

exchanger Specification Forms and Buyer's Practices are also covered in a brief survey. The section on Information Sources, both published and confidential can also be useful, but is not exhaustive.

The reader should not expect information on actual design, which the author wisely omitted. The expert will find an occasional oversimplification which, however, should not detract from the main strength of the book which is a very useful down-to-ground general review of heat exchanger applications.

Jerry Taborek  
Heat Transfer Research Inc.  
2165 Canyon Road  
Arcadia, Ca. 91006

**History of Chemical Engineering**, William F. Furter, Editor, *Advances in Chemistry*, Series 190, American Chemical Society, Washington, D.C. (1980) 435 pages, \$39.00.

The Symposium sponsored by ACS Division of The History of Chemistry and of In-

dustrial and Engineering Chemistry contained twenty-two papers, (9) United States; (5) Canada; (4) United Kingdom; (1) Italy; (1) Japan; (1) Germany; and (1) India. Educators traced the development of their schools during the past 100 years, engineers in industry set forth the part of chemical engineering in developing modern process plants.

The diffuse nature of chemical engineering and the lack of clarity when craftsmen and technologist become chemical engineers make it difficult to sort out a definition from the historical treatment, this brings the question "Who is a Chemical Engineer?" The bringing together of the sciences to identify, analyse, and predict the parameters which control the several steps in processing material so as to permit improved designs did not seem to stand out to a reader. The advent of the unit operations era in the late 1920's pointed out by educators along with the design construction, and operation of plants including the separation of uranium, isotopes and fluidized cracking of petroleum described industrial personnel included this

representation of chemical engineering.

Historical material generally shows evidence of transition to new areas. Scant reference is made to the combined use of mathematics and computers, to data analysis, solution to complex problems, utility in design, and simulation for optimization. Likewise, one would not surmise the large involvement of universities and industry in biomedical engineering endeavors taking place.

The articles represent a broad view of chemical technology and education during the past century and make interesting reading. The many claims of "firsts", no doubt, would be contradicted by others but established a general sequence of events for the reader. Many authors documented their statements, some 600 references in all. The editor deserves credit for covering the western world and completing this fine historical book.

Donald L. Katz  
University of Michigan  
Ann Arbor, MI

## LETTERS TO THE EDITOR

### To the editor:

In a recent paper, Wey and Jagannathan (1982) evaluated the effect of errors in solubility on the apparent kinetic order of crystal growth from solution. They determined that a 0.21% error in the solubility could cause a variation in the kinetic order from one to two thus making any conclusions about the crystal growth mechanism questionable. They conclude the variations in solubility of this order can occur due to the "differential solubility" of individual crystal faces and reference the work of Ritzel (1911) as proof of this concept. We feel that this conclusion is incorrect and that the authors have misinterpreted the results reported by Ritzel and will, therefore, attempt to clarify several points addressed in the paper.

Solubility is the solute concentration established after a crystal-solvent system has reached thermodynamic equilibrium. The crystal form is then unique for a given substance solvent, temperature and pressure is approximately described by the Wulff theorem. It is, therefore, incorrect to discuss solubility of cubic and octahedral NaCl crystals since only the cubic crystals are equilibrium forms. The octahedral crystals have a transient character in aqueous solution (Kern 1969).

Ritzel (1911) did not measure and establish differences in solubility of cubic and octahedral NaCl crystals as stated by Wey and Jagannathan. Ritzel measured the rate at which cubic and octahedral faces of NaCl crystals dissolved. From this data, Ritzel

calculated the solubility of *infinite* cubic and octahedral NaCl faces undisturbed by the presence of edges. Ritzel correctly realized that for a real crystal, the solute concentration adjacent to the faces of a crystal in equilib-

rium with its solution must be equal. Ritzel's observations can be explained in terms of the different rates of approach towards thermodynamic equilibrium of the cubic and octahedral faces of NaCl during their disso-

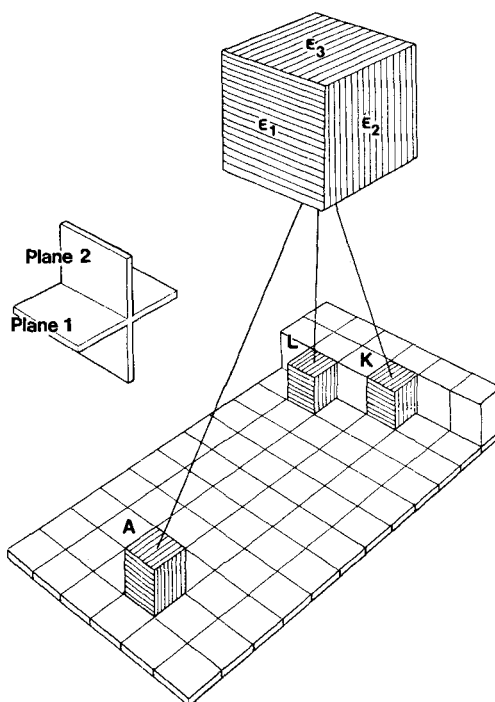


Figure 1. A portion of a stepped surface with adatom (A), ledge (L) and kink (K) adsorption sites.

lution. The chemical potential driving force during the dissolution of the nonequilibrium (111) (Octahedral) face changes with time as the equilibrium crystal configuration is approached. Even though Ritzel stated that the surface retained its original configuration during dissolution, it is doubtful that he would have been able to detect any changes given the fact that the average thickness of a slice of a face dissolved was less than 0.1 mm.

The thermodynamic driving force for growth of a crystal face  $i$  is given by the difference in the chemical potentials of a monomer in solution  $\mu^L$  and an attachment site,  $\mu_i^s$ .

$$\Delta\mu_i = \mu^L - \mu_i^s \quad (1)$$

From crystal growth theory, there are several different types of sites on a stepped surface where a growth unit can enter the crystal lattice. These sites include kink sites (K), ledge sites (L) and adatom sites (A). The chemical potential of an attachment site on face  $i$  can be given by the relation:

$$\mu_i^s = \sum_j P_{ij} \mu_{ij}^s \quad (2)$$

where  $\mu_{ij}^s$  is the chemical potential of a growth unit adsorbed at a site  $j$  (where  $j = K, L$  or  $A$ ) on face  $i$  and  $P_{ij}$  is the probability of the process. Let us assume that the growth units are orthogonal blacks packed together with anisotropic bond enthalpies  $2\epsilon_1$ ,  $2\epsilon_2$  and  $2\epsilon_3$  as shown in Figure 1. The chemical potential corresponding to each type of site on the plane 1, can be expressed by the relations:

$$\mu_{1A}^s - \mu^* \cong 2\epsilon_1 + 2\epsilon_2 + \epsilon_3 \quad (3)$$

$$\mu_{1L}^s - \mu^* \cong \epsilon_1 + 2\epsilon_2 + \epsilon_3 \quad (4)$$

$$\mu_{1K}^s - \mu^* \cong \epsilon_1 + \epsilon_2 + \epsilon_3 \quad (5)$$

where  $\mu^*$  is the standard chemical potential (taken as that of an infinite solid). To estimate the relative importance of the three types of sites  $K$ ,  $L$ , and  $A$  it is assumed that the probabilities can be given by the relation:

$$P_{ij} \sim \exp(-\mu_{ij}^s/kT) \quad (6)$$

Assuming a representative value of  $\epsilon$  equal to  $4kT$  yields:

$$\frac{P_{1K}}{P_{1L}} = \exp(\epsilon_2/kT) \cong 50 \quad (7)$$

$$\frac{P_{1K}}{P_{1A}} = \exp\left(\frac{\epsilon_1 + \epsilon_2}{kT}\right) \cong 3 \times 10^3 \quad (8)$$

The kink positions are thus prominent (and self-perpetuating) sites of attachment.

For plane 2 perpendicular to plane 1 (see Figure 1), the chemical potential of a monomer at each type of site can be expressed as:

$$\mu_{2A}^s - \mu^* \cong \epsilon_1 + 2\epsilon_2 + 2\epsilon_3 \quad (9)$$

$$\mu_{2L}^s - \mu^* \cong \epsilon_1 + 2\epsilon_2 + \epsilon_3 \quad (10)$$

or

$$\epsilon_{2L}^s - \mu^* \cong \epsilon_1 + \epsilon_2 + 2\epsilon_3 \quad (11)$$

depending on step orientation, and

$$\epsilon_{2K}^s - \mu^* \cong \epsilon_1 + \epsilon_2 + \epsilon_3 \quad (12)$$

Thus the driving force of growth given by equations 1 and 2 is identical for the two crystal faces 1 and 2. Similar results can be obtained for the other faces. When kink sites are the prominent incorporation sites ( $P_{iL} \cong P_{iA} \ll P_{iK}$ ) and their density is sufficient to accommodate the surface diffusional flux of growth units, the thermodynamic driving force for growth will be equal for all faces growing by this mechanism. The surface potential of atomically smooth planes however is highly anisotropic.

The effect of uncertainty in solubility data on the calculated kinetic order of crystallization has been discussed by several investigators including Ritzel (1911) (his Figure 3) and VanHook (1969). The calculations of Wey and Jagannathan show that a small error in solubility can result in significant changes in the calculated kinetic order. The solubility uncertainty, however, cannot be attributed to differential solubility of crystal faces.

#### LITERATURE CITED

- Kern, R., "Crystal Growth and Adsorption," in "Growth of Crystals" N. N. Sheftal, ed., vol. 8, 1969.  
Ritzel, A., "The Crystal Shape of Sodium Chloride in Its Dependence on the Solvent," *Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem.*, **49**, 152 (1911).  
VanHook, A., "Sucrose Crystallization Mechanism of Growth from Aqueous Solutions," *J. Crystal. Growth*, **5**, 305 (1969).  
Wey, J. S. and R. Jagannathan, "Determination of Growth Kinetics of Polyhedral Crystals," *AIChE J.*, **28**, 697 (1982).

Michael Saska and Allan S. Myerson  
School of Chemical Engineering  
Georgia Institute of Technology  
Atlanta, GA 30332

#### Reply:

We appreciate the interest shown by Saska and Myerson to our paper (Wey and Jagannathan, 1982) but disagree with most of their comments, which appeared to result from misreading and misinterpreting our paper. First, we considered different equilibrium solute concentration  $C_e$  (rather than "solubility"  $C_s$ ) for different crystal faces in a polyhedral crystal. We will clarify this concept in more detail later. Second, our analysis, which illustrated the effect of errors in  $C_e$  on the apparent kinetic order of crystal growth from solution, was quite general. We referred to the work of Ritzel (1911) merely as possible experimental evidence that a small difference in  $C_e$  could exist for different crystal

faces. Third, we did not state that Ritzel measured  $C_e$  values for cubic and octahedral NaCl crystals. Instead, as stated in the fourth paragraph of our paper, we clearly indicated that Ritzel obtained a 0.35% difference in  $C_e$  (referred to as "solubility" by Ritzel) between cubic and octahedral NaCl crystals from the measurement of dissolution rates.

Our concept of different  $C_e$  for different crystal faces in a polyhedral crystal was not based on the Wulff theorem, which considered a minimization of the chemical potential for the entire crystal. Instead, our concept was based on the minimization of the chemical potential for each individual crystal face. That is, we considered that the equilibrium chemical potential of a crystal face was dependent on the crystallographic nature of the surface and was related to its " $\alpha_{hkl}$  factor". This equilibrium chemical potential may be determined by minimizing the excess free energy associated with the random transfer of growth species from the bulk solution to the specific crystal surface. This concept was first discussed by Jackson (1958) and was recently considered in more detail by Jagannathan (1982). We do not believe that the theoretical concept proposed by Saska and Myerson in their letter was adequate because they did not consider the differences in the crystallographic nature of the crystal faces.

We do not disagree with the comment of Saska and Myerson that solubility is the solute concentration established after a crystal-solvent system has reached thermodynamic equilibrium. However, the equilibrium solute concentration  $C_e$  associated with a growing crystal surface can be different from the solubility  $C_s$  obtained at thermodynamic equilibrium of the entire crystal-solution system. The main thrust of our paper was to illustrate the importance of using the true equilibrium solute concentration  $C_e$  for the determination of the face growth kinetics of a polyhedral crystal. The apparent kinetic order determined can be significantly different from the true value if  $C_e$  is replaced by the nominal solubility  $C_s$  for the calculation of solution supersaturation.

#### LITERATURE CITED

- Jackson, K. A., *Liquid Metals and Solidification*, ASM, Cleveland (1958), p. 174.  
Jagannathan, R., "Equilibrium Chemical Potential for Crystal Growth—A Surface Property", submitted to *J. Crystal Growth* (1982).  
Ritzel, A., "The Crystal Shape of Sodium Chloride in Its Dependence on the Solvent", *Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem.*, **49**, 152 (1911).  
Wey, J. S. and R. Jagannathan, "Determination of Growth Kinetics of Polyhedral Crystals", *AIChE J.*, **28**, 697 (1982).

J. S. Wey and R. Jagannathan  
Research Laboratories  
Eastman Kodak Company  
Rochester, New York 14650