

COMMENTS

Comment on "Entropy Production and the Ostwald Step Rule"

Sir: Ostwald's step rule teaches that crystallization from solution commonly proceeds via thermodynamically unstable phases. This means that a process is described in which successive phases are formed as a function of time. Ostwald's step rule applies to a situation that is far from steady state. Concentrations change as a function of a time.

The paper by Casey studies a consecutive reaction scheme, by solving its kinetic equation with the steady-state assumption, a condition where Ostwald's step rule has no relevance.

Casey shows that if the steady condition is satisfied all processes occur with identical net overall rate of entropy production. This is a well-known result from irreversible thermodynamics, as is the result not demonstrated by Casey that at steady state entropy production is a minimum.¹

Casey also claims that an earlier paper² contains an error. In fact relations 13 and 18 of ref 2 are identical to Casey's expression 15 and 18. So mathematically the results of both papers do not

differ. However, in ref 2 an extra relation, valid under steady-state conditions, is used, between the rate constant of the overall indirect process and the rate constants of the individual steps. One then finds that under stationary conditions entropy production in the indirect process becomes less than in the direct process, if one supposes that the rate constant of the direct process equals that of the individual steps in the indirect process.

So Casey's conclusion, that a difference in overall reaction rate is required to find differences in entropy production between reaction taking place with multiple reaction paths, is correct if the steady-state condition is satisfied. However, this result is already contained in formula 18 derived in ref 2. Since the Ostwald step rule applies to non-steady-state conditions, the postulate proposed in the earlier paper,² that the rate of entropy condition can become less if the number of intermediate steps increases, cannot be considered to have been rejected. The physical picture explaining this behavior is that the reaction by using intermediate steps proceeds closest to reversible conditions, which minimizes entropy production.

Koninklijke/Shell Laboratorium
Shell Research B.V.
1003AA Amsterdam, The Netherlands

R. A. van Santen

(1) See Prigogine, I. *Etude thermodynamique des phenomenes irreversibles*; Desver: Liege, 1947.

(2) van Santen, R. A. *J. Phys. Chem.* 1984, 88, 5768.

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