

DISCUSSION

Smoluchowski, R.: The occurrence of a Varley type mechanism in bromides would be expected to be less probable than in chlorides because of the dependence of the Auger process on the atomic number. Perhaps bromides require still another type of mechanism.

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Effect of Hydrostatic Pressure on the Rate of Atomic Movement in Noble Metals*

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In recent years it has become possible to estimate some physical constants and properties of vacancies in noble metals. Of these determinations the volume of a vacancy is one of the most uncertain quantities due to the fact that the volume is estimated indirectly by the combination of two or more independent experiments. In order to offer more direct approach to this problem, Nachtrieb, Lawson and their co-workers measured the self-diffusion rates in sodium and lead in a pressurized liquid system. For noble metals it is necessary to employ pressurized gas systems due to the requirement of high temperatures.

The vacancy volume obtained by this method (activation volume) is the volume of a vacancy at a saddle point configuration, *i. e.*, the volume of a vacancy in motion. The measurement of self-diffusion rates in single crystals of silver at high pressures up to 8KB was carried out in a pressurized argon system. The activation volume thus obtained was 90 percent of the atomic volume. This value represents the sum of the two volumes: the volume of a vacancy at rest (ΔV_f) and the volume expansion introduced by the migration of a vacancy into a saddle point configuration

(ΔV_m). This latter quantity was estimated by Emrick in gold by measuring the pressure effect on the annealing rate of the quenched-in vacancies in gold. The value of 15 percent of the atomic volume was obtained by this method. If it can be assumed that a similar value holds for silver, then the static volume of a vacancy in silver is 75 percent of the atomic volume. This is considerably larger than the values estimated by indirect methods or by theoretical calculations.

It is necessary, however, to perform the quenching experiment under pressure in order to obtain the static vacancy volume directly. This can be accomplished if a sufficiently large quenching rate can be achieved at high pressure. Preliminary experiments indicate that the quenching rate of 10^4 deg./sec is possible at the pressure range of 2.5KB to 9KB. In order to increase the quenching rate and remove some difficulties associated with a dc heating, a pulse heating method is currently being tested.

It is hoped that the quenching experiment at high pressure, combined with the self-diffusion and vacancy annealing at high pressure, all of which are in progress in this laboratory, will yield significant information which can be added to the present knowledge of the vacancies in noble metals.

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DISCUSSION

Lazarus, D.: It might be pointed out that measurements of the effect of pressure on diffusion may shed some light on the mechanism of diffusion, particularly for those b.c.c. systems where the vacancy mechanism is not established. In this connection, it might be noted that preliminary measurements by Dr. Y. Adda, at C.E.N., Saclay, reveal that the activation volume for self-diffusion in γ -Uranium may be negative, possibly implying an interstitial mechanism.

Sosin, A.: The results in silver appear queer to me, not being familiar with activation volumes. I would expect the activation volumes to be roughly proportional to activation energies. This is not true in silver. Could you enlarge on this point?

Tomizuka, C.: S. A. Rice and Nachtrieb derived an expression between the activation energy and the activation volume by employing the law of corresponding states. This relation, however, requires the knowledge of the volume change upon melting as well as the heat of fusion. The reliable value for the former quantity was not available.

I believe that the simple proportionality between ΔH (activation energy) and ΔV can not be taken too seriously.

Lidiard, A. B.: In connection with your remark on the relation of ΔH to ΔV in reply to Dr. Sosin, I would like to make this comment. The equivalence of the ratio ($\Delta H/\Delta V$) for diffusion to that for melting is not, as has sometimes been claimed, a consequence of the dynamical theory of diffusion but is a purely thermodynamic deduction from the empirical result that the pressure dependence of diffusion coefficient is given by

$$D = D_0 \exp(-bT/T_m(p))$$

in which D_0 and b are constants and where $T_m(p)$ is the melting temperature at pressure p .

Tomizuka, C.: The relationship I was referring to is

$$\frac{\Delta H}{\Delta H_m} = \frac{\Delta V}{\Delta V_m}$$

where ΔH_m is the heat of fusion and ΔV_m is the volume change upon melting.

I agree with you entirely that the law of corresponding states is an empirical rule. S. A. Rice and N. Nachtrieb combined this rule with thermodynamic considerations to derive the above relation.
