CHAPTER - I

GENERAL INTRODUCTION AND REVIEW OF THE PREVIOUS WORKS

The process of thermal diffusion which was predicted theoretically before it was observed experimentally arises when a temperature gradient is established in a uniform gas mixture of two or more pure components. The larger and the heavier molecules move towards the colder region while the smaller and the lighter ones in the reverse direction producing thereby an appearance of difference in concentrations of the mixture components in the direction of lowering the temperature. Thus the thermal diffusion is regarded as the second order kinetic effect. This difference in concentrations in a uniform mixture set up by the temperature gradient produces the concentration gradient to allow the ordinary diffusion which acts in the opposite direction tending to annul the thermal diffusion flux. As a result of the joint action of these two processes, a steady state is reached when an equilibrium concentration gradient sets in due to the temperature gradient.

There are several reasons for the investigation of the process of thermal diffusion:

(i) It is particularly a convenient experimental tool to separate stable isotopes,

(ii) It can be used as a perturbation factor in various physico-chemical processes,

(iii) It has a wide application in a number of natural phenomena, such as flames, astrophysical problems and nabulae and

(iv) It is very much sensitive to intermolecular forces between unlike molecules in a mixture and hence it is widely used to study the nature of unlike forces between the components of the gas mixtures.

The phenomenon of thermal diffusion can not be explained by simple molecular kinetic theory which we use with some success to explain the ordinary diffusion. This is why thermal diffusion was not discovered for such a long time. It was found that an appreciable part in this phenomenon is played forces of repulsion between molecules of the components upon their collision. It may be considered that these forces diminish with an increasing distance r between the molecules to an approximate force law $F = f(\frac{1}{r^n})$. If $n > 5$, thermal diffusion proceeds in the direction indicated above, if $n < 5$, the sign of the thermal diffusion difference in concentrations is reversed, and finally if $n = 5$ thermal diffusion is, in general impossible.

The equation of ordinary diffusion is

$$c_i(V_i - V) = c_i c_j (V_i - V_j) = -D_{ij} \text{ grad } c_i \qquad (1.1)$$

where,

V_i and V_j are the relative velocities of the components i and j.

V = mean velocity.

c_i and c_j are the mass fractions of the components i and j.

The existence of thermal diffusion makes it necessary to add another term to eqn (1.1) so that we have

$$c_i(V_i - V) = -D_{ij} \text{ grad } c_i + \frac{D_T}{T} \text{ grad } T \qquad (1.2)$$

where, D_{ij} is the interdiffusion co-efficient and D_T is the co-efficient of thermal diffusion, its dimension is obviously the same as that of D_{ij} in gm^2/sec. But unlike the co-efficient of diffusion, D_T is virtually independent of the concentrations, the co-efficient D_T the thermal diffusion co-efficient is proportional to the product of the concentration of both the components i.e. c_i and c_j

$$\therefore \quad \frac{D_T}{D_{ij}} = \alpha_T c_i c_j$$

$$\text{or} \quad D_T = \alpha_T c_i c_j D_{ij}$$

where, c_i and c_j are the concentration of the lighter and the heavier ones. Hence the eqn. (1.2) becomes

$$c_i(V_i - V) = -D_{ij} \text{ grad } c_i + \frac{D_{ij} c_i c_j \alpha_T}{T} \text{ grad } T$$
$$= D_{ij}(\alpha_T c_i c_j \text{ grad log } T - \text{grad } c_i) \qquad (1.3)$$

Since grad log $T = \frac{1}{T}$ grad T,

where α_T is defined as the so called thermal diffusion factor. It is exactly the constant that depends upon the properties of a mixture being separated particularly on the exponent n in the above mentioned force law i.e. $F = f\left(\frac{1}{r^n}\right)$ the law of diminishing of roce of repulsion between molecules.

There are several arrangements to perform the thermal diffusion experiments in the laboratory. The apparatuses commonly used are two bulb, trennschaukel or swing separator and the thermal diffusion column in fact abbreviated by T.D. column.

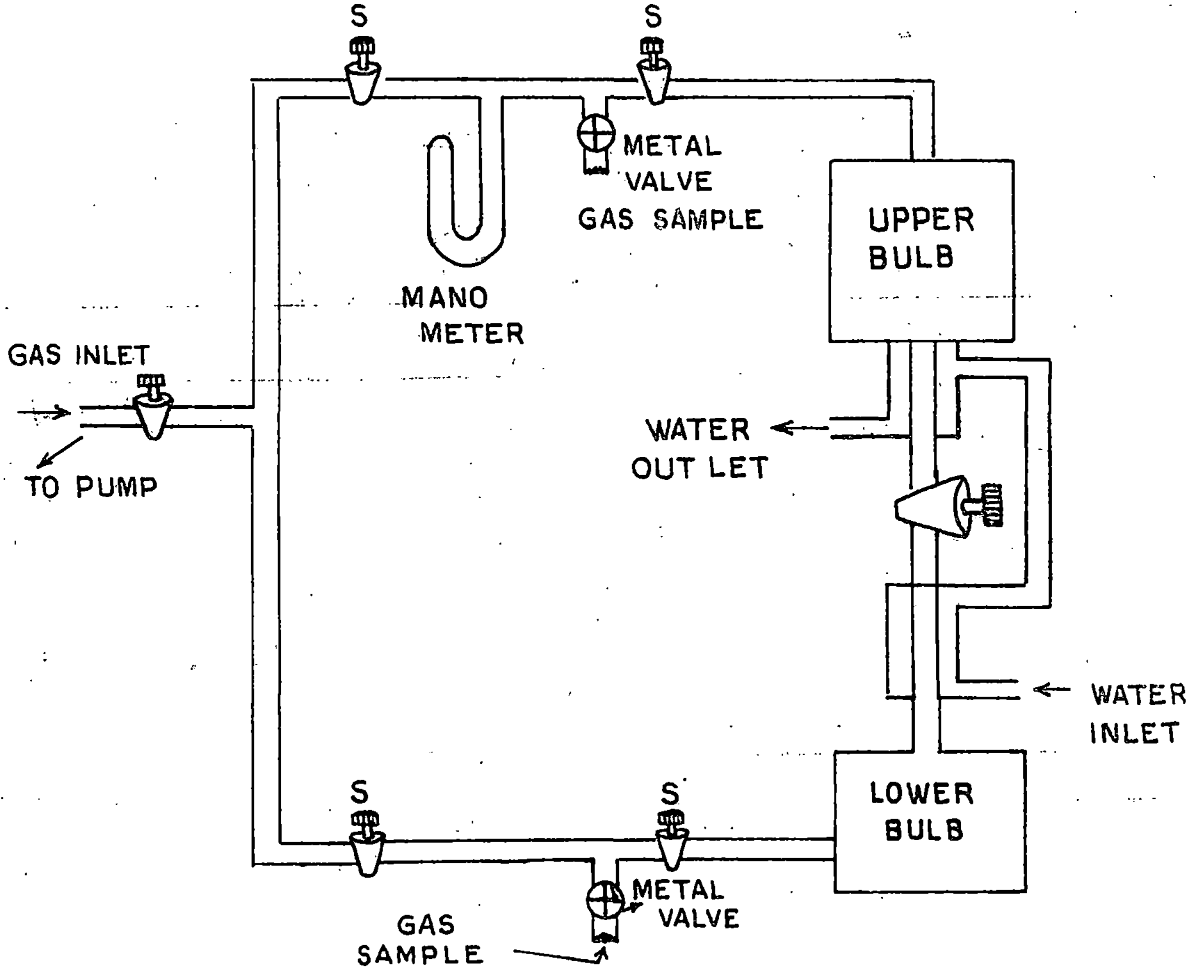

Fig 1.1. The schematic diagram of two bulb apparatus.

Thermal diffusion column may exist in two forms : hot wire column and hot wall column. The investigation under the present thesis is concerned with T.D. columns either hot wall or hot wire available in the literature.

THE TWO BULB APPARATUS:

It is the simplest apparatus to measure the thermal diffusion factors in a gas mixture. It was first used by Champman and Dootson[1] in their first experimental demonstration of the thermal diffusion phenomenon in gas mixture. It consists of two bulbs joined by a tube having a stop cock (Fig. 1.1). The apparatus is filled up by a gas mixture of known concentration and a temperature gradient is established by keeping the two bulbs at two different temperatures. The top bulb is always maintained at a higher temperature in order to avoid the convection current. When the steady state is reached a resultant concentration gradient is set up due to the applied temperature gradient. The samples of gases are then taken from the top and the bottom bulbs in order to analyse the compositions. For a two component mixture under a given temperature gradient the general diffusion equation can be written as

$$V_i - V_j = \frac{n^2}{n_i\, n_j}\left[D_{ij}\right]\left\{\frac{\partial}{\partial r}\left(\frac{n_i}{n}\right) + k_T\,\frac{\partial \ln T}{\partial r}\right\}$$

where V_i and V_j are the diffusion velocities of the ith and the jth components respectively. n_i and n_j are the number densities of the ith and jth species and n is the total number of density. $[D_{ij}]$, is the diffusion co-efficients and k_T is the thermal diffusion ratio. When the equilibrium condition is reached so that the diffusion velocities are zero, we have from the above equation

$$\frac{\partial}{\partial r}\left(\frac{n_i}{n}\right) = -k_T \frac{\partial \ln T}{\partial r} \tag{1.4}$$

Eqn (1.4) when expressed in terms of the thermal diffusion factor α_T where $\alpha_T = \frac{k_T}{x_i\, x_j}$ becomes

$$\frac{\partial x_i}{\partial r} = -\alpha_T\, x_i\, x_j \frac{\partial}{\partial r} \ln T \tag{1.5}$$

where x_i and x_j are the mole fractions of the components i and j of pure gases forming a mixture. It is immaterial whether we use c_i and c_j in place of mole fractions x_i and x_j to signify the mass fractions of the lighter and the heavier components of the mixture respectively, because of the very definition of q_e, the equilibrium separation factor of any binary mixture.

If $(x_i/x_j)_{top}$ and $(x_i/x_j)_{bottom}$ represent the ratios of the mole fractions of the lighter and the heavier components of a mixture at the top, the upper bulb and at the bottom, the lower bulbs respectively at the temperatures T_h and T_c respectively, we then write by integrating the eqn (1.5) in the form:

$$\int_{\text{bottom}}^{\text{Top}} \frac{dx_i}{x_i x_j} = \alpha_T \int_{T_c}^{T_h} d \ln T$$

$$\text{or,} \quad \ln \frac{(x_i/x_j)_{\text{top}}}{(x_i/x_j)_{\text{bottom}}} = \alpha_T \ln \frac{T_h}{T_c}$$

$$\text{or,} \ln q_e = \alpha_T \ln \frac{T_h}{T_c} \tag{1.6}$$

where $q_e = \frac{(x_i/x_j)_{\text{top}}}{(x_i/x_j)_{\text{bottom}}}$ is known as the equilibrium separation factor. Thus the direct evaluation of the thermal diffusion factor α_T is possible from eqn (1.6) only by measuring T_h, T_c and $\ln q_e$

$$\therefore \alpha_T = \frac{\ln q_e}{\ln(T_h/T_c)} \tag{1.7}$$

which is supposed to be a mean value of the thermal diffusion factor in the temperature range T_c to T_h. Brown[2] had shown that for given values T_h and T_c a temperature $\bar{T}$ could be found out corresponding to the actual value of α_T at that temperature

$$\bar{T} = \frac{T_h + T_c}{T_h - T_c} \ln \frac{T_h}{T_c} \tag{1.8}$$

The two bulb apparatus though it is believed to yield the actual thermal diffusion factor of a gas mixture at a temperature given by eqn (1.8), it has a few limitation. The separation in this apparatus for isotopic and isobaric gas mixtures is very low thus inviting an enormous error in the value of q_e and hence of α_T. When the mass difference between the components of a gas mixture is very large, two bulb apparatus can be used with greater advantage. Moreover after the attainment of steady state the middle stop cock can be closed and the sampling of the gas mixture could be done without disturbing the system. The difference of temperature T_h and T_c should also be made very large in order to obtain the appreciable separation. This fact also invites a larger error in estimating the mean temperature $\bar{T}$ for α_T to be measured.

However, for measuring the small α_T values of isotopic gas mixtures an improved apparatus known as trennschaukel or the swing separator is commonly used.

THE SWING SEPARATOR:

It is usually called trennschaukel first designed by Clusius and Huber[3,4] in order to get enhanced separation of a binary gas mixture. They connected a number of two bulb apparatus in series. This device is also called a swing separator. It effectively obtains multiple separation with considerably less operational effort, and is accordingly used to measure isotopic thermal diffusion for which α_T is small. It is also useful for measurement in which α_T is not small, since smaller temperature differences are needed and the temperature assignment for the mean temperature is therefore more accurate.

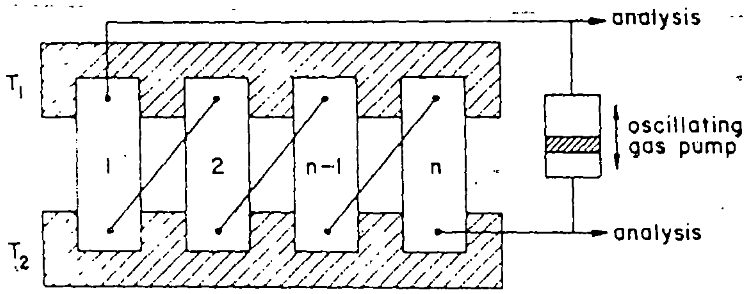

FIG. 1·2 Schematic diagram of the swing separator, or "Trennschaukel."

A schematic diagram of the swing separator is shown in Fig. (1.2). Each two bulb stage of separation is constructed as a vertical cylinder of uniform diameter. The stages are joined in series by capillaries which connect the bottom of stage I to the top of stage 2, the bottom of stage 2 to the top of the stage 3 and so on. An oscillatory motion is given to the gas so that the volumes of gas are continually interchanged between the bottom of one stage and the top of the following stage. As a result of this mechanical mixing, the gas compositions become equal at the bottom and at the top of two adjacent stages, and the overall separation factor Q_e of the apparatus as described above is simply the product of the separation factor q_e for the individual stage.

$$\therefore \qquad Q_e = q_e^n \tag{1.9}$$

for n stages. To maintain the constant temperature at the end regions it is also considered that the equilibrium time should be as small as possible. The equilibrium time for an assembly of n tubes is proportional to n^2 which means that small number of tubes should be employed. The thermal diffusion factor α_T of any binary gas mixture can be found out in the following way.

For a single stage of a trennschaukel

$$(\alpha_T)_{\text{single stage}} = \frac{\ln q_e}{\ln (T_h/T_c)} \tag{1.10}$$

Thus for n stages we have

$$\alpha_T = \frac{\ln q_e}{\ln(T_h/T_c)} = \frac{\ln Q_e^{1/n}}{\ln(T_h/T_c)} = \frac{1}{n}\,\frac{\ln Q_e}{\ln(T_h/T_c)} \tag{1.11}$$

where, $Q_e = (x_i/x_j)_T \; / \; (x_i/x_j)_B$, where x_i and x_j being mole fraction of the lighter and the heavier components at the top and the bottom of a tube. The swing separator functioning in the manner as described was demonstrated by Clusius and Huber (1955) with a six-stages apparatus with $H_2 - CO_2$ mixture for which α_T had been previously measured by the two bulb technique. The swing separator has since been recognized as being a valuable instrument for the measurement of isotopic thermal diffusion factors α_T. The apparatus is thus clearly a useful device capable of yielding accurate result, but it is susceptible to more types of errors than in the simple two bulb apparatus.

Thermal diffusion Column:

When the mass difference between the components of a binary gas mixture is very small as in the case of isotopic gases and even for the isobaric gas mixtures like N_2-CO. N_2O-CO_2, He-HT etc., where the mass difference are practically nill, the thermal diffusion column technique could advantageously be used to separate them. It was first invented by Clusius and Dickel[5,6] in the year of 1939. There are two types of thermal diffusion columns usually used in practice namely (i) Hot wire type thermal diffusion and (ii) Hot wall type thermal diffusion column.

The hot wire type thermal diffusion column consists of a long vertical wire surrounded by a coaxial cylindrical tube, the outside of which is jacketted through which water is circulated to cool the outer side of the cylindrical tube. The wire which runs along the axis of the coaxial cylinder can be heated electrically. The temperatures T_h and T_c of the electrically heated wire and the cold wall of the tube produces a temperature gradient along the horizontal direction. A gas mixture of known concentration is introduced into the annular space between the hot wire and the cold wall of the vertical cylindrical tube. The transverse temperature gradient between T_h and T_c of the hot wire and the cold wall thus applied gives rise to the horizontal concentration gradient in a uniform binary mixture due to thermal diffusion. A vertical convective motion of the gas starts along the hot wire in the vertically upward direction and along the inner wall of the tube in the vertically downward direction respectively. The heavier components which move towards the cold wall and the lighter components towards the hot wire due to thermal diffusion, are thus taken by this convection current to the bottom and at the top of the column respectively. Finally an enrichment of lighter component at the top and the heavier components at the bottom of a column occurs. Although the separation produced by thermal diffusion is balanced by the remixing effect due to the convection currents and the back diffusion caused by the longitudinal concentration gradient still the separation in this type of device is many times larger than those of trennschaukel and two bulb apparatuses which are commonly used to observe the thermal diffusion phenomenon.

For some gas mixtures which may decompose when it will come in contact with the heated wire, the hot wire column can not be used to separate them. For this reason and to get the larger values of the separation factors than a hot wire type Brewer and Bramley[7] modified the hot wire column by replacing the central hot wire by an indirectly heated tube coaxial to the outer cold wall tube. This modified thermal diffusion column is known as concentric cylindrical hot wall thermal diffusion column. The construction of such column although is very difficult still a more accurate geometry can be achieved with it. The main advantage of using the hot wire type thermal diffusion column is that it is easy to construct and a larger temperature gradient can be established across it.

Recently Vasaru et al[8] have improved the column techniques to obtain the higher separation and hence the yield of rare isotopes of a particular type per day. Vasaru et al found the condition of optimum yield for a large number of columns, some of which are placed in series and some are connected in parallel.

A large number of workers C.J.G. Slieker[10] (1965), T.I. Moran and W.W. Watson[11] (1958), J.W. Corbett and W.W. Watson[12] (1956), S.C. Saxena and S. Raman[13] (1962), J.L. Navarro, J.A.

Madariaga and J.M. Saviron[14] (1983), J.M. Saviron, C.M. Santamaria, J.A. Carrion and J.C. Yrza[15] (1975) etc. tried to improve the column theory in order to obtain the exact values of the thermal diffusion factors of a large number of binary gas mixtures, but their results could hardly be explained with the theoretical α_T's based on either elastic and inelastic collisions included in the formal Kinetic theory.[16,17,18,19,20,21] However W.M. Rutherford et al from 1965 to 1982 performed thermal diffusion experiments on a large number of isotopic mixtures of noble gases by thermal diffusion columns of comparatively long geometrical lengths and the values of $\ln q_e$ thus obtained are found to be large which at once demands the accuracy of the measurements of $\ln q_e$ to a large amount. In recent years E.I. Leyarovski, A.J. Zahariev and J.K. Georgiev[22] (1987) set up thermal diffusion column of length 230 cm and $r_h = 1.5$ cm, $r_c = 2.5$ cm and determined α_T with a thermal diffusion column over a large intervals of temperatures and pressures. It can be used for the investigation and optimisation of the influence of main thermodynamic parameters in the process of separation of gas mixtures in a thermal diffusion column. They deduced an equation from Rozen[23] (1960) which is given by:

$$\alpha_T = \frac{\ln(N + \ln Q_L)/(N - \ln Q_H)}{\ln(T_h^*/T_c^*)} \qquad (1.12)$$

where $Q_L = \frac{x_1}{x_2}$ and $Q_H = (1 - x_2)/(1 - x_1)$.

$N = \frac{h}{h_0}$,

$h_0 = h_c + h_d$,

but
$$h_c = \frac{\rho g \Delta T \delta^4}{1008 \eta D \bar{T}}$$

$$h_d = \frac{360 \eta D \bar{T}}{\rho g \Delta T \delta^2}$$

$$\Delta T = T_h - T_c$$

and
$$\bar{T} = \frac{T_c T_h}{T_h - T_c} \ln \frac{T_h}{T_c}$$

$$T_h^* = \frac{T_h + \bar{T}}{2}$$

and
$$T_c^* = \frac{T_c + \bar{T}}{2}$$

where h_o is the transfer unit height (TUH); h_c and h_d are the components of TUH; N is the number of TUH, h is the geometrical length of the column, Q_L and Q_H are the degrees of separation of the light component and the heavy component respectively which are the functions of the pressure at constant average temperature. $\bar{T}$ is the logarithmic averaged temperature; ρ is the density of the gas mixture; D is the coefficient of mutual diffusion; η is the viscosity of the gas mixture and g is the acceleration due to gravity. x_1 and x_2 are the gas concentration of the light and the heavy component, T_h is the temperature of the hot wall and T_c is the temperature of the cold wall of the column respectively.

The equation (1.12) is derived starting from the Rozen[23] (1960) equation

$$\ln(Q_H - Q_L^{\ 1/q}) = (H/K)h \qquad (1.13)$$

where q is the coefficient of separation being a function of pressure, and is given by

$$q = (T_H^* / T_C^*)^{\alpha_T} ;$$

H and K are the well known transport coefficients of Furry, Jones, Onsager (FJO) theory. Obviously, in the case of isotopic or very dilute binary mixtures, where $(q-1) \ll 1$ eq. (1.13) is essentially equivalent to the general equation of the FJO[25] theory

$$\ln Q = \ln (Q_H - Q_L) = (H/K)h \qquad (1.14)$$

It should be noted that eq. (1.12) is somewhat different from the equation derived from the 'classical Furry, Jones, Onsager[25] (FJO) theory and commonly used in determination of α_T in thermal diffusion column (TDC). Rutherford and Kaminski (1967) have shown that the FJO[25] theory is applicable mainly in the case of isotopic binary mixtures or in the case of a mixture in which one of the components is in a trace concentration in a relatively lower total pressure of the binary mixture. The FJO[25] theory was shown to be valid in such conditions, the theoretical values of column coefficients being obtained (Rutherford 1982) by computer

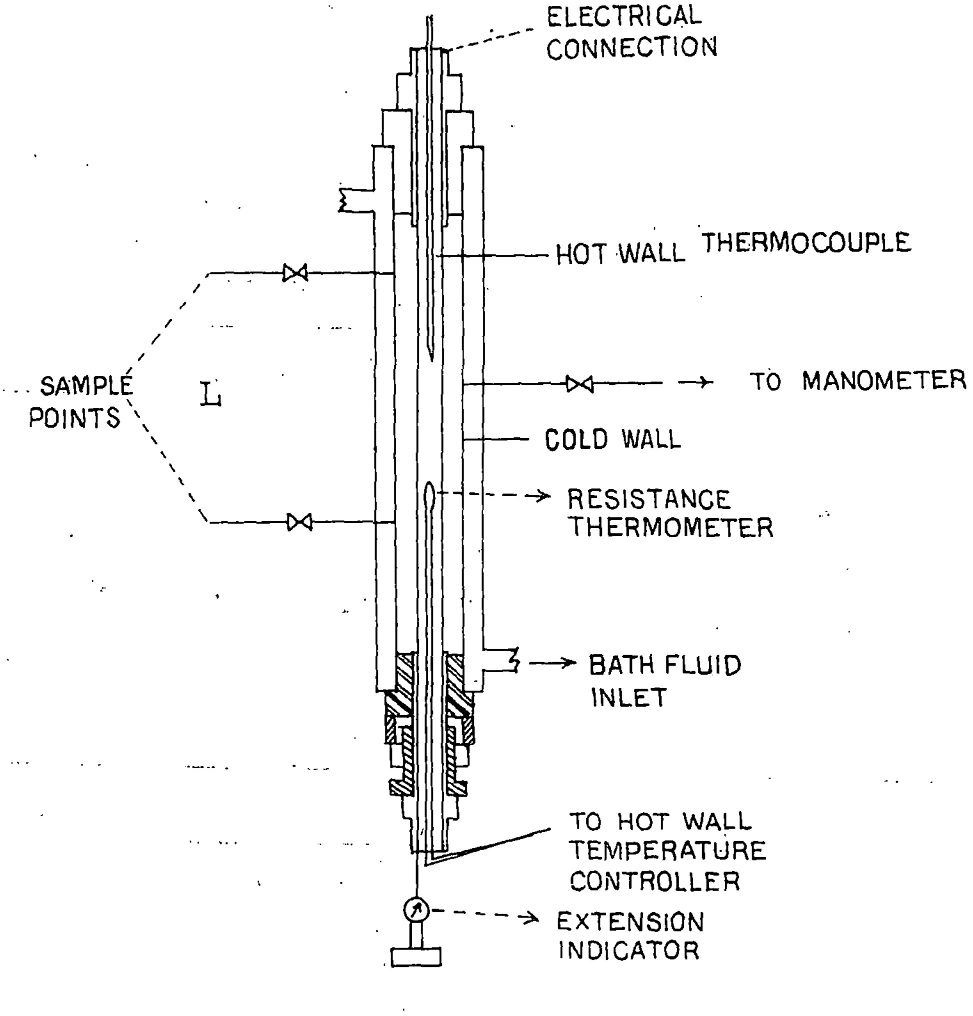

Fig 1.3. Simplified schematic diagram of experimental thermal diffusion column.

integration of the appropriate FJ[24] expressions for comparison with experiments, performed by Rutherford and Kaminski[17] (1967).

Let us now consider a thermal diffusion column as shown in Fig. (1.3), which consists of two concentric cylinders as the hot and cold surfaces. The outer surface is of radius r_c and is kept cooled at a temperature T_c called the cold wall temperature by circulating water through a concentric jacket surrounding the cold wall. The inner one is of radius r_h called the hot wall radius and is maintained at a temperature T_h called the hot wall temperature such that $r_c > r_h$ and $T_c < T_h$. The annular gap is filled up with a uniform gaseous mixture to be separated.

The hydrodynamical equation in cartesian coordinates[24] is given by $(\text{div}\,\eta\,\text{grad})\,v = \text{grad}\ p - \rho g$ (1.15) which reduces to the following form in the cylindrical coordinates (r, z) as θ is symmetric w.r. to velocity v:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\eta\frac{dv}{dr}\right) = \frac{dp}{dz} - \rho g \qquad (1.16)$$

where v is the convection velocity parallel to Z-axis, p = pressure of the gas, g is the acceleration of gravity at a place, and η is the coefficient of viscosity of the mixture of mass density ρ. In the region of the column tube the temperature gradient is determined by the conduction of thermal energy alone. If $2\pi Q$ measures the rate of flow of heat per unit area per unit length

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of the T.D. column we have

$$2\pi Q = 2\pi r\lambda\left(-\frac{dT}{dr}\right)$$

or, $$Q = -r\lambda\left(\frac{dT}{dr}\right)$$

or, $$\frac{1}{dr} = -\frac{Q}{r\lambda}\,\frac{1}{dT}$$

or, $$\frac{\partial}{\partial r} = -\frac{Q}{r\lambda}\,\frac{\partial}{\partial T} \qquad (1.17)$$

which shows that $\frac{\partial}{\partial r}$ is an operator which could, however, be replaced in terms of the operator $\frac{\partial}{\partial T}$. The symbol λ is the coefficient of thermal conductivity of the binary gas mixture. Eq. (1.16) thus becomes with the help of eqn. (1.17)

$$\frac{Q^2}{r^2\lambda}\,\frac{\partial}{\partial T}\left(\frac{\eta}{\lambda}\,\frac{\partial v}{\partial T}\right) = \frac{\partial p}{\partial z} - \rho g \qquad (1.18)$$

with the boundary conditions that $v(T_h) = v(T_c) = 0$ i.e. the velocities of the fluids at $T = T_h$ and $T = T_c$ vanishes.

Now, the equation for the transport of the species 1 i.e. the lighter component along the tube is J_1 where

$$J_1 = \rho c_1 v_1 + \rho D_{12}\left(-\mathrm{grad}\, c_1 + \alpha_T c_1 c_2\, \mathrm{grad}\, \ln T\right) \qquad (1.19)$$

where c_1 and c_2 are the mass fractions of the lighter and the heavier components of the gas mixtures. D_{12} is the diffusion coefficient of the mixture, and v_1 is the velocity of the lighter component along the tube.

The equation of continuity in the case of fluid motion is

$$\frac{\partial}{\partial t}(\rho c_1) + \operatorname{div} J_1 = 0 \qquad (1.20)$$

which, in the case if stationary condition is div $J_1 = 0$, as $\frac{\partial \rho}{\partial t} = 0$. On taking divergence on both sides of eq. (1.19) we have

since $\operatorname{div} F = \frac{1}{r}\frac{\partial}{\partial r}(r F_r) + \frac{1}{r}\frac{\partial F_\theta}{\partial \theta} + \frac{\partial F_z}{\partial z}$,

$$\operatorname{div} J_1 = \operatorname{div}(\rho c_1 v_1) + \operatorname{div}\left[\rho D_{12}\left(-\operatorname{grad} c_1 + \frac{\alpha_T c_1 c_2}{T}\frac{\partial T}{\partial r}\right)\right]$$

$$\left[\because \operatorname{grad} \ln T = \frac{1}{T}\frac{\partial T}{\partial r}\right]$$

$$= \frac{1}{r}\frac{\partial}{\partial r}\left(r \rho c_1 v_{1r}\right) + \frac{\partial}{\partial z}\left(\rho c_1 v_{1z}\right) + \frac{1}{r}\frac{\partial}{\partial r}\left[r\left\{\rho D_{12}\left(-\frac{\partial c_1}{\partial r} + \frac{\alpha_T c_1 c_2}{T}\frac{\partial T}{\partial r}\right)\right\}\right] + \frac{\partial}{\partial z}\left[\rho D_{12}\left(-\frac{\partial c_1}{\partial z}\right)\right] = 0$$

or, $$\frac{\partial}{\partial z}\left(\rho c_1 v_{1z}\right) + \frac{\partial}{\partial r}\left[\rho D_{12}\left\{-\frac{\partial c_1}{\partial r} + \frac{\alpha_T c_1 c_2}{T}\frac{\partial T}{\partial r}\right\}\right] - \rho D_{12}\frac{\partial}{\partial z}\left(\frac{\partial c_1}{\partial z}\right) = 0$$

or, $$\rho v_{1z}\frac{\partial c_1}{\partial z} + \frac{\partial}{\partial r}\left[-\rho D_{12}\frac{\partial c_1}{\partial r} + \rho D_{12}\frac{\alpha_T c_1 c_2}{T}\frac{\partial T}{\partial r}\right] - \rho D_{12}\frac{\partial^2 c_1}{\partial z^2} = 0 \qquad (1.21)$$

Since v_{1z} is not a function of Z and $\frac{\partial\rho}{\partial z} = 0$ for the stationary condition of the gas mixture, we have

$$\frac{\partial}{\partial r}\rho D_{12}\left[-\frac{\partial c_1}{\partial r} + \frac{\alpha_T c_1 c_2}{T}\frac{\partial T}{\partial r}\right] = -\rho v_{1z}\frac{\partial c_1}{\partial z} + \rho D_{12}\frac{\partial^2 c_1}{\partial z^2} \tag{1.22}$$

which in terms of $\frac{\partial}{\partial T}$ operator in places of $\frac{\partial}{\partial r}$ as given by eq. (1.17) becomes

$$\frac{Q^2}{r^2\lambda}\frac{\partial}{\partial T}\left(\frac{\rho D_{12}}{\lambda}\right)\left[\frac{\partial c_1}{\partial T} - \frac{\alpha_T c_1 c_2}{T}\right] = \rho v_{1z}\frac{\partial c_1}{\partial z} - \rho D_{12}\frac{\partial^2 c_1}{\partial z^2} \tag{1.23}$$

As done by Furry, Jones and Onsagar[25] we can, at present omit the term $\rho D_{12}\frac{\partial^2 c_1}{\partial z^2}$ which gives rise to the effect of longitudinal diffusion. This can however be included later on in a very simpler way. Hence eq. (1.23) is then

$$\frac{\partial}{\partial T}\left(\frac{\rho D_{12}}{\lambda}\right)\left[\frac{\partial c_1}{\partial T} - \frac{\alpha_T c_1 c_2}{T}\right] = \frac{r^2\lambda}{Q^2}\rho v_{1z}\frac{\partial c_1}{\partial z} \tag{1.24}$$

Let us now introduce a function G(Z,T) defined by

$$\frac{\partial c_1}{\partial z} G(z,T) = \frac{r\lambda Q^3}{[\rho D_{12}]_1} J_{1r}$$

where J_{1r} is the radial component of the flux of the species 1 per unit area and per unit time given from eq. (1.22) by

$$J_{1r} = \rho D_{12}\left[-\frac{\partial c_1}{\partial r} + \frac{\alpha_T c_1 c_2}{T}\frac{\partial T}{\partial r}\right]$$

$$= \rho D_{12}\frac{Q}{r\lambda}\left[\frac{\partial c_1}{\partial T} - \frac{\alpha_T c_1 c_2}{T}\right] \tag{1.25}$$

Thus

$$\frac{\partial c_1}{\partial z}G(z,T) = \frac{r\lambda Q^3}{\rho D_{12}}\rho D_{12}\frac{Q}{r\lambda}\left[\frac{\partial c_1}{\partial T} - \frac{\alpha_T c_1 c_2}{T}\right]$$

$$= Q^4\left[\frac{\partial c_1}{\partial T} - \frac{\alpha_T c_1 c_2}{T}\right]$$

$$\text{or, }\left[\frac{\partial c_1}{\partial z} - \frac{\alpha_T c_1 c_2}{T}\right] = \frac{1}{Q^4}\frac{\partial c_1}{\partial z}G(z,T) \qquad (1.26$$

Eq. (1.24) with the help of eq.(1.26) finally becomes

$$\frac{\partial}{\partial T}\left(\frac{\rho D_{12}}{\lambda}\right)\frac{1}{Q^4}\frac{\partial c_1}{\partial z}G(z,T) = \frac{\lambda r^2}{Q^2}\rho v_{1z}\frac{\partial c_1}{\partial z}$$

$$\text{or, }\frac{\partial}{\partial T}\left(\frac{\rho D_{12}}{\lambda}\right)\frac{\partial c_1}{\partial z}G(z,T) = \lambda r^2 Q^2 \rho v_{1z}\frac{\partial c_1}{\partial z}$$

(1.27)

from which we can obtain v_{1Z}, cancelling $\frac{\partial C_1}{\partial Z}$ from both sides of eq. (1.27)

$$v_{1Z} = \frac{1}{\lambda r^2 Q^2 \rho} \frac{\partial}{\partial T}\left(\frac{\rho D_{12}}{\lambda}\right) G(Z,T)$$

$$= \frac{1}{\lambda r^2 Q^2 \rho} \frac{\partial}{\partial T}\left\{\frac{\rho D_{12}}{\lambda} G(Z,T)\right\} \tag{1.28}$$

where G(Z,T) is the master flow function and it can be shown that it is a function of temperature alone i.e. G(T).

The hydrodynamical equation so far deduced by eq. (1.18) can now be written as in terms of v_{1Z} where v_{1Z} is the convective velocity of the lighter component up the column, as shown by eqn. (1.28), becomes

$$\frac{Q^2}{r^2\lambda}\frac{\partial}{\partial T}\left(\frac{\eta}{\lambda}\right)\frac{\partial}{\partial T}\left[\frac{1}{\lambda r^2 Q^2 \rho}\frac{\partial}{\partial T}\left\{\frac{\rho D_{12}}{\lambda} G(T)\right\}\right] = \frac{\partial p}{\partial Z} - \rho g$$

or, $$\frac{1}{r^2\lambda}\frac{\partial}{\partial T}\left(\frac{\eta}{\rho}\right)\frac{\partial}{\partial T}\left(\frac{1}{\lambda r^2 \rho}\right)\frac{\partial}{\partial T}\left\{\frac{\rho D_{12}}{\lambda} G(T)\right\} = \frac{\partial p}{\partial Z} - \rho g \tag{1.29}$$

which on differentiation with respect to temperature T gives us

$$\frac{d}{dT}\left(\frac{1}{r^2\lambda}\right)\frac{d}{dT}\left(\frac{\eta}{\lambda}\right)\frac{d}{dT}\left(\frac{1}{\lambda r^2\rho}\right)\frac{d}{dT}\left(\frac{\rho D_{12}}{\lambda}G(T)\right)$$
$$= -g\frac{\partial\rho}{\partial T} \qquad (1.30)$$

neglicting the term $\frac{\partial^2 p}{\partial T\partial z}$ which is nearly equal to zero, the temperature variation of density in the case of column is nearly constant.

Eq. (1.30) is the hydrodynamical equation whose solution is the master flow function G(T). Here η is the shear coefficient of viscosity, ρ is the density and g is the acceleration due to gravity. The boundary condition is

$$G(T_c) = G(T_h) = G'(T_c) = G'(T_h) = 0 \qquad (1.31)$$

let us now proceed to find out the total upward transport of the species i up the column tube.

Let

$$\tau_1 = 2\pi\int_{r_c}^{r_h}\rho c_1 v_{1z}\, r\, dr$$

$$= -\frac{2\pi}{Q}\int_{T_c}^{T_h} c_1\rho\lambda v_{1z}\, r^2\, dT$$

$$\left[\because dr = -\frac{r\lambda}{Q}\, dT\right]$$

which with the help of eq. (1.28) becomes

$$\tau_1 = -\frac{2\pi}{Q}\int_{T_c}^{T_h} c_1\rho\lambda r^2 \frac{1}{\lambda r^2 Q^2\rho}\frac{\partial}{\partial T}\left\{\frac{\rho D_{12}}{\lambda}G(T)\right\}dT$$

$$= -\frac{2\pi}{Q^3}\int_{T_c}^{T_h} c_1 \frac{\partial}{\partial T}\left\{\left(\frac{\rho D_{12}}{\lambda}\right)G(T)\right\}dT$$

$$= -\left[\frac{2\pi}{Q^3}\left\{c_1\left(\frac{\rho D_{12}}{\lambda}\right)G(T)\right\}\Bigg|_{T_c}^{T_h} - \frac{2\pi}{Q^3}\int_{T_c}^{T_h}\frac{dc_1}{dT}\right.$$
$$\left.\times\left(\frac{\rho D_{12}}{\lambda}\right)G(T)\,dT\right]$$

Since $G(T_c) = G(T_h) = 0$ we have

$$\tau_1 = \frac{2\pi}{Q^3}\int_{T_c}^{T_h}\frac{dc_1}{dT}\left(\frac{\rho D_{12}}{\lambda}\right)G(T)\,dT \qquad (1.32)$$

as the total transport τ_1 up along the tube.

Again from eq. (1.26) we have

$$\frac{\partial c_1}{\partial z}G(T) = Q^4\left[\frac{\partial c_1}{\partial T} - \frac{\alpha_T c_1 c_2}{T}\right]$$

$$\text{or, } \frac{\partial c_1}{\partial T} = \frac{dc_1}{dT} = \frac{1}{Q^4}\frac{dc_1}{dz}G(T) + \frac{\alpha_T c_1 c_2}{T}$$

and hence eq. (1.32) finally becomes

$$\tau_1 = \frac{2\pi}{Q^3}\int_{T_c}^{T_h}\left[\left\{\frac{1}{Q^4}\frac{dc_1}{dz}G(T) + \frac{\alpha_T c_1 c_2}{T}\right\}\frac{\rho D_{12}}{\lambda}\,G(T)\right]dT$$

$$= \frac{2\pi}{Q^7}\int_{T_c}^{T_h}\frac{dc_1}{dz}\,\frac{\rho D_{12}}{\lambda}G^2(T)\,dT + \frac{2\pi}{Q^3}\int_{T_c}^{T_h}\frac{\alpha_T c_1 c_2}{T}\left(\frac{\rho D_{12}}{\lambda}\right)dT$$

$$= \left\{\frac{2\pi}{Q^7}\int_{T_c}^{T_h}\left(\frac{\rho D_{12}}{\lambda}\right)G^2(T)\,dT\right\}\frac{dc_1}{dz} + \left\{\frac{2\pi}{Q^3}\int_{T_c}^{T_h}\frac{\alpha_T G(T)}{T}\left(\frac{\rho D_{12}}{\lambda}\right)dT\right\}\times c_1 c_2$$

$$= H c_1 c_2 + K_c\frac{dc_1}{dz} \tag{1.33}$$

To obtain the correct equation of transport of species i up the tube let us now add to the eq. (1.33) a term which gives the effect of longtitudinal diffusion along the tube since this effect was omitted previously. Thus the term

$$\frac{dc_1}{dz}2\pi\int_{T_c}^{T_h}(\rho D_{12})\,r\,dr = -\frac{dc_1}{dz}\frac{2\pi}{Q}\int_{T_c}^{T_h}\lambda(\rho D_{12})\,r^2\,dT$$

$$\left[\because\ dr = -\frac{r\lambda}{Q}\,dT\right]$$

must be added to eq. (1.33) in order to get the correct transport equation of the gas mixtures through the annular gap of the T.D. column i.e.

$$\tau_1 = HC_1C_2 - (K_c + K_d)\frac{dc_1}{dz} \tag{1.34}$$

where the initial transport coefficient H, the convective remixing coefficient K_c and the diffusive remixing coefficient K_d are given the following expressions:

$$H = \frac{2\pi}{Q^3}\int_{T_c}^{T_h}\left(\frac{\rho D_{12}}{\lambda}\right)\frac{\alpha_T}{T}\,G(T)\,dT \tag{1.35}$$

$$K_c = \frac{2\pi}{Q^7}\int_{T_c}^{T_h}\left(\frac{\rho D_{12}}{\lambda}\right)G^2(T)\,dT \tag{1.36}$$

and $$K_d = \frac{2\pi}{Q}\int_{T_c}^{T_h} r^2\lambda\rho D_{12}\,dT \tag{1.37}$$

Since in the steady state condition the total transport up the tube is zero we have

$$HC_1C_2 - (K_c + K_d)\frac{dC_1}{dZ} = 0 \tag{1.38}$$

where $c_1 = c$ and $c_2 = 1 - c$ since $c_1 + c_2 = 1$

or, $\frac{dc}{C(1-C)} = \frac{H}{K_c + K_d}\,dZ$ which on integration on both sides for $Z = 0$ to $Z = L$ where L is the geometrical length of the column yields that

$$\int_{Z=0}^{Z=L} \frac{dc}{C(1-C)} = \frac{H}{K_c + K_d} \int_{Z=0}^{Z=L} dZ \quad \text{or,} \quad \log \frac{(C/1-C)_{Z=L}}{(C/1-C)_{Z=0}} = \frac{HL}{K_c+K_d}$$

or, $$\ln q_e = \frac{HL}{K_c + K_d} \qquad (1.39)$$

where $q_e = (c_i/c_j)_T / (c_i/c_j)_B$, is called the equilibrium separation factor defined as the ratio of the mass fractions or rather the mole fractions of the lighter and the heavier components of the binary gas mixture at the top and the bottom of the column of geometrical length L.

For a hot wire column the expressions for the transport coefficients H, K_c and K_d are given by

$$H = \frac{2\pi}{6!} \left\{ \frac{\alpha_T \rho^2 g}{\eta} \right\}_1 r_c^4 \, h \qquad (1.40)$$

$$K_c = \frac{2\pi}{9!} \left\{ \frac{\rho^3 g^2}{\eta^2 D_{12}} \right\}_1 r_c^8 \, k_c \qquad (1.41$$

and $$K_d = 2\pi \left\{ \rho D_{12} \right\} r_c^2 \, k_d \qquad (1.42)$$

where r_c = radius of the cold wall and the quantities in the curly braces are to be evaluated at the cold wall temperature T_c. The h, k_c and k_d are known as dimensionless shape factors which are functions of the two ratios (r_h/r_c) and (T_H/T_C) respectively. T_H and T_C are the temperatures of the hot and the cold wall of a thermal diffusion column. The above H, K_c and K_d as determined by h, k_c and k_d and the transport parameters of the gas mixtures evaluated at the cold wall temperature T_c, are called the Lennard-Jones method.

But for a concentric cylindrical type column and r_h/r_c is not very large, the transport coefficients can also be given by a model known as Maxwellian one. Thus,

$$H = \frac{2\pi}{6!}\left\{\frac{\alpha_T \rho^2 g}{\eta}\right\}_1 \frac{1}{2}(r_c+r_h)(r_c-r_h)^3(2u)^2 h' \tag{1.43}$$

$$K_c = \frac{2\pi}{9!}\left\{\frac{\rho^3 g^2}{\eta^2 D_{12}}\right\}_1 \frac{1}{2}(r_c+r_h)(r_c-r_h)^7(2u)^2 k'_c \tag{1.44}$$

and

$$K_d = 2\pi\left\{\rho D_{12}\right\} \frac{1}{2}(r_c+r_h)(r_c-r_h) k'_d \tag{1.45}$$

Here again r_c and r_h are the radii of the cold and hot walls respectively at temperatures T_c and T_h and $u = \frac{\Delta T}{2\bar{T}} = \frac{(T_h - T_c)}{(T_h + T_c)}$. The quantities in carly braces i.e. ρ = the density of the mixtures, η = the coefficient of viscosity and D_{12} = the diffusion coefficient of a gas mixture are to be evaluated at the mean temperature $\bar{T}$ of the column i.e. $\bar{T} = \left[(T_h + T_c)/2 \right]$; and g = acceleration of gravity of a place.

The shape factors involved in the above transport equations starting from equations (1.40) to (1.45) have been evaluated and then tabulated by Furry and Jones[24] for Maxwellian model, by Saxena and Raman[26] for rigorous sphere model and by McInteer and Reisfield[27,28] for Lennard-Jones model respectively. Recently for the last model E. Von Halle and R.K. Hoglund[29] (1966) reported the thermal diffusion column shape factors in Rept. No. K 1679 (1966). These shape factors are supposed to be the most accurate one to evaluate the column transport coefficient for the Lennard-Jones (12:6) model.

Slieker[10] however in 1965 presented another set of formulations of column constants without assuming any molecular model. It is also assumed that the transport coefficients may be regarded constant within the experimental temperature range and their values are evaluated at the mean temperature $\bar{T}$. The expressions for H, K_c and K_d for a concentric cylindrical column are

$$c_1 = [SF]_1 \, r_c^4 \left\{ \frac{\rho^2 g \alpha_T}{\eta} \right\}_1 \left(\frac{\Delta T}{\bar{T}} \right)^2 \tag{1.46}$$

$$c_2 = \pi \left\{ \rho D_{12} \right\}_1 r_c^2 \left(1 - a^2 \right) \tag{1.47}$$

and

$$c_3 = [SF]_3 \, r_c^8 \left\{ \frac{\rho^3 g^2}{\eta^2 D} \right\} \frac{\Delta T}{\bar{T}} \tag{1.48}$$

The shape factors $[SF]_1$, $[SF]_3$ and $\prod(1-a^2)$ used in the formulations given above from equations (1.46) to (1.48) are binary molecular model independent, but depends entirely on the shape and size of the column. The values of the shape factors used to calculate H, K_c and K_d i.e. C_1, C_3 and C_2 of Slieker's theory are tabulated in C.J.G. Slieker[10] (1965). Here $a = \frac{r_h}{r_c}$ and the other molecular parameters for the binary mixtures are to be evaluated at the mean temperature $\bar{T}$ where $\bar{T} = (T_h + T_c)/2$ to estimate the experimental thermal diffusion factor of any binary gas mixture.

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