Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Quantum Mechanical Aspects of Order Evolution Processes - The Case of Nanoporous Aluminum Oxide - Supplementary

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Supplementary

derivation of eq. 1

Our considerations are based on the assumption of an isothermal process. Hence, our model is based on the assumption of a constant temperature. This choice is also directly comprehensible as the extent of the electric field as a driving force should be much higher according to the high voltages used which are effective only in a short distance from the anode. Hence, the field strength is very high in the regarded volume.

The first time derivative of entropy production can be divided into two parts to create a coupling with the electrical current density $j = \frac{i}{A}$[1]

$$T\frac{d_{in}^2 S}{dt^2} = \frac{d}{dt}\frac{d_{in}S}{dt}\frac{dQ}{dQ} = \frac{d}{dQ}\frac{d_{in}S}{dt}\frac{dQ}{dt} = \Pi A j \tag{1}$$

The factor $\Pi = \frac{d}{dQ}\frac{d_{in}S}{dt}$ can be transformed into $\Pi_{P'} = \frac{d}{dP'}\frac{d_{in}S}{dt}$ where P' is the electric power given by $P' = EjV$ (E...electric field, j...current density, V...volume). As $P' = EjV$, it follows that

$$\frac{dP'}{dQ} = \frac{V}{A}\left[\frac{dQ}{dt}\frac{dE}{dQ} + \frac{d}{dQ}\frac{dQ}{dt}E\right] = 2\frac{V}{A}\frac{dE}{dt} \tag{2}$$

where V and A are considered independent on Q. Therefore,

$$A\Pi = A\frac{dP}{dQ}\Pi_P = 2V\frac{dE}{dt}\Pi_{P'} \tag{3}$$

and

$$T\frac{d_{in}^2 S}{dt^2} = 2V\frac{dE}{dt}\Pi_{P'} j \tag{4}$$

with the entropy production

$$T\frac{d_{in}S}{dt} = 2V\int \frac{dE}{dt}\Pi_{P'}jdt = 2V\int \Pi_{P'}jdE > 0 \tag{5}$$

which is assumed true for all non-equilibrium processes. It follows therefore for a stationary process with $\Pi_{P'} = 0$, that

$$T\frac{d_{in}S}{dt} = 2VC > 0 \tag{6}$$

where C is a constant term. The process of PAOX-formation is driven by the electric field. The net amount heat between bath and system is 0, which is due to the assumed instantaneous compensation of the heat which evolves from the process by the attached cryostat. Nevertheless, the amount of heat produced by the process is referred to an external entropy production $\frac{d_{ex}S}{dt}$. At the same time, in case of a steady state,[2] it has to be equal to the negative of internal entropy production $\frac{d_{in}S}{dt}$, i.e.

$$\frac{d_{ex}S}{dt} = -\frac{d_{in}S}{dt} \tag{7}$$

Using the common eqs. $G = U + pV - TS$, $H = U + pV$ and $G = H - TS$, it follows that

$$\frac{dG}{dt} - \frac{dH}{dt} = -TdS = -\frac{d_{in}S}{dt} - \frac{d_{ex}S}{dt} \tag{8}$$

in case of a constant temperature. Associating $\frac{d_{ex}S}{dt}$ to $\frac{dH}{dt}$, the main eq. $-\frac{dG}{dt} = T\frac{d_{in}S}{dt} = 2V\int_E j\Pi_{P'}dE$ follows.

relationship between current density and electric field strength at extremum entropy production

The reciprocal of the total differential of P' is given by

$$\begin{aligned}\frac{d}{dP'} &= \left(\frac{d}{dP'}\right)_E + \left(\frac{d}{dP'}\right)_j \\ &= \frac{1}{E}\frac{\delta}{\delta j} + \frac{1}{j}\frac{\delta}{\delta E}\end{aligned} \tag{9}$$

Owning an extremum entropy production leads to

$$\Pi_{P'} = \frac{d}{dP'}\frac{d_{in}S}{dt} = 0 \tag{10}$$

which leads to

$$T\frac{d_{in}S}{dt} = 2V\int 0dE = 2VC > 0 \tag{11}$$

in case of an indetermined integral owning the constant C. In the vicinity of this extremum it follows that

$$\frac{d}{dP'}\frac{d_{in}S}{dt} = \tau\left(t, P\right) \tag{12}$$

where $\tau\left(t, P'\right)$ describes small differences from the actual extremum which implies the condition

$$\begin{aligned}|\frac{1}{j}\frac{\delta}{\delta E}| &= |\frac{1}{E}\frac{\delta}{\delta j}| \\ |\frac{E}{j}| &= |\frac{\delta E}{\delta j}|\end{aligned} \tag{13}$$

Thus, at the extremum mentioned, the ratio between E and j stays constant. In contrast, around the extremum the ratio fluctuates with $\tau\left(t, P'\right)$, i.e.

$$|\frac{E}{j}| = |\tau'\left(t, P'\right) - \frac{\delta E}{\delta j}| \tag{14}$$

with $\tau'\left(t, P'\right) = E\frac{\delta E}{\delta\frac{d_{in}S}{dt}}\tau\left(t, P'\right)$

Having a constant ratio E and j accounts for the fact that both functions directly reflect on each other. If therefore E and j have this kind of linear relation, E reflects the properties of j linearely. Hence, $E = C * j$, which is Ohm's law.

Gibb's enthalpy minimization condition

G is described by

$$G = G_0 + \frac{\gamma}{r} \tag{15}$$

where γ is the surface tension of the pore and r its radius. Considering a time dependent process, it follows that

$$\frac{dG}{dt} = \frac{dH}{dt} - T\frac{d_{in}S}{dt} \tag{16}$$

The internal energy change in the regarded system is in general defined by

$$dU = TdS - pdV + \mu dn = Td_{in}S + Td_{ex}S \tag{17}$$

According to $H = U + pV$ and $dH = dU + VdP + pdV$ it follows that

$$dH = Td_{in}S + Td_{en}S \tag{18}$$

Hence, in case of a steady state process ($Td_{in}S = -Td_{ex}S > 0^2$) it follows that $dH = 0$. In case of equal packing densities of equal sized packings and non-equal sized packings the need to lower the enthalpy of the system leads therefore to a homogeneous size distribution. Therefore, the development of entropy production sets a fundamental limit to G (and vice versa) as

$$-\frac{dG}{dt} = T\frac{d_{in}S}{dt} \tag{19}$$

with $dG < 0$ and $T\frac{d_{in}S}{dt} > 0$.

References

(1) Heinschke, S.; Schneider, J. J. On the Prediction of Well Ordered Porous Anodic Alumina Films. *J. Phys. Chem. C* **2020**, *124*, 11913–11921.

(2) Endres, R. G. Entropy production selects nonequilibrium states in multistable systems. *Scientific Reports* **2017**, *7*, 14437.