

# Measurement of the diffusion coefficient of naphthalene into air

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**Abstract**—An experimental technique which is often used to study convective heat transfer by investigating analogous naphthalene sublimation situations requires a knowledge of the diffusion coefficient of naphthalene into air to couple the two systems. Only two previous measurements of the diffusion coefficient have appeared in the literature (Mack, *J. Am. Chem. Soc.* **47**, 2468–2482 (1925) and Caldwell, *J. Chem. Engng Data* **29**, 60–62 (1984)). Both measurements were taken at single but different temperatures and their values differed by approximately 29%. In view of this uncertainty, an experiment was performed to measure the diffusion coefficient of naphthalene into air over the temperature range  $15^{\circ}\text{C} \leq T \leq 55^{\circ}\text{C}$ . Two different geometrical systems were used as a check on possible systematic errors. The repeatability of the data is 2% and the estimated possible systematic error is  $\pm 3\%$ . The data result in Schmidt and Lewis numbers which have a weak temperature dependence of  $25^{\circ}\text{C}$ .

## INTRODUCTION

THE DIFFUSION of gases relates to many phenomena such as the movement of gases in the earth's strata, purification by adsorption, cooling of nuclear reactors, the permeability of various packing materials, etc.

Diffusion is the process which transports material from one part of a system to another as a result of random molecular motions in the absence of mixing. It is more complicated than single species viscous flow or heat conduction because mixtures have to be considered. Ordinary diffusion occurs in isothermal, isobaric systems with no external-force-field gradients. It transfers mass from one region to another because of concentration gradients when the mixture is stationary or in laminar flow in the direction of the concentration gradient.

The diffusion rate is described by Fick's first law of diffusion which states that the mass flux of a component per unit area is proportional to the concentration gradient. The proportionality factor in Fick's law, known as the diffusion coefficient, is a property of the species involved system, and is almost composition independent, increases with temperature and varies inversely with pressure for low density gases.

The boundary-layer equations for heat transfer and the equations for isothermal mass transfer are analogous when the heat transfer situation corresponds to

the mass transfer situation with analogous boundary conditions and similar geometries. In this case, the Sherwood number ( $Sh$ ) can replace the Nusselt number ( $Nu$ ) for heat transfer when the Prandtl number ( $Pr$ ) is replaced by the Schmidt number ( $Sc$ ) and the Rayleigh number ( $Ra$ ) is replaced by the Rayleigh number of mass transfer ( $Ra_M$ ). This analogy applies to turbulent as well as laminar flow. However, the analogy only exists in cases of no heat sources in the heat transfer process and no chemical reactions in the mass transfer process.

The naphthalene sublimation technique employs the heat and mass transfer analogy to determine heat transfer coefficients in convection flows by measuring mass transfer coefficients. This is discussed in detail in ref. [1]. The basic characteristic of this technique is that the heat transfer problem to be investigated is replaced by an analogous mass transfer problem. Thus, only mass transfer experiments need be made and the analogy is used to solve the heat transfer problem. Naphthalene is often utilized in this technique for performing the mass transfer experiments mainly due to its desirable properties such as subliming at room temperature, low toxicity, and good casting and machining characteristics.

The naphthalene sublimation technique, which employs the heat-mass transfer analogy, requires accurate values of the diffusion coefficient of naphthalene into air ( $D_{na}$ ). Only two previous measurements of  $D_{na}$  have appeared in the literature [2, 3]. Both measurements were made at single but different temperatures (25 and  $30^{\circ}\text{C}$ , respectively) and their values differ by approximately 29% when the temperature effect on the diffusion coefficient is not considered.

Mack [2] employed an evaporation tube method and determined the diffusion coefficient of naphtha-

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## NOMENCLATURE

$A_n$	surface area of naphthalene pellet [cm <sup>2</sup> ]	$\rho_n^*$	saturated mass concentration of naphthalene per unit volume [g cm <sup>-3</sup> ].
$d_n$	diameter of naphthalene pellet [cm]	<b>Subscripts</b>	
$D_{na}$	binary diffusion coefficient of naphthalene into air [cm <sup>2</sup> s <sup>-1</sup> ]	a	air
$h$	heat transfer coefficient [W m <sup>-2</sup> °C <sup>-1</sup> ]	LSE	least square equation
$h_D$	mass transfer coefficient [cm s <sup>-1</sup> ]	n	naphthalene
$L$	diffusion length [cm]	na	naphthalene-air mixture
$m_n$	naphthalene mass flux per unit time [g s <sup>-1</sup> ]	1 atm	1 atm pressure.
$P$	diffusion system pressure [atm]	<b>Superscript</b>	
$P_{vn}^*$	saturated vapor pressure of naphthalene [Pa]	*	saturation state.
$R_n$	gas constant of naphthalene (64 859.6 Pa cm <sup>3</sup> g <sup>-1</sup> K <sup>-1</sup> )	<b>Dimensionless parameters</b>	
$T$	absolute temperature [K]	$Le$	Lewis number, $Pr/Sc = \alpha/D_{na,1 atm,LSE}$
$t$	time [s].	$Nu$	Nusselt number, $hx/k$
<b>Greek symbols</b>		$Pr$	Prandtl number, $\nu/\alpha = \mu C_p/k$
$\Delta$	change or increment	$Sc$	Schmidt number, $\nu/D_{na,1 atm,LSE}$
$\rho_n$	mass concentration of naphthalene per unit volume [g cm <sup>-3</sup> ]	$Sh$	Sherwood number, $h_D x/D_{na,1 atm,LSE}$

lene into air by measuring the steady state sublimation rate of naphthalene through an air space at constant pressure and temperature ( $25 \pm 0.01^\circ\text{C}$ ). A brass cup at the tube top end was filled with melted naphthalene and after solidification, it was weighed in a glass bottle on a balance to an accuracy of 0.00001 g in a room at constant temperature ( $\pm 0.1^\circ\text{C}$ ). After being weighed, the inverted cup was placed over the open end of a glass tube containing powdered charcoal (80–100 mesh) at the other end so that the naphthalene diffused through the air space and was absorbed by the charcoal.

Mack's assumptions were as follows. The first is the steady state assumption that the concentration gradient between the naphthalene surface and the charcoal surface was constant. The second is the air insolubility assumption that the air was not absorbed by the charcoal and thus that the air in the tube was conserved. The third concerns the boundary conditions of the system in that the vapor concentration at the naphthalene air interface was constant and could be calculated from the equilibrium vapor pressure at the naphthalene surface temperature and that the vapor concentration at the charcoal surface was zero. The fourth is that the naphthalene vapor and air are ideal gases, so that the compositions could be expressed in terms of partial pressures. Based on those assumptions, he obtained the diffusion coefficient of naphthalene into air from his data by applying the steady-state diffusion equation and using Barker's vapor pressure data for naphthalene [4] at  $25^\circ\text{C}$

(13.71 Pa). Barker's data point has a higher value (by about 22%) than the more accurate data of Ambrose *et al.* [5], which will be used in the present work (at  $25^\circ\text{C}$ , 11.23 Pa). Since the deviation in the vapor pressure is inversely proportional to the deviation in the diffusion coefficient, Mack's diffusion coefficient of naphthalene into air has to be corrected by an increase of 22% from his reported value of  $0.0611 \text{ cm}^2 \text{ s}^{-1}$  at  $25^\circ\text{C}$  and 1 atm. Other possible error sources in Mack's work in addition to the vapor pressure are discussed below.

First, Mack measured a mass loss of the order of 1 mg which is difficult to accomplish accurately considering such effects as the mass loss during movements between the balance and the system, static electricity effects on mass measurements, dust in the room, air currents around the object, etc. However, he did not discuss such possible errors. In addition, the possible adsorption of naphthalene vapor into the tube wall should be considered since it affects the diffusion rate at the naphthalene surface. His system had an area ratio of the tube wall to the diffusing naphthalene surface of 2.9. Since these error sources generally tend to increase the mass loss, Mack's measured value for the diffusion coefficient of naphthalene into air could be higher than the true value. Possible errors due to free convection, Dufour effects and the dependence of the diffusion coefficient on mixture composition are thought to be negligible. Since the mass density of naphthalene-air mixtures is greater than that of air, free convection may occur when the naphthalene

pellet is located at the top of the air space. However, Mack did not consider this possible error source.

Before 1984, the Schmidt number for a naphthalene-air mixture at 25°C was assumed to be 2.57 based on Mack's experiment. The Schmidt number is the dimensionless parameter that connects the mass and heat transfer processes and contains the diffusion coefficient. However, Caldwell [3] reported that Mack's value was in serious error, mainly due to his use of an inaccurate vapor pressure. Caldwell performed independent experiments using a modified Stefan tube technique which did not require vapor pressure data. He measured the concentration of the naphthalene vapor in air leaving the diffusion cell by using a gas chromatograph detector. His diffusion cell consisted of 52 tubes of 5.48 mm bore and 100 mm length with upper and lower chambers. The lower chamber contained the solid naphthalene while the upper chamber contained an airflow to carry away the diffused naphthalene. He reported a diffusion coefficient of 0.086 cm<sup>2</sup> s<sup>-1</sup> at 30.04°C and 0.1013 MPa and a Schmidt number of 1.805.

Some possible error sources are considered here for Caldwell's measurements. The adsorption of naphthalene vapor by tube walls could affect the diffusion rate at the naphthalene surface as mentioned previously. In his system, the area ratio of all tube walls to the diffusing naphthalene surface was approximately 73, which is 25 times larger than that of Mack's system. Thus, it might be suspected that Caldwell's value will be higher than Mack's and that they are both higher than the true value. Second, turbulence effects at the diffusion tube outlet could be a deleterious factor.

As discussed so far, the two diffusion coefficients of naphthalene into air measured by Mack and Caldwell differed considerably and were measured only at a single temperature. Since the naphthalene sublimation technique requires reliable diffusion coefficient data as the function of temperature, the purpose of the present work was to determine experimentally the diffusion coefficient of naphthalene in air as a function of temperature over the range of approximately 15–55°C. In addition, the Schmidt number (*Sc*) and the Lewis number (*Le*) were to be calculated over the same temperature range in order to be able to utilize the naphthalene sublimation technique with greater accuracy.

The present apparatus is similar in principle to Mack's but has been improved as follows:

(1) Use of a larger diameter naphthalene pellet in order to reduce the naphthalene surface area to tube wall area ratio. In this way, possible tube wall adsorption effects can be reduced.

(2) Use of a larger naphthalene surface to increase the total sublimed mass for greater measurement accuracy.

(3) Using a variable temperature control system so that the diffusion coefficient could be measured at more than one temperature.

(4) Measurement of the naphthalene temperature.

(5) Continuous monitoring of the total pressure and the relative humidity.

(6) The use of the most reliable naphthalene vapor pressure data for data reduction.

(7) Use of two experimental systems with different diffusion lengths and masses as a check on possible wall adsorption effects.

## EXPERIMENTAL APPARATUS AND PROCEDURE

The present study employed a steady-state method for the measurements of the diffusion coefficients of naphthalene into air, shown in schematic form in Fig. 1. In this apparatus, a naphthalene pellet with a diameter  $d_n$  was placed at the top of a diffusion tube at a diffusion length ( $L$ ) from a flat activated charcoal powder surface located at the bottom of the diffusion system. The space between them was filled with atmospheric air so that the naphthalene vapor would diffuse to the charcoal surface through the air. With the mass loss of the naphthalene pellet measured at a certain temperature ( $T$ ) for a certain time period ( $\Delta t$ ), the diffusion coefficient of naphthalene into air can be calculated from the following equation which is derived from Fick's first law:

$$D_{na} = \frac{\Delta m_n L}{A_n \Delta t \rho_n^*} \quad (1)$$

The main advantage of the present method is the large mass loss of the naphthalene pellet, which reduces the overall uncertainties in the mass measurements to less than 0.5%. The time period for reaching steady state can be estimated from a solution of Fick's second law with proper initial and boundary conditions, by assuming that it is the time period until the concentration at the middle of the diffusion length reaches 99.9% of the steady-state concentration. The solution to this problem is given in ref. [6]. For the present diffusion systems with diffusion lengths of 0.5 and 1 cm and considering the temperature range between 15 and 55°C, that time period is less than

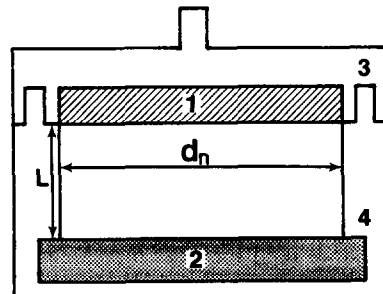
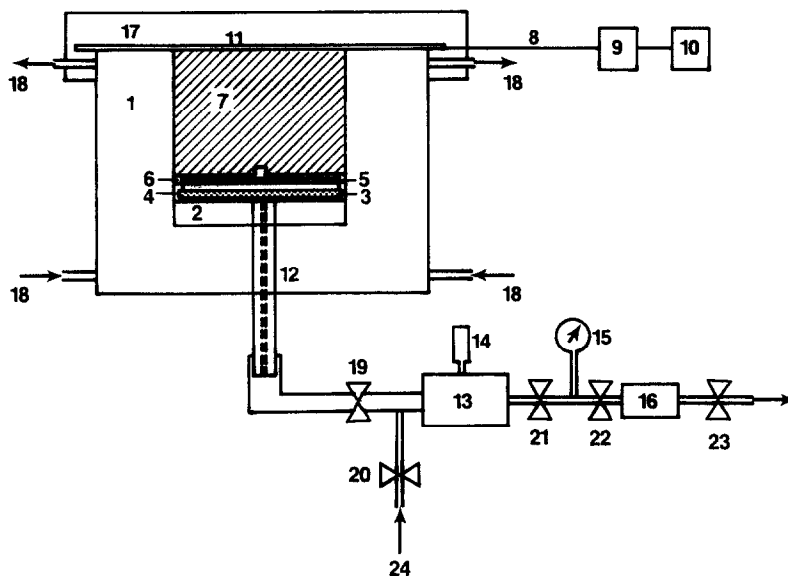


FIG. 1. Simple diagram of diffusion system: 1, naphthalene pellet; 2, activated charcoal; 3, naphthalene holder; 4, charcoal holder.



NO	PART NAME	NO	PART NAME
1	Water Jacket	13	Humidity Cell
2	Bottom Support	14	Humidity Meter
3	Activated Charcoal	15	Manometer
4	Charcoal Holder	16	Desiccator Box
5	Naphthalene Pellet	17	Fiberfrax Insulation Material
6	Naphthalene Holder	18	From and To Water Bath
7	Top Support	19	No 1 Valve
8	Type T Thermocouple	20	No 2 valve
9	Thermocouple Switching Box	21	No 3 Valve
10	Hewlett-Packard Multimeter	22	No 4 Valve
11	Glass Plate	23	No 5 Valve
12	Capillary glass Tube	24	From the other Diffusion System

FIG. 2. Schematic diagram of present apparatus.

9 s. This factor will be considered for determining the lower limit of the diffusion time.

The proper diffusion length was investigated by considering wall adsorption effects on the diffusion coefficients, the ratio of the change of naphthalene pellet thickness to the diffusion length and the disturbance effect on the charcoal surface due to placing the naphthalene pellet in the apparatus. The sizes and materials selected for each part of the present apparatus were determined by considering all these factors.

#### Description of present apparatus

A more detailed schematic diagram of the present apparatus is shown in Fig. 2. The naphthalene was reagent-grade naphthalene manufactured by J. T. Baker Inc. (Phillipsburg, New Jersey). The naphthalene was cast into a pellet inside the naphthalene holder which holds the pellet firmly and allows it to sublime only through its front surface.

The balance used for mass measurements (Model number B5, Mettler Inst. Co., Hightstown, New Jersey) could measure up to 200 g with a readability of 0.1 mg. The naphthalene pellet diameter was selected to be 8.357 cm. The thickness of the naphthalene pellet

was determined by considering the maximum balance limit of 200 g, the effect of the thickness change of the naphthalene on the diffusion length and the difficulties of casting. This thickness change of the naphthalene pellet and its effect on the determination of the diffusion length was one factor in selecting the diffusion length to be large enough that the ratio of the pellet thickness change to the diffusion length was less than 1%.

From the above pellet diameter and thickness, the range of the diffusing mass of naphthalene during the diffusion time period was determined so that the overall uncertainties including the uncertainty in the mass measurements were negligible compared with the diffusing mass. Thus, diffusion masses of the order of 250 and 400 mg were selected. One purpose of choosing two different diffusing masses was to check possible adsorption effects of the diffusion tube wall.

In addition, two different diffusion systems with diffusion lengths of 0.5 and 1 cm were used. The main reason for using two systems with different diffusion lengths was to compare the results of both systems for possible wall adsorption effects. Thus, the diffusion time period turned out to be from approximately 2 h to 4 days over the temperature range from 15 to 55°C.

Type T (copper–constantan) insulated thermocouple wires from the Thermoelectric Co. (AWG No. 26) were used for making 12 thermocouples at various locations in the two systems. They were connected to the thermocouple switching box (part No. 9 in Fig. 2) from Leeds & Northrop Co. (North Wales, Pennsylvania) and well insulated with fiberfrax insulating material. The thermocouple and RTD readings were made by a Hewlett–Packard multimeter with four-wire junctions (part No. 10 in Fig. 2).

The aluminum naphthalene holder consists of a center pouring hole with four air holes to assist in the naphthalene casting. A peripheral groove fits onto the charcoal holder to prevent any naphthalene vapor leaks. After the naphthalene pellet was cast, the air holes were sealed to prevent any sublimation through them. At the top of the naphthalene holder, there are two hemispherical depressions, one located near the center pouring hole and the other near the edge of the naphthalene pellet to contain the thermocouples for measuring the naphthalene temperature. The naphthalene holder cover fits on the naphthalene holder and was designed to prevent any mass loss during the naphthalene mass measurements.

Activated carbon (part No. 3 in Fig. 2) is a carbonaceous material specially treated to give it extremely high internal porosity and thus good adsorptive properties. The particular activated carbon used was selected by considering its density, mesh size, adsorption capability for naphthalene vapor, etc. A simple test showed that Norit A charcoal (American Norit Co., Inc., Jacksonville, Florida) was the best among the eight different samples considered (six samples from American Norit Co., Inc., two samples from Barnebey & Sutcliffe Corp., Columbus, Ohio). The Norit A charcoal has a surface area of  $750 \text{ m}^2 \text{ g}^{-1}$  and a bulk density of  $0.460 \text{ g ml}^{-1}$ . Its particle sizes are distributed so that 4% are greater than  $150 \mu\text{m}$ , 18% greater than  $74 \mu\text{m}$ , 36% greater than  $44 \mu\text{m}$  and 77% greater than  $10 \mu\text{m}$ .

Two charcoal holders were made so that two experiments could be conducted simultaneously. At the bottom center of the charcoal holder, a small piece of stainless steel capillary tube was placed to measure the pressure inside the diffusion system. Since the charcoal surface had to be flat inside the charcoal holder at a specified distance from the naphthalene, two aluminum spacer blocks were constructed. These were placed inside the diffusion tube and pressed against the charcoal to create a smooth surface.

Since the naphthalene vapor pressure which is used in the calculation of the diffusion coefficient varies by about 1% for a  $0.1^\circ\text{C}$  change, a glass water jacket (part No. 1 in Fig. 2) was fabricated with outer and inner glass tubes for controlling the temperature of the diffusion system. The top of this glass water jacket was ground flat and a thick glass plate and Dow Corning high-vacuum grease was used to seal the system. Fiberfrax insulating material (part No. 17 in Fig. 2) was placed on the top of the flat glass plate.

One system was connected to a Haake water bath which was used for experiments above room temperature. The other system water jacket was controlled by a combination of a Haake FE2 bath and a Fisher refrigerated bath and was used for experiments below room temperature. The temperature fluctuations in each bath system were within  $0.01^\circ\text{C}$  as determined by calibrated thermocouples and two resistance thermometers (RTDs). They were calibrated against a standard RTD (traceable to National Bureau of Standards) with a Guideline Galvanometer made by the Leeds & Northrop Co.

The purposes of the top support (No. 7 in Fig. 2) were to maintain the diffusion length by pushing down the naphthalene and charcoal holders with the weight of the support and to reduce the air space inside the diffusion system to eliminate back-leaks of naphthalene vapor. Since it had a large thermal mass, it was located inside the diffusion system long enough to come to the experimental temperature.

The capillary glass tube (part No. 12 in Fig. 2) was connected to a humidity box (part No. 13 in Fig. 2). Valves No. 1 and No. 2 in both diffusion systems were opened and closed appropriately for checking the humidity and the system total pressure. The humidity box contained the sensors of a calibrated humidity meter manufactured by Omega Eng. Inc. (Stamford, Connecticut) which measure the relative humidity from 0 to 97% within  $\pm 2\%$  accuracy. The humidity box was connected to a manometer (part No. 15 in Fig. 2) manufactured by Wallace & Tiernan Inc. (Belleville, New Jersey) for measuring pressures from 0 to 80.0 cm of mercury with accuracies of 0.052 cm Hg. The measured system pressure was used for correcting the diffusion coefficient to 1 atm pressure. The desiccator box (part No. 16 in Fig. 2) contains  $\text{CaSO}_4$  and is used with the No. 5 valve for eliminating any water vapor from the outside.

#### *Description of experimental procedure*

The top supports with thermocouples were put into each diffusion system in order for them to reach thermal equilibrium before the experiment began. Then, Dow Corning high-vacuum grease was applied to the glass plate and the ground surface on the water jackets. The activated charcoal was prepared by putting it into the charcoal holder and pushing it down with the depth gauges in order to make the charcoal surface flat. The charcoal and its holder were placed in the Mettler balance and their mass was measured. They were then inserted into the diffusion system and the top support was added. The temperatures were checked with the thermocouples until they were close to the water bath temperature. During the waiting time, the naphthalene pellet was made by casting inside the naphthalene holder.

After placing on the naphthalene holder cover, the total mass was measured after shooting it with an anti-static gun to prevent static electricity effects on the mass measurement. During the measuring period,

the temperature and relative humidity inside the balance were recorded. The naphthalene holder with the naphthalene pellet was slowly moved and placed inside the diffusion system which already contained the charcoal. Then the top support was placed on the naphthalene holder and the thermocouples and other grooves were placed in their proper positions. The diffusion system was then closed. The temperatures at different positions were measured periodically by the thermocouples and RTDs, as were the system pressure and relative humidity until the diffusion experiments were finished. The diffusion time period varied from 2 to 95 h depending on the diffusion system, mass losses and the system temperature.

The experimental diffusion time period was determined by a Fisher stopwatch which could be read to 0.01 s. Then, the total mass of the naphthalene system was measured (naphthalene pellet, naphthalene holder and naphthalene holder cover) and after that the total mass of the charcoal system (charcoal, charcoal holder) was measured.

When the system temperature was different from room temperature, the naphthalene mass measurements were repeated after about 20–30 min from the first measurements in order to check any effect of temperature non-equilibrium. Usually, the change on the naphthalene side during this period was less than 1 mg. The average of the two measurements on the naphthalene side was taken as the zero time mass for the calculation of the diffusion coefficients. The mass increases on the charcoal side did not balance with the naphthalene mass losses, mainly due to water vapor absorption by the charcoal.

The run temperature, pressure and relative humidity reported in the Results section are averages based on the measurements made during each time period. For all experiments, the system temperature was controlled within a maximum of 0.01°C which causes about 0.1% uncertainty in the vapor pressure of naphthalene. The system pressure varied a maximum of 0.34 kPa while the relative humidity changed a maximum of 15%.

#### Analysis of the present apparatus

For one-dimensional steady isothermal diffusion of a binary mixture with non-reacting components naphthalene and air

$$\frac{m_n}{A_n} = D_{na} \left( \frac{d\rho_n}{dx} \right). \quad (2)$$

The present work assumes that the naphthalene pellet surface has a saturated concentration of naphthalene at the given temperature and the charcoal surface has zero concentration. Also, since steady-state diffusion has a constant concentration gradient, the concentration gradient term in equation (2) can be written as  $\rho_n^*/L$ , where the distance between the naphthalene surface and the charcoal surface is the diffusion length  $L$  and the saturated concentration of

naphthalene is  $\rho_n^*$ . Since  $\Delta m_n$  is the total mass loss of the naphthalene pellet for the diffusion time period  $\Delta t$ ,  $m_n$  can be changed to  $\Delta m_n/\Delta t$ . Thus, equation (2) can be written as

$$\Delta m_n = \frac{D_{na} A_n \Delta t \rho_n^*}{L}. \quad (3)$$

The ideal-gas law can be applied with negligible errors for a dilute mixture such as naphthalene–air. Thus

$$\rho_n^* = \frac{P_{vn}^*}{R_n T} \quad (4)$$

and

$$A_n = \frac{\pi}{4} d_n^2. \quad (5)$$

Thus, by substituting equations (4), (5) and the values of  $R_n$  into equation (1)

$$D_{na} = 82\,581.8 \frac{\Delta m_n T L}{d_n^2 \Delta t P_{vn}^*}. \quad (6)$$

Since  $D_{na}$  is inversely proportional to  $P$

$$D_{na,1\text{atm}} = 82\,581.8 \frac{\Delta m_n T L}{d_n^2 \Delta t P_{vn}^*} \left( \frac{P}{P_{1\text{atm}}} \right). \quad (7)$$

Thus, the present work employs equations (6) and (7), which indicate that the diffusion coefficients of naphthalene into air can be determined by measuring the total mass loss of naphthalene for the diffusion time period at a certain temperature and pressure in a certain diffusion system.

The saturated vapor pressure of naphthalene is a function of temperature. Thus, it is determined by applying the measured temperature to the vapor pressure equation. The least square equation for the saturated vapor pressure of naphthalene proposed by Ambrose *et al.* [5] was adopted in the present work from all the vapor pressure relations suggested from 28 sources surveyed. Their measurements were made over a wide enough temperature range for the present study with a small standard deviation of 1.6%. Also, his equation agrees well with other equations, as shown in ref. [7], and has been widely used in mass transfer measurements.

A separate investigation was made to determine if the system could be affected by free convection. Under the worst conditions, the mass transfer Rayleigh number was one order of magnitude less than the critical Rayleigh number as reported by Gebhart *et al.* [8]. Thus, it was assumed that the system was stable and that free convection effects were absent.

An error analysis [7] predicted the maximum systematic errors in  $D_{na,1\text{atm}}$  to be  $-3.36$  to  $3.32\%$  for the 0.25 g case and  $-2.96$  to  $2.78\%$  for the 0.4 g case in the 0.5 cm diffusion system and  $-2.56$  to  $2.66\%$  for the 0.25 g case and  $-2.39$  to  $3.46\%$  for the 0.4 g case in the 1 cm diffusion system. The major uncertainties

arise from the vapor pressure equation and the diffusion length.

### EXPERIMENTAL RESULTS AND DISCUSSION

The present work determined the diffusion coefficients of naphthalene into air by measuring the mass loss of naphthalene ( $\Delta m_n$ ) at 10 different nominal temperatures for four different cases consisting of two different nominal diffusion lengths (0.5 and 1 cm) and two different nominal mass losses (0.25 and 0.4 g).

Several diffusion coefficient runs were made at each point to check the data repeatability over the working temperature range from 14.50 to 53.96°C at 10 different nominal temperatures. The diffusion coefficient data at the system pressure ( $D_{na}$ ) were converted to diffusion coefficients at 1 atm pressure ( $D_{na,1 atm}$ ) by applying the inverse proportionality relationship between  $D_{na}$  and the system pressure. The system pressure in the present work differed by  $-1.1$  to  $1.8\%$  from 1 atm. The  $D_{na,1 atm}$  results corrected for system pressure are shown in Fig. 3. As shown in Fig. 3, the repeatability over the working temperature range was within 0.18–2.66%.

Diffusion coefficient measurements for four different cases were carried out in order to check the assumed negligible diffusion tube wall adsorption of naphthalene vapor. This was done by using two different diffusion tube lengths and two different diffusion masses for each system temperature.

As the naphthalene to wall surface ratio changes any wall adsorption effects should give different experimental values of the diffusion coefficients. As seen in Fig. 3, the values for the 1 cm system are an average of 1.9% higher than for the 0.5 cm system. These systematic errors between both diffusion systems are considered to be mainly caused by the wall adsorption

effect. Any wall adsorption effect cannot be included in the systematic error analysis mentioned previously [7]. The above measurements, however, indicate that the wall adsorption effect, if it exists, is less than the sum of other systematic errors.

The zero wall adsorption effect was also checked by measuring the diffusion coefficient for the two mass loss cases for each diffusion system. It could be expected that wall adsorption effects would change when the walls were exposed to the diffusing naphthalene vapor for different periods of time. However, no significant difference was observed for the two different mass loss cases. The percent deviations were from 0.13 to 1.68% for the different mass loss cases for each diffusion system, as shown in Fig. 3. This percent deviation is also less than the sum of the other predicted systematic errors.

In the present work, the relative humidity inside the diffusion system varied from 60 to 77%. Any effect of relative humidity change on the determination of the diffusion coefficients could not be detected. Naphthalene with two different naphthalene lot numbers but made by the same company was used in the present work. No difference due to different lot numbers could be detected.

A least squares equation (LSE) for the diffusion coefficients of naphthalene into air at 1 atm pressure ( $D_{na,1 atm}$ ) was developed by considering all the diffusion coefficient data for the four different cases, a total of 59 data points

$$D_{na,1 atm} = 8.17708 \times 10^{-7} T^{1.983} \quad (14.50^\circ\text{C} \leq T \leq 53.96^\circ\text{C}). \quad (8)$$

The temperature ( $T$ ) in equation (8) has units of Kelvin (K) and the diffusion coefficient has units  $\text{cm}^2 \text{s}^{-1}$ . All diffusion coefficient data are within a maximum of  $\pm 3\%$  from the LSE and their coefficient of correlation is 0.981.

It is useful to compare equation (8), the LSE, with the two existing data by Mack and Caldwell, respectively, Mack's corrected value with the Ambrose  $P_{vn}^*$  equation and with other semi-empirically and empirically correlated  $D_{na,1 atm}$  values. The comparisons for  $D_{na,1 atm}$  and the percent deviations from the LSE of the present work are shown in Figs. 4(a) and (b). The comparisons were made over the present working temperature range. The percent deviations in Fig. 4 are defined as follows:

$$\% \text{ Dev. } (\%) = \frac{D_{na,1 atm, \text{correlated}} - D_{na,1 atm, \text{LSE}}}{D_{na,1 atm, \text{LSE}}} \times 100(\%) \quad (9)$$

In Figs. 4(a) and (b), the zero percent line is for the experimental LSE of the present work. Mack's result deviates by  $-7.4\%$  from  $D_{na,1 atm, \text{LSE}}$  and his corrected value using Ambrose's  $P_{vn}^*$  has a 13.0% deviation. It is believed that the main reason for the deviation is the adsorption of naphthalene vapor by the tube wall which affects the diffusion rate at the naphthalene

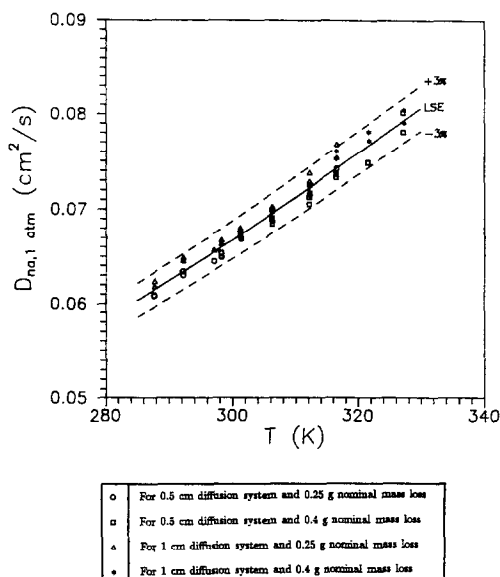


FIG. 3. Present experimental  $D_{na,1 atm}$  vs  $T$  with present LSE.

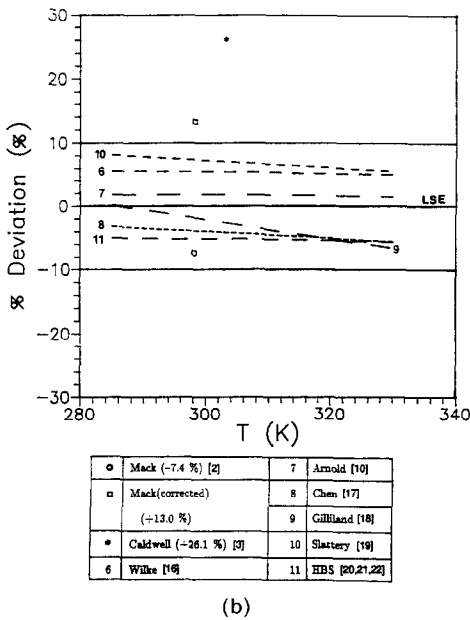
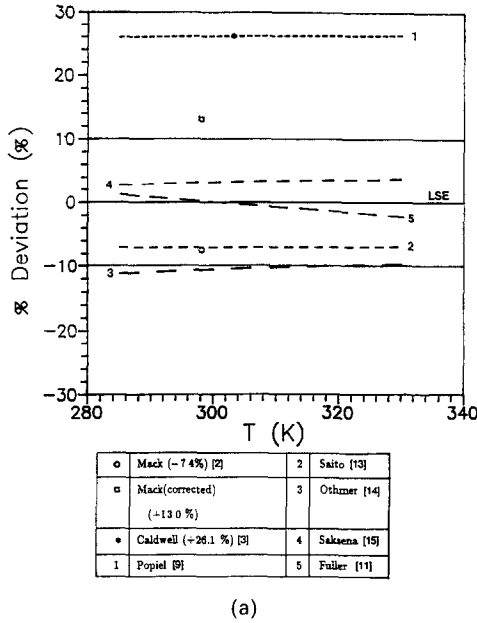


FIG. 4. (a) Percent deviation of  $D_{na,1 atm}$  and other correlated LSEs vs  $T$  from present LSE. (b) Percent deviation of  $D_{na,1 atm}$  and other correlated LSE vs  $T$  from present LSE.

surface. His system had an area ratio of the tube wall to the diffusing naphthalene surface of 2.9 while the ratios in the present apparatus were 0.24 for the 0.5 cm system and 0.48 for the 1 cm system.

The  $D_{na,1 atm}$  from Popiel and Boguslawski's empirical correlation [9] shows a constant percent deviation of about 26% over the working temperature range. The percent deviation is the same as that of Caldwell's measurement because Popiel and Boguslawski employed Caldwell's only point and assumed a power of two in the temperature term. His  $D_{na,1 atm}$  values have the largest deviation of all the correlated equations shown in Figs. 4(a) and (b).

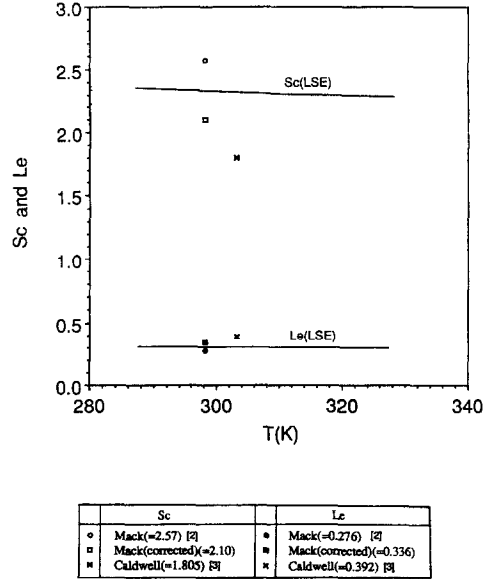


FIG. 5. Comparison of  $Sc$  and  $Le$  vs  $T$  to present LSE and other existing data.

From an examination of Figs. 4(a) and (b), it is seen that the semi-empirical correlations by Arnold [10] and Fuller *et al.* [11] agree best with the present experimental data. Their predictions are within the error range of the LSE shown in the figures.

Previous to the time that Caldwell reported a Schmidt number of 1.805 at 30.04°C for a dilute naphthalene-air mixture in 1984, the Schmidt number was generally assumed to be 2.57 based on Mack's experiment. The Schmidt number calculated with Mack's  $D_{na,1 atm}$  corrected by Ambrose's  $P_{vn}^*$  is 2.10. They are compared with the Schmidt numbers which were obtained from dividing the kinematic viscosity of air [12] by the  $D_{na,1 atm,LSE}$  in the present work.

A least squares equation for the Schmidt number was developed over the temperature range from 14.50 to 53.96°C

$$Sc = 8.0743T^{-0.2165} \quad (10)$$

The temperature ( $T$ ) in equation (10) is in Kelvin (K). Figure 5 shows a comparison with other data. The change of Schmidt number with temperature is similar to the change of Prandtl number with temperature. They both decrease with increasing temperature.

If percent deviations for the Schmidt number are calculated with respect to equation (10), Mack's value and his corrected value have 9.3 and -10.7% deviations, respectively, while Caldwell's value has a -23.0% deviation. It is believed that the Schmidt numbers obtained from the present work can be applied to the naphthalene sublimation technique over the temperature range from 14.50 to 53.96°C with greater accuracy as compared to other existing data.

Lewis numbers were calculated by dividing the Prandtl number of air [11] by the calculated Schmidt



numbers from equation (10). A least squares equation for the Lewis number was calculated for the temperature range from 14.50 to 53.96°C

$$Le = 0.164845T^{0.1059}. \quad (11)$$

The temperature ( $T$ ) in equation (11) is in Kelvin (K). Both the Schmidt and Lewis numbers are shown in Fig. 5 for easy and quick application to the naphthalene sublimation technique. As shown in Fig. 5, the Lewis number calculated from equation (11) is essentially constant at 0.30 within a maximum change of 1.7% over the indicated temperature range. The Lewis numbers obtained from Mack's data and his corrected value are 0.276 and 0.338, respectively, while that obtained from Caldwell's data is 0.392. The calculated deviations from equation (11) show that Mack's value and his corrected value have -8.3 and 12.3% deviations and Caldwell's value has a 29.8% deviation.

### SUMMARY AND CONCLUSIONS

Diffusion coefficients of naphthalene into air were measured for four different cases with two different nominal diffusion lengths (0.5 and 1 cm) and two different diffusion masses (0.25 and 0.4 g) over the temperature range from 14.50 to 53.96°C. The predicted systematic errors are approximately  $\pm 3\%$ . The repeatability of the data is within 2%.

After the diffusion coefficients were adjusted to the values at 1 atm pressure, a least squares equation was calculated over the working temperature range. The diffusion coefficients calculated from this LSE were compared with the previous data of Mack [2] and Caldwell [3] which indicated differences of -7.4 and 26.1%, respectively. Mack's value corrected by an increase of 22% from his reported value was also compared to the LSE and had a difference of 13.0%. When the diffusion coefficients from the present LSE were compared with 12 semi-empirical and empirical correlations, the semi-empirical equation by Arnold shows the closest agreement to the present work with a deviation less than 2% over the working temperature range.

Least squares equations for the Schmidt and Lewis numbers were developed and suggested as the most appropriate for use in the naphthalene sublimation technique. The Schmidt number has a similar temperature dependence as the Prandtl number which results in essentially a constant Lewis number. The Schmidt and Lewis numbers have values of 2.35 and 0.30, respectively, at a temperature of 25°C.

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## MESURE DU COEFFICIENT DE DIFFUSION DU NAPHTALÈNE DANS L'AIR

**Résumé**—La sublimation du naphthalène demande une étude du coefficient de diffusion dans l'air pour éclairer la technique expérimentale analogique souvent utilisée pour simuler le transfert convectif de la chaleur. Seules sont connues deux mesures du coefficient de diffusion (Mack, *J. Am. Chem. Soc.* **47**, 2468–2482 (1925) et Caldwell, *J. Chem. Engng Data* **29**, 60–62 (1984)). Chaque mesure étant faite à une seule température, les résultats diffèrent de 29% environ. Pour éclairer cette incertitude, une expérience est conduite pour mesurer le coefficient de diffusion du naphthalène dans l'air, pour un domaine de température  $15^{\circ}\text{C} \leq T \leq 55^{\circ}\text{C}$ . Deux systèmes géométriquement différents sont utilisés comme test des erreurs systématiques possibles. La répétabilité des données est de 2% et l'erreur systématique possible est estimée à  $\pm 3\%$ . Les données conduisent aux nombres de Schmidt et Lewis qui ont une température faible de  $25^{\circ}\text{C}$ .

## MESSUNG DES DIFFUSIONSKOEFFIZIENTEN VON NAPHTHALIN IN LUFT

**Zusammenfassung**—Eine häufig angewandte Versuchstechnik zur Untersuchung des konvektiven Wärmeübergangs basiert auf dem analogen Vorgang der Naphthalinsublimation. Dabei wird der Diffusionskoeffizient von Naphthalin in Luft zur Kopplung der beiden Systeme benötigt. Aus der Literatur sind bisher nur zwei Messungen des Diffusionskoeffizienten bekannt (Mack, *J. Am. Chem. Soc.* **47**, 2468–2482 (1925) und Caldwell, *J. Chem. Engng Data* **29**, 60–62 (1984)). Beide Messungen wurden bei einzelnen jedoch unterschiedlichen Temperaturen ausgeführt, und die Ergebnisse unterscheiden sich um ungefähr 29%. Aufgrund dieser Unsicherheit wurde der Diffusionskoeffizient von Naphthalin in Luft noch einmal gemessen, und zwar im Temperaturbereich zwischen  $15^{\circ}\text{C}$  und  $55^{\circ}\text{C}$ . Zur Ermittlung möglicher systematischer Fehler wurden zwei unterschiedliche geometrische Konfigurationen verwendet. Die Reproduzierbarkeit der Daten beträgt 2%, der berechnete mögliche systematische Fehler  $\pm 3\%$ .

## ОПРЕДЕЛЕНИЕ КОЭФФИЦИЕНТА ДИФФУЗИИ НАФТАЛИНА В ВОЗДУХЕ

**Аннотация**—Экспериментальный метод, основанный на сублимации нафталина и часто используемый для исследования конвективного теплопереноса, требует знания коэффициента диффузии нафталина в воздухе с целью установления связи между обеими системами. В литературе приводились результаты только двух измерений этого коэффициента диффузии (Mack, *J. Am. Chem. Soc.* **47**, 2468–2482 (1925) и Caldwell, *J. Chem. Engng Data* **29**, 60–62 (1984)). Каждое из этих измерений проводилось при фиксированной температуре, которая в этих работах была различна, при этом результаты отличаются друг от друга примерно на 29%. Ввиду указанной неопределенности в настоящей работе эксперименты по определению коэффициента диффузии нафталина в воздухе проводились в диапазоне изменения температуры  $15^{\circ}\text{C} \leq T \leq 55^{\circ}\text{C}$ . Для исключения возможных систематических ошибок использовались две различные геометрические системы, при этом систематическая погрешность составляет  $\pm 3\%$ .