CHAPTER 13

ONSAGER'S RECIPROCAL RELATIONS

§13.01 *Introduction*

We recall the fundamental properties of entropy stated in §1.19. The entropy of a system can change in two distinct ways namely by external and internal changes. This is expressed symbolically by

$$dS = d_e S + d_i S \tag{13.01.1}$$

where $d_e S$ denotes the part of dS due to interaction with the surroundings and $d_i S$ denotes the part due to changes taking place in the system. We have the now familiar equality

$$d_e S = q/T \tag{13.01.2}$$

where T is the thermodynamic temperature of the system. As regards $d_i S$ the only property hitherto stressed is the inequality

$$d_i S > 0. \tag{13.01.3}$$

We shall in this chapter consider more quantitatively the value of $d_i S$ or rather of $d_i S/dt$ which is the rate of internal production of entropy. Such considerations constitute a subject often called *thermodynamics of irreversible processes.* It is a subject on which whole books* have been written and it is not practicable to devote sufficient space here for an exhaustive discussion. For the sake of brevity it has been decided to exclude from the present discussion the interesting field of thermal diffusion.

§13.02 *Electric insulators and conductors*

We introduce the subject of internal entropy production by considering electric conductors which we shall compare and contrast with electric

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* De Groot, Thermodynamics of Irreversible Processes, North-Holland 1951; Denbigh, The Thermodynamics of the Steady State, Methuen 1951; Prigogine and Defay, Etude Thermodynamique des Phénomènes Irréversibles, Dunod 1947.

insulators. We begin with the simplest case of isotropic media and then pass on to the more interesting case of anisotropic media.

The Helmholtz function of an electric insulator is related to the *electric field strength* $\boldsymbol{E}$ and the *electric displacement* $\boldsymbol{D}$, under isothermal conditions, by

$$\mathrm{d}\mathcal{F} = V\boldsymbol{E}\,\mathrm{d}\boldsymbol{D}. \qquad 13.02.1$$

This follows immediately from formula (11.06.1). We recall that $\boldsymbol{D}$ is related to $\boldsymbol{E}$ by

$$\boldsymbol{D} = \varepsilon \boldsymbol{E} \qquad 13.02.2$$

where ε is the permittivity. Under ordinary conditions ε is independent of $\boldsymbol{E}$ and this will be assumed here.

In an isotropic medium $\boldsymbol{D}$ and $\boldsymbol{E}$ have the same direction and ε is a scalar quantity. In an anisotropic medium $\boldsymbol{D}$ and $\boldsymbol{E}$ generally have different directions. A quantity such as ε relating two non-parallel vectors $\boldsymbol{D}$ and $\boldsymbol{E}$ according to (2) is called a tensor. Without any prior knowledge of tensors we can see what this means by considering the cartesian components of (2). The relations for these components have the form

$$D_x = \varepsilon_{xx} E_x + \varepsilon_{xy} E_y + \varepsilon_{xz} E_z \qquad 13.02.3$$

$$D_y = \varepsilon_{yx} E_x + \varepsilon_{yy} E_y + \varepsilon_{yz} E_z \qquad 13.02.4$$

$$D_z = \varepsilon_{zx} E_x + \varepsilon_{zy} E_y + \varepsilon_{zz} E_z \qquad 13.02.5$$

where all the quantities are scalars.

Since we are assuming that ε is independent of $\boldsymbol{E}$, we can substitute (2) into (1) and integrate obtaining, apart from a trivial integration constant,

$$\mathcal{F}/V = \tfrac{1}{2}\varepsilon \boldsymbol{E}^2. \qquad 13.02.6$$

In an isotropic medium ε is as we have already mentioned a scalar and there is no difficulty. In an anisotropic medium the meaning of (6) is by no means so simple and its interpretation requires at least an elementary knowledge of tensors. However all that we need to record here is that the existence of the Helmholtz function related to $\boldsymbol{E}$ and $\boldsymbol{D}$ by (1) requires the symmetry conditions

$$\varepsilon_{xy} = \varepsilon_{yx} \qquad \varepsilon_{yz} = \varepsilon_{zy} \qquad \varepsilon_{zx} = \varepsilon_{xz}\,. \qquad 13.02.7$$

In the terminology of tensors we say that ε must be a symmetrical tensor. When the relations (7) are assumed, the expression for the Helmholtz function becomes

$$\mathcal{F}/V = \tfrac{1}{2}\varepsilon_{xx} E_x^2 + \tfrac{1}{2}\varepsilon_{yy} E_y^2 + \tfrac{1}{2}\varepsilon_{zz} E_z^2 + \varepsilon_{xy} E_x E_y + \varepsilon_{yz} E_y E_z + \varepsilon_{zx} E_z E_x\,. \qquad 13.02.8$$

When we assume (8) and (7) we can immediately derive (3), (4), and (5) by means of (1). Without the relations (7) it is impossible to find any formula for the Helmholtz function consistent with (1).

We now turn from insulators to conductors. If we denote electric field by $\boldsymbol{E}$ and current density by $\boldsymbol{J}$ we may write

$$\boldsymbol{J}=\sigma \boldsymbol{E} \qquad 13.02.9$$

where σ denotes the electric conductivity. Under ordinary conditions σ is independent of $\boldsymbol{E}$ and we shall assume this. In an isotropic medium $\boldsymbol{J}$ and $\boldsymbol{E}$ have the same direction and σ is a scalar quantity. In an anisotropic medium $\boldsymbol{J}$ and $\boldsymbol{E}$ generally have different directions so that σ is a tensor. The relations between the cartesian components have the form

$$J_x=\sigma_{xx}E_x+\sigma_{xy}E_y+\sigma_{xz}E_z \qquad 13.02.10$$

$$J_y=\sigma_{yx}E_x+\sigma_{yy}E_y+\sigma_{yz}E_z \qquad 13.02.11$$

$$J_z=\sigma_{zx}E_x+\sigma_{zy}E_y+\sigma_{zz}E_z \qquad 13.02.12$$

where all the quantities are scalars.

Let us now determine the rate of internal production of entropy in the simple case of an isotropic medium so that $\boldsymbol{J}$ has the same direction as $\boldsymbol{E}$. It is simplest to assume that the conductor is maintained at a constant temperature and that $\boldsymbol{J}$ and $\boldsymbol{E}$ are independent of the time. The conductor is then maintained in an unchanging state so that

$$\mathrm{d}S/\mathrm{d}t=0. \qquad 13.02.13$$

Substituting from (13.01.1) and (13.01.2) into (13) we obtain

$$\mathrm{d_i}S/\mathrm{d}t=-\mathrm{d_e}S/\mathrm{d}t=-T^{-1}\mathrm{d}q/\mathrm{d}t \qquad 13.02.14$$

where $-q$ is the heat given up to the thermostat. From elementary electrical theory we have

$$-\mathrm{d}q/\mathrm{d}t=V\boldsymbol{J}\boldsymbol{E}. \qquad 13.02.15$$

Substituting (15) into (14) we obtain

$$T\mathrm{d_i}S/\mathrm{d}t=V\boldsymbol{J}\boldsymbol{E}. \qquad 13.02.16$$

Finally substituting (9) into (16) we obtain

$$T\mathrm{d_i}S/\mathrm{d}t=V\sigma E^2. \qquad 13.02.17$$

In the more complicated and more interesting case of an anisotropic conductor, we obtain by similar but more difficult reasoning

$$V^{-1}T\mathrm{d_i}S/\mathrm{d}t=J_xE_x+J_yE_y+J_zE_z. \qquad 13.02.18$$

Substituting (10), (11), and (12) into (18) we derive

$$V^{-1}T\mathrm{d_i}S/\mathrm{d}t=\sigma_{xx}E_x^2+\sigma_{yy}E_y^2+\sigma_{zz}E_z^2$$
$$+(\sigma_{xy}+\sigma_{yx})E_xE_y+(\sigma_{yz}+\sigma_{zy})E_yE_z+(\sigma_{zx}+\sigma_{xz})E_zE_x. \qquad 13.02.19$$

If we compare (19) with (8) we notice a superficial resemblance but also two differences which are interrelated. In the first place $\mathscr{F}$ occurring on the left of (8) is a function of the state of the medium while $\mathrm{d_i}S/\mathrm{d}t$ occurring on the left of (19) is not. In the second place, and as a consequence of the first difference, there is no compelling reason from classical thermodynamics why relations between the σ's analogous to the relations (7), namely

$$\sigma_{xy}=\sigma_{yx} \qquad \sigma_{yz}=\sigma_{zy} \qquad \sigma_{zx}=\sigma_{xz} \qquad 13.02.20$$

should always be true. They must in fact be true for reasons of geometrical symmetry except for crystals of low symmetry, namely those in which the only element of symmetry is an axis of rotation. It was however suggested by Clerk Maxwell* that (20) is always true. Even earlier Stokes† had surmised the truth of relations analogous to (20) for thermal conductivity.

There are moreover reasons based on the kinetic principle of detailed balancing‡, which we shall not here go into, for assuming such relations and they are in good agreement with experiment. The equations (20) constitute one of the simplest examples of *Onsager's reciprocal relations.*

§13.03 *Onsager's reciprocal relations*

We are now ready for a more general statement of Onsager's reciprocal relations. We denote by J_i the flux in a certain direction of something such as electric charge, as in the previous section, or a particular molecular or ionic species, or a quantity of energy. We denote by X_i the *driving force* corresponding to J_i. We make our meaning more precise by the statement that the rate of internal production of entropy per unit volume is given by

$$V^{-1}T\mathrm{d_i}S/\mathrm{d}t=\sum_i J_iX_i. \qquad 13.03.1$$

For example when J_i is electric current density, then X_i is the electric field. When J_i is the flux of a molecular species i, then X_i is minus the gradient of its chemical potential. When J_i is the flux of an ionic species i, then X_i

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* Maxwell, Electricity and Magnetism, Oxford University, 1st ed. 1873; 3rd ed. 1892 ch. 8.

† Stokes, Cambridge and Dublin Math. J. 1851 **6** 235.

‡ Onsager, Phys. Rev. 1931 **37** 405; De Groot, Thermodynamics of Irreversible Processes, North-Holland 1951.

is minus the gradient of its electrochemical potential. When J_i is the flux of energy then X_i must be closely related to the temperature gradient.

Provided the gradients X_i are not too great the fluxes J_i will generally be linear functions of the driving forces. This may be expressed as

$$J_i = \sum_k L_{ik} X_k \qquad (L_{ik} \text{ const.}). \qquad 13.03.2$$

In the simple case of only two kinds of flow (2) reduces to

$$J_1 = L_{11} X_1 + L_{12} X_2 \qquad 13.03.3$$

$$J_2 = L_{21} X_1 + L_{22} X_2 . \qquad 13.03.4$$

We now state Onsager's reciprocal relations in the general form

$$L_{ik} = L_{ki} \qquad (\text{all } i, k). \qquad 13.03.5$$

In the simple case of only two kinds of flow (5) reduces to

$$L_{12} = L_{21} . \qquad 13.03.6$$

§13.04 *Electrokinetic effects*

Electrokinetic phenomena occur when a liquid which is a poor electric conductor flows through a tube. Generally the tube walls and the liquid have opposite electric charges together constituting an electric double layer. There is a consequent interplay between the flow of matter and the flow of electric charge.

We consider a tube of length l and uniform cross-section A. We denote the electric current density by $\boldsymbol{J}$ and the electric field, which is equal and opposite to the electric potential gradient, by $\boldsymbol{E}$. We measure the rate of flow of liquid by the volume per unit time and we denote this by fA. We denote the pressure gradient by P_l. It can be verified that the rate of internal production of entropy per unit volume is given by

$$V^{-1} T \mathrm{d}_\mathrm{i} S/\mathrm{d}t = \boldsymbol{J}\boldsymbol{E} + f P_l . \qquad 13.04.1$$

From the form of (1) we see that we may regard $\boldsymbol{E}$ and P_l as the driving forces corresponding to the fluxes $\boldsymbol{J}$ and f respectively. We assume the linear relations

$$\boldsymbol{J} = L_{11} \boldsymbol{E} + L_{12} P_l \qquad 13.04.2$$

$$f = L_{21} \boldsymbol{E} + L_{22} P_l . \qquad 13.04.3$$

We then have Onsager's reciprocal relation

$$L_{12} = L_{21} . \qquad 13.04.4$$

Let us now consider briefly the physical significance of the L's. In the absence of a pressure gradient (2) reduces to

$$J = L_{11} E \qquad (P_l = 0) \tag{13.04.5}$$

from which we see that L_{11} is just the *electric conductivity*. In the absence of an electric field (3) reduces to

$$f = L_{22} P_l \tag{13.04.6}$$

from which we have according to Poiseuille's law

$$L_{22} = r^2/8\eta \tag{13.04.7}$$

where η is the viscosity and r the radius of the tube (or the effective radius if the cross-section is not circular).

The essential consequence of Onsager's relation is this. All the electrokinetic effects require for their quantitative description a knowledge of the electric conductivity, the viscosity, and *one other coefficient*, not two. We shall now formulate briefly the relations for some of the most important electrokinetic effects.*

In the first place we have the *streaming potential*, defined as the electric potential difference per unit pressure difference in a stationary state with zero electric current. According to (2) it is given by

$$E/P_l = -L_{12}/L_{11} \qquad (J = 0). \tag{13.04.8}$$

In the second place we have *electro-osmosis*, which is the flow of liquid per unit electric current in a state with zero pressure gradient. According to (2) and (3) it is given by

$$f/J = L_{21}/L_{11} \qquad (P_l = 0). \tag{13.04.9}$$

The third effect is the *electro-osmotic pressure*, which is the pressure difference per unit potential difference in the stationary state with zero material flow. According to (3) it is given by

$$P_l/E = -L_{21}/L_{22} \qquad (f = 0). \tag{13.04.10}$$

The fourth effect is the *streaming current*, which is the electric current per unit material flow for the steady state of zero electric field. According to (2) and (3) it is given by

$$J/f = L_{12}/L_{22} \qquad (E = 0). \tag{13.04.11}$$

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* De Groot, Thermodynamics of Irreversible Processes, North-Holland 1951 p. 187.

As a consequence of Onsager's reciprocal relation (4) we deduce from (8) and (9)

$$(E/P_l)_{J=0} = -(f/J)_{P_l=0} \qquad 13.04.12$$

and from (10) and (11)

$$(P_l/E)_{f=0} = -(J/f)_{E=0}. \qquad 13.04.13$$

Formula (13), known as Saxén's relation, has been verified experimentally with an accuracy of about 2 per cent*. Formula (12) has also been confirmed experimentally but only with an accuracy of about 15 per cent.*

§13.05 *Electric double layer*

We have seen in the previous section how the several electrokinetic effects can be expressed quantitatively in terms of the conductivity, the viscosity, and one further parameter denoted by $L_{12}=L_{21}$. It was not necessary to consider the physical significance of L_{12}. We shall now show that this quantity is closely related to the strength of the electric double layer at the boundary between the wall of the tube and the liquid in the tube. It does not matter which of the electrokinetic effects we consider in order to establish the required relation. We choose to consider electro-osmosis.

We consider a thin strip of liquid near to and parallel to the wall. We denote by du the difference of velocity along the tube between the inner and outer surface of this strip. We denote by dτ the strength of the electric double layer in this strip, that is to say the electric moment per unit area of the strip. We consider a steady state of motion under an applied electric field E. We now equate the two opposing couples due to the viscous effect of the velocity gradient on the one hand and the effect of the electric field on the dipoles on the other. We thus obtain the condition

$$\eta \, \mathrm{d}u = E \, \mathrm{d}\tau. \qquad 13.05.1$$

Integrating from the wall, where the liquid is stationary, to the interior we obtain for the velocity u in the interior of the liquid

$$\eta u = E\tau \qquad 13.05.2$$

where τ is the strength of the whole double layer, that is to say the total electric moment per unit area of the wall.

The flow fA expressed as volume of liquid per unit time is related to u by

$$fA = uA' \qquad 13.05.3$$

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* Miller, Chem. Rev. 1960 **60** 20.

where A' is an area less than the total internal cross-section A of the tube but greater than the cross-section of liquid having a velocity inappreciably different from u. In practice the thickness of the double layer is small compared with the width of the tube and consequently the difference between the cross-sections A and A' is negligible. We may then regard A' as the internal cross-section of the tube and substituting (2) into (3) we have

$$f = \tau E/\eta \qquad 13.05.4$$

while from (13.04.3) we have

$$f = L_{21} E \qquad (P_l = 0). \qquad 13.05.5$$

Comparing (4) with (5) we deduce

$$L_{21} = \tau/\eta. \qquad 13.05.6$$

Formula (6) expresses a relation essentially due to Helmholtz* although he did not use the same notation. Most authors instead of using Helmholtz's strength of the double layer here denoted by τ prefer to consider another quantity introduced by Perrin† and subsequently denoted by ζ by Freundlich.‡ This quantity has the dimensions of an electric potential and is called the ζ-potential. It is derived from τ by division by the rational permittivity. The introduction of this subsidiary quantity adds nothing except unnecessary complications.§

§13.06 *Electrochemical cells with transference*

We shall now use Onsager's reciprocal relations to obtain a stricter derivation of formula (8.18.16) for the electromotive force of the cell with transference described by (8.18.2). We shall not repeat the whole of the textual argument, but shall merely revise the formulae. The first change is that we replace (8.18.3) by the less restrictive assumption

$$J_i = -\sum_k L_{ik} \, \mathrm{d}\mu_k/\mathrm{d}y. \qquad 13.06.1$$

The condition for zero electric current then becomes instead of (8.18.9)

$$\sum_i \sum_k z_i L_{ik} \, \mathrm{d}\mu_k/\mathrm{d}y = 0. \qquad 13.06.2$$

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* Helmholtz, Ann. Phys. Lpz. 1879 **7** 337.

† Perrin, J. Chim. Phys. 1904 **2** 601.

‡ Freundlich, Colloid and Capillary Chemistry, Methuen 1926 p. 242.

§ Guggenheim, Trans. Faraday Soc. 1940 **36** 139, 722.

We still have for the electromotive force formula (8.18.7)

$$F\,\mathrm{d}E/\mathrm{d}y = z_{\mathrm{Cl}^-}^{-1}\,\mathrm{d}\mu_{\mathrm{Cl}^-}/\mathrm{d}y. \tag{13.06.3}$$

Combining (2) with (3) we have

$$\begin{aligned}\sum_i\sum_k z_i z_k L_{ik}(-z_k^{-1}\,\mathrm{d}\mu_k/\mathrm{d}y + z_{\mathrm{Cl}^-}^{-1}\,\mathrm{d}\mu_{\mathrm{Cl}^-}/\mathrm{d}y)&\\ = \sum_i\sum_k z_i z_k L_{ik} z_{\mathrm{Cl}^-}^{-1}\,\mathrm{d}\mu_{\mathrm{Cl}^-}/\mathrm{d}y&\\ = \sum_i\sum_k z_i z_k L_{ik} F\,\mathrm{d}E/\mathrm{d}y.&\end{aligned} \tag{13.06.4}$$

Consequently, instead of (8.18.11) we have

$$F\,\mathrm{d}E/\mathrm{d}y = \sum_k \{(-z_k^{-1}\,\mathrm{d}\mu_k/\mathrm{d}y + z_{\mathrm{Cl}^-}^{-1}\,\mathrm{d}\mu_{\mathrm{Cl}^-}/\mathrm{d}y)(z_k\sum_i z_i\,L_{ik}/\sum_l\sum_m z_l z_m L_{lm})\}. \tag{13.06.5}$$

We now, as in §8.18, turn to the different condition where the two electrode solutions are identical and an external potential difference $\mathrm{d}E^{\mathrm{e}}$ is applied across the electrodes. We have by (8.18.12)

$$z_k^{-1}\,\mathrm{d}\mu_k = F\,\mathrm{d}E^{\mathrm{e}} \qquad (\text{all } k) \tag{13.06.6}$$

so that by (1)

$$J_i = -\sum_k z_k L_{ik} F\,\mathrm{d}E^{\mathrm{e}}/\mathrm{d}y. \tag{13.06.7}$$

The electric current per unit cross-section carried by the ionic species i will be

$$z_i F J_i = -z_i \sum_k z_k L_{ik} F^2\,\mathrm{d}E^{\mathrm{e}}/\mathrm{d}y. \tag{13.06.8}$$

The transport number t_i, being the fraction of the total current carried by the ionic species i, is therefore

$$t_i = z_i \sum_k z_k L_{ik}/\sum_i\sum_k z_i z_k L_{ik}. \tag{13.06.9}$$

The transport number of the ionic species k is likewise

$$t_k = z_k \sum_i z_i L_{ki}/\sum_k\sum_i z_k z_i L_{ki} = z_k \sum_i z_i L_{ki}/\sum_l\sum_m z_l z_m L_{lm}. \tag{13.06.10}$$

Comparing (5) with (10) we have

$$F\,\mathrm{d}E/\mathrm{d}y = \sum_k t_k(-z_k^{-1}\,\mathrm{d}\mu_k/\mathrm{d}y + z_{\mathrm{Cl}^-}^{-1}\,\mathrm{d}\mu_{\mathrm{Cl}^-}/\mathrm{d}y)\sum_i z_i L_{ik}/\sum_i z_i L_{ki}. \tag{13.06.11}$$

Finally by use of Onsager's relation

$$L_{ik}=L_{ki} \tag{13.06.12}$$

(11) reduces to

$$F\,\mathrm{d}E/\mathrm{d}y=\sum_k t_k(-z_k^{-1}\,\mathrm{d}\mu_k/\mathrm{d}y+z_{\mathrm{Cl}^-}^{-1}\,\mathrm{d}\mu_{\mathrm{Cl}^-}/\mathrm{d}y) \tag{13.06.13}$$

which is the same as formula (8.18.16).

We note that in the derivation given in §8.18 instead of Onsager's relation (12) we used the more restrictive assumption

$$L_{ik}=0 \qquad (i\neq k). \tag{13.06.14}$$

The author believes that the assumption (14) is in fact true although this has not been proved.

§13.07 *Thermoelectricity*

We shall now discuss the most important and most interesting application of Onsager's relations to a non-isothermal system, namely a system in which electric current is coupled with energy flow. This phenomenon is called *thermoelectricity*. The following treatment is similar to that of Callen.*

We consider a straight uniform metallic wire in a non-uniform temperature through which an electric current can result from a flow of electrons. If the wire lies in the y-direction the rate of internal production of entropy per unit volume is given by

$$V^{-1}\,\mathrm{d_i}S/\mathrm{d}t=-J_{\mathrm{e}^-}\,\mathrm{d}(\mu/T)/\mathrm{d}y+J_U\,\mathrm{d}(T^{-1})/\mathrm{d}y \tag{13.07.1}$$

where μ is the electrochemical potential of the electrons, $-FJ_{\mathrm{e}^-}$ is the electric current density, and J_U is the energy flux.

From the form of (1) we may regard $\mathrm{d}(\mu/T)/\mathrm{d}y$ and $\mathrm{d}(T^{-1})/\mathrm{d}y$ as the driving forces corresponding to the fluxes $-J_{\mathrm{e}^-}$ and J_U respectively. We accordingly assume the linear relations

$$-J_{\mathrm{e}^-}=L'_{11}\,\mathrm{d}(\mu/T)/\mathrm{d}y+L'_{12}\,\mathrm{d}(T^{-1})/\mathrm{d}y \tag{13.07.2}$$

$$J_U=L'_{21}\,\mathrm{d}(\mu/T)/\mathrm{d}y+L'_{22}\,\mathrm{d}(T^{-1})/\mathrm{d}y. \tag{13.07.3}$$

We could use formulae (2) and (3) as the basis of our discussion and should of course obtain correct results, but by a simple transformation we obtain formulae in which the coefficients L have a more direct physical significance.

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* Callen, Thermodynamics, Wiley 1960 ch. 17.

We define J_q by

$$J_q = J_U - \mu J_{\mathrm{e}^-} \tag{13.07.4}$$

and substitute into (2) and (3) obtaining

$$-J_{\mathrm{e}^-} = L_{11} T^{-1} \mathrm{d}\mu/\mathrm{d}y + L_{12} \mathrm{d}(T^{-1})/\mathrm{d}y \tag{13.07.5}$$

$$J_q = L_{21} T^{-1} \mathrm{d}\mu/\mathrm{d}y + L_{22} \mathrm{d}(T^{-1})/\mathrm{d}y \tag{13.07.6}$$

where

$$L_{11} = L'_{11} \tag{13.07.7}$$

$$L_{12} = L'_{12} + L'_{11}\mu \tag{13.07.8}$$

$$L_{21} = L'_{21} + L'_{11}\mu \tag{13.07.9}$$

$$L_{22} = L'_{22} + (L'_{12} + L'_{21})\mu + L'_{11}\mu^2. \tag{13.07.10}$$

We can also verify that the determinant

$$D = L_{11}L_{22} - L_{12}L_{21} = L'_{11}L'_{22} - L'_{12}L'_{21}. \tag{13.07.11}$$

From (8) and (9) we see that Onsager's relation $L'_{21} = L'_{12}$ is equivalent to $L_{21} = L_{12}$.

We next determine the physical interpretation of L_{11} and L_{22}. If we consider the case of an isothermal flow of current we obtain for the *electric conductivity*

$$\sigma = -F^2 J_{\mathrm{e}^-}/(\mathrm{d}\mu/\mathrm{d}y) \qquad (\mathrm{d}T/\mathrm{d}y = 0) \tag{13.07.12}$$

so that by use of (5)

$$T\sigma/F^2 = L_{11}. \tag{13.07.13}$$

Similarly if we consider a flow of energy with zero electric current we obtain for the *thermal conductivity* κ

$$\kappa = -J_U/(\mathrm{d}T/\mathrm{d}y) = -J_q/(\mathrm{d}T/\mathrm{d}y) \qquad (J_{\mathrm{e}^-} = 0) \tag{13.07.14}$$

so that from (5) and (6)

$$T^2\kappa = D/L_{11}. \tag{13.07.15}$$

From (13) and (15) we derive

$$T^3\kappa\sigma/F^2 = D. \tag{13.07.16}$$

§13.08 *Seebeck effect and thermoelectric power*

When there is no electric current we have according to (13.07.5)

$$\mathrm{d}\mu/\mathrm{d}y = (L_{12}/L_{11}T)\mathrm{d}T/\mathrm{d}y \tag{13.08.1}$$

and integrating from one end of the wire denoted by the subscript 1 to the other end denoted by the subscript 2 we have

$$\mu_2-\mu_1=\int_{T_1}^{T_2}(L_{12}/L_{11}\,T)\mathrm{d}T \qquad 13.08.2$$

or

$$\mu_2-\mu_1=-F\int_{T_1}^{T_2}\varepsilon\,\mathrm{d}T \qquad 13.08.3$$

where ε, called the *thermoelectric power*, is given by

$$FT\varepsilon=-L_{12}/L_{11}\,. \qquad 13.08.4$$

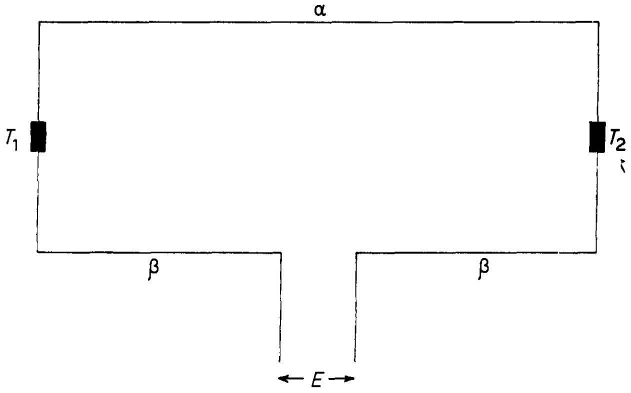

Fig. 13.1. Thermocouple

We now consider the thermocouple, shown in figure 13.1, consisting of a pair of wires of different metals α and β with their two junctions 1 and 2 at temperatures T_1 and T_2. Since μ is continuous at both metal–metal junctions, it follows that the difference between the values μ_l and μ_r of μ at the left and right terminals is given by

$$\mu_r-\mu_l=F\int_{T_1}^{T_2}(\varepsilon^{\beta}-\varepsilon^{\alpha})\mathrm{d}T. \qquad 13.08.5$$

But since the two terminals are at the same temperature T' the electric potential difference between the two terminals or the electromotive force E of the thermocouple is given by

$$E=-(\mu_r-\mu_l)/F=\int_{T_1}^{T_2}(\varepsilon^{\alpha}-\varepsilon^{\beta})\mathrm{d}T. \qquad 13.08.6$$

The occurrence of this electromotive force in a thermocouple is called the *Seebeck effect*.

From (4) and (13.07.13) we deduce

$$-T^2\sigma\varepsilon/F = L_{12}. \qquad 13.08.7$$

§13.09 *Peltier effect*

Consider an isothermal junction of two metals α and β through which flows an electric current of density $-FJ_{e^-}$. Then the flux of energy is discontinuous across the junction and the difference in energy flux appears as heat at the junction. Since both μ and J_{e^-} are continuous across the junction it follows from (13.07.4) that

$$J_U^\alpha - J_U^\beta = J_q^\alpha - J_q^\beta \qquad (T^\alpha = T^\beta) \qquad 13.09.1$$

and from (13.07.5) and (13.07.6) that

$$(J_U/J_{e^-})^\beta - (J_U/J_{e^-})^\alpha = (J_q/J_{e^-})^\beta - (J_q/J_{e^-})^\alpha = (L_{21}/L_{11})^\alpha - (L_{21}/L_{11})^\beta. \qquad 13.09.2$$

The *Peltier coefficient* $\pi^{\alpha\beta}$, defined as the heat that must be supplied per unit time to the junction to keep its temperature constant when unit electric current passes from α to β, is given by

$$F\pi^{\alpha\beta} = (L_{21}/L_{11})^\alpha - (L_{21}/L_{11})^\beta. \qquad 13.09.3$$

§13.10 *Kelvin's second relation*

We recall that the *thermoelectric power* ε of a metal is given by (13.08.4)

$$FT\varepsilon = -L_{12}/L_{11} \qquad 13.10.1$$

so that for a pair of metals

$$FT(\varepsilon^\beta - \varepsilon^\alpha) = (L_{12}/L_{11})^\alpha - (L_{12}/L_{11})^\beta. \qquad 13.10.2$$

The *Peltier coefficient* $\pi^{\alpha\beta}$ is given by (13.09.3)

$$F\pi^{\alpha\beta} = (L_{21}/L_{11})^\alpha - (L_{21}/L_{11})^\beta. \qquad 13.10.3$$

When we introduce *Onsager's relation*

$$L_{21} = L_{12} \qquad 13.10.4$$

into (2) and (3) we obtain

$$\pi^{\alpha\beta} = T(\varepsilon^\beta - \varepsilon^\alpha) \qquad 13.10.5$$

which is called *Kelvin's second relation*. This has been verified within an accuracy of one per cent or better for about twenty pairs of metals.*

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* Miller, Chem. Rev. 1960 **60** 19.

§13.11 *Thomson effect*

Hitherto we have considered a thermocouple on open circuit only. We now consider a thermocouple balanced by a different cell with an electromotive force opposite to and differing infinitesimally from that of the thermocouple. We then have a flow of current which is reversible apart from the Joule effect which may be neglected because it is proportional to the square of the current and is consequently a second-order small quantity. When the electric current flows in a temperature gradient there is a flow of heat between the wire and its surroundings of the form $\tau \mathrm{d}T$ called the *Thomson heat* superposed on the negligible Joule heat.

We now apply the first law of thermodynamics to this thermocouple when the two metal–metal junctions are at temperatures T and $T+\mathrm{d}T$. The heat q absorbed is

$$q = -\pi^{\alpha\beta}(T) + \tau^{\alpha}\mathrm{d}T + \pi^{\alpha\beta}(T+\mathrm{d}T) - \tau^{\beta}\mathrm{d}T \qquad 13.11.1$$

and the work done on the thermocouple is

$$w = (\varepsilon^{\beta} - \varepsilon^{\alpha})\mathrm{d}T. \qquad 13.11.2$$

By the first law of thermodynamics we have for a steady state

$$q + w = 0. \qquad 13.11.3$$

Combining (1), (2), and (3) we obtain

$$\mathrm{d}\pi^{\alpha\beta}/\mathrm{d}T + \tau^{\alpha} - \tau^{\beta} - \varepsilon^{\alpha} + \varepsilon^{\beta} = 0. \qquad 13.11.4$$

We emphasize that this relation is a consequence of the *first law* only. When we combine (4) with (13.10.5) we obtain

$$T\mathrm{d}(\varepsilon^{\beta} - \varepsilon^{\alpha})/\mathrm{d}T = \tau^{\beta} - \tau^{\alpha}. \qquad 13.11.5$$

Formula (5) is called *Kelvin's first relation.* The author is not aware of its having been verified experimentally.

§13.12 *Interdiffusion of two fluids*

We shall now consider briefly the interdiffusion along the y-axis, at constant temperature and constant pressure, of two fluids denoted by the subscripts $_1$ and $_2$ respectively. We denote the mass fractions of the two components by $\tilde{x}_1$ and $\tilde{x}_2$ so that

$$\tilde{x}_1 + \tilde{x}_2 = 1. \qquad 13.12.1$$

We denote the specific fluxes or fluxes per unit mass by $\tilde{J}_1$ and $\tilde{J}_2$. We denote the specific chemical potentials or chemical potentials divided by the proper masses by $\tilde{\mu}_1$ and $\tilde{\mu}_2$. We take as origin for the coordinate y the centre of mass of the fluid. This implies that

$$\tilde{J}_1+\tilde{J}_2=0. \qquad 13.12.2$$

The Gibbs–Duhem relation may be written as

$$\tilde{x}_1\,\mathrm{d}\tilde{\mu}_1+\tilde{x}_2\,\mathrm{d}\tilde{\mu}_2=0. \qquad 13.12.3$$

From (2) and (3) it follows that

$$-\tilde{x}_2\tilde{J}_1/(\mathrm{d}\mu_1/\mathrm{d}y)=-\tilde{x}_1\tilde{J}_2/(\mathrm{d}\tilde{\mu}_2/\mathrm{d}y) \qquad 13.12.4$$

and we call this quantity L. We then have, using (1),

$$\tilde{J}_1=-\tilde{J}_2=L(\mathrm{d}\tilde{\mu}_2/\mathrm{d}y-\mathrm{d}\tilde{\mu}_1/\mathrm{d}y)=-(L/\tilde{x}_2)\mathrm{d}\tilde{\mu}_1/\mathrm{d}y=(L/\tilde{x}_1)\mathrm{d}\tilde{\mu}_2/\mathrm{d}y. \qquad 13.12.5$$

From (5) we see that $\tilde{J}_1$, $\tilde{J}_2$ are related to $\mathrm{d}\tilde{\mu}_1/\mathrm{d}y$, $\mathrm{d}\tilde{\mu}_2/\mathrm{d}y$ by the single coefficient L. Consequently in this system there is no reciprocal relation.

§13.13 *Interdiffusion of two solutes in dilute solution*

Having seen that the interdiffusion of two fluids is describable by a single coefficient L, we now turn to a system of three fluids and shall derive the reciprocal relations. We use the same notation as in §13.12 with the subscripts $_1$, $_2$, and $_3$ relating to the three components. Taking as origin the centre of mass of the fluid we have by analogy with (13.12.1), (13.12.2), and (13.12.3)

$$\tilde{x}_1+\tilde{x}_2+\tilde{x}_3=1 \qquad 13.13.1$$

$$\tilde{J}_1+\tilde{J}_2+\tilde{J}_3=0 \qquad 13.13.2$$

$$\tilde{x}_1\,\mathrm{d}\tilde{\mu}_1+\tilde{x}_2\,\mathrm{d}\tilde{\mu}_2+\tilde{x}_3\,\mathrm{d}\tilde{\mu}_3=0. \qquad 13.13.3$$

The rate of entropy production σ per unit volume is given by

$$T\sigma=-\tilde{J}_1\,\mathrm{d}\tilde{\mu}_1/\mathrm{d}y-\tilde{J}_2\,\mathrm{d}\tilde{\mu}_2/\mathrm{d}y-\tilde{J}_3\,\mathrm{d}\tilde{\mu}_3/\mathrm{d}y. \qquad 13.13.4$$

Substituting from (1), (2), and (3) into (4) we obtain

$$\begin{aligned}-T\sigma&=(\tilde{J}_2+\tilde{J}_3)\{(\tilde{x}_2/\tilde{x}_1)\mathrm{d}\tilde{\mu}_2/\mathrm{d}y+(\tilde{x}_3/\tilde{x}_1)\mathrm{d}\tilde{\mu}_3/\mathrm{d}y\}+\tilde{J}_2\,\mathrm{d}\tilde{\mu}_2/\mathrm{d}y+\tilde{J}_3\,\mathrm{d}\tilde{\mu}_3/\mathrm{d}y\\&=\tilde{J}_2\{(1+\tilde{x}_2/\tilde{x}_1)\mathrm{d}\tilde{\mu}_2/\mathrm{d}y+(\tilde{x}_3/\tilde{x}_1)\mathrm{d}\tilde{\mu}_3/\mathrm{d}y\}\\&\quad+\tilde{J}_3\{(\tilde{x}_2/\tilde{x}_1)\mathrm{d}\tilde{\mu}_2/\mathrm{d}y+(1+\tilde{x}_3/\tilde{x}_1)\mathrm{d}\tilde{\mu}_3/\mathrm{d}y\}.\end{aligned} \qquad 13.13.5$$

If we take as origin for the coordinate y the centre of mass of the component 1, which we now call the solvent, instead of the centre of mass of the mixture, we have instead of (2)

$$\tilde{J}_1 = 0 \qquad 13.13.6$$

and instead of (4) we have

$$T\sigma = -\tilde{J}_2 \, \mathrm{d}\tilde{\mu}_2/\mathrm{d}y - \tilde{J}_3 \, \mathrm{d}\tilde{\mu}_3/\mathrm{d}y. \qquad 13.13.7$$

For the sake of brevity and simplicity we shall henceforth confine ourselves to the case of a dilute solution of 2 and 3 in the solvent 1. We then have

$$\tilde{x}_2 \ll \tilde{x}_1 \qquad \tilde{x}_3 \ll \tilde{x}_1 \qquad 13.13.8$$

and we may accordingly replace (5) by the approximation

$$T\sigma = -\tilde{J}_2 \, \mathrm{d}\tilde{\mu}_2/\mathrm{d}y - \tilde{J}_3 \, \mathrm{d}\tilde{\mu}_3/\mathrm{d}y \qquad 13.13.9$$

which is identical with (7). Moreover if we had chosen a slightly different origin for y formula (9) would be unaffected.

We now introduce the linear relations

$$\tilde{J}_2 = -L_{22} \, \mathrm{d}\tilde{\mu}_2/\mathrm{d}y - L_{23} \, \mathrm{d}\tilde{\mu}_3/\mathrm{d}y \qquad 13.13.10$$

$$\tilde{J}_3 = -L_{32} \, \mathrm{d}\tilde{\mu}_2/\mathrm{d}y - L_{33} \, \mathrm{d}\tilde{\mu}_3/\mathrm{d}y \qquad 13.13.11$$

or the equivalent relations

$$J_2 = -L_{22} \, \mathrm{d}\mu_2/\mathrm{d}y - L_{23} \, \mathrm{d}\mu_3/\mathrm{d}y \qquad 13.13.12$$

$$J_3 = -L_{32} \, \mathrm{d}\mu_2/\mathrm{d}y - L_{33} \, \mathrm{d}\mu_3/\mathrm{d}y \qquad 13.13.13$$

where J_2 and J_3 denote the fluxes per unit amount of 2 and 3 respectively. Onsager's reciprocal relation is

$$L_{23} = L_{32}. \qquad 13.13.14$$

Whereas the equation (14) relates to a solution of given composition, with values of L_{23} or L_{32} dependent on the composition, the available experimental measurements give only values of diffusion coefficients averaged over a wide range of composition. Consequently the attempt* to verify (14) is unconvincing. The most that can be said is that there is no experimental evidence at variance with (14).

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* Miller, Chem. Rev. 1960 **60** 19.