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# Thermal diffusion factors in gaseous mixtures from irreversible thermodynamics

Jalil Moghadasi *, Ahmad Razavizadeh, Ali Boushehri
*Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran*

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**Abstract**—Study of diffusion thermoeffect can yield quantitative information about the other transport coefficients, particularly thermal diffusion factor. The diffusion thermoeffect is investigated for five different gaseous mixtures: $N_2$–Ar, $N_2$–$CO_2$, $N_2$–$N_2O$, $O_2$–$CO_2$, $O_2$–$N_2O$. We employed a non-steady state method with a Loschmidt-type apparatus. The values of the thermal diffusion factor were calculated for the above mixtures from experimental data on the basis of the irreversible thermodynamics. All measurements were made at 293.15 K and 101.3 kPa. The results of these measurements are compared to the values from direct thermal diffusion measurements, and also those calculated from the kinetic molecular theory of gases. Comparison of these measured values of thermal diffusion factors with those of thermal diffusion measurements which are in literature shows good agreement. There is no information for thermal diffusion factors of the $O_2$–$CO_2$ and $O_2$–$N_2O$ pairs in literature which were measured in this experiment. © 2001 Éditions scientifiques et médicales Elsevier SAS

**diffusion thermoeffect / irreversible thermodynamics / kinetic theory of gases / Loschmidt apparatus / nonclassical thermodynamics / thermal diffusion factor / transport coefficients**

## Nomenclature

| | | |
|---|---|---|
| $C$ | mass fraction | |
| $C_P$ | heat capacity at constant pressure | $J{\cdot}K^{-1}{\cdot}mol^{-1}$ |
| $C^*$ | ratio of collision integrals | |
| $C_6^*$ | short range dispersion coefficient | |
| $D$ | diffusion coefficient | $m^2{\cdot}s^{-1}$ |
| $\boldsymbol{J}_i$ | flux density vector of mass | $mol{\cdot}m^{-2}{\cdot}s^{-1}$ |
| $\boldsymbol{J}_u$ | flux density vector of energy | $J{\cdot}m^{-2}{\cdot}s^{-1}$ |
| $K$ | apparatus constant | $J{\cdot}m^{-2}{\cdot}s^{-1}$ |
| $k$ | Boltzmann constant | $J{\cdot}K^{-1}$ |
| $k_T$ | higher-order correction of thermal diffusion factor | |
| $M$ | molar mass | $kg{\cdot}mol^{-1}$ |
| $R$ | gas constant | $J{\cdot}K^{-1}{\cdot}mol^{-1}$ |
| $t$ | time | s |
| $T$ | temperature | K |
| $T^*$ | reduced temperature $= T\varepsilon/k$ | |
| $x$ | mole fraction | |

*Greek symbols*

| | | |
|---|---|---|
| $\alpha_T$ | thermal diffusion factor | |
| $\varepsilon$ | potential well depth | J |
| $\mu_i$ | chemical potential | $J{\cdot}mol^{-1}$ |
| $\Delta C$ | difference mass fraction in two chambers | |
| $\Delta T$ | temperature difference | K |
| $\Delta T_{max}$ | maximum temperature change | K |
| $\Delta x$ | distance between thermocouple junctions | m |
| $\lambda$ | thermal conductivity coefficient | $J{\cdot}m^{-1}{\cdot}s^{-1}{\cdot}K^{-1}$ |
| $\rho$ | mass density | $kg{\cdot}m^{-3}$ |
| $\sigma$ | entropy production | $J{\cdot}K^{-1}{\cdot}s^{-1}$ |

## 1. INTRODUCTION

When a difference in concentration of a physical property exists for any properties of a system from one region to adjacent region, a net transport of this property occurs.

The transport properties can yield information about intermolecular forces that are one of the most important

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* Correspondence and reprints.
*E-mail addresses:* moghadasi@chem.susc.ac.ir (J. Moghadasi), razavi@chem.susc.ac.ir (A. Razavizadeh), boushehri@chem.susc.ac.ir (A. Boushehri).

tools for determination of many chemical and physical properties of matter. In this respect the determination of transport coefficients is of great importance.

Among the transport phenomena diffusion thermoeffect is of great significance.

The diffusion thermoeffect is the transfer of thermal energy due to a mass gradient, and therefore, it can be regarded as the inverse of thermal diffusion. Thermal diffusion depends on the nature of the forces between unlike molecules, more than most of gas phenomena. In addition, thermal diffusion factors are used in difficult separation of gas mixtures. The thermal diffusion factors are also obtained from the diffusion thermoeffect. These can be used in determining other transport coefficients.

Diffusion thermoeffect was discovered by Dufour [1] in 1872 and is known as the Dufour effect. The Dufour effect was not investigated until it was rediscovered by Clusius and Waldmann [2] in 1942.

A study of the pressure dependence of the diffusion thermoeffect was made by Mason et al. [3]. An experimental study of the temperature dependence of the Dufour effect was made by Boushehri [4]. Effect of thermocouple separation and pressure on diffusion thermoeffect was investigated by Boushehri and Moghadasi [5]. Finally, Bordbar et al. [6] modified the thermal diffusion factor equation by using the perturbation technique and deriving a new formula. In this paper we report thermal diffusion factors for $N_2$–Ar, $N_2$–$CO_2$, $N_2$–$N_2O$, $O_2$–$CO_2$, $O_2$–$N_2O$ from irreversible thermodynamics.

## 2. CALCULATION OF THERMAL DIFFUSION FACTOR ON THE BASIS OF IRREVERSIBLE THERMODYNAMICS

When two transport processes take place simultaneously, they may interfere and produce cross phenomena. An example is interference of diffusion and heat conduction, which gives rise to diffusion thermoeffect. In this effect a transient temperature difference arises from a concentration gradient for two gases (labeled by subscripts 1 and 2) at the same initial temperature diffusing into each other.

Entropy production, $\sigma$, for an isotropic medium in which only mass and energy transfer occur is given by

$$\sigma = \boldsymbol{J}_u \cdot \nabla\left(\frac{1}{T}\right) - \sum \boldsymbol{J}_i \cdot \nabla\left(\frac{\mu_i}{T}\right) \qquad (1)$$

For a two-component gaseous mixture at constant pressure $P$ and constant temperature $T$, equation (1) is written as

$$\sigma = -\frac{1}{T^2}\boldsymbol{J}_q \cdot \nabla T - \frac{1}{C_2 T}\left(\frac{\partial \mu_1}{\partial C_1}\right)_{T,P,C_2} \boldsymbol{J}_1 \cdot \nabla C_1 \qquad (2)$$

where

$$\boldsymbol{J}_q = \boldsymbol{J}_u - \sum \frac{\partial}{\partial T}\left(\frac{\mu_i}{T}\right)_P \boldsymbol{J}_i \qquad (3)$$

The thermal diffusion factor $\alpha_T$ is defined as

$$\alpha_T = \frac{L_{1q}}{L_{11}C_1}\left(\frac{\partial \mu_1}{\partial C_1}\right)_{T,P}^{-1} \qquad (4)$$

where $L_{1q}$ and $L_{11}$ are phenomenological coefficients. By using the Onsager reciprocity relation, $L_{1q} = L_{q1}$, it can be shown that

$$\boldsymbol{J}_q = -\lambda \nabla T - \rho_1 \left(\frac{\partial \mu_1}{\partial C_1}\right)_{T,P} D_{12}\alpha_T \nabla C_1 \qquad (5)$$

By using local form of conservation of energy and in the absence of convection, it can be shown that

$$\rho C_P \left(\frac{\partial T}{\partial t}\right) = \nabla \cdot \left[\lambda \nabla T + \rho_1 \left(\frac{\partial \mu_1}{\partial C_1}\right)_{T,P} D_{12}\alpha_T \nabla C_1\right] \qquad (6)$$

Some time after interdiffusion of gases into each other, maximum temperature difference, $\Delta T_{\max}$, is created in the system. At this condition, from equation (6) thermal diffusion factor will be obtained as [7]

$$\alpha_T = \frac{(K\Delta x - \lambda \Delta T_{\max})\{C_1[M_1 - C_1(M_1 - M_2)]\}}{\rho_1 R T D_{12} \Delta C_1} \qquad (7)$$

The apparatus constant, $K$, depends on the geometry of the cell (in particular, the position of thermocouples) and must be determined experimentally. It is possible to leave $K = 0$ as Rastogi and Madan [8] did, but this is not the most general equation. Equation (7) was used in this work to calculate $\alpha_T$ from observations of $\Delta T_{\max}$.

From the kinetic theory of gases, the thermal diffusion factor $\alpha_T$ for binary gas mixture according to revised principle of corresponding states is given by the following expression [9]:

$$\alpha_T = \left(6C_{ij}^* - 5\right)\left(\frac{x_1 S_1 - x_2 S_2}{x_1^2 Q_1 + x_2^2 Q_2 + x_1 x_2 Q_{12}}\right)(1 + k_T) \qquad (8)$$

where $k_T$ is a higher-order correction term and usually negligibly small. $S_1$, $S_2$, $Q_1$, $Q_2$, and $Q_{12}$ are functions of masses, collision integrals, and collision diameters.

The collision integrals are calculated on the basis of the revised principle of corresponding states as follows [9]:

- *molecular gases:*

$$1 \le T^* \le 10$$

$$\Omega^{(2,2)*} = \exp\big[0.46641 - 0.56991 \ln T^* + 0.19591\big(\ln T^*\big)^2 - 0.03879\big(\ln T^*\big)^3 + 0.00259\big(\ln T^*\big)^4\big] \quad (9)$$

$$\Omega^{(1,1)*} = \exp\big[0.295402 - 0.510069 \ln T^* + 0.189395\big(\ln T^*\big)^2 - 0.045427\big(\ln T^*\big)^3 + 0.0037928\big(\ln T^*\big)^4\big] \quad (10)$$

- *noble gases:*

$$T^* \le 1.2$$

$$\Omega^{(2,2)*} = 1.1943\left(\frac{C_6^*}{T^*}\right)^{1/3}\big[1 + a_1\big(T^*\big)^{1/3} + a_2\big(T^*\big)^{2/3} + a_3 T^* + a_4\big(T^*\big)^{4/3} + a_5\big(T^*\big)^{5/3} + a_6\big(T^*\big)^2\big] \quad (11)$$

where

$$a_1 = 0.18$$
$$a_2 = 0$$
$$a_3 = -1.20407 - 0.195866\big(C_6^*\big)^{-1/3}$$
$$a_4 = -9.86374 + 20.2221\big(C_6^*\big)^{-1/3}$$
$$a_5 = 16.6295 - 31.3613\big(C_6^*\big)^{-1/3}$$
$$a_6 = -6.73805 + 12.6611\big(C_6^*\big)^{-1/3}$$

$$\Omega^{(1,1)*} = 1.1874\left(\frac{C_6^*}{T^*}\right)^{1/3}\big[1 + b_1\big(T^*\big)^{1/3} + b_2\big(T^*\big)^{2/3} + b_3\big(T^*\big) + b_4\big(T^*\big)^{4/3} + b_5\big(T^*\big)^{5/3} + b_6\big(T^*\big)^2\big] \quad (12)$$

where

$$b_1 = 0$$
$$b_2 = 0$$
$$b_3 = 10.0161 - 10.5395\big(C_6^*\big)^{-1/3}$$
$$b_4 = -40.0394 + 46.0048\big(C_6^*\big)^{-1/3}$$
$$b_5 = 44.3202 - 53.0817\big(C_6^*\big)^{-1/3}$$
$$b_6 = -15.2912 + 18.8125\big(C_6^*\big)^{-1/3}$$

$$1 \le T^* \le 10$$

$$\Omega^{(2,2)*} = \text{same as equation (9)}$$

$$\Omega^{(1,1)*} = \exp\big[0.357588 - 0.472513 \ln T^* + 0.0700902\big(\ln T^*\big)^2 + 0.0165741\big(\ln T^*\big)^3 - 0.00592022\big(\ln T^*\big)^4\big] \quad (13)$$

## 3. EXPERIMENTAL

The measurements are reported here were made with an apparatus essentially similar to that used by Boushehri and Ghoharshadi [10]. The apparatus consists of two double-walled glass cylinders, with each inner cylinder having volume of 380 ml. A two-junction thermocouple and a Leeds & Northrup potentiometer were used by which $\Delta T$ could be measured to ±0.005 K. The two half-cells were connected by a stopcock having a bore of 23 mm diameter. Temperature of the apparatus was kept constant in a water bath at 293.15 K with an uncertainty of ±0.2 K. The experiments were carried out under constant pressure of 101.3 kPa. The apparatus allowed reaching thermal equilibrium in the water bath for 2 hours. Then, the annular spaces between the double walls of the cells were evacuated to minimize heat loss. It was allowed to remain for 2 hours to ensure constancy of temperature. When the stopcock was opened, interdiffusion of two gases caused a temperature gradient across the two junctions of the thermocouple which was measured with the potentiometer. The maximum temperature change and time for its attainment were recorded.

The gases used in this research are Ar, $N_2$, $O_2$, $CO_2$, and $N_2O$. The minimum purity of these gases was at least 99.5 %, and they were used without further purification.

The studied mixtures were: Ar–$N_2$, $N_2$–$CO_2$, $N_2$–$N_2O$, $O_2$–$CO_2$, and $O_2$–$N_2O$.

## 4. RESULTS AND DISCUSSION

The observed values of $\Delta T_{\max}$ are listed in *table I*. The apparatus constant, $K$, was estimated by setting the known value of thermal diffusion factor, $\alpha_T$, for $O_2$–$CO_2$ mixture in equation (7). This value of $\alpha_T$ was calculated from equation (8). This value of $K$ was used for the calculation of the thermal diffusion factor from experimental data by equation (7).

TABLE I
Thermal diffusion factors $\alpha_T$ for gaseous mixtures.

| System | $\Delta T_{\max}$ (K) | $\alpha_{\text{exp}}$ from equation (7) | $\alpha_{\text{theo}}$ from equation (8) | $\alpha$ from thermal diffusion measurements |
|---|---|---|---|---|
| $N_2+Ar$ | 0.077 | 0.0437 | 0.0561 | 0.071[a] |
| $N_2+CO_2$ | 0.069 | 0.0588 | 0.0734 | 0.061[a] |
| $N_2+N_2O$ | 0.053 | 0.0589 | 0.0696 | 0.048[a] |
| $O_2+CO_2$ | 0.058 | 0.0520[b] | 0.0520 | –[c] |
| $O_2+N_2O$ | 0.050 | 0.0519 | 0.0561 | –[c] |

[a] These values are reported in [13].

[b] This value is calculated from equation (7).

[c] There are no experimental values available for these mixtures.

The thermal diffusion factors also were calculated from kinetic theory of gases at equimolar concentration according to equation (8).

In the pervious works [4, 5, 7, 10], Lennard-Jones potential was used for calculating the collision integrals for polyatomic gases, but here we used the revised principle of corresponding states [9].

The comparison between experimental data and theoretical thermal diffusion factor shows the error lower than 25 %. The uncertainty in $\Delta T$ is of the order of $\pm 0.005$ K, the error in $\alpha_T$, however, cannot be obtained on the basis of this error in $\Delta T$ alone. Considerable uncertainty enters the calculated values of $\alpha_T$ because of the uncertainty in $\lambda_1$, $\rho_1$, and $D_{12}$. For $\lambda$ and $\rho$ the values of the pure components were used, since typical values of $\Delta C_1$ were close to unity. $D_{12}$ was calculated from equation (C4) of [9] by using the revised principle of corresponding states.

In addition, we assumed that the gases are ideal and neglecting a correction in evaluating the thermal diffusion factor for the heat transport due to the imperfection of the gases.

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## APPENDIX

The values of $C_1$ could not be measured directly, they can be obtained by using integrated form of Fick's second law of diffusion, which is written as [11]

$$C_t = \frac{1}{2} C_0 \left[ 1 - \operatorname{erf}\left( \frac{x}{2\sqrt{D_{12} t}} \right) \right] \tag{A.1}$$

$$C_1 = 1 - C_t \tag{A.2}$$

where $D_{12}$ is the diffusion coefficient, $x$ is the distance between thermocouples and diffusion interface and equal to $\Delta x/2$, $t$ is time when $\Delta T$ reaches a maximum value and obtained from experiment, $C_t$ is the mass fraction of the particular component in the second chamber at time $t$, and $C_0$ is the mass fraction of the lighter component at time zero, which is equal to unity, erf is the error function and is described by [11]

$$\operatorname{erf}(x) = 2\pi^{-1/2} \int_0^x e^{-\eta^2}\, d\eta, \qquad \operatorname{erf}(\infty) = 1 \tag{A.3}$$

The values of error function are tabulated in [11, 12].