

C H A P T E R - II

GENERAL PREFACE AND SCOPE OF THE
PRESENT WORKS

The present position of thermal diffusion column experiments is really very encouraging. The process of thermal diffusion was actually theoretically predicted in 1911 by Chapman and Cowling¹ in the course of development of the formal kinetic theory based on collision processes. It was first experimentally detected by Dootson² in the year of 1917. The column techniques to separate isotopes were soon developed by different atomic energy commissions in different countries, Clusius and Dickel³, Grew et al⁴ and hence several monographs were published. It was in 1939, a rigorous hydrodynamical theory of transport of isotopic constituents in a cylindrical column either hot wall and hot wire was first arrived at in a classic paper by W.H. Furry, R.C. Jones and L. Onsager⁵. In 1946 a review work on it was made by R.C. Jones and W.H. Furry⁶ and W.H. Furry and R.C. Jones⁷. Since then a large number of workers^{8,9,10,11,12} tried to improve the experimental techniques to get the experimental equilibrium separation factor q_e defined by

$$q_e = (x_i/x_j)_T / (x_i/x_j)_B \quad (2.1)$$

where x_i and x_j represent the mole fractions of the i th and the j th components of a binary gas mixture at the top T and the bottom B of a column of geometrical length L.

To support the theoretical prediction of Furry, Jones and Onsager⁵, recently a rigorous phenomenological development of experiment and theory of the process of thermal diffusion was made by E.A. Mason, R.J. Munn and F.J. Smith¹⁸ (Advances in

atomic and molecular Phy - Vol-II (1966) 31). Most of the recent experimental works in this field of research have been directed towards the estimation of the experimental thermal diffusion factor α_T of different binary gas mixtures either isotopic, isobaric and non isotopic binary gases and the data thus obtained may be compared with the theoretical α_T 's based on elastic and inelastic collision theories. But the experimental results of thermal diffusion factor α_T thus obtained from experimental $\ln q_e$ data were hardly explained by both the elastic and inelastic theories of thermal diffusion as deduced by Chapman and Cowling¹⁹ (1964) and Mason, Sandler and Monchick²⁰ (1968). Another group of workers like Saviron et al¹³, E. I. Leyarovski et al¹⁴ (1987), S. Acharyya et al^{16,17} attempted either to extend or to modify the theory of Furry, Jones and Onsager⁵ in order to get the correct experimental thermal diffusion factors α_T of a large number of systems from the experimental $\ln q_e$ data of eq. (2.1) sometimes by new methods suggested by them. On the other hand several groups guided by different workers like Vasaru et al¹⁵ are engaged themselves to set up a large number of the thermal diffusion columns in a cascade system i.e. some T.D. columns in series and some in parallel to have the optimum isotopic yield per day. Now-a-days this is an important aspect of column technique towards the enrichment of isotopes both radio-active and non-radioactive ones. Under such situation as described above, we have tried to get the actual experimental α_T values of a large number of gases of isotopic, nonisotopic and isobaric

binary gas mixtures like Helium-Hydrogen isotopic binary mixtures, several inert gases of natural isotopic abundances etc. from the available data of $\ln q_e$ by introducing a factor F_s called the column calibration factor in the relation:

$$\ln q_{\max} = \alpha_T F_s (r_c, r_h, \bar{T}, L) \quad (2.2)$$

This F_s is simply an apparatus constant. It depends entirely on the geometry of the column.

Thus in absence of reliable theoretical possibility to estimate the actual α_T through the use of the rigorous column theory (Furry-Jones-Onsager⁵) which is supposed to include the column geometry by using column shape factors^{24,25}, we use these F_s values to get the experimental α_T 's of any binary gas mixture. The experimental α_T 's thus obtained are found to be of the same order of magnitudes maintaining the same trend with respect to temperature and compositions as predicted by the reported data available elsewhere¹⁶. This at once suggests that there exists some functional relationship of F_s with the cold and the hot wall radii r_c and r_h , mean temperature \bar{T} and the geometrical length L of the column.

The subject matter of this thesis has been broadly divided into two parts : Part A and Part B. Each part is then divided into several chapters.

In part A several binary gas pairs were chosen from the available data to throw much light on the column calibration

factor F_s of the T.D. columns. The valuable data of F_s in columns thus estimated, were then utilised to obtain the temperature dependence of the T.D. factors α_T of several isotopic and nonisotopic binary gas mixtures.

In part B we discussed the composition dependences of thermal diffusion factor α_T of a large number of binary gas mixtures. The composition dependence of α_T is much more important to study the like and unlike interactions between the molecules under investigation.

An attempt was then made to interpret the estimated thermal diffusion factor α_T from the available theories^{19,20} of thermal diffusion. Chapman and Cowling¹⁹ however put forward the classical theory based on elastic collisions between the pairs of molecules to obtain the theoretical α_T . The comparison however yields that the agreement between the theoretical and the experimental data are very encouraging then hitherto known for these isotopic gas mixtures and for the molecules of spherical symmetry. The development of a formal kinetic theory for gases and gas mixtures involving spherically symmetric molecules is more or less satisfactory except for finer details but the situation is quite different in cases of polyatomic gases and gas mixtures.

The first rigorous treatment of the kinetic theory for gases having nonspherical shaped molecules has been given by Wang Chang, Uhlenbeck and de Boer²¹ who considered the translational

motions of the molecules classically²² and the internal motion quantum mechanically. The expression for the coefficient of thermal conductivity and thermal diffusion factors of gas mixtures are derived from this theory. The theoretical thermal diffusion factor α_T can thus be obtained for polyatomic gases and gas mixtures based on inelastic collision by Mason, Sandler and Monchick²⁰ in recent years, because there are many experimental evidences that the heat conductivity and the thermal diffusion are greatly influenced by inelastic collisions between the molecules.

The comparison of thermal diffusion factor α_T obtained from inelastic collision theory²⁰ and the α_T obtained experimentally from column²³ showed a remarkable success particularly in cases of hydrogenic isotopes in Helium in trace concentrations. All these discussions in the last part of the synopsis which we are going to represent systematically chapterwise in this thesis indicate that our column calibration factor F_s has an important role in determining the experimental thermal diffusion factors α_T both its temperature and the composition dependence. Moreover, the column calibration factor may be regarded as an apparatus constant having probably the same nature concerning the temperature variation²³. This is really an experimental problem to be resolved only by careful and extensive experimental works.

It is found that the dimensionless shape factors h' , k'_c & k'_d and h , k_c & k_d due to Maxwell and Lennard-Jones respectively are the functions of T_h/T_c and r_c/r_h for a given column. The latter quantities however depend on dimensionless quantity T_c^*

where

$$T_c^* = T_c / (\epsilon_{12}/k)$$

where r_c and r_h are the radii of the cold wall and the hot wall of the thermal diffusion column maintained at the temperature T_c and T_h respectively. ϵ_{12}/k is the depth of the molecular potential and k is the Boltzmann constant.

In order to obtain the accurate experimental α_T by the existing methods using molecular models, the accurate and reliable column shape factors are required. Though a large number of workers in this field tried to obtain the accurate value of this quantities, it is found that simply the graphical interpolation method very often invites a personal judgement on the location of the values of the column shape factors. The evidence of these facts are however realised in the Chapter VII, where the columns of varying sizes and different T_h/T_c are studied to yield the temperature dependence of the thermal diffusion factor α_T of inert gas mixtures like Ar³⁶ - Ar⁴⁰, Kr⁸⁰ - Kr⁸⁶, Xe¹²⁸ - Xe¹³⁶ and Ne²⁰ - Ne²². The situation is however the worst when we consider the gas mixtures of polyatomic molecules in which the appreciable quantity of energy is transported for the internal degrees of freedom of the molecules. In this sense our column calibration factor F_s opened a new and vast scope to study the composition as well as the temperature dependence of α_T of any binary gas mixtures. Unlike Sliker in 1965, who presented the column shape factors depending entirely on the geometry of the

column, but still it is a crude one in representing the experimental α_T , our column calibration factor method which is free from any binary molecular interaction and depends on the geometry of the column is found to give the relative, accurate and small α_T of the same order of magnitude as well as of almost the same trends with respect to temperature and composition respectively of any binary gas mixture. Here lies the utility of using our column calibration factor method in estimating the experimental α_T to detect the very existence of elastic and inelastic collisions between the molecules in thermal diffusion.

P A R T : A

CHAPTER V : Chapter V deals with the theoretical development of the estimation of the thermal diffusion factor α_T of the hydrogenic trace mixtures in Helium at three different experimental mean temperatures \bar{T} . The temperatures are 338°K, 378°K and 423°K respectively. The theory so presented has been extended from the well known hydrodynamical part of the column theory of Furry, Jones and Onsager⁵ (1939). In this chapter the variation of column calibration factor F_s with respect to temperature change has been attained for a given column constructed by C.J.G. Sliker and A.E. de Vries²⁶ *J chim Phys* 50 (1963) 172_7. The most probable temperature dependence of F_s of this column can be given by a fitted equation in \bar{T} :

$$F_s = -66.52202 + 0.3502286 \bar{T} - 4.1879 \times 10^{-4} \bar{T}^2 \quad (2.3)$$

which is similar to the equation as obtained by us in connection with T.D. columns of I.A.C.S. Calcutta-32 by B.N. Srivastava et al¹¹ [*J Chem Phys* 47 (1967) 3470] and D.G. Alvarez et al²⁷ [*J Chem Phys* 50 (1969) 3936], except that the coefficients of A, B and C in the eq. (2.3) i.e.

$$F_s = A + B \bar{T} + C \bar{T}^2$$

differ from the previous ones regarding their signs. The temperature variation of F_s of the latter two columns were arrived at:

$$F_s = 34.030495 - 0.15472984 \bar{T} + 1.9101183 \times 10^{-4} \bar{T}^2 \quad (2.4)$$

and

$$F_s = 68.94796 - 0.3174514 \bar{T} + 3.71383 \times 10^{-4} \bar{T}^2 \quad (2.5)$$

It is interesting to note that the magnitudes of A, B and C of eq. (2.3) and eq. (2.5) are identically the same except to their signs while those of B.N. Srivastava et al¹¹ (1967) are simply half the coefficients of those of D.G. Alvarez et al²⁷ (1969). This at once indicates that the temperature variation of F_s really depends on the ratios of cold wall and hot wall radii r_c and r_h and the geometrical length L of the column. This also suggests that an extensive and careful experimental observation of F_s with respect to temperature change is really necessary to arrive at the functional relationship of F_s with the geometry of the columns.

The temperature variation of the experimental thermal diffusion factors of He-T₂, He-HT and He-DT trace mixtures so estimated, were then compared with the theoretical α_T 's based on elastic (1964) and inelastic collision (1968) theories, only to detect the existence of inelastic collision effects in these mixtures as already predicted by T.K. Chattopadhyay and S.Acharyya [J Phys B (London) 7 (1974) 2277]. An attempt has been finally made to interpret α_T 's thus obtained in terms of the available elastic and inelastic collision theories of thermal diffusion to establish the importance of the column calibration factor in column measurements.

CHAPTER VI : Chapter VI contains the experimental evaluation of the thermal diffusion factors of He-HT and He-DT trace mixtures by the process of estimation of $\ln q_{\max}$ from

$$\ln q_{\max} = a' / 2\sqrt{b'} \quad (2.6)$$

in terms of the estimated values of a' and b' . The values of a' and b' of these mixtures are estimated by fitting the following equations with experimental data measured at different pressures in atmosphere of these mixtures mentioned above:

$$\begin{aligned} \sum p^4 \ln q_e &= a' \sum p^2 - b' \sum \ln q_e \\ \sum p^6 \ln q_e &= a' \sum p^4 - b' \sum p^2 \ln q_e \end{aligned} \quad (2.7)$$

The values of a' and b' thus obtained are found to obey the column theory of the variation of the experimental $p^2/\ln q_e$ against p^4 resulting in straight lines having certain slopes and intercepts. For He-DT and He-HT trace mixtures the following equations were arrived at

$$p^2/\ln q_e = 0.8161 + 0.7758 p^4 \text{ at } \bar{T} = 338^\circ \text{K}$$

$$p^2/\ln q_e = 0.4938 + 0.7294 p^4 \text{ at } \bar{T} = 378^\circ \text{K}$$

$$p^2/\ln q_e = 0.3964 + 0.6024 p^4 \text{ at } \bar{T} = 423^\circ \text{K}$$

and

$$p^2/\ln q_e = 9.0749 + 14.8368 p^4 \text{ at } \bar{T} = 338^\circ \text{K}$$

$$p^2/\ln q_e = 13.5999 + 64.6412 p^4 \text{ at } \bar{T} = 378^\circ \text{K}$$

$$p^2/\ln q_e = 14.6461 + 411.5226 p^4 \text{ at } \bar{T} = 423^\circ \text{K}$$

respectively.

Unlike He-DT, the entire experimental $\ln q_e$ data of He-HT are not found to fit the hydrodynamical part of the column theory so excellently, sometimes they have tendency to yield negative intercepts of $p^2/\ln q_e$ against p^4 . This is absurd. That is why we are bound to select some six to seven data from the reported graphs of C.J.G. Sliker and A.E. de Vries²⁶ [*J Chim Phys* 60 (1963) 172-7]. Under this restricted conditions the computed a' and b' , in case of He-HT, which is also an isobaric system, fit the values of $\ln q_{\max}$ the same as those of reported ones and hence the temperature variation of α_T , as determined by our calibration factor method are the accurate ones. Unlike He-T₂,

He-DT trace mixture the He-HT shows a peculiar behaviour. As \bar{T} increases $\ln q_e$ values for this system decreases. It is evident that at and beyond a certain temperature \bar{T} K, $\ln q_e$ may be zero or negative. Beyond this critical temperature $\bar{T} = \bar{T}_c$ inversion of $\ln q_e$ or rather α_T may occur. Thus He-HT trace mixture as well as its 1:1 mixture demands a thorough investigation. But unfortunately due to experimental difficulties with T.D. column and nonavailability of a precision type of mass spectrometer we are to be satisfied with the experimental observations made by C.J.G. Sliker and A.E. de Vries²⁶ (1963).

CHAPTER VII : Chapter VII deals with several T.D. columns in order to arrive at the unique nature of the temperature variation of the column calibration factors F_s given in a mathematical form :

$$F_s = A + B \bar{T} + C \bar{T}^2 \quad (2.8)$$

where A, B and C are three arbitrary constants depending entirely on the geometry of the columns under investigation. The temperature dependence of F_s of a column³¹ (of comparatively higher geometrical length $L = 487.7$ cm) (W.J. Roos and W.M. Rutherford : J Chem Phys 50 (1969) 424) using $Kr^{80} - Kr^{86}$ gas mixture as a calibrating gas (S. Acharyya et al¹⁷ : J Phys Soc (Japan) 51 (1982) 1469) the following fitted equation can be obtained in terms the mean column temperature \bar{T} by :

$$F_s = 67.194 - 8.5052 \times 10^{-2} \bar{T} + 1.09925 \times 10^{-4} \bar{T}^2 \quad (2.9)$$

which is more or less similar to the expression of F_s [eq. (2.5)] attained by S. Acharyya et al¹⁷ (1982) in a T.D. column of D.G. Alvarez et al²⁷ [J Chem Phys 50 (1969) 3936]. The magnitudes of B and C involved in eq. (2.9) are slightly less than those for the latter column while that of A agrees better. The temperature variation of F_s in a T.D. column of comparatively smaller geometrical length L than the former one, constructed by W.M. Rutherford²⁹ [J Chem Phys 58 (1973) 1613] was obtained with the reliable experimental α_T of Ar³⁶ - Ar⁴⁰ as a calibrating gas [F. Vander Valk Ph.D dissertation (1963)] by a fitted equation

$$F_s = 91.153 - 0.315561 \bar{T} + 3.34456 \times 10^{-4} \bar{T}^2 \quad (2.10)$$

Here all the coefficients involved in eq. (2.10) are almost the same for B & C but the value of A is higher, although the temperature variation of F_s for this column is nearly similar to those of previous observations by S. Acharyya et al^{16,17} (1981-82).

The column calibration factors of a column available (W.M. Rutherford and K.J. Kaninski³⁰ [J Chem Phys 47 (1967) 5427] had also been computed with the reliable experimental α_T 's of naturally occurring isotopes Ne²⁰ - Ne²² gas due to F Vander Valk [Ph.D. dissertation (1963)]. The most probable behaviour of F_s against \bar{T} is

$$F_s = -56.722813 + 0.246176 \bar{T} - 0.749691 \times 10^{-4} \bar{T}^2 \quad (2.11)$$

which like our previous observations [S. Acharyya et al²³ : J. Phys Soc (Japan) 56 (1987) 105_] has both the coefficients A and C are negative while B is positive. But the difference is that all the coefficients involved in eq. (2.11) are really smaller in magnitudes. These facts, perhaps arise due to different values of r_c/r_h of the columns. The temperature dependence of the thermal diffusion factors of the inert gases with their natural isotopic abundances like Ne²⁰ - Ne²², Ar³⁶ - Ar⁴⁰, Kr⁸⁰ - Kr⁸⁶ and Xe¹²⁸ - Xe¹³⁶ were then estimated by using the column calibration factors cited above (for a wide temperature range of nearly 400° lying between 300K to 700K) and then compared with the experimental [S. Acharyya¹⁷ (1982)] and theoretical α_T 's based on elastic collisions. These studies further indicate that the column calibration factor is really an important parameter of column measurement and hence its functional relationship with r_c , r_h and L of a column where r_c , r_h are the cold wall and hot wall radii of the column of the geometrical length L, is to be found out for a column by extensive experimental and careful theoretical works. The functional form of F_s with r_c , r_h , L and \bar{T} of a column will then be a reliable tool to estimate the thermal diffusion factors which are very sensitive to intermolecular interaction of like and unlike molecules.

P A R T : B

Part B is concerned with the estimation of the composition dependence of the thermal diffusion factors α_T of isobaric gas mixtures like $N_2 - CO$ as measured in a column of B.N. Srivastava et al¹¹ (1967) and some isotopic and nonisotopic gas mixtures in a column constructed by D.G. Alvarez et al²⁷ (1969).

CHAPTER VIII : The available concentration variation of $\ln q_e$ data³³ [I.L. Saha et al : J Phys Soc (Japan) 56 (1987) 2381] of isobaric $N_2 - CO$ gas mixtures in a hot wall thermal diffusion column has been utilised to calculate the composition dependence of thermal diffusion factor α_T at three experimental temperatures 350.1, 368.1 and 432.0° K. It is found that there is always an inversion of α_T as a function of composition for these experimental temperatures indicating further that this inversion phenomenon occurs in a well defined temperature range 248.6 K to 610.1 K. If the experimental conditions on composition and temperature fall within the area enclosed by the inversion curve and the temperature axis, in general N_2 enriches at the top of the column; if they are outside, then N_2 enriches at the bottom.

CHAPTER IX : In the this chapter, we are interested to deal with some inert gas mixtures like Helium-Argon (He-Ar), Neon-Xenon (Ne-Xe) and neon having its natural isotopic abundances, to study the composition dependence of the thermal diffusion factors α_T of these gas mixtures because of the availability of the experimental $\ln q_e$ data for these mixtures. The $\ln q_e$ values

at different compositions of the mixture at a fixed temperature ($\bar{T} = 340 \pm 5^\circ \text{K}$) against pressure in atmosphere were observed by J.M. Saviron et al¹³ [*J Chem Phys* 63 (1975) 5318] in a column of $r_c = 1.37 \text{ cm}$, $r_h = 0.6 \text{ cm}$ and geometrical length $L = 149 \text{ cm}$ respectively. The column calibration factor in the above mentioned column constructed by D.G. Alvarez et al²⁷ [*J Chem Phys* 50 (1969) 3936] is already determined by S. Acharyya et al¹⁷ [*J Phys Soc (Japan)* 1982]. The temperature distribution of the column calibration factor is

$$F_s = 68.94796 - 0.3174514 \bar{T} + 3.71383 \times 10^{-4} \bar{T}^2$$

The value of F_s came out to be 3.946 at $\bar{T} = 340 \pm 5^\circ \text{K}$ with $T_h = 381 \pm 5$ and $T_c = 301 \pm 2^\circ \text{K}$. This value of F_s and the estimated value of the logarithm of maximum separation factor i.e. $\ln q_{\max} = \frac{a'}{2\sqrt{b'}}$ where a' and b' are the experimental parameters to satisfy the variation of experimental $\ln q_e$ against pressure in atmosphere as obtained by the least-square technique are then used to obtain the thermal diffusion factor α_T from

$$\alpha_T = \frac{\ln q_{\max}}{F_s} = \frac{a'}{2\sqrt{b'}} \frac{1}{F_s} \quad (2.12)$$

only to establish the role of the column calibration factor F_s in determining the composition dependence of α_T which is very sensitive to like and unlike intermolecular interaction. An attempt is then made to interpret all these experimental values of α_T 's in terms of the theory of thermal diffusion based on the

elastic collision between the interacting molecules. The comparison however indicates that the column calibration factor is truly a theoretical tool to estimate the experimental α_T 's, unlike the existing theoretical methods due to Maxwell and Lennard-Jones models as well as the model independent Sliker's method.

R E F E R E N C E S

1. D. Enskog, Z. Physik 12 (1911) 533.
and
S. Chapman and T.G. Cowling, The mathematical theory of
non uniform gases: Cambridge University Press
(1953)
2. S. Chapman and F.W. Dootson, Phil Mag. 33 (1977)248.
and
S. Chapman, Phil Trans A217 (1917) 184.
3. K. Clusius and G. Dickel, Naturwiss, 26 (1938) 546.
4. K.E. Grew and T.L. Ibbs, Thermal Diffusion in gases,
Cambridge University Press, N.Y. (1952).
5. W.H. Furry, R.C. Jones and L. Onsager, Phys. Rev.
55 (1939) 1083.
6. R.C. Jones and W.H. Furry, Rev. Mod. Phys 18 (1946) 151.
7. W.H. Furry and R.C. Jones, Phys Rev 69 (1946) 459 M.D.
8. A. Youssef, M.M. Hanna and Migahed Z. Naturf 20 (1965) 655.
9. S. Raman, B.P. Mathur, A.J. Howard, J.W. Champlin and
W.W. Watson, J Chem Phys 49 (1968) 4877.
10. B.P. Mathur and W.W. Watson, J Chem Phys 49 (1968) 5537.
11. B.N. Srivastava, A.K. Batabyal, A.N. Roy and A.K. Ghosh,
J Chem Phys 47 (1967) 3470.
12. S.C. Saxena and S. Raman, Rev Mod Phys 34 (1962) 252.
13. J.M. Saviron, C.M. Santamaria, J.A. Carrion and
J.C. Yarza, J Chem Phys 63 (1975) 5318.
14. E.I. Ieyarovski, A.L. Zahariev and J.K. Georgiev,
J Phys E Sct Instrum 20 (1987) 1192-1195.
15. G. Vasaru, P. Ghete, I. Covaci, M. Atanasiu; "Stable
Isotopes in the Life Sciences", International
Atomic Energy Agency (Vienna), (1977) 29.
16. S. Acharyya, A.K. Das, P. Acharyya, S.K. Datta and
I.L. Sah, J Phys Soc (Japan) 50 (1981) 1603.

17. S. Acharyya, I.L. Saha, P. Acharyya, A.K. Das and S.K. Datta, J. Phys Soc (Japan) 51 (1982) 1469.
18. E.A. Mason, R.J. Munn and Francis J. Smith, Advances in atomic and Molecular Physics edited by D.R. Bates and Immanuel Estermann, Vol. II (1966) 31-91.
19. J.O. Hirschfelder, C.F. Curtiss and R.B. Bird, Molecular theory of gases and liquids, John Willey and Sons N Y (1964).
20. L. Monchick, S. I. Sandler and E.A. Mason, J Chem Phys 49 (1968) 1178.
21. C.S. Wang Chang, G.E. Uhlenbeck and J. de Boer, The heat conductivity and viscosity of polyatomic gases in studies in statistical Mechanics (John Wiley and Sons Inc, N.Y. (1964)).
22. N. Taxman, Phys Rev 110 (1958) 1235.
23. S. Acharyya, I.L. Saha, A.K. Datta and A.K. Chatterjee, J Phys Soc (Japan) 56 (1987) 105.
24. B.B. Mc Inteer and M.J. Reisfield, Los Alamos Scientific Laboratory report, LAMS 2517 (1961).
25. E. Green, R.L. Hoglund and E. Von Halle, US atomic energy commission Res. Development-K-1469 (1966).
26. C.J.G. Slieker and A.E. de Vries, J Chim Phys 60 (1963)172.
27. D. Gonzalez Alvarez, J.M. Saviron and J.C. Yarza, J Chem Phys 50 (1969) 3936.
28. T.K. Chattopadhyay and S. Acharyya, J Phys B (London) 7 (1974) 2277.
29. W.M. Rutherford, J Chem Phys 58 (1973) 1613.
30. W.M. Rutherford and K.J. Kaminski, J Chem Phys 47 (1967) 5427.
31. W.J. Roos and W.M. Rutherford, J Chem Phys 50 (1969) 424.
32. W.J. Roos and W.M. Rutherford, J Chem Phys 52 (1970)1684.
33. I.L. Saha, A.K. Datta, A.K. Chatterjee and S. Acharyya, J Phys Soc (Japan) 56 (1987) 2381.