

§ 7. *A homogeneous plate.* In this case we have to put in (17) $N_1 = N_2 = N$, $\nu_1 = \nu_2 = \nu$, $h_1 = 1$, $b_1 + b_2 = b$, $y_1 = y_0 + b_1$. With a simple calculation the formula for $w_2(x, y)$ appears in the same form as $w_1(x, y)$. Hence, we have only to evaluate the expressions $C(\xi)$, $D(\xi)$ and $G(\xi)$ entering in the first formula (17). Using (14.1) and (15.1) a rather troublesome calculation gives

$$C(\xi) = 2[2 \operatorname{ch} b\xi + (1 - \nu) b\xi \operatorname{sh} b\xi],$$

$$D(\xi) = 2[(1 - \nu)b\xi \operatorname{ch} b\xi + (1 + \nu) \operatorname{sh} b\xi],$$

$$G(\xi) = -4[(1 + \nu)^2 \operatorname{sh}^2 b\xi - 4 \operatorname{ch}^2 b\xi - (1 - \nu)^2 b^2 \xi^2].$$

Inserting this into the first formula (17) one obtains finally the complicated solution

$$w(x, y) = \frac{P}{\pi N} \int_0^{\infty} \frac{\cos(x - s)\xi}{\xi^3[(1 + \nu)^2 \operatorname{sh}^2 b\xi - 4 \operatorname{ch}^2 b\xi - (1 - \nu)^2 b^2 \xi^2]} \{ [2 \operatorname{ch} b\xi + (1 - \nu)b\xi \operatorname{sh} b\xi] [\xi(y - y_0) \operatorname{ch} \xi(y - y_0) - \operatorname{sh} \xi(y - y_0)] - [(1 - \nu)b\xi \operatorname{ch} b\xi + (1 + \nu) \operatorname{sh} b\xi] \xi(y - y_0) \operatorname{sh} \xi(y - y_0) \} d\xi, \\ -\infty < x < +\infty, y_0 \leq y \leq y_0 + b. \quad (18)$$

For technical purposes the rapidly convergent integral in (18) is to be evaluated by numerical methods.

§ 8. *Remarks.*

1. The above solution represents, in the well-known sense, the basis for solving more complicated problems on composite plates (e.g. under the action of generally distributed normal forces and twisting moments at the free edge $y = y_n$).

2. Our preceding deductions may serve as a kind of guide in treating other questions, not only from the statics, but also from the dynamics of composite continua.

3. Generally, the method of matrix analysis is very convenient whenever one has to do with problems leading to chains of differential equations. Of course, the results are usually complicated^{1) 2)}.

Received 14th July, 1958.

REFERENCES

- 1) Vodička, V., Z. angew. Math. Mech. **37** (1957) 44.
2) Vodička, V., Quart. Appl. Math. **16** (1958) 11.

Applied Sci. Res., Vol. A8, 1959

THE MACROSCOPIC EQUATIONS FOR SIMULTANEOUS HEAT AND MASS TRANSFER IN ISOTROPIC, CONTINUOUS AND CLOSED SYSTEMS

by H. J. MERK

Koninklijke/Shell-Laboratorium Amsterdam
(N.V. De Bataafse Petroleum Maatschappij), the Netherlands

Summary

In the literature concerning the phenomenological theory of heat and mass transfer in multicomponent systems various formulations of the macroscopic equations are found. In order to decide which formulations are correct, a more or less complete survey of the macroscopic equations is given. Since no disagreements exist concerning the ultimate formulation of the equation of motion, special attention is given to the diffusion equations and the thermal energy equation. The ultimate formulation of the latter equation given in the present paper differs in some details from that found in the literature, the difference being caused by the effect of the diffusing heat capacities and by the dependence of the enthalpy on the concentration. In order to find a proper driving force for the mass transfer, use is made of formulae taken from the thermodynamics of irreversible processes. It appears that for binary systems the barycentric description of the diffusion is the most suitable, especially when convection phenomena play an important role. For multicomponent systems it seems better to relate the diffusion fluxes to the activity. In this case Maxwell's diffusion laws are easily obtained, showing that relations, hitherto only derived in a first approximation for ideal gases, are generally valid for ideal as well as non-ideal systems. From the exact relations simplified descriptions of the diffusion may be derived. If it is, for instance, assumed that Maxwell's diffusion coefficients are all equal and that the system is ideal, then diffusion equations can be derived which are analogous to those for binary systems. In addition, a simplified version of the thermal energy equation is indicated, which differs somewhat from that given by Spalding and Emmons.

List of symbols

- a_i = activity of component i
 c_i = fractional mass concentration
 c_i^* = fractional number concentration

- C_{ij} = coefficient of diffusion resistance
 C_p = specific heat capacity of the system for constant pressure
 $C_{p,i}$ = partial specific heat capacity of component i for constant pressure
 C_p^* = molar heat capacity of the system for constant pressure
 $C_{p,i}^*$ = partial molar heat capacity of component i for constant pressure
 d_i = vector for binary systems defined by (70) and for multicomponent systems defined by (102)
 d_i^* = vector for binary systems defined by (77) and for multicomponent systems defined by (96)
 d_i^a = vector defined by (52)
 D_{ij} = binary diffusion coefficient
 D_i^T = thermal diffusion coefficient
 D_{ij}^a = multicomponent diffusion coefficient
 D_{ij}^m = Maxwell's diffusion coefficient
 e = specific internal energy of the system
 F_i = exterior force exerted on a unit mass of component i
 h = specific enthalpy of the system
 h_i = partial specific enthalpy of component i
 \mathbf{l} = unit tensor of second order
 J_i = barycentric mass flux of component i
 J_i^* = molar number flux of component i
 J_q = barycentric heat flux
 K_i = mass of component i created by chemical reactions per unit volume and unit time
 K_i^* = quantity being defined by (18)
 $l_{T,i}$ = partial latent heat of component i defined by (32)
 l_T = latent heat of the system defined by (35)
 Le = Lewis number
 m = mean molar mass of the system
 m_i = molar mass of component i
 n = total number of moles per unit volume
 n_i = number of moles of component i per unit volume
 N = number of components
 p = hydrostatic pressure
 q = reduced heat flux
 Q_p = heat of reaction for constant pressure, measured per unit time and unit volume
 R_A = molar gas constant of Avogadro
 t = time
 T = absolute temperature
 v = specific volume of the system
 v_i = partial specific volume of component i
 v = mass velocity
 v^* = number velocity
 v_i = velocity of component i
 V_i = diffusion velocity of component i

- V_i' = vector defined by (80)
 X_i = thermodynamic force
 Z = function defined by (47)
 α_p = pressure diffusion factor for binary systems
 $\alpha_{p,ij}$ = pressure diffusion factor for multicomponent systems
 α_T = thermal diffusion factor for binary systems
 $\alpha_{T,ij}$ = thermal diffusion factor for multicomponent systems
 β_{ij} = phenomenological coefficient
 η = coefficient of shear viscosity
 κ = coefficient of bulk viscosity
 λ = coefficient of heat conductivity
 μ_i = specific chemical potential of component i
 ρ = density of the system
 ρ_i = mass concentration of component i
 τ = viscous stress tensor
 Φ_η = dissipation function

Subscripts

- i, j = component
 k, l = summation indices

Superscripts

- $()^*$ = molar quantity
 $()^+$ = transposed tensor of second order

§ 1. *Introduction.* The calculation of transfer processes involving convection and molecular diffusion is based upon a system of partial differential equations and boundary conditions. The partial differential equations are called here the macroscopic equations and are derived from the laws of conservation of matter, momentum and energy. In these derivations no fundamental difficulties are encountered. However, the so-called thermodynamic fluxes (i.e. chemical reaction rates, mass or number fluxes of the components, heat flux, viscous stresses) introduced during the derivations have to be related to the thermodynamic forces. Although the means for finding these relations are well known nowadays, various proposals concerning the relations for the mass and number fluxes are found in the present literature. Investigation of the various relations proposed shows that they are not always consistent with each other. Moreover, the ultimate formulations of the diffusion equations and the thermal energy equation sometimes differ appreciably.

The choice of a proper description of diffusion and the driving force for the rate of mass transfer has caused much confusion and is

in fact a subtle one. Probably Nusselt¹⁾ was one of the first authors to investigate convective mass transfer in relation to an engineering application. Considering only mass transfer by ordinary diffusion, Nusselt¹⁾²⁾ remarked that under certain circumstances the differential equations and the boundary conditions for heat and mass transfer respectively are mathematically equivalent, so that these processes are similar. If this similarity holds, then the laws governing mass transfer may be derived from the laws governing heat transfer and vice versa. Schmidt³⁾ has formulated the similarity theory of heat and mass transfer for free convection. Nusselt¹⁾²⁾ and Schmidt³⁾ both developed their similarity relations on the assumption that the mass flux of a component caused by ordinary diffusion is proportional to the negative gradient of the mass concentration of the component considered. This means that these authors assumed that the diffusion potential of ordinary diffusion is given by the mass concentration. This assumption had already been introduced many years previously by Fick⁴⁾ and is sometimes called Fick's diffusion law. It is somewhat surprising that Nusselt should have introduced the mass concentration as the diffusion potential, since he mentions that for gases and vapours the partial pressure difference is the driving force in diffusion processes. Ackermann⁵⁾ tried to show that for simultaneous heat and mass transfer it is better to use the partial pressure as diffusion potential. This point of view has been accepted by several authors, see e.g. Eckert⁶⁾ and Jakob⁷⁾, although other authors, like Sherwood and Pigford⁸⁾, defined the number concentration as the diffusion potential.

Spalding⁹⁻¹²⁾ remarks that simultaneous heat and mass transfer may be described in a very convenient way if the fractional mass concentration is used as the diffusion potential. However, Spalding's derivations are not correct, since he did not interpret the barycentric description of the diffusion in the right manner. The formulation of the thermal energy equation given by Spalding is not correct either, since he did not account for the dependence of the enthalpy on the composition of the system or for the diffusion of heat capacities, the latter effect having already been mentioned by Ackermann⁵⁾. In calculating the burning rate of liquid fuel Emmons¹³⁾ also omitted to account for these effects.

The diffusion equation given by Berman¹⁴⁾ is not very suitable

for application to engineering problems, since it contains the velocity of the component considered and not the mass velocity occurring in the equation of motion. The thermal energy equation given by Kirkwood and Crawford¹⁵⁾ may be transformed further into a more suitable equation.

In recent years mass transfer in gases at high pressure has become very important for chemical engineering applications. The pressures are generally too high for assuming the gases to be ideal. Opfell and Sage¹⁶⁾ therefore proposed to use the fugacity as the diffusion potential. This proposal is not based upon exact derivations, however, but upon a conjectured extension of the formulae given by Chapman and Cowling¹⁷⁾ for ideal gases. It may be remarked that Onsager and Fuoss¹⁸⁾ and Jost¹⁹⁾ had already proposed introducing the fugacity or activity as the diffusion potential for non-ideal gases and liquids.

The various definitions of the diffusion potential lead to different definitions of the diffusion coefficients and mass transfer coefficients. It seems therefore worthwhile to discuss the correct formulation of the macroscopic equations and the thermodynamic fluxes occurring in these equations. For the derivation of the thermodynamic fluxes two general bases are available: the kinetic theory of matter and the thermodynamics of irreversible processes. Unfortunately the kinetic theory of liquids is not sufficiently advanced to be a reliable guide in the treatment of diffusion in liquids. Our considerations will therefore be based upon the theory of irreversible thermodynamics, since this theory appears to furnish a considerable amount of information for gases as well as for liquids. It may be remarked that Prigogine²⁰⁾ has shown that for gases the results obtained by the thermodynamics of irreversible processes agree with the results obtained in the so-called first approximation of the kinetic theory.

From the thermodynamics of irreversible processes no unique definitions of the diffusion potential and diffusion coefficients can be derived (see e.g. Ubbelohde²¹⁾ and Wirtz²²⁾). Because a more or less arbitrary choice of these quantities seems to be inevitable, we shall be guided by the following requirements: 1) the relations for the mass fluxes have to be as simple as possible, 2) the diffusion coefficients have to be defined in such a way that for ideal gases they agree with the usual definitions given in the kinetic theory. The

first-mentioned requirement leads us to define the activity as the diffusion potential for multicomponent systems, while for binary systems the most suitable diffusion potential is the fractional mass concentration. Moreover, it will be shown that relations, hitherto only derived in the first approximation of the kinetic theory of gases, may also be derived from the thermodynamics of irreversible processes. This means that these relations are more general than might be expected from their kinetic derivation.

§ 2. Laws of conservation.

a. Law of conservation of matter. Let us consider a system consisting of N components. The number density of the moles of component i is denoted by n_i and the molar mass of this component by m_i . Hence, the mass concentration of component i is given by

$$\rho_i = n_i m_i, \quad (i = 1, 2, \dots, N). \quad (1)$$

The statistical mean value of the molar velocity of component i measured with respect to a fixed reference system is represented by the vector \mathbf{v}_i . Now, the law of conservation of matter of component i yields

$$\frac{\partial \rho_i}{\partial t} = -\operatorname{div}(\rho_i \mathbf{v}_i) + K_i, \quad (2)$$

where K_i is the mass of component i produced per unit time and unit volume by chemical reactions. Since the system is assumed to be "closed", no matter is introduced into the system, so that we must have

$$\sum_{k=1}^N K_k = 0. \quad (3)$$

Summing in (2) over the index i and making use of (3), the well-known equation of continuity for closed systems is obtained, viz.

$$\frac{\partial \rho}{\partial t} = -\operatorname{div}(\rho \mathbf{v}), \quad (4)$$

where ρ is the total density of the system and \mathbf{v} the mass velocity; hence

$$\rho = \sum_{k=1}^N \rho_k, \quad (5)$$

$$\mathbf{v} = \sum_{k=1}^N c_k \mathbf{v}_k \quad \text{with} \quad c_i = \rho_i / \rho. \quad (6)$$

The quantity c_i represents the fractional mass concentration. The mass velocity \mathbf{v} may be interpreted as the velocity of the centre of mass of a volume element of the system. This velocity may be used to define the barycentric derivative according to

$$\frac{D}{Dt} \equiv \frac{\partial}{\partial t} + \mathbf{v} \cdot \operatorname{grad}. \quad (7)$$

Using (7), the equation of continuity may also be written as

$$\frac{D\rho}{Dt} + \rho \operatorname{div} \mathbf{v} = 0. \quad (4')$$

Furthermore, we introduce the mass flux of component i :

$$\mathbf{J}_i = \rho_i (\mathbf{v}_i - \mathbf{v}). \quad (8)$$

From (6) and (8) we get

$$\sum_{k=1}^N \mathbf{J}_k = 0. \quad (9)$$

Making use of (4'), (7) and (8), equation (2) may be written as

$$\rho \frac{Dc_i}{Dt} = -\operatorname{div} \mathbf{J}_i + K_i. \quad (10)$$

In (8) the mass fluxes are described with respect to the mass velocity. We shall therefore call the description of the diffusion by means of (8) and (10) the barycentric description (see also de Groot²³), pages 108–111). It appears that the barycentric description of the diffusion is the most useful for the treatment of convective mass transfer problems. In the literature, however, other descriptions of the diffusion are also given. One which is often applied is the so-called molar description, which may be derived as follows: we first introduce the number velocity \mathbf{v}^* and the fractional number or molar density c_i^* defined by

$$\mathbf{v}^* = \sum_{k=1}^N c_k^* \mathbf{v}_k, \quad c_i^* = n_i/n, \quad n = \sum_{k=1}^N n_k. \quad (11)$$

Further we introduce the number flux defined by

$$\mathbf{J}_i^* = n_i (\mathbf{v}_i - \mathbf{v}^*). \quad (12)$$

From (11) and (12) we obtain in analogy to (9)

$$\sum_{k=1}^N \mathbf{J}_k^* = 0. \quad (13)$$

Dividing (2) by m_i , we get

$$\frac{\partial n_i}{\partial t} = -\operatorname{div}(n_i \mathbf{v}_i) + K_i/m_i. \quad (14)$$

Summation with respect to the index i leads to

$$\frac{\partial n}{\partial t} = -\operatorname{div}(n\mathbf{v}^*) + \sum_{k=1}^N K_k/m_k. \quad (15)$$

In analogy to the barycentric derivative we introduce now the molar derivative according to

$$\frac{D^*}{Dt} \equiv \frac{\partial}{\partial t} + \mathbf{v}^* \cdot \operatorname{grad} = \frac{D}{Dt} + (\mathbf{v}^* - \mathbf{v}) \cdot \operatorname{grad}. \quad (16)$$

From (12), (14), (15) and (16) we obtain

$$n \frac{D^* c_i^*}{Dt} = -\operatorname{div} \mathbf{J}_i^* + K_i^*, \quad (17)$$

where

$$K_i^* = \frac{K_i}{m_i} - c_i^* \sum_{k=1}^N \frac{K_k}{m_k}. \quad (18)$$

(12) and (17) represent the molar description of the diffusion. In the following discussions we restrict ourselves to these barycentric and molar descriptions.

b. Law of conservation of momentum. The law of conservation of momentum leads to the following vectorial equation:

$$\rho \frac{D\mathbf{v}}{Dt} = -\operatorname{grad} p + \sum_{k=1}^N \rho_k \mathbf{F}_k + \operatorname{Div} \tau, \quad (19)$$

where p is the hydrostatic pressure, \mathbf{F}_i the exterior force exerted per unit mass upon component i and τ the viscous stress tensor^{*}). In a continuous and isotropic system the relations expressing the

^{*}) In equation (19) and the subsequent equations and formulae use is made of Milne's tensor notation, see e.g. Chapman and Cowling¹⁷⁾ or Rosenfeld²⁴⁾.

viscous stresses in terms of the thermodynamic forces are well-known; they can be found in various text books on aerodynamics, thermodynamics of irreversible processes and kinetic theory of matter. These relations read

$$\tau = \eta [\operatorname{Grad} \mathbf{v} + (\operatorname{Grad} \mathbf{v})^+] + (\kappa - \frac{2}{3}\eta)(\operatorname{div} \mathbf{v}) \mathbf{l}, \quad (20)$$

where η is the coefficient of shear viscosity, κ the coefficient of bulk viscosity and \mathbf{l} the unit tensor. From the kinetic theory of gases it follows that for ideal gases $\kappa = 0$, but for liquids it is not always permissible to neglect κ . If chemical reactions occur in the system, then according to the thermodynamics of irreversible processes and Curie's theorem the second order tensor τ may also depend on the scalar chemical affinities. Cross-effects between viscous stresses and chemical reactions do not seem as yet to be confirmed by experiments and are, therefore, generally neglected.

Substituting (20) in (19), we obtain

$$\rho \frac{D\mathbf{v}}{Dt} = -\operatorname{grad} p + \sum_{k=1}^N \rho_k \mathbf{F}_k + \operatorname{Div}(\eta \operatorname{Grad} \mathbf{v}) + \operatorname{grad}[(\kappa + \frac{1}{3}\eta) \operatorname{div} \mathbf{v}] + (\operatorname{grad} \eta) \cdot [(\operatorname{Grad} \mathbf{v})^+ - \mathbf{l} \operatorname{div} \mathbf{v}]. \quad (21)$$

For constant values of η and κ the last equation becomes

$$\rho \frac{D\mathbf{v}}{Dt} = -\operatorname{grad} p + \sum_{k=1}^N \rho_k \mathbf{F}_k + \eta(\Delta \mathbf{v} + \frac{1}{3} \operatorname{grad} \operatorname{div} \mathbf{v}) + \kappa \operatorname{grad} \operatorname{div} \mathbf{v}. \quad (22)$$

For $\kappa = 0$ equation (22) is identical with the well-known equation of motion of Navier-Stokes. It may be stressed that in the usual formulation of the equation of motion only mass velocities occur and no number velocities.

c. Law of conservation of energy. Application of the law of conservation of energy to a volume element moving with the mass velocity yields the following energy equation:

$$\rho \frac{D}{Dt} (e + \frac{1}{2} \mathbf{v}^2) = -\operatorname{div} \mathbf{J}_q - \operatorname{div}(p\mathbf{v}) + \sum_{k=1}^N \rho_k \mathbf{v}_k \cdot \mathbf{F}_k + \operatorname{div}(\tau \cdot \mathbf{v}), \quad (23)$$

where e is the specific internal energy of the system and \mathbf{J}_q the

(barycentric) heat flux. Eliminating the barycentric kinetic energy from (23) by means of (19), we obtain

$$\rho \frac{De}{Dt} = -\operatorname{div} \mathbf{J}_q - p \operatorname{div} \mathbf{v} + \sum_{k=1}^N \mathbf{J}_k \cdot \mathbf{F}_k + \Phi_\eta, \quad (24)$$

where Φ_η is the heat developed by the viscous stresses; hence:

$$\Phi_\eta = \tau : \operatorname{Grad} \mathbf{v}. \quad (25)$$

Equation (24) no longer contains the barycentric kinetic energy and will therefore be called the thermal energy equation. For the calculation of convective transport processes it is convenient to transform (24). For that purpose we introduce the reduced heat flux \mathbf{q} defined by Prigogine according to

$$\mathbf{J}_q = \mathbf{q} + \sum_{k=1}^N h_k \mathbf{J}_k, \quad (26)$$

where h_i is the partial specific enthalpy of component i (*). From (4') it follows that

$$-p \operatorname{div} \mathbf{v} = \frac{p}{\rho} \frac{D\rho}{Dt} = \frac{Dp}{Dt} - \rho \frac{D}{Dt} \frac{p}{\rho}. \quad (27)$$

Substituting (26) and (27) in (24), we obtain

$$\rho \frac{Dh}{Dt} + \operatorname{div} \left(\sum_{k=1}^N h_k \mathbf{J}_k \right) = -\operatorname{div} \mathbf{q} + \frac{Dp}{Dt} + \sum_{k=1}^N \mathbf{J}_k \cdot \mathbf{F}_k + \Phi_\eta, \quad (28)$$

where h is the specific enthalpy of the system; hence

$$h = e + p/\rho = \sum_{k=1}^N c_k h_k. \quad (29)$$

In some cases (28) can be applied to the calculation of convective transfer processes, but in others it is often convenient to express the enthalpy h in terms of the temperature T . This has to be done carefully, because at this point many derivations given in the literature are not correct. First of all we note that from (29) it follows that

$$dh = \sum_{k=1}^N h_k dc_k + \sum_{k=1}^N c_k dh_k. \quad (30)$$

*) As is done in most textbooks on thermodynamics, Prigogine and Defay²⁵⁾ introduce partial molar quantities, but for our purpose it is more convenient to introduce partial specific quantities.

We now assume that h_i depends explicitly only on p , T and the composition of the system. (In the thermodynamics of irreversible processes this is a conventional assumption.) Hence, we get

$$dh_i = \sum_{k=1}^N \left(\frac{\partial h_i}{\partial \rho_k} \right)_{p,T} d\rho_k + C_{p,i} dT + (l_{T,i} + v_i) dp, \quad (31)$$

where v_i is the partial specific volume of component i and

$$C_{p,i} = \left(\frac{\partial h_i}{\partial T} \right)_{p,\rho_k}, \quad l_{T,i} = \left(\frac{\partial h_i}{\partial p} \right)_{T,\rho_k} - v_i. \quad (32)$$

$C_{p,i}$ represents the partial specific heat of component i for constant pressure and composition, while $l_{T,i}$ is a sort of partial latent heat. Because the enthalpy is an extensive thermodynamic variable, we have (see e.g. Prigogine and Defay²⁵⁾)

$$\sum_{k=1}^N \rho_k \left(\frac{\partial h_k}{\partial \rho_i} \right)_{p,T} = 0. \quad (33)$$

From (30), (31) and (33) it follows that

$$dh = \sum_{k=1}^N h_k dc_k + C_p dT + (l_T + v) dp, \quad (34)$$

where

$$C_p = \sum_{k=1}^N c_k C_{p,k}, \quad l_T = \sum_{k=1}^N c_k l_{T,k}, \quad v = 1/\rho = \sum_{k=1}^N c_k v_k. \quad (35)$$

With the use of (10) and (34), the thermal energy equation (28) may be written as

$$\rho C_p \frac{DT}{Dt} + \sum_{k=1}^N \mathbf{J}_k \cdot \operatorname{grad} h_k = -\operatorname{div} \mathbf{q} - \rho l_T \frac{Dp}{Dt} + Q_p + \sum_{k=1}^N \mathbf{J}_k \cdot \mathbf{F}_k + \Phi_\eta, \quad (36)$$

where Q_p is the heat developed for constant pressure by the chemical reactions per unit time and unit volume; hence

$$Q_p = - \sum_{k=1}^N h_k K_k. \quad (37)$$

The thermal energy equation (36) is often applied in the literature, but mostly the sum at the left-hand side is left out. Furthermore, we note that Q_p occurs only in (36) and not in (28). Spalding¹⁰⁾ and Emmons¹³⁾ have given an equation analogous to (28) con-

taining the heat of reaction. These authors derived this equation from (36) (without the sum at its left hand side) by writing $dh = C_p dT$; i.e. they did not account for the concentration dependence of the enthalpy.

For ideal systems (36) may be somewhat simplified. In that case we have

$$v_i = 1/(nm_i) \text{ and } p = nR_A T = R_A T / (m_i v_i), \quad (38)$$

R_A being the universal constant of Avogadro. For ideal gases we have furthermore

$$dh_i = C_{p,i} dT, \quad (39)$$

where $C_{p,i}$ is a constant. From (32) and (39) follows

$$l_{T,i} = -v_i.$$

By means of these relations (36) becomes

$$\rho C_p \frac{DT}{Dt} + \sum_{k=1}^N C_{p,k} \mathbf{J}_k \cdot \text{grad } T = -\text{div } \mathbf{q} + \frac{Dp}{Dt} + Q_p + \sum_{k=1}^N \mathbf{J}_k \cdot \mathbf{F}_k + \Phi_\eta. \quad (40)$$

The existence of the sum at the left-hand side of (40) has already been mentioned by Ackermann⁵⁾. This author called this sum the "effect of the diffusing heat capacities". Since Ackermann's publication this effect has been ignored in the literature, probably because Ackermann's derivation was not exact.

If the molar heats of the components are all equal, then the left-hand side of (40) may be transformed further. Writing

$$C_{p,i}^* = m_i C_{p,i} = C_p^* \text{ for all } i,$$

we obtain from (6), (8), (11) and (35)

$$\sum_{k=1}^N C_{p,k} \mathbf{J}_k = n C_p^* (\mathbf{v}^* - \mathbf{v}) = \rho C_p (\mathbf{v}^* - \mathbf{v}).$$

Making use of this relation and (16), equation (40) becomes

$$\rho C_p \frac{D^* T}{Dt} = -\text{div } \mathbf{q} + \frac{Dp}{Dt} + \sum_{k=1}^N \mathbf{J}_k \cdot \mathbf{F}_k + Q_p + \Phi_\eta. \quad (41)$$

The left-hand side of this equation is analogous to that of (17). From its derivation it follows that (41) is only valid under restrictive conditions. We remark further that (41) may be obtained directly

from the energy equations given by Chapman and Cowling¹⁷⁾. This must be so since these authors consider ideal gases for which $C_{p,i}^* = \frac{5}{2} R_A$ for all values of i . This demonstrates that equations derived from the conventional kinetic theory of gases have only restricted validity.

§ 3. *Vectorial transport processes.* In the macroscopic equations derived in the foregoing section we have to relate the diffusion fluxes and the heat flux to the thermodynamic forces. For that purpose we use the results given by the thermodynamics of irreversible processes, which may be found in text books and articles on this subject (see e.g. de Groot²³⁾ or Hirschfelder, Curtiss and Bird²⁶⁾, pages 694-720). According to the thermodynamics of irreversible processes we have

$$\left. \begin{aligned} \mathbf{q} &= \beta_{00} \mathbf{X}_0 + \sum_{k=1}^N \beta_{0k} \mathbf{X}_k, & (a) \\ \mathbf{J}_i &= \beta_{i0} \mathbf{X}_0 + \sum_{k=1}^N \beta_{ik} \mathbf{X}_k, & (b) \end{aligned} \right\} \quad (42)$$

where the coefficients β_{ij} ($i, j = 0, 1, 2, \dots, N$) are the so-called phenomenological coefficients, while the vectors \mathbf{X}_i are the thermodynamic forces which are given by

$$\left. \begin{aligned} \mathbf{X}_0 &= -(\text{grad } T)/T, & (a) \\ \mathbf{X}_i &= -[T \text{ grad } (\mu_i/T) + h_i (\text{grad } T)/T - \mathbf{F}_i], & (b) \end{aligned} \right\} \quad (43)$$

μ_i being the partial specific chemical potential of component i . For the coefficients β_{ij} the following relations exist:

$$\beta_{ij} = \beta_{ji}, \quad (i, j = 0, 1, 2, \dots, N) \quad (44)$$

and

$$\sum_{k=1}^N \beta_{ik} = 0, \quad (i = 0, 1, 2, \dots, N). \quad (45)$$

Relations (44) are Onsager's reciprocal relations, while (45) are derived from (9) and from the fact that the production of entropy by heat conduction and diffusion has to be positive. From (44) and (45) it follows that there are $\frac{1}{2}N(N+1)$ independent phenomenological coefficients.

Introducing the activity a_i of component i , the specific chemical potential of that component may be written as (see e.g. Prigogine

and Defray²⁵), page 153)

$$\mu_i = \mu_i^0(T, p) + \frac{R_A T}{m_i} \ln a_i. \quad (46)$$

For ideal gases we have $a_i = c_i^*$, but for non-ideal systems a_i is a thermodynamic function depending on p , T and the composition of the system. The thermal equation of state is written as

$$p = nR_A T Z, \quad (47)$$

where Z generally depends on p , T and the composition of the system; for ideal systems $Z = 1$, while for small deviations from the ideal state Z may be expressed in terms of the virial coefficients.

From (46) it follows that μ_i depends only on the composition by way of a_i , so that

$$T d\left(\frac{\mu_i}{T}\right) = \frac{R_A T}{m_i} \frac{(da_i)_{p,T}}{a_i} + \left(\frac{\partial \mu_i}{\partial p}\right)_{T, c_i^*} dp + T \left(\frac{\partial \mu_i/T}{\partial T}\right)_{p, c_i^*} dT$$

or, introducing the well-known thermodynamic formulae for the partial derivatives of the chemical potential,

$$T d\left(\frac{\mu_i}{T}\right) = \frac{R_A T}{m_i} \frac{(da_i)_{p,T}}{a_i} + v_i dp - h_i \frac{dT}{T}. \quad (48)$$

From (42b), (43) and (48) we obtain

$$\mathbf{J}_i = - \sum_{k=1}^k \frac{\beta_{ik}}{m_k} \left[R_A T \frac{(\text{grad } a_k)_{p,T}}{a_k} + m_k v_k \text{grad } p - m_k \mathbf{F}_k \right] - D_i^T \frac{\text{grad } T}{T}, \quad (49)$$

where the thermal (multicomponent) diffusion coefficients are introduced according to

$$D_i^T = \beta_{i0}, \quad (i = 1, 2, \dots, N). \quad (50)$$

From (44), (45) and (50) it follows that

$$\sum_{k=1}^N D_k^T = 0, \quad (51)$$

so that there are apparently $N - 1$ independent thermal diffusion coefficients. In order to write (49) in a more convenient manner, we introduce

$$\mathbf{d}_i^a = \frac{c_i^*}{a_i} (\text{grad } a_i)_{p,T} + c_i Z (\rho v_i - 1) \frac{\text{grad } p}{p} - \frac{c_i Z}{p} (\rho \mathbf{F}_i - \sum_{k=1}^N \rho_k \mathbf{F}_k). \quad (52)$$

This definition is chosen such that

$$\sum_{k=1}^N \mathbf{d}_k^a = 0. \quad (53)$$

It is easily seen that after summation the terms on the right-hand side of (52) cancel out, except for the first term, which disappears by virtue of the relation of Gibbs-Duhem. This relation may be written as

$$\sum_{k=1}^N n_k m_k (d\mu_k)_{p,T} = 0$$

or with (46)

$$\sum_{k=1}^N \frac{n_k}{a_k} (da_k)_{p,T} = 0 \quad \text{or} \quad \sum_{k=1}^N \frac{c_k^*}{a_k} (da_k)_{p,T} = 0. \quad (54)$$

From (54) relation (53) follows directly. From the definitions of the fractional mass and number concentrations given by (6) and (11) respectively it follows that

$$c_i = m_i c_i^* / m, \quad (55)$$

where m is the mean molar mass of the system given by

$$m = \rho / n = \sum_{k=1}^N c_k^* m_k = \left(\sum_{k=1}^N c_k / m_k \right)^{-1}. \quad (56)$$

Making use of (47), (55) and (56), we derive from (49) and (52):

$$\mathbf{J}_i = - \frac{p}{Z} \sum_{k=1}^N \frac{\beta_{ik}}{\rho_k} \mathbf{d}_k^a - D_i^T \frac{\text{grad } T}{T}. \quad (57)$$

In this relation the diffusion by thermal effects is separated from the diffusion by mechanical effects, the latter being represented by the vectors \mathbf{d}_i^a . The mechanical diffusion consists of three parts, namely ordinary diffusion (terms with $\text{grad } a_i$), pressure or baric diffusion (terms with $\text{grad } p$) and diffusion by external forces. The multicomponent diffusion coefficients are now defined by

$$\mathbf{J}_i = + \frac{n^2}{\rho} \sum_{k=1}^N \sum_{k \neq i} m_i m_k D_{ik}^a \mathbf{d}_k^a - D_i^T \frac{\text{grad } T}{T}. \quad (58)$$

From (53), (57) and (58) it follows that

$$D_{ij}^a = - \frac{p \rho}{n^2 m_i m_j Z} \left(\frac{\beta_{ij}}{\rho_j} - \frac{\beta_{ii}}{\rho_i} \right), \quad (59)$$

note: $v_k \neq \frac{1}{\rho_k}!$

$\rho = \sum_{k=1}^N \rho_k$

$\rho_i v_i = \frac{\rho_i}{\rho} = \frac{h_i}{h}$

so that

$$D_{ii}^a = 0. \quad (60)$$

Apparently we have introduced $N(N-1)$ multicomponent diffusion coefficients. These coefficients, however, are not independent. In order to find the relations between them, (59) is solved for β_{ij} . The result reads

$$\beta_{ij} = \frac{n^2 n_j m_i m_j}{p \rho^2} Z (-\rho m_j D_{ij}^a + \sum_{k=1}^N \rho_k m_k D_{ik}^a). \quad (61)$$

From (44) and (61) it follows that

$$\rho(\rho_j D_{ij}^a - \rho_i D_{ji}^a) = \sum_{k=1}^N \rho_k m_k (n_j D_{ik}^a - n_i D_{jk}^a), \quad (62)$$

representing $\frac{1}{2}N(N-1)$ relations, so that we have $\frac{1}{2}N(N-1)$ independent multicomponent diffusion coefficients. From (61) other relations may also be obtained. Combining (61) with (44) and (45), we get

$$m_i \sum_{k=1}^N m_k D_{ki}^a = m_j \sum_{k=1}^N m_k D_{kj}^a \left(= \frac{p \rho}{Z n^2} \sum_{k=1}^N \frac{\beta_{kk}}{\rho_k} \right). \quad (63)$$

This relation may also be obtained from (62). Hirschfelder, Curtiss and Bird²⁶ have derived (63) from the kinetic theory of gases, so that this relation would appear to be valid only in the first-order approximation for ideal gases. From its derivation above, however, it follows that (63) is generally valid for ideal and non-ideal systems, provided that the activity is considered as the diffusion potential.

Our further considerations are based upon (58), while relations for the reduced heat flux are given in § 4 for binary systems and in § 5 for multicomponent systems.

§ 4. *Vectorial transport processes in binary systems.* Let us now consider binary systems with the components i and j . From (53) and (58) we obtain

$$\mathbf{J}_i = - \frac{n^2}{\rho} m_i m_k D_{ij}^a \mathbf{d}_i^a - D_i^T \frac{\text{grad } T}{T}. \quad (64)$$

For binary systems (52) may be written as

$$\mathbf{d}_i^a = \frac{c_i^*}{a_i} (\text{grad } a_i)_{p,T} + \rho c_i c_j Z (v_i - v_j) \left[\frac{\text{grad } p}{p} - \frac{\mathbf{F}_i - \mathbf{F}_j}{p(v_i - v_j)} \right]. \quad (65)$$

From (55) and (56) we obtain

$$dc_k^* = \frac{m^2}{m_i m_j} dc_k, \quad (k = i, j). \quad (66)$$

Since $c_i^* + c_j^* = 1$, we may consider a_i as a function of p, T and c_i^* . In (65) the gradient of a_i has to be calculated for constant p and T , so that

$$\frac{c_i}{a_i} (\text{grad } a_i)_{p,T} = \left(\frac{\partial \ln a_i}{\partial \ln c_i^*} \right)_{p,T} \text{grad } c_i^* = \frac{m^2}{m_i m_j} \left(\frac{\partial \ln a_i}{\partial \ln c_i^*} \right)_{p,T} \text{grad } c_i, \quad (67)$$

where (55) and (66) have also been used. Combining (64), (65) and (67), we obtain

$$\mathbf{J}_i = - \rho \mathcal{D}_{ij} \mathbf{d}_i - D_i^T \frac{\text{grad } T}{T}, \quad (68)$$

where

$$\mathcal{D}_{ij} = \left(\frac{\partial \ln a_i}{\partial \ln c_i^*} \right)_{p,T} D_{ij}^a = - \frac{p \beta_{ij}}{n^2 m_i m_j c_i c_j Z} \left(\frac{\partial \ln a_i}{\partial \ln c_i^*} \right)_{p,T} \quad (69)$$

and

$$\mathbf{d}_i = \text{grad } c_i + \alpha_p c_i c_j \left[\frac{\text{grad } p}{p} - \frac{\mathbf{F}_i - \mathbf{F}_j}{p(v_i - v_j)} \right], \quad (70)$$

α_p being defined by

$$\alpha_p = \frac{\rho(v_i - v_j) m_i m_j Z}{m^2} \left| \left(\frac{\partial \ln a_i}{\partial \ln c_i^*} \right)_{p,T} \right|. \quad (71)$$

α_p may be called the pressure diffusion factor; for ideal systems this factor becomes

$$\alpha_p = (m_j - m_i)/m, \quad (72)$$

showing that α_p depends on the composition of the system by way of m . The pressure diffusion factor is analogous to the thermal diffusion factor, the latter being defined by

$$D_i^T / (\rho \mathcal{D}_{ij}) = m_i m_j c_i^* c_j^* \alpha_T / m^2 = c_i c_j \alpha_T. \quad (73)$$

Introduction of α_T in (68) leads to

$$\mathbf{J}_i = - \rho \mathcal{D}_{ij} \left(\mathbf{d}_i + \alpha_T c_i c_j \frac{\text{grad } T}{T} \right). \quad (74)$$

It should be noted that Green²⁷) in dealing with liquids also introduced pressure diffusion coefficients. The definition of the binary coefficient of ordinary diffusion is chosen such that for ideal systems it agrees with that introduced by Chapman and Cowling¹⁷) and Hirschfelder, Curtiss and Bird²⁶). The definition of the thermal diffusion coefficient differs from that given by Chapman and Cowling, but agrees with the definition given by Hirschfelder, Curtiss and Bird.

For the barycentric description of the diffusion (74) represents a useful relation. Substitution of (74) in (10) yields a differential equation for c_i , the barycentric diffusion equation. For the molar description of the diffusion (74) is less adequate, since it would then be necessary to relate the mass concentration to the number concentration. We shall therefore now derive a relation for the diffusion flux more suitable for the molar description of the diffusion. For that purpose we derive from (8), (12) and (55) the following relation:

$$\mathbf{J}_i^* = n_i n_j (\mathbf{v}_i - \mathbf{v}_j) / n = nm^2 \mathbf{J}_i / (\rho m_i m_j). \quad (75)$$

After a simple calculation we obtain from (55), (66), (74) and (75)

$$\mathbf{d}_i^* = -n D_{ij} \mathbf{d}_i^* + \alpha_T c_i^* c_j^* \text{grad } T/T, \quad (76)$$

where

$$\mathbf{d}_i^* = \text{grad } c_i^* + \alpha_p c_i^* c_j^* \left[\frac{\text{grad } p}{p} - \frac{\mathbf{F}_i - \mathbf{F}_j}{p(v_i - v_j)} \right]. \quad (77)$$

Substitution of (76) in (17) now yields a differential equation for c_i^* , the molar diffusion equation. We may call (74) Fick's barycentric diffusion law and (76) Fick's molar diffusion law.

From the formulae derived in this section it appears that in the barycentric description of the diffusion the fractional mass concentration is the most useful potential of the ordinary diffusion, but in the molar description of the diffusion it seems more convenient to define the fractional number concentration as the diffusion potential. In the latter case we may also introduce p_i/p as the diffusion potential, since the partial pressure p_i may be defined by $p_i = c_i^* p$ (see e.g. Prigogine and Defay²⁵). The various proposals concerning the diffusion potential mentioned in § 1 may therefore be right, provided that they are consistent with the chosen description of the diffusion. Much confusion, however, has been

caused by the fact that several authors did not account for the differences in the various descriptions of the diffusion.

For the calculation of convective transfer phenomena the barycentric description of the diffusion has a formal advantage. If this description is chosen, then the macroscopic equations contain only mass velocities, while in the molar description of the diffusion the equation of motion contains mass velocities and the diffusion equation number velocities. If the difference between the mass and number velocities is overlooked, the results are only valid when all the components of the system have the same molar mass.

The physical results have, of course, to be independent of the chosen description of the diffusion, so that the advantage of the barycentric description can only be formal. Spalding¹⁰) remarked that the barycentric description of the diffusion yields better results than the molar description. This cannot be true if both descriptions are applied in the correct manner. The differences put forward by Spalding are caused by the fact that it makes a difference whether the fluid properties are assumed to be constant in the barycentric or in the molar description. In the barycentric description Spalding¹⁰) puts $\rho = \text{constant}$, for example, while in the molar description Sherwood and Pigford⁸) put $n = \text{constant}$, etc. It may happen that the former approximation yields better results than the latter, but this can only be proved experimentally or theoretically when it is known how the fluid properties depend on p , T and the composition of the fluid. For many gases the fluid properties have been calculated (see e.g. Hirschfelder, Bird, and Spatz²⁸)²⁹), but investigation of the fluid properties is beyond the scope of this paper. In taking the barycentric to be the most suitable description of the diffusion, our choice is guided solely by the formal advantage it displays, especially when convection phenomena play an important role.

A relation for the reduced heat flux is easily derived from (42) and (43). Making use also of (44) and (45), we get

$$\mathbf{q} = -\lambda \text{grad } T + p(v_i - v_j) \alpha_T \mathbf{J}_i / \alpha_p, \quad (78)$$

where λ is the thermal conductivity given by

$$\lambda = \frac{\beta_{00} \beta_{ii} - \beta_{0i}^2}{\beta_{ii} T}.$$

The second term at the right-hand side of (78) represents the Dufour effect. For gases this effect is of the same order of magnitude as the Soret effect (effect of the thermal diffusion), while for liquids the Dufour effect is mostly negligible. (For gases, Smith³⁰) accounts only for the Soret effect, but not for the Dufour effect. In so doing he apparently does not make a consistent approximation).

§ 5. *Maxwell's diffusion laws for multicomponent systems.* For multicomponent systems it is not in general possible to derive relations for the diffusion fluxes containing the gradient of one component only. In many investigations the mass fluxes given by (58) are not completely adequate and Maxwell's description of the diffusion is more attractive. We shall now show how Maxwell's description can be derived in a straightforward manner from (58). For that purpose we introduce the diffusion velocity

$$\mathbf{V}_i = \mathbf{v}_i - \mathbf{v}. \quad (79)$$

For a convenient notation we further introduce

$$\mathbf{V}_i' = \mathbf{V}_i + \frac{D_i^T}{\rho_i} \frac{\text{grad } T}{T}. \quad (80)$$

From (8), (58) and (80) we obtain

$$c_i^* c_j^* \mathbf{V}_i' = \frac{n_j}{\rho} \sum_{k=1}^N m_k D_{ik}^a \mathbf{d}_k^a. \quad (81)$$

We now introduce the coefficients of diffusion resistance C_{ij} and derive from (81)

$$\begin{aligned} \sum_{k \neq i} C_{ik} c_i^* c_k^* (\mathbf{V}_k' - \mathbf{V}_i') &= \\ &= \frac{1}{\rho} \sum_{k \neq i} \sum_{l \neq k} C_{ik} (n_l m_l D_{kl}^a - n_k m_l D_{il}^a + n_k m_k D_{ik}^a) \mathbf{d}_l^a. \end{aligned} \quad (82)$$

The coefficients C_{ij} are determined in such a way that the following relations are satisfied

$$\sum_{k=1}^N C_{ik} (n_l m_l D_{kj}^a - n_k m_j D_{ij}^a + n_k m_k D_{ik}^a) = \rho \delta_{ij}. \quad (83)$$

In the sum at the left-hand side the terms with $k = i$ cancel because

of (60), if it is assumed that C_{ii} is finite. Substitution of (83) in (82) yields

$$\mathbf{d}_i^a = \sum_{k=1}^N C_{ik} c_i^* c_k^* (\mathbf{V}_k' - \mathbf{V}_i'). \quad (84)$$

These relations may be considered as Maxwell's diffusion laws, since Maxwell³¹) formulated these laws in a form analogous to (84). The reciprocal values of the coefficients of diffusion resistance may be called Maxwell's diffusion coefficients

$$D_{ij}^m = 1/C_{ij} \text{ for } i \neq j. \quad (85)$$

Curtiss and Hirschfelder³²) have shown that for ideal gases in a first approximation Maxwell's diffusion coefficients are equal to the binary diffusion coefficients; hence

$$D_{ij}^m \approx D_{ij} \text{ for ideal gases.} \quad (86)$$

Because the binary diffusion coefficients are mostly better known than the multicomponent diffusion coefficients, (86) is a very important relation, which cannot be derived from the thermodynamics of irreversible processes.

By means of (80) and (85) Maxwell's diffusion laws (84) may be written as

$$\sum_{k \neq i} \frac{c_i^* c_k^*}{D_{ik}^m} (\mathbf{V}_k - \mathbf{V}_i) = \mathbf{d}_i^a - \frac{\text{grad } T}{T} \sum_{k \neq i} \frac{c_i^* c_k^*}{D_{ik}^m} \left(\frac{D_k^T}{\rho_k} - \frac{D_i^T}{\rho_i} \right). \quad (87)$$

For ideal gases (87) is equal to the equations derived by Curtiss and Hirschfelder³²). If no exterior forces are present and if pressure and thermal diffusion are neglected, it follows from (52) and (87) that

$$\text{grad } a_i + a_i \sum_{k \neq i} \frac{c_k^*}{D_{ik}^m} (\mathbf{V}_i - \mathbf{V}_k) = 0. \quad (88)$$

These equations should be equivalent to those given by Opfell and Sage¹⁶). This is not the case, so that the more or less conjectural diffusion laws proposed by Opfell and Sage are not correct in all their details.

We shall now show that for ideal gases the diffusion coefficients introduced above are indeed the same as those introduced by Curtiss and Hirschfelder³²) and Hirschfelder, Curtiss and

Bird²⁶). (83) represents N^2 equations for the $N(N - 1)$ coefficients C_{ij} . Since the equations (83) are not independent, it is easy to derive $N(N - 1)$ equations from (83). Putting $j = i$ in (83) and subtracting (83), when $i \neq j$, from the equation obtained, we get

$$\sum_{k \neq i} C_{ik}(n_k m_j D_{ij}^a - n_i m_j D_{kj}^a + n_i m_i D_{ki}^a) = \rho(1 - \delta_{ij}). \quad (89)$$

Since for $i = j$ (89) is identically satisfied, we have indeed obtained $N(N - 1)$ equations. For ideal gases Curtiss and Hirschfelder³²) have shown that (89) exists at least to a first approximation. Since for ideal gases the multicomponent diffusion coefficients are the same as those introduced by Curtiss and Hirschfelder, (63), (85) and (89) show that Maxwell's diffusion coefficients are also equivalent to these and thus (86) is indeed valid.

From the derivation of (89) given above it appears that this relation is generally valid for ideal as well as non-ideal systems. Putting $j = h$ in (89) and subtracting (89) from the obtained equation, we get

$$\sum_{k \neq i} C_{ik}(n_i m_h D_{kh}^a - n_i m_j D_{kj}^a - n_k m_h D_{ih}^a + n_k m_j D_{ij}^a) = \rho(\delta_{ih} - \delta_{ij}). \quad (90)$$

These equations have been given by Hirschfelder, Curtiss and Bird²⁶) as a first approximation for ideal gases. Making use of (63), we may solve (90) for D_{ij}^a and obtain relations which are also found in the book of Hirschfelder, Curtiss and Bird, so that for further details we refer the reader to these authors. It is only stressed that from the thermodynamics of irreversible processes it follows that the relevant relations are exact and not approximative.

In § 3 we introduced $\frac{1}{2}N(N - 1)$ independent multicomponent diffusion coefficients. It is to be expected that we shall also have the same number of independent Maxwell diffusion coefficients. From (89) or (90) it seems to follow that there are $N(N - 1)$ coefficients C_{ij} . However, (89) and (90) do not represent independent equations either, but have to be combined with (63). We are therefore left indeed with $\frac{1}{2}N(N - 1)$ independent equations. The relations (85) and (86) suggest that at least for ideal gases the coefficients C_{ij} and D_{ij}^m are symmetrical because the binary diffusion coefficients are symmetrical. If this symmetry holds also for the general case, then the number of independent coefficients C_{ij} and corresponding Maxwell diffusion coefficients should be $\frac{1}{2}N(N - 1)$. However, we

have not succeeded in proving the symmetry for the general case, although there is strong evidence for it. From (63) and (90) it is, for instance, easy to prove that for ternary systems the symmetry of C_{ij} has to exist for ideal as well as for non-ideal systems.

Finally the reduced heat flux for multicomponent systems may be calculated from (42a), (43), (45), (48) and (52). The result is given by

$$\mathbf{q} = -\beta_{00} \frac{\text{grad } T}{T} - \frac{p}{Z} \sum_{k=1}^N \frac{\beta_{0k}}{\rho_k} \mathbf{d}_k^a.$$

Making use of (44), (50), (85) and (87), the last relation becomes

$$\mathbf{q} = -\lambda \text{grad } T + \frac{R_A T}{n} \sum_{k,l} \frac{n_l}{D_{kl}^m} \frac{D_k^T}{m_k} (\mathbf{V}_k - \mathbf{V}_l), \quad (91)$$

where λ is given by

$$\lambda = \frac{\beta_{00}}{T} - \frac{R_A}{n} \sum_{k,l} \frac{n_k n_l}{D_{kl}^m} \frac{D_k^T}{\rho_k} \left(\frac{D_k^T}{\rho_k} - \frac{D_l^T}{\rho_l} \right).$$

For ideal gases (91) agrees with the equivalent relation given by Hirschfelder, Curtiss and Bird²⁶).

§ 6. *Simplified description of the diffusion for multicomponent systems.* The formulae developed in the foregoing sections show that the calculation of convective transfer phenomena in multicomponent systems is generally very complicated. In order to make these problems tractable, drastic simplification of the equations and formulae is needed. Such a simplification has been proposed by Spalding^{9) 10)}, but his derivations are not correct. We shall now try to derive Spalding's equations from those given in the foregoing sections. As a first and important simplification we assume that all Maxwell diffusion coefficients are equal; hence

$$D_{ij}^m = D^m \text{ for } i, j = 1, 2, \dots, N. \quad (92)$$

On this assumption (87) becomes

$$\sum_k c_k^* (\mathbf{V}_k - \mathbf{V}_i) = \frac{D^m}{c_i^*} \left(\mathbf{d}_i^a + \sum_k \alpha_{T,ik} c_i^* c_k^* \frac{\text{grad } T}{T} \right), \quad (93)$$

where $\alpha_{T,ij}$ is the thermal diffusion factor for a multicomponent

system defined by

$$\alpha_{T,ij} = \left(\frac{D_i^T}{\rho_i} - \frac{D_j^T}{\rho_j} \right) \Big| D^m. \quad (94)$$

For binary systems (94) is equivalent to (73). For a further simplification of (93) we derive from (11) and (79).

$$\mathbf{v}^* = \mathbf{v} + \sum_{k=1}^N c_k^* \mathbf{V}_k.$$

Hence, making use also of (12), we get

$$\sum_{k=1}^N c_k^* (\mathbf{V}_k - \mathbf{V}_i) = \mathbf{v}^* - \mathbf{v}_i = -\mathbf{J}_i^*/n_i.$$

Introducing this relation into (93), we obtain

$$\mathbf{J}_i^* = -nD^m \left(\mathbf{d}_i^a + \sum_{k=1}^N \alpha_{T,ik} c_i^* c_k^* \frac{\text{grad } T}{T} \right). \quad (95)$$

This shows that for multicomponent systems assumption (92) leads to a diffusion law which is equivalent to that for binary systems (compare (95) with (76)). This analogy may be completed if we consider ideal systems, for which

$$Z = 1, a_i = c_i^*, v_i = 1/nm_i.$$

Assuming furthermore that the external forces are the same for all components (this assumption is for instance satisfied in gravitational fields), then (52) becomes

$$\mathbf{d}_i^a = \mathbf{d}_i^* = \text{grad } c_i^* + \sum_{k=1}^N \alpha_{p,ik} c_i^* c_k^* \frac{\text{grad } p}{p}, \quad (96)$$

where

$$\alpha_{p,ij} = (m_j - m_i)/m. \quad (97)$$

The coefficient $\alpha_{p,ij}$ is clearly equivalent to the coefficient α_p for binary systems (compare (97) with (72)). Together with equation (17), (95) and (96) represent the formulation of the molar description of the diffusion. We shall now indicate how the barycentric description of the diffusion may be obtained from (95) and (96). For that purpose we derive first from (6), (8), (11), (12) and (55)

$$\mathbf{J}_i = \frac{m_i}{m} \sum_{k=1}^N m_k (c_k^* \mathbf{J}_i^* - c_i^* \mathbf{J}_k^*). \quad (98)$$

From (55) and (56) we obtain

$$\frac{\rho}{n} \text{dc}_i = \frac{m_i}{m} \sum_{k=1}^N m_k (c_k^* \text{dc}_i^* - c_i^* \text{dc}_k^*). \quad (99)$$

Furthermore we remark that from (94) it follows that

$$\alpha_{T,ik} - \alpha_{T,jk} = \alpha_{T,ij}. \quad (100)$$

Making use of (55), (96) and (100), substitution of (95) in (98) leads to the following relation:

$$\mathbf{J}_i = -\rho D^m \left(\mathbf{d}_i + \sum_{k=1}^N \alpha_{T,ik} c_i c_k \frac{\text{grad } T}{T} \right), \quad (101)$$

where

$$\mathbf{d}_i = \frac{n}{\rho} \frac{m_i}{m} \sum_{k=1}^N m_k (c_k^* \mathbf{d}_i^* - c_i^* \mathbf{d}_k^*),$$

or, making use of (96) and (99),

$$\mathbf{d}_i = \text{grad } c_i + \sum_{k=1}^N \alpha_{p,ik} c_i c_k \frac{\text{grad } p}{p}. \quad (102)$$

From (10), (101) and (102) the barycentric diffusion equation is obtained which is, as a result of assumption (92), analogous to the barycentric diffusion equation for binary systems. The most simple formula for the mass flux is apparently

$$\mathbf{J}_i = -\rho D^m \text{grad } c_i. \quad (103)$$

Substitution of (103) in (10) leads to

$$\rho \frac{Dc_i}{Dt} = \text{div} (\rho D^m \text{grad } c_i) + K_i. \quad (104)$$

This represents the diffusion equation upon which Spalding's calculations are based. From the derivation of (104) it follows that the assumptions underlying this equation may be summarized as follows:

- 1) all Maxwell diffusion coefficients are equal,
- 2) the system is ideal,
- 3) the exterior forces exerted on the components are equal,
- 4) the pressure diffusion is negligible,
- 5) the thermal diffusion is negligible.

The first assumption differs from that of Spalding, who is also forced to assume that the molar masses of the components are equal. The latter assumption is not necessary if the derivation of (104) is based upon assumption 1.

If chemical reactions occur in the system, the source term K_t occurring in (104) may be eliminated in a manner indicated by Spalding⁹⁾ 10). Straightforward calculation of the mass transfer is then possible without the use of chemical kinetics.

The thermal energy equation is also considerably simplified if the five assumptions named above are accepted. In that case we obtain from (28), (91) and (103)

$$\rho \frac{Dh}{Dt} = \text{div} [\rho D^m (C_p Le \text{ grad } T + \sum_{k=1}^N h_k \text{ grad } c_k)] + \frac{Dp}{Dt} + \Phi_\eta, \quad (105)$$

where Le represents the Lewis number, here defined by $Le = \lambda / (\rho C_p D^m)$. For gases Le is in most cases approximately equal to 1 and we thus introduce as a 6th assumption: $Le = 1$. Furthermore, making use of (30), (35) and (39), equation (105) becomes

$$\rho \frac{Dh}{Dt} = \text{div} (\rho D^m \text{ grad } h) + \frac{Dp}{Dt} + \Phi_\eta, \quad (106)$$

This equation is also very simple and does not contain the heat of reaction. Its absence is not in accordance with Spalding and Emmons for reasons mentioned in § 2c.

In the literature other simplifications are also proposed. These may be verified in a manner indicated in this section. In this connection we mention for instance the simplifications given by Wilke³³⁾, who considered the diffusion of one component through stagnant layers consisting of several components. For ideal systems the transformation from the molar to the barycentric description of the diffusion may again be performed by means of (98) and (99).

The author wishes to express his thanks to Prof. Dr. J. A. Prins of the Technological University at Delft for his valuable discussions and suggestions.

Received 19th July, 1958

REFERENCES

- 1) Nusselt, W., Z. Ver. dtsh. Ing. (VDI) **60** (1916) 102, 541 and 569.
- 2) Nusselt, W., Z. angew. Math. Mech. **10** (1930) 105, or Natl Advisory Comm. Aeronaut., Techn. Mem. 1367, 1954.
- 3) Schmidt, E. Gesundh. Ing. **52** (1929) 525.
- 4) Fick, A., Pogg. Ann. Phys. **94** (1855) 59, and Phil. Mag. (10) **4** (1855) 30.
- 5) Arckermann, G., V.D.I.-Forschungsheft **382**, 1937.
- 6) Eckert, E., Einführung in die Wärme- und Stoffaustausch, Springer-Verlag, Berlin, 1949, or Introduction to the transfer of heat and mass, McGraw-Hill, N.Y., 1950.
- 7) Jakob, M., Heat transfer I, John Wiley and Sons Inc., New York, Chapter 28, 1949.
- 8) Sherwood, T. K. and R. L. Pigford, Absorption and extraction, McGraw-Hill, New York, 1952.
- 9) Spalding, D. B., Fourth Symposium on Combustion, Williams and Wilkins Co., Baltimore, 1953, p. 847.
- 10) Spalding, D. B., Proc. Instn. Mech. Engrs **168** (1954) 545.
- 11) Spalding, D. B., Proc. Roy. Soc. (London) **A 221** (1954) 78 and 100.
- 12) Spalding, D. B., Some fundamentals on combustion, Gas Turbine series, vol. 2, Butterworths Sci. Publ., London, 1955.
- 13) Emmons, H. W., Z. angew. Math. Mech. **36** (1956) 60.
- 14) Berman, K., J. Appl. Mech. **22** (1955) 197.
- 15) Kirkwood, J. G. and B. J. Crawford, Phys. Chem **56** (1952) 1048.
- 16) Opfell, J. B. and B. H. Sage, Industr. Eng. Chem. **47** (1955) 918.
- 17) Chapman, S. and T. G. Cowling, The mathematical theory of non-uniform gases, Cambridge Univ. Press, Cambridge, 1939.
- 18) Onsager, L. and R. M. Fuoss, J. Phys. Chem. **36** (1932) 2689.
- 19) Jost, W., Diffusion und chemische Reaktionen in festen Stoffen, Steinkopf, Dresden and Leipzig, 1937.
- 20) Prigogine, I., Physica **15** (1949) 272.
- 21) Ubbelohde, A. R., Trans. Faraday Soc. **33** (1937) 599.
- 22) Wirtz, K., Z. Naturforsch. **3a** (1948) 672.
- 23) Groot, S. R. de, Thermodynamics of irreversible processes, North-Holland Publ. Co., Amsterdam, 1952.
- 24) Rosenfeld, L., Theory of electrons, North-Holland Publ. Co., Amsterdam, 1951.
- 25) Prigogine, I. and R. Defay, Chemical thermodynamics, Longmans Green and Co., London, 1954.
- 26) Hirschfelder, J. O., C. F. Curtiss and R. B. Bird, Molecular theory of gases and liquids, John Wiley and Sons Inc., New York, 1954.
- 27) Green, H. S., Molecular theory of fluids, North-Holland Publ. Co., Amsterdam, 1952.
- 28) Hirschfelder, J. O., R. B. Bird and E. L. Spotz, J. Chem. Phys. **16** (1948) 968.
- 29) Hirschfelder, J. O., R. B. Bird and E. L. Spotz, Chem. Rev. **44** (1949) 205, and Trans. Amer. Soc. Mech. Engrs **71** (1949) 921.
- 30) Smith, J. W., J. Aero. Sci. **21** (1954) 154.
- 31) Maxwell, J. C., Sci. Papers 2, Cambridge Univ. Press, Cambridge, 1890, p. 625.
- 32) Curtiss, C. F. and J. O. Hirschfelder, J. Chem. Phys. **17** (1949) 550.
- 33) Wilke, C. R., Chem. Eng. Progr. **46** (1950) 95.