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Heat, Mass and Charge Transport, and Chemical Reactions at Surfaces

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Abstract

In this work we derive the excess entropy production rate for heat, mass and charge transport into, out of and across a surface, using as basic variables the excess densities proposed by Gibbs. With the help of these variables we define the surface as an autonomous system (i.e. a surface in local equilibrium) and find its excess entropy production rate. This then determines the conjugate fluxes and forces. Equivalent forms of the entropy production rate are given. The forms contain finite differences of intensive variables into and across the surface as driving forces. The general form of the force-flux relations is given. The expressions for the fluxes serve as boundary conditions for integration across heterogeneous systems. Two examples are discussed in more detail. The first example is the practically important coupled transport of heat and mass into and through a liquid-vapor surface. The second example concerns phenomena at electrode surfaces: the coupled transport of heat, mass and charge and a chemical reaction. By assuming that the two sides of the surface can be described as resistances in series, we are able to reduce the number of unknown transport coefficients considerably. For both examples it is shown that the coupling coefficients for heat and mass flow are large at the surface, when the homogeneous phases have a large enthalpy difference. As a consequence it is not sufficient to use, for instance, Fourier's law for transport of heat across surfaces.

Keywords: Non-equilibrium thermodynamics, local equilibrium, transport through surfaces, phase transitions, electrochemical reactions.

1. Introduction

The second law of thermodynamics says that the entropy change of the system plus its surroundings is positive for irreversible processes and zero for reversible processes. The law gives the direction of a process; it does not give its rate. In this work we shall use nonequilibrium thermodynamics to derive rate equations for surface area elements. Nonequilibrium thermodynamics assumes that the second law remains valid locally, also for such surface area elements. The entropy production is then obtained as an excess quantity, using Gibbs excess densities as a basis.

A general expression for the excess entropy production rate of a surface was already given some time ago (Bedeaux et al., 1976; Bedeaux, 1986; Albano and Bedeaux, 1987). That analysis was not only for curved surfaces, but also for surfaces that were allowed to move in space and change their curvature. The analysis was done using time dependent orthogonal coordinate systems. For a majority of systems this leads to unnecessary complications, however, so we find that a more dedicated presentation may be useful. We have thus chosen to present equations of transport of heat, mass and charge for transport into and across surfaces where reactions take place, in much more detail than before, and for some important specific cases. The general framework mentioned above (Bedeaux et al., 1976; Bedeaux, 1986; Albano and Bedeaux, 1987) will be followed, however. It adds to similar results for continuous (de Groot and Mazur, 1984) and discontinuous systems (Katchalsky and Curran, 1975). A surface does not exist without its bounding phases, and the transport processes in question therefore address a heterogeneous system: the system made up by two homogeneous (bulk) phases and the surface (or interface) between these. The aim of the present work is to contribute to the understanding and modeling of such heterogeneous systems with transport of heat, mass and charge with the possibility of chemical reactions at surfaces. We shall conclude that it is not enough to invoke the first law in the modeling of such systems, as is common in the literature according to a recent review of fuel cell modeling (Weber and Newman, 2004). Also the second law need be used to obtain a thermodynamically consistent model of non-isothermal systems.

Heterogeneous systems with transport of heat, mass and charge are important in industry as well as in nature. Evaporation or condensation is one such central example of heat and mass transport. The phase transformations of water in nature, and of organic liquids in the distillation industry are thus widely studied (Pao, 1971; Pao, 1971, Cippola Jr. et al., 1974; Cippola Jr. et al., 1974, Bedeaux et al., 1990; Bedeaux et al., 1992; Fang and Ward, 1999a; Fang and Ward, 1999b; Røsjorde et al., 2001; Kjelstrup and deKoeijer, 2003). All electrochemical cells have such transport processes at their electrodes. Here chemical reactions take place at the electrode surfaces during conversion of electric into chemical energy or vice versa. We shall give general transport equations for both example systems, consistent with the second law of thermodynamics.

We lay the foundation in Section 2 by presenting Gibbs' definition (Gibbs, 1961) of excess mass densities for the surface. Concepts like the equimolar surface are introduced. The excess internal energy, enthalpy, entropy as well as the surface tension are defined in the same way. Gibbs gave an extensive discussion of these definitions for equilibrium systems. In Section 3 we give the thermodynamic identities between the excess densities for the equilibrium surface. We introduce the hypothesis of local equilibrium for the surface in a nonequilibrium system in Section 4. For a surface element, we say that there is local equilibrium when the thermodynamic identities discussed in Section 3 are valid.

The hypothesis of local equilibrium implies that the nonequilibrium surface is treated as an autonomous thermodynamic system. We follow Bakker (1928) and Guggenheim (1985) in this respect. Whether the nonequilibrium surface is autonomous has been questioned by, for instance, Defay et al. (1966). There is, however, convincing evidence from nonequilibrium molecular dynamics simulations (Røsjorde et al., 2000; Simon et al., 2004) and from the nonequilibrium van der Waals square gradient model (Johannessen and Bedeaux, 2003), that this assumption is appropriate for many systems. It follows, using this as a premise, that in Section 5 we can explain how to obtain the excess entropy production rate for the surface. The first step is done in Section 6, where we give the energy and mass balance equations for the surface. In Section 7 we then find the excess entropy production rate for the surface, using the entropy balance equation given in Section 5, the energy and mass balance equations given in Section 6 and the Gibbs equation for the surface. This makes it then possible to give the general linear force-flux relations in Section 8. Some practical reduced forms of these equations are discussed first for coupled transport of heat and mass, and then for coupled transport of heat, mass and charge combined with a chemical reaction at the surface. The equations predict jumps at the surface in the temperature, and the chemical and electric potentials, depending on the magnitude of the fluxes, and imply that simple transport equations, like Fourier's law, are not enough to correctly describe transport at the surface.

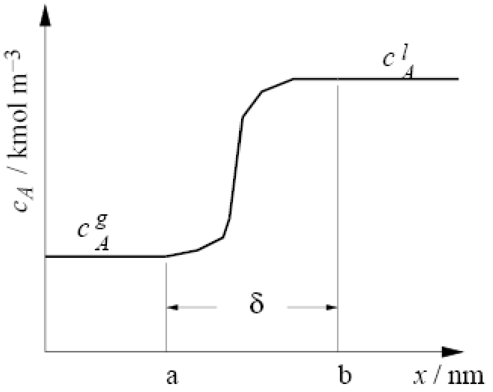

Figure 1. Variation in the molar density of a fluid going from the gas to the liquid state. The vertical line indicates the extension of the surface. The scale of the x-axis is measured in nanometer

2. Thermodynamic Excess Densities of a Surface

A surface is the thin layer between two homogeneous phases. We shall use the two words surface and interface interchangeably. We examine flat surfaces and choose the x-axis perpendicular to the surface. The thermodynamic properties of the interface are given by the values of the excess densities of the interface. The value of these densities and the location of the interface will be defined through the example of a gas-liquid interface. We shall correspondingly indicate these phases with the superscripts g or l.

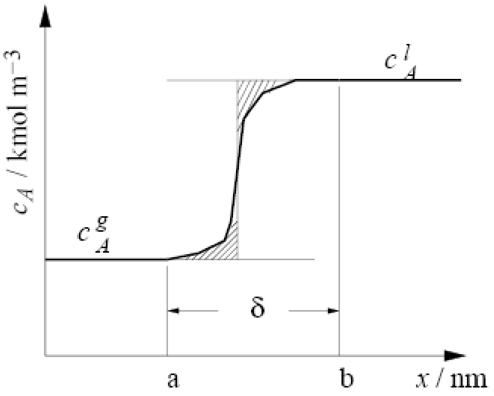

Figure 2. Determination of the position of the equimolar surface of component A. The vertical line is drawn so that the areas between the curve and the bulk densities are the same

Figure 1 shows the variation in concentration of A, in a mixture of several components, as we go from the gas to the liquid phase. The surface thickness is somewhere between a fraction of a nm and a μm. The x-axis of *Figure 1* has coordinates in nm, it has a molecular scale. A continuous variation in the concentration is seen. Gibbs (1961) defined the closed surface as a transition region with a finite thickness bounded by planes of similarly chosen points. In *Figure 1* such planes are indicated by vertical lines. The position a is the point in the gas, left of the closed surface where $c_A(x)$ starts to differ from the concentration of the gas, $c_A{}^g$, and the position b is the point in the liquid right of the closed surface, where $c_A(x)$ starts to differ from the concentration of the liquid, $c_A{}^1$. The surface thickness is then δ=b-a. It refers to component A. Other components may yield somewhat different planes.

Gibbs defined the dividing surface as ”a geometrical plane, going through points in the interfacial region, similarly situated with respect to conditions of adjacent matter”. Many different planes of this type can be chosen. While the position of the dividing surface depends on this choice, it is normally somewhere between the vertical lines in *Figure 1*. The planes that separate the closed surface from the homogeneous phases are parallel to the dividing surface. The continuous density, integrated over δ, gives the excess surface concentration of component A as a function of the position (y, z), along the surface:

$$\Gamma_A(y,z) = \int_a^b \Big[c_A(x,y,z) - c_A^g(a,y,z)\Theta(d-x) - c_A^1(b,y,z)\Theta(x-d) \Big] dx \qquad (1)$$

where d is the position of the dividing surface.

The surface concentration is often called the adsorption (in mol/m^2). The Heaviside function, Θ, is by definition unity when the argument is positive and zero when the argument is negative. Normally a < d < b. The adsorptions of other components are defined in the same way. Other excess variables, like the excess internal energy, the excess enthalpy, the surface tension and the excess entropy, are also defined in the same way.

All excess properties of a surface can be given by integrals like equation (1). The excess variables are the extensive variables of the surface. They describe how the surface differs from adjacent homogeneous phases. It is clear from *Figure 1* that one may shift the position a to the left and b to the right without changing the adsorption. This shows why the precise location of a and b is not important for the value of the adsorption. Given d, the adsorption has a precise definition, however.

The equimolar surface of component A is a special choice of the dividing surface. The location is such that the surplus of moles of the component on one side of the surface is equal to the deficiency of moles of the component on the other side of the surface. The vertical line is drawn so that the areas between the curve and the bulk densities are the same, see *Figure 2*. The position d of the equimolar surface obeys therefore:

$$\int_a^d \Big[c_A(x,y,z) - c_A^g(a,y,z) \Big] dx = -\int_d^b \Big[c_A(x,y,z) - c_A^1(b,z,y) \Big] dx \qquad (2)$$

According to equations (1) and (2), $\Gamma_A=0$, when the surface has this position. The shaded areas in the figure are equal. In multi-component systems, each component has its ”equimolar” surface, but we have to make one choice for the surface position. We choose the position of the surface as the equimolar surface of the reference component. This component has then no excess concentration, while another component B, like the one sketched in *Figure 3*, has an excess concentration. Thermodynamic properties of homogeneous systems are usually plotted on scales with greater dimension than nm. In *Figure 4*, $c_A(x)$ is plotted on a μm scale. The fine details of *Figure 1* disappear, and the surface appears as a discontinuity. When plotted on a macroscopic scale, a non-zero excess surface density, like component B, will appear as a singularity at the position of the dividing surface. On this scale the different possible choices of the dividing surface are no longer visible, and the surface can be regarded as a two-dimensional thermodynamic system with properties that are integrated out in the x-direction and are given per surface area. The dependence on the coordinates y and z remains.

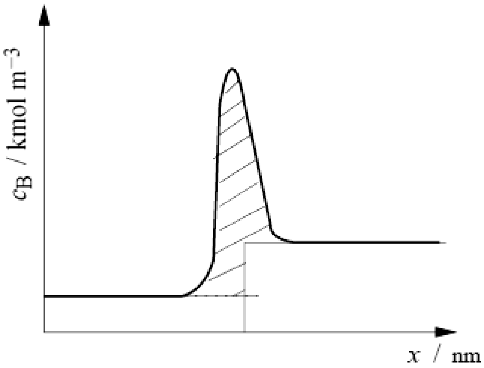

Figure 3. Variation of the density of component B across the surface. The excess surface concentration of component B is the integral under the curve in the figure

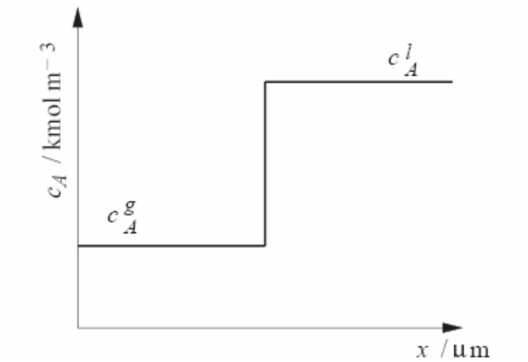

Figure 4. The equimolar surface, plotted on a micrometer scale, appears as a jump between bulk densities

For the usual interface, as for instance between a liquid and a vapor, the thickness is not more than a nanometer. In the application of the above methods using excess densities and fluxes there is no reason to restrict oneself to surfaces that are so thin, however. If one considers a polymer fuel cell and uses a carbon electrode with platinum catalyst, one has a three phase surface region of about a micron thick. This whole region can also be described using excess quantities such as the excess platinum density and others. On an even larger scale one may in fact describe the whole atmosphere of the earth, which is about 20 km thick, using excess densities of the constituents of air and describe the flow of air in terms of excess fluxes. This leads to a two-dimensional picture of the weather, very much like it is presented during the weather forecast.

3. Local Thermodynamic Identities for the Surface

When excess surface densities are defined in this manner, the normal thermodynamic relations, like the first and the second law and derived relations, apply for the variables (Gibbs, 1961). The Gibbs equation for the surface becomes:

$$dU^s = TdS^s + \gamma d\Omega + \sum_{j=1}^{n} \mu_j dN_j^s \tag{3}$$

where U is the internal energy, T is the temperature, S is the entropy, γ is the surface tension, Ω is the area, μ_j is the chemical potential of component j and N_j is the number of moles of this component. The number of independent components is n. A surface property is indicated by superscript s. By integration for constant surface tension, temperature and composition, we obtain:

$$U^s = TS^s + \gamma\Omega + \sum_{j=1}^{n} \mu_j N_j^s \tag{4}$$

The Gibbs-Duhem equation for the surface follows by differentiation of this equation and subtracting equation (3):

$$0 = S^s dT + \Omega d\gamma + \sum_{j=1}^{n} N_j^s d\mu_j \tag{5}$$

In order to use these equations in combination with the continuity equations, we need the local variables given per unit of surface area. These are the excess internal energy density $u^s = U^s/\Omega$, the adsorptions $\Gamma_j = N_j^s/\Omega$ and the excess entropy density, $s^s = S^s/\Omega$. When we introduce these variables into equation (3) and use equation (4), we obtain Gibbs equation for the surface in a density form:

$$du^s = Tds^s + \sum_{j=1}^{n} \mu_j d\Gamma_j \tag{6}$$

The surface excess internal energy density is:

$$u^s = Ts^s + \gamma + \sum_{j=1}^{n} \mu_j \Gamma_j \tag{7}$$

and the Gibbs-Duhem equation becomes

$$0 = s^s dT + d\gamma + \sum_{j=1}^{n} \Gamma_j d\mu_j \tag{8}$$

An overview of thermodynamic relations for the surface is given below for the surface internal energy, surface internal energy density, Gibbs equation, Gibbs-Duhem equation, surface Gibbs energy density and the surface Helmholtz energy density, respectively:

$$
\begin{aligned}
U^s &= TS^s + \gamma\Omega + \textstyle\sum_{j=1}^{n}\mu_j N_j^s \\
u^s &= Ts^s + \gamma + \textstyle\sum_{j=1}^{n}\mu_j\Gamma_j \\
du^s &= Tds^s + \textstyle\sum_{j=1}^{n}\mu_j d\Gamma_j \\
0 &= s^s dT + d\gamma + \textstyle\sum_{j=1}^{n}\Gamma_j d\mu_j \\
g^s &= u^s - Ts^s - \gamma = \textstyle\sum_{j=1}^{n}\mu_j\Gamma_j \\
f^s &= u^s - Ts^s = \gamma + \textstyle\sum_{j=1}^{n}\mu_j\Gamma_j
\end{aligned}
\qquad (9)
$$

All these relations are analogous to the ones valid in the homogeneous phases (Kjelstrup and Bedeaux, 2001).

4. The Hypothesis of Local Equilibrium for the Surface

We have so far considered systems that are in global equilibrium, i.e. the temperature and the chemical potentials are constant throughout the whole system. In global equilibrium the thermodynamic forces and fluxes are everywhere zero, so that both the total and the local entropy productions are zero. The central hypothesis in the systematic development of the theory of nonequilibrium thermodynamics for continuous systems is that the system is everywhere in local equilibrium. For a more detailed definition and discussion of this property we refer to the discussion in Section 8. For a surface element, we say that there is local equilibrium whenever the thermodynamic relations (6)-(8) are locally valid. The Gibbs' relation (6) becomes:

$$
\begin{aligned}
du^s(y,z,t) &= T^s(y,z,t)\ \ ds^s(y,z,t) \\
&\quad + \sum_{j=1}^{n}\mu_j^s(y,z,t)\,d\Gamma_j(y,z,t)
\end{aligned}
\qquad (10)
$$

The excess internal energy (7) is given by

$$
\begin{aligned}
u^s(y,z,t) &= T^s(y,z,t)s^s(y,z,t) + \gamma(y,z,t) \\
&\quad + \sum_{j=1}^{n}\mu_j^s(y,z,t)\Gamma_j(y,z,t)
\end{aligned}
\qquad (11)
$$

and the Gibbs-Duhem equation (8) by

$$
\begin{aligned}
0 &= s^s(y,z,t)\,dT^s(y,z,t) + d\gamma(y,z,t) \\
&\quad + \sum_{j=1}^{n}\Gamma_j(y,z,t)\,d\mu_j^s(y,z,t)
\end{aligned}
\qquad (12)
$$

The relations are valid at any time t and positions y, z. Similarly, local equilibrium implies that all the thermodynamic relations given in equation (9) are valid locally. The intensive thermodynamic variables for the surface are given by the derivatives:

$$
T^s = \left(\frac{du^s}{ds^s}\right)_{\Gamma_j} \quad \text{and} \quad \mu_j^s = \left(\frac{du^s}{d\Gamma_j}\right)_{s^s,\Gamma_k} \qquad (13)
$$

The temperature and chemical potentials, defined in this manner, depend only on the surface excess variables, not on the value of variables in the homogeneous phases close to the surface. By introducing these definitions we therefore allow for the possibility that the surface has a different temperature or chemical potential than the adjacent homogeneous systems. Nonequilibrium molecular dynamics simulations support the validity of the hypothesis of local equilibrium for surfaces (Røsjorde et al., 2000; Simon et al., 2004). The hypothesis of local equilibrium, as formulated above, does not imply that there is local *chemical* equilibrium (de Groot and Mazur, 1984). In that case the Gibbs energy of the reaction is also zero. The thermodynamic variables for the surface depend on the position along the surface and the time. As we shall not consider transport along the surface, we shall further restrict ourselves to cases where the variables are independent of y and z and the fluxes are in the x-direction.

We shall see that an essential and surprising aspect of the local equilibrium hypothesis for the surface and the adjacent homogeneous phases is that the temperature and chemical potentials on both sides of the surface may differ, not only from each other, but also from the values found for the surface. This is, however, similar to and compatible with the fact that an electric potential difference can be generated across a surface, and that the Nernst equation applies to the surface at electrochemical equilibrium.

5. The Entropy Balance for the Surface

The change of the excess entropy density in a surface is a result of the flow of entropy in and out of the surface element and of the excess entropy production rate, $\sigma^s(t)$, inside:

$$
\frac{d}{dt}s_s(t) = J_s^{i,o}(t) - J_s^{o,i}(t) + \sigma^s(t) \qquad (14)
$$

where $J_s^{i,o}(t)$ is the asymptotic value of the entropy flux in the adjacent phase i left of the surface and into the surface, and $J_s^{o,i}(t)$ is similarly the entropy flux in the phase o to the right of the surface and out of the surface, see *Figure 5*. All excess properties of a surface, like the excess entropy production rate, are given by integrals like equation (1). The excess entropy production rate describes how the entropy production rate in the surface differs from the one in the adjacent homogeneous phases.

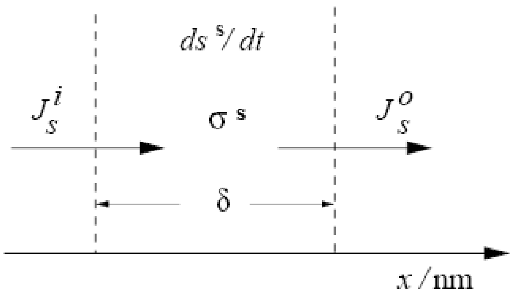

Figure 5. The change of the surface entropy due to entropy fluxes in and out of the surface and the entropy production rate in the surface

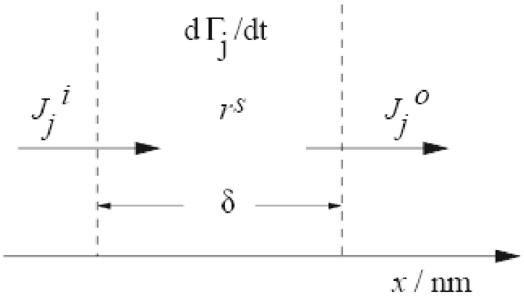

Figure 6. The mass balance for a surface with reaction

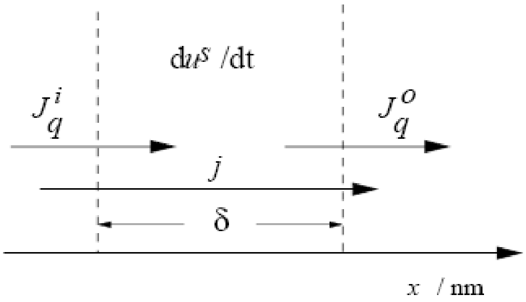

Figure 7. The energy change in the surface with total heat fluxes and an electric current

In order to emphasize that the two phases are not necessarily a gas and a liquid, we now indicate the two phases by i and o rather than by g and l. The asymptotic fluxes are defined by:

$$J_s^{i,o}(t) \equiv J_s^i(a,t) \quad \text{and} \quad J_s^{o,i}(t) \equiv J_s^o(b,t), \quad (15)$$

compare *Figure 1*. The first roman superscript gives the phase, i, s or o in this case. The second superscript, o or i, indicates a value close to the surface in phase i or o. The combination i, o means therefore the value in phase i as close as possible to the o-phase. The excess entropy production rate is $\sigma^s(t) \geq 0$. We shall find explicit expressions for $\sigma^s(t)$ by combining:

- mass balances
- the first law of thermodynamics
- the local form of the Gibbs equation.

In the derivation we follow references (Bedeaux et al., 1976; Bedeaux, 1986; Albano and Bedeaux, 1987). We shall see that $\sigma^s(t)$ can be written as the product sum of thermodynamic fluxes and forces in the system. These are the conjugate fluxes and forces for the surface. Electroneutral nonequilibrium systems, with and without chemical reactions, are of interest as these are the systems that we encounter most often in nature and also in industry. We shall give equations of transport for heat, mass and charge for surfaces where reactions occur. Electrochemical reactions need surfaces to occur and are especially important.

The excess entropy production rate for the surface shall be derived along the same lines as for the homogeneous phase (Kjelstrup and Bedeaux, 2001). Consider a surface area element, Ω, of an electroneutral surface that is in local equilibrium. The surface element has a temperature T^s, chemical potentials μ_j^s (j =1, 2,..., n for the n components), and surface tension γ. Electroneutrality of the surface means that the integral of the excess charge density is equal to zero. This property is valid, or more precisely, assumed to be valid if one extends the integration domain far enough to include, for instance, a possible double layer in an electrolyte. It does not depend on the choice of the dividing surface. The concept electroneutral surface differs in this respect from a concept like equimolar surface for a given component, which specifies the location of the dividing surface.

6. Balance Equations

The balance equation for a neutral component j, when a chemical reaction takes place, is:

$$\frac{d}{dt}\Gamma_j(t) = J_j^{i,o}(t) - J_j^{o,i}(t) \pm \nu_j r^s(t) \quad (16)$$

The accumulation of component j is equal to the flux into the surface, $J^{o,i}_j$ (t), minus the flux out of the surface, $J^{o,i}_j$ (t), plus or minus the (positive) stoichiometric constants, ν_j, of a chemical reaction times its rate, $r^s(t)$, in the surface element. There are n neutral components. Straight derivatives apply because the surface variables depend only on the time, not on the position along the surface. The positive direction of transport is chosen to be from left to right, cf. *Figure 6*. All fluxes are given in a frame of reference in which the surface is at rest.

The surface can accumulate mass and/or energy. The extension of the surface can and will always be chosen such that the integral of the excess charge density is zero. The surface can include, for instance, the electric double layer in an electrolyte adjacent to the electrode. The surface is electroneutral with these choices. The conservation equation for charge in the surface is therefore:

$$j^{i,o}(t) = j^{o,i}(t) \tag{17}$$

The adjacent homogeneous phases are also electroneutral, giving $j^{i,o}(t)=j^{i}(t)$ and $j^{o,i}(t)=j^{o}(t)$. We conclude that the electric current is constant throughout the system:

$$j^{i}(t) = j^{o}(t) = j(t) \tag{18}$$

The balance equation for the internal energy for the electroneutral surface is:

$$\begin{aligned}\frac{du^{s}(t)}{dt} &= J_q^{i,o}(t) - J_q^{o,i}(t) \\ &-j(t)\left(\phi^{o,i}(t) - \phi^{i,o}(t)\right)\end{aligned} \tag{19}$$

The change in the excess energy density of the surface, du^{s}, during the time, dt, is given by the total heat flux into the surface from the left, $J^{i,o}_{q}$, minus the total heat flux out of the surface to the right, $J^{o,i}_{q}$ plus the electric work per area done to the surface, $-j\left(\phi^{o,i} - \phi^{i,o}\right)$. Here $\phi^{o,i}$ and $\phi^{i,o}$ are the electric potentials in the bulk regions close to the surface.

7. The Excess Entropy Production Rate

The surface has an excess entropy production rate, in line with its other excess variables. This shall now be derived. The Gibbs equation in its local form (cf. equation (10)) is:

$$du^{s} = T^{s} ds^{s} + \sum_{j=1}^{n} \mu_j^{s} d\Gamma_j \tag{20}$$

The time derivative of the entropy density is:

$$\frac{ds^{s}}{dt} = \frac{1}{T^{s}}\frac{du^{s}}{dt} - \frac{1}{T^{s}}\sum_{j=1}^{n}\mu_j^{s}\frac{d\Gamma_j}{dt} \tag{21}$$

The entropy flux in or out of the surface, Js, is related to the total heat flux by:

$$J_s = \frac{1}{T}J_q - \sum_{j=1}^{n}\frac{\mu_j}{T}J_j \tag{22}$$

By introducing equations. (19) and (16) into equation (21), using equation (22), and comparing the result to the entropy balance equation (14), we find the excess entropy production rate in the surface frame of reference:

$$\begin{aligned}\sigma^{s} &= J_q^{i,o}\left(\frac{1}{T^{s}} - \frac{1}{T^{i,o}}\right) + J_q^{o,i}\left(\frac{1}{T^{o,i}} - \frac{1}{T^{s}}\right) \\ &+\sum_{j=1}^{n} J_j^{i,o}\left[-\left(\frac{\mu_j^{s}}{T^{s}} - \frac{\mu_j^{i,o}}{T^{i,o}}\right)\right] + \sum_{j=1}^{n} J_j^{o,i}\left[-\left(\frac{\mu_j^{o,i}}{T^{o,i}} - \frac{\mu_j^{s}}{T^{s}}\right)\right] \\ &+j\left[-\frac{1}{T^{s}}\left(\phi^{o,i} - \phi^{i,o}\right)\right] + r^{s}\left(-\frac{1}{T^{s}}\Delta_n G^{s}\right)\end{aligned} \tag{23}$$

where $\Delta_n G^{s}$ is the contribution from the neutral species to the Gibbs energy of the reaction. The surface frame of reference is the frame of reference in which the normal velocity of the surface is zero. In equation (23) the entropy production is a sum of products of pairs of conjugate forces and fluxes. Using equation (22), we may alternatively write this expression using the entropy fluxes:

$$\begin{aligned}\sigma^{s} &= J_s^{i,o}\left(-\frac{\Delta_{i,s}T}{T^{s}}\right) + J_s^{o,i}\left(-\frac{\Delta_{s,o}T}{T^{s}}\right) \\ &+\sum_{j=i}^{n} J_j^{i,o}\left(-\frac{\Delta_{i,s}\mu_j}{T^{s}}\right) + \sum_{j=1}^{n} J_j^{o,i}\left(-\frac{\Delta_{s,o}\mu_j}{T^{s}}\right) \\ &+ j\left[-\frac{1}{T^{s}}\Delta_{i,o}\phi\right] + r^{s}\left(-\frac{1}{T^{s}}\Delta_n G^{s}\right)\end{aligned} \tag{24}$$

For definitions of the deltas, we refer to subsection 7.1. Alternatively we may write this expression using the measurable heat flux, which is related to the entropy and the total heat fluxes by:

$$J_q = TJ_s + \sum_{j=1}^{n}\mu_j J_j = J'_q + \sum_{j=1}^{n} H_j J_j \tag{25}$$

on both sides of the surface. Here H_j is the molar enthalpy of component j. Using the thermodynamic identity $\partial(\mu_j/T)/\partial(1/T) = H_j$ one may then show that:

$$\begin{aligned}\sigma^{s} &= J'^{\,i,o}_q \Delta_{i,s}\left(\frac{1}{T}\right) + J'^{\,o,i}_q \Delta_{s,o}\left(\frac{1}{T}\right) \\ &+\sum_{j=1}^{n} J_j^{i,o}\left(-\frac{1}{T^{s}}\Delta_{i,s}\mu_{j,T}\left(T^{s}\right)\right) \\ &+\sum_{j=1}^{n} J_j^{o,i}\left(-\frac{1}{T^{s}}\Delta_{s,o}\mu_{j,T}\left(T^{s}\right)\right) \\ &+ j\left(-\frac{1}{T^{s}}\Delta_{i,o}\phi\right) + r^{s}\left(-\frac{1}{T^{s}}\Delta_n G^{s}\right)\end{aligned} \tag{26}$$

The outcome of the derivation is that in equation (26), the chemical potentials must be calculated at the temperature of the surface. In all cases the surface frame of reference is used for the fluxes. For the interpretation of experiments it is convenient to use measurable heat fluxes, which are independent of the frame of reference. This is what we shall do in the rest of the paper. In equations (24) and (26) the entropy production is written as a sum of products of conjugate forces and fluxes. As is clear from the derivation of these equations, a change in the fluxes leads to a corresponding change in the conjugate forces.

It is interesting to compare equation (26) for the excess entropy production rate with the expression for the entropy production that was derived for a homogeneous phase (de Groot and Mazur, 1984; Kjelstrup and Bedeaux, 2001):

$$\begin{aligned}\sigma = J'_q \nabla\left(\frac{1}{T}\right) + \sum_{j=1}^{n} J_j\left(-\frac{1}{T}\nabla\mu_{j,T}\right) \\ + j\left(-\frac{1}{T}\nabla\phi\right) + r\left(-\frac{1}{T}\Delta_n G\right)\end{aligned} \tag{27}$$

The gradients of (1/T) and ($\mu_{j,T}$) that are forces in the homogeneous phase have been replaced by jumps in these variables into and out of the surface; the fluxes are the same. The gradient of $-\phi$ has been replaced by a jump across the surface. These replacements represent the discrete nature of the surface and are typical for transport between different homogeneous parts of a system. Most of the contributions to the excess entropy production rate of a planar, isotropic surface given above are due to fluxes of heat, mass and charge in the homogeneous phases outside the surface. The contribution from the chemical reaction is, however, a specific surface contribution. For a more extended discussion we refer to Bedeaux (1986), Albano and Bedeaux (1987), Bedeaux and Kjelstrup Ratkje (1996).

At the surface, the system is no longer isotropic in the normal direction, so that all the normal fluxes, unlike in a homogeneous phase, are scalar under rotations and reflections in the plane of the surface. We therefore have coupling between chemical reactions and fluxes of heat, mass and charge at a surface; coupling that does not exist in isotropic homogeneous phases. Mass transport that is fueled by energy from a chemical reaction is called active transport in biology. One may also have active transport in non-isotropic homogeneous media. Equation (26) can be used to describe active transport which takes place at surfaces between isotropic homogeneous phases. Coupling of fluxes at the surface is also responsible for conversion of chemical to electrical energy. The extended coupling between fluxes at the surface gives a very important difference between transport processes in a homogeneous and in a heterogeneous system.

When the surface position is an equimolar surface for one particular component, this component has zero excess density in the surface and the flux of the component is continuous through the surface. The corresponding two contributions to the excess entropy production then combine into one and the constant flux has as a main driving force the chemical potential difference across the surface. When the surface does not move, the frame of reference given by the equimolar surface is the same as the laboratory frame of reference. Common frames of reference have been discussed by many authors, see e.g. Kjelstrup and Bedeaux (2001).

7.1 A remark on notation

We introduced the following notation for jumps in a variable at the surface, using the temperature as an example:

$$\begin{aligned}\Delta_{i,o}T &\equiv T^{o,i} - T^{i,o} \\ \Delta_{i,s}T &\equiv T^{s} - T^{i,o} \\ \Delta_{s,o}T &\equiv T^{o,i} - T^{s}\end{aligned} \tag{28}$$

The subscript T indicates a chemical potential difference at constant temperature. The differences with the surface chemical potentials at constant temperature are given in terms of the values in the homogeneous phases close to the surface, in points c and d, at the temperature of the surface:

$$\begin{aligned}\Delta_{i,s}\mu_{j,T}\left(T^s\right) &= \mu_j^s\left(T^s\right) - \mu_j^{i,o}\left(T^s\right) \\ \Delta_{s,o}\mu_{j,T}\left(T^s\right) &= \mu_j^{o,i}\left(T^s\right) - \mu_j^s\left(T^s\right)\end{aligned} \tag{29}$$

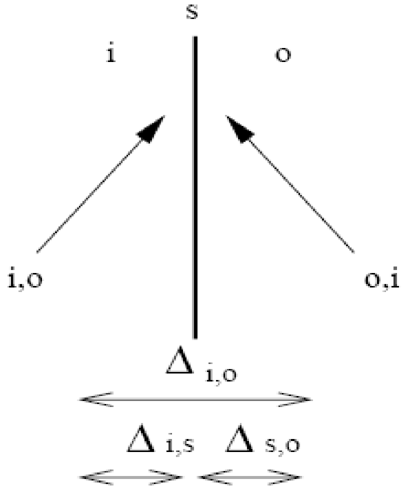

Figure 8. Standard notation used for transport across surfaces

Each jump is written as the value to the right minus the value to the left. This choice gives the jumps the same sign as the gradients in the homogeneous phases for increasing or decreasing variables. The subscripts of Δ refer to the two locations between which the difference is taken. The notation is further illustrated in *Figure 8*.

8. Force-flux Relations at the Surface

8.1 The surface coefficients

The number of independent force-flux pairs in equation (26), is equal to 2n+4 (we considered only one reaction). The linear relations between these forces and fluxes therefore contain $(2n+4)^2$ coefficients. The Onsager symmetry relations reduce the number of independent coefficients to (2n+4)(2n+5)/2. Even for one component and no reaction the number of independent coefficients is equal to 15. It is clear that one must find ways to simplify the description in order to make progress. This is usually possible, for instance, by introducing stationary state conditions. This gives relations between incoming fluxes on one side of the surface and outgoing fluxes on the other side, and the number of independent coefficients reduces to (n+3)(n+4)/2. The original 15 coefficients have then been reduced to 6, a rather more manageable number. Still, knowledge about these coefficients is limited for most applications. A few exceptions exist: reaction rates are usually well documented. Kinetic theory provides some important expressions for liquid-vapor transitions (Pao,1971; Pao, 1971; Cippola Jr. et al., 1974; Cippola Jr. et al., 1974; Bedeaux et al., 1990; Bedeaux et al., 1992). Experiments (Fong and Ward; 1999a; Fang and Ward, 1999b) and molecular dynamics simulations (Rosjorde et al., 2001) have recently become available for phase transitions. Apart from these studies, there is a lot of work still to be done to obtain surface transport coefficients. It may therefore be useful not only to examine the general flux-force equations, but also to consider simplifications of these that still contain the proper Onsager symmetry and are therefore compatible with the second law of thermodynamics. This shall be done in the following two subsections. A possibility for simplification of the linear laws, giving a set that still captures the major effects, is to neglect the resistivities that describe coupling across the surface, but keep the resistivities that describe coupling between fluxes on the same side of the surface. The reason for this simplification is that the two sides of the surface have, in fact, a slightly different location. Coupling resistivities for the forces and fluxes on the different sides of the surface would thus describe non-local effects. It seems reasonable to assume that these are negligible. This simplification is equivalent to looking at the surface as, in some respects, having two resistivity matrices in series. We want to emphasize that it is not necessary to make this simplification; it is, however, very convenient.

8.2 Heat and mass transport at the surface

As an example we now consider the transport of heat and one component (1) across a surface. The other component (2) is not moving. The entropy production rate is from equation (26):

$$\begin{aligned}\sigma^s &= J_q'^{\,i,o}\Delta_{i,s}\left(\frac{1}{T}\right)+J^{i,o}\left(-\frac{\Delta_{i,s}\mu_{1,T}\left(T^s\right)}{T^s}\right)\\ &+J_q'^{\,o,i}\Delta_{s,o}\left(\frac{1}{T}\right)+J^{o,i}\left(-\frac{\Delta_{s,o}\mu_{1,T}\left(T^s\right)}{T^s}\right)\end{aligned} \tag{30}$$

The equimolar surface of component 2 is used as the frame of reference. The notation of the forces was illustrated in *Figure 8*. For the surface temperature one superscript is sufficient. The forces are given as linear functions of the fluxes by:

$$\begin{aligned}\Delta_{i,s}\left(\frac{1}{T}\right) &= r_{qq}^{s,ii}J_q'^{\,i,o}+r_{qq}^{s,io}J_q'^{\,o,i}\\ &\quad +r_{q\mu}^{s,ii}J_1^{i,o}+r_{q\mu}^{s,io}J_1^{o,i}\\ \Delta_{s,o}\left(\frac{1}{T}\right) &= r_{qq}^{s,oi}J_q'^{\,i,o}+r_{qq}^{s,oo}J_q'^{\,o,i}\\ &\quad +r_{q\mu}^{s,oi}J_1^{i,o}+r_{q\mu}^{s,oo}J_1^{o,i}\\ -\frac{\Delta_{i,s}\mu_{1,T}\left(T^s\right)}{T^s} &= r_{\mu q}^{s,ii}J_q'^{\,i,o}+r_{\mu q}^{s,io}J_q'^{\,o,i}\\ &\quad +r_{\mu\mu}^{s,ii}J_1^{i,o}+r_{\mu\mu}^{s,io}J_1'^{\,o,i}\\ -\frac{\Delta_{s,o}\mu_{1,T}\left(T^s\right)}{T^s} &= r_{\mu q}^{s,oi}J_q'^{\,i,o}+r_{\mu q}^{s,oo}J_q'^{\,o,i}\\ &\quad +r_{\mu\mu}^{s,oi}J_1^{i,o}+r_{\mu\mu}^{s,oo}J_1'^{\,o,i}\end{aligned} \tag{31}$$

All resistivities have the dimensionality of the resistivities for the homogeneous phases times a length (the surface thickness). In equation (30), the matrix of resistivity coefficients is symmetric. We have, using these Onsager relations, ten independent resistivities, while there are three in the bulk regions. The resistivities have superscripts before the comma. The first superscript after the comma gives the region for which the flux is evaluated, and the second gives the region to which the force couples. The subscripts indicate the flux involved in the coupling. The linear relations between forces and fluxes are valid as long as the system is close to local equilibrium. This condition has been found to apply also for very large temperature gradients (Rosjorde et al., 2001; Rosjorde et al., 2000). It should be emphasized that a system in local equilibrium can be far from global equilibrium (de Groot and Mazur, 1984). It is also important to realize that a linear relation between forces and fluxes, nevertheless, gives rise to a non-linear description of the system. This is due to a variety of reasons, for instance, the non-linear character of the equations of state and the dependence of the resistivities on the surface temperature and the adsorptions of the various components. The name linear nonequilibrium thermodynamics is in this respect somewhat misleading. The validity of the linear laws given in equation (31) is not restricted to systems close to global equilibrium. See also the discussion section regarding this matter.

The coupling resistivities may be divided into three groups. The first group contains coupling of fluxes and forces on the incoming side of the surface, the second group contains coupling of fluxes and forces on the outgoing side, and the third group has resistivities that describe coupling of fluxes on one side to forces on the other side. Because entropy or enthalpy is carried along with the mass flux, the coefficients in the first two groups are important, as we shall see below. As we argued in the previous subsection, we expect the third group of resistivities to be negligible. We shall neglect these coefficients:

$$\begin{aligned} r_{qq}^{s,io} &= r_{qq}^{s,oi} = r_{q\mu}^{s,io} = r_{q\mu}^{s,oi} \\ &= r_{\mu q}^{s,io} = r_{\mu q}^{s,oi} = r_{\mu\mu}^{s,io} = r_{\mu\mu}^{s,oi} = 0 \end{aligned} \tag{32}$$

In that case the flux equations simplify to:

$$\begin{aligned} \Delta_{i,s}\left(\frac{1}{T}\right) &= r_{qq}^{s,ii} J_q'^{i,o} + r_{q\mu}^{s,ii} J_1^{i,o} \\ -\frac{1}{T^s}\Delta_{i,s}\mu_{1,T}\left(T^s\right) &= r_{\mu q}^{s,ii} J_q'^{\,i,o} + r_{\mu\mu}^{s,ii} J_1^{i,o} \end{aligned} \tag{33}$$

for the left side of the surface and to

$$\begin{aligned} \Delta_{s,o}\left(\frac{1}{T}\right) &= r_{qq}^{s,oo} J_q'^{o,i} + r_{q\mu}^{s,oo} J_1^{o,i} \\ -\frac{1}{T^s}\Delta_{s,o}\mu_{1,T}\left(T^s\right) &= r_{\mu q}^{s,oo} J_q'^{\,o,i} + r_{\mu\mu}^{s,oo} J_1^{o,i} \end{aligned} \tag{34}$$

for the right side of the surface. When the resistivities across the surface are neglected, cf. equation (32), the resistivities of the two sides of the surface to transport through the surface are in series. The approximation may in principle be tested, but the experiments involved are extremely difficult to do since it is difficult to control variables at the surface. We expect that a deviation from equation (32) is most likely for surfaces of molecular thickness, and that the assumption is good for relatively thick surfaces. Using the assumption, the number of independent resistivities decreases from ten to six, three for each side of the surface. A benefit of this formulation is that it combines well with corresponding equations for the homogeneous phases; and that the coupling coefficient is the same at the surface and in the homogeneous phases.

The heats of transfer for both sides of the surface are defined in the usual way by:

$$\begin{aligned} q^{*i,o} &= \left(\frac{J_q'^{\,i,o}}{J_1^{i,o}}\right)_{\Delta_{i,s}T=0} = -\frac{r_{q\mu}^{s,ii}}{r_{qq}^{s,ii}} \\ q^{*0,i} &= \left(\frac{J_q'^{\,o,i}}{J_1^{o,i}}\right)_{\Delta_{s,o}T=0} = -\frac{r_{q\mu}^{s,oo}}{r_{qq}^{s,oo}} \end{aligned} \tag{35}$$

The heats of transfer for the surface are ratios of the asymptotic values of the bulk fluxes at a constant (independent of position) temperature. They are therefore equal to the asymptotic values of the heats of transport in the adjacent bulk phases. This is a useful property as it reduces the number of new unknown resistivities for the surface to two on either side.

Defining the Fourier thermal conductivities for constant molar fluxes, $J_1^{i,o}$ and $J_1^{o,\,i}$, by:

$$\begin{aligned} \lambda^{s,i} &= \frac{1}{T^s T^{i,o} r_{qq}^{s,ii}} \\ \lambda^{s,o} &= \frac{1}{T^s T^{o,i} r_{qq}^{s,oo}} \end{aligned} \tag{36}$$

we may write equations (33) and (34) as:

$$\begin{aligned} J_q'^{i,o} &= -\lambda^{s,i}\Delta_{i,s}T + q^{*i,o} J_1^{i,o} \\ -\frac{1}{T^S}\Delta_{i,s}\mu_{1,T}\left(T^s\right) &= \\ &= q^{*i,o}\frac{\Delta_{i,s}T}{T^s T^{i,o}} + \left[r_{\mu\mu}^{s,ii} - \frac{\left(q^{*i,o}\right)^2}{T^s T^{i,o}\lambda^{s,i}} \right] J_1^{i,o} \\ &= q^{*i,o}\frac{\Delta_{i,s}T}{T^s T^{i,o}} + \left(r_{\mu\mu}^{s,ii} - \frac{r_{\mu q}^{s,ii} r_{q\mu}^{s,ii}}{r_{qq}^{s,ii}} \right) J_1^{i,o} \end{aligned} \tag{37}$$

and

$$
\begin{aligned}
J_q'^{\,o,i} &= -\lambda^{s,o}\Delta_{s,o}T + q^{*o,i}J_1^{o,i} \\
-\frac{1}{T^S}\Delta_{s,i}\mu_{1,T}\left(T^s\right) &= \\
&= q^{*o,i}\frac{\Delta_{s,o}T}{T^S T^{o,i}} + \left[r_{\mu\mu}^{s,oo} - \frac{\left(q^{*o,i}\right)^2}{T^S T^{o,i}\lambda^{s,o}}\right]J_1^{o,i} \quad (38) \\
&= q^{*o,i}\frac{\Delta_{s,o}T}{T^S T^{o,i}} + \left(r_{\mu\mu}^{s,oo} - \frac{r_{\mu q}^{s,oo}\, r_{q\mu}^{s,oo}}{r_{qq}^{s,oo}}\right)J_1^{o,i}
\end{aligned}
$$

There is mass transport into the surface due to the temperature difference between the surface and the bulk, cf. equations (37b) and (38b), similar to the Soret effect in the bulk phase [23]. Conversely, there is also a heat effect associated with adsorption or desorption, a Dufour effect, cf. equations (37a) and (38a). The direction of this contribution to the heat flux follows the direction of the molar flux; it is reversible in this sense. These heats of transfer are accessible by experiment on the homogeneous phases. They are small in vapor mixtures, somewhat larger in liquid mixtures (Bird et al., 1960). In homogeneous phases, they can sometimes, with good approximation, be neglected. In the linear relations (37) and (38) only the four main coefficients, $\lambda^{s,i}$, $\lambda^{s,o}$, $r_{\mu\mu}^{s,ii}$, $r_{\mu\mu}^{s,oo}$ remain to be determined for the surface. To summarize so far: the above set of equations is required in a calculation which takes the surface temperature along as a variable. Arguing that the heats of transfer are relatively small quantities, one may then question the reason for going to this sophistication. We shall see below, however, that as soon as the mass flux becomes substantial, the jump in temperature and chemical potential across the surface become large, thereby giving a rationale for taking the terms containing the coupling coefficients along also here.

In order to examine the behavior of the surface layer as a whole, we introduce the stationary state conditions that follow from equations (16), (19) and (25):

$$
\begin{aligned}
J_1^{o,1} &= J_1^{i,o} \equiv J_1 \\
J_q'^{o,i} &= J_q'^{i,o} - J_1\left(H_1^{o,i} - H_1^{i,o}\right) = J_q'^{i,o} - J_1\Delta_{i,o}H_1
\end{aligned}
\qquad (39)
$$

There are therefore only two independent fluxes. Using J_1 and $J_1{}^{'i,o}$ in equations (37) and (38) we obtain:

$$
\begin{aligned}
\Delta_{i,s}T &= -\frac{1}{\lambda^{s,i}}\left(J_q'^{i,o} - q^{*i,o}J_1\right) \\
-\frac{1}{T^s}\Delta_{i,s}\mu_{1,T}\left(T^s\right) &= -\frac{1}{T^S T^{i,o}\lambda^{s,i}}q^{*i,o}J_q'^{i,o} + r_{\mu\mu}^{s,ii}J_1
\end{aligned}
\qquad (40)
$$

for the jumps from the left side to the surface.

For the jumps across the surface we then obtain:

$$
\begin{aligned}
\Delta_{i,o}T &= -\left(\frac{T^{o,i}}{T^S\lambda^{s,i}} + \frac{T^{i,o}}{T^S\lambda^{s,o}}\right) J_q'^{i,o} + \\
&\left[\frac{T^{o,i}}{T^S\lambda^{s,i}}q^{*i,o} + \frac{T^{i,o}}{T^S\lambda^{s,o}}\left(Q^{*o,i} + \Delta_{i,o}H_1\right)\right]J_1 \\
& \qquad\qquad\qquad\qquad\qquad\qquad (41) \\
-\frac{1}{T^{o,i}}\Delta_{i,o}\mu_{1,T}\left(T^{o,i}\right) &= -\left[\frac{1}{T^S T^{i,o}\lambda^{s,i}}q^{*i,o} + \right. \\
&\left.\frac{1}{T^S T^{0,i}\lambda^{s,o}}\left(q^{*o,i} + \Delta_{i,o}H_1\right)\right]J_q'^{i,o} + \\
&\left[r_{\mu\mu}^{s,ii} + r_{\mu\mu}^{s,oo} + \frac{1}{T^S T^{o,i}\lambda^{s,o}}\Delta_{i,o}H_1\left(2q^{*o,i} + \Delta_{i,o}H_1\right)\right]J_1
\end{aligned}
$$

where we used the thermodynamic identity:

$$
\begin{aligned}
&\frac{1}{T^s}\Delta_{i,o}\mu_{1,T}\left(T^s\right) \\
&= \frac{1}{T^{o,i}}\Delta_{i,o}\mu_{1,T}\left(T^{o,i}\right) \\
&\qquad + \left[\frac{\partial\left(\Delta_{i,o}\mu_1(T)/T\right)}{\partial(1/T)}\right]_{T=T^{o,i}}\left(\frac{1}{T^s} - \frac{1}{T^{o,i}}\right) \qquad (42) \\
&= \frac{1}{T^{o,i}}\Delta_{i,o}\mu_{1,T}\left(T^{o,i}\right) + \Delta_{i,o}H_1\left(T^{o,i}\right)\frac{\Delta_{s,o}T}{T^S T^{o,i}} \\
&= \frac{1}{T^{o,i}}\Delta_{i,o}\mu_{1,T}\left(T^{o,i}\right) - \frac{\Delta_{i,o}H_1\left(T^{o,i}\right)}{T^S T^{o,i}\lambda^{s,o}}\left(J_q'^{o,i} - q^{*o,i}J_1\right) \\
&= \frac{1}{T^{o,i}}\Delta_{i,o}\mu_{1,T}\left(T^{o,i}\right) \\
&\qquad - \frac{\Delta_{i,o}H_1\left(T^{o,i}\right)}{T^S T^{o,i}\lambda^{s,o}}\left(J_q'^{\,i,o} - \left(q^{*o,i} + \Delta_{i,o}H_1\right)\ J_1\right)
\end{aligned}
$$

In the last two identities we used equations (38a) and (39b). The T^s in equation (41) is due to the definitions of $\lambda^{s,i}$ and $\lambda^{s,o}$, which contain the surface temperature. They can be eliminated using equation (40). This leads to contributions to the forces which are nonlinear in the fluxes. In the theory of nonequilibrium thermodynamics, such nonlinear terms should be neglected. This implies that one may replace T^s by either $T^{i,o}$ or $T^{o,i.}$. Suppressing, furthermore, the dependence of the enthalpy on the temperature, which is small, equation (41) becomes:

$$
\begin{aligned}
\Delta_{i,o}T &= -\left(\frac{1}{\lambda^{s,i}} + \frac{1}{\lambda^{s,o}}\right)J_q'^{\,i,o} \\
&\quad + \left[\frac{1}{\lambda^{s,i}}q^{*i,o} + \frac{1}{\lambda^{s,o}}\left(q^{*i,o} + \Delta_{i,o}H_1\right)\right]J_1 \\
& \qquad\qquad\qquad\qquad\qquad\qquad (43) \\
\Delta_{i,o}\mu_{1,T}\left(T^{o,i}\right) &= \frac{1}{T^{o,i}}\left[\frac{1}{\lambda^{s,i}}q^{*i,o} + \right. \\
&\left.\frac{1}{\lambda^{s,o}}\left(q^{*o,i} + \Delta_{i,o}H_1\right)\right]J_q'^{\,i,o} - \left[T^{o,i}\left(r_{\mu\mu}^{s,ii} + r_{\mu\mu}^{s,oo}\right) + \right. \\
&\left.\frac{1}{T^{o,i}\lambda^{s,o}}\Delta_{i,o}H_1\left(2q^{*o,i} + \Delta_{i,o}H_1\right)\right]J_1
\end{aligned}
$$

These equations make it possible to calculate the jumps of the temperature and the chemical potential across the surface. The equation contains only three unknown surface coefficients, $\lambda^{s,i}$ and $\lambda^{s,o}$ and the sum $r_{\mu\mu}^{s,ii}+r_{\mu\mu}^{s,oo}$. This is reasonable, given the assumption we made in the outset that the surface behaves as two resistances in series. The sum $r_{\mu\mu}^{s,ii}+r_{\mu\mu}^{s,oo}$ is the surface resistance to mass transfer, measured for isothermal conditions. The sum of the inverse of the thermal conductivities is the total thermal resistivity, measured at zero mass flux.

We see now that in spite of $q^{*o,i}$ and $q^{*i,o}$ being small, the coupling coefficient, the expressions in the square brackets in equation (43), may become large when the enthalpy difference between the sides is large. Many systems have a large enthalpy of evaporation, and large surface temperature jumps and jumps in chemical potentials can thus be expected at such surfaces, as soon as the mass flux becomes sizeable. A mass flux will generate heat transport according to the term in front of J_1 in equation (43a). And conversely, a mass flux will, to a large degree, be affected by the presence of a heat flux, as expressed by equation (43b). It can thus not be approximated by an equation with one term only. It is therefore not enough to use Fourier's law for heat transfer across the surface in these systems, when there is a simultaneous mass flux. Similarly, it is not enough to use Fick's law for mass transport across the surface. Olivier (2002) estimated the error made by neglecting coupling terms, and found that a 20% error in the heat flux on the vapor side was common for evaporation of hydrocarbons.

A special case of interest is evaporation and condensation for a one-component fluid. In that case the heats of transfer in both the liquid and the vapor phase are zero. Equation (43) then reduces to:

$$\begin{aligned}
\Delta_{i,o}T &= -\left(\frac{1}{\lambda^{s,i}}+\frac{1}{\lambda^{s,o}}\right)J_q'^{\,i,o}+\frac{1}{\lambda^{s,o}}\Delta_{i,o}H_1J_1 \\
\Delta_{i,o}\mu_{1,T}\left(T^{o,i}\right) &= \frac{1}{T^{o,i}\lambda^{s,o}}\Delta_{i,o}H_1J_q'^{\,i,o} \qquad (44)\\
&-\left[T^{o,i}\left(r_{\mu\mu}^{s,ii}+r_{\mu\mu}^{s,oo}\right)+\frac{1}{T^{o,i}\lambda^{s,o}}\left(\Delta_{i,o}H_1\right)^2\right]J_1
\end{aligned}$$

The enthalpy of evaporation, $-\Delta_{i,o}H_1$, is equal to $2.5RT^{o,i}$ for a low density vapor or larger. It is therefore eminently clear that the coupling terms are important. Notice also that the coupling terms have the proper Onsager symmetry. In kinetic theory the resistivities for the liquid-vapor interface have been calculated (Pao, 1971; Pao, 1971; Cippola Jr. et al., 1974; Cippola Jr. et al., 1974; Bedeaux et al.,1990). Using these results one obtains with $-\Delta_{i,o}H_1=2.5RT^{o,i}$,

$$\begin{aligned}
\frac{1}{\lambda^{s,i}} &= \frac{\sqrt{\pi}}{5Rc^{i,o}v_{mp}}\left(1+\frac{22}{5\pi}\right)\\
\frac{1}{\lambda^{s,o}} &= \frac{\sqrt{\pi}}{20Rc^{i,o}v_{mp}}\left(1+\frac{16}{5\pi}\right) \qquad (45)\\
r_{\mu\mu}^{s,ii}+r_{\mu\mu}^{s,oo} &= \frac{2R\sqrt{\pi}}{c^{i,o}v_{mp}}\left(\sigma_w^{-1}+\frac{1}{2\pi}-\frac{28}{32}\right)
\end{aligned}$$

Here σ_w is the condensation coefficient, $v_{mp}=(2RT^{i,o}/M)^{1/2}$ is the most probable thermal velocity and M is the molar mass. Furthermore $c^{i,o}$ is the molar density in the gas close to the surface. For the heat of transport of the surface on the vapor side one finds:

$$\begin{aligned}
q^{*s,i} &\equiv \left(\frac{J_q'^{\,i,o}}{J_1}\right)_{\Delta_{i,o}T=0} = \frac{\lambda^{s,i}\Delta_{i,o}H_1}{\lambda^{s,i}+\lambda^{s,o}} \qquad (46)\\
&= -\frac{5\left(5\pi+16\right)RT^{o,i}}{2\left(25\pi+104\right)}
\end{aligned}$$

and on the liquid side:

$$\begin{aligned}
q^{*s,o} &\equiv \left(\frac{J_q'^{\,o,i}}{J_1}\right)_{\Delta_{i,o}T=0}\\
&= \left(\frac{J_q'^{\,i,o}}{J_1}\right)_{\Delta_{i,o}T=0} - \Delta_{i,o}H_1 = q^{*s,i}-\Delta_{i,o}H_1 \qquad (47)\\
&= -\frac{\lambda^{s,o}\Delta_{i,o}H_1}{\lambda^{s,i}+\lambda^{s,o}} = \frac{10\left(5\pi+22\right)RT^{o,i}}{\left(25\pi+104\right)}
\end{aligned}$$

We see that the condensation of one mole leads to the transport of a fraction of $-\Delta_{i,o}H_1$, into the liquid and the rest into the vapor, the fraction being given by the ratio of the thermal conductivity of the liquid side of the surface and the total surface conductivity. It is therefore natural that $q^{*s,i}$ is negative, while $q^{*s,o}$ is positive. It is not correct to assume that kinetic theory describes only the vapor side of the surface. The boundary conditions in kinetic theory contain a model of the surface, and contain therefore information about both $q^{*s,i}$ and $q^{*s,o}$.

Common in engineering is now to solve the system's conservation equations in combination with simple transport laws. For the stationary surface, the conservation equations were given in equation (39). By introducing Fourier's law for $J_q'^{\,i,o}$ into equation (39a), and Fick's law into (39b), we obtain:

$$\begin{aligned} J_1^{i,o} &= J_1 = -D\Delta_{i,o}c \\ J_q'^{i,o} &= -\lambda^{i,o}\Delta_{i,o}T \end{aligned} \tag{48}$$

On the other side of the surface these linear laws imply:

$$\begin{aligned} J_1^{i,o} &= J_1 = -D\Delta_{i,o}c \\ J_q'^{o,i} &= J_q'^{i,o} - J_1\Delta_{i,o}H_1 \\ &= -\lambda^{i,o}\Delta_{i,o}T - \Delta_{i,o}H_1J_1 \end{aligned} \tag{49}$$

We see then that the symmetric choice of the linear laws in equation (48) imply that the linear laws on the other side of the surface lack the proper symmetry required by Onsager (1931, 1931). This set of equations can be shown to violate the second law of thermodynamics. Nevertheless, a set like this is used most often in engineering applications.

8.3 Heat, mass and charge transport at an electrode surface

Our next example is the anode of a polymer electrolyte fuel cell. The bulk anode material consists of porous carbon. On the surface of the carbon, catalytic platinum is adsorbed. The layer that contains the platinum is our two-dimensional surface. Humidified hydrogen gas comes through the pores in the carbon to the platinum in the surface, where it reacts to form protons and electrons. The protons go into the electrolyte; the proton conducting membrane, while the electrons go into the carbon matrix (Kjelstrup and Røsjorde, 2005). We consider stationary states from the outset. Conservation of energy across the interface between the porous carbon matrix and the water-filled proton exchange membrane gives for a stationary state that

$$\begin{aligned} J_u &= J_q'^{i} + j^i\phi^{i,o} + J_{H_2}^i H_{H_2}^{i,o} + J_w^i H_w^{i,o} \\ &= J_q'^{o} + j^o\phi^{o,i} + J_w^o H_w^{o,i} \end{aligned} \tag{50}$$

The flux of hydrogen stops at the surface, while the water flux and the electric current density are continuous through the surface:

$$J_w^i = J_w^o \equiv J_w \quad \text{and} \quad j^i = j^o \equiv j \tag{51}$$

The molecular hydrogen flux is given by:

$$J_{H_2}^i = \frac{j}{2F} \tag{52}$$

There is a discontinuity in the measurable heat flux at the surface, so we distinguish between the heat flux into the surface, $J_q'^{i}$, and out of the surface, $J_q'^{o}$. Substituting equation (51) into equation (50) one obtains:

$$j\Delta_{i,o}\phi = -J_q'^{o} + J_q'^{i} + J_{H_2}^i H_{H_2}^{i,o} - J_w\Delta_{i,o}H_w \tag{53}$$

The enthalpy of hydrogen is, in this stationary process, converted into electric energy and heat. There is also a change in the enthalpy as water goes from the vapor state to the condensed state in the membrane. This is also converted into electric energy and heat. The difference in the electric potential between the two sides of the surface $\phi^o - \phi^i = \Delta_{i,o}\phi$ is therefore generated by the heat and enthalpy changes.

The entropy production of an electrode surface was given by Bedeaux, Kjelstrup and coworkers (1976, 1987, 1996, 1999, 2005):

$$\begin{aligned} \sigma^{s,i} &= J_q'^{i}\Delta_{i,s}\left(\frac{1}{T}\right) + J_q'^{o}\Delta_{s,o}\left(\frac{1}{T}\right) \\ &\quad - J_w^i\frac{1}{T^s}\Delta_{i,s}\mu_{w,T}\left(T^s\right) - J_w^o\frac{1}{T^s}\Delta_{s,o}\mu_{w,T}\left(T^s\right) \\ &\quad - j\frac{1}{T^s}\left(\Delta_{i,o}\phi - \frac{\mu_{H_2}^{i,o}\left(T^s\right)}{2F}\right) \end{aligned} \tag{54}$$

Subscript i,s for the thermal force means that the difference is taken between the surface and the anode backing. Subscript s,o means that the difference is taken between the membrane and the surface. The electrochemical reaction takes place at the surface, and the reaction rate at the stationary state is equal to j/F . We have also used the stationary state value for the hydrogen flux.

We use again the assumption that the coupling of the forces on one side of the surface and the forces on the other side can be neglected (see subsection 8.1). The linear force-flux equations then become:

$$\begin{aligned} \Delta_{i,s}\left(\frac{1}{T}\right) &= R_{qq}^{s,i}J_q'^{i} + R_{q\mu}^{s,i}J_w^i + R_{q\phi}^{s,i}j \\ -\frac{1}{T^s}\Delta_{i,s}\mu_{w,T}\left(T^s\right) &= R_{\mu q}^{s,i}J_q'^{i} + R_{\mu\mu}^{s,i}J_w^i + R_{\mu\phi}^{s,i}j \end{aligned} \tag{55}$$

for the left hand side of the surface, and:

$$\begin{aligned} \Delta_{s,o}\left(\frac{1}{T}\right) &= R_{qq}^{s,o}J_q'^{o} + R_{q\mu}^{s,o}J_w^o + R_{q\phi}^{s,o}j \\ -\frac{1}{T^s}\Delta_{s,o}\mu_{w,T}\left(T^s\right) &= R_{\mu q}^{s,o}J_q'^{o} + R_{\mu\mu}^{s,o}J_w^o + R_{\mu\phi}^{s,o}j \end{aligned} \tag{56}$$

for the right hand side of the surface. For the electric potential one obtains:

$$\begin{aligned} -\frac{1}{T^s}\left(\Delta_{i,o}\phi - \frac{\mu_{H_2}^{i,o}\left(T^s\right)}{2F}\right) &= R_{\phi q}^{s,i}J_q'^{i} + R_{\phi q}^{s,o}J_q'^{o} \\ &\quad + R_{\phi\mu}^{s,i}J_w^i + R_{\phi\mu}^{s,o}J_w^o + R_{\phi\phi}^{s}j \end{aligned} \tag{57}$$

The coefficients satisfy Onsager's reciprocal relations. It is convenient for our present purpose to also give the heat and water fluxes in terms of their conjugate forces and the electric flux. Solving J'^{i}_{q} and J^{i}_{w} from equation (55) one obtains:

$$\begin{aligned} J'^{i}_{q} &= \ell^{s,i}_{qq}\Delta_{i,s}\left(\frac{1}{T}\right) - \ell^{s,i}_{q\mu}\frac{1}{T^{s}}\Delta_{i,s}\mu_{w,T}\left(T^{s}\right) + \pi^{i}\frac{j}{F} \\ J^{i}_{w} &= \ell^{s,i}_{\mu q}\Delta_{i,s}\left(\frac{1}{T}\right) - \ell^{s,i}_{\mu\mu}\frac{1}{T^{s}}\Delta_{i,s}\mu_{w,T}\left(T^{s}\right) + t^{i}_{w}\frac{j}{F} \end{aligned} \qquad (58)$$

for the left hand side of the surface, and for J'^{o}_{q} and J^{o}_{w} one obtains from equation (56)

$$\begin{aligned} J'^{o}_{q} &= \ell^{s,o}_{qq}\Delta_{s,o}\left(\frac{1}{T}\right) - \ell^{s,o}_{q\mu}\frac{1}{T^{s}}\Delta_{s,o}\mu_{w,T}\left(T^{s}\right) + \pi^{o}\frac{j}{F} \\ J^{o}_{w} &= \ell^{s,o}_{\mu q}\Delta_{s,o}\left(\frac{1}{T}\right) - \ell^{s,o}_{\mu\mu}\frac{1}{T^{s}}\Delta_{s,o}\mu_{w,T}\left(T^{s}\right) + t^{o}_{w}\frac{j}{F} \end{aligned} \qquad (59)$$

for the right hand side of the surface. The conductivity and resistivity matrices are related by:

$$\begin{aligned} \ell^{s,j}_{qq} &= \frac{R^{s,j}_{\mu\mu}}{R^{s,j}_{qq}R^{s,j}_{\mu\mu} - R^{s,j}_{\mu q}R^{s,j}_{q\mu}} \\ \ell^{s,j}_{q\mu} = \ell^{s,j}_{\mu q} &= -\frac{R^{s,j}_{q\mu}}{R^{s,j}_{qq}R^{s,j}_{\mu\mu} - R^{s,j}_{\mu q}R^{s,j}_{q\mu}} \\ \ell^{s,j}_{\mu\mu} &= \frac{R^{s,j}_{qq}}{R^{s,j}_{qq}R^{s,j}_{\mu\mu} - R^{s,j}_{\mu q}R^{s,j}_{q\mu}} \end{aligned} \qquad (60)$$

while the Peltier coefficients and the transference coefficient for water are given by:

$$\begin{aligned} \pi^{j} &= F\left(\frac{J'^{j}_{q}}{j}\right)_{\Delta T=0,\Delta\mu=0} = F\frac{R^{s,j}_{\mu\phi}R^{s,j}_{\mu q} - R^{s,j}_{\mu\mu}R^{s,j}_{q\phi}}{R^{s,j}_{qq}R^{s,j}_{\mu\mu} - R^{s,j}_{\mu q}R^{s,j}_{q\mu}} \\ t^{j}_{w} &= F\left(\frac{J^{j}_{w}}{j}\right)_{\Delta T=0,\Delta\mu=0} = F\frac{R^{s,j}_{q\phi}R^{s,j}_{\mu q} - R^{s,j}_{qq}R^{s,j}_{\mu\phi}}{R^{s,j}_{qq}R^{s,j}_{\mu\mu} - R^{s,j}_{\mu q}R^{s,j}_{q\mu}} \end{aligned} \qquad (61)$$

where j=i or o. The ΔT and $\Delta\mu$ differences are taken zero on the side of the surface for which these ratios are calculated.

By substituting equations (58) and (59) in equation (57), we obtain (after some algebra) the potential difference across the surface:

$$\begin{aligned} \Delta_{i,o}\phi - \frac{\mu^{i,o}_{H_2}\left(T^{s}\right)}{2F} &= -\frac{\pi^{i}}{T^{i}F}\Delta_{i,s}T - \frac{\pi^{o}}{T^{o}F}\Delta_{s,o}T \\ &- \frac{t^{i}_{w}}{F}\Delta_{i,s}\mu_{w,T}\left(T^{s}\right) - \frac{t^{o}_{w}}{F}\Delta_{s,o}\mu_{w,T}\left(T^{s}\right) - r^{s}j \end{aligned} \qquad (62)$$

where r^{s} is the ohmic resistivity of the surface. This ohmic resistivity can be found from the 5x5 resistivity matrix by inversion of this matrix into the 5x5 conductivity matrix. Using capital L's for the elements of this matrix, one finds that $r^{s} = T^{s}/L^{s}_{\phi\phi}$. We furthermore introduce the heats of transfer:

$$q^{*j} \equiv \left(\frac{J'^{j}_{q}}{J^{j}_{w}}\right)_{\Delta T=0,j=0} = -\frac{R^{s,j}_{q\mu}}{R^{s,j}_{qq}} = \frac{\ell^{s,j}_{q\mu}}{\ell^{s,j}_{\mu\mu}} \qquad (63)$$

The transference coefficients, the Peltier coefficients and the heats of transfer are all given as ratios of bulk fluxes. These coefficients are therefore equal to the coefficients that can be defined for the bulk phases, and have the same value as these coefficients have in the bulk regions next to the surface. This reduces the number of new coefficients for the surface in equations (58), (59) and (62) to five, being: $\ell^{s,i}_{qq}$, $\ell^{s,i}_{\mu\mu}$, $\ell^{s,o}_{qq}$, $\ell^{s,j}_{\mu\mu}$ and r^{s}. The equations (58) and (59) can finally be written in the following form:

$$\begin{aligned} \Delta_{i,s}T &= -\frac{1}{\lambda^{s,i}}\left[J'^{i}_{q}\right] - q^{*i}\left(J^{i}_{w} - t^{i}_{w}\frac{j}{F}\right) - \pi^{i}\frac{j}{F} \\ \Delta_{i,s}\mu_{w,T}\left(T^{s}\right) &= -\frac{q^{*i}}{T^{i,o}}\Delta_{i,s}T - \frac{T^{s}}{\ell^{s,i}_{\mu\mu}}\left(J^{i}_{w} - t^{i}_{w}\frac{j}{F}\right) \end{aligned} \qquad (64)$$

for the left hand side of the surface and:

$$\begin{aligned} \Delta_{s,o}T &= -\frac{1}{\lambda^{s,o}}\left[J'^{o}_{q} - q^{*o}\left(J^{o}_{w} - t^{o}_{w}\frac{j}{F}\right) - \pi^{o}\frac{j}{F}\right] \\ \Delta_{s,o}\mu_{w,T}\left(T^{s}\right) &= -\frac{q^{*o}}{T^{o,i}}\Delta_{s,o}T - \frac{T^{s}}{\ell^{s,o}_{\mu\mu}}\left(J^{o}_{w} - t^{o}_{w}\frac{j}{F}\right) \end{aligned} \qquad (65)$$

for the right hand side of the surface. The stationary state thermal conductivities for the two sides of the surface were defined by:

$$\lambda^{s,j} \equiv \frac{1}{R^{s,j}_{qq}T^{s}T^{j}} \qquad (66)$$

By using equations (62), (64) and (65) we obtain expressions for the driving forces across the surface that contain the transference coefficients, t^{i}_{w} and t^{o}_{w}, the Peltier coefficients, π^{i} and π^{o}, and the heats of transfer, q^{*i} and q^{*o}. Furthermore they contain five diagonal coefficients specific for the surface, $\lambda^{s,i}$, $\ell^{s,i}_{\mu\mu}$, $\lambda^{s,o}$, $\ell^{s,j}_{\mu\mu}$ and r^{s}. These have to be found by measuring transport across and into the surface. As we have explained in detail in the previous subsection, and as follows from equation (53), the coupling between the forces is large, since thermodynamic variables like $H^{i,o}_{H_2}$ and $\Delta_{i,o}H_w$ appear in the expressions for the difference between J'^{i}_{q} and J'^{o}_{q}. The larger the heat flux and the water flux into the membrane are, and the larger the electric current density is, the larger are the jumps in the temperature and the chemical potential of water across the surface. Indeed, relatively large temperature jumps have recently been measured (Vie and Kjelstrup, 2004).

The purpose of the derivations above has been to present one possible version of flux force relations at the anode in the polymer electrolyte fuel cell. Emphasis was made on how to simplify the rather complicated full description. In order to model the surface transport phenomena in agreement with the second law, it is mandatory to introduce assumptions in a way that preserves the Onsager symmetry relations. This was done above. As we explained in the previous subsection, this is not usually done in the modeling of phase transitions. In a recent review on fuel cell modeling, Weber and Newman (2004) explained that most of the transport properties of the surface in good approximation can be dismissed. Our derivations show that this may lead to violation of the second law.

9. Discussion

In the sections above we have given the development of a nonequilibrium thermodynamics theory for surfaces that have transport of heat, mass and charge through and into the surface and chemical reactions at the surfaces. A heterogeneous system was divided into three- and two-dimensional subsystems, corresponding to the homogeneous phases and the surface, or alternatively called interface in between. The systematic approach designed by Gibbs, who defined excess densities for the surface, was invoked to obtain a proper thermodynamic description of the surface. By doing this we have avoided the problems posed by a completely continuous transport model for the total system, see Weber and Newman (2004). We were thereby able to assign to the surface properties that are specific to the surface.

The governing equations that derive from the entropy production rate of the surface appear in this method as being discontinuous at the surface, in contrast to their counterparts for the homogeneous phases which are continuous. The force flux relations for the surface therefore have the form of boundary conditions to the corresponding transport equations that apply in the neighboring bulk phases. These boundary conditions are more complicated than those normally used in thermodynamic descriptions of heterogeneous systems, but the complications are required to not violate the second law of thermodynamics, and to properly describe the interaction of all transport phenomena such that they satisfy the Onsager reciprocal relations. One of the main new results of the analysis was that this interaction or coupling is large and cannot be neglected. These points can only be addressed on the background of nonequilibrium thermodynamics, and have therefore largely been missing in the literature on electrochemical cells, see however (Kjelstrup et al., 1999; Vie and Kjelstrup, 2004; Kjelstrup and Røsjorde, 2005). The situation for one-component evaporation is better, as the large effort in kinetic theory has produced theoretical estimates for transport coefficients including the cross coefficient (Pao, 1971; Pao, 1971; Cippola Jr. et al., 1974; Cippola Jr. et al., 1974; Bedeaux et al., 1990; Bedeaux et al., 1992).

The linear force-flux relations can be used when the system is not too far from *local* equilibrium. This implies both, that one may use the usual thermodynamic relations everywhere in the system (the hypothesis of local equilibrium), and that the forces and fluxes are not too large. For chemical reactions this is a serious restriction, see e.g. (de Groot and Mazur, 1987). On the other hand, it is found, in molecular dynamics simulations, that forces like temperature gradients across the system, and in particular across the surface, can be very large, while the system is still everywhere in local equilibrium and satisfies the linear force-flux relations (Rosjorde et al., 2001; Rosjorde et al., 2000; Hafskjold and Kjelstrup Ratkje, 1995). The validity of the linear force-flux relations does not imply that the description using nonequilibrium thermodynamics is linear. De Groot and Mazur emphasized this point in the preface of the Dover edition of their book (de Groot and Mazur, 1984). We quote: ”This theory gives rise to partial differential equations for the state variables which are non-linear for a variety of reasons, such as (i) the presence of convection terms and of (ii) quadratic source terms in, e.g., the energy equation, (iii) the non-linear character of the equation of state and (iv) the dependence of the phenomenological transport coefficients on the state variables. The name”linear thermodynamics of irreversible processes” (their quotes) is therefore slightly misleading. Of course, the formalism may be fully linearized and is then applicable to situations in which one is not only too far from local equilibrium, but even near to overall, global, equilibrium.” In the literature the phrase ”close to equilibrium” is generally used without specifying whether one is close to local or close to global equilibrium. To give an example we quote from the recent book by Demirel, page 356 (Demirel, 2002):”Linear nonequilibrium thermodynamics has some fundamental limitations..... it is based on the local-equilibrium hypothesis and therefore confined to systems in the vicinity of equilibrium”. Leaving aside whether the author meant local (which it should be) or global equilibrium, it is statements like this which have contributed to the rather common impression that the range of validity of nonequilibrium thermodynamics is limited to systems close to global equilibrium. This is unfortunate. Also Prigogine contributes to this misunderstanding. Quoting from a short self-biography, reproduced in Appendix C from Demirel’s book, Prigogine says: ”From the very beginning, I knew that the minimum entropy production was valid only for the linear branch of irreversible phenomena, the one to which the famous reciprocity relations of Onsager are valid”. This is also confusing because the minimum entropy production principle has only been proven close to global equilibrium, while the Onsager relations are valid close to local equilibrium. Of course there are systems close to local and global equilibrium and systems which are far from local and global equilibrium. The majority of systems are, however, close to local equilibrium and far from global equilibrium. These systems satisfy the linear laws and are nevertheless very non-linear. One may, e.g., describe the transition to turbulence and the Rayleigh-Benard instability using the non-linear partial differential equations for the state variable which follow using linear nonequilibrium thermodynamics.

Two relatively simple cases were used to bring out the essential features of the method, the coupled transport of heat and mass and the coupled transport of heat, mass and charge at an electrode surface. We did not detail the possibility of having a chemical reaction out of chemical equilibrium. This situation can also be dealt with in nonequilibrium thermodynamics, but may require a description on the mesoscopic level as was done by (Rubi and Kjelstrup,2003). Special for the surface is that the discontinuous description puts all transport phenomena on the same footing; i.e. they are all scalar phenomena. This is in contrast to the situation in the bulk phase, where heat, mass and charge transport phenomena are vectors, while chemical reactions are scalar. The fact that the normal component of the forces and fluxes are scalar at the surface, make a coupling possible between chemical reactions and the other fluxes. The coupling of scalar phenomena at the surface is special, and we have seen that the coupling coefficients are large. The existence of large coupling coefficients may have a bearing on the description of many other similar cases. It is also clear that a large effort is needed to find the value and nature of surface coefficients.

10. Conclusion

We have seen above that fluxes for transport of heat, mass and charge into, out of and across surfaces are coupled with large coupling coefficients, when the fluxes are formulated in agreement with the second law of thermodynamics. The reason that the coupling effects cannot be neglected is that they contain contributions from thermodynamic properties related to the phase transition or the reaction at the surface, contributions which make the surface transport coefficient different from their counter values in the homogeneous phases. The terms must be accounted for in correct thermodynamic modeling of dynamic processes at surfaces.

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