

# Mass Transfer at Heterogeneous Surfaces

by

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## **Abstract**

It is often necessary to predict rates of mass transfer to or from “heterogeneous” surfaces which contain discrete “active” areas, having characteristic dimensions (size, spacing) comparable to the thickness of a concentration boundary layer. Examples of heterogeneous surfaces include porous membranes, dispersed catalysts and various electrochemical systems. Although it is expected that mass transfer coefficients for such surfaces are lower than for uniformly active surfaces under the same conditions, the theoretical and experimental information available for predicting mass transfer rates for heterogeneous surfaces is limited.

The customary approach in modeling heterogeneous systems has been to apply a stagnant film approximation to the fluid phase adjacent to a representative active site. The validity of this approach was tested theoretically through analysis of a pair of two-dimensional model problems with spatially periodic active areas. Each involved laminar flow in the fully developed mass transfer region located far downstream from the point at which contacting begins. In both the falling film and cylindrical tube geometries considered, a key parameter was the Peclet number ( $Pe$ ) based on the film thickness or tube diameter and maximum velocity. Flow tangential to the surface had the effect of smoothing concentration variations between neighboring active sites, making the surface behave as if it were homogeneous. This convective enhancement of mass transfer became substantial in either case when  $Pe$  was increased beyond  $\sim 10$ - $10^2$ , depending on the site spacing and fraction of active area.

In a further investigation of the effects of surface heterogeneity on mass transfer, limiting current measurements were made at partially masked platinum electrodes in a rotating disk apparatus. These electrochemical measurements enabled the experimental determination of mass transfer coefficients in a fully three-dimensional system with known hydrodynamics. The electrode surfaces, which were fabricated with photolithography techniques used in microelectronics processing, encompassed a wider range of active area fractions, active site dimensions and active site distributions that was previously available. Several regular and random distributions, with active area fractions ranging from 0.001 to 1.0 and active site dimensions ranging from 0.0025 cm to 0.040 cm were considered. The predominant effects noted were an increase in mass transfer rates with increasing active area fractions, and increased mass transfer rates with decreasing ratios of site spacing to boundary layer thickness. These observations were in agreement with the trends predicted by the two theoretical convective-diffusion models.

Moreover, the rates of transport measured at the partially masked electrodes were always underpredicted by an equivalent stagnant film model. This result is again in qualitative agreement with the previous theoretical analyses when considered in view of the Pe values estimated for the experimental conditions, which always exceeded  $10^3$ . Measured rates of transport did not exhibit any marked dependence on the particular details of surface topology for a given active area fraction.

These results are relevant to the general problem of estimating average mass transfer coefficients at heterogeneous surfaces. Convective interactions between neighboring active areas may make a surface appear more homogeneous than suggested by its active area fraction. Because these effects become important at magnitudes of the local Peclet number which are representative of those occurring in practice, caution is advised in applying the results of stagnant film analyses.

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