

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,

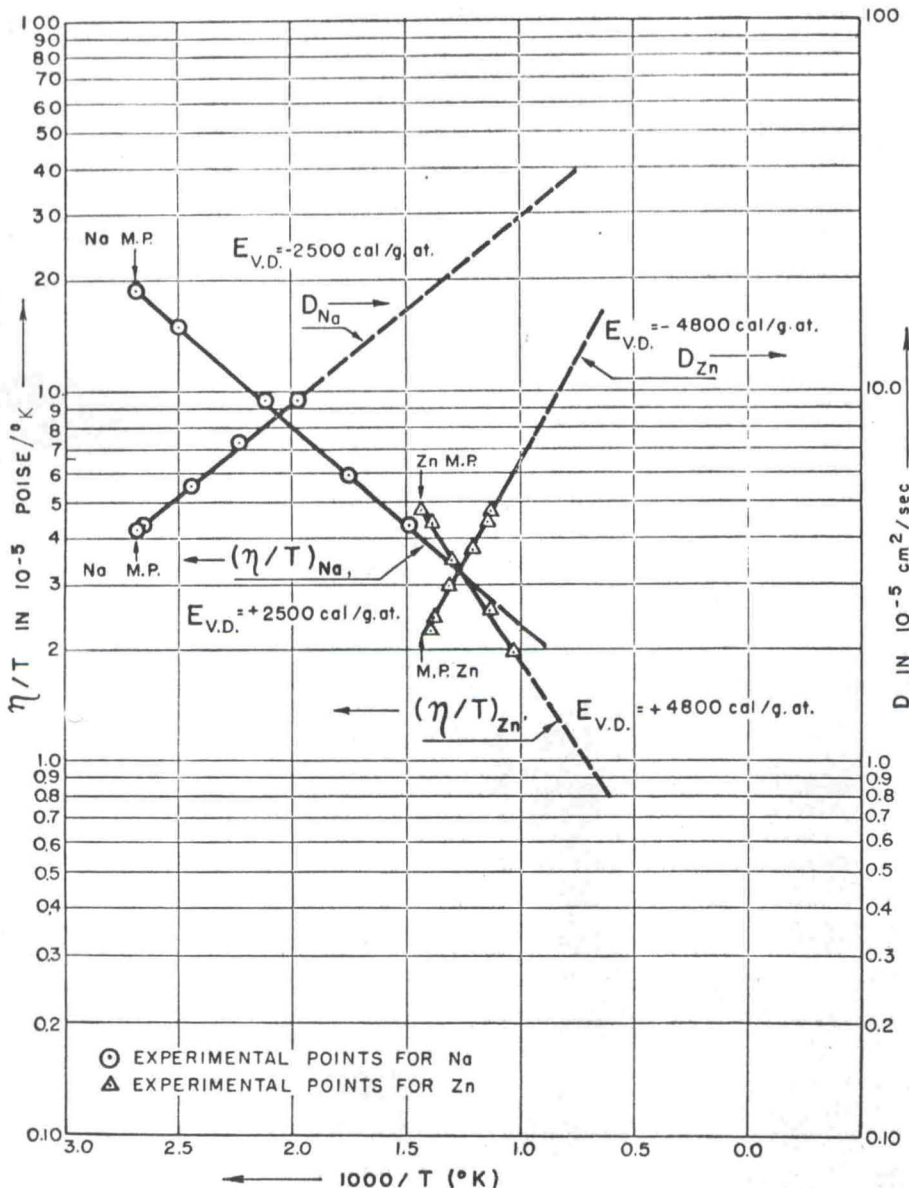


Fig. 1. A comparison of the experimental results obtained for the viscosity and diffusion of Na and Zn with two sets of straight lines of the same numerical slope, but of opposite sign, for viscosity and diffusion.

if one uses for V_{at} (in Eqs. 4 and 5) the liquid atomic volume at the melting point and not more.

The viscosity at the melting point, η_{mp} , can be estimated for any metal from Andrade's well known expression:

$$\eta_{mp} = 5.7 ([\text{at.wt.}] \times T_{mp})^{1/2} / (10^4 \times V_{at}^{2/3}) \quad (8)$$

More data supporting the above relationship, as well as a detailed discussion of the theory, will be presented elsewhere. Suffice it to show here two typical examples, namely, Na and Zn. The diffusion measurements are due to Nachtrieb and his associates (4) while those on viscosity are taken from the *Liquid Metals Handbook* (5).

Figure 1 shows four series of experimental results—that is, the viscosity and diffusion of Na and Zn, respectively, are compared with two sets of straight lines of the same numerical slope, but of opposite sign, for viscosity and diffusion. The four specific equations of these straight lines, in the form of the general equations 2 and 3, are as follows [η in poises, D in cm^2/sec , T in deg K, $R = 1.9865 \text{ cal}(\text{deg K})^{-1} (\text{g-atom})^{-1}$].

For Na

$$\eta = 0.84 \times 10^{-9} T e^{-0.28} e^{+2500/RT}$$

$$D = 7.95 \times 10^{-4} T e^{+0.41} e^{-2500/RT}$$

and for Zn

$$\eta = 2.00 \times 10^{-9} T e^{-0.29} e^{+4800/RT}$$

$$D = 4.64 \times 10^{-4} T e^{+0.42} e^{-4800/RT}$$

The constants B and D_0 of Eqs. 2 and 4 and Eqs. 3 and 5 were calculated by using Debye temperatures, θ_D , of 192°K and 213°K and liquid atomic volumes at the melting point, V_{at} , of 24.76 and 9.45 $\text{cm}^3/\text{g-atom}$ for

Na and Zn, respectively.

Figure 1 shows that the experimental points fit the theoretical lines very well and that the same E_{VD} , that is, 2500 cal/g-atom for Na and 4800 cal/g-atom for Zn, describes both viscosity (η/T) and self-diffusion equally well, within the accuracy of the measurements.

The adjustment of experimental points to the theoretical lines involving B , D_0 , θ_D , and E_{VD} , is possible essentially only by adjustment of Frenkel's e^γ or $e^{-\gamma}$ factor; it is close to unity and for a perfect agreement γ should be identical in Eqs. 2 and 3.

Finally, from the general equation for E_{VD} (that is, Eq. 6) we obtain for Zn and Na, with their $T_{mp} = 693^\circ\text{K}$ and 371°K , respectively, heats of activation of 4700 and 2400 cal/g-atom.

In summary, one can estimate from the above relationships the viscosity or self-diffusion of any liquid metal, over a substantial temperature range, from its known melting point.

ARISTID V. GROSSE

Research Institute of Temple University,
Philadelphia, Pennsylvania 19144

References and Notes

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