Meetings

Surface Phenomena

Surface phenomena include all those physical and chemical areas that are pertinent to the surface of a solid, or to the interface between a solid and a gas, a liquid, or another solid. Four interrelated branches of the study of surface phenomena are surface thermodynamics, nucleation, diffusion, and fine particle technology. All four topics were discussed at the 3rd annual symposium on fundamental phenomena in the material sciences, Boston, Massachusetts, 25–26 January 1965. P. L. de Bruyn (Massachusetts Institute of Technology) discussed certain fundamental concepts of surface technology in the framework of the classical thermodynamics, as derived principally by Gibbs. First, the concept of a dividing surface was considered. Following a review of Gibbs's treatment of surfaces and interfaces, de Bruyn pointed out that in most thermodynamic treatments of multiphases it is assumed that when the main interest is in bulk properties, the surface may be completely ignored. He further pointed out that when two contiguous phases are brought into juxtaposition, for the study of the boundary between them (namely, the interface) it is convenient to introduce a mathematical surface (the dividing surface), with respect to which all excess "surface" properties may be defined. This mathematical surface and all surface properties defined by it must take into account that there is a definite gradient in properties in the vicinity of any interface.

Accordingly, with recognition of this gradient, there is a two-dimensional representation of the interfacial region across which the properties of the system vary from one bulk phase to the other. The smaller this difference in properties between two contiguous phases, the greater will be the extent of the surface layer—the dividing surface—or the closer the system is to its critical temperature.

In the same context of the classical thermodynamic equations, de Bruyn went on to define the concept of surface tension as a direct calculated entity which is experimentally obtainable only for liquid-liquid or liquid-gas interfaces. He demonstrated that: when an interface is planar in nature, the value of this surface tension will be independent of the arbitrary position of the interface. But when the interface is curved, this is not the case; then it is necessary to define a surface of tension (Gibbs), the location of which is characterized by a minimum in the surface tension. It follows that the surface tension is directly proportional to the pressure differences across the interface boundary.

Further examination of the classical equations showed that the equilibrium vapor pressure of a small droplet, because of its dependence on the radius of curvature, must be larger than that of a large body of liquid.

E. W. Hart (General Electric Research Laboratory) discussed the application of the recently developed thermodynamic theory for equilibrium in homogeneous systems to the problem of the surface tension of the interface between two fluid phases. The results of the experimentation, he said, were unexpected; they were also inconsistent with earlier conclusions regarding the existence of a minimum surface tension and the concept of a surface of tension. It was found that the surface tension of the planar interface was given by the difference of two quantities, characteristic solely of the two homogeneous bulk phases. The nature of that conclusion supports the general validity of Antonoff's rule. Another problem treated was that of the equilibrium, unstable droplet of condensed phase in an undercooled vapor. The invariant work of formation of the droplet was shown to be zero. This result has important bearing on the Gibbs theory of the surface and on the current theory of nucleation kinetics.

K. C. Russell (M.I.T.) introduced the discussion on nucleation with the impressive reminder that at present there is a 1- to 7-order-of-magnitude difference between the experimentally determined and the theoretically predicted behavior of homogeneous nucleation, as observed in cloud chamber experiments. The most this situation could be improved by is about 1 order of magnitude.

The type of sophisticated experimentation, however, that Russell believed would result in more substantial improvement of this situation was such as would focus attention on those additional energy and entropy effects that may be meaningful. He also believes there would be similar benefit from more detailed statistical mechanical calculation of the surface tension of droplets and crystallites.

J. P. Hirth (Ohio State University) spoke on nucleation processes in deposition onto substrates. In a review of the classic theory of heterogeneous nucleation, he demonstrated how, through minimization of the free energy of formation, it is possible to determine a critical nucleus size above which it can be expected that crystal growth will begin. From this point it is possible similarly to determine, in order, the volume density of critical sized nuclei and an observable nucleation rate. Plotting the nucleation rate as a function of vapor supersaturation can produce information giving the surface energy and the difference between the desorption and surface diffusion energies.

But several different mechanisms of nucleation are possible, depending principally on the substrate temperature. At high temperatures, for instance, the nucleation rate is no longer related to the surface diffusion energy; the impinging atoms form a two-dimensional gas that is not tied to an oscillating substrate atom.

The influence of surface imperfections and the phenomenon of epitaxy were also treated. It was pointed out that nucleation can actually be favorably influenced by a certain type of surface blemish—a step or ledge—inclined at a certain angle to the flat portion of the crystal. It was stated generally that nucleation rates were influenced by such steps or ledges, and the degree and nature of influence related to the geometry created by the contact angle of the nucleus and the substrate angle of the surface imperfection. The conditions under which epitaxial growth is most favorable were said to be high substrate temperatures, small driving forces, and intermediate values of contact angle.

F. P. Price (General Electric Research Laboratory) discussed nucleation and growth of single-crystal organic polymers, and presented evidence that classical nucleation theory applies equally satisfactorily to polymer crystals and to materials of low molecular weight. Specifically, it was shown (i) that the thermal history of organic solids controls the size of crystalline spherulites and (ii) that for polychlorotrifluoroethylene there is correlation between spherulite size and fatigue life. In particular, rapid quenching results in small crystals, capable of greater reverse bending before fracture occurs; whereas slow cooling creates crystals of such size that single bending causes failure. The stress-strain curves of polypropylene exhibited similar characteristics but, through annealing for increased periods of time, the total possible elongation can be reduced. This in turn possibly results in immediate fracture after the initial upper yield.

P. G. Shewmon (Carnegie Institute of Technology) introduced the subject of surface diffusion with an examination of the experimental techniques used in the determination of the surface diffusion coefficient D_s. The controversy as to whether volume or surface diffusion plays the major role in the process of fine powder sintering was then explored. Shewmon suggested that surface diffusion is the all-important factor to be considered, contrary to the conclusions arrived at in most of the literature on this subject. Recent extensive computer studies, however, substantiate this minority belief, he pointed out. The basic argument was developed as an extension of the observed results of scratch smoothing experiments; these experiments showed the wavelength of a grating surface to be an important parameter in the determination of the ratio of surface to bulk diffusion.

C. E. Birchenall and J. M. Williams (University of Delaware) took the general position that these subjects—surface diffusion, surface diffusion versus bulk diffusion, and the relation of these to the sintering process—were more complex and should be more closely considered. Among the factors that should be examined, for example, in any consideration of surface diffusion are surface impurity size and distribution, crystalline anisotropies, divacancy migration through the surface, the long mean free paths at high temperatures, and the chemical effects that "pin" atoms to adsorbed species. Commenting particularly on the sintering process, Birchenall and Williams thought that neck size, not particle size, as is usually thought, was more important in a determination of a surface diffusion mechanism. They also discussed tracer technique experiments which they had been performing recently. The conclusion, however, was that the end results of these experiments might not shed any more light on these general problems than presently existed.

J. M. Blakely and C. Y. Li (Cornell University) discussed the formation of surface point defects on ionic crystals and showed that about 2.12 ev of energy is required to create a divacancy on a (100) NaCl crystal surface, compared to 1.95 ev for the creation of a similar double effect in the bulk material. The legitimacy of the use of the bulk dielectric constant in the neighborhood of a surface was questioned. It was pointed out that a correction to this value would have the effect of increasing the polarization component of the removal energy, thus making it more difficult to create a surface defect pair.

I. R. Kramer (Martin Company) spoke on surface-initiated failures in structural materials. His basic premise was that the mechanical behavior of materials, particularly metals, is markedly affected by the surface; that all of the usual mechanical properties—tensile behavior, fatigue, creep, stress-rupture—can be altered by suitable surface changes. For example, copper-plated zinc crystals reduce creep rate to negligible values. It was also pointed out that various atmospheres produce different and readily observable effects on materials. For example, specimens tested in vacuum are able to deform plastically more readily than those tested in air.

J. Turkevich (Princeton University) spoke broadly on the subject of ultra-fine particles in gases. Regarding the nucleation, growth, and aggregation of fine aerosol particles he suggested that their formation and also their texture are due to a certain degree of information or memory in an organized aggregate of materials. His view has been documented by electron-microscopy examinations of particles in a finely divided state. Other unusual characteristics of the growth of such particles in gases are that, in contrast to the case of crystallites, there are no driving forces to promote growth, and that these particles are so nearly perfect that the so-called "growth sites" associated with dislocations are not found to exist. It was explained that in the preparation of such fine particles it was always necessary to perform some preliminary burning off of debris (carbon). This burning is not as simple a task as might be presumed, because the burning rate—dependent on surface area—will decrease as the particles become smaller. Another problem associated with the formation of such fine particles is the dissipation of the energy generated at the surface. Usually this is accomplished through absorption by the "bulk." With such fine particles, however, there is usually no bulk; thus the carbon burning cannot be sustained. Room-temperature burning, using oxygen produced in a discharge tube, however, can be accomplished to a finer degree, and no side effects are introduced into the materials from which the carbon is removed. Next, it was explained that, contrary to usual belief, magnesium atoms do not aggregate to form well-defined hexagonal crystals. With the addition of small amounts of copper impurities, crystal growth is promoted and such perfect hexagons do appear. In closing, it was shown that there is a very practical application of these aerosol studies—namely, the use of fine particle technology in the study of radioactive fallout.

The sponsor of the symposium was the Ilikon Corporation, Natick Industrial Center, Natick, Massachusetts. A symposium volume is being prepared; requests for copies should be addressed to Ilikon Corporation.

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Forthcoming Events

December

26–31. **American Assoc. for the Advancement of Science**, annual, Berkeley, Calif. (R. L. Taylor, AAAS, 1515 Massachusetts Ave., NW, Washington, D.C.)

In addition to the 20 sections of the Association and five AAAS committees, the following organizations have arranged sessions at the AAAS annual meeting:

Mathematics

American Mathematical Soc. (R. S. Pierce, Univ. of Washington, Seattle)