

Viscosity and Self-Diffusion of Liquid Metals

Abstract. It is demonstrated that the empirical relationship between activation energy of viscosity and the melting point of a metal is also true for the energy of self-diffusion, in view of the Stokes-Einstein relation. The provision is that viscosity and self-diffusion be expressed in a self-consistent manner, as provided, for example, by the J. Frenkel's theory of liquids. Thus, one can now estimate either the viscosity or the self-diffusion of any metal over a substantial temperature range from its known melting point.

A few years ago (1, 2) we drew attention to the empirical fact that the activation energy of viscosity, H_η , of metals is a straight line function of their melting points, T_{mp} , when plotted on a log-log graph (see 1, p. 788, Fig. 9).

Self-diffusion, D , is directly related to viscosity, η , by means of the Stokes-

Einstein relation (in its Eyring version):

$$\eta D = \frac{kT}{6\delta} \quad (1)$$

where T is the temperature in deg K, k is the Boltzman constant, and $\delta = (V_{at}/N_{avog})^{1/3}$, V_{at} being the atomic volume and N_{avog} , Avogadro's number.

It therefore follows that the above empirical relationship should also hold between the activation energy for self-diffusion (2) and the T_{mp} of the metal, since the two energies are equal except in sign, and provided both η and D are expressed in a self-consistent manner.

If the simplest form of theory of liquids is used, namely, Frenkel's kinetic theory (3)

$$\eta = B T e^{-\gamma} e^{E_{VD}/RT} \quad (2)$$

and

$$D = D_0 e^{\gamma} e^{-E_{VD}/RT} \quad (3)$$

where B , D_0 and γ are constants, E_{VD} is the activation energy for both viscosity and diffusion (in cal/g-atom) and R is the gas constant; η is the viscosity (in poises), D in cm^2/sec . It follows further from Frenkel's theory that the constants B and D_0 can be calculated for any metal from the expressions

$$B = h N_{avog} / \theta_D V_{at} \quad (4)$$

and

$$D_0 = (k/6 h N_{avog}^{2/3}) \theta_D V_{at}^{2/3} \quad (5)$$

where h is Plank's constant, θ_D and V_{at} are the Debye temperature in deg K and the liquid atomic volume of the metal (at the melting point), respectively. Thus defined, it is evident that the product ηD gives the Stokes-Einstein relation. The Frenkel factor $e^{-\gamma}$ (or its reciprocal e^γ) is close to unity and for the moment may be considered as an adjustment of $B_{\text{exptl}}/B_{\text{theor}}$ (or $e^\gamma = D_0^{\text{exptl}}/D_0^{\text{theor}}$) for each metal; it can be considered as the entropy of E_{VD} .

The activation energy for viscosity or self-diffusion—that is, E_{VD} (in cal/g-atom) is, like H_η (1, 2), a straight line function of the melting point of the metal, T_{mp} , (in deg K) on a log-log graph and may be expressed as

$$E_{VD} = 3.53 T_{mp}^{1.10} \quad (6)$$

The E_{VD} here differs from our original H_η (1, 2) and is equal to:

$$E_{VD} = H_\eta \left[\frac{\ln(\eta_1/T_1)}{\ln(\eta_2/T_2)} \right] \quad (7)$$

if η_1 and η_2 are the viscosities at temperatures T_1 and T_2 .

The above formulas obviously are not exact for an infinite temperature range. They are functions of T only, whereas actually the volume of the liquid metal is also a variable, since it expands—or the number of atoms per cubic centimeter decreases—although slowly, with temperature. Thus, they cover practically a range of about 500°K from the melting point upward,

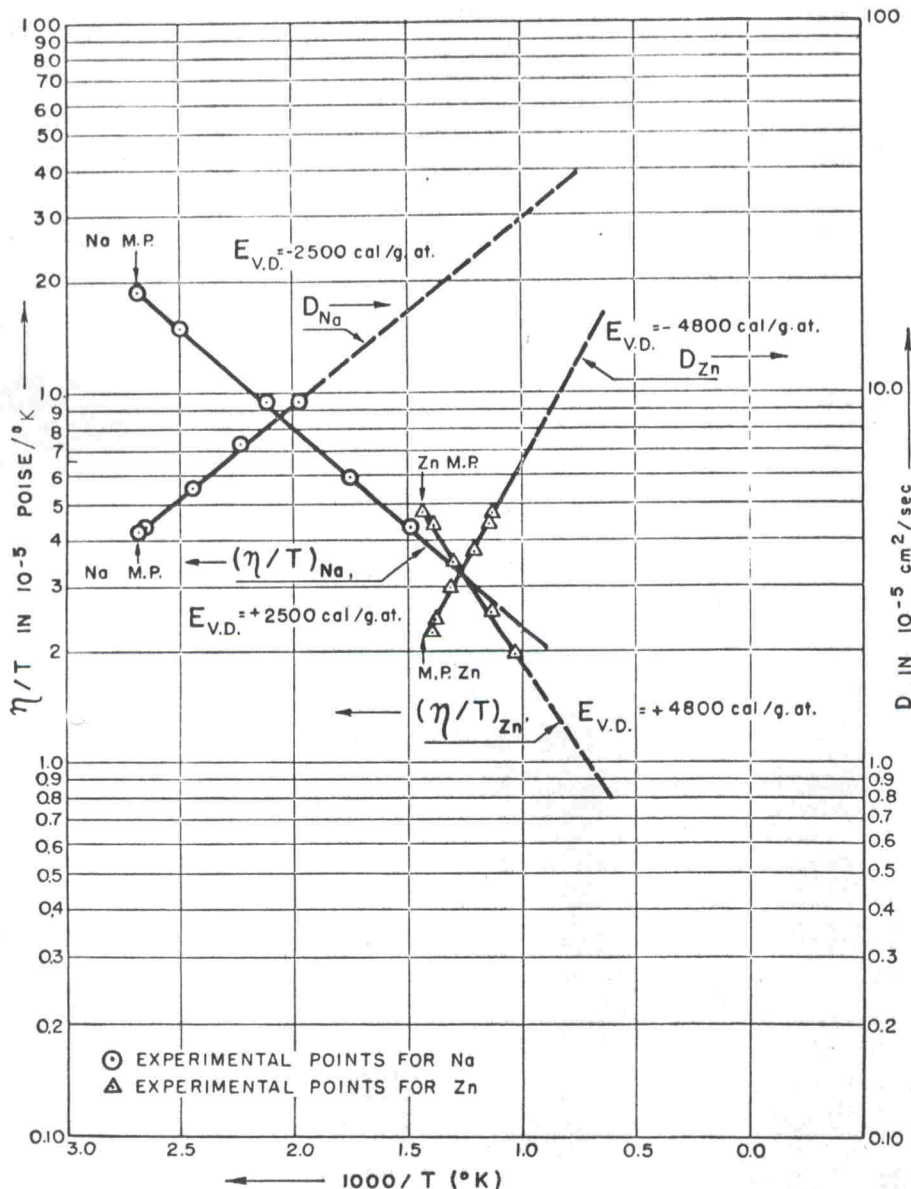


Fig. 1. A comparison of the experimental results obtained for the viscosity and diffusion of Na and Zn with two sets of straight lines of the same numerical slope, but of opposite sign, for viscosity and diffusion.