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THE THERMAL DIFFUSION IN BINARY GASEOUS MIXTURES UNDER PRESSURES, I

Hydrogen-Carbon Dioxide System

BY TADASHI MAKITA

The thermal diffusion in H_2–CO_2 system has been measured at pressures up to 120 atm and a mean temperature of 339.6~346.0°K. A "two-bulb" type apparatus has been employed here, because accurate estimation of thermal diffusion factor is possible. The thermal diffusion cells used are made of glass at 1~11.5 atm, and of steel at higher pressures. The composition at a steady state is analysed chemically. The experimental results obtained are as follows: 1) At 0.5~3.5 atm, the effect of pressure upon the thermal diffusion factor α is very small, and α is nearly constant as predicted by the kinetic theory. 2) The change in α with the composition is examined at the moderate pressure range of 1~11.5 atm, and it is found that the maximum separation is obtained near 0.6 of mole fraction of H_2, and that α increases with increasing mole fraction of H_2. 3) The theoretical equation of thermal diffusion at the atmospheric pressure is only qualitative for this system. 4) At pressures up to 120 atm, α increases continuously with increasing pressure, and the present results are found to have a good agreement with Becker's up to 81 atm.

Introduction

When the temperature gradient is applied to a homogeneous fluid mixture, the concentration gradient results. This phenomenon is a kind of mass-transfer and is known as thermal diffusion, one of the transport properties of fluids. The thermal diffusion is important both for practical separation processes and for theoretical treatment on the intermolecular forces.

This phenomenon in gaseous mixtures was first predicted theoretically by Enskog[1] and independently by Chapman[2], and verified experimentally by Chapman and Dootson[3]. Since the discovery, a number of measurements have been done at the atmospheric pressure, because the experimental methods and procedures are simpler and easier than in the study of other transport properties of gases. Most of the investigations employed a single stage apparatus, the so-called "two-bulb" method. Since multi-stage separation was discovered by Clusius and Dickel[4], the theoretical treatment of thermal diffusion columns has been developed by several investigators[5],

1) D. Enskog, *Physik. Z.*, **12**, 56, 533 (1911); *Ann. Physik*, **38**, 731 (1912)
2) S. Chapman, *Phil. Trans.*, **A 211**, 433 (1912); **A 216**, 279 (1916); **A 217**, 115 (1917)
3) S. Chapman and F. W. Dootson, *Phil. Mag.*, (6) **33**, 248 (1917)
4) K. Clusius and G. Dickel, *Naturwissenschaften*, **26**, 546 (1938); *Z. Phys. Chem.*, **B 44**, 397, 451 (1939)
5) W. H. Furry, R. C. Jones and L. Onsager, *Phys. Rev.*, **55**, 1083 (1939)
   R. C. Jones and W. H. Furry, *Rev. Mod. Phys.*, **18**, 151 (1946)
   H. G. Drickamer, V. J. O'Brien, J. C. Bresee and C. E. Ockert, *J. Chem. Phys.*, **16**, 122 (1948)
   H. G. Drickamer, E. W. Mellow and L. H. Tung, *ibid.*, **18**, 945 (1950)

and a column method for the measurement of thermal diffusion has been also employed success-
fully at least near the atmospheric pressure. On the other hand, considerable interests in the
theoretical treatment of thermal diffusion had arisen from its sensitivity to the nature of inter-
action between unlike molecules, and therefore, the study of thermal diffusion was one of the best
means of the investigation of these forces. The refined kinetic theory[6] has been well developed
on the several molecular models[7], and gives a good agreement with experiments at the ordinary
pressure.

However, investigations on the effect of pressure on the thermal diffusion in gaseous mixtures
are very scarce, as the author has recently reviewed[8]. An earnest work under high pressures
was first done by Becker and his coworker[9]. They carried out measurements for several gas-pairs
under pressures from 3 to 81 atm, and their apparatus consisted of two cylinders, each capacity
of 140 cc, connected by a steel tube, and the top cylinder was maintained at 160°C and the bottom
one at 14°C. After allowing time for a steady state to be attained, the composition in each cylinder
was analysed chemically or by a thermal conductivity bridge. They found that the thermal
diffusion factor increased with increasing pressure, with the exception of N_2–CH_4. In 1950~1953,
several ambitious works by use of thermal diffusion columns were reported by Drickamer and
coworkers[10]. Their investigations for several gas-pairs, contained isotopic mixtures, succeeded in
covering over much wider range of pressures, up to 225 atm, and partly over the critical region,
where the large change in thermal diffusion factor was found. However, as the theory of columns
is only semi-quantitative in dense media, Walther and Drickamer[11] recently made measurements
on a series of binary mixtures of gases up to 500 or 1000 atm by means of the two-bulb type
apparatus. Their cell consisted of a large hot chamber and a small cold one, separated by a layer
of porous glass, the temperature difference averaged 8°C. The analysis was performed by use of
a thermal conductivity bridge. They found that mixtures far from the critical temperature show
only small effects, and that, for systems where one component is near its critical temperature, a
large negative value of the thermal diffusion factor is obtained. On the other hand, in spite of
several theoretical attempts on this phenomenon under high pressures, neither kinetic theories[6,7]
nor the thermodynamics of irreversible processes[12] offer a satisfactory explanation of experimental

6) S. Chapman and T. G. Cowling. *The Mathematical Theory of Non-Uniform Gases*, Cambridge Univ.
Press, London (1939)
7) J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *The Molecular Theory of Gases and Liquids*, John
Wiley & Sons, Inc., New York (1954)
8) T. Makita, *J. of the Society of High Pressure Gas Industry (Japan)*, 24, No. 1, 18 (1960)
9) E. W. Becker and A. Schulzeff, *Naturwissenschaften*, 35, 218 (1948)
   E. W. Becker, *Z. Naturforsch.*, 5a, 457 (1950) ; *J. Chem. Phys.*, 19, 131 (1951)
10) H. G. Drickamer, E. W. Mellow and L. H. Tung, *J. Chem. Phys.*, 18, 945 (1950)
   N. C. Pierce, R. B. Duffield and H. G. Drickamer, *ibid.*, 18, 950 (1950)
   E. B. Giller, R. B. Duffield and H. G. Drickamer. *ibid.*, 18, 1027 (1950)
   L. H. Tung and H. G. Drickamer, *ibid.*, 18, 1031 (1950)
   F. E. Caskey and H. G. Drickamer, *ibid.*, 21, 153 (1953)
11) J. E. Walther and H. G. Drickamer, *J. Phys. Chem.*, 62, 421 (1958)
12) R. Haase, *Z. Physik*, 127, 1 (1949); *Z. Phys. Chem.*, A 196, 219 (1950); *Z. Elektrochem.*, 54, 450 (1950)
   W. L. Robb and H. G. Drickamer, *J. Chem. Phys.*, 18, 1380 (1950); 19, 818 (1951)

results.

In the present investigation, some detailed measurements have been attemped in the system of H_2 and CO_2 by use of the two-bulb method.

Experimentals

Experimental apparatus   For the measurement of thermal diffusion in gas mixtures, the two-bulb technique and column method have been used, as mentioned above. Although the theory of thermal diffusion column has been well developed, its applicability in dense media is very doubtful. Therefore, the former method, by which the accurate estimation of thermal diffusion factor is possible, has been applied in this investigation.

The apparatus consists of two cylindrical chambers and a narrow tube connecting between them. The tube contains a stopcock or a valve, isolating one chamber from the other for analysis. Some preliminary examinations on the two-bulb type apparatus were done by Kiyama and Saiuchi[13] in earlier years, and as some relations were obtained between the relaxation time (the time required to the steady state) and the cell dimensions——volume of each chamber, length and diameter of the connecting tube, and diameter of the cock-hole, the dimensions of the apparatus are chosen
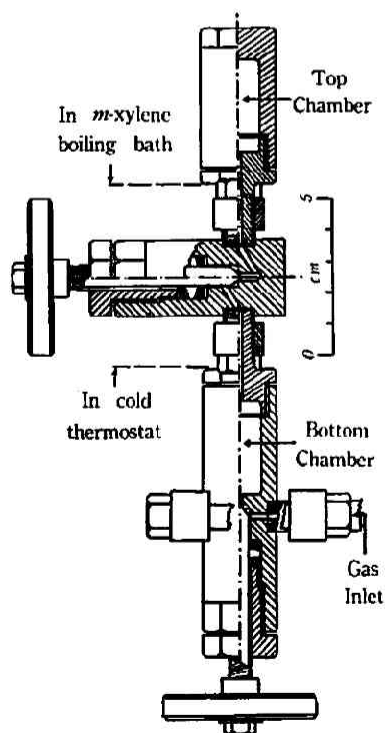

Fig. 1   Thermal diffusion apparatus (steel)

13) R. Kiyama and K. Saiuchi, *unpublished.*

50 . T. Makita

to be suitable for conditions of measurements. A glass apparatus with each chamber of 125 cc capacity is used for measurements at 0.5 ~ 3.5 atm. At the pressures of 3 ~ 12 atm, a thick-walled glass apparatus, each of 25 cc, is employed. which has a chuck of the glass-cock and a metal joint. For higher pressures, a steel apparatus, each of 5 cc capacity, is used, which is shown in Fig. 1. The apparatus is mounted vertically and, to avoid convection, the top chamber is maintained at a high temperature and the bottom one at a lower temperature. A boiling m-xylene bath (138.8°C) is used for the top temperature and a liquid thermostat (10.0° or 20.0°C) for the bottom. These temperatures are chosen to be adequate by reasons of : 1) it had been found that, in the measurements of thermal diffusion in mixtures containing CO_2, the thermal diffusion ratio changed from one definite value to a higher definite one at a temperature of about 146°C[14, 15], and 2) in Becker's work[9] which is only one measurement in H_2–CO_2 system under high pressures, hot and cold temperatures were near the present ones as described above.

Materials   The sample gases used were obtained from commercial sources, and H_2 was dryed by passage through a trap of silica-gel and CO_2 was purified by means of redistillation from liquid. The purity of both gases is more than 99.95%. The gas mixtures were made up in large cylinders and were used for measurements at least after one week.

Procedures   The bulbs of thermal diffusion apparatus are maintained at each temperature and, after evacuated, are filled with a gas mixture from the high pressure cylinder. If necessary, the gas mixture is compressed through a pressure-intensifier, in which the pressure is transmitted by an oil pump. After allowing time for a steady state to be attained, the gas in each chamber is analysed. For the measurement at one condition. 5 ~ 6 runs are taken over the relaxation time, in order to ensure the attainment to the steady state conditions.

Method of analysis   The composition of a gas mixture in feed and at equilibrium is analysed chemically. That is, CO_2 in mixtures is absorbed by 33 wt. % KOH solution, which is kept in H_2 atmosphere, in order to eliminate the error resulting from the solubility of H_2. Then, as the vapour pressure of the solution is corrected. the accuracy of analysis could be attained to 0.02%.

Experimental Determination of Thermal Diffusion Factor

A temperature gradient in a mixture initially of uniform composition leads to the development of a concentration gradient. Since this concentration gradient causes ordinary diffusion tending to eliminate the gradient, a steady state is possible in which the separation of thermal diffusion is balanced by the remixing effect of the ordinary diffusion. At such equilibrium condition, the solution of the equation of diffusion in a binary mixture is as follows[7, 8] :

$$\alpha(\bar{T}) = \frac{(x_1)_b - (x_1)_t}{x_1 x_2 \ln(T_t/T_b)} = \frac{\Delta x}{x_1 x_2 \ln(T_t/T_b)},\qquad(1)$$

14)   T. L. Ibbs and A. C. R. Wakeman, *Proc. Roy. Soc., London*, A 134, 613 (1932)

15)   R. E. Bastick, H. R. Heath and T. L. Ibbs, *ibid.*, A 173, 543 (1939)

assuming that the composition change is usually so small that the variation in thermal diffusion factor α due to this variation may be neglected, and taking α at some mean temperature $\bar{T}$ lying between temperatures of top chamber T_t and of bottom one T_b. In this equation x_1 and x_2 are the mole fraction of components in feed, and $(x_1)_b$ and $(x_1)_t$ are the mole fraction of heavy component in bottom and top chamber, respectively, at equilibrium. On the other hand, Brown[16] suggested the following relation semi-theoretically for $\bar{T}$:

$$\bar{T} = \frac{T_t T_b}{T_t - T_b} \ln\left(\frac{T_t}{T_b}\right). \qquad (2)$$

In this investigation, the thermal diffusion factor is calculated by Eq. 1 at the mean temperature assigned by Eq. 2.

Results and Considerations

The pressure effect near the atmospheric pressure   The effect of pressure on the thermal diffusion factor for a mixture of equal proportions has been measured at the pressure range of 0.59～3.44 atm. by use of the large glass apparatus maintained at temperatures of the top chamber, 138.8°C and the bottom one, 10°C ($\bar{T}$=339.6°K). As the results are shown in Fig. 2, the pressure effect is very small, α increases slightly, and the change in separation $\varDelta x$ is only
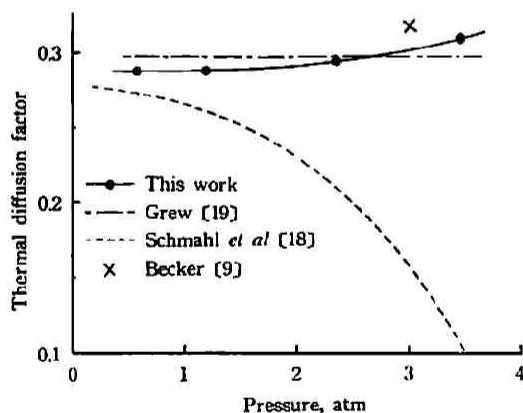

Fig. 2   Thermal diffusion factor in H₂-CO₂ system near the atmospheric pressure

0.002 within this pressure range.   According to the theory of Enskog and Chapman[6,7], the thermal diffusion factor should be independent of pressure.   Its experimental evidence is scarce and a contrary result has been also obtained.   That is. this independence of pressure was first found over small pressure range of 0.3～1 atm by Ibbs and coworkers[17].   While, Schmahl and Schewe[18] made measurements of thermal separation in mixtures of H₂ with CO₂ and H₂S at pressures of 0.2～3.5

16)   H. Brown, *Phys. Rev.*, **58**, 661 (1940)

17)   T. L. Ibbs, K. E. Grew and A. A. Hirst, *Proc. Phys. Soc.*, **41**, 456 (1929)

18)   N. G. Schmahl and J. Schewe, *Z. Elektrochem.*, **46**, 203 (1940)

52   T. Makita

atm and found the distinct decrease in the separation with increasing pressure, but Grew[19] obtained some data for H_2-CO_2 over the same pressure range and indicated that the thermal diffusion factor is independent of pressure.   In Fig. 2, the data in the H_2-CO_2 system of Schmahl et al and Grew are also plotted, where the former values are calculated from the values of the separation read from their diagram.   The present results would support Grew's one, taking into consideration high accuracy in analysis of this measurement.   It seems that the results of Schmahl et al would be caused by troublesome convection currents in the connecting tube, or by insufficiency of the time for separation, the effect of which would be more severe at high pressures.

   The effect of initial concentration under moderate pressures   The separation and the thermal diffusion factor in this mixtures have been determined at pressures $1.2 \sim 11.5$ atm. by means of the two glass apparatus described above.   The temperature of cold chamber is taken 20.0°C. and therefore $\bar{T}$=346.0°K.   The isobars in a diagram of separation $\varDelta x$ and initial concentration x_{H_2} are shown in Fig. 3.   A maximum separation is obtained near x_{H_2}=0.6.   The same tendency had been seen in other works[18, 20, 21] at the ordinary pressure.   The present results show that the composition of maximum separation is not affected by pressure within this range. The thermal diffusion factors obtained at the three pressures are plotted as a function of x_{H_2} in Fig. 4.   It is found that the thermal diffusion factor α is now not independent of pressure at an
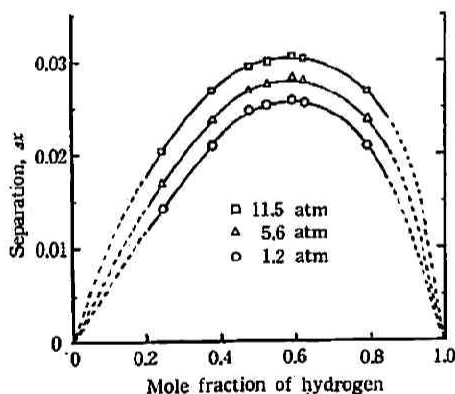

Fig. 3   Thermal separation in H_2-CO_2 system at moderate pressures
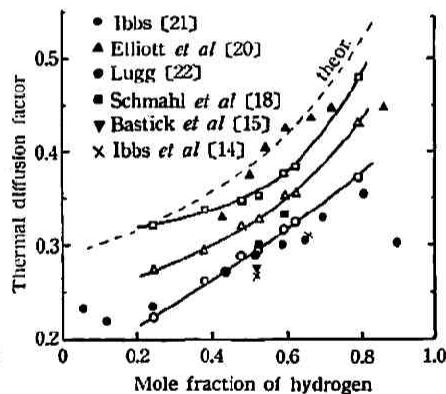
Fig. 4   Thermal diffusion factor in H_2-CO_2 system at moderate pressures

initial concentration, and that α increases slowly with increasing x_{H_2} at a constant pressure.   Then, the pressure effect on α is larger at low x_{H_2}, where the pseudocritical temperature of the system is considerably near the experimental temperature.   Some results, which are calculated from data at 1 atm published by several investigators[14, 15, 18, 20~22], are also shown in Fig. 4.   It seems that the present data at 1.2 atm agree roughly with those of other workers, with an exception of

   19) K. E. Grew, *Nature*, **156**, 267 (1945)
   20) G. A. Elliott and I. Masson, *Proc. Roy. Soc., London,* A **108**, 378 (1925)
   21) T. L. Ibbs, *ibid.,* A **107**, 470 (1925)
   22) J. W. H. Lugg, *Phil. Mag.,* **8**, 1019 (1929)

Elliott *et al* who measured at higher temperatures of the top chamber, 480~494°C.

On theoretical values at the ordinary pressure   The rigorous theory of thermal diffusion in gaseous phase, which is fully treated by Chapman and Cowling[6], is very complex, and three expressions for α are available[23,24], depending on the approximation procedures employed, the first approximation and second one of Chapman and Cowling and the first approximation of Kihara[25]. A few example calculation of α indicated that the second approximation of Chapman and Cowling and the first one of Kihara are more accurate than the other. But, the second one is rather complicated and quite tedious for numerical calculation. It seems, therefore, satisfactory for the present purpose to use Kihara's expression, and it is given by[3,23,24]

$$\alpha = (6C^* - 5)\frac{x_1 S_1 - x_2 S_2}{x_1^2 Q_1 + x_2^2 Q_2 + x_1 x_2 Q_{12}}, \qquad (3)$$

where S's and Q's are quantities that involve reduced masses, diameters and collision cross-sections of the colliding particles, and C^* is a function of reduced collision integral.

The numerical calculation of S's, Q's and C^* depends on the molecular model used. To this investigation, Lennard-Jones (12–6) model is applied, which has been the best intermolecular potential used to date for the study of transport phenomena, and is expressed by a repulsion term varying as the inverse twelfth power of the distance of separation between the centers of two molecules and an attraction term varying as the sixth power of the separation distance. The force constants of pure components, γ and ε, obtained from viscosity data are used as follows[7]:

$$CO_2: \quad \gamma_1 = 3.996\,A, \quad \varepsilon_1/k = 190°K.$$
$$H_2: \quad \gamma_2 = 2.968\,A, \quad \varepsilon_2/k = 33.3°K,$$

where k is the Boltzmann constant. And the force constants γ_{12} and ε_{12} of the potential between unlike molecules can be given by the following simple combination rule:

$$\left. \begin{array}{l} \gamma_{12} = \frac{1}{2}(\gamma_1 + \gamma_2) \\[2mm] \varepsilon_{12} = (\varepsilon_1 \cdot \varepsilon_2)^{1/2}. \end{array} \right\} \qquad (4)$$

The numerical values of reduced collision integral are obtained from tables[7] as a function of kT/ε.

The calculated values are plotted as a dotted-curves in Fig. 4. It seems that the theoretical values are only qualitative in the case of this system. This discrepancy between theory and experiment may be caused by the fault of the basic theory, of an inadequate potential form, or of the simple combination rule. That is, the theory involves several assumptions, of which spherically symmetrical force fields and elastic collisions are the most important in this case. Although these assumption would be reasonably valid for H_2, CO_2 cannot be treated as a spherical molecule.

23) E. A. Mason, *J. Chem. Phys.*, **23**, 49 (1955)

24) B. N. Srivastava and K. P. Srivastava, *Physica*, **23**, 103 (1957)

25) T. Kihara, *Imperfect Gases*, Asakusa Bookstore, Tokyo (1949)

54   T. Makita

Mason and Rice[26] have recently described on a modified Buckingham (exp-6) potential, which is more realistic than Lennard-Jones potential, and showed that CO_2 can not be handled by the method used for spherical molecules. and that the best that can be done is to assign different parameters for each property.

Thermal diffusion factors under high pressures   The effect of pressure upon the thermal diffusion factor in H_2–CO_2 system is measured under the range of $11.5 \sim 115.2$ atm by using a steel apparatus.   A mixture of initial concentration $x_{H_2}=0.4905$ has been separated between temperatures of the top chamber 138.8°C and the bottom 20.0°C ($\bar{T}=346.0$°K).   The results are
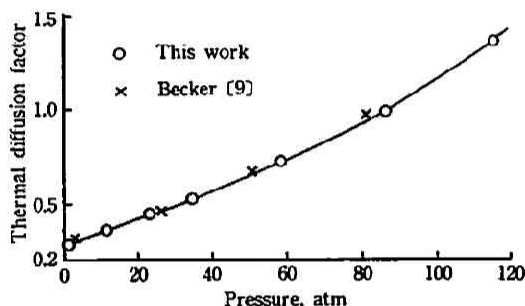

Fig. 5   Thermal diffusion factor in H_2–CO_2 system under high pressures

shown in Fig. 5, where Becker's data which are only one investigation existing to date are also plotted.   The agreement is satisfactory over the all pressure range.   The increase in α is entirely smooth. and the separation Δx becomes from 0.031 at 11.5 atm to 0.116 at 115.2 atm, and the relaxation time determined roughly increases from 7 to 60 hours in the same pressure range.

Acknowledgment

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26)   E. A. Mason, *J. Chem. Phys.*, **22**, 169 (1954)
      E. A. Mason and W. E. Rice, *ibid.*, **22**, 522, 843 (1954)