, 105 (1949).

¹ J. R. Baron, *Am. Rocket Soc. J.* **32**, 1053 (1962); *Int. J. Heat Mass Transfer* **6**, 1025 (1963).

² O. E. Tewfik, E. R. G. Eckert, and L. S. Jurewicz, *Astronaut. Aeron.* **1**, 1537 (1963), and previous papers.

³ E. M. Sparrow, W. J. Minkowycz, and E. R. G. Eckert, *Trans. ASME* **86C**, 508 (1964); and previous papers.

⁴ L. S. Kotousov, *Soviet Phys.—Tech. Phys.* **10**, 1698, 1702 (1966) [*Zh. Tekh. Fiz.* **35**, 2215, 2221 (1965)].

⁵ L. Waldmann, *Z. Phys.* **124**, 2 (1947).

⁶ L. Miller, *Z. Naturforsch.* **4a**, 262 (1949).

* This work was supported in part by the U.S. Atomic Energy Commission in its initial stages, and by the U.S. Army Research Office, Durham, during its later stages.

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¹ K. Clusius and L. Waldmann, *Naturwiss.* **30**, 711 (1942). For an interesting but brief historical review, see K. Clusius, *Helv. Phys. Acta* **22**, 135 (1949).

² R. P. Rastogi and G. L. Madan, *J. Chem. Phys.* **43**, 4179 (1965).

designs differ mainly in the methods of connecting the two tube halves and in mounting the resistance wires.

A diagram of the apparatus is shown in Fig. 1, approximately to scale. Each half-tube is mounted on a circular plate; rotation of the two plates relative to each other brings the tubes together for diffusion or isolates them for filling. This type of variation on the Loschmidt apparatus was proposed long ago¹³ and has been used many times since. The novel feature of the present apparatus is the method of making a gas-tight seal for high pressures. The usual seal is made by having the plates lapped flat and pressed together by a center bolt, but this is unsatisfactory at high pressures. In the present apparatus the rotating plates fit into a large short cylinder, and O rings at the edges make the seals. The plates therefore do not need to be lapped, or even made especially smooth, but they must be kept from blowing apart at high pressures by a 10-ton hydraulic press. The apparatus is also usable below 1 atm; the press is then not needed, but a ball bearing is inserted between the plates to facilitate rotation.

The dimensions of the apparatus involve some compromises. On the one hand, it is desirable to have a large tube diameter, otherwise the temperature differences are much reduced by heat conduction to the walls. On the other hand, the forces pushing the apparatus apart increase as the square of a dimension. The diameters of the rotating plates are 6 in.; a gas pressure of 50 atm exerts on this area a force of approximately 10 tons, which is the limit of the hydraulic press. The length of each half-tube is 4 in., and the internal diameter is $1\frac{5}{8}$ in. Part of the inside wall consists of cylindrical plastic rings on which the resistance thermometer wires can be mounted. The distance of the thermometers from the diffusion interface can be varied by interchanging plastic rings. The thermometer wires are parallel to the diffusion interface and ideally lie along the diameter of the tube, so that they measure the average temperature across the diameter. In practice, the wires form a band about 0.5 in. wide and so measure the average temperature over this area. The construction of the thermometers from 0.0004-in. Wollaston wire, and the method of recording the temperature as a function of time with a rotating drum camera, have been described elsewhere.¹⁴ The electrical leads of the thermometers are brought out through the ends of the apparatus through simple insulated pressure seals constructed of ordinary spark plugs modified for O rings. Only one insulated lead per thermometer is needed, the other lead being grounded to the apparatus.

The filling and starting procedure at high pressures merits a few comments. The two rotating plates were first pressed tightly together by the 10-ton press to isolate the two half-tubes, which were then filled to the

desired gas pressure separately. Pressures were equalized by opening an external bypass valve. The sensitive resistance thermometer can be used to check pressure equality, as very small pressure differences give clear adiabatic temperature changes when the bypass valve is opened. The rotating plates cannot be moved when pressed tightly together. The 10-ton press was therefore carefully bled until the top plate moved up about 0.01 in. (as read on a micrometer dial gauge), which is enough to allow free rotation while still keeping the half-tubes sealed from each other by an O ring. The bypass valve, closed during the latter operation, was opened again before the upper plate was rotated by hand to bring the diffusion tubes into alignment. The few seconds duration of the rotation was marked on the photographic recording paper by a microswitch-operated light signal. This duration was not reproducible from run to run, and hence the length of time during which the diffusion tubes only partially overlapped was variable, introducing some uncertainty in the location of $t=0$.

All runs were made at room temperature (about 23°C), which was always constant over the time required to perform a run. Tank gases from commercial sources were used without further purification. Minimum purity was at least 99.5%, and the present results are expected to be insensitive to small impurities.

B. Results

Temperature-time curves for H_2 -Ar and H_2 -CO₂ are shown in Figs. 2 and 3, for different pressures between 1 and 20 atm. The thermometer was located $\frac{7}{8}$ in. either

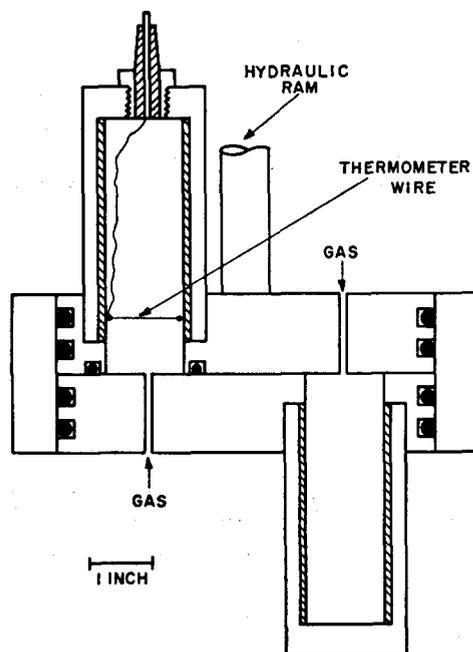


FIG. 1. Diagram of high-pressure diffusion apparatus. Electrical connections in the lower half are not shown.

¹³ L. E. Boardman and N. E. Wild, Proc. Roy. Soc. (London) **A162**, 511 (1937); H. F. Coward and E. H. M. Georgeson, J. Chem. Soc. **1937**, 1085.

¹⁴ L. Miller and E. A. Mason, Phys. Fluids **9**, 711 (1966).

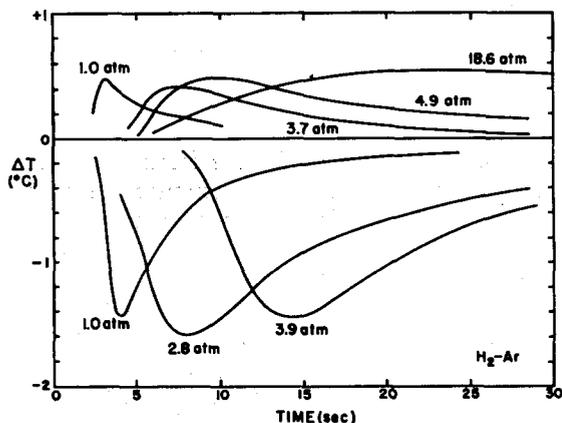


FIG. 2. Diffusion thermoeffect in H_2 -Ar mixtures as a function of pressure above and below the diffusion interface (7/8 in.).

above or below the diffusion interface. The origin of time is taken to be the instant at which rotation of the plates started; since the time taken to rotate the plates differed from run to run, the curves in Figs. 2 and 3 all have somewhat different true time origins.

Several general features are immediately apparent in these results. First of all, an increase of pressure slows the diffusion and in effect expands the time scale. Secondly, the temperature effect is greater below the diffusion interface than above it, an effect which has been noted before.^{11,12} Thirdly, the maximum temperature change increases approximately linearly with pressure, until at about 20 atm it is larger than at 1 atm by a factor of 1.2 for H_2 -Ar and 1.5 for H_2 -CO₂.

The results for H_2 -CH₄ are very much like those for H_2 -Ar, and so are not shown separately. The temperature change is a little less, but the effect of pressure is almost identical, an increase by about a factor of 1.2 from 1 to 20 atm.

A plot of the maximum temperature change, ΔT_{\max} , as a function of pressure is shown in Fig. 4 for all three systems. These results all refer to the upper (hydrogen-rich) side of the diffusion interface. The effect of pressure is clearly much greater for H_2 -CO₂ than for H_2 -Ar or H_2 -CH₄, and might be nonlinear at high pressures.

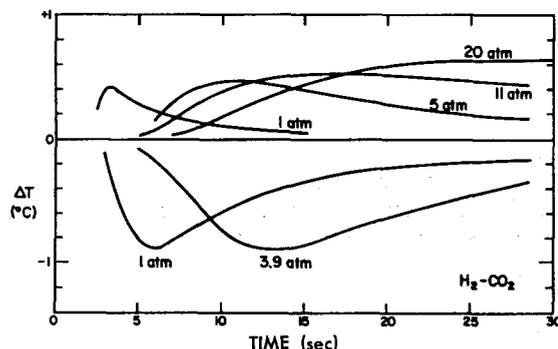


FIG. 3. Diffusion thermoeffect in H_2 -CO₂ mixtures as a function of pressure above and below the diffusion interface (7/8 in.).

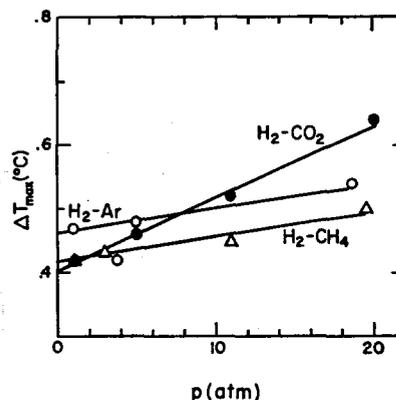


FIG. 4. Effect of pressure on the maximum temperature difference above the diffusion interface.

The present experimental accuracy does not permit us to say with any assurance whether ΔT_{\max} is linear or nonlinear with pressure for H_2 -Ar and H_2 -CH₄. Only straight lines are drawn in Fig. 4.

III. THEORETICAL

In this section we attempt to account, at least semi-quantitatively, for the results shown in Figs. 2-4. For this we need to know the composition and pressure dependences of the thermal diffusion factor α_T and the thermal conductivity, λ ; these are indicated (as well as they are known) for H_2 -Ar and H_2 -CO₂ in Figs. 5-8, as taken from a variety of sources.¹⁵⁻²⁰ In addition, the

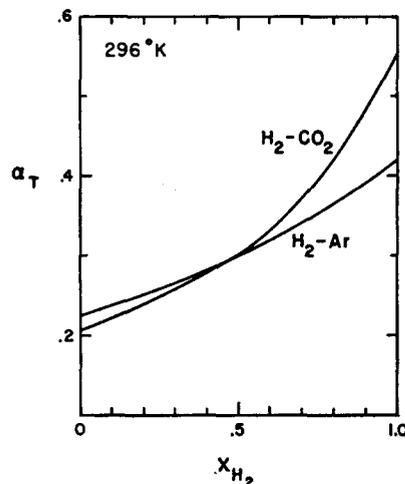


FIG. 5. Composition dependence of α_T at 1 atm, from Ref. 15.

¹⁵ E. A. Mason, S. Weissman, and M. Islam, *Phys. Fluids* **7**, 174 (1964); S. C. Saxena and E. A. Mason, *Mol. Phys.* **2**, 379 (1959).

¹⁶ T. Makita, *Rev. Phys. Chem. Japan* **29**, 47, 55 (1960); T. Makita and T. Takagi, *ibid.* **32**, 1 (1963).

¹⁷ T. L. Ibbs and A. A. Hirst, *Proc. Roy. Soc. (London)* **A123**, 134 (1929).

¹⁸ L. A. Guildner, *J. Res. Natl. Bur. Std.* **A66**, 341 (1962).

¹⁹ B. M. Rosenbaum, S. Oshen, and G. Thodos, *J. Chem. Phys.* **44**, 2831 (1966).

²⁰ N. V. Tsederberg, *Thermal Conductivity of Gases and Liquids* (MIT Press, Cambridge, Mass., 1965).

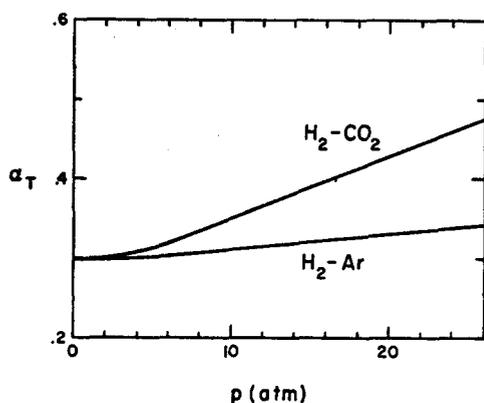


FIG. 6. Pressure dependence of α_T for approximately equimolar mixtures, from Ref. 16.

diffusion coefficient D_{12} at 296°K and 1 atm is¹⁵ 0.80 cm²/sec for H₂-Ar and 0.68 cm²/sec for H₂-CO₂. For H₂-Ar, the product pD_{12} decreases by about 7% on increasing pressure to 20 atm,²¹ and for H₂-CO₂ pD_{12} is essentially constant.²² Data for H₂-CH₄ are more scarce. The value of α_T at 296°K and 1 atm is 0.24 for an equimolar mixture,²³ and the value of D_{12} is 0.72 cm²/sec at the same conditions.²⁴ The value of λ for CH₄ at 296°K and 1 atm is²⁵ 8.06×10^{-5} cal/cm sec °C, and increases by about 8% on increasing pressure to 20 atm.²⁰

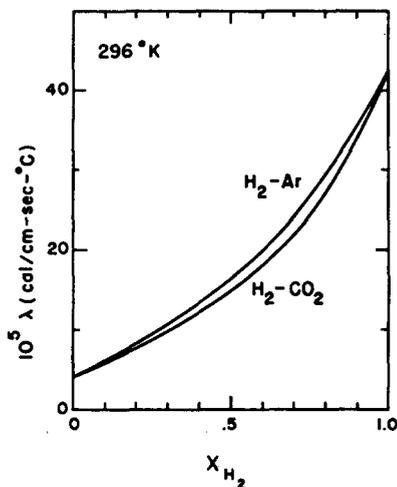


FIG. 7. Composition dependence of λ at 1 atm, scaled to 296°K from the measurements at 273°K given in Ref. 17.

²¹ I. F. Golubev and A. G. Bondarenko, *Gaz. Prom.* **8**, 46 (1963).

²² C.-H. Chou and J. J. Martin, *Ind. Eng. Chem.* **49**, 758 (1957).

²³ H. G. Drickamer, S. L. Downey, and N. C. Pierce, *J. Chem. Phys.* **17**, 408 (1949).

²⁴ C. A. Boyd, N. Stein, V. Steingrimsson, and W. F. Rumpel, *J. Chem. Phys.* **19**, 548 (1951).

²⁵ H. L. Johnston and E. R. Grilly, *J. Chem. Phys.* **14**, 233 (1946).

The foregoing data indicate that the asymmetry in ΔT above and below the diffusion interface is dominated by the composition dependence of λ . Although α_T is greater on the hydrogen-rich side by about a factor of 2 (Fig. 5), the value of λ on that side is greater by about a factor of 10 (Fig. 7); the faster heat loss by conduction results in a smaller temperature change.

Some progress can also be made in understanding the pressure dependence of the ΔT vs t curves without the need for a full mathematical description of the phenomenon. In the ideal-gas region (low pressures), α_T and λ are independent of pressure and D_{12} is inversely proportional to pressure. One might therefore expect that an increase of pressure would slow down the diffusion without slowing down the heat leak to the walls, so that ΔT_{\max} would decrease with increasing pressure. In fact, ΔT_{\max} remains nearly constant at low pressures, as indicated by Figs. 2-4, because the heat

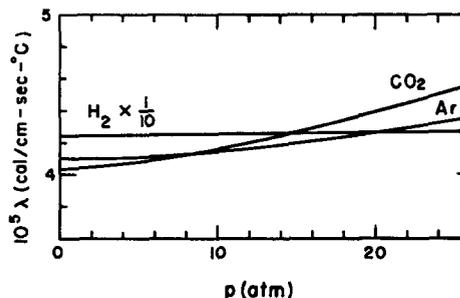


FIG. 8. Pressure dependence of λ for H₂, Ar, and CO₂, from Refs. 18-20. The behavior of a mixture is presumably intermediate between the behavior of its pure components.

leak is controlled not by λ but by the thermal diffusivity, $K = \lambda / \rho \bar{c}_p$, where ρ is the mass density and \bar{c}_p the specific heat. Since D_{12} and K both vary inversely with pressure, the only effect of pressure on the ΔT vs t curve is to change the time scale. This suggests that the ΔT vs t curves for the same system at different pressures could be brought into correspondence by replacing the t abscissa by t/p . This can easily be tested, although it is best to choose the origin to be at t_{\max} because of the uncertainty in the opening time, and to measure all temperatures relative to ΔT_{\max} . Plots of $\Delta T / \Delta T_{\max}$ vs $(t - t_{\max}) / p$ are found to bring runs at different pressures on the same system into coincidence, within the accuracy of reading the photographic record of ΔT vs t . However, this procedure does not correlate the results above and below the diffusion interface, even for the same system, because of the markedly different thermal diffusivities.

The preceding argument further suggests that the ΔT vs t curves for systems with different values of D_{12} but the same values of K might be brought into cor-

response by replacing t by $D_{12}t$. Thus plots of $\Delta T/\Delta T_{\max}$ vs $\log[(t-t_{\max})/p]$ should be superposable on each other by parallel translation along the time axis, the amount of translation giving the ratios of the D_{12} for the different systems. H_2 -Ar and H_2 -CO₂ have nearly the same K , and such plots are superposable for these systems; the ratio $D_{12}(H_2-CO_2)/D_{12}(H_2-Ar)$ is 0.85 ± 0.04 from the measurements above the interface, and 0.86 ± 0.06 from the measurements below the interface (except for an anomalously slow decay in the 1-atm H_2 -CO₂ results). These are in good agreement with the experimental value of 0.85. The value of K for H_2 -CH₄ is only slightly different above the interface than the values for H_2 -Ar and H_2 -CO₂ and the logarithmic plots for this system can be made to coincide reasonably well with those for H_2 -Ar and H_2 -CO₂. The ratio $D_{12}(H_2-CH_4)/D_{12}(H_2-Ar)$ is thus found to be about 0.92 ± 0.08 , in agreement with the experimental value of 0.90.

Further understanding of the experimental results requires a mathematical description of the phenomenon. It is important that this description be kept on a phenomenological basis, since we are dealing here with the pressure dependence of transport coefficients, for which no satisfactory molecular theory presently exists.²⁶ Waldmann⁶ has given such a description on the basis of irreversible thermodynamics. In a binary mixture without pressure gradients or external forces, the linear phenomenological equations for the heat flux

J_q and the diffusion fluxes J_1 and J_2 are⁶

$$J_q = (h_1 J_1 + h_2 J_2) - \lambda \nabla T$$

$$-nD_{12}\alpha_T x_1 x_2 \left(\frac{\partial \mu_1}{\partial x_1} + \frac{\partial \mu_2}{\partial x_2} - \frac{\partial \mu_1}{\partial x_2} - \frac{\partial \mu_2}{\partial x_1} \right) \nabla x_1, \quad (1)$$

$$J_1 = -nD_{12} \nabla x_1 - nD_{12}\alpha_T x_1 x_2 \nabla \ln T = -J_2, \quad (2)$$

where h_1 and h_2 are the partial molar enthalpies of Components 1 and 2, x_1 and x_2 are their mole fractions, μ_1 and μ_2 their chemical potentials, and n is the total molar density (moles per cubic centimeter). The heavy component is conventionally designated as 1. These equations may be regarded as essentially definitions of the transport coefficients λ , D_{12} , and α_T . The value of α_T is determined experimentally by application of Eq. (2) to steady-state ($J_1=0$) gas-unmixing experiments; the results shown in Figs. 5 and 6 were obtained in this way. Similarly, the value of λ is usually determined experimentally by application of Eq. (1) to a steady-state system in which the diffusive fluxes are zero; the last term in Eq. (1) is often negligible in magnitude. Applying the equation of continuity and remembering that the temperature change in the Dufour effect is small, we obtain from Eq. (2) the equation for the composition as a function of time and position,

$$\partial x_1 / \partial t \approx nD_{12} \nabla^2 x_1. \quad (3)$$

Similarly, applying the equation of energy balance, we obtain from Eq. (1) the result⁶

$$\rho \bar{c}_p (\partial T / \partial t) = - (J_1 \cdot \nabla h_1 + J_2 \cdot \nabla h_2) + \nabla \cdot (\lambda \nabla T) + nD_{12} \nabla \cdot \left[\alpha_T x_1 x_2 \left(\frac{\partial \mu_1}{\partial x_1} + \frac{\partial \mu_2}{\partial x_2} - \frac{\partial \mu_1}{\partial x_2} - \frac{\partial \mu_2}{\partial x_1} \right) \nabla x_1 \right]. \quad (4)$$

For nearly ideal gases, for which the second virial coefficient suffices in the equation of state, Eq. (4) can be transformed to

$$\partial T / \partial t = K \nabla^2 T + A \nabla^2 x_1 + B (\nabla x_1)^2 + C (\nabla x_1) \cdot (\nabla T), \quad (5)$$

where $K = \lambda / \rho \bar{c}_p = \lambda / nC_p$, and

$$A = \frac{RTD_{12}\alpha_T}{C_p} \left(1 + \frac{2px_1x_2B^*}{RT} \right), \quad (6)$$

$$B = \frac{RTD_{12}}{C_p} \left[\frac{\partial \alpha_T}{\partial x_1} + \frac{2p}{RT} \left(b^* + (x_2 - x_1)\alpha_T B^* + x_1x_2B^* \frac{\partial \alpha_T}{\partial x_1} \right) \right], \quad (7)$$

$$C = \frac{1}{nC_p} \frac{\partial \lambda}{\partial x_1} + \frac{RD_{12}\alpha_T}{C_p} \left[1 + \frac{2px_1x_2}{RT} (2B^* - b^*) \right] + \frac{D_{12}(C_{p1} - C_{p2})}{C_p} - \frac{2pD_{12}\beta^*}{TC_p}, \quad (8)$$

$$B^* = B_{11} - 2B_{12} + B_{22},$$

$$b^* = b_{11} - 2b_{12} + b_{22}, \quad b_{ij} = B_{ij} - T(dB_{ij}/dT),$$

$$\beta^* = x_1\beta_{11} + (x_2 - x_1)\beta_{12} - x_2\beta_{22}, \quad \beta_{ij} = T^2(d^2B_{ij}/dT^2),$$

in which B_{ij} are second virial coefficients and C_p is the molar heat capacity. The terms in B^* , b^* , and β^* are various nonideality effects, some of which are negligible for the present experiments. The most important terms on the right-hand side of Eq. (5) are $K\nabla^2 T$ and $A\nabla^2 x_1$. The importance of the $\partial \alpha_T / \partial x_1$ term in the coefficient B was first pointed out by Kotousov.¹⁰

* E. G. D. Cohen, Lectures Theoret. Phys. 8A, 145 (1966).

Kotousov¹⁰ has considered solutions of Eqs. (3) and (5) for the important case of diffusion in cylinders of finite radius a and arbitrary length L , with constant-temperature walls. For a first approximation, we neglect the terms involving B and C , assume ideal gases, and assume that the length of the diffusion tube is much larger than the distance of the thermometer from the diffusion interface. None of these approximations is of high accuracy for the present experiments, but some insight can be gained from this simplified case. The solution of Eq. (3), the diffusion equation, is

$$x_1(z, t) - x_1^\infty = (x_1^0 - x_1^\infty) \operatorname{erf}[z/2(D_{12}t)^{1/2}], \quad (9)$$

where z is the distance from the diffusion interface, and x_1^0 and x_1^∞ are the mole fractions at zero and infinite time, respectively. The solution of Eq. (5) for the temperature change δT is then¹⁰

$$\delta T(r, z, t) = \frac{zRTD_{12}\alpha_T(x_1^0 - x_1^\infty)}{C_p(K - D_{12})(\pi K)^{1/2}} \sum_{k=1}^{\infty} \frac{J_0(\gamma_k r/a)}{\gamma_k J_1(\gamma_k)} \exp(-\sigma_2^2 t) \int_t^{D_{12}t/K} \tau^{-3/2} \exp(\sigma_1^2 \tau) \exp\left(\frac{-z^2}{4K\tau}\right) d\tau, \quad (10)$$

where J_0 and J_1 are Bessel functions of orders zero and one, the γ_k are the roots of $J_0(\gamma_k) = 0$, and

$$\sigma_1^2 = \frac{K^2}{D_{12} - K} \left(\frac{\gamma_k}{a}\right)^2, \quad \sigma_2^2 = \frac{KD_{12}}{D_{12} - K} \left(\frac{\gamma_k}{a}\right)^2. \quad (11)$$

The actual reading on a diametric thermometer is

$$\Delta T(z, t) = a^{-1} \int_0^a \delta T(r, z, t) dr. \quad (12)$$

Although Eq. (10) is very cumbersome to handle accurately, sufficient accuracy for the present purposes can be obtained by keeping only the first term of the summation and evaluating the integral approximately, as follows:

$$\int_t^{D_{12}t/K} \tau^{-3/2} \exp(\sigma_1^2 \tau) \exp\left(\frac{-z^2}{4K\tau}\right) d\tau \approx \left(\frac{D_{12}t}{K}\right)^{-3/2} \exp\left(\frac{-z^2}{4D_{12}t}\right) \int_t^{D_{12}t/K} \exp(\sigma_1^2 \tau) d\tau \approx \left(\frac{D_{12}t}{K}\right)^{-3/2} \exp\left(\frac{-z^2}{4D_{12}t}\right) \left(\frac{-1}{\sigma_1^2}\right), \quad (13)$$

from which we obtain

$$\Delta T(z, t) \approx \frac{z\phi D_{12}\alpha_T(x_1^\infty - x_1^0)}{\pi^{1/2}\lambda} \left[\frac{0.61}{\gamma_1 J_1(\gamma_1)} \left(\frac{a}{\gamma_1}\right)^2 \right] \times (D_{12}t)^{-3/2} \exp\left(\frac{-z^2}{4D_{12}t}\right). \quad (14)$$

If the thermometer wires covered the total cross-sectional area of the diffusion cell the corresponding expression for $\Delta T(z, t)$ would be the same as Eq. (14) but with the numerical factor 0.61 replaced by 0.43. The actual situation is somewhere between these limits.

This result has the correct qualitative behavior, although it is too approximate to reproduce the detailed shapes of the experimental ΔT vs t curves, especially when K is greatly different from D_{12} . Even so, the magnitudes predicted by Eq. (14) are not grossly in error; the value of ΔT_{\max} for H_2 -Ar above the interface is predicted to be within the limits 0.89° and 0.63°C, whereas the experimental value is about 0.5°C.

The greatest usefulness of Eq. (14) is that it indicates the major dependence of the experimental results on the parameters of the system. For instance, it explicitly exhibits the dependence of ΔT vs t on D_{12} which was discussed above, and even gives a reasonable result for the absolute value of D_{12} . That is, if a plot of $\Delta T/\Delta T_{\max}$ vs $\log[D_{12}(t - t_{\max})]$ from Eq. (14) is compared with a plot of the experimental quantities $\Delta T/\Delta T_{\max}$ vs $\log[(t - t_{\max})/\phi]$, the two should be superposable by translation along the time axis, the amount of translation giving directly the value of D_{12} at 1 atm pressure.

On treating the results on H_2 -Ar above the interface in this way, we obtain a value for D_{12} of 0.85, in reasonable agreement with the known value of 0.80.

Three further experimental comparisons are suggested by Eq. (14). First of all, it indicates that the values of ΔT_{\max} above and below the interface should be in the same ratio as the values of α_T/λ above and below. Secondly, it indicates that the values of ΔT_{\max} for different systems at the same pressure should be in the same ratio as their values of $\alpha_T D_{12}/\lambda$. Finally, it indicates that the variation of ΔT_{\max} with pressure for a given system should be the same as the variation of $\alpha_T \phi D_{12}/\lambda$ with pressure. These three predictions can be tested for the present experiments.

The experimental ratios of ΔT_{\max} above and below the interface are about 0.30 ± 0.03 for H_2 -Ar and 0.47 ± 0.02 for H_2 -CO₂ at low pressures, according to Figs. 2 and 3. According to Eqs. (14) and (9), the composition at t_{\max} is $x_1 - x_1^\infty = 0.92(x_1^0 - x_1^\infty)$; from Figs. 5 and 7 we therefore predict that the ΔT_{\max} ratios should be 0.22 for H_2 -Ar and 0.29 for H_2 -CO₂. This agreement is only fair, and unfortunately is very sensitive to the value used for t_{\max} , which determines the compositions. For instance, if t_{\max} is somewhat greater,

so that $x_1 - x_1^\infty = 0.80(x_1^0 - x_1^\infty)$, the predicted ΔT_{\max} ratios increase to 0.28 for $\text{H}_2\text{-Ar}$ and 0.36 for $\text{H}_2\text{-CO}_2$. This agreement is still only fair for $\text{H}_2\text{-CO}_2$.

For the second comparison, we note from Figs. 2 and 3 that the ratio $\Delta T_{\max}(\text{H}_2\text{-CO}_2)/\Delta T_{\max}(\text{H}_2\text{-Ar})$ is 0.95 ± 0.06 above the interface and 0.58 ± 0.03 below. The corresponding ratios of $\alpha_T D_{12}/\lambda$, which are relatively insensitive to the value of t_{\max} , are 1.10 and 0.86, which is again only fair agreement.

The third and most interesting comparison is the effect of pressure on ΔT_{\max} . The only possible explanation, according to Eq. (14), for the increase of ΔT_{\max} with pressure shown in Fig. 4 would be the increase of α_T with pressure, since the pressure dependences of pD_{12} and λ are negligible or in the wrong direction. But the pressure dependence of α_T could increase ΔT_{\max} from 1 to 20 atm by only a factor of 1.1 for $\text{H}_2\text{-Ar}$ and a factor of 1.4 for $\text{H}_2\text{-CO}_2$. In both cases the predicted increase is less than the observed.

The experimental results thus indicate that Eq. (14) is only semiquantitative, and that some effects have been neglected. Likely candidates are the neglected terms of Eq. (5). Keeping only terms of importance at t_{\max} for the present experiments, we can rewrite the coefficients of Eq. (5) as

$$A = RTD_{12}\alpha_T/C_p, \quad (15)$$

$$B = \frac{RTD_{12}}{C_p} \left[\frac{\partial \alpha_T}{\partial x_1} + \frac{2pb^*}{RT} + \frac{2p(x_2 - x_1)B^*}{RT} \right], \quad (16)$$

$$C = \frac{1}{\rho \bar{c}_p} \frac{\partial \lambda}{\partial x_1} + \frac{RD_{12}}{C_p} \left[\alpha_T + \left(\frac{C_{p1} - C_{p2}}{R} \right) - \frac{2p\beta^*}{RT} \right]. \quad (17)$$

Without going through the formal integration of the differential equation, we can see that ΔT_{\max} , instead of varying as $(z p D_{12} \alpha_T / \lambda)$ according to Eq. (14), will be altered by a factor of approximately

$$1 + \frac{B(\nabla x_1)^2}{A \nabla^2 x_1} + \frac{C(\nabla x_1) \cdot (\nabla T)}{A \nabla^2 x_1}. \quad (18)$$

Using Eq. (9) to evaluate $\nabla^2 x_1$ and $(\nabla x_1)^2$, and Eq. (14) to find ∇T , we find the numerical values of (18) as listed in Table I. It can be seen that none of the corrections is of great importance, although they would not be negligible in an accurate study. The smallness of the corrections is caused by the rather large value of z used in the present experiments. For small values of z , the term $\partial \alpha_T / \partial x_1$ in the coefficient B can dominate at large times and cause a sign reversal in the ΔT vs t curve, as was pointed out by Kotousov.¹⁰ The non-ideality terms involving b^* , B^* , and β^* are negligible at 1 atm, but not at 20 atm.

The effect of the corrections in Table I on the agreement between theory and experiment is to worsen the agreement slightly for the ratios of ΔT_{\max} above and below the interface, and to improve it slightly for the ratios of ΔT_{\max} for different systems. This is probably

TABLE I. Values of correction terms at t_{\max} and 1 atm, above and below the diffusion interface (7/8 in.).

| System | $B(\nabla x_1)^2/A \nabla^2 x_1$ | | $C(\nabla x_1) \cdot (\nabla T)/A \nabla^2 x_1$ | |
|--------------------------|----------------------------------|-------|---|-------|
| | Above | Below | Above | Below |
| $\text{H}_2\text{-Ar}$ | -0.04 | +0.02 | -0.05 | +0.16 |
| $\text{H}_2\text{-CO}_2$ | -0.08 | +0.03 | -0.06 | +0.05 |

not significant in view of the approximations still inherent in Eq. (14) for ΔT , namely that the diffusion apparatus is very long and that the transport coefficients α_T and λ can be taken as constants in integrating the differential equation for the temperature, Eq. (5).

The effect of increasing pressure on the corrections to ΔT_{\max} is interesting. The gas-unmixing experiments¹⁶ indicate that the magnitude of $\partial \alpha_T / \partial x_1$ decreases markedly with increasing pressure, and Figs. 7 and 8 suggest that $\partial \lambda / \partial x_1$ probably also decreases. The result of this is to cause ΔT_{\max} to increase faster with pressure than α_T / λ does. However, the nonideality terms involving b^* , B^* , and β^* have the opposite effect. The net effect is a slight improvement of a few percent in the agreement between theory and experiment.

IV. CONCLUSIONS

We conclude that there is a distinct dependence on pressure of the diffusion thermoeffect, which parallels the pressure dependence of the thermal diffusion factor as found from gas-unmixing experiments. The present accuracy is insufficient to establish whether or not the increase with pressure is linear; measurements at higher pressures than 20 atm would be useful. The decay of the temperature difference with time gives a good measure of the relative diffusion coefficients for different systems, and fair absolute values of diffusion coefficients are obtainable with even a rather simplified mathematical theory.

Further refinements will be necessary before quantitative information on other transport coefficients can be extracted from measurements of the diffusion thermoeffect. The variation of α_T and λ with position, due to their dependence on composition, can be reduced experimentally by working with as small values of $(x_1^0 - x_1^\infty)$ as practicable, but there will remain non-negligible effects proportional to $\partial \alpha_T / \partial x_1$ and $\partial \lambda / \partial x_1$. It may be possible to disentangle these effects by study of the variation of ΔT with both position and time.¹⁰ In short, the diffusion thermoeffect is complicated, but the complications contain useful information.

ACKNOWLEDGMENTS

Special thanks are due the Council for Scientific and Industrial Research, Pretoria, South Africa, for making these studies possible by granting leave of absence to L.M. Thanks are due to Dr. H. W. Schamp, Jr., for helpful discussions concerning the apparatus design.