Letter to the Editor

A Note on the Use of the Word 'Reversible'

A. A. SAAMAN and P. BERGVELD

Department of Electrical Engineering, Twente University of Technology, P.O. Box 217, 7500 AE Enschede (The Netherlands)

(Received December 19, 1984, accepted February 19, 1985)

Introduction

As an important requirement for chemical sensors it is often stated that the sensor must behave 'reversibly'. 'Irreversible' sensor operation is generally considered a drawback for its application, although this need not necessarily be so. We would like to point out that the word 'reversible' has several meanings and may therefore only be used with caution.

1 Thermodynamic definition

The word 'reversible' has a thermodynamic origin. When a system is brought from an initial equilibrium state S_i to a final equilibrium state S_f , the process is said to be 'reversible' if the continuum of intermediate states S_{i+1} , S_{i+2} , ..., S_{f-2} , S_{f-1} are equilibrium states too. For such a thermodynamically 'reversible' process

$$(TdS)_{\text{rev process}} = dq \quad (1a)$$

where T = absolute temperature, dS = infinitesimal entropy change of the system and dq = infinitesimal amount of heat supplied to the system. For a thermodynamically 'irreversible' process always

$$(TdS)_{\text{irr process}} > dq \quad (1b)$$

which reflects the key concept of entropy production [3].

2 Electrochemical definition

Electrochemists have long been aware of the problems that arise when using the concept of 'reversibility' [2]. They classify electron transfer reactions at electrodes as 'reversible', 'quasi-reversible' or 'irreversible', depending on the magnitude of the standard heterogeneous rate constant k_{sh} and

the time behaviour of the applied signal that is driving the system out of equilibrium. In this case the use of the word 'reversible' is related to the concept of 'reversibility' as discussed in Section 1, since for 'quasi-reversible' and 'irreversible' behaviour the rate of entropy production is inversely proportional to the standard heterogeneous rate constant

$$\text{entropy production/unit time} \sim \frac{1}{k_{\text{sh}}} \quad (2)$$

So, for a reaction with $k_{\text{sh}} \rightarrow \infty$ no entropy production occurs and the process is indeed thermodynamically 'reversible'. It is to be noted that the standard heterogeneous rate constant usually emerges in a kinetic, not in a thermodynamic discussion of electrode reactions.

3 Chemical definition

There is also a much simpler concept of 'reversibility' used by chemists. A reaction that may proceed from left to right in the reaction equation as well as in the opposite direction is also often named 'reversible'. As a simple example, one may think of the reaction of molecular oxygen (O_2) with haemoglobin (Hb) to form oxyhaemoglobin (HbO_2)

The reaction from left to right proceeds in the lungs, the reverse reaction (the release of oxygen) proceeds elsewhere in the body. The oxygen is said to be 'reversibly' bonded to the haemoglobin. Many more examples of reactions that are 'reversible' in this sense can be given. This concept of chemical 'reversibility' is not necessarily related to the concept of 'reversibility' as discussed in Sections 1 and 2, i.e., a chemically 'reversible' process may be thermodynamically 'irreversible' as equilibrium conditions may not be maintained at each stage of the process.

4 The 'reversibility' of chemical sensors

In papers dealing with chemical sensors, usually attention is paid to the 'reversibility' of the chemical sensing reaction. Generally 'reversibility' is then to be understood in the sense discussed in Section 3. For instance, a pH-sensitive ISFET is a 'reversible' sensor, because the sensing reaction

proceeds equally well from left to right as in the reverse direction, but it is not certain whether the system is at equilibrium at each stage of the process.

There is also a tendency, however, towards a further extension of the concept of 'reversibility'. Consider the following example [1]

“Pd MOS structures have also been used to monitor NH_3 and H_2S () In the case of H_2S it was observed that in an inert atmosphere (argon) the surface was poisoned () Introduction of air cured the structures again We saw, probably, a reversible sulfur poisoning of the catalytic surface ”

Also in this case ‘reversibility’ is a keyword describing the process It is used in a wider sense than discussed in Sections 1, 2 and 3, as it is meant to indicate that the sensor can be restored into a condition that resembles its initial state, not taking into account, however, the chemical transformation of the sulfur-bearing species from H_2S into SO_2

Summarizing, a line of reasoning can be discerned in which the concept of ‘reversibility’ is subjected to gradual changes with increasing neglect of its thermodynamic origin Originally, ‘reversibility’ is a key concept in chemical equilibrium thermodynamics The electrochemical concept of ‘reversibility’ is still directly related to this thermodynamic origin The much simpler and often implicitly used concept of chemical ‘reversibility’ gives up this thermodynamic origin Finally, for chemical sensors a kind of operational ‘reversibility’ is defined when after a sensor reaction relatively simple chemical manipulations restore the sensor (nearly) perfectly to its original physico-chemical state

Although it is not desirable to have a word with four different meanings, there is no objection against its use, provided it is made unambiguously clear as to which meaning is appropriate in the context used

Acknowledgements

The authors are indebted to Professor Dr M J Sparnaay and Dr A van Silfhout of the solid state physics department for their continuous and stimulating interest in these studies

These investigations in the programme of the Foundation for Fundamental Research on Matter (FOM) have been supported by the Foundation for Technical Research (STW), future Technical Science Branch/Division of the Netherlands Organization for the Advancement of Pure Research (ZWO)

References

- 1 I Lundstrom, Hydrogen sensitive MOS-structures Part 1 Principles and applications, *Sensors and Actuators*, 1 (1981) 403 - 425
- 2 Further discussion may be found in A J Bard and L B Faulkner, *Electrochemical Methods*, John Wiley & Sons, New York, 1980, pp 44 - 47
- 3 I Prigogine, *Thermodynamics of Irreversible Processes*, Interscience Publishers, New York, 1955