P into metallic P involves a substantial intermediate formation of the A7 phase.

When starting from point A (Fig. 1) the sample is cooled down to low temperatures under constant load; the sample becomes superconducting with a rather sharp transition at about 4.7°K. This transition temperature corresponds reproducibly to the precipitous drop of the electrical resistance. If the pressure is increased at room temperature in two steps to points B and C in Fig. 1, the room-temperature resistance shows only a small further decrease. The superconducting transition temperature, however, is shifted to much higher values, as shown in Fig. 2. The monotonic increase with pressure indicates a pure pressure effect rather than any new crystallographic phase change. Thus it appears that P is the first nontransition metal to show a large positive pressure coefficient of T_c.

The low-temperature resistivity of all samples was about one-half of the room-temperature resistance, thus indicating a rather imperfect and strained lattice for the superconducting polymorph. After complete release of pressure, the resistance of the sample was about four orders of magnitude higher than in the metallic state (Fig. 1). This value is to be expected from the specific resistivity of semiconducting black P. In addition, the black color of the sample and the negative temperature coefficient of the resistance down to 1.2°K are convincing proofs that black P has been formed irreversibly on the pressure-releasing cycle.

The onset of superconductivity in P may depend on the prior history of the sample, and at the same time there may be more than one superconducting modification of P. But apart from these questions, the discovery of superconductivity in P is further proof that every truly metallic sp element will be found to be superconducting (9).

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Concentration-Gradient-Driven Convection: Experiments

Abstract. Concentration-gradient-driven convection was studied by measurement of the rate of dissolution of the lower face of a KCl single crystal in contact with various solvents. The rate of mass transfer due to convective stirring appeared to follow the Rayleigh number to the one-third power law. A regular pattern of etch pits due to the convective stirring action was observed in the crystal face after exposure to water for 5 minutes. Schlieren photographs of the early stages of dissolution showed a regular pattern of spikes having approximately the same dimensions as the etch pits in the crystals.

Differences between salt rejection in unstirred hyperfiltration systems (1), when membranes are placed above feed solutions and when membranes are placed below feed solutions, indicated marked differences in concentration polarization with orientation. The difference was attributed to stirring that arose from the density gradients formed near the interface where salt is rejected.

Natural-convection stirring of horizontal fluid layers is common (2, 3) when an adverse density gradient is produced by heating of a fluid from below. The enhancement of the rate of heat transfer between two horizontal solid surfaces by natural-convection stirring has been studied experimentally (2, 4, 5) and theoretically (6). These studies show that the Nusselt number for heat transfer (the dimensionless heat-transfer rate) N_{Nu} is a function of the Rayleigh number N_{Ra}:

$$N_{Nu}/(N_{Nu})_0 = C (N_{Ra})^n \qquad (1)$$

where $(N_{Nu})_0$ is the Nusselt number in the absence of natural-convection stirring. For Rayleigh numbers greater than 20 times the critical, the value of n is $\frac{1}{3}$ and C is about 0.089. It is of interest to note that shear flow apparently has little effect on either the critical Rayleigh number (1) or the increase in Nusselt number due to natural-convection stirring.

A related stability problem occurs when two different fluids, having a common plane boundary, experience an acceleration in a direction perpendicular to their interface (8). When the acceleration is directed from the less-dense to the denser medium, the interface becomes unstable; as the instability develops, the denser fluid jets out in long spikes.

Little is known about the effect of concentration-gradient-driven natural convection on the rate of mass transfer at a liquid-solid interface. Since such stirring was believed (1) to be responsible for the effect of orientation on the differences in rejection in the hyperfiltration experiments, we chose to study concentration-gradient-driven convection by measuring the rate of dissolution of the lower surface of a single crystal of KCl in contact with solvent. Such a technique has the advantage of eliminating high-pressure systems and permitting visualization of flow, but has
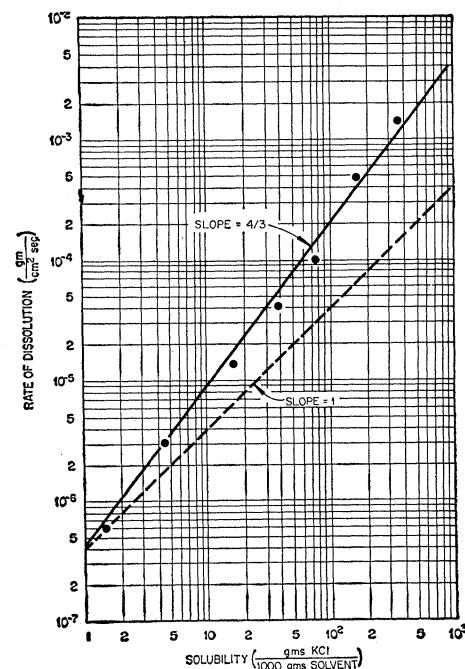

Fig. 1. The effect of solubility of KCl on rate of dissolution in ethanol-water solutions.
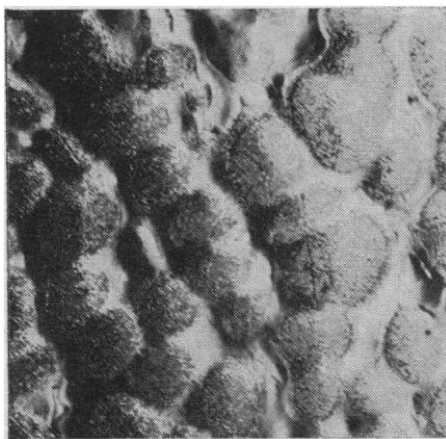
Fig. 2. Hydrodynamic etch pits observed in 100 plane of a single crystal of KCl exposed to water for 5 minutes.

the disadvantage of having no analog to the flow toward the membrane.

The experimental procedure was to cement single crystals of KCl (3.8 by 3.8 by 0.8 cm) to a stainless steel holder. The 100 cleavage plane of the crystal was polished by rubbing the crystal against moist cheesecloth backed by a glass plate. The crystal was polished before every experiment and was dried and stored in a desiccator before weighing. After weighing, the crystal and mount were lowered until the lower surface of the KCl contacted the solvent; after exposure to the solvent for a given time, the crystal was dried and reweighed. The solvent container was rectangular, 13 by 20 by 14 cm deep.
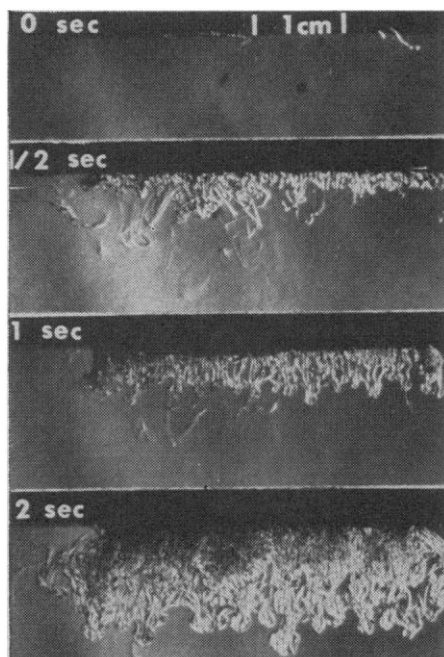

Fig. 3. Schlieren photographs of "spikes" observed during early stages of dissolution of a KCl crystal in water.

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The solvents were mixtures of ethanol and water; solubilities, obtained from a smooth curve through reported data (9), varied from 358 to 1.45 g/1000 g. The density difference between saturated solutions and solvent [the driving force for concentration-gradient-driven convection (10)] is directly proportional to the solubility.

At each solvent concentration, the weight loss per square centimeter of exposed crystal area was directly proportional to duration of exposure to solvent for durations from 5 to 10^4 seconds. The longer exposures were required in the low-solubility tests to give a measurable weight loss. Figure 1 shows the weight loss per square centimeter per second as a function of solubility of KCl. If there were no natural-convection stirring, the rate of weight loss (and the Nusselt number for mass transfer) would be directly proportional to the solubility of the salt. However, if Eq. 1 applies equally to mass transfer and heat transfer, the rate of weight loss should be proportional to the 4/3 power of the solubility. Our data are not inconsistent with the 4/3-power relation.

An interesting aspect of these studies was the opportunity to observe the dissolution of KCl from above the transparent salt crystal. Within less than 1 second of contact with water, a regular "pebbled" appearance was observed at the crystal-water interface. The size of each "pebbled" area was approximately 1 mm. The thickness of salt dissolved from the crystal in 1 second is estimated to be less than 20 μ. Inspection of the crystal face after 1- to 5-second contact with water showed that the surface was still smooth and transparent. As dissolution continued, the dissolved-salt solution layer thickened and obscured the "pebbled" structure.

After 300-second exposure to the solvent, the surface of the crystal was pitted in a regular pattern (Fig. 2). Identification of the "pebbled" pattern as pits rather than bumps was confirmed by cleavage of a crystal in a plane perpendicular to the exposed face. The pits appeared to have somewhat larger diameter toward the crystal edge than in the center; the diameters of the pits in the two regions followed a logarithmic normal distribution, with the same standard deviation $\sigma = 1.27$. The mean diameter of the pits in the central region was 0.91 mm; in the outer region, 1.14 mm. It is virtually certain that the pits observed by us were due to fluid motion rather than preferential

etching along crystal dislocations, because normally about 10^6 dislocations per square centimeter are observed with potassium chloride crystals (11). Thus the average size of a dislocation is 10^{-2} mm—about 1 percent of the size observed by us.

The difference in refractive index between saturated solution of KCl and water was sufficiently great to permit visualization of flow with a simple schleiren system that used a 100-watt mercury-vapor lamp as a light source. Typical photographs taken at the instant of contact of the salt crystal with water and after 0.5-, 1-, and 2-second exposure to water, in different experiments, are shown in Fig. 3. The water-crystal interface is the dark line at the top of the photograph. The saturated salt solution formed at the crystal-water interface appears to be falling through the solvent as "spikes" about 1 mm wide, substantially the same size as the hydrodynamic etch pits observed in the crystal face.

The question of whether the mechanism responsible for this particular example of concentration-gradient-driven convection is Rayleigh instability or Rayleigh-Taylor instability remains to be determined; its resolution is of some significance because in one case a critical difference in density is required for initiation of convective stirring, while in the other case no threshold is required.

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