

# **CHAPTER 1**

## **General Introduction : Experimental Details**

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Thermal diffusion in gases was first theoretically predicted by Enskog and Chapman<sup>1)</sup>. But the existence of thermal diffusion in gases was experimentally detected by Dootson<sup>2)</sup> in 1917 with H<sub>2</sub>-CO<sub>2</sub> binary gas mixture in a Thermal diffusion column (TDC). Since then it has been drawing the attention of a large number of workers. The instrument of TD column was devised by Clusius and Dickel<sup>3)</sup>. The elementary effect of separation of a component in a gas mixture caused by thermal diffusion in a TDC is multiplied in a simple way.

However, TD experiments can be performed with three different types of apparatuses. These are:

- (i) the two bulb apparatus
- (ii) the swing separator or trennschaukel and
- (iii) the thermal diffusion column (TDC).

**1.1) Two Bulb Apparatus :** A two bulb apparatus consists of two metal brass bulbs of volumes  $V_1$  and  $V_2$  maintained at two different experimental temperatures. The temperature of the hot bulb is  $T_h$  and that of the cold bulb is  $T_c$ . A schematic diagram of the two bulb apparatus is shown in Fig 1.1. To prevent gravitational convective flow of the gas mixture the apparatus is held in a vertical position with its hot bulb at the top. The bulbs are usually connected by a narrow metal tube of length  $L$  and cross sectional area  $Q$ .

Under the influence of temperature gradient upon the gas mixture of uniform pressure, there is always a diffusion flow of a gas in a binary gas mixture. The equation of diffusion which governs the transport of the desired component of a gas mixture is :

$$\vec{J} = \frac{-p}{RT} \left[ D_{ij} \text{ grad } x - D_T \frac{1}{T} \text{ grad } T \right] \quad \dots(1.1)$$

where  $\vec{J}$  is the flux density and  $x$  is the molefraction of a component in a mixture at any given pressure  $p$ .  $D_T$  and  $D_{ij}$  are the thermal diffusion coefficient

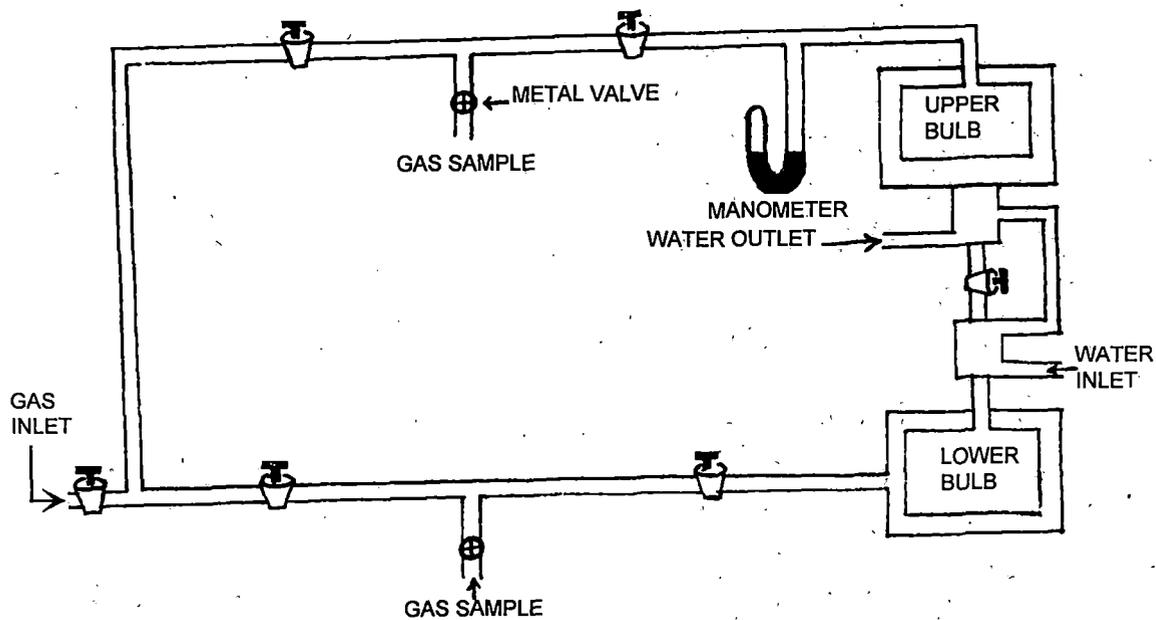


Fig. 1.1. Schematic diagram of the Two Bulb Apparatus

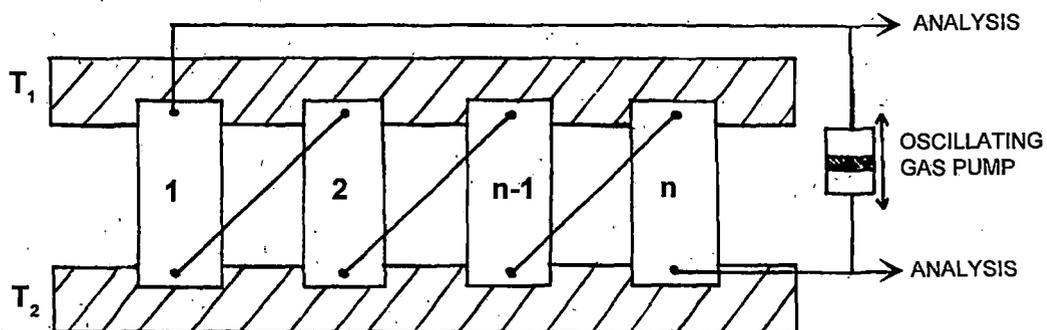


Fig. 1.2. Schematic diagram of the Swing Separator or Trennschaukel

and diffusion coefficient respectively. The partial separation of the components under temperature gradient is determined by  $D_T$  at any temperature  $T$  K. The thermal diffusion ratio  $K_T$  on the other hand, defined by  $K_T = D_T/D_{ij}$ , is strongly dependent on the composition of the gas mixture. It is thus desirable to introduce a composition independent factor, called the Thermal Diffusion Factor (TDF), denoted by  $\alpha_T$  given by

$$\alpha_T = \frac{K_T}{x(1-x)} \dots\dots\dots(1.2)$$

The flux density  $\vec{J}$  is finally given by

$$\vec{J} = \frac{-pD_{ij}}{RT} [\text{grad } x - \alpha_T x(1-x) \text{ grad } \ln T] \dots\dots\dots(1.3)$$

At steady state condition  $\vec{J} = 0$ . Eq (1.3) can then be integrated to yield  $\ln q_e$  where it becomes :

$$\ln q_e = \int_{T_c}^{T_h} \alpha_T d \ln T \dots\dots\dots (1.4)$$

The equilibrium separation factor  $q_e$  is defined by

$$q_e = \frac{(x_i/x_j)_{\text{top}}}{(x_i/x_j)_{\text{bottom}}}$$

Thus the TDF  $\alpha_T$  depends strongly on the temperature, but slowly on the compositions of a gas mixture. The integration of the right hand side of eq (1.4) gives only an average thermal diffusion factor  $\alpha_T$  at any intermediate temperature  $\bar{T}$ . Here, the concentration dependence of the trace components of any gas mixture is, neglected.

The  $\alpha_T$  can also be found out from the slope of the curve of  $\ln q_e$  against  $\ln(T_h/T_c)$  by the relation :

$$\alpha_T = \frac{d \ln q_e}{d \ln (T_h/T_c)} \dots\dots\dots (1.5)$$

$\alpha_T$  is taken to be positive if the lighter component concentrates in the hotter part of the system.

## 1.2. The Swing Separator or Trennschaukel

The Swing separator or trennschaukel consists of a series of two bulbs connected by small capillary tubes as shown in Fig. 1.2. The capillaries connect the bottom of stage 1 to the top of stage 2, the bottom of stage 2 to the top of stage 3 and so on. A wobbling mercury pump is used to maintain equilibrium between the hot part of stage 1 and the cold part of stage 2. The pump produces an oscillating motion of the gas mixture in the swing separator. Thus the gas composition becomes equal at the bottom and the top of the adjacent stages and over-all separation factor  $Q$  is given by

$$Q = q_e^n \quad \dots\dots\dots (1.6)$$

where  $q_e$  is the equilibrium separation factor of the individual stage and  $n$  is the number of stages.

Due to oscillation in the gas mixture, the volume of the gas will disturb the steady state separation in the individual separation tube. The back diffusion through the capillaries will thus reduce the oscillating effect with respect to high or low speed of the pump. The optimum speed of the pump can, however, be estimated from the theory developed by Wearden<sup>4</sup>.

Finally, in a swing separator, eq (1.5) becomes :

$$\alpha_T = \frac{1}{n} \frac{d \ln q_e}{d \ln (T_h/T_c)} \quad \dots\dots\dots (1.7)$$

The swing separator has been recognised as a valuable instrument specially designed to measure  $\alpha_T$  of isotopic mixture when the separation is very small in a two bulb apparatus. Wearden <sup>4</sup>) had argued that the simple relation  $Q = q_e^n$  are not sufficient enough for the swing separator. Here, the equality of composition at the ends of the capillary connectors are not attained in finite pumping time. Although the swing separator is a useful device to yield more accurate results, it is susceptible to various types of errors in comparison to the simple two bulb apparatus.

### 1.3. Thermal Diffusion Column

Thermal Diffusion Column (TDC) is a unique device to concentrate impurities of a gas mixture. The column consists of two cylindrical surfaces of which one is kept at higher temperature  $T_h$  and the other at lower temperature  $T_c$ . Unlike two bulb apparatus and swing separator in a thermal diffusion column a temperature gradient is arranged horizontally to cause convection, as a result cumulative effect occurs. To produce separation in the binary mixture by a TDC it is thus subjected to two effects. These are :

- a) thermal diffusion in a horizontal direction due to temperature gradient between hot wall or wire and the cold wall of a TDC and
- b) convective motion of the lighter component of a gas mixture upward near the hot wall or wire and downward for the heavier component near the cold wall of a TDC.

From the equation of continuity the differential equation in vector notation for the separation of a gas mixture in a TDC is given by :

$$\vec{\tau}_o = - \rho_{ij} D_{ij} \{ \text{grad } x + \alpha_T x (1-x) \text{ grad } \ln T \} + \rho \vec{v} x \quad \dots\dots (1.8)$$

where  $\tau_o$  is the transport of the desired component through a cross section of the column per unit time,  $x$  is the molefraction of the component,  $D_{ij}$  is the diffusion coefficient and  $\rho_{ij}$  is the density of the binary gas mixture. Now, considering the thermal diffusion column as a square cascade, the column equation is given by:

$$\mu \frac{\delta x}{\delta t} = (K_c + K_d) \frac{\delta^2 x}{\delta z^2} - \frac{\delta}{\delta z} \{ P x + H x (1-x) \} \quad \dots\dots\dots (1.9)$$

where  $\mu$  is the mass of the gas transported per unit length of the column,  $H$  is the initial transport coefficient which determines the enrichment of a component of the gas mixture in a TDC,  $K_c$  is the loss of enrichment due to axial counter current and  $K_d$  represents the axial back diffusion. The product stream is  $P$  in the vertical  $z$  direction. In the steady state condition  $\vec{\tau}_o$  is no longer a function

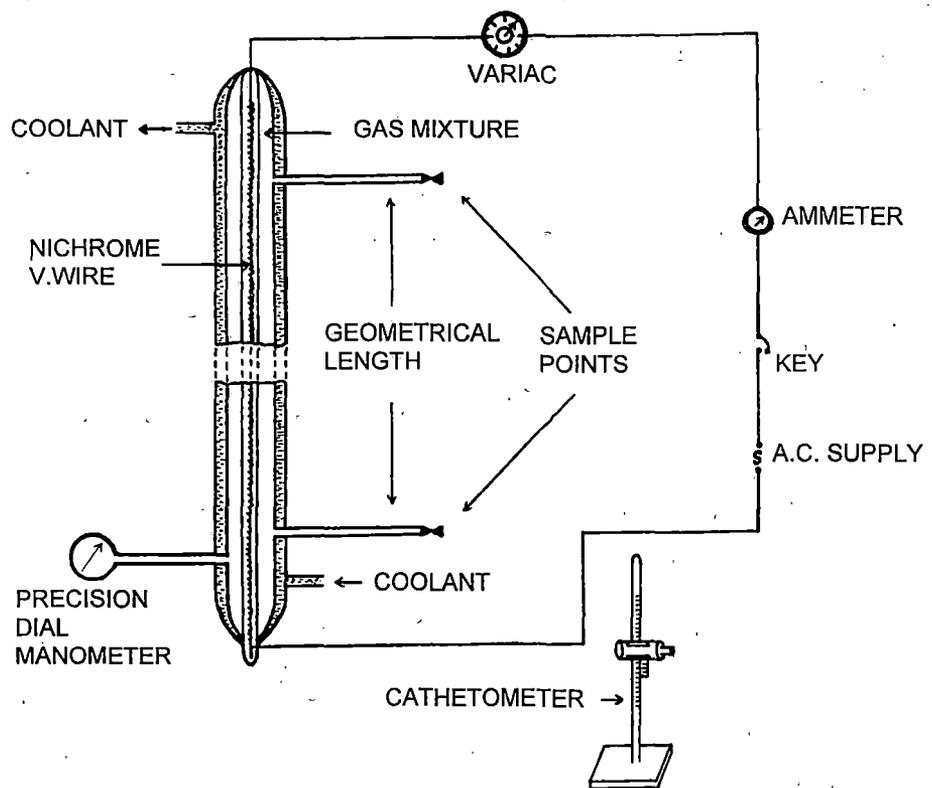


Fig. 1.3. One Stage Thermal Diffusion Column

of  $z$  and is equal to  $Px_p$ , where  $x_p$  is the molefraction of the product. Using Cohens equation<sup>5)</sup> i.e.,

$$\frac{\delta \bar{\tau}_o}{\delta z} = -\mu \frac{\delta x}{\delta t}$$

eq (1.9) after integration becomes :

$$\bar{\tau}_o = Px + Hx(1-x) - (K_c + K_d) \frac{\delta x}{\delta z} \quad \dots\dots\dots (1.10)$$

At total reflux i.e., with zero production rate we have  $P = 0$ . The eq (1.10) thus yields

$$\bar{\tau}_o = Hx(1-x) - (K_c + K_d) \frac{\delta x}{\delta z}$$

As the TDC starts to work, the concentration gradient in a uniform gas mixture contained in a column is zero everywhere. This leads to

$$(\bar{\tau}_o)_{t=0} = Hx(1-x)$$

which represents the initial transport. At the steady state the concentration in the reservoir of the column is time independent and the net transport becomes zero. Thus for a thermal diffusion column working at total reflux we have,

$$Hx(1-x) = (K_c + K_d) \frac{\delta x}{\delta z} \quad \dots\dots\dots (1.11)$$

Introducing the equilibrium separation factor  $q_o$  and integrating eq (1.11) for a TDC of length  $L$  one gets

$$\ln q_o = \frac{HL}{K_c + K_d} \quad \dots\dots\dots (1.12)$$

$x_i$  and  $x_j$  are the molefractions of the lighter and the heavier components respectively at the steady state condition.

When the temperature difference between the walls of a TDC is small, the expressions for the column parameters  $H$ ,  $K_c$  and  $K_d$  are given by Jones and Furry<sup>6)</sup>, Fleischmann and Jenson<sup>7)</sup>, Sliker<sup>8)</sup>, and others. The coefficient of viscosity  $\eta_{ij}$ , the coefficient of thermal conductivity  $\lambda_{ij}$ , the diffusion coefficient  $D_{ij}$ , thermal diffusion factor  $\alpha_T$  and the density  $\rho_{ij}$  occurring in the formulae for  $H$ ,  $K_c$  and  $K_d$  are taken at the mean temperature  $\bar{T} = (T_h + T_c)/2$ . The convective

velocity  $v$  which specify the flow of a component of a gas mixture in the TDC can be obtained from the well known Navier - Stokes equation. For a square cascade TD column the equation which describes the vertical flow of a gas as a function of horizontal  $x$  - coordinate is given by <sup>8)</sup>

$$v = - \frac{1}{12} \frac{\rho_{ij} g}{\eta_{ij}} \frac{\Delta T}{T} \frac{x}{d} (2x-d) (x-d). \quad \dots\dots\dots (1.13)$$

With some suitable boundary conditions the column parameters are finally given by <sup>8)</sup> :

$$\left. \begin{aligned} H &= \frac{d^3 \rho_{ij}^2 \alpha_T g}{6 \eta_{ij}} B \left( \frac{\Delta T}{T} \right)^2, \\ K_c &= \frac{d^7 \rho_{ij}^3 g^2}{9 \eta_{ij}^2 D_{ij}} B \left( \frac{\Delta T}{T} \right)^2 \text{ and} \\ K_d &= \rho_{ij} D_{ij} B d. \end{aligned} \right\} \dots\dots\dots (1.14)$$

Here,  $B$  is the mean circumference of the parallel plates of a TDC at a distance  $d$  apart and  $g$  is the acceleration due to gravity.

From eqs (1.12) and (1.14) for a plane parallel plate type thermal diffusion column we have

$$\ln q_0 = \frac{L}{1.2d} \alpha_T \left( \frac{\Delta T}{T} \right) \frac{m}{1+m^2} \quad \dots\dots\dots (1.15)$$

$$\text{where } m = \frac{d^3 \rho_{ij} g}{602.4 \eta_{ij} D_{ij}} \left( \frac{\Delta T}{T} \right). \quad \dots\dots\dots (1.16)$$

$\eta_{ij}$  is independent of pressure  $p$  while  $\rho_{ij}$  and  $D_{ij}$  are proportional to  $p$  and  $p^{-1}$  respectively.  $\alpha_T$  is pressure independent function and hence  $\ln q_0$  is only a function of pressure through  $m$ ,  $m$  is proportional to  $p^2$ .

From eq (1.15) it is obvious that as pressure  $p$  increases  $\ln q_0$  increases

and eventually assumes a maximum value for  $m = 1$ . Thus on maximization eq (1.15) becomes

$$\ln q_{\max} = \frac{L}{2.4d} \alpha_T \left( \frac{\Delta T}{\bar{T}} \right) \dots\dots\dots (1.17)$$

and the optimum pressure  $p_{\text{opt}}$  can be obtained as :

$$p_{\text{opt}}^2 = 602.4 \frac{\eta_{ij} D'_{ij}}{d^3 \rho'_{ij} g} \left( \frac{\bar{T}}{\Delta T} \right) p_0^2$$

where the transport coefficients are to be evaluated at any reference pressure  $p_0$ .

In order to develop the theory of a plane parallel type TDC<sup>9-10)</sup> it is assumed that there is a nonturbulent convective flow of gas mixture in the column. In a thermal diffusion column it depends upon the Grashof - Prandtl number<sup>9)</sup>. The authors are in the habit to express the Grashof - Prandtl number, Gr. Pr, as the Reynolds number  $R_e$  where

$$R_e = \frac{\rho_{ij}^2 g d^3}{384 \eta_{ij}^2} \left( \frac{\Delta T}{\bar{T}} \right).$$

It follows that

$$\text{Gr. Pr.} = \frac{C_p \eta_{ij}}{\lambda_{ij}} 384 R_e \dots\dots\dots (1.18)$$

It had been shown experimentally by Onsager and Watson<sup>11)</sup> in a TDC that the maximum possible value of  $R_e < 25$ . According to Donaldson and Watson<sup>12)</sup> and Jones and Furry<sup>6)</sup>  $R_e < 14$  and  $R_e < 10$  respectively. Grew and Ibbs<sup>13)</sup> argued that spacing should be so adjusted that  $5 < K_o/K_d < 25$ . Summarizing all these facts for laminar flow in a TDC we have

$$5 < R_e < 10.$$

For diffusion of trace components where  $R_e = 0.78$  the condition for laminar flow becomes

$$2.5 P_{\text{opt}} < P < 3.6 P_{\text{opt}}$$

The other limitations of the theory of concentric cylindrical type TDC can

be summarized as follows :

- (a) the concentration and temperature dependence of the transport coefficients like  $\rho_{ij}$ ,  $\eta_{ij}$ ,  $D_{ij}$ ,  $\lambda_{ij}$  and  $\alpha_T$  are not taken into account,
- (b) for a concentric cylindrical type TDC the coefficients are measured at the mean gas temperature<sup>9)</sup>  $\bar{T}$  where

$$\bar{T} = T_c + \frac{0.56}{\ln(r_o/r_h)} \Delta T \text{ and}$$

- (c) the temperature distribution along the x - axis of the TDC is determined by the conduction of heat energy alone.

For the concentric cylinder type TDC the expressions for the column parameters are given by Jones and Furry<sup>6)</sup>, Fleischman and Jenson<sup>7)</sup>, Slieker<sup>8)</sup> and others. Velds et al<sup>9)</sup> have, however, used these column parameters for column of cold wall radius  $r_c=10$  mm and hot wall radii  $r_h=4$ mm, 6.7 mm and 8.3 mm respectively with cold wall temperature  $T_c=293$ K and hot wall temperature  $T_h=633$ K. The calculated values of column parameters  $H$ ,  $K_c$  and  $K_d$  for concentric cylinder type columns were compared with the values for the expressions of plane parallel plates<sup>9)</sup>. There is a clear difference between the results of column parameters  $H$ ,  $K_c$  and  $K_d$  for concentric cylinder type and plane parallel plate type columns. The column parameters using Jones and Furry<sup>6)</sup> column shape factors (CSF) were larger in magnitude than the parallel plate type in contrast with those by using either Fleischmann and Jenson's<sup>7)</sup> CSF or Slieker's CSF. However, for simplicity many of the authors<sup>9-10)</sup> had used the plane parallel type column behaviour.

It is assumed that the approximations for the theoretical developments of a plane parallel plate type TDC do not give serious deviations between the theory and experiment. Further, the deviations are caused by the imperfectness of the TDC such as nonverticality of the TDC and non uniformity in the diameter of the tubes. These usually invite remixing. Jones and Furry<sup>6,14)</sup> had added a term  $K_p$  proportional to  $p^4$  to the denominator of eq (1.12) for this remixing effects. However, different authors have made different approximations in the

formulation for  $H$ ,  $K_c$  and  $K_d$  of the concentric cylinder type TDC. The agreement between the theoretical and experimental results are still not satisfactory. Better experimental results of interesting pair of molecules are, therefore, needed for the column parameters  $H$ ,  $K_c$  and  $K_d$  of a concentric cylinder type TDC.

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