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POSSIBILITIES OF SURFACE REACTION COUPLING WITH TRANSPORT PHENOMENE

G. BERTRAND¹ & R. PRUD'HOMME²

Abstract The thermodynamic approach of nonequilibrium phenomena allows, through the construction of entropy production, appropriate fluxes generalized forces to be identified, and the possibility of coupling to be detected. For the interface phase the expression entropy production consists of two parts: one for irreversible phenomena in the surface (chemical reactions and transport); and the second for transport processes between volumic phases due to the discontinuity of intensive surface parameters.

Accordingly, in the linear range, the phenomenological relations establishing the thermodynamic coupling between fluxes and forces of the same tensorial order may cause couplings, forbidden in homogeneous medium, to occur. For instance the thermal force which is the temperature gradient vector in homogeneous medium is split at the surface into a surface gradient (vector) and temperature jumps (scalar); the latter, thus, can be inserted into the flux-force relation of surface reaction. Various consequences resulting from this formal analysis are considered.

1. Introduction

Reactive media are a fruitful field of investigation in nonequilibrium thermodynamics. However, while there are numerous studies devoted to homogeneous phase reactions, few of them deal with interface chemical reactions despite the major interest in interface phenomena, i.e. catalytic or electrochemical reactions, adsorption, phase transformation, membrane processes. The reason for this paucity may be essentially due to the complexity of the problem of interface, where even the actual theoretical definition of interface is problematic. However, applications of nonequilibrium thermodynamics to interface media have become more and more numerous [1] and at this time it appears that fresh results, proper to this medium, may be predicted. Such is the case as will be shown, for surface chemical reactions. In the present paper, the application of the linear laws of thermodynamics will be considered; the stability of interface phenomena or of the interface itself will not be examined - the reader is advised to refer to the valuable papers by A. Sanfeld et al. [2] concerning those subjects.

First, the major results regarding nonuniform, homogeneous media, i.e. without surface phenomena, will be viewed. These may reveal the actual importance of couplings as predicted by the thermodynamics of irreversible processes; the interface will then be approached in a similar way.

2. Study of Nonuniform, Reactive, Homogeneous Media

A. Formalism of the Thermodynamics of Irreversible Processes

The expression of the entropy production is of major importance in nonequilibrium thermodynamics. The formulation found in numerous studies (see, for instance. Refs. [3]- [5]) may be written

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$$\sigma(S) = -\frac{1}{T} \sum_{j=1}^N g_j \dot{W}_j - \frac{1}{T} (\pi - p) \nabla \cdot \mathbf{v} - \frac{1}{T^2} \mathbf{q} \cdot \nabla T - \frac{1}{T} \sum_{j=1}^N \mathbf{J}_{Dj} \cdot \left[T \nabla \left(\frac{g_j}{T} \right) - \mathbf{f}_j \right] - \frac{1}{T} \boldsymbol{\tau} : \mathbf{G}_s \quad (1)$$

A list of the notations and symbols used is presented at the end of the paper. We may also write

$$-\frac{1}{T} \sum_{j=1}^N g_j \dot{W}_j = \sum_{k=1}^R \mathcal{A}_k \dot{w}_k \quad (2)$$

in order to distinguish the chemical affinities \mathcal{A}_k and rates \dot{w}_k of the R chemical reactions.

Expression (1) is the sum of the contributions of each phenomenon of dissipation: chemical reaction, heat and mass transfer, viscosity phenomena. It is a bilinear expression, i.e., a sum of products of generalized forces X_k , chemical affinities or gradients, by generalized currents or fluxes J_k .

Table I shows the decomposition of Eq. (1) depending on fluxes and forces. A precise tensorial order is apparent

At thermodynamic equilibrium, fluxes and forces cancel each other simultaneously for all irreversible processes and the entropy production is zero. Close to equilibrium, linear relations between fluxes and forces can be written. They are the phenomenological relations

$$J_k = \sum_i l_{ki} X_i \quad (3)$$

Tensorial order	Fluxes J_k	Forces X_k	
0 scalar	$\pi - p$ \dot{W}_j (or \dot{w}_k)	$-\nabla \cdot \mathbf{v}/T$ $-g_j/T$ (or \mathcal{A}_k)	Bulk viscosity Chemical reaction
1 vector	\mathbf{q} \mathbf{J}_{Dj}	$\nabla(1/T)$ $-(\nabla(g_j/T) - \mathbf{f}_j/T)$	Heat transfer Diffusion
2 tensor	$\boldsymbol{\tau}$	$-\mathbf{G}_s/T$	viscosity

Table I

The coefficients l_{ki} are called phenomenological coefficients. Two types of coefficients may be defined: first, those which are on the diagonal of the matrix (l_{kk}); they relate flux to the corresponding force. Secondly, extradiagonal coefficients termed *coupling coefficients* or *cross-coefficients*.

These coefficients are the elements of a matrix which must obey several principles

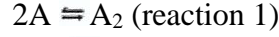
(1) The Onsager principle which states that coefficients l_{ki} and l_{ik} are equal.

(2) The Curie-Prigogine principle or symmetry principle: it results in writing a priori nonzero coefficients only for a flux and a force of the same tensorial order. We shall, thereby, find relations between scalars, distinct group between vectors, and, finally a set for tensors of order two.

In the so-called strictly linear region, the phenomenological coefficients are constant. But in the case of systems sufficiently far from equilibrium and where a nonlinearity at system level occurs it may still prove useful to write *local* linear relations [4].

B. Thermodynamic Coupling

Let us consider an example, namely, two chemical reactions



with heat transfer and diffusion.

In this case, we have expressed the production of entropy:

$$\begin{aligned} \sigma(S) = & \frac{1}{T} A_1 \dot{w}_1 + \frac{1}{T} A_2 \dot{w}_2 - \frac{1}{T^2} \mathbf{q} \cdot \nabla T - \mathbf{J}_{DA} \cdot \nabla \left(\frac{g_A}{T} \right) \\ & - \mathbf{J}_{DB} \cdot \nabla \left(\frac{g_B}{T} \right) - \mathbf{J}_{DAB} \cdot \nabla \left(\frac{g_{AB}}{T} \right) - \mathbf{J}_{DA_2} \cdot \nabla \left(\frac{g_{A_2}}{T} \right) \end{aligned} \quad (4)$$

and the resulting phenomenological relation

$$\mathbf{J}_{Di} = -l_{ii} \nabla \left(\frac{g_i}{T} \right) - \sum_{j \neq i} \nabla \left(\frac{g_j}{T} \right) - l_{iT} \frac{\nabla T}{T^2} \quad (5)$$

(i, j=A, A₂, B, AB)

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(A)

(B)

$$\mathbf{q} = -l_{TT} \frac{\nabla T}{T^2} - \sum_j l_{Tj} \nabla \left(\frac{g_j}{T} \right) \quad (6)$$

(D)

(B)

$$\dot{w}_r = l_{rr} \frac{A_r}{T} + l_{rs} \frac{A_s}{T} \quad (7)$$

(r=1, 2)

The coupling between transport phenomena are well known: they are called binary diffusion (A) and thermal diffusion (B). When no coupling occurs, Fick's law (C) and Fourier law (D) are evidenced.

Chemical reactions cannot be coupled with transport phenomena by such relations. We would like to stress the fact that the prediction of couplings resulting strictly from the expression of entropy production has been experimentally confirmed. The values of some cross-coefficients can be determined: they are of interest because of the applications to crystal growth [6], to ultrafiltration and selective permeation phenomena [7], to transport processes in membranes [8], to the nonisothermal diffusion of water vapor [9], in engineering [10], etc. Often, however, as noted by Tambour and Gal-Or [10], a number of investigations "have neglected thermodynamic couplings or an *a priori* basis (i.e., before any estimation of expected results under the expected operating conditions)."

These beings so, let us now consider the same problem for the interface medium.

3. Nonequilibrium Thermodynamics of Interfaces

A. Production of Interface Entropy

The thermodynamic investigation of the interface beforehand requires a certain number of choices [1, 11-15] to be made: Gibbs' discontinuous interface model (dividing surface) or continuous model (three-dimensional region of some undetermined thickness)? Assumption of autonomy and local equilibrium or that of interface nonautonomy? In addition, we may assume that the interface does or does not possess internal properties (material surface), that it is a monolayer (discontinuity of bulk quantity at the surface) or not, that it is mobile or not [12-21].

Our assumption [5] is that of a mobile, singular Gibbs' surface of arbitrary shape with internal properties and having an autonomous phase.

The interface is then likened to a geometrical surface (Σ) of the form

$$f(x, y, z, t) = 0 \quad (8)$$

The normal ξ at same point on the surface, at any time t , is defined by

$$\xi = \frac{\nabla f}{|\nabla f|} \quad (9)$$

The geometrical velocity \mathbf{V} of the interface fulfils equation

$$\mathbf{V} \cdot \xi = -\frac{\partial f}{\partial t} / |\nabla f| \quad (10)$$

defining the projection of \mathbf{V} on the normal at the interface.

Finally, an operator $\bar{\nabla}$ is defined. It is written as

$$\bar{\nabla} = (\mathbf{1} - \xi \otimes \xi) \cdot \nabla - (\nabla \cdot \xi) \xi \quad (11)$$

Relation (11) consists of a term representing the projection of vector \mathbf{V} on the plane tangent to the surface at the point considered and of a term collinear to the normal ξ which accounts for the surface curvature. It is the operator $\bar{\nabla}$ and not the conventional derivation operator ∇ which appears in the thermodynamic expressions of the interface. It should be noted, that this term is assimilated into the surface gradient only in the particular case of a plane interface.

Under the assumption of an autonomous phase, Gibbs' relation for the interface is to be recalled:

$$d\hat{s} = \frac{1}{\hat{T}} d\hat{e} - \frac{\gamma}{\hat{T}} d\left(\frac{1}{\sigma}\right) - \sum_j \frac{\hat{g}_j}{\hat{T}} d\hat{Y}_j \quad (12)$$

Taking into account relation (12) and the laws for conservation of mass, momentum, energy, and entropy as applied to the interface [5], we find the expression of the production of interface entropy, which is given by Eq.(13). This equation implies that the volumic phases are isotropic and that the surface has a two-dimensional isotropy.

$$\begin{aligned}
\hat{\sigma}(S) = & -\sum_{j=1}^N \frac{\hat{g}_j}{\hat{T}} \hat{W}_j + \hat{\mathbf{q}} \cdot \nabla \frac{1}{\hat{T}} - \frac{1}{\hat{T}} \sum_{j=1}^N \hat{\mathbf{J}}_{Dj} \cdot \left[\hat{T} \nabla \left(\frac{\hat{g}_j}{T} \right) - \hat{f}_j \right] + \frac{1}{T} \mathbf{\Gamma} : \nabla \otimes \hat{\mathbf{v}} \\
& + \left[\left(\frac{1}{T} - \frac{1}{\hat{T}} \right) (\mathbf{q} + \rho(\mathbf{v} - \mathbf{V})h) \right] \cdot \xi \\
& - \sum_j \left[\left(\frac{g_j}{T} - \frac{\hat{g}_j}{\hat{T}} \right) (J_{Dj} + \rho(\mathbf{v} - \mathbf{V})Y_j) \right] \cdot \xi \\
& - \frac{1}{\hat{T}} \left[(\mathbf{v} - \hat{\mathbf{v}}) \cdot \left(\mathbf{\Pi} + \frac{1}{2} \rho(\mathbf{v} - \hat{\mathbf{v}}) \otimes (\mathbf{v} - \mathbf{V}) \right) \right] \cdot \xi
\end{aligned} \tag{13}$$

(Notations are explained in the list of symbols at [end of this paper.]) $[A]$ denotes

$$[A] = A^+ - A^- \tag{14}$$

where A^+ and A^- are the values of the quantity A on either side of the interface: the normal ξ is oriented from - to +.

To distinguish the interface chemical reactions, we may write

$$\sum_{j=1}^N \frac{\hat{g}_j}{\hat{T}} \hat{W}_j = \sum_{k=1}^R \hat{\mathcal{A}}_k \hat{W}_k \tag{15}$$

Finally, the relative mass flux \mathbf{J} is defined by

$$\mathbf{J} = \rho(\mathbf{v} - \mathbf{V}) \tag{16}$$

Equation (13) can be divided into two parts. The first which contains the first four terms, consists of the contribution of the interface irreversible processes: surface chemical reactions, heat transfer and diffusion in the interface, surface tensions. It is to be related to expression (1) transposing the three-dimensional space to the two-dimensional manifold prescribed by the surface.

The second part explains the contribution of the dissipation phenomena resulting at the interface level from discontinuities of temperature, chemical potential of the constituents, and flow velocity.

Each term between square brackets is the product of such a discontinuity by the corresponding flux: it consists of the normal component of a volumic flow of the adjacent phases at interface level and of a relative convective flow, namely, of values incorporated by the relative flow of matter.

In Table II, we present the fluxes and generalized forces included in equation (13), and show their tensorial order. We did not decompose the viscosity terms; in the general case it is a delicate operation; an application has been considered by Kovac [18].

Fresh results are obtained compared to those of Table 1; e.g. the thermal force was the temperature gradient in the continuous medium, Now we have three terms, one being the surface temperature “gradient,” the other two being the surface temperature jumps. The former keeps the vectorial character whereas the latter two, now, become scalar values.

B. Coupling at the Interface

The phenomenological relation between fluxes and forces can now be considered. Following our previous remark, it is obvious that new possibilities of coupling will occur. The principles of reciprocity and symmetry are still assumed to be valid.

Table II contains examples where the phenomenological relations are expressed in simpler cases. Thus, interactions which would be forbidden in a homogeneous medium can be considered, e.g., the coupling between the surface-heat flow and the sliding friction [24, 25]. The cross-effect will be termed thermal slip.

The nonequilibrium state changes presented in Table III should be commented on. Waldman and Rubsamen [21] put forward a procedure to determine the phenomenological coefficients from the interface temperature jump. Cipolla et al.[22].

Tensorial order	Fluxes	Forces
0 scalar	\dot{W}_j (or \dot{w}_k) $(\mathbf{q}^+ + \mathbf{J}^+ h^+) \cdot \boldsymbol{\xi}$ $(\mathbf{q}^- + \mathbf{J}^- h^-) \cdot \boldsymbol{\xi}$ $(\mathbf{J}_{Dj}^+ + \mathbf{J}^+ Y_j^+) \cdot \boldsymbol{\xi}$ $(\mathbf{J}_{Dj}^- + \mathbf{J}^- Y_j^-) \cdot \boldsymbol{\xi}$	$-g_j/T$ (or \mathcal{A}_k) surface chemical reaction $\left. \begin{array}{l} \frac{1}{T^+} - \frac{1}{\hat{T}} \\ -\left(\frac{1}{T^-} - \frac{1}{\hat{T}} \right) \end{array} \right\}$ temperature jumps $\left. \begin{array}{l} -\left(\frac{g_j^+}{T^+} - \frac{\hat{g}_j}{\hat{T}} \right) \\ \frac{g_j^-}{T^-} - \frac{\hat{g}_j}{\hat{T}} \end{array} \right\}$ chemical potential jumps
1 vector	\mathbf{q} \mathbf{J}_{Dj} $\left(\boldsymbol{\Pi}^+ + \frac{1}{2} \mathbf{J}^+ \otimes (\mathbf{v}^+ - \mathbf{V}) \right) \cdot \boldsymbol{\xi}$ $\left(\boldsymbol{\Pi}^- + \frac{1}{2} \mathbf{J}^- \otimes (\mathbf{v}^- - \mathbf{V}) \right) \cdot \boldsymbol{\xi}$	$\mathcal{X} \left(\frac{1}{\hat{T}} \right)$ surface heat flow $-(\mathcal{X} \left(\frac{\hat{g}_j}{\hat{T}} \right) - \frac{\hat{\mathbf{f}}_j}{\hat{T}})$ surface diffusion $\left. \begin{array}{l} -(\mathbf{v}^+ - \hat{\mathbf{v}}) \\ \mathbf{v}^- - \hat{\mathbf{v}} \end{array} \right\}$ sliding friction
(2+0) tensor	$\boldsymbol{\Gamma}$	$\frac{1}{\hat{T}} \mathcal{X} \otimes \hat{\mathbf{v}}$ surface viscosity (shear stress)

Table II. Examples of possible couplings at interface

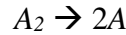
Bornhorst and Hatsopoulos [20] Waldmann and Rubsamen [21] Cipolla, Jr. et al. [22] Bertrand and Prud'homme [23]	temperature jump and chemical potential jump	evaporation and condensation kinetics
Prud'homme [24] Bedeaux et al. [25]	surface heat flow and sliding friction	cross-effect (thermal slip)
Kovac [18]	shear stress surface heat (flow, sliding friction and diffusion bulk viscosity, thermal jumps, chemical potential jumps and velocity jumps	adsorption damping of surface wave in a two component fluid

Table III. Some references

report experimental results validating the existence of the interface coupling: these authors, in this case, establish the symmetry of Onsager's matrix. Finally, Bertrand and Prud'homme [23] show that some features in the kinetics of evaporation (Smith-Topley effect) are accounted for by those couplings.

B. Surface Chemical Reactions

We now consider the possibility of a coupling involving surface chemical reaction. Let us consider a catalytic surface reaction such as



The fluid reactant consisting of A_2 and A is inserted between two infinite parallel planes; the lower plane only is catalytic. The reaction is not athermal and gives rise to heat transfer. Viscosity is neglected. The solid is assumed impermeable and adiabatic.

In this case, the production of interface entropy may be expressed easily:

$$\begin{aligned}
-\hat{\sigma}(S) = & \frac{\hat{A}}{\hat{T}} \hat{w} + \hat{\mathbf{q}} \cdot \nabla \left(\frac{1}{T} \right) + \left(\frac{1}{T^+} - \frac{1}{T^-} \right) (\mathbf{q}^+ + \rho^+ \mathbf{v}^+ h^+) \cdot \boldsymbol{\xi} \\
& - \left(\frac{g_A^+}{T^+} - \frac{\hat{g}_A}{\hat{T}} \right) (\mathbf{J}_{DA} + \rho^+ \mathbf{v}^+ Y_A^+) \cdot \boldsymbol{\xi} \\
& - \left(\frac{g_{A_2}^+}{T^+} - \frac{\hat{g}_{A_2}}{\hat{T}} \right) (\mathbf{J}_{DA_2} + \rho^+ \mathbf{v}^+ Y_{A_2}^+) \cdot \boldsymbol{\xi}
\end{aligned} \tag{17}$$

When linear relation can be used, the flux-force relations are deduced by developing the matrix of phenomenological coefficients:

$$\begin{pmatrix} \dot{w} \\ (q^+ + \rho^+ v^+ h^+) \cdot \xi \\ (J_{DA}^+ + \rho^+ v^+ Y_{A^+}) \cdot \xi \\ (J_{DA2}^+ + \rho^+ v^+ Y_{A2^+}) \cdot \xi \\ \dot{q} \end{pmatrix} = \begin{pmatrix} l_{11} & l_{12} & l_{13} & l_{14} & 0 \\ l_{21} & l_{22} & l_{23} & l_{24} & 0 \\ l_{31} & l_{32} & l_{33} & l_{34} & 0 \\ l_{41} & l_{42} & l_{43} & l_{44} & 0 \\ 0 & 0 & 0 & 0 & l_{55} \end{pmatrix} \begin{pmatrix} \frac{\mathcal{A}}{\hat{T}} \\ \frac{1}{T^+} - \frac{1}{\hat{T}} \\ -\left(\frac{g_A^+}{T^+} - \frac{\hat{g}_A}{\hat{T}}\right) \\ -\left(\frac{g_{A2}^+}{T^+} - \frac{\hat{g}_{A2}}{\hat{T}}\right) \\ \hat{\nabla} \left(\frac{1}{\hat{T}}\right) \end{pmatrix} \quad (18)$$

We thus show the dependence of reaction rate i not only on chemical affinity but also on temperature jump and surface chemical potential jumps. Coupling between the chemical reaction and transfers along the surface remains forbidden.

These conclusions are quite general and should apply to any surface reaction. In fact, to assert, according to the Curie principle, that no thermodynamic coupling can occur between the surface reaction and the transport phenomena in the adjacent phases, one must consider that the interface does not constitute a discontinuity surface either for temperature or for the chemical potential of the reactives and reactants (see, for instance. Ref. [26]).

Another remark results from the examination of flux-force relation; (Eq. (18)). It appears that even if the chemical affinity of the surface reaction could lie kept zero, the occurrence of an interface temperature jump would result in a reactive kinetics.

4. Conclusion

In this survey, we have essentially theoretically justified, from the viewpoint of irreversible thermodynamics, the coupling of surface chemical reactions with transport phenomena. From this point of view, we have insisted on the difference between surface and volume reaction.

We have, therefore, shown the important part played by couplings, citing for this purpose significant results where the predictions yielded by nonequilibrium thermodynamics are confirmed.

The results, relative to surface reactions, derive from an identical formal analysis; but so far no accurate experimental example exists as an illustration. However, the problem of active transport through biological membranes, some examples of which were reported at this Colloquium [27], may be evoked. This phenomenon is usually regarded as a case of coupling between the chemical reaction and the transmembrane movement. The actuality of these couplings may be logically considered from phenomenological interface relations.

List of Symbols

Volume	Interface	
\mathcal{A}_i	$\hat{\mathcal{A}}_i$	chemical affinity of the i^{th} reaction
e	\hat{e}	mass internal energy
$f(x, y, z, t)$		interface equation
\mathbf{f}_j	\hat{f}_j	external force acting on species j
\mathbf{G}_S		symmetric part of the tensor $\nabla \cdot \mathbf{v}$ (with zero trace)
g_j	\hat{g}_j	mass chemical potential of species j
h	\hat{h}	mass enthalpy
	J^k	generalized thermodynamic force
\mathbf{J}_{Dj}	\mathbf{J}_{Dj}	diffusion flow of species j
	\mathbf{J}	relative mass flux defined in Eq. (17)
	l_{ki}	phenomenological coefficient
	N	number of chemical species in the mixture
p		thermodynamic pressure
\mathbf{q}	$\hat{\mathbf{q}}$	heat flow vector
	R	number of chemical reactions
s	\hat{s}	mass entropy
T	\hat{T}	temperature
\mathcal{T}		viscous stress tensor
	\mathbf{V}	actual velocity of interface progression
\mathbf{v}	$\hat{\mathbf{v}}$	particle velocity
\dot{W}_j	\hat{W}_j	mass rate of production of species
\dot{w}_j	\hat{w}_j	molar rate of the i^{th} chemical reaction
	X_k	generalized flux
Y_j	\hat{Y}_j	mass fraction of species j
	$\mathbf{\Gamma}$	interface stress tensor
	γ	surface tension
	ξ	normal to a surface
Π		tensor of viscosity stresses
π		hydrostatic pressure
ρ		mass density
	σ	density per unit area (or surface mass)
	σ_j	surface mass of species j
$\sigma(S)$	$\hat{\sigma}(S)$	entropy production rate
	∇	space derivation operator
	\boxtimes	surface derivation operator defined by Eq. (12)
	\mathbf{A}	vector \mathbf{A}
	\mathbf{A}	tensor of order two \mathbf{A}
	$\mathbf{A} \cdot \mathbf{B}$	scalar product
	$\mathbf{A} \otimes \mathbf{B}$	tensorial product
	$\mathbf{A} : \mathbf{B}$	diadic product

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