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THERMODYNAMICS OF IRREVERSIBLE ELECTROCHEMICAL PHENOMENA

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Synopsis

A discussion from first principles is given of the energy and entropy laws in electrochemical systems. It is found that it is possible to clarify such controversial concepts as the form of the second law and the role of the electrochemical potential in the systems concerned.

1. *Introduction.* The correct formalism and interpretation of the thermodynamics of processes, in which electrical and chemical phenomena play a role, has been a controversial subject for a long time^{1) 2)}. Recently, however, in the "thermodynamics of irreversible processes" it has been possible to clear up this matter^{3) 4) 5) 6)}. It was shown that all relevant macroscopic equations can be written in the proper "local" form, *i.e.*, as differential equations between quantities which are continuous functions of space and time variables. The treatment permits the solution of problems such as writing down the first law for open systems⁷⁾ (thus giving a clear definition of the various energy terms) and including the electromagnetic field in the general thermodynamic scheme⁴⁾. It seems worthwhile to state and discuss a few general conclusions of physical importance, which can be drawn from the formalism.

2. *First law of thermodynamics for electrochemical systems.* In its local form the law of conservation of total energy can be written, for any system,

$$\partial u_{tot,v} / \partial t = - \operatorname{div} \mathbf{J}_u, \quad (1)$$

where $u_{tot,v}$ is the density of total energy, and \mathbf{J}_u the corresponding flow density.

We now consider a system consisting of charged particles placed in an electromagnetic field, with electric field strength \mathbf{E} and magnetic field strength \mathbf{H} . For simplicity we consider a system without electric and magnetic polarization *). The density of total energy is then given by

$$u_{tot,v} = u_v + \frac{1}{2}\rho \mathbf{v}^2 + \frac{1}{8\pi} (\mathbf{E}^2 + \mathbf{H}^2). \quad (2)$$

The three terms on the right-hand side of (2) are the density of internal energy, the density of macroscopic kinetic energy (ρ is the mass density, \mathbf{v} the barycentric velocity), and the localized energy of the (macroscopic) electromagnetic field.

For a non-viscous medium the energy flow density will be of the form

$$\mathbf{J}_u = u_v \mathbf{v} + \frac{1}{2}\rho \mathbf{v}^2 \mathbf{v} + p \mathbf{v} + \mathbf{J}_q + \mathbf{S}. \quad (3)$$

Here p is the thermostatic pressure, \mathbf{J}_q the heat flow and \mathbf{S} the flux of electromagnetic energy (Poynting vector). Thus equation (3) defines the heat flow \mathbf{J}_q .

By means of the law of conservation of momentum and the Maxwell field equations, one then deduces by straightforward transformations a balance equation for the internal energy u_v

$$\partial u_v / \partial t = -\text{div} (u_v \mathbf{v} + p \mathbf{v} + \mathbf{J}_q) + \mathbf{i} \cdot \{\mathbf{E} + c^{-1} \mathbf{v} \wedge \mathbf{H}\}, \quad (4)$$

(with \mathbf{i} the irreversible electrical current) or alternatively, introducing the internal energy per unit mass $u = u_v / \rho$, and substantial time derivatives $d/dt = \partial/\partial t + \mathbf{v} \cdot \text{grad}$,

$$du/dt = dq/dt - p dv/dt + \mathbf{i} \cdot \{\mathbf{E} + c^{-1} \mathbf{v} \wedge \mathbf{H}\} / \rho, \quad (5)$$

with $dq/dt = \rho^{-1} \text{div} \mathbf{J}_q$ the heat added per unit mass and $v = \rho^{-1}$ the specific volume of the system.

Equation (5) is the local form of the first law of thermodynamics for electrochemical systems without polarization. The last term of (5) represents the amount of electromagnetic energy irreversibly transformed into *internal* energy.

3. *Second law of thermodynamics for electrochemical systems.* In the absence of a (macroscopic) electromagnetic field the second law (Gibbs' equation) for a system of several (charged or uncharged) components is given by

$$T ds/dt = du/dt + p dv/dt - \sum_k \mu_k dc_k/dt, \quad (6)$$

*) These latter cases are treated in references 4) 5) 6).

where s is the entropy per unit mass, p the thermostatic pressure, μ_k the chemical potential, and c_k the mass fraction of component k .

If the system is placed in an electromagnetic field, equation (6) will be unchanged in agreement with statistical theories: the entropy s will still be the same function of the *internal* energy u , the specific volume v and the mass fractions c_k .

If one now calculates from (6) the entropy production for irreversible changes of the system using also (4) or (5) and the laws of conservation of mass, it is found that the thermodynamic "force" acting on the k th charged component is at uniform temperature given by

$$\mathbf{X}_k = e_k \{ \mathbf{E} + c^{-1} \mathbf{v} \wedge \mathbf{H} \} - \text{grad } \mu_k, \quad (7)$$

where e_k is the charge per unit mass of component k .

Writing for the electric field \mathbf{E}

$$\mathbf{E} = -\text{grad } \varphi - c^{-1} \partial \mathbf{A} / \partial t, \quad (8)$$

where φ and \mathbf{A} are the scalar and the vector potentials, and introducing the "electrochemical potential"

$$\tilde{\mu}_k = \mu_k + e_k \varphi, \quad (9)$$

equation (7) becomes

$$\mathbf{X}_k = e_k \{ c^{-1} \mathbf{v} \wedge \mathbf{H} - c^{-1} \partial \mathbf{A} / \partial t \} - \text{grad } \tilde{\mu}_k. \quad (10)$$

In particular for an observer moving with the center of mass velocity and at the stationary state, this reduces to

$$\mathbf{X}_k = -\text{grad } \tilde{\mu}_k. \quad (11)$$

For complete thermodynamical and mechanical equilibrium one therefore finds the well-known result that $\tilde{\mu}_k$ is uniform throughout the system. On the other hand according to (10) $-\text{grad } \tilde{\mu}_k$ is only part of the "force" acting on the k -th component in the most general case. This is in agreement with the fact that the electromagnetic and the thermodynamic contributions to this "force" cannot both be derived from a scalar potential. This point has already been stressed ⁴⁾ ⁵⁾ and seems to be a strong argument against the exclusive use of the electrochemical potential. A "force" $-\text{grad } \tilde{\mu}_k$ could for instance never explain eddy currents in a variable magnetic field, which are entirely due to the term $\partial \mathbf{A} / \partial t$. It is therefore also obvious that a separation of $\tilde{\mu}_k$ into a chemical and an electrical part has a real physical significance, since according

to electromagnetic theory the two potentials φ and \mathbf{A} are closely related (see equation 8).

4. *Alternative form of the second law.* Let us now introduce the energy \tilde{u} per unit mass of the system defined by

$$\tilde{u} = u + e\varphi, \quad (12)$$

where $e = \sum_k c_k e_k$ is the total charge per unit mass.

With (12) and (9), the definition of the electrochemical potential $\tilde{\mu}_k$, the second law (6) can be rewritten in the equivalent form

$$T ds/dt = d\tilde{u}/dt + p dv/dt - \sum_k \tilde{\mu}_k dc_k/dt - ed\varphi/dt. \quad (13)$$

This form of the second law has been used by two of us³⁾ in our second treatment of the thermodynamics of electrochemical systems. The thermodynamical "force" acting on the k th charged component deduced from (13) is still given by (7) or in special cases by (11), as should be expected, since equations (6) and (13) are completely equivalent. In fact, this second method has only been introduced as a formal means of obtaining equations containing μ_k and $e_k\varphi$ as far as possible only in the combination $\tilde{\mu}_k$. At the same time this mathematical transformation reveals that the entropy equation containing quantities \tilde{u} and $\tilde{\mu}_k$ also contains the new term $-e d\varphi/dt$.

5. *Conclusive remarks.* Recently K e m p²⁾, in opposition to the point of view of the present authors, claims to have derived correct results from the equation

$$T ds/dt = d\tilde{u}/dt + p dv/dt - \sum_k \tilde{\mu}_k dc_k/dt. \quad (14)$$

The energy appearing in (14) is clearly our \tilde{u} , although K e m p apparently confuses this quantity with our u , the internal energy^{*)}:

In connection with K e m p's point of view, we would like to make the following remarks.

a. It seems rather surprising that one should also arrive as K e m p states at the expressions (7) or (11) for the thermodynamic force from equation (14) which is equivalent neither with (6) nor with (13) (whatever the definition of K e m p's energy).

^{*)} In K e m p's own words: "the intrinsic energy u does by definition include the totality of the energy contained in the system, so that the addition of the term $e\varphi$ is tantamount to including the electrical energy *twice over*". Thus Kemp's u is our \tilde{u} and not our internal energy, which by definition (cf. equation (2)) does not contain the (macroscopic) electric (or electromagnetic) energy.

b. According to K e m p: "Since the change in u is quite independent of the path followed, it is quite correct to apply this equation (equation (6) or (14)) to any process whatever occurring in the system, reversible or irreversible". However, the application of Gibbs' equation to irreversible processes, *i.e.*, outside equilibrium, is, from a macroscopic point of view, an assumption only to be justified by statistical methods. In fact it has been shown that the use of Gibbs' equation is only a good approximation for "small" deviations from equilibrium ⁸).

c. Finally we would like to illustrate once more the importance of the term $-e d\varphi/dt$ in (13), as well as the paradoxical results arrived at with formula (14) (cf. also ³).

We introduce the free energy densities

$$f_v = u_v - Ts_v, \quad (15)$$

$$\tilde{f}_v = \tilde{u}_v - Ts_v, \quad (16)$$

$s_v = \varrho s$ being the density of entropy.

From (6), (13) and (14) we then deduce the corresponding formulae

$$df_v = -s_v dT + \sum_k \mu_k d\varrho_k, \quad (6a)$$

$$d\tilde{f}_v = -s_v dT + \sum_k \tilde{\mu}_k d\varrho_k + \varrho e d\varphi, \quad (13a)$$

$$d\tilde{f}_v = -s_v dT + \sum_k \tilde{\mu}_k d\varrho_k, \quad (14a)$$

where ϱ_k is the density of component k .

We now consider an isothermal reversible cycle. The potential is initially φ and the space charge e is zero. We first add to the unit of volume an amount $\Delta\varrho_k$ of the k -th charged component. Then according to (6a), (13a) and (14a) we find for the change in free energy Δf_v and $\Delta \tilde{f}_v$

$$\text{I. } \Delta f_v = \int_0^{\Delta\varrho_k} \mu_k d\varrho_k \quad (6a), \quad \Delta \tilde{f}_v = \int_0^{\Delta\varrho_k} (\mu_k + e_k \varphi) d\varrho_k \quad (13a),$$

$$\Delta \tilde{f}_v = \int_0^{\Delta\varrho_k} (\mu_k + e_k \varphi) d\varrho_k. \quad (14a)$$

The potential is now changed from φ to $\varphi + \Delta\varphi$ (either by moving the system into the field or by changing the external field).

The respective changes in free energy are

$$\text{II. } \Delta f_v = 0 \quad (6a), \quad \Delta \tilde{f}_v = e_k \Delta\varphi \Delta\varrho_k \quad (13a), \quad \Delta \tilde{f}_v = 0. \quad (14a)$$

The next step is to change the amount of the k -th component by $-\Delta\varrho_k$ so that

$$\text{III. } \Delta f_v = \int_{\Delta\varrho_k}^0 \mu_k d\varrho_k \quad (6a), \quad \Delta \tilde{f}_v = \int_{\Delta\varrho_k}^0 \{\mu_k + e_k(\varphi + \Delta\varphi)\} d\varrho_k \quad (13a),$$

$$\Delta \tilde{f}_v = \int_{\Delta\varrho_k}^0 \{\mu_k + e_k(\varphi + \Delta\varphi)\} d\varrho_k. \quad (14a)$$

Finally the potential is again brought to its initial value φ .
The corresponding changes in free energy are

$$\text{IV. } \Delta f_v = 0 \text{ (6a), } \Delta f_v^{\bar{x}} = 0 \text{ (13a), } \Delta f_v^{\bar{x}} = 0. \quad (14a)$$

For the total change in the whole cycle one therefore finds

$$\Delta f_v = 0 \text{ (6a), } \Delta f_v^{\bar{x}} = 0 \text{ (13a), } \Delta f_v^{\bar{x}} = -e_k \Delta \varphi \Delta \rho_k. \quad (14a)$$

Thus in conclusion it is clear that only formulae (6a) or (13a) lead to correct results.

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