

lished). Also, creeping does not occur if the KCl solution is unsaturated, or if a beaker containing a saturated solution is stoppered. In the case of an unsaturated solution, if any crystals were formed on the sides of the beaker they would be dissolved as the unsaturated solution was drawn into any fissures or crevices in the crystal and the creeping could not occur. In the case of a covered beaker, no creeping occurs because the atmosphere inside the beaker is saturated with water vapour, preventing evaporation of the solution which is necessary for the crystal front to form and advance.

Regarding the creeping which occurs through a 'seamless' glass tube connector; the authors do not specifically mention whether the joint was greased or ungreased. In the former case, we would not expect any creeping to occur, however, in the later case, small fissures and crevices are certain to be present in the joint allowing the creeping to occur. In fact, this ability of the KCl solution to creep into small fissures is put to good use by electrochemists in constructing reference electrodes². Instead of using a porous frit or a salt bridge to maintain solution contact, a platinum wire is sealed in glass and contact is maintained by way of the small fissures which form between the platinum and glass on cooling.

The alkali halides form two separate isomorphous groups³: the lithium and sodium salts; and the potassium, rubidium, and caesium salts. If the creeping results simply from the wick effect by the crystals, one would not expect it to be unique, and in fact, compounds such as potassium bromide, potassium iodide, and caesium chloride that are crystallographically isomorphous with KCl also exhibit this creeping phenomenon (A. M. Yacynych, unpublished). Sodium fluoride, chloride, bromide and iodide which are not isomorphous with KCl do not creep. Perhaps their crystal formation does not have the small fissures and crevices necessary for the wick action.

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¹ Huang, B. J., and Huang, J. C., *Nature*, 261, 36-38 (1976).

² Heineman, W. R., and Kuwana, T., *Analyt. Chem.*, 44, 1972-1978 (1972).

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CONCERNING the paper by Huang and Huang¹, may I suggest that the well known Marangoni Effect may provide the authors with an explanation for their observations. A good account of different types of Marangoni Effect may be found in ref. 2.

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Matters arising

Matters Arising is meant as a vehicle for comment and discussion about papers that appear in *Nature*. The originator of a Matters Arising contribution should initially send his manuscript to the author of the original paper and both parties should, wherever possible, agree on what is to be submitted. Neither contribution nor reply (if one is necessary) should be longer than 300 words and the briefest of replies, to the effect that a point is taken, should be considered.

HUANG and Huang¹ describe the flow of potassium chloride solutions over surfaces and conclude by saying the results are "inexplicable" but that they might be attributed to "interactions of the ions with the surface of the beaker or tube and the surrounding gaseous molecules". In 1950 I observed the same effect in aqueous solutions of potassium ferricyanide, but results of several experiments were not published because I was unable to obtain reproducible quantitative results. I attributed the phenomenon to surface mobility of ions and molecules.

Evidence for surface mobility of adsorbed atoms was first given by Volmer and Estermann in 1921. They set up an experiment in which mercury evaporated from a bath at -10°C to a glass plate at -65°C . Hexagonal crystal plates of mercury formed on the glass. The crystals should have grown at the rate G/ρ in which G is the rate at which mercury molecules struck unit area of crystal at the glass surface and ρ is the density of the crystal. But the dimensions of the crystals grew $1,000\times$ faster than that. Volmer and Estermann concluded the

mercury atoms moved over the surface of the glass to become attached to the crystals.

A few years later, Volmer and Adhikari placed a benzophenone crystal between 0.02 to 0.09 mm from the edge of a glass plate; a mercury drop just touched the edge of the glass. The crystal dissolved in the mercury due to the mobility of benzophenone molecules over the surface of glass (vapour pressure negligible); it was estimated that the resistance to diffusion over the glass was one hundredth of that in the liquid state.

Wicke in 1940 was the first to suggest that molecules adsorbed from the vapour phase contribute to total flow through porous materials; and the following year Wicke and Kallenbach flowed mixtures of CO_2 and N_2 past one face of a charcoal membrane, at 600 torr total pressure and pure N_2 past the other face at the same pressure. In the absence of a pressure gradient there was no flow through the membrane but diffusion of CO_2 into N_2 could occur and the diffusion coefficient could be determined by analysis. Experiments were done in the range $0-300^{\circ}\text{C}$. From the laws of gas kinetics, the diffusion should increase with temperature and this was observed at high temperatures. At low temperatures, however, the diffusion coefficient increased as temperature was decreased, which was attributed to the greater adsorption of CO_2 at lower temperatures. Mobility in the adsorbed phase contributed as much as 50% of the total flow of CO_2 at the lowest temperature.

So, when crystals are in contact with another solid surface an adsorbed layer of atoms (or molecules) can form on the solid surface in dynamic (mobile) equilibrium with the crystal. When a vapour (or gas) is in equilibrium with a solid surface there will be an adsorbed phase on the solid in kinetic equilibrium with the vapour; atoms or molecules will be mobile over the surface within the adsorbed phase. Evidence for this is considerable²⁻⁴. Adsorption also occurs when liquid mixtures and solutions are in contact with solid surfaces and various forms of adsorption isotherm have been found experimentally, see for example, Kipling⁵. Atoms and molecules will be mobile within that adsorbed layer.

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⁴ Roberts, G. T., *J. Phys. A.*, 6, 570 (1973).

⁵ Kipling, J. J., *Adsorption from Solutions of Nonelectrolytes* (Academic, London and New York, 1965).