

ON THE PRESSURE DEPENDENCE OF THE THERMAL  
DIFFUSION FACTOR

W.A. OOST

Universiteit Leiden



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ON THE PRESSURE DEPENDENCE OF THE THERMAL  
DIFFUSION FACTOR

for binary mixtures up to 50 atmospheres

PROEFSCHRIFT

TER VERLEGING VAN DE GRAAD VAN DOCTOR IN DE WIS-  
KUNDE EN NATUURWETENSCHAPPEN AAN DE UNIVERSITEIT  
WIJNTJE TE LEIDEN, OP ORDE VAN DE RECTOR MAGISTRUS  
DE L. KROONHUIS DE. TH. ALLENBAUM EN DE FACULTEIT DER  
LETTAREN, DIE OVERSTAAN VAN EEN COMMISSIE UIT DE  
BENAAMTE VERENIGING OF WAKENING TOEGESCHIEDT VAN  
DE GRAAD VAN DOCTOR

DOOR

WILHELM AALBERT OOST

GEBOREN TE AMSTERDAM IN 1894

TE WETENSCAPEN - Afdeling

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# ON THE PRESSURE DEPENDENCE OF THE THERMAL DIFFUSION FACTOR

for binary mixtures up to 80 atmospheres

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE WIS-  
KUNDE EN NATUURWETENSCHAPPEN AAN DE RIJKSUNIVER-  
SITEIT TE LEIDEN, OP GEZAG VAN DE RECTOR MAGNIFICUS  
DR. L. KUKENHEIM Ezn, HOOGLERAAR IN DE FACULTEIT DER  
LETTEREN, TEN OVERSTAAN VAN EEN COMMISSIE UIT DE  
SENAAT TE VERDEDIGEN OP WOENSDAG 18 DECEMBER 1968  
TE KLOKKE 15.15 UUR

DOOR

WIEBE AALDERT OOST

GEBOREN TE AMSTERDAM IN 1938

DRUKKERIJ ELINKWIJK - UTRECHT

ON THE PRESSURE DEPENDENCE OF THE THERMAL  
DIFFUSION FACTOR

for binary mixtures up to 80 atmospheres

PROEFSCHRIFT

PROMOTOR: PROF. DR J. KISTEMAKER

1958

WILHELM AALBERT OOST

GEBOREN TE AMSTERDAM IN 1928

DRUKKERIJ "DE WERKMAN" ROTTERDAM

## STELLINGEN

1. De door van der Waerden behandelde correcties, nodig voor een juiste beoordeling van de in een scheidingswip verkregen ontmenging, kunnen verwaarloosd worden indien voor de concentratie-nivellering tussen de afzonderlijke elementen van de opstelling gebruik wordt gemaakt van thermo-syphon werking.

B.L. van der Waerden, Z. Naturforsch. 12A, (1957), 583.

Dit proefschrift, hoofdstuk I.

2. Bij enkelvoudige ionisatie van krypton door electronen is de bijdrage van de N=3 schil klein, in tegenspraak met de bewering van Lotz.

W. Lotz, Z. f. Physik 206, (1967), 205.

3. De oscillaties, gevonden in de differentiële en onvolledige totale botsingsdoorsnede voor de interactie van alkalimetaalionen en edelgas-atomen, kunnen behalve door de invloed van een lading-geïnduceerde dipool ook verklaard worden door effecten, die optreden bij verstrooiing aan een monotone repulsieve potentiaal.

H. Boersch und G. Forst, Z. f. Physik 176, (1963), 221.

H. Schoenebeck, Z. f. Physik 177, (1964), 111.

F.J. Smith, E.A. Mason and J.T. Vanderslice, J. Chem. Phys. 42, (1965), 3257.

4. De wijze waarop in het boek van Hirschfelder, Curtiss en Bird de gereduceerde  $\Omega$ -integralen geïntroduceerd worden, suggereert een onjuiste interpretatie van het gebruikelijke begrip moleculaire diameter.

J.O. Hirschfelder, C.F. Curtiss and R.B. Bird, Molecular theory of gases and liquids, New York, (1954).

5. Ten onrechte verwaarlozen Nezlin et al. de mogelijkheid, dat instabiele golven in een plasma gereflecteerd worden in de plasmashath aan een metalen wand.

M.V. Nezlin, G.I. Sapozhnikov and A.M. Solntsev, Sov. Phys. JETP 23, (1966), 232.

6. Bij de experimentele bepaling van dimeerconcentraties in gassen verdienen nauwkeurige absorptiemetingen de voorkeur boven massaspectrometrische bepalingen.
7. De extreem grote negatieve waarden, die Walther en Drickamer vinden voor de thermodiffusiefactor, kunnen verklaard worden als zijnde het gevolg van de vorming van veelvoudige moleculen in het koude deel van het apparaat.

J.E. Walther and H.G. Drickamer, J. Phys. Chem. 62, (1958), 421.  
H.A. Cataldi and H.G. Drickamer, J. Chem. Phys. 18, (1950), 650.
8. Woodmansee en Decius uitten de veronderstelling (welke door anderen is overgenomen), dat de vibratie-relaxatie-tijd voor andere gassen dan kooldioxide niet bepaald kan worden door het in een spectrofoon opgevangen signaal te meten als functie van de moduleringsfrequentie. In de argumentatie voor deze veronderstelling is ten onrechte de drukafhankelijkheid van de relaxatie-tijd verwaarloosd.

W.E. Woodmansee and J.C. Decius, J. Chem. Phys. 36, (1962), 1831.  
A.D. Wood, thesis, Purdue University, (1963).  
R.J. Vargovick, thesis, Purdue University, (1965).
9. Wegens de in toenemende snelheid voortgaande aantasting van het biologisch milieu dient als één der op nationaal zowel als internationaal niveau te nemen maatregelen de studie der oecologie hoogste prioriteit te krijgen.
10. De sinds de winter 1962/1963 in Rotterdam gemeten daling van de luchtverontreiniging (althans wat betreft het gehalte aan zwaveldioxide) is grotendeels te danken aan gunstige meteorologische omstandigheden. Een dankwoord aan de industrie voor de door haar genomen maatregelen is dus vooralsnog prematuur.

Jaarverslag over 1967 van de commissie Bodem, Water en Lucht te Rotterdam.  
Perspublicaties naar aanleiding van de ingebruikneming van de Centrale Meld- en Regelkamer te Rotterdam.



*Twee zijn beter dan één, omdat zij een goede beloning hebben bij hun zwoegen. Want, indien zij vallen, dan richt de een de ander weer op; maar wee de éne, die valt zonder dat een metgezel hem opricht!*

(Pred. 4 : 9,10)

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*Aan Thea*

*Aan mijn ouders*

1. Het is experimenteel bewezen dat de afwijkingen van de ideale wetten van de natuurkunde, die voortvloeien uit de relativiteitstheorie, in de praktijk niet meetbaar zijn. Dit is het resultaat van de experimenten van Michelson en Morley, die in 1887 werden uitgevoerd. Het resultaat van deze experimenten is dat de afwijkingen van de ideale wetten van de natuurkunde, die voortvloeien uit de relativiteitstheorie, in de praktijk niet meetbaar zijn.

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The work described in this thesis is part of the research program of the "Stichting voor Fundamenteel Onderzoek der Materie" (Foundation for Fundamental Research on Matter) and was made possible by financial support from the "Nederlandse Organisatie voor Zuiver-Wetenschappelijk Onderzoek" (Netherlands Organization for the Advancement of Pure Research).

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## V O O R W O O R D

Teneinde te voldoen aan de wens van de Faculteit der Wiskunde en Natuurwetenschappen volgt hier een kort overzicht van mijn studie.

Nadat ik in 1955 met goed gevolg het eindexamen H.B.S.-B had afgelegd aan de Christelijke H.B.S.-B met vijfjarige cursus te Amsterdam liet ik mij inschrijven als student aan de Vrije Universiteit te Amsterdam. Hier legde ik in 1959 mijn candidaalexamen wis- en natuurkunde A af. Gedurende de studie voor dit examen volgde ik de colleges van en legde ik tentamens af bij Prof.Dr. H.R. Woltjer, Prof.Dr. P. Mullender, Prof.Dr. J.F. Koksma, Prof.Dr. G.J. Sizoo, Prof.Dr. G.H.A. Grosheide F.Wzn, Prof. Dr. R. Hooykaas en Prof.Dr. J.P. van Rooijen.

Tijdens de studie voor het doctoraalexamen, waarvoor ik de tentamens aflegde bij de hoogleraren Prof.Dr. J.P. van Rooijen, Prof.Dr. J.F. Koksma, Prof.Dr. P. Mullender, Prof.Dr. P. Groen en Prof.Dr. C.C. Jonker, verrichtte ik praktisch werk op het gebied van de kernphysica en wel onder leiding van Drs. J.J. Vasmel betreffende het ijken van een neutronenbron. Gedurende ruim twee jaar was ik als assistent verbonden aan het natuurkundig practicum voor studenten medicijnen en biologie. In 1962 legde ik het doctoraalexamen natuurkunde met bijvakken wiskunde en mechanica af.

In oktober 1962 werd ik verbonden aan het F.O.M.-Instituut voor Atoom- en Molecuulfysica (toentertijd F.O.M.-Laboratorium voor Massaspectrografie) als wetenschappelijk medewerker in gewoon verband. Aanvankelijk betroffen mijn werkzaamheden het meten van diffusiecoëfficiënten, later het in dit proefschrift beschreven onderzoek.

In januari 1967 aanvaardde ik een functie als docent natuurkunde aan het Christelijk Lyceum West (thans Christelijke Scholengemeenschap "Pascal") te Amsterdam. Gaarne wil ik op deze plaats mijn dank betuigen aan rector en conrectores van deze school voor de wijze waarop bij de roostersamenstelling rekening gehouden is met mijn wensen, voortvloeiend uit dit promotieonderzoek. Ook wil ik mijn collega, Drs. C. Oranje, dank zeggen voor zijn bereidheid de lessen in de hogere klassen voor zijn rekening te nemen. De ervaringen bij het tijdelijk overnemen van deze lessen hebben mij getoond hoeveel tijdsbesparing deze taakverdeling mij heeft opgeleverd.

Hen, die meer betrokken zijn geweest bij het onderzoek, wil ik graag bedanken voor de geboden medewerking.

Zeergeleerde Velds, beste Dick, de wijze waarop jij het onderzoek aan mij hebt overgedragen, heeft het mij mogelijk gemaakt binnen de tijd waarin ik mij geheel aan dit onderzoek kon wijden tot de eerste resultaten te komen. Zonder die start betwijfel ik of dit proefschrift ooit geschreven was.

Zeergeleerde Los, beste Joop, jouw adviezen en kritiek in droeve en minder droeve dagen, je voortdurende aandacht voor en je bijdragen aan dit onderzoek zijn voor mij een belangrijke stimulans geweest om het tot een goed einde te brengen.

Zeergeleerde de Vries, beste Dolf, de vele discussies die we over dit onderzoek hebben gehad en je meeleven met de voortgang ervan hebben het voor mij tot een stuk teamwerk gemaakt, waarbij ik dankbaar gebruik heb kunnen maken van je ervaring op het gebied van de thermodiffusie.

Alle medewerkers van de groep molecuulfysica dank ik voor de wijze, waarop zij mij terzijde hebben gestaan. Speciaal Mej. A. Tom en de heer A. Haring wil ik hierbij noemen voor de technische bijstand in diverse situaties.

De medewerking van de heer F. Vitalis bij het gereedmaken van de rekenprogramma's en de verwerking hiervan is voor mij van groot belang geweest. Ook zijn assistenten de heren A.O. Akihary en W. v.d.Kaay betuig ik hierbij mijn dank.

De rekendienst van het Mathematisch Centrum dank ik voor de correcte en vlotte afwerking van de programma's.

I'd like to thank Dr. R. Paul, now at the Indian Association for the Cultivation of Science, for his critical remarks concerning the reference system. Ook Dr. J. v.d.Ree (nu verbonden aan de Technische Hogeschool te Eindhoven), die mede de aandacht op deze kwestie vestigde, betuig ik hiervoor mijn erkentelijkheid.

De hulp, ondervonden van de instrumentmakerij onder leiding van de heer A.F. Neuteboom, van de heer J.A. van Wel (glasblaaswerk), Mej. M.J. Benavente (tekenwerk) en de heren F.L. Monterie en Th.A. van Dijk (fotografie), waren voor mij van groot belang. De medewerking van de administratie van het F.O.M.-Instituut voor Atoom- en Molecuulfysica onder leiding van de heer K. Bijleveld is voor de uiteindelijke uitvoering van deze dissertatie van wezenlijk belang geweest.

Tenslotte wil ik mijn vrouw danken voor de nauwgezette en toegewijde wijze, waarop zij van dit proefschrift een gezamenlijke productie heeft gemaakt.

## CHAPTER I

### SURVEY OF THEORY AND EXPERIMENT

#### a. INTRODUCTION

The first experiments on the phenomenon, now known as thermal diffusion, were done in 1856 by C. Ludwig (Lu 1856), who investigated the change in composition when a temperature gradient was introduced in an initially homogeneous solution. In 1873 W. Feddersen (Fe 1873) speaks already about thermal diffusion (Thermodiffusion) and in 1879 C. Soret (So 1879) publishes the experiments that connect his name with thermal diffusion, which is called the Soret-effect when it takes place in liquids. In 1890 a publication of M.P. Van Berghem (Bg 1890) gives results for thermal diffusion experiments on gases dissolved in water. But it was in the theoretical work, published in a number of articles, of Chapman and Enskog, that the stimulus was received for a systematic and thorough research of this phenomenon. The fact that the first article of Enskog on this subject dates back to 1911 (En 11), while the first article of Chapman on thermal diffusion was published in 1912 (Ch 12) does not mean, however, that thermal diffusion by now has become a clear and easily understood phenomenon. The restrictions Chapman and Enskog had to make in their theory are only partly removed and theory and experiment on thermal diffusion often meet each other on the basis of serious disagreement.

One of the points for which still no dependable predictions can be made is the pressure dependence of the thermal diffusion factor. In this thesis we try to find an explanation on the basis of several theories. To see where pressure may have influence on thermal diffusion we will give a short survey of the way in which the transport coefficients are calculated in the so-called distribution function method. The alternative procedure, the time-correlation function method up till now has not led to numerical results for the thermal diffusion factor and so will be left out of the discussion.

To prevent circumlocutions we will indicate densities for which the mean free path is small compared with the dimensions of the vessel and large compared with the dimensions of the molecules of the gas as low densities. This will cause no confusion as we will restrict ourselves to pressures well outside the Knudsen region.

The calculation of the transport properties by means of the distribution function method for these densities is started with the derivation of the Boltzmann-equation from the Liouville-equation. The Boltzmann-equation gives the relation between the variation with time of the one-particle distribution function and the molecular encounters. When we multiply this equation with mass, momentum or kinetic energy and integrate the result over velocity space the conservation laws give us the possibility to find relations between the time-dependence of the local values of these physical quantities and their respective fluxes: the equations of change. Then, by means of the H-theorem the equilibrium distribution is found, whereafter the distribution function for the non-equilibrium situation is written as the sum of the equilibrium distribution function and the product of this function and a supposedly small perturbation function. In the now linearized problem our task is the determination of this perturbation function. We make the approximation that only first powers of first derivatives of the equilibrium distribution, the Maxwell distribution, are maintained. Then, from the Boltzmann-equation and the equations of change the general outlook of the perturbation function follows immediately as a sum of inner products of vectors and tensors. From each term in this sum one of the two factors is a thermodynamical force, such as a gradient in the composition or in the temperature. The other factor, the unknown vector or tensor, is split into the product of a known vector or tensor and a scalar. The scalars are found by expanding them into Sonine polynomials using a limited number of terms or by means of variational calculus. Here several methods exist, differing in the way in which the infinite system that must be solved is handled. Successive approximations are found by taking an increasing number of terms. Using the now known distribution function in the definitions of the diffusion velocity, the pressure tensor and the energy flux and comparing the result with the definitions of the various fluxes, formulae for the transport coefficients are found. As a last step the Sonine-polynomials are replaced by so-called  $\Omega$ -integrals, which are directly related to the intermolecular potential energy functions.

The first moment that the pressure comes in is in the derivation of the Boltzmann-equation. During this derivation certain suppositions are made; one of them is that of molecular chaos: during the time between two collisions the system returns to a situation in which no correlation can be found in the motion of particles, that has resulted from the collision. This supposition will be exactly true as long as the molecules may be considered as hard spheres, independent of the pressure (Je 04). As soon as we consider real molecules, still interacting when they are on a distance from each other, the interaction will



cause a certain correlation between the motion of neighbouring molecules. This correlation will be negligible when the molecules are outside each other's fields of force for most of the time. As soon as we increase the density the molecules will be in each other's neighbourhood for a larger percentage of the time, thus making the correlation more important. This problem can be dealt with by taking into account the two-particle distribution function. This function, to which we will return in chapter II, gives the probability that, at the same time, one molecule with momentum  $\vec{p}$  is at the place  $\vec{r}$  and an other one, with momentum  $\vec{p}'$  is at  $\vec{r}'$ .

A second aspect of the Boltzmann-equation which is valid only at low densities is the fact that simultaneous collisions of three or more molecules are left out of the discussion. Once again when the molecules are to be considered as hard spheres, this approximation will be sufficient to pretty high densities, although it is never exact. With real molecules however, it is quite well possible that two molecules are still within each other's interaction sphere when a third one strikes the system. This three-particle collision can be considered as a collision of a two-particle system with a single molecule, so that the net effect is that a third kind of molecule (viz. the two-particle system) is added to the mixture.

When the pressure is raised the number of collisions of this type will increase and we have here another aspect of the influence of pressure on transport properties. We will treat this problem in an approximate way by taking into account those systems of two molecules that are more or less stable. We will look after the influence of this type of molecules on thermal diffusion in chapter III.

In the use of the Boltzmann-equation one of the next steps is the derivation of the equations of change. Here we only take into account the transport of mass, momentum and energy during the free flight of the molecules. While this is strictly true with mass, momentum and energy can be transported in another way, namely during the collision: then energy and momentum are transferred from the center of one molecule to that of an other which gives an extra transport term for these quantities. This collisional transfer has been calculated for hard spheres by Enskog (En 22) for pure gases, while the theory has been extended to mixtures by H.H. Thorne, as mentioned in the book of Chapman and Cowling (Ch 39). Probably due to the unrealistic assumption of hard spheres however, the theory does not hold even qualitatively, as has been found by Walther and Drickamer (Wl 58) and Velds (Ve 66). Therefore we will not

not try to find an explanation of the pressure dependence of the thermal diffusion factor on the base of this theory. We shall consider the influence of collisional transfer on the thermal diffusion factor in the last part of chapter II by means of the two-particle distribution function.

Apart from the distribution function method there are two other related methods. The first one, describing the whole process in terms of probability statements and using a so-called "Master-equation" is due mainly to Brout and Prigogine (Br 56a and Br 56b). The second one is due to Bogolubov (Bo 46) and gives a new basic equation from which the Boltzmann-equation may be derived under certain limiting conditions. Although the last equation gives the heat conduction and viscosity coefficients in terms of the local density we will not consider it here, as no results have been obtained for the thermal diffusion factor or, in general, for a mixture involving more than one gas. The Master-equation approach can be used only for spatially homogeneous systems.

Apart from these kinetic methods some phenomenological equations for the pressure dependence of the thermal diffusion factor have been derived. We will return to these in chapter II.

## b. THE THERMAL DIFFUSION FACTOR AND THE DIFFUSION COEFFICIENT AT LOW DENSITIES

As we will need the values of the thermal diffusion factor and the diffusion coefficient at low pressures in some of our calculations, we will give the results of the first Chapman-Enskog approximations for the diffusion coefficient as well as for the thermal diffusion factor and also the first Kihara approximation for the thermal diffusion factor.

In the derivation of the formulae for the transport coefficients a system of integral equations is solved by changing it into an infinite system of linear equations, as mentioned in the introduction. This infinite system is solved by conventional techniques by taking only a very limited number of terms. Here two fundamentally different approaches exist: the first one, due to Chapman and Cowling (Ch 39) takes as a first approximation the terms on the main diagonal of the determinant, as a second approximation some elements next to the main diagonal; the other one, due to Kihara (Kh 49) starts also with the elements of the main diagonal, but then expresses the off-diagonal elements in terms of the  $\Omega$ -integrals and their temperature derivatives. The

successive approximations are found by including first, second, third etc. time-derivatives. The last method has the most physical background and will be used if possible. A second advantage of the Kihara method is that the resulting formulae are much simpler than those of the Chapman-Cowling scheme. In the first approximation, both in the Chapman-Cowling and Kihara system, the thermal diffusion factor is zero. Therefore the first approximation to the thermal diffusion factor is necessarily the second step in the approximation scheme.

Part of our considerations will be the calculation of the thermal diffusion factor in multicomponent mixtures. No formulae exist for such mixtures in the Kihara approximation. We will therefore have to use the Chapman-Cowling method, as here the generalization to multicomponent mixtures has been made by Van der Valk (Va 63), following the work of Waldmann (Wa 58). This formalism uses the first Chapman-Cowling approximation to the thermal diffusion factor. An important factor in the use of transport coefficients in general is the choice of a reference system. As has been shown by Waldmann (loc.cit.p.357) the reference system most suited for the description of both diffusion and thermal diffusion is the one in which the mean particle velocity  $v$  is zero.  $v = \sum_i x_i v_i$ , in which  $x_i$  is the mole-fraction of component  $i$  in the mixture and  $v_i$  is the mean velocity of the molecules of component  $i$  with respect to the laboratory system. We will use this system throughout this thesis.

Again the name of Waldmann turns up when we consider the diffusion coefficient. In the general scheme for the derivation of explicit expressions for the transport coefficients as discussed in part a. of this chapter, one degree of freedom is left in the derivation of the diffusion coefficient about which can be disposed at will. Here several choices can be made. Hirschfelder, Curtiss and Bird (Hi 54), for example, made their choice in such a way that the multicomponent diffusion coefficients, which are found from the general treatment reduce to the binary diffusion coefficient as defined by Fick's law in the binary case. Waldmann (Wa 58), on the other hand, uses the degree of freedom left to introduce the property  $\sum_i x_i D_{ik} = 0$ , where the  $D_{ik}$  are the multicomponent diffusion coefficients. The result is that the multicomponent diffusion coefficients no longer reduce directly to the binary diffusion coefficients according to Fick's law in the case of a binary mixture, but the  $D_{ik}$  are symmetrical (i.e.  $D_{ik} = D_{ki}$ ) and the relation between the binary diffusion coefficients and the multicomponent ones is a system of linear equations for each number of

components, at least in the first Chapman-Cowling approximation. As this approximation is pretty good for the diffusion coefficient we have a simple way here to calculate multicomponent diffusion coefficients from binary ones, for which closed formulae exist.

After these general arguments we will proceed now by giving the pertinent formulae.

#### b). THE DIFFUSION COEFFICIENT

The diffusion velocity  $\vec{W}_i$  with respect to the average particle velocity is given as

$$\vec{W}_i = -\sum_k D_{ik} \vec{d}_k - D_{Ti} \text{grad ln } T \quad (1.1)$$

The summation is extended over all components of the mixture. The  $D_{ik}$  are the multicomponent diffusion coefficients, the  $\vec{d}_k$  are summations over the three factors giving rise to diffusion viz.  $\text{grad } x_i$  (concentration diffusion),  $\text{grad ln } p$  (pressure diffusion) and the external forces. Of these only the concentration diffusion will be considered so that for our purposes

$$\vec{d}_k = \text{grad } x_k \quad (1.2)$$

The  $D_{Ti}$  are thermal diffusion coefficients in a polynary mixture, whereas  $T$  is the absolute temperature.

For the  $D_{ik}$  Waldmann (Wa 58) derived the following relation with the binary diffusion coefficients :

$$\sum_j x_j (D_{ik} - D_{jk}) / D(i,j) = \delta_{ik} / x_i - 1 \quad (1.3a)$$

which is correct up to the first Chapman-Cowling approximation. Here the  $D(i,j)$  are the binary diffusion coefficients, whereas the  $\delta_{ik}$  is the well-known delta-function. (1.3a) may be rewritten as the following set of linear equations :

$$\left( \sum_{j, j \neq i} x_j / D(i, j) \right) D_{ik} - \sum_{j, j \neq i} (x_j / D(i, j)) D_{jk} = \delta_{ik} / x_i - 1 \quad (1.3b)$$

This linear system makes possible the calculation of the polynary diffusion coefficients from the first Chapman-Cowling approximation of the binary diffusion coefficient (see f.i. Wa 58, part 68,51)

$$D(i, j) = \frac{3k\sqrt{k}}{8\sqrt{\pi}} \frac{\sqrt{T^3(m_i + m_j) / (2m_i m_j)}}{p \sigma_{ij}^2 \Omega_{ij}^{(1,1)\star}} \quad (1.4a)$$

where  $k$  is the Boltzmann constant,  $m_i$  the mass of a molecule of type  $i$ ,  $p$  the pressure and  $\sigma_{ij}$  the distance between the centers of two colliding molecules, one of type  $i$  and one of type  $j$  if these molecules are considered as rigid spheres. It is common practice to use the molecular diameter belonging to the potential model used instead of the rigid sphere diameter (which is energy dependent). An approximation, implicit in this formula, originates from the use of the ideal gas law for the transition from particle density to pressure in its derivation.

The reduced  $\Omega$ -integral  $\Omega_{ij}^{(1,1)\star}$  is the value of a function which depends on the type of interaction potential, the temperature and some parameters which are characteristic for the molecule under consideration.  $\Omega_{ij}^{(1,1)\star}$  is found by dividing the  $\Omega$ -integral for the potential model that is supposed to be valid by the  $\Omega$ -integral for a rigid sphere type of interaction. These  $\Omega$ -integrals do depend on the same quantities as the reduced  $\Omega$ -integrals, but they are dimensionless; their evaluation involves integrations over all possible distances and relative velocities of the molecules (see e.g. Ch 39, part 9.33 or Hi 54, page 525). Values of the  $\Omega$ -integrals for several potential models are tabulated in the book of Hirschfelder et al. (Hi 54).

Expressing  $m_i$  and  $m_j$  as molecular weights, writing down  $p$  in atmospheres and  $\sigma_{ij}$  in Ångström-units (1.4a) becomes (Hi 54, page 539)

$$D(i, j) = 0.002628 \frac{\sqrt{T^3(m_i + m_j) / (2m_i m_j)}}{p \sigma_{ij}^2 \Omega_{ij}^{(1,1)\star}} \quad (1.4b)$$

The second Chapman-Cowling approximation to the binary diffusion coefficient is a pretty complicated function which gives a value for the diffusion coefficient which is only slightly different from the first approximation. In the correction factor, given by Hirschfelder et al. (Hi 54, p. 606)  $\Omega$ -integrals different from the earlier mentioned appear; the difference lies in an other way of averaging about the angle of deflection of a molecule in a collision and the relative velocities of the two colliding molecules; this is indicated by the values of the superscripts for the  $\Omega$ -integral (e.g.  $\Omega^{(1,2)}$ ,  $\Omega^{(2,2)}$  etc.).

## b2. THE THERMAL DIFFUSION COEFFICIENT

We will proceed now by discussing the thermal diffusion coefficient  $D_{Ti}$  in a polynary mixture. As in the case of the diffusion coefficient an extra condition must be imposed to obtain unequivocal values for the  $D_{Ti}$ , for which, using the convention of Waldmann, we have

$$\sum_i x_i D_{Ti} = 0 \quad (1.5)$$

because of the already introduced relation between the polynary diffusion coefficients and the definition of the diffusion velocity, which was taken with respect to the mean particle velocity. Following Waldmann (Wa 58, part 69) we introduce now the multicomponent thermal diffusion ratios  $k_{Tk}$  by the relation

$$\sum_k (D_{ik} - D_{jk}) k_{Tk} = D_{Ti} - D_{Tj} \quad (1.6)$$

By defining so-called polynary thermal diffusion factors  $\alpha_{ij}$  in the first Chapman-Cowling approximation to the thermal diffusion coefficient (second approximation in the general scheme), we get the following relations :

$$k_{Ti} = x_i \sum_j x_j \alpha_{ij} ; \alpha_{ij} = -\alpha_{ji} ; \alpha_{ii} = 0 \quad (1.7)$$

In a binary mixture the  $\alpha_{ij}$  reduce to the experimentally found thermal diffusion factor; in a polynary mixture they have only a mathematical meaning. Van der Valk (Va 63) worked out this scheme and obtained the following relations for an n-component mixture :

$$\alpha_{ij} = - \left| \begin{array}{cccccc} a_{11} & a_{12} & \cdot & \cdot & a_{1n} & 1 \\ a_{21} & a_{22} & \cdot & \cdot & a_{2n} & 1 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ a_{n1} & a_{n2} & \cdot & \cdot & a_{nn} & 1 \\ b_{1,ij} & b_{2,ij} & \cdot & \cdot & b_{n,ij} & 0 \end{array} \right| : \left| \begin{array}{cccccc} a_{11} & a_{12} & \cdot & \cdot & a_{1n} \\ a_{21} & a_{22} & \cdot & \cdot & a_{2n} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ a_{n1} & a_{n2} & \cdot & \cdot & a_{nn} \end{array} \right| \quad (1.8)$$

where 
$$a_{rs} = x_s \frac{m_r m_s}{(m_s + m_r)^2} \frac{F_{rs}^*}{E_{sr}} + \delta_{rs} \sum_l x_l \frac{F_{sl}}{E_{sl}}$$

$$b_{k,ij} = \left( -\delta_{ki} \frac{m_j}{E_{ij}} + \delta_{kj} \frac{m_i}{E_{ji}} \right) \frac{6 C_{ij}^* - 5}{m_i + m_j}$$

$$E_{ij} = \frac{2}{5} \sqrt{\frac{2m_i}{m_i + m_j} \frac{\Omega_{ii}^{(2,2)\star}}{\Omega_{ij}^{(1,1)\star}}} \left\{ \frac{\sigma_{ii}}{\sigma_{ij}} \right\}^2$$

$$F_{ij} = \{6m_i^2 + (5 - 2.4B_{ij}^*)m_j^2 + 3.2m_i m_j A_{ij}^*\} / (m_i + m_j)^2$$

$$F_{ij}^* = -11 + 2.4 B_{ij}^* + 3.2 A_{ij}^*$$

The functions  $A_{ij}^*$ ,  $B_{ij}^*$  and  $C_{ij}^*$  are ratios of reduced  $\Omega$ -integrals and can be found also from the book of Hirschfelder et al. (Hi 54).

The foregoing formulae are based on the first step in the Chapman-Cowling scheme that gives a non-zero value for the thermal diffusion coefficient. A better approximation is the earlier mentioned second Kihara approximation which can be written as follows :

$$\alpha_{ij} = (6C_{ij}^* - 5) \frac{S_i x_i - S_j x_j}{x_i^2 Q_i + x_i x_j Q_{ij} + x_j^2 Q_j} ; i, j = 1, 2 ; i \neq j \quad (1.9)$$

$$\text{where } S_i = \frac{m_i}{m_j} \sqrt{\frac{2m_j}{m_i+m_j}} \frac{\Omega_{ii}^{(2,2)\star}}{\Omega_{ij}^{(1,1)\star}} \left\{ \frac{\sigma_{ii}}{\sigma_{ij}} \right\}^2 - (4m_i A_{ij}^{\star} + 7.5(m_j - m_i)) \frac{m_j}{(m_i+m_j)^2}$$

$$Q_i = \frac{2}{m_j(m_i+m_j)} \sqrt{\frac{2m_j}{m_i+m_j}} \frac{\Omega_{ii}^{(2,2)\star}}{\Omega_{ij}^{(1,1)\star}} \left\{ \frac{\sigma_{ii}}{\sigma_{ij}} \right\}^2 (m_i^2 + 3m_j^2 + 1.6m_i m_j A_{ij}^{\star})$$

$$Q_{12} = Q_{21} = \{15(m_1 - m_2)^2 + 32m_1 m_2 A_{12}^{\star}\} (m_1 + m_2)^2 + 1.6 \frac{m_1 + m_2}{\sqrt{m_1 m_2}} \frac{\Omega_{11}^{(2,2)\star} \Omega_{22}^{(2,2)\star}}{(\Omega_{12}^{(1,1)\star})^2} \left\{ \frac{\sigma_{11} \sigma_{22}}{\sigma_{12}^2} \right\}^2$$

### c. EXPERIMENTAL METHODS

Three methods are used for the experimental determination of the thermal diffusion factor :

1. The two-bulb apparatus
2. The thermal diffusion column
3. The swing-separator ("Trennschaukel")

Of these three only the first and second one have been used to determine the thermal diffusion factor at higher densities. The two-bulb apparatus consists of two volumes, kept at different temperatures, connected by a tube. The temperature difference causes one of the components, in general the lighter one, to go to the volume with the highest temperature, while the other one goes to the colder volume. The separation process is halted as soon as the back-diffusion caused by the concentration difference equals the demixing. In this case the net diffusive flux is zero as long as we have a non-reacting mixture, so that in (1.1) the term on the left side is zero. Combining (1.1), (1.6) and (1.7), written down for two components, we obtain the relation

$$\text{grad } x_1 = - \alpha_{12} x_1 x_2 \text{ grad } \ln T \quad (1.10)$$



Remembering that  $x_1 = 1 - x_2$  and supposing  $\alpha_{12}$  independent of temperature and composition we may integrate this to obtain

$$x_1/x_2 = C T^{-\alpha_{12}}$$

where C is some constant.

Using this for the higher and lower temperature part we find

$$q = \frac{(x_1/x_2)_{\text{high}}}{(x_1/x_2)_{\text{low}}} = \left\{ \frac{T_{\text{high}}}{T_{\text{low}}} \right\}^{-\alpha_{12}}$$

$$\text{or} \quad \ln q = -\alpha_{12} \ln \left\{ \frac{T_h}{T_l} \right\} \quad (1.11)$$

$q$  is called the separation factor.

This is the way in which the thermal diffusion factor is found from experiment in a two-bulb apparatus.

The fact that  $\alpha_{12}$  depends both on temperature and concentration is accounted for by taking a suitable mean temperature and mean concentration to which the value of  $\alpha_{12}$  belongs. General practice is to take the geometric mean for the value of  $T$ .

The separation factor can be found experimentally in two ways. One is an analysis at the pressure of the experiment, e.g. by means of heat conduction measurements or infra-red gas analysis. The second way is to take a sample from both volumes and analyse these samples at low pressure, e.g. in a mass-spectrometer. Although these methods need not be distinguished for low pressure experiments (i.e. up to a density comparable to normal circumstances) it will be useful to make the distinction for experiments at somewhat higher pressures.

The demixing found with a two-bulb apparatus is in general pretty small. Among the methods used to enlarge the separation the thermal diffusion column invented by Clusius and Dickel (Cl 39) is the most drastic one. Here two concentric tubes (or a wire and a tube) are kept at different temperatures, so that each cross-section acts as a two-bulb apparatus, causing the light component to concentrate around the (hot) inner tube. Convective action then causes the light component to go upwards, while the heavier one

goes down along the outer tube. The final separation between the lower and upper parts of the tube is determined again by back-diffusion. Although this type of apparatus has the advantage of causing a strong demixing, it has the drawback that for the evaluation of  $\alpha$  from the separation obtained no straight-forward method exists. Its main meaning for fundamental research comes from the determination of relative values of the thermal diffusion factor under identical circumstances. A great number of experiments has been made, both with two-bulb apparatuses and thermal diffusion columns to obtain values of the thermal diffusion factor at elevated pressures. We will only use in this thesis the results of experiments with two-bulb apparatuses, as we wish to study the change of the thermal diffusion factor with pressure. A change in pressure changes the conditions in a thermal diffusion column in such a way that no straightforward comparison between experiments at different pressures can be made. The two-bulb experiments which we have chosen are those of Becker (Be 50), performed at temperatures higher than room temperature with 50%-50% mixtures and those of Van Ee (Ee 66), performed at low temperatures with mixtures of different composition. Together with our own experiments, performed at temperatures above room temperature with 10%-90% mixtures we have a range of temperatures and compositions sufficient for a reasonable comparison between theory and experiment.

No experiments have been made at pressures higher than one atmosphere with the third kind of apparatus, the swing-separator or Trennschaukel. This type of thermal separation unit, originally described by Clusius and Huber (Cl 55), is in fact a number of two-bulb apparatuses in a series arrangement. Each tube (two-bulb apparatus) has a cold and a hot side; the hot side of each tube is connected by means of a piece of capillary tubing to the cold side of the next one. The hot side of one end tube and the cold side of the other one are connected with a pumping arrangement which pushes a certain amount of gas to one side through all tubes and capillaries and then pulls it back again. This rocking motion of the gas causes a leveling of the concentrations at both ends of a capillary. In this way each following tube builds up a concentration difference on top of the one already obtained. Between the end tubes we find a separation which is the  $n^{\text{th}}$  power of the one obtained with a two-bulb apparatus, if  $n$  is the number of tubes.

Although the situation is somewhat more complex than this short discussion shows, the physical effects, which lead to a wrong value of  $\alpha$  found

from experiment, become less important at higher pressures, as can be seen from the article by Van der Waerden (Wr 57), so that a Trennschaukel apparatus seems very suitable for the measurement of thermal diffusion factors at higher pressures. If technical difficulties with the rocking arrangement under high pressure would show insurmountable the concentration leveling might be achieved by connecting the tubes each time with two capillaries, kept at different temperatures, to each of their neighbours.

Thermo-syphon action then would replace the rocking of the gas. This type of experiments is desired as the bigger separation obtained gives higher accuracy in the values of  $\alpha$ , which is necessary to see the effect of small pressure changes and in this way to decide when the several effects occurring at higher pressures start being important.

#### d. SCOPE OF THIS STUDY

In this thesis we will treat some theoretical aspects of the pressure dependence of the thermal diffusion factor and give the results of a number of experiments. These experiments were performed at densities which were well away from the critical. This was done because the phenomena in the critical region are very complicated and no dependable quantitative predictions can be made. Moreover, small fluctuations in the temperature will cause large changes in the mixture under investigation thus making accurate measurements extremely difficult. From the work of other experimenters e.g. that of Velds (Ve 66,67), performed at this institute, we knew that large changes in the thermal diffusion factor could be obtained well outside the critical region. However, this large demixing caused a pretty big change in the mean concentration ratio between the two bulbs. This change is mainly due to the unequal volumes of upper and lower bulb. Therefore we chose for our experiments such conditions that the demixing obtained was pretty small.

In the theoretical part we will give in chapter II some theories, both old and new, which are based on a thermodynamical approach of the problem. Chapter III contains a new theory based on the fact that molecules tend to form clusters. The number of clusters and the number of molecules in a cluster both depend on temperature and pressure in the same way : when the pressure is raised or the temperature is lowered both numbers will

increase. As we have restricted ourselves to densities far from the critical the most important clusters for us are clusters of two molecules, called dimers. Chapter IV contains the experimental part. We have performed our experiments on mixtures for which no earlier data concerning the pressure dependence of the thermal diffusion factor existed, viz. 10%-90% mixtures at temperatures higher than ambient. Chapter V contains a survey of the calculations performed and a discussion of the theoretical and experimental data obtained.

## CHAPTER II

### THE THERMAL DIFFUSION FACTOR AT HIGHER PRESSURES

#### a. THE THERMAL DIFFUSION FACTOR ACCORDING TO NON-EQUILIBRIUM THERMODYNAMICS

A phenomenological approach to the thermal diffusion factor can be made from the point of view of non-equilibrium thermodynamics. Following the monograph of De Groot (Gt 59) we write down the phenomenological equations for a non-reacting n-component mixture :

$$\begin{aligned} \vec{J}_i &= \sum_{k=1}^n L_{ik} \vec{X}_k + L_{iu} \vec{X}_u \\ \vec{J}_q &= \sum_{k=1}^n L_{uk} \vec{X}_k + L_{uu} \vec{X}_u \end{aligned} \quad (2.1)$$

where  $\vec{J}_i$  denotes the mass-flux of component  $i$  and  $\vec{J}_q$  denotes the heat flux, both due to the thermodynamic forces  $\vec{X}_k$  and  $\vec{X}_u$ . The  $L_{ik}$ ,  $L_{uk}$ ,  $L_{iu}$  and  $L_{uu}$  are phenomenological coefficients. The thermodynamic forces are

$$\begin{aligned} \vec{X}_k &= \vec{F}_k - T \text{grad}(\mu_k/T) \\ \vec{X}_u &= - \text{grad} T / T \end{aligned} \quad (2.2)$$

Here  $\vec{F}_k$  denotes the external forces per unit mass, working on the system (e.g. gravity or an external magnetic field) and  $\mu_k$  is the chemical potential per unit mass of species  $k$ ;  $T$  is the temperature. The formalism, as it will be given here, is valid in a center-of-mass system and with mass fractions instead of molar fractions. The transcription to our usual system will be made in the final formula. For the derivation of a closed formula for the thermal diffusion factor it is convenient to introduce new coefficients  $Q_k^*$  by

$$L_{iu} = \sum_{k=1}^{n-1} L_{ik} Q_k^* = L_{ui} \quad (i=1,2, \dots, n-1) \quad (2.3)$$

where the last equality follows from the Onsager relations. The fluxes of (2.1) can now be written as

$$\vec{J}_i = \sum_{k=1}^{n-1} L_{ik} (\vec{X}_k - \vec{X}_n + Q_k^* \vec{X}_u) \quad (i=1,2, \dots, n-1) \quad (2.4)$$

$$\vec{J}_q = \sum_{k=1}^{n-1} L_{uk} (\vec{X}_k - \vec{X}_n) + L_{uu} \vec{X}_u$$

The physical interpretation of the  $Q_1^*$  is as follows: when there is no temperature gradient ( $\vec{X}_u = 0$ )  $Q_1^*$ , the so-called heat of transfer, is the amount of heat, transported with the unity of mass of component 1.

Introducing the equations (2.2) into the mass-fluxes in (2.4) we find

$$\vec{J}_i = \sum_{k=1}^{n-1} L_{ik} [\vec{F}_k - \vec{F}_n - T \text{grad}\{(\mu_k - \mu_n)/T\} - Q_k^* \text{grad}(T)/T]$$

or, supposing that the only force present is gravity and remembering that the force is per unit mass, so that  $\vec{F}_k = \vec{F}_n$

$$\vec{J}_i = \sum_{k=1}^{n-1} L_{ik} [-T \text{grad}\{(\mu_k - \mu_n)/T\} - Q_k^* \text{grad}(T)/T] \quad (2.5)$$

$\text{grad } \mu_k$  can be written as a linear combination of temperature, pressure and concentration gradients; when we suppose mechanical equilibrium the pressure gradient is zero, so that we have for two components

$$\vec{J}_1 = -\vec{J}_2 = -L_{11} \left\{ \frac{1}{c_2} \frac{\partial \mu_1}{\partial c_1} \text{grad } c_1 + (Q_1^* - h_1 + h_2) \text{grad } \ln T \right\}$$

where the Gibbs-Duhem relation

$$c_1 \delta \mu_1 + c_2 \delta \mu_2 = 0 ; T \text{ and } p \text{ constant}$$

has been used and  $h_k = \mu_k + T \cdot s_k$  is the partial specific enthalpy per unit mass of substance  $k$ .

As soon as equilibrium has been reached  $J_1 = J_2 = 0$ , or

$$\frac{1}{c_2} \frac{\partial \mu_1}{\partial c_1} \text{grad } c_1 + (Q_1^* - h_1 + h_2) \text{grad } \ln T = 0 \quad (2.6a)$$

which leads to a relation comparable with (1.10). To obtain full agreement between these two equations we will only have to replace concentrations by mole-fractions, as, in the equilibrium situation in our system both the center-of-mass and the center-of-particles are at rest, so that no change of coordinate system is needed. The mole-fractions in our two-component system are connected with the mass-fractions through

$$c_i = \frac{x_i M_i}{x_1 M_1 + x_2 M_2}$$

where the  $M_i$  are the molecular weights and which changes (2.6a), multiplied with  $x_1 \cdot x_2$  into

$$\frac{x_1 M_1 + x_2 M_2}{M_2} x_1 \frac{\partial \mu_1}{\partial x_1} \text{grad } x_1 + x_1 x_2 (Q_1^* - h_1 + h_2) \text{grad } \ln T = 0 \quad (2.6b)$$

giving

$$\alpha_{12} = \frac{-\text{grad } x_1}{x_1 x_2 \text{grad } \ln T} = \frac{M_2}{x_1 M_1 + x_2 M_2} \frac{Q_1^* - h_1 + h_2}{x_1 \frac{\partial \mu_1}{\partial x_1}} = \frac{Q_1^* - h_1 + h_2}{c_1 \frac{\partial \mu_1}{\partial c_1}} \quad (2.7a)$$

or, using molar quantities, denoted by the superposition of a wave, so that e.g.  $Q_1 = M_1 \cdot Q_1^*$

$$\alpha_{12} = \frac{M_2 \tilde{Q}_1^* - M_2 \tilde{h}_1 + M_1 \tilde{h}_2}{x_1 (x_1 M_1 + x_2 M_2) \partial \tilde{\mu}_1 / \partial x_1} \quad (2.7b)$$

Up to this point the discussion has been fully general. We can now introduce for  $h_i$  and  $\mu_i$  (or  $\tilde{h}_i$  and  $\tilde{\mu}_i$ ) expressions derivable from the equation of state that is supposed to be valid. For  $Q_1^*$  this is less simple, so that one or more new assumptions have to come in as soon as we wish to use the equations (2.11) for predicting values of  $\alpha_{12}$  at higher pressures.

#### b. HAASE THEORY

The simplest assumption for  $Q_1^*$  (or  $\tilde{Q}_1^*$ ) is to take it independent of the pressure. This supposition was introduced by Haase (Ha 49) and used extensively by Drickamer and co-workers (Dr 50-53) for several equations of state. The procedure is to take (2.7a) or (2.7b) and write it down twice: once for the low pressure situation where only the non-equilibrium contribution to the separation is important and once for the pressure of the experiment. From these two equations  $Q_1^*$  can be eliminated under the assumption made. The result is

$$\alpha_{12} = \left\{ \frac{(x_1 M_1 + x_2 M_2) \alpha_{12}^0 + RT + M_1 (\tilde{h}_2 - \tilde{h}_2^0) - M_2 (\tilde{h}_1 - \tilde{h}_1^0)}{x_1 M_1 + x_2 M_2} \right\} / x_1 \frac{\partial \tilde{\mu}_1}{\partial x_1} \quad (2.8)$$

where the superscript 0 indicates the low pressure value of the pertinent quantity and use has been made of the thermodynamical relation, valid for ideal gases

$$x_1 \frac{\partial \tilde{\mu}_1}{\partial x_1} = RT$$

For a given equation of state  $\alpha_{12}$  can now be calculated if the low pressure thermal diffusion factor is known.



### c. FUGACITY-THEORY

The experimental work of Becker (Be 50) showed that a description of the higher pressure behavior of the thermal diffusion factor can be found by separating the total demixing in a low-pressure contribution (the thermal diffusion factor in the usual sense) and a contribution due to the non-ideal behavior of the component gases. In fact, this partition can be seen in (2.8), although here the separation is not complete, due to the factor in the denominator. Velds, Los and De Vries (Ve 67) worked out this idea by ascribing the non-ideality contribution to the fact that for higher pressures not the partial pressures but the partial fugacities have to be the same throughout the apparatus. No cross-effects will exist with thermal diffusion, due to the Curie principle, as thermal diffusion has a vectorial and the fugacity demixing a scalar character.

The way in which this splitting was introduced by Velds et al. is somewhat confusing as the thermal diffusion contribution is considered as due to ideal properties of the gaseous mixture, whereas in an ideal gas no thermal diffusion exists. A better proposition is the term quasi-ideal, used by Becker (Be 50).

The observed demixing  $Q_{\text{obs}}$  can now be written as

$$Q_{\text{obs}} = Q_{\text{th.d.}} + Q_{\text{fug}} \quad (2.9a)$$

where  $Q_{\text{th.d.}}$  is the separation due to thermal diffusion and  $Q_{\text{fug}}$  the one due to the fugacity. Using a similar notation (2.9a) leads to

$$\alpha_{\text{obs}} = \alpha_{\text{th.d.}} + \alpha_{\text{fug}} \quad (2.9b)$$

The fugacity  $f_i$  of component  $i$  in a mixture is defined by the equation (see e.g. (Hi 54), p.389)

$$\ln f_i(T, p, x_i) = \ln(x_i, p) + \frac{1}{RT} \int_0^p \left( \tilde{V}_i - \frac{RT}{p} \right) dp \quad (2.10)$$

in which  $R$  is the gas-constant and  $\tilde{V}_i$  the partial molar volume. It is

clear that the value of  $f_i$  will depend on the equation of state that is used. Velds et al. worked out in detail the formulae for the Van der Waals equation and the simplified Beattie-Bridgeman equation of state. The last mentioned equation has the form

$$p \bar{V} = RT + Bp \quad (2.11a)$$

where  $\bar{V}$  is the molar volume of the mixture and  $B$  is a function of temperature and composition :

$$B = B_{11}x_1^2 + 2B_{12}x_1x_2 + B_{22}x_2^2 \quad (2.11b)$$

$$B_{ij} = (B_0)_{ij} - (A_0)_{ij}/RT - c_{ij}/T^3 \quad (2.11c)$$

$(A_0)_{ii}$ ,  $(B_0)_{ii}$  and  $c_{ii}$  are empirical constants for the pure gases; the constants with unequal suffixes are found from those for the pure gases by the use of combination rules.

Formula (2.11a) is also a form of the virial equation of state. This equation can be written as an expansion in negative powers of the specific volume  $\bar{V}$  or in positive powers of the pressure  $p$ . Using this last type of expansion and cutting off after the second term gives equation (2.11a). The concentration dependence (2.11b) of  $B$  is the same as in the simplified Beattie-Bridgeman equation but the temperature dependence (2.11c) is not the same and is determined by the type of interaction potential used.

The basic statement of the fugacity theory is that the fugacity  $f_i$  of each component gas is the same in the hot and in the cold part of the apparatus or

$$f_i(T_c) = f_i(T_h) \quad (2.12)$$

where  $T_c$  denotes the temperature of the cold and  $T_h$  of the hot part of the apparatus. For the simplified Beattie-Bridgeman equation of state we have in a two-component system (Ve 67)

$$\ln f_i(T, p, x_i) = \ln(p x_i^{(T)}) + \frac{p}{RT} \{ B_{ii}(T) + (1 - x_i^{(T)})^2 \Delta(T) \} \quad (2.13)$$

with

$$\Delta(T) = 2B_{12}(T) - B_{11}(T) - B_{22}(T)$$

the superscript (T) indicating that the value of  $x_i$  is meant in the region with temperature T. Combining (2.12) and (2.13) we have the relation

$$\ln \left\{ \frac{x_i^{(T_h)}}{x_i^{(T_c)}} \right\} = \frac{p}{R} \left\{ - \frac{B_{ii}(T_h)}{T_h} - \frac{\Delta(T_h)(1 - x_i^{(T_h)})^2}{T_h} + \frac{B_{ii}(T_c)}{T_c} + \frac{\Delta(T_c)(1 - x_i^{(T_c)})^2}{T_c} \right\} \quad (2.14)$$

Writing down (2.14) twice, once for  $i=1$  and once for  $i=2$  and subtracting the two equations, we find for the separation

$$Q = \frac{x_1^{(T_h)}/x_2^{(T_h)}}{x_1^{(T_c)}/x_2^{(T_c)}} \quad (2.15)$$

due to the equilibrium properties of the mixture

$$\ln Q_{\text{fug}} = \frac{p}{R} \left\{ \frac{B_{11}(T_c) - B_{22}(T_c) + (x_2^{(T_c)} - x_1^{(T_c)}) \Delta(T_c)}{T_c} - \frac{B_{11}(T_h) - B_{22}(T_h) + (x_2^{(T_h)} - x_1^{(T_h)}) \Delta(T_h)}{T_h} \right\} \quad (2.16)$$

(2.16), with the omission of the superscripts ( $T_h$ ) and ( $T_c$ ) of the  $x_i$  is the formula used by Velds. The values of the  $x_i$  he used are the initial molar fractions. We wish to maintain the superscripts for the following reasons :

1. From the basic formula (2.12) it follows that the equilibrium part of the separation is found from the local values of temperature, concentration etc., in the upper volume and, separately, in the lower volume. This

means that it is in principle incorrect to use an intermediate value for the concentration and, moreover, the neglect of a factor contributing to the separation.

2. Using the initial concentration ratio for the mean value means that no account is taken of the conservation of the number of particles present of each species. If we introduce this conservation law into our considerations we find that the value of the separation will change with the ratio of the upper and lower volumes.
3. Although, as stated, no cross-effects exist between the equilibrium and non-equilibrium properties, the values of  $x_i^{(T_h)}$  and  $x_i^{(T_c)}$  to be used in (2.16) are the actual values, i.e. the values after both effects have changed the concentrations. This enhances the effect mentioned under 2. in the case that the two kinds of separation reinforce each other, otherwise decreases it.

The reasons, mentioned as 2. and 3., are valid for all calculations of thermal diffusion factors. That they are mentioned here comes from the fact that here it is possible - at least approximately - to take them into account. In other calculations, starting from a thermal diffusion factor at some intermediate temperature, this is less simple.

The use of (2.16) instead of a formula with mean values of the  $x_i$  complicates the mathematical treatment, inasmuch as the equation has now become transcendental. Moreover, we have to introduce other equations as the system is no longer sufficiently described by (2.14). To solve the problem we have started from the actual filling procedure used in our and most other experiments. First one gas is introduced into the system until the desired pressure  $p_1$  has been reached. Using again the simplified Beattie-Bridgeman equation (2.11) for one component we find for the number  $N_1$  of moles present :

$$N_1 = \frac{p_1 V_c}{RT_c + B_{11}(T_c)p_1} + \frac{p_1 V_h}{RT_h + B_{11}(T_h)p_1} \quad (2.17a)$$

where  $V_h$  and  $V_c$  are resp. the hot (upper) and cold (lower) volume. Then the second gas is introduced until the final pressure  $p$  has been reached.

The total number  $N$  of moles present is :

$$N = \frac{pV_c}{RT_c + B(T_c)p} + \frac{pV_h}{RT_h + B(T_h)p} = C_c + C_h \quad (2.17b)$$

Here  $C_c$  denotes the total number of moles present in the cold,  $C_h$  in the hot volume. It will be clear from the definitions that

$$N_1 = C_c x_1^{(T_c)} + C_h x_1^{(T_h)} \quad (2.18)$$

and

$$x_1^{(T_c)} + x_2^{(T_c)} = 1 \quad (2.19)$$

$$x_1^{(T_h)} + x_2^{(T_h)} = 1$$

The system is now fully described: (2.16), together with (2.15), the values of  $N$ ,  $N_1$ ,  $C_c$  and  $C_h$  and the equations (2.18) and (2.19) form a system of four equations in four unknowns, viz.  $x_1^{(T_c)}$ ,  $x_2^{(T_h)}$ ,  $x_2^{(T_c)}$  and  $x_2^{(T_h)}$ . The method used for the solution of this system will be discussed in chapter V.

The same procedure could be followed with any other equation of state. The fact that we have chosen the simplified Beattie-Bridgeman equation instead of e.g. the Van der Waals equation comes from the easy mathematical tractability of the formulae and is not to be considered as a fundamental choice.

#### d. PAIR-CORRELATION THEORY

As discussed below eqn.(2.7b), the thermal diffusion factor can be calculated when the heat of transfer  $Q_1^*$  is known. To find this quantity one can suppose that only two-body forces are acting between the various molecules. This restricts the discussion to the one-particle and two-particle distribution functions, the last one giving the distribution of pairs of molecules as a function of position, momentum and time. A number of authors have been using this supposition to calculate  $Q_1^*$ , the most complete treatment having been given by Bearman, Kirkwood and Fixman (Bm 58). Starting from the Liouville equation they derive an expression for the heat flux  $\vec{q}$

in a two-component system, using the assumption mentioned and supposing further that the molecules interact with central forces and that no external fields of force are present. Their expression consists of a part  $\vec{q}_k$  that gives the kinetic contribution and a part  $\vec{q}_\phi$  giving the effect of the intermolecular forces on the heat flux. The calculation of the kinetic contribution can be performed without difficulties; for the calculation of the contribution of the intermolecular forces a number of approximations must be made. The most important of these is the supposition that a number of friction coefficients in pair space are direct sums of comparable coefficients in singlet space.

These friction coefficients are needed to express in terms of molecular velocities the deviations of the mean thermodynamical forces from the values these forces would have if the system was in equilibrium. This means that the interaction between two molecular pairs is split into two times the interaction of two separate molecules, which is true in the case of a large distance between the molecules of the pair. The final formula for the heat of transport consists of two parts, one using equilibrium quantities, the other containing the non-equilibrium contribution. We have used only the equilibrium part as this may be expected to give the most important contribution to the heat of transfer and the non-equilibrium part can not be calculated in a simple way to a useful degree of accuracy. We will give the derivation of the equilibrium contribution from the formula for the heat flux in a two-component system given by Bearman et al. (loc.cit.), which is a generalization of the formula given by Irving and Kirkwood (Ir 50) for one component (see also (Hi 54), chapter 9). This expression reads as follows :

$$\vec{q} = \vec{q}_k + \vec{q}_\phi \quad (2.20)$$

$$\text{with } \vec{q}_k(\vec{r}) = \sum_{\alpha=1}^2 \int \frac{m_\alpha}{2} \left| \frac{\vec{p}_1}{m_\alpha} - \vec{v}_0 \right|^2 \left( \frac{\vec{p}_1}{m_\alpha} - \vec{v}_0 \right) f_\alpha^{(1)} d\vec{p}_1$$

$$\vec{q}_\phi(\vec{r}) = \frac{1}{2} \sum_{\alpha=1}^2 \sum_{\beta=1}^2 \int \left\{ \phi_{\alpha\beta}(\vec{R}) \vec{U} - \phi'_{\alpha\beta}(\vec{R}) \frac{\vec{R}\vec{R}}{R} \right\} \left\{ \vec{j}_{\alpha\beta,1}^{(2)}(\vec{r}, \vec{R}) - \vec{v}_0 n_{\alpha\beta}^{(2)}(\vec{r}, \vec{R}) \right\} d\vec{R}$$

$$\vec{j}_{\alpha\beta,1}^{(2)}(\vec{r}, \vec{R}) = \iint \frac{\vec{p}}{m_\alpha} f_{\alpha\beta}^{(2)}(\vec{r}, \vec{r}', \vec{p}, \vec{p}') d\vec{p} d\vec{p}'$$

In these formulae is  $f_{\alpha}^{(1)}(\vec{r}, \vec{p})$  the one-particle,  $f_{\alpha\beta}^{(2)}(\vec{r}, \vec{r}', \vec{p}, \vec{p}')$  the two-particle distribution function,  $\vec{R}$  is the intermolecular position vector,  $\phi_{\alpha\beta}(R)$  the intermolecular potential,  $\phi'_{\alpha\beta}(R)$  its derivative;  $n_{\alpha\beta}^{(2)}(\vec{r}, \vec{R})$  is the number density of molecular pairs with one molecule located at  $\vec{r}$ , the other at  $\vec{r}' = \vec{r} + \vec{R}$ . The other quantities have their usual meaning, the suffixes denoting the molecular species. From the formulae for  $\vec{q}_{\phi}$  and  $\vec{j}_{\alpha\beta,1}^{(2)}$  (the last one is the projection of the six-dimensional pair flux vector on the space of  $\vec{r}$ ), we see that

$$\vec{q}_{\phi}(\vec{r}) = \frac{1}{2} \sum_{\alpha=1}^2 \sum_{\beta=1}^2 \int \{ \phi_{\alpha\beta}(\vec{R}) \vec{U} - \phi'_{\alpha\beta}(\vec{R}) \frac{\vec{R}\vec{R}}{R} \} \left\{ \int \left( \frac{\vec{p}}{m_{\alpha}} - \vec{v}_0 \right) f_{\alpha\beta}^{(2)} d\vec{p} d\vec{p}' \right\} d\vec{R} \quad (2.21)$$

We now suppose

$$\begin{aligned} \int \left( \frac{\vec{p}}{m_{\alpha}} - \vec{v}_0 \right) f_{\alpha\beta}^{(2)} d\vec{p} d\vec{p}' &= \int \left( \frac{\vec{p}}{m_{\alpha}} - \vec{v}_0 \right) f_{\alpha}^{(1)}(\vec{r}, \vec{p}) d\vec{p} \int f_{\beta}^{(1)}(\vec{r}', \vec{p}') d\vec{p}' g(\vec{r}, \vec{R}) = \\ &= n_{\alpha}(\vec{r}) \vec{v}_{\alpha} n_{\beta}(\vec{r}') g(\vec{r}, \vec{R}) \end{aligned} \quad (2.22)$$

using for the last change the definitions of the one-particle distribution function and the diffusion velocity  $\vec{v}_{\alpha}$  of component  $\alpha$ .  $n_{\alpha}(\vec{r})$  and  $n_{\beta}(\vec{r}')$  are number densities in singlet space;  $g(\vec{r}, \vec{R})$  is the radial distribution function, which is supposed not to depend on the composition of the mixture. (2.22) assumes that no relation exists between the velocities of the components of the pair.

Introducing (2.22) into (2.21) we find

$$\vec{q}_{\phi} = \frac{1}{2} \sum_{\alpha=1}^2 \sum_{\beta=1}^2 n_{\alpha}(\vec{r}) \vec{v}_{\alpha} n_{\beta}(\vec{r}') \left\{ \phi_{\alpha\beta} \vec{U} - \frac{d\phi_{\alpha\beta}}{dR} \frac{\vec{R}\vec{R}}{R} \right\} g(\vec{r}, \vec{R}) d\vec{R}$$

or, to a good approximation, as the number density will not vary much over distances of the order of the intermolecular distance

$$\vec{q}_{\phi} = \frac{1}{2} \sum_{\alpha=1}^2 \sum_{\beta=1}^2 n_{\alpha}(\vec{r}) n_{\beta}(\vec{r}) \vec{v}_{\alpha} \int \left\{ \phi_{\alpha\beta} \vec{U} - \frac{d\phi_{\alpha\beta}}{dR} \frac{\vec{R}\vec{R}}{R} \right\} g(\vec{r}, \vec{R}) d\vec{R} \quad (2.23)$$

(2.23) is now split into two contributions following the expression between braces :

$$\vec{q}'_{\phi} = \frac{1}{2} \sum_{\alpha=1}^2 \sum_{\beta=1}^2 n_{\alpha}(\vec{r}) n_{\beta}(\vec{r}) \vec{v}_{\alpha} \int \phi_{\alpha\beta} \vec{U} g(\vec{r}, \vec{R}) d\vec{R} \quad (2.24)$$

$$\vec{q}''_{\phi} = \frac{1}{2} \sum_{\alpha=1}^2 \sum_{\beta=1}^2 n_{\alpha}(\vec{r}) n_{\beta}(\vec{r}) \vec{v}_{\alpha} \int \frac{d\phi_{\alpha\beta}}{d\vec{R}} \frac{\vec{R}\vec{R}}{R} d\vec{R} \quad (2.25)$$

The internal energy per molecule in a one-component system, due to the intermolecular potential energy, can be given as

$$u_{\phi}(\vec{r}) = \frac{1}{2} n(\vec{r}) \int \phi(R) g(\vec{r}, \vec{R}) d\vec{R}$$

Assuming equilibrium we can substitute  $q'_{\phi}$  by  $u_{\phi}$  in a one-component system (no summation,  $\alpha=\beta=1$ ). To find the relation between  $q'_{\phi}$  and  $u_{\phi}$  in a two-component system we shall use the following considerations: as the potential energy of a molecule is the sum of the potential energies resulting from the interaction of this molecule with every single molecule in the vessel, the supposition of two-body forces allows us to write for the potential energy of a molecule of species 1 in a mixture of components 1 and 2

$$u_{\phi_1}(\vec{r}) = \frac{1}{2} \{ n_1(\vec{r}) \int \phi_{11}(R) g(\vec{r}, \vec{R}) d\vec{R} + n_2(\vec{r}) \int \phi_{12}(R) g(\vec{r}, \vec{R}) d\vec{R} \}$$

and the mean potential energy of a molecule is

$$\begin{aligned} u_{\phi}(\vec{r}) &= x_1 u_{\phi_1}(\vec{r}) + x_2 u_{\phi_2}(\vec{r}) \\ &= \frac{1}{2n} \sum_{\alpha=1}^2 \sum_{\beta=1}^2 n_{\alpha}(\vec{r}) n_{\beta}(\vec{r}) \int \phi_{\alpha\beta} g(\vec{r}, \vec{R}) d\vec{R} \\ &= \sum_{\alpha=1}^2 \sum_{\beta=1}^2 x_{\alpha} x_{\beta} u_{\phi, \alpha\beta} \end{aligned} \quad (2.26)$$



when we denote particle fractions with  $x_i$ .

The total energy per molecule in a gas is made up of a potential and a kinetic contribution. As the last one is the only one present in an ideal gas, we may write, taking the quantities per molecule

$$u_{\phi, \alpha\beta}(\vec{r}) = u_{\alpha\beta} - u_{\alpha\beta}^{(0)} \quad (2.27)$$

the superscript zero indicating that the value for an ideal gas is meant.

The pressure tensor for a gas is, just as the internal energy, made up of a potential and a kinetic part. In the case of a single gas in equilibrium the total pressure tensor becomes diagonal with elements

$$p = nkT - \frac{1}{6} n^2 \int \frac{d\phi}{dR} g(R) 4\pi R^3 dR \quad (2.28)$$

the second term on the right hand side representing the potential contribution. Using the same kind of reasoning as with the potential energy we can generalize this expression for a two-component mixture as

$$p = nkT - \frac{1}{6} \sum_{\alpha=1}^2 \sum_{\beta=1}^2 n_{\alpha}(\vec{r}) n_{\beta}(\vec{r}) \int \frac{d\phi_{\alpha\beta}(R)}{dR} g(R) 4\pi R^3 dR \quad (2.29)$$

Comparing this with the virial equation of state truncated after the second virial coefficient

$$p = nkT + \frac{nB(T)kT}{V} = nkT + \frac{kT}{nV} \sum_{\alpha=1}^2 \sum_{\beta=1}^2 n_{\alpha}(\vec{r}) n_{\beta}(\vec{r}) B_{\alpha\beta}(T) \quad (2.30)$$

we find the desired interpretation of (2.25) if  $q_{\phi}^{\dagger}$  is taken in the equilibrium situation.

In (2.30) is  $\bar{V}$  the molar volume and  $B_{\alpha\beta}(T)$  are the virial coefficients specific for the interaction between the various components. Combining eqns. (2.23) to (2.30), all for the equilibrium situation, we find

$$\bar{q}_{\phi}^{\dagger} = n \sum_{\alpha=1}^2 \sum_{\beta=1}^2 x_{\alpha} x_{\beta} \bar{v}_{\alpha} (u_{\alpha\beta} - u_{\alpha\beta}^{(0)}) + \frac{kT}{V} x_{\alpha} x_{\beta} B_{\alpha\beta} \bar{v}_{\alpha} \quad (2.31)$$

The contribution to the heat of transfer of  $\vec{q}_\phi$  is then found by dividing  $\vec{q}_\phi$  by the mass-flux  $J_1$ , given as

$$\vec{J}_1 = n_1 m_1 \vec{v}_1 = - n_2 m_2 \vec{v}_2 \quad (2.32)$$

the last form resulting from the supposition that the center of mass of the system is at rest. This gives, using  $n_i = x_i \cdot n$ ,

$$Q_{1,\phi}^* = \frac{x_1(u_{11} - u_{11}^{(0)}) + x_1 \frac{kT}{V} B_{11} + x_2(u_{12} - u_{12}^{(0)}) + x_2 \frac{kT}{V} B_{12}}{m_1} - \frac{x_1(u_{12} - u_{12}^{(0)}) + x_1 \frac{kT}{V} B_{12} + x_2(u_{22} - u_{22}^{(0)}) + x_2 \frac{kT}{V} B_{22}}{m_2}$$

or, multiplying both numerator and denominator with Avogadro's number,

$$Q_{1,\phi}^* = \frac{x_1(\bar{u}_{11} - \bar{u}_{11}^{(0)}) + x_1 \frac{RT}{V} B_{11} + x_2(\bar{u}_{12} - \bar{u}_{12}^{(0)}) + x_2 \frac{RT}{V} B_{12}}{\bar{m}_1} - \frac{x_1(\bar{u}_{12} - \bar{u}_{12}^{(0)}) + x_1 \frac{RT}{V} B_{12} + x_2(\bar{u}_{22} - \bar{u}_{22}^{(0)}) + x_2 \frac{RT}{V} B_{22}}{\bar{m}_2} \quad (2.33)$$

a wave denoting a quantity per mole.

From the relations between the thermodynamic properties and the equation of state it is easily derived (see e.g. (Hi 54), chapter 3) that for the virial equation of state in the approximation earlier used

$$\frac{RT}{V} B_{ij} = (\bar{h}_{ij} - \bar{h}_{ij}^{(0)}) - (\bar{u}_{ij} - \bar{u}_{ij}^{(0)})$$

wherein  $h_{ij}$  denotes the specific enthalpy, calculated for a hypothetical ( $i \neq j$ ) or real ( $i=j$ ) gas, consisting of molecules  $i$  or molecules with a combination of the properties of molecules  $i$  and  $j$  and which changes (2.33) into

$$Q_{1,\phi}^* = \frac{x_1(\tilde{h}_{11} - \tilde{h}_{11}^{(0)}) + x_2(\tilde{h}_{12} - \tilde{h}_{12}^{(0)})}{\tilde{m}_1} - \frac{x_1(\tilde{h}_{12} - \tilde{h}_{12}^{(0)}) + x_2(\tilde{h}_{22} - \tilde{h}_{22}^{(0)})}{\tilde{m}_2} \quad (2.34)$$

As will be clear from (2.24)  $Q_{1,\phi}^*$  goes to zero with the pressure.

Supposing that the pressure dependence of  $Q_{1,\phi}^*$  is fully contained in  $Q_{1,\phi}^*(0)$  we may write, according to (2.7a) and (2.7b),

$$\alpha^{(0)} = \frac{Q_{1,\phi}^*(0) - h_1^{(0)} + h_2^{(0)}}{c_1 \partial \mu_1^{(0)} / \partial c_1}$$

with

$$Q_{1,\phi}^*(0) = Q_1^* - Q_{1,\phi}^*$$

Combination of these formulae with (2.7a) gives

$$\alpha = \alpha^{(0)} \frac{c_1 \partial \mu_1^{(0)} / \partial c_1}{c_1 \partial \mu_1 / \partial c_1} + \frac{x_1(\tilde{h}_{11} - \tilde{h}_{11}^{(0)}) + x_2(\tilde{h}_{12} - \tilde{h}_{12}^{(0)}) - (\tilde{h}_1 - \tilde{h}_1^{(0)})}{\tilde{m}_1 c_1 \partial \mu_1 / \partial c_1} - \frac{x_1(\tilde{h}_{12} - \tilde{h}_{12}^{(0)}) + x_2(\tilde{h}_{22} - \tilde{h}_{22}^{(0)}) - (\tilde{h}_2 - \tilde{h}_2^{(0)})}{\tilde{m}_2 c_1 \partial \mu_1 / \partial c_1}$$

or, using the virial equation of state to second order and the corresponding formulae for the specific enthalpy and thermodynamic potential,

$$\alpha = \frac{\alpha_0 + p/RT \{ (B_{22} - T dB_{22}/dT) - (B_{11} - T dB_{11}/dT) + (x_1 - x_2)(\Delta - T d\Delta/dT) \}}{1 - 2p\Delta x_1 x_2 / RT} \quad (2.35)$$

in which

$$\Delta(T) = 2B_{12}(T) - B_{11}(T) - B_{22}(T)$$

The final formula of (Bm 58) for the equilibrium contribution is identical with (2.34) up to terms of the order of the third virial coefficient and a correction factor

$$1 + p B(T)/RT$$

It must be kept in mind, however, that the thermal diffusion factor can not be calculated from the formula given in (Bm 58) for  $Q_1^*$  in combination with the expression for  $\bar{J}_1$  in that publication, as this will introduce an error of a factor

$$\frac{m_1}{m_2} x_1 + x_2$$

with respect to the common definition of the thermal diffusion factor, due to the choice of the reference system in combination with molecular units.

## CHAPTER III

### THE FORMATION OF DIMERS AND ITS EFFECTS ON THERMAL DIFFUSION

#### a. THE DIMER CONCEPT

As early as 1904 Jeans (Je 04) mentioned the possible existence of double molecules. Several investigators did detect them in adiabatically expanding molecular beams (Gr 1) as well as in systems where this expansion and the consequent cooling did not take place (Le 66). The amount of double molecules to be expected in a given gaseous system was calculated by Hill (Hl 55), Stogryn and Hirschfelder (St 59), Kim and Ross (Ki 65) and others (Gr 2). In this thesis we will mainly use the results of Stogryn and Hirschfelder, which are partly based on those of Hill.

For the calculation of the dimer concentration we start from a known interaction potential  $\phi(r)$  which is only dependent on the intermolecular distance. Throughout this part we will neglect internal degrees of freedom. After the well-known reduction of the three-dimensional scattering problem to a two-dimensional one by the use of center-of-mass coordinates (Hi 54) we may write down the laws of conservation of angular momentum and conservation of energy in polar coordinates :

$$\mu b g = \mu r^2 \dot{\theta} \tag{3.1a}$$

$$\frac{1}{2} \mu g^2 = \frac{1}{2} \mu (\dot{r}^2 + r^2 \dot{\theta}^2) + \phi(r) \tag{3.1b}$$

In this formula is  $\mu$  the reduced mass of the colliding pair,  $b$  the impact parameter,  $g$  the relative velocity and  $\theta$  the angle of deflection. Eliminating  $\dot{\theta}$  we find

$$\frac{1}{2} \mu g^2 = \frac{1}{2} \mu \dot{r}^2 + \frac{1}{2} \mu g^2 \left( \frac{b^2}{r^2} \right) + \phi(r) \tag{3.2}$$

Here the only variable left is  $r$ , so that we have reduced our scattering problem to a one-dimensional equivalent as far as the separation of the

molecules is concerned. This separation is the only thing of interest for the dimer concept, so that (3.2) gives the whole description of our problem.

We may consider (3.2) as giving the motion of a particle with mass  $\mu$  in a potential  $\phi_{\text{eff}}(r)$ , the effective potential, given as

$$\phi_{\text{eff}}(r) = \phi(r) + \mu g^2 \left( \frac{b^2}{r} \right) \quad (3.3)$$

The relative kinetic energy of the two particles, which is  $1/2 \mu g^2$ , will be indicated by the letter E; the factor  $E b^2$  is called L. Taking for  $\phi(r)$  a known potential, for instance the Lennard-Jones (6-12) potential

$$\phi(r) = 4 \epsilon \left\{ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right\} \quad (3.4)$$

we may draw the curves for  $\phi_{\text{eff}}$  for different values of L, as has been done in fig.3.1. The zero of energy is defined as the potential energy of the particles at infinite separation.

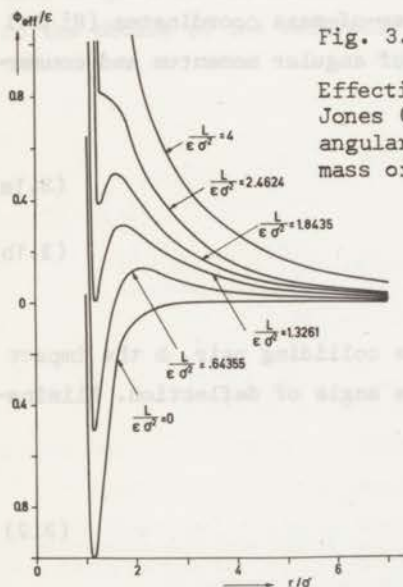


Fig. 3.1

Effective potential energy curves for the Lennard-Jones (6-12) potential for different values of the angular momentum L.  $L = I^2/2\mu$  where  $\mu$  is the reduced mass of the colliding molecules.

From this figure we see that for values of  $L$  different from zero, but not too big,  $\phi_{\text{eff}}(r)$  has a maximum beside the minimum due to  $\phi(r)$ . As the value of  $L$  increases the minimum and the maximum coincide in an inflection point for  $L = L_c = 2.4624 \epsilon \sigma^2$ . For values of  $L$  bigger than  $L_c$  no extremum exists any longer. The value of  $\phi_{\text{eff}}(r)$  in the inflection point is indicated as  $E_c$ .

Two kinds of dimers may be introduced now. In the case of a three-particle collision one particle may gain a certain amount of energy, leaving the other two trapped in each other's potential well. Here two possibilities arise :

- a. The relative potential energy of the two particles is less than zero.
- b. The relative potential energy of the two particles is bigger than zero, but less than the maximum in the effective potential.

Case a. has been discussed by Hill (Hl 55). The double molecule that has been formed is called a stable dimer; neither classically nor quantum-mechanically the two particles will separate without external disturbances.

Case b. has been introduced by Stogryn and Hirschfelder (St 59) and is called a metastable dimer. Classically the particles stay together, quantum-mechanically the tunnelling process will finally allow them to separate. As long as the lifetime of such a metastable dimer is longer than the time between two collisions these molecular complexes behave like stable dimers. Stogryn and Hirschfelder calculated the lifetimes of these metastable dimers with the help of the W.K.B. approximation for the Lennard-Jones potential. They took three, about equally spaced, values for  $L$  and calculated the lifetimes of the metastable dimers for four values of  $E$  for each of these  $L$ -values. The  $L$ -values covered the range in which metastable dimers can be expected ( $0$  to  $L_c$ ) and the  $E$ -values covered the range determined by the  $L$ -value (minimum to maximum in  $\phi_{\text{eff}}$ ). The results are given for the case of Ar, where the vast majority of metastable dimers has a lifetime exceeding the time between two collisions at temperatures not too far from ambient and atmospheric pressure.

We calculated the lifetimes for the metastable dimers of several other gases:  $H_2$ , He,  $CH_4$ ,  $N_2$ ,  $CO_2$  and  $C_2H_4$ . For  $CH_4$ ,  $N_2$ ,  $C_2H_4$ ,  $CO_2$  and Kr the results were comparable to those of Ar. For  $H_2$  and He however the lifetimes varied between  $10^{-9}$  and  $10^{-12}$  seconds, with all values except one smaller than  $10^{-9}$  seconds. As this is shorter than the time between two collisions we may conclude that the role of metastable dimers is negligible

here. As the mean temperature in our apparatus is higher than ambient and the pressure well above one atmosphere it will be permitted to consider the metastable species as real dimers, except for  $H_2$  and He.

A third kind of dimer has been introduced by Kim and Ross (Ki 65). Starting from the fact that for a value of  $E$  somewhat bigger than the maximum in the effective potential the phenomenon of orbiting will occur, which means that two particles stay revolving around each other for some time before separating again, they extended the region of  $E$  where dimers could be formed: regardless of the value of  $L$  they consider as dimers two-particle systems where  $E \leq E_c$ . The extra amount of dimers is referred to as quasi-dimers. Although the mean lifetime of quasi-dimers is too short to take them into account as real dimers, their importance mainly comes from the fact that for their existence only a two-particle collision is needed. Because their mean lifetime is longer than the mean duration of a collision, they enhance the possibility for the three-particle collisions needed for the coming into existence of the stable and metastable species.

#### b. PREDICTIONS OF THE DIMER CONCENTRATION

For the calculation of the concentration of stable and metastable dimers, in which we will follow the treatment given by Hill and by Stogryn and Hirschfelder (loc.cit.), we consider the formation of dimers as a chemical equilibrium



For such a reaction the equilibrium constant  $K$  is defined as

$$K = a_{c2} N_2 V / a_{c1}^2 N_1^2 \quad (3.6a)$$

where the  $a_{ci}$  are activity coefficients and the  $N_i$  are the numbers of monomers ( $N_1$ ) and dimers ( $N_2$ ) present in the system. As it is more convenient for us to express  $K$  in mole fractions  $x_i$  instead of numbers of molecules  $N_i$





with the Hamiltonian

$$H = \frac{1}{4m}(p_x^2 + p_y^2 + p_z^2) + \frac{1}{mr^2}(p_\theta^2 + \frac{p_\psi^2}{\sin^2\theta}) + \frac{p_r^2}{m} + \phi(r) \quad (3.9b)$$

$x$ ,  $y$  and  $z$  are the coordinates of the center of mass and  $\theta$ ,  $\psi$  and  $r$  are the relative (polar) coordinates of the two molecules. Making the change of variables

$$P_\theta = \frac{p_\theta}{(mr^2kT)^{1/2}}; P_\psi = \frac{p_\psi}{(mr^2kT\sin^2\theta)^{1/2}}; P_r = \frac{p_r}{(mkT)^{1/2}}$$

and integrating over  $x$ ,  $y$ ,  $z$ ,  $\theta$  and  $\psi$  we get for (3.8a,b)

$$Q_2 = 2V\pi^{-3/2}\Lambda^{-6} \int r^2 \exp\left\{-\frac{\phi(r)}{kT} - P_\theta^2 - P_\psi^2 - P_r^2\right\} dr dP_\theta dP_\psi dP_r \quad (3.10)$$

Up to this point the calculations of Hill (stable dimers) and Stogryn and Hirschfelder (metastable dimers) are the same, but now each one goes his way by the choice of the limits of the integration to be performed. The terms between braces in the integrand of (3.10) together form the total energy divided by  $kT$  of the two-molecule system. Hill now considers the system to be a dimer when this total energy is less than or equal to zero, in formula

$$P_\theta^2 + P_\psi^2 + P_r^2 \leq -\phi(r)/kT \quad (3.11)$$

(3.10) may be split up in two separate integrals :

$$Q_2 = 2V\pi^{-3/2}\Lambda^{-6} \left[ \int r^2 \exp\left\{-\frac{\phi(r)}{kT}\right\} dr \right] \left[ \int \exp\left\{-(P_\theta^2 + P_\psi^2 + P_r^2)\right\} dP_\theta dP_\psi dP_r \right] \quad (3.10a)$$

The region of integration of the triple integral in (3.10a) is determined by (3.11) and the fact that a sum of squares of real quantities is larger than or equal to zero. The integration over  $P_\theta$ ,  $P_\psi$  and  $P_r$  may now be

performed and the result is expressed in the gamma function and incomplete gamma function :

$$\int \exp\{-(P_{\theta}^2 + P_{\psi}^2 + P_r^2)\} dP_{\theta} dP_{\psi} dP_r = \pi^{3/2} \frac{\Gamma\{\frac{3}{2}, -\frac{\phi(r)}{kT}\}}{\Gamma(\frac{3}{2})} \quad (3.10b)$$

The limits of integration for  $r$  are the values of  $r$  between which  $\phi(r) \leq 0$ . Taking for  $\phi(r)$  a potential which is negative for values of  $r$  larger than a certain  $\sigma$  we have at last

$$Q_{2b} = 2V\pi\Lambda^{-6} \int_{\sigma}^{\infty} r^2 e^{-\phi(r)/kT} [\Gamma\{\frac{3}{2}, -\frac{\phi(r)}{kT}\} / \Gamma(\frac{3}{2})] dr \quad (3.12)$$

For the calculation of  $Q_{2m}$  we start again from (3.10). The term between braces is equal to the relative energy of the particles, divided by  $kT$ , so that

$$E = kT(P_{\theta}^2 + P_{\psi}^2) + kTP_r^2 + \phi(r) \quad (3.13a)$$

The centrifugal part of  $\phi_{\text{eff}}(r)$  (See(3.3)) is found to be

$$kT(P_{\theta}^2 + P_{\psi}^2) = Eb^2/r^2 \quad (3.13b)$$

As only the sum of the squares of  $P_{\theta}$  and  $P_{\psi}$  comes into play we may introduce a kind of polar coordinates instead of  $P_{\theta}$  and  $P_{\psi}$  for the integration, so that

$$\int dP_{\theta} dP_{\psi} = \frac{\pi}{kT} \int \frac{1}{r^2} d(Eb^2) \quad (3.13c)$$

Introducing (3.13a,b,c) into (3.10), substituting  $E$  for  $P_r$  with the help of (3.13a) and remembering that  $P_r$  may be negative and positive to give positive values of  $E$ , we find

$$Q_2 = 2V\pi^{1/2}(kT)^{-3/2}\Lambda^{-6} \int \{E - \phi(r) - Eb^2/r^2\}^{-1/2} e^{-E/kT} d(Eb^2) dr dE \quad (3.14)$$

The regions of integration must now be found. For  $E$  this is simple enough:  $E$  has to be larger than 0 - otherwise we would have a stable dimer - and less than  $E_c$ . For a fixed value of  $E$  only a certain range of values for  $Eb^2$  gives rise to metastable dimers as will be clear from fig.3.1. The limits for the integration over  $r$ , however, do depend on the value of  $Eb^2$ . At the turning points of motion of the two particles in each other's effective potential,  $r_f(E)$  and  $r_h(E)$ , the kinetic energy has to be equal to  $\phi_{\text{eff}}$ :

$$E = \phi(r) + Eb^2/r^2$$

or

$$Eb^2 = r^2 \{E - \phi(r)\}$$

This gives the integration area for the combined integrations over  $Eb^2$  and  $r$ . (3.14) may now be written as

$$Q_2 = Q_{2b} + Q_{2m} \quad (3.15)$$

$$Q_{2m} = 4V\pi^{1/2}(kT)^{-3/2}\Lambda^{-6} \int_0^{E_c} \int_{r_f(E)}^{r_h(E)} r^2 \{E - \phi(r) - Eb_f^2/r^2\}^{-1/2} e^{-E/kT} dr dE$$

where  $b_f(E)$  is the value of  $b$  for which the initial kinetic energy is equal to the height of the hump in  $\phi_{\text{eff}}$ .

The combination of (3.6b), (3.8), (3.12) and (3.15) gives in principle the possibility to calculate the dimer-concentration for a gas with a given potential and under given experimental conditions. Stogryn and Hirschfelder did calculate the integrals (3.12) and (3.15) for the square well, Sutherland and Lennard-Jones (6-12) potentials. Their results for the Lennard-Jones potential (which were obtained partly numerically) have been used in our calculations.

### c. THERMAL DIFFUSION IN MIXTURES CONTAINING ONE DIMER-FORMING COMPONENT

The formation of dimers, as discussed in the foregoing paragraphs, can be considered as a chemical reaction with equilibrium constant given in eq.(3.6b).  $K$  is only temperature dependent, the pressure dependence of  $x_2/x_1^2$  is contained in  $n$ . When we raise the pressure of a mixture of two gases in which one component is able to form dimers we have two effects that do influence the thermal diffusion in such a system :

1. The formation of dimers changes the mixture from a two-component to a three-component one.
2. The temperature dependence of  $K$  gives an other equilibrium value for the dimer-monomer ratio in the high-temperature part of a thermal-diffusion apparatus than in the low-temperature part. This gives an extra unmixing in the two-component system.

To work this out in detail we will make two assumptions :

- a. The chemical reaction (3.5) is fast compared with thermal diffusion so that local "chemical" equilibrium between  $A$  and  $A_2$  is established.
- b. Thermal diffusion and dimerisation do not have cross-effects. This follows from the Curie principle, as the dimerisation has a chemical and therefore a scalar character, whereas thermal diffusion is a vectorial phenomenon.

As a consequence of the first of the two effects, mentioned above we will have to use a formalism for thermal diffusion in ternary mixtures, for which we choose the formalism given by Van der Valk (Va 63) which is based on that of Waldmann (Wa 58).

The analysis of a thermal diffusion experiment is usually done at low pressures (e.g. in a mass-spectrometer) where the reaction (3.5) has gone completely to the left side. This means that we have to distinguish two kinds of mole fractions:  $x_1$ ,  $x_2$  and  $x_3$ , respectively the mole fractions of monomer, dimer and second component at the pressure of the experiment and  $\bar{x}_A$  and  $\bar{x}_B$ , the mole fractions of first (dimer-forming) and second component at low pressure. The relations between them are

$$\bar{x}_A = \frac{x_1 + 2x_2}{1 + x_2} \quad (3.16a)$$

$$\bar{x}_B = \frac{x_3}{1 + x_2} \quad (3.16b)$$

The experimentally obtained thermal diffusion factor is

$$\bar{\alpha}_{AB} = \frac{\text{grad } \bar{x}_B}{\bar{x}_A \bar{x}_B \text{ grad } \ln T} \quad (3.17)$$

We will see now how this thermal diffusion factor does depend on the amount of molecules A forming dimers.

First of all we will have to find a relation between the diffusion velocities or fluxes in the system. Because we have a reacting mixture we will have to distinguish different velocities because even in the equilibrium situation the mean particle velocities in the center of particles and in the laboratory system are not the same. Denoting the diffusion velocities in the laboratory system as  $\vec{v}_i$  and those in the center-of-particles system as  $\vec{w}_i$  we have the relation

$$\vec{w}_i = \vec{v}_i - \vec{w} ; i = 1, 2, 3 \quad (3.18)$$

where  $\vec{w}$  is the velocity of the center-of-particles with respect to the laboratory system. According to the definition of  $\vec{w}$  we may write

$$\vec{w} = \sum_i x_i \vec{v}_i \quad (3.19)$$

In the equilibrium situation we have as a consequence of the fact that the center of mass of both component A and component B is at rest :

1.  $\vec{v}_3 = 0$ ; this means that  $\vec{w} = -\vec{v}_3$
2.  $m_1 n_1 \vec{v}_1 + m_2 n_2 \vec{v}_2 = 0$ . Because  $m_2 = 2m_1$ , this gives, when we divide by the total particle concentration  $n$  and  $m_1$

$$x_1 \vec{v}_1 + 2x_2 \vec{v}_2 = 0 \quad (3.20)$$

Both results can also be derived by a way of reasoning based on the fact that the velocity of the center-of-particles of both components is zero. By subtracting (3.19) once from (3.20) and remembering that  $\vec{v}_3 = 0$

we find

$$x_2 \vec{v}_2 = - \vec{w} \quad (3.21a)$$

or, with the help of (3.18)

$$x_2 \vec{w}_2 - (1+x_2) \vec{w}_3 = 0 \quad (3.21b)$$

(3.21b) is the equation which forms the basis for our evaluation of the thermal diffusion factor in a gas mixture where dimers are formed.

In the notation of Waldmann (loc.cit.) we have

$$\vec{w}_i = - \sum_j D_{ij} \text{grad } x_j - D_{Ti} \text{grad } \ln T \quad (3.22)$$

where the  $D_{ij}$  are multicomponent diffusion coefficients and the  $D_{Ti}$  multicomponent thermal diffusion coefficients.

In this expression one of the concentration gradients can be eliminated by means of

$$\sum_i x_i = 1 \quad (3.23a)$$

or

$$\sum_i \text{grad } x_i = 0 \quad (3.23b)$$

so that

$$\vec{w}_2 = -(D_{12} - D_{23}) \text{grad } x_1 - (D_{22} - D_{23}) \text{grad } x_2 - D_{T2} \text{grad } \ln T \quad (3.24a)$$

$$\vec{w}_3 = -(D_{13} - D_{33}) \text{grad } x_1 - (D_{23} - D_{33}) \text{grad } x_2 - D_{T3} \text{grad } \ln T \quad (3.24b)$$

The relation between  $x_2$  and  $x_1$  given in (3.6b) gives the possibility to eliminate  $x_2$  by supposing that chemical equilibrium is established. From this equation we find

$$x_2 = (nK) x_1^2 \quad (3.25a)$$

so that

$$\text{grad } x_2 = x_1^2 \text{grad}(nK) + 2x_1(nK)\text{grad } x_1$$

As  $nK$  is dependent on pressure and reduced temperature only while the pressure is constant throughout the apparatus we may substitute  $\text{grad}(nK)$  by an expression in which the gradient of  $T$  or  $\ln T$  appears as the only gradient.

Introducing a quantity  $\lambda$  by means of

$$\lambda = \frac{x_2}{x_1} = (nK)x_1 \quad (3.25b)$$

we see that

$$\text{grad } x_2 = x_2(nK)'T\text{grad } \ln T + 2\lambda\text{grad } x_1 \quad (3.26)$$

where the prime denotes the derivative to  $T$ .

When (3.24a) and (3.24b) are combined in (3.21b) the thermal diffusion coefficients are combined as

$$-x_2 D_{T2} + (1+x_2) D_{T3}$$

The  $D_{Tk}$  can be expressed in formal multicomponent thermal diffusion factors in the way as given by Van der Valk (Va 63) :

$$D_{Tk} = \sum_{i,j} D_{kj} x_i x_j \alpha_{ij} \quad (3.27)$$



The combination of (3.21b), (3.24a), (3.24b) and (3.26) gives us an equation in which the only gradients are those of  $x_1$  and  $\ln T$  :

$$\begin{aligned} & [ \{-x_2(D_{12}-D_{23})+(1+x_2)(D_{13}-D_{33})\} + 2\lambda \{-x_2(D_{22}-D_{23})+(1+x_2)(D_{23}-D_{33})\} ] \text{grad } x_1 + \\ & + [ x_1^2(nK)'T \{-x_2(D_{22}-D_{23})+(1+x_2)(D_{23}-D_{33})\} - x_2 D_{T2} + (1+x_2) D_{T3} ] \text{grad } \ln T = 0 \quad (3.28) \end{aligned}$$

$D_{T2}$  and  $D_{T3}$  can be eliminated by means of (3.27).

To find an expression for the right side of (3.17) we have to find a relation between  $\text{grad } x_1$  and  $\text{grad } \bar{x}_B$ . This is done by using the inverse formulae of (3.16a) and (3.16b), found with these formulae and (3.25b) :

$$x_1 = \frac{\bar{x}_A}{1+\lambda+\lambda\bar{x}_B} \quad ; \quad x_2 = \frac{\lambda\bar{x}_A}{1+\lambda+\lambda\bar{x}_B} \quad ; \quad x_3 = \frac{(1+2\lambda)\bar{x}_B}{1+\lambda+\lambda\bar{x}_B} \quad (3.29)$$

The first of these equations gives (remembering that  $\bar{x}_A + \bar{x}_B = 1$ , so that  $\text{grad } \bar{x}_A = -\text{grad } \bar{x}_B$ ) :

$$-(1+\lambda x_1)^2 \text{grad } \bar{x}_B = (1+2\lambda) \text{grad } x_1 + x_1(2-x_1) \text{grad } \lambda$$

$\text{grad } \lambda$  is found from the second expression for  $\lambda$  in (3.25b) as

$$\text{grad } \lambda = x_1(nK)'T \text{grad } \ln T + (nK) \text{grad } x_1$$

so that

$$-(1+\lambda x_1)^2 \text{grad } \bar{x}_B = (1+4\lambda-2x_1^2) \text{grad } x_1 + (2-x_1)x_1^2(nK)'T \text{grad } \ln T \quad (3.30)$$

Combination of (3.28) and (3.30) would give an expression in which  $\text{grad } \bar{x}_B$  and  $\text{grad } \ln T$  are the only gradients. Before writing it down we will make two more changes. First we replace the  $x_i$  by  $\bar{x}_A$  and  $\bar{x}_B$  according to (3.29) because we know from the experimental conditions the values of these quantities and not of the  $x_i$ . In the second place we substitute the multi-

component  $D_{ij}$  by the binary diffusion coefficients  $D(i,j)$ . This is done by the method given by Waldmann, which is valid up to the first Chapman-Enskog approximation. The general formula for this substitution is

$$\sum_j \frac{x_j (D_{ik} - D_{jk})}{D(i,j)} = \frac{\delta_{ik}}{x_i} - 1 \quad (3.31)$$

from which explicit expressions can be found for the differences of two multicomponent diffusion coefficients. Doing this for the three-component mixture we have at hand, making use of (3.27) and substituting the  $x_i$  by  $\bar{x}_A$  and  $\bar{x}_B$ , we find from (3.30) and (3.28) the following expression for  $\bar{x}_{AB}$ :

$$\begin{aligned} \bar{\alpha}_{BA} = -\bar{\alpha}_{AB} = & \left[ \{\bar{x}_A D(1,3)D(2,3) - 2D(1,2)D(2,3) + (1+\bar{x}_B)D(1,2)D(1,3)\} \bar{x}_A (nK)^{-1} T - \right. \\ & - (1+2\lambda+2\lambda\bar{x}_B) \{D(1,3) - 2D(2,3)\} \lambda \alpha_{12} \bar{x}_A D(1,2) + \\ & + (1+2\lambda) \bar{x}_A D(1,3)D(2,3) (\alpha_{13} - \lambda \alpha_{23}) + \\ & \left. + (1+2\lambda) \bar{x}_B D(1,2) \{ \alpha_{13} D(1,3) + 2\lambda \alpha_{23} D(2,3) \} \right] \\ & \left[ (1+2\lambda)(1+\lambda+\lambda\bar{x}_B) \{ (1+2\lambda) \bar{x}_A D(1,3)D(2,3) + \bar{x}_B D(1,2)D(1,3) + \right. \\ & \left. + 4\lambda \bar{x}_B D(1,2)D(2,3) \} \right]^{-1} \quad (3.32) \end{aligned}$$

To find  $\lambda$  it is not necessary to know  $x_2$  and  $x_1$ : from (3.25b) and (3.29) it is easily found that

$$\lambda = \{-1 + \sqrt{1 + 4(nK)(1 - \bar{x}_B^2)}\} / \{2(1 + \bar{x}_B)\} \quad (3.33)$$

We calculate the ternary thermal diffusion factors  $\alpha_{ij}$  (the  $\alpha$ 's are ternary, the  $\bar{\alpha}$ 's binary quantities) with the formulae given by Van der Valk (loc.cit. formulae (13), (14), (16), (17) and (18) and the binary diffusion coefficients in the first Chapman-Cowling approximation.

$\lambda$  is calculated from (3.20); for this we use the value of  $\bar{x}_A$ , known

from the low-pressure analysis, the value of  $K$  according to Stogryn and Hirschfelder and a value of  $n$  which was found by applying the ideal gas law to a ternary mixture. For the mean temperature of the experiment we used the geometric mean of the temperatures of the two bulbs of the apparatus; a control calculation where the value of  $\alpha$  thus obtained was used to find the concentrations at various points in the diffusion tube and using these values to find a second approximation showed that this supposition was good enough for our purposes: on a thermal diffusion factor of about 0.4 the second order correction was 0.004 i.e. 1%.

The numerator of (3.32) may be split into two groups: the one that is multiplied with  $\bar{x}_A(nK)'T$  and the one that is multiplied with  $(1+2\lambda+2\lambda\bar{x}_B)$ . The first one gives a contribution due to the fact that  $nK$  is temperature dependent, whereas the second one gives the change in  $\alpha$  due to the mere presence of a third component.

#### d. THERMAL DIFFUSION IN MIXTURES WHERE BOTH COMPONENTS MAY FORM DIMERS

Again we consider a mixture of two gases A and B, but now both components may form dimers. A third kind of dimer will be present then, namely a dimer formed from one molecule of component A and one of component B. We will refer to this kind of dimer as a mixed or hetero-molecular dimer. The dimers consisting of two similar molecules will be indicated as homo-molecular.

Supposing, as in part c. of this chapter, that the analysis of a thermal diffusion experiment takes place at low pressure where all dimers have changed into two monomers we have as our experimentally determined thermal diffusion factor

$$\bar{\alpha}_{AB} = \frac{\text{grad } \bar{x}_B}{\bar{x}_A \bar{x}_B \text{ grad } \ln T} = \frac{-\text{grad } \bar{x}_A}{\bar{x}_A \bar{x}_B \text{ grad } \ln T} \quad (3.34)$$

where  $\bar{x}_A$  and  $\bar{x}_B$  denote the mole fractions during the analysis i.e. at low pressure.

For the five components of the mixture present during the experiment

we will use the following notation :

suffix 1 : monomer A

suffix 2 : dimer  $A_2$

suffix 3 : dimer AB

suffix 4 : dimer  $B_2$

suffix 5 : monomer B

The rest of the notation and the reference system will be along the same lines as in part c. of this chapter. We now have three reactions :



(3.35a) and (3.35c) have equilibrium constants

$$K_2 = \frac{x_2}{x_1^2 n} \quad (3.36a)$$

$$K_4 = \frac{x_4}{x_5^2 n} \quad (3.36c)$$

just as in (3.6b). For mixed dimers a corresponding formula applies

(St 59) :

$$K_3 = \frac{x_3}{x_1 x_5 n} \quad (3.36b)$$

We have to keep in mind that, for the case of equal a priori probabilities for the formation of dimers, the concentration of homo-molecular dimers is proportional to  $x_1^2$  or  $x_5^2$ , whereas the concentration of hetero-molecular dimers is proportional to  $2x_1 x_5$  if we use the same proportionality constant. As in part c. we will use a notation for mole ratios :

$$\lambda_2 = \frac{x_2}{x_1} \quad ; \quad \lambda_4 = \frac{x_4}{x_5} \quad ; \quad \lambda_{31} = \frac{x_3}{x_1} \quad ; \quad \lambda_{35} = \frac{x_3}{x_5} \quad (3.37)$$

First we will try to find an expression comparable to (3.21b). We will proceed along the same lines as used there. (3.18) and (3.19) stay valid with  $i = 1, 2, 3, 4, 5$ . As in the equilibrium situation the center of mass of component A is at rest it is clear that for the diffusion velocities in the laboratory system the following relation must hold

$$n_1 m_1 \vec{v}_1 + n_2 m_2 \vec{v}_2 + \frac{m_1}{m_3} n_3 m_3 \vec{v}_3 = 0$$

As  $m_2 = 2m_1$ , this is equivalent to

$$x_1 \vec{v}_1 + 2x_2 \vec{v}_2 + x_3 \vec{v}_3 = 0 \quad (3.38)$$

where we have divided by  $n$ , the total number of molecules. The same expression is found when we start from the center of particles of component A being at rest. From (3.19) written down for five components we find with (3.38)

$$x_1 \vec{v}_1 + x_5 \vec{v}_5 = 2\vec{w}$$

Using (3.18) we can derive from the last expression a relation between  $\vec{w}$ ,  $\vec{w}_1$ ,  $\vec{w}_5$  and the  $x_i$  which, when introduced in (3.38) after substitution of the  $\vec{v}_i$  by the  $\vec{w}_i$  and  $\vec{w}$  gives the following result :

$$-x_1(x_1+2x_2+x_3)\vec{w}_1 - x_2(2-x_1-x_5)\vec{w}_2 + x_4(2-x_1-x_5)\vec{w}_4 + x_5(x_3+2x_4+x_5)\vec{w}_5 = 0 \quad (3.39)$$

In the derivation of (3.39) we have used also (3.23a) written down for five components. (3.39) is the parallel formula of (3.21b) in the simple case; putting  $x_3$  and  $x_4$  equal to zero gives (3.21b) from (3.39).

In (3.39) we substitute the  $\vec{w}_i$  by the expressions used by Waldmann and given in (3.22); next we eliminate  $\text{grad } x_3$  by means of (3.23b). The  $D_{Ti}$

are substituted by multicomponent diffusion coefficients and multicomponent thermal diffusion factors with the help of (3.27). Introducing a new function

$$DS_{ij} = -x_1(x_1+2x_2+x_3)(D_{1i}-D_{1j})-x_2(2-x_1-x_5)(D_{2i}-D_{2j})+ \\ +x_4(2-x_1-x_5)(D_{4i}-D_{4j})+x_5(x_5+2x_4+x_3)(D_{5i}-D_{5j}) \quad (3.40)$$

which has the properties

$$DS_{ij} = -DS_{ji} \quad ; \quad DS_{ii} = 0 \quad (3.41a)$$

$$DS_{ij} + DS_{jk} = DS_{ik} \quad (3.41b)$$

it is a matter of some calculations to show that using (3.36) and (3.37) we can write (3.39) in the following form

$$(DS_{13}+2\lambda_2 DS_{23})\text{grad } x_1 + (DS_{53}+2\lambda_4 DS_{43})\text{grad } x_5 + \\ +\{x_1^2(nK_2)'\text{T } DS_{23}+x_5^2(nK_4)'\text{T } DS_{43}+\frac{1}{2} \sum_{j,k} DS_{jk} x_j x_k \alpha_{jk}\}\text{grad } \ln T = 0 \quad (3.42)$$

where the primes denote the derivative with respect to T.

As we have to find a relation between a concentration gradient and a gradient of the temperature we have to eliminate one of the concentration gradients for which we choose grad  $x_5$ . The procedure to do this uses (3.23b) with (3.36) substituted into it. The result is

$$(1+2\lambda_2+\lambda_{3i})\text{grad } x_1+(1+2\lambda_4+\lambda_{35})\text{grad } x_5+ \\ +\{x_1^2(nK_2)'+x_1x_5(nK_3)'+x_5^2(nK_4)'\}\text{T grad } \ln T = 0 \quad (3.43a)$$

or, with a kind of shorthand notation

$$\text{grad } x_5 = -\frac{a_1}{a_5} \text{grad } x_1 - \frac{a_T}{a_5} \text{T grad } \ln T \quad (3.43b)$$

Introducing (3.43b) into (3.42) we find

$$\begin{aligned} & \{DS_{13} + 2\lambda_2 DS_{23} + \frac{a_1}{a_5} DS_{35} + 2\lambda_4 \frac{a_1}{a_5} DS_{34}\} \text{grad } x_1 + \left\{ \frac{a_T}{a_5} T DS_{35} + 2\lambda_4 \frac{a_T}{a_5} T DS_{34} + \right. \\ & \left. + x_1^2 (nK_2)' T DS_{23} - x_5^2 (nK_4)' T DS_{34} + \frac{1}{2} \sum_{j,k} DS_{jk} x_j x_k \alpha_{jk} \right\} \text{grad } \ln T = \\ & A_{11} \text{grad } x_1 + A_{T1} \text{grad } \ln T = 0 \end{aligned} \quad (3.44)$$

From (3.44) we find the ratio of grad  $x_1$  and grad  $\ln T$ . We have to find however the ratio of grad  $\bar{x}_A$  and grad  $\ln T$ . To do this we use the equation that links  $\bar{x}_A$  and the  $x_i$

$$\bar{x}_A = \frac{x_1 + 2x_2 + x_3}{1 + x_2 + x_3 + x_4} = \frac{1 + 2(nK_2)x_1^2 + (nK_3)x_1x_5}{1 + (nK_2)x_1^2 + (nK_3)x_1x_5 + (nK_4)x_5^2} \quad (3.45a)$$

Taking the gradient of  $\bar{x}_A$  from this expression and remembering that the gradient of  $(nK_i)$  is dependent only on  $T$ , as the pressure is constant throughout the apparatus we find that

$$\begin{aligned} \text{grad } \bar{x}_A &= \left[ \left\{ (a_1 + 2\lambda_4 a_1 + 2\lambda_2 a_5)(2 - x_1 - x_5) + a_1 x_1 (a_5 - a_1) \right\} \text{grad } x_1 + \right. \\ & \left. + (2 - x_1 - x_5) \left\{ 2a_5 x_1^2 (nK_2)' + a_5 x_1 x_5 (nK_3)' - a_T \lambda_{35} \right\} - a_1 - a_1 x_1 \right] T \text{grad } \ln T \\ & \left\{ a_5 (2 - x_1 - x_5)^2 \right\}^{-1} \\ &= \frac{A_{12}}{A_5} \text{grad } x_1 + \frac{A_{T2}}{A_5} T \text{grad } \ln T \end{aligned} \quad (3.46)$$

From (3.46) and (3.44) we find an expression for (3.34) :

$$\bar{\alpha}_{AB} = \frac{A_{12} A_{T1} - A_{11} A_{T2} T}{\bar{x}_A \bar{x}_B A_5 A_{11}} \quad (3.47)$$

To evaluate the coefficients in (3.47) we have to find the concentrations  $x_i$  during the experiment from the experimentally measured  $\bar{x}_A$  and  $\bar{x}_B$ . To do this we use (3.23a) and (3.45a) and its parallel expression

$$\bar{x}_B = \frac{x_5 + 2(nK_4)x_5^2 + (nK_3)x_1x_5}{1 + (nK_2)x_1^2 + (nK_3)x_1x_5 + (nK_4)x_5^2} \quad (3.45b)$$

Taking twice (3.23a) and using the ratio of  $\bar{x}_A$  and  $\bar{x}_B$  from (3.45) we have

$$x_1 + x_5 + \left(1 + \frac{\bar{x}_A}{\bar{x}_B}\right) \{x_5 + 2(nK_4)x_5^2 + (nK_3)x_1x_5\} = 2 \quad (3.48)$$

From this equation we find  $x_1$  expressed in  $x_5$ ,  $\bar{x}_B$  and the  $(nK_i)$ ; inserting this expression in (3.23a) we find a fourth order equation for  $x_5$ :

$$\begin{aligned} & (nK_4) \{4(nK_2)(nK_4) - (nK_3)^2\} x_5^4 + \\ & + \{2(nK_4) \{2(nK_2) - (nK_3)\} + \bar{x}_B \{4(nK_2)(nK_4) - (nK_3)^2\}\} x_5^3 + \\ & + \{(nK_4)\bar{x}_B(\bar{x}_B - 2) + (nK_2)(1 + \bar{x}_B)^2 - (nK_3)(1 + \bar{x}_B^2) + (nK_3)^2(2\bar{x}_B - 1) - 8(nK_2)(nK_4)\bar{x}_B\} x_5^2 - \\ & - \{\bar{x}_B \{1 + 4(nK_2)\} + \bar{x}_B^2 \{2(nK_2) - (nK_3)\}\} x_5 + \bar{x}_B^2 \{1 + 4(nK_2)\} = 0 \end{aligned} \quad (3.49)$$

From this equation we find  $x_5$ , from (3.48) and from (3.36)  $x_2$ ,  $x_3$  and  $x_4$ . From the complicated expressions it will be clear that no closed final formula can be given in this case: (3.34) can be calculated with the help of (3.47), (3.44), (3.46), (3.43) and (3.49);  $\bar{x}_B$  and  $T$  are experimental parameters whereas the  $(nK_i)$  and  $(nK_i)'$  may be found f.i. from the work of Stogryn and Hirschfelder. The calculation of the  $D_{ij}$  and  $\alpha_{ij}$  is postponed until chapter V.



## CHAPTER IV

### EXPERIMENTS

#### a. APPARATUS AND PROCEDURE

The apparatus used for our experiments was the two-bulb apparatus used by Velds (Ve 66) with some minor changes. (fig.4.1)

Thermal diffusion takes place between the reservoirs  $V_1$  and  $V_2$ , the hotter one at the top to avoid convection between these two bulbs. As, for some earlier experiments, an ionization chamber analysis of the contents of the upper volume was needed, this volume was divided into two parts, connected by two tubes. The upper space was kept on room temperature because of the ionization chamber analysis; the real high temperature part  $V_2$  was welded together and thermally isolated from the rest of the apparatus by the oil-cooled flanges F and W. To avoid thermal diffusion between  $V_2$  and I, the gas was flushed continuously from  $V_2$  to I and back through the by-pass B. This flushing was accomplished by convective action when the temperature difference between  $V_2$  and I was big enough; for lower temperatures of  $V_2$  a heater around B maintained a flow by means of thermo-syphon action.

By means of E and S samples could be taken for analysis; the apparatus could be evacuated and filled through S.

The pressure in the apparatus was measured with a bourdon-manometer. The temperature of O was kept constant and measured by means of a photo-transistor regulator (made by Nieaf, Utrecht, Holland), acting on the thermocouple T.

Only one of the heating elements was switched on and off; the other elements were used only during the first heating period. The lower part of the apparatus (from F downward) was placed in a thermostatted space. Here the thermostate consisted of a contact thermometer, blower and heater. The temperature was controlled with an accuracy of about one degree centigrade in this part. During the course of our experiments the temperature was kept on  $36 \pm 1$  °C.

A typical run started with the evacuation of the apparatus through S, after which the component of the mixture that was to have the lowest concentration was admitted through a valve at S. When the pressure of this gas had reached the desired value, this valve was closed and the filling system at

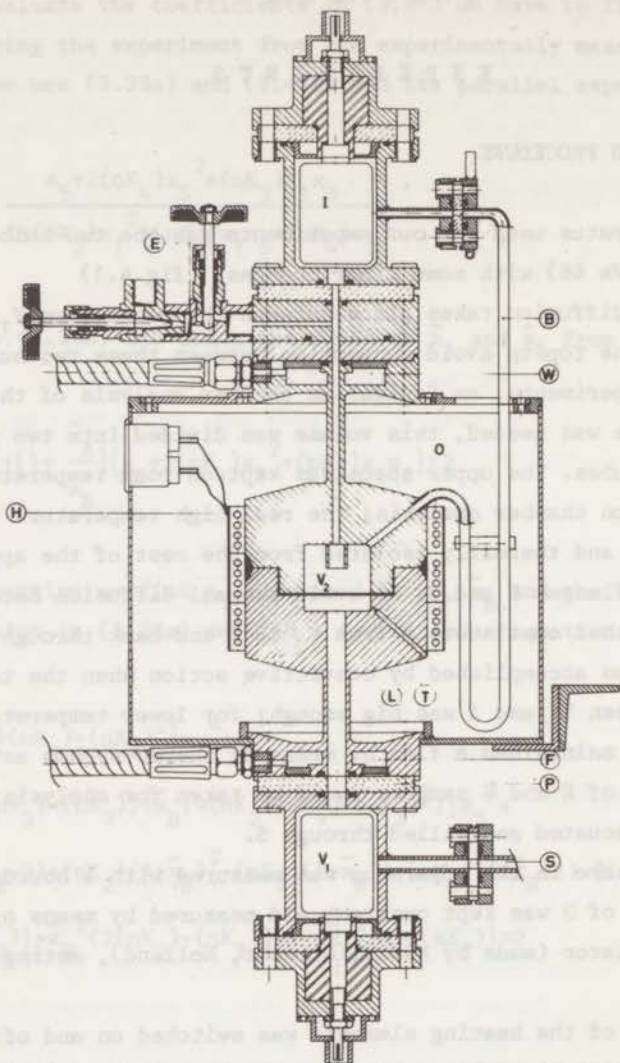


Fig. 4.1

The two-bulb apparatus.

- |   |                  |   |                 |                |                 |
|---|------------------|---|-----------------|----------------|-----------------|
| B | by-pass          | L | connecting tube | V <sub>1</sub> | lower reservoir |
| E | expansion volume | O | oven            | V <sub>2</sub> | hot reservoir   |
| F | cooled flange    | S | side tube       | I              | upper reservoir |
| H | heating elements | T | thermocouple    | W              | cooled flange   |

the back of it depressurized and evacuated. After that the second component was allowed to enter, until the manometer indicated the desired total pressure. The admittance of the second component gave rise to a turbulency that assured a mixing of the components.

After the filling procedure the system was left apart for at least seven times the relaxation time  $t_r$ ; this is the time needed to reach the final concentration gradient to within 1%. An estimate of  $t_r$  was inferred from an article of Saxena and Mason (Sa 59) :

$$t_r = \frac{L}{A} \left( \frac{T_1}{V_1} + \frac{T_2}{V_2} \right)^{-1} \left\langle \frac{T}{D} \right\rangle_{Av}$$

in which L is the length and A the cross-sectional area of the connecting tube between  $V_1$  and  $V_2$ .  $T_1$  and  $T_2$  are the temperatures of resp.  $V_1$  and  $V_2$ ; in our situation  $V_2$  is the volume of  $V_2$  and I, as the gas is flushing through both volumes.  $\langle T/D \rangle_{Av}$  is the average value of the quotient of temperature and diffusion coefficient along the thermal diffusion path. The validity of this formula was checked by taking samples after times longer than  $7 \cdot t_r$ ; no difference with the samples taken after  $7 \cdot t_r$  were found that exceeded the experimental error, which shows that the formula gives at least an upper limit. The value of  $t_r$  is about proportional to the pressure. For Kr-CO<sub>2</sub> mixtures at 50 atm with  $T_1 = 36^\circ\text{C}$  and  $T_2 = 260^\circ\text{C}$  we calculated for  $7 \cdot t_r$  15 days. Smaller temperature intervals would make  $t_r$  longer, due to the fact that the binary diffusion coefficient depends on T with a power that is roughly 1.5.

When the final separation has been attained with sufficient accuracy samples are taken at S and E to give the concentration ratios in the low and in the high temperature part of the apparatus. The analysis of the samples was carried out in a mass-spectrometer (Atlas, model CH4) except for the nitrogen-ethane samples. Mass-spectrometric analysis was not possible here because of the almost equal masses of the N<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> molecules. Here the analysis was performed with the apparatuses given schematically in fig.4.2a and 4.2b.

The procedure for an analysis with the apparatus of fig.4.2a is as follows: a certain amount of the sample S is introduced into the liquid nitrogen cooled trap K and circulated by means of the Töppler pump T through

a closed system. Each time the gas passes K the  $C_2H_4$  remaining in the sample may be frozen to the wall. After this procedure has been ended the  $N_2$  is introduced into the constant volume manometer and measured. After the  $N_2$  has been pumped off the  $C_2H_4$  is allowed to evaporate again, introduced into the constant volume manometer and measured separately. From the two measurements the composition of the sample is derived.

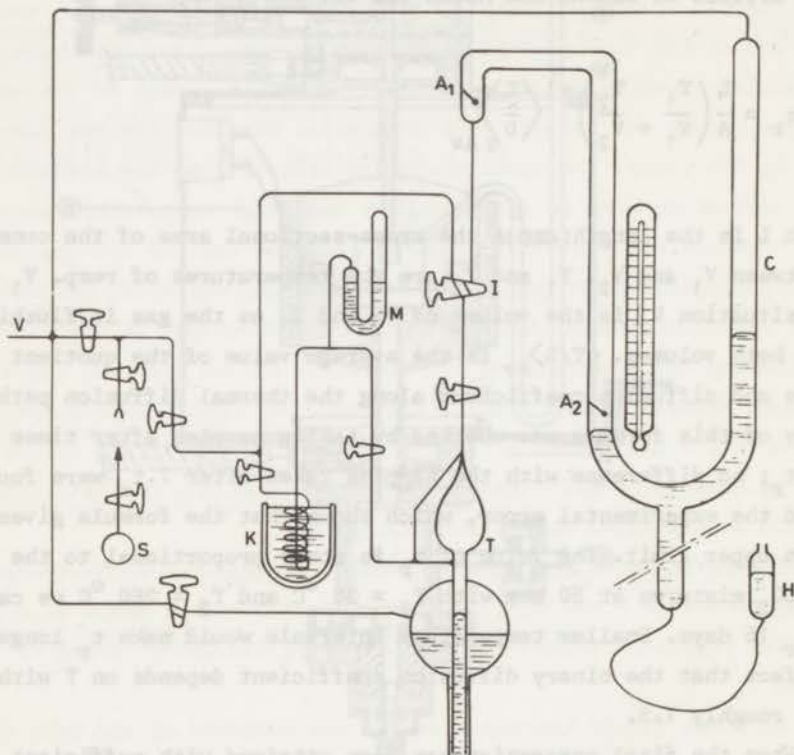


Fig. 4.2a

Apparatus for the analysis of  $N_2-C_2H_4$  mixtures by means of a constant volume manometer.

- |   |                             |            |                           |
|---|-----------------------------|------------|---------------------------|
| V | vacuum system               | C          | constant volume manometer |
| S | sample                      | $A_1, A_2$ | indication needles        |
| K | liquid nitrogen cooled trap | H          | mercury reservoir         |
| M | mercury manometer           | T          | thermometer               |
| P | Töppler pump                | I          | valve                     |

For the mixtures containing much  $C_2H_4$  the reproducibility was good enough to obtain an experimental error of about 1%. The mixtures containing much  $N_2$  however showed a pretty bad reproducibility, due to unknown causes. Therefore we devised another method, using a precision pressure gauge. This instrument (made by Texas Instruments Inc., Houston, Texas, U.S.A.) consists of a fused quartz bourdon-tube in a vacuum-sealed housing. The difference in pressure between the housing (reference pressure) and the inside of the bourdon-tube is found by measuring the torque of the bourdon-tube with an electro-optical system. The calibrated absolute accuracy of this instrument is 0.05 Torr in the 25 to 376 Torr region, 0.008 Torr for lower pressures; errors due to temperature sensitivity and resolution are less than 0.01% under the experimental conditions.

The rest of the unit used for the analysis is shown in fig.4.2b.

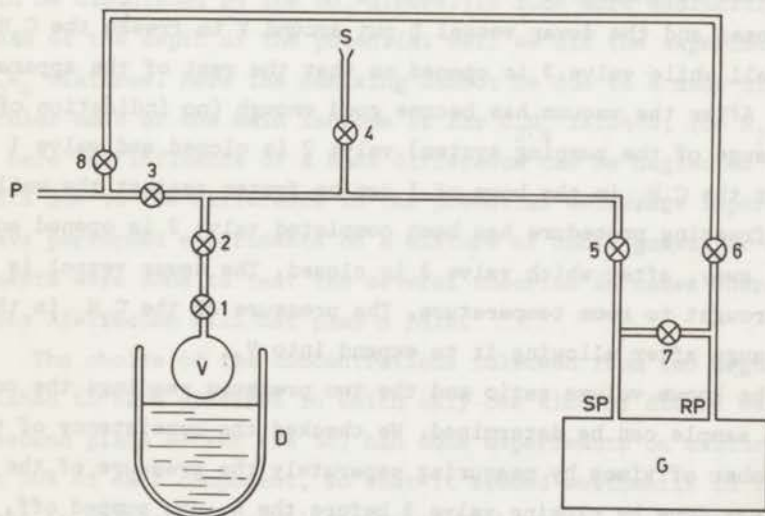


Fig. 4.2b

Apparatus for the analysis of  $N_2-C_2H_4$  mixtures with a quartz precision gauge.

- |   |                 |     |                                  |
|---|-----------------|-----|----------------------------------|
| P | pumping system  | G   | pressure gauge                   |
| V | freezing volume | SP  | sample port of pressure gauge    |
| S | sample inlet    | RP  | reference port of pressure gauge |
| D | dewar vessel    | 1-8 | valves                           |

At S the sample is introduced, P goes to the vacuum system; SP and RP are the sample port and the reference port of the pressure gauge; V is a glass bulb. The pressure at RP is kept zero; throughout the analysis RP is connected with the pumping system by way of valves 6 and 8.

As we need to know the ratio of volume V plus the bore of stopcock 1 to the total volume, bounded by valves 3, 4 and 7 and the bourdon-tube of the pressure gauge we introduce a certain amount of gas in the last mentioned volume, measure the pressure, close valve 1, pump off through valve 3, close this valve, open valve 1 and measure the pressure again. The ratio of the pressures gives the ratio of the volumes; it was found as  $0.45385 \pm 0.0018$ .

The analysis now proceeds along the following lines. A certain amount of the sample is introduced into the volume bounded by valves 3, 4 and 7 (which will be indicated as  $V_1$ ) and the pressure is read. Then valve 1 is closed and the dewar vessel D put around V to freeze the  $C_2H_4$  against the wall while valve 3 is opened so that the rest of the apparatus is evacuated. After the vacuum has become good enough (no indication of gas on a McLeod gauge of the pumping system) valve 2 is closed and valve 1 opened so that the  $C_2H_4$  in the bore of 1 can be frozen against the wall of V. After the freezing procedure has been completed valve 2 is opened and the  $N_2$  pumped away, after which valve 3 is closed. The dewar vessel is removed and V brought to room temperature. The pressure of the  $C_2H_4$  is then read on the gauge after allowing it to expand into  $V_1$ .

From the known volume ratio and the two pressure readings the composition of the sample can be determined. We checked the consistency of the analysis a number of times by measuring separately the pressure of the nitrogen. This was done by closing valve 3 before the  $N_2$  was pumped off, allowing the nitrogen to expand into  $V_1$  while the ethane stayed frozen and measuring the pressure of the  $N_2$ . After correction for the temperature and the volume the amounts of  $C_2H_4$  and  $N_2$  added up to the measured total amount of gas to within one percent.

This method of analysis not only was much faster than the one with the constant volume manometer, but the accuracy too had improved greatly: the experimental scatter in the analysis of one sample was now well below one percent, so that all later analyses of  $N_2$ - $C_2H_4$  samples were done by this method.

## b. EXPERIMENTS PERFORMED AND RESULTS

The mixtures on which we did our experiments were chosen for a number of different reasons. The Ar-CO<sub>2</sub> mixture was chosen to see if the regularities observed by Velds (Ve 67) in He-CO<sub>2</sub> mixtures were also present in an other noble gas-CO<sub>2</sub> mixture. The fact of the near to equal masses of the constituent gases made them interesting from the point of view of the dimer-theory; if dimers had an appreciable influence their relative effect had to be larger in the case of Ar-CO<sub>2</sub> than in the one of He-CO<sub>2</sub>, provided that only the CO<sub>2</sub> molecules were forming dimers. In the He-CO<sub>2</sub> case CO<sub>2</sub> was already much heavier than He, so that the extra mass of (CO<sub>2</sub>)<sub>2</sub> could be expected to be less important than in the Ar-CO<sub>2</sub> case. For the same reason we used the Kr-CO<sub>2</sub> mixture, be it that here the mean relative mass-difference should be diminished by the CO<sub>2</sub>-dimers. To look more explicitly to the influence of the depth of the potential well we did the experiments on N<sub>2</sub>-C<sub>2</sub>H<sub>4</sub> mixtures. Here the demixing cannot be due to a mass-difference (the molecular mass of the main isotope is for C<sub>2</sub>H<sub>4</sub> 28.0403, for N<sub>2</sub> 28.0151) so that here the influence of a mass difference can be neglected and only the effects due to the difference in the potential wells are important. Finally we have performed experiments on a mixture of noble gases: Ar-He. These experiments were done to test the several theories in cases where the internal degrees of freedom will not play a rôle.

The choice of the concentrations followed from two arguments: first we wished to have mixtures in which only one kind of dimers was formed, in the second place Becker (Be 50) had done experiments on mixtures containing about 50% of each component, so that it seemed worthwhile to take the other extreme in view of the small amount of high-pressure thermal diffusion factors that have been measured. Although our first argument did not hold, as we found out later, the choice of the concentrations gave us a clear picture of the concentration dependence of the high-pressure effects.

The errors given in the tables are the errors indicating the spread in the measured values. To this error the systematic ones inherent to the measuring apparatuses should be added. These errors (e.g. calibration errors) are believed to be in general an order of magnitude smaller than the spread in the measured values of  $\alpha$ .

1. CO<sub>2</sub>-Ar

We performed experiments at 5 and at 50 atmospheres, with the upper volume at a temperature of about 260 °C. Two mixtures were used: one with 90% CO<sub>2</sub> (10% Ar) and one with 10% CO<sub>2</sub> (90% Ar). As the potential well for CO<sub>2</sub> is deeper than the one of Ar, we expected the biggest effect of a change of pressure in the mixture containing much CO<sub>2</sub>. To the experiments for this

TABLE 4.1

Experimental values of the separation factor  $q$  and the thermal diffusion factor  $\alpha$  for mixtures containing CO<sub>2</sub> and Ar. Temperature lower volume 308 °K, temperature upper volume 535 °K. A bar denotes an average value.

p in atm.	% CO <sub>2</sub>	$q$	$\bar{q}$	$\ln \bar{q}$	$\bar{\alpha}$
5	90	1.014			
5	90	1.012	1.014±0.001	0.014±0.001	0.026±0.002
5	90	1.016			
20	90	1.047			
20	90	1.048	1.048±0.0003	0.047±0.0003	0.086±0.001
20	90	1.048			
50	90	1.104			
50	90	1.106	1.104±0.001	0.099±0.001	0.181±0.002
50	90	1.103			
5	10	1.014			
5	10	1.015			
5	10	1.016	1.015±0.0005	0.015±0.0005	0.027±0.001
5	10	1.014			
5	10	1.016			
50	10	1.042			
50	10	1.024	1.035±0.004	0.034±0.004	0.062±0.007
50	10	1.037			
50	10	1.038			



mixture we later added measurements at 20 atm as it was clear from the results of the 5 and 50 atm experiments that the value of the separation at 20 atm could be expected to lie outside the limit of error of those at 5 and 50 atm. The analyses were done mass-spectrometrically; the results of the experiments are given in table 4.1.

## 2. Kr-CO<sub>2</sub>

The Kr-CO<sub>2</sub> experiments were done at 5, 20 and 50 atm. Only a 10% Kr-90% CO<sub>2</sub> mixture was used, as there was no special interesting point in a 10% CO<sub>2</sub>-90% Kr mixture, that would justify the pretty costly experiment. The temperature of V<sub>2</sub> was 255 °C; analyses were performed on the mass-spectrometer. Table 4.2 gives the results of these experiments.

TABLE 4.2

Experimental values of the separation factor  $q$  and the thermal diffusion factor  $\alpha$  for a mixture containing 10% Kr and 90% CO<sub>2</sub>. Temperature lower volume 308 °K, temperature upper volume 535 °K. A bar denotes an average value.

p in atm.	$q$	$\bar{q}$	$\ln \bar{q}$	$\bar{\alpha}$
5	1.015			
5	1.021	1.018±0.002	0.018±0.002	0.033±0.004
5	1.020			
5	1.014			
20	1.000			
20	0.998	1.000±0.001	0.000±0.001	0.000±0.002
20	1.001			
50	0.967			
50	0.970	0.966±0.001	-0.034±0.001	-0.063±0.002
50	0.966			
50	0.962			
50	0.967			
50	0.967			

3.  $C_2H_4-N_2$ 

Experiments were done at 5, 20 and 50 atm on a mixture containing 10%  $N_2$  and 90%  $C_2H_4$  and at 5 and 50 atm on a mixture containing 10%  $C_2H_4$  and 90%  $N_2$ . The temperature of  $V_2$  for all experiments was 255 °C. The ex-

TABLE 4.3

Experimental values of the separation factor  $q$  and the thermal diffusion factor  $\alpha$  for mixtures containing  $C_2H_4$  and  $N_2$ . Temperature lower volume 308 °K, temperature upper volume 535 °K. A bar denotes an average value.

p in atm.	% $C_2H_4$	$q$	$\bar{q}$	$\ln \bar{q}$	$\bar{\alpha}$
5	90	1.049			
5	90	1.036	1.039±0.007	0.038±0.007	0.069±0.013
5	90	1.052			
5	90	1.020			
20	90	1.062			
20	90	1.055	1.056±0.001	0.054±0.001	0.097±0.002
20	90	1.052			
50	90	1.122			
50	90	1.153			
50	90	1.207	1.171±0.012	0.157±0.010	0.29 ±0.02
50	90	1.194			
50	90	1.179			
50	90	1.171			
5	10	1.004			
5	10	1.022	1.014±0.004	0.014±0.004	0.026±0.008
5	10	1.017			
5	10	1.012			
50	10	1.033			
50	10	1.039	1.041±0.003	0.040±0.003	0.074±0.006
50	10	1.049			
50	10	1.043			

periment at 20 atm was not done with the last mentioned mixture as here the effect of pressure on the thermal diffusion factor was pretty small. Analyses were performed with the apparatuses of fig.5.2a and 5.2b. The results are given in table 4.3.

#### 4. Ar-He

The experiments were done at 5 and 50 atm, both with the 10% Ar-90% He and the 90% Ar-10% He mixture. The analyses were performed mass-spectrometrically. The results are given in table 4.4.

TABLE 4.4

Experimental values of the separation factor  $q$  and the thermal diffusion factor  $\alpha$  for mixtures containing Ar and He. Temperature lower volume 308 °K, temperature upper volume 535 °K. A bar denotes an average value.

p in atm.	% Ar	$q$	$\bar{q}$	$\ln \bar{q}$	$\bar{\alpha}$
5	90	1.183			
5	90	1.191	1.187±0.002	0.171±0.002	0.305±0.004
5	90	1.186			
50	90	1.244			
50	90	1.246	1.245±0.001	0.219±0.001	0.393±0.002
50	90	1.244			
5	10	1.404			
5	10	1.378	1.395±0.009	0.333±0.006	0.595±0.011
5	10	1.403			
50	10	1.321			
50	10	1.313	1.326±0.009	0.282±0.007	0.505±0.013
50	10	1.343			

## CHAPTER V

### CALCULATIONS, RESULTS AND DISCUSSION

#### a. CALCULATIONS

We will compare the experimental results of Becker (Be 50), Van Ee (Ee 66) and ourselves with the theories given in chapter II and chapter III. As some of the calculations needed for this comparison are quite lengthy (especially those for the extended dimer theory), we have used the calculational facilities of the Mathematisch Centrum at Amsterdam, where the work was done on an Electrologica EL-X8 computer. In the next subsections we give the pertinent details for each programme.

For the temperature belonging to the value of the thermal diffusion factor we used the geometric mean between the upper and lower temperatures. The correct way to find this temperature would have been to repeat the experiments for a number of temperatures and to derive  $\alpha$  from a  $\ln Q$  vs.  $\ln T_h/T_l$  plot. This however would have asked for a far greater series of experiments and we decided to take the geometric mean, which gave us the possibility to do a number of gases in a reasonable time, whereas the assumption is not unreasonable. For the concentrations we took mean values, found from the filling procedure. This is certainly permitted as the upper and lower volumes do not differ very much and the concentration differences are fairly small. A number of calculations, made with slightly different temperatures and concentrations, gave negligible differences with the values obtained with those using the earlier mentioned assumptions.

#### a1. HAASE THEORY

In the basic formula (2.12) an equation of state must be introduced, for which we choose the simplified Beattie-Bridgeman equation, given in formula (2.15a,b,c). From this equation it follows (see e.g. (Ha 56)) for a two-component mixture that

$$\tilde{h}_i - \tilde{h}_i^{(0)} = p \left\{ B_{ii} - T \frac{\partial B_{ii}}{\partial T} + (1-x_i)^2 \left( \Delta - T \frac{\partial \Delta}{\partial T} \right) \right\} \quad (5.1a)$$

and

$$x_1 \frac{\partial \bar{u}_1}{\partial x_1} = R T - 2 p \Delta x_1 x_2 \quad (5.1b)$$

with

$$\Delta = 2 B_{12} - B_{11} - B_{22}$$

As long as no use is made of the expression (2.15c) for the  $B_{ij}$ , (5.1a) and (5.1b) stay valid also if we use a virial type equation of state and cut it off after the second term.

As soon as we introduce (2.15c) into (5.1a) the computation is a straightforward procedure. The value of  $\alpha_{12}^0$  has been calculated in the second Kihara approximation (1.9); for the collision parameters, reduced  $\Omega$ -integrals and the functions  $A^*$ ,  $B^*$  and  $C^*$  the tables for the Lennard-Jones (6-12) potential from the book of Hirschfelder et al. (Hi 54) have been used. Also from this book came the parameters and combination rules for the Beattie-Bridgeman equation needed for the calculations. The parameters used are given in table 5.1 (non-equilibrium values) and table 5.2.

## a2. FUGACITY THEORY

The calculations for the fugacity theory are somewhat more complicated inasmuch as a system of four equations with four unknowns, given by eqns (2.19), (2.20), (2.22) and (2.23) must be solved numerically. This was done in the following way:  $x_1^{(T_h)}$ ,  $x_2^{(T_c)}$  and  $x_2^{(T_h)}$  are expressed in  $x_1^{(T_c)}$  and the quantities  $N_1$ ,  $C_c$  and  $C_h$  (which are known from the experimental conditions) by means of the eqns (2.22) and (2.23). These expressions are introduced in the right hand side of (2.20) so that this expression can be written as

$$\ln Q_{\text{fug}} = \frac{P}{R} \{k_1(B) + k_2(B)x_1^{(T_c)}\} \quad (5.2)$$

TABLE 5.1

Force constants for the Lennard-Jones (6-12) potential used in the calculations.  $\epsilon/k$  denotes the depth of the potential well in  $^{\circ}\text{K}$ ,  $\sigma$  is the zero-energy collision diameter in  $\text{\AA}$ .  $l$  indicates values for temperatures below,  $h$  for temperatures above room temperature.

gas	non-equilibrium values		equilibrium values	
	$\epsilon/k$	$\sigma$	$\epsilon/k$	$\sigma$
$\text{H}_2(l)$	33.3	2.968	29.2	2.87
$\text{H}_2(h)$	38.0	2.915		
$\text{D}_2$	39.3	2.95	31.1	2.87
He	10.22	2.576	6.03	2.63
$\text{CH}_4$	144	3.796	148.2	3.82
$\text{N}_2(l)$	91.5	3.68	95.1	3.70
$\text{N}_2(h)$	79.8	3.749		
$\text{C}_2\text{H}_4$	205	4.232	199.2	4.523
Ar	116	3.465	120	3.41
$\text{CO}_2$	213	3.897	203.3	3.91
Kr	190	3.61	158	3.60

where, using (2.15a) and (2.15b)

$$k_1(B) = \frac{B_{11}(T_h) - B_{22}(T_h) - \Delta(T_h)}{T_h} - \frac{B_{11}(T_l) - B_{22}(T_l) - \Delta(T_l)}{T_l} - \frac{2N_1 \Delta(T_h)}{C_h T_h}$$

and

$$k_2(B) = \left\{ \frac{C_c}{C_h} \frac{\Delta(T_h)}{T_h} + \frac{\Delta(T_l)}{T_l} \right\}$$

TABLE 5.2

Constants for the Beattie-Bridgeman equation of state used in the calculations. For the meaning of these constants see eqn (2.11).

gas	$A_0$	$B_0$	$c$
H <sub>2</sub>	0.1975	0.02096	504
D <sub>2</sub>	0.2125	0.02060	1010
He	0.0216	0.01400	40
CH <sub>4</sub>	2.2769	0.05587	128300
N <sub>2</sub>	1.3445	0.05046	42000
C <sub>2</sub> H <sub>4</sub>	6.1520	0.12156	226800
Ar	1.2907	0.03931	59900
CO <sub>2</sub>	5.0065	0.10476	660000
Kr	2.4230	0.05261	148900

Now we take a trial value  $x_{10c}^{(T)}$  for  $x_{1c}^{(T)}$  (viz. the mean value of  $x_1$ , known from the filling procedure), which differs from the real value by an amount  $\delta x$ , so

$$x_{1c}^{(T)} = x_{10c}^{(T)} + \delta x$$

Eqs (2.22) and (2.23) give the values  $x_{10h}^{(T)}$ ,  $x_{20c}^{(T)}$  and  $x_{20h}^{(T)}$  for  $x_{1h}^{(T)}$ ,  $x_{2c}^{(T)}$  and  $x_{2h}^{(T)}$  when  $x_{1c}^{(T)} = x_{10c}^{(T)}$  and the changes in  $x_{1h}^{(T)}$ ,  $x_{2h}^{(T)}$ ,  $x_{2c}^{(T)}$  and  $x_{2h}^{(T)}$  in going from  $x_{1c}^{(T)}$  to  $x_{10c}^{(T)}$ . From these changes and the definition (2.19) we see that

$$Q = \frac{x_{1c}^{(T)} x_{2h}^{(T)}}{x_{1h}^{(T)} x_{2c}^{(T)}} = \frac{(x_{10c}^{(T)} + \delta x)(x_{20h}^{(T)} + c_c \delta x / C_h)}{(x_{10c}^{(T)} - c_c \delta x / C_h)(x_{20c}^{(T)} - \delta x)}$$

With a linear approximation in  $\delta x$ , which is supposed to be small, this leads to the relation

$$Q = \frac{x_{10c}^{(T)} x_{20h}^{(T)}}{x_{10h}^{(T)} x_{20c}^{(T)}} \left[ 1 + \left\{ \frac{c_c}{c_h} \frac{1}{x_{10h}^{(T)}} + \frac{1}{x_{20h}^{(T)}} + \frac{1}{x_{10c}^{(T)}} + \frac{1}{x_{20c}^{(T)}} \right\} \delta x \right] \quad (5.3)$$

Introducing  $x_{10c}^{(T)}$  instead of  $x_{1c}^{(T)}$  in (5.2), using (2.22) and (2.23) and introducing the result in the logarithm of the expression (5.3), gives the value of  $\delta x$ . Using the value of  $x_{10c}^{(T)} + \delta x$  as a new  $x_{10c}^{(T)}$  we can find  $Q$  to any desired accuracy by iteration.

The equation used for the  $B_{ij}$  was again the Beattie-Bridgeman expression (2.15c). The computations can be performed now, using (2.21a), (2.21b) and the formulae and method outlined above. The result is that we find a value for the separation  $Q_{fug}$  of eqn (2.13a). To this must be added the separation  $Q_{th.d.}$  to find the total separation: in the actual computations we derived the value of  $\alpha_{fug}$  from  $Q_{fug}$  and then added  $\alpha_{th.d.}$  calculated in the second Kihara approximation to find the total thermal diffusion factor. All parameters used, as well as the values for the  $\Omega^*$ -integrals and related functions, were found from the book of Hirschfelder (Hi 54); the potential used was again the Lennard-Jones (6-12) potential, the equation of state the Beattie-Bridgeman equation. The parameters used are given again in table 5.1 (non-equilibrium values) and table 5.2.

### a3. PAIR-CORRELATION FUNCTION

A complete final formula was derived (eqn (2.39)), so that the calculation was a straightforward procedure. The equation of state chosen was the virial equation, cut off after the second virial coefficient. For the calculation of the low-pressure value of  $\alpha$  the second Kihara approximation (1.9) was used. The values of  $B_{ij}(T)$  and its temperature-derivative, as well as those of the  $\Omega$ -integrals and related functions (or, better, their reduced values) were found from the tables for the Lennard-Jones potential in (Hi 54). A procedure was introduced into the programme that derived the values needed from the tables by linear interpolation, thus reducing the



amount of work needed for the composition of the number tapes. The parameters used are given in table 5.1 (equilibrium values).

#### a4. DIMER THEORY

For the simplified dimer theory a complete final formula was derived (eqn (3.32)), so that no substantial difficulties are met in the calculations; for the  $\alpha_{ij}$  we have used the formulae for ternary thermal diffusion factors given by Van der Valk (Va 63) which are correct up to the first Chapman-Cowling approximation. The determinants given by Van der Valk have been written out and calculated for the Lennard-Jones (6-12) potential. The diffusion coefficients  $D(i,j)$  have been calculated to the first Chapman-Cowling approximation (1.4a), also for the Lennard-Jones potential, with the parameters given in table 5.1 (non-equilibrium values).

For the extended dimer theory more complications arise. The first problem is the calculation of the functions  $nK_1$  and  $(nK_1)'$ ;  $nK_2$  and  $nK_4$ , as well as their temperature derivatives, can be calculated with the formula given by Stogryn and Hirschfelder (St 59) for the Lennard-Jones potential, taking into account the lifetimes of the metastable dimers as discussed in the beginning of chapter III. For the  $nK_3$  and  $(nK_3)'$  we have used the same formula; the values for the potential parameters that we used in this case were derived from those of components A and B with the usual combination rules: for the depth of the potential well we took the geometric, for the molecular diameter the arithmetic mean of the values for A and B. With the  $nK_1$  known eqn (3.49) can be written down, from which we have to find  $x_5$ . This is done by using a trial value  $x_0$  for  $x_5$  (viz. the value of  $\bar{x}_B$ ) which differs from  $x_5$  by a supposedly small amount  $\delta x$ . Introducing  $x_5 = x_0 + \delta x$  in (3.49) and linearizing with respect to  $\delta x$  gives the possibility to find  $x_5$  to any required accuracy by iteration; (3.48) then gives  $x_1$  and (3.36)  $x_2$ ,  $x_3$  and  $x_4$ .

We do need the potential parameters of the various monomers and dimers to calculate their influence on the transport coefficients. Those for the monomers were used already for the calculation of the  $nK_1$  and  $(nK_1)'$ . For the calculation of the parameters for the homo-molecular dimers we used the empirical rules given for dimer-monomer interaction by Stogryn and Hirschfelder (St 59), together with the well-known combination rules. This

leads to the following relations :

$$\begin{aligned}
 (\epsilon/k)_{\text{dimer}} &= 1.32^2 (\epsilon/k)_{\text{monomer}} \\
 \sigma_{\text{dimer}} &= 1.06 \sigma_{\text{monomer}}
 \end{aligned}
 \tag{5.4}$$

where  $\epsilon/k$  denotes the depth of the potential well and  $\sigma$  the zero-energy collision diameter. The potential parameters for the hetero-molecular dimers were found also from (5.4) with the values used in the calculation of  $nK_3$  and  $(nK_3)'$  inserted for  $(\epsilon/k)_{\text{monomer}}$  and  $\sigma_{\text{monomer}}$ .

The next problem is the calculation of the five-component diffusion coefficients  $D_{ik}$  and five-component thermal diffusion factors  $\alpha_{ij}$ . For the  $D_{ik}$  we will use eqn (1.3b) and the relation

$$\sum_i x_i D_{ik} = 0
 \tag{5.5}$$

As the five equations of the type (1.3b) that we get for each value of  $i$  are linearly dependent, we omit the equation for  $i=k$  and replace it by (5.5). In this way we get for each  $i$  a system of five independent linear equations with five unknowns in which the coefficients and known terms consist of combinations of binary diffusion coefficients and concentrations. The binary diffusion coefficients are calculated up to the second Chapman-Cowling approximation for the Lennard-Jones potential. The system is solved by the computer, using the procedures AP 204, AP 205 and AP 207 of the Mathematisch Centrum at Amsterdam.

The  $\alpha_{ij}$  can be found in the same way as for the three-component system, although here we did not develop the determinants constituting the final formula of Van der Valk, but used a combination of some of his formulae from which the  $\alpha_{ij}$  for an  $n$ -component system can be found as the inner product of coefficients  $A_k$  and  $b_{k,ij}$ . The  $A_k$  are the roots of a system of  $n$  independent linear equations with  $n$  unknowns, which was solved by the computer. The  $b_{k,ij}$  can be calculated from given expressions so that, with the  $A_k$  and  $b_{k,ij}$  known, the  $\alpha_{ij}$  can be calculated as

$$\alpha_{ij} = \sum_k b_{k,ij} A_k$$

The remaining calculations are straightforward, using the eqns (3.40), (3.44), (3.46) and (3.47). To facilitate the composition of the number tapes (for each temperature and each combination of gases 125 values of  $\Omega^*$ -integrals and related functions were needed) a procedure of the same kind as used with the pair-correlation calculations was inserted in the programme.

For the computation of the  $\alpha$ 's, taking into account the dimer-concentrations measured by Leckenby and Robbins (Le 66), the same procedure was used. The correction was performed by the introduction of extra factors in the formulae for the  $nK_i$  and  $(nK_i)'$ .

## b. RESULTS

The theoretical predictions for the values of the thermal diffusion factor at different pressures, obtained via the calculations described in part a. of this chapter, are given in table 5.3. Table 5.3a contains the results for our own experiments, table 5.3b those for the experiments of Becker and table 5.3c those for the experiments of Van Ee, at least a part of them. The experimental values are indicated with  $\alpha_{\text{exp}}$ , while for the indication of the various theories the following notation is used in the suffixes :

Haase	: Haase theory
fug	: fugacity theory
p.c.	: pair-correlation theory
s.d.	: simplified dimer theory
e.d.	: extended dimer theory
e.d.c.	: extended dimer theory with corrections according to the experimental results of Leckenby and Robbins (Le 66).

Pressures are indicated with  $p$  and given in atmospheres,  $x_1$  is the mole fraction of the first mentioned (i.e. heavier) component of the mixture.

For the comparison of the various predictions with each other and with the experimental values we have used the following method: from the values of  $\alpha$  for different pressures we obtained a mean pressure dependence  $\delta_p(\alpha) = \delta\alpha / \delta p$  where  $\delta\alpha$  resp.  $\delta p$  are the change in  $\alpha$  resp.  $p$  on going from the lowest pressure used to the pressure of the experiment. These pressure dependences are tabulated in the first part of table 5.4a and table 5.4b,

TABLE 5.3a

Experimental and theoretical values of the thermal diffusion factor  $\alpha$  for our experiments.  
For the meaning of abbreviations: see page

mixture	$x_1$	p	$\alpha_{\text{exp}}$	$\alpha_{\text{Haase}}$	$\alpha_{\text{fug}}$	$\alpha_{\text{p.c.}}$	$\alpha_{\text{s.d.}}$	$\alpha_{\text{e.d.}}$	$\alpha_{\text{e.d.c.}}$
CO <sub>2</sub> -Ar	0.1	5	0.027	0.053	0.055	0.043	0.032	0.030	0.035
		50	0.062	0.223	0.244	0.112	0.011	-0.002	0.040
CO <sub>2</sub> -Ar	0.9	5	0.026	0.065	0.071	0.041	0.042	0.031	0.055
		20	0.086	0.175	0.201	0.078	0.075	0.039	0.127
		50	0.181	0.396	0.465	0.157	0.122	0.048	0.239
Kr-CO <sub>2</sub>	0.1	5	0.033	0.021	0.047	0.073	0.068	0.050	0.009
		20	0.000	-0.135	-0.033	0.055	0.026	-0.013	-0.162
		50	-0.063	-0.449	-0.195	0.017	-0.010	-0.132	-0.445
C <sub>2</sub> H <sub>4</sub> -N <sub>2</sub>	0.1	5	0.026	0.045	0.045	0.038	0.018	0.020	0.023
		50	0.074	0.251	0.261	0.144	0.000	0.011	0.037
C <sub>2</sub> H <sub>4</sub> -N <sub>2</sub>	0.9	5	0.069	0.065	0.069	0.044	0.034	0.029	0.034
		20	0.097	0.206	0.221	0.114	0.075	0.055	0.073
		50	0.29	0.491	0.530	0.268	0.131	0.088	0.133
Ar-He	0.1	5	0.595	0.668	0.659	0.662	0.636	0.637	-
		50	0.505	0.764	0.668	0.672	0.636	0.642	-
Ar-He	0.9	5	0.305	0.344	0.350	0.343	0.295	0.295	-
		50	0.393	0.442	0.499	0.411	0.334	0.339	-

TABLE 5.3b

Experimental and theoretical values of the thermal diffusion factor  $\alpha$  for the experiments of Becker (Be 50). For the meaning of abbreviations: see page

mixture	$x_1$	P	$\alpha_{\text{exp}}$	$\alpha_{\text{Haase}}$	$\alpha_{\text{fug}}$	$\alpha_{\text{p.c.}}$	$\alpha_{\text{e.d.}}$	$\alpha_{\text{e.d.c.}}$
CO <sub>2</sub> -H <sub>2</sub>	0.52	3	0.32	0.38	0.04	0.40	0.33	0.35
		26	0.46	0.54	0.33	0.52	0.39	0.51
		51	0.67	0.72	0.71	0.64	0.43	0.62
		81	0.98	0.97	1.25	0.82	0.47	0.70
CO <sub>2</sub> -N <sub>2</sub>	0.48	3	0.05	0.11	0.03	0.10	0.09	0.11
		26	0.12	0.27	0.25	0.17	0.10	0.24
		52	0.25	0.45	0.51	0.25	0.09	0.33
		81	0.40	0.67	0.81	0.36	0.08	0.39
CO <sub>2</sub> -Ar	0.46	3	0.03	0.05	0.03	0.04	0.03	0.04
		26	0.08	0.24	0.23	0.10	0.02	0.12
		50	0.15	0.44	0.46	0.18	0.01	0.16
		80	0.25	0.70	0.75	0.28	-0.02	0.17
CO <sub>2</sub> -CH <sub>4</sub>	0.48	3	0.07	0.12	0.02	0.12	0.10	0.12
		26	0.12	0.12	0.18	0.17	0.04	0.12
		51	0.22	0.13	0.36	0.22	-0.02	0.11
		81	0.37	0.14	0.57	0.28	-0.01	0.06
N <sub>2</sub> -CH <sub>4</sub>	0.50	4	0.07	0.09	-0.01	0.09	0.09	0.09
		20	0.03	0.03	-0.05	0.07	0.04	0.04
		38	0.02	-0.04	-0.09	0.05	0.00	0.00
		80	0.00	-0.21	-0.20	0.01	-0.09	-0.09
N <sub>2</sub> -H <sub>2</sub>	0.50	3	0.35	0.41	0.01	0.42	0.37	0.36
		26	0.36	0.44	0.05	0.44	0.37	0.36
		50	0.39	0.47	0.10	0.46	0.38	0.36
		78	0.44	0.51	0.16	0.49	0.38	0.36

TABLE 5.3c

Experimental and theoretical values of the thermal diffusion factor  $\alpha$  for a number of the experimental values of Van Ee (Ee 66). For the meaning of abbreviations: see page

mixture	$x_1$	p	T	$\alpha_{\text{exp}}$	$\alpha_{\text{p.c.}}$	$\alpha_{\text{e.d.}}$	$\alpha_{\text{e.d.c.}}$
$\text{N}_2\text{-H}_2$	0.726	0.1	290	0.26	0.34	0.30	0.30
		1.9		0.26	0.34	0.30	0.30
		4.0		0.26	0.35	0.30	0.30
		0.1	200	0.24	0.30	0.26	0.26
		1.9		0.25	0.31	0.27	0.26
		4.0		0.27	0.32	0.27	0.26
		0.1	100	0.13	0.16	0.14	-
		1.9		0.18	0.21	0.18	-
		4.0		0.37	0.28	0.21	-
	0.500	0.1	300	0.30	0.40	0.36	0.36
		4.0		0.30	0.41	0.36	0.36
		7.0		0.30	0.41	0.36	0.36
		0.1	200	0.27	0.35	0.31	0.31
		4.0		0.29	0.36	0.32	0.31
		7.0		0.32	0.38	0.33	0.31
		0.1	100	0.13	0.19	0.17	-
		4.0		0.21	0.29	0.21	-
		7.0		0.42	0.37	0.24	-
	0.241	0.1	290	0.37	0.49	0.46	0.46
		7.0		0.38	0.50	0.46	0.45
		13.0		0.39	0.50	0.46	0.45
		0.1	200	0.34	0.43	0.40	0.40
		7.0		0.35	0.45	0.41	0.40
		13.0		0.39	0.47	0.41	0.40
0.1		100	0.16	0.23	0.22	-	
7.0			0.25	0.36	0.24	-	
13.0			0.45	0.48	0.25	-	

TABLE 5.3c (continued)

mixture	$x_1$	P	T	$\alpha_{\text{exp}}$	$\alpha_{\text{p.c.}}$	$\alpha_{\text{e.d.}}$	$\alpha_{\text{e.d.c.}}$
$\text{N}_2\text{-D}_2$	0.498	0.1	290	0.29	0.36	0.33	0.33
		4.0		0.29	0.37	0.33	0.33
		7.0		0.29	0.37	0.34	0.33
		0.1	200	0.26	0.32	0.29	0.29
		4.0		0.27	0.34	0.30	0.29
		7.0		0.30	0.35	0.30	0.29
		0.1	100	0.10	0.17	0.16	-
		4.0		0.19	0.27	0.20	-
		7.0		0.36	0.35	0.22	-
$\text{N}_2\text{-He}$	0.492	0.1	290	0.40	0.44	0.39	0.39
		1.9		0.41	0.44	0.40	0.39
		6.0		0.43	0.45	0.40	0.39
		0.1	200	0.40	0.43	0.38	0.38
		1.9		0.41	0.44	0.39	0.38
		6.0		0.43	0.46	0.40	0.39
		0.1	100	0.32	0.36	0.33	-
		1.9		0.33	0.42	0.36	-
		6.0		0.43	0.56	0.43	-

table 5.4a referring to our own experiments and 5.4b to those of Becker. From the values of the mean pressure dependence we calculated the relative error  $\mu(\delta_p(\alpha))$  of the theoretical predictions with respect to the experimental results with the formula

$$\mu(\delta_p(\alpha)) = \{(\delta\alpha/\delta p)_{\text{th}} - (\delta\alpha/\delta p)_{\text{exp}}\} / (\delta\alpha/\delta p)_{\text{exp}} \quad (5.6)$$

where  $(\delta\alpha/\delta p)_{\text{th}}$  denotes a theoretical prediction for the mean pressure dependence. The values of  $\mu(\delta_p(\alpha))$  are given in the second part of tables 5.4a and 5.4b. To have a criterion which gives us an indication for the reliability of the various theories we have added the absolute values of the relative

TABLE 5.4a

Experimental and theoretical values of the mean pressure dependence  $\delta_p(\alpha)$  of the thermal diffusion factor  $\alpha$  and the relative error  $\mu(\delta_p(\alpha))$  of the theoretical predictions, calculated with formula (5.6), using values from our experiments. Also given are the sum of the absolute values of  $\mu(\delta_p(\alpha))$  and its mean value. For abbreviations: see page

				$\delta_p(\alpha) \cdot 10^4$							$\mu(\delta_p(\alpha))$						
mixture	$x_1$	$p_0$	$p$	exp	Haase	fug	p.c.	s.d.	e.d.	e.d.c.	Haase	fug	p.c.	s.d.	e.d.	e.d.c.	
CO <sub>2</sub> -Ar	0.1	5	50	8	38	42	15	- 5	- 7	1	3.84	4.38	0.96	-1.60	-1.91	-0.86	
CO <sub>2</sub> -Ar	0.9	5	20	40	73	87	25	22	5	48	0.83	1.18	-0.38	-0.45	-0.88	0.20	
			50	34	74	88	26	18	4	41	1.18	1.59	-0.24	-0.47	-0.88	0.21	
Kr-CO <sub>2</sub>	0.1	5	20	- 22	-104	- 53	- 12	- 28	- 42	-114	3.73	1.41	-0.45	0.27	0.91	6.18	
			50	- 21	-104	- 54	- 12	- 17	- 40	-101	3.95	1.57	-0.43	-0.19	0.90	5.81	
C <sub>2</sub> H <sub>4</sub> -N <sub>2</sub>	0.1	5	50	11	46	48	24	- 4	- 2	3	3.18	3.36	1.18	-1.36	-1.18	-0.73	
C <sub>2</sub> H <sub>4</sub> -N <sub>2</sub>	0.9	5	20	19	94	101	47	27	17	26	3.95	4.32	1.47	0.42	-0.11	0.37	
			50	49	95	102	50	22	13	22	0.94	1.08	0.02	-0.55	-0.73	-0.55	
Ar-He	0.1	5	50	- 20	21	2	2	0	1	1	2.05	1.10	1.10	1.00	1.05	1.05	
Ar-He	0.9	5	50	20	22	33	15	9	10	10	0.10	0.65	-0.25	-0.55	-0.50	-0.50	
											$\Sigma  \mu(\delta_p(\alpha)) $	22.57	20.64	6.48	6.86	9.05	16.46
											$ \mu(\delta_p(\alpha)) _{\text{gem}}$	2.26	2.06	0.65	0.69	0.91	1.65



TABLE 5.4b

Experimental and theoretical values of the mean pressure dependence  $\delta_p(\alpha)$  of the thermal diffusion factor  $\alpha$  and the relative error  $\mu(\delta_p(\alpha))$  of the theoretical predictions, calculated with formula (5.6); values for the experiments of Becker (Be 50). Also given are the sum of the absolute values of  $\mu(\delta_p(\alpha))$  and its mean value. For abbreviations: see page

mixture	p <sub>0</sub>	p	$\delta_p(\alpha) \cdot 10^4$						$\mu(\delta_p(\alpha))$				
			exp	Haase	fug	p.c.	e.d.	e.d.c.	Haase	fug	p.c.	e.d.	e.d.c.
CO <sub>2</sub> -H <sub>2</sub>	3	26	61	70	126	52	26	70	0.15	1.07	0.85	-0.57	0.15
		51	73	71	140	50	21	56	-0.03	0.92	-0.32	-0.71	-0.23
		81	85	76	155	54	18	45	-0.11	0.82	-0.36	-0.79	-0.47
CO <sub>2</sub> -N <sub>2</sub>	3	26	30	70	96	30	4	57	1.33	2.20	0.00	-0.87	0.90
		52	41	69	98	31	0	45	0.68	1.39	-0.24	-1.00	0.10
		81	45	72	100	33	-1	36	0.60	1.22	-0.27	-0.98	-0.20
CO <sub>2</sub> -Ar	3	26	22	83	87	26	-4	35	2.77	2.95	0.18	-1.18	0.59
		50	26	83	91	30	-4	26	2.19	2.50	0.15	-1.15	0.00
		80	29	84	94	31	-6	17	1.90	2.24	0.07	-1.21	-0.41
CO <sub>2</sub> -CH <sub>4</sub>	3	26	22	0	70	22	-26	0	-1.00	2.18	0.00	-2.18	-1.00
		51	31	2	71	21	-25	-2	-0.94	1.29	-0.32	-1.81	-1.06
		81	38	3	71	21	-14	-8	-0.92	0.87	-0.45	-1.37	-1.21
N <sub>2</sub> -CH <sub>4</sub>	4	20	-25	-38	-25	-13	-31	-31	0.52	0.00	-0.48	0.24	0.24
		38	-15	-38	-24	-12	-26	-26	1.53	0.60	-0.20	0.73	0.73
		80	-9	-39	-25	-11	-24	-24	3.33	1.78	0.22	1.67	1.67
N <sub>2</sub> -H <sub>2</sub>	3	26	4	13	17	9	0	0	2.25	3.25	1.25	1.00	1.00
		50	9	13	19	9	2	0	0.44	1.11	0.00	-0.78	-1.00
		78	12	13	20	9	1	0	0.08	0.67	-0.25	-0.92	-1.00
								$\Sigma  \mu(\delta_p(\alpha)) $	20.77	27.06	5.61	19.16	11.96
								$ \mu(\delta_p(\alpha)) _{gem}$	1.15	1.50	0.31	1.06	0.66

TABLE 5.5

Sums of the differences between the theoretical and experimental values of the change in thermal diffusion factor  $\alpha$  on going from a pressure of 0.1 atm to the pressure of the experiment. Values for the experiments of Van Ee (Ee 66) given in table 5.1c for 300, 290 and 200 °K. Also given are the sums of the experimental values for the change in  $\alpha$ . For abbreviations: see page

mixture	$x_1$	Haase	p.c.	e.d.	e.d.c.	$\delta\alpha_{\text{exp}}$
N <sub>2</sub> -H <sub>2</sub>	0.726	0.03	0.02	0.02	0.04	0.04
	0.500	0.06	0.04	0.04	0.07	0.07
	0.241	0.03	0.03	0.06	0.11	0.09
N <sub>2</sub> -D <sub>2</sub>	0.498	0.04	0.03	0.04	0.05	0.05
N <sub>2</sub> -He	0.492	0.06	0.03	0.03	0.07	0.08
sum		0.22	0.15	0.19	0.34	

errors for each theory in tables 5.4a and 5.4b. From this sum we calculated a mean relative error per experiment.

We have not used this method for the work of Van Ee; due to the small changes of  $\alpha$  in the majority of cases a difference of 1 in the last decimal would give an unrealistically large relative error, even if we take the theoretical value of  $\delta\alpha/\delta p$  as the denominator in (5.6) in the case of no change in the experimental value of  $\alpha$  and a change 0.01 in the theoretical value. In table 5.5 we have added the absolute values of the differences between the theoretical and the experimental change in  $\alpha$  on going from the lowest pressure used to the pressure of the experiment. In this way we use the ratio of the experimental and theoretical values of the change in  $\alpha$  with the experimental value of this change as weight function as indication for the reliability of the various theories. We have done this for the pair-correlation theory, the two versions of the extended dimer theory and the Haase

theory; the values for the last-mentioned theory were derived from (Ee 66). We have given in table 5.5 the sum of the differences outlined above for the temperatures 290 (or 300) and 200 °K; for 100 °K an unrealistically large extrapolation had to be made to obtain values for the correction factor, needed for the e.d.c.-values, from the measurements of Leckenby and Robbins; therefore we left out this temperature. In the table are inserted also the values for the sum of the changes in  $\alpha$  found from experiment.

### c. DISCUSSION

To test the applicability of various theories we shall not use tables 5.3a, b or c, as a basic inaccuracy in these tables is the error in the value of the low-pressure thermal diffusion factor. This value, calculated to the second Kihara or first Chapman-Cowling approximation (depending upon the theory under consideration), is a more or less additive factor in the Haase, fugacity and pair-correlation theory. Its influence in the dimer theories is far more complicated as can be seen from the pertinent formulae. A better indication for the reliability of the various theories is found in the pressure dependence of  $\alpha$  as given in table 5.4a and table 5.4b.

Starting with table 5.4a we see from the sum of the relative errors that the Haase theory and the fugacity theory are the two theories which give the worst agreement with the experimental values. This is confirmed by table 5.4b, be it that here the e.d.-predictions fall in the same category. That these theories give no satisfying predictions could be expected as in both cases gross simplifications have been introduced: for the Haase theory the basic supposition of no pressure dependence of the heat-of-transfer, for the fugacity theory the neglect of back-diffusion for the equilibrium contribution to the separation. In the last case the implication is that the predictions for the absolute value of the equilibrium contribution to the separation are too high. This is true in all cases of table 5.4a and table 5.4b, except for the Ar-He mixture with 10% Ar in table 5.4a; this mixture is a strange case as all theoretical predictions indicate positive change or no change at all, while the experimentally obtained change is negative. No satisfactory explanation (such as a possible experimental error)

could be found for this discrepancy.

The next best group of predictions is those of the dimer theories. The predictions of the simplified theory for our own experiments are surprisingly good and better than the e.d.-predictions. This is contrary to our expectations for the following reason: neglecting for a moment the fact that dimers are constantly being formed and disappearing again the three kinds of dimers can be considered as heavy gasmolecules in a mixture of two lighter gases, made up of the monomers. Taking equal a priori probabilities for the three kinds of dimers we find as the ratio of the dimer-concentrations in a mixture of 10% of gas A and 90% of gas B :

$$x_{B_2} : x_{AB} : x_{A_2} = 0.81 : 0.18 : 0.01$$

As all three types of dimers have the greatest concentration in the colder part of the vessel, the separation obtained depends only on their concentration and composition compared to the one of the mixture as a whole. The  $B_2$  dimers have a comparatively high concentration, but, due to the fact that their composition does not differ appreciably from the one of the mixture, their influence will be reduced. The  $A_2$  dimers are present in very low concentration, so that, although they have a composition which is very different from the one of the mixture, their influence can be neglected. The hetero-molecular dimers AB, however, have a reasonable concentration and a composition (50% A, 50% B) differing greatly from the one of the mixture (10% A, 90% B), so that their influence will be pretty important in 10% - 90% mixtures, at least when the a priori probabilities for the formation of the various types of dimers are comparable. The reasonably good agreement between the simplified dimer predictions and the experimental values is therefore somewhat surprising. The fact that the e.d.-predictions are worse instead of better than those of the simplified theory can not be explained by a physical picture. The reason for it seems to lie mainly in the fact that diffusion coefficients and thermal diffusion factors are calculated up to a certain approximation, in this case the first Chapman-Cowling approximation, which is pretty accurate as regards the diffusion coefficients but is less precise for the thermal diffusion factors. It will be clear from the way in which the diffusion coefficients  $D_{ij}$  and thermal diffusion factors  $\alpha_{ij}$  were calculated from the coefficients determining them (part a. of this chapter) that inaccuracies in these coefficients give

rise to larger errors in the  $D_{ij}$ 's and  $\alpha_{ij}$ 's for a five-component system than for a three-component system.

Comparing the e.d. and the e.d.c.-values in tables 5.4a and 5.4b a remarkable inconsistency shows up: for our own experiments the e.d.c.-values are worse than the e.d.-values, for the experiments of Becker we see the reverse. The inconsistency is caused by the theoretical predictions for only one mixture viz. Kr-CO<sub>2</sub>. If we leave this mixture out of discussion (a possible justification for this will be given hereafter), the sum of relative errors of table 5.4a goes down to 5.40 for the p.c., to 6.40 for the s.d., to 7.24 for the e.d. and to 4.48 for the e.d.c.-values and the inconsistency has disappeared: the correction gives a distinct improvement over the e.d.-values in almost all cases of tables 5.4a and 5.4b: only in the case of the N<sub>2</sub>-H<sub>2</sub> mixture in table 5.4b the e.d.c.-values are still slightly worse than the e.d.-values. The same mixture has been used by Van Ee (Ee 66) and here again the e.d.-values are better than the e.d.c.-predictions, not only for N<sub>2</sub>-H<sub>2</sub>, but also for the N<sub>2</sub>-D<sub>2</sub> and N<sub>2</sub>-He mixtures. This could mean that the correction for N<sub>2</sub> is in error e.g. because the supposition of rotational disruption does not hold here.

We checked this by calculating e.d.c.-values for the mixture CO<sub>2</sub>-N<sub>2</sub> while using only the correction factor for CO<sub>2</sub>. The result was that the sum of the relative errors for the experiments of Becker on this mixture went up from 1.20 to 2.34, so an error in the correction factor for N<sub>2</sub> does not seem to offer an explanation for the different behavior of the other mixtures containing N<sub>2</sub>. Comparing the differences between theory and experiment given in table 5.5 we see that the difference between the experimental values and the e.d.c.-values is the biggest for the mixture containing the largest amount of H<sub>2</sub>, so it seems probable that the origin of the different behavior of these mixtures lies in the second component, for which no experimental values of the dimer-concentration are known.

This brings us to the point that for the majority of the mixtures used the dimer-concentration of only one component is known, as Leckenby and Robbins gave quantitative results only for CO<sub>2</sub>, N<sub>2</sub> and Ar. The unknown dimer-concentration of the second component may have caused also the wrong sign of the correction for the Kr-CO<sub>2</sub> mixture. To avoid this incompleteness we will compare the e.d.c.-predictions with those of the pair-correlation theory only using the values for the mixtures CO<sub>2</sub>-Ar and CO<sub>2</sub>-N<sub>2</sub>. The values of the relative errors, calculated for these mixtures, are given again in table 5.6.

TABLE 5.6

The relative error  $\mu(\delta_p(\alpha))$ , calculated with formula (5.6) for the experiments in which two correction factors are known for the dimer-calculations. The values given are for the p.c. and the e.d.c. predictions and contain also the sum of the absolute values of  $\mu(\delta_p(\alpha))$  and its mean value.  $p_0$ : lowest pressure used in atm; other abbreviations: see page

mixture	$x_1$	$p_0$	$p$	p.c.	e.d.c.
CO <sub>2</sub> -Ar	0.1	5	50	0.96	0.86
CO <sub>2</sub> -Ar	0.9	5	20	0.38	0.20
			50	0.24	0.21
CO <sub>2</sub> -N <sub>2</sub>	0.48	3	26	0.00	0.90
			52	-0.24	0.10
			81	-0.27	-0.20
CO <sub>2</sub> -Ar	0.46	3	26	0.18	0.59
			50	0.15	0.00
			80	0.07	-0.41
$\Sigma  \mu(\delta_p(\alpha))  = 2.49$					3.47
$ \mu(\delta_p(\alpha)) _{gem} = 0.28$					0.39

From this table it is clear that, although the value of the mean relative error for the e.d.c.-values has become smaller, the pair-correlation predictions are the best. This fact and the relatively simple calculations needed to find the p.c.-predictions make the pair-correlation theory in the present situation the most suitable theory for a semi-quantitative prediction of the value of the thermal diffusion factor at slightly elevated

pressures. Still better approximations may be obtained as soon as a useful formalism has been found for the calculation of the non-equilibrium radial distribution function.

After having compared the numerical results of the dimer- and pair-correlation theories we will compare them on a somewhat more fundamental base.

For the dimer theory one cause of its inaccuracy has been mentioned already, viz. the fact that the concentrations of dimers may differ appreciably from the values predicted by Stogryn and Hirschfelder. This may be caused by a number of factors, such as the influence of internal degrees of freedom and the inadequacy of the Lennard-Jones potential. The fact that we have used in our calculations either all metastable dimers or no metastable dimers at all, while the real number of metastables that survive the time between two collisions will lie somewhere in between is another factor that leads to erroneous predictions. Furthermore, a small number of quasi-dimers will live long enough to survive also the time between two collisions and we have left this quasi-dimers fully out of the discussion. The problem of the right number of dimers exists also for  $\text{CO}_2$  and  $\text{N}_2$ , as we accepted the rotational disruption supposition to find our correction factors. No experimental or theoretical indications exist that indeed all rotational energy is converted into translational energy.

Apart from the number of dimers their behavior during a collision is also a possible source of errors; this problem is in fact a three-particle problem in which the internal degrees of freedom can not be neglected.

The dimer theory itself is also an approximation: no attention has been paid to collisional transfer, neither to clusters of more than two molecules. For all transport properties only the low-pressure values are used and even these only to the first Chapman-Cowling approximation.

The fact that with all these inaccuracies the theory still gives results that are reasonably in line with the experiments gives us the conviction that the physical picture that forms the basis of the theory is correct: dimers do have appreciable influence on the thermal diffusion factor when the pressure is raised.

The good correspondence between the experimental and pair-correlation values shows that our supposition that the equilibrium contribution to the heat-of-transfer as the biggest one was correct. The remaining discrepancy between theory and experiment may be attributed to the non-equilibrium

contribution, although other factors too may be present, such as the influence of internal degrees of freedom.

Concerning the pair-correlation theory we may conclude that the most important quantities in the final formula for the p.c.-predictions are the second virial coefficients. The values for these quantities are found from the tables in (Hi 54) with potential parameters derived from the experimental determination of the virial coefficients, thus in an indirect way using the experimental values themselves. This means that in the calculation of a high-pressure values are used and therefore effects due to dimers or collisional transfer are automatically taken into account. This is true for the second virial coefficients for the pure components. A fair comparison between the pair-correlation and dimer theories would be possible only if all dimer-concentrations needed were known from experiment. For the time being the conclusion is:

*for the calculation of the thermal diffusion factor at pressures where the third virial coefficient has no appreciable influence the pair-correlation theory gives the most reliable results.*



The experimental results have been compared with those obtained from the study of the effect of temperature on the rate of reaction of the system. The results show that the rate of reaction is independent of temperature in the range 20°C to 40°C. This is in agreement with the results obtained from the study of the effect of temperature on the rate of reaction of the system. The results show that the rate of reaction is independent of temperature in the range 20°C to 40°C. This is in agreement with the results obtained from the study of the effect of temperature on the rate of reaction of the system. The results show that the rate of reaction is independent of temperature in the range 20°C to 40°C. This is in agreement with the results obtained from the study of the effect of temperature on the rate of reaction of the system.

## S U M M A R Y

The investigations, described in this thesis, are concerned with the pressure dependence of the thermal diffusion factor in the region where three-particle collisions are not yet important. The immediate motive was the work of Velds on the He-CO<sub>2</sub> mixtures, where was shown that a growing concentration of CO<sub>2</sub> caused an increasing pressure dependence of the thermal diffusion factor. This was ascribed to the fact that the CO<sub>2</sub> behaves less like an ideal gas than He does.

To see which contribution to the non-ideality of the gas is important in this respect, we used the fact that at higher pressures molecules tend to cling together forming double molecules or dimers. By changing the components of the mixture and their respective concentrations we can influence the number of dimers that is formed and in this way change the thermal diffusion factor in a predictable way. These considerations determined our experimental programme: by giving first one, then the other component of a binary mixture the biggest concentration, the number of dimers of each component is changed and we can predict that the thermal diffusion factor becomes lower or higher. These ideas have been worked out in chapter III, where at first we supposed that only one component was able to form dimers and later removed this restriction thus allowing both components to form dimers, also with each other. For the calculation of the number of dimers present use has been made of the predictions of Stogryn and Hirschfelder and the experimentally found numbers of dimers in the work of Leckenby and Robbins.

In the choice of the last mixture we used (Ar-He) other considerations came into play: the difference between the number of dimers calculated by Stogryn and Hirschfelder and the experimental results of Leckenby and Robbins gave rise to the suspicion that internal degrees of freedom of the molecules played a rôle in the formation of dimers. Therefore we used a mixture consisting of molecules where internal degrees of freedom could not have any influence.

The experiments have been performed in the two-bulb apparatus earlier described by Velds. The lower temperature for all experiments was about 36 °C, the upper temperature about 255 °C; the pressure was varied from 5 to 50 atmospheres.

The experimental results have been compared also with some other

predictions. In the first place we have to mention the theory of Haase, in which the assumption is used that the so-called heat-of-transfer is pressure independent. This heat-of-transfer is a quantity which appears in the treatment of the thermal diffusion factor in the book of De Groot about the thermodynamics of irreversible processes.

A better approximation to the heat-of-transfer is given by Bearman, Fixman and Kirkwood. Their results - though derived in a somewhat other fashion, using an equilibrium treatment - are used in chapter II. As the basic idea in this theory is the interaction between pairs of molecules, we speak about the pair-correlation theory.

Attention has further been paid to a theory, given already by Velds, in which the influence of the non-ideality comes from the fact that in a non-ideal mixture of gases not the partial pressures, but the fugacities of the components of the mixture have to be equal throughout the apparatus.

To make the comparison between computed and experimental values as complete as possible, we have used also the experimental results published by Becker and Van Ee.

From the experimental results it followed that the physical picture of dimer-formation (which is in fact the first stage of condensation) is correct, but that it is very hard to calculate precisely the consequences for thermal diffusion among other things because of the many, often badly known, parameters involved.

From the comparison of the values found by experiment and by calculation we can draw the conclusion that the predictions of the pair-correlation theory give the best agreement with the experimental results.

In the first place we have to consider the theory of gases. It is well known that the molecules of a gas are in constant motion. This motion is not only in the direction of the force of gravity, but also in the direction of the force of the walls of the container. The result of this motion is that the molecules of a gas exert a pressure on the walls of the container. This pressure is the same in all directions. This is the theory of the pressure of a gas.

The second part of the theory is the theory of the diffusion of gases. It is well known that if two different gases are mixed together, they will gradually mix themselves together. This is the theory of the diffusion of gases. It is the result of the random motion of the molecules of the two gases. The molecules of the two gases will eventually mix themselves together, and the result will be a uniform mixture of the two gases. This is the theory of the diffusion of gases.

The third part of the theory is the theory of the viscosity of gases. It is well known that if two different gases are mixed together, they will gradually mix themselves together. This is the theory of the viscosity of gases. It is the result of the random motion of the molecules of the two gases. The molecules of the two gases will eventually mix themselves together, and the result will be a uniform mixture of the two gases. This is the theory of the viscosity of gases.

## S A M E N V A T T I N G

Het in dit proefschrift beschreven onderzoek betreft de drukafhankelijkheid van de thermodiffusiefactor in een gebied, waar drie-deeltjes botsingen nog niet van belang zijn. De directe aanleiding vormde het werk van Velds aan He-CO<sub>2</sub> mengsels, waarbij bleek dat een toenemende concentratie van CO<sub>2</sub> een toenemende drukafhankelijkheid van de thermodiffusiefactor ten gevolge had. Dit werd toegeschreven aan het feit, dat CO<sub>2</sub> zich minder als een ideaal gas gedraagt dan He.

Om na te gaan hoe dit verder geïnterpreteerd zou moeten worden is aanvankelijk gebruik gemaakt van het feit, dat bij hogere drukken de moleculen de neiging vertonen zich twee aan twee samen te voegen tot zgn. dimeren (tweelingmoleculen). Door nu de componenten en hun concentraties te wijzigen kan de concentratie van de mogelijke dimeren beïnvloed worden, hetgeen tot voorspelbare veranderingen van de thermodiffusiefactor zou moeten leiden. Dit bepaalde in feite de keuze van het meetprogramma: door nu eens de ene dan weer de andere component de hoogste concentratie te geven kan men het aantal gevormde dimeren wijzigen en kan voorspeld worden of de thermodiffusiefactor groter of kleiner wordt. Dit is in hoofdstuk III nader uitgewerkt, waarbij aanvankelijk verondersteld werd dat slechts één van de aanwezige componenten dimeren kon vormen, terwijl later de mogelijkheid dat beide componenten dimeren vormen (ook met elkaar) in ogenschouw genomen werd. Voor de berekening van de aanwezige hoeveelheden dimeren is gebruik gemaakt van de voorspellingen hieromtrent door Stogryn en Hirschfelder en van de door Leckenby en Robbins gemeten aantallen.

Bij de keuze van het mengsel, dat als laatste is opgenomen, speelde nog een andere overweging mee: het verschil tussen de door Stogryn en Hirschfelder berekende en door Leckenby en Robbins gevonden waarden gaf aanleiding tot het vermoeden dat interne vrijheidsgraden van de moleculen een rol speelden bij de vorming van dimeren, weshalve een experiment gedaan is waarbij deze interne vrijheidsgraden geen invloed konden hebben.

De experimenten zijn uitgevoerd in een twee-bollen apparaat dat eerder beschreven werd door Velds. De ondertemperatuur was bij alle experimenten ongeveer 36 °C, de boventemperatuur ongeveer 255 °C; de druk varieerde tussen 5 en 50 atmosfeer.

Behalve met berekeningen betreffende de invloed van dimeren zijn de experimentele resultaten ook vergeleken met enkele andere voorspellingen.

In de eerste plaats moet hierbij genoemd worden de theorie van Haase, waarin verondersteld wordt dat de zgn. heat-of-transfer niet afhangt van de druk. Deze heat-of-transfer is een grootheid die optreedt in de behandeling van de thermodiffusiefactor in het boek van de Groot over de thermodynamica van irreversibele processen.

Een betere benadering van de heat-of-transfer is gegeven door Bearman, Fixman en Kirkwood. Van hun resultaten - benaderd opnieuw afgeleid in een evenwichtsbeschouwing - is gebruik gemaakt in hoofdstuk II. Aangezien het hier gaat om beschouwingen die de onderlinge interactie van molecuul-paren in rekening brengen, wordt hier gesproken over de paar-correlatie theorie.

Verder is nog aandacht besteed aan een door Velds reeds behandelde invloed van de niet-idealiteit van de componenten van het mengsel: niet de partiële drukken, maar de fugaciteiten van de componenten van het mengsel zijn overal in het vat gelijk.

Om de vergelijking tussen berekende en experimentele waarden zo volledig mogelijk te maken, is nog gebruik gemaakt van de experimentele resultaten, gepubliceerd door Becker en door van Ee.

Uit de experimentele resultaten volgde, dat het fysische beeld van de dimeervorming - in feite het begin van het condensatie-proces - wel juist is, doch dat de consequenties voor de thermodiffusie o.m. door de vele, vaak slecht bekende, parameters die in de berekening voorkomen, moeilijk precies te berekenen zijn.

Uit de vergelijking van de experimenten met de verschillende beschouwingen kan de conclusie getrokken worden, dat de paar-correlatie berekeningen de beste overeenkomst met de verkregen experimentele resultaten opleveren.

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