THERMODYNAMICS OF IRREVERSIBLE PROCESSES IN ROTATING SYSTEMS

G. J. HOOYMAN

STELLINGEN

I

De formule van Svedberg voor de sedimentatie-snelheid in binaire mengsels kan worden afgeleid met behulp van de thermodynamica der irreversibele processen. De daarin optredende grootheden worden hierbij ondubbelzinnig gedefinieerd, terwijl het geldigheidsgebied kan worden aangegeven.

Hoofdstuk I van dit proefschrift.

II

Het door Johnston en Ogston gevonden anomale concentratieverloop en de door Schachman en Harrington waargenomen terugstroming bij sedimentatie in ternaire mengsels worden in beginsel beschreven door de fenomenologische vergelijkingen, zoals die gegeven worden door de thermodynamica van irreversibele processen.

Hoofdstuk III van dit proefschrift.

III

De door Meixner gegeven transformatieformules voor de thermodynamische stromen en krachten (waarbij de Onsager-relaties hun vorm behouden) kunnen worden afgeleid uit de eis, dat de uitdrukking voor de *afwijking* der entropie van de evenwichtswaarde invariant is.

Hoofdstuk V van dit proefschrift.

IV

Ten onrechte beweert Haase, dat de formule voor de sedimentatiesnelheid in binaire mengsels kan worden afgeleid met behulp van de thermodynamica van irreversibele processen zonder aanvullende onderstellingen (zoals de onderstelling, dat de partiële volumina niet van de samenstelling van het mengsel afhangen).

R. Haase, Kolloid-Z. **138** (1954) 105.
G. J. Hooyman, P. Mazur, und S. R. de Groot, Kolloid-Z. **140** (1955) 165.

V

Voor de beschrijving van de Bose-Einstein-condensatie heeft London de benaderingsmethode van een continu energiespectrum gebruikt. Het optreden van een overgangstemperatuur met een discontinuïteit in de soortelijke warmte kan echter ook met bepaalde discrete energieniveaux gevonden worden, zonder de daarbij optredende sommen door integralen te vervangen. De door London ad hoc gepostuleerde niveaudichtheid blijkt dan te ontstaan door een speciale keuze der niveaux bij de grensovergang naar een continu spectrum.

F. London, J. phys. Chem. **43** (1939) 49.
S. R. de Groot, G. J. Hooyman and C. A. ten Seldam, Proc. roy. Soc. London A **203** (1950) 266.

VI

De kinetische uitdrukking, die Wigner geeft voor de temperatuurgradiënt, zou moeten luiden

$$\operatorname{grad} T(\mathbf{x}) = (2/kN)\, \Sigma_i\, \mathbf{q}_i\, \{p_i^2/2m - 3kT(\mathbf{x})/2\}/q_i^2,$$

waarbij gesommeerd wordt over de N deeltjes binnen een bol met middelpunt $\mathbf{x}$ en een straal, klein genoeg om hogere afgeleiden van T en van de dichtheid te kunnen verwaarlozen. $\mathbf{q}_i$ is de plaatsvector van het $i^{\text{-de}}$ deeltje ten opzichte van $\mathbf{x}$.

E. P. Wigner, J. chem. Phys. **22** (1954) 1912.

VII

Lax beweert, dat het door Berlin en Kac ingevoerde sferische model van een ferromagneticum een volstrekt geldig voorbeeld is ter vergelijking van het canonieke en het microcanonieke formalisme van de statistische mechanica en toont aan, dat deze voor dit model niet steeds gelijkwaardig zijn. Hiertegen valt op te merken, dat het sferische model zich voor dergelijke aequivalentie-problemen niet leent.

T. H. Berlin and M. Kac, Phys. Rev. **86** (1952) 821.
M. Lax, Phys. Rev. **97** (1955) 1419.

VIII

Teneinde effecten van de anharmoniciteit op de thermische eigenschappen van kristallen te beschrijven worden in recente onderzoekingen normale trillingen ingevoerd, die van de temperatuur afhankelijk zijn. Hierbij dient men zich af te vragen, of deze normale trillingen ook werkelijk fysisch voorkomen of slechts een formele betekenis hebben.

M. Born, Festschrift Akad. Wiss. Göttingen I (1951).
D. J. Hooton, Phil. Mag. **46** (1955) 422; 433.

IX

De wijze waarop Lansraux bij de behandeling van de buigingsintegraal poogt, de invloed van de begrenzing van de uittreepupil in rekening te brengen, is onjuist. Bij het toepassen van de Fourier-transformatie houdt hij niet voldoende rekening met het feit, dat de optredende functies niet kwadratisch integreerbaar zijn.

G. Lansraux, *Diffraction instrumentale*, Éd. de la Revue d'Optique, Paris, 1953, Ch. II.

X

Het binnen redelijke grenzen vermijden van buitenlandse termen bij natuurwetenschappelijke voordrachten in het eigen taalgebied kan een gunstige invloed uitoefenen op de voordrachtstechniek, in het bijzonder op een betere verzorging van de eigen taal.

XI

In zuiver fysische discussies worden veelal ten onrechte begrippen ingevoerd met een wijsgerige inhoud. Een voorbeeld hiervan is het begrip individualiteit.

E. Persico, *Fundamentals of quantum mechanics*, New York, 1950, p. 446.
H. Margenau, *The nature of physical reality*, New York, 1950, p. 440.

XII

De door Whittaker gegeven formuleringen van de bewijzen voor het Godsbestaan zijn onderhevig aan critiek, zowel van natuurwetenschappelijke als van wijsgerige aard.

E. Whittaker, *Space and Spirit*, Nelson and Sons, London, 1946.
G. J. Hooyman en F. E. M. Ongering, K.C.T. Streven **3** (1950) 78.

THERMODYNAMICS OF IRREVERSIBLE PROCESSES IN ROTATING SYSTEMS

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PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN
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Promotor: PROF. DR S. R. DE GROOT

Aan mijn Moeder

Aan de nagedachtenis van mijn Vader

CONTENTS

INTRODUCTION AND SUMMARY

The phenomenological theory of sedimentation phenomena in rotating systems can be developed from the viewpoint of thermodynamics of irreversible processes. With the help of this theory one can find the appropriate form of the phenomenological equations, describing the irreversible phenomena, and establish the reciprocity relations, which, according to Onsager's theory and its extensions, exist between the phenomenological coefficients. In particular, this formalism allows a systematic description of diffusion and sedimentation phenomena in centrifugal fields, which is the main purpose of this thesis. In addition, we want to discuss some related problems, which also play a part in other applications of thermodynamics of irreversible processes.

The central quantity in thermodynamics of irreversible processes is the entropy production, the change in entropy of a system which results from the action of irreversible processes, taking place inside the system. In chapter I an explicit expression for this quantity is derived for a rotating system, containing a mixture of charged and uncharged components in the presence of an electric field. Chemical reactions and viscous forces are not taken into account.

This expression has already been the starting point for the treatment of electrokinetic effects in rotating systems by De Groot, Mazur and Overbeek. With the neglection of transverse effects and of non-uniformities in temperature or concentrations, these authors were able to show that an Onsager relation connects the sedimentation potential with a quantity, called barycentric electrophoresis. The latter quantity turned out to be ordinary electrophoresis for a colloidal solution under certain limiting, but frequently realized circumstances.

In the present treatment we shall confine ourselves to sedimentation phenomena in mixtures of uncharged components, taking into account the existence of concentration gradients. This problem is of practical interest, since it allows a systematic description of the sedimentation equilibrium in the ultracentrifuge as well as a straightforward derivation of the phenomenological equations for sedimentation velocities, both of these being of use for the determination of molecular masses by means of ultracentrifugation measurements. Detailed considerations concerning temperature gradients will not be given since in actual experiments they are avoided by all means, as they could give rise to convection currents, thus invalidating the experimental results of sedimentation analysis.

In the second part of chapter I we consider monodisperse systems. The well-known Svedberg equation for the distribution of the solute in sedimentation equilibrium is found as the condition for thermostatic equilibrium, which means the vanishing of the entropy production. The explicit expression for the latter quantity also leads to the appropriate form of the phenomenological equation for the relative sedimentation flow. Neglecting transverse effects and introducing the boundary condition for a closed vessel, which for liquids leads to the vanishing of the volume flow throughout the system, we then find the sedimentation velocity of the solute. For dilute ideal solutions the obtained expression reduces to the familiar Svedberg equation for the sedimentation rate in monodisperse systems.

Although this equation has been widely and successfully used for a long time already, the usual derivations repeatedly have given rise to discussions about two questions: one concerning the proper meaning of the quantities involved (in particular, the density and the specific volume), the other regarding the frame of reference. It is the advantage of thermodynamics of irreversible processes that it allows a rigorous definition of all quantities involved and that the non-equilibrium equation can be put on a basis, which meets the requirements of exactness to be used in macroscopic physics.

In order to extend the treatment to paucidisperse systems, one needs an appropriate description of diffusion in multicomponent systems. Therefore, in chapter II the phenomenological description of diffusion in isotropic mixtures is developed from the expression for the entropy production and the relations between the diffusion coefficients, resulting from the Onsager relations, are derived. The results are specified for ternary mixtures.

In chapter III we consider sedimentation in paucidisperse systems. The expression for the entropy production, deduced in chapter I, enables us once again to formulate the phenomenological equations for the fluxes of matter as the net result of sedimentation and diffusion. As in chapter I, the spatial distribution of the components in sedimentation equilibrium is re-established from the condition of vanishing entropy production. The result is specified for ideal solutions, in terms of molar quantities as well as in terms of mass quantities. The non-equilibrium equations contain phenomenological tensors for which the Onsager relations hold. We shall give these relations in the general form, taking into account the anisotropy, due to the presence of an over-all rotation. The sedimentation rates of the components are derived from the general non-equilibrium equations by neglecting transverse effects and by introducing the boundary condition of vanishing volume flow. The coefficients, relating the sedimentation rates to the centrifugal force and the concentration gradients, can be expressed in terms of the diffusion coefficients, introduced in chapter II.

Although very little is known about the coefficients of cross diffusion as to sign and order of magnitude, the obtained equations allow some simple conclusions, which might account for two effects, established in experimental sedimentation study. The first effect is related to an anomalous behaviour of slowly sedimenting materials above the boundary layer of more rapidly sedimenting components. The form of the obtained expressions suggests a contribution to this effect, caused by the presence of a density gradient of the rapidly sedimenting component. The other effect is the decrease in sedimentation rate, due to the presence of other sedimenting materials, which even can lead to a backward flow, as was shown in experiments with the so-called synthetic boundary cell. For ideal ternary mixtures the equations actually show the possibility of a slowing down. This effect, in turn, might contribute to the above mentioned boundary anomaly.

In chapter IV and V we discuss some problems arising in various applications of thermodynamics of irreversible processes. The influence of linear dependencies between the fluxes or between the forces, occurring in the expression for the entropy production, on the phenomenological coefficients and the Onsager reciprocal relations is investigated in chapter IV. If both sets of variables are dependent, the phenomenological coefficients are not uniquely defined (such a situation may arise in the theory of diffusion, as is indicated in chapter II). It is shown, that they always can be chosen such as to satisfy the Onsager relations.

The invariance of the Onsager relations under simultaneous linear transformations of the fluxes and forces is investigated in chapter V for the cases of scalar phenomena and of vectorial phenomena (heat conduction and diffusion). The connection between these transformations follows in a natural way from the invariance of the deviation of the entropy from its equilibrium value. The latter condition, rather than the invariance of the entropy production, guarantees the invariance of the Onsager relations. An application of the transformations in question to the various diffusion flows was discussed in chapter II.

In chapter VI we discuss the linear equations between the elements of the viscous pressure tensor and the rates of deformation for the case of a rotating fluid or for the equivalent case of an isotropic fluid in an external magnetic field. Since these equations can be incorporated within the thermodynamics of irreversible processes, the Onsager reciprocity relations hold for the scheme of phenomenological coefficients. For the cases under investigation the viscous behaviour is seen to be described by 8 coefficients, between which one Onsager relation exists. The remaining 7 independent coefficients can be linearly combined in such a way as to yield 5 coefficients of ordinary viscosity, the other 2 coefficients then describing the volume viscosity and a cross-effect between the ordinary and the volume viscosity, resp. For the special case of vanishing volume viscosity the equations are compared with those, derived from kinetic theory by Chapman and Cowling for an ionized gas in a magnetic field.

CHAPTER I

THE ENTROPY BALANCE EQUATION FOR ROTATING MEDIA AND ITS APPLICATION TO SEDIMENTATION IN MONODISPERSE SYSTEMS

§ 1. *Introduction.* The application of thermodynamics of irreversible processes to continuous media requires the calculation of the entropy balance equation and, in particular, the derivation of the expression for the source strength of the entropy production, occurring in this balance equation. In the present chapter we first shall derive the general expression for this quantity in the case of a rotating system, containing a mixture of charged and uncharged components in the presence of an electric field. In the second part the application to sedimentation phenomena in monodisperse uncharged systems will be given.

In § 2 the conservation laws and the second law of thermodynamics are formulated, with the help of which the entropy balance is derived in § 3. The contribution of the centrifugal force and the Coriolis force to the entropy production is discussed in § 4.

In the obtained expression for the entropy production the fluxes of matter refer to the centre of mass velocity. Assuming the system to be at mechanical equilibrium, we can replace this velocity by an arbitrary other reference velocity according to a theorem, due to Prigogine. The application of this theorem in § 5*A* leads to the final form of the expression for the entropy production, which will also be used in subsequent chapters.

As a first specification we consider in § 5*B* systems, for which transverse effects and non-uniformities in temperature or concentrations can be neglected. At vanishing volume flow the expression for the entropy production then yields the basic equation for the treatment of the sedimentation potential and electrophoresis, given by De Groot, Mazur and Overbeek[1]).

In the remaining part of this chapter we confine ourselves to sedimentation phenomena in uncharged monodisperse systems. This case is of practical interest, since the sedimentation of large molecules in ultracentrifugal fields provides a means for the determination of molecular masses, which can be calculated either from the distribution of the solute in sedimentation equilibrium or from the observed sedimentation rate. For the latter quantity a theoretical expression was given in 1925 by Svedberg[2]) for the case of dilute ideal solutions. Although this formula has been widely used, its derivation repeatedly has given rise to discussions with regard to the proper meaning of the quantities involved and the frame of reference, to be chosen [3]) [4]) [5]) [6]). It therefore seems worthwhile to develop the description of sedimentation from the viewpoint of thermodynamics of irreversible processes, which allows a rigorous definition of the quantities involved and from which it can be seen what approximations are necessary in order to arrive at the Svedberg equation.

In § 6 we consider the distribution of the solute in sedimentation equilibrium. The familiar equilibrium equation for ideal solutions is re-established from the condition of vanishing entropy production. In § 7*A* we first give a proper definition of the diffusion coefficient in binary mixtures, with the help of which the various forms of Fick's law can easily be expressed. In § 7*B* the equation for the sedimentation rate in centrifugal fields is derived from the non-equilibrium equation with the neglection of transverse effects and with the assumption of vanishing volume flow. For dilute ideal solutions the obtained expression reduces to the well-known Svedberg equation.

In the appendices we successively give a discussion of the boundary condition (which for liquid solutions leads to the vanishing of the volume flow throughout the vessel), the derivation of some thermodynamical formulae used in this chapter, and the proof of Prigogine's theorem.

§ 2. *The fundamental equations.* We consider a system rotating with a constant angular velocity $\boldsymbol{\omega}$. Fixed to the system we choose a right-handed cartesian coordinate system. The state variables of the system are supposed to be continuous functions of space coordinates and of time. The system is composed of n non-reacting components (labelled $k = 1, 2, \ldots, n$), m of which carry electrical charges e_k per unit mass ($k = 1, 2, \ldots, m$) whereas $e_{m+1} = \ldots = e_n = 0$. The entropy balance is derived from the four following fundamental equations (see also [7]) [8])).

I. The law of conservation of mass. If ϱ_k is the density of component k (mass per unit volume), $\partial/\partial t$ the local time derivative and $\mathbf{v}_k$ the velocity of substance k, this law can be written

$$\partial \varrho_k/\partial t = -\operatorname{div} \varrho_k \mathbf{v}_k. \tag{1}$$

Introducing the total density

$$\varrho = \Sigma_k\, \varrho_k = 1/v \tag{2}$$

(with v the specific volume) and the centre of mass velocity

$$\mathbf{v} = (\Sigma_k\, \varrho_k \mathbf{v}_k)/\varrho, \tag{3}$$

and with the help of the barycentric substantial time derivative

$$\mathrm{d}/\mathrm{d}t = \partial/\partial t + \mathbf{v}\cdot\mathrm{grad} \tag{4}$$

and the flow of substance k with respect to $\mathbf{v}$

$$\mathbf{J}_k = \varrho_k(\mathbf{v}_k - \mathbf{v}), \tag{5}$$

one can write the balance equation (1) in the alternative form

$$\mathrm{d}\varrho_k/\mathrm{d}t = -\,\varrho_k\,\mathrm{div}\,\mathbf{v} - \mathrm{div}\,\mathbf{J}_k. \tag{6}$$

From (3) and (5) it follows that

$$\Sigma_1^n{}^{k}\,\mathbf{J}_k = 0. \tag{7}$$

Summed over all substances k equation (6) thus leads to

$$\mathrm{d}\varrho/\mathrm{d}t = -\,v^{-2}\,\mathrm{d}v/\mathrm{d}t = -\,\varrho\,\mathrm{div}\,\mathbf{v} \tag{8}$$

and finally, with $c_k = \varrho_k/\varrho$ the mass fraction of k, to

$$\varrho\,\mathrm{d}c_k/\mathrm{d}t = -\,\mathrm{div}\,\mathbf{J}_k. \tag{9}$$

II. The force law (conservation of momentum) reads in the present case if viscous forces are not taken into account

$$\varrho\,\mathrm{d}\mathbf{v}/\mathrm{d}t = -\,\mathrm{grad}\,P + \Sigma_1^n{}^{k}\,\varrho_k\,\mathbf{F}_k, \tag{10}$$

where P is the pressure and $\mathbf{F}_k$ the external force on component k per unit mass, consisting of the centrifugal force, the Coriolis force and the electric force

$$\mathbf{F}_k = \omega^2\,\mathbf{r} + 2\mathbf{v}_k \wedge \boldsymbol{\omega} + e_k\,\mathbf{E}. \tag{11}$$

Here $\mathbf{r}$ is the distance from the axis of rotation, $\mathbf{E}$ the electric field strength and $\wedge$ stands for vectorial multiplication.

III. The law of conservation of energy reads

$$\varrho\mathrm{d}(\tfrac{1}{2}\mathbf{v}^2 + u)/\mathrm{d}t = -\,\mathrm{div}\,(P\mathbf{v} + \mathbf{J}_q) + \Sigma_k\,\varrho_k\,\mathbf{F}_k\cdot\mathbf{v}_k. \tag{12}$$

Here u is the internal specific energy and $\mathbf{J}_q$ the heat flow given by

$$-\,\mathrm{div}\,\mathbf{J}_q = \varrho\,\mathrm{d}q/\mathrm{d}t, \tag{13}$$

where $\mathrm{d}q$ is the heat supplied to the unit of mass of the mixture.

IV. The second law (Gibbs' equation) is

$$T\,\mathrm{d}s/\mathrm{d}t = \mathrm{d}u/\mathrm{d}t + P\,\mathrm{d}v/\mathrm{d}t - \Sigma_k\,\mu_k\,\mathrm{d}c_k/\mathrm{d}t, \tag{14}$$

where T is the temperature, s the specific entropy and μ_k the chemical potential (partial specific Gibbs function) of k.

§ 3. *The entropy balance.* This equation follows from (8), (9), (10), (12), (14) and can be written as

$$\varrho \, \mathrm{d}s/\mathrm{d}t = -\operatorname{div} \mathbf{J}_s + \sigma, \tag{15}$$

where

$$T\mathbf{J}_s = \mathbf{J}_q - \Sigma_k \, \mu_k \, \mathbf{J}_k, \tag{16}$$

$$T\sigma = \mathbf{J}_q \cdot \mathbf{X}_q + \Sigma_k \, \mathbf{J}_k \cdot \mathbf{X}_k \geq 0, \tag{17}$$

with

$$\mathbf{X}_q = -(\operatorname{grad} T)/T, \tag{18}$$

$$\mathbf{X}_k = \mathbf{F}_k - T \operatorname{grad} (\mu_k/T). \tag{19}$$

Equation (15) has the form of a balance equation in which $\mathbf{J}_s$ is the flow of entropy and σ is the source strength of the entropy production caused by the irreversible processes. In (17) $T\sigma$ is seen to be a sum of products of "fluxes" $\mathbf{J}_q$ and $\mathbf{J}_k$ and of "forces" $\mathbf{X}_q$ and $\mathbf{X}_k$. In thermodynamics of irreversible processes linear relationships between the components of the fluxes and forces are introduced. To these relations, which are called phenomenological equations, we shall return in subsequent sections.

§ 4. *The centrifugal force, the Coriolis force and the entropy production.* From (11) and (19) the explicit contributions of the centrifugal force and the Coriolis force to the entropy production (17) can be calculated. The first is $\omega^2 \mathbf{r} \cdot \Sigma_k \, \mathbf{J}_k$ which vanishes according to (7). The second is

$$\begin{aligned} 2 \, \Sigma_k \, \mathbf{J}_k \cdot \mathbf{v}_k \wedge \boldsymbol{\omega} &= 2 \, \Sigma_k \, \varrho_k \, \mathbf{v}_k \cdot \mathbf{v}_k \wedge \boldsymbol{\omega} - 2 \, \Sigma_k \, \varrho_k \, \mathbf{v} \cdot \mathbf{v}_k \wedge \boldsymbol{\omega} = \\ &= 0 + 2 \, \Sigma_k \, \varrho_k \, \mathbf{v}_k \cdot \mathbf{v} \wedge \boldsymbol{\omega} = 2 \varrho \, \mathbf{v} \cdot \mathbf{v} \wedge \boldsymbol{\omega} = 0, \end{aligned} \tag{20}$$

where (3) and (5) have been used. It is thus formally proved that neither the centrifugal force nor the Coriolis force gives any *explicit* contribution to the entropy production (this reversible character is as is to be expected for motion under the influence of a purely mechanical force).

However, from this result it cannot be concluded that these forces do not give any contribution to the entropy production at all. To make this clear we rewrite $T\sigma$ from (17) with the help of (11), using also (20), and, choosing T, P and the c_k as state variables, we express grad μ_k in the gradients of these variables

$$T\sigma = \{\mathbf{J}_q - \Sigma_k \, h_k \mathbf{J}_k\} \cdot \mathbf{X}_q + \Sigma_k \, \mathbf{J}_k \cdot \{e_k \, \mathbf{E} - v_k \operatorname{grad} \mathrm{P} - (\operatorname{grad} \mu_k)_{P,T}\}, \tag{21}$$

where h_k and v_k are the partial specific enthalpy and volume of k, respectively. For the case of mechanical equilibrium ($\mathrm{d}\mathbf{v}/\mathrm{d}t = 0$), which is of particular interest, the force law (10) shows the connection between grad P and the external forces. It is then seen that in this case these forces contribute *implicitly* to $T\sigma$, because they give rise to a pressure gradient which appears in the expression (21).

§ 5. *The case of mechanical equilibrium and the condition of vanishing volume flow*. The setting up of mechanical equilibrium is a very much quicker process than any thermodynamical phenomenon. It will virtually be reached as soon as ω has attained a constant value. We first want to consider this case without making any further approximation.

A. Mechanical equilibrium. In this case, where $\mathrm{d}\mathbf{v}/\mathrm{d}t = 0$, we can apply a theorem which is due to Prigogine[7][8]. In order to do this in the general non-isothermal case we perform a linear transformation of the fluxes and forces in (17) leaving $T\sigma$ invariant

$$T\sigma = \mathbf{J}'_q \cdot \mathbf{X}'_q + \Sigma_{1}^{n}{}_{k}\, \mathbf{J}'_k \cdot \mathbf{X}'_k. \tag{22}$$

If we choose as new fluxes

$$\mathbf{J}'_q = \mathbf{J}_q - \Sigma_k\, h_k \mathbf{J}_k, \tag{23}$$

$$\mathbf{J}'_k = \mathbf{J}_k, \tag{24}$$

we find, identifying (17) and (22)

$$\mathbf{X}'_q = \mathbf{X}_q = -\,(\mathrm{grad}\ T)/T, \tag{25}$$

$$\mathbf{X}'_k = \mathbf{X}_k + h_k\, \mathbf{X}_q = \mathbf{F}_k - (\mathrm{grad}\ \mu_k)_T. \tag{26}$$

Prigogine has shown that, assuming mechanical equilibrium and using forces and fluxes of the form (23)–(26) (with $\mathbf{F}_k$ the force from the force law (10)), one can replace the barycentric velocity $\mathbf{v}$ in the flows $\mathbf{J}'_k$ appearing in (22) by an arbitrary other velocity (*cf.* Appendix III).

Let us introduce an arbitrary mean velocity

$$\mathbf{v}^a \equiv \Sigma_{1}^{n}{}_{k}\, w_k\, \mathbf{v}_k, \tag{27}$$

where the w_k are weight factors, normalized to unity

$$\Sigma_k\, w_k = 1. \tag{28}$$

With this velocity we can define the flows

$$\mathbf{J}^a_k \equiv \varrho_k(\mathbf{v}_k - \mathbf{v}^a), \tag{29}$$

for which

$$\Sigma_{1}^{n}{}_{k}\, w_k \mathbf{J}^a_k/\varrho_k = 0 \tag{30}$$

holds.

The use of $\mathbf{J}^a_k$ instead of $\mathbf{J}'_k$ in (22) leads to

$$T\sigma = \mathbf{J}'_q \cdot \mathbf{X}'_q + \Sigma_{1}^{n}{}_{k}\, \mathbf{J}^a_k \cdot \{(1 - \varrho v_k)\,(\omega^2\, \mathbf{r} + 2\mathbf{v} \wedge \boldsymbol{\omega}) + (e_k - \varrho v_k e)\, \mathbf{E} - \\ - (\mathrm{grad}\ \mu_k)_{P,T}\}, \tag{31}$$

where we have applied

$$\mathrm{grad}\ \mu_k = -\, s_k\, \mathrm{grad}\ T + v_k\, \mathrm{grad}\ P + \Sigma_{1}^{n-1}\, (\partial\mu_k/\partial c_i)_{P,T}\ \mathrm{grad}\ c_i, \tag{32}$$

(s_k being the partial specific entropy of component k) and the condition of mechanical equilibrium,

$$\operatorname{grad} P = \varrho\omega^2\mathbf{r} + 2\varrho\mathbf{v}\wedge\boldsymbol{\omega} + \varrho e\,\mathbf{E}, \tag{33}$$

derived from (10) and (11); we also have used the equality

$$\begin{aligned}\Sigma_k\, \mathbf{J}_k^a\cdot\mathbf{v}_k\wedge\boldsymbol{\omega} = \Sigma_k\, \mathbf{J}_k^a\cdot\mathbf{v}^a\wedge\boldsymbol{\omega} = \varrho(\mathbf{v}-\mathbf{v}^a)\cdot\mathbf{v}^a\wedge\boldsymbol{\omega} = \\ = \varrho(\mathbf{v}-\mathbf{v}^a)\cdot\mathbf{v}\wedge\boldsymbol{\omega} = \Sigma_k\, \mathbf{J}_k^a\cdot\mathbf{v}\wedge\boldsymbol{\omega}.\end{aligned} \tag{34}$$

Finally, e stands for the total charge per unit mass

$$e = \Sigma_k\, c_k\, e_k. \tag{35}$$

Let us consider some special choices of $\mathbf{v}^a$ and the relative flows (see also [8] [9]):

a) Barycentric velocity, $w_k = c_k$. This leads to the centre of mass velocity $\mathbf{v}$ defined already in (3) and to the barycentric description used in the foregoing sections.

b) Mean molar velocity, $w_k = n_k$. With M_k the molar mass of substance k, $N_k = \varrho_k/M_k$ the molar concentration, $N = \Sigma_k N_k$ the molar density and $n_k = N_k/N$ the mole fraction of k, the mean molar velocity is

$$\mathbf{v}^m = \Sigma_k\, n_k\, \mathbf{v}_k. \tag{36}$$

With this velocity it is sometimes of advantage to use molar flows instead of mass flows, *i.e.*

$$\mathbf{J}^m_{k,mol} \equiv N_k(\mathbf{v}_k - \mathbf{v}^m) = \mathbf{J}_k^m/M_k, \tag{37}$$

for which, of course,

$$\Sigma_k\, \mathbf{J}^m_{k,mol} = 0 \tag{38}$$

holds, analogous to (7).

c) Mean volume velocity, $w_k = \varrho_k v_k$. Here we have

$$\mathbf{v}^\circ = \Sigma_k\, \varrho_k\, v_k \mathbf{v}_k, \tag{39}$$

and

$$\Sigma_k\, \varrho_k\, v_k = 1. \tag{40}$$

d) Velocity of component i, $w_i = 1$, $w_k = 0$ ($k \neq i$). The use of material flows with respect to one of the components is of special interest for dilute solutions where one can take the solvent for component i.

The use of Prigogine's theorem is not restricted to the introduction of mean velocities (27). One also could choose a constant velocity, *e.g.* $\mathbf{v}^a = 0$, thus passing on to absolute flows $\varrho_k\mathbf{v}_k$. For this choice, equation (31) still holds.

B. Vanishing volume flow. From (31) it is seen that at mechanical equilibrium, the entropy production $T\sigma$ contains contributions of the centrifugal force

$$\Sigma_k\, \mathbf{J}_k^a\cdot(1-\varrho v_k)\,\omega^2\mathbf{r} = \varrho(\mathbf{v}-\mathbf{v}^\circ)\cdot\omega^2\,\mathbf{r}, \tag{41}$$

of the Coriolis force

$$2\,\Sigma_k\,\mathbf{J}_k^a\cdot(1-\varrho v_k)\,\mathbf{v}\wedge\boldsymbol{\omega}=2\varrho\mathbf{v}\cdot\mathbf{v}^\circ\wedge\boldsymbol{\omega}, \tag{42}$$

and of the electrical phenomena

$$\Sigma_k\,\mathbf{J}_k^a\cdot(e_k-\varrho\,v_k\,e)\,\mathbf{E}=(\mathbf{I}-\varrho e\mathbf{v}^\circ)\cdot\mathbf{E}, \tag{43}$$

with $\mathbf{v}^\circ$ the mean volume velocity (39), and $\mathbf{I}$ the electrical current

$$\mathbf{I}=\Sigma_k\,\varrho_k\,e_k\,\mathbf{v}_k. \tag{44}$$

As a first approximation, one could *neglect all transverse effects,* thus neglecting the Coriolis force with respect to the centrifugal force. This is justified since $|\mathbf{v}_k| \ll \omega r$. In practical cases, the boundary condition for a liquid confined to a vessel can then be expressed by the vanishing of the total volume flow through any section (*cf.* Appendix I) or

$$\mathbf{v}^\circ=0. \tag{45}$$

If, moreover, the gradients of temperature and concentrations could be neglected, (31) would reduce to

$$T\sigma=\mathbf{J}\cdot\omega^2\mathbf{r}+\mathbf{I}\cdot\mathbf{E}, \tag{46}$$

with the total mass flow

$$\mathbf{J}=\varrho\mathbf{v}=\Sigma_k\,\varrho_k\mathbf{v}_k, \tag{47}$$

or, eliminating the absolute flow $\varrho_n\mathbf{v}_n$ by means of (39) and (45), to

$$T\sigma=\Sigma_1^{n-1}{}_k\,\varrho_k\,\mathbf{v}_k\cdot\{e_k\,\mathbf{E}+(1-v_k/v_n)\,\omega^2\mathbf{r}\}, \tag{48}$$

which were the basic equations for the treatment of the sedimentation potential and electrophoresis given by De Groot, Mazur and Overbeek[1]).

§ 6. *The sedimentation equilibrium for an uncharged monodisperse system in the ultracentrifuge.* The foregoing treatment until § 5*B* is applicable to the particular case of an isothermal solution of one uncharged solute in a solvent, which case is of practical interest for determining molecular masses by means of sedimentation in an ultracentrifuge. With $n=2$, grad $T=0$ and $e_1=e_2=0$, equation (31) reads

$$T\sigma=\mathbf{J}_1^a\cdot w_2^{-1}\{(1-\varrho v_1)\,(\omega^2\mathbf{r}+2\mathbf{v}\wedge\boldsymbol{\omega})-(\operatorname{grad}\mu_1)_{P,T}\}\geq 0, \tag{49}$$

where we have eliminated $\mathbf{J}_2^a$ by means of (30) and made use of the Gibbs-Duhem relation

$$\Sigma_1^n{}_k\,\varrho_k\,(\operatorname{grad}\mu_k)_{P,T}=0 \tag{50}$$

and the identity

$$\Sigma_k\,\varrho_k\,(1-\varrho v_k)=0. \tag{51}$$

According to the general procedure in thermodynamics of irreversible processes [7]) [8]) we can assume linear phenomenological relations between the fluxes and forces occurring in the entropy production:

$$\mathbf{J}_1^a = \mathsf{L}\, w_2^{-1} \{(1 - \varrho\, v_1)\, (\omega^2 \mathbf{r} + 2\mathbf{v} \wedge \boldsymbol{\omega}) - (\mathrm{grad}\, \mu_1)_{P,T}\}. \tag{52}$$

Here L is a tensor of the second order.

We first consider thermostatic equilibrium, *i.e.*, the vanishing of the entropy production. Then from (49) and (52) it follows that fluxes and forces also vanish. Therefore, since in that case $\mathbf{v}_1 = \mathbf{v}_2$, which for a closed vessel means that $\mathbf{v} = 0$, we have

$$(1 - \varrho v_1)\, \omega^2 \mathbf{r} - (\mathrm{grad}\, \mu_1)_{P,T} = 0. \tag{53}$$

This equation allows us to describe the distribution of the solute in sedimentation equilibrium with the help of

$$(\mathrm{grad}\, \mu_1)_{P,T} = (\partial \mu_1/\partial n_1)_{P,T}\, \mathrm{grad}\, n_1 = (\partial \mu_1/\partial c_1)_{P,T}\, \mathrm{grad}\, c_1 = \\ = (\partial \mu_1/\partial \varrho_1)_{P,T}\, \mathrm{grad}\, \varrho_1. \tag{54}$$

For an ideal solution

$$(\partial \mu_1/\partial n_1)_{P,T} = RT/M_1 n_1, \tag{55}$$

and with the help of

$$\mathrm{d}n_1/\mathrm{d}c_1 = n_1 n_2/c_1 c_2 \tag{56}$$

and

$$(\partial \varrho_1/\partial c_1)_{P,T} = \varrho^2 v_2 \tag{57}$$

(*cf.* Appendix II) we find

$$n_1^{-1}\, \partial n_1/\partial r = M_1(1 - \varrho v_1)\, \omega^2 r/RT, \tag{58}$$

$$c_1^{-1}\, \partial c_1/\partial r = \{1 - c_1\, (1 - M_2/M_1)\}\, M_1(1 - \varrho v_1)\, \omega^2 r/RT, \tag{59}$$

$$\varrho_1^{-1}\, \partial \varrho_1/\partial r = N_1^{-1}\, \partial N_1/\partial r = M_1[1 - \varrho v_1\{1 + c_1\, (1 - \varrho v_1)\}]\, \omega^2 r/RT\, n_2. \tag{60}$$

Equation (58) is the well-known Svedberg equation (*cf.* [10]) p. 46, equ. (91*a*)) for the sedimentation equilibrium. In practical applications to the determination of the molecular mass M_1 the expressions on the left-hand sides of (58)–(60) are taken to be equal. From the above it can be seen which approximations are necessary in order to justify this procedure. In practical cases $M_2 \ll M_1$. Generally the solution will be molar diluted, so $n_2 \approx 1$. If the solution is so highly diluted that also $c_2 \approx 1$ the right-hand sides of (59) and (60) reduce to the right-hand side of (58).

§ 7. *The sedimentation velocity for an uncharged monodisperse system.* Before considering the sedimentation process we want to give a proper definition of the diffusion coefficient.

A. Definition of the diffusion coefficient[9]). As can be seen, *e.g.*, from (49), in the case of isothermal diffusion in a binary uncharged system in the absence of external forces the entropy production at mechanical equilibrium (where the pressure P is uniform, *cf.* (33)) is given by

$$T\sigma = -\mathbf{J}_1^a \cdot w_2^{-1}\,(\partial\mu_1/\partial c_1)_{P,T}\,\mathrm{grad}\,c_1. \tag{61}$$

In general, the phenomenological relation between $\mathbf{J}_1^a$ and the "force" occurring in (61) will be a tensorial relation. If transverse effects are negligible this relation reduces to a vectorial one for an isotropic fluid and can be written

$$\mathbf{J}_1^a = -w_2\,c_2^{-1}\,\varrho\,D\,\mathrm{grad}\,c_1, \tag{62}$$

which is Fick's law and defines the diffusion coefficient D. (In the presence of external forces, the right-hand side of (62) would contain these forces as well, but one still could define $w_2\,c_2^{-1}\varrho\,D$ as the coefficient of $-$ grad c_1). From the invariance of $T\sigma$ it follows that D is independent of the special choice of the w_k, which can be seen immediately by inserting (62) in (61). Moreover, the relation (62) is symmetric in the two components: with (30) it follows from (62) that

$$\mathbf{J}_2^a = -w_1\,c_1^{-1}\,\varrho\,D\,\mathrm{grad}\,c_2. \tag{63}$$

Finally, D has the same dimensions as a surface area divided by a time *).

Of course, (62) allows us to express the flow (molar or in mass units) in terms of the gradient of n_1, ϱ_1 or N_1. One has, *e.g.*,

$$\mathbf{J}_{1,mol}^a = -w_2 n_2^{-1}\,ND\,\mathrm{grad}\,n_1, \tag{64}$$

or, with the help of (57),

$$\mathbf{J}_1^a = -w_2\,(\varrho_2 v_2)^{-1}\,D\,\mathrm{grad}\,\varrho_1. \tag{65}$$

It is now easy to derive the various forms in which Fick's law is usually stated. We will give some of them here.

The *barycentric* description ($w_k = c_k$) of the diffusion phenomenon leads to

$$\mathbf{J}_1 \equiv \varrho_1(\mathbf{v}_1 - \mathbf{v}) = -\varrho\,D\,\mathrm{grad}\,c_1. \tag{66}$$

With the *molar* description ($w_k = n_k$) (64) yields

$$\mathbf{J}_{1,mol}^m \equiv N_1(\mathbf{v}_1 - \mathbf{v}^m) = -ND\,\mathrm{grad}\,n_1. \tag{67}$$

If one prefers to consider the diffusion with respect to the *mean volume velocity* ($w_k = \varrho_k v_k$), the most convenient relations, fitting in this scheme, are

$$\mathbf{J}_1^\circ \equiv \varrho_1(\mathbf{v}_1 - \mathbf{v}^\circ) = -D\,\mathrm{grad}\,\varrho_1, \tag{68}$$

and

$$\mathbf{J}_{1,mol}^\circ \equiv N_1(\mathbf{v}_1 - \mathbf{v}^\circ) = -D\,\mathrm{grad}\,N_1. \tag{69}$$

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*) The introduction of the flows $\mathbf{J}_k^a$ and of the diffusion coefficient D having the properties stated here is not restricted to the case of mechanical equilibrium or to the absence of a temperature gradient.

Finally, taking relative flows with respect to the *velocity of component* 2, we have

$$\mathbf{J}_1^r \equiv \varrho_1(\mathbf{v}_1 - \mathbf{v}_2) = - c_2^{-1}\, \varrho D \,\mathrm{grad}\, c_1 \tag{70}$$

and

$$\mathbf{J}^r_{1,mol} \equiv N_1(\mathbf{v}_1 - \mathbf{v}_2) = - n_2^{-1}\, ND \,\mathrm{grad}\, n_1. \tag{71}$$

Several authors 8) 9) have given relations between the diffusion coefficients, occurring in the various descriptions of the diffusion phenomenon. It is the advantage of the definition (62) of D that it immediately connects the various phenomenological coefficients which occur according to the choice of the reference velocity, the kind of flow and the gradient to which this flow is related.

B. The sedimentation velocity. Another important method for determining molecular masses in the ultracentrifuge consists in following the sedimentation rate of the layer between solution and pure solvent.

In order to find an expression for this velocity we start again from the relation (52). If we neglect, as we did in §§ 5*B* and 7*A*, transverse effects, the Coriolis force in (52) can be left out and the tensor L reduces for an isotropic fluid to a scalar L. Since by (62) the diffusion coefficient D is defined by taking the coefficient of $-\,\mathrm{grad}\, c_1$ equal to $w_2 c_2^{-1} \varrho D$, we have

$$L = w_2^2 \varrho c_2^{-1} (\partial \mu_1/\partial c_1)^{-1}_{P,T}\, D, \tag{72}$$

or for an ideal solution

$$L = w_2^2 \varrho_1 M_1\, D/RT\, n_2. \tag{73}$$

As long as the system is still far from equilibrium the solution is homogeneous over a large region between the boundary (separating solution and pure solvent) and the outer wall, *i.e.*, $\mathrm{grad}\, c_1 = 0$. Therefore, in this region (52) becomes

$$\mathbf{J}_1^a = w_2 \varrho_1\, M_1 D(1 - \varrho\, v_1)\, \omega^2 \mathbf{r}/RT\, n_2. \tag{74}$$

Introducing the mobility

$$U_1^a = |\mathbf{v}_1 - \mathbf{v}^a|\, / M_1(1 - \varrho v_1)\, \omega^2 r, \tag{75}$$

we can write equ. (74), using also (29),

$$U_1^a = w_2 D/RT\, n_2, \tag{76}$$

which can be considered as a generalization of the Einstein relation between diffusion coefficient and mobility. With the molar description ($w_k = n_k$) it takes the form

$$U_1^m = D/RT. \tag{77}$$

We now can consider the flow (74) with respect to the mean volume velocity $\mathbf{v}^\circ$, which can be taken zero according to the boundary condition (45). We thus have from (29)

$$\mathbf{v}_1 = \varrho_2 v_2 M_1 D(1 - \varrho v_1)\, \omega^2 \mathbf{r}/RT\, n_2, \tag{78}$$

or *)

$$M_1 = n_2 RT|\mathbf{v}_1|/[1 - \varrho v_1 \{1 + c_1 (1 - \varrho v_1)\}]\, D\omega^2 r. \tag{79}$$

In the same way as in § 6 one can make the approximation $n_2 \approx 1$ or the more restrictive approximation $c_2 \approx 1$. The latter one would lead to the well-known Svedberg equation

$$M_1 = RT\, |\mathbf{v}_1|/(1 - \varrho v_1)\, D\omega^2 r. \tag{80}$$

The equations (78)–(80) are valid throughout the region where grad c_1 is negligible. In practice one measures $|\mathbf{v}_1|$ by observing a part of the boundary layer of which the motion also follows from (78)–(80).

The Svedberg equations have thus been derived in the framework of thermodynamics of irreversible processes which allows a rigorous definition of all quantities involved. Thus we have found the result (79) and as an approximation the customary relation (80), both containing well-defined quantities (D and ϱv_1). In this way the non-equilibrium equation has been put on a basis which meets the same requirements of exactness as the equilibrium equation.

APPENDIX I

The condition of vanishing volume flow [1]. The mean volume velocity $\mathbf{v}^\circ$, defined in (39), can be shown to be zero if one can neglect transverse effects and if the partial specific volumes v_k do not appreciably depend on pressure and concentrations.

From the identity (40) it follows that

$$\Sigma_k\, v_k\, \partial \varrho_k/\partial t + \Sigma_k\, \varrho_k\, \partial v_k/\partial t = 0. \tag{81}$$

With the help of this identity and the conservation of mass (1) one obtains

$$\operatorname{div} \mathbf{v}^\circ = \Sigma_k\, \varrho_k (\partial v_k/\partial t + \mathbf{v}_k \cdot \operatorname{grad} v_k). \tag{82}$$

The expression at the right-hand side in parentheses is seen to be the substantial time derivative of v_k in the direction of $\mathbf{v}_k$ and is zero according to the above assumption.

The same assumption allows us to write

$$\operatorname{rot} \mathbf{v}^\circ = \Sigma_k \operatorname{rot} v_k \mathbf{J}_k + \operatorname{rot} \mathbf{v} = \Sigma_k\, v_k \operatorname{rot} \mathbf{J}_k + \operatorname{rot} \mathbf{v}. \tag{83}$$

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*) The above treatment also holds for a non-ideal solution if RT is replaced by $(\partial \overline{\mu}_1/\partial \ln n_1)_{P,T}$ where $\overline{\mu}_1$ is the partial molar Gibbs function. The formulae thus obtained correspond with those given by Lamm [4]).

As was stated in § 3, linear relations exist between the components of the fluxes and forces occurring in the entropy production. As can be seen from (17), this means that a tensorial relation exists between $\mathbf{J}_k$ and the forces $\mathbf{X}_q$ and $\mathbf{X}_i$ ($i = 1, \ldots, n$) given in (18) and (19). If we then can neglect transverse effects (and in particular disregard the Coriolis force), the isotropy of the fluid reduces this tensorial relation to a vectorial one of the form

$$\mathbf{J}_k = \Sigma_j\, L_{kj} \operatorname{grad} Y_j, \tag{84}$$

and in consequence

$$\operatorname{rot} \mathbf{J}_k = \Sigma_j \operatorname{grad} L_{kj} \wedge \operatorname{grad} Y_j. \tag{85}$$

This expression vanishes since, in accordance with the neglecting of transverse effects, grad L_{kj} is parallel to grad Y_j.

The supposition, made throughout the whole treatment, that viscous phenomena do not give an appreciable contribution to the entropy production, allows us to neglect the quantities $\partial v_i/\partial x_j + \partial v_j/\partial x_i$ (i, j cartesian coordinates). Since the tangential component of $\mathbf{v}$ vanishes at the wall, this gives rot $\mathbf{v} = 0$.

As a consequence, rot $\mathbf{v}^\circ = 0$, which combines with div $\mathbf{v}^\circ = 0$ and the fact that the normal component of $\mathbf{v}^\circ$ vanishes at the boundary to yield the condition of vanishing volume flow $\mathbf{v}^\circ = 0$.

APPENDIX II

Derivation of some thermodynamic formulae. Equation (56) is readily derived from the definition of the mole fractions

$$n_i = (c_i/M_i)/(c_1/M_1 + c_2/M_2), \quad (i = 1, 2). \tag{86}$$

In order to arrive at equation (57) we consider a homogeneous mixture of n components containing the masses m_k ($k = 1, \ldots, n$) in a volume V. The partial specific volumes v_k are then defined by

$$v_k = (\partial V/\partial m_k)_{P,T,m_i}. \tag{87}$$

Since V is a homogeneous function of the first degree of the m_k, we have the Euler relation

$$V = \Sigma_1^n{}_k\, m_k v_k, \tag{88}$$

and hence

$$\delta V = \Sigma_1^n{}_k\, v_k\, \delta m_k + \Sigma_1^n{}_k\, m_k\, \delta v_k. \tag{89}$$

On the other hand, we have with constant P and T

$$\delta V = \Sigma_1^n{}_k\, (\partial V/\partial m_k)_{P,T,m_i}\, \delta m_k = \Sigma_1^n{}_k\, v_k\, \delta m_k, \tag{90}$$

which combines with (89) to yield for constant P and T

$$\Sigma_1^n{}_k\, m_k\, \delta v_k = 0. \tag{91}$$

Introducing the density $\varrho_k = m_k/V$, we can write equations (88) and (91) in the form

$$1 = \Sigma_{\substack{k\\1}}^{n} \varrho_k v_k \tag{92}$$

and

$$\Sigma_{\substack{k\\1}}^{n} \varrho_k \, \delta v_k = 0, \tag{93}$$

respectively. From these relations it then follows that for constant P and T

$$\Sigma_{\substack{k\\1}}^{n} v_k \, \delta \varrho_k = 0. \tag{94}$$

For a binary system we can take P, T and c_1 as state variables and (94) leads to

$$v_1 \, (\partial \varrho_1/\partial c_1)_{P,T} + v_2 \, (\partial \varrho_2/\partial c_1)_{P,T} = 0 \tag{95}$$

or, writing ϱ_2 as $\varrho_1(c_1^{-1} - 1)$,

$$(\partial \varrho_1/\partial c_1)_{P,T} = \varrho^2 v_2. \tag{96}$$

Equation (58) follows immediately from (53), (54) and (55). In order to derive (59) one needs $(\partial \mu_1/\partial c_1)_{P,T}$ which can be calculated from (55) and (56):

$$(\partial \mu_1/\partial c_1)_{P,T} = RT \, n_2/M_1 c_1 c_2 = RT/M_1 c_1 \, \{1 - c_1 \, (1 - M_2/M_1)\}, \tag{97}$$

where the definition (86) of n_2 has been used. Finally, we can write, taking P, T and ϱ_1 as state variables,

$$\delta \mu_1 = (\partial \mu_1/\partial \varrho_1)_{P,T} \, \delta \varrho_1, \tag{98}$$

for constant P, T. Passing on to P, T and c_1 as state variables, we then find that

$$(\partial \mu_1/\partial c_1)_{P,T} = (\partial \mu_1/\partial \varrho_1)_{P,T} \, (\partial \varrho_1/\partial c_1)_{P,T} \tag{99}$$

which combines with (97) and (57) to give $(\partial \mu_1/\partial \varrho_1)_{P,T}$ and so equation (60).

APPENDIX III

Prigogine's theorem for mechanical equilibrium. In order to prove Prigogine's theorem [7] [8], used in § 5*A*, we first derive that at mechanical equilibrium

$$\Sigma_{k=1}^{n} \varrho_k \mathbf{X}'_k = 0, \tag{100}$$

$\mathbf{X}'_k$ being the thermodynamic force, introduced in (22),

$$\mathbf{X}'_k = \mathbf{F}_k - (\text{grad} \, \mu_k)_T, \tag{101}$$

with $\mathbf{F}_k$ the external force per unit mass of component k.

In fact, if g is the mean specific Gibbs function,

$$g = \Sigma_{k=1}^{n} c_k \mu_k, \tag{102}$$

we have

$$\delta g = - s\delta T + v\delta P + \Sigma_{k=1}^{n} \mu_k \delta c_k, \qquad (103)$$

hence

$$\Sigma_{k=1}^{n} \varrho_k \delta\mu_k = - \varrho s \delta T + \delta P. \qquad (104)$$

For constant temperature we thus have

$$\Sigma_{k=1}^{n} \varrho_k \, (\text{grad}\ \mu_k)_T = \text{grad}\ P. \qquad (105)$$

At mechanical equilibrium the force law (10) yields

$$\Sigma_{k=1}^{n} \varrho_k \mathbf{F}_k = \text{grad}\ P. \qquad (106)$$

Combining (105) and (106) we find (100).

Prigogine's theorem states that in the fluxes of matter, occurring in the entropy production, one can replace the barycentric velocity **v** by an arbitrary other velocity $\mathbf{v}^a$ if the system is at mechanical equilibrium, or (*cf.* (22))

$$T\sigma_v \equiv \Sigma_{k=1}^{n} \varrho_k (\mathbf{v}_k - \mathbf{v}) \cdot \mathbf{X}_k' = \Sigma_{k=1}^{n} \varrho_k (\mathbf{v}_k - \mathbf{v}^a) \cdot \mathbf{X}_k'. \qquad (107)$$

The proof of this theorem immediately follows from (100).

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CHAPTER II

DIFFUSION IN MULTICOMPONENT SYSTEMS

§ 1. *Introduction.* In chapter I of this thesis we have introduced the phenomenological description of the diffusion phenomenon and have given an appropriate definition of the diffusion coefficient for a binary mixture (*cf.* § I.7*A*). It is the purpose of the present chapter to extend this description to the case of a multicomponent system and to derive the relations between the diffusion coefficients resulting from the Onsager relations.

As was already done in the case of a binary mixture, the diffusion of the components can be described with respect to various reference velocities, giving rise to different matrices of diffusion coefficients. The relations between these matrices follow from the transformations between the sets of diffusion flows, to which these matrices correspond (for ternary mixtures similar calculations have been given by Prigogine[1])).

The transformation formulae relating the various types of diffusion flows are derived in § 2. The corresponding transformation of the conjugated thermodynamic forces follows with the help of the treatment to be developed in chapter V.

Starting from the expression for the entropy production, we can describe the diffusion most easily with respect to one of the components (*e.g.*, the solvent). This is done in § 3, where the corresponding phenomenological equations (Fick's law in the first form) and the diffusion matrix D are formulated and where the relations between the diffusion coefficients resulting from the Onsager relations are given. In § 4 the description with respect to an arbitrary mean velocity is derived from § 3 with the help of the transformation formulae of § 2. The connection with the coefficient of binary diffusion, introduced in § I.7*A*, is discussed in § 5. The differential equations for the diffusion (Fick's law in the second form) are deduced in § 6 and in § 7 the results are specified for a ternary mixture.

Since the phenomenological equations relate the diffusion flows to the gradients of the chemical potentials, one has to introduce the derivatives of the chemical potentials with respect to the concentrations in order to find Fick's law in the usual form. For these derivatives the

Gibbs-Duhem relations hold and, in addition, a number of relations which (like Maxwell's relations) follow by cross differentiation of thermodynamic functions. They are derived in Appendix I. In Appendix II we give the derivatives of concentrations with respect to fractions and conversely for a ternary mixture.

§ 2. *Transformation formulae for the diffusion flows.* For a mixture of n components (labelled $k = 1, \ldots, n$) with velocities $\mathbf{v}_k$ we can introduce an arbitrary mean velocity

$$\mathbf{v}^a \equiv \Sigma_{k=1}^n w_k \mathbf{v}_k, \qquad (\Sigma_{k=1}^n w_k = 1), \tag{1}$$

and define the diffusion flows $\mathbf{J}_k^a$ with respect to $\mathbf{v}^a$

$$\mathbf{J}_k^a \equiv \varrho_k(\mathbf{v}_k - \mathbf{v}^a), \qquad (k = 1, \ldots, n), \tag{2}$$

which, according to the definition (1) of $\mathbf{v}^a$, satisfy the identity

$$\Sigma_{k=1}^n w_k \mathbf{J}_k^a / c_k = 0, \tag{3}$$

(c_k is the mass fraction ϱ_k/ϱ of component k). Examples of $\mathbf{v}^a$ have been given in Ch. I. § 5*A*.

Let $\mathbf{v}^b$ be an other mean velocity

$$\mathbf{v}^b \equiv \Sigma_{k=1}^n u_k \mathbf{v}_k, \qquad (\Sigma_{k=1}^n u_k = 1), \tag{4}$$

and

$$\mathbf{J}_k^b \equiv \varrho_k(\mathbf{v}_k - \mathbf{v}^b), \qquad (k = 1, \ldots, n), \tag{5}$$

the corresponding flows satisfying the identity

$$\Sigma_{k=1}^n u_k \mathbf{J}_k^b / c_k = 0. \tag{6}$$

If $w_n \neq 0$ and $u_n \neq 0$ the $n - 1$ independent flows $\mathbf{J}_1^a, \ldots, \mathbf{J}_{n-1}^a$ can be expressed in the independent flows $\mathbf{J}_1^b, \ldots, \mathbf{J}_{n-1}^b$ by a linear transformation

$$\mathbf{J}_k^a = \Sigma_{i=1}^{n-1} P_{ki} \mathbf{J}_i^b, \qquad (k = 1, \ldots, n-1), \tag{7}$$

where the matrix P is given by

$$P_{ki} = \delta_{ki} + (w_n u_i / u_n - w_i) c_k / c_i, \qquad (i, k = 1, \ldots, n-1), \tag{8}$$

as follows in a straightforward manner by expressing both sides of (7) in terms of the independent velocities $\mathbf{v}_1, \ldots, \mathbf{v}_n$, subsequently equating the coefficients of these velocities appearing on both sides of the equation. The inverse matrix P^{-1} follows from (8) by interchanging the weight factors u and w

$$P_{ki}^{-1} = \delta_{ki} + (u_n w_i / w_n - u_i) c_k / c_i, \qquad (i, k = 1, \ldots, n-1). \tag{9}$$

The flows $\mathbf{J}_n^a$ or $\mathbf{J}_n^b$ are determined by the remaining $n - 1$ independent flows through (3) or (6).

If the contribution of the flows $\mathbf{J}_k^a$ to the entropy production (per unit time and volume) is

$$\sigma_1 = \Sigma_{k=1}^{n-1} \mathbf{J}_k^a \cdot \mathbf{X}_k^a, \tag{10}$$

one can apply the linear transformation P^{-1} to the flows $\mathbf{J}_k^a$ and rewrite the entropy production in the form

$$\sigma_1 = \Sigma_{k=1}^{n-1} \mathbf{J}_k^b \cdot \mathbf{X}_k^b. \tag{11}$$

As phenomenological equations one introduces linear relationships between the flows $\mathbf{J}_k^a$ and the corresponding thermodynamic forces $\mathbf{X}_k^a$ and similarly between the flows $\mathbf{J}_k^b$ and the forces $\mathbf{X}_k^b$. From the treatment in chapter V it follows that the validity of the Onsager reciprocity relations between the phenomenological coefficients is not affected by the transformation if the transformation matrix of the forces $\mathbf{X}_k^a$ equals $\tilde{P}$ (the symbol $\sim$ indicates the transposed matrix), *i.e.*,

$$\mathbf{X}_k^b = \Sigma_{i=1}^{n-1} P_{ik} \mathbf{X}_i^a, \qquad (k = 1, \ldots, n-1). \tag{12}$$

Finally, we may remark that the above transformation can also be performed in the absence of mechanical equilibrium.

§ 3. *Description of diffusion with respect to one of the components.* In order to describe diffusion phenomena in a multicomponent system we consider for the sake of brevity the simple case of an isotropic mixture of n non-reacting components which are not subject to external forces. Temperature gradients and viscous forces will not be taken into consideration. From the equation of motion (I. 10) it follows that the pressure will be uniform as soon as the system is at mechanical equilibrium ($\mathrm{d}\mathbf{v}/\mathrm{d}t = 0$).

We first write down the expression for the entropy production σ for this case which follows from the more general expression, given in § I. 3. With the assumption of mechanical equilibrium we can replace the centre of mass velocity in the diffusion flows occurring in the expression for σ by an arbitrary other reference velocity as was done in § I. 5*A*. Thus, for the present case we can take as a starting point equation (I.31) which reduces to

$$T\sigma = -\Sigma_{k=1}^{n} \mathbf{J}_k^a \cdot (\mathrm{grad}\, \mu_k)_{P,T}. \tag{13}$$

If we take the velocity $\mathbf{v}_n$ of the nth component (*e.g.*, the solvent in a solution) for the reference velocity $\mathbf{v}^a$ and denote

$$\mathbf{J}_k^r \equiv \varrho_k(\mathbf{v}_k - \mathbf{v}_n), \tag{14}$$

we are left with $n-1$ independent flows in (13). Choosing P, T and the concentrations $\varrho_1, \ldots, \varrho_{n-1}$ as the state variables we can rewrite (13) as

$$T\sigma = -\Sigma_{k=1}^{n-1} \mathbf{J}_k^r \cdot \Sigma_{i=1}^{n-1} \mu_{ki}\, \mathrm{grad}\, \varrho_i, \tag{15}$$

where

$$\mu_{ki} \equiv (\partial\mu_k/\partial\varrho_i)_{P,T,\varrho_j}, \qquad (i, j = 1, \ldots, n-1). \tag{16}$$

In view of (15) we introduce as phenomenological equations

$$\mathbf{J}^r_k = -\Sigma_{j=1}^{n-1} L_{kj}\, \Sigma_{i=1}^{n-1} \mu_{ji} \operatorname{grad} \varrho_i = -\Sigma_{i=1}^{n-1} D_{ki} \operatorname{grad} \varrho_i, \quad (k=1, \ldots, n-1), \tag{17}$$

which defines the coefficients of diffusion with respect to one of the components

$$D_{ki} \equiv \Sigma_{j=1}^{n-1} L_{kj}\, \mu_{ji}, \qquad (D = L\mu), \tag{18}$$

(between parentheses we have indicated the relation between the diffusion coefficients and the L_{kj} in matrix notation).

The Onsager reciprocal relations read

$$L_{kj} = L_{jk}, \qquad (\tilde{L} = L), \tag{19}$$

or in terms of the diffusion coefficients

$$\Sigma_{j=1}^{n-1} D_{jk}\, \mu_{ji} = \Sigma_{j=1}^{n-1} \mu_{jk}\, D_{ji}, \qquad (\tilde{D}\mu = \tilde{\mu} D), \tag{20}$$

which reduces the number of independent diffusion coefficients from $(n-1)^2$ to $\frac{1}{2}n(n-1)$.

§ 4. *Diffusion with respect to an arbitrary mean velocity.* In the foregoing section the diffusion has been described with respect to one of the components of the mixture. We now want to pass on to a description with respect to an arbitrary mean velocity. In order to do this we can take the phenomenological equations (17) as a starting point and transform from the flows $\mathbf{J}^r_k$ to the flows $\mathbf{J}^a_k$ defined by (2). With

$$\mathbf{J}^a_k = \Sigma_{i=1}^{n-1} P_{ki}\, \mathbf{J}^r_i, \tag{21}$$

where in view of (8) the matrix P is

$$P_{ki} = \delta_{ki} - w_i c_k / c_i, \tag{22}$$

it follows from (17) that

$$\mathbf{J}^a_k = -\Sigma_{j=1}^{n-1} P_{kj}\, \Sigma_{i=1}^{n-1} D_{ji} \operatorname{grad} \varrho_i = -\Sigma_{i=1}^{n-1} D^a_{ki} \operatorname{grad} \varrho_i, \tag{23}$$

which defines the diffusion coefficients D^a_{ki}. The diffusion matrix D^a is related to D by

$$D^a_{ki} = \Sigma_{j=1}^{n-1} P_{kj}\, D_{ji}, \qquad (D^a = PD). \tag{24}$$

The Onsager relations now read

$$\Sigma_{j,l=1}^{n-1} D^a_{jk}\, P^{-1}_{lj}\, \mu_{li} = \Sigma_{j,l=1}^{n-1} \mu_{lk}\, P^{-1}_{lj}\, D^a_{ji}, \qquad (\tilde{D}^a \tilde{P}^{-1} \mu = \tilde{\mu} P^{-1} D^a), \tag{25}$$

or with

$$\nu_{ji} \equiv \Sigma_{l=1}^{n-1} P^{-1}_{lj}\, \mu_{li}, \qquad (\nu \equiv \tilde{P}^{-1} \mu), \tag{26}$$

also

$$\Sigma_{j=1}^{n-1} D^a_{jk}\, \nu_{ji} = \Sigma_{j=1}^{n-1} \nu_{jk}\, D^a_{ji}, \qquad (\tilde{D}^a \nu = \tilde{\nu} D^a). \tag{27}$$

In deriving (23) we have taken the phenomenological equation (17) as a starting point and we have applied a linear transformation of the flows. Of course, the results of this section can also be achieved by a simultaneous transformation of fluxes *and* forces according to equations (7) and (12), subsequently introducing linear relationships between the transformed fluxes and forces. The phenomenological coefficients in these relations then will be connected to the coefficients L_{kj} of (17) in the same way as in equation (V.41). Again, we can introduce the diffusion matrix D^a and re-establish (24).

A third way to reach the above equations is to retain the general expression (13). However, since the n fluxes (and also the n forces) in (13) are interdependent, it is then necessary to eliminate one of the fluxes and one of the forces.

§ 5. *The connection with the binary diffusion coefficient D.* Of course, the foregoing descriptions also apply to binary mixtures. For that case we have defined in § I.7*A* a diffusion coefficient D which did not depend on the special choice of the weight factors w_k. In order to extend the description given in § I.7*A* to multicomponent systems, we introduce as the reference velocity the mean volume velocity

$$\mathbf{v}^\circ \equiv \Sigma_{k=1}^{n} \varrho_k v_k \mathbf{v}_k, \qquad (\Sigma_{k=1}^{n} \varrho_k v_k = 1), \tag{28}$$

and consider the phenomenological equations (23) for this special choice

$$\mathbf{J}_k^\circ \equiv \varrho_k(\mathbf{v}_k - \mathbf{v}^\circ) = -\, \Sigma_{i=1}^{n-1} D_{ki}^\circ \operatorname{grad} \varrho_i. \tag{29}$$

On comparison of this equation with (I.68) we see that (29) reduces for $n = 2$ to (I.68) with $D = D_{11}^\circ$. The general definition (I.62) or (I.65) of D is also included in the present description and can be derived from (29). As a matter of fact, if we express the diffusion matrix D^a defined by (23) in terms of the D_{ki}° by

$$D_{ki}^a = \Sigma_{j=1}^{n-1} Q_{kj} D_{ji}^\circ, \qquad (D^a = QD^\circ), \tag{30}$$

where analogous to (8)

$$Q_{ki} = \delta_{ki} + (w_n \varrho_i v_i / \varrho_n v_n - w_i) c_k / c_i, \tag{31}$$

we can rewrite (23) in the form

$$\mathbf{J}_k^a = -\, \Sigma_{i=1}^{n-1} (QD^\circ)_{ki} \operatorname{grad} \varrho_i. \tag{32}$$

For $n = 2$ this reduces to

$$\mathbf{J}_1^a = -\, w_2 (\varrho_2 v_2)^{-1} D_{11}^\circ \operatorname{grad} \varrho_1, \tag{33}$$

which is equation (I.65). So the matrix D° should be considered as the generalization of the binary diffusion coefficient D. The reciprocal relations for D° are included in (27).

In his paper on liquid diffusion Onsager 2) also considers diffusion flows with respect to $\mathbf{v}^\circ$, but states that "it seems impossible to devise a simple general scheme of description for an n-component system which reduces directly to Fick's law with one single diffusion coefficient for the case $n = 2$". From the above it is clear how such a general scheme could be obtained. The reason why this reduction is not possible with Onsager's description is that in the latter treatment n^2 coefficients are introduced for $n > 2$, but only one single coefficient for $n = 2$. Thus n interdependent diffusion flows are chosen for $n > 2$ which are related to n interdependent concentration gradients. The situation thus met with is quite analogous to the one described in chapter IV: there exists a number of relations between the phenomenological coefficients and, moreover, a certain arbitrariness in the definition of these coefficients. The transition to the case $n = 2$ with the use of independent quantities then cannot be performed directly but follows from the treatment to be developed in chapter IV, if one introduces in the phenomenological equations the appropriate thermodynamic forces, which are to be taken from the expression for the entropy production (these forces are the quantities $(\operatorname{grad}\mu_k)_{P,T}$).

§ 6. *The differential equation for the diffusion.* In the absence of chemical reactions conservation of mass is expressed by

$$\partial\varrho_k/\partial t = -\operatorname{div}\varrho_k\mathbf{v}_k = -\operatorname{div}\mathbf{J}_k^a - \operatorname{div}\varrho_k\mathbf{v}^a. \tag{34}$$

For a closed vessel the boundary condition can always be expressed by the vanishing of some average of the absolute flows $\varrho_k\mathbf{v}_k$ which means that for a certain choice of the weight factors w_k

$$\mathbf{v}^a \equiv \Sigma_{k=1}^{n} w_k\mathbf{v}_k = 0, \tag{35}$$

(*e.g.*, if the partial specific volumes vary only slightly throughout the vessel, the mean volume velocity can be taken zero, *cf.* Ch. I, App. I). For this special choice of the reference velocity we can insert (23) in the conservation law (34):

$$\partial\varrho_k/\partial t = \operatorname{div}\Sigma_{i=1}^{n-1} D_{ki}^a \operatorname{grad}\varrho_i = \Sigma_{i=1}^{n-1}\{D_{ki}^a\,\Delta\varrho_i + \operatorname{grad}D_{ki}^a\cdot\operatorname{grad}\varrho_i\}. \tag{36}$$

If, moreover, these special diffusion coefficients D_{ki}^a would depend only slightly on the densities ϱ_i, the last term of (36) could be neglected and the differential equation would take the simple form

$$\partial\varrho_k/\partial t = \Sigma_{i=1}^{n-1} D_{ki}^a\,\Delta\varrho_i. \tag{37}$$

§ 7. *Ternary mixtures.* For the case of a ternary mixture we have 4 diffusion coefficients between which one Onsager relation exists. For diffusion with respect to a 'solvent' this relation reads

$$D_{11}\mu_{12} - D_{12}\mu_{11} = D_{22}\mu_{21} - D_{21}\mu_{22} \tag{38}$$

and for diffusion with respect to an arbitrary mean velocity analogously

$$D^a_{11}\nu_{12} - D^a_{12}\nu_{11} = D^a_{22}\nu_{21} - D^a_{21}\nu_{22}. \tag{39}$$

For this case the differential equations are

$$\partial\varrho_k/\partial t = D^a_{k1}(\partial^2\varrho_1/\partial x^2) + D^a_{k2}(\partial^2\varrho_2/\partial x^2), \quad (k = 1, 2), \tag{40}$$

if the diffusion is a one-dimensional phenomenon.

APPENDIX I

In the derivation of (13) (*viz.*, in the proof of Prigogine's theorem which leads to (13)) use is made of the Gibbs-Duhem relation, which may be written

$$\Sigma^n_{j=1}\, \varrho_j\, \mu_{jk} = 0, \qquad (k = 1, \ldots, n-1). \tag{41}$$

It should be noted that apart from these equations a number of additional relations exists between the derivatives μ_{kj} (and analogously between the ν_{kj}). Similar relations (*e.g.*, for the derivatives of chemical potentials or activities with respect to molalities, mole fractions or mole numbers) can be found in the literature 3) 4) 5).

In order to derive the relations which do apply in the present treatment, we choose P, T and the mass fractions $c_1, \ldots, c_{n-1}$ as state variables and start from the thermostatic equation

$$\mathrm{d}g = -\,s\mathrm{d}T + v\mathrm{d}P + \Sigma^n_{i=1}\, \mu_i \mathrm{d}c_i = -\,s\mathrm{d}T + v\mathrm{d}P + \Sigma^{n-1}_{i=1}\, (\mu_i - \mu_n)\mathrm{d}c_i, \tag{42}$$

where g, s and v are the mean specific Gibbs function, entropy and volume, resp. By cross differentiation we find

$$\{\partial(\mu_k - \mu_n)/\partial c_i\}_{P,T,c_j} = \{\partial(\mu_i - \mu_n)/\partial c_k\}_{P,T,c_j}, \tag{43}$$

or

$$\partial\mu_k/\partial c_i - \partial\mu_i/\partial c_k = \partial\mu_n/\partial c_i - \partial\mu_n/\partial c_k, \quad (i, k = 1, \ldots, n-1). \tag{44}$$

With the help of the Gibbs-Duhem relation in the form

$$\Sigma^n_{j=1}\, c_j(\partial\mu_j/\partial c_k)_{P,T,c_l} = 0, \qquad (k = 1, \ldots, n-1), \tag{45}$$

we can eliminate μ_n from (44):

$$\partial\mu_k/\partial c_i - \partial\mu_i/\partial c_k = c_n^{-1}\, \Sigma^{n-1}_{j=1}\, c_j(\partial\mu_j/\partial c_k - \partial\mu_j/\partial c_i). \tag{46}$$

(An alternative starting point for the derivation of (44) is provided by the Euler relation

$$g = \Sigma^n_{l=1}\, c_l\mu_l, \tag{47}$$

from which one can easily derive (44) making use of

$$\partial^2 g/\partial c_i\,\partial c_k = \partial^2 g/\partial c_k\,\partial c_i \tag{48}$$

and of the Gibbs-Duhem relation).

For $i \neq k$ we have $\frac{1}{2}(n-1)(n-2)$ non-trivial relations (44) which are independent of the $n-1$ Gibbs-Duhem relations (45). Thus, the number of independent derivatives $\partial\mu_l/\partial c_i$ (with $l = 1, \ldots, n$; $i = 1, \ldots, n-1$) is diminished from $n(n-1)$ to $\frac{1}{2}n(n-1)$.

We now can pass on to the use of the densities ϱ_i, instead of the fractions c_i. With (16) we have

$$(\partial\mu_k/\partial c_i)_{P,T,c_l} = \Sigma_{j=1}^{n-1}\,\mu_{kj}\,(\partial\varrho_j/\partial c_i)_{P,T,c_l}. \tag{49}$$

For a ternary mixture the derivatives $\partial\varrho_j/\partial c_i$ are given in App. II (59). For this case there is only one relation (46) which by means of (49) and (59) can be written as

$$\varrho_1 v_2 \mu_{11} - (1-\varrho_2 v_2)\mu_{12} = \varrho_2 v_1 \mu_{22} - (1-\varrho_1 v_1)\mu_{21}. \tag{50}$$

This relation gives rise to a corresponding one between the quantities ν_{kj} occurring in the description of diffusion with respect to an arbitrary mean velocity (cf. (26)):

$$\begin{aligned}&\varrho_1\nu_{11}\{v_2(w_1-1)+w_2(1-\varrho_1 v_1)/\varrho_2\}+\nu_{12}\{(1-\varrho_2 v_2)(1-w_1)-w_2\varrho_1 v_1\}=\\&=\varrho_2\nu_{22}\{v_1(w_2-1)+w_1(1-\varrho_2 v_2)/\varrho_1\}+\nu_{21}\{(1-\varrho_1 v_1)(1-w_2)-w_1\varrho_2 v_2\}.\end{aligned} \tag{51}$$

This relation takes a very simple form for $w_k = \varrho_k v_k$ (which means that the mean volume velocity is taken as the reference velocity of diffusion), *viz.*,

$$\nu_{12} = \nu_{21}. \tag{52}$$

Hence the Onsager relation reads

$$D^\circ_{12}\,\nu_{11} - D^\circ_{21}\,\nu_{22} = \nu_{12}\,(D^\circ_{11} - D^\circ_{22}) \tag{53}$$

for this case.

APPENDIX II

The phenomenological laws (17) and (23) connect the diffusion flows with the gradients of the *densities* of the components. Of course, we could as well have introduced the *fractions* of the various components as state variables. Then the diffusion coefficients would have referred to the gradients of these fractions. The advantage of this choice would manifest itself in the corresponding derivatives of the chemical potentials. For several cases (ideal solutions, regular solutions) these derivatives take a very simple form if they are taken with respect to the mole fractions (though the foregoing treatment has been set up for mass quantities it is obvious that we could have used molar quantities as well.) However, the law of conservation of mass takes its most simple form if densities are used and the same holds for the diffusion equations in the differential form.

In order to express the μ_{ki} in terms of the derivatives $\partial\mu_k/\partial c_i$ (for derivatives with respect to molar quantities the calculation goes along the same lines) in the case of a ternary mixture we start with (49) where we still have to find the $\partial\varrho_j/\partial c_i$. From

$$\Sigma_{k=1}^{3}\, v_k(\delta\varrho_k)_{P,T} = 0 \tag{54}$$

(*cf.* (I.94)) and

$$(\delta\varrho_k)_{P,T} = (\partial\varrho_k/\partial c_1)_{P,T,c_2}\,\delta c_1 + (\partial\varrho_k/\partial c_2)_{P,T,c_1}\,\delta c_2 \tag{55}$$

it follows that

$$\Sigma_{i=1}^{2}\,\{\Sigma_{k=1}^{3}\, v_k(\partial\varrho_k/\partial c_i)\}\,\delta c_i = 0, \tag{56}$$

or, since the δc_i are independent,

$$\Sigma_{k=1}^{3}\, v_k(\partial\varrho_k/\partial c_i) = 0, \qquad (i = 1, 2). \tag{57}$$

Writing $\varrho_1 = c_1\varrho$, $\varrho_2 = c_2\varrho$, $\varrho_3 = (1 - c_1 - c_2)\varrho$ we then find

$$\partial\varrho/\partial c_i = \varrho^2(v_3 - v_i), \tag{58}$$

and finally

$$\partial\varrho_j/\partial c_i = \varrho\delta_{ij} + \varrho\varrho_j(v_3 - v_i), \qquad (i, j = 1, 2). \tag{59}$$

The Jacobian determinant of these four derivatives equals $\varrho^3 v_3$. By inversion we find

$$\left.\begin{aligned} \partial c_1/\partial\varrho_1 &= \{1 + \varrho_2(v_3 - v_2)\}/\varrho^2 v_3, \\ \partial c_1/\partial\varrho_2 &= -\,\varrho_1(v_3 - v_2)/\varrho^2 v_3. \end{aligned}\right\} \tag{60}$$

The other derivatives are found by interchanging the subscripts 1 and 2.

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CHAPTER III

SEDIMENTATION IN PAUCIDISPERSE SYSTEMS

§ 1. *Introduction.* In the first chapter we have derived the general expression for the entropy production in rotating mixtures and formulated the phenomenological equations for sedimentation in monodisperse uncharged systems. In the present chapter we want to extend this treatment to paucidisperse systems with particular emphasis on a description of the sedimentation process in ternary mixtures. The coefficients of diffusion for multicomponent systems, introduced in the preceding chapter, will be used.

The general form of the Onsager relations for vectorial phenomena in rotating systems is given in § 2. With the help of the expression for the entropy production, we formulate in § 3 the phenomenological equations for the fluxes of matter in rotating isothermal mixtures of uncharged components. In particular, we consider the fluxes with respect to the mean volume velocity. The spatial distribution of the components in sedimentation equilibrium is given in § 4 and is specified for ideal solutions.

The equations for the sedimentation velocities in paucidisperse systems are considered in detail in § 5. They are derived from the phenomenological equations by neglecting transverse effects and by introducing the boundary condition for a closed vessel, which for liquids leads to the vanishing of the mean volume velocity, previously chosen as the reference velocity.

For ternary mixtures the equations describe the effect of a boundary layer of one of the sedimenting components on the sedimentation velocity of the other. As is discussed in § 5*A*, this effect might in part account for a boundary anomaly, encountered in experimental investigations. The change in sedimentation velocity, due to the presence of other sedimenting materials is explicitly calculated in § 5*B* for ideal solutions. From the final equations it is clear, that in the region where both components have a finite density, each of the components can be slowed down by the other. This effect might explain the occurrence of a 'backward flow', encountered in sedimentation experiments where slowly sedimenting materials are mixed with more rapidly sedimenting ones. This effect also might contribute to the above mentioned boundary anomaly.

In the Appendix we give the formulae for the derivatives of the densities with respect to the chemical potentials for ideal solutions, used in § 5*A*.

§ 2. *The Onsager relations for vectorial phenomena in a rotating system or in a magnetic field.* In this section we give the Onsager reciprocal relations for vectorial processes in an isotropic medium, which is subject to an over-all rotation or placed in a uniform external magnetic field; the angular velocity or the magnetic field will be denoted by the comprehensive symbol H.

The contribution of the vectorial processes to the entropy production σ (per unit time and volume) can be written

$$T\sigma_v = \Sigma_{k=1}^{\nu}\, \mathfrak{J}_k \cdot \mathfrak{X}_k, \tag{1}$$

with ν independent fluxes $\mathfrak{J}_k$ and ν independent thermodynamic forces $\mathfrak{X}_k$. We then introduce the phenomenological equations

$$\mathfrak{J}_k = \Sigma_{i=1}^{\nu}\, \mathsf{L}_{ki} \cdot \mathfrak{X}_i, \qquad (k = 1, \ldots, \nu). \tag{2}$$

Each tensor L_{ki} can be split into a symmetrical and an antisymmetrical tensor with respect to space coordinates

$$\mathsf{L}_{ki} = \mathsf{L}_{ki}^{s} + \mathsf{L}_{ki}^{a}. \tag{3}$$

If the z-axis is chosen in the direction of H it follows from the isotropy of the medium that the relations (2) are invariant for rotation about the z-axis, hence

$$\mathsf{L}_{ki} = \begin{bmatrix} L_{ki}^{11} & L_{ki}^{12} & 0 \\ -L_{ki}^{12} & L_{ki}^{11} & 0 \\ 0 & 0 & L_{ki}^{33} \end{bmatrix} \tag{4}$$

or

$$\mathsf{L}_{ki}^{s} = \begin{bmatrix} L_{ki}^{11} & 0 & 0 \\ 0 & L_{ki}^{11} & 0 \\ 0 & 0 & L_{ki}^{33} \end{bmatrix} \quad \text{and} \quad \mathsf{L}_{ki}^{a} = \begin{bmatrix} 0 & L_{ki}^{12} & 0 \\ -L_{ki}^{12} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}. \tag{5}$$

The number of phenomenological coefficients is thus reduced from $9\nu^2$ to $3\nu^2$. Moreover, it follows from the isotropy that the relations (2) are invariant for a rotation about an axis, perpendicular to the z-axis, by an angle π. From this it follows, that L_{ki}^{s} is an even function of H and L_{ki}^{a} is an odd function of H.

The Onsager reciprocal relations read ¹) ²)

$$\mathsf{L}_{ki}(\mathrm{H}) = \mathsf{L}_{ik}^{\dagger}(-\mathrm{H}), \tag{6}$$

(where † indicates transposing of the Cartesian components), which can be written as

$$\mathsf{L}_{ki}(\mathrm{H}) = \mathsf{L}_{ik}(\mathrm{H}), \tag{7}$$

since

$$\begin{aligned} \mathsf{L}^s_{ki}(\mathrm{H}) &= \mathsf{L}^s_{ik}(-\mathrm{H}) = \mathsf{L}^s_{ik}(\mathrm{H}), \\ \mathsf{L}^a_{ki}(\mathrm{H}) &= \mathsf{L}^{a\dagger}_{ik}(-\mathrm{H}) = -\,\mathsf{L}^{a\dagger}_{ik}(\mathrm{H}) = \mathsf{L}^a_{ik}(\mathrm{H}), \end{aligned} \tag{8}$$

where we have used the parities of $\mathsf{L}^s_{ik}(\mathrm{H})$ and $\mathsf{L}^{a\dagger}_{ik}(\mathrm{H})$. So by means of the Onsager relations the number of independent coefficients is further reduced to $\frac{3}{2}\nu(\nu + 1)$.

§ 3. *The phenomenological equations for sedimentation in paucidisperse systems.* As in chapter I we consider a system of n non-reacting components, rotating with an angular velocity $\boldsymbol{\omega}$. At mechanical equilibrium the entropy production is again given by (I.31), where the flows $\mathbf{J}^a_k$ are taken with respect to the mean velocity $\mathbf{v}^a$. For this reference velocity we choose the velocity of the nth component (the solvent), the flow $\mathbf{J}^r_n$ then being zero. If the components do not carry electrical charges and if the system is isothermal, equation (I.31) then reduces to

$$T\sigma = \Sigma_{k=1}^{n-1}\, \mathbf{J}^r_k \cdot \{(1 - \varrho v_k)\,(\omega^2\mathbf{r} + 2\mathbf{v} \wedge \boldsymbol{\omega}) - (\mathrm{grad}\,\mu_k)_{P,T}\}, \tag{9}$$

which is an extension of (II.15), since (9) gives the entropy production for diffusion in the presence of an external field.

According to (2) we introduce as phenomenological equations

$$\mathbf{J}^r_k = \Sigma_{i=1}^{n-1}\, \mathsf{L}_{ki} \cdot \{(1 - \varrho v_i)(\omega^2\mathbf{r} + 2\mathbf{v} \wedge \boldsymbol{\omega}) - (\mathrm{grad}\,\mu_i)_{P,T}\}, \quad (k = 1, \ldots, n-1), \tag{10}$$

which is the extension of (II.17) to the present case. The tensors L_{ki} satisfy the Onsager relations (7) with $\mathrm{H} = \boldsymbol{\omega}$.

In the same way as in chapter II (*cf.* §§ 4 and 5) we can find from (10) the phenomenological equations for the flows $\mathbf{J}^\circ_k$ with respect to the mean volume velocity

$$\mathbf{v}^\circ = \Sigma_{k=1}^{n}\, \varrho_k v_k \mathbf{v}_k, \tag{11}$$

making use of the matrix P which transforms the flows $\mathbf{J}^r_k$ into the flows $\mathbf{J}^\circ_k$,

$$\mathbf{J}^\circ_k \equiv \varrho_k(\mathbf{v}_k - \mathbf{v}^\circ) = \Sigma_{i=1}^{n-1}\, P_{ki}\, \mathbf{J}^r_i, \quad (k = 1, \ldots, n-1), \tag{12}$$

where, according to (II.22) for $w_i = \varrho_i v_i$,

$$P_{ki} = \delta_{ki} - \varrho_k v_i. \tag{13}$$

The phenomenological equations (10) then yield

$$\mathbf{J}^\circ_k = \Sigma_{i=1}^{n-1}\, \mathsf{L}'_{ki} \cdot \{(1 - \varrho v_i)\,(\omega^2\mathbf{r} + 2\mathbf{v} \wedge \boldsymbol{\omega}) - (\mathrm{grad}\,\mu_i)_{P,T}\}, \tag{14}$$

where

$$\mathsf{L}'_{ki} = \Sigma_{j=1}^{n-1}\, P_{kj}\, \mathsf{L}_{ji}. \tag{15}$$

The phenomenological equations (14) are the basic equations for our description of sedimentation in paucidisperse systems.

N.B. We might remark that for the tensors L'_{ki} the Onsager relations do not hold in the form (7), since in passing on from (10) to (14) we have not performed a simultaneous transformation of the thermodynamic forces (*cf.* chapter V).

§ 4. *The sedimentation equilibrium.* Inasmuch as thermostatic equilibrium is characterized by the vanishing of the entropy production, it follows from (9) and (10) or (14) that the flows and the corresponding thermodynamic forces vanish. The vanishing of the fluxes means, that $\mathbf{v}_1 = \ldots = \mathbf{v}_n = 0$ in a closed vessel. Thus, the centre of mass velocity $\mathbf{v}$ equals zero and we find for $k = 1, \ldots, n-1$ the well-known equilibrium equation

$$(1 - \varrho v_k)\omega^2\mathbf{r} - (\operatorname{grad} \mu_k)_{P,T} = 0, \tag{16}$$

which, as a consequence, also holds for $k = n$ (this follows immediately with the help of (I.50) and (I.51)).

These equations describe the distribution of the components in sedimentation equilibrium. Choosing P, T and the mole fractions $n_1, \ldots, n_{n-1}$ as state variables we can rewrite (16) as

$$\Sigma_{i=1}^{n-1} (\partial\mu_k/\partial n_i)_{P,T,n_j} \operatorname{grad} n_i = (1 - \varrho v_k)\omega^2\mathbf{r}. \tag{17}$$

For ideal solutions, where

$$(\partial\mu_k/\partial n_i)_{P,T,n_j} = RT\delta_{ki}/M_k n_k, \tag{18}$$

we find for each of the n components

$$n_k^{-1} \operatorname{grad} n_k = M_k(1 - \varrho v_k)\omega^2\mathbf{r}/RT, \tag{19}$$

analogous to (I.58).

In order to express the equilibrium distribution in terms of the mass fractions c_i we need the derivatives

$$\partial c_k/\partial n_i = c_i\,\{M_i\delta_{ki} - c_k(M_i - M_n)\}/M_i n_i, \quad (k, i = 1, \ldots, n-1), \tag{20}$$

with the help of which we find

$$c_k^{-1} \operatorname{grad} c_k = \{M_k(1 - \varrho v_k) - \Sigma_{i=1}^{n} c_i M_i(1 - \varrho v_i)\}\,\omega^2\mathbf{r}/RT, \tag{21}$$

which also holds for $k = n$ and includes (I.59) for binary mixtures.

§ 5. *The sedimentation velocity in paucidisperse systems.* The phenomenological equations (14) enable us to find expressions for the sedimentation velocity in paucidisperse systems.

If we neglect, as we also did in chapter I, all transverse effects, the Coriolis force in (14) can be left out and the tensors L'_{ki} reduce for an isotropic solution to scalar coefficients L'_{ki}, hence

$$\mathbf{J}_k^\circ = \Sigma_{i=1}^{n-1} L'_{ki}\,\{(1 - \varrho v_i)\,\omega^2\mathbf{r} - \Sigma_{j=1}^{n-1} \mu_{ij} \operatorname{grad} \varrho_j\}. \tag{22}$$

The derivatives μ_{ij} are defined in (II.16). The coefficient of $-$ grad ϱ_j in this equation is the diffusion coefficient D°_{kj}, introduced in (II.29). So we can write

$$\Sigma_{i=1}^{n-1} L'_{ki}\,\mu_{ij} = D^\circ_{kj}, \qquad (L' = D^\circ \mu^{-1}). \tag{23}$$

The coefficients D°_{kj} satisfy the Onsager relations in the form (II.27).

In particular, we want to consider a ternary mixture, a case that is frequently met with in ultracentrifuge measurements. As was shown in chapter I, App. I, the boundary condition for a closed vessel can be expressed by the vanishing of the mean volume velocity $\mathbf{v}^\circ$ with the assumption that the partial specific volumes v_k do not appreciably depend on pressure and concentrations. For a ternary mixture the sedimentation velocities are then given by

$$\varrho_k \mathbf{v}_k = \Sigma_{j=1}^{2} D^\circ_{kj}\,\{\Sigma_{i=1}^{2}\,\mu_{ji}^{-1}\,(1 - \varrho v_i)\,\omega^2 \mathbf{r} - \operatorname{grad} \varrho_j\}, \quad (k = 1, 2). \tag{24}$$

In these equations four diffusion coefficients occur, which are interrelated by the Onsager relation

$$\nu_{11}^{-1}\,D^\circ_{21} - \nu_{22}^{-1}\,D^\circ_{12} = \nu_{12}^{-1}(D^\circ_{11} - D^\circ_{22}), \quad (\widetilde{D^0 \nu^{-1}} = D^\circ \nu^{-1}), \tag{25}$$

(cf. (II.27) or (II.53)), where the coefficients ν_{ki}^{-1} follow from the μ_{kj}^{-1} according to (II.26)

$$\nu_{ki}^{-1} = \Sigma_{j=1}^{2}\,\mu_{kj}^{-1}\,P_{ij}, \qquad (\nu^{-1} = \mu^{-1}\,\tilde{P}), \tag{26}$$

or, with (13),

$$\nu_{ki}^{-1} = \mu_{ki}^{-1}\,(1 - \varrho_i v_i) - \mu_{kj}^{-1} \varrho_i v_j, \quad (i, j, k = 1, 2; i \neq j). \tag{27}$$

The coefficients μ_{ki}^{-1} (the derivatives $(\partial \varrho_k / \partial \mu_i)_{P,T,\mu_j}$) together form the matrix μ^{-1}, which is the inverse of the matrix μ of derivatives μ_{ki}. For an ideal solution μ^{-1} is given in the Appendix.

From (24) one could in principle derive the mutual influence of the components on the sedimentation velocities and, by solving the differential equation resulting from the insertion of (24) in the law of conservation of mass (analogous to § II.6), determine the distribution of the components in the course of the sedimentation process. This would require the knowledge of the derivatives μ_{ki}^{-1} and the diffusion coefficients, in particular the cross coefficients D°_{12} and D°_{21}. However, some simple conclusions can be drawn already from (24), which might account for two effects, established in experimental sedimentation study. These will be described in the following sections.

A. The influence of boundary layers on sedimentation velocities. As was first discovered by Johnston and Ogston[3][4], an anomalous behaviour in the sedimentation patterns of mixtures is caused by a boundary anomaly. There is an apparent increase (a 'build up') of the amount of the less rapidly sedimenting component with a corresponding decrease in the amount of the other in the region above the boundary of faster mobility. The magnitude of the effect always increases with increase in solute concentration.

One contribution to this effect seems to be described immediately by the equations (24). In fact, let the boundary layer of 2 be closer to the outer wall than the boundary of 1 (component 2 may be the more rapidly sedimenting one). In the boundary region of 2, grad ϱ_2 is positive and very large, whereas on both sides of this layer grad ϱ_2 is negligible. According to (24), grad ϱ_2 contributes to $\varrho_1\mathbf{v}_1$ by the term $-\overset{\circ}{D}_{12}$ grad ϱ_2. If now $\overset{\circ}{D}_{12}$ is positive, $\mathbf{v}_1$ will be *smaller* in the boundary region of 2 than on both sides of this boundary, even if $\overset{\circ}{D}_{12}$ is small. This situation will give rise to an increase of the amount of 1 over and above its original value in the region above the boundary of 2.

Since grad ϱ_2 increases for larger values of ϱ_2 (the width of the boundary layer in first approximation being independent of ϱ_2), the magnitude of this effect indeed increases with increase in solute concentration, as was indicated by the experimental analysis.

Another possible contribution to the 'build up' will be described below.

B. Slowing down and backward flow during ultracentrifugation. In the foregoing we considered the influence of a density *gradient* of one of the components on the sedimentation velocity of the other. The description of the influence of the *densities* ϱ_1 and ϱ_2 on the sedimentation rates would require the knowledge of the derivatives μ_{ji}^{-1} and the dependence of the diffusion coefficients $\overset{\circ}{D}_{kj}$ on the composition.

In the following we shall assume ideality of the solution. We then find (*cf.* Appendix)

$$\mu_{ji}^{-1} = \varrho_j \{M_j\delta_{ji} - \varrho_i(\bar{v}_i - \bar{v}_3)\}/RT, \tag{28}$$

hence (24) reads

$$\begin{aligned}\varrho_2\mathbf{v}_2 = \varrho_2\overset{\circ}{D}_{22}\,[(1-\varrho v_2)\{M_2 - \varrho_2(\bar{v}_2-\bar{v}_3)\} - \varrho_1(1-\varrho v_1)(\bar{v}_1-\bar{v}_3)]\omega^2\mathbf{r}/RT \\ + \varrho_1\overset{\circ}{D}_{21}\,[(1-\varrho v_1)\{M_1 - \varrho_1(\bar{v}_1-\bar{v}_3)\} - \varrho_2(1-\varrho v_2)(\bar{v}_2-\bar{v}_3)]\omega^2\mathbf{r}/RT \\ - \overset{\circ}{D}_{22}\,\mathrm{grad}\,\varrho_2 - \overset{\circ}{D}_{21}\,\mathrm{grad}\,\varrho_1.\end{aligned} \tag{29}$$

The analogous expression for $\mathbf{v}_1$ follows by interchanging the subscripts 1 and 2. $\bar{v}_i$ is the partial molar volume

$$\bar{v}_i = M_i v_i. \tag{30}$$

We suppose the velocity of the boundary layer 1 to be given by $\mathbf{v}_1(A)$ in the region A between the two layers (where $\varrho_2 = 0$) and, likewise, the velocity of layer 2 by $\mathbf{v}_2(B)$ in the region B between layer 2 and the outer wall. Within these regions grad ϱ_1 = grad $\varrho_2 = 0$.

As long as the region A exists, the sedimentation rate of component 1 is given by

$$\mathbf{v}_1(A) = (1 - \varrho v_1) D_{11}^{\circ} \{M_1 - \varrho_1(\bar{v}_1 - \bar{v}_3)\} \omega^2 \mathbf{r}/RT, \tag{31}$$

which equals (I.78), as it should be, because in this period component 1 sediments as in the case of a monodisperse system. We can rewrite (31) as

$$\mathbf{v}_1(A) = (1 - \varrho v_1) D_{11}^{\circ} M_1 \{1 - \varrho_1 v_1 (1 - \bar{v}_3/\bar{v}_1)\} \omega^2 \mathbf{r}/RT. \tag{32}$$

Usually, the partial molar volume of component 1 is very large in comparison with the partial molar volume of the solvent ($\bar{v}_1 \gg \bar{v}_3$). We then have

$$\mathbf{v}_1(A) = (1 - \varrho v_1) D_{11}^{\circ} M_1 (1 - \varrho_1 \bar{v}_1) \omega^2 \mathbf{r}/RT, \tag{33}$$

which for a dilute solution ($\varrho_1 \bar{v}_1 \ll 1$) reduces to the Svedberg equation (I.80) with $D = D_{11}^{\circ}$.

Let us now consider the region B, where both components are present. $\mathbf{v}_2$ is given by (29) with grad ϱ_1 = grad $\varrho_2 = 0$.

If M_2 is not too small with respect to M_1 (we suppose $M_3 < M_2 < M_1$), the factors occurring after D_{22}° and D_{21}° in (29) are of the same order of magnitude in practical cases. Inasmuch as cross coefficients tend to zero for dilute solutions ($|D_{21}^{\circ}| \ll D_{22}^{\circ}$), $\mathbf{v}_2$ will then be determined by the first term on the right-hand side of (29), which can be written

$$\mathbf{v}_2(B) = (1 - \varrho v_2) D_{22}^{\circ} \{M_2 - \varrho_2(\bar{v}_2 - \bar{v}_3) - \varrho_1(\bar{v}_1 - \bar{v}_3)\} \omega^2 \mathbf{r}/RT, \tag{34}$$

since v_1 and v_2 are nearly the same. Similarly we then have

$$\mathbf{v}_1(B) = (1 - \varrho v_1) D_{11}^{\circ} \{M_1 - \varrho_1(\bar{v}_1 - \bar{v}_3) - \varrho_2(\bar{v}_2 - \bar{v}_3)\} \omega^2 \mathbf{r}/RT. \tag{35}$$

These equations describe the decrease in velocity of each component, due to the presence of the other component and, in particular, the slowing down of component 2 in the region B and hence a decrease in the sedimentation rate of 2, due to the finite value of ϱ_1.

We also can express this result in terms of sedimentation coefficients. In the absence of component 1 we have, analogous to (31),

$$\mathbf{v}_2 \equiv s_2^0 \omega^2 \mathbf{r} = (1 - \varrho v_2) D_{22}^{\circ} \{M_2 - \varrho_2 (\bar{v}_2 - \bar{v}_3)\} \omega^2 \mathbf{r}/RT, \tag{36}$$

which defines s_2^0, the sedimentation coefficient for component 2 in the absence of component 1. Here D_{22}° is a binary diffusion coefficient. We can rewrite (34) as

$$\begin{aligned} \mathbf{v}_2(B) \equiv s_2 \omega^2 \mathbf{r} = (1 - \varrho v_2) D_{22}^{\circ} \{M_2 - \varrho_2 (\bar{v}_2 - \bar{v}_3)\} \times \\ \times [1 - \varrho_1(\bar{v}_1 - \bar{v}_3)/\{M_2 - \varrho_2(\bar{v}_2 - \bar{v}_3)\}] \omega^2 \mathbf{r}/RT, \end{aligned} \tag{37}$$

which defines the sedimentation coefficient s_2 of component 2 in the ternary mixture. For infinite dilution of component 1 the coefficient D_{22}° in (37) will tend to the value for binary diffusion, occurring in (36). Taking the same value of ϱ in (36) and (37), neglecting $\bar{v}_3$ with respect to $\bar{v}_2$ and $\bar{v}_1$ and assuming $\varrho_2 v_2 \ll 1$, we therefore have in good approximation

$$s_2 = s_2^0(1 - \varrho_1 v_1 M_1/M_2). \tag{38}$$

If $M_2 \ll M_1$, the second term of (29) in general cannot be neglected in the region B. Since this term will have the sign of D_{21}°, its contribution to $\mathbf{v}_2(B)$ will depend on the sign of D_{21}° and on the magnitude of $|D_{21}^{\circ}|$ as compared with D_{22}°. If D_{21}° is negative, the term under consideration gives an extra contribution to the slowing down of component 2, caused by the presence of the other component. In order to estimate the change in $\mathbf{v}_2$ if D_{21}° is positive, we can take together all the terms in (29) containing ϱ_1. If we assume $\bar{v}_3 \ll \bar{v}_2$ (as is the case in sedimentation experiments) we have as a consequence $\bar{v}_3 \ll \bar{v}_1$ and the result of the presence of component 1 then can be seen to depend essentially on the sign of

$$-\varrho_2 v_1 D_{22}^{\circ} + (1 - \varrho_1 v_1) D_{21}^{\circ}. \tag{39}$$

Thus, also in this case component 2 will be slowed down if $D_{21}^{\circ}/D_{22}^{\circ}$ is smaller than $\varrho_2 v_1/(1 - \varrho_1 v_1)$.

According to the foregoing discussion, the equation (29) might account for the backward flow of slowly sedimenting materials in the presence of more rapidly sedimenting components, which occurs in experiments with the 'synthetic boundary cell' [5]): if 1 is more rapidly sedimenting than 2, the boundary of 1 overtakes the boundary of 2, merges with it and finally appears on the other side. The experiments showed that during the first part of the run there may be a backward flow of component 2. This effect might be explained by the foregoing description if the contribution of the term with D_{21}° is either negligible or negative.

The above treatment also suggests another contribution to the effect, mentioned in the preceding section A: the 'build up' of component 1 in the region A. From the discussion of equation (29) it is clear that, if $M_1 \lesseqgtr M_2$ (as was the case in actual experiments), component 1 will be slowed down in the region B as a result of the presence of component 2, the decrease in $\mathbf{v}_1$ being proportional to ϱ_2 (*cf.* (35)). This in turn might contribute to a build up of component 1 in the region A, the effect increasing for larger values of ϱ_2.

APPENDIX

In order to calculate the derivatives μ_{ji}^{-1} for ideal ternary mixtures we first take P, T and the mole fractions n_1, n_2 as state variables. We then have

$$\partial \mu_k / \partial n_i = RT \delta_{ki} / M_k n_k, \tag{40}$$

and inversely

$$\partial n_k/\partial \mu_i = M_k n_k \delta_{ki}/RT. \tag{41}$$

The derivatives μ_{ji}^{-1} follow from

$$\mu_{ji}^{-1} \equiv \partial \varrho_j/\partial \mu_i = \sum_{k=1}^{2} (\partial \varrho_j/\partial n_k)(\partial n_k/\partial \mu_i), \tag{42}$$

where we still have to find the $\partial \varrho_j/\partial n_k$. Since

$$\varrho_j = M_j n_j N, \tag{43}$$

(N is the total molar density) and, analogous to (II.58),

$$\partial N/\partial n_k = N^2(\bar{v}_3 - \bar{v}_k), \tag{44}$$

where $\bar{v}_k$ is the partial molar volume of component k, we find

$$\partial \varrho_j/\partial n_k = \varrho_j\{n_j^{-1}\delta_{jk} - N(\bar{v}_k - \bar{v}_3)\}. \tag{45}$$

The insertion of (41) and (45) into (42) yields (28).

The coefficients ν_{ki}^{-1}, occurring in the Onsager relation (25), are given by (27). For an ideal solution they follow by combining (27) and (28).

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Chapter IV

PHENOMENOLOGICAL EQUATIONS AND ONSAGER RELATIONS

§ 1. *Introduction.* In the thermodynamics of irreversible processes [1]) [2]) the entropy production can generally be written as a sum of products of fluxes and corresponding forces. The phenomenological equations describing the irreversible phenomena are introduced as linear equations between these two sets of quantities. For the scheme of phenomenological coefficients the Onsager reciprocal relations then hold.

Since in the proof of the Onsager relations the fluxes as well as the forces are assumed to be independent, this formalism should be applied with care if linear dependencies exist among the fluxes or among the forces. This is, *e.g.*, the case with the flows of matter in a mixture of several components if these flows are taken with respect to some mean velocity [1]), as was also done in the preceding chapters. Another example is the condition of vanishing volume flow in a closed vessel (*cf.* Ch. I, App. I), which reduces the number of independent absolute flows of matter [3]). Likewise, the number of independent forces may be diminished by a linear dependency such as can result, *e.g.*, from the condition of mechanical equilibrium [1]) [2]) (*cf.* Ch. I, App. III). An analogous situation arises for the chemical affinities in the case of a triangular reaction [1]).

A linear dependency for only one of the two classes of variables gives rise to additional relations among the phenomenological coefficients which leave the symmetry of the coefficient scheme unimpaired [1]) [4]), as is shown in § 2. However, when both classes of variables, fluxes and forces, are dependent, the phenomenological coefficients are not uniquely defined and the validity of the Onsager relations can no longer be guaranteed. Such a situation has been met with by Holtan in his treatment of thermocells [5]) (*l.c.* p. 44). The same problem may arise in the phenomenological theory of diffusion (§ II. 5.).

It is the purpose of this chapter to show that in the latter case the coefficients can always be chosen in such a way that the Onsager relations hold.

We shall restrict ourselves to the case of one single linear relation for each class of variables and only write down the formalism for vectorial irreversible phenomena in isotropic media.

§ 2. *The case of dependent fluxes.* When only vectorial irreversible phenomena occur, the entropy production σ can be written in the form

$$\sigma = \Sigma_{k=1}^{n} \mathbf{J}_k \cdot \mathbf{X}_k . \tag{1}$$

If the fluxes $\mathbf{J}_k$ as well as the forces $\mathbf{X}_k$ each constitute a set of independent quantities the phenomenological equations for isotropic media read

$$\mathbf{J}_k = \Sigma_{l=1}^{n} L_{kl} \mathbf{X}_l, \quad (k = 1, \ldots, n), \tag{2}$$

and in the absence of a magnetic field the Onsager reciprocal relations [6]) state that

$$L_{kl} = L_{lk}, \quad (l, k = 1, \ldots, n). \tag{3}$$

The system (2) can be solved for the $\mathbf{X}_l$, the new scheme of phenomenological coefficients again being symmetric.

Let us now suppose that one of the sets of quantities is independent whereas the other quantities are interrelated in a linear way, *e.g.*,

$$\Sigma_{k=1}^{n} a_k \mathbf{J}_k = 0. \tag{4}$$

With $a_n \neq 0$ we then can eliminate $\mathbf{J}_n$ from (1)

$$\sigma = \Sigma_{i=1}^{n-1} \mathbf{J}_i \cdot \{\mathbf{X}_i - a_i \mathbf{X}_n / a_n\}, \tag{5}$$

so that we are left with $n - 1$ independent fluxes and forces. Taking this expression for σ as a starting point it follows by straightforward calculation that the phenomenological equations (2) as well as the reciprocal relations (3) still hold although now a number of relations exist between the coefficients L_{kl}. In fact, starting from (5) we can write for the phenomenological equations

$$\mathbf{J}_i = \Sigma_{j=1}^{n-1} l_{ij} (\mathbf{X}_j - a_j \mathbf{X}_n / a_n), \quad (i = 1, \ldots, n - 1), \tag{6}$$

and on comparison with (2) making also use of (4) we find for $i, j = 1, \ldots, n - 1$

$$\left.\begin{aligned} L_{ij} &= l_{ij}, & L_{in} &= - \Sigma_{j=1}^{n-1} a_j l_{ij} / a_n, \\ L_{ni} &= - \Sigma_{j=1}^{n-1} a_j l_{ji} / a_n, & L_{nn} &= \Sigma_{i,j=1}^{n-1} a_i a_j l_{ij} / a_n^2 . \end{aligned}\right\} \tag{7}$$

From (7) it is clear that the coefficients L_{kl} now are interrelated by

$$\left.\begin{aligned} \Sigma_{l=1}^{n} a_l L_{kl} &= 0, \\ \Sigma_{k=1}^{n} a_k L_{kl} &= 0, \end{aligned}\right\} \quad (k, l = 1, \ldots, n), \tag{8}$$

a set of $2n - 1$ independent relations which could also be derived directly from (1), (2) and (4) (*cf.* [1]) p. 102).

Since the Onsager relations are valid for the coefficients l_{ij} it follows from (7) that equation (3) still holds.

Of course, equations (2) or (6) can no longer be solved for the n quantities $\mathbf{X}_l$ but only for the $n - 1$ quantities $\mathbf{X}_j - a_j \mathbf{X}_n / a_n$.

§ 3. *Dependent fluxes and forces.* In addition to (4) we shall next assume a linear relation

$$\Sigma_{k=1}^{n} b_k \mathbf{X}_k = 0 \tag{9}$$

with $b_n \neq 0$. By eliminating both $\mathbf{J}_n$ and $\mathbf{X}_n$ from (1) we find

$$\sigma = \Sigma_{i=1}^{n-1} \mathbf{J}_i \cdot \{\mathbf{X}_i + (a_i/a_n) \Sigma_{p=1}^{n-1} b_p \mathbf{X}_p / b_n\}. \tag{10}$$

The phenomenological equations are now

$$\begin{aligned} \mathbf{J}_i &= \Sigma_{j=1}^{n-1} l_{ij} \{\mathbf{X}_j + (a_j/a_n) \Sigma_{p=1}^{n-1} b_p \mathbf{X}_p / b_n\} = \\ &= \Sigma_{j=1}^{n-1} \mathbf{X}_j \{l_{ij} + (b_j/b_n) \Sigma_{p=1}^{n-1} a_p l_{ip} / a_n\}, \quad (i = 1, \ldots, n-1), \end{aligned} \tag{11}$$

and thus in view of (4)

$$\mathbf{J}_n = - \Sigma_{j=1}^{n-1} \mathbf{X}_j \Sigma_{i=1}^{n-1} \{l_{ij} + (b_j/b_n) \Sigma_{p=1}^{n-1} a_p l_{ip}/a_n\} a_i/a_n. \tag{12}$$

These equations can again be written in the form (2). However, since the forces $\mathbf{X}_k$ are no longer independent (*v.* (9)) there is a certain arbitrariness with respect to the coefficients L_{kl}: in each row of the L_{kl} scheme (*i.e.*, for each value of k) one of the n coefficients can be chosen arbitrarily. On the other hand, because of (4) there exist $n - 1$ linear relations between the L_{kl}. To find these we first eliminate $\mathbf{X}_n$ from (2) by means of (9). The flows are then expressed in terms of independent forces

$$\mathbf{J}_k = \Sigma_{j=1}^{n-1} \mathbf{X}_j (L_{kj} - b_j L_{kn}/b_n), \quad (k = 1, \ldots, n). \tag{13}$$

Now it follows from (4) that

$$\Sigma_{k=1}^{n} a_k (L_{kj} - b_j L_{kn}/b_n) = 0, \quad (j = 1, \ldots, n-1). \tag{14}$$

These $n - 1$ relations combine with the n-fold arbitrariness to leave a sensible set of $(n-1)^2$ coefficients L_{kl}.

From the foregoing it is clear that the L_{kl} scheme need not be symmetric, as the phenomenological coefficients are not uniquely defined. However, it can easily be shown that they can be chosen in such a way as to satisfy the Onsager relations (3). As a matter of fact, by comparing (11) and (12) with (13) we get for $i, j = 1, \ldots, n-1$

$$L_{ij} - b_j L_{in}/b_n = l_{ij} + (b_j/b_n) \Sigma_{p=1}^{n-1} a_p l_{ip}/a_n, \tag{15}$$

$$L_{ni} - b_i L_{nn}/b_n = - \Sigma_{q=1}^{n-1} (a_q/a_n) \{l_{qi} + (b_i/b_n) \Sigma_{p=1}^{n-1} a_p l_{qp}/a_n\}, \tag{16}$$

a system of $n(n-1)$ equations for the n^2 coefficients L_{kl}. A possible solution is again given by (7). Since the coefficients l_{ij} are subject to the Onsager relations this solution satisfies (3).

The most general symmetric solution is reached from (15) and (16) by superimposing the conditions

$$L_{in} = L_{ni}, \quad (i = 1, \ldots, n-1). \tag{17}$$

If we then solve the equations for L_{ij} making use of the symmetry in the l_{ij} scheme we find

$$L_{ij} = l_{ij} + b_i b_j \{L_{nn} - \Sigma_{p,q=1}^{n-1} a_p a_q l_{pq}/a_n^2\}/b_n^2, \quad (i, j = 1, \ldots, n-1), \tag{18}$$

an expression which is symmetric in i and j.

The $n(n-1)$ equations (15) and (16) leave an n-fold arbitrariness in the n^2 coefficients L_{kl}. By the conditions (17) one is left with only one single arbitrary choice. If we choose the coefficient L_{nn} in an arbitrary way, the complete scheme is determined.

§ 4. *External magnetic field or over-all rotation.* The foregoing treatment is only slightly modified if the system is placed in an external magnetic field H or if it rotates with an angular velocity H. The Onsager relations (3) then read

$$L_{kl}(\mathrm{H}) = L_{lk}(-\mathrm{H}), \quad (k, l = 1, \ldots, n), \tag{19}$$

The coefficients l_{ij} now satisfy the Onsager relations

$$l_{ij}(\mathrm{H}) = l_{ji}(-\mathrm{H}), \quad (i, j = 1, \ldots, n-1), \tag{20}$$

and it can easily be verified that the conclusions of § 2 and § 3 are unimpaired if the coefficients a_k are all either even or odd functions of H. In the case of § 3 the most general solution satisfying (19) is reached by superimposing the conditions

$$L_{in}(\mathrm{H}) = L_{ni}(-\mathrm{H}), \quad (i = 1, \ldots, n-1), \tag{21}$$

while L_{nn} should of course be an even function of H.

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Chapter V

TRANSFORMATION PROPERTIES OF THE ONSAGER RELATIONS

§ 1. *Introduction.* In thermodynamics of irreversible processes [1]) [2]) the entropy production can generally be written as a sum of products of fluxes and corresponding forces, between which linear relationships are assumed. For the scheme of phenomenological coefficients occurring in these equations the Onsager reciprocal relations hold.

Meixner [3]) has been the first to investigate the invariance of the Onsager relations under simultaneous linear transformations of the fluxes and forces. With a given linear transformation of the fluxes, the linear transformation of the forces is derived from the invariance of the entropy production and with the help of these transformation formulae the invariance of the Onsager relations is established (*cf.* also [1]) § 78).

However, as Davies [4]) has pointed out, if the transformations are only subject to the condition of leaving the entropy production invariant, they also include transformations which destroy the Onsager relations. Verschaffelt [5]) previously had given an example.

It is the purpose of this chapter to show that the latter type of transformations should be discarded. As a starting point we will take the expression for the deviation of the entropy from its equilibrium value. Then Meixner's result for the connection between the transformation formulae and the invariance of the Onsager relations follow in a natural way.

The same idea is implicit in a paper by Prigogine [6]) where he discusses the invariance of the Onsager relations for transformations between 'equivalent systems of chemical reactions'.

§ 2. *Treatment based on the invariance of the entropy production.* In the scheme of thermodynamics of irreversible processes [1]) [2]) the entropy production σ (per unit volume per unit time) can generally be written as a sum of products of a number of independent fluxes J_i (together called j in matrix notation) and corresponding forces X_i (in matrix notation x)

$$\sigma = \tilde{j}x, \tag{1}$$

where the symbol $\sim$ indicates the transposed matrix. Linear relationships are assumed between the fluxes and forces, which we can write as

$$j = Lx. \tag{2}$$

The Onsager reciprocal relations state that the matrix L of phenomenological coefficients be symmetric

$$\tilde{L} = L. \tag{3}$$

We now consider a linear transformation of the fluxes

$$j' = Pj, \text{ with } \det P \neq 0, \tag{4}$$

and a simultaneous transformation of the forces

$$x' = Qx. \tag{5}$$

In the treatment given by Meixner[3]) and De Groot[1]) the matrix Q is generally derived from the condition that the expression (1) for σ remain invariant

$$\sigma = \tilde{j}x = \tilde{j}'x'. \tag{6}$$

From (4), (5) and (6) it is then concluded that

$$Q = \tilde{P}^{-1}. \tag{7}$$

With (7) the phenomenological equations (2) transform into

$$j' = L'x' = PL\tilde{P}x', \tag{8}$$

and the Onsager relation (3) is seen to be invariant since

$$L' = PL\tilde{P} = \tilde{L}'. \tag{9}$$

However, as Davies[4]) has pointed out, the condition that the expression for σ be invariant does not uniquely lead to (7). As a matter of fact, from this condition alone a more general solution for the matrix Q can be found, which includes (7) as a special case. This can be seen by inserting the phenomenological equation (2) in the entropy production (1)

$$\tilde{j}x = \tilde{x}\tilde{L}x \tag{10}$$

and likewise

$$\tilde{j}'x' = \tilde{j}\tilde{P}Qx = \tilde{x}\tilde{L}\tilde{P}Qx. \tag{11}$$

The condition (6) thus leads to

$$\tilde{L} = \tilde{L}\tilde{P}Q + A \text{ or } PL = \tilde{Q}^{-1}(L + A), \tag{12}$$

where A is an arbitrary antisymmetric matrix

$$\tilde{A} = -A, \tag{13}$$

which may differ from zero. The transformed matrix L' follows from (2), (4), (5) and (12)

$$L' = PLQ^{-1} = \tilde{Q}^{-1}(L + A)Q^{-1}. \tag{14}$$

In view of (3) it is thus seen that L' will contain a symmetric part $\tilde{Q}^{-1}LQ^{-1}$ but also an antisymmetric part $\tilde{Q}^{-1}AQ^{-1}$ and so the Onsager relation will break down unless one takes $A = 0$ as was done in (7) and (9).

Davies showed that it is the including of the antisymmetric matrix A which has led Verschaffelt[5]) to an example of a linear transformation which leaves the entropy production invariant and yet which destroys the Onsager reciprocal relations. In this example P is taken unity and Q equals $1 - L^{-1}A$. In his note Davies argues that such transformations can be of no physical importance since they depend explicitly on the phenomenological coefficients contained in L and from this argument he concludes the restriction to the case $A = 0$.

However, Davies does not make it clear why the dependence of the transformation matrix on the phenomenological coefficients should be physically meaningless. Actually, there is no reason why such a dependence should be excluded and there exists a number of important cases in which transformations of this type are applied successfully, *e.g.*, in the theories of the thermomolecular pressure difference, the thermomechanical effect, the Soret effect and the Dufour effect, where the transformation matrices contain so-called quantities of transfer depending on the phenomenological coefficients (for examples of these cases, *cf.* [1]) [7])).

Yet, the connection between the transformations P and Q of fluxes and forces should be as given in (7) and the antisymmetric matrix A should be taken zero. The reason is that the proper condition for these transformations is the invariance of the *deviation of the entropy* from its equilibrium value. If this condition is satisfied, the invariance of the *entropy production* as well as the invariance of the Onsager relations are easily deduced, as will be shown in the following.

§ 3. *Transformation properties derived from the expression for the deviation of the entropy.* We consider an adiabatically insulated system, the thermodynamical state of which is described by a number n of independent variables which are continuous functions of space and time coordinates. The deviations of these variables from their thermostatic equilibrium values are denoted by $a_i (i = 1, \ldots, n)$. Since the entropy S of the system has a maximum in the thermostatic state, the deviation ΔS of the entropy from its equilibrium value can be written as [8]) [9])

$$\Delta S = -\tfrac{1}{2} \iint \Sigma_{i=1}^{n} \Sigma_{k=1}^{n} \, a_i(\mathbf{r}) \, g_{ik}(\mathbf{r}, \mathbf{r}') \, a_k(\mathbf{r}') \, \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{r}', \tag{15}$$

where of course

$$g_{ik}(\mathbf{r}, \mathbf{r}') = g_{ki}(\mathbf{r}', \mathbf{r}), \tag{16}$$

$\mathbf{r}$ and $\mathbf{r}'$ denoting coordinate vectors. Introducing the quantities

$$X_j(\mathbf{r}) \equiv \partial \Delta S / \partial a_j(\mathbf{r}) = -\int \Sigma_k \, g_{jk}(\mathbf{r}, \mathbf{r}') \, a_k(\mathbf{r}') \, \mathrm{d}\mathbf{r}', \quad (j = 1, \ldots, n), \tag{17}$$

we can write

$$\Delta S = \tfrac{1}{2} \int \Sigma_i \, \alpha_i(\mathbf{r}) \, X_i(\mathbf{r}) \, \mathrm{d}\mathbf{r} \tag{18}$$

and the time derivative $\Delta\dot{S}$ (the entropy production per unit time) is given by

$$\Delta\dot{S} = \int \Sigma_i \, \dot{\alpha}_i(\mathbf{r}) \, X_i(\mathbf{r}) \, \mathrm{d}\mathbf{r}. \tag{19}$$

In the same way the system could be described by a new set of state variables $a_i(\mathbf{r})$ which are related to the original variables $\alpha_i(\mathbf{r})$ in the following way

$$a_i(\mathbf{r}) = \Sigma_{j=1}^{n} P_{ij} \, \alpha_j(\mathbf{r}) \text{ or } \alpha_i(\mathbf{r}) = \Sigma_{j=1}^{n} P_{ij}^{-1} \, a_j(\mathbf{r}), \quad (i = 1, \ldots, n). \tag{20}$$

This leads to

$$\begin{aligned} \Delta S = &- \tfrac{1}{2} \iint \Sigma_{j,l} \, \Sigma_{i,k} \, P_{ij}^{-1} \, a_j(\mathbf{r}) \, g_{ik}(\mathbf{r}, \mathbf{r}') \, P_{kl}^{-1} \, a_l(\mathbf{r}') \, \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{r}' = \\ &= - \tfrac{1}{2} \iint \Sigma_{j,l} \, a_j(\mathbf{r}) \, h_{jl}(\mathbf{r}, \mathbf{r}') \, a_l(\mathbf{r}') \, \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{r}', \end{aligned} \tag{21}$$

with

$$h_{jl}(\mathbf{r}, \mathbf{r}') = \Sigma_{i,k} \, P_{ij}^{-1} \, g_{ik}(\mathbf{r}, \mathbf{r}') \, P_{kl}^{-1} = h_{lj}(\mathbf{r}', \mathbf{r}). \tag{22}$$

Instead of the quantities $X_j(\mathbf{r})$ we now have quantities

$$Y_j(\mathbf{r}) \equiv \partial \Delta S / \partial a_j(\mathbf{r}) = - \int \Sigma_l \, h_{jl}(\mathbf{r}, \mathbf{r}') \, a_l(\mathbf{r}') \, \mathrm{d}\mathbf{r}' = \Sigma_i \, P_{ij}^{-1} \, X_i(\mathbf{r}), \tag{23}$$

which shows how the $X_j(\mathbf{r})$ are transformed.

Analogous to (18) and (19) we find

$$\Delta S = \tfrac{1}{2} \int \Sigma_i \, a_i(\mathbf{r}) Y_i(\mathbf{r}) \, \mathrm{d}\mathbf{r}, \tag{24}$$

$$\Delta\dot{S} = \int \Sigma_i \, \dot{a}_i(\mathbf{r}) \, Y_i(\mathbf{r}) \, \mathrm{d}\mathbf{r}. \tag{25}$$

The present theory could be developed for arbitrary combinations of scalar, vectorial and tensorial phenomena in anisotropic media. However, for the sake of clarity we shall only consider two special cases, *viz.*, scalar irreversible processes (chemical reactions, relaxation phenomena) and vectorial ones (heat conduction and diffusion).

A. Transformations between scalar phenomena. If only scalar processes occur the state variables are uniform throughout the system and the expression for the entropy production in local form follows from (19) and (25)

$$\sigma = \Sigma_i \, \dot{\alpha}_i \, X_i = \Sigma_i \, \dot{a}_i \, Y_i. \tag{26}$$

The quantities $\dot{\alpha}_i$ and X_i are the irreversible fluxes and the forces occurring in equation (1). From the foregoing it is clear that the transformation of the forces (23) logically follows from the transformation of the fluxes and the expression for ΔS. Comparing (20) with (23) we see that these transformations are connected in the way of equation (7) and that no antisymmetric matrix (as in (12)) can occur. The transformation also leaves the entropy production invariant.

Since the Onsager theory can be applied in terms of the variables α_i as well as in terms of the variables a_i, the invariance of the validity of the Onsager reciprocal relations is guaranteed beforehand. In order to prove it explicitly we consider the phenomenological equations in both descriptions

$$\dot{\alpha}_i = \Sigma_j L_{ij} X_j, \tag{27}$$

$$\dot{a}_i = \Sigma_j M_{ij} Y_j. \tag{28}$$

With the help of (20) and (23) we find

$$M_{ij} = \Sigma_{k,l} P_{ik} L_{kl} P_{jl}. \tag{29}$$

The symmetry of the M_{ij} scheme then immediately follows from the symmetry of the L_{ij} and *vice versa*.

B. Transformations between vectorial phenomena. In the case of vectorial phenomena the irreversible fluxes are no longer time derivatives of thermodynamic state variables nor are the thermodynamic forces given by such linear expressions in these variables as occur in (17). The connection between the thermodynamic fluxes and the state variables is now given by the conservation laws (*e.g.*, of mass and energy) and in the absence of scalar processes (*e.g.*, for diffusion and heat conduction at constant volume) we can write

$$\partial \alpha_i / \partial t = -\operatorname{div} \mathbf{J}_i, \qquad (i = 1, \ldots, n), \tag{30}$$

where $\mathbf{J}_i$ is the flux connected with the state variable α_i. Thus (19) can be rewritten as

$$\dot{\Delta S} = -\int \Sigma_i X_i(\mathbf{r}) \operatorname{div} \mathbf{J}_i(\mathbf{r}) \mathrm{d}\mathbf{r} = \int \Sigma_i \mathbf{J}_i(\mathbf{r}) \cdot \operatorname{grad} X_i(\mathbf{r}) \mathrm{d}\mathbf{r}, \tag{31}$$

where we have applied Gauss' theorem and the fact that the flows $\mathbf{J}_i$ vanish at the boundary of the system. The integrand on the right-hand side of (31) is the entropy production σ per unit time and volume [1])

$$\sigma(\mathbf{r}) = \Sigma_i \mathbf{J}_i(\mathbf{r}) \cdot \operatorname{grad} X_i(\mathbf{r}). \tag{32}$$

The thermodynamic force conjugated to the flow $\mathbf{J}_i(\mathbf{r})$ is now grad $X_i(\mathbf{r})$. With the linear transformation (20) of the state variables the expression (19) for $\dot{\Delta S}$ transforms into (25). The conservation laws (30) transform into

$$\partial a_i / \partial t = -\operatorname{div} \mathbf{I}_i, \qquad (i = 1, \ldots, n), \tag{33}$$

with

$$\mathbf{I}_i(\mathbf{r}) = \Sigma_j P_{ij} \mathbf{J}_j(\mathbf{r}). \tag{34}$$

In the same way as (31) followed from (19) with the help of (30), so (25) and (33) lead to

$$\dot{\Delta S} = \int \Sigma_i \mathbf{I}_i(\mathbf{r}) \cdot \operatorname{grad} Y_i(\mathbf{r}) \mathrm{d}\mathbf{r}, \tag{35}$$

where

$$\operatorname{grad} Y_i(\mathbf{r}) = \Sigma_j P_{ji}^{-1} \operatorname{grad} X_j(\mathbf{r}), \tag{36}$$

and the local expression for the entropy production is

$$\sigma(\mathbf{r}) = \Sigma_i \mathbf{I}_i(\mathbf{r}) \cdot \operatorname{grad} Y_i(\mathbf{r}). \tag{37}$$

Again, the transformations (34) and (36) of the fluxes and the forces, resp., are connected in the way of equation (7) and $\sigma(\mathbf{r})$ is invariant.

The Onsager theory (as extended by De Groot and Mazur [8]) could again be applied in both descriptions and the invariance of the Onsager reciprocal relations is guaranteed beforehand. This is also seen explicitly from the phenomenological equations

$$\mathbf{J}_i = \Sigma_j \, \mathsf{L}_{ij} \cdot \mathrm{grad}\, X_j, \tag{38}$$

$$\mathbf{I}_i = \Sigma_j \, \mathsf{M}_{ij} \cdot \mathrm{grad}\, Y_j, \tag{39}$$

where the L_{ij} and M_{ij} are tensors of the second order. The Onsager relations state that in the absence of a magnetic field or an over-all rotation of the system

$$\mathsf{L}_{ij} = \mathsf{L}_{ji}^{\dagger}, \tag{40}$$

where the symbol † indicates transposing of the Cartesian coordinates. In view of (34), (36), (38) and (39) we have

$$\mathsf{M}_{ij} = \Sigma_{k,l} \, P_{ik} \mathsf{L}_{kl} P_{jl}, \tag{41}$$

so that the Onsager relation

$$\mathsf{M}_{ij} = \mathsf{M}_{ji}^{\dagger} \tag{42}$$

follows from (40) and conversely.

In the foregoing treatment the transformation matrix P_{ij} is supposed to be uniform throughout the system. In practice, P_{ij} might depend explicitly on the phenomenological coefficients contained in L_{ij} which are functions of the state variables and thus of space coordinates. However, since the Onsager theory is based on expressions for ΔS which are quadratic in the state variables we can restrict ourselves to coefficients P_{ij} which are functions only of the equilibrium values of the state parameters (compare equation (15) with (21)). In the absence of external fields these equilibrium values are uniform throughout the system and the above treatment is justified. If the system is placed in an external field, the state parameters need not be uniform. If then the P_{ij} are slowly varying functions of space coordinates (as is generally the case) the whole treatment can be applied to small subsystems where P_{ij} can be taken uniform.

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CHAPTER VI

COEFFICIENTS OF VISCOSITY FOR A FLUID IN A ROTATING SYSTEM OR IN A MAGNETIC FIELD

§ 1. *Introduction.* The macroscopic description of viscosity can be developed from the viewpoint of the thermodynamics of irreversible processes [1]) [2]) [3]). In this theory an expression for the entropy production σ (per unit time and volume) due to the irreversible phenomena occurring within a system is derived by means of the conservation laws and the second law of thermodynamics. For the contribution σ_v of viscous flow one then finds

$$T\sigma_v = -\mathbf{\Pi} : \text{Grad } \mathbf{v}, \tag{1}$$

where T is the temperature, $\mathbf{\Pi}$ the viscous pressure tensor, $\mathbf{v}$ the barycentric velocity and $:$ denotes the interior product of two tensors, contracted twice. We shall restrict ourselves to the case usually met with that $\mathbf{\Pi}$ is a symmetric tensor and denote the six independent cartesian components as

$$\begin{aligned} \pi_{xx} &= \pi_1, & \pi_{yz} &= \pi_4, \\ \pi_{yy} &= \pi_2, & \pi_{xz} &= \pi_5, \\ \pi_{zz} &= \pi_3, & \pi_{xy} &= \pi_6. \end{aligned} \tag{2}$$

In (1) the tensor Grad $\mathbf{v}$ then can be replaced by its symmetric part which we shall denote by $\boldsymbol{\epsilon}$ with components

$$\begin{aligned} \varepsilon_{xx} &= \varepsilon_1, & \varepsilon_{yz} &= \tfrac{1}{2}\varepsilon_4, \\ \varepsilon_{yy} &= \varepsilon_2, & \varepsilon_{xz} &= \tfrac{1}{2}\varepsilon_5, \\ \varepsilon_{zz} &= \varepsilon_3, & \varepsilon_{xy} &= \tfrac{1}{2}\varepsilon_6, \end{aligned} \tag{3}$$

such that we have

$$T\sigma_v = -\mathbf{\Pi} : \boldsymbol{\epsilon} = -\Sigma_{i=1}^{6}\, \pi_i \varepsilon_i. \tag{4}$$

According to the thermodynamics of irreversible processes we next assume linear relationships between the elements of $\mathbf{\Pi}$ and $\boldsymbol{\epsilon}$ which occur in (4) as 'fluxes' and 'forces' in the thermodynamic sense. These 'phenomenologica equations' can be written as

$$-\pi_i = \Sigma_{k=1}^{6} L_{ik}\, \varepsilon_k, \qquad (i = 1, \ldots, 6), \tag{5}$$

(we shall not consider cross-effects between viscosity and other irreversible phenomena although such effects might exist).

We now suppose the fluid (*e.g.*, an ionized gas) to be placed in a homogeneous external magnetic field or to rotate with a constant angular velocity. The magnetic field strength or the angular velocity will be denoted by the comprehensive symbol H. Supposing that the fluid itself is isotropic we then want to investigate the symmetry properties of the phenomenological equations (5).

§ 2. *Derivation.* a. *Spatial symmetry.* If we choose the x-axis in the direction of H it follows from the isotropy of the fluid that the relations (5) are invariant with respect to rotations about the x-axis. By straightforward calculation (*e.g.*, introducing an infinitesimal rotation) one then finds for the scheme of phenomenological coefficients

$$\begin{array}{c|cccccc}
 & \varepsilon_1 & \varepsilon_2 & \varepsilon_3 & \varepsilon_4 & \varepsilon_5 & \varepsilon_6 \\
\hline
-\pi_1 & L_{11} & L_{12} & L_{12} & 0 & 0 & 0 \\
-\pi_2 & L_{21} & L_{22} & L_{23} & L_{24} & 0 & 0 \\
-\pi_3 & L_{21} & L_{23} & L_{22} & -L_{24} & 0 & 0 \\
-\pi_4 & 0 & -L_{24} & L_{24} & \frac{1}{2}(L_{22}-L_{23}) & 0 & 0 \\
-\pi_5 & 0 & 0 & 0 & 0 & L_{55} & L_{56} \\
-\pi_6 & 0 & 0 & 0 & 0 & -L_{56} & L_{55}
\end{array} \tag{6}$$

in which only 8 coefficients are left.

b. *Parity.* Since any axis perpendicular to the x-direction is a 2-fold axis of rotation, the relations (5) are invariant for a rotation of the coordinate system by an angle π about the z-axis. This leads to

$$L_{ik}(\mathrm{H}) = (-1)^n L_{ik}(-\mathrm{H}), \tag{7}$$

if the index z figures n times in π_i and ε_k together (*cf.* (2) and (3)). Hence we find that

$$\left.\begin{array}{l}
L_{11}, L_{12}, L_{21}, L_{22}, L_{23} \text{ and } L_{55} \text{ are even functions of H,} \\
L_{24} \text{ and } L_{56} \qquad\qquad\qquad ,, \quad \text{odd} \quad ,, \qquad ,, \ \text{H.}
\end{array}\right\} \tag{8}$$

c. *The Onsager relations.* For the phenomenological coefficients the Onsager reciprocal relations [3] [4]

$$L_{ik}(\mathrm{H}) = L_{ki}(-\mathrm{H}) \tag{9}$$

hold. In view of (6) and the parity relations (8) we are left with only one true Onsager relation, *viz.*,

$$L_{12} = L_{21}, \tag{10}$$

by which the number of independent coefficients is further reduced to 7 (5 of these being even functions of H and 2 odd).

d. *Ordinary viscosity, volume viscosity and their cross-effect.* Each of the tensors $\mathbf{\Pi}$ and $\boldsymbol{\epsilon}$ can be split up into a tensor with zero trace and a scalar multiple of the unit tensor $\boldsymbol{\delta}$

$$\left.\begin{aligned} \mathbf{\Pi} &= \mathring{\mathbf{\Pi}} + \tfrac{1}{3}\pi\boldsymbol{\delta}, \\ \boldsymbol{\epsilon} &= \mathring{\boldsymbol{\epsilon}} + \tfrac{1}{3}\vartheta\boldsymbol{\delta}, \end{aligned}\right\} \tag{11}$$

where π and ϑ are the traces

$$\left.\begin{aligned} \pi &= \Sigma_{i=1}^{3}\, \pi_i, \\ \vartheta &= \Sigma_{i=1}^{3}\, \varepsilon_i = \operatorname{div} \mathbf{v}. \end{aligned}\right\} \tag{12}$$

The expression (4) for the entropy production then can be rewritten as

$$-\,T\sigma_v = \mathring{\mathbf{\Pi}} : \mathring{\boldsymbol{\epsilon}} + \tfrac{1}{3}\pi\vartheta. \tag{13}$$

We now can write the phenomenological equations in a form corresponding to (13). From (5) and (12) we find, using also (6) and (10),

$$-\pi = (L_{11}+2L_{12})\,\mathring{\varepsilon}_1 + (L_{12}+L_{22}+L_{23})(\mathring{\varepsilon}_2+\mathring{\varepsilon}_3) + \tfrac{1}{3}(L_{11}+4L_{12}+2L_{22}+2L_{23})\vartheta, \tag{14}$$

and therefore

$$\left.\begin{aligned} -\mathring{\pi}_1 &= \tfrac{2}{3}(L_{11}-L_{12})\,\mathring{\varepsilon}_1 + \tfrac{1}{3}(2L_{12}-L_{22}-L_{23})(\mathring{\varepsilon}_2+\mathring{\varepsilon}_3) + \tfrac{2}{9}(L_{11}+L_{12}-L_{22}-L_{23})\vartheta, \\ -\mathring{\pi}_2 &= \tfrac{1}{3}(-L_{11}+L_{12})\,\mathring{\varepsilon}_1 + \tfrac{1}{3}(-L_{12}+2L_{22}-L_{23})\,\mathring{\varepsilon}_2 + \tfrac{1}{3}(-L_{12}-L_{22}+2L_{23})\,\mathring{\varepsilon}_3 + \\ &\qquad + \tfrac{1}{9}(-L_{11}-L_{12}+L_{22}+L_{23})\,\vartheta + L_{24}\,\varepsilon_4, \\ -\mathring{\pi}_3 &= \tfrac{1}{3}(-L_{11}+L_{12})\,\mathring{\varepsilon}_1 + \tfrac{1}{3}(-L_{12}-L_{22}+2L_{23})\,\mathring{\varepsilon}_2 + \\ &\qquad + \tfrac{1}{3}(-L_{12}+2L_{22}-L_{23})\,\mathring{\varepsilon}_3 + \tfrac{1}{9}(-L_{11}-L_{12}+L_{22}+L_{23})\,\vartheta - L_{24}\,\varepsilon_4. \end{aligned}\right\} \tag{15}$$

Since $\mathring{\varepsilon}_1 + \mathring{\varepsilon}_2 + \mathring{\varepsilon}_3 = 0$ these equations can be given a more symmetrical form. Writing

$$\left.\begin{aligned} 2L_{11} - 4L_{12} + L_{22} + L_{23} &\equiv 6\mu_1, & L_{55} &\equiv \mu_3, \\ L_{11} - 2L_{12} + 2L_{22} - L_{23} &\equiv 6\mu_2, & L_{24} &\equiv \eta_1, \\ L_{11} + 4L_{12} + 2L_{22} + 2L_{23} &\equiv 9\mu_v, & L_{56} &\equiv \eta_2, \\ L_{11} + L_{12} - L_{22} - L_{23} &\equiv 3\zeta, & & \end{aligned}\right\} \tag{16}$$

we find the following scheme of phenomenological coefficients connecting the two sets of quantities which occur in (13):

$$\begin{array}{r|ccccccc}
 & \mathring{\varepsilon}_1 & \mathring{\varepsilon}_2 & \mathring{\varepsilon}_3 & \varepsilon_4 & \varepsilon_5 & \varepsilon_6 & \frac{1}{3}\vartheta \\
\hline
-\mathring{\pi}_1 & 2\mu_1 & 0 & 0 & 0 & 0 & 0 & 2\zeta \\
-\mathring{\pi}_2 & 0 & 2\mu_2 & 2(\mu_1-\mu_2) & \eta_1 & 0 & 0 & -\zeta \\
-\mathring{\pi}_3 & 0 & 2(\mu_1-\mu_2) & 2\mu_2 & -\eta_1 & 0 & 0 & -\zeta \\
-\pi_4 & 0 & -\eta_1 & \eta_1 & 2\mu_2-\mu_1 & 0 & 0 & 0 \\
-\pi_5 & 0 & 0 & 0 & 0 & \mu_3 & \eta_2 & 0 \\
-\pi_6 & 0 & 0 & 0 & 0 & -\eta_2 & \mu_3 & 0 \\
-\pi & 2\zeta & -\zeta & -\zeta & 0 & 0 & 0 & 9\mu_v
\end{array} \qquad (17)$$

μ_1, μ_2, μ_3, μ_v and ζ are even functions of H, η_1 and η_2 are odd.

The coefficients μ_1, μ_2, μ_3, η_1 and η_2 describe ordinary viscosity, μ_v is the coefficient of volume (or bulk) viscosity and ζ describes a cross-effect between ordinary and volume viscosity.

With regard to symmetry and parity the scheme (17) can be compared with the equations given by Chapman and Cowling 5) for the stress tensor of a simple gas in a magnetic field, derived from kinetic theory. The scheme is in agreement with these equations apart from an apparent error of sign in the latter (the coefficients of $2\mathring{e}_{yz}$ in p_{yy} and p_{zz}, resp., should be the opposite of the coefficients of $\mathring{e}_{yy}$ and $\mathring{e}_{zz}$, resp., in p_{yz}; this follows from the spatial symmetry and is confirmed by the Onsager relations (9)). It may be noted that in Chapman and Cowling's approximation μ_v and ζ vanish.

e. *The case of isotropy.* If $\mathrm{H} = 0$ the above equations reduce to the well-known linear relationships between the stresses and rates of deformation in an isotropic system. As a matter of fact, for complete isotropy we have in addition to (6)

$$\left.\begin{array}{ll} L_{12} = L_{21} = L_{23}, & L_{24} = L_{56} = 0, \\ L_{11} = L_{22}, & L_{55} = L_{44}, \end{array}\right\} \qquad (18)$$

so that only two independent coefficients are left (the Onsager relations become trivial for this case). By (16) this means

$$\mu_1 = \mu_2 = \mu_3, \qquad \zeta = \eta_1 = \eta_2 = 0, \qquad (19)$$

and (17) reduces to a diagonal scheme, pertaining to the equations

$$\left.\begin{aligned} -\mathbf{\Pi} &= 2\mu_1 \mathring{\boldsymbol{\epsilon}}, \\ -\pi &= 3\mu_v \vartheta, \end{aligned}\right\} \qquad (20)$$

or

$$-\mathbf{\Pi} = 2\mu_1 \mathring{\boldsymbol{\epsilon}} + \mu_v \vartheta\, \boldsymbol{\delta} = 2\mu_1\, \boldsymbol{\epsilon} + \lambda\vartheta\, \boldsymbol{\delta}, \qquad (21)$$

where λ is the 'second coefficient of viscosity' defined by

$$\mu_v \equiv \lambda + \tfrac{2}{3}\mu_1. \qquad (22)$$

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LIST OF FREQUENTLY USED SYMBOLS

c_k	mass fraction of component k (I.2)
D	binary diffusion coefficient (I.7A)
D_{ki}	coefficient of diffusion with respect to component n (II.3)
D_{ki}^{a}	coefficient of diffusion with respect to the mean velocity $\mathbf{v}^{a}$ (II.4)
D_{ki}°	coefficient of diffusion with respect to the mean volume velocity $\mathbf{v}^{\circ}$ (II.5)
e	total electrical charge per unit mass
e_k	electrical charge per unit mass of component k
$\mathbf{E}$	electric field vector
$\mathbf{F}_k$	external force per unit mass of component k
H	comprehensive symbol for angular velocity vector or magnetic field vector (III.2)
$\mathbf{I}$	electric current density (I.5)
$\mathbf{J}_k$	flux of substance k with respect to the barycentric velocity $\mathbf{v}$ (I.2)
$\mathbf{J}_k^{a}$	flux of substance k with respect to the mean velocity $\mathbf{v}^{a}$ (I.5)
$\mathbf{J}_k^{\circ}$	flux of substance k with respect to the mean volume velocity $\mathbf{v}^{\circ}$ (I.7)
$\mathbf{J}_k^{r}$	flux of substance k with respect to the velocity of component n (I.7)
M_k	molar mass of substance k
N	total molar density
N_k	molar density of component k
n_k	mole fraction of component k (I.5)
s	specific entropy
v	specific volume of mixture
v_k	partial specific volume of component k
$\bar{v}_k$	partial molar volume of component k
$\mathbf{v}$	barycentric velocity (I.2)
$\mathbf{v}_k$	velocity of component k
$\mathbf{v}^{a}$	mean velocity (I.5)
$\mathbf{v}^{\circ}$	mean volume velocity
w_k	weight factor of component k in the mean velocity $\mathbf{v}^{a}$ (I.5)
$\mathbf{X}_k$	thermodynamic force, conjugate to $\mathbf{J}_k$
μ_k	chemical potential of component k (partial specific Gibbs function)

μ_{ki}	derivative of μ_k with respect to ϱ_i (II.3)
ν_{ki}	auxiliary quantity (II.4)
ϱ	total density
ϱ_k	density of component k
σ	entropy production per unit time and volume (I.3)
$\boldsymbol{\omega}$	angular velocity vector

RÉSUMÉ

Le but principal de cette thèse est la description macroscopique de la diffusion et de la sédimentation dans des systèmes en rotation à l'aide de la thermodynamique des processus irréversibles. Nous discutons en outre quelques problèmes qui interviennent dans la présente application de ladite théorie, ainsi que dans quelques-unes de ses autres applications.

La thermodynamique des phénomènes irréversibles a déjà été appliquée aux milieux rotatoires par De Groot, Mazur et Overbeek pour l'étude des phénomènes électrocinétiques. Ces auteurs ont montré que le potentiel de sédimentation est lié par une relation d'Onsager à une grandeur qu'ils ont appelée l'électrophorèse barycentrique et qui pour un système colloïdal, sous des conditions spéciales, se réduit à l'électrophorèse ordinaire. Dans cette application on n'a pas tenu compte de la non-uniformité des concentrations.

Dans cette thèse nous considérons des systèmes dans lesquels des gradients de concentration sont formès par suite de la sédimentation; nous nous limitons aux mélanges dont les constituants ne sont pas chargès. Notre analyse s'applique immédiatement à la sédimentation des molécules lourdes dans un champ centrifuge intense. Les méthodes expérimentales de détermination des poids moléculaires à l'aide d'ultracentrifuges sont fondées soit sur l'observation de la vitesse de sédimentation, soit sur la détermination de la distribution de la substance dissoute quand l'équilibre de sédimentation est atteint.

Dans le premier chapitre on obtient l'expression générale de la production d'entropie (qui est la grandeur fondamentale en thermodynamique des processus irréversibles), notamment pour un mélange en rotation, formé de constituants chargés ou non, et placé dans un champ électrique. Le cas des réactions chimiques ou des phénomènes de viscosité n'est pas considéré. Cette expression générale contient comme cas particulier les phénomènes électrocinétiques.

La deuxième partie de ce chapitre discute les systèmes monodisperses et non chargés. La formule bien connue pour l'équilibre de sédimentation est retrouvée comme conséquence du fait que la production d'entropie est nulle à l'équilibre thermodynamique. En négligeant les effets transversaux et en faisant usage de la condition (valable pour un liquide contenu dans un réservoir) que le débit à travers toute section du système doit être nul, nous établissons une expression pour la vitesse de sédimentation. Pour des solutions parfaites extrêmement diluées il en résulte l'équation donnée déjà en 1925 par Svedberg et valable pour le cas en question. Comparée aux méthodes antérieures, la méthode ici suivie présente l'avantage de définir de manière univoque les grandeurs employées et de mettre en lumière les approximations nécessaires pour arriver à la formule de Svedberg.

La théorie phénoménologique de la diffusion dans les systèmes à plusieurs constituants est développée dans le second chapitre. On y établit les relations qui existent entre les coefficients de diffusion comme conséquence des relations d'Onsager.

Le troisième chapitre est consacré à la sédimentation dans les systèmes paucidisperses. Les équations phénoménologiques pour les courants de matière résultant de la sédimentation et de la diffusion, sont formulées à l'aide de l'expression de la production d'entropie. Comme au premier chapitre on retrouve les équations régissant l'équilibre de sédimentation et on établit des expressions pour les vitesses de sédimentation des constituants. Les coefficients phénoménologiques qui y figurent s'expriment à l'aide des coefficients de diffusion introduits dans le second chapitre. Les équations trouvées pourraient fournir l'explication de deux effets établis expérimentalement: une anomalie dans la distribution spatiale des substances sédimentant lentement en présence des substances sédimentant plus vite et le reflux de la limite d'une substance sédimentante lorsque cette limite se trouve en présence d'une substance sédimentant beaucoup plus vite.

L'influence des dépendances linéaires entre les flux et (ou) les forces thermodynamiques intervenant dans la production d'entropie sur les coefficients phénoménologiques et les relations d'Onsager est discutée dans le quatrième chapitre.

Dans le cinquième chapitre on examine, pour les phénomènes scalaires et pour les processus vectoriels les plus importants, l'invariance des relations d'Onsager vis à vis de transformations linéaires simultanées des flux et des forces.

Dans le sixième chapitre les relations d'Onsager sont appliquées aux phénomènes de viscosité dans les milieux isotropes plongés soit dans un système en rotation, soit dans un champ magnétique extérieur. Il en résulte 7 coefficients de viscosité indépendants: 5 coefficients de viscosité ordinaire, 1 coefficient de viscosité de volume et 1 coefficient d'un effet croisé entre ces deux. Dans le cas où la viscosité de volume est négligeable, le système obtenu permet une comparaison avec les équations pour un gaz ionisé dans un champ magnétique, obtenues par Chapman et Cowling à partir de la théorie cinétique.

SAMENVATTING

Het hoofddoel van dit proefschrift is de macroscopische beschrijving van diffusie en sedimentatie in roterende systemen met behulp van de thermodynamica van irreversibele processen. Daarnaast worden enkele problemen besproken, die zich in deze en in andere toepassingen van genoemde theorie voordoen.

Reeds eerder hebben De Groot, Mazur en Overbeek de thermodynamica van irreversibele processen toegepast op roterende media ter bestudering van electrokinetische verschijnselen en daarbij aangetoond, dat er een Onsager-relatie bestaat tussen de sedimentatiepotentiaal en een grootheid, die zij barycentrische electroforese noemden en die voor colloidale oplossingen onder bepaalde omstandigheden samenviel met de gewone electroforese. In deze toepassing werden concentratie-gradiënten niet in rekening gebracht.

In dit proefschrift worden systemen beschouwd, waarin concentratie-gradiënten ontstaan als gevolg van sedimentatie, onder beperking tot mengsels van ongeladen componenten. Dit probleem heeft directe toepassing op de sedimentatie van zware moleculen in sterke centrifugale velden. De experimentele methoden ter bepaling van molecuulgewichten met behulp van ultracentrifuges berusten hetzij op de waarneming van de sedimentatie-snelheid, hetzij op de bepaling van de verdeling der opgeloste stof in het sedimentatie-evenwicht.

In hoofdstuk I wordt de algemene uitdrukking afgeleid voor de entropie-productie (de centrale grootheid in het formalisme van de thermodynamica der irreversibele processen) en wel voor een roterend mengsel, dat zowel electrisch geladen als ongeladen componenten bevat en geplaatst is in een electrisch veld. Chemische reacties en visceuze verschijnselen worden daarbij buiten beschouwing gelaten. Deze algemene uitdrukking omvat de electrokinetische verschijnselen als bijzonder geval.

Het tweede deel van dit hoofdstuk handelt over ongeladen monodisperse systemen. De bekende formule voor het sedimentatie-evenwicht wordt teruggevonden uit de voorwaarde, dat de entropie-productie nul is in thermodynamisch evenwicht. Onder verwaarlozing van dwarseffecten en met behulp van de randvoorwaarde voor een afgesloten systeem (die voor vloeistoffen meebrengt, dat de volumestroom nul is) wordt een uitdrukking afgeleid voor de sedimentatie-snelheid. Voor sterk verdunde ideale oplossingen volgt hieruit de reeds in 1925 door Svedberg voor dit geval gegeven vergelijking. Boven eerder gegeven afleidingen hiervan heeft de hier gevolgde methode het voordeel, de optredende grootheden ondubbelzinnig te definiëren en te laten zien, welke benaderingen tot de formule van Svedberg leiden.

In hoofdstuk II wordt de fenomenologische theorie van diffusie in systemen van meer dan twee componenten beschreven. De betrekkingen, die als gevolg van Onsager-relaties bestaan tussen de diffusiecoëfficiënten, worden afgeleid.

Hoofdstuk III is gewijd aan sedimentatie in paucidisperse systemen. De fenomenologische vergelijkingen voor de materiestromen, die uit sedimentatie en diffusie resulteren, worden geformuleerd aan de hand van de uitdrukking voor de entropie-productie. Op dezelfde wijze als in hoofdstuk I worden de vergelijkingen voor het sedimentatie-evenwicht teruggevonden en uitdrukkingen afgeleid voor de sedimentatie-snelheden der componenten. De in deze laatste voorkomende fenomenologische coëfficiënten kunnen worden uitgedrukt in de in hoofdstuk II ingevoerde diffusiecoëfficiënten. De gevonden vergelijkingen zouden een beschrijving kunnen geven van een tweetal experimenteel waargenomen effecten, nl. een anomalie in het concentratieverloop van langzaam sedimenterende stoffen bij aanwezigheid van sneller sedimenterende stoffen en het terugstromen van de grenslaag van een sedimenterende stof indien ter plaatse van deze grenslaag een zeer veel sneller sedimenterende component aanwezig is.

In hoofdstuk IV wordt de invloed van lineaire afhankelijkheden tussen de stromen en/of de thermodynamische krachten, die in de entropieproductie voorkomen, op de fenomenologische coëfficiënten en de Onsager-relaties besproken.

De invariantie van de Onsager-relaties bij gelijktijdige lineaire transformaties van stromen en krachten wordt in hoofdstuk V onderzocht voor scalaire verschijnselen en voor de belangrijkste vectoriële processen.

In hoofdstuk VI worden de Onsager-relaties toegepast op visceuze verschijnselen in isotrope media, geplaatst in een roterend stelsel of in een uitwendig magnetisch veld. Er blijken 7 onafhankelijke viscositeitscoëfficiënten te zijn: 5 voor gewone viscositeit, 1 voor volume-viscositeit en 1 voor een kruiseffect tussen beide. Het verkregen stelsel kan voor het geval van verwaarloosbare volume-viscositeit vergeleken worden met de langs kinetische weg door Chapman en Cowling verkregen vergelijkingen voor een geïoniseerd gas in een magnetisch veld.

Op verzoek van de Faculteit der Wis-en Natuurkunde volgt hier een beknopt overzicht van mijn studie.

In November 1940 begon ik mijn studie aan de Rijksuniversiteit te Utrecht. Na een onderbreking van 1942 tot 1945 legde ik aan deze Universiteit in Juli 1946 het candidaatsexamen wis- en natuurkunde (D) af. Het doctoraalexamen met hoofdvak theoretische natuurkunde en bijvakken wiskunde en mechanica behaalde ik in February 1951.

Van 1948 af was ik, aanvankelijk als assistent, werkzaam aan het Instituut voor Theoretische Natuurkunde aan de Universiteit te Utrecht onder Prof. Dr S. R. de Groot (van 1954 af onder Prof. Dr L. Ch. P. Van Hove). In de jaren 1950–1953 vervulde ik daarnaast een gedeeltelijke betrekking als leraar aan het Katholiek Gelders Lyceum te Arnhem.

Samen met C. A. ten Seldam verrichtte ik onder leiding van Prof. S. R. de Groot theoretisch onderzoek over wiskundige problemen betreffende de Bose-Einstein-condensatie van een ideaal gas.

In 1952 begon ik onder leiding van Prof. S. R. de Groot en Dr P. Mazur aan het onderzoek betreffende de toepassing van de thermodynamica van irreversibele processen op roterende systemen.

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In November 1945 begon ik mijn studie aan de [illegible]. Na een onderbreking van 1946 tot 1948 [illegible] candidaatsexamen [illegible] examen met hoofdvak theoretische natuurkunde en bijvakken wiskunde en [illegible] in Februari 1951.

Van 1950 af was ik [illegible] Instituut voor Theoretische Natuurkunde van de Universiteit te [illegible] Prof. Dr. S. R. de Groot; van 1954 af onder Prof. Dr [illegible] van [illegible] In de jaren 1950–1952 [illegible] het [illegible] te [illegible].

Samen met C. A. ten Seldam [illegible] onder leiding van Prof. S. R. de Groot [illegible] van een [illegible].

In 1952 begon ik onder leiding van Prof. S. R. de Groot en [illegible] het [illegible] van de thermodynamica van [illegible] processen [illegible] systemen.

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