EXPERIMENTAL AND THEORETICAL THERMAL DIFFUSION FACTORS IN BINARY AND TERNARY MIXTURES

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PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN
DOCTOR IN DE WIS- EN NATUURKUNDE
AAN DE RIJKSUNIVERSITEIT TE LEIDEN
OP GEZAG VAN DE RECTOR MAGNIFICUS
MR. J. E. JONKERS, HOOGLERAAR IN DE
FACULTEIT DER RECHTSGELEERDHEID,
TEGEN DE BEDENKINGEN VAN DE FACULTEIT DER WIS- EN NATUURKUNDE TE VERDEDIGEN OP DONDERDAG 5 NOVEMBER 1959
TE 16.00 UUR

DOOR

MANUEL FERNANDES LARANJEIRA

GEBOREN TE CABANAS-CARREGAL DO SAL (PORTUGAL) IN 1928

KLEIN OFFSETDRUKKERIJ POORTPERS N.V.

1959

Promotor: Prof.Dr J.Kistemaker

To my wife and my son

To my parents

The work done in connection with this thesis was partially financed by the Foundation for Pure and Scientific Research, (Z.W.O.), in The Hague. It was part of the scientific programme of the Foundation for Fundamental Research of Matter (F.O.M.).

ACKNOWLEDGEMENT

At the end of my pleasant stay in the Netherlands I thank all those people who have helped to make this time as useful and agreeable as it has been.

I should like to thank my promotor, Prof.Dr J.Kistemaker, for his attention and criticism during my stay in his laboratory and for the interest he always gave to this thesis.

The fundamental part of this work was done at the Laboratorium voor Massaspectrografie. It is quite impossible to mention here all the individual help which I have always received from the staff of this laboratory. Friendship is not enough to express the gratitude which I feel after a stay of two years. More specially in connection with this thesis, I want to thank Dr Heymann and Drs van der Valk for their criticism, and Dr de Vries, Dr Boerboom, Drs Rol, Bob Schutten, Miss de Vletter, Meester Janssen, Frans Monterie, Ton Haring, Maarten Hoogervorst and all the people of the workshops for their kind help.

I should also like to thank Prof.Herculano de Carvalho, Prof. Julio Palacios and Prof.Abreu Faro and all the people of the Laboratório de Física da Comissão de Estudos for their interest in this work.

I want to thank the Stichting voor Fundamenteel Onderzoek der Materie for the kind hospitality and the Comissão de Estudos de Energia Nuclear do Instituto de Alta Cultura for supporting my stay in Amsterdam.

CONTENTS

MOST IMPORTANT NOTATIONS USED IN THIS THESIS

a_i	quantity related to the 'hardness' of the gas i (eq. 14.IV).
$a_{ij} = (a_i + a_j)/2$	
3A	numerical factor which depends on the intermolecular force (eq. 23.III).
$A_A = c_1^{(b)}A_1 + c_2^{(b)}A_2$	for a gas A consisting of two isotopes, 1 and 2.
$A_i = (m_i/\eta_i)^{½}$	if the gas consists of several isotopes the coefficient of viscosity for each isotope is identified with that of the natural gas.
$A_i' = \frac{1 - a_j}{1 - a_{ij}} A_i$	
$A_{kji}^{(res)} = [\alpha_{kj}^{(b)}(res)]_k - [\alpha_{ki}^{(b)}(res)]_k$	
$A_{kji}^{(sm)} = [\alpha_{kj}^{(b)}(sm)]_k - [\alpha_{ki}^{(b)}(sm)]_k$	
c_A	molar concentration of the gas A. If the gas consists of two isotopes of the kinds 1 and 2, then $c_A = c_1 + c_2$.
$c_i = n_i/n$	molar concentration $\sum_{k=1}^{s} c_k = 1$.
$c_i^{II}; c_i^{I}$	molar concentrations at absolute temperatures T^{II} and T^{I}.
$c_i^{(b)}$	molar concentration of the gas i in a binary mixture (i,k).
$(c_i/c_j)^{II}; (c_i/c_j)^{I}$	molar concentration ratios at absolute temperatures T^{II} and T^{I}.
D_{ij}	Meyer's coefficient of concentration diffusion in a binary mixture.
D_{ii}	coefficient of self-diffusion.
$[D_{ij}]_1$	first approximation for D_{ij}.
$[D_{ii}]_1$	first approximation for D_{ii}.
F_{ij}	force acting between molecules of kinds i and j.
k	Boltzmann's constant.
$k_{ij}; k_{ij}'$	force constants.
K_{pi}	general notation for the pressure diffusion ratio of the gas i.

K_{pi}(Chap); $[K_{pi}(\text{Chap})]_1$	Chapman-Enskog's pressure diffusion ratio.
K_{pi}(elem); $[K_{pi}(\text{elem})]_1$	elementary pressure diffusion factor. Only used for comparison with Chapman-Enskog's theory.
K_{Ti}	general notation for the thermal diffusion ratio of the gas i.
K_{Ti}(Chap); $[K_{Ti}(\text{Chap})]_1$	thermal diffusion ratio of the gas i given by Chapman-Enskog's theory.
K_{Ti}(elem); $[K_{Ti}(\text{elem})]_1$	thermal diffusion ratio, as given by our treatment, for comparison with Chapman-Enskog's theory only.
l_i	mean free path for number density transfer.
l'_i	mean free path related to thermal diffusion. In our treatment it is called mean free path for 'mean thermal speed' transfer.
l''_i	mean free path for momentum transfer.
${}_M l_i$	Maxwell's mean free path.
${}_P l_i$	Maxwell's mean free path for number density transfer corrected for 'persistence of velocities'.
$[{}_P l_i]_1$	first approximation for ${}_P l_i$, eq. (28, 30.III).
${}_P l''_i$	Maxwell's mean free path for momentum transfer corrected for 'persistence of velocities'. (Eq.17.III), given by Jeans and Whalley and Winter.
m_i	molecular mass.
$M_{ij} = m_i/(m_i + m_j)$; $M_{ji} = m_j/(m_i + m_j)$.	
$n = \sum_{k=1}^{s} n_k$.	
n_i	number density of the gas i (molecular density).
p	pressure.
$q_{ij} = \dfrac{(c_i/c_j)^{II}}{(c_i/c_j)^{I}}$	separation factor achieved by thermal diffusion for the gases i and j, in this succession.
Q_i; Q_j; Q_{ij}	see equations (17.IV) for our elementary theory.

$R_{ij} = \frac{[\alpha_{ij}(sm)]_1}{[\alpha_{ij}(res)]_1}$	theoretical thermal separation ratio defined by elementary thermal diffusion factors.
$R_{ij}(exp) = \frac{\alpha_{ij}(exp)}{[\alpha_{ij}(res)]_1}$	experimental thermal separation ratio, always referred to our elementary first approximation to the thermal diffusion factor for ‘rigid elastic spheres’.
$[R_{ij}]_k$	limiting value for R_{ij} as $c_k = 1$. Mostly used in multicomponent mixtures.
$R_{ij}^{(b)}$	thermal separation ratio of gases i and j in a binary mixture (i,j). Only used in the theory of multicomponent mixtures.
$[R_{ij}^{(b)}]_i$	limiting value of $R_{ij}^{(b)}$ as $c_i^{(b)} = 1$. Mostly used in multicomponent mixtures.
$R_T = \frac{\alpha_{ij}(exp)}{[\alpha_{ij}(Chap)]_1}$	experimental separation ratio of gases i and j, always referred to Chapman-Cowling's first approximation for the thermal diffusion factor for rigid elastic spheres.
$R_T(elem) = \frac{[\alpha_{ij}(elem)]_1}{[\alpha_{ij}(Chap)]_1}$	theoretical thermal separation ratio of our elementary treatment referred to Chapman-Cowling's first approximation.
R_{kji}	see equation (53.V).
S_i; S_j	see equation (18.IV) for our elementary theory.
$S_i = c_i^{II} - c_i^{I}$	separation achieved by thermal diffusion for the gas i.
T	absolute temperature.
T^{II} and T^{I}	absolute temperatures at respectively the hot and the cold part of a thermal diffusion apparatus.
u_i	thermal speed.
$\bar{u}_i$	mean thermal speed.
$\vec{u}_i$	thermal velocity.
$\vec{U}_i$	flux velocity.
$\vec{U}_i - \vec{U}_j$	velocity of mutual diffusion for gases i and j in this succession.
$v_i = 1.086\,\bar{u}_i$	root-mean square of thermal velocities (square root of the mean square of thermal velocities).

$(\alpha_p)_{ij}$; $[(\alpha_p)_{ij}]_1$	general notation for the pressure diffusion factor of gases i and j in this succession.
$[(\alpha_p)_{ij}(\text{elem})]_1$	elementary first approximation to the pressure diffusion factor.
$[(\alpha_p)_{ij}(\text{Chap})]_1$	Chapman-Cowling's first approximation to the pressure diffusion factor.
α_{ij}; $[\alpha_{ij}]_1$	general notation for the thermal diffusion factor of gases i and j, in this succession, when no confusion arises with the pressure diffusion factor.
$[\alpha_{ij}(\text{Chap})]_1$	Chapman-Cowling's first approximation to the thermal diffusion factor for rigid elastic spheres.
$\alpha_{ij}(\text{elem})$; $[\alpha_{ij}(\text{elem})]_1$	elementary thermal diffusion factor for 'rigid elastic spheres'. Only used for comparison with Chapman-Enskog's theory.
$\alpha_{ij}(\text{exp})$	experimental thermal diffusion factor.
$\alpha_{ij}(\text{res})$; $[\alpha_{ij}(\text{res})]_1$	elementary thermal diffusion factor for 'rigid elastic spheres'.
$\alpha_{ij}(\text{sm})$; $[\alpha_{ij}(\text{sm})]_1$	theoretical thermal diffusion factor for 'soft' molecular interactions. Only used for our elementary treatment.
$[\alpha_{ij}(\text{sm})]_k$; $[\alpha_{ij}(\text{res})]_k$	limiting values of $\alpha_{ij}(\text{sm})$ and $\alpha_{ij}(\text{res})$ as $c_k = 1$. Mostly used for multicomponent mixtures.
$\alpha_{ij}^{(b)}(\text{sm})$; $[\alpha_{ij}^{(b)}(\text{sm})]_1$	elementary thermal diffusion factors for a binary mixture of gases i and j. Only used in the theory of multicomponent mixtures.
$[\alpha_{ij}^{(b)}(\text{sm})]_i$; $[\alpha_{ij}^{(b)}(\text{res})]_i$	limiting values of $\alpha_{ij}^{(b)}(\text{sm})$ and $\alpha_{ij}^{(b)}(\text{res})$ respectively, as $c_i^{(b)} = 1$. Mostly used in multicomponent mixtures.
$[\alpha_{ij}^{(b)}(\text{sm})]_j$; $[\alpha_{ij}^{(b)}(\text{res})]_j$	limiting values of $\alpha_{ij}^{(b)}(\text{sm})$ and $\alpha_{ij}^{(b)}(\text{res})$ respectively, as $c_j^{(b)} = 1$. Mostly used in multicomponent mixtures.
$(\alpha_T)_{ij}$; $[(\alpha_T)_{ij}]_1$	general notation for the thermal diffusion factor of gases i and j in this succession.
σ_i;	molecular diameters.
σ_{ij}	mutual collision diameter for the molecules of kinds i and j. For rigid elastic spheres $\sigma_{ij} = (\sigma_i + \sigma_j)/2$.

ν_i; ν_j; ν_{ij};	power force constants.
$\Delta_{ij}(\text{res}) = \dfrac{[\alpha_{ij}(\text{res})]_1}{[\alpha_{ij}^{(b)}(\text{res})]_1}$	in multicomponent mixtures only. Molar concentrations are such that $c_i/c_i^{(b)} = c_j/c_j^{(b)}$.
$\Delta_{ij}(\text{sm}) = \dfrac{[\alpha_{ij}(\text{sm})]_1}{[\alpha_{ij}^{(b)}(\text{sm})]_1}$	in multicomponent mixtures only. Molar concentrations are such that $c_i/c_i^{(b)} = c_j/c_j^{(b)}$.
$[\Delta_{ij}(\text{sm})]_k$	limiting value of $\Delta_{ij}(\text{sm})$ as $c_k = 1$.
$[\Delta_{ij}(\text{res})]_k$	limiting value of $\Delta_{ij}(\text{res})$ as $c_k = 1$.
η_i	coefficient of viscosity of the gas i.
$[\eta_i]_1$	first approximation for η_i.
ρ_i	density of the gas i.

CHAPTER I

INTRODUCTORY SURVEY ON THERMAL DIFFUSION

§ 1. *Introduction*

From the exact theory of transport phenomena in gases, diffusion should arise because of non-homogeneity of composition, temperature and pressure. For example, in a binary mixture with uniform temperature and pressure but non-uniform concentration, the components move in opposite directions, each down its concentration gradient. Diffusion originated in this way is called ordinary or *concentration diffusion*.

If in a mixture, initially with uniform concentrations and pressure, a temperature gradient is set up, a relative motion of the components may occur leading to the development of concentration gradients. This type of diffusion is called *thermal diffusion*.

Since the concentration gradients originated by thermal diffusion in turn cause concentration diffusion, a steady state may exist which balances these two processes. Thermal diffusion thus gives rise to a partial separation of the components of the initially uniform mixture.

According to Chapman (C1) the general equation of diffusion in a binary mixture contains a term representing diffusion due to a pressure gradient. Diffusion arising from this way is called *pressure diffusion*. Pressure diffusion, however, has been studied little because of the difficulties which experimental work gives rise to.

Thermal diffusion was first discovered experimentally in liquids by Ludwig and more fully investigated by Soret (1879-81). Soret filled a straight vertical tube with various salt solutions and set up a temperature gradient in it by heating the upper part and cooling the lower. After about fifty days the solute was more concentrated in the lower, cooler part than in the other.

In contrast, thermal diffusion in gases was first discovered theoretically by Enskog (E1,E2,E3) and independently by Chapman (C2,C3,C4,C5). Experimental confirmation was first given by Chapman and Dootson (C6). In their experiments two bulbs were connected by a tube and the system was filled with a mixture of Hydrogen and Carbon Dioxide or Hydrogen and Sulfur Dioxide.

One bulb was heated to about 200° C. and the other was at room temperature. After some hours the Hydrogen content of the mixture in the hot bulb was enriched by two or three per cent. relatively to the cold bulb.

In 1939 Clusius and Dickel (C7) proposed their famous thermal diffusion column and showed how the small elementary effect could be increased by tremendous factors in a very easy way. In short, the column was a vertical glass tube along the axis of which there was a nichrome wire which was heated electrically. The horizontal temperature gradient set up in the mixture produces an elementary thermal diffusion separation, at any instant, in the gases within the glass wall and the hot wire; a continuous convective flow of the gases, up the hotter surface and down the cooler, changes, at any instant, the concentration gradients established by the former process. Such a convective flow tends, therefore, to reduce the concentration gradients first formed. For this reason another elementary thermal diffusion separation will follow between the components of the mixture; and so forth. As a consequence of those two processes the column provides a strong separation between the components of the mixture, one concentrating at the upper part and the other at the lower end of the column.
By this way Clusius and Dickel could separate, almost completely, first the isotopes of Chlorine and subsequently those of several other elements, showing the practical interest of thermal diffusion.

§ 2. *Thermal diffusion and molecular interactions*

One important feature of the exact theory of thermal diffusion is that this transport phenomenon should be strongly dependent on the forces acting between the molecules in collision, providing one of the best means for investigating these forces. The most important molecular models which have been treated so far are the following:

1 - Rigid elastic sphere model (C1,G3).This is the simplest model. The molecules are regarded as 'billiard-balls' with diameters σ. The forces acting between like and unlike molecules in collision are equal to zero except at the instant of collision when they become infinitely large.

The practical interest of this model is rather small because numerical predictions are well far from experimental data of thermal diffusion.

2 - *The inverse power repulsion model.* In this model the molecules are regarded as centers of repulsive forces, F_{ij}, which vary as the $-\nu_{ij}$ power of the mutual distance, r:

$$F_{ij} = k_{ij}\, r^{-\nu_{ij}} \tag{1.I}$$

where k_{ij} and ν_{ij} are the force constants.

According to the theory, the coefficient of viscosity should vary with temperature as

$$T^{\frac{1}{2} + \frac{2}{\nu_i - 1}} \tag{2.I}$$

which provides a way to determine the force index ν_i of a pure gas relative to collisions of like molecules. Usually a gas is called 'hard' if ν_i is large and 'soft' if ν_i is small.

The coefficient of diffusion should vary with temperature as

$$T^{\frac{3}{2} + \frac{2}{\nu_{ij} - 1}} \tag{3.I}$$

where ν_{ij} is the force index for collisions of unlike molecules.

Thermal diffusion effect is dependent on the forces acting between like and unlike molecules but its magnitude is mostly determined by collisions of the type (i,j) being roughly proportional to

$$\frac{\nu_{ij} - 5}{\nu_{ij} - 1} \tag{4.I}$$

Therefore the magnitude of the thermal diffusion effect is strongly dependent on the 'hardness' of molecular interactions. If molecules repel each other as the fifth power of the distance no thermal diffusion separation occurs. This is the well known case of 'Maxwellian' gases to which the coefficient of viscosity should vary with temperature as T and the coefficient of concentration diffusion as T^2.

The rigid elastic sphere model may be considered as a particular case of the inverse power repulsion model assuming that the force indices ν_i, ν_j and ν_{ij} for collisions of the types (i,i), (j,j) and (i,j) are all equal to infinity. Therefore, the coefficients of viscosity of gases i and j theoretically vary with temperature as $T^{1/2}$ and the coefficient of concentration diffusion as $T^{3/2}$. The ratio of the coefficient of thermal diffusion, as given by the inverse power repulsion model, to the corresponding value of the rigid elastic sphere model is roughly equal to (4.I). For most natural gases the force index ν_{ij} is of the order of 5 to 15. Therefore marked differences occur between theoretical predictions of thermal diffusion according to both models.

Though giving a better agreement with experiments, the inverse power repulsion model is not adequate to explain thermal diffusion data, particularly the variation usually observed with temperature, which according to this model should be mostly expressed by the factor (4.I) which theoretically should be regarded as a constant. However, rough predictions may be obtained considering that the force indices change with temperature. Usually the values of ν_i and ν_j at any temperature are estimated from the variation of the coefficients of viscosity of the gases with temperature and a mean value for ν_{ij} is chosen. Conversely, if experimental thermal diffusion data are available, an 'averaged force index' ν_{ij} is obtained assuming that temperature variation is mostly expressed by the factor (4.I).

3 - *The Lennard-Jones model* (C1,G3,H8). In this model the intermolecular forces are assumed to be simultaneously repulsive and attractive:

$$F_{ij} = k_{ij}\, r^{-\nu_{ij}} - k'_{ij}\, r^{-\nu'_{ij}} \qquad (5.I)$$

where k_{ij} and ν_{ij} refer to the repulsive force, and k'_{ij} and ν'_{ij} to the attractive force.

Sutherland's model which represents a molecule as a rigid sphere of diameter σ surrounded by an attractive force field, can be regarded as a special case of Lennard-Jones model.

Rather few specialisations to particular values of the force constants appearing into equation (5.I) have been done. This part of theoretical development presents, however, many mathematical difficulties. The best studied case is the so-called 13-7 model for the force indices ν_{ij} and ν'_{ij} respectively. It provides rather good agreement with experiments even in such a sensitive process as thermal diffusion, in magnitude as well as temperature dependence, for a large number of observations which have been reported.

Unfortunately the Lennard-Jones model involves high mathematical complexity and it has not yet sufficiently been worked out. A few other specialisations have been proposed, viz. the 9-6 model, but they do not cover experimental results so well.

4 - As we have already referred, thermal diffusion was first theoretically discovered by Enskog and independently by Chapman. The works of these authors were based on classical mechanics. They have been treated so far in binary mixtures according to the models given above. In 1939 Hellund and Uehling (H1) extended Chapman-Enskog's theory taking into account quantum corrections. Modifications required by quantum theory are, however, mainly important at low temperatures in gases consisting of light molecules.

Exact theories of transport phenomena in complex mixtures have been presented by Hellund (H2) and Curtiss and Hirschfelder (C8), the former taking into account quantum corrections and the latter as an extension of Chapman's theory. Both involve high mathematical complexity.

Only a few observations have been reported for complex mixtures.

§ 3. *Elementary theories of thermal diffusion*

Several attempts have been made to give an explanation of thermal diffusion by means of elementary considerations as, for example, similar to those of a free path treatment of concentration diffusion, viscosity or conduction of heat.

In 1939 Gillespie (G9) showed that the heavier component of a binary mixture should diffuse down the temperature gradient. It is usually in accordance with Chapman-Enskog's exact theory. However, the author assumes a very restrictive hypothesis considering that all kinds of molecules of the mixture have the same free path.

By means of an interesting explanation Frankel (F1) could show, in agreement with the exact theory, that thermal diffusion should not occur between maxwellian molecules, i.e. molecules which repel each other inversely as the fifth power of their mutual distances. Following the way applied by Frankel, Furry (F2) presented in 1948 another approximate theory sacrifying, however, the elementary character of the treatment to a large extent.

The most satisfactory of the proposed elementary theories is that of Fürth (F3). Indeed, it can explain, at least qualitatively, all the essential features of thermal diffusion and just follows the general lines of a free path treatment of diffusion.

A general equation of diffusion should have three terms: one related to concentration diffusion which has been known since long ago, another related to thermal diffusion and another one to pressure diffusion. Fürth's theory only took into account concentration and thermal diffusion. Nevertheless an easy generalisation can also explain pressure diffusion.

In short, Fürth considered two kinds of mean free paths: one, l_i, being the mean distance over which the molecules of kind i should carry the attribute of the number density (molecular density), n_i; and another one, l_i', being the mean distance to carry the attribute of the root-mean square of the thermal velocities, v_i (square root of the mean square of thermal velocities). The root-mean square of thermal velocities was identified to the mean thermal speed, $\bar{u}_i$, which must be regarded as an approach, for we have, in general, $v_i = 1.086\ \bar{u}_i$. It is assumed that Maxwell's distribution law of thermal velocities is appropriated to the local temperature and density. Both n_i and v_i were supposed to be developed in power series in the vicinity of any point P inside the gas mixture.

The 'hardness' of molecular interactions was expressed by the ratios of mean free paths, l_i'/l_i and l_j'/l_j which Fürth assumed to be equal.

In 1949 Whalley and Winter (W1) worked out Fürth's theory extending it to complex mixtures of molecules behaving as rigid elastic spheres. Their general equation of diffusion contains already a term referring to pressure diffusion.

At least for binary mixtures, theoretical values agree rather well with those of the exact rigid elastic sphere model. However, the practical interest of Whalley and Winter's theory is small, indeed, because numerical computations are generally just as laborious as those of the exact Chapman-Enskog theory. Also, no reference is made to 'softer' molecular interactions. This is an important lack of Whalley and Winter's treatment because it is a well established feature that thermal diffusion is strongly dependent on the force fields surrounding the molecules.

The theory now proposed in this paper is similar to those of Fürth, and Whalley and Winter. It is, however, more general and it has been sufficiently worked out in binary as well as in complex mixtures, for thermal and pressure diffusion.

Two kinds of mean free paths have been considered: one, l_i, for number density transfer, and another one, l'_i, for 'mean thermal speed transfer', which are related by

$$l'_i = (1+a_i)\, l_i \qquad (6.I)$$

where a_i certainly depends on the force laws acting between colliding molecules: For the sake of simplicity, probably not reflecting the real situation, we assumed that a_i mostly depends on the force field surrounding the molecules of kind i.

We also use approximate formulae to the mean free path, l_i, obtained through the known mean free path for number density transfer corrected for 'persistence of velocities'. The resulting equations for thermal and pressure diffusion are then very simple to handle in binary as well as in multicomponent mixtures. This should be a characteristic of any elementary treatment. Our theory shows several unknown characteristics of thermal and pressure diffusion, namely that the inverse of the thermal diffusion factor - a quantity frequently used in experiments - should be linearly dependent on concentrations, at a first approximation, at least if molecular masses and diameters increase simultaneously, or if the mass ratio is not too close to unity when $m_j > m_i$ but $\sigma_j < \sigma_i$. This conclusion agrees closely with experience and Chapman-Enskog's theory.

CHAPTER II

A GENERAL EQUATION OF DIFFUSION BY A FREE PATH THEORY

§ 1. *Remarks on free path theories* (J1)

It is well known that the essential hypotheses of free path theories are the following: (1) Maxwell's law is locally applied to the distribution of velocities, at a first approximation; (2) the molecules may be regarded as transporters of their attributes of quality (transfer of molecules themselves), momentum and energy over small distances, the free paths.

Transfer of quality is related to diffusion; transfer of momentum is related to viscosity, and of energy to conduction of heat.

It is also considered that each attribute only slightly changes within a distance of a free path and it may thus be developed into a power series.

The simplest treatment assumes that the mean free paths for transfer of number density, mean momentum and mean energy are all equal to Maxwell's mean free path. For more elaborate theories different mean free paths are considered for each attribute transfer, due to several corrections which have been proposed, leading indeed to better agreement with exact Chapman-Enskog's theory and experiments. For instance: the transformation of Maxwell into Tait's mean free path by multiplying the first one by a factor nearly equal to 1.051; the use of Stefan-Maxwell's mean free path which only considers collisions of unlike molecules when treating concentration diffusion; corrections due to 'persistence of velocities' when studying concentration diffusion and viscosity.

In free path theories we are dealing, of course, with a mathematically inexact treatment, for a gas or a mixture in which transport phenomena occur is not in a steady state and therefore it does not obey Maxwell's law of distribution of velocities. Nevertheless, free path theories have been rather successful to predict the magnitude of the effects.

One important lack by which such theories have been faced was due to inability to explain thermal diffusion which is an important phenomenon after the theoretical work of Chapman and Enskog and after them has also been applied successfully by Clusius and others for separating isotopes. Now we may say that such inability was only apparent and actually due to the implicit assumption of ordinary theories that temperature was kept constant through the gas mixture. If not only temperature but also pressure is non-uniform, then a general equation of diffusion should have three terms related to concentration, temperature and pressure diffusion due to non-uniformity of composition, temperature and pressure, respectively.

§ 2. *General equation of diffusion in gaseous multicomponent mixtures*

2.1. Let there be a mixture of s gases of kinds 1,2,...,s each consisting of identical molecules of masses $m_1, m_2, \ldots, m_s$. Suppose n_i the local average number of molecules of kind i per unit volume (*number density*) and $\bar{u}_i$ the local mean thermal speed.

We assume that absolute temperature, T, and pressure, p, are not uniform, but Maxwell's law of distribution of thermal velocities is locally valid. Therefore we have, if no external forces act between the molecules of the gas mixture,

$$\bar{u}_i = \left(\frac{8kT}{\pi m_i}\right)^{1/2} \tag{1.II}$$

and

$$k\,T \sum_{i=1}^{s} n_i = p \tag{2.II}$$

where k is the Boltzmann's constant.

If we consider relatively to the gas mixture a fixed frame (OX,Y,Z), then the number densities, $n_1, n_2, \ldots, n_s$, the temperature and pressure, and therefore the mean thermal speeds, $\bar{u}_1, \bar{u}_2, \ldots, \bar{u}_s$, will be functions of the co-ordinates of the point P inside the gas they refer to. Making the hypothesis that in the vicinity of any point Q, the number density and the mean thermal speed only slightly change within a distance PQ, we may admit the following power series for $(n_i)_P$ and $(\bar{u}_i)_P$:

$$(n_i)_P = (n_i)_Q + x\left(\frac{\partial n_i}{\partial x}\right)_Q + y\left(\frac{\partial n_i}{\partial y}\right)_Q + z\left(\frac{\partial n_i}{\partial z}\right)_Q$$

$$(\bar{u}_i)_P = (\bar{u}_i)_Q + x\left(\frac{\partial \bar{u}_i}{\partial x}\right)_Q + y\left(\frac{\partial \bar{u}_i}{\partial y}\right)_Q + z\left(\frac{\partial \bar{u}_i}{\partial z}\right)_Q \tag{3.II}$$

where x,y,z are the components of the vector (P-Q).

The first equation of (3.II) is a consequence of non-uniformity of composition of the gas mixture. It is the only one which is considered by an ordinary free path theory of diffusion (concentration diffusion). The second one is now proposed in order to take into account thermal diffusion. Pressure diffusion does not need an additional hypothesis besides the known equation (2.II).

Let us consider an element of area, dS, around the point Q, on the plane Z_Q perpendicular to OZ (fig.1.II). Positive side of dS is directed to OZ increasing.

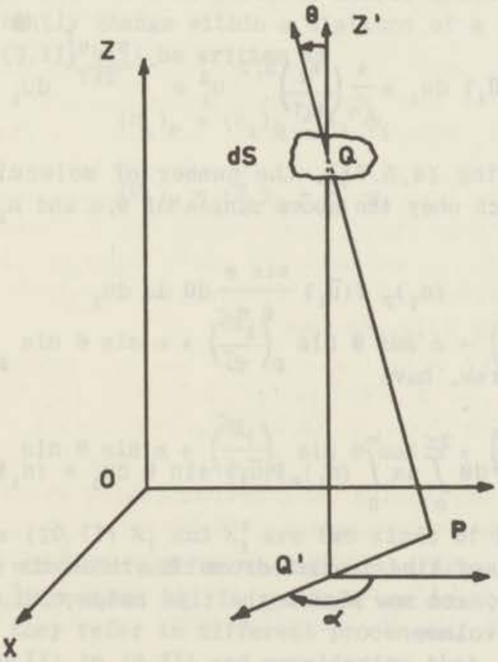

Fig. 1.II

The flow of molecules is assumed to be positive when they cross dS from the negative to the positive side. Regarding the parameters θ and α of fig.1, the total flow of molecules coming to dS and just crossing it, will be determined by integration over all the values of α from 0 to 2π, and over all the values of θ from 0 to π. The flow is positive for values of θ between 0 and $\pi/2$ and negative between $\pi/2$ and π.

2.2. We will now determine the number of molecules of kind i which cross dS in a small range of time t, dt.

Assuming the Maxwellian symmetrical distribution of thermal velocities, the probability that molecules come to Q, from an element of volume around P, within the angle ranges $\theta, d\theta$ and $\alpha, d\alpha$ is given by

$$\frac{\sin\theta \, d\theta \, d\alpha}{4\pi} \qquad (4.\mathrm{II})$$

On the other hand, the probability that a molecule of kind i has a thermal speed, in any direction of space, within a range u_i, du_i is (J1)

$$f(\vec{u}_i)\, du_i = \frac{4}{\sqrt{\pi}} \left(\frac{m_i}{2kT}\right)^{3/2} u_i^2 \, e^{-\frac{m_i u_i^2}{2kT}} \, du_i \qquad (5.\mathrm{II})$$

Hence, by using (4,5.II), the number of molecules per unit volume at P which obey the above ranges of θ, α and u_i is given by

$$(n_i)_P \, f(\vec{u}_i) \, \frac{\sin\theta}{4\pi} \, d\theta \, d\alpha \, du_i \qquad (6.\mathrm{II})$$

We must, of course, have

$$\frac{1}{4\pi} \int_0^{\pi} d\theta \int_0^{2\pi} d\alpha \int_0^{\infty} (n_i)_P f(\vec{u}_i) \sin\theta \, du_i = (n_i)_P \qquad (7.\mathrm{II})$$

The molecules of kind i which cross dS within the ranges $\theta, d\theta$; $\alpha, d\alpha$ and u_i, du_i, and now within the time range t, dt, must occupy the element of volume

$$(W_z + u_i \cos\theta) \, dS \, dt \qquad (8.\mathrm{II})$$

where W_z is the OZ component of the common stream velocity, $\vec{W}$, relative to which the thermal velocities are supposed to be of spherical symmetry.

Now, the number of molecules per unit volume, $(\Gamma_{iz})_Q$ dS dt, coming from an element of volume around P within the time range t,dt is therefore equal to the product of expressions (6.II) and (8.II). The total flow, $(\Gamma_{iz})_Q$, per unit area at Q, per unit time, in the direction of OZ increasing is thus,

$$(\Gamma_{iz})_Q = \frac{1}{4\pi}\int_0^{\pi} d\theta \int_0^{2\pi} d\alpha \int_0^{\infty} (n_i)_P \left[W_z + u_i \cos\theta \right]_P f(\vec{u}_i) \sin\theta \, du_i \tag{9.II}$$

2.3. Let us now evaluate the integral equation (9.II). In accordance with the principles of ordinary free path theory we consider that the molecules coming to Q have suffered their last collisions at P. Therefore the molecules of kind i which transfer their attributes of number density and thermal speed through the elementary surface, dS, will come from a distance of a free path.

If we assume that the attributes of number density and thermal speed only slightly change within a distance of a free path, the power series (3.II) will be written as

$$(n_i)_P = (n_i)_Q - \lambda_i \varphi_i$$

$$(\bar{u}_i)_P = (\bar{u}_i)_Q - \lambda_i' \psi_i \tag{10.II}$$

where

$$\varphi_i = \left(\frac{\partial n_i}{\partial x}\right)_Q \sin\theta \sin\alpha + \left(\frac{\partial n_i}{\partial y}\right)_Q \sin\theta \cos\alpha + \left(\frac{\partial n_i}{\partial z}\right)_Q \cos\theta$$

$$\psi_i = \left(\frac{\partial \bar{u}_i}{\partial x}\right)_Q \sin\theta \sin\alpha + \left(\frac{\partial \bar{u}_i}{\partial y}\right)_Q \sin\theta \cos\alpha + \left(\frac{\partial \bar{u}_i}{\partial z}\right)_Q \cos\theta \tag{11.II}$$

In equations (10.II) λ_i and λ_i' are two kinds of free paths for number density transfer and for 'thermal speed transfer', respectively, in the direction PQ. In general, we do not identify λ_i with λ_i' since they refer to different processes.

By using (10.II) in (9.II) and considering that
(1) the terms including products of derivatives may be neglected;

(2) λ_i and λ'_i may be regarded as independent of θ and α since the attributes of the molecules change only slightly within a distance of a free path;

(3) the common stream velocity, as used in ordinary free path theories, is not a function of position,

the general equation of flow of molecules per unit area and time, in the direction of OZ increasing is thus,

$$(\Gamma_{iz})_Q = (n_i)_Q W_z - \frac{1}{3} (\bar{u}_i)_Q \left(\frac{\partial n_i}{\partial z}\right)_Q l_i - \frac{1}{3} (n_i)_Q \left(\frac{\partial \bar{u}_i}{\partial z}\right)_Q l'_i \qquad (12.II)$$

where l_i is the mean value of λ_i averaged over all the values of thermal speeds from 0 to infinity, namely

$$l_i = \frac{\int_0^\infty \lambda_i u_i f(\vec{u}_i)\, du_i}{\int_0^\infty u_i f(\vec{u}_i)\, du_i} \qquad (13.II)$$

Following Tait and Boltzmann, Jeans (J1) gives l_i as 1.051 times Maxwell's mean free path. We call l_i *the mean free path for number density transfer.*

The mean free path, l'_i, should accordingly be defined. We call it the *'mean free path for thermal speed transfer'*.

Since l_i and l'_i refer to different processes of attribute transfer they may be different in general. In our treatment we furthermore assume that the ratio $l'_i/l_i = 1+a_i$ may express the 'hardness' of the force fields surrounding the molecules of kind i.

Equation (12.II) without the third term on the right hand side is the well known flux equation as given by the ordinary free path theory (J1). The new term

$$\frac{1}{3} (n_i)_Q \left(\frac{\partial \bar{u}_i}{\partial z}\right)_Q l'_i \qquad (14.II)$$

is just a consequence of non-uniformity of temperature being therefore related with thermal diffusion.

Since point Q and direction OZ were arbitrarily chosen, the flux equation (12.II) can be presented into a vectorial form. By using equations (1,2.II) and introducing the molar concentration,

$$c_i = n_i / \sum_{k=1}^{s} n_k = n_i/n \qquad (15.II)$$

we obtain

$$\vec{\Gamma}_i = n_i\vec{W} - \frac{1}{3} n_i\bar{u}_i[l_i \text{ grad} \ln c_i + l_i \text{ grad} \ln p - (l_i - l_i'/2) \text{ grad} \ln T] \tag{16.II}$$

2.4. General equation of diffusion in multicomponent mixtures. By means of equation (16.II) we can define a flux velocity of molecules of kind i in a mixture of s gases as

$$\vec{U}_i = \vec{\Gamma}_i/n_i \tag{17.II}$$

We say that two gases, i and j, are mutually diffusing when $\vec{U}_i$ and $\vec{U}_j$ are not equal. The rate of mutual diffusion is given by $\vec{U}_i - \vec{U}_j$. By using (16,17.II) we obtain

$$\vec{U}_i - \vec{U}_j = -\frac{1}{3}(\bar{u}_i l_i \text{ grad} \ln c_i - \bar{u}_j l_j \text{ grad} \ln c_j) - \tag{18.II}$$

$$-\frac{1}{3}(\bar{u}_i l_i - \bar{u}_j l_j) \text{ grad} \ln p + \frac{1}{3}[\bar{u}_i(l_i - l_i'/2) - \bar{u}_j(l_j - l_j'/2)] \text{ grad} \ln T$$

This equation shows that *the velocity of diffusion has three terms due to non-uniformity of composition, pressure and temperature.* If temperature and pressure are kept constant through the gas mixture, then (18.II) reduces to the ordinary free path equation of concentration diffusion.

Introducing (1.II) into (18.II) we obtain the following equivalent equation of diffusion:

$$\vec{U}_i - \vec{U}_j = -\left(\frac{8kT}{9\pi}\right)^{1/2} [(X_i \text{ grad} \ln c_i - X_j \text{ grad} \ln c_j) + \tag{19.II}$$

$$+ Z_{ij} \text{ grad} \ln p - \frac{1}{2} Z_{ij}' \text{ grad} \ln T]$$

where, in a general form,

$$X_k = l_k m_k^{-1/2} \; ; \; Z_{ij} = X_i - X_j = l_i m_i^{-1/2} - l_j m_j^{-1/2} \tag{20.II}$$

$$\frac{1}{2} Z_{ij}' = (l_i - l_i'/2) m_i^{-1/2} - (l_j - l_j'/2) m_j^{-1/2}$$

Notice that the quantity Z_{ij}' which determines the magnitude of thermal diffusion velocity, is strongly dependent on the differences $(l_i - l'_i/2)$ and $(l_j - l'_j/2)$. For example, if $l'_i = 2\ l_i$ and also $l'_j = 2\ l_j$, then no thermal diffusion occurs between gases of kinds i and j. This immediately suggests that the difference of the mean free path for 'mean thermal speed transfer' from the corresponding mean free path for number density transfer may somehow express the 'hardness' of the force fields surrounding the molecules.

For a mixture of s gases we have s-1 independent equations similar to (19.II). The thermal diffusion velocity may be zero for the gases i and j and, a priori, not zero for the gases i and k. Therefore the simplest assumption, probably not reflecting the real situation, is to consider that the difference $(l_i - l'_i/2)$ mostly depends on the 'hardness' of the gas i. This hypothesis will be taken in the following chapter. It seems to be rather satisfactory to explain experimental thermal diffusion data.

2.5. *Formal comparison with Fürth's, and Whalley and Winter's theories* (F3,W1). Following Fürth's treatment of thermal diffusion in binary mixtures, Whalley and Winter could obtain a general equation of diffusion which differs from our equation (19.II) only in the numerical factor which is given by the authors as $(k\ T/3)^{1/2}$. This is a result of the identification of the mean thermal speed to the root-mean square of thermal velocities which has been made by Fürth through all of his theory. From the foregoing paragraphs we may conclude that the error resulting from such an identification may easily be avoided without any increasing complexity in the mathematical treatment of free path theory.

Whalley and Winter worked out their theory according to a rigid elastic sphere model. l_i is identified to the mean free path for number density transfer corrected for 'persistence of velocities'; l'_i was identified to the mean free path for momentum transfer to which an approximate formula is proposed, also corrected for 'persistence of velocities'.

Fürth's equation of diffusion does not take into account pressure diffusion, and it has been given for binary mixtures only. It can be obtained assuming into (19.II) $c_i + c_j = 1$ and changing the numerical factor into $(kT/3)^{1/2}$.

§ 3. *General equation of diffusion for binary mixtures. Formal comparison with exact Chapman-Enskog theory*

In the particular case of binary mixtures (i,j), molar concentrations are such that $c_i + c_j = 1$. Hence, by means of (18, 19.II), the equation of diffusion is written as

$$\vec{U}_i - \vec{U}_j = - \frac{D_{ij}}{c_i c_j} (\text{grad } c_i - K_{Ti} \text{ grad } \ln T + K_{pi} \text{ grad } \ln p) \qquad (21.II)$$

where

$$D_{ij} = \frac{1}{3} (\bar{u}_i l_i c_j + \bar{u}_j l_j c_i) \qquad (22.II)$$

$$K_{Ti} = c_i c_j (\alpha_T)_{ij} \; ; \; K_{pi} = c_i c_j (\alpha_p)_{ij} \qquad (23.II)$$

$$(\alpha_T)_{ij} = \frac{1}{2} \cdot \frac{\bar{u}_i (2l_i - l_i') - \bar{u}_j (2l_j - l_j')}{\bar{u}_i l_i c_j + \bar{u}_j l_j c_i} \qquad (24.II)$$

$$(\alpha_p)_{ij} = \frac{\bar{u}_i l_i - \bar{u}_j l_j}{\bar{u}_i l_i c_j + \bar{u}_j l_j c_i} \qquad (25.II)$$

or equivalently,

$$(\alpha_T)_{ij} = \frac{1}{2} \cdot \frac{(2l_i - l_i') m_j^{1/2} - (2l_j - l_j') m_i^{1/2}}{l_i c_j m_j^{1/2} + l_j c_i m_i^{1/2}} \qquad (26.II)$$

$$(\alpha_p)_{ij} = \frac{l_i m_j^{1/2} - l_j m_i^{1/2}}{l_i c_j m_j^{1/2} + l_j c_i m_i^{1/2}} \qquad (27.II)$$

Equation of diffusion (21.II) shows the existence of three terms relating respectively to concentration diffusion, thermal and pressure diffusion due to non-uniformity of composition, temperature and pressure. It is formally identical to that given, by the exact Chapman-Enskog theory (C1). D_{ij} as given by equation (22.II) is the well known *coefficient of concentration diffusion* for a binary mixture (i,j), usually called *Meyer's coefficient of diffusion.*

The quantities K_{Ti} and $(\alpha_T)_{ij}$ are respectively the *thermal diffusion ratio* of the gas of kind i and the *thermal diffusion* *factor* of gases i and j, *in this succession*, usually indicated in binary mixtures as K_T and α respectively. Notice that the sign of the thermal diffusion factor must be fixed by convention. In practice it is usual to consider that the thermal diffusion factor is positive when the lighter molecules diffuse into hotter regions. When a steady state is reached, $\vec{U}_i - \vec{U}_j = 0$ and then,

$$\text{grad } c_i = K_{Ti} \text{ grad } \ln T - K_{pi} \text{ grad } \ln p \qquad (28.\text{II})$$

According to the above practical convention, if subscript i refers to the lighter gas, K_{Ti} and thus also $(\alpha_T)_{ij}$ would be positive when only the masses of the molecules determine the magnitude of thermal diffusion. As we shall see, this occurs with our equation (24.II) for $(\alpha_T)_{ij}$. Since the thermal diffusion factor has been given into a certain succession of the gases i and j, we have,

$$K_{Ti} = - K_{Tj} \; ; \; (\alpha_T)_{ij} = - (\alpha_T)_{ji} \qquad (29.\text{II})$$

The quantities K_{pi} and $(\alpha_p)_{ij}$ are similarly called the *pressure diffusion ratio* of the gas i and the *pressure diffusion factor* of the gases i and j, *in this succession*. If subscript i refers to the lighter molecules, these quantities are usually positive. Therefore the molecules of kind i would diffuse down the pressure gradient.

In connection with experiments, it is convenient to express (28.II) in the concentration ratio, (c_i/c_j). We can easily obtain

$$\text{grad } \ln (c_i/c_j) = (\alpha_T)_{ij} \text{ grad } \ln T - (\alpha_p)_{ij} \text{ grad } \ln p \qquad (30.\text{II})$$

By integration of equation (28.II) giving grad c_i we obtain the so-called *separation*, S_i,

$$S_i = c_i^{II} - c_i^{I} \qquad (31.\text{II})$$

well known when dealing with experimental thermal diffusion. Then c_i^{II} and c_i^{I} are the molar concentrations of the gas of kind i in the regions at absolute temperatures T^{II} and T^{I} respectively.

By integration of grad ln (c_i/c_j) we obtain the *separation factor*, q_{ij},

$$q_{ij} = \frac{(c_i/c_j)^{II}}{(c_i/c_j)I} \qquad (32.\text{II})$$

where $(c_i/c_j)^{II}$ and $(c_i/c_j)^{I}$ refer to the concentration ratio of gases i and j at absolute temperatures T^{II} and T^{I} respectively. Experimental observations of thermal diffusion are frequently carried out by means of the separation factor.

CHAPTER III

APPROXIMATE FORMULAE TO MAXWELL'S MEAN FREE PATH AND TO THE COEFFICIENTS OF DIFFUSION AND VISCOSITY CORRECTED FOR PERSISTENCE OF VELOCITIES

§ 1. *Approximate equation to Maxwell's mean free path for number density transfer*

It is well known that if one uses the common Maxwell's mean free path

$$1/{}_{M}l_{i} = \pi\, n \sum_{k=1}^{s} c_{k}\, \sigma_{ik}^{2}\, \left(1 + \frac{m_{i}}{m_{k}}\right)^{\frac{1}{2}} \qquad (1.\mathrm{III})$$

into Meyer's formula (22.II), the coefficient of concentration diffusion, D_{ij}, is strongly dependent on the proportion of the components. This is in disagreement with experiments as well as with Chapman-Enskog's theory (J1, C1).

Better results are obtained if Maxwell's mean free path is corrected for 'persistence of velocities' regarding to number density transfer, namely (J1,C1),

$$1/{}_{P}l_{i} = \pi\, n \sum_{k=1}^{s} c_{k}\, \sigma_{ik}^{2}\, \psi_{ik} \qquad (2.\mathrm{III})$$

where

$$\sigma_{ik} = (\sigma_{i} + \sigma_{k})/2 \;;\; M_{ik} = 1 - M_{ki} = \frac{m_{i}}{m_{i} + m_{k}} \qquad (3.\mathrm{III})$$

$$\psi_{ik} = (1 - \theta_{ik})\, M_{ki}^{-\frac{1}{2}} \qquad (4.\mathrm{III})$$

$$\theta_{ik} = \frac{1}{2} M_{ik} + \frac{1}{2} M_{ik}^{2}\, M_{ki}^{-\frac{1}{2}} \cdot \ln\left[\left(M_{ik}^{\frac{1}{2}} + 1\right) M_{ki}^{-\frac{1}{2}}\right] \qquad (5.\mathrm{III})$$

θ_{ik} is the *mean persistence ratio*. It increases from zero to unity as the mass ratio, m_i/m_k, increases from zero to infinity; its value for collisions of like molecules is approximately equal to 0.406.

Unfortunately, equation (2.III) is too complex for a reasonable use in practice. Therefore we have tried to search a satisfactory approach. We found that the following equations can be used with reasonable accuracy:

$$\theta_{ik} \simeq \frac{1}{2} M_{ik} \ (1 + M_{ik}^{1/2}) \tag{6.III}$$

$$\psi_{ik} \simeq 1.16 \ M_{ki}^{1/2} \tag{7.III}$$

In Table 1.III we give approximate and exact values of θ_{ik} and ψ_{ik} over the mass ratio from 0 to infinity. According to our approximate equations, θ_{ik} changes from 0 to unity with increasing values of m_i/m_k; for collisions of like molecules $\theta_{ii} = 0.427$. Approximate values of ψ_{ik} change from 1.160 to 0.000 and for like molecules $\psi_{ii} = 0.820$ whereas the correct values are respectively 1.000; 0.000 and 0.840.

Table 1.III

Correct and approximate values for θ_{ik} and ψ_{ik}

mass ratio m_i/m_k	M_{ik}	θ_{ik}		ψ_{ik}	
		(exact)	(approx.)	(exact)	(approx.)
0	0.000	0.000	0.000	1.000	1.160
0.1	0.091	0.054	0.059	0.993	1.106
0.2	0.167	0.107	0.117	0.978	1.059
0.4	0.286	0.203	0.219	0.943	0.981
0.6	0.375	0.283	0.302	0.907	0.912
0.8	0.444	0.350	0.370	0.872	0.864
1	0.500	0.406	0.427	0.840	0.820
2	0.667	0.588	0.606	0.714	0.670
3	0.750	0.683	0.699	0.634	0.580
4	0.800	0.736	0.758	0.590	0.519
9	0.900	0.869	0.877	0.414	0.367
20	0.952	0.940	0.941	0.291	0.255
∞	1.000	1.000	1.000	0.000	0.000

By using our approximate equation (7.III) into (2.III), the approximate formula to Maxwell's mean free path corrected for 'persistence of velocities' is thus given as

$$1/{}_P l_i = 1.16 \ \pi \ n \sum_{k=1}^{s} c_k \ \sigma_{ik}^2 \ M_{ki}^{1/2} \tag{8.III}$$

§ 2. *Approximate formula to Meyer's coefficient of diffusion*

Introducing (8.III) into (22.II) and using Tait's mean free path l_i (see eq.13.II) which is 1.051 times Maxwell's mean free path, we obtain for the coefficient of concentration diffusion of a binary mixture the following equation:

$$D_{ij} = \frac{0.385}{n\,\sigma_{ij}^2}\left[\frac{k\,T\,(m_i + m_j)}{2\,\pi\,m_i\,m_j}\right]^{\frac{1}{2}} \cdot f_{ij} \qquad (9.\text{III})$$

where

$$f_{ij} = \frac{c_i^2 M_{ij}(\sigma_i/\sigma_{ij})^2 + c_j^2 M_{ji}(\sigma_j/\sigma_{ij})^2 + 2c_i c_j M_{ij}^{\frac{1}{2}} M_{ji}^{\frac{1}{2}}}{c_i^2 M_{ij}(\sigma_i/\sigma_{ij})^2 + c_j^2 M_{ji}(\sigma_j/\sigma_{ij})^2 + c_i c_j M_{ij}^{\frac{1}{2}} M_{ji}^{\frac{1}{2}}[1 + (\sigma_i^2\sigma_j^2/\sigma_{ij}^4]}$$

$$(10.\text{III})$$

When either $c_i = 1$ or $c_j = 1$, then $f_{ij} = 1$. In general, whatever the mass ratio may be, f_{ij} is only slightly dependent on concentrations and always close or equal to unity. Indeed, we may assume for gases

$$\sigma_{ij} = (\sigma_i\,\sigma_j)^{\frac{1}{2}} \qquad (11.\text{III})$$

since molecular diameter only slightly changes with molecular mass. Furthermore, products $M_{ij}^{\frac{1}{2}}\,M_{ji}^{\frac{1}{2}}$ approach to zero with increasing mass ratio.

Therefore we may assume, at a first approximation for real gases,

$$[D_{ij}]_1 = \frac{0.385}{n\,\sigma_{ij}^2}\left[\frac{k\,T\,(m_i + m_j)}{2\,\pi\,m_i\,m_j}\right]^{\frac{1}{2}} \qquad (12.\text{III})$$

As a conclusion: *the coefficient of concentration diffusion should be nearly independent on concentrations of the gases in a binary mixture, if we use into Meyer's formula our approximate equation for mean free path for number density transfer corrected for 'persistence of velocities'.*

This is an even better result than that obtained by using the equation for the mean free path (3.III). Indeed, then the corresponding equation for the coefficient of diffusion still exhibits a strong dependence on the proportion of the gases. The ratio of the limiting values as $c_j = 1$ and $c_i = 1$ is thus equal to

$$\frac{(D_{ij})_{c_j=1}}{(D_{ij})_{c_i=1}} = \frac{m_j\ (1 - \theta_{ji})}{m_i\ (1 - \theta_{ij})} \tag{13.III}$$

To take an example, for $m_j/m_i = 10$ (Argon-Helium) the ratio (13.III) is equal to 1.324. Such concentration dependence shows a clear disagreement with experimental data after Schmidt and Lonius (C1, p.248) as well as with the second approximation to the coefficient of diffusion by Chapman-Enskog's exact theory which gives the above ratio as 1.072. Chapman-Enskog's first approximation is independent of concentrations and equal to our value, $[D_{ij}]_1$, equation (12.III), except for the numerical factor which is then equal to 0.375 when molecules behave as rigid elastic spheres.

The foregoing analyses show that the approach we have introduced into Maxwell's mean free path is satisfactory and may be used with advantage in practical cases.

§ 3. *The coefficients of self-diffusion and viscosity*

In the special case of self-diffusion all the molecules, i and j, are equal. Meyer's formula thus becomes,

$$D_{ii} = \frac{1}{3}\ l_i\ \overline{u}_i \tag{14.III}$$

According to the approximate equation (8.III) for the mean free path ${}_p l_i$, we have then

$$D_{ii} = \frac{0.385}{n_i\ \sigma_i^2}\left[\frac{k\ T}{\pi m_i}\right]^{1/2} \tag{15.III}$$

This result could also be obtained by making $m_i = m_j$ into (9,12.III).

The coefficient of viscosity, η_i, of a gas i is given by the free path theory (J1) as

$$\eta_i = \frac{1}{3}\, \rho_i\, l''_i\, \bar{u}_i \qquad (16.\text{III})$$

where

ρ_i is the density of the gas, and

l''_i is the mean free path for momentum transfer.

If 'persistence of velocities' is considered, Jeans suggested (J1) that the corrections which have to be introduced into Maxwell's mean free path regarding to number density transfer and to momentum transfer should be different. He proposed an equation of the form,

$$1/_{P}\, l''_i = \pi\, n \sum_{k=1}^{s} c_k\, \sigma^2_{ik}\, \psi''_{ik} \qquad (17.\text{III})$$

where

$$\psi''_{ik} = (1 - F_{ik}\, \theta_{ik})\, M_{ki}^{-\frac{1}{2}} \qquad (18.\text{III})$$

θ_{ik} is the mean persistence ratio as given by (5.III) and F_{ik} is a quantity which is probably a function of the masses of the colliding molecules. For collisions of like molecules Jeans assumed $F_{ii} = \frac{1}{2}$. In their theory of thermal diffusion Whalley and Winter had also considered this question and proposed the relationship

$$F_{ik} = \frac{m_i}{m_i + m_k} = M_{ik} \qquad (19.\text{III})$$

Assuming Jeans' hypothesis, the mean free path for momentum transfer between like molecules is thus

$$1/_{P}\, l''_i = \sqrt{2}\, \pi\, n\, \sigma^2_i\, (1 - \frac{1}{2}\, \theta_{ii}) \qquad (20.\text{III})$$

For the sake of consistency of our theory, we use into (20.III) the approximate value $\theta_{ii} = 0.427$ as given by our equation (6.III). The approximate equation for the coefficient of viscosity is accordingly,

$$\eta_i = \frac{0.284}{\sigma^2_i} \left[\frac{k\, T\, m_i}{\pi} \right]^{\frac{1}{2}} \qquad (21.\text{III})$$

By means of this equation and (14.III) we obtain the following relationship:

$$D_{ii} = 1.356 \frac{\eta_i}{\rho_i} \qquad (22.\mathrm{III})$$

Common mean free path theory corrected for 'persistence of velocities' gives the numerical factor of this equation as 1.342. The result we have obtained shows again, in addition to that of the preceding paragraph, that all the approaches which we have proposed either for the mean persistence ratio, θ_{ik}, or ψ_{ik} are satisfactory for treating diffusion and viscosity and they give rise to relative simple equations for mean free paths.

It is of interest to consider now the exact Chapman-Enskog theory. According to it the above relationship is given, at a first approximation, as

$$[D_{ii}]_1 = 3A \frac{[\eta_i]_1}{\rho_i} \qquad (23.\mathrm{III})$$

where A is a numerical factor depending on the molecular fòrces. For example, when the molecules repel each other with a force inversely proportional to the ν_ith power of the distance, theoretical values of 3A are as follows:

Table 2.III

Values of 3A for the inverse power repulsion model (after Chapman and Cowling (C1))

ν_i	3A
5	1.551 (Maxwellian gas)
9	1.434
11	1.395
15	1.350
∞	1.200 (Rigid elastic spheres)

In Table 3.III (see p.27) we report experimental values of the ratio $\rho_i D_{ii}/\eta_i$ = 3A for several gases. D_{ii} has been identified, at a first approximation, with the coefficient of diffusion of isotopes of the same gas.

As we have already pointed out, the inverse power repulsion model may hardly explain experimental data. For examplê, the values of the force index, ν_i, obtained for each gas by compar-

Table 3.III

Experimental values of 3A (from ref. (C1))

gas	$\rho_i D_{ii}/\eta_i$ = 3A	Reference for D_{ii}
H_2	1.37	(H3)
N_2	1.48	(W2)
CH_4	1.33	(W3)
ClH	1.33	(B1)
Ne	1.28	(G1)
A	1.34	(H4)
Kr	1.30	(G2)
Xe	1.24	(G2)

ison of Tables 2 and 3.III are frequently in disagreement with those deduced from the variation of viscosity with temperature. To take a definite example, viscosity data show that Neon should be markedly 'harder' than Xenon. This is also confirmed by thermal diffusion. From Table 3.III it would be just the contrary.

For our purposes it is, however, enough to show that the ratio $\rho_i D_{ii}/\eta_i$ is dependent on the forces acting upon molecules in collision and that the numerical factor which we have determined by mean free path considerations must be regarded as being a satisfactory approximation. On the other hand, we may consider the equations (14.III) and (16.III) for the coefficients of self-diffusion and viscosity respectively, independent of any formulae for the mean free paths l_i and l''_i. We have then,

$$D_{ii} = \frac{l_i \eta_i}{l''_i \rho_i} \tag{24.III}$$

If a formal comparison is established with Chapman-Enskog's theory, then

$$3A = l_i/l''_i \tag{25.III}$$

For rigid elastic spheres we have 3A = 1.200 and for maxwellian gases 3A = 1.551. Accordingly, we may say that the ratio of the mean free path for number density transfer to the mean free path for momentum transfer would be related to the 'hardness' of molecular interactions. This may be taken into account in case of generalisation. Also, the ratio l_i/l''_i should be larger than unity, usually increasing with decreasing 'hardness' of the molecules. For real gases rather small variations are observed.

§ 4. *Another approximate formula to Maxwell's mean free path for number density transfer*

When dealing with thermal and pressure diffusions we will introduce another equation for the mean free path for number density transfer which can be obtained from equation (8.III) by making into it further approaches.

For gases we may usually assume the mutual collision diameter as given by

$$\sigma_{ik} = (\sigma_i \, \sigma_k)^{1/2} \tag{26.III}$$

because molecular diameter only slightly changes with mass. For Xenon and Hydrogen whose mass ratio is about 65, the ratio of molecular diameters is only about 2. Equation (26.III) then gives the mutual collision diameter 6% smaller than the correct value $\sigma_{ik} = (\sigma_i + \sigma_k)/2$.

Introducing (26.III) into (8.III) and after some developments, we have:

$$1/_P l_i = \frac{1.16\,\pi}{\sqrt{2}} \, n \, \sigma_i \, m_i^{-1/4} \sum_{k=1}^{s} c_k \, \sigma_k \, m_k^{1/4} \cdot \sqrt{2} \, M_{ik}^{1/4} \, M_{ki}^{1/4} \tag{27.III}$$

Now, if the mass ratios, m_i/m_k, are not far from unity, the quantities $\sqrt{2}\, M_{ik}^{1/4}\, M_{ki}^{1/4}$ may be assumed, at a first approximation, as equal to unity. To take definite examples, for mass ratios equal to 1, 2, 4 and 9 (or equivalently equal to 1, 0.5, 0.25 and 0.111) those quantities are respectively equal to 1, 0.971, 0.894 and 0.775. Therefore, with the above restriction, we may consider, at a first approximation,

$$1/[_P l_i]_1 = K \, \sigma_i \, m_i^{-1/4} \tag{28.III}$$

where K is a constant *for each gas mixture*, namely,

$$K = \frac{1.16\,\pi}{\sqrt{2}} \, n \sum_{k=1}^{s} c_k \, \sigma_k \, m_k^{1/4} \tag{29.III}$$

Introducing into (27.III) the coefficient of viscosity as given by (21.III) we obtain an equivalent equation, namely,

$$[_P l_i]_1 = K' \eta_i^{1/2} \tag{30.III}$$

where K′ is another constant for each gas mixture.

As we shall see in Chapter IV the above approximate equations for the mean free path, ${}_{p}l_{i}$, give rise to very simple formulae for the thermal and pressure diffusion factors. A priori, the resulting equations would only be valid for a rather narrow range of mass ratios. However, in Chapter IV we will show that they can fortunately be used for any mass ratio, except for m_i/m_k very close to unity if simultaneously $m_k > m_i$ but $\sigma_k < \sigma_i$ (when a change of sign of the thermal diffusion factor may occur for a particular value of the concentration ratio).

When $m_i = m_k$ and also $\sigma_i = \sigma_k$ no error is committed relative to our equation (8.III). Therefore the coefficients of self-diffusion and viscosity are given by equations (15,21.III) as well. Meyer's coefficient of diffusion is accordingly obtained as

$$D_{ij} \sim \frac{0.385}{n\sigma_i\sigma_j}\left[\frac{k\ T\ (m_i + m_j)}{2\ \pi\ m_i\ m_j}\right]^{1/2} \cdot \sqrt{2}\ M_{ij}^{1/4}\ M_{ji}^{1/4} \qquad (31.\text{III})$$

which can be compared with (9,12.III) only if m_i/m_j is not far from unity. Concentration dependence was practically not affected by the approaches which we have proposed in the foregoing analysis.

The errors which are introduced when the above equations are used for thermal and pressure diffusions will be studied afterwards.

CHAPTER IV

THERMAL DIFFUSION AND PRESSURE DIFFUSION IN BINARY MIXTURES

§ 1. *Definitions*

In this paragraph we will define several quantities which are used in theoretical and experimental investigations of thermal diffusion. Similar quantities could also be considered for pressure diffusion but they will be disregarded here since no observations have been found in literature because of the difficulties which experiments involve.

1.1. Measurements of thermal diffusion. The most simple system for experimental determinations of the thermal diffusion effect is the so-called 'two bulb apparatus' which consists of two containers joined by a tube of small diameter. These two bulbs, V^I and V^{II}, are kept at constant absolute temperatures, T^I and T^{II} respectively, and pressure is equal everywhere.

The temperature gradient set up, in a binary mixture for example, tends to separate out the components and in time a steady state may be reached which balances the opposing effects of thermal and concentration diffusion. Then, by means of equation (28.II),

$$\text{grad}\ c_i = K_{Ti}\ \text{grad}\ \ln T \qquad (1.\text{IV})$$

where K_{Ti} is the *thermal diffusion ratio* of the gas of kind i, usually indicated in literature by K_T for binary mixtures. For the sake of generalisation which becomes necessary in complex mixtures, we have added the subscript i referring to the gas i.

K_{Ti} is a small quantity, usually less than 0.1, and is generally treated as a constant into the equation (1.IV). If c_i^I and c_i^{II} represent the molar concentrations of the gas i in the bulbs V^I and V^{II} at the temperatures T^I and T^{II} respectively, we obtain by integration of (1.IV),

$$S_i = c_i^{II} - c_i^I = K_{Ti}\ \ln\ (T^{II}/T^I) \qquad (2.\text{IV})$$

The difference, S_i, of molar concentrations, is termed *separation* and it is usually represented in binary mixtures by S only. The subscript i has been added for the sake of generalisation.

Equation (2.IV) is frequently used for experimental determinations of the thermal diffusion ratio, K_{Ti}, introducing in it experimental data of separation and temperatures.

Instead of equation (1.IV) we may consider equation (30.II) which takes the following form when only thermal diffusion is regarded:

$$\operatorname{grad} \ln (c_i/c_j) = (\alpha_T)_{ij} \operatorname{grad} \ln T \qquad (3.IV)$$

where $(\alpha_T)_{ij}$ is the *thermal diffusion factor* of gases i and j, in this succession, usually represented in literature by α only. It has first been introduced by Furry, Jones and Onsager (F4), usually being regarded as a constant for integration of equation (3.IV). This is theoretically to be preferred to considering K_{Ti} as a constant into (1.IV) because $(\alpha_T)_{ij}$ is indeed less dependent on concentrations and it remains finite as c_i or c_j approach to zero. For binary mixtures we have the relationship (23.II), namely,

$$K_{Ti} = (\alpha_T)_{ij}\, c_i c_j \qquad (4.IV)$$

As we shall see in Chapter V, this equation is not valid for multicomponent mixtures. Nevertheless, equations (1.IV) and (3.IV) which define, respectively, the thermal diffusion ratio and the thermal diffusion factor are formally identical.

By integration of (3.IV) we obtain

$$\ln q_{ij} = (\alpha_T)_{ij} \ln (T^{II}/T^{I}) \qquad (5.IV)$$

where

$$q_{ij} = \frac{(c_i/c_j)^{II}}{(c_i/c_j)^{I}} \qquad (6.IV)$$

$(c_i/c_j)^{II}$ and $(c_i/c_j)^{I}$ are the concentration ratios in the bulbs at temperatures T^{II} and T^{I} respectively.

The quantity q_{ij} is called the *separation factor* of gases i and j *in this succession* (notice that $q_{ij} = 1/q_{ji}$).

Equation (5.IV) is frequently used to determine experimental values for the thermal diffusion factor.

1.2. The thermal separation ratio. In the discussion of experimental results there has been introduced a quantity denoted by R_T which is named thermal separation ratio. It is determined by the ratio of the experimental value of the thermal diffusion ratio, $K_{Ti}(\mathrm{exp})$, or of the thermal diffusion factor, $(\alpha_T)_{ij}(\mathrm{exp})$, to the corresponding theoretical value of Chapman-Enskog's first approximation for the rigid elastic sphere model, i.e.,

$$R_T = \frac{K_{Ti}(\mathrm{exp})}{[K_{Ti}(\mathrm{Chap})]_1} = \frac{(\alpha_T)_{ij}(\mathrm{exp})}{[(\alpha_T)_{ij}(\mathrm{Chap})]_1} \tag{7.IV}$$

R_T is therefore a measure of the approach to the ideal rigid elastic sphere interaction or, as usually said, a measure of the *'hardness'* of molecular interaction. Molecular interaction is called *'hard'* when R_T approaches to unity and *'soft'* when it is small or even negative.

Sometimes the separation ratio is applied to theoretical values as well given by any particular model in comparison to the corresponding r.e.s. first approximation. R_T is then represented by $R_T(\mathrm{th})$, and K_{Ti} and $(\alpha_T)_{ij}$ by $K_{Ti}(\mathrm{th})$ and $(\alpha_T)_{ij}(\mathrm{th})$.

In this paper a comparison is made between our elementary thermal diffusion factor and the corresponding value given by the r.e.s. Chapman-Enskog's first approximation. The separation ratio is then represented by $R_T(\mathrm{elem})$ defined by

$$R_T(\mathrm{elem}) = \frac{(\alpha_T)_{ij}(\mathrm{elem})}{[(\alpha_T)_{ij}(\mathrm{Chap})]_1} \tag{8.IV}$$

For the sake of the simplicity in the notation, the subscript T which refers to temperature, will usually be omitted if no confusion arises with pressure diffusion.

In our theory we also assume a 'rigid elastic sphere model' for which a first approximation for the thermal diffusion factor was obtained. The thermal separation ratio corresponding to our elementary first approximation is represented by $R_{ij}(\mathrm{exp})$ and is defined as

$$R_{ij}(\mathrm{exp}) = \frac{\alpha_{ij}(\mathrm{exp})}{[\alpha_{ij}(\mathrm{res})]_1} \tag{9.IV}$$

This definition is assumed for binary mixtures as well as for multicomponent mixtures.

Our theory also provides equations for 'soft' molecular interactions. The corresponding thermal diffusion factors will be represented by

$$\alpha_{ij}(\mathrm{sm}) \text{ and for the first approximation by } [\alpha_{ij}(\mathrm{sm})]_1$$

The corresponding thermal separation ratios are termed as

$$R_{ij} = \frac{\alpha_{ij}(\mathrm{sm})}{[\alpha_{ij}(\mathrm{res})]_1} \quad \text{and} \quad [R_{ij}]_1 = \frac{[\alpha_{ij}(\mathrm{sm})]_1}{[\alpha_{ij}(\mathrm{res})]_1} \qquad (10.\mathrm{IV})$$

1.3. Limiting values of quantities. In the following chapters we frequently use asymptotic values of the thermal diffusion factor and of the thermal separation ratio if the molar concentration of one of the components of the mixture approaches unity. This will be represented by adding to the normal notation the letter (or number) of the kind of gas for which the molar concentration has to be taken as equal to unity. For example:

$$[R_{ij}]_i = \lim_{c_i=1} R_{ij}$$

$$\{[R_{ij}]_1\}_k = \lim_{c_k=1} [R_{ij}]_1 \quad \text{(in multicomponent mixtures only)}$$

$$\{[\alpha_{ij}(\mathrm{res})]_1\}_j = \lim_{c_j=1} [\alpha_{ij}(\mathrm{res})]_1 \qquad (11.\mathrm{IV})$$

§ 2. *The mean free paths for number density transfer and for mean thermal speed transfer*

Two kinds of mean free paths appear into the general equation of diffusion, equation (18.II), namely:

1) l_i which is the *mean free path for number density transfer*. It is the only one which has been considered in Meyer's equation of concentration diffusion, equation (22.II) being known since long ago. In the following theory we use for it the approximate equations which have been deduced in Chapter III, namely,

$$1/{}_p l_i = 1.16\,\pi\, n \sum_{k=1}^{s} c_k\, \sigma_{ik}^2\, M_{ki}^{1/2} \qquad (12.\mathrm{IV})$$

which is nearly equivalent to Maxwell's mean free path corrected for 'persistence of velocities'. According to this equation, Meyer's coefficient of diffusion is practically independent on concentrations which is in satisfactory agreement with experience and Chapman-Enskog's theory.

For mass ratios not far from unity, the above equation may be written as (see equations 28 and 30.III)

$$1/[{}_{P}l_i]_1 = K\ \sigma_i m_i^{-1/4}\ ;\ [{}_{P}l_i]_1 = K'\ \eta_i^{1/2} \qquad (13.IV)$$

which give rise to very simple equations for the thermal diffusion factor.

2) l_i' was called the *mean free path for mean thermal speed transfer*. It is a result of the power series (3,10.II) assumed for thermal speeds. It might be a matter of discussion whether this mean free path would have to be identified with any other mean free path already known. However, this will be disregarded here.

As shown by equation (26.II) for the thermal diffusion factor in a binary mixture, the magnitude of α_{ij} will be strongly dependent on the relationship assumed for the mean free paths, l_i, l_i' and l_j, l_j'. If $l_i' = 2l_i$ and $l_j' = 2l_j$ then $\alpha_{ij} = 0$ and no thermal diffusion should occur. By comparison with Chapman-Enskog's theory this case should be equivalent to a mixture of Maxwellian gases (C1). If we assume a relationship of the form

$$l_i' = (1+a_i)\ l_i \qquad (14.IV)$$

the quantity a_i might be a 'measure' of the molecular interactions, which should be equal to unity for Maxwellian molecules.

Let us now consider the case of rigid elastic sphere molecules. The simplest hypothesis is to assume that the transfer of quality (molecules themselves) and of thermal speed just occurs at the points where the molecules collide. Even then the mean free paths, l_i and l_i', will probably not be equal. Indeed,

1) for the mean free path, l_i', for mean thermal speed transfer all kinds of collisions of the types (i,i), (i,j), (i,k),...,(i,s) would be of interest because they would somehow change the local distribution of thermal velocities of molecules of kind i;

2) for the mean free path, l_i, for number density transfer, it is physically doubtful that collisions (i,i) of like molecules can hinder the process of diffusion of molecules of kind i. Stefan and Maxwell have accordingly suggested that only collisions

between unlike molecules of the types (i,j), (i,k),...,(i,s) should be regarded for l_i.

Since the number of collisions which should then be considered for l_i is smaller than that considered for l_i', the mean free path for number density transfer, l_i, should accordingly be *larger* than the corresponding one for mean thermal speed transfer, l_i'. Therefore, the quantity a_i of equation (14.IV) should thus be *negative*. A negative value for a_i for rigid elastic spheres is confirmed by experimental data for the thermal diffusion factor of Neon isotopes at higher temperatures as we shall see in the next paragraph.

As is well known, Neon is indeed one of the 'hardest' gases, therefore approaching to the ideal rigid elastic sphere interaction.

For the sake of simplicity of the corresponding equations, we assume $a_i = 0$ for *'rigid elastic spheres'*. This assumption is not too bad in practice because only for a few exceptions, the exexperimental thermal diffusion factor brings about small, negative values for a_i.

In our treatment we further assume that the quantity a_i mostly depends on the force field surrounding the molecules of kind i.

This assumption might also be regarded as a physical approach because a_i would probably be considered as dependent on the 'hardness' of molecular interactions (i,i), (i,j), (i,k),...,(i,s) and similarly a_j as dependent on molecular interactions (j,j), (j,i), (j,k),...,(j,s).

§ 3. *The thermal diffusion factor for isotopic mixtures*

As usually done for these mixtures, we consider that the mass ratio, m_j/m_i, is close to unity and furthermore all the quantities relating to the molecules will be nearly equal. Hence we may assume $l_i = l_j$; $l_i' = l_j'$ and a mean value, a_{ij}, may be chosen for the quantities a_i and a_j. Therefore, by using equations (26.II) and (14.IV), the thermal diffusion factor for isotopes i and j is given by

$$[\alpha_{ij}(sm)]_1 = \frac{1 - a_{ij}}{2} \cdot \frac{m_j^{1/2} - m_i^{1/2}}{c_i m_i^{1/2} + c_j m_j^{1/2}} \qquad (15.\mathrm{IV})$$

For 'rigid elastic spheres' we assume in equation (15.IV) that $a_{ij} = 0$.

If the thermal diffusion factor is experimentally available, then the quantity a_{ij} which may be regarded as a measure of the 'hardness' of the gas consisting of two isotopes, i and j, can be determined.

In Table 4.IV we report experimental data of thermal diffusion factors for several isotopic mixtures. The corresponding values for a_{ij} are usually positive numbers, smaller than unity.

Table 1.IV
Variation of experimental thermal diffusion factor for ^{20}Ne-^{22}Ne and $^{14}NH_3$-$^{15}NH_3$ with temperature

Mean temp. T_r (°K)	$\alpha_{20,22}$(exp)	$a_{20,22}$	Mean temp. T_r (°K)	$\alpha_{17,18}$(exp)	$a_{17,18}$
129	+ 0.0162	+ 0.34	239	- 0.0100	+ 1.69
238	+ 0.0233	+ 0.049	268	- 0.0039	+ 1.27
298	+ 0.0254	- 0.037	366	+ 0.0105	+ 0.28
712	+ 0.0346	- 0.412	...	...	...

In Table 1.IV we report the variation of the experimental thermal diffusion factor with temperature for ^{20}Ne-^{22}Ne and $^{14}NH_3$-$^{15}NH_3$ mixtures which have been observed by Stier (S1) and Watson and Woernley (W4) respectively. The corresponding values for the quantities $a_{20,22}$ and $a_{17,18}$ from our equation (15.IV) are also given in the Table. The mean temperature, T_r, reported by the authors, is given by equation (61.IV).

For ^{20}Ne-^{22}Ne, the experimental thermal diffusion factor, corresponds to *negative* values for $a_{20,22}$ *at higher temperatures*, at which the behaviour of Neon molecules approaches to that of rigid elastic spheres. Negative values for $a_{20,22}$ therefore show that our 'rigid elastic sphere model' ($a_{ij} = 0$) is only a kind of mathematical assumption, even then not too bad in practice because the most frequent range observed for isotopic mixtures is $0 < a_{ij} < 1$.

For $^{14}NH_3$-$^{15}NH_3$ which is known as having 'soft' molecular interactions, a change of sign of the thermal diffusion factor has been observed at lower temperatures. At these temperatures we have $a_{17,18} > 1$, i.e., the gas is even 'softer' than a Maxwellian one ($a_{ij} = 1$).

§ 4. *The thermal diffusion factor for non-isotopic mixtures*

4.1. General equation for the thermal diffusion factor. Introducing (12,14.IV) in (26.II) we obtain the following equation for the thermal diffusion factor:

$$\alpha_{ij}(\mathrm{sm}) = \frac{1-a_{ij}}{2} \cdot \frac{c_j S_j - c_i S_i}{c_i^2 Q_i + c_j^2 Q_j + c_i c_j Q_{ij}} \qquad (16.\mathrm{IV})$$

where

$$M_{ij} = m_i/(m_i + m_j); \; a_{ij} = (a_i + a_j)/2 \qquad (17.\mathrm{IV})$$

$$Q_i = \frac{\sqrt{2}}{2} (\sigma_i/\sigma_{ij})^2 M_{ij}^{\frac{1}{2}} \; ; \; Q_{ij} = 2 M_{ij}^{\frac{1}{2}} M_{ji}^{\frac{1}{2}}$$

$$S_i = \frac{1-a_j}{1-a_{ij}} Q_i - \frac{1-a_i}{1-a_{ij}} (Q_{ij}/2) \qquad (18.\mathrm{IV})$$

and analogous equations for Q_j and S_j by interchanging the subscripts i and j in (17,18.IV).

All the essential features of thermal diffusion can be explained by our elementary equation (16.IV) which is formally identical with the first approximation of the thermal diffusion factor as given by the rigorous Chapman-Enskog theory (C1).

When molecules behave as 'rigid elastic spheres' ($a_i = a_j = a_{ij} = 0$) and assuming that the subscript i refers to the lighter gas ($m_j > m_i$), the thermal diffusion factor, α_{ij}(res), is *positive* for $\sigma_j > \sigma_i$ ($S_j > 0$ and $S_i < 0$) over all the concentration ratio. If. $\sigma_j < \sigma_i$, then three cases have to be considered, namely:

1) $S_j > 0$ and $S_i < 0$. Then $\alpha_{ij}(\mathrm{res}) > 0$. This is the most frequent case, at least if the mass ratio, m_j/m_i, is not too small.

2) $S_j < 0$ and $S_i > 0$. Then $\alpha_{ij}(\mathrm{res}) < 0$. Usually for small mass ratios only.

3) S_j and S_i are both of the same sign. Then *the thermal diffusion factor changes sign with concentration.* This may occur for mass ratios nearly equal to unity.

The *'hardness' of gases* is mainly expressed into (16.IV) by the factor ($1-a_{ij}$). According to the hypotheses of § 2.IV, the usual range of ($1-a_{ij}$) should be in between 0 (Maxwellian case) and 1 (our 'r.e.s.' model). This conclusion has been confirmed for a large number of binary mixtures (see Table 4.IV).

For a few mixtures, $(1-a_{ij})$ is larger than unity (see in Table 4.IV the following mixtures: H_2-D_2 (ref. H5), H_2-Ne (T2), He-Ne (A1), ^{20}Ne-^{22}Ne). The corresponding values for a_{ij} are then negative ones.

A change of sign of the thermal diffusion factor with temperature has been observed by several authors (T1,W4) at lower temperatures. This feature of thermal diffusion can be explained by our equation (16.IV) assuming in it that $a_{ij} < 1$ above the temperature at which the reversal of sign occurs, and $a_{ij} > 1$ below that temperature.

4.2. First approximation for the thermal diffusion factor. Although the general formula (16.IV) given above is most wonderful, for practical applications it is just too complicated. We will therefore now give a deduction of a first approximation to $\alpha_{ij}(sm)$, named $[\alpha_{ij}(sm)]_1$.

By using in (26.II) the first approximation (13.IV) for the mean free path for number density transfer, the thermal diffusion factor is given, at a first approximation, as

$$[\alpha_{ij}(sm)]_1 = \frac{1-a_{ij}}{2} \cdot \frac{m_j^{1/4}\sigma_j' - m_i^{1/4}\sigma_i'}{c_i m_i^{1/4}\sigma_i + c_j m_j^{1/4}\sigma_j} \qquad (19.IV)$$

or equivalently,

$$[\alpha_{ij}(sm)]_1 = \frac{1-a_{ij}}{2} \cdot \frac{A_j' - A_i'}{c_i A_i + c_j A_j} \qquad (20.IV)$$

where

$$a_{ij} = (a_i + a_j)/2$$

$$\sigma_i' = \frac{1-a_j}{1-a_{ij}}\,\sigma_i \quad \text{and similarly for } \sigma_j' \qquad (21.IV)$$

$$A_i' = \frac{1-a_j}{1-a_{ij}}\,A_i \; ; \; A_i = (m_i/\eta_i)^{1/2} \qquad (22.IV)$$

and analogous equations for A_j and A_j' by interchanging subscripts i and j in the above equations.

Let us now examine how far the above first approximation for the thermal diffusion factor may be compared with equation (16.IV).

As a first remark we notice that a *reversal of sign with concentration cannot be explained* by equations (19,20.IV). For practical cases this is, however, not too bad because such a change of sign may only occur for very unusual mass and diameter ratios and frequently for ‘soft’ gases only. As we shall see this is the most important disadvantage of the above first approximation.

Equation (19.IV) can be written into the following form, though without interest in practice:

$$[\alpha_{ij}(\mathrm{sm})]_1 = \frac{1}{2} \cdot \frac{(1-a_i)Q_j^{\frac{1}{2}} - (1-a_j)Q_i^{\frac{1}{2}}}{c_i\ Q_i^{\frac{1}{2}} + c_j\ Q_j^{\frac{1}{2}}} = \frac{1-a_{ij}}{2} \cdot \frac{c_j\ S_j' - c_i\ S_i'}{c_i^2 Q_i + c_j^2 Q_j + c_i c_j Q_{ij}'} \qquad (23.\mathrm{IV})$$

where

$$S_i' = \frac{1-a_j}{1-a_{ij}} \cdot Q_i - \frac{1-a_i}{1-a_{ij}}\ (Q_{ij}'/2) \qquad (24.\mathrm{IV})$$

and analogous equation for S_j' by interchanging the subscripts;

$$Q_{ij}' = 2\ Q_i^{\frac{1}{2}}\ Q_j^{\frac{1}{2}} = (\sigma_i \sigma_j / \sigma_{ij}^2)\ Q_{ij}^{\frac{1}{2}} \qquad (25.\mathrm{IV})$$

Q_i, Q_j and Q_{ij} are given by equations (17.IV).

According to (16.IV) and (23.IV), $[\alpha_{ij}(\mathrm{sm})]_1$ can be compared with $\alpha_{ij}(\mathrm{sm})$ as far as Q_{ij}' can be identified with Q_{ij}. When m_j/m_i and σ_j/σ_i increase simultaneously from unity to infinity both quantities Q_{ij} and Q_{ij}' change from unity to zero. *In both limiting cases we have then* $[\alpha_{ij}(\mathrm{sm})]_1 = \alpha_{ij}(\mathrm{sm})$.

Let us now show that *if* S_j *and* S_i *are opposite in sign, a single concentration ratio exists such that*

$$\alpha_{ij}(\mathrm{sm}) = [\alpha_{ij}(\mathrm{sm})]_1 \qquad (26.\mathrm{IV})$$

For the sake of simplicity we only consider here the case that molecules are regarded as ‘rigid elastic spheres’ ($a_i = a_j = a_{ij} = 0$) and also $m_j > m_i$; $\sigma_j > \sigma_i$. Therefore $\alpha_{ij}(\mathrm{res})$ and $[\alpha_{ij}(\mathrm{res})]_1$ are positive over all the concentration ratios.

By means of (16,17,18.IV) and of (23,24.IV) we obtain,

$$\left\{\begin{aligned} &\lim_{c_i=1} \alpha_{ij}(\mathrm{res}) = -\frac{S_i}{Q_i} = \frac{(Q_{ij}/2) - Q_i}{Q_i} > 0 \\ &\lim_{c_i=1} [\alpha_{ij}(\mathrm{res})]_1 = \frac{(Q'_{ij}/2) - Q_i}{Q_i} > 0 \end{aligned}\right. \qquad (27.\mathrm{IV})$$

$$\left\{\begin{aligned} &\lim_{c_j=1} \alpha_{ij}(\mathrm{res}) = \frac{S_j}{Q_j} = \frac{Q_j - (Q_{ij}/2)}{Q_j} > 0 \\ &\lim_{c_j=1} [\alpha_{ij}(\mathrm{res})]_1 = \frac{Q_j - (Q'_{ij}/2)}{Q_j} > 0 \end{aligned}\right. \qquad (28.\mathrm{IV})$$

The corresponding asymptotic values given above only differ on the quantities $(Q_{ij}/2)$ and $(Q'_{ij}/2)$. Now, since molecular diameters vary slightly with molecular masses we may assume in equation (25.IV) $\sigma_i\sigma_j = \sigma_{ij}^2$. Then, $Q'_{ij} = Q_{ij}^{1/2}$. On the other hand, $Q_{ij} = 2\, M_{ij}^{1/2}\, M_{ji}^{1/2}$, equation (17.IV), is always smaller than unity if m_j is different from m_i. Therefore $Q_{ij}^{1/2} > Q_{ij}$. Then, by using equation (25.IV),

$$Q'_{ij} = Q_{ij}^{1/2} > Q_{ij} \qquad (29.\mathrm{IV})$$

Accordingly, we obtain from equations (27.IV) and (28.IV),

$$\lim_{c_i=1} \alpha_{ij}(\mathrm{res}) < \lim_{c_i=1} [\alpha_{ij}(\mathrm{res})]_1 \qquad (30.\mathrm{IV})$$

$$\lim_{c_j=1} \alpha_{ij}(\mathrm{res}) > \lim_{c_j=1} [\alpha_{ij}(\mathrm{res})]_1 \qquad (31.\mathrm{IV})$$

Since the directions of (30.IV) and (31.IV) are opposite, then a concentration ratio exists such that $\alpha_{ij}(\mathrm{res}) = [\alpha_{ij}(\mathrm{res})]_1$. The general equation (26.IV), namely $\alpha_{ij}(\mathrm{sm}) = [\alpha_{ij}(\mathrm{sm})]_1$, could be obtained following a similar discussion.

From the analysis given above we conclude that *the first approximation,* $[\alpha_{ij}(\mathrm{sm})]_1$, *may be used for any mass ratio as well as* $\alpha_{ij}(\mathrm{sm})$, *though with somewhat different concentration dependence, except for the unusual cases to which a change of sign of the thermal diffusion factor with concentration may occur,* i.e., when m_j/m_i is nearly equal to unity and at the same time $m_j > m_i$ but $\sigma_j < \sigma_i$.

As far as general cases are concerned, equation (19.IV) shows that the thermal diffusion factor of gases i and j, in this succession, will usually be positive if $m_j > m_i$, at least if the mass ratio is not too small and $a_{ij} < 1$. Therefore, by means of equations (1,4.IV), *the gas consisting of lighter molecules tends usually to diffuse into the hotter regions.*

We also obtain for general cases that $\lim\limits_{c_i=1} [\alpha_{ij}(sm)]_1 > \lim\limits_{c_j=1} [\alpha_{ij}(sm)]_1$.

Therefore *the thermal diffusion factor usually tends to increase with increasing concentration of the lighter gas.*

The above conclusions are well known features of thermal diffusion observations.

An interesting conclusion of equations (19,20.IV) is that *the inverse of the thermal diffusion factor should be linearly dependent on concentrations, at a first approximation, at least if molecular masses and diameters increase simultaneously* ($m_j > m_i$; $\sigma_j > \sigma_i$) *or if the mass ratio is not too close to unity when* $m_j > m_i$ *but* $\sigma_j < \sigma_i$.

This conclusion which may be very useful in practice, does appear to be confirmed by experiments. It also agrees closely with exact Chapman-Enskog's first approximation for the thermal diffusion factor as we shall see for a few binary mixtures in § 6.IV.

Equation (20.IV) is so easily applied to 'rigid elastic spheres' ($a_i=a_j=a_{ij}=0$) that it will be of value to determine the magnitude of the thermal diffusion factor in binary mixtures.

§ 5. *General comparison with Chapman-Enskog's theory*

In the preceding paragraph we have shown that our elementary treatment accounts for most characteristics of thermal diffusion in a qualitative form. The order of numerical agreement with Chapman-Enskog's theory may be established by means of the following limiting cases, when molecules behave as 'rigid elastic spheres'.

5.1. Lorentzian mixtures. In the limiting case of these mixtures we have:

$$m_j/m_i \rightarrow \infty \text{ and either } c_i \rightarrow 0 \text{ or } \sigma_j/\sigma_i \rightarrow \infty \qquad (32.\text{IV})$$

When molecules behave as rigid elastic spheres Chapman and Cowling (C1) give the first approximation for the thermal diffusion ratio as

$$[K_{Ti}(\mathrm{Chap})]_1 = \frac{5}{13}\, c_i = 0.385\, c_i \qquad (33.\mathrm{IV})$$

For these kinds of mixtures the true value of the thermal diffusion ratio can be determined (C1) being equal to

$$K_{Ti}(\mathrm{Chap}) = \frac{1}{2}\, c_i \qquad (34.\mathrm{IV})$$

By means of both elementary equations (16.IV) and (19.IV) we also obtain,

$$K_{Ti}(\mathrm{elem}) = [K_{Ti}(\mathrm{elem})]_1 = \frac{1}{2}\, c_i \qquad (35.\mathrm{IV})$$

Therefore, *in the limiting case of Lorentzian mixtures the elementary and Chapman's theories agree quantitatively.*

Regarding Chapman-Cowling's first approximation our treatment gives the thermal separation ratio as

$$R_T(\mathrm{elem}) = \frac{\tfrac{1}{2}}{0.385} = 1.30 \qquad (36.\mathrm{IV})$$

5.2. *Isotopic mixtures.* It was first shown by Furry, Jones and Onsager (F4) that Chapman-Cowling's first approximation for the thermal diffusion factor can approximately be given for rigid elastic spheres as

$$[\alpha_{ij}(\mathrm{Chap})]_1 = \frac{105}{118} \cdot \frac{m_j - m_i}{m_j + m_i} = 0.89\, \frac{m_j - m_i}{m_j + m_i} \qquad (37.\mathrm{IV})$$

However, a small concentration dependence is not incompatible with further approaches of the theory (C1).

Multiplying both terms of the fraction on the right hand side of our equation (15.IV) by $(m_j^{\frac{1}{2}} + m_i^{\frac{1}{2}})$, the elementary first approximation for the thermal diffusion factor for isotopic mixtures, may be written for 'rigid elastic spheres' as

$$[\alpha_{ij}(\mathrm{elem})]_1 = \frac{1}{2} \cdot \frac{m_j^{\frac{1}{2}} - m_i^{\frac{1}{2}}}{c_i m_i^{\frac{1}{2}} + c_j m_j^{\frac{1}{2}}} \simeq \frac{1}{2} \cdot \frac{m_j - m_i}{m_j + m_i} \qquad (38.\mathrm{IV})$$

Therefore, by means of (37,38.IV) the thermal separation ratio of our treatment for isotopic mixtures is approximately,

$$R_T(\text{elem}) = \frac{\frac{1}{2}}{0.89} = 0.56 \qquad (39.\text{IV})$$

5.3. Mixture of gases consisting of molecules of equal masses and different size. Considering $m_j = m_i$ and also $\sigma_{ij} = (\sigma_i \sigma_j)^{1/2}$ we can show that Chapman-Cowling's first approximation for the thermal diffusion factor can be given as

$$[\alpha_{ij}(\text{Chap})]_1 = \frac{10}{59} \cdot \frac{\sigma_j - \sigma_i}{c_i\ \sigma_i + c_j\ \sigma_j} \qquad (40.\text{IV})$$

By using our equations (16.IV) and (19.IV) the numerical factor of the equation corresponding to (40.IV) is obtained as ½. The elementary thermal separation is thus,

$$R_T(\text{elem}) = 2.95 \qquad (41.\text{IV})$$

5.4. Conclusion. From the foregoing paragraphs we can conclude:

1) For intermediate and large mass ratios, the magnitude of the thermal diffusion factor is mainly determined by mass ratio because the variation of molecular diameters with mass is usually small. Hence, by means of (36,39.IV), the thermal separation ratio of our elementary theory should usually increase from 0.56 (isotopic mixtures) to 1.30 (Lorentzian mixtures) with increasing mass ratio.

This conclusion can be inferred from Table 4.IV where corresponding values for $[\alpha_{ij}(\text{elem})]_1$ and $[\alpha_{ij}(\text{Chap})]_1$ are given for a large number of binary mixtures. *Except for very large mass ratio, the thermal separation ratio of our elementary theory is smaller than unity.*

2) For small mass ratios, the magnitude of the thermal diffusion factor can be markedly determined by molecular diameters. As we have shown, equations (39,41.IV), $R_T(\text{elem}) = 0.56$ for isotopic mixtures and $R_T(\text{elem}) = 2.95$ if $m_j = m_i$. We therefore see that such so different values may bring about quite different values for the thermal diffusion factors $[\alpha_{ij}(\text{elem})]_1$ and $[\alpha_{ij}(\text{Chap})]_1$.

If $m_j > m_i$ and also $\sigma_j > \sigma_i$, then $[\alpha_{ij}(\text{elem})]_1$ and $[\alpha_{ij}(\text{Chap})]_1$ are both positive and the range for the thermal separation ratio is (isot. mix.) $0.56 < R_T(\text{elem}) < 2.95$ ($m_i = m_j$).

If $m_j > m_i$ but $\sigma_j < \sigma_i$ three cases may occur, namely:

(a) predominance of the mass effect in both theories. Then, $[\alpha_{ij}(\text{elem})]_1 > 0$; $[\alpha_{ij}(\text{Chap})]_1 > 0$ and then $R_T(\text{elem}) > 0$,

(b) predominance of diameter effect in both theories. Then, $[\alpha_{ij}(\text{elem})]_1 < 0$; $[\alpha_{ij}(\text{Chap})]_1 < 0$ and then $R_T(\text{elem}) > 0$.

(c) predominance of mass effect in Chapman-Cowling's first approximation, and predominance of diameter effect in the elementary first approximation because diameter effect is of higher influence in our treatment for small mass ratios. Then,

$$[\alpha_{ij}(\text{elem})]_1 < 0 \quad \text{but} \quad [\alpha_{ij}(\text{Chap})]_1 > 0. \text{ Then } \quad R_T(\text{elem}) < 0.$$

The discussion given above for small mass ratios can be confirmed by Table 2.IV.

Table 2.IV

First approximations for the thermal diffusion factor for mixtures of equal proportions of H_2-D_2, C_2H_4-N_2, NH_3-Ne and H_2-He.

Gas mixture	m_j/m_i	σ_j/σ_i	$[\alpha_{ij}(\text{elem})]_1$	$[\alpha_{ij}(\text{Chap})]_1$	$R_T(\text{elem})$
H_2-D_2	2.00	1.01	+ 0.172	+ 0.276	+ 0.623
N_2-C_2H_4	1.0005	1.32	+ 0.137	+ 0.046	+ 2.95
NH_3-Ne	1.186	0.56	- 0.0230	- 0.0146	+ 1.58
H_2-He	2.00	0.80	- 0.0268	+ 0.241	- 0.111

The mixtures reported in Table 2.IV have been observed experimentally except N_2-C_2H_4. We give the general features below:

H_2-D_2 and H_2-He. The thermal diffusion factor is positive for higher temperatures but it changes sign at lower temperatures (ref.T1. Temperature range T^{II} = 293 °K; T^{I} from 90 to 20 °K).

NH_3-Ne. The thermal diffusion factor changes sign with concentration at about 75% Neon (G4). By our elementary 'r.e.s.' model as well as by Chapman-Cowling's r.e.s. first approximation, the thermal diffusion factor would be negative over all the concentration ratios.

§ 6. *Inert gas mixtures. Comparison between elementary and Chapman-Cowling's first approximation for thermal diffusion factor*

The following mixtures will be considered:

Neon-Argon $m_A/m_{Ne} = 1.979$; $\sigma_A/\sigma_{Ne} = 1.362$
Helium-Neon $m_{Ne}/m_{He} = 5.045$; $\sigma_{Ne}/\sigma_{He} = 1.182$
Helium-Argon $m_A/m_{He} = 9.984$; $\sigma_A/\sigma_{He} = 1.649$
Helium-Krypton $m_{Kr}/m_{He} = 20.92$; $\sigma_{Kr}/\sigma_{He} = 1.912$
Helium-Xenon $m_{Xe}/m_{He} = 32.56$; $\sigma_{Xe}/\sigma_{He} = 2.263$

Notice that diameter ratio increases with increasing mass ratio, *except for Helium-Neon mixtures.*

Equations (19,20.IV) show that the inverse of the thermal diffusion factor should have a linear dependence on concentrations, at a first approximation. The corresponding equations to $[\alpha_{ij}(\text{res})]_1$ for the above mixtures are the following. The notation $[\alpha_{ij}(\text{elem})]_1$ has been used for the sake of comparison with Chapman-Cowling's equations.

$$1/[\alpha_{Ne,A}(\text{elem})]_1 = 3.250\, c_{Ne} + 5.250\, c_A \qquad (42.\text{IV})$$

$$1/[\alpha_{He,Ne}(\text{elem})]_1 = 2.593\, c_{He} + 4.593\, c_{Ne} \qquad (43.\text{IV})$$

$$1/[\alpha_{He,A}(\text{elem})]_1 = 1.035\, c_{He} + 3.035\, c_A \qquad (44.\text{IV})$$

$$1/[\alpha_{He,Kr}(\text{elem})]_1 = 0.648\, c_{He} + 2.648\, c_{Kr} \qquad (45.\text{IV})$$

$$1/[\alpha_{He,Xe}(\text{elem})]_1 = 0.454\, c_{He} + 2.454\, c_{Xe} \qquad (46.\text{IV})$$

The corresponding Chapman-Cowling's first approximations (A1), are the following:

$$[\alpha_{Ne,A}(\text{Chap})]_1 = \frac{0.593\, c_{Ne} + 0.603\, c_A}{1.214\, c_{Ne}^2 + 2.368\, c_A^2 + 3.616\, c_{Ne} c_A} \qquad (47.\text{IV})$$

$$[\alpha_{He,Ne}(\text{Chap})]_1 = \frac{0.783\, c_{He} + 0.638\, c_{Ne}}{1.046\, c_{He}^2 + 1.713\, c_{Ne}^2 + 3.062\, c_{He} c_{Ne}} \qquad (48.\text{IV})$$

$$[\alpha_{He,A}\,(Chap)]_1 = \frac{0.603\ c_{He} + 0.718\ c_A}{0.444\ c_{He}^2 + 1.879\ c_A^2 + 2.139\ c_{He}c_A} \qquad (49.IV)$$

$$[\alpha_{He,Kr}(Chap)]_1 = \frac{0.361\ c_{He} + 0.602\ c_{Kr}}{0.207\ c_{He}^2 + 1.570\ c_{Kr}^2 + 1.296\ c_{He}c_{Kr}} \qquad (50.IV)$$

$$[\alpha_{He,Xe}(Chap)]_1 = \frac{0.248\ c_{He} + 0.550\ c_{Xe}}{0.113\ c_{He}^2 + 1.433\ c_{Xe}^2 + 0.899\ c_{He}c_{Xe}} \qquad (51.IV)$$

The inverse of the above Chapman-Cowling's equations can be written as

$$1/[\alpha_{Ne,A}\,(Chap)]_1 = 2.047\ c_{Ne} + 3.927\ c_A + \frac{0.053\ c_{Ne}c_A}{0.603\ c_A + 0.593\ c_{Ne}} \qquad (52.IV)$$

$$1/[\alpha_{He,Ne}(Chap)]_1 = 1.336\ c_{He} + 2.685\ c_{Ne} + \frac{0.008\ c_{He}c_{Ne}}{0.638\ c_{Ne} + 0.783\ c_{He}} \qquad (53.IV)$$

$$1/[\alpha_{He,A}\,(Chap)]_1 = 0.736\ c_{He} + 2.617\ c_A + \frac{0.033\ c_Ac_{He}}{0.603\ c_{He} + 0.718\ c_A} \qquad (54.IV)$$

$$1/[\alpha_{He,Kr}(Chap)]_1 = 0.573\ c_{He} + 2.608\ c_{Kr} + \frac{0.010\ c_{He}c_{Kr}}{0.361\ c_{He} + 0.602\ c_{Kr}} \qquad (55.IV)$$

$$1/[\alpha_{He,Xe}(Chap)]_1 = 0.456\ c_{He} + 2.605\ c_{Xe} + \frac{0.0002\ c_{He}c_{Xe}}{0.248\ c_{He} + 0.550\ c_{Xe}} \qquad (56.IV)$$

All the fractions on the right hand side of the above equations are comparatively small and may be disregarded within an error less than 1 per cent. *In practice we may assume the inverse of Chapman-Cowling's first approximation for the thermal diffusion factor as linear on concentrations.*

This feature of Chapman-Cowling's first approximation has also been verified in a large number of binary mixtures, namely in all the combinations of inert gases examined by Atkins, Bastick and Ibbs (A1). Experimental observations also seem to show such linear dependence as we shall see in § 7.2.

Let us now compare the concentration dependence of the elementary approximation, $[\alpha_{ij}(\text{elem})]_1$, to that corresponding to Chapman and Cowling's formula for the rigid elastic sphere model. Table 3.IV reports theoretical values of the thermal separation ratio,

$$R_T(\text{elem}) = \frac{[\alpha_{ij}(\text{elem})]_1}{[\alpha_{ij}(\text{Chap})]_1} \qquad (57.\text{IV})$$

for the inert gas mixtures given above, over the concentration range of the lighter gas from 0 to 1.

Table 3.IV

Theoretical separation ratios, R_T(elem), of the elementary first approximation for Ne-A, He-Ne, He-Kr and He-Xe mixtures

Concentr. of the lighter gas	Ne-A	He-Ne	He-A	He-Kr	He-Xe
0.000	0.745	0.586	0.861	0.987	1.062
0.100	0.742	0.585	0.859	0.983	1.060
0.300	0.726	0.578	0.847	0.976	1.057
0.500	0.708	0.570	0.830	0.968	1.054
0.700	0.684	0.554	0.802	0.952	1.045
0.900	0.651	0.532	0.752	0.919	1.027
1.000	0.631	0.515	0.711	0.885	1.004

This table shows that the separation ratio of the elementary first approximation *decreases* with *increasing concentration* of the lighter gas of the mixture. On the other hand, Chapman and Cowling's first approximation always *increases with increasing concentration* of the lighter component. Hence, *the elementary first approximation,* $[\alpha_{ij}(\text{elem})]_1$, *is less dependent on the concentration ratio than the corresponding first approximation of the exact Chapman-Enskog theory.* The variation of the elementary thermal separation ratio is, however, rather satisfactory, being of the order of 6-20 per cent. (He-Xe and He-A, respectively) in the above mixtures of inert gases.

Table 3.IV shows that *the thermal separation ratio of the elementary first approximation increases with increasing mass ratio,* except for He-Ne mixtures. In mixtures of equal proportions, R_T(elem) is equal to 0.708, 0.830, 0.968 and 1.054, respectively for Ne-A, He-A, He-Kr and He-Xe mixtures. For He-Ne, R_T(elem) is only 0.570. Increasing values of the thermal separation ratio with increasing mass ratio is a usual feature of the

elementary theory, as we have shown in § 5.IV. It is common either to the thermal diffusion factor, α_{ij}(elem) or its corresponding first approximation, $[\alpha_{ij}(\mathrm{elem})]_1$, when in a series of binary mixtures both the mass and the diameter ratios increase in the same direction.

In the above series of inert gas mixtures, the ratio σ_{Ne}/σ_{He} is even smaller than σ_A/σ_{Ne} which explains the lower value of R_T(elem) for He-Ne mixtures.

§ 7. *Comparison with experimental data*

For the sake of comparison with experimental results of thermal diffusion we shall use the 'r.e.s.' elementary first approximation only, namely

non-isotopic mixtures

$$[\alpha_{ij}(\mathrm{res})]_1 = \frac{1}{2}\cdot\frac{A_j - A_i}{c_i A_i + c_j A_j} \tag{58.IV}$$

where $A_i = (m_i/\eta_i)^{½}$ and $A_j = (m_j/\eta_j)^{½}$.

For *isotopic mixtures*, we use equation (15.IV), namely

$$[\alpha_{ij}(\mathrm{sm})]_1 = \frac{1-a_{ij}}{2}\cdot\frac{m_j^{½} - m_i^{½}}{c_i m_i^{½} + c_j m_j^{½}} \tag{59.IV}$$

Theoretically, we may obtain in this case the value for $a_{ij} \simeq a_i \simeq a_j$ by identifying $[\alpha_{ij}(\mathrm{sm})]_1$ with the corresponding experimental value for the thermal diffusion factor.

When molecules behave as *'rigid elastic spheres'*, equation (59.IV) reduces to

$$[\alpha_{ij}(\mathrm{res})]_1 = \frac{1}{2}\cdot\frac{m_j^{½} - m_i^{½}}{c_i m_i^{½} + c_j m_j^{½}} \tag{60.IV}$$

7.1. Binary mixtures of equal proportions. In Table 4.IV we present experimental values for the thermal diffusion factor for several mixtures of equal proportions. Comparison is made to the first approximations according to our elementary treatment and the exact Chapman-Enskog theory when molecules behave as rigid elastic spheres.

When a temperature range is reported in the Table, the experimental thermal diffusion factor is a mean value in this range; when a single temperature is given the thermal diffusion factor corresponds to a mean temperature assumed by the authors. Usually, $\bar{T}$ is determined by the following equations:

$$\bar{T} = T_r = \frac{T^I T^{II}}{T^{II} - T^I} \ln (T^{II}/T^I); \ (T^{II} > T^I) \qquad (61.IV)$$

This equation has been deduced by Harrison Brown (B3) assuming that the thermal diffusion factor varies with temperature according to the relation

$$\alpha_{ij}(\exp) = (\alpha^{*}_{ij})_o \cdot (1 + A/T_r) \qquad (62.IV)$$

where A is a constant and $(\alpha_{ij})_o$ is the limiting value of the thermal diffusion factor at higher temperatures. Equation (61.IV) holds fairly well at higher temperatures (D2).

Another equation for the mean temperature to which the experimental thermal diffusion factor should be referred, has been proposed by Holleran (H7), namely,

$$\bar{T} = T_m = (T^I T^{II})^{1/2} \qquad (63.IV)$$

which has been found assuming that

$$\alpha_{ij}(\exp) = A + B \ln T_m \qquad (64.IV)$$

where A and B are constants.

Equation (64.IV) is usually satisfactory at lower temperatures (D2).

Quasi-theoretical values for the 'r.e.s.' elementary first approximation have been determined by using in (58.IV) experimental coefficients of viscosity taken from 'Handbook of Chemistry and Physics', 36th edition (H6). They refer to the highest quoted values of temperatures, because the behaviour of molecules at these temperatures tends to come close to that of rigid elastic spheres. Quasi-theoretical values for Chapman-Cowling's first approximation for the thermal diffusion factor are mainly taken from ref. (G3).

Table 4.IV

Calculated and experimental values
of the thermal diffusion factor, α_{ij},
in binary mixtures of equal proportions

Mixture	Chapman r.e.s.	Elem. 'r.e.s.'	Exp.	Temp. Range $T^{I}-T^{II}$ (°K)	Reference
H_2-D_2	0.276	0.172	0.173	288-373	H5
H_2-Ne	0.495	0.267	0.280	290- 90	T2
			0.254	284-671	This paper
H_2-N_2	0.568	0.455	0.340	288-373	I1
H_2-A	0.571	0.467	0.28	288-456	I2
H_2-CO_2	0.609	0.536	0.298	288-373	I1
^3He-^4He	0.127	0.0670	0.059	273-613	N1
He-Ne	0.488	0.295	0.388	288-373	A1
			0.275	284-660	This paper
He-N_2	0.577	0.486	0.36	287-373	G7
He-A	0.592	0.491	0.39	369	G8
			0.376	289-663	This paper
He-Kr	0.627	0.607	0.448	465	G8
He-Xe	0.652	0.688	0.434	465	G8
$^{14}NH_3$-$^{15}NH_3$	0.0254	0.0145	0.0105	366	W4
^{20}Ne-^{22}Ne	0.0424	0.0245	0.0254	195-490	S1
			0.0275	289-660	This paper
Ne-A	0.332	0.224	0.191	465	G8
			0.144	288-665	This paper
Ne-Kr	0.514	0.394	0.32	465	G8
Ne-Xe	0.584	0.468	0.37	465	G8
N_2-CO_2	0.236	0.108	0.051	372	W5
N_2-N_2O	0.240	0.0839	0.048	288-400	B4
$^{16,16}O_2$-$^{16,18}O_2$	0.0270	0.0148	0.0145	443	W6
^{36}A-^{40}A	0.0468	0.0257	0.0250	638-835	S1
			0.0145	287-660	This paper
A-Kr	0.313	0.158	0.149	465	G8
A-Xe	0.452	0.264	0.176	465	G8

Table (4.IV) shows that our elementary first approximation for the thermal diffusion factor is usually closer to experimental data than Chapman-Cowling's value. For higher mass ratios, the value predicted by the elementary theory comes close to that of Chapman and Cowling, in accordance to the analysis made in § 5.1.IV. This can be observed for H_2-CO_2 and He-Kr mixtures to which the mass ratios are respectively 21.8 and 20.92. For He-Xe (m_j/m_i = = 32.56) the elementary thermal diffusion factor is already somewhat larger than the one corresponding to Chapman-Cowling's first approximation.

For He-Ne, the experimental value after Atkins, Bastick and Ibbs (A1) is larger than $[(\alpha_{ij}(\text{elem})]_1$, whereas our observation is smaller though corresponding to higher mean temperature than that of Atkins' observation. (Our experimental results are given and discussed in Chapter VI.)

For the isotopic mixture ^{20}Ne-^{22}Ne with natural Neon the elementary theoretical value is also somewhat smaller than that observed by Stier (S1) in the range T^I = 195 °K, T^{II} = 490 °K. Our value is even higher for it corresponds to higher mean temperature.

Smaller theoretical values are also obtained by the elementary theory in H_2-D_2 and H_2-Ne.

Table 4.IV is only a short survey on experimental observations at normal temperatures. For more detailed data see, for example, ref. (G3).

The order of magnitude of $(1 - a_{ij})$ (and therefore of a_i and a_j) may be determined assuming that $\alpha_{ij}(\text{exp}) \sim (1 - a_{ij}) \cdot$ $\cdot$ $[\alpha_{ij}(\text{res})]_1$. From Table 4.IV it follows that the most probable range for a_{ij} (and therefore for a_i and a_j) is in between 0.10 and 0.40. In a few cases only, we have $a_{ij} < 0$. According to equation (14.IV), the most probable range for the ratio, l_i'/l_i, of the mean free path for mean thermal speed transfer to the mean free path for number density transfer should be in between 1.10 and 1.40.

7.2. Inert gas mixtures. Concentration dependence of thermal diffusion factor. Tables 5, 6, 7, 8 and 9.IV, and figures 1, 2, 3, 4 and 5.IV report experimental thermal diffusion factors in Ne-A, He-Ne, He-A, He-Kr and He-Xe mixtures obtained by Atkins, Bastick and Ibbs (A1) who determined the separation as a function of composition, for constant temperatures $T^{I} = 288\ ^{\circ}K$ and $T^{II} = 373\ ^{\circ}K$. The katharometer method of analysis has been used. Experimental errors are about 5 per cent.

We have also made several measurements with Ne-A and He-A mixtures over large ranges of composition. Analysis has been carried out by mass spectrometry using the isotopic peaks of ^{20}Ne (90.51% in natural Neon), ^{40}A (99.633%) and ^{4}He (~ 100%). The range of temperature was about 286-667 °K. Experimental errors are about 3 per cent. Our results which will be mainly discussed in Chapter VI of this paper, are also given in the above Tables and figures.

Elementary first approximations for the 'r.e.s.' thermal diffusion factor are given by quasi-theoretical equations: (42,..., 46.IV).

Equations (52,..., 56.IV) corresponding to the inverse of r.e.s. Chapman and Cowling's first approximation are also drawn in the figures. As we have already pointed out in § 6, these equations are closely linear in concentrations.

According to the theory given in § 4.2.IV we should have: *Even when molecules do not behave as 'rigid elastic spheres' the inverse of thermal diffusion factors should be, usually, linear on concentrations, at a first approximation.*

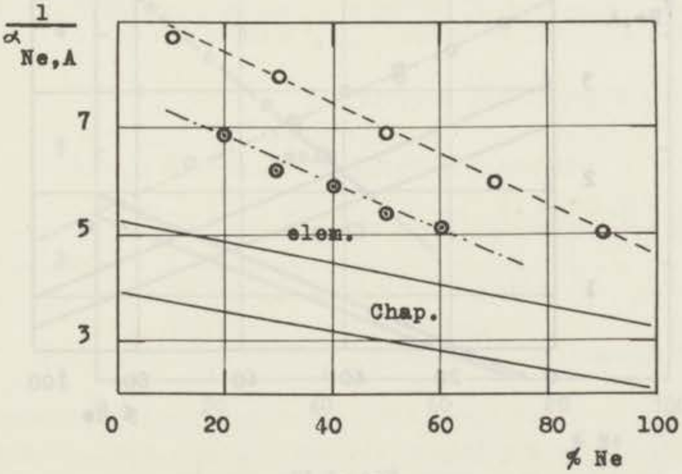

Fig. 1.IV.
The inverse of the thermal diffusion factor for Neon-Argon mixtures.
⊙ Experimental data after Atkins et al. (A1)
O our experiments.
Chap. Chapman-Cowling's r.e.s. first approximation
elem. Elementary 'r.e.s.' first approximation.

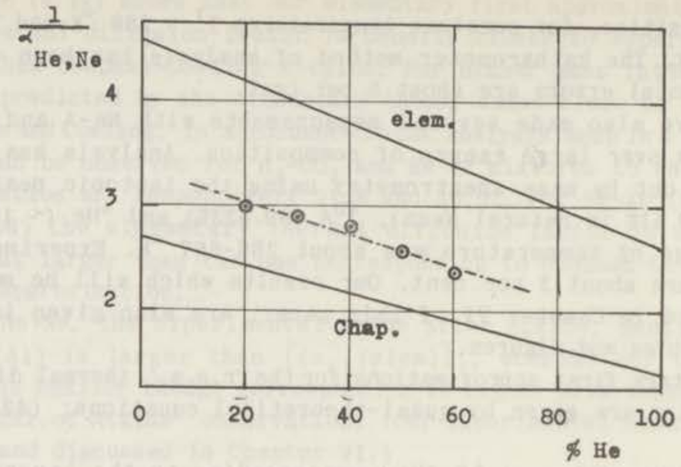

Fig. 2.IV.
The inverse of the thermal diffusion factor for Helium-Neon mixtures.
⊙ Experimental data after Atkins et al. (A1)
Chap. Chapman-Cowling's r.e.s. first approximation
elem. Elementary 'r.e.s.' first approximation.

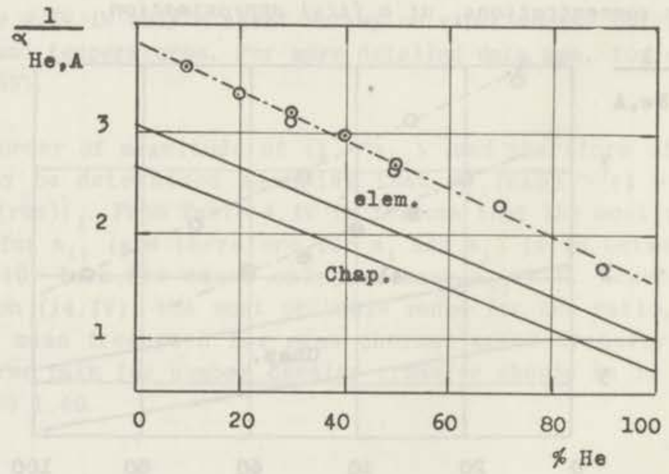

Fig. 3.IV.
The inverse of the thermal diffusion factor for Helium-Argon mixtures.
⊙ Experimental data after Atkins et al. (A1)
O Our experiments
Chap. Chapman-Cowling's r.e.s. first approximation
elem. Elementary 'r.e.s.' first approximation.

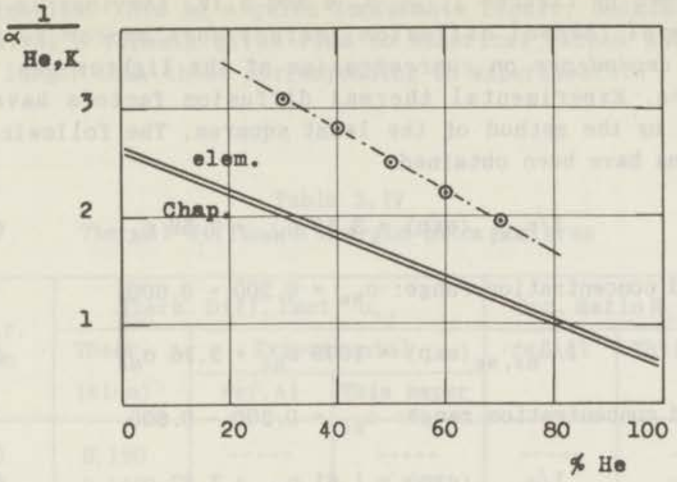

Fig. 4.IV.
The inverse of the thermal diffusion factor for Helium-Krypton mixtures.
⊙ Experimental data after Atkins et al. (A1)
Chap. Chapman-Cowling's r.e.s. first approximation
elem. Elementary 'r.e.s.' first approximation.

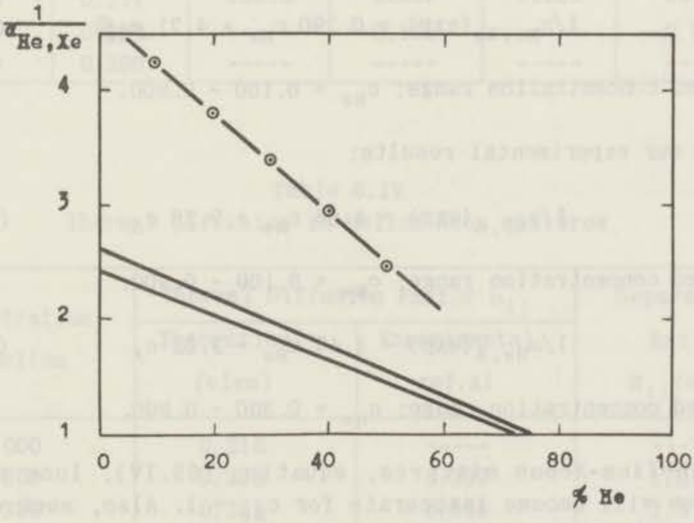

Fig. 5.IV.
The inverse of the thermal diffusion factor in Helium-Xenon mixtures.
⊙ Experimental data after Atkins et al. (A1)
Chap. Chapman-Cowling's r.e.s. first approximation
elem. Elementary 'r.e.s.' first approximation.

As shown by figures 1, 2, 3, 4 and 5.IV, *the inverse of experimental thermal diffusion factors does appear to have a linear dependence on concentration* of the lighter gas of the mixtures. Experimental thermal diffusion factors have been treated by the method of the least squares. The following mean equations have been obtained:

$$1/\alpha_{Ne,A}(\mathrm{exp}) = 3.39\ c_{Ne} + 7.58\ c_A \qquad (65.IV)$$

Observed concentration range: $c_{Ne} = 0.200 - 0.600$.

$$1/\alpha_{He,Ne}(\mathrm{exp}) = 1.79\ c_{He} + 3.36\ c_{Ne} \qquad (66.IV)$$

Observed concentration range: $c_{He} = 0.200 - 0.600$.

$$1/\alpha_{He,A}(\mathrm{exp}) = 1.61\ c_{He} + 3.82\ c_A \qquad (67.IV)$$

Concentration range observed: $c_{He} = 0.100 - 0.500$.

$$1/\alpha_{He,Kr}(\mathrm{exp}) = 1.08\ c_{He} + 3.96\ c_{Kr} \qquad (68.IV)$$

Observed concentration range: $c_{He} = 0.300 - 0.700$.

$$1/\alpha_{He,Xe}(\mathrm{exp}) = 0.290\ c_{He} + 4{,}71\ c_{Xe} \qquad (69.IV)$$

Observed concentration range: $c_{He} = 0.100 - 0.500$.

From our experimental results:

$$1/\alpha_{Ne,A}(\mathrm{exp}) = 4.65\ c_{Ne} + 9.28\ c_A \qquad (70.IV)$$

Observed concentration range: $c_{Ne} = 0.100 - 0.900$.

$$1/\alpha_{He,A}(\mathrm{exp}) = 1.47\ c_{He} + 3.82\ c_A \qquad (71.IV)$$

Observed concentration range: $c_{He} = 0.300 - 0.900$.

For Helium-Xenon mixtures, equation (69.IV), long extrapolation will become inaccurate for $c_{He} = 1$. Also, such extrapolation might be very unfavourable because the thermal diffusion factor can be expected to be markedly dependent on concentration regarding the large mass ratio, $m_{Xe}/m_{He} = 32.56$. According to (69.IV) the limiting value for the thermal diffusion factor at $c_{He} = 1$ should be 1.57 times the r.e.s. Chapman-Cowling's first approximation. This is a quite improbable result, because Chapman-Cowling's formula gives rise to numerical values which are always larger than those corresponding to experiments.

Table 5.IV
Thermal diffusion in Argon-Neon mixtures

Concentr. of Neon	Therm. Diff. Fact. α_{ij}			Sep. Ratio R_{ij} (exp)	
	Theor. (elem)	Experimental		ref.A1	This paper
		ref.A1	This paper		
0.000	0.190	-----	-----	-----	-----
0.100	0.198	-----	0.114	-----	0.576
0.200	0.206	0.146	-----	0.709	-----
0.300	0.215	0.161	0.125	0.749	0.581
0.400	0.225	0.170	-----	0.756	-----
0.500	0.235	0.183	0.145	0.779	0.617
0.600	0.247	0.195	-----	0.789	-----
0.700	0.260	-----	0.166	-----	0.638
0.800	0.274	-----	-----	-----	-----
0.900	0.290	-----	0.195	-----	0.672
1.000	0.308	-----	-----	-----	-----

Table 6.IV
Thermal diffusion in Helium-Neon mixtures

Concentration of Helium	Thermal Diffusion Factor α_{ij}		Separation Ratio R_{ij} (exp)
	Theoretical (elem)	Experimental ref.A1	
0.000	0.218	-----	-----
0.200	0.238	0.332	1.395
0.300	0.251	0.345	1.375
0.400	0.264	0.360	1.364
0.500	0.278	0.388	1.396
0.600	0.295	0.418	1.417
1.000	0.386	-----	-----

Table 7.IV

Thermal diffusion in Helium-Argon mixtures

Concentr. of Helium	Therm. Diff. Fact. α_{ij}			Sep. Ratio R_{ij}(exp)	
	Theor. (elem)	Experimental		ref.A1	This paper
		ref.A1	This paper		
0.000	0.329	-----	-----	-----	-----
0.100	0.353	0.278	-----	0.788	-----
0.200	0.379	0.298	-----	0.786	-----
0.300	0.411	0.314	0.323	0.764	0.786
0.400	0.447	0.338	-----	0.756	-----
0.500	0.491	0.372	0.376	0.758	0.766
0.700	0.612	-----	0.454	-----	0.742
0.900	0.810	-----	0.594	-----	0.733
1.000	0.966	-----	-----	-----	-----

Table 8.IV

Thermal diffusion in Helium-Krypton mixtures

Concentration of Helium	Thermal diffusion factor α_{ij}		Separation Ratio R_{ij}(exp)
	Theoretical (elem)	Experimental ref.A1	
0.000	0.378	-----	-----
0.300	0.488	0.322	0.660
0.400	0.541	0.355	0.656
0.500	0.607	0.400	0.659
0.600	0.691	0.450	0.651
0.700	0.802	0.509	0.635
1.000	1.544	-----	-----

Table 9.IV

Thermal diffusion in Helium-Xenon mixtures

Concentration of Helium	Thermal diffusion factor α_{ij}		Separation Ratio R_{ij}(exp)
	Theoretical (elem)	Experimental ref.A1	
0.000	0.407	-----	-----
0.100	0.444	0.234	0.527
0.200	0.487	0.264	0.542
0.300	0.539	0.294	0.545
0.400	0.605	0.338	0.559
0.500	0.688	0.403	0.586
1.000	2.203	-----	-----

Let us now compare the concentration dependence of the thermal diffusion factor as given by (1) the 'r.e.s.' elementary first approximation, (2) the r.e.s. Chapman-Cowling's formula and (3) by experimental data, for Ne-A, He-Ne, He-A and He-Kr mixtures. For this purpose Table 10.IV reports the ratios of the thermal diffusion factors in the limiting case as $c_i = 1$ to the corresponding values as $c_j = 1$, namely $[\alpha_{ij}]_i/[\alpha_{ij}]_j$.

Table 10.IV shows that the experimental ratio, $[\alpha_{ij}(\exp)]_i/[\alpha_{ij}(\exp)]_j$, is closer to that given by our theory for He-A and He-Kr mixtures, whereas it is closer to Chapman-Cowling's value for A-Ne mixtures. The experimental ratio is in between the theoretical ones for He-Ne mixtures.

Table 10.IV

Theoretical and experimental ratios $[\alpha_{ij}]_i/[\alpha_{ij}]_j$.

Mixture	Chapman and Cowling (res)	Elementary ('r.e.s.')	Experimental	
			ref.A1	This paper
A-Ne	1.918	1.615	2.23	1.99
He-Ne	2.010	1.771	1.88	----
He-A	3.556	2.932	2.37	2.60
He-Kr	4.551	4.086	3.67	----

Experimental thermal separation ratios, $R_{ij}(\exp)$, referred to our elementary 'r.e.s.' first approximations for the thermal diffusion factors of A-Ne, He-Ne, He-A, He-Kr and He-Xe mixtures are also given in Tables 5, 6, 7, 8 and 9.IV. For mixtures of equal proportions of A-Ne, He-A, He-Kr and He-Xe, $R_{ij}(\exp)$ is equal to 0.779, 0.858, 0.659 and 0.586.

For He-Ne, $R_{ij}(\exp) = 1.396$ which seems to be an abnormal value when compared with those of the above series of inert gas mixtures. As we have shown in paragraph 6 (see Table 3.IV), the elementary first approximation for 'r.e.s.' thermal diffusion factor for He-Ne mixtures, $[\alpha_{He,Ne}(res)]_1$, is rather small when compared to the corresponding first approximations for A-Ne, He-A, He-Kr and He-Xe because the diameter ratio σ_{Ne}/σ_{He} is too small in the above series of mixtures (even smaller than σ_A/σ_{Ne}). This may explain so high a result for $R_{ij}(\exp)$ for He-Ne mixtures.

§ 8. *Pressure diffusion in binary mixtures*

Only a short reference will be made since pressure diffusion has been a non-important phenomenon up to now, because of the difficulties of experiments.

According to the elementary theory, the pressure diffusion ratio is given by equation (23.II), namely,

$$K_{pi}(\mathrm{elem}) = c_i c_j \cdot \frac{l_i m_j^{½} - l_j m_i^{½}}{l_i c_j m_j^{½} + l_j c_i m_i^{½}} \qquad (72.\mathrm{IV})$$

It follows than that pressure diffusion ratio would probably be independent of the model for the intermolecular interactions. This is in agreement with the exact theory, to which Chapman and Cowling (C1) give the first approximation, $[K_{pi}(\mathrm{Chap})]_1$, as

$$[K_{pi}(\mathrm{Chap})]_1 = c_i c_j \cdot \frac{m_j - m_i}{c_i m_i + c_j m_j} \qquad (73.\mathrm{IV})$$

Equation (73.IV) is, however, also independent on molecular diameters what does not usually occur in (72.IV).

The elementary first approximation, $[(\alpha_p)_{ij}(\mathrm{elem})]_1$ for the pressure diffusion factor obtained by using (13.II) into (72.IV) will be given by

$$[(\alpha_p)_{ij}(\mathrm{elem})]_1 = \frac{A_j - A_i}{c_i A_i + c_j A_j} \; ; \; A_i = (m_i/\eta_i)^{½} \qquad (74.\mathrm{IV})$$

Hence the pressure diffusion factor should be twice the 'r.e.s.' thermal diffusion factor.

The clearest disagreement between the elementary and the exact Chapman-Enskog theory is shown by the concentration dependence of the pressure diffusion factor. The variation of this factor with concentration is usually very much larger in Chapman-Enskog's theory. Whereas the ratio $[(\alpha_p)_{ij}]_i/[(\alpha_p)_{ij}]_j$ is equal to the mass ratio, m_j/m_i, in the exact Chapman-Enskog theory, our elementary treatment gives it as

$$\frac{[(\alpha_p)_{ij}(\mathrm{elem})]_i}{[(\alpha_p)_{ij}(\mathrm{elem})]_j} = \left[\frac{m_j}{m_i}\right]^{½} \cdot \left[\frac{\eta_i}{\eta_j}\right]^{½} \qquad (73.\mathrm{IV})$$

which is indeed markedly different from m_j/m_i for large mass ratios.

In Table 11.IV we give the theoretical values of the pressure diffusion factor for mixtures of equal proportions of A-Ne, Ne-He, A-He and Kr-He mixtures. Values of the ratios $[(\alpha_p)_{ij}]_i/$ $/[(\alpha_p)_{ij}]_j$, and $(\alpha_p)_{ij}/(\alpha_T)_{ij}$ for mixtures of equal proportions are also given by the exact Chapman-Enskog and the elementary theories. For the elementary treatment we always have $(\alpha_p)_{ij}/$ $/(\alpha_T)_{ij}(\text{res}) = 2.00$ as we have pointed out before.

Table 11.IV

Pressure diffusion by the exact Chapman-Enskog and the elementary theories

Mixture	Press.Diff. Factors $(\alpha_p)_{ij}$ $(c_i=c_j=0.500)$		$[(\alpha_p)_{ij}]_i/[(\alpha_p)_{ij}]_j$		$(\alpha_p)_{ij}/(\alpha_T)_{ij}$ $(c_i=c_j=0.500)$	
	Chapman-Enskog	Elem.	Chapman-Enskog	Elem.	Chapman-Enskog	Elem.
A-Ne	0.668	0.470	1.979	1.62	2.01	2.00
Ne-He	1.340	0.556	5.045	1.77	2.74	2.00
A-He	1.635	0.982	9.984	2.93	2.76	2.00
Kr-He	1.813	1.214	20.92	4.09	2.89	2.00

CHAPTER V

THERMAL AND PRESSURE DIFFUSION IN MULTICOMPONENT MIXTURES

§ 1. *General theory*

In Chapter II (equation (19.II)), we have shown that the velocity of mutual diffusion for gases i and j was given by

$$\vec{U}_i - \vec{U}_j = -\left[\frac{8kT}{9\pi}\right]^{1/2} \left[(X_i \operatorname{grad} \ln c_i - X_j \operatorname{grad} \ln c_j) + Z_{ij} \operatorname{grad} \ln p - \frac{1}{2} Z'_{ij} \operatorname{grad} \ln T\right] \tag{1.V}$$

where, in a general form,

$$X_k = l_k m_k^{-1/2} \; ; \; Z_{ij} = X_i - X_j = l_i m_i^{-1/2} - l_j m_j^{-1/2}$$
$$\frac{1}{2} Z'_{ij} = (l_i - l'_i/2)\, m_i^{-1/2} - (l_j - l'_j/2)\, m_j^{-1/2} \tag{2.V}$$

In a mixture of s gases in which molar concentrations, temperature and pressure are not uniform, we will have s-1 independent equations analogous to (1.V).

When the steady state is reached, all of these equations will be equal to zero. Also,

$$\sum_{k=1}^{s} \operatorname{grad} c_k = \sum_{k=1}^{s} c_k \operatorname{grad} \ln c_k = 0 \tag{3.V}$$

Hence, at equilibrium we obtain the following system of s equations:

$$X_i \operatorname{grad} \ln c_i - X_1 \operatorname{grad} \ln c_1 = \frac{1}{2} Z'_{i1} \operatorname{grad} \ln T - Z_{i1} \operatorname{grad} \ln p$$

. . . .

$$X_i \operatorname{grad} \ln c_i - X_j \operatorname{grad} \ln c_j = \frac{1}{2} Z'_{ij} \operatorname{grad} \ln T - Z_{ij} \operatorname{grad} \ln p$$

. . . .

$$X_i \operatorname{grad} \ln c_i - X_s \operatorname{grad} \ln c_s = \frac{1}{2} Z'_{is} \operatorname{grad} \ln T - Z_{is} \operatorname{grad} \ln p$$

$$c_i \text{ grad } \ln c_i + \dots + c_j \text{grad } \ln c_j + \dots + c_s \text{ grad } \ln c_s = 0 \qquad (4.\text{V})$$

In connection with experiments, it is convenient to solve the system (4.V) in order to obtain grad c_i and grad ln (c_i/c_j). By integration of the equation involving grad c_i we obtain the *separation*, $S_i = c_i^{II} - c_i^{I}$, well known when dealing with thermal diffusion. Then c_i^{II} and c_i^{I} refer to the molar concentration of the gas of kind i in the regions at absolute temperature T^{II} and T^{I} respectively.

By integration of grad ln (c_i/c_j) we can obtain the *separation factor*, $q_{ij} = (c_i/c_j)^{II}/(c_i/c_j)^{I}$ where $(c_i/c_j)^{II}$ and $(c_i/c_j)^{I}$ refer to the concentration ratio of gases i and j at temperatures T^{II} and T^{I}, respectively.

By using the system (4.V) we can obtain

$$\text{grad } c_i = K_{Ti} \text{ grad } \ln T - K_{pi} \text{ grad } \ln p \qquad (5.\text{V})$$

$$\text{grad } \ln (c_i/c_j) = (\alpha_T)_{ij} \text{ grad } \ln T - (\alpha_p)_{ij} \text{ grad } \ln p \qquad (6.\text{V})$$

where

$$K_{Ti} = \frac{1}{2} \cdot \frac{\sum_{k=1}^{s} c_i c_k \, Z'_{ik}/X_i X_k}{\sum_{k=1}^{s} c_k/X_k} \qquad (7.\text{V})$$

$$K_{pi} = \frac{\sum_{k=1}^{s} c_i c_k \, Z_{ik}/X_i X_k}{\sum_{k=1}^{s} c_k/X_k} \qquad (8.\text{V})$$

$$(\alpha_T)_{ij} = \frac{1}{2} \cdot \frac{\sum_{k=1}^{s} c_k \, [Z'_{ik}/X_i X_k - Z'_{jk}/X_j X_k]}{\sum_{k=1}^{s} c_k/X_k} \qquad (9.\text{V})$$

$$(\alpha_p)_{ij} = \frac{\sum_{k=1}^{s} c_k \, [Z_{ik}/X_i X_k - Z_{jk}/X_j X_k]}{\sum_{k=1}^{s} c_k/X_k} = \frac{Z_{ij}/X_i X_j}{\sum_{k=1}^{s} c_k/X_k} \qquad (10.\text{V})$$

The quantities Z'_{ik}, Z_{ik} and X_k are given in general by (2.V). The quantity K_{Ti} and $(\alpha_T)_{ij}$ are respectively the *thermal diffusion ratio* of the gas i and the *thermal diffusion factor* of gases i and j, in this succession.

In the same way we indicate K_{pi} as the *pressure diffusion ratio* of the gas i in a complex mixture of s gases and $(\alpha_p)_{ij}$ as the *pressure diffusion factor* of the gases i and j, in this succession.

The thermal diffusion ratio K_{Ti} is related to thermal diffusion factors, as

$$K_{Ti} = \sum_{k=1}^{s} c_i c_k \, (\alpha_T)_{ik} \tag{11.V}$$

Also,

$$K_{pi} = \sum_{k=1}^{s} c_i c_k \, (\alpha_p)_{ik} \tag{12.V}$$

By means of equation (6.V), we can easily obtain,

$$(\alpha_T)_{ij} = - (\alpha_T)_{ji} \; ; \; (\alpha_p)_{ij} = - (\alpha_p)_{ji} \tag{13.V}$$

$$(\alpha_T)_{ik} + (\alpha_T)_{kj} = (\alpha_T)_{ij} \; ; \; (\alpha_p)_{ik} + (\alpha_p)_{kj} = (\alpha_p)_{ij} \tag{14.V}$$

All the equations given above will be valid, whatever formulae are applied for the mean free paths, l_k and l'_k.

In Whalley and Winter's theory (W1) for complex mixtures, K_{Ti} is given in a rather complex form, though equivalent to our equation (7.V). The pressure diffusion ratio, K_{pi}, is only given for binary mixtures. Thermal and pressure diffusion factors, $(\alpha_T)_{ij}$ and $(\alpha_p)_{ij}$, were not determined for complex mixtures.

Whalley and Winter worked out their theory assuming a rigid elastic sphere model. l_k was identified with Maxwell's mean free path corrected for persistence of velocities, equation (2.III). l'_k was indicated as a mean free path for momentum transfer to which the authors proposed an approximate formula (see equations 17, 18, 19.III).

If we assume for the mean free paths l_i and l'_i a relationship of the form

$$l'_i = (1 + a_i) \, l_i$$

the thermal diffusion factor for gases i and j, in this succession, is given by

$$(\alpha_T)_{ij} = \frac{(1 - \sum_{k=1}^{s} c_k a_k)}{2} \cdot \frac{m_j^{1/2}/l_j - m_i^{1/2}/l_i}{\sum_{k=1}^{s} c_k m_k^{1/2}/l_k} - \frac{a_i - a_j}{2} \qquad (15.V)$$

which is a general equation independent of any specification for the quantities a_k.

§ 2. *First approximation for the thermal diffusion factor*

Though formally simple, the above equation (15.V) for the thermal diffusion factor will become very laborious in practical cases of multicomponent mixtures if in it we use the common equations for the mean free path, l_k, for number density transfer. The equation will be even more complicated if the quantities a_k are not equal to zero.

Following the lines used in Chapter IV, we consider in our treatment that the quantities a_k depend predominantly on the 'hardness' of the force field surrounding the molecules of kind k. For 'rigid elastic spheres' we assume that all the quantities a_k are equal to zero. This assumption is only a kind of mathematical approach and even then not too bad for practical cases. The thermal diffusion factor will be given in this Chapter *at a first approximation* only, by using our equation (30.III) for the mean free path for number density transfer, namely,

$$[{}_p l_i]_1 = K' (\eta_i)^{1/2} \qquad (16.V)$$

where K′ is a constant for each gas mixture.

As we have shown, equation (16.V) can be satisfactorily applied to thermal diffusion in binary mixtures, provided that the mass ratio is not too close to unity when $m_j > m_i$ and $\sigma_j < \sigma_i$ (when a change of sign of the thermal diffusion factor with concentration may occur).

By using (16.V) in (15.V) we obtain the following equation for the first approximation to the thermal diffusion factor of gases i and j, in this succession. The subscript 1, referring to the first approximation, will always be omitted in this Chapter for the sake of simplicity in notation. Subscript T referring to thermal is omitted as well, when no confusion arises with pressure diffusion.

$$\alpha_{ij}(\mathrm{sm}) = \frac{1 - \sum_{k=1}^{s} c_k a_k}{2} \cdot \frac{A_j - A_i}{\sum_{k=1}^{s} c_k A_k} - \frac{a_i - a_j}{2} \qquad (17.\mathrm{V})$$

where, in general,

$$A_k = (m_k/\eta_k)^{1/2} \qquad (18.\mathrm{V})$$

When molecules are regarded as 'rigid elastic spheres' we assume in (17.V) $a_i = a_j = \ldots = a_s = 0$.

For Maxwellian mixtures we have $a_i = a_j = \ldots = a_s = 1$.

For a binary mixture (i,j), equation (17.V) reduces to (20.IV), namely,

$$\alpha_{ij}^{(b)}(\mathrm{sm}) = \frac{1}{2} \cdot \frac{(1-a_i)A_j - (1-a_j)A_i}{c_i^{(b)} A_i + c_j^{(b)} A_j} \qquad (19.\mathrm{V})$$

The notation (b) has been added because the thermal diffusion factor of the binary mixture (i,j) will afterwards be compared with the corresponding one of a multicomponent mixture.

If (19.V) is compared to the corresponding value of our 'r.e.s.' model, the binary thermal separation ratio, $R_{ij}^{(b)}$, is given by

$$R_{ij}^{(b)} = \frac{\alpha_{ij}^{(b)}(\mathrm{sm})}{\alpha_{ij}^{(b)}(\mathrm{res})} = \frac{(1-a_i)A_j - (1-a_j)A_i}{A_j - A_i} \qquad (20.\mathrm{V})$$

This equation will be used in the next dicussion.

According to equation (20.V), the binary separation ratio, $R_{ij}^{(b)}$, would be independent of concentration, at a first approximation. As we have seen in § 7.2.IV, a small variation is usually observed in experiments.

If the gases i and j are isotopes, equation (17.V) should bring about equation (15.IV) for binary isotopic mixtures:

$$\alpha_{ij}^{(b)}(\mathrm{sm}) = \frac{1 - a_{ij}}{2} \cdot \frac{m_j^{1/2} - m_i^{1/2}}{c_i^{(b)} m_i^{1/2} + c_j^{(b)} m_j^{1/2}} \qquad (21.\mathrm{V})$$

where $a_{ij} = a_i = a_j$. This equation has been obtained by making the particular assumption that $l_i = l_j$ and also $l_i' = l_j'$ for isotopic mixtures.

In order to reduce (17.V) to (21.V) in the limiting case of a binary isotopic mixture (i,j), a kind of approach has to be considered: *we assume that the coefficients of viscosity of isotopes, η_i and η_j, are both equal to the coefficient of viscosity, η_A, of the gas with natural isotopic composition.* As a result of that approximation, quasi-theoretical values for A_i and A_j for isotopes i and j are the one *increased* and the other *decreased*, relative to the actual value which should be taken, depending on the concentration of each isotope in the natural gas A. Therefore, the difference between the quasi-theoretical values $\alpha_{ik}(\mathrm{res})$ and $\alpha_{jk}(\mathrm{res})$, as well as the difference between $\alpha_{ik}^{(b)}(\mathrm{res})$ and $\alpha_{jk}^{(b)}$, has been *increased* somewhat artificially. Even then, the error which is committed, is, indeed, rather small.

§ 3. *Effect of addition of gases to a binary mixture*

In this paragraph we will compare the thermal diffusion factor in a multicomponent mixture (i, j,...,s) to that of a binary mixture (i,j). In particular we consider in what way the thermal diffusion factor of gases i and j would be changed by addition of a gas k to the initial mixture (i,j).

Let us suppose that gases k, ..., s are added to the binary mixture of gases i and j, with concentrations $c_i^{(b)}$ and $c_j^{(b)}$, respectively. Consider, c_i, c_j, c_k, ..., c_s, the resulting concentrations in the multicomponent mixture. Since the proportion of the gases i and j has not been changed, we have

$$c_i/c_i^{(b)} = c_j/c_j^{(b)} = c_i + c_j \qquad (23.\mathrm{V})$$

We first determine the thermal separation ratio, R_{ij}, of gases i and j in the multicomponent mixture. By means of (17.V) we have

$$R_{ij} = \frac{\alpha_{ij}(\mathrm{sm})}{\alpha_{ij}(\mathrm{res})} = 1 - \sum_{k=1}^{s} c_k a_k - \frac{a_i - a_j}{A_j - A_i} \cdot \sum_{k=1}^{s} c_k A_k \qquad (23.\mathrm{V})$$

Since $\sum_{k=1}^{s} c_k = 1$, the above equation can be written as

$$R_{ij} = \sum_{k=1}^{s} c_k \frac{2\,A_k}{A_j - A_i}\left[\frac{(1-a_k)A_j - (1-a_j)A_k}{2\,A_k} - \frac{(1-a_k)A_i - (1-a_i)A_k}{2\,A_k}\right] \tag{24.V}$$

Now, by using (19.V), we have,

$$\frac{A_j - A_i}{2\,A_k} = \frac{A_j - A_k}{2\,A_k} - \frac{A_i - A_k}{2\,A_k} = [\alpha_{kj}^{(b)}(\mathrm{res})]_k - [\alpha_{ki}^{(b)}(\mathrm{res})]_k \tag{25.V}$$

$$\frac{(1-a_k)A_j - (1-a_j)A_k}{2\,A_k} - \frac{(1-a_k)A_i - (1-a_i)A_k}{2\,A_k} = [\alpha_{kj}^{(b)}(\mathrm{sm})]_k - [\alpha_{ki}^{(b)}(\mathrm{sm})]_k \tag{26.V}$$

Subscript k, which has been added, is the notation used for the asymptotic values of binary thermal diffusion factors when $c_k^{(b)} = 1$ (see § 1.3.IV - Limiting values of quantities).

Introducing (25,26.V) in (24.V), we obtain

$$R_{ij} = \sum_{k=1}^{s} c_k \,.\, \frac{[\alpha_{kj}^{(b)}(\mathrm{sm})]_k - [\alpha_{ki}^{(b)}(\mathrm{sm})]_k}{[\alpha_{kj}^{(b)}(\mathrm{res})]_k - [\alpha_{ki}^{(b)}(\mathrm{res})]_k} \tag{27.V}$$

Then,

$$R_{ij} = c_i \;[R_{ij}^{(b)}]_i + c_j \;[R_{ij}^{(b)}]_j + \sum_{\substack{k=1\\ k\neq i,j}}^{s} c_k \, A_{kji}^{(\mathrm{sm})}/A_{kji}^{(\mathrm{res})} \tag{28.V}$$

where

$$A_{kji}^{(\mathrm{sm})} = [\alpha_{kj}^{(b)}(\mathrm{sm})]_k - [\alpha_{ki}^{(b)}(\mathrm{sm})]_k \tag{29.V}$$

and an analogous equation for $A_{kji}^{(\mathrm{res})}$ changing (sm) by (res) into (29.V).

Since the proportion of gases i and j is not changed by the addition of gases k, ..., s, equation (22.V) is valid. Then

$$c_i \;[R_{ij}^{(b)}]_i + c_j \;[R_{ij}^{(b)}]_j = (c_i + c_j)\{\, c_i^{(b)}[R_{ij}^{(b)}]_i + c_j^{(b)}[R_{ij}^{(b)}]_j \} \tag{30.V}$$

As shown by equation (20.V), the binary thermal separation ratio, $R_{ij}^{(b)}$, should be theoretically regarded as a constant, at a first approximation. Even then equation (30.V) also holds for a linear variation of $R_{ij}^{(b)}$ with concentration. Then $c_i^{(b)}[R_{ij}^{(b)}]_i + c_j^{(b)}[R_{ij}^{(b)}]_j$ is the value of the thermal separation ratio for the binary mixture (i,j) with molar concentrations $c_i^{(b)}$ and $c_j^{(b)}$, to which the gases k, ..., s have been added.

Introducing (30.V) in (28.V), the *thermal separation ratio of gases i and j in a multicomponent mixture* is given by

$$R_{ij} = (c_i + c_j)\, R_{ij}^{(b)} + \sum_{\substack{k=1\\ k\neq i,j}}^{s} c_k\, A_{kji}^{(sm)}/A_{kji}^{(res)} \qquad (31.V)$$

This equation theoretically predicts a *linear variation of the thermal separation ratio with molar concentrations, c_k, of the gases which have been 'added' to the initial binary mixture* (i,j). If binary thermal diffusion factors are experimentally available, equation (31.V) provides a very simple way to study thermal diffusion in multicomponent mixtures. Elementary 'r.e.s.' thermal diffusion factors which have to be used in (31.V) can be obtained by means of (19,21.V).

The variation of the thermal diffusion factor of gases i and j with addition of gases k, ..., s is better discussed by using the quantity $\Delta_{ij}(sm)$ which is defined as

$$\Delta_{ij}(sm) = \frac{\alpha_{ij}(sm)}{\alpha_{ij}^{(b)}(sm)} \qquad (32.V)$$

where $\alpha_{ij}^{(b)}(sm)$ refers to the concentrations $c_i^{(b)}$ and $c_j^{(b)}$.

According to (32.V) the thermal diffusion factor of gases i and j *should increase by addition of a gas k if* $\Delta_{ij}(sm) > 1$. *Conversely, it should decrease if* $\Delta_{ij}(sm) < 1$.

Since (32.V) can be written as

$$\Delta_{ij}(sm) = \frac{\alpha_{ij}(res)}{\alpha_{ij}^{(b)}(res)} \cdot \frac{\alpha_{ij}(sm)}{\alpha_{ij}(res)} \cdot \frac{\alpha_{ij}^{(b)}(res)}{\alpha_{ij}^{(b)}(sm)} \qquad (33.V)$$

we obtain, by using (31.V) and (17.V)

$$\Delta_{ij}(\mathrm{sm}) = \Delta_{ij}(\mathrm{res}) \left[(c_i + c_j) + \sum_{\substack{k=1 \\ k\neq i,j}}^{s} \frac{c_k}{R_{ij}^{(b)}} \cdot \frac{A_{kji}^{(\mathrm{sm})}}{A_{kji}^{(\mathrm{res})}} \right] \qquad (34.\mathrm{V})$$

where $\Delta_{ij}(\mathrm{res})$ is the value of $\Delta_{ij}(\mathrm{sm})$ for 'r.e.s.' molecules ($a_i = a_j = \ldots = a_s = 0$), namely,

$$1/\Delta_{ij}(\mathrm{res}) = \frac{\alpha_{ij}^{(b)}(\mathrm{res})}{\alpha_{ij}(\mathrm{res})} = (c_i + c_j) + \sum_{\substack{k=1 \\ k\neq i,j}}^{s} \frac{c_k A_k}{c_i^{(b)} A_i + c_j^{(b)} A_j} \qquad (35.\mathrm{V})$$

Let us now discuss the above equations (34, 35.V)

1) *If molecules are regarded as 'rigid elastic spheres'* or if $R_{ij}^{(b)} = [R_{kj}^{(b)}]_k = [R_{ki}^{(b)}]_k$ it can be shown that $A_{kji}^{(\mathrm{sm})}/R_{ij}^{(b)} \cdot A_{kji}^{(\mathrm{res})} = 1$. Hence, $\Delta_{ij}(\mathrm{sm}) = \Delta_{ij}(\mathrm{res})$. We have then

$$\Delta_{ij}(\mathrm{res}) \gtrless 1 \text{ if } \sum_{\substack{k=1 \\ k\neq i,j}}^{s} c_k A_k \lesseqgtr c_i^{(b)} A_i + c_j^{(b)} A_j. \text{ Then } \alpha_{ij}^{(b)}(\mathrm{sm}) \lesseqgtr \alpha_{ij}(\mathrm{sm}) \qquad (36.\mathrm{V})$$

On the other hand, the quantities $A_k = (m_k/\eta_k)^{½}$ are proportional to $m_k^{¼}\sigma_k$. Therefore we can withdraw the following conclusion: *If molecules are regarded as 'rigid elastic spheres' or if all the binary thermal separation ratios are equal, the thermal diffusion factor of gases i and j should increase by addition of gases consisting of lighter or smaller molecules* ($A_k < A_i, A_j$). *Conversely, the thermal diffusion factor should decrease by addition of heavier or larger molecules* ($A_k > A_i, A_j$).

2) *In general cases* the variation of the thermal diffusion factor with addition of gases to the binary mixture (i,j) may be quite different from that predicted by the 'r.e.s.' model, as it can be inferred by means of equation (34.V), if the binary separation ratios $R_{ij}^{(b)}$, $[R_{kj}^{(b)}]_k$, $[R_{ki}^{(b)}]_k$ are markedly different. Indeed, we have,

$$A_{kji}^{(\mathrm{sm})} = [\alpha_{kj}^{(b)}(\mathrm{sm})]_k - [\alpha_{ki}^{(b)}(\mathrm{sm})]_k$$
$$A_{kji}^{(\mathrm{res})} = [\alpha_{kj}^{(b)}(\mathrm{res})]_k - [\alpha_{ki}^{(b)}(\mathrm{res})]_k \qquad (37.\mathrm{V})$$

If the ratio $A_{kji}^{(\mathrm{sm})}/A_{kji}^{(\mathrm{res})} > R_{ij}^{(b)}$, then by means of (34.V) $\Delta_{ij}(\mathrm{sm}) > \Delta_{ij}(\mathrm{res})$, and the thermal diffusion factor increases more than if molecules are regarded as 'rigid elastic spheres', provided that the added gas k consists of lighter or smaller molecules (Δ_{ij}(res) > 1).

If $A_{kji}^{(sm)}$ and $A_{kji}^{(res)}$ are *opposite in sign*, then *the thermal diffusion factor changes sign* with concentration of the added gas, as shown by (34.V).

§ 4. *Addition of a third gas to a binary isotopic mixture*

4.1. Introduction. This particular system of the general case studied in the preceding paragraph is one of interest because thermal diffusion is extensively used for separating isotopes.

Addition of a gas to isotopic mixtures has been reported by several authors, in order to achieve better experimental conditions for isotopic enrichment (C10,C11,C12,V1). Usually, the added gas, B, is chosen so that it concentrates between isotopes 1 and 2, and can be separated afterwards by chemical or physical methods. In the thermal diffusion column, each of the isotopes concentrate at either side of the region mostly occupied by the gas B. Schematically, we get the sequence

1 - 1B - B - B2 - 2

which shows that the addition of B reduces the loss of isotopic material in the hold-up of the column, i.e., in the transition portion between the regions mostly enriched on isotopes 1 and 2 respectively. This is of great importance when the amount of the isotopic mixture to be separated is very small.

As a generalisation of the same principle, separation of more than two isotopes may be performed by addition of a convenient gas consisting of several isotopic molecules. Clusius and Schumacher (C12) could almost completely separate the isotopes of natural Argon, ^{36}A, ^{38}A and ^{40}A by using hydrogen chloride. In the column the following sequence is schematically established:

$$^{36}A - H^{35}Cl - D^{35}Cl - {}^{38}A - H^{37}Cl - D^{37}Cl - {}^{40}A$$

Transition regions between isotopes of Argon are enlarged and ^{38}A could be withdrawn with appreciable enrichment. 0.6 cm^3 were obtained with a concentration higher than 90%. With Argon alone, in which natural abundance of ^{38}A is 0.060% only, the separation of this isotope would be nearly impossible.

In the preceding cases the molecular mass of the added gas is close to that of the isotopes to be separated. A.E.de Vries (V1) refers to another method, used by R.H.Davies at Harwell, for separation of ^{3}He and ^{4}He. Hydrogen is added to natural Helium, in which the abundance of the desired isotope, ^{3}He, is 1.3 x 10^{-4}% only. The top reservoir of the thermal diffusion column is kept filled with Hydrogen in order to reduce the effective top volume occupied by Helium enriched in ^{3}He. As a result, the time to reach stationary conditions is appreciably shortened.

In the examples given above, the addition of a gas tends to decrease the concentration of the desired isotope in transition regions, or to shorten the relaxation time of the column. Variations of the thermal diffusion factors, as a consequence of interactions of the added gas upon the molecules of the initial mixture, are not considered or only mass and diameter effects are considered. However, it would be very important if the thermal diffusion factors themselves could be increased or, at least, not markedly decreased. Therefore, the following discussion may be of value to choose the gas which should be added to the isotopic mixture, in order to get better experimental conditions for separation.

4.2. Variation of the isotopic thermal diffusion factor and separation ratio with addition of a third gas. Let us take a gas A consisting of two isotopes, 1 and 2, with molar concentrations $c_1^{(b)}$ and $c_2^{(b)}$, respectively.

If a third gas, of kind B, is added to the initial isotopic mixture, concentrations c_1, c_2 and c_B in the resulting ternary mixtures must be such that

$$c_1/c_1^{(b)} = c_2/c_2^{(b)} = c_1 + c_2 = c_A \tag{38.V}$$

and also

$$c_A + c_B = 1 \tag{39.V}$$

By using equations (17.V), the thermal diffusion factor, $\alpha_{12}(\mathrm{sm})$, for isotopes 1 and 2 in a ternary mixture (1,2,B) consisting of 'soft gases', is given by

$$\alpha_{12}(\mathrm{sm}) = \frac{1 - c_A a_A - c_B a_B}{2} \cdot \frac{A_2 - A_1}{c_A A_A + c_B A_B} - (a_1 - a_2)/2 \tag{40.V}$$

where

$$
\begin{aligned}
a_A &= c_1^{(b)} a_1 + c_2^{(b)} a_2 \\
A_A &= c_1^{(b)} A_1 + c_2^{(b)} A_2
\end{aligned}
\qquad (41.V)
$$

A priori the quantities a_1, a_2 and a_A as well as A_1, A_2 and A_A would be closely equal since they refer to isotopes of the same gas A.

If $a_1 = a_2 = a_B$, i.e. if all the force fields are equal, then *the inverse of the isotopic thermal diffusion factor should be linear on concentration*, c_B, *of the gas added* to the isotopic binary mixture (1,2). In practical cases it may be convenient to look for such eventual linear dependence because (40.V) is only given at a first approximation.

Let us now consider the isotopic separation ratio, R_{12}, for a ternary mixture (1,2,B). By using (31.V) we obtain,

$$R_{12} = \frac{\alpha_{12}(\mathrm{sm})}{\alpha_{12}(\mathrm{res})} = c_A R_{12}^{(b)} + c_B A_{B21}^{(\mathrm{sm})}/A_{B21}^{(\mathrm{res})} \qquad (42.V)$$

where, by means of (29.V)

$$
\begin{aligned}
A_{B21}^{(\mathrm{sm})} &= [\alpha_{B2}^{(b)}(\mathrm{sm})]_B - [\alpha_{B1}^{(b)}(\mathrm{sm})]_B \\
A_{B21}^{(\mathrm{res})} &= [\alpha_{B2}^{(b)}(\mathrm{res})]_B - [\alpha_{B1}^{(b)}(\mathrm{res})]_B
\end{aligned}
\qquad (43.V)
$$

or equivalently

$$\frac{A_{B21}^{(\mathrm{sm})}}{A_{B21}^{(\mathrm{res})}} = \frac{A_2 - A_B}{A_2 - A_1}.\ [R_{2B}^{(b)}]_B - \frac{A_1 - A_B}{A_2 - A_1}.\ [R_{1B}^{(b)}]_B \qquad (44.V)$$

The separation ratio $R_{12}^{(b)}$ is a constant; the ratio $A_{B21}^{(\mathrm{sm})}/A_{B21}^{(\mathrm{res})}$ is also a constant. Therefore equation (42.V) shows that *the isotopic thermal separation ratio*, R_{12}, *for ternary mixtures (1,2,B) should be linear on molar concentration of the gas added to the isotopic mixture (1,2), at a first approximation.*

Equation (42.V) also shows an important feature of thermal diffusion in ternary mixtures. If experimental data of the thermal diffusion factor $\alpha_{12}(\mathrm{sm})$ are available over a sufficiently large concentration range of the gas B, indirect values for the binary separation ratio, $R_{12}^{(b)}$, might be obtained by extrapolation of the above equation to the limiting case as $c_A = c_1 + c_2 = 1$. Also, a relationship between $[R_{1B}^{(b)}]_B$ and $[R_{2B}^{(b)}]_B$ might be obtained without any measurement of non-isotopic thermal diffusion factors, which might be of practical interest.

The variation of the isotopic thermal diffusion factor with addition of B is better discussed by using the quantity $\Delta_{12}(\mathrm{sm})$, equation (34.V), which can in this case be written as

$$\Delta_{12}(\mathrm{sm}) = \frac{\alpha_{12}(\mathrm{sm})}{\alpha_{12}^{(b)}(\mathrm{sm})} = \Delta_{12}(\mathrm{res}) \left[c_A + c_B \,.\, \frac{A_{B21}^{(\mathrm{sm})}}{R_{12}^{(b)} \,.\, A_{B21}^{(\mathrm{res})}} \right] \qquad (45.\mathrm{V})$$

where $\Delta_{12}(\mathrm{res})$ gives the variation of the thermal diffusion factor for 'r.e.s.' molecules, namely, equations (35,41.V),

$$1/\Delta_{12}(\mathrm{res}) = c_A + c_B . A_B / A_A \qquad (46.\mathrm{V})$$

According to equation (45.V), the variation of the thermal diffusion factor with addition of a third gas should depend on the following effects:

1) *Mass and diameter effects*. They are mainly determined by the quantity $\Delta_{12}(\mathrm{res})$. We assume then $R_{12}^{(b)} = [R_{1B}^{(b)}]_B = [R_{2B}^{(b)}]_B$. Therefore, by means of (46.V), *the isotopic thermal diffusion factor tends to increase by addition of a gas consisting of lighter or smaller molecules* ($A_B < A_A$). *Conversely, it tends to decrease when the gas added to the isotopic mixture (1,2) consists of heavier or larger molecules* ($A_B > A_A$).

This conclusion has also been obtained by Whalley and Winter (W1) in the limiting case, as the concentration of the added gas was equal to unity and molecules are regarded as rigid elastic spheres.

The variation of the quantity A_B with molecular mass, m_B, is usually rather small, hardly increasing or decreasing the thermal diffusion factor by a factor of two.

2) *Hardness effect*. This effect is expressed in (45.V) by the ratio $A_{B21}^{(\mathrm{sm})}/[R_{12}^{(b)} . A_{B21}^{(\mathrm{res})}]$ (see also eq. 44.V).

One would say that we could assume in (44.V) that $[R_{1B}^{(b)}]_B = [R_{2B}^{(b)}]_B$ because both thermal separation ratios refer to isotopes. *This is not true* for our elementary theory. As we have pointed out in § 2.V, we have indeed to consider, as an approximation necessary for our treatment, that the coefficients of viscosity for isotopes 1 and 2 are both equal to that for the gas A with natural isotopic composition. Therefore, the difference between the quantities A_1 and A_2 and therefore the difference between $\alpha_{1B}^{(b)}(res)$ and $\alpha_{2B}^{(b)}(res)$ has been increased artificially. Since in practical applications the separation ratios, $R_{1B}^{(b)}$ and $R_{2B}^{(b)}$, are defined by $\alpha_{1B}^{(b)}(exp)/\alpha_{1B}^{(b)}(res)$ and $\alpha_{2B}^{(b)}(exp)/ /\alpha_{2B}^{(b)}(res)$, *the difference between the experimental values of* $R_{1B}^{(b)}$ *and* $R_{2B}^{(b)}$ *has been increased artificially.*

To take a definite example obtained from our experiments with ternary mixtures (^4He; ^{36}A, ^{40}A), we report the following values:

$$[R_{4,36}^{(b)}]_4(exp) = 0.737 \pm 0.006; \quad [R_{4,40}^{(b)}]_4 = 0.707 \pm 0.005$$

$$[R_{4,36}^{(b)}]_{36}(exp) = 0.833 \pm 0.006; \quad [R_{4,40}^{(b)}]_{40} = 0.796 \pm 0.006$$

The percentage difference between $R_{4,36}^{(b)}$ and $R_{4,40}^{(b)}$ is a constant within the magnitude of experimental errors (from 4.2 ± 1.5 to 4.5 ± 1.5%).

As we may expect from the above example, the difference between $[R_{1B}^{(b)}]_B$ and $[R_{2B}^{(b)}]_B$ would usually be a small one for most pairs of isotopes. Even then it cannot be disregarded in equation (44.V) except when $R_{12}^{(b)}$ is markedly different from $[R_{1B}^{(b)}]_B$ and $[R_{2B}^{(b)}]_B$. For the latter case a qualitative conclusion may be drawn by assuming $[R_{1B}^{(b)}]_B = [R_{2B}^{(b)}]_B$. We have then, by using equations (44,45.V), $\frac{A_{B21}^{(sm)}}{A_{B21}^{(res)}} = [R_{1B}^{(b)}]_B$ and then,

$$\Delta_{12}(sm) = \Delta_{12}(res)\left[c_A + c_B \cdot \frac{[R_{1B}^{(b)}]_B}{R_{12}^{(b)}}\right] \qquad (47.V)$$

Now, by means of (21.V) and assuming $a_1 = a_2 = a_{12}$, we have $R_{12}^{(b)} = (1-a_1)$. Then, by using (20.V), we obtain

$$[R_{1B}^{(b)}]_B - R_{12}^{(b)} = \frac{A_1(a_1-a_B)}{A_1 - A_B} \qquad (48.V)$$

If $A_1 > A_B$, i.e. if the gas which has been added to the isotopic mixture consists of lighter and smaller molecules, then $R_{1B}^{(b)} > R_{12}^{(b)}$ if $a_1 > a_B$, which means, in accordance with the discussion made in § 2.IV, that the gas B is 'harder' than isotopes 1 and 2.

Therefore, by using (46,47.V), we may conclude: *If the binary isotopic separation ratio, $R_{12}^{(b)}$, is appreciably different from $R_{1B}^{(b)}$ and $R_{2B}^{(b)}$, the thermal diffusion factor of isotopes tends to increase by addition of a gas B consisting of lighter, smaller ($A_B < A_A$) and 'harder' molecules ($R_{1B}^{(b)}, R_{2B}^{(b)} > R_{12}^{(b)}$).*

Conversely, it tends to decrease by addition of heavier, larger and 'softer' molecules.

3) *Concentration effect.* According to equation (45.V) a possibility exists that the thermal diffusion factor changes sign with concentration of the added gas if $A_{B21}^{(sm)}$ and $A_{B21}^{(res)}$ are opposite in sign. Such a change of sign will probably be unusual as can be inferred from equations (43.V).

4.3. Non-isotopic thermal diffusion factors. By means of (17.V), the 's.m.' thermal diffusion factor, $\alpha_{1B}(sm)$, of the isotope 1 and the added gas B is given, at a first approximation, by

$$\alpha_{1B}(sm) = \frac{1 - c_A a_A - c_B a_B}{2} \cdot \frac{A_B - A_1}{c_A A_A + c_B A_B} - (a_1 - a_B)/2 \quad (49.V)$$

The quantities a_A and A_A are given by (41.V). For 'r.e.s.' molecules we assume in (49.V) $a_1 = a_A = a_B = 0$.

A similar equation is obtained for $\alpha_{2B}(sm)$, changing the subscript 1 into 2 in (49.V).

For most ternary mixtures (1,2,B) *the inverse of non-isotopic thermal diffusion factors, $\alpha_{1B}(sm)$ and $\alpha_{2B}(sm)$, can practically be assumed as linear on concentration of the gas B which has been added to the binary isotopic mixture (1,2).* This conclusion will be very useful in treating experimental results. The error which is usually made is small indeed, as can be seen by the following discussion.

Let us consider the quantity $\alpha'_{1B}(sm)$ defined as

$$\alpha'_{1B}(sm) = \frac{1}{2} \cdot \frac{(1-a_1)A_B - (1-a_B)A_1}{c_A A_A + c_B A_B} \quad (50.V)$$

The *inverse* of this equation *is linear on concentrations of the gases.*

Also, by comparison of (50.V) with (19.V) it follows that $\alpha'_{1B}(sm)$ is close to $\alpha_{1B}^{(b)}(sm)$ since A_1 and A_A (eq. 41.V) are isotopic quantities.

The ratio $\alpha'_{1B}(\mathrm{sm})/\alpha_{1B}(\mathrm{res})$ *is just equal to the binary separation ratio* $R^{(b)}_{1B}$ (see equation 20.V) which should be regarded as a constant, at a first approximation.

By means of (49,50.V), we have then

$$\alpha_{1B}(\mathrm{sm}) = \alpha'_{1B}(\mathrm{sm}) \cdot [R_{1B}/R^{(b)}_{1B}] \qquad (51.\mathrm{V})$$

Introducing now equation (31.V) for the separation ratio R_{1B}, we can obtain, after some developments,

$$\alpha_{1B}(\mathrm{sm}) = \alpha'_{1B}(\mathrm{sm}) \, \{[c^{(b)}_1 + c^{(b)}_2 \cdot R_{2B1}] \, c_A + c_B\} \qquad (52.\mathrm{V})$$

where $c^{(b)}_1$ and $c^{(b)}_2$ are the molar concentrations of isotopes in the initial binary mixture (1,2) and R_{2B1} is a quantity theoretically independent of concentrations, at a first approximation, given by

$$R_{2B1} = \frac{A_B - A_2}{A_B - A_1} \cdot \frac{R^{(b)}_{2B}}{R^{(b)}_{1B}} - \frac{A_1 - A_2}{A_B - A_1} \cdot \frac{R^{(b)}_{12}}{R^{(b)}_{1B}} \qquad (53.\mathrm{V})$$

Equation (53.V) shows that the quantity R_{2B1} will usually be close to unity. Indeed, the first term on the right hand side of this equation will usually be close to unity and is, furthermore, the predominant one.

Therefore, equation (52.V) shows that $\alpha_{1B}(\mathrm{sm})$ will usually be close to $\alpha'_{1B}(\mathrm{sm})$ and the linear dependence may usually be assumed for $1/\alpha_{1B}(\mathrm{sm})$. This conclusion can be seen better in Chapter VI (experiments).

In connection with experiments further considerations have to be made in respect to the quantity R_{2B1} (eq. 53.V). At a first approximation the binary separation ratios $R^{(b)}_{1B}$ and $R^{(b)}_{2B}$ are constants and R_{2B1} is a constant as well. In practice both $R^{(b)}_{1B}$ and $R^{(b)}_{2B}$ will usually vary somewhat with different concentrations. For consistency of this theory we assume that *both binary separation ratios are referred to the same concentration of the gas B* which has been added to the binary isotopic mixture (1,2). With this assumption the ratio $R^{(b)}_{2B}/R^{(b)}_{1B}$, which has to be used in (53.V), will very probably be a constant and then only a small variation of R_{2B1} with concentration may occur due to the second term on the right hand side of (53.V).

By dividing both terms of equation (52.V) by $\alpha_{1B}(\text{res})$, we have the following relationship for ternary and binary separation ratios

$$R_{1B} = R_{1B}^{(b)} \{[c_1^{(b)} + c_2^{(b)} R_{2B1}] c_A + c_B\} \tag{54.V}$$

For consistency with equation (52.V), both thermal separation ratios should be referred to the same concentration of the gas B.

If only ternary thermal diffusion data are available, the binary thermal separation ratio $R_{1B}^{(b)}$ can be obtained by a method of successive approximations.

From the general equations (13,14.V) we obtain the following relationship for the isotopic and non-isotopic thermal diffusion factors of a ternary mixture (1,2,B):

$$\alpha_{12}(\text{sm}) = \alpha_{1B}(\text{sm}) - \alpha_{2B}(\text{sm}) \tag{55.V}$$

This equation brings about a kind of final test for all of the theory given in § 4.2 and 4.3.V, when it is applied to the most probable experimental equations for $\alpha_{1B}(\text{exp})$, $\alpha_{2B}(\text{exp})$ and $\alpha_{12}(\text{exp})$.

§ 5. *Mixture of two gases each consisting of a pair of isotopes*

This case can be regarded as a generalisation of that of the preceding paragraph. Therefore we present only the most important conclusions and equations.

Let us consider two gases, A and B, each consisting of a pair of isotopes, (1,2) and (3,4), respectively, with concentrations c_A and c_B. The proportions of each pair of isotopes do not change with the ratio c_A/c_B and then

$$\begin{aligned} c_1/c_1^{(b)} &= c_2/c_2^{(b)} = c_1 + c_2 = c_A \\ c_3/c_3^{(b)} &= c_4/c_4^{(b)} = c_3 + c_4 = c_B \end{aligned} \tag{56.V}$$

where $c_1^{(b)}$, $c_2^{(b)}$ are the molar concentrations of isotopes 1 and 2 in the gas A, and c_1 and c_2 the corresponding molar concentrations in the mixture (A,B). Similarly for the isotopes 3 and 4 of the gas B.

5.1. Isotopic thermal diffusion factor and separation ratio. They are given by the following equations:

$$\alpha_{12}(\mathrm{sm}) = \frac{1 - c_A a_A - c_B a_B}{2} \cdot \frac{A_2 - A_1}{c_A A_A + c_B A_B} - (a_1 - a_2)/2 \quad (57.\mathrm{V})$$

where a_A, a_B and A_A, A_B are given by equations similar to (41.V) for each pair of isotopes.

For 'r.e.s.' molecules we assume in (57.V) $a_1 = a_2 = a_A = a_B = 0$. A similar equation is obtained for $\alpha_{34}(\mathrm{sm})$.

If the force fields are all equal, the inverse of isotopic thermal diffusion factors will be linear on concentrations c_A and c_B. In practice it might be convenient to look for such eventual linear dependence because isotopic thermal diffusion factors are only given at a first approximation.

The isotopic separation ratio is given by

$$R_{12} = \frac{\alpha_{12}(\mathrm{sm})}{\alpha_{12}(\mathrm{res})} = c_A R_{12}^{(b)} + c_B \left[c_3^{(b)} \cdot \frac{A_{321}^{(\mathrm{sm})}}{A_{321}^{(\mathrm{res})}} + c_4^{(b)} \cdot \frac{A_{421}^{(\mathrm{sm})}}{A_{421}^{(\mathrm{res})}} \right] \quad (58.\mathrm{V})$$

where the quantities $A_{kji}^{(\mathrm{sm})}/A_{kji}^{(\mathrm{sm})}$ are analogous to (43,44.V).

According to (58.V), the isotopic separation ratios, R_{12} and R_{34}, should be linear on concentrations c_A and c_B of gases A and B, respectively.

The variation of the isotopic thermal diffusion factor can be studied by means of the quantity $\Delta_{12}(\mathrm{sm}) = \alpha_{12}(\mathrm{sm})/\alpha_{12}^{(b)}(\mathrm{sm})$ where $\alpha_{12}^{(b)}$ is the thermal diffusion factor of isotopes 1 and 2 for the gas A alone. We have,

$$\Delta_{12}(\mathrm{sm}) = \Delta_{12}(\mathrm{res}) \left\{ c_A + c_B \left[c_3^{(b)} \frac{A_{321}^{(\mathrm{sm})}}{R_{12}^{(b)} \cdot A_{321}^{(\mathrm{res})}} + c_4^{(b)} \frac{A_{421}^{(\mathrm{sm})}}{R_{12}^{(b)} \cdot A_{421}^{(\mathrm{res})}} \right] \right\} \quad (59.\mathrm{V})$$

where $\Delta_{12}(\mathrm{res})$ represents the variation of the thermal diffusion factor for 'r.e.s.' molecules, namely,

$$1/\Delta_{12}(\mathrm{res}) = c_A + c_B A_B / A_A \quad (60.\mathrm{V})$$

If binary separation ratios $R_{32}^{(b)}$, $R_{31}^{(b)}$, $R_{42}^{(b)}$, $R_{41}^{(b)}$ are not too close to $R_{12}^{(b)}$ we can conclude: the thermal diffusion factor of isotopes 1 and 2 of the gas A usually tends to increase with increasing concentration of the gas B consisting of lighter, smaller and 'harder' molecules. Conversely, the thermal diffusion factor for isotopes 3 and 4 of the gas B will decrease then with increasing concentration of the gas A.

5.2. Non-isotopic thermal diffusion factors and separation ratios. The thermal diffusion factor of isotope 1 of the gas A and the isotope 3 of the gas B is given by,

$$\alpha_{13}(\mathrm{sm}) = \frac{1 - c_A a_A - c_B a_B}{2} \cdot \frac{A_3 - A_1}{c_A A_A + c_B A_B} - (a_1 - a_3)/2 \quad (61.\mathrm{V})$$

If we define a quantity $\alpha'_{13}(\mathrm{sm})$ as

$$\alpha'_{13}(\mathrm{sm}) = \frac{1}{2} \cdot \frac{(1-a_1)A_3 - (1-a_3)A_1}{c_A A_A + c_B A_B} \quad (62.\mathrm{V})$$

then,

$$\alpha_{13}(\mathrm{sm}) = \alpha'_{13}(\mathrm{sm}) \left\{ \left[c_1^{(b)} + c_2^{(b)} R_{231}\right] c_A + \left[c_3^{(b)} + c_4^{(b)} R_{431}\right] c_B \right\} \quad (63.\mathrm{V})$$

where the quantities R_{231} and R_{431} are usually close to unity. They are given by equations analogous to (53.V). The ratios $R_{23}^{(b)}/R_{13}^{(b)}$ and $R_{14}^{(b)}/R_{13}^{(b)}$ are assumed constants referring to the same concentrations, c_A and c_B.

The inverse of non-isotopic thermal diffusion factors $\alpha_{13}(\mathrm{sm})$, $\alpha_{14}(\mathrm{sm})$, $\alpha_{23}(\mathrm{sm})$ and $\alpha_{24}(\mathrm{sm})$ may usually be assumed as linear on concentrations c_A and c_B.

We also have,

$$\frac{\alpha'_{13}(\mathrm{sm})}{\alpha_{13}(\mathrm{res})} = R_{13}^{(b)} \quad (64.\mathrm{V})$$

and

$$R_{13} = R_{13}^{(b)} \left\{ \left[c_1^{(b)} + c_2^{(b)} R_{231}\right] c_A + \left[c_3^{(b)} + c_4^{(b)} R_{431}\right] c_B \right\} \quad (65.\mathrm{V})$$

The following equations connect isotopic and non-isotopic thermal diffusion factors:

$$\begin{aligned}\alpha_{12}(\mathrm{sm}) &= \alpha_{13}(\mathrm{sm}) - \alpha_{23}(\mathrm{sm}) = \alpha_{14}(\mathrm{sm}) - \alpha_{24}(\mathrm{sm}) \\ \alpha_{34}(\mathrm{sm}) &= \alpha_{14}(\mathrm{sm}) - \alpha_{13}(\mathrm{sm}) = \alpha_{24}(\mathrm{sm}) - \alpha_{23}(\mathrm{sm})\end{aligned} \tag{66.V}$$

§ 6. *Mixture of isotopes*

For a mixture of s isotopes we assume

$$l_1 = l_2 = \dots = l_s \ ; \ a_1 = a_2 = \dots = a_s = \bar{a} \tag{67.V}$$

Equation (15.V) thus reduces to

$$\alpha_{ij}(\mathrm{sm}) = \frac{1 - \bar{a}}{2} \cdot \frac{m_j^{1/2} - m_i^{1/2}}{\sum\limits_{k=1}^{s} c_k \, m_k^{1/2}} \tag{68.V}$$

If we consider a binary mixture of any pair of isotopes (m,n), we will usually have $c_m^{(b)} \, m_m^{1/2} + c_n^{(b)} \, m_n^{1/2}$ closely equal to the summation $\sum\limits_{k=1}^{s} c_k m_k^{1/2}$ of the above equation (68.V). Therefore the thermal diffusion factor of isotopes i and j would be almost the same for binary and multicomponent mixtures.

§ 7. *Pressure diffusion*

Only a small reference will be made here. According to our elementary theory, pressure diffusion can be studied readily because it is related to thermal diffusion by the following simple equations.

When molecules are regarded as 'rigid elastic spheres' we assume $a_k = 0$. Then, by means of (14.IV), we have $l_k = l_k'$, which, introduced into (2.V), gives $Z_{ij}'/2 = Z_{ij}$. Hence, by using (9, 10.V), we obtain

$$(\alpha_p)_{ij} = 2(\alpha_T)_{ij}(\mathrm{res}) \tag{69.V}$$

Therefore pressure diffusion should be independent of molecular forces. This feature suggests immediately that if a cascade method could easily be realized in practice, pressure diffusion would be a comparatively better process for separating isotopes.

CHAPTER VI

EXPERIMENTAL THERMAL DIFFUSION IN COMPLEX MIXTURES

§ 1. *Introduction*

In this chapter we present experimental thermal diffusion data for mixtures of natural Argon-Helium, Neon-Helium and Neon-Hydrogen regarded as ternary mixtures (^{36}A, ^{40}A; ^{4}He), (^{20}Ne, ^{22}Ne; H_2) respectively.

The main subject of our experiments was to observe the influence of the 'added' gas - Helium and Hydrogen - upon isotopic separations of ^{20}Ne-^{22}Ne and of ^{36}A-^{40}A. Isotopic thermal diffusion factors have been determined by means of mass spectrometric analyses over a large concentration range of the added gases.

According to our elementary theory we may roughly say that the isotopic thermal diffusion factor would increase with addition of a gas consisting of lighter and 'harder' molecules. Conversely, it would decrease by addition of heavier and 'softer' molecules.

Experimental results show that isotopic thermal diffusion factors increase with concentration of Helium in (^{36}A, ^{40}A; ^{4}He) mixtures and decrease in (^{20}Ne, ^{22}Ne; ^{4}He) and even more in (^{20}Ne, ^{22}Ne; H_2) mixtures.

To heighten the accuracy of determinations of the isotopic thermal diffusion factor, we have always chosen the best set of conditions of the mass spectrometer for carrying out the analyses for each pair of isotopes, namely ^{20}Ne-^{22}Ne and ^{36}A-^{40}A. As a consequence, our machine could not simultaneously provide accurate analyses for ^{4}He and H_2. For that reason only a few non-isotopic thermal diffusion factors have even then been determined comparatively with somewhat large experimental errors.

Experiments have also been made with natural Neon-Argon mixtures. Isotopic analyses of ^{20}Ne-^{22}Ne and of ^{36}A-^{40}A could be carried out satisfactorily by mass spectrometry over large concentration ranges of Neon and Argon. Since we were interested mostly in the influence of each gas upon the isotopic separation of the other, Neon-Argon mixtures have been regarded roughly as 'quaternary' mixtures (^{20}Ne, ^{22}Ne; ^{36}A, ^{40}A).

Experimental data show that the thermal diffusion factor of Neon isotopes decreases markedly with increasing concentration of Argon. Conversely, the thermal diffusion factor of Argon isotopes increases with increasing concentration of Neon. This is qualitatively in accordance with our theory because Argon molecules are heavier and 'softer' than those of Neon.

Non-isotopic thermal diffusion factors could be determined over a large concentration range of the added gas in (He-A) and (Ne-A) mixtures. It was observed that the inverse of non-isotopic thermal diffusion factors was linear on concentrations of Neon and Argon, which is in accordance with our theory.

2.1. The measurement of the thermal diffusion factor. For measuring the thermal diffusion factors we have used the 'swinging separator' (Trennschaukel) described by Clusius (C13). A block diagram is given in fig. 1.VI. It consists essentially of 9 stainless steel tubes connected in series, the upper part of each tube with the lower part of the following one, via a stainless steel capillary tube.

The upper part of the tubes is forced into a copper block which is heated by a 200 W. heating element. The mains voltage supplied to this element could be varied by means of a transformer in order to obtain any desired 'hot' temperature, T^{II}, in between 373 and 750° Kelvin.

The lower part of the tubes is cooled by a water stream. The 'cold' temperature T^{I} was practically independent of T^{II}.

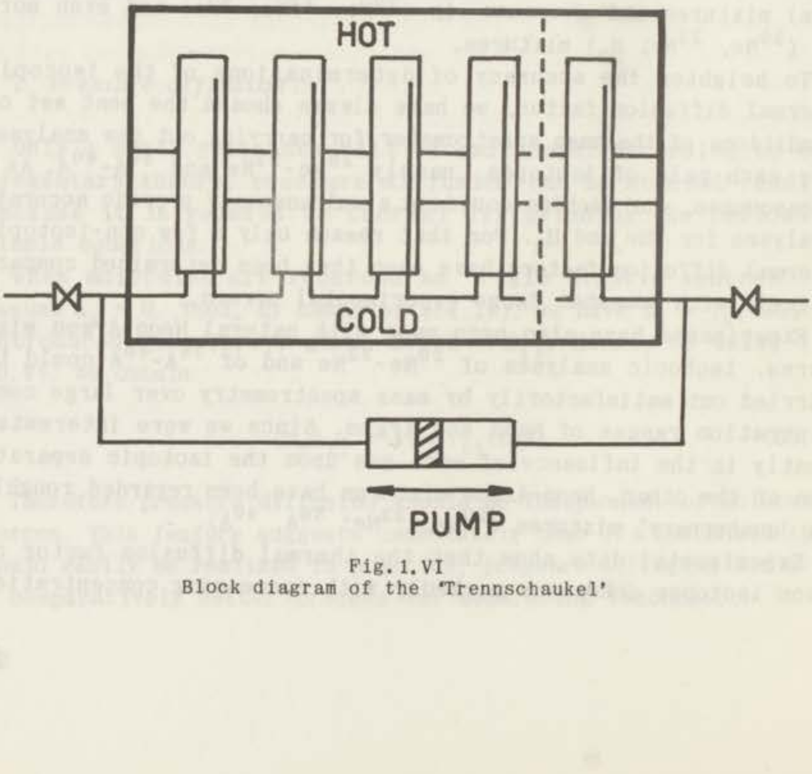

Fig. 1.VI
Block diagram of the 'Trennschaukel'

About 1 cm^3 of the gas mixture was pumped to and fro periodically by means of a glass U tube, partially filled with mercury, which was swung by an electromotor and an eccentric wheel. Therefore, concentrations of the gases in the hot and cold regions of two consecutive tubes should be equalized. If a separation factor, q_{ij}, of gases of kinds i and j, namely,

$$q_{ij} = \frac{(c_i/c_j)^{II}}{(c_i/c_j)^{I}} \qquad (1.VI)$$

is obtained by an elementary thermal diffusion process in each tube, the total separation factor achieved with a 'Trennschaukel' of n tubes should be

$$Q_{ij} = q_{ij}^{n} \qquad (2.VI)$$

Experimental values of the thermal diffusion factor of the gases i and j can thus be obtained by means of equation (18.IV), namely,

$$\ln Q_{ij} = n\ \alpha_{ij}(sm)\ \ln (T^{II}/T^{I}) \qquad (3.VI)$$

2.2. *Temperature stability of the Trennschaukel.* Stabilisation of temperature of the hot and cold regions of the 'Trennschaukel' should be good enough in order to obtain experimental values of the thermal diffusion factors with reasonable accuracy.

Figure 2.VI (see p.86) shows the approach to the steady state of temperature for 187 V. set up on the transformer, with the system filled with natural Neon at a pressure of about 1 atm. Stability is reached after about 2 hours and maintained during 48 hours within a variation of 2° for a mean temperature of 666° Kelvin in the hot region, and within 0.5° for a mean temperature in the cold region of 286,5° Kelvin. Experimental values of thermal diffusion factors were practically not affected by these temperature variations during the observations which had been carried out for about 24 hours. The most important errors arise from the concentration measurements.

The variation of the temperature, T^{II}, with voltage supplied to the heating element is shown in figure 3.VI. The slope of this curve at increased temperatures is about 2° per volt. Since the voltage scale of the transformer was rather narrow, it was somewhat difficult to preselect a given temperature T^{II}

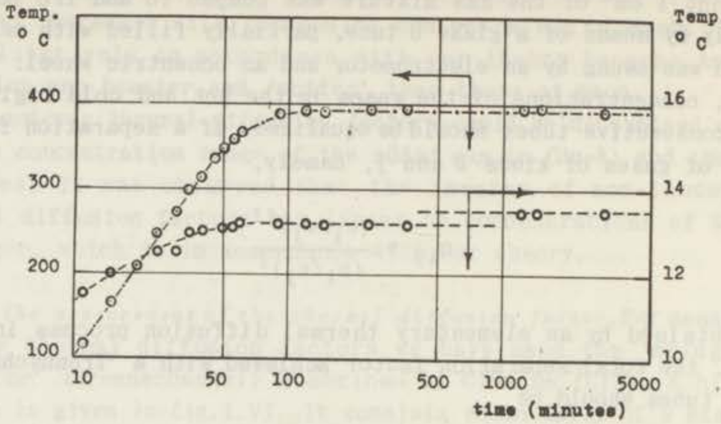

Fig. 2. VI

The approach to temperature stabilisation in the 'Trennschaukel'.
⊙ Temperature T^{II} (hot region).
○ Temperature T^{I} (cold region).

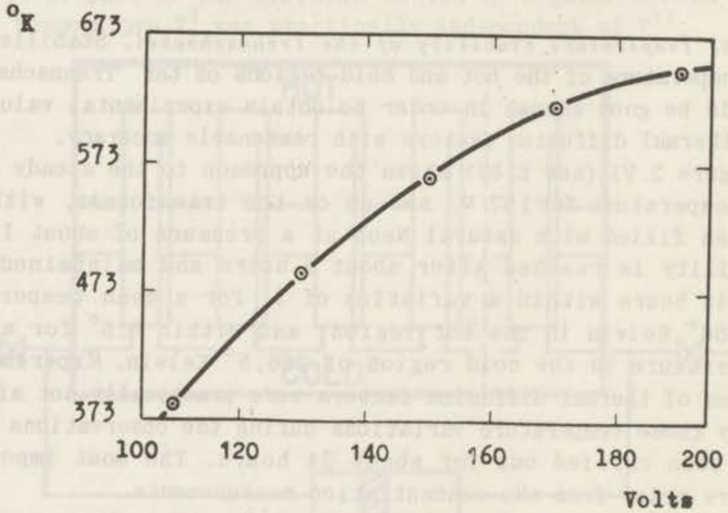

Fig. 3. VI

Variation of the temperature, T^{II}, with voltage supplied to the heating element.

accurately. For that reason the temperatures at which experiments have been carried out sometimes differ from one to another.

2.3. The approach to the steady state. The theory of the 'Trennschaukel' has been given by van der Waerden (W7). The approach to the steady state should be an exponential one and the 'half-life' was given by

$$t_h = (t_P \frac{V}{2a} + t_D) \left[\frac{n+1}{\pi}\right]^2 \ln 2 \qquad (4.VI)$$

where

$$t_D = l^2/D_{ij} \qquad (5.VI)$$

V = volume of each tube (in our case $V \simeq 23$ cm^3), 2a = volume which is pumped to and fro (1.5 cm^3 to 1 cm^3), t_P = period of the pump (5 seconds), l = length of each connecting capillary (10.4 cm), D_{ij} = coefficient of diffusion, n = number of tubes of the 'Trennschaukel' (9).

For values of the coefficient of diffusion in between 0.1 and 0.8 cm^2/sec the 'half-life' to the exponential approach changes between 8 and 45 minutes for our 'Trennschaukel'.

Our experiments have been carried out over 24 hours at least and are therefore safe enough for our purposes.

A rough experimental determination of the approach to the steady state with Neon alone has been made. After stabilisation of temperature, the 'Trennschaukel' was filled with a sample of pure Neon at a small over-pressure. At any time t_1, t_3, t_5,... a sample of about 1 cm^3 N.T.P. from the cold region (the lower end of the 9th tube) was brought into the mass spectrometer through a capillary tube for analyses of Neon isotopes. The ratio, $(c_{20}/c_{22})^I$, of concentrations of ^{20}Ne and ^{22}Ne was then determined in arbitrary units which only depended on the characteristics of our mass spectrometer. At any time, t_2, t_4, t_6,... a sample from the hot region (the upper end of the first tube) was also analysed and the ratio $(c_{20}/c_{22})^{II}$, was determined to the same arbitrary units.

The values of $(c_{20}/c_{22})^I$ and $(c_{20}/c_{22})^{II}$ were plotted versus time and smooth curves were obtained. A mean total separation factor as a function of time was then determined:

$$Q_{20,22}(t) = \frac{(c_{20}/c_{22})^{II}}{(c_{20}/c_{22})^{I}} \qquad (6.VI)$$

Values of $Q_{20,22}(t)$ are plotted on a logarithmic scale in fig.4.VI. They do appear to obey an equation of the form

$$Q_{20,22}(t) = Q_{20,22}(\infty)\ (1 - e^{-\lambda t}) \qquad (7.VI)$$

where $Q_{20,22}(\infty)$ represents the total experimental separation factor achieved after 24-48 hours, and λ is a constant. Since the 'half-life' of this exponential approach is

$$t_h = (\ln 2)/\lambda \qquad (8.VI)$$

and the corresponding relaxation time is

$$t_r = 1/\lambda \qquad (9.VI)$$

we obtain, from fig.4.VI, t_h = 90 minutes. The theoretical value according to equation (4.VI) should be 10 minutes approximately. Such a marked difference between experimental and theoretical

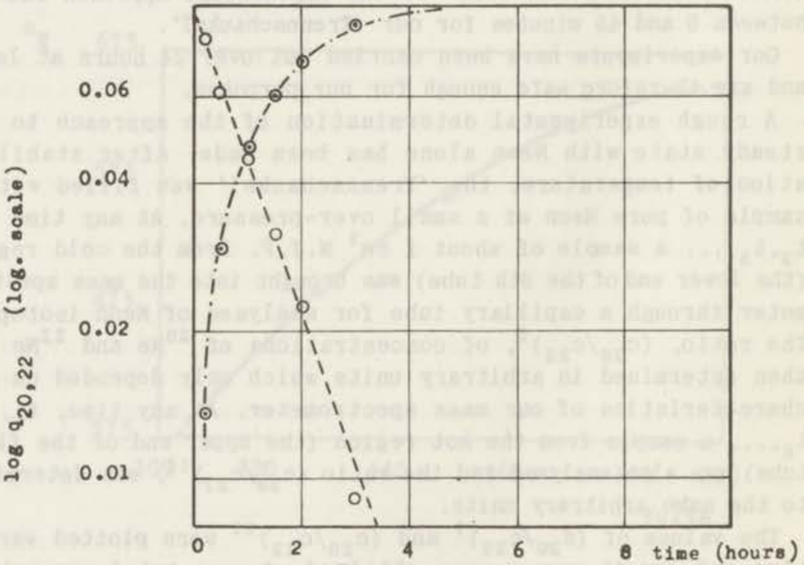

Fig.4.VI

Experimental approach to the steady state with Neon isotopes.

O Experimental values of log $Q_{20,22}(t)$.

O Values of log $Q_{20,22}(\infty)$ - log $Q_{20,22}(t)$. Half-life about 90 minutes.

values is probably due to the disturbances which have been introduced by successive withdrawals of gas from the 'Trennschaukel' during the beginning of the thermal diffusion enrichment. Indeed, each analysis needs a volume of about 1 cm^3, and 10 cm^3 in total have been withdrawn during the initial two and a half hours to follow the isotopic separation. Nevertheless, the 24 hours that have been taken for each approach to a steady state are compared long enough with the observed 'half-life'.

§ 3. *Mixtures Helium-Argon regarded as ternary mixtures* (^{4}He; ^{36}A, ^{40}A)

3.1. Experimental data. Natural isotopic abundances of Argon and Helium are the following:

^{36}A	0.307 %	^{3}He	1.3×10^{-4} %
^{38}A	0.060 %	^{4}He	99.9999 %
^{40}A	99.633 %		

Therefore it is reasonable to consider A-He mixtures as ternary mixtures (^{36}A, ^{40}A; ^{4}He) in which the initial ratio of molar concentrations, c_{36}/c_{40}, is the same in each of the Helium-Argon mixtures.

Three thermal diffusion factors have to be considered, namely $\alpha_{36,40}$; $\alpha_{4,36}$ and $\alpha_{4,40}$. Experimental values are given in Table 1.VI.

Table 1.VI

Experimental thermal diffusion factors for (^{4}He; ^{36}A, ^{40}A)

Concentr. of Argon	Absolute Temp. T^I-T^{II}	$\alpha_{36,40}$	$\alpha_{4,36}$	$\alpha_{4,40}$
1.000	287-655	$0.014_7 \pm 0.001_0$	...	...
1.000	286-666	0.0142 ± 0.0008	...	...
1.000	286-667	0.0149 ± 0.0008	...	...
0.900	286-667	$0.014_9 \pm 0.001_0$	...	...
0.700	288-660	$0.015_3 \pm 0.001_3$	0.308 ± 0.004	0.323 ± 0.004
0.500	289-663	$0.017_6 \pm 0.001_3$	0.358 ± 0.003	0.376 ± 0.003
0.300	288-660	$0.020_7 \pm 0.001_0$	0.433 ± 0.005	0.454 ± 0.005
0.100	288-660	$0.022_2 \pm 0.001_4$	0.572 ± 0.006	0.594 ± 0.006

The system was filled to about 2-2,5 cm Hg over-pressure to prevent eventual inleakage. Anyway, the peak at mass 28 corresponding to N_2, was always measured so as to have a check on the experimental technique. Experiments in which the peak height of N_2 exceeds the normal background of the mass spectrometer by two or three times were dropped.

Each peak, ^{4}He, ^{36}A and ^{40}A, was measured 6 times. Mean values were then obtained and the standard errors computed.

We can see in the Table that the absolute errors of the non-isotopic thermal diffusion factors are larger than those corresponding to isotopic ones, the consequence of which will be discussed in 3.3.2.

3.2. Comparison of the isotopic thermal diffusion factor for Argon alone and the thermal diffusion factor for ^{4}He and ^{40}A with earlier results. Table 2.VI and fig.5.VI report the values of $\alpha^{(b)}_{36,40}$ given by Stier (S1). In the Table our values are also given for comparison. In the figure only the mean of the three values is represented. The mean temperatures, T_m, to which the thermal diffusion factors would be referred, are the algebraic mean value of absolute temperatures T^{I} and T^{II}.

Table 2.VI

The variation of the thermal diffusion factor for Argon isotopes with temperature

Absolute Temperatures T^{I}-T^{II}	Mean Temperature $T_m = (T^{I}T^{II})^{½}$	$\alpha^{(b)}_{36,40}$	Reference
90 - 195	132	0.0031	S 1
90 - 296	163	0.0071	S 1
195 - 296	240	0.0116	S 1
195 - 495	310	0.0146	S 1
273 - 623	412	0.0182	S 1
455 - 635	537	0.0218	S 1
638 - 835	729	0.0250	S 1
287 - 655	433	0.0147	This paper
286 - 666	437	0.0142	This paper
287 - 667	437	0.0149	This paper

Figure 5.VI shows that our mean value is somewhat lower than that corresponding to Stier's mean curve which gives the isotopic

thermal diffusion factor as 0.0190 for $T_m = 437°$ K whereas our mean value is 0.0146 ± 0.0009. Errors of Stier's observations are about 5%.

Table 3.VI gives the thermal diffusion factor for a mixture of equal concentrations of natural Helium and Argon at different temperatures, after Atkins, Bastick and Ibbs (A1); Puschner (P1); Grew (G8); and van Itterbeek and de Troyer (I3). We compare these values with our observations for ^{4}He and ^{40}A*). Mean temperature, T_m, is defined as before.

Table 3.VI
Thermal diffusion factor for Helium-Argon mixtures of equal proportions

Mean Temperature T_m (°K)	$\alpha_{He,A}$	Reference
157	0.31	I 3
185	0.36	G 8
293	0.38	G 8
328	0.372	A 1
346	0.42	P 1
369	0.39	G 8
438	0.376	This paper

Tabulated values are plotted in figure 6.VI, which shows that our result agrees well with earlier data, as far as a mean curve is concerned. Puschner's value is clearly too high.

3.3. *Interpretation of experimental data by the elementary theory.*

3.3.1. Isotopic thermal diffusion factor. According to the theory given in § 4.2.V experimental values for the thermal diffusion factor of Argon isotopes, ^{36}A and ^{40}A, in ternary mixtures (^{36}A, ^{40}A; ^{4}He), will be worked out considering:

a) The inverse of the isotopic thermal diffusion factor may eventually be linear on concentration of the added gas, Helium.

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*) We have measured the concentrations of ^{40}A and ^{4}He, whereas the other authors have made measurements of Argon and Helium concentrations. The differences, however, of both procedures can be disregarded since the concentration of ^{36}A is so small.

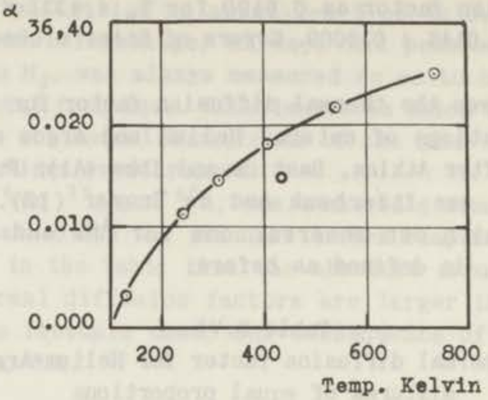

Fig.5.VI
Variation of the thermal diffusion factor of ^{36}A and ^{40}A with temperature.

⊙ Experimental data after Stier (S1).
O Our mean value.

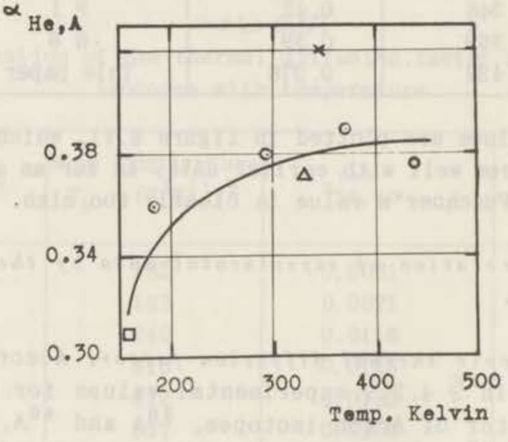

Fig.6.VI
Variation of the thermal diffusion factor of mixtures of equal concentrations of Helium-Argon with temperature.

Experimental values:
△ After Atkins, Bastick and Ibbs (A1).
x After Puschner (P1).
⊙ After Grew (G8).
□ After van Itterbeek and de Troyer (I3).
O Our experiment.

This is theoretically acceptable, at a first approximation, if the force fields are not too different.

b) Isotopic separation ratio, $R_{36,40}$, would be linearly dependent on the concentration of the added gas (Helium) at a first approximation (see equations 42,44.V).

In Chapter V we usually worked with the indication (sm) for ‘soft molecules’ meaning to indicate real molecules. In this experimental Chapter we will mostly use the indication (exp) instead.

Experimental values of $R_{36,40}$ are determined by the ratio of the observed isotopic thermal diffusion factor to the corresponding value of the ‘rigid elastic sphere model’, given by the general equation,

$$\alpha_{36,40}(\text{res}) = \frac{1}{2} \cdot \frac{A_{40} - A_{36}}{c_4 A_4 + c_A A_A} \qquad (11.VI)$$

where $A_A = c_{36}^{(b)} A_{36} + c_{40}^{(b)} A_{40}$.

The concentrations $c_{36}^{(b)}$ and $c_{40}^{(b)}$ of ^{36}A and ^{40}A are the following, assuming natural Argon as consisting of those isotopes only, since natural concentration of ^{38}A has been neglected:

$$c_{36}^{(b)} = 0.0031$$

$$c_{40}^{(b)} = 0.9969$$

The quantities A_4, A_{36} and A_{40} are given in general by $A_k = (m_k/\eta_k)^{1/2}$. For the reason already explained in § 2.V, we consider that the coefficients of viscosity of Argon isotopes are both equal to that of natural Argon.

The values for the coefficients of viscosity of Argon and Helium have been taken from ref. (H6). They refer to the mean temperature $\bar{T} = 437°$ K. The corresponding quasi-theoretical values for the quantities A_4, A_{36}, A_{40} and A_A, which have been used in equation (11.VI), are the following:

$$A_4 = 0.09119 \ \mu \text{ poise}^{-1}$$

$$A_{36} = 0.2528$$

$$A_{40} = 0.2665$$

$$A_A = 0.2664_6$$

The subscript 4 will always be referred to Helium and the subscript A to Argon.

The 'r.e.s.' isotopic thermal diffusion factor is then given by the equation,

$$1/\alpha_{36,40}(\mathrm{res}) = 38.90\ c_A + 13.31\ c_4 \qquad (12.\mathrm{VI})$$

This equation is used for computations of experimental isotopic thermal separation ratios, $R_{36,40}(\mathrm{exp})$, corresponding to observed values for isotopic thermal diffusion factors, $\alpha_{36,40}(\mathrm{exp})$.

Equation (12.VI) brings about the following limiting values for the 'r.e.s.' isotopic thermal diffusion factor:

for $c_A = 1$:

$$[\alpha_{36,40}(\mathrm{res})]_A = \alpha^{(b)}_{36,40}(\mathrm{res}) = 0.0257$$

$$(13.\mathrm{VI})$$

for $c_4 = 1$:

$$[\alpha_{36,40}(\mathrm{res})]_4 = 0.0751$$

The 'r.e.s.' thermal diffusion factor of Argon isotopes therefore *increases* with *increasing* concentrations of Helium. In the limiting case as $c_4 = 1$, the quantity $\Delta_{36,40}(\mathrm{res})$ which shows the influence of the addition of Helium upon the 'r.e.s.' thermal diffusion factor of Argon isotopes, is given by

$$[\Delta_{36,40}(\mathrm{res})]_4 = \frac{[\alpha_{36,40}(\mathrm{res})]_4}{\alpha^{(b)}_{36,40}(\mathrm{res})} = \frac{0.0751}{0.0257} = 2.92 \qquad (14.\mathrm{VI})$$

Let us now consider the experimental values for $\alpha_{36,40}(\mathrm{exp})$ and $R_{36,40}(\mathrm{exp})$. In figures 7.VI and 8.VI we report experimental data for $1/\alpha_{36,40}(\mathrm{exp})$ and $R_{36,40}(\mathrm{exp})$ respectively. They both appear to satisfy a linear dependence on molar concentrations, within the magnitude of experimental errors. The most probable equations determined by least squares are respectively:

$$\text{a)}\ 1/\alpha_{36,40}(\mathrm{exp}) = (69._4 \pm 3._5)\ c_A + (42._4 \pm 2._0)\ c_4 \qquad (15.\mathrm{VI})$$

$$\text{b)}\ R_{36,40}(\mathrm{exp}) = (0.56_6 \pm 0.02_5)\ c_A + (0.34_4 \pm 0.02_0)\ c_4 \qquad (16.\mathrm{VI})$$

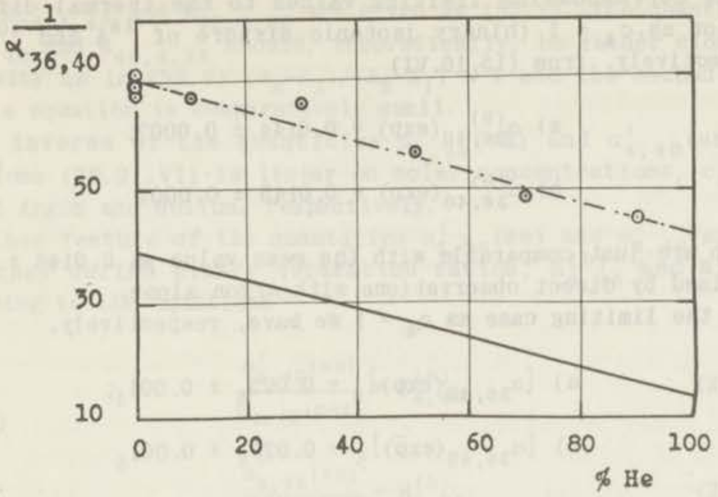

Fig. 7. VI
Variation of the inverse of the thermal diffusion factor for ^{36}A-^{40}A with addition of Helium.

⊙ Experimental data.

—— Elementary 'r.e.s.' first approximation.

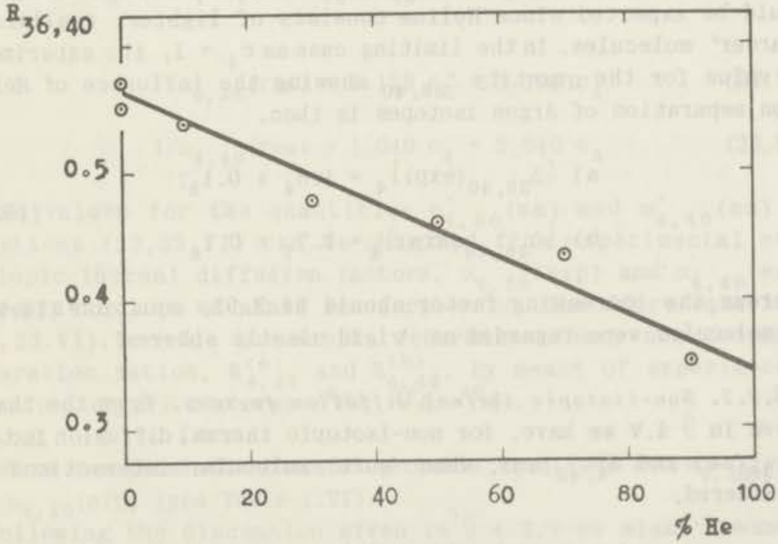

Fig. 8. VI
Variation of the thermal separation ratio for ^{36}A-^{40}A with addition of Helium.

⊙ Experimental data.

The corresponding limiting values to the thermal diffusion factor as $c_A = 1$ (binary isotopic mixture of ^{36}A and ^{40}A) are respectively, from (15,16.VI)

$$\begin{aligned} &\text{a)}\ \alpha^{(b)}_{36,40}(\text{exp}) = 0.0144 \pm 0.0007; \\ &\text{b)}\ \alpha^{(b)}_{36,40}(\text{exp}) = 0.0145 \pm 0.0007 \end{aligned} \qquad (17.\text{VI})$$

which are just comparable with the mean value as 0.0146 ± 0.0009 obtained by direct observations with Argon alone.

In the limiting case as $c_4 = 1$ we have, respectively.

$$\begin{aligned} &\text{a)}\ [\alpha_{36,40}(\text{exp})]_4 = 0.023_6 \pm 0.001_1; \\ &\text{b)}\ [\alpha_{36,40}(\text{exp})]_4 = 0.025_8 \pm 0.001_5 \end{aligned} \qquad (18.\text{VI})$$

The agreement is not so good as before but may be considered rather satisfactory within the magnitude of the errors. Theoretically, the second value would be preferred.

By means of (17,18.VI) the *isotopic thermal diffusion factor* thus *increases with increasing concentration of Helium*. This would be expected since Helium consists of lighter, smaller and 'harder' molecules. In the limiting case as $c_4 = 1$, the experimental value for the quantity $\Delta_{36,40}$ showing the influence of Helium upon separation of Argon isotopes is then,

$$\begin{aligned} &\text{a)}\ [\Delta_{36,40}(\text{exp})]_4 = 1.6_4 \pm 0.1_5; \\ &\text{b)}\ [\Delta_{36,40}(\text{exp})]_4 = 1.7_7 \pm 0.1_8 \end{aligned} \qquad (19.\text{VI})$$

whereas the increasing factor should be 2.92, equation (14.VI), if molecules were regarded as 'rigid elastic spheres'.

3.3.2. Non-isotopic thermal diffusion factors. From the theory given in § 4.V we have, for non-isotopic thermal diffusion factors, $\alpha_{4,36}(\text{sm})$ and $\alpha_{4,40}(\text{sm})$, when 'soft' molecular interactions are considered,

$$\alpha_{4,40}(\text{sm}) = \alpha'_{4,40}(\text{sm})\ [(c^{(b)}_{40} + c^{(b)}_{36}.R_{36,4,40})\ c_A + c_4] \qquad (20.\text{VI})$$

$$\alpha_{4,36}(\text{sm}) = \alpha'_{4,36}(\text{sm})\ [(c^{(b)}_{36} + c^{(b)}_{40}.R_{40,4,36})\ c_A + c_4] \qquad (21.\text{VI})$$

where $R_{36,4,40}$ and $R_{40,4,36}$ are given by (53.V). The quantities $R_{36,4,40}$ and $R_{40,4,36}$ should, theoretically, be rather close to the unity as in (53.V) $(A_B-A_2)/(A_B-A_1) \sim 1$ and the second term of this equation is comparatively small.

The inverse of the quantities $\alpha'_{4,36}(sm)$ and $\alpha'_{4,40}(sm)$ of equations (20,21.VI) is linear on molar concentrations, c_A and c_4, of Argon and Helium, respectively.

Another feature of the quantities $\alpha'_{4,36}(sm)$ and $\alpha'_{4,40}(sm)$ is that they define binary separation ratios, $R^{(b)}_{4,36}$ and $R^{(b)}_{4,40}$, according to the equations

$$\frac{\alpha'_{4,40}(sm)}{\alpha_{4,40}(res)} = R^{(b)}_{4,40} \qquad (22.VI)$$

$$\frac{\alpha'_{4,36}(sm)}{\alpha_{4,36}(res)} = R^{(b)}_{4,36} \qquad (23.VI)$$

The values for 'r.e.s.' non-isotopic thermal diffusion factors, $\alpha_{4,40}(res)$ and $\alpha_{4,36}(res)$, which have to be used in equations (22,23.VI) are obtained by introducing in equation (49.V) the values of $A_4 = (m_4/\eta_4)^{1/2}$, A_{36}, A_{40} and A_A given in § 3.3.1. We obtain,

$$1/\alpha_{4,36}(res) = 1.128\ c_4 + 3.298\ c_A \qquad (24.VI)$$

$$1/\alpha_{4,40}(res) = 1.040\ c_4 + 3.040\ c_A \qquad (25.VI)$$

The values for the quantities $\alpha'_{4,36}(sm)$ and $\alpha'_{4,40}(sm)$ of equations (22,23.VI) can be obtained from experimental non-isotopic thermal diffusion factors, $\alpha_{4,36}(exp)$ and $\alpha_{4,40}(exp)$ respectively, as we shall see further on. Therefore equations (22,23.VI) provide the way to determine binary non-isotopic separation ratios, $R^{(b)}_{4,36}$ and $R^{(b)}_{4,40}$, by means of experimental data for ternary mixtures (^4He; ^{36}A, ^{40}A).

Let us now determine the most probable equations for $\alpha_{4,36}(exp)$ and $\alpha_{4,40}(exp)$ (see Table 1.VI).

Following the discussion given in § 4.3.V we might assume a priori that $1/\alpha_{4,40}(exp)$ and $1/\alpha_{4,36}(exp)$ were linearly dependent on concentrations of Helium and Argon. By means of (20.VI), such linear dependence can easily be inferred for $1/\alpha_{4,40}(exp)$ because the concentration of ^{36}A in Argon alone is only $c^{(b)}_{36} = 0.0031$, (therefore the brackets on the right hand side of (20.VI) are always very close to unity) and $1/\alpha'_{4,40}(\mathrm{sm})$ is theoretically linearly dependent on concentrations.

On the other hand, the linear dependence of $1/\alpha_{4,36}(\mathrm{exp})$ with concentrations is not so evident a priori because the term $c_{40}^{(b)}.R_{40,4,36} = 0.9969\ R_{40,4,36}$ is the predominant one in equation (21.VI) whereas $c_{36}^{(b)}$ is practically of no influence. In order to show that the error which is committed, assuming $1/\alpha_{4,36}(\mathrm{exp})$ linearly dependent on concentrations, is even then negligible within the magnitude of experimental errors, we use the following method of successive approximations which is only based on the theoretical assumption that the inverses of the quantities $\alpha'_{4,36}(\mathrm{sm})$ and $\alpha'_{4,40}(\mathrm{sm})$ are linear on concentrations.

As a FIRST APPROXIMATION we consider $\alpha'_{4,36}(\mathrm{sm}) = \alpha_{4,36}(\mathrm{exp})$ and also $\alpha'_{4,40}(\mathrm{sm}) = \alpha_{4,40}(\mathrm{exp})$. Since $1/\alpha'_{4,36}(\mathrm{sm})$ and $1/\alpha'_{4,40}(\mathrm{sm})$ are theoretically linear on concentrations we obtain, from experimental data given in Table 1.VI,

$$1/\alpha'_{4,40}(\mathrm{exp}) = 1/\alpha_{4,40}(\mathrm{exp}) = (1.47 \pm 0.01)\ c_4 + (3.82 \pm 0.03)\ c_A \tag{26.VI}$$

$$1/\alpha'_{4,36}(\mathrm{exp}) = 1/\alpha_{4,36}(\mathrm{exp}) = (1.53 \pm 0.01)\ c_4 + (4.02 \pm 0.03)\ c_A \tag{27.VI}$$

By means of (22,25,26.VI), we obtain an equation for the binary non-isotopic separation ratio, $R_{4,40}^{(b)}$. Similarly, by means of (23,24,27.VI) we obtain a first approximation for $R_{4,36}^{(b)}$. We only give here the limiting values for these quantities, namely,

$$[R_{4,40}^{(b)}(\mathrm{exp})]_4 = 0.707 \pm 0.005;\quad [R_{4,40}^{(b)}(\mathrm{exp})]_{40} = 0.796 \pm 0.006 \tag{28.VI}$$

and

$$[R_{4,36}^{(b)}(\mathrm{exp})]_4 = 0.738 \pm 0.006;\quad [R_{4,36}^{(b)}(\mathrm{exp})]_{36} = 0.821 \pm 0.006 \tag{29.VI}$$

Equations for $R_{36,4,40}$ and $R_{40,4,36}$ which appear in (20,21.VI) can now be determined, at a first approximation, by using in (53.V) the values for $R_{4,36}^{(b)}$ and $R_{4,40}^{(b)}$ already obtained. We also need a value for the binary isotopic separation ratio $R_{36,40}^{(b)}$. We have, from the results of § 3.3.1, $R_{36,40}^{(b)}(\mathrm{exp}) = 0.566$.

We only give here the limiting values for $R_{40,4,36}$ and $R_{36,4,40}$.

$$[R_{40,4,36}]_4 = 0.97_4 \pm 0.01_5; \quad [R_{40,4,36}]_A = 0.98_2 \pm 0.01_5 \qquad (30.VI)$$

$$[R_{36,4,40}]_4 = 1.02_5 \pm 0.01_5; \quad [R_{36,4,40}]_A = 1.01_8 \pm 0.01_5 \qquad (31.VI)$$

As we can see, they are not far from the unity which is in accordance with the theory.

SECOND APPROXIMATION. We now have approximate equations for the quantities $R_{36,4,40}$ and $R_{40,4,36}$. Hence, by using equations (20,21.VI), we obtain, from experimental data for non-isotopic thermal diffusion factors, a second approximation for $\alpha'_{4,36}(\mathrm{exp})$ and $\alpha'_{4,40}(\mathrm{exp})$. The natural abundance of ^{36}A being $c_{36}^{(b)} = 0.0031$, the correction considered here is only of interest for $\alpha'_{4,36}(\mathrm{exp})$. The most probable equation is then,

$$1/\alpha'_{4,36}(\mathrm{exp}) = (1.53 \pm 0.01)\, c_4 + (3.95 \pm 0.03)\, c_A \qquad (32.VI)$$

At a THIRD APPROXIMATION we obtain:

$$1/\alpha'_{4,36}(\mathrm{exp}) = (1.53 \pm 0.01)\, c_4 + (3.96 \pm 0.03)\, c_A \qquad (33.VI)$$

which just confirms the preceding equation. Accordingly,

$$[R_{4,36}^{(b)}(\mathrm{exp})]_4 = 0.737 \pm 0.006; \quad [R_{4,36}^{(b)}(\mathrm{exp})]_{36} = 0.833 \pm 0.006 \qquad (34.VI)$$

By means of (28,34.VI) we obtain, at a third approximation,

$$\frac{[R_{4,36}^{(b)}(\mathrm{exp})]_4}{[R_{4,40}^{(b)}(\mathrm{exp})]_4} = 1.04_2 \pm 0.01_5; \quad \frac{[R_{4,36}^{(b)}(\mathrm{exp})]_{36}}{[R_{4,40}^{(b)}(\mathrm{exp})]_{40}} = 1.04_5 \pm 0.01_5 \qquad (35.VI)$$

These results are just in accordance with the hypothesis assumed in theory that the quotient of non-isotopic binary separation ratios, both referred to the same concentration ratio, would be regarded as a constant.

Also, we obtain, at a third approximation, an equation for $R_{40,4,36}$. Limiting values are the following:

$$[R_{40,4,36}]_4 = 0.97_6 \pm 0.01_5;[R_{40,4,36}]_A = 0.98_4 \pm 0.01_5 \quad (36.VI)$$

Finally, the most probable equations which according to the elementary theory satisfy experimental values of non-isotopic thermal diffusion factors in (^{4}He, ^{36}A, ^{40}A) mixtures are the following:

$$1/\alpha_{4,40}(\exp) = (1.47 \pm 0.01)\, c_4 + (3.82 \pm 0.03)\, c_A \quad (37.VI)$$

and

$$1/\alpha_{4,36}(\exp) = \frac{(1.53 \pm 0.01)\, c_4 + (3.96 \pm 0.03)\, c_A}{c_4 + (0.0031 + 0.9969\, R_{40,4,36})\, c_A} \quad (38.VI)$$

which for practical purposes is very closely equivalent to

$$1/\alpha_{4,36}(\exp) = (1.53 \pm 0.01)\, c_4 + (4.03 \pm 0.03)\, c_A \quad (39.VI)$$

Equation (39.VI) is experimentally equivalent to (27.VI) which shows that the error which is committed, assuming a priori that $1/\alpha_{4,36}(\exp)$ was linearly dependent on concentrations, is negligible.

Therefore, *the inverses of non-isotopic thermal diffusion factors of ternary mixtures (^{4}He, ^{36}A, ^{40}A) are considered to be linear on concentrations of Argon and Helium within the magnitude of experimental errors.*

Experimental most probable equations (37,39.VI) and the observed values of $1/\alpha_{4,40}(\exp)$ and $1/\alpha_{4,36}(\exp)$ are represented in figures 9.VI and 10.VI, respectively.

According to the theory, the equations determined for $1/\alpha_{4,36}(\exp)$ and $1/\alpha_{4,40}(\exp)$ should explain the observed experimental data for the isotopic thermal diffusion factor. Indeed, we have, for each concentration ratio, c_A/c_4, the general relationship,

$$\alpha_{36,40} = \alpha_{4,40} - \alpha_{4,36} \quad (40.VI)$$

The error of this difference is, of course, very large compared to the corresponding value of $\alpha_{36,40}$.

By means of (37,39,40.VI) we obtain, approximately,

$$1/\alpha_{36,40}(\exp) = (38 \pm 13)\, c_4 + (73 \pm 27)\, c_A \quad (41.VI)$$

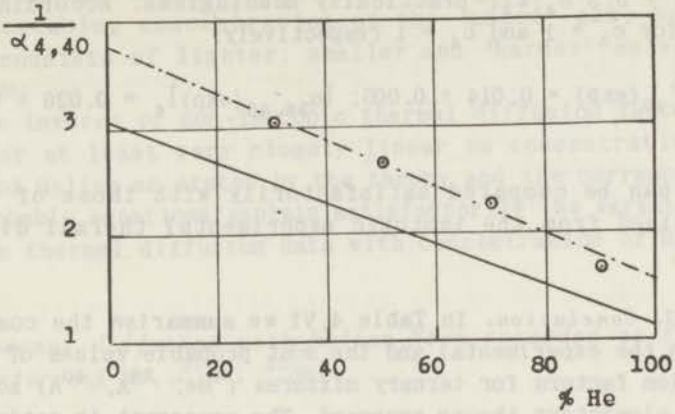

Fig. 9.VI

The inverse of the thermal diffusion factor of ^{4}He-^{40}A in ternary mixtures (^{4}He; ^{36}A, ^{40}A).

⊝ Experimental data.

—— Elementary 'r.e.s.' first approximation.

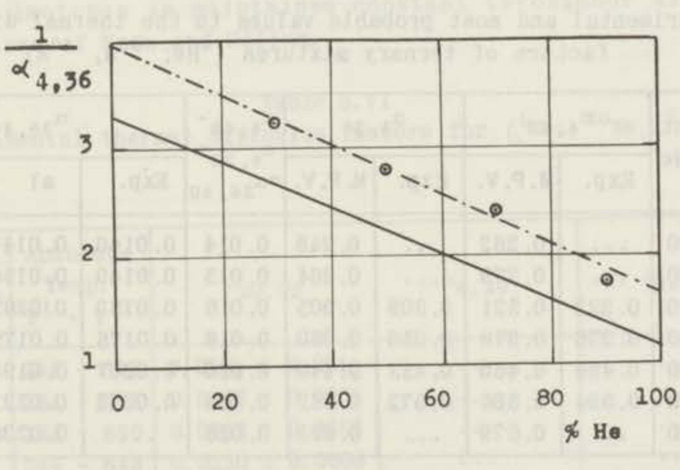

Fig. 10.VI

The inverse of the thermal diffusion factor of ^{4}He-^{36}A in ternary mixtures (^{4}He; ^{36}A, ^{40}A).

⊝ Experimental data.

—— Elementary 'r.e.s.' first approximation.

From the terms which have been disregarded, the most important one is $+\ 0.5\ c_4\ c_A$, practically meaningless. Accordingly, we have, for $c_A = 1$ and $c_4 = 1$ respectively:

$$\alpha^{(b)}_{36,40}(\exp) = 0.014 \pm 0.005;\ [\alpha_{36,40}(\exp)]_4 = 0.026 \pm 0.009 \tag{42.VI}$$

which can be compared satisfactorily with those of § 3.3.1 determined from the isotopic experimental thermal diffusion factor.

3.3.3. Conclusion. In Table 4.VI we summarise the comparison between the experimental and the most probable values of thermal diffusion factors for ternary mixtures (^{4}He; ^{36}A, ^{40}A) according to the elementary theory proposed. The agreement is satisfactory and all the essential features of thermal diffusion are correctly explained by the theory, namely,

a) $1/\alpha_{36,40}$ is linear on concentration of the 'added' gas, Helium. This is theoretically explained as the binary thermal separation ratios $R^{(b)}_{36,40}$; $R^{(b)}_{4,36}$ and $R^{(b)}_{4,40}$ are not too different;

b) the isotopic separation ratio, $R_{36,40}(\exp)$, is also linear as stated by the theory;

Table 4.VI
Experimental and most probable values to the thermal diffusion factors of ternary mixtures (^{4}He; ^{36}A, ^{40}A)

Concent. of ^{4}He	$\alpha_{4,40}$		$\alpha_{4,36}$		$\alpha_{4,40}-\alpha_{4,36}=\alpha_{36,40}$	$\alpha_{36,40}$		
	Exp.	M.P.V.	Exp.	M.P.V.		Exp.	a)	b)
0.000	...	0.262	...	0.248	0.014	0.0146	0.0144	0.0145
0.100	...	0.279	...	0.264	0.015	0.0149	0.0150	0.0149
0.300	0.323	0.321	0.308	0.305	0.016	0.0153	0.0163	0.0160
0.500	0.376	0.378	0.358	0.360	0.018	0.0176	0.0179	0.0174
0.700	0.454	0.460	0.433	0.440	0.020	0.0207	0.0198	0.0195
0.900	0.594	0.586	0.572	0.562	0.024	0.0222	0.0221	0.0231
1.000	...	0.679	...	0.653	0.026	...	0.0236	0.0258

M.P.V. most probable values.

a) Assuming $1/\alpha_{36,40}(\exp)$ linear on Helium concentration.

b) Assuming $R_{36,40}(\exp)$ linear on Helium concentration.

c) the isotopic thermal diffusion factor, $\alpha_{36,40}$(exp), increases with increasing concentration of the 'added' gas, because Helium consists of lighter, smaller and 'harder' molecules. molecules;

d) the inverse of non-isotopic thermal diffusion factors is linear or at least very closely linear on concentrations of Argon and Helium as stated by the theory and the corresponding most probable equations explain satisfactorily the variation of isotopic thermal diffusion data with concentration of Helium.

§ 4. *Thermal diffusion with Helium-Neon regarded as ternary mixtures* (^{4}He, ^{20}Ne, ^{22}Ne).

4.1. Experimental data. Natural isotopic abundance of Neon and Helium is the following:

^{20}Ne	90.51 %	^{4}He	99.9999 %
^{21}Ne	0.28 %	^{3}He	1.3 x 10^{-4} %
^{22}Ne	9.21 %		

Therefore we may consider Helium-Neon mixtures as ternary mixtures (^{4}He; ^{20}Ne, ^{22}Ne) in which the concentration ratio of Neon isotopes is maintained constant throughout all the proportions of Neon and Helium.

Table 5.VI

Experimental thermal diffusion factors for (^{4}He; ^{20}Ne, ^{22}Ne)

Concentr of Neon	Absolute Temp. T^I - T^{II}	$\alpha_{20,22}$	$\alpha_{4,20}$	$\alpha_{4,22}$
1.000	284 - 658	$0.027_7 \pm 0.001_0$	...	...
1.000	284 - 658	0.0267 ± 0.0004	...	...
0.900	284 - 650	0.0242 ± 0.0005	...	...
0.800	284 - 648	0.0230 ± 0.0008	...	...
0.800	284 - 673	$0.024_2 \pm 0.001_1$	...	...
0.600	284 - 658	0.0209 ± 0.0009	...	...
0.400	284 - 667	$0.017_7 \pm 0.001_0$	0.267 ± 0.005	0.285 ± 0.005
0.200	285 - 661	0.0164 ± 0.0009	...	...
0.100	285 - 670	$0.015_8 \pm 0.001_3$	0.332 ± 0.004	0.348 ± 0.005

In Table 5.VI (see p. 103) we report experimental thermal diffusion factors, namely, $\alpha_{20,22}$, $\alpha_{4,20}$ and $\alpha_{4,22}$. As for Argon-Helium mixtures, non-isotopic observations are given with low accuracy because of the difficulties of Helium measurements in our mass spectrometer. Only two values for $\alpha_{4,20}$ and $\alpha_{4,22}$ are given which have been obtained by paying careful attention to Helium measurements.

Notice, as a first remark, that the isotopic thermal diffusion factor decreases with increasing concentration of Helium.

4.2. Comparison of the thermal diffusion factor for Neon alone and of the thermal diffusion factor for ^{4}He and ^{20}Ne with earlier results. Table 6.VI and fig. 11.VI report the values of $\alpha^{(b)}_{20,22}$ given by Stier (S1) in studying the temperature dependence of the thermal diffusion factor of Neon isotopes. Our values are also given for comparison. The mean temperature, T_m, is defined, as in § 3.2, by the algebraic mean value of the absolute temperatures T^{I} and T^{II}.

From fig. 11.VI it follows that our experimental values are somewhat smaller, but within reasonable agreement with Stier's observations.

Table 6.VI

The variation of the thermal diffusion factor for Neon isotopes with temperature

Absolute Temp. T^{I} - T^{II}	Mean Temp. T_m	$\alpha^{(b)}_{20,22}$	Reference
90 - 195	132	0.0162	S1
90 - 296	163	0.0187	S1
195 - 296	240	0.0233	S1
195 - 490	309	0.0254	S1
302 - 645	441	0.0302	S1
460 - 638	542	0.0318	S1
691 - 819	752	0.0346	S1
284 - 658	430	0.0277	This paper
284 - 658	430	0.0267	This paper

In Table 7.VI we report experimental data of the thermal diffusion factor for Helium-Neon mixtures of equal concentrations, after de Troyer, van Itterbeek and van den Berg (T2, 1950); Grew (G8, 1947); Puschner (P1, 1937); Atkins, Bastick and Ibbs (A1, 1939) and our value, $\alpha_{4,20}$, obtained by extrapolation of experimental data of Table 5.VI. The earlier results refer to global analyses of natural Helium and Neon, therefore they would not be exactly equivalent to our value of $\alpha_{4,20}$ since the concentration of the isotope ^{22}Ne is not negligible. Their thermal diffusion factor, $\alpha_{He,Ne}$, would be in between $\alpha_{4,20}$ and $\alpha_{4,22}$ and even then closer to $\alpha_{4,20}$. Our extrapolated value for $\alpha_{4,22}$ is also given in Table 7.VI.

Table 7.VI

Thermal diffusion factor for Helium-Neon mixtures of equal proportions

Absolute Temp. $T^I - T^{II}$	Mean Temp. T_r	$\alpha_{He,Ne}$	Reference
20 - 293	58	0.242	T2
90 - 293	154	0.330	T2
200 - 600	330	0.316	G8
300 - 400	343	0.364	P1
288 - 373	325	0.388	A1
284 - 660	420	$\alpha_{4,20} = 0.280$	This paper
284 - 660	420	$\alpha_{4,22} = 0.299$	This paper

The experimental data available seem to confirm an equation of the form

$$\alpha_{He,Ne} = (\alpha_{He,Ne})_o \; (1 + A/T_r) \qquad (43.VI)$$

where T_r is a mean temperature defined by

$$T_r = \frac{T^I \; T^{II}}{T^{II} - T^I} \ln (T^{II}/T^I) \qquad (44.VI)$$

(see equations 61,62.IV)

In figure 12.VI we give experimental values of $\alpha_{He,Ne} . T_r$ which according to (43.V) should be linearly dependent on the mean temperature, T_r. Most recent values of the thermal diffusion factor (de Troyer and Grew) give rise to the equation:

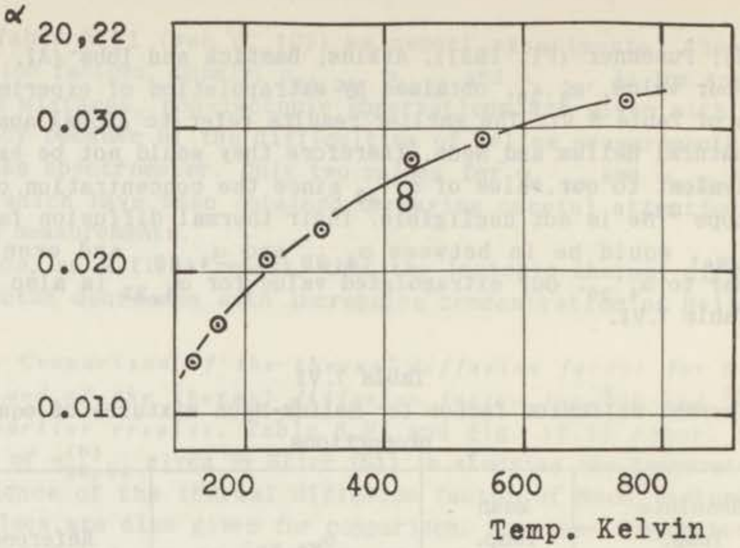

Fig. 11.VI
Variation of the thermal diffusion factor of ^{20}Ne and ^{22}Ne with temperature.

⊙ Experimental data after Stier (S1).
○ Our experiments.

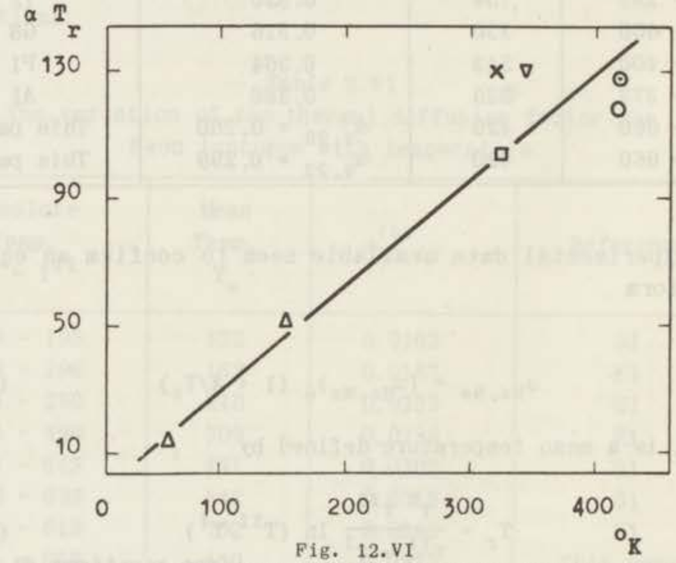

Fig. 12.VI
Variation of the thermal diffusion factor of mixtures of equal concentrations of Helium-Neon with temperature.
Experimental data for $\alpha_{He,Ne} \cdot T_r$:

△ After de Troyer, van Itterbeek and van den Berg (T2, 1950).
□ After Grew (G8, 1947).
▽ After Puschner (P1, 1937).
x After Atkins, Bastick and Ibbs (A1).
⊙ From our observation for $\alpha_{4,22}$(exp).
○ From our observation for $\alpha_{4,20}$(exp).

$$\alpha_{He,Ne} = 0.331 - \frac{4.57}{T_r} \qquad (45.VI)$$

Accordingly, our value of $\alpha_{He,Ne}$ at $T_r = 430°$ K should be 0.320 whereas we have obtained

$$\alpha_{4,20}(exp) = 0.280; \ \alpha_{4,22}(exp) = 0.299$$

4.3. Interpretation of experimental data by the elementary theory

4.3.1. Isotopic thermal diffusion factor. The treatment of experimental data is just analogous to that of § 3.3.1. The values which have been used in elementary equations are the following:

$c_{20}^{(b)} = 0.9076$
$c_{22}^{(b)} = 0.0924$
(Assuming natural Neon as consisting of ^{20}Ne and ^{22}Ne only)

$A_4 = 0.09119 \ \mu$ poise^{-1}
$A_{20} = 0.1665$
$A_{22} = 0.1747$
$A_{Ne} = 0.1673$

When molecules are regarded as 'rigid elastic spheres' we have:

$$1/\alpha_{20,22}(res) = 40.80 \ c_{Ne} + 22.24 \ c_4 \qquad (46.VI)$$

This equation will be used to determine experimental thermal separation ratios, $R_{20,22}(exp) = \alpha_{20,22}(exp)/\alpha_{20,22}(res)$.

Limiting values for the 'r.e.s.' isotopic thermal diffusion factor are the following:

for $c_{Ne} = 1$:

$$[\alpha_{20,22}(res)]_{Ne} = \alpha_{20,22}^{(b)}(res) = 0.0245$$

(47.VI)

for $c_4 = 1$:

$$[\alpha_{20,22}(res)]_4 = 0.0450$$

The limiting value of the quantity $\Delta_{20,22}(\text{res})$ when $c_4 = 1$ is then

$$[\Delta_{20,22}(\text{res})]_4 = \frac{[\alpha_{20,22}(\text{res})]_4}{\alpha^{(b)}_{20,22}(\text{res})} = 1.83 \qquad (48.\text{VI})$$

According to (48.VI), the 'r.e.s.' isotopic thermal diffusion factor, $\alpha_{20,22}(\text{res})$, *increases* with *increasing* concentration of Helium.

Let us now consider *experimental* isotopic data given in Table 5.VI. As a first remark we notice that the isotopic thermal diffusion factors, $\alpha_{20,22}(\text{exp})$, *decrease* in reality with *increasing* concentration of Helium. As we shall see, such surprising results can be explained by the values of $R^{(b)}_{20,22}$ and $R^{(b)}_{4,20}$, $R^{(b)}_{4,22}$.

In figures 13 and 14.VI we report experimental values of $1/\alpha_{20,22}(\text{exp})$ and $R_{20,22}(\text{exp})$ versus Helium concentration. Most probable linear equations are the following:

$$\text{a) } 1/\alpha_{20,22}(\text{exp}) = (37._0 \pm 1._0)\, c_{Ne} + (66._9 \pm 2._5)\, c_4 \qquad (49.\text{VI})$$

$$\text{b) } R_{20,22}(\text{exp}) = (1.07 \pm 0.05)\, c_{Ne} + (0.25_0 \pm 0.04_0)\, c_4$$

The corresponding limiting values to the thermal diffusion factor are given by
for $c_{Ne} = 1$

$$\text{a) } \alpha^{(b)}_{20,22}(\text{exp}) = 0.0270 \pm 0.0007$$

$$\text{b) } \alpha^{(b)}_{20,22}(\text{exp}) = 0.026_1 \pm 0.001_2 \qquad (50.\text{VI})$$

for $c_4 = 1$

$$\text{a) } [\alpha_{20,22}(\text{exp})]_4 = 0.0149 \pm 0.0006$$

$$\text{b) } [\alpha_{20,22}(\text{exp})]_4 = 0.011_3 \pm 0.001_8 \qquad (51.\text{VI})$$

Notice that the standard errors corresponding to the isotopic separation ratio, $R_{20,22}(\text{exp})$, equations (49,50,51b.VI), are *larger* than those of the experimental observations given in Table 5.VI. This result probably means that the linear dependence of $R_{20,22}(\text{exp})$ is not correct.

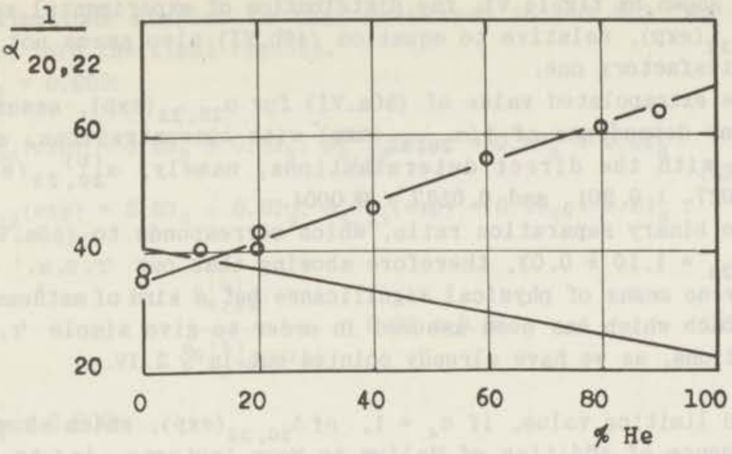

Fig. 13.VI
Variation of the inverse of the thermal diffusion factor for ^{20}Ne-^{22}Ne with addition of Helium.
O Experimental data.
——— elementary 'r.e.s.' first approximation.

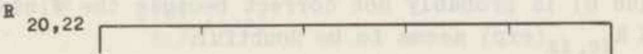

Fig. 14.VI
Variation of the thermal separation ratio for ^{20}Ne-^{22}Ne with addition of Helium.
x Experimental data.

As shown by fig. 14.VI, the distribution of experimental values, $R_{20,22}(\mathrm{exp})$, relative to equation (49b.VI) also seems not to be a satisfactory one.

The extrapolated value of (50a.VI) for $\alpha_{20,22}(\mathrm{exp})$, assuming a linear dependence of $1/\alpha_{20,22}(\mathrm{exp})$ with concentrations, agrees well with the direct determinations, namely, $\alpha^{(b)}_{20,22}(\mathrm{exp}) = 0.027_7 \pm 0.001_0$ and 0.0267 ± 0.0004.

The binary separation ratio, which corresponds to (50a.VI) is $R^{(b)}_{20,22} = 1.10 \pm 0.03$, therefore showing that our 'r.e.s.' model is by no means of physical significance but a kind of mathematical approach which has been assumed in order to give simple 'r.e.s.' equations, as we have already pointed out in § 2.IV.

The limiting value, if $c_4 = 1$, of $\Delta_{20,22}(\mathrm{exp})$, which shows the influence of addition of Helium to Neon isotopes, is, by means of (50,51.VI),

$$\begin{aligned} &\text{a)}\ [\Delta_{20,22}(\mathrm{exp})]_4 = 0.55 \pm 0.04 \\ &\text{b)}\ [\Delta_{20,22}(\mathrm{exp})]_4 = 0.44 \pm 0.09 \end{aligned} \qquad (52.\mathrm{VI})$$

The value b) is probably not correct because the linear dependence of $R_{20,22}(\mathrm{exp})$ seems to be doubtful.

When molecules are regarded as 'rigid elastic spheres', we have, equation (48.VI), $[\Delta_{20,22}(\mathrm{res})]_4 = 1.83$ which has to be compared with the experimental values (52.VI). The effect of addition of Helium upon the thermal diffusion factor of Neon isotopes is therefore quite different from the 'r.e.s.' predictions and the pronounced decrease of $\alpha_{20,22}(\mathrm{exp})$ with increasing Helium concentration, as experimentally observed, could not be expected a priori.

4.3.2. Non-isotopic thermal diffusion factors. A full treatment similar to that of § 3.3.2 for (^{4}He; ^{36}A, ^{40}A) cannot be given because we only have two pairs of observations for non-isotopic thermal diffusion factors $\alpha_{4,20}(\mathrm{exp})$ and $\alpha_{4,22}(\mathrm{exp})$ ($c_4 = 0.600$ and $c_4 = 0.900$).

By introducing in (54.V) the values of $R_{4,20}(\mathrm{exp})$ and $R_{4,22}(\mathrm{exp})$ which correspond to the values of $\alpha_{4,20}(\mathrm{exp})$ and $\alpha_{4,22}(\mathrm{exp})$ given in Table 5.VI, the values of the binary separation ratios, $R^{(b)}_{4,20}$ and $R^{(b)}_{4,22}$ can be determined by a method of successive

approximations similar to that described in § 3.3.2. We only present here the final results.
for $c_4 = 0.600$:

$$\begin{aligned} R_{4,20}(\mathrm{exp}) &= 0.86_2 \pm 0.01_5;\ R^{(b)}_{4,20}(\mathrm{exp}) = 0.86_5 \pm 0.01_6 \\ R_{4,22}(\mathrm{exp}) &= 0.83_0 \pm 0.01_6;\ R^{(b)}_{4,22}(\mathrm{exp}) = 0.79_7 \pm 0.01_8 \end{aligned} \tag{53.VI}$$

$$\frac{R^{(b)}_{4,22}(\mathrm{exp})}{R^{(b)}_{4,20}(\mathrm{exp})} = 0.92 \pm 0.04 \tag{54.VI}$$

For $c_4 = 0.900$:

$$\begin{aligned} R_{4,20}(\mathrm{exp}) &= 0.87_1 \pm 0.01_2;\ R^{(b)}_{4,20} = 0.87_2 \pm 0.01_2 \\ R_{4,22}(\mathrm{exp}) &= 0.82_3 \pm 0.01_3;\ R^{(b)}_{4,22} = 0.81_6 \pm 0.01_5 \end{aligned} \tag{55.VI}$$

$$\frac{R^{(b)}_{4,22}(\mathrm{exp})}{R^{(b)}_{4,20}(\mathrm{exp})} = 0.94 \pm 0.03 \tag{56.VI}$$

As shown by equations (54,56.VI) the ratio $R^{(b)}_{4,22}(\mathrm{exp})/R^{(b)}_{4,20}(\mathrm{exp})$ may be assumed constant, as we have stated in § 4.3.V, within the magnitude of experimental errors.

Since the extrapolation for $c_4 = 1$ of binary separation ratios $R^{(b)}_{4,20}$ and $R^{(b)}_{4,22}$ is a short one and, furthermore, it may appear, by means of (53, ..., 56.VI), that the experimental values at concentrations $c_4 = 0.600$ and $c_4 = 0.900$ are consistent together, we obtain by a linear extrapolation,

$$[R^{(b)}_{4,20}(\mathrm{exp})]_4 = 0.87;\ [R^{(b)}_{4,22}(\mathrm{exp})]_4 = 0.82 \tag{57.VI}$$

within an error of about 2%.

Introducing (57.VI) into (42.V) we can obtain the limiting value for $R_{20,22}(\mathrm{exp})$, when $c_4 = 1$, as $[R_{20,22}(\mathrm{exp})]_4 = 0{,}34$, of course given with very large error (about 40%). Multiplying this value by $[\alpha_{20,22}(\mathrm{res})]_4$, equation (47.VI) we get

$$[\alpha_{20,22}(\mathrm{exp})]_4 = 0.015 \tag{58.VI}$$

which is just equivalent to the value of (51a.VI), obtained from extrapolation of the experimental isotopic thermal diffusion factor, when $c_4 = 1$, assuming a linear dependence of $1/\alpha_{20,22}$(exp) with concentration. We may then conclude that the observed decreasing of $\alpha_{20,22}$(exp) with increasing Helium concentration is explained from the non-isotopic behaviour of the thermal diffusion factors, $\alpha_{4,20}$(exp) and $\alpha_{4,22}$(exp).

§ 5. *Mixtures of Hydrogen-Neon regarded as ternary mixtures* (H_2; ^{20}Ne, ^{22}Ne).

5.1. Experimental data. Isotopic abundance of Deuterium in natural Hydrogen is 0.0156% only. We may therefore consider Hydrogen-Neon mixtures as ternary mixtures (H_2; ^{20}Ne, ^{22}Ne).

Our experimental data for thermal diffusion factors are given in Table 8.VI.

Table 8.VI

Experimental thermal diffusion factors of ternary mixtures (H_2; ^{20}Ne, ^{22}Ne)

Concent. of H_2	Absolute Temp. $T^I - T^{II}$	$\alpha_{20,22}$	$\alpha_{2,20}$	$\alpha_{2,22}$
0.000	286 - 658	$0.027_7 \pm 0.001_0$	...	...
0.000	284 - 658	0.0267 ± 0.0004	...	...
0.250	284 - 657	0.0192 ± 0.0009	...	...
0.400	284 - 668	$0.016_7 \pm 0.001_1$	...	...
0.500	284 - 671	0.0160 ± 0.0005	0.254 ± 0.003	0.270 ± 0.003
0.500	284 - 668	$0.015_6 \pm 0.001_4$	...	...
0.600	284 - 658	0.0128 ± 0.0009	...	...
0.700	284 - 661	0.0126 ± 0.0006	...	...
0.800	284 - 653	$0.011_1 \pm 0.001_2$	...	...
0.900	284 - 653	0.0105 ± 0.0008	0.314 ± 0.003	0.324 ± 0.003

5.2. Comparison of the thermal diffusion factor for H_2 *and* ^{20}Ne *with earlier data.* Only a few observations have been found in literature for the thermal diffusion factor $\alpha_{H_2,Ne}$. They are given in Table 9.VI as well as our values for $\alpha_{2,20}$(exp) and

$\alpha_{2,22}$(exp). Temperature dependence cannot be studied satisfactorily. Even then our experimental values seem to be rather low.

Table 9.VI
Experimental thermal diffusion factors for Hydrogen-Neon of equal concentrations

Absolute Temp. $T^{I} - T^{II}$	$\alpha_{H_2,Ne}$	References
20 - 290	0.174	(T2)
90 - 290	0.280	(T2)
128 - 288	0.36	(G6)
284 - 671	$\alpha_{2,20} = 0.254$	This paper
284 - 671	$\alpha_{2,22} = 0.270$	This paper

5.3. *Interpretation of experimental data for* (H_2; ^{20}Ne, ^{22}Ne) *by the elementary theory*

5.3.1. Isotopic thermal diffusion factor. By using the values of $c_{20}^{(b)}$, $c_{22}^{(b)}$; A_{20}, A_{22}, A_{Ne}; given in § 4.3.1 and $A_2 = 0.09679$ μ poise^{-1}, we obtain the following equation for the 'r.e.s.' isotopic thermal diffusion factor, $\alpha_{20,22}$(res),

$$1/\alpha_{20,22}(\text{res}) = 40.80\ c_{Ne} + 23.61\ c_2 \qquad (59.\text{VI})$$

which brings about the following limiting values:
for $c_{Ne} = 1$:

$$[\alpha_{20,22}(\text{res})]_{Ne} = \alpha_{20,22}^{(b)}(\text{res}) = 0.0245 \qquad (60.\text{VI})$$

for $c_2 = 1$

$$[\alpha_{20,22}(\text{res})]_2 = 0.0424 \qquad (61.\text{VI})$$

and by means of (60,61.VI),

$$[\Delta_{20,22}(\text{res})]_2 = \frac{[\alpha_{20,22}(\text{res})]_2}{\alpha_{20,22}^{(b)}(\text{res})} = 1.73 \qquad (62.\text{VI})$$

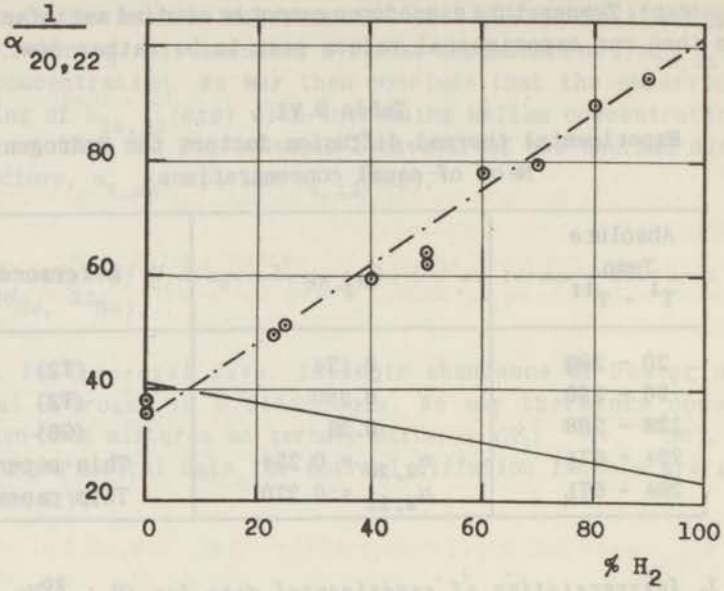

Fig. 15.VI
Variation of the inverse of the thermal diffusion factor for ^{20}Ne-^{22}Ne with addition of Hydrogen.
⊙ Experimental data.
——— Elementary 'r.e.s.' first approximation.

which shows that the 'r.e.s.' thermal diffusion factor, $\alpha_{20,22}(\mathrm{res})$ *increases* with *increasing* concentration of Hydrogen.

On the other hand, the experimental thermal diffusion factor $\alpha_{20,22}(\mathrm{exp})$ *decreases* markedly with *increasing* concentration of Hydrogen. In fig. 15.VI we give experimental values for $1/\alpha_{20,22}(\mathrm{exp})$ versus Hydrogen concentration. The linear dependence appears to be satisfactory and the most probable equation is

$$1/\alpha_{20,22}(\mathrm{exp}) = (35._2 \pm 1._0)\, c_{Ne} + (100 \pm 7)\, c_2 \qquad (63.\mathrm{VI})$$

Limiting values for $\alpha_{20,22}(\mathrm{exp})$ when $c_{Ne} = 1$ and $c_2 = 1$ are respectively,

$$\alpha^{(b)}_{20,22}(\mathrm{exp}) = 0.0284 \pm 0.0008 \qquad (64.\mathrm{VI})$$

whereas direct observations give it as $0.027_7 \pm 0.001_0$ and 0.0267 ± 0.0004;
for $c_2 = 1$:

$$[\alpha_{20,22}(\mathrm{exp})]_2 = 0.0100 \pm 0.0007 \qquad (65.\mathrm{VI})$$

By means of (64,65.VI) we obtain

$$[\Delta_{20,22}(\mathrm{exp})]_2 = \frac{[\alpha_{20,22}(\mathrm{exp})]_2}{\alpha^{(b)}_{20,22}} = 0.35 \pm 0.09 \qquad (66.\mathrm{VI})$$

which shows the pronounced decrease of $\alpha_{20,22}(\mathrm{exp})$ with increasing concentration of Hydrogen.

A linear dependence of the isotopic separation ratio, $R_{20,22}(\mathrm{exp})$, on the concentration of Hydrogen was not observed. Contrary it was bent.

Considering the decrease of the thermal diffusion factor of Neon isotopes which has been observed with addition of Helium (§ 4.3.1), we might also expect a decrease of $\alpha_{20,22}(\mathrm{exp})$ with increasing concentration of Hydrogen. Indeed, Hydrogen molecules are appreciably larger than those of Helium, which brings about that $[\Delta_{22,20}(\mathrm{res})]_2 = 1.73$ whereas for (^{4}He; ^{20}Ne, ^{22}Ne) we have $[\Delta_{22,20}(\mathrm{res})]_4 = 1.83$. Also Hydrogen molecules are 'softer' than those of Helium. Therefore both diameter and 'softness' of the Hydrogen molecule try to decrease the thermal diffusion factor of Neon isotopes even more than in the case of addition of Helium.

5.3.2. *Non-isotopic thermal diffusion factors.* Experimental values of $\alpha_{2,20}(\mathrm{exp})$ and $\alpha_{2,22}(\mathrm{exp})$ which are given in Table 8.VI give rise to the following binary separation ratios:
for $c_2 = 0.500$:

$$R_{2,20} = 0.96_2 \pm 0.01_1;\ R^{(b)}_{2,20} = 0.96_5 \pm 0.01_2$$
$$R_{2,22} = 0.91_5 \pm 0.01_0;\ R^{(b)}_{2,22} = 0.86_2 \pm 0.01_3 \qquad (67.\mathrm{VI})$$

for $c_2 = 0.900$:

$$R_{2,20} = 0.936 \pm 0.009;\ R^{(b)}_{2,20} = 0.93_7 \pm 0.01_0$$
$$R_{2,22} = 0.864 \pm 0.009;\ R^{(b)}_{2,22} = 0.85_5 \pm 0.01_1 \qquad (68.\mathrm{VI})$$

By means of (67,68.VI) we obtain,

$$\text{for } c_2 = 0.500:\quad \frac{R^{(b)}_{2,20}}{R^{(b)}_{2,22}} = 1.12 \pm 0.02 \qquad (69.\mathrm{VI})$$

$$\text{for } c_2 = 0.900: \quad \frac{R^{(b)}_{2,20}}{R^{(b)}_{2,22}} = 1.10 \pm 0.02$$

Equations (69.VI) show that $R^{(b)}_{2,20}/R^{(b)}_{2,22}$ can be regarded as a constant, within the magnitude of experimental errors, as stated in our theory.

By extrapolation of the above values for $R^{(b)}_{2,20}$ and $R^{(b)}_{2,22}$ when $c_2 = 1$, we obtain

$$[R^{(b)}_{2,20}]_2 = 0.93 \text{ and } [R^{(b)}_{2,22}]_2 = 0.85 \qquad (70.\text{VI})$$

which give rise to the following limiting value of the isotopic thermal diffusion factor when $c_2 = 1$, using a procedure similar to that given in § 4.3.2:

$$[\alpha_{20,22}(\text{exp})]_2 = 0.008 \qquad (71.\text{VI})$$

This value is thus in accordance with that obtained by observations of the isotopic thermal diffusion factor, equation (55.VI), namely $[\alpha_{20,22}(\text{exp})]_2 = 0.0100 \pm 0.0007$.

§ 6. *Mixtures Argon-Neon regarded as multicomponent mixtures*

Analyses of the Argon isotopes ^{36}A and ^{40}A as well as of Neon isotopes ^{20}Ne and ^{22}Ne could be carried out simultaneously in our mass spectrometer. On the other hand, measurements of ^{21}Ne were obtained with low accuracy, being therefore disregarded.

Neon-Argon mixtures cannot be assumed as quaternary mixtures (^{20}Ne, ^{22}Ne; ^{36}A, ^{40}A) because the isotopic abundance of ^{21}Ne in natural Neon is of the same order of ^{36}A (see § 3.1 and § 4.1). For that reason we do not give in this paragraph a full treatment of experimental data, pointing out only the most important features experimentally observed.

6.1. Experimental data. Observed values for thermal diffusion factors are given in Table 10.VI. Notice, as a first remark, that $\alpha_{36,40}(\text{exp})$ *increases* markedly with *increasing* Neon concentration as would be expected, because Argon consists of heavier, larger and 'softer' molecules. Conversely, $\alpha_{20,22}(\text{exp})$ *decreases* with *increasing* Argon concentration and even *changes sign* at about $c_A = 0.600$.

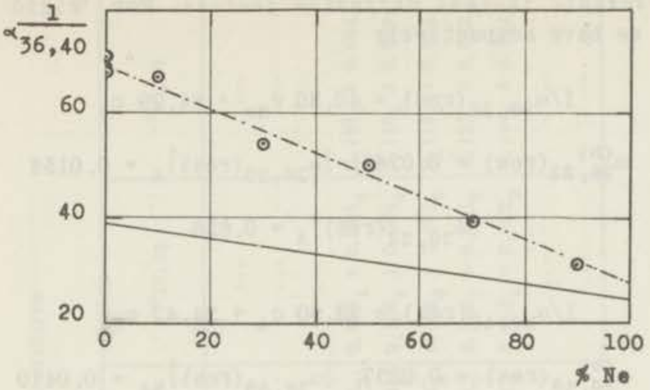

Fig. 16.VI
Variation of the inverse of the thermal diffusion factor for ^{36}A-^{40}A with addition of Neon.
⊙ Experimental data.
—— Elementary 'r.e.s.' first approximation.

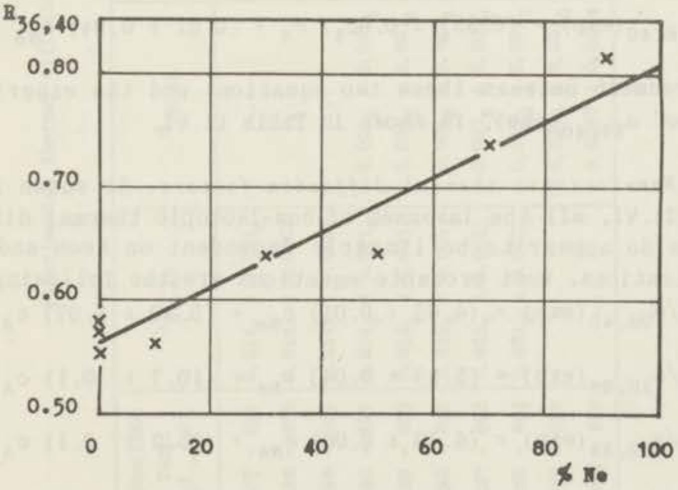

Fig. 17.VI
Variation of the thermal separation ratio for ^{36}A-^{40}A with addition of Neon.
x Experimental data.

6.2.1. Isotopic thermal diffusion factors. For ‘rigid elastic spheres’ we have respectively

$$1/\alpha_{20,22}(\mathrm{res}) = 40.80\ c_{Ne} + 64.99\ c_A$$

$$\alpha^{(b)}_{20,22}(\mathrm{res}) = 0.0245;\ [\alpha_{20,22}(\mathrm{res})]_A = 0.0154 \tag{72.VI}$$

$$[\Delta_{20,22}(\mathrm{res})]_A = 0.628$$

$$1/\alpha_{36,40}(\mathrm{res}) = 38.90\ c_A + 24.42\ c_{Ne}$$

$$\alpha^{(b)}_{36,40}(\mathrm{res}) = 0.0257;\ [\alpha_{36,40}(\mathrm{res})]_{Ne} = 0.0410$$

$$[\Delta_{36,40}(\mathrm{res})]_{Ne} = 1.59$$

Experimental values of $1/\alpha_{20,22}(\mathrm{exp})$ and $R_{20,22}(\mathrm{exp})$ are not linearly dependent on c_{Ne} and c_A. On the other hand, such linear dependence is well satisfied for $1/\alpha_{36,40}(\mathrm{exp})$ and $R_{36,40}(\mathrm{exp})$ as shown in fig. 16 and 17. Most probable equations are the following

$$1/\alpha_{36,40}(\mathrm{exp}) = (69._0 \pm 2._5)\ c_A + (27._4 \pm 1._5)\ c_{Ne} \tag{74.VI}$$

$$R_{36,40}(\mathrm{exp}) = (0.55_4 \pm 0.02_5)\ c_A + (0.81 \pm 0.04)\ c_{Ne} \tag{75.VI}$$

The agreement between these two equations and the experimental values of $\alpha_{36,40}(\mathrm{exp})$, is shown in Table 11.VI.

6.2.2. Non-isotopic thermal diffusion factors. As shown in fig. 18 ... 21.VI, all the inverses of non-isotopic thermal diffusion factors do appear to be linearly dependent on Neon and Argon concentrations. Most probable equations are the following:

$$1/\alpha_{20,40}(\mathrm{exp}) = (4.65 \pm 0.01)\ c_{Ne} + (9.30 \pm 0.07)\ c_A$$

$$1/\alpha_{20,36}(\mathrm{exp}) = (5.59 \pm 0.04)\ c_{Ne} + (10.7 \pm 0.1)\ c_A$$

$$1/\alpha_{22,36}(\mathrm{exp}) = (6.48 \pm 0.06)\ c_{Ne} + (10.2 \pm 0.1)\ c_A$$

$$1/\alpha_{22,40}(\mathrm{exp}) = (5.27 \pm 0.04)\ c_{Ne} + (8.9_5 \pm 0.1_0)\ c_A$$

The agreement between isotopic and non-isotopic thermal diffusion factors is shown in Table 11.VI.

Table 10.VI

Experimental thermal diffusion factors in natural Neon-Argon mixtures

Concent. of Neon	Absolute Temp. $T^I - T^{II}$	$\alpha_{36,40}$	$\alpha_{20,22}$	$\alpha_{20,40}$	$\alpha_{22,40}$	$\alpha_{20,36}$	$\alpha_{22,36}$
0.000	287 - 655	$0.014_7 \pm 0.001_0$	...	...	...	...	...
0.000	286 - 676	0.0142 ± 0.0008	...	...	...	...	...
0.000	286 - 667	0.0149 ± 0.0008	...	...	...	...	...
0.100	286 - 667	$0.014_8 \pm 0.001_0$	$- 0.001_9 \pm 0.001_5$	0.1139 ± 0.0009	$0.115_8 \pm 0.001_3$	$0.099_1 \pm 0.001_3$	$0.101_0 \pm 0.001_7$
0.300	288 - 667	$0.018_5 \pm 0.001_2$	$- 0.004_3 \pm 0.001_5$	$0.124_8 \pm 0.001_0$	$0.129_1 \pm 0.001_3$	$0.106_3 \pm 0.001_4$	$0.110_6 \pm 0.001_7$
0.500	288 - 665	$0.019_9 \pm 0.001_6$	$+ 0.004_8 \pm 0.001_3$	$0.143_9 \pm 0.001_1$	$0.139_1 \pm 0.001_4$	$0.124_0 \pm 0.001_5$	$0.119_2 \pm 0.001_7$
0.700	287 - 663	$0.025_7 \pm 0.002_0$	$+ 0.007_5 \pm 0.001_0$	0.1663 ± 0.0008	$0.158_8 \pm 0.001_2$	$0.140_6 \pm 0.001_8$	$0.133_1 \pm 0.002_2$
0.900	286 - 661	$0.031_5 \pm 0.002_6$	$+ 0.019_2 \pm 0.001_2$	$0.195_3 \pm 0.001_0$	$0.176_1 \pm 0.001_4$	$0.163_8 \pm 0.002_2$	$0.144_6 \pm 0.002_6$
1.000	286 - 658	...	$+ 0.027_7 \pm 0.001_0$	...	...	...	...
1.000	284 - 658	...	$+ 0.0267 \pm 0.0004$	...	...	...	...

Table 11.VI

Experimental and most probable values for isotopic thermal diffusion factors, $\alpha_{36,40}$(exp) and $\alpha_{20,22}$(exp), in Neon-Argon mixtures

c_{Ne}	$\alpha_{36,40}$(exp)	M.P.V. a)	M.P.V. b)	$\alpha_{20,40}-\alpha_{20,36} = \alpha_{36,40}$	$\alpha_{22,40}-\alpha_{22,36} = \alpha_{36,40}$	$\alpha_{20,22}$(exp)	$\alpha_{20,40}-\alpha_{22,40} = \alpha_{20,22}$	$\alpha_{20,36}-\alpha_{22,36} = \alpha_{20,22}$
0.000	0.0147	0.0145	0.0142	0.0142	0.0140	...	- 0.0042	- 0.0045
0.000	0.0142	idem	idem	idem	idem	...	idem	idem
0.000	0.0149	idem	idem	idem	idem	...	idem	idem
0.100	0.0148	0.0154	0.149	0.0152	0.0150	- 0.0019	- 0.0034	- 0.0036
0.300	0.0185	0.0177	0.0183	0.0176	0.0176	- 0.0043	- 0.0010	- 0.0010
0.500	0.0199	0.0207	0.0216	0.0208	0.0210	+ 0.0048	+ 0.0027	+ 0.0029
0.700	0.0257	0.0251	0.0256	0.0252	0.0254	+ 0.0075	+ 0.0086	+ 0.0088
0.900	0.0315	0.0317	0.0304	0.0318	0.0316	+ 0.0192	+ 0.0183	+ 0.0184
1.000	...	0.0365	0.0333	0.0364	0.0356	+ 0.0277	+ 0.0255	+ 0.0257
1.000	...	idem	idem	idem	idem	+ 0.0267	idem	idem

M.P.V. Most probable value

a) assuming $1/\alpha_{36,40}$(exp) linearly dependent on concentrations of Neon and Argon

b) assuming $R_{36,40}$(exp) linearly dependent on concentrations of Neon and Argon

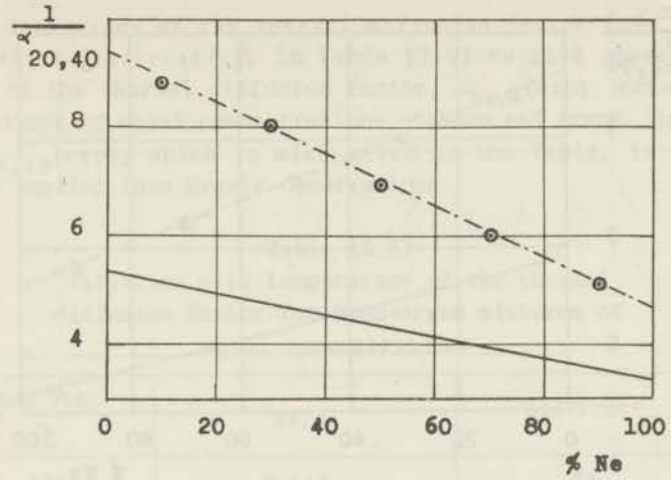

Fig. 18.VI
The inverse of the thermal diffusion factor for ^{20}Ne-^{40}A in Neon-Argon mixtures.
Θ Experimental data.
——— Elementary 'r.e.s.' first approximation.

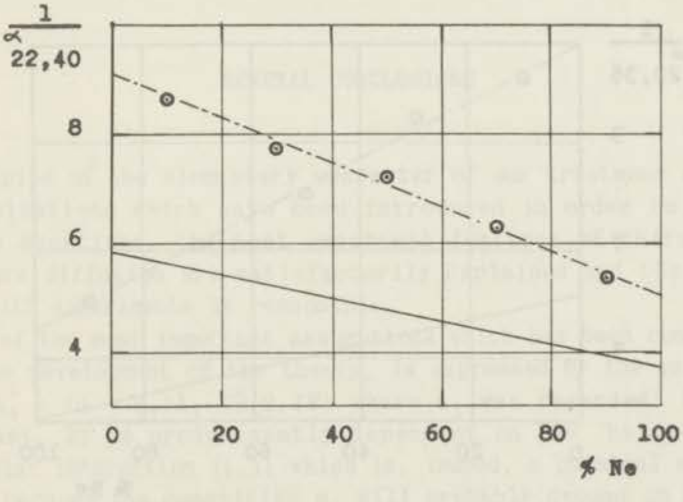

Fig. 19.VI
The inverse of the thermal diffusion factor for ^{22}Ne-^{40}A in Neon-Argon mixtures.
Θ Experimental data.
——— Elementary 'r.e.s.' first approximation.

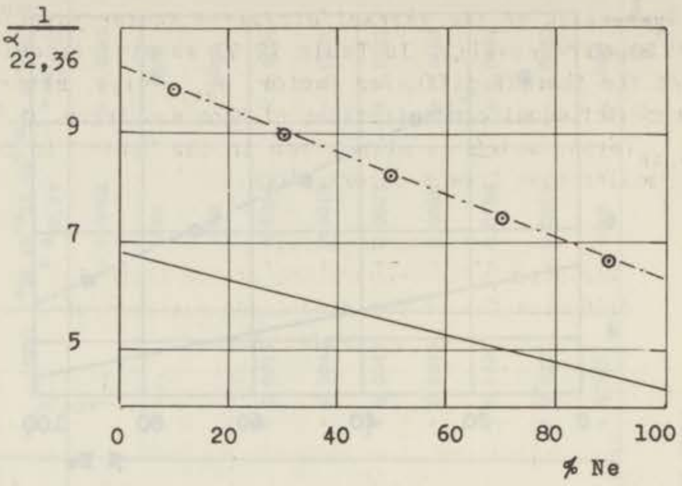

Fig. 20.VI
The inverse of the thermal diffusion factor for ^{22}Ne-^{36}A in Neon-Argon mixtures.
⊙ Experimental data.
—— Elementary 'r.e.s.' first approximation.

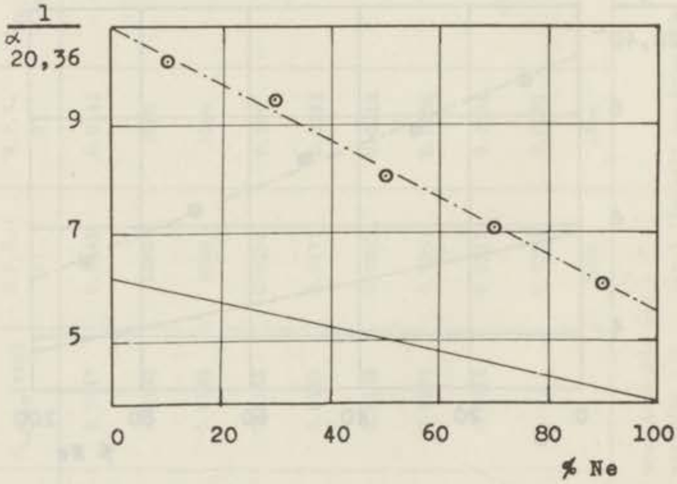

Fig. 21.VI
The inverse of the thermal diffusion factor for ^{20}Ne-^{36}A in Neon-Argon mixtures.
⊙ Experimental data.
—— Elementary 'r.e.s.' first approximation.

6.3. Comparison of the thermal diffusion factor for ^{20}Ne *and* ^{40}A *with earlier results.* In Table 12.VI we give experimental values of the thermal diffusion factor, $\alpha_{Ne,A}$(exp), after Grew, for mixtures of equal concentrations of Neon and Argon. Our value for $\alpha_{20,40}$(exp), which is also given in the Table, is comparatively smaller than Grew's observations.

Table 12.VI

Variation with temperature of the thermal diffusion factor for Neon-Argon mixtures of equal concentrations

Mean Temp. T_r	$\alpha_{Ne,A}$	Reference
185	0.148	G8
293	0.174	G8
369	0.19	G8
465	0.191	G8
420	$\alpha_{20,40}$ = 0.144	This paper

GENERAL CONCLUSIONS

In spite of the elementary character of our treatment and the approximations which have been introduced in order to obtain simple equations, the most important features of thermal and pressure diffusion are satisfactorily explained and the agreement with experiments is reasonable.

One of the most important assumptions which has been considered for the development of the theory, is expressed by the relationship $l_i' = (1 + a_i)l_i$ (§ 2.IV) where a_i was regarded: 1) as a constant, 2) as predominantly dependent on the 'hardness' of molecular interaction (i,i) which is, indeed, a physical approach only, because the quantities a_i will probably depend on all the molecular interactions of the types (i,i), (i,j), ..., (i,s).

The constancy of a_i may be considered a satisfactory approach since the linear dependence of the inverse of the thermal diffusion factor appears to be confirmed by experiments and, furthermore, the ratio of limiting values, $[\alpha_{ij}^{(b)}(\exp)]_i/[\alpha_{ij}^{(b)}(\exp)]_j$, is usually close to the corresponding one given by our 'r.e.s.' model (§ 7.2 and Table 10.IV).

The assumption that a_i depends predominantly on the 'hardness' of interactions of kind (i,i), cannot readily be confirmed by experiments because it would first be necessary to obtain a satisfactory equation for the r.e.s. thermal diffusion factor. Our 'r.e.s.' model ($a_i = 0$) is not sufficient for this purpose as can be inferred from the discussion of § 5.IV. Indeed, our 'r.e.s'. model is correct only for Lorentzian mixtures (R_T(elem) = 1, § 5.1.IV). For isotopic mixtures (§ 5.2.IV) a_i is definitely a negative value of the order of - 0.8 for r.e.s. molecules. Also it depends on diameter ratio as shown by § 5.3.IV. As a general conclusion we may say that a_i will usually depend on mass and diameter ratios, in case of the r.e.s. model, in such a way that $a_i = 0$ for Lorentzian mixtures.

For the reasons given above we do not present any value for a_i and only qualitative discussions have been given for this quantity.

The increase of the isotopic thermal diffusion factor, $\alpha_{36,40}(\exp)$, which has been observed with increasing concentration of Helium and Neon in Argon-Helium and Argon-Neon mixtures respectively, was expected a priori, since Helium and Neon consist of lighter, smaller and 'harder' molecules. For the same reason, decreasing values of $\alpha_{20,22}(\exp)$ with increasing concentration of Argon could be foreseen as well.

On the other hand, the decrease observed for the thermal diffusion factor of Neon isotopes with increasing concentration of Helium and Hydrogen was quite a surprise. In addition to our experiments, it would be very interesting to carry out measurements for H_2-D_2 and for ^{3}He-^{4}He with addition of Neon. The isotopic thermal diffusion factors for H_2-D_2 and ^{3}He-^{4}He should increase with increasing concentration of Neon.

Mixtures of two isotopes and an added gas realize the simplest ternary non-isotopic mixtures. They provide quite a new field of thermal diffusion observations which, indeed, do not involve any additional experimental difficulties and may be of great theoretical importance. The variation of the isotopic thermal diffusion factor with addition of a third gas is by no means negligible and seems to be strongly dependent on the molecular interactions (1,B) and (2,B).

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SUMMARY

Following the lines of a free path treatment of diffusion a general equation is presented which takes into account concentration, thermal and pressure diffusion. Two kinds of mean free path have been considered: 1) one, l_i, is the mean free path for number density transfer which is the only one appearing in Meyer's equation of concentration diffusion; 2) another one, l_i', is related to transfer of thermal speed, only appearing in the equations for thermal diffusion. We assume that $l_i' = (1 + a_i)l_i$, where a_i is regarded as a constant predominantly depending on the 'hardness' of molecular interactions (i,i). For the sake of simplicity of equations for the thermal diffusion factor, we have considered for 'rigid elastic spheres' that $a_i = 0$. For Maxwellian molecules $a_i = 1$.

We propose an approximate equation for l_i corrected for persistence of velocities. The inverse of the corresponding thermal diffusion factor of a binary mixture is at a first approximation linearly dependent on concentrations (except when a change of sign of the thermal diffusion factor with concentrations may occur). Such linear dependence has been confirmed by experiments and is also observed in general cases for Chapman's first approximation to the thermal diffusion factor for rigid elastic sphere model.

Multicomponent mixtures have also been considered in our treatment. Our equations can easily be handled in practice. In particular, we have studied ternary mixtures of two isotopes (1 and 2) with fixed concentration ratio, to which a third gas, B, has been added. It is shown that the isotopic thermal diffusion factor α_{12} should usually increase by addition of a gas consisting of lighter, smaller and 'harder' molecules. The isotopic thermal separation ratio, R_{12}, (defined according to our 'r.e.s.' model) and the inverses of non-isotopic thermal diffusion factors (α_{1B} and α_{2B}) are linearly dependent on concentration c_B, at a first approximation. The inverse of the isotopic thermal diffusion factor (α_{12}) is linearly dependent on c_B as well, if the force fields are not too different.

Observations have been carried out with the mixtures (^{4}He; ^{36}A, ^{40}A), (^{4}He; ^{20}Ne, ^{22}Ne), (H_2; ^{20}Ne, ^{22}Ne) and also with Neon-Argon regarded as a multicomponent mixture. Experimental data are given in the Tables of pages 89, 103, 112 and 120 respectively.

The linear dependence predicted by the theory was observed for all the inverses of non-isotopic thermal diffusion factors and for the inverse of the isotopic thermal diffusion factor as well, except for ^{20}Ne-^{22}Ne in Neon-Argon mixtures. The linear dependence of the isotopic thermal separation ratio, R_{12}, was not so well confirmed by experiments.

The thermal diffusion factor of Argon isotopes ^{36}A-^{40}A increases in Helium-Argon and Neon-Argon mixtures, with increasing concentration of Helium and Neon, as was expected. Marked decrease was observed for the thermal diffusion factor of ^{20}Ne-^{22}Ne with increasing concentrations of Helium, Hydrogen and Argon, and moreover a change of sign was observed for $\alpha_{20,22}$(exp) in Neon-Argon mixtures.

SAMENVATTING

Met behulp van een vrije-weglengte-methode is een algemene diffusievergelijking opgesteld, die rekening houdt met diffusie tengevolge van een concentratie-, een temperatuur- en een drukgradient. Hierbij zijn twee verschillende vrije weglengten ingevoerd, nl.: 1) l_i, de gemiddelde vrije weglengte voor 'number density transfer', welke de enige is die voorkomt in de vergelijking voor concentratiediffusie volgens Meyer; 2) l_i', de gemiddelde vrije weglengte voor 'thermal speed transfer', welke alleen voorkomt in de vergelijking voor thermodiffusie. Aangenomen is dat $l_i' = (1 + a_i)l_i$, waarin a_i beschouwd wordt als een constante, die afhangt van het krachtenveld om de moleculen i. Om de vergelijkingen voor de thermodiffusiefactor te vereenvoudigen is voor harde elastische bollen $a_i = 0$ gesteld; voor 'Maxwellse' moleculen is $a_i = 1$.

Een benaderde uitdrukking voor l_i is opgesteld, die 'persistence of velocities' in aanmerking neemt. Deze uitdrukking is eenvoudiger hanteerbaar dan de gebruikelijke en wijkt minder dan 15% van deze af tussen een massaverhouding gelijk aan 0 en oneindig. Het omgekeerde van de thermodiffusiefactor α van een binair mengsel die met behulp van deze l_i wordt afgeleid is in eerste benadering recht evenredig met de concentratie (behalve in gevallen waarin α over het concentratiegebied van teken omkeert). Dit lineaire verband is bevestigd door de experimenten en blijkt ook een eigenschap te zijn van Chapman's vergelijking voor de eerste benadering van de thermodiffusiefactor van harde elastische bollen.

Meercomponentensystemen zijn eveneens beschouwd en wel in het bijzonder mengsels van twee isotopen (A1 en A2) in een vaste concentratieverhouding, waaraan een derde gas (B) wordt toegevoegd. De afgeleide vergelijking voor de thermodiffusiefactor is eenvoudig van vorm en kan gemakkelijk toegepast worden voor berekeningen. Het blijkt dat de thermodiffusiefactor α_{12} voor de isotopen in het algemeen toeneemt bij toevoeging van een gas dat bestaat uit lichtere, kleinere of 'hardere' moleculen. De thermodiffusiescheidingsfactor R_{12} voor de isotopen en de reciproken van de niet-isotope-thermodiffusiefactoren (α_{1B} en α_{2B}) zijn in eerste benadering recht evenredig met de concentratie c_B van het toegevoegde gas.

Het omgekeerde van de thermodiffusiefactor α_{12} van de isotopen is eveneens recht evenredig met c_B als de krachtenvelden om de twee soorten moleculen ongeveer gelijk zijn.

Thermodiffusiefactoren zijn gemeten van de mengsels (^{4}He; ^{36}A, ^{40}A), (^{4}He; ^{20}Ne, ^{22}Ne), (H_2; ^{20}Ne, ^{22}Ne) en (^{20}Ne, ^{22}Ne; ^{36}A, ^{40}A) als functie van de concentratie, tussen 10 en 400° C. De experimentele uitkomsten zijn ondergebracht in de tabellen op pag. 89, 103, 112 en 120.

De lineaire afhankelijkheid van 1/α van de concentratie, die de theorie voorspelt, werd gevonden voor alle niet-isotope- en voor de isotope thermodiffusiefactoren met uitzondering van die voor ^{20}Ne-^{22}Ne in neon-argon mengsels.

Het lineaire verband tussen R_{12} en c_B bleek niet in alle gevallen te bestaan.

Het blijkt dat de thermodiffusiefactor van ^{36}A-^{40}A in helium-argon en neon-argon mengsels toeneemt met toenemende concentratie van He resp. Ne, zoals theoretisch verwacht werd. De experimentele thermodiffusiefactor van ^{20}Ne-^{22}Ne neemt sterk af met toenemende concentratie van argon doch ook met die van helium en waterstof. In neon-argon mengsels keert $\alpha_{20,22}$ zelfs van teken om bij 60% A.

SUMÁRIO

Baseando-nos no conceito do livre precurso médio das moléculas, apresentamos uma equação generalizada da difusão gasosa em que se interpretam as diffusões de concentração, de pressão e termodifusão. Dois tipos de livres precursos médios são considerados: 1) um, l_i, é o livre precurso médio para transferência da densidade molecular, que aparece na conhecida fórmula de Meyer para a difusão de concentração; 2) outro, l_i', está relacionado com a transferência dos módulos das velocidades térmicas e aparece nas fórmulas para a termodifusão agora propostas. Os dois livres precursos médios foram equacionados pela exprassão $l_i' = (1 + a_i)l_i$, onde a_i é considerado como uma constante, dependente dos campos de forças moleculares. Quando as moléculas são consideradas como 'esferas rígidas e perfeitamente elásticas' assumimos $a_i = 0$. Para gases maxwellianos o fenómeno da termodifusão não se verifica e $a_i = 1$.

Propõe-se uma equação aproximada para l_i, corrigida para o fenómeno da persitência das velocidades térmicas. As equações correspondentes mostram que o inverso do factor de termodifusão para misturas binárias é usualmente linear nas concentrações molares dos componentes (excepto quando possa teòricamente ocorrer uma variação de sinal com as concentrações para o factor de termodifusão). Esta dependência linear foi experimentalmente confirmada e igualmenta se observa, em casos gerais, para a primeira aproximação do factor de termodifusão segundo Chapman e Cowling.

Misturas complexas foram também estudadas, com especial ênfase para misturas constituidas por dois isótopos, 1 e 2, (com razão de concentração fixa) e um terceiro gas B. O factor de termodifusão isotopica (α_{12}) usualmenta aumenta com a adição dum terceiro gas constituido por moléculas mais leves, menores e rodeadas de campos de força menos intensos. A razão de separação térmica isotópica, R_{12} (definida da acordo com o modelo de 'esferas rígidas' proposto) e os inversos dos factores não isotópicos de termodifusão (α_{1B} e α_{2B}) são linearmente dependentes na concentração, c_B, do gás adicionado à mistura isotópica (1,2), em primeira aproximação. O inverso do factor de termodifusão isotópica (α_{12}) é igualmente linear em c_B, se os campos de forças moleculares dos tipos (1,2), (1,B) e (2,B) não forem marcadamente diferentes.

Realizaram-se experiências com as seguintes misturas:

(^{4}He; ^{36}A, ^{40}A), (^{4}He; ^{20}Ne, ^{22}Ne), (H_2; ^{20}Ne, ^{22}Ne) e igualmente com misturas Neon-Argon consideradas como complexas. Os resultados experimentais são dados nas páginas 89, 103, 112 e 120, respectivamente.

A dependência linear com a concentração, teòricamente prevista para os factores isotópicos e não isotópicos de termodifusão, foi experimentalmente observada, excepto para ^{20}Ne-^{22}Ne em misturas de Neon e Argon. A dependência linear da razão de separação isotópica, R_{12}, apresenta maior número de excepções.

O factor de termodifusão dos isótopos de Argon, ^{36}A e ^{40}A, aumenta nas misturas Helio-Argon e Neon-Argon, com a concentração de Hélio e Neon, como era previsível. Acentuada diminuição com crescentes concentrações de Hélio, Hidrogénio e Argon, foi observada para o factor de termodifusão dos isótopos de Neon e uma inversão de sinal foi notada para este factor em misturas Neon-Argon.

PROPOSITIONS

1

Stier's experiments on the temperature variation of thermal diffusion factors of Argon and Neon isotopes can be represented satisfactorily by using the correct mean temperature in the equations $R_T(\text{exp}) = a \ln (\bar{T}/b)$.

Stier, L.G.; Phys.Rev., *62*, 548 (1942).
Davenport, A.N. and Winter, E.R.S.; Trans.Faraday Soc., *47*, 1160 (1951).

2

The method for determining the range of β-particles as proposed by Harley and Hallden may only be applied to particular geometric counting conditions.

Harley, J.H. and Hallden, W.; Nucleonics, *13*, 1, 32 (1955).

3

Furry's criticism of mean free path theory of diffusion is contradictory in itself.

Furry, W.H.; Amer.J.Phys., *16*, 63 (1948).

4

The result of Cacciapuoti's theory of thermal diffusion can be applied to isotopic mixtures only, although he treats this subject in a general way.

Cacciapuoti, B.N.; Nuovo Cimento, (IX), 1, 126 (1943).

5

The use of soft glass instead of pyrex-glass should be preferred for the storage and maintenance of radon at least for activities higher than 0.5 Curie.

6

It is doubtful whether Whalley and Winter's assumption about l_i' being the mean free path for momentum transfer is correct.

This thesis Chapters II and III.

Whalley, E. and Winter, E.R.S.; Trans.Faraday Soc., *46*, 517 (1950).

7

It is of theoretical interest to identify, in our general equations (26.II) and (9.V), the mean free path l_i with Stefan-Maxwell's one and l_i' with the common Maxwell mean free path.

This thesis Chapters II and V.

8

The discrepancy between the charge exchange cross-sections, determined by Keene and by Stedeford can be explained from an incorrect interaction path length.

9

It is advisable to use stabilised stainless steel for ultra high vacuum systems.

10

There are indications that impulse transfer in crystals results in focussing of impulse momentum inside the crystal in closed packed directions.

11

The geographic situation of the Netherlands and Portugal may somehow give a partial understanding of the interesting parallelism which we find between several Dutch and Portuguese characters.