

Thermodynamics of Irreversible Electrochemical Processes

IN a recent paper, DeGroot and Tolhoek¹ have attempted, by means of an application of the thermodynamics of irreversible processes, to extend Guggenheim's² ideas concerning the activities of ions and the electrical potential difference between two phases. To this end they have considered a medium showing a bulk motion and in which chemical reactions and flows of energy, matter and electricity are occurring; two different mathematical treatments of this system are given.

As a result of their second treatment, these authors deduce that electrical potential differences are (in principle) measurable apart from differences in ionic chemical potentials, provided that an electrical space charge is present, that is, in nearly insulating media but not in media showing any appreciable degree of electrical conductivity. This conclusion is obtained from the fact that the thermodynamic equations of this method of treatment, provided that there is no space charge, contain the chemical potential μ_i of the i th ionic species and the electrical term $e_i\phi$ (where ϕ is the electrical potential of the medium and e_i the ionic charge) only in the combination $\bar{\mu}_i = \mu_i + e_i\phi$, that is, as the electrochemical potential of i ; if a space charge exists, however, the equations contain additional terms involving ϕ but not μ_i .

Now both the second and first methods of treatment involve the use of the following thermostatic equation for the change in intrinsic energy of a system:

$$dU = TdS - pdV + \sum_i \mu_i dn_i, \quad (1)$$

where the symbols have their usual thermodynamic meaning. Since the change in U is quite independent of the path followed, it is quite correct to apply this equation to any process whatever occurring in the system, reversible or irreversible. However, it is subject to the restriction that the system does no specialized work, that is, no work which cannot be included in the second and third terms on the right of (1). It is therefore quite erroneous to apply it to a system containing electrical charges and potentials, which can perform electrical work.

It is readily ascertained from thermostatic first principles that, when a system can perform specialized work, a term representing the maximum specialized work that it is capable of performing under reversible conditions must be added to (1). The equation is then still applicable to an irreversible change, for the same reason as before; but it must be noted that the specialized work term is then not equal to the specialized work which has actually been performed in the process. In the case of electrical work, the correct form of the equation is obtained by replacing the chemical potentials μ_i in (1) by the electrochemical potentials $\bar{\mu}_i$ as defined above:

$$dU = TdS - pdV + \sum_i \bar{\mu}_i dn_i. \quad (2)$$

It is this expression, not (1), which must be taken as the basis of the thermodynamic treatment of an irreversible electrochemical process, although the erroneous use of (1) has apparently been in vogue for a number of years³.

If now the first method of DeGroot and Tolhoek is carried through using (2) in place of (1) as the only modification, it will be found that the equations finally obtained do indeed contain μ_i and ϕ only in

the combination $\bar{\mu}_i$; in particular, the thermodynamic force acting on the i th ion is given by:

$$X_i = F_i - T \text{grad}(\bar{\mu}_i/T), \quad (3)$$

where F_i is the non-electrical external force acting on the ion (the effect of external electrical forces is already included in the ϕ term of $\bar{\mu}_i$). Equation (3) leads to the usual and well-known results when applied in any particular problem. Thus from this first treatment alone it is seen that no thermodynamic measurement can ever determine separately either the electrical or non-electrical part of $\bar{\mu}_i$, no matter whether or not a space charge exists in the system.

The second method of DeGroot and Tolhoek can also be carried through with the same modification, but then some rather peculiar equations result. In this method, instead of the intrinsic energy U , used in the first case, a quantity \bar{U} is employed; this is said to be the "intrinsic energy, including electrical energy", and is defined as:

$$\bar{U} = U + e\phi, \quad (4)$$

where e is the total electric charge in the system. However, the intrinsic energy U does, by definition, include the totality of the energy contained in the system, so the addition of the term $e\phi$ is tantamount to including the electrical energy twice over. Thus \bar{U} as defined by (4) is a new thermodynamic function which might conceivably have some particular applications, but which certainly cannot be used in place of U in equations (1) and (2).

The whole of this second method of treatment must therefore be considered invalid. This leaves us with the conclusion, drawn from the revised first treatment, that thermodynamic measurements on any system will never give us anything other than the electrochemical potentials $\bar{\mu}_i$ of the ionic species concerned. This is in complete agreement with Guggenheim's original conclusions. The question of whether or not the electrical and non-electrical parts into which the $\bar{\mu}_i$ may be formally split have any real physical significance is, however, quite another matter and cannot be discussed here.

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¹ DeGroot, S. R., and Tolhoek, H. A., *Proc. K. Ned. Akad. Wet.*, **54**, B, 42 (1951).

² Guggenheim, E. A., *J. Phys. Chem.*, **33**, 842 (1929); **34**, 1540 (1930).

³ DeGroot, S. R., "Thermodynamics of Irreversible Processes" (Amsterdam, 1951). Denbigh, K. G., "The Thermodynamics of the Steady State" (London, 1951).

Thermal Decomposition of Normal Paraffins

DURING the past two years, four papers dealing with the thermal decomposition of normal paraffin hydrocarbons by Sir Cyril Hinshelwood and his collaborators have been published in the *Proceedings of the Royal Society*. The work described in them is based upon the following assumptions: (1) that primary decomposition, in the simplest case, involves the formation of methane, and the corresponding olefine; (2) that reaction is inhibited by the addition of nitric oxide to the paraffin, and may therefore be assumed to be initiated by free radicals, and carried forward by a chain mechanism; (3) that the rate of the process mentioned under (1) can be measured by observing the rate of change of pressure at constant volume and temperature.