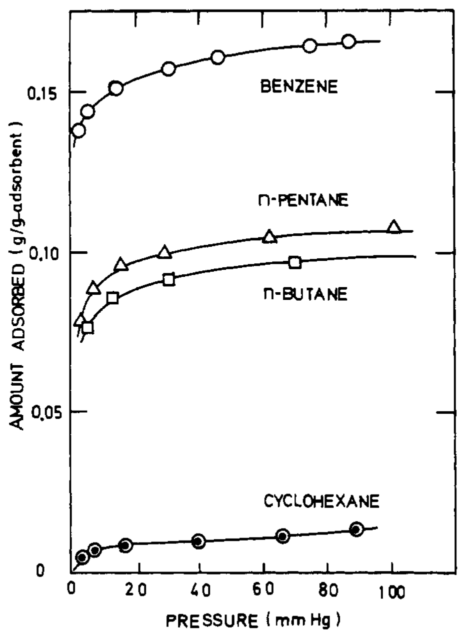

Figure 5. Molecular sieving effect for benzene and cyclohexane by MSC-5A at 30°C and isotherms of *n*-butane and *n*-pentane at 30°C as reference

therms shows the Type I isotherm according to the classification by Brunauer et al. (*1*). Figures 4 and 5 show this type of isotherm for *n*-butane and other hydrocarbons, respectively.

Isotherms of Type I are associated with the systems in which adsorption does not proceed beyond a monomolecular layer. For the methane system, in which the temperatures are above the critical, the adsorption does not reach saturation at the pressure below 650 mm Hg (Figure 2). For the ethylene and ethane systems, in which the temperatures are both below and above the critical, the shape of the isotherms is also similar to Type I. For the adsorbent like MSC-5A having the pores of molecular size diameter, the pore volumes are filled with adsorbate at relatively low pressures, giving the same results as the monomolecular adsorption. It also means that the adsorption inside the macropores is almost negligible. Adsorption on saran charcoals, the molecular sieving action of which is well known, has typical Type I isotherms (*3*).

The data by Kawazoe et al. (*5*) for ethane at 0° and 30°C are presented together with our data in Figure 3. The molecular sieving effect is obvious because the adsorbed amount of cyclohexane is $^1/_{15}$ the benzene adsorption amount at 30°C (Figure 5). The *n*-butane and *n*-pentane adsorption at 30°C is shown in the same figure for comparison. Details of the molecular sieving action of this material are reported by Eguchi (*2*).

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Diffusion Thermoeffect in Gases

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A study of the diffusion thermoeffect (the Dufour effect) was made for five different gas mixtures: H_2–N_2, H_2–CH_4, He–A, He–CO_2, and He–N_2. Measurements were made at several different temperatures and pressures. The values of the thermal diffusion factors were calculated for the five gas mixtures from the experimental data and were compared with the values obtained by other workers from direct thermal diffusion measurements.

The diffusion thermoeffect is of interest both in its own right as a little-investigated transport phenomenon and because it enables us to obtain quantitative information on other transport coefficients, particularly the thermal diffusion factor. In this work five different gas mixtures are investigated. No previous measurements of the temperature dependence of the diffusion thermoeffect are known to have been made for the H_2–N_2, CH_4–H_2, He–A, CO_2–He, and N_2–He mixtures.

The Dufour effect involves the measurement of the transient temperature gradient which results from an initial concentration gradient, and it is therefore related to the phenomenon of thermal diffusion. The effect was discovered by Dufour (*3*) in 1872 but was not extensively investigated until after its rediscovery by Clusius and Waldmann (*1*) in 1942. Apart from the classic studies of Waldmann, little work has been done in this field. Rastogi and Madan (*8*) studied the Dufour effect with an apparatus similar to the one used in the present work. Sawford et al. (*9*) also recently published some measurements on this effect. A study of the pressure dependence of the diffusion thermoeffect was made by Mason et al. (*7*).

Suppose two gases (labeled with subscripts 1 and 2), initially at the same temperature, diffuse into each other. On the basis of irreversible thermodynamics (*2*), it may be shown that:

$$\lambda \frac{\Delta T}{\Delta x} + \frac{\rho_1 RTD_{12}\alpha}{C_1\,[M_1 - C_1(M_1 - M_2)]}\,\frac{\Delta C_1}{\Delta x} = K \qquad (1)$$

where λ and D_{12} are the heat conductivity and diffusivity coefficients, respectively; α is the thermal diffusion fac-

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Table I. Dufour Effect in Gaseous Systems at Different Pressures and Temperatures

ΔT_{max} in °C

	$p = 700$ torr			$p = 500$ torr			
Systems	0°C	25°C	65°C	0°C	25°C	65°C	Warm side
A+He	0.29	0.26	0.21	0.20	0.18	0.13	Helium
$He+CO_2$	0.32	0.30	0.27	0.24	0.22	0.16	Helium
N_2+He	0.25	0.22	0.17	0.17	0.14	0.10	Helium
H_2+CH_4	0.14	0.13	0.10	0.10	0.09	0.07	Hydrogen
N_2+H_2	0.18	0.18	0.15	0.13	0.13	0.09	Hydrogen

Table II. Thermal Diffusion Factors for Gas Mixtures

Systems	α, from Equation 1	α, from thermal diffusion measurements	Ref.
N_2+H_2	0.44	0.35	*5*
He+A	0.33	0.37	*4*
CH_4+H_2	0.29	0.29	*4*
$He+CO_2$	0.44	0.45[a]	*6*
N_2+He	0.25	0.36	*4*

[a] The value of α for $He-CO_2$ was estimated using Figure 3 of Lonsdale and Mason (*6*).

tor; ρ_1 and C_1 are the mass density and mass fraction of component 1, respectively; ΔT is the maximum temperature difference; Δx is the distance between the thermocouples; and M_1 and M_2 are the molecular weights.

K is a constant which depends on the geometry of the cell (in particular, the position of the thermocouples) and must be determined experimentally. It is possible to leave $K = 0$ as Rastogi and Madan (*8*) do, but this is not the most general equation. Equation 1 was used in this work to calculate the thermal diffusion factor α from observations of ΔT_{max}.

Experimental

The measurements reported here were made with an apparatus similar to that of Rastogi and Madan (*8*). This apparatus consisted of two double-walled glass bulbs (250-ml capacity each) with a three-junction thermocouple in each. The bulbs were connected via a stopcock having a bore of 2 cm in diameter. The distance between the thermocouples (Δx) was 28.0 cm. The apparatus was kept in an oil bath except at 0°C where an ice-slush was used. The bath temperature was controlled to within ±0.1°C. The experiments were carried out under constant pressure conditions. The annular space between the double walls of the bulbs was evacuated to minimize heat loss. In each experimental determination, different gases were confined in the two bulbs at the same pressure. The temperature difference between the thermocouples was obtained as a function of time after the stopcock between the bulbs was opened and interdiffusion was allowed to occur.

A major difference from the Rastogi–Madan apparatus was the use of an operational amplifier circuit and pen recorder attached to the thermocouples. This overcame the difficulty in measuring the maximum temperature difference, ΔT_{max}, which occurs a short time (of the order of 10 sec) after the gases begin to diffuse. The resulting continuous curve of ΔT as a function of time could be used to estimate ΔT_{max} with an accuracy of ±0.01°C. It is doubtful whether an accurate measurement could be obtained with a potentiometer as in Rastogi and Madan's work.

The gases were supplied by the Matheson Co. and were used without further purification since the results were not expected to be sensitive to the presence of trace impurities. The purities of the gases were claimed by the supplier to be: Argon, 99.998%; carbon dioxide, 99.8%; methane, 99.0%; hydrogen, 99.95%; helium, 99.995%; and nitrogen, 99.9%.

Results and Discussion

The temperature and pressure dependence of ΔT_{max} are given in Table I. Measurements were carried out at three different temperatures for each of two different pressures. It may be noted that the maximum temperature difference in the diffusion thermoeffect increases with increasing pressure. This was to be expected since an approximate linear dependence of ΔT_{max} on pressure is predicted theoretically for the range of pressures under consideration. Also, Table I shows that ΔT_{max} does not change or shows only a slight decrease with increasing temperature.

Equation 1 was used to estimate the values of the thermal diffusion factor (α) from the values of ΔT_{max}. These are shown in Table II. The value of ΔC_1 in Equation 1 could not be measured directly, and it was estimated using the integrated form of Fick's second law of diffusion, since the time when ΔT reaches its maximum value was known from the experiments. This is the same procedure used by Rastogi and Madan (*8*). Since ΔC_1 was close to unity, we used the values of λ and ρ_1 for the pure component in Equation 1. The apparatus constant K was estimated to be 2.24×10^{-5} by setting the value of α equal to 0.29 for the methane–hydrogen mixture (*4*). Since the apparatus geometry remained the same in all experiments, this value of K was used in calculating α for the other systems.

In Table II the values of the thermal diffusion factors obtained directly from thermal diffusion measurements are also shown for comparison purposes. These values are of the correct order of magnitude but do not agree precisely with those obtained from our experiments. This may be due to convective mixing effects in our experiments or to the use of pure component values of λ and ρ_1 in Equation 1.

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