

LETTERS TO THE EDITOR

To the Editor:

In "Determination of Growth Kinetics of Polyhedral Crystals" [*AIChE J.*, **28**, 697 (1982)] Wey and Jagannathan have discussed a number of aspects of solubility and supersaturation in relation to the interpretation of crystal growth rate data. The objective of this note is to clarify some of the important issues which they have raised.

Solubility is an equilibrium property and the assertion, of Wey and Jagannathan that it can have different values for different crystallographic planes is incorrect. A simple illustration of this fact is achieved by considering a solution in contact with a single crystal of the solute. Physicochemical equilibrium between these two bulk phases occurs when

$$\mu_{\text{solid}} = \mu_{\text{solute}} \quad (1)$$

The solution of this equation gives a unique solubility value for the substance under given conditions and is independent of the morphology of the crystal. At equilibrium the chemical potential of any surface must equal that of both bulk phases. If this were not the case then solute species would flow either to or from the surface (i.e. growth or dissolution) until equilibrium was established. A proof of this thermodynamic argument can be found in the papers of Willard Gibbs (1948) and is discussed by Defay et al (1966).

Different crystal faces will, indeed, have different α -factors. This occurs, however, not due to different solubilities, but because of different lateral bonding interactions in the surfaces. It is the balance between these lateral interactions and the surface disorder which determines the roughness of the interface.

If a solution is supersaturated the surface of a crystal will grow and, as discussed by Davey (1982), the α -factor now becomes important in determining the operative growth mechanism because it is a measure of the surface roughness and hence the population of kink sites. In terms of chemical potentials, in a supersaturated solution

$$\mu_{\text{solid}} < \mu_{\text{surface}} < \mu_{\text{solute}} \quad (2)$$

and hence a bulk and surface supersaturation can be defined, viz:

$$\sigma \equiv (\mu_{\text{solute}} - \mu_{\text{solid}})/RT$$

$$\sigma_s = (\mu_{\text{surface}} - \mu_{\text{solid}})/RT$$

For many systems a measure of the bulk supersaturation can be obtained from the difference between the actual concentration and the equilibrium value (i.e. ΔC). The surface supersaturation is an inhomogeneous quan-

tity and its evaluation is an important part of growth theories as discussed by Garside (1977).

For surface controlled growth processes the growth rate may be a linear, quadratic or exponential function of supersaturation. Mass transfer controlled processes are identified by studying the influence of solution flow on the growth rate as illustrated by Mullin et al (1970).

Since crystallographically different faces will have different α -factors it is not surprising that different kinetic expressions exist for each crystal face as indeed is the case for $(\text{NH}_4)_2\text{SO}_4$ where Mullin et al (1970) found first order kinetics for the (100) face and second order for the (001) face.

Wey and Jagannathan's concern about the data of Mullin et al (1970) centres on the fact that for only a 0.21% decrease in the equilibrium solubility the kinetic order of the (100) face changes from one to two. This deserves closer attention since the original data of Mullin et al were obtained by measurement of undercooling and subsequent calculation of supersaturation. In this respect a 0.21% change in equilibrium solubility represents an error of 0.6°C in temperature measurement which is well above their quoted accuracy of $\pm 0.1^\circ\text{C}$. There thus seems to be no reason to question the original conclusion of Mullin et al (1970) that the interfacial kinetics for the (100) face are linear.

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Notation

μ_{solid}	= chemical potential of solute in solid phase
μ_{solute}	= chemical potential of solute in solution phase
μ_{surface}	= chemical potential of solute in surface phase
σ	= bulk supersaturation
σ_s	= surface supersaturation

LITERATURE CITED

- Davey, R. J., in *Current Topics in Materials Science*, Vol. 8, Chpt. 6, North Holland, Amsterdam. Ed. E. Kaldis (1982).
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Garside, J., in *Current Topics in Materials Science*,

Vol. 2, p. 483, North Holland, Amsterdam. Ed. E. Kaldis (1977).

- Gibbs, J. W., "The Collected Works of J. Willard Gibbs" Vol. I—Thermodynamics, Yale University Press, New Haven, (1948).
Mullin, J. W., Chakraborty, M. and Mehta, K., *J. Appl. Chem.*, **20**, (1970), 367.
Wey, J. A. and Jagannathan, R., *AIChE J.*, **28**, (1982) 697.

To the Editor:

Herskowitz and Smith have recently published a review of trickle-bed reactors. The stated purpose of their review was to summarize recent developments in interphase mass transfer, partial catalyst wetting and reactor design. Although the review cites 110 papers and one of my papers was referenced, the six papers listed below were not mentioned. These papers are most relevant to the subject of trickle-bed reactors and should be of interest to your readers.

1. Sylvester, Nicholas D. and Punya Pitayagulsarn, "Effect of Transport Processes on Conversion in a Trickle-Bed Reactor," *AIChE J.*, **19**, 3 (May 1973), pp. 640-644.
2. Sylvester, Nicholas D. and Punya Pitayagulsarn, "Effect of Catalyst Wetting on Conversion in a Trickle Bed Reactor," *The Canadian Journal of Chemical Engineering*, **52**, (Aug. 1974), pp. 539-540.
3. Sylvester, N. D., A. A. Kulkarni, and J. J. Carberry, "Slurry and Trickle-Bed Reactor Effectiveness," *The Canadian Journal of Chemical Engineering*, **53**, (June 1975), pp. 313-316.
4. Sylvester, Nicholas D. and Punya Pitayagulsarn, "Mass Transfer for Two-Phase Cocurrent Downflow in a Packed Bed," *Ind. Eng. Chem., Process Des. Dev.*, **14**, 4 (1975), pp. 421-426.
5. Dharwadkar, Ajit and N. D. Sylvester, "Liquid-Solid Mass Transfer in Trickle Beds," *AIChE J.*, **23**, 3 (May 1977), pp. 376-378.
6. Sakornwimon, Wirat and Nicholas D. Sylvester, "Effectiveness Factors for Partially Wetted Catalysts in Trickle-Bed Reactors," *I&EC Process Des. Dev.*, **21**, 1 (1982), pp. 16-25.

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