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Note on the Curie principle

The formalism of irreversible thermodynamics affords a potent method for the study of membrane transport. Since active transport is of great biological significance, several attempts have been made to define active transport in terms of such a formalism. Kedem[1] has suggested that a metabolic reaction could be coupled to transport by means of a vectorial cross-coefficient. However, Jardetzky[2], on the basis of Curie's principle, excluded the possibility of such direct coupling. Later, Katchalsky and Kedem[3] stated, "Langeland showed that Curie's principle applies only to isotropic media but not to an anisotropic membrane capable of active transport". However, Langeland's[4] abstract does not contain a discussion of the matter and since that time explicit justification of his conclusion has not appeared. Therefore the following discussion of Curie's principle, based upon the presentation of De Groot and Mazur[5], is offered.

Irreversible phenomena leading to dissipation or entropy production may be of different tensorial character. For example, a chemical reaction is a scalar phenomenon and the entropy production rate is the product of two scalar quantities, namely the reaction rate and the affinity divided by the temperature. The reaction rate plays the role of a generalized "flux" or "effect", while the affinity plays the role of a generalized "force" or "cause". Similarly, the flow of heat in an isotropic material is a vector phenomenon and the rate of entropy production is given by the scalar product of these vectors: the heat flux and the gradient of the reciprocal temperature. Viscous phenomena have the character of second rank tensors and the entropy production rate is the doubly contracted product of two second rank tensors, the viscous stress tensor and the gradient of the velocity vector, divided by the temperature.

The linear phenomenological laws relating these phenomena may be written either in terms of the cartesian components of the individual fluxes or in a more compact manner, namely

$$\begin{aligned} J_s &= L_{ss} X_s + L_{sv} \cdot \mathbf{X}_v + L_{st} : \mathbf{X}_t \\ \mathbf{J}_v &= L_{vs} X_s + L_{vv} \cdot \mathbf{X}_v + L_{vt} : \mathbf{X}_t \qquad (1) \\ \mathbf{J}_t &= L_{ts} X_s + L_{tv} \cdot \mathbf{X}_v + L_{tt} : \mathbf{X}_t \end{aligned}$$

Here the simultaneous occurrence of one flux of each tensorial character is assumed, and the tensorial nature of the "flux" J or "force" X is denoted by the appropriate subscript. The nature of the phenomenological coefficients (the L's) is apparent from inspection: L_{ss} must be a scalar; L_{sv}, L_{vs} must be vectors; L_{st}, L_{ts}, L_{vv} must be tensors of rank 2; L_{vt}, L_{tv} must be tensors of rank 3; and finally L_{tt} must be a tensor of rank 4.

In the absence of spatial symmetry of the system in which the irreversible phenomena take place, such as in an anisotropic system for example, Onsager's relations hold between the coefficients L but no further simplification of the system of coefficients can be made.

If the system, on the other hand, has some spatial symmetry properties then the coordinate transformations corresponding to these symmetry properties of the system of coefficients yield additional conditions which lead to a simplification of the system of coefficients. This is the content of CURIE's principle. In particular, in a completely isotropic system one finds that complete spatial symmetry of the system leads to the fact that most cross-coupling coefficients in Eqns. 1 must vanish so that no coupling can exist between phenomena of different tensorial character, except for a possible coupling between the scalar flux and the "trace" of the tensor flux. In general, no coupling can occur in a completely isotropic medium between phenomena whose tensorial orders differ by an odd integer[6,7].

A very simple illustration of the above is provided by a situation in which a scalar flux and a vector flux occur simultaneously. In this case the phenomenological equations simplify to:

$$\begin{aligned} J_s &= L_{ss} X_s + \mathbf{L}_{sv} \cdot \mathbf{X}_v \\ \mathbf{J}_v &= \mathbf{L}_{vs} \cdot X_s + L_{vv} \cdot \mathbf{X}_v \end{aligned} \tag{2}$$

One of the requirements of isotropy is that under an inversion of the coordinate system (sign reversal of all three axes) the phenomenological coefficients must be invariant. This is obviously true for the scalar L_{ss}. The vector $\mathbf{L}_{sv}$ under such a transformation would change sign. (A vector in the positive x-direction is oriented in the negative x′-direction if x = −x′.) It can only remain invariant if it is equal to zero. Thus $\mathbf{L}_{sv} = \mathbf{L}_{vs} = 0$. By considering the invariance of L_{vv} under an arbitrary rotation, as required by isotropy, it may also be shown that L_{vv} must, in fact, be a scalar L_{vv}.

Thus if one considers diffusion and a chemical reaction, occurring simultaneously in a system which is isotropic, the two phenomena cannot be coupled phenomenologically. In the case, however, of one-dimensional diffusion across a membrane occurring simultaneously with a chemical reaction, the system is not isotropic and the above conditions do not necessarily apply. The "membrane" for this discussion need not be a structural body but can be simply an interfacial boundary between two contiguous phases as described by GIBBS[8]. We may consider two cases. In the first case the membrane is contained within the system and the reaction takes place within the system on both sides of the membrane. Here the vector coefficient $\mathbf{L}_{sv}$ must be invariant under a reversal of the axis normal to the membrane. This can occur only for $\mathbf{L}_{sv} = 0$; *i.e.*, there is again no coupling between the scalar and the vector phenomena. The second case consists of a system bounded by a membrane. The chemical reaction occurs within the system and acts, as it were, as a pump promoting the diffusion across the membrane boundary. Here we may adopt two points of view: one, more formal, which states that the reversal of the axis normal to the membrane moves the region the pump is situated (*i.e.*, where the reaction occurs) from the side of the "inward" normal to the membrane to the side of the "outward" normal. Thus under such a transformation the sign of $\mathbf{L}_{sv}$ changes. The other point of view states that in the system described diffusion loses its vectorial character since it can be oriented only in or out of the system. Both these views lead to the possibility of coupling between a scalar reaction and one-dimensional diffusion or transport.

Thus it appears that in an anisotropic system coupling between a metabolic reaction and transport is allowed. This possibility arises not because CURIE's principle "fails to hold", but because of the asymmetry of the system. CURIE's[9] interest was particularly in phenomena that occur because of the asymmetric properties of the system. Actually his proposition was stated in these terms: "Autrement dit, certains éléments de symétrie peuvent coexister avec certains phénomènes, mais il ne sont pas nécessaires. Ce qui est nécessaires, c'est que certains éléments de symétrie n'existent pas. C'est la dissymétrie qui crée le phénomène."

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Ionization of tyrosyl group in angiotensin II

The thermodynamical quantities for the ionization of tyrosyl group have been used as a basis for speculating on its functional behaviour on the tertiary structure of proteins[1]. Experiments on surface activity of polypeptides of the angiotensin group demonstrated the convenience of knowing beforehand the ionization constant of its tyrosyl group, its temperature dependence, and the thermodynamical parameters ΔF, ΔH, and ΔS in bulk solutions of angiotensin II.

The spectrophotometric method was used, employing a Beckman DK-2 ratio-recording spectrophotometer. Temperatures were measured directly inside the cells and were always within ± 0.1°, using a special circulation system from an external, thermostatically controlled, water bath. A stream of dry nitrogen was used to prevent water condensation on the cells.

The synthetic angiotensins II used were: (a) a mixture of 90% β-asp^1, val$_5$-angiotensin II and 10% α-asp^1, val$_5$-angiotensin II and (b) val$_5$-angiotensin II β-aspartylamide; both were kindly provided by Drs. R. Schwyzer, F. Gross and B. Iselin from Ciba Ltd. (Basle). 1 mole of acetic acid and 5 moles of water per mole of octapeptide were also present in these preparations. Deionized water freshly distilled in an all-glass apparatus was used throughout. Prior to use it was boiled to