

Energetics of the Kirkendall effect

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In 1942, Kirkendall established through a definitive experiment that different atoms can migrate at different rates during binary diffusion in an alloy, accompanied by measurable local volume change and displacement of reaction interface. Over the six decades since, the Kirkendall effect has continued to attract much attention among metallurgists, material scientists and physicists. To explain the observed displacement and volume change, the most widely used concept is the vacancy mechanism. If, because of unequal diffusion rates, there is net loss of atoms from a region in an alloy, the loss creates an excess number of vacancies. These vacancies also diffuse out of the region, leading to a local volume decrease. Although logical, this explanation does not probe into the nature of the forces and energies that underlie observed deformation. That is, the vacancy mechanism does not provide a dynamical explanation. The purpose of this article is to explore what a rational framework might be if one were to analyse the Kirkendall effect from a dynamical perspective. To this end, the Kirkendall effect is examined based on concepts related to binary diffusion in gases and liquids developed during the nineteenth century, and the extent to which such ideas may have relevance to diffusion in solids. Additionally, deformation due to local depletion of energy is also considered by analogy with deformation of water-saturated porous solids associated with diffusional drainage. The ideas presented have to be critically evaluated before acceptance. Nevertheless, it seems reasonable to state that the present insufficiency of knowledge of energetics governing the Kirkendall effect merits attention and remedy.

Keywords: Deformation, diffusion, energetics, Kirkendall effect, vacancy mechanism.

ERNEST KIRKENDALL¹ investigated inter-diffusion of copper and zinc in brass at high temperatures, observed a noticeable volume reduction in brass, and concurrent shift in brass-copper interface to accommodate the volume change. He concluded that the reduction in volume was evidence for the movement of zinc atoms out of brass at a faster rate than the influx of copper atoms. Smigelskas and Kirkendall² repeated the experiment under more carefully controlled conditions and confirmed the earlier observations. Kirkendall's work thus invalidated the prevalent perception that binary diffusion in substitutional solid

solutions involved the same diffusion rates for both species. His contribution is regarded as an important milestone in understanding solid diffusion. More recently, there has been renewed interest in the Kirkendall effect in the study of nano materials. The widely accepted explanation of the Kirkendall effect is based on the vacancy mechanism³. Although the vacancy mechanism qualitatively accounts for the Kirkendall effect, it does not throw light on the forces that underlie the volume change and interface displacement. In essence, the vacancy mechanism does not provide a dynamical elucidation.

Assuming that the observed volume change of brass is a deformational strain, the purpose of this article is to inquire as to what a logical framework might be for a dynamical explanation of the Kirkendall effect. To this end, the Kirkendall effect is examined based on ideas of binary diffusion in gases and liquids developed during the nineteenth century, and from the perspective of deformation of water-saturated porous materials consequent to diffusive depletion of water from the pore spaces. A voluminous literature exists on the application of thermodynamics to the Kirkendall effect. This work is an attempt to take a conceptual look at the phenomenon through a self-consistent approach independent of thermodynamics. The motivation is to stimulate interest towards an understanding of the Kirkendall effect from a dynamical perspective.

Kirkendall's contribution

The experiments

In 1942, Kirkendall experimentally investigated phase relationships as β -brass was changed to α -brass by the diffusive addition of copper in disc-shaped samples (Figure 1). A cylindrical bar of β -brass (60.6% Cu and 39.3% Zn; melting point 900–940°C) with a diameter of 0.5965 in (1.515 cm) was electroplated with a 0.4 in (about 1 cm) shell of pure copper. The composite bar was maintained at a temperature of 780°C for a prolonged period of time. As zinc diffused out and copper diffused in, a shell of copper-rich α -brass formed and grew around a gradually diminishing core of β -brass. Since α -brass is intrinsically denser than β -brass, the shell was expected to have a slightly smaller volume than the β -brass it replaced. However, a careful study of photomicrographs showed that the actual volume change was significantly larger, requiring explanation beyond just the effects of phase change. The observed changes are schematically shown in Figure 1.

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In Figure 1, the dashed circle represents the interface between β -brass and copper at the beginning of the experiment ($t = 0$). For purposes of diffusion calculations, Kirkendall used this circle as the reference, and hence called this diffusion interface. The annulus indicated by B represents the newly-formed shell of α -brass. The circle with diameter indicated as D represents the position, determined on the basis of microscopic columnar structure, of the initial β -brass and copper interface at time $t > 0$, referred to as original interface. The distance A indicates the actual displacement at time t of the initial β -brass–copper interface. The volume associated with cylindrical annulus A is the actual volume change of α -brass. The inner circle denotes the outer limit of β -brass at time t .

Convinced that the displacement A could not be explained merely by phase change, Kirkendall¹ stated,

‘It has already been mentioned that the location of the original interface shifts. This can be accounted for to a small extent by the fact that the beta brass changes to a denser, higher copper alpha brass. In itself, this shrinkage in volume would account for less than one fifth of the shift in position of the original interface’ (p. 107).

In order to account for volume change in excess of what could be accounted for by phase change, Kirkendall proposed a new explanation¹,

‘In order to explain the rest of the shift in the original interface, the author proposes that the zinc diffuses more rapidly than the copper in alpha brass. The diffusing out of the zinc faster than the copper can diffuse in, necessitates a reformation of the lattice (without destroying the columnar grain structure in this case). The reformation of the lattice without some of the

zinc atoms causes a contraction and a shift in position of the original interface in the direction of the high-zinc brass’ (p. 107).

Five years later, Smigelskas and Kirkendall² repeated the experiment under more controlled conditions to confirm the earlier findings and establish repeatability of the experiment. Instead of a bar of circular cross-section, they used a bar of rectangular cross-section (Figure 2), so that displacements could be measured perpendicular to a plane, thereby avoiding the need for applying corrections to interface areas as the circumference decreased during diffusion. Two other modifications were made. First, in order to avoid large volume changes in going from β - to α -brass, a bar of wrought brass (69.5% Cu and 30.5% Zn) was used. Also, insoluble molybdenum wires were imbedded at initial contact between wrought brass and copper to readily observe the displacement of the boundary. Photomicrographs taken at the end of 56 days clearly showed that the molybdenum wires and the original interface had moved together (Figure 3).

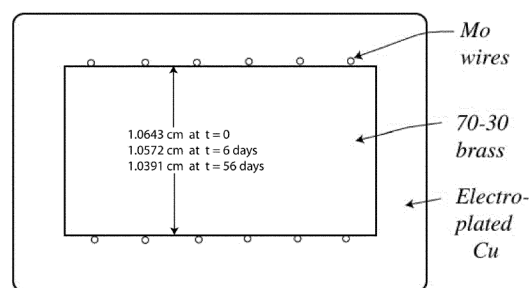


Figure 2. Schematic cross-section of bar used by Smigelskas and Kirkendall² (figure 1, redrawn).

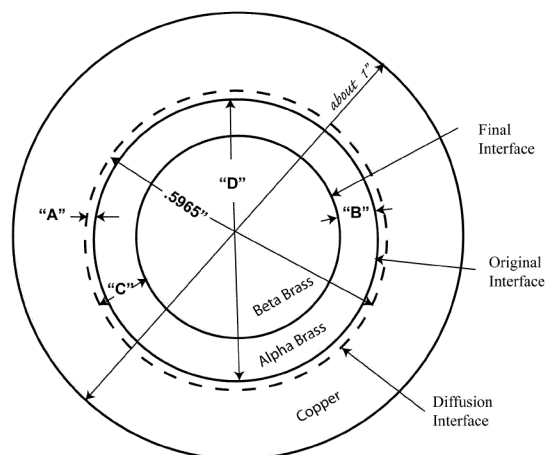


Figure 1. Cross-section of diffusion sample identifying various interfaces. (Source: Kirkendall¹; figure 1 redrawn.)

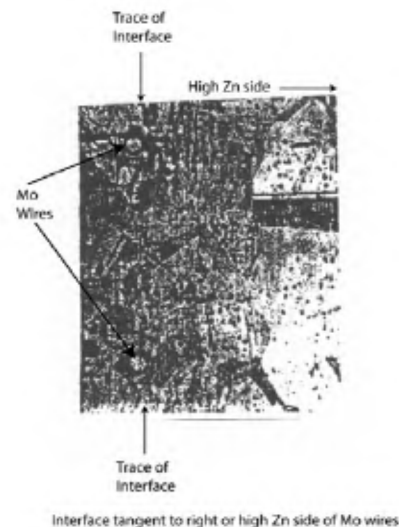


Figure 3. Photomicrograph showing disposition of original interface and Mo wires at the end of 56 days (Smigelskas and Kirkendall²; labels added).

Kirkendall's principal suggestion was that a reformation of the lattice was necessary to accommodate the loss of excess zinc atoms, and that the reformation was responsible for the observed contraction. Contemporaneously with Kirkendall, Huntington and Seitz⁴ had suggested that the vacancy mechanism provided a satisfactory explanation for self-diffusion of metallic copper. In 1950, a seminar on atom movements held during the 32nd National Meeting of the American Society of Metals, devoted much attention to the Kirkendall effect. The consensus at the end of this meeting was that the vacancy mechanism proposed by Huntington and Seitz⁴ provided the most plausible explanation for the Kirkendall effect, and that different diffusion coefficients had to be used for Cu and Zn³. A large body of literature exists on the theory of the Kirkendall effect combining vacancy mechanism, principles of thermodynamics, and Fick's law extended to multiple-species diffusion. In what follows, we look at the Kirkendall effect from a different, self-consistent dynamical perspective.

Towards a dynamical interpretation

Although eminently reasonable in qualitatively explaining the Kirkendall effect, the vacancy mechanism does not address the issue of the forces that are responsible for the contraction observed by Kirkendall. Clearly, these shrinkages are indicative of local strains within a solid body, and these strains must be associated with local stresses. If so, what logical framework may one employ to make dynamical sense of the Kirkendall effect? Two lines of reasoning are suggested below. The first involves dynamic coupling between pure diffusion and pressure-driven flow first noticed during the early nineteenth century, while the second involves deformation associated with depletion of energy, by analogy with deformation water-saturated porous media caused by drainage of water.

Dynamics of binary diffusion in gases and liquids

Evolution of ideas: The first ever diffusion experiments were conducted by Thomas Graham in Scotland during the early nineteenth century. He studied counter-diffusion of atmospheric air and a number of gases through a porous material. He found that binary diffusion tended to increase pressure within the chamber holding the gas, thereby affecting the diffusion measurements. Graham carefully controlled the experiments to maintain a constant pressure in the chamber, so that the measurements pertained solely to gas diffusion⁵. The observations led to what is now known as Graham's law, stating that the rate of diffusion of a gas is inversely proportional to the square root of its density. A decade later, Graham⁶ studied the flow of gases in capillary tubes and discovered that this pressure-driven flow was of a different kind, and did not conform to the diffusion law he had discovered earlier. Graham had found

that pure diffusion or molecular diffusion of gases is dynamically coupled with pressure-driven flow of gas mixtures during binary diffusion. Remarkably, this important finding was overlooked for over a century until it was experimentally confirmed by Kramers and Kistemaker^{7,8}.

Graham then went on to investigate the rate of diffusion of solutes in aqueous solutions and compiled an impressive set of data, but without synthesizing the information to elucidate the underlying process. Fick⁹ took it upon himself to complete the task left unfinished by Graham. Using Fourier's heat equation as a metaphor, he proposed that the diffusive flux of a salt in an aqueous solution is directly proportional to its concentration gradient. In the same paper, Fick also suggested that the diffusion of salt in one direction is accompanied by the simultaneous movement of water in the opposite direction. In suggesting this, Fick drew upon earlier experimental studies. In particular, he was influenced by Dutrochet¹⁰, who had suggested in 1827, that transport across an osmotic membrane involves a solute current and a solvent current, and had coined the terms 'endosmosis' and 'exosmosis'.

It is important to note that although Fick's law mathematically accounts only for salt movement and treats water to be stationary, his conceptual model considered liquid diffusion to be a binary process¹¹. Binary diffusion in an aqueous solution is similar to that in gases, but with an important difference. In an aqueous solution, one of the diffusing species is water, a condensed phase. The nature of its movement is different from that of a diffusing solute or gas molecule. Moreover, this type of water movement is of a different kind than the bulk movement of the solution as a whole, with water and solutes moving in the same direction.

In 1887, van't Hoff provided an explanation for osmotic pressure in aqueous solutions. Analysing the data published by previous workers, he showed that osmotic pressure exerted by a dilute non-electrolyte conforms to a law that is the same as the ideal gas law¹². Essentially, van't Hoff demonstrated that osmotic pressure represents the pressure exerted by the mobile solute molecules confined within a finite space, just as free-moving gas molecules exert pressure when confined in a finite space. This work also introduced the notion of 'colligative' property, that is, a property that depends solely on the number of particles, regardless of their nature or quality. In the following year, Nernst¹³ looked at Fick's law in the light of van't Hoff's osmotic pressure, and pointed out that the use of concentration in Fick's law failed to give any consideration to the forces responsible for salt diffusion, and that for a dynamical understanding of the process it is necessary to express flux as a function of gradient of osmotic pressure. He also argued that at high concentrations diffusion coefficient would vary with concentration, and therefore, the linear Fick's law was valid only in dilute solutions. In dilute solutions, concentration is related to osmotic pressure through a single constant.

In his celebrated paper on Brownian motion, Einstein¹⁴ drew upon the contributions of van't Hoff and Nernst in formulating his molecular-kinetic theory of heat. Einstein argued that osmotic pressure could not be explained by thermodynamics, and that kinetic theory would do so. Einstein's expression for the diffusion coefficient of a colloidal particle in an aqueous emulsion in terms of particle size, fluid viscosity, and Avogadro's number was a direct outcome of writing Fick's law in terms of osmotic pressure.

From the foregoing, the following important ideas emerge.

- In gases, partial pressure is a manifestation of the kinetic energy of the component gas molecules, expressed as energy per unit volume. Pure diffusion consists in the movement of each gas component in the direction of its decreasing partial pressure. Distinct from this mode of transport is the movement of the entire gas mixture in the direction of decreasing total pressure. This is pressure-driven flow or viscous flow.
- In aqueous solutions, solutes move freely within the solvent, a condensed phase. van't Hoff found that the movement of the solutes is analogous to the movement of gas molecules. Thus, osmotic pressure is analogous to partial pressure. Accordingly, osmotic pressure of a given solute component is equal to its kinetic energy per unit volume of the solution. In an aqueous solution, the external pressure acting on the solution (analogous to total pressure of a gas mixture) is equal to the sum of osmotic pressure of the solutes plus the pressure of the water component. However, since water is a condensed phase, the water-component pressure is of a different nature than osmotic pressure. Thus, if the sum of the osmotic pressures exceeds the external pressure, the water-component pressure could be negative. That water could be under tension in a solution has been suggested by Hulett¹⁵. This is an important difference between gases and liquids.

Implications to the Kirkendall effect: How may the above ideas be used to interpret the Kirkendall effect? There are two aspects to this question. The first is to extend the concept of pressure exerted by free-moving particles (gas pressure or osmotic pressure) to solid diffusion. The second pertains to how a solid may respond to changing internal stresses.

Note that osmotic pressure is an expression of the kinetic energy of diffusing particles normalized per unit volume of the solution. Given this, there is no reason why the concept of osmotic pressure cannot be extended to diffusion in solids. At a given temperature in a solid, most atoms occupy fixed positions at which they vibrate by virtue of their vibrational energy. However, a small number of the atoms may possess sufficiently high vibrational energy to get out of the fixed position, move freely and diffuse. These mobile atoms possess kinetic energy. This kinetic

energy, expressed per unit volume of the solid is osmotic pressure. Thus, it is reasonable to postulate that the rate of diffusion of an atom in an alloy is proportional to spatial variation of its osmotic pressure. We now proceed to apply this reasoning to the Kirkendall effect.

The counter-diffusion of copper and zinc is pure diffusion, with each species driven by its gradient of osmotic pressure. At a given location, we may consider osmotic pressure of each species as well as the total osmotic pressure being equal to the sum of osmotic pressures. As time proceeds, there will be an accumulation of excess zinc atoms on the copper side. This should be expected to increase total osmotic pressure on the copper side in relation to the brass side. The difference in total osmotic pressure should be expected to drive a mixture of copper and zinc atoms towards the brass side. The movement of the copper-zinc mixture, impelled by the gradient of total osmotic pressure, can be thought of as exerting a viscous drag on the solid matrix, leading to local deformation.

Energy depletion and deformation

We now consider a second model. For this, we use as metaphor, the deformation of a water-saturated porous medium consequent to diffusive drainage of water.

Karl Terzaghi founded the field of soil mechanics with experimental studies of deformation of water-saturated clays. He was interested in the time-dependent settlement of clay foundations caused by a gradual draining away of water¹⁶. To rationalize the deformation of the water-solid mixture, Terzaghi postulated that at any point within the soil, the stresses tending to compress the soil (external stress) are borne partly by the solid matrix (matrix stress) and partly by the fluid (water pressure), and that the volume of the porous solid skeleton is solely a function of matrix stress, and independent of water pressure. He further postulated that matrix stress is equal to the external stress less the water pressure. This difference is referred to as the 'effective stress', or the stress that effectively governs the porous solid's volumetric strain. That is, matrix stress is equal to effective stress (Figure 4).

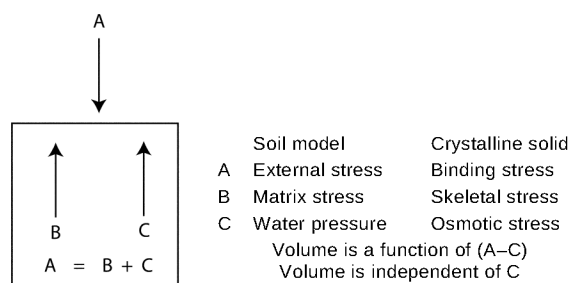


Figure 4. Schematic comparison of stress relationships in soils and crystalline solids.

Suppose a small quantity of water is removed from the soil (say, by pumping), and the water pressure is decreased by a certain magnitude at the point of removal. Then, according to Terzaghi's postulate, matrix stress will be increased by the same magnitude, and this will cause the volume of the soil to decrease by an amount depending on the compressibility of the soil. This soil consolidation model is widely used to explain land subsidence associated with withdrawal of groundwater, oil and natural gas in various parts of the world. The central idea is that the energy removed along with the water is ultimately responsible for volume decrease.

We now use the soil consolidation model as an analogy for the Kirkendall effect. At any location within the solid, the bonding force holds the atoms together in a stable configuration so that the solid has stiffness and shear strength. Let this bonding force per unit area be referred to as the 'bonding stress'. Opposing this are two stresses. One stems from the vibrational energy of atoms that occupy stable positions (skeletal stress), and the other stems from the kinetic energy of diffusing mobile atoms (osmotic stress). Thus,

$$\sigma_{\text{bond}} = \sigma_{\text{sk}} + \sigma_{\text{osm}}. \quad (1)$$

By analogy with Terzaghi's model, we postulate that solid volume is solely a function of skeletal stress and independent of osmotic stress. Hence, the stress that effectively controls volume is

$$\sigma_{\text{eff}} = \sigma_{\text{sk}} = \sigma_{\text{bond}} - \sigma_{\text{osm}}. \quad (2)$$

If, at a given temperature, we assume the bonding stress to be constant, then the change in effective stress that controls volume change is given by

$$\delta\sigma_{\text{eff}} = -\delta\sigma_{\text{osm}}. \quad (3)$$

Consequently, if osmotic stress decreases locally, skeletal stress will effectively increase, and volume will decrease. In Kirkendall's experiment, the zinc atoms that diffused out of brass in excess of the copper atoms carried kinetic energy out of the brass, leading to a decrease in osmotic stress in brass. This decrease in osmotic stress caused an increase in skeletal stress, and an accompanying volume decrease of α -brass.

Three-dimensional soil consolidation, based on Terzaghi's conceptualization, was formally brought within the framework of elasticity theory by Biot¹⁷. The Kirkendall effect must be amenable to this type of stress-strain analysis.

Consider now the magnitudes of energy and pressure involved. The pressure p exerted by n atoms at 780°C (1053 K), confined to a volume V is given by

$$p = \frac{nkT}{V}, \quad (4)$$

where k is the Boltzmann's constant and T the temperature. Using $k = 1.38 \times 10^{-23}$ J/K and $T = 1053$ K, we get an osmotic pressure of 1.45×10^{-20} Pa per particle in a cubic metre, or 1.45×10^{-14} Pa per particle in a cubic centimetre. If we take V as 1 cubic cm and set n to be 10^{20} (0.02% mol), the osmotic pressure works out to 1.45 MPa or about 14.5 atm, or about 205 psi, suggesting that even a relatively small number of excess mobile atoms can potentially mobilize sufficient stresses to strain the material.

Considering stress and strain, it follows that volume decrease will be more pronounced in materials of relatively low bulk modulus (or higher compressibility) than in materials of relatively high bulk modulus. Moreover, as vacancies migrate and coalesce, the resulting change in volume will depend much on the ability of the material to accommodate vacancy accumulation through increased porosity. It should be expected that the Kirkendall effect will be more pronounced in materials with relatively higher compressibility and less pronounced in materials that can internally absorb the vacancies through augmented porosity.

Discussion

In the foregoing, it has been argued that the Kirkendall effect needs to be looked at from the perspective of deformation mechanics. Two conceptual models have been presented providing a framework for the purpose. It is now pertinent to discuss the extent to which deformation has been addressed in the literature with regard to the Kirkendall effect, and the limitations of the two models presented above.

Diffusion and deformation in metals

Kirkendall's observations came at a time when attempts to understand the mechanics of solid diffusion had just begun. In 1921, Groh and Hevesy¹⁸, having successfully measured self-diffusion in lead at temperatures close to melting, intuitively suggested a 'softening' of the solid structure that facilitated diffusion. Shortly thereafter, Langmuir^{19,20} suggested that relatively lesser magnitudes of stresses would be needed to enable diffusion if several rows of atoms moved simultaneously in different directions, producing a species of circulation. Presumably, Hevesy and Langmuir believed that all the lattice positions were filled with atoms. At this time, Frenkel²¹ proposed the vacancy mechanism, allowing for more space for movement of atoms.

One consequence of Langmuir's ring mechanism was that opposing fluxes of the diffusing species must be equal in binary diffusion in substitutional alloys. However, the observed displacement of the phase boundary indicated to Kirkendall that more zinc was leaving brass than copper was diffusing in. Accordingly, he abandoned

Langmuir's model (which he had accepted earlier²²), and concluded that the crystal lattices must reform without destroying the columnar structure to accommodate volume decrease. Subsequently, this simple explanation came to be reinforced by invoking Frenkel's vacancy mechanism. Kirkendall's intuitive explanation was kinematic; it did not concern itself with causative forces. It was tacitly assumed that vacancies somehow coalesce to cause contraction.

However, the mechanics of diffusion was being addressed by others, not necessarily concerned with the Kirkendall effect. Herring²³, following a suggestion by Nabarro, developed a theory for creep-deformation of a polycrystalline solid at high temperatures subjected to an applied shear stress. The central assumption of this theory was that any crystal can change its shape by self-diffusion in such a way as to yield to an applied stress, analogous to a viscous fluid. In other words, diffusion is induced by an applied stress. McCartney²⁴ reviewed the literature on vacancy diffusion and pointed out that existing theory had made no attempt to incorporate the mechanical behaviour of the crystal. To remedy this, he presented a theory for the irreversible thermodynamic processes occurring in the interior of a stressed, single-component crystal, and proposed a phenomenological equation based on fundamental laws of continuum mechanics.

Caveats

The two models suggested in the foregoing are propositions that need to be critically examined before acceptance, refinement or rejection. Potential arguments against the models are discussed below.

Role of osmotic pressure: Central to both models is the assumption that the role of diffusive atoms in deformation can be rationalized in terms of osmotic pressure. It may be argued that in order to invoke osmotic pressure, each lattice plane in a crystal must be treated as a dynamic membrane with time-varying characteristics. Additionally, the accumulation of vacancies with time would also have to be accounted for in treating lattice planes as membranes. In this regard, it is necessary to point out that an osmotic pressure, defined by van't Hoff to be analogous to partial pressure of a gas, exists regardless of the presence of a membrane. It is simply that when a membrane exists, osmotic pressure may be physically observed or quantitatively measured. The notion that osmotic pressure drives molecular diffusion is implicit in van't Hoff's expression for osmotic pressure, $p_{\text{osm}} = (mRT)/V$, where m is the number of moles of the dissolved substance, R the universal gas constant, T the absolute temperature and V the volume of solution. This definition was used by Einstein¹⁴ in his paper on Brownian motion to derive an expression for molecular diffusion coefficient for a spherical particle randomly moving in a viscous fluid.

Plastic vs elastic deformation: Assuming that the deformation observed by Kirkendall is a mechanical strain, the question arises whether it is due to plastic or elastic deformation. Since plastic deformation can only cause distortion without volume change, the strain must be elastic in nature. If so, how does elastic strain occur in a free body?

This question necessitates a consideration of how vacancy migration may lead to volume shrinkage. Considering the simple case of Kirkendall's binary system, if the excess vacancies created in α -brass get filled by other atoms pushed in to fill the vacancies, the resulting lattice reorganization can be expected to lead to a volume decrease as visualized by Kirkendall¹. This shrinkage will be accompanied by a reduction in porosity. For this to happen, low-energy atoms occupying stable positions in the neighbourhood must be pushed to fill the excess vacancies. Force will be needed for this.

If, on the other hand, the migrating vacancies get absorbed at local grain boundaries, then the resulting increase in porosity may tend to reduce the Kirkendall shift. Thus the stress-strain relationship in this simple binary system may depend on the attributes of the grain boundaries, notably on their ability to absorb vacancies, in addition to other factors that commonly influence stress-strain relationships.

This consideration raises the possibility that stress-strain relationship for a solid subject to external loads may differ from that which relates to reorganization of internal stresses. A granular solid with inter-grain boundaries, when subjected to external compressive stresses, will respond by slippage along grain-to-grain contacts. In polycrystalline metallic materials at high temperatures, Herring²³ pointed out that creep-deformation will be mediated by self-diffusion in such a way as to yield to an applied stress, analogous to a viscous fluid. However, if the same material were to be subjected to internally generated stresses arising from unequal diffusion rates, volume change will be influenced by the opportunities for vacancies to accumulate locally to enhance porosity or to diffuse out freely, leading to volume decrease.

As to the question whether elastic strain can occur in a free body, there is no reason why it cannot. Internal redistribution of stresses in a free body can reasonably be expected to redistribute strain locally in such a way as to compensate shrinkage at some locations with extension at others.

Multi-component diffusion: In case of multi-component systems in which several species inter-diffuse, net vacancy flows may yield additional time-dependence of Kirkendall shifts and fluxes of individual components. These are referred to as vacancy wind effects. How will the dynamical models based on osmotic pressure account for these effects?

In the case of multi-component systems, different species may migrate at different rates and in different directions. Consequently, it is reasonable to expect that some parts of the solid will experience energy depletion, while others will experience energy accumulation. The former will have a tendency to experience compression and contract, while the latter will tend to experience tension and expand. Under these conditions, how the vacancies may behave will depend on several factors, including the ability of grain boundaries to absorb vacancies. From a stress-strain perspective, the problem will involve a multiplicity of neighbouring regions to experience varying magnitudes of tension and compression interacting with each other.

In the literature, vacancy wind effects are generally handled on the basis of chemical potentials and thermodynamics. However, it seems quite possible that such effects arising from multi-component diffusion will be amenable to credible analysis based on solid mechanics. Indeed, such an analysis may even yield novel insights about the Kirkendall effect.

Interstitial diffusion: The energy-based models presented above suggest that the Kirkendall effect should also be observed in the case of systems involving interstitial diffusion. Is there any evidence for this?

It is reasonable to expect that structural strength and related mechanical properties of the solid will be dominated by the large atoms that occupy major lattice positions. Smaller interstitial atoms may only influence these properties in a subordinate role. If so, in systems restricted to interstitial binary diffusion, the Kirkendall effect may be expected to be significantly attenuated. It should be interesting to find out if this speculation can be justified by available data.

Two-dimensional systems: Finally, it may be noted that the Kirkendall effect has been proposed for diffusion of solutes along two-dimensional interfaces such as grain boundaries. How can such observations be subjected to stress-strain analysis? The two models presented in this work are strictly restricted to three-dimensional solid bodies. They are not directly applicable to two dimensional systems. Nevertheless, it is worth mentioning that even in systems idealized to be two-dimensional, one has to allow for a finite thickness in the third dimension. Moreover, the surfaces on which atoms diffuse do offer resistance. These surfaces may also attract and hold atoms at fixed locations. On these surfaces there may exist high-energy mobile atoms and low-energy fixed atoms.

Concluding remarks

Binary diffusion was first discovered in gases and then in liquids during the nineteenth century. Contributions by van't Hoff and Nernst during the 1880s provided a

framework for an integrated dynamical understanding of binary diffusion in gases and liquids. Thus, partial pressure of gas components and osmotic pressure of solute molecules are analogous, both conforming to ideal gas laws under certain conditions. Binary diffusion in liquids is different from gas diffusion in that the migration of water, a condensed phase, differs from diffusion of a gas component. Whereas the partial pressure of a gas is always positive, the pressure of the water component in an aqueous solution can be negative, because water can sustain tension in the presence of solids. Graham's work during the nineteenth century also established a dynamic coupling between diffusion of individual components and pressure-driven viscous flow of mixtures.

Following Kirkendall's seminal contribution, attention has been almost exclusively devoted to using thermodynamics for explaining volume changes and displacement of reaction interfaces. Although the interconnection between diffusion and stress has been addressed by some workers (e.g. Herring²³), little attention has been given to a dynamical understanding of the Kirkendall effect in terms of stress-strain relationships.

Looking at how ideas have developed in the understanding of material diffusion in gases, liquids and solids, it appears reasonable to extend the concept of osmotic pressure to address atoms with sufficiently high kinetic energy that have vacated their stable position in a lattice and are free to diffuse. The two models presented in the foregoing show how osmotic pressure provides a conceptual basis to approach the Kirkendall effect from a dynamical perspective.

1. Kirkendall, E. O., Diffusion of zinc in alpha brass. *Trans. Am. Inst. Min. Metall. Eng.*, 1942, **147**, 104–110.
2. Smigelskas, A. D. and Kirkendall, E. O., Zinc diffusion in alpha brass. *Trans. Am. Inst. Min. Metall. Eng.*, 1947, **171**, 130–142.
3. Nakajima, H., The discovery and acceptance of Kirkendall effect: The result of a short research career. *JOM*, 1997, **49**, 15–19.
4. Huntington, H. B. and Seitz, F., Mechanism for self-diffusion in metallic copper. *Phys. Rev.*, 1942, **61**, 315–425.
5. Graham, T., On the law of diffusion of gases. *Philos. Mag. J. Sci.*, 1833, **2**, 175–191; 269–276; 351–358.
6. Graham, T., Of the motion of gases. *Philos. Trans.*, 1846, **136**, 573–632.
7. Mason, E. A., Thomas Graham and the kinetic theory of gases. *Philos. J. Trans. R. Philos. Soc. Glasgow*, 1970, **7**, 99–115.
8. Kramers, H. A. and Kistemaker, J., On the slip of a diffusing gas mixture along a wall. *Physica*, 1943, **10**, 699–713.
9. Fick, A., On liquid diffusion. *Philos. Mag. J. Sci.*, 1855, **10**, 31–39.
10. Dutrochet, R. J. H., New observations on endosmosis and exosmosis, and on the cause of this dual phenomenon. *Ann. Chim. Phys.*, 1827, **35**, 393–400.
11. Narasimhan, T. N., Fick's insights on liquid diffusion. *EOS Trans. Am. Geophys. Union*, 2004, **85**, 499; 501.
12. van't Hoff, J. H., Die Rolle des osmotischen Druckes in der Analogie zwischen Lösungen und Gasen (Role of osmotic pressure in the analogy between solutions and gases). *Z. Phys. Chem.*, 1887, **1**, 481–493.

13. Nernst, W., Zur kinetik der losung befindlichen Körper (On kinetics of dissolved substances). *Z. Phys. Chem.*, 1888, **2**, 613–622; 634–637.
14. Einstein, A., Über die von der molekularkinetischen Theorie der wärme geordnete Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen (On the motion of small particles suspended in a stationary solution required by the molecular-kinetic theory of heat). *Ann. Phys.*, 1905, **322**, 549–560.
15. Hulett, G. A., Beziehung zwitschen negativem Druck und osmotischem Druck (Relation between negative pressure and osmotic pressure), *Z. Phys. Chem.*, 1903, 353–368.
16. Terzaghi, K., Die Berechnung der Durchlässigkeitsziffer des Tones aus dem Verlauf der hydrodynamischen Spannungsercheinungen (The calculation of permeability number of the clay out of the process of the hydrodynamic phenomenon tension). *Sitzungsber. Akad. Wiss. Wien. Math-Naturwiss. Kl., Part Iia*, 1923, **32**, 125–138.
17. Biot, M. A., General theory of three-dimensional consolidation. *J. Appl. Phys.*, 1941, **12**, 155–164.
18. Groh, J. and Hevesy, G. V., Die Selbstdiffusion in festern Blei (Self-diffusion in solid lead). *Ann. Phys.*, 1921, **370**, 216–222.
19. Rosenhein, W., The inner structure of alloys. *J. Inst. Met.*, 1923, **30**, 17.
20. Jeffries, J., The trend in the science of metals. *Trans. Am. Inst. Min. Metall. Eng.*, 1924, **120**, 310.
21. Frenkel, J., Theorie der Adsorption und verwandter Erscheinungen (Theory of adsorption and related phenomena). *Z. Phys.*, 1924, **26**, 117–138.
22. Kirkendall, E. O., Thomassen, L. and Upthegrove, C., Rates of diffusion of copper and zinc in alpha brass. *Trans. Am. Inst. Min. Metall. Eng.*, 1939, **133**, 186–203.
23. Herring, C., Diffusional viscosity of a polycrystalline solid. *J. Appl. Phys.*, 1950, **21**, 437–445.
24. McCartney, L. N., Vacancy diffusion in a crystal. *Acta Metall.*, 1975, **23**, 769–777.

ACKNOWLEDGEMENTS. Thanks are due to Ramamoorthy Ramesh and two anonymous reviewers for critical review and comments. I also thank M. A. Dayananda for comments on an earlier version of the manuscript.

Received 22 February 2007; revised accepted 29 August 2007