

## NON-EQUILIBRIUM THERMODYNAMICS AND LIQUID HELIUM II

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### Synopsis

The thermodynamics of irreversible processes, based on the Onsager reciprocal relations, is applied to a system consisting of a mixture of two substances, of which one can go over into the other. The mixture is enclosed in two communicating reservoirs at different temperatures  $T$  and  $T + \Delta T$ . The situations, in which systems arrive, when one, two or more differences between the values of state parameters in the two reservoirs are kept fixed, are called "stationary states of first, second etc. order". For the stationary state of the first order with fixed  $\Delta T$  the corresponding pressure difference  $\Delta P$  is calculated. This gives the thermomolecular pressure effect

$$\Delta P/\Delta T = -Q^*/vT = (h - U^*)/vT,$$

where  $h$  and  $v$  are the mean specific enthalpy and volume. This equation shows the connection with the mechano-caloric effect  $Q^*$ , since application of the Onsager relations shows that  $Q^*$  is the "heat of transfer" i.e. the heat supplied per unit of time from the surroundings to the reservoir at temperature  $T$ , when one unit of mass is transferred from one reservoir to the other in the stationary state of the second order with fixed  $\Delta P$  and  $\Delta T = 0$  (uniform temperature). Similarly  $U^*$  is the "energy of transfer". The influence of  $\Delta T$  on the relative separation (thermal effusion) and the "chemical affinity" of the two components is also calculated. The heat conduction can be split into an "abnormal" part due to the coupling of diffusion and chemical reaction between the components and a "normal" part also present when no reaction takes place.

The results can be applied to liquid helium II, considered in the two-fluid theory as a mixture of "normal" (1) and "superfluid" (2) atoms, capable of the "chemical reaction"  $1 \rightleftharpoons 2$ . When it is supposed that chemical equilibrium is immediately established and that only superfluid atoms can pass through a sufficiently narrow capillary, the above mentioned equation leads to Gorter's formula

$$v \Delta P/\Delta T = x_1 \partial s/\partial x_1,$$

where  $x_1$  is the fraction of normal atoms and  $s$  the mean specific entropy of the mixture. Under the same circumstances only the "normal" part of the heat conduction subsists.

§ 1. *Introduction.* In the two fluid theory of liquid helium II this substance is supposed to consist of two components, which we may call the "normal" and the "condensed" or "superfluid" atoms. In G o r t e r's version of the theory <sup>1)</sup> equations of motion for both components are written down and expressions derived, which describe several peculiar properties of liquid helium II. For the derivation of the diffusion force formulae G o r t e r uses a pseudo-thermodynamic method, but he mentions that "they could probably also be derived by the aid of O n s a g e r's relations" <sup>1)</sup>.

One of the aims of this paper is to show that the thermodynamics of irreversible processes, based on the O n s a g e r reciprocal relations, actually can be applied to the two fluid model of liquid helium II. We have not assumed that the "chemical equilibrium" between the two components is immediately reached, as was supposed in G o r t e r's first paper. We also did not consider from the beginning the special case of helium, but have taken a mixture of two arbitrary "isomers" 1 and 2 capable of the "chemical reaction"



which transforms one substance into the other. The mixtures are supposed to be contained in two vessels, communicating by a narrow capillary. The vessels are artificially kept at temperatures, differing by an amount  $\Delta T$ , and we calculate for the stationary state the resulting pressure difference  $\Delta P$  and concentration difference  $\Delta x_1$  between both reservoirs, where  $x_1$  is the relative proportion of the isomer 1 in the mixture. This means that we arrive at an expression for  $\Delta P/\Delta T$ , which is called the thermomolecular pressure difference, and for  $\Delta x_1/\Delta T$ , called the thermal effusion effect (sometimes thermal diffusion, although this latter name could better be used only for systems without capillaries or membranes). We also considered the mechano-caloric effect i.e. the heat transfer at fixed  $\Delta P$  and  $\Delta T = 0$ .

We have specially focused attention to the two limiting cases of absence of chemical reaction and immediate chemical equilibrium. The first is the ordinary thermal effusion phenomenon for a mixture of two non-reacting components, considered already by P r i g o i n e <sup>2)</sup>. The second case was taken in G o r t e r's calculation. For arbitrary substances we do not immediately obtain G o r t e r's expression, but as it should be, only when we make the assumption,

usually accepted for liquid helium II, that no "normal" atoms can pass through a narrow capillary <sup>3</sup>).

The present paper can also be considered as a refinement of the calculation made by one of us <sup>4</sup>), where liquid helium II was considered as one single substance.

§ 2. *Entropy production and phenomenological equations.* Let us suppose that the mixture of isomers 1 and 2 enclosed in two communicating reservoirs I and II, of volumes  $V_I$  and  $V_{II}$ , kept at temperatures  $T_I$  and  $T_{II} = T_I + \Delta T$ . The pressures in the vessels I and II are  $P_I$  and  $P_{II} = P_I + \Delta P$ , the fraction of component 1 is  $x_1^I$  in the first and  $x_1^{II} = x_1^I + \Delta x_1$  in the second reservoir. The fraction of component 2 is given by  $x_1 + x_2 = 1$ . We suppose that the "chemical reaction" (1) is possible between the components. For simplicity's sake we consider the case that the sub-systems have equal masses  $M^I = M^{II}$ .

The first step in the thermodynamics of irreversible processes is to calculate the entropy production corresponding with transfer of energy and mass from I to II, and with the advancement of the chemical reaction in I and II.

Let us write first the G i b b s formula

$$T^I dS^I = dU^I + P^I dV^I - \mu_1^I dM_1^I - \mu_2^I dM_2^I, \quad (2)$$

where  $S^I$  is the entropy,  $U^I$  the energy,  $\mu_1^I$  and  $\mu_2^I$  the chemical potentials (partial specific G i b b s functions),  $M_1^I$  and  $M_2^I$  the masses of isomers 1 and 2,  $P^I$  the pressure and  $V^I$  the volume, all quantities referring to reservoir I. It is convenient to split the differential masses into a part indicated by  $d_i$  which refers to the transfer of mass from one reservoir to the other, and a part marked by  $d_r$ , which gives the change, resulting from chemical reaction, e.g.

$$dM_1^I = d_i M_1^I + d_r M_1^I. \quad (3)$$

We have, of course, for the chemical reaction (1)

$$d_r M_1^I + d_r M_2^I = 0, \quad (4)$$

and similarly for II. With the help of (3) and (4), formula (2) gets the alternative form

$$T^I dS^I = dU^I + P^I dV^I - \mu_1^I d_i M_1^I - \mu_2^I d_i M_2^I - A^I d_r M_1^I, \quad (5)$$

where

$$A^I \equiv \mu_1^I - \mu_2^I \quad (6)$$

is called the De Donder chemically affinity of the reaction (1).

For the conservation of mass we can write

$$d_r M_k^I + d_i M_k^{II} = 0 \quad (k = 1, 2). \quad (7)$$

The change of energy  $dU^I$  may be split into an external part  $d_e U^I$ , the energy exchanged with the surroundings, and an internal part  $d_i U^I$ , the energy exchanged with vessel II. A similar splitting holds for  $dU^{II}$ . The conservation of energy can then be expressed as

$$d_i U^I + d_i U^{II} = 0. \quad (8)$$

By means of (7) and (8) we find from equation (5) and a similar one for reservoir II for the change of entropy of the total system

$$dS = (d_e U^I + P^I dV^I)/T^I + (d_e U^{II} + P^{II} dV^{II})/T^{II} + (\Delta T/T^2) d_i U^I + \Delta(\mu_1/T) d_i M_1^I + \Delta(\mu_2/T) d_i M_2^I - (A^I/T^I) d_r M_1^I - (A^{II}/T^{II}) d_r M_1^{II}, \quad (9)$$

where the symbol  $\Delta$  is used for the difference of a quantity in II and the corresponding one in I.

Expression (9) can be split into two parts: one, giving the entropy supply from the surroundings (cf. appendix)

$$d_e S = (d_e U + P^I dV^I)/T^I + (d_e U^{II} + P^{II} dV^{II})/T^{II}, \quad (10)$$

the other giving the internal production of entropy, resulting from the taking place of irreversible processes

$$d_i S = (\Delta T/T^2) d_i U^I + \Delta(\mu_1/T) d_i M_1^I + \Delta(\mu_2/T) d_i M_2^I - (A^I/T^I) d_r M_1^I - (A^{II}/T^{II}) d_r M_1^{II}. \quad (11)$$

We now define the "energy flow"  $J_u$ , the flows  $J_k$  of components  $k = 1$  or  $2$ , and the chemical reaction rates  $J_I$  in vessel I and  $J_{II}$  in vessel II, as follows

$$\left. \begin{aligned} J_u &\equiv -d_i U^I/dt = d_i U^{II}/dt \\ J_k &\equiv -d_i M_k^I/dt = d_i M_k^{II}/dt \\ J_I &\equiv -d_r M_1^I/dt = d_r M_2^I/dt \\ J_{II} &\equiv -d_r M_1^{II}/dt = d_r M_2^{II}/dt. \end{aligned} \right\} \quad (k = 1, 2) \quad (12)$$

$J_u$  and  $J_k$  are counted positive for flow from reservoir I to II,  $J_I$  and  $J_{II}$  are positive when the reaction takes places in the direction  $1 \rightarrow 2$ . After insertion of (12) in (11) we find for the production of entropy per unit time

$$\sigma \equiv d_i S/dt = -J_u \Delta T/T^2 - J_1 \Delta(\mu_1/T) - J_2 \Delta(\mu_2/T) + J_I A^I/T^I + J_{II} A^{II}/T^{II}. \quad (13)$$

This gives the entropy production as a sum of products of "flows"  $J$  and corresponding "forces", which we can describe as arising from energy conduction, diffusion and chemistry. We will now write down the phenomenological equations i.e. the "flows" as linear functions of the "forces". Doing this we must take care not to put quantities of different tensorial character in relation to each other. The application of this rule, which is called Curie's theorem<sup>5</sup>), forbids us to combine the vectorial flows  $J_u$ ,  $J_1$  and  $J_2$  with the scalar forces  $A^I$  and  $A^{II}$  and also the scalar flows  $J_I$  and  $J_{II}$  with the vectorial forces. This leads us therefore to the relations

$$\left. \begin{aligned} J_1 &= -L_{11} \Delta(\mu_1/T) - L_{12} \Delta(\mu_2/T) - L_{13} (\Delta T/T^2) \\ J_2 &= -L_{21} \Delta(\mu_1/T) - L_{22} \Delta(\mu_2/T) - L_{23} (\Delta T/T^2) \\ J_u &= -L_{31} \Delta(\mu_1/T) - L_{32} \Delta(\mu_2/T) - L_{33} (\Delta T/T^2) \\ J_I &= L_{44} A^I/T^I \\ J_{II} &= L_{44} A^{II}/T^{II}. \end{aligned} \right\} \quad (14)$$

In the last two equations we have inserted the same coefficient  $L_{44}$  since there is obviously no physical difference between the reactions in I and II (we use here the supposition  $M^I = M^{II}$ ). We also omitted chemical cross-terms as there is admittedly no interaction between the chemical reactions in the two vessels. Finally we still have the three Onsager reciprocal relations<sup>6</sup>)

$$L_{12} = L_{21}, \quad L_{13} = L_{31} \quad \text{and} \quad L_{23} = L_{32}, \quad (15)$$

so that we are left with seven independent phenomenological coefficients in (15).

Inserting (14) into (13) we have

$$\begin{aligned} \sigma &= L_{11} \{\Delta(\mu_1/T)\}^2 + L_{22} \{\Delta(\mu_2/T)\}^2 + L_{33} (\Delta T/T^2)^2 + \\ &+ (L_{12} + L_{21}) \Delta(\mu_1/T) \Delta(\mu_2/T) + (L_{31} + L_{13}) \Delta(\mu_1/T) \Delta T/T^2 + \\ &+ (L_{32} + L_{23}) \Delta(\mu_2/T) \Delta T/T^2 + L_{44} \{(A^I/T^I)^2 + (A^{II}/T^{II})^2\}, \end{aligned} \quad (16)$$

i.e. the production of entropy per unit time is given as a quadratic function of the set of the "forces"  $\Delta(\mu_1/T)$ ,  $\Delta(\mu_2/T)$ ,  $\Delta T/T^2$ ,  $A^I/T^I$  and  $A^{II}/T^{II}$ . According to (6) only four of these parameters are independent variables.

§ 3. *The stationary states.* Formula (16) is an example of a general property of the production of entropy per unit time for any process

under consideration:  $\sigma$  can always be written as a quadratic function of a set of variables, which we may call in general  $y_1, \dots, y_n$ . In our case (16) we had  $n = 4$ , viz. the four independent parameters mentioned at the end of the preceding section; or eventually four independent functions thereof.

Now, by means of some external influence, one can fix the values of some of them, e.g.  $y_1, \dots, y_k$ , where  $k$  takes the values  $0, 1, \dots, n$ . The function  $\sigma$ , which is positive definite, will always tend to a minimum value in course of time, which value is reached when the partial derivatives  $\partial\sigma/\partial y_i$  with  $i = k + 1, \dots, n$  are zero. These states of lowest entropy production are stationary, because, once these states are reached, the different variables  $y_i$  ( $i = 1, \dots, n$ ) will be constant in time.

We can distinguish between "stationary states of various order  $k$ ", when different numbers  $k$  of the variables  $y_i$  are kept constant during the evolution of the system to the stationary state. This concept of the order of the stationary state is very convenient for the characterization of physical situations<sup>8)</sup>. We note that the stationary state of zeroth order, where none of the variables  $y_i$  is kept at constant value during this evolution, is simply the state of thermostatic equilibrium.

For our purpose the stationary state of the first order, reached when  $\Delta T$  is kept constant, is of special interest. In this case we have for the derivatives of (16) with respect to the other independent variables

$$\left. \begin{aligned} \partial\sigma/\partial\Delta(\mu_1/T) &= 0 \\ \partial\sigma/\partial\Delta(\mu_2/T) &= 0 \\ \partial\sigma/\partial(A^I/T^I) &= 0. \end{aligned} \right\} \quad (17)$$

Making use of the relation which follows from the definition (6) of the affinities

$$A^{II}/T^{II} = A^I/T^I + \Delta(\mu_1/T) - \Delta(\mu_2/T), \quad (18)$$

these equations become

$$\left. \begin{aligned} 2L_{11}\Delta(\mu_1/T) + (L_{12} + L_{21})\Delta(\mu_2/T) + (L_{13} + L_{31})\Delta T/T^2 + 2L_{44}A^{II}/T^{II} &= 0 \\ 2L_{22}\Delta(\mu_2/T) + (L_{12} + L_{21})\Delta(\mu_1/T) + (L_{23} + L_{32})\Delta T/T^2 - 2L_{44}A^{II}/T^{II} &= 0 \\ 2L_{44}A^I/T^I + 2L_{44}A^{II}/T^{II} &= 0. \end{aligned} \right\} \quad (19)$$

From these equations we can derive two important results regarding this stationary state of the first order:

A) Applying the Onsager reciprocal relations  $L_{ij} = L_{ji}$  in (19) we have from (14), (12) and (3)

$$\left. \begin{aligned} J_1 - J_{II} &= dM_1^I/dt = 0 \\ J_2 + J_{II} &= dM_2^I/dt = 0 \\ J_I + J_{II} &= -d_r M_1/dt = d_r M_2/dt = 0. \end{aligned} \right\} \quad (20)$$

Equations (20) can be regrouped to give

$$\left. \begin{aligned} J_1 + J_I &= -dM_1^I/dt = 0 \\ J_2 - J_I &= -dM_2^I/dt = 0, \end{aligned} \right\} \quad (21)$$

and summarized as

$$J_1 = -J_2 = -J_I = J_{II}. \quad (22)$$

Clearly these formulae express physically that equal amounts of 1 and 2 pass in opposite directions through the capillary and that in both reservoirs the amounts of in- or outflowing mass of each component are just compensated by the chemical reaction taking place.

Also the net total chemical reaction rate of each component in both reservoirs when taken together is zero. It was already remarked by Meixner<sup>7)</sup> that the fluxes in (22) are not separately zero at the stationary state.

B) The equations (19) are three linear, homogeneous equations in the four variables  $\Delta(\mu_1/T)$ ,  $\Delta(\mu_2/T)$ ,  $A^I/T^I$  and  $\Delta T$ . We can get an alternative and more convenient form when we write the diffusion "force" explicitly as

$$\Delta(\mu_k/T) = -h_k \Delta T/T^2 + v_k \Delta P/T + (\partial\mu_k/\partial x_1)_{P,T} \Delta x_1/T \quad (k=1,2), \quad (23)$$

where  $h_k$  and  $v_k$  are the partial specific enthalpy and volume of component  $k$ . We also need the Gibbs-Duhem relation

$$x_1(\partial\mu_1/\partial x_1)_{P,T} + x_2(\partial\mu_2/\partial x_1)_{P,T} = 0. \quad (24)$$

Then, finally, the three equations (17) for the stationary state of the first order with  $\Delta T$  constant are linear and homogeneous in the four variables  $\Delta P$ ,  $\Delta x_1$ ,  $A^I/T^I$  and  $\Delta T$ . As  $\Delta T$  has a fixed, given value, we can calculate the other three mentioned variables in terms of  $\Delta T$ . After a lengthy, but elementary calculation we find the following results

$$\Delta P/\Delta T = (h + x_1 L_1 + x_2 L_2)/vT, \quad (25)$$

where the abbreviations

$$\tau_1 \equiv \frac{\frac{1}{2}(L_{12} + L_{21}) \frac{1}{2}(L_{23} + L_{32}) - L_{22} \frac{1}{2}(L_{13} + L_{31}) - \frac{1}{2}L_{44} \{ \frac{1}{2}(L_{13} + L_{31}) + \frac{1}{2}(L_{23} + L_{32}) \}}{L_{11}L_{22} - \{ \frac{1}{2}(L_{12} + L_{21}) \}^2 + L_{44} \frac{1}{2}(L_{11} + L_{22} + L_{12} + L_{21})} \quad (26)$$

$$L_2 \equiv \frac{\frac{1}{2}(L_{12} + L_{21}) \frac{1}{2}(L_{13} + L_{31}) - L_{11} \frac{1}{2}(L_{23} + L_{32}) - \frac{1}{2}L_{44} \{ \frac{1}{2}(L_{13} + L_{31}) + \frac{1}{2}(L_{23} + L_{32}) \}}{L_{11}L_{22} - \{ \frac{1}{2}L_{12} + L_{21} \}^2 + L_{44} \frac{1}{2}(L_{11} + L_{22} + L_{12} + L_{21})} \quad (27)$$

are used and where  $h$  and  $v$  are the mean specific enthalpy and volume

$$h = x_1 h_1 + x_2 h_2 = x_1(h_1 - h_2) + h_2, \quad (28)$$

$$v = x_1 v_1 + x_2 v_2 = x_1(v_1 - v_2) + v_2. \quad (29)$$

Further for the separation per unit temperature difference

$$\Delta x_1 / \Delta T = x_2 \{ v_2(L_1 + h_1) - v_1(L_2 + h_2) \} / vT(\partial\mu_1/\partial x_1)_{P,T}. \quad (30)$$

The third result is the chemical "force" divided by  $\Delta T$

$$\begin{aligned} A^I / T^I \Delta T &= -A^{II} / T^{II} \Delta T = -\frac{1}{2} \Delta(A/T) / \Delta T = (L_2 - L_1) / 2T^2 = \\ &= \frac{1}{2T^2} \left[ \frac{\frac{1}{2}(L_{12} + L_{21}) \{ \frac{1}{2}(L_{13} + L_{31}) - \frac{1}{2}(L_{23} + L_{32}) \} - L_{11} \frac{1}{2}(L_{23} + L_{32}) + L_{22} \frac{1}{2}(L_{13} + L_{31})}{L_{11}L_{22} - \{ \frac{1}{2}(L_{12} + L_{21}) \}^2 + L_{44} \frac{1}{2}(L_{11} + L_{22} + L_{12} + L_{21})} \right]. \end{aligned} \quad (31)$$

In order to show the full symmetry and occurrence of the same combinations  $L_1$  and  $L_2$  of phenomenological coefficients in all three equations (25), (30) and (31), the Onsager relations (15) have not yet been inserted.

The Onsager relations must however be applied to give physical significance to combinations of the phenomenological constants  $L_{ik}$  (see sections 5, 6 and 7). To make this interpretation possible, we shall first discuss the stationary state of second order, with fixed  $\Delta P$  and  $\Delta T$ .

§ 4. *Stationary state of second order and energies of transfer.* Let us again suppose  $\sigma$  to be written as a function of the four parameters  $\Delta P$ ,  $\Delta T$ ,  $\Delta x_1$  and  $A^I$  and let us now consider the stationary state of second order where  $\Delta T$  and  $\Delta P$  are kept at constant values, with  $\Delta T = 0$ . In this case we have only two free independent variables  $\Delta x_1$  and  $A^I$ .

For the state of lowest entropy production we have, from (16)

$$\begin{aligned} \partial\sigma/\partial\Delta x_1 &= -(2/x_1 T^2) (\partial\mu_2/\partial x_1) \{ L_{11} x_2 \Delta\mu_1 + \frac{1}{2}(L_{12} + L_{21}) (x_2 \Delta\mu_2 - x_1 \Delta\mu_1) \\ &\quad - L_{22} x_1 \Delta\mu_2 + L_{44} A^{II} \} = 0. \end{aligned} \quad (32)$$

$$\partial\sigma/\partial A^I = (2L_{44}/T^2) (A^I + A^{II}) = 0, \quad (33)$$

where terms of higher order in  $\Delta x_1$  and  $\Delta P$  have been neglected. For the sake of simplicity use has been made in these equations of the parameters  $\Delta\mu_1$  and  $\Delta\mu_2$ . Between these exists the connection, which follows from (18), (32) and (33)



$$\left. \begin{aligned} \frac{\Delta\mu_1}{\Delta\mu_2} &= \frac{L_{22}x_1 - \frac{1}{2}(L_{12} + L_{21})x_2 + \frac{1}{2}L_{44}}{L_{11}x_2 - \frac{1}{2}(L_{12} + L_{21})x_1 + \frac{1}{2}L_{44}} \end{aligned} \right\} \quad (34)$$

Making use of the phenomenological equations (14) and the Onsager relations (15), equations (32) and (33) can also be written as

$$x_2 J_1 - x_1 J_2 - J_{II} = 0, \quad (35)$$

$$J_I + J_{II} = 0. \quad (36)$$

With the use of (12) these equations can be given the alternative simple form ( $x_1^I = M_1^I/(M_1^I + M_2^I)$  etc.)

$$dx_1^I/dt = dx_1^{II}/dt = 0. \quad (37)$$

Formulae (37) and (36) express physically that in this state the *composition* in both vessels is constant in time and that the net total chemical production rate is zero.

We can introduce now the so-called "quantities of transfer" which play an important rôle in the thermodynamics of irreversible processes<sup>8)</sup>. The "energies of transfer"  $U^*$  and  $U_k^*$  ( $k = 1, 2$ ) are defined as the energies transported with one unit of mass of the mixture and of the component  $k$  in the stationary state of second order with fixed  $\Delta P$  and fixed  $\Delta T = 0$  (uniform temperature). Stated explicitly we have

$$J_u \equiv U^* (J_1 + J_2) \quad (38)$$

$$J_u \equiv U_1^* J_1 + U_2^* J_2. \quad (39)$$

Writing the first three equations (14) for  $\Delta T = 0$

$$\left. \begin{aligned} J_1 &= -L_{11} \Delta\mu_1/T - L_{12} \Delta\mu_2/T \\ J_2 &= -L_{21} \Delta\mu_1/T - L_{22} \Delta\mu_2/T \\ J_u &= -L_{31} \Delta\mu_1/T - L_{32} \Delta\mu_2/T \end{aligned} \right\} \quad (40)$$

and substituting these equations into (38) we find, using (34), the energy of transfer

$$\begin{aligned} U^* &= - \frac{x_1 \{ \frac{1}{2}(L_{12} + L_{21}) L_{32} - L_{22} L_{31} - \frac{1}{2} L_{44} (L_{31} + L_{32}) \} +}{L_{11} L_{22} + \frac{1}{2} L_{44} (L_{11} + L_{22} + L_{12} + L_{21}) -} \\ &+ \frac{x_2 \{ \frac{1}{2}(L_{12} + L_{21}) L_{31} - L_{11} L_{32} - \frac{1}{2} L_{44} (L_{31} + L_{32}) \}}{-\frac{1}{2}(L_{12} + L_{21}) (L_{12} x_1 + L_{21} x_2) + \frac{1}{2}(L_{11} x_2 - L_{22} x_1) (L_{12} - L_{21})}. \end{aligned} \quad (41)$$

If we substitute (40) into (39), identifying the coefficients of the forces in both members, we find

$$L_{3k} = L_{1k} U_1^* + L_{2k} U_2^* \quad (k = 1, 2) \quad (42)$$

These relations give for the energies of transfer  $U_k^*$

$$U_1^* = (L_{31}L_{22} - L_{32}L_{21})/(L_{11}L_{22} - L_{12}L_{21}), \quad (43)$$

$$U_2^* = (L_{32}L_{11} - L_{31}L_{12})/(L_{11}L_{22} - L_{12}L_{21}), \quad (44)$$

expressed in terms of the phenomenological coefficients.

In equations (41), (43) and (44) we have found the desired results viz. the energies of transfer expressed in terms of the phenomenological coefficients  $L_{ik}$  and the relative proportions  $x_1$  and  $x_2$  of the components.

We want to stress one result which concerns the relation between the energies of transfer which follows from (38) and (39)

$$U^* = \{J_1/(J_1 + J_2)\} U_1^* + \{J_2/(J_1 + J_2)\} U_2^*. \quad (45)$$

We remark that in general

$$J_1/(J_1 + J_2) \neq x_1 \quad \text{and} \quad J_2/(J_1 + J_2) \neq x_2, \quad (45a)$$

because we have from (35) and (36)

$$x_1 = (J_1 + J_I)/(J_1 + J_2) \quad \text{and} \quad x_2 = (J_2 - J_I)/(J_1 + J_2). \quad (45b)$$

So we see that only if the chemical reaction rate  $J_I (= -J_{II})$  vanishes, the fractions occurring in (45) correspond to the relative proportions  $x_1$  and  $x_2$  of the two components in the vessels for this stationary state.

Finally we want to point out that we have not yet made use of the Onsager relations (15) in order to apply them only at a moment, where their full physical significance can be shown. Incidentally we remark that (41) is already considerably simplified by the one Onsager relation  $L_{12} = L_{21}$ .

§ 5. *The thermomolecular pressure effect.* Equation (25) with (26) and (27) gives the pressure effect in the stationary state of the first order with fixed  $\Delta T$ . It contains a combination of the phenomenological coefficients. It is at this stage of the derivation that we introduce the Onsager relations (15). As always in the thermodynamics of irreversible processes they enable us to give a physical significance to the hitherto uninterpreted combinations of coefficients. Here we have from (15), (26), (27) and (41) the relation

$$x_1 L_1 + x_2 L_2 = -U^*, \quad (46)$$

so that the thermomolecular pressure effect can now be expressed in terms of the energy of transfer  $U^*$

$$\Delta P/\Delta T = (h - U^*)/vT. \quad (47)$$

With the help of (45) and (45b), this equation can alternatively be written as

$$\Delta P/\Delta T = [h - x_1 U_1^* - x_2 U_2^* + \{J_I/(J_1 + J_2)\} (U_1^* - U_2^*)]/vT. \quad (48)$$

These equations are valid for arbitrary values of the coefficient  $L_{44}$ .

Two special cases are interesting  $L_{44} = 0$  and  $L_{44} \rightarrow \infty$ . The first gives the results for non-reacting components. As  $J_I (= -J_{II}) = 0$  in this case, we find from (48)

$$\Delta P/\Delta T = (h - x_1 U_1^* - x_2 U_2^*)/vT, \quad (49)$$

equivalent to an equation, derived by Prigogine<sup>2</sup>).

The other limiting case would lead to infinitely quick chemical reaction for finite affinity. As this is impossible, we expect that  $A^I$  will tend to zero. This means that the situation with  $L_{44} \rightarrow \infty$  is the case of immediate chemical equilibrium. In fact we find for  $L_{44} \rightarrow \infty$  from (31)  $A^I = 0$  i.e. zero chemical affinity ( $\mu_1 = \mu_2$ ). From this we have

$$(\partial g/\partial x_1)_{P,T} = h_1 - h_2 - T(s_1 - s_2) = h_1 - h_2 - T(\partial s/\partial x_1)_{P,T} = 0 \quad (50)$$

where  $g$  and  $s$  have the meaning of mean specific Gibbs function  $x_1 \mu_1 + x_2 \mu_2$  and mean specific entropy of the mixture  $x_1 s_1 + x_2 s_2$  respectively, and where the Gibbs-Duhem relation has been used for the entropy (same relation as (24) but  $s_k$  instead of  $\mu_k$ ). Equations (28), (47) and (50) give

$$v \Delta P/\Delta T = x_1 (\partial s/\partial x_1)_{P,T} + (h_2 - U^*)/T \quad (51)$$

a formula to be discussed in §9 for liquid helium. It should be kept in mind that in the limit  $L_{44} \rightarrow \infty$ , and therefore  $A^I \rightarrow 0$ , we may not conclude that  $J_I \rightarrow 0$ , as can be easily verified from (14) (fourth equation) and (31).

§ 6. *The thermal effusion effect.* Equation (30) gives the difference between the fractions of component 1 in the two vessels, in the first order stationary state with  $\Delta T$  kept at constant value. We will consider again the two limiting values for  $L_{44} = 0$  and  $L_{44} \rightarrow \infty$ .

For non-reacting components ( $L_{44} = 0$ ) we have, applying the

Onsager relations (15) to (26) and (27), again an interpretation in terms of the energies of transfer (43) and (44)

$$L_1 = (L_{21}L_{32} - L_{31}L_{22})/(L_{11}L_{22} - L_{12}L_{21}) = -U_1^*. \quad (52)$$

$$L_2 = (L_{31}L_{12} - L_{32}L_{11})/(L_{11}L_{22} - L_{12}L_{21}) = -U_2^*. \quad (53)$$

Thus we get from (30)

$$\Delta x_1/\Delta T = x_2 \{v_1(U_2^* - h_2) - v_2(U_1^* - h_1)\}/vT(\partial\mu_1/\partial x_1)_{P,T} \quad (54)$$

equivalent to Prigogine's formula <sup>2)</sup> for thermal effusion in a non-reacting mixture.

For immediate chemical equilibrium  $L_{44} \rightarrow \infty$  we find from (26), (27) and (41)

$$L_1 = L_2 = -(L_{13} + L_{23})/(L_{11} + L_{12} + L_{21} + L_{22}) = -U^*, \quad (55)$$

where the Onsager relations (15) have again been used. From (30) we then have

$$\Delta x_1/\Delta T = x_2 \{h_1v_2 - h_2v_1 + (v_1 - v_2)U^*\}/vT(\partial\mu_1/\partial x_1)_{P,T}. \quad (56)$$

§ 7. *The chemical effect.* This is the deviation from the equilibrium value zero of the affinity  $A^I = \mu_1^I - \mu_2^I$  in the stationary state of first order with a fixed temperature difference  $\Delta T$ . It is given in general by equation (31).

For non-reacting components ( $L_{44} = 0$ ) we have from (31), (52) and (53)

$$A^I/T^I \Delta T = (U_1^* - U_2^*)/2T^2. \quad (57)$$

For the case  $L_{44} \rightarrow \infty$  equation (31) reads, using (55)

$$A^I/T^I \Delta T = 0, \quad (58)$$

as it should be at chemical equilibrium.

§ 8. *The mechano-caloric effect and heats of transfer.* In the stationary state of second order with fixed  $\Delta P$  and  $\Delta T (= 0)$ , the transfer of energy from one system to the other may give rise to a caloric effect i.e. an amount of heat may be produced in the vessels. This effect is called the *mechano-caloric* effect.

In our case of isothermal processes the production of heat in a vessel will be compensated by a "heat flow" from its surroundings. Applying the first law of thermodynamics for open systems <sup>2)</sup> to system I, we have

$$dU^I = dQ^I - P^I dV^I + h^I dM^I; \quad (dM^I = d_r M_1^I + d_r M_2^I). \quad (59)$$

For the stationary state under consideration the composition of the vessels is constant in time (37) and the temperature and the pressure are kept at constant values. Thus we have also constant mean specific energy  $u^I$  and mean specific volume  $v^I$  in the mixture in vessel I and consequently

$$dU^I = u^I dM^I \quad \text{and} \quad dV^I = v^I dM^I \quad (60)$$

Inserting (60) into (59) we find

$$(u^I + P^I v^I - h^I) dM^I = dQ^I \quad \text{and thus} \quad dQ^I = 0. \quad (61)$$

Splitting  $dQ^I$  into an external part  $d_e Q^I$  (supply from the surroundings) and an internal part  $d_i Q^I$  we have from (61)

$$d_e Q^I + d_i Q^I (= dQ^I) = 0, \quad (62)$$

so that, by means of the relation

$$d_i Q^I = d_i U^I - h^I dM^I, \quad (63)$$

(see appendix) we find, also using the notations (12)

$$d_e Q^I/dt = -d_i U^I/dt + h^I dM^I/dt = J_u - h(J_1 + J_2), \quad (64)$$

where the superscript of  $h^I$  has been dropped.

We now introduce the "heat of transfer"  $Q^*$  as the heat supplied from the surroundings to vessel I per unit of time, when one unit of mass is transferred from one vessel to the other in this stationary state of second order with constant  $\Delta P$  and  $\Delta T (= 0)$ . Stated explicitly, we have

$$Q^* = (d_e Q^I/dt)/(J_1 + J_2) \quad (65)$$

or

$$Q^* = U^* - h, \quad (66)$$

where (64) and (38) have been used. Equations (65) and (66) describe the mechano-caloric effect i.e. the heat flow per unit of total mass transfer.

Some formulae get a simpler form when the heats of transfer are used instead of the energies of transfer: e.g. equation (47) can be written with the help of (66) in the form

$$\Delta P/\Delta T = -Q^*/vT, \quad (67)$$

thus establishing a very close connexion between the thermomolecular pressure effect  $\Delta P/\Delta T$  and the mechano-caloric effect  $Q^*$ .

§ 9. *Liquid helium II*. According to the two fluid model of liquid helium II this substance is just under the circumstances described in the preceding sections. Therefore, without additional assumptions, the full formalism should also be applied to helium II.

In his first papers however G o r t e r assumed that the "chemical" equilibrium between normal and superfluid atoms is immediately established. In that case formulae (51), (56) and (58) are valid. When we make further the usual assumption that no normal atoms (taken as component 1) but only superfluid atoms (component 2) can pass through a sufficiently narrow capillary, the energy of transfer can immediately be given. As a matter of fact we have in general for the transport of matter in bulk that the energy of transfer is equal to the specific energy of the transported mass added to the external work against the pressure in the vessel, which is then equal to the product of this pressure and the specific volume; or in other words the energy of transfer is equal to the specific enthalpy of the transported mass. In our case we have therefore for the transport of component 2 (superfluid atoms)

$$U^* = u_2 + Pv_2 = h_2. \quad (68)$$

When this is inserted into equation (51) we get the remarkable result viz.

$$v \Delta P / \Delta T = x_1 (\partial s / \partial x_1)_{P,T}, \quad (69)$$

G o r t e r's equation for the fountain effect, which is thus confirmed by the thermodynamical theory of irreversible processes. Formulae (56) and (58) become with (68)

$$\Delta x_1 / \Delta T = x_2 v_2 (h_1 - h_2) / v T (\partial \mu_1 / \partial x_1)_{P,T} \quad (70)$$

and

$$A^I = A^{II} = 0. \quad (71)$$

We recall that the assumptions leading from the general formulae (25), (30) and (31) for the stationary state to (69), (70) and (71) were 1st: immediate chemical equilibrium ( $L_{44} \rightarrow \infty$ ), 2nd: transfer of superfluid atoms only and 3rd: transfer in bulk. To which extent the first assumption is legitimate, it not yet completely known. Some physical considerations are given in reference <sup>1</sup>). It is perhaps of some importance to dwell on the validity of the last two conditions. If for instance the tube is so wide that normal atoms can also pass, the more general formulae (51) and (56) must be used. The same

would be necessary if by any means the third assumption is falsified; in this connection it must be remarked that by transfer in bulk we mean transport as one whole or, in atomic terms, in such a way that the mean free path of the atoms is small compared with the diameter of the tube. Then, and only then, equation (68) containing the external work term  $Pv_2$  is correct. This is very probably true in the dense liquid state, but in the contrary case, e.g. if the substance would pass under "Knudsen gas circumstances" (mean free path large compared with tube diameter) the expression (68) for  $U^*$  would not be correct (cf. 4)), but of course equations (51), (56) and (58) will remain valid.

§ 10. *Energy and heat conduction in the first order stationary state.* In order to find the influence of the chemical reaction (1) on heat and energy conduction we will examine the stationary state of first order with fixed  $\Delta T$ .

The energy conduction is given by the third equation (14). The quantities  $\Delta(\mu_1/T)$  and  $\Delta(\mu_2/T)$  can be expressed in terms of  $\Delta T$  and in the phenomenological coefficients  $L_{ik}$  for the state considered.

From (18) and (19) we find

$$\Delta(\mu_1/T) = L_1 \Delta T/T^2 \quad (72)$$

$$\Delta(\mu_2/T) = L_2 \Delta T/T^2 \quad (73)$$

where the abbreviations  $L_1$  and  $L_2$  are defined by (26) and (27). Inserting these equations into the third equation (14), we get

$$J_U = -(L_{31}L_1 + L_{32}L_2 + L_{33}) \Delta T/T^2. \quad (74)$$

We now define the heat flow as

$$J_Q = -d_i Q^I/dt, \quad (75)$$

where  $d_i Q^I$  is the internal part of  $dQ^I$  defined by (59). This is, according to (63) and (12), also equal to

$$J_Q = J_U - h(J_1 + J_2), \quad (76)$$

omitting the superscript I of the specific enthalpy, just as has been done in (23).

As we have in a stationary state of the first kind with  $\Delta T = \text{constant}$   $J_1 + J_2 = 0$  (22), the heat flow is equal to the energy flow (74)

$$J_Q = J_U = -(L_{31}L_1 + L_{32}L_2 + L_{33}) \Delta T/T^2. \quad (77)$$

For  $L_{44} = 0$  this equation reduces with the help of (52) and (53) to

$$J_Q = (L_{31}U_1^* + L_{32}U_2^* - L_{33}) \Delta T/T^2. \quad (78)$$

In view of this result we may rewrite (77) for arbitrary  $L_{44}$  in the form

$$J_Q = -\{L_{31}(L_1 + U_1^*) + L_{32}(L_2 + U_2^*)\} \Delta T/T^2 + \\ + (L_{31}U_1^* + L_{32}U_2^* - L_{33})\Delta T/T^2, \quad (79)$$

thus splitting the heat flow into two parts, the first of which accounts for an "abnormal" heat conduction due to the coupling of chemical reaction and diffusion, and the second giving a "normal" transport of heat also present when no reaction takes place.

We will consider again the heat flow for the two limiting values  $L_{44} = 0$  and  $L_{44} \rightarrow \infty$ .

It has already been seen that the first case (non-reacting components) leads to (78) i.e. a so-called "normal" transport of heat.

For immediate chemical equilibrium ( $L_{44} \rightarrow \infty$ ) we have from (55) and (79)

$$J_Q = \{L_{31}(U^* - U_1^*) + L_{32}(U^* - U_2^*)\} \Delta T/T^2 + \\ + (L_{31}U_1^* + L_{32}U_2^* - L_{33}) \Delta T/T^2 = \\ = \{(L_{31} + L_{32})U^* - L_{33}\} \Delta T/T^2. \quad (80)$$

This equation may be applied to the case of liquid helium II in arbitrary slits where the normal component still has a finite speed. In very narrow slits, where we make the usual assumption  $J_1 \equiv 0$ , we have  $L_{ik} \equiv 0$  ( $k = 1, 2, 3$ ). Making use of the Onsager relations (15) we have therefore also  $L_{31} \equiv 0$ . Furthermore  $U^* = U_2^*$  according to (45), so that equation (80) reduces to

$$J_Q = (L_{32}U_2^* - L_{33}) \Delta T/T^2, \quad (81)$$

i.e. the heat conduction does not include a part due to the coupling of chemical reaction and diffusion, or in other words we have only a "normal" heat conduction in this case.

We see that some features of heat conduction of liquid helium II, such as the different results obtained in slits of various width may be explained by the above treatment. The fact that no cube root dependence of  $\Delta T$  is found for the total heat flow does not impair this treatment as such a dependence will be the result of non-linear phenomenological relations which lie beyond the region of validity of the present treatment. Formally however we may always consider a region of linear dependence for sufficiently small  $\Delta T$ , although this region may be inaccessible to experiment in some cases. Indeed a



linear dependence of  $\Delta T$  has been found experimentally for the heat flow in slits of width between 5 and 15 microns at small  $\Delta T$  and  $T$  <sup>1)</sup>. That such a dependance has not been found for the same values of  $\Delta T$  and  $T$  in very large slits and capillaries can easily be understood with the usual assumption that the mean velocity of the normal component will be larger since larger slits, since a higher velocity may give rise to a non-linear phenomenological relation.

§ 11. *Appendix.* The first law of thermodynamics can be applied separately to the two vessels, which are then considered as open systems, or to the total system, taken as a materially closed one. We have therefore the three relations

$$dQ^I = dU^I + P^I dV^I - h^I dM^I \quad (82)$$

$$dQ^{II} = dU^{II} + P^{II} dV^{II} - h^{II} dM^{II} \quad (83)$$

$$dQ = dU + P^I dV^I + P^{II} dV^{II}. \quad (84)$$

Splitting  $dQ^I$ ,  $dQ^{II}$ ,  $dU^I$  and  $dU^{II}$  into external and internal parts, and considering that

$$dQ = d_e Q^I + d_e Q^{II} \quad (85)$$

and

$$dU = d_e U^I + d_e U^{II} \quad (\text{or } d_i U^I + d_i U^{II} = 0) \quad (86)$$

we find

$$d_e Q^I + d_e Q^{II} = d_e U^I + P^I dV^I + d_e U^{II} + P^{II} dV^{II}. \quad (87)$$

The sizes of I and II being independent, it is furthermore obvious from (87) that

$$d_e Q^I = d_e U^I + P^I dV^I, \quad (88)$$

and similarly for II.

Formula (10) for the entropy supply can now be written as

$$d_e S = d_e Q^I / T^I + d_e Q^{II} / T^{II}, \quad (89)$$

thereby justifying the separation of  $dS$  into  $d_e S$  (entropy supply) and  $d_i S$  (entropy production) as given by (10) and (11).

Subtracting (88) from (82) we find

$$d_i Q^I = d_i U^I - h^I dM^I, \quad (90)$$

that is relation (63) which has been used in § 8.

A relation similar to (90) is also valid for vessel II, so that equation (8) for the conservation of energy can now be given in the following form

$$(d_i Q^I + h^I dM^I) + (d_i Q^{II} + h^{II} dM^{II}) = 0 \quad (91)$$

already derived by Prigogine<sup>2)</sup> 8).

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