THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 29, NO. 2, MAR. 1960

THE THERMAL DIFFUSION IN BINARY GASEOUS MIXTURES UNDER PRESSURES, II

A New Thermal Diffusion Apparatus

BY TADASHI MAKITA

(Received February 13, 1960)

A new "two-bulb" type thermal diffusion apparatus has been constructed, in which the concentration of a mixture and its variation with time can be deduced continuously under high pressures, from the velocity of ultrasonics. The bottom chamber of the themal diffusion apparatus is designed to be a constant-volume, variable-path ultrasonic interferometer, which contains a quartz transducer, facing a reflector-piston that can be driven by means of a micrometer screw. The electrical circuits consist of a Hartley oscillator, an amplifier and a detector. And the position of nodes is recorded on a photographic paper by the light spot of a galvanometer. The frequency of the driving oscillator is determined by a heterodyne frequency-meter at the same time. The overall accuracy of this instrument would be 0.2% in the estimation of the velocity of sound, as shown by the data of that in argon at 25.0°C under pressures up to 150 atm.

After the evaluation of the relations between the velocity of sound and the composition in hydrogen-carbon dioxide system, thermal diffusion factor α in these mixtures of various compositions has been measured under 9.7~98.1 atm and at a mean temperature of 349.1°K. It has been found that α increases continuously with increasing pressure at a definite composition, and the effect of pressure is larger at the lower mole fraction of hydrogen.

Introduction

In spite of the importance of the thermal diffusion both for the practical separation processes and for the theoretical treatment of intermolecular force, some data obtained under pressures are still unsufficient, as described in the author's recent review paper1). The effect of pressure and concentration upon the thermal diffusion in hydrogen-carbon dioxide system has been investigated in details by using a two-bulb method in the previous paper2). In that apparatus, some troublesome problems arose, that is, it was considerably difficult to determine the relaxation time and the rate of approach to the steady state. and it took long time to confirm that the system was at the steady state condition, because runs of each point were made at several time-length to ensure that condition. Therefore, an apparatus, in which the composition of a mixture can be continuously analysed even under pressures, would be desirable.

At the atmospheric pressure, there are more immediate and convenient methods depending on the variation with composition of properties such as density, thermal conductivity, viscosity,

---

1) T. Makita, *J. of the Society of High Pressure Gas Industry (Japan)*, 24, No. 1, 18 (1960)

2) T. Makita, *This Journal*, 29, 47 (1959)

optical refractivity and velocity of sound. The development in recent years of mass spectrometers has also made it possible to adapt a method to determine the composition of mixtures. Another technique is by radioactivity, which is applicable in a mixture containing a radioactive isotope. This is the only method that was ever employed under high pressures3).

Since measurements of thermal diffusion by use of the velocity of sound were first made under low pressures by van Itterbeek and coworkers4), in the present investigation, the velocity of sound, measured under pressures by several workers5), has been chosen from the following points of view: 1) the measurement would be possible in a small space, 2) the measurement of the property has not severe effects on a gas, such as convection or heating, 3) the property would be continuous from the ordinary pressure to high pressure, 4) the absolute values of the property could be directly estimated, without using other properties under pressures, 5) the mechanism of the apparatus is not so complicated. A new thermal diffusion apparatus has been constructed in which the bottom chamber is an ultrasonic interferometer, and some measurements have been made by means of this apparatus.

Instrument

The instrument used in this work consists of four parts: a thermal diffusion cell where the bottom chamber is an interferometer, electrical circuits, the low pressure system for gas analysis, and the high pressure system, as shown in Fig. 1, which is self-explanatory.

Ultrasonic interferometer The measurement of the velocity of sound consists of determinations of the wave length λ and of the frequency f in a medium. Then the velocity of sound C is given by

$$C=f\cdot\lambda. \qquad (1)$$

Experimental determination of the wave length was performed by several methods, in which an interferometer method would be more suitable for measurements using ultrasonic waves of rather low frequency, than other methods, from the point of view of accuracy. For the purpose of this work, a variable path acoustic interferometer was designed as shown in Fig. 2.

The main cylinder contains a quartz transducer F, facing parallel to the carefully finished face of a reflector-piston H. When the revolution of the main shaft is transmitted to the piston by

---

3) H. G. Drickamer *et al*, *J. Chem. Phys.*, **18**, 1027 (1950); **19**, 1242, 1504 (1951); **20**, 981 (1952)
J. J. Martin *et al*, *Ind. Eng. Chem.*, **47**, 2081 (1955); **49**, 758 (1957)
T. R. Mifflin and C. O. Bennett, *J. Chem. Phys.*, **29**, 975 (1958)

4) A. van Itterbeek, G. Forrez and P. Mariens, *Physica*, **19**, 525 (1953)

5) A. H. Hodge, *J. Chem. Phys.*, **5**, 974 (1937)
C. M. Herget, *ibid.*, **8**, 537 (1940)
A. Lacan and J. Noury, *Compt. rend.*, **223**, 377 (1946); **233**, 516 (1951); **234**, 303, 1036 (1952); **236**, 362, 589 (1953); *J. Phys. Radium*, **14**, 348, 351, 426, 427 (1953); **15**, 301, 381 (1954)
W. G. Schneider *et al*, *Can. J. Research*, **28 A**, 509 (1950); *Can. J. Chem.*, **29**, 243 (1951); *J. Chem. Phys.*, **20**, 1777 (1952)
H. D. Parbrook and E. G. Richardson, *Proc. Phys. Soc.*, **64 B**, 437 (1952)

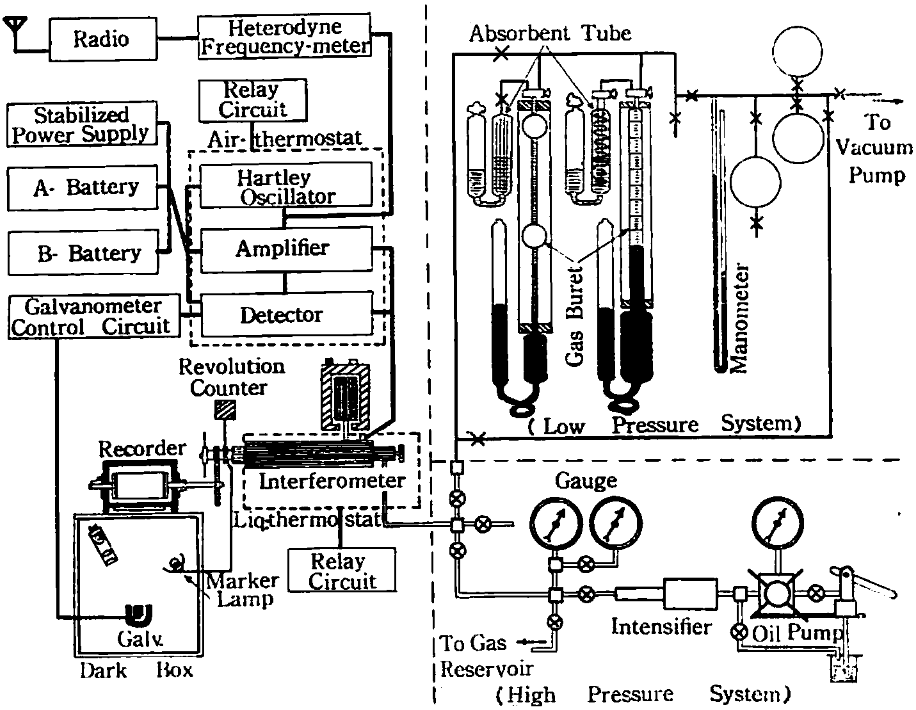


Fig. 1 Schematic diagram of a new thermal diffusion apparatus

a micrometer-screw I, the piston is movable without revolution by a key G inlaid, which slides along a guide-groove on the main cylinder. A narrow groove and small hole in the reflector-piston are provided to allow free passage of gas to both sides of the piston. The main shaft is held at a definite position by a spring K and ball-bearings J and L. Two gears N and O on the main shaft are connected with a revolution-counter and a recorder-drum, respectively. A contact-point M is used to mark revolutions on the recorder. The power driving crystal is led through a high-tension electrode D, which is insulated from the cylinder by polystyrene-resin.

The chief merits of this apparatus would be: 1) The capacity of gas space is taken to be a minimum size, without diminution of accuracy in the measurement of the velocity of sound, 2) the dead space in the chamber is minimized as possible for the measurement of thermal diffusion, 3) the volume of the chamber remains constantly when the reflector-piston would be driven, and therefore the pressure is also maintained constant, 4) any force is not transmitted to the precision micrometer-screw, 5) the procedures of opening and resealing are rather easy and simple, and 6) the apparatus would be applicable to the measurement of other properties in binary mixtures—-for example, ordinary diffusion, rate of chemical reactions, phase equilibrium, *etc.*—-if partly improved.

Electrical circuits The source of ultrasonic waves is a X-cut quartz-crystal, shown as F in Fig. 2, which is chosen as 24 mm in diameter and about 6 mm thick. The circuits used for driving the crystal and for detecting the nodal positions are of a conventional type, as can

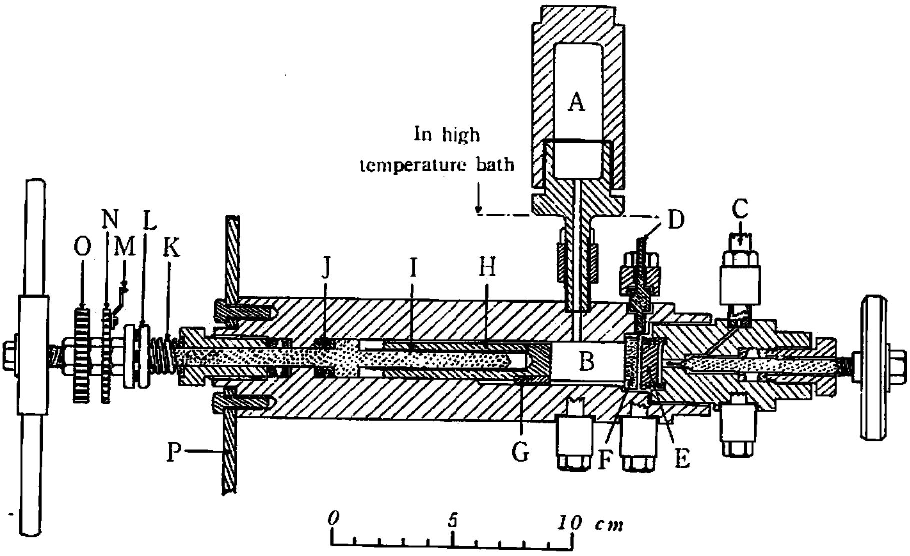
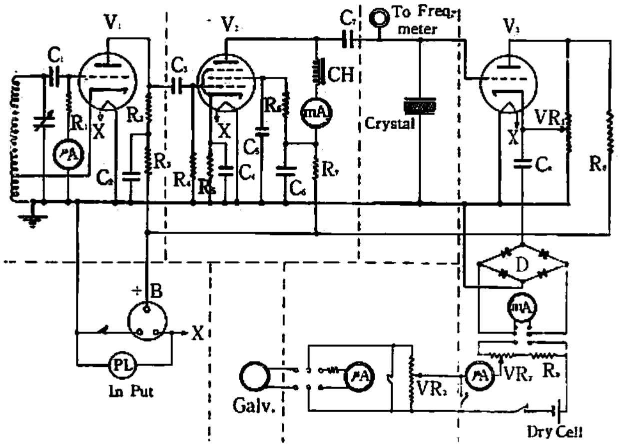


Fig. 2 Thermal diffusion apparatus——the bottom chamber is a constant-volume, variable-path ultrasonic interferometer.

A: Top chamber
B: Bottom chamber
C: Gas inlet
D: Electrode
E: Back plate
F: Quartz crystal
G: Key
H: Reflector piston
I: Micrometer screw
J: Ball bearing
K: Spring
L: Ball bearing
M: Contact point for marking
N: Gear connecting with revolution counter
O: Gear connecting with recorder drum
P: Thermostat wall



V_1: 6J5-GT
V_2: 6F6-GT
V_3: UY-76
D: Germanium diode (1NA4)
C_1: 250 pF
C_2: 0.1 μF
C_3: 0.005 μF
C_4: 0.1 μF
C_5: 0.1 μF
C_6: 0.1 μF
C_7: 250pF
C_8: 0.01 μF

VR_1: 0~250 kΩ
VR_2: 0~2 kΩ
VR_3: 0~5 kΩ
R_1: 30 kΩ
R_2: 300 Ω
R_3: 15 kΩ
R_4: 100 kΩ
R_5: 420 Ω
R_6: 10 kΩ
R_7: 1 kΩ
R_8: 20 kΩ
R_9: 1 kΩ
CH: 2.5 mH

Fig. 3 Electrical circuits for ultrasonic interferometer

be seen from Fig. 3 and explanatorily in Fig. 1. Powers for electronic-tubes are supplied from batteries. The frequency of the driving oscillator is checked in each run by a precision heterodyne frequency-meter, which is calibrated against the JJY standard transmissions (accurate to

2×10^{-8}). The circuits for detecting nodes, as the reflector is moved, are a simple electronic-tube voltmeter which contains a germanium-diode bridge. A potentiometer circuit is employed to balance out the steady component of the current. The amplitude of light from the galvanometer is controlled by a variable shunt-resistance.

Recording In order to eliminate personal errors in reading the moving light from the galvanometer and to check the wave form, the light spot is recorded on a photographic paper, which is made to move connectedly with the main shaft of the interferometer as shown schematically in Fig. 1.

Accuracy As the measurement of the frequency of the oscillator is made within at least less than 0.05%, the accuracy in the estimation of the velocity of sound would be determined by that in the determination of wave length of ultrasonics. Since the micrometer-screw has a pich of 0.5 mm and is calibrated to 0.001 mm, it is possible to read a displacement of the reflector of 0.001 mm. 16 revolutions of the main shaft (the reflector moves by about 0.08 mm) are recorded on a paper, in which we can read the distance between the waves within the accuracy of 0.1%. The overall accuracy depending upon the precision of the micrometer-screw would be 0.2% in this instrument.

Measurements of the Velocity of Sound

Measurements of the velocity of ultrasonic waves in hydrogen, carbon dioxide and argon have been made at 25.0°C and under pressures up to 150 atm, in order to examine the accuracy and reproducibility of the present instrument.

The gases used were obtained from commercial sources. H_2 and CO_2 were purified as mentioned in the previous paper[1], and both have the purity of more than 99.95%. Although argon was not further purified, the purity of the high-grade argon is 99.9% as indicated by the manufacturer.

The interferometer, where the top chamber A in Fig. 2 had been removed away, was immersed in a liquid-paraffin bath maintained at a constant temperature of 25.0 ± 0.02°C. After evacuation, the sample gas was introduced into the interferometer and compressed to a desired pressure by a pressure-intensifier. The electrical circuits had been kept at a constant temperature by an air-thermostat. After one hour or more, the relations between the node and the position of reflector were recorded at 16 revolutions of the main shaft near an end apart from crystal, and the frequency of driving oscillator was also measured at the same time. Then repeating the process, measurements were carried out under other desired pressures.

One of the results obtained is given in Table 1, where the present data in argon are compared with those of other investigators[6,7,8]. The agreement between them is excellent. The scattering of an experimental point is found to be within less than 0.2% over the whole pressure range for the three gases.

---

6) National Bureau of Standards, *Tables of Thermal Properties of Gases*, Washington (1955)

7) A. Lacan and J. Noury, *Compt. rend.*, **236**, 362 (1953)

8) A. van Itterbeek, W. van Dael and W. Grevendonk, *Physica*, **25**, 640 (1959)

Table 1 Velocity of ultrasonic waves in argon at 25°C

Pressure (atm)	f (kc)	λ (mm)	C (m/sec)			
			This work	NBS.[6)]	Lacan & Noury[7)]	van Itterbeek *et al*[8)] (26.6°C)
1.0	470.4	0.682_9	$321._2$	321.4	—	322.7
19.4	470.7	$.687_2$	$323._5$	323.3	—	325.4
39.9	470.9	$.689_1$	$324._5$	324.8	—	328.3
69.1	471.3	$.702_3$	$331._0$	331.3	—	332.6
98.1	471.7	$.715_4$	$337._6$	337.4	336.0	—
146.2	472.4	$.743_2$	$351._1$	—	351.5	—

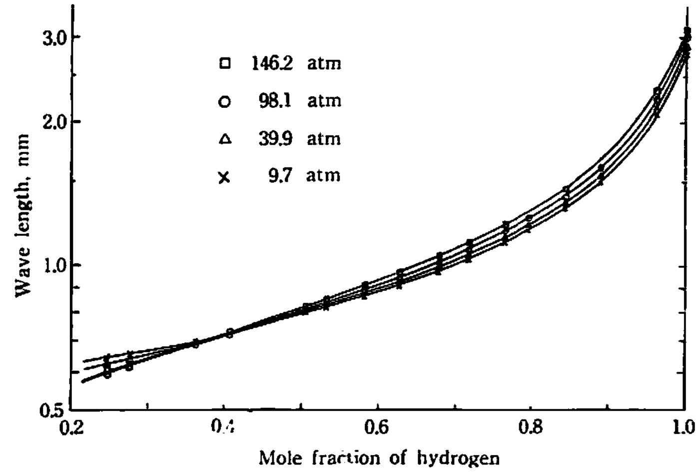


Fig. 4 Wave length of ultrasonics of 470.0 kc in H_2–CO_2 system at 25°C

For the purpose of this investigation, the velocity of sound has been estimated in H_2-CO_2 mixtures of various compositions at 25.0°C and under several pressures. As the frequency of driving oscillator is fixed at 470.0 kc in this measurement, the wave length is taken to be functions of composition and pressure, as shown in Fig. 4. The isobars in this figure could be employed as an indirect method of determining the composition under these pressures. As shown from these curves in Fig. 4, the analysis of the composition could be done with the accuracy of 0.002 of the mole fraction of H_2 at $x_{H_2}=0.3\sim0.7$ and of 0.001 at higher concentrations.

Thermal Diffusion Factor in H_2–CO_2 System

The thermal diffusion in the mixtures of several compositions has been measured under the pressure range of 9.7 ~ 98.1 atm, by use of the new apparatus shown in Fig. 2. The top and bottom chambers are maintained at constant temperatures of 138.8° and 25.0°C, respectively, and, therefore, the mean temperature[9)] $\bar{T}$ is 349.1°K.

[9)] H. Brown, *Phys. Rev.*, 58, 661 (1940)

In order to estimate the thermal diffusion factor, the compositions in both chambers are required when a steady state condition has been attained. Although the change of composition in the bottom chamber $(\Delta x)_b$ can be known from Fig. 4, that in the top one $(\Delta x)_t$ cannot be measured. It must be, however, evaluated by a simple material balance if $(\Delta x)_b$ and the composition in feed are known. That is, assuming that the mean composition in the connecting tube at the equilibrium condition is nearly equal to the initial composition of the mixture,

$$(\Delta x)_t = (\Delta x)_b \frac{V_b T_t Z_t}{V_t T_b Z_b}, \qquad (2)$$

where V's and T's are the volume and the temperature of chambers, respectively, and z's are the compressibility, and the subscripts t, b show the top and bottom. As the V_t and V_b were designed to be $(\Delta x)_t \fallingdotseq (\Delta x)_b$ in the present apparatus, that assumption would be satisfied, and we could use Eq. 2 for evaluation of $(\Delta x)_t$. Therefore, the separation Δx and the thermal diffusion factor α is given by

$$\Delta x = (\Delta x)_t + (\Delta x)_b, \qquad (3)$$

$$\alpha = \frac{\Delta x}{x_1 x_2 \ln(T_t/T_b)}. \qquad (4)$$

For the use of Eq. 2, each volume of the two chambers has been determined by filling each chamber with H_2 at pressures of about 2 atm, then carefully bleeding off the gas into a gas buret. The pressures were measured by means of a mercury-manometer. By careful control and replication of the measurement, the following values have been obtained; $V_t = 17.77 \pm 0.03$ cc and $V_b = 12.39 \pm 0.02$ cc. And, the compressibility factors were obtained from a generalized compressibility-factor chart[10] and a table[11], by reason of the lack of experimental data or adequate

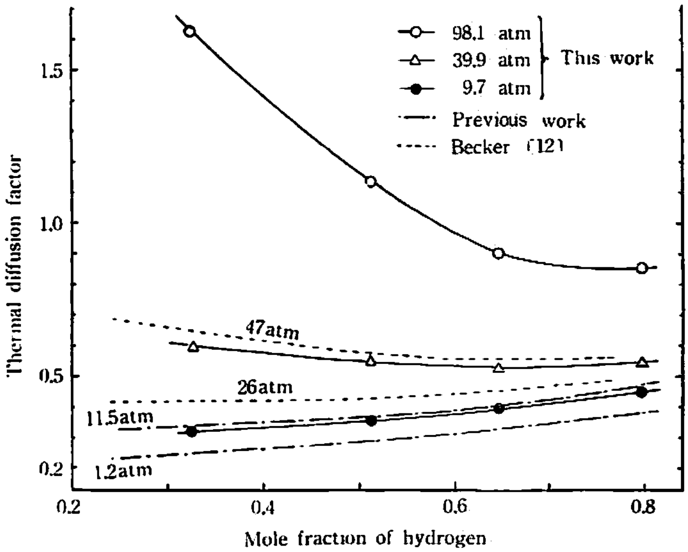


Fig. 5 Thermal diffusion factor in H_2-CO_2 system as a function of composition at different pressures

---

10) L. C. Nelson and E. F. Obert, *Trans. ASME*, **76**, 1057 (1954)

11) A. L. Lydersen, R. A. Greenkorn and O. A. Hougen, *Univ. of Wisc. Eng. Expt. Sta. Rept.* **4**, October, 1955

12) E. W. Becker, *Z. Naturforsch.*, **5a**, 457 (1950)

Table 2 Thermal diffusion in H_2-CO_2 system ($T=349.1°K$)

Pressure (atm)	x_{H_2}	$(x_{H_2})_b$	Z_t/Z_b	Δx	α
9.7	0.326	0.315	1.015	0.023	0.32
98.1	〃	.305	1.064	.043	0.61
39.9	〃	.273	1.210	.116	1.63
9.7	0.512	0.498	1.008	0.028	0.35
39.9	〃	.490	1.039	.045	0.56
69.1	〃	.480	1.058	.065	0.80
98.1	〃	.469	1.083	.090	1.11
9.7	0.647	0.632	1.006	0.029	0.39
39.9	〃	.627	1.016	.039	0.53
98.1	〃	.613	1.038	.067	0.91
9.7	0.798	0.786	1.001	.024	0.46
39.9	〃	.784	1.004	.029	0.56
98.1	〃	.776	1.013	.045	0.86

equations of the states. Therefore, although the variation of the ratio Z_t/Z_b is considerably small with pressure or temperature, this would be the most part of the error in α estimated.

The experimental results are given in Table 2 and Fig. 5. The data obtained at the initial concentration $x_{H_2}=0.512$ are found to have a good agreement with the values obtained by a direct method in the previous paper²⁾ and with Becker's data¹²⁾. As shown in Fig. 5, although α increases continuously with increasing pressure at a constant x_{H_2}, the variation in α with x_{H_2} is rather complex, that is, α increases with x_{H_2} under low pressures, but it decreases with x_{H_2} under pressures above about 40 atm. This phenomenon was first suggested from Becker's results, which are also plotted in Fig. 5, and now is distinctly shown by an isobar at 98.1 atm in the present work. It seems that the effect of pressure on α is larger at the smaller x_{H_2}, where the large content of CO_2 makes the pseudocritical temperature of the mixture approach to the experimental temperature.

Acknowledgment

The author has great pleasure in expressing his sincere thanks to Prof. Wasaburo Jono and Dr. Jiro Osugi for their valuable guidance and encouragement throughout the course of this work. The author wishes to thank the investigators in the Laboratory of Physical Chemistry, Kyoto University, for their valuable discussion and Mr. Naozo Matsumoto for his advice and assistance.

This research was partially financed by the Grant in Aid for Fundamental Scientific Individual Research of the Ministry of Education.

Chemical Institute
Fuculty of Industrial Arts
Kyoto Technical University
Kyoto, Japan