The thermal diffusion factors of gas mixtures can be investigated by three methods viz. 1) the two bulb method 2) the Trennschaukel or swing separator method and 3) the thermal diffusion column method. In our experimental work we have carried out measurements by the two bulb apparatus and Trennschaukel. We shall therefore give detailed descriptions of these two apparatuses, together with the Column device in brief.

**Two Bulb Apparatus**

As the name indicates, it consists of two bulbs joined vertically by a tube of small cross-section. The apparatus is filled up with a gas mixture of known composition and a temperature gradient is established by maintaining the bulbs at different temperatures. To avoid convection, the apparatus is mounted vertically. In the steady state, a concentration gradient is established such that the effect of thermal diffusion is partially balanced by the ordinary diffusion. From an analysis of the composition of the mixture in both the bulbs, the thermal diffusion factor can be calculated.

For a binary mixture, subject to no external force, under a temperature gradient, the equation for the diffusion velocity can be written as

$$\vec{V}_1 - \vec{V}_2 = -\frac{n_1}{n_1 n_2} D_{12} \left\{ \frac{\partial}{\partial T} \left( \frac{n_1}{n} \right) + K_T \frac{\delta}{\delta T} \ln T \right\}$$
where \( V_1 \) and \( V_2 \) are the diffusion velocities, \( n_1 \) and \( n_2 \) are the number densities of component 1 and 2, component 1 being the heavier one, \( n \) is the total number of density, \( D_{12} \) is the coefficient of ordinary diffusion and \( K_T \) is the thermal diffusion ratio. When equilibrium is established, we have \( \nabla V_1 - \nabla V_2 = 0 \).

Hence

\[
\frac{\delta}{\delta T} \left( \frac{n_1}{n} \right) = -K_T \frac{\delta}{\delta T} \left( \ln T \right)
\]

In terms of the thermal diffusion factor \( \alpha_T \) defined by the relation

\[
\alpha_T = \frac{K_T}{x_1 x_2}
\]

we have,

\[
\frac{\delta}{\delta T} \left( x_i \right) = -\alpha_T x_1 x_2 \frac{\delta}{\delta T} \left( \ln T \right)
\]

where \( x_1 \) and \( x_2 \) are the molefractions of component 1 and 2 respectively. Let the concentration in the top and bottom bulbs be denoted by \( (x_1/x_2)_{\text{top}} \) and \( (x_1/x_2)_{\text{bottom}} \) respectively and corresponding temperature by \( T_H \) and \( T_C \). Then assuming \( \alpha_T \) to be independent of temperature, we have,

\[
\ln \left( \frac{(x_1/x_2)_{\text{top}}}{(x_1/x_2)_{\text{bottom}}} \right) = -\alpha_T \ln \frac{T_H}{T_C}
\]

The quantity \( \frac{(x_1/x_2)_{\text{top}}}{(x_1/x_2)_{\text{bottom}}} \) is known as the separation factor and is denoted by 'q'. Generally in experiments we take component 1 to be the lighter one. Then we have,

\[
\alpha_T (T) = \frac{\ln q}{\ln \frac{T_H}{T_C}}
\]

The value of \( \alpha_T \) calculated by the above formula is a mean value.
over a temperature range $T_C$ to $T_H$. Assuming the temperature dependence of $\alpha_T$ to be of the form given by

$$\alpha_T = A - \frac{B}{T}$$

where $A$ and $B$ are constants, Brown showed this value of $\alpha_T$ can be identified with the actual value of $\alpha_T$ at some intermediate temperature $\bar{T}$, given by

$$\bar{T} = \frac{T_H \times T_c}{T_H - T_c} \ln \left( \frac{T_H}{T_c} \right)$$

Holleran suggested that $\alpha_T = A + B \ln T$ which yields

$$\bar{T} = (T_H \times T_C)^{\frac{1}{2}}$$

Paul et al. suggested that by assuming $\alpha_T = A + BT$, $T$ may be expressed as,

$$\bar{T} = \frac{(T_H - T_C)}{\ln (T_H/T_C)}$$

Relaxation Time

Jones and Furry showed theoretically that the approach toward the steady state in thermal diffusion is exponential which was verified by Nettley, Van Itterbeck and Nihoul, Lansdale and Mason. Saxena and Mason put the theory on firm experimental basis and according to them, the relaxation time $\tau$ for a binary mixture is given by,

$$\tau = K \cdot \frac{L}{A} \left( \frac{T_H}{V_1} + \frac{T_c}{V_2} \right)^{-l} \left\langle \frac{T}{D} \right\rangle_{AV}$$

$$\left\langle \frac{T}{D} \right\rangle_{AV} = \frac{L}{T} \int \frac{T}{D} \, dz$$

where 'L' is the length of the tube connecting the two bulbs,
'A' its area of cross-section, \( D \) is the mutual diffusion coefficient of the molecules and \( V_1 \) and \( V_2 \) are the volumes of the two bulbs which are kept at temperatures \( T_R \) and \( T_C \) respectively. 'K' is an apparatus constant which is very nearly equal to unity. From its physical significance, \( \tau \) is the time required for any process to attain its \( \left( 1 - \frac{1}{e} \right) \)th of the steady state value. Calculation shows that a time of \( 5 \tau \) is sufficient to complete 99% of the process. So in all our experiments we allowed a time greater than \( 5 \tau \) to obtain a steady state.

One disadvantage of this apparatus lies in the fact that a small separation occurs when there is a small relative mass difference between the components of the gas mixture and almost similar force fields i.e. isotropic mixture. So, to obtain a considerable separation in those cases we have to use another apparatus which is called Trennschaukel or swing separator which is described below.

**Trennschaukel or Swing Separator**

In order to obtain a considerable separation for the system where mass difference is small, Clasius and Huber described a device known as Trennschaukel or swing separator.

The apparatus consists of a number of two-bulbs connected in series. A schematic diagram of the apparatus is shown in fig. 2. It consists of an array of vertical tubes with the top of one tube connected to the bottom of the next by capillary tubing and so on.
Fig. 2. Schematic diagram of a conventional tren scheuchel.
While the top of the first tube and bottom of the last tube are connected to a gas swinging arrangement for imparting an oscillatory motion to gas mixture filling the apparatus. All the top ends are kept at a temperature $T_H$ and the bottom ends are kept at a temperature $T_c$ such that $T_H > T_c$. Each vertical tube may be considered as a two-bulb apparatus in which a separation is produced due to thermal diffusion. If now due to mechanical mixing by push and pull arrangement the composition of the gas at the bottom of one tube becomes equal to that at the top of the next and the entire assembly which includes all the stages in series becomes a number of two-bulb in cascade, resulting in a large separation compared to a single two-bulb apparatus operating in the same temperature range.

The theory of this apparatus has been presented in detail by Van der Waerden\textsuperscript{12} and in a more simplified way by Joshi and Saxena\textsuperscript{13}. Each tube can be considered as a two-bulb apparatus in which there is a separation factor $q$, given by

$$\ln q = \ln \left( \frac{x_1}{x_2} \right) = \alpha_T \ln \left( \frac{T_H}{T_c} \right)$$

$x_1$ and $x_2$ being the molefraction of the lighter and heavier component respectively. As a result of cascading of individual stages due to mechanical mixing, the over-all separation factor 'Q' for the whole apparatus is the product of the separation factor 'q' of all stages. Thus for 'N' stages, we have

$$Q = q^N$$
Therefore, 

\[ \alpha_T = \frac{1}{N} \frac{\ln Q}{\ln \left( \frac{T_0}{Tg} \right)} \]

where \( Q \) is the over-all separation factor as measured from the ratios \( x_i/x_j \) at the top and bottom of the two-end tubes. Thus, we see that separation factor obtained is \( N \) times that of the simple two-bulb apparatus.

The relaxation time \( \tau \) for a Trennschaukel is given by \(^{10}\)

\[ \tau = \frac{Vt_p}{2A} \left\{ N + \frac{2\left( V'\right)^2}{\pi} \right\} \]

where \( V \) is the volume of the main tube, \( V' \) is the volume of the gas on either side of the piston of the pump connecting to two ends tubes, \( t_p \) is the period of gas swing and \( 2a \) is the volume of the gas displaced at each stroke. The above derivation assumed an infinitely fast concentration diffusion in the main tube. In a more realistic case of finite rate of diffusion, the correct time \( \tau' \) is given by

\[ \tau' = \tau \left( 1 + \frac{2A t_D}{Vt_p} \right) \]

where \( t_D \) is the characteristic diffusion time given by \( t_D = L^2/D \)

where \( L \) is the length of the main tube. The perfect cascading of all stages is limited by several factors which are described below.

1) **Back diffusion through the capillaries**

There is a temperature gradient in the capillary tube connecting the top and bottom ends of two consecutive stages. This gives rise to thermal diffusion causing the lighter component to go in a direction opposite to that due to Trennschaukel operation.
as a whole. The fractional change in the measured separation due to this effect is given by \(12\)

\[
\frac{\Delta S}{S} = \frac{\nu}{2A} \cdot \frac{t_p}{t_D}
\]

where \(V\) is the volume of the capillary connection, \(2A\) is the volume of the gas displaced, \(t_p\) is the time period of swing and \(t_D\) is the time of diffusion. Thus the decrease in separation can be reduced by decreasing the capillary volume and the period of swing and increasing the volume of displaced gas.

2) Decay in the amplitude of the gas swing towards the central tube

The volume of the gas displaced cycle decreases progressively from the ends towards the middle tubes because the flow of gas through capillary requires a pressure gradient. This effect causes a decrease in the over-all separation and thus the value of decreases. It was shown by Joshi and Saxena\(^{13}\) that to minimise this effect the number of stages must be small and the cross-section of the capillary should be high.

3) Perturbation of the steady state

If the volume of the gas moved per cycle is too large, the steady state in each tube is disturbed. The effect becomes prominent near the ends of the process when equilibrium has almost been attained. The details of this effect was considered by Saxena and Joshi\(^{13}\). They showed that the effect can be minimised by making the volume of the main bulb large compared to the volume of the displaced gas per cycle.
Other sources of systematic error

a) When the gas jets are released in the end bulb, they cause vortex motion in the gas column which remixes the gas and alters the concentration distribution \(^{13}\).

b) These jets release gas at a different temperature than that of the tube and this may raise or lower the effective temperature of the tube as the case may be \(^{13}\).

Recently, Ghosh, Batabyal and Barua \(^{14}\) improved the design of the Trennschaukel mentioning all the defects inherent in the Trennschaukel operation. This will be discussed later.

The thermal diffusion column

The thermal diffusion column or Trennrohr is a device invented by Clusius and Dickel \(^{15}\). It consists of a long vertical tube, cooled on outer side, with a hot wire running along its axis. A gas mixture introduced into the tube is thus subjected to a transverse temperature gradient causing a concentration gradient due to thermal diffusion. The temperature gradient causes a vertical convective motion of gas upward along the hot wire and downward motion along the cold wall. The heavier molecules of the mixture which move towards the cold wall due to thermal diffusion are thus carried downward, while the lighter molecules diffusing towards the hot wire are carried upward. In the ultimate equilibrium state the separation produced by thermal diffusion is balanced by the remixing produced by the convection current.
The exact qualitative theory for the thermal diffusion column is yet to be developed. The existing theories have been given by Jones and Furry, Saxena and Raman and Drickammar.

**Methods of Analysis**

Since the change in composition in thermal diffusion experiment is small, it is a difficult task to measure this change in composition unless the method of analysis is a sensitive one. We here give the different methods of analysis used so far and mention the advantages and disadvantages in each case.

1) **Mass spectrometer**

The analysis with the help of mass spectrometer is a very suitable one for the thermal diffusion in polyatomic gases can be measured with this technique. The main drawback lies in the fact that it is very difficult to analyse gases possessing overlapping peaks in the mass scale.

All of our measurements were carried out with an MS-3 type mass spectrometer supplied by Associated Electrical Industries, U.K. This is a 90° sector type instrument with a spectrometer tube of 10 cm radius and using an electron impact source. The mass spectrometer was operated with 2kV ion accelerating voltage, 70 V accelerating voltage for the ionizing electrons, 3V ion repeller voltage, 100 A. trap current and 1 mA cage current. Peaks were tuned by magnetic scanning. The instrument has a mass range 2 - 130, which can be extended up to 150. A double inlet system allows simultaneous analysis of two samples.
2) **Tracer Technique**

If one of the components of the gas mixture is radioactive, one can employ this technique to study the thermal diffusion. This method suffers from several drawbacks which are stated below.

1) One of the components must be radioactive.
2) The whole composition range can not be studied.
3) Thermal diffusion in polynary systems can not be studied.
4) It is very difficult to use this technique with a swing separator.
5) The separation in one bulb can be measured and the temperature of the observation bulb can not be varied much, which leads to uncertainty in the temperature assignment of \( \alpha_T \) if one wants to measure \( \alpha_T \) at high temperature.

The advantage of this method lies in the fact that it allows one to study the separation of gases without perturbing the diffusion process.

3) **Chemical Method**

This method is seldom used at present. The method is also not suitable for the analysis of inert gases and small change in concentration cannot be measured accurately.

4) **Optical and Ultrasonic Method**

The variation of refractive index of a gas mixture with composition can be employed as a method of analysis. However
a long path of light is required which limits the applicability of this method.

The velocity of sound in a gas mixture varies with composition. Using an acoustic interferometer for the measurement of sound velocity, the change in composition in thermal diffusion can be measured.

5) Measurement of Viscosity

The change in viscosity of a gas mixture with the relative proportion of its component, can be used as one of the method for determining the change in composition in thermal diffusion. The method was developed by Van Itterbeck and Van Pamel\textsuperscript{17} using an oscillating disc viscometer.

6) Measurement of thermal conductivity

The principle of this method is based on the fact that heat conductivity of a mixture changes with the relative concentration of the ingredients. The conductivity measurements are carried out with hot-wire type conductivity cell. For high degree of accuracy one can use differential conductivity analyser, sometimes called a 'Katharometer' in which two thermal conductivity cells are used as two arms of a wheatstone bridge, the other two arms being fixed standard resistances. The analyser is first calibrated with mixture of known composition. Such analyser have been used by Ibbs\textsuperscript{18} and Grew\textsuperscript{19} for most of their thermal diffusion analysis.
References


