

Figure 7 demonstrates that the unique correlation is only possible for very small differences between the meshes.

### Conclusion

In a thin rectangular channel, an expanded structure is a fairly less efficient turbulence promoter of the wall-to-liquid mass transfer; its promoting effect depends on the mesh orientation with respect to the flow but is much smaller than the effect of a SU-grid which appears less efficient than previously reported. For not very different meshes of expanded materials it is possible to obtain a unique mass-transfer correlation if the promoting effect is included in a parameter. However, caution must be applied to a generalization of the beneficial use of this parameter.

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### LIST OF SYMBOLS

$A, A_C, A_L$	mean aperture of the mesh
$A_e$	cathodic surface area
$a_s$	specific surface area of the promoter
$C^*$	bulk ferricyanide concentration
$D$	diffusion coefficient
$d_h = \frac{2lh}{l+h}$	hydraulic diameter of the channel
$e_a$	apparent thickness of the expanded structure
$h$	thickness of the channel
$I_L$	limiting diffusion current
$k_d$	overall mass-transfer coefficient
$l$	channel width
$L$	channel length
$L_T$	length of the transfer surface
$\Delta P$	pressure drop
$r$	apparent mean roughness of a pore
$R = 2R_h$	equivalent pore radius

$Re = \frac{\bar{v}d_h}{\nu}$	Reynolds number based on $d_h$
$Re^* = \frac{\bar{v}R_h}{\nu}$	Reynolds number based on $R_h$
$Re_h = \frac{\bar{v}h}{\nu}$	Reynolds number based on $h$
$R_h = \frac{\bar{\epsilon}}{a_s(1-\bar{\epsilon})}$	hydraulic radius
$Sc = \nu/D$	Schmidt number
$Sh = \frac{\bar{k}_d d_h}{D}$	Sherwood number based on $d_h$
$Sh^* = \frac{\bar{k}_d R_h}{D}$	Sherwood number based on $R_h$
$\bar{v}$	superficial velocity in the empty channel
$\bar{\epsilon}$	mean porosity of the promoter
$\nu$	kinematic viscosity
$\nu_e$	number of electrons in the electrochemical reaction
$\rho$	density of the liquid

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## Technical Notes



## Response of Systems with Gaussian or Exponential Energy Distributions

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Albery and co-authors (1) have recently published an interesting treatment of the small-signal ac response of semi-conductors to an ac modulated light source. To analyze the frequency response results of this powerful technique, they assume a Gaussian distribution of free energies and obtain expressions for frequency-dependent real and imaginary response functions. In addition, in earlier work (2) they applied the same Gaussian distribution assumption to the area of dispersed kinetics in heterogeneous systems, leading to time-concentration and time-current transient response results which were compared with experiment. In this note, I point out earlier energy-distribution-assumption work in the electrochemistry and dielectric areas relevant to the above papers but not cited

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there and indicate the greater generality of some of the prior work.

The assumption of a Gaussian distribution of the logarithm of relaxation times (inverse reaction rate constants) goes back to at least the 1913 work of Wagner (3), and perhaps earlier. For a thermally activated situation, such a distribution may be directly associated with a Gaussian dispersion of the Gibbs free energy of activation, involving either a distribution of entropy or of enthalpy or both (4-8). Such a Gaussian free energy distribution was probably first suggested and discussed in some detail by Kauzmann (4) in 1942. In the usual case, where the enthalpy is distributed, one speaks of a distribution of activation energies (DAE), with such a distribution associated with physical conditions such as a dispersion of reaction barrier heights,

trap energies, hopping distances, waiting times, etc. Since the pioneering work of Kauzmann, a great many Gaussian distribution of activation energies (GDAE) treatments have appeared; several are cited in Ref. (8) and (9).

One theoretical defect of many of the earlier treatments, including those of Albery and his co-workers, is the assumption that the range of the Gaussian distributed variable, which we shall hereafter term the activation energy,  $E$ , extends from minus to plus infinity. But in real systems such energies must lie between a minimum energy, possibly as small as zero but not negative, and a maximum positive energy, which must be less than infinite for any actual situation (5-10). When the distribution is narrow enough and/or the mean activation energy is sufficiently far from zero, the infinite range assumption makes no practical difference since the probability density is then vanishingly small outside the physically possible range of  $E$ . When these conditions are not met, however, finite and non-negative range limits of  $E/RT$  must be employed, thereby introducing one or two new parameters into the treatment. These considerations are even more important for those DAE's which decrease less rapidly than Gaussian, such as the exponential DAE (EDAE) (6-10).

First, consider transient response. An early, and perhaps the first, thorough analytical DAE treatment was that of Macdonald (6), which involved a type of EDAE. Unlike the later work of Albery *et al.*, it took account of the finite range of  $E$  and included the possibilities of dispersion of the enthalpy, the entropy, or both. It was based on a probability density made up of two joined exponential parts with possibly different strength parameters. It led to closed-form transient response involving joined regions of possibly different log-log slopes,  $t^{-m}$  and  $t^{-n}$ , with these exponents independent of time. Such response, with a single exponent (one constant slope) or with two different ones, is very frequently found experimentally and often extends over five or more decades in time.

On the other hand, the GDAE transient response solution of Albery *et al.* (2) can only be expressed in integral form and does not lead to transient response with a single, or even two slopes. Instead, it predicts time response more or less of the form  $t^{-p}$ , where  $p$  continuously increases with time, behavior also similar to that of stretched exponential response (9). In some situations there may be a possibility of confusion between the transient predictions of the EDAE and the GDAE, or even the stretched exponential. When  $m$  and  $n$  are different, there is a transition region in EDAE response from a slope parameter of  $m$  to one of  $n$ . This varying slope, curved region can extend over two or more decades in normalized current and might be confused with similar GDAE response unless the measurement time span extends well into the constant-slope  $n$  and  $m$  straight-line regions on either side of the transition.

A detailed EDAE frequency response model has been published which uses the same probability density function mentioned above (7, 8). It can lead to wide regions of frequency where the admittance or impedance vary as  $\omega^{\pm m}$  and/or  $\omega^{\pm n}$ , where  $\omega$  is the angular frequency and again  $m$  and  $n$  are frequency-independent constant slopes in a log-(immittance) vs. a log(frequency) plot. Such behavior, say with  $0 < m = n < 1$ , often called constant phase angle or constant phase element (CPE) response (7-13), is exceedingly common in both electrolyte and dielectric experimental results. Further, because of its provision of two adjustable (slope) constants and its restriction to a physically realizable range of  $E$ , the EDAE can lead to arcs in the complex frequency plane (imaginary part of an immittance plotted against the real part) which are either symmetric or asymmetric, as found experimentally. In fact, it has been shown (7, 8) that such EDAE response can fit very well nearly all prior empirical and theoretical frequency response functions, such as those of Cole and Cole (14) and Davidson and Cole (15). Thus it should also fit all the data that have been fitted by them. Further, unlike most other theories, it yields specific predictions for the temperature dependence of the slope parameters, predictions which

are usually in agreement with experiment for both conducting and dielectric systems (7, 8).

By contrast, the GDAE frequency response model of Albery *et al.* (1), leads to only symmetric response in the complex plane and to no finite-length regions of constant slope in log-log plots. An earlier GDAE frequency response model of the present author (8), however, involves somewhat more general assumptions than that of Albery *et al.* and uses a finite range of  $E$ . Although it can lead to both symmetric and asymmetric complex plane response, it also does not yield any regions of constant slope except those present at limiting high and low frequencies because of the absence of relaxation times beyond these limits (6, 7, 16). The Albery model does not directly yield an immittance but instead involves a transfer function between a light input and the resulting photocurrent. Nevertheless, it turns out that when the earlier GDAE treatment (8) is specialized so as to involve the same assumptions as those of Albery *et al.*, its normalized immittance and Albery's normalized response are given by the same equation, and thus corresponding complex plane plots presented in the two publications are also essentially identical.

In the frequency domain, both EDAE and GDAE response functions are presented only as integrals and thus require numerical evaluation. Perhaps for this reason, Albery *et al.* do not attempt to fit their experimental results to their GDAE model by least squares. By contrast, the EDAE and GDAE models of the present author have been incorporated, along with many other distributed circuit elements (10, 12), in a wide variety of equivalent circuits whose parameters may be estimated by nonlinear least squares (or by robust regression) fitting (17) of either frequency dependent data (complex data fitting) or (real) time domain data.

The very general computer program which carries out such fitting is available from the author. It provides a wide variety of weighting choices, including an automatic optimization procedure for best weighting of real and imaginary parts, and also contains a robust regression fitting approach, often superior to least squares fitting. The program has been used to determine whether the GDAE or the EDAE yielded the best fit for specific experimental data (8). Many important material/electrode parameters may be estimated from such fitting to help determine the best characterization of the system (7-9).

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