

# ***This Week's Citation Classic***

**Darken L S.** Diffusion, mobility and their interrelation through free energy in binary metallic systems. *Trans. AIME* 175:184-201, 1948. [US Steel Corp., Res. Lab., Kearny, NJ]

**Since the 'Kirkendall effect'<sup>1</sup> is incompatible with the concept of simple exchange of atoms on adjacent sites as the mechanism of diffusion in solid alloys, the mobilities of different atomic species must differ. On this basis a quantitative explanation of the 'Kirkendall effect' is developed. It is further shown quantitatively that the diffusivity is a function not only of the two mobilities (or tracer diffusivities) but also of the thermodynamic properties. [The *SCI*<sup>®</sup> indicates that this paper has been cited over 195 times since 1961.]**

Lawrence S. Darken  
Department of Geosciences  
Pennsylvania State University  
University Park, PA 16802

April 25, 1978

"A year before this paper was presented at the 1948 American Institute of Mining and Metallurgical Engineers (AIME) annual meeting, Kirkendall had presented at an AIME meeting a paper showing that inert markers implanted in a diffusion 'sandwich' moved relative to each other during the diffusion process.<sup>1</sup> This created quite a stir, and there was much formal and informal discussion at the meeting as well as afterward, of what came to be known as the 'Kirkendall effect' The reason for this stir was the apparent conflict between this observed phenomenon and the metallurgically popular belief that diffusion in solid alloys took place by a simple exchange of atoms on adjacent sites. Physicists had previously proposed other mechanisms but communication was

much poorer then. Much of the long discussion suggested that the effect was 'spurious' in some way, arising from porosity, cracks or lattice parameter change.

"However, I was convinced of the basic validity of the 'Kirkendall effect' — perhaps because I already had the feeling that it was past time for a new look at diffusion in alloys. Further, R.F. Mehl went out of his way to persuade me to see what I could do on the subject. I devoted much time and turmoil to the problem. Rather than compete with the physicists on the development and elaboration of detailed atomistic mechanisms, I took a purely phenomenological approach. The basic assumption was the adoption of Fick's law, that the flux is proportional to the concentration gradient for each component; but since the gradient is independent of the reference frame whereas the flux is not, the choice of frame is of dominant importance; this was chosen as the markers themselves. It was subsequently shown that Fick's law fails at sufficiently high gradients. The original restriction to essentially constant lattice parameter was subsequently lifted both by myself and others. The final equation, relating the diffusivity to that of tracer isotopes of the components, has been found to be a good approximation for crystalline solutions. However, it is inadequate for many organic liquid solutions.

"Thus, in view of the often quoted statement, 'A theory is never discarded on account of discordant facts, but only when it is replaced by a better theory,' I must conclude that this paper is so frequently cited not because it is in such wonderful agreement with all subsequent findings but because no one has yet come up with a better interpretation."

1. Snigelskas A C & Kirkendall E O. Zinc diffusion in alpha brass. *Trans. AIME* 171:130-5, 1947.