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, $H\eta$, 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):

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

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.

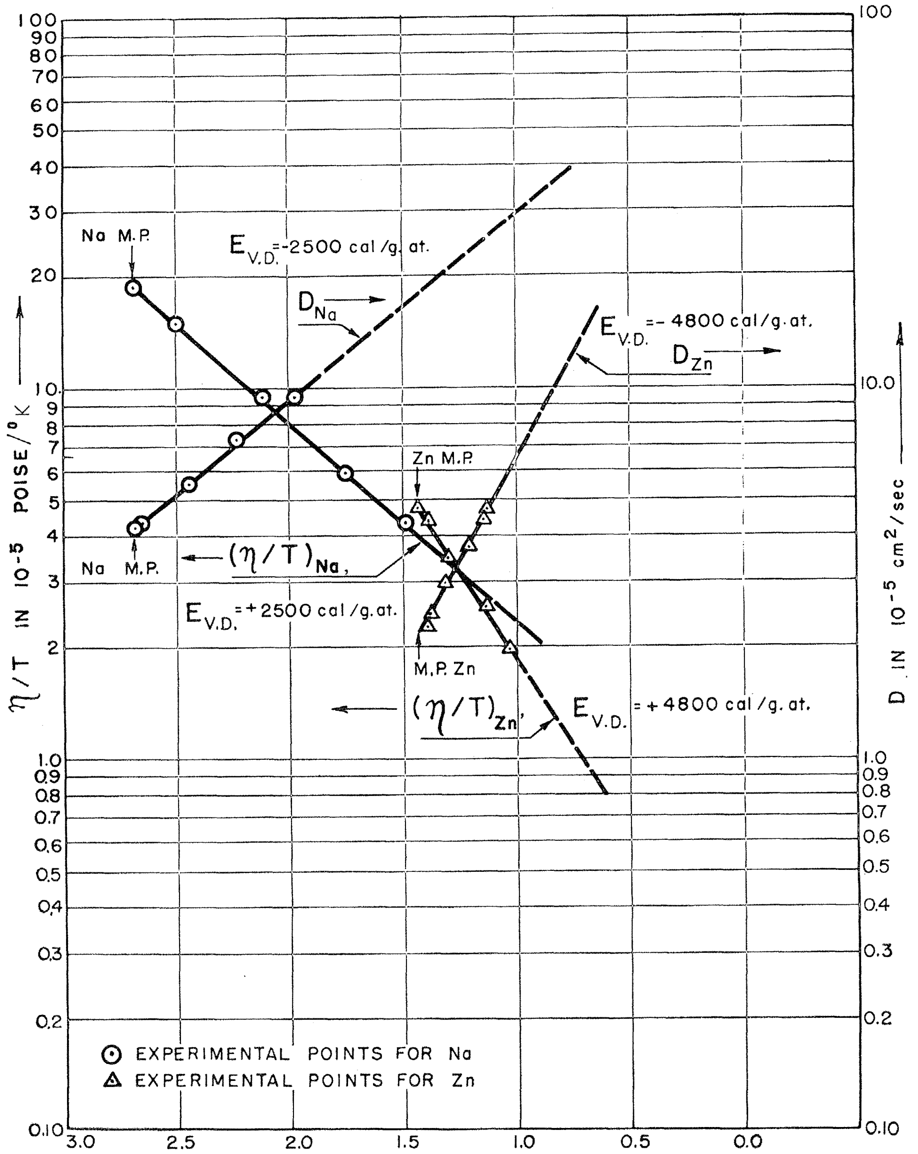

Fig. 1. A comparison of the experimental results obtained for the viscosity and diffusion of Na and Zn with two sets of straight lines of the same numerical slope, but of opposite sign, for viscosity and diffusion.

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*)

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

and

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

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 cm²/sec. It follows further from Frenkel's theory that the constants B and D_0 can be calculated for any metal from the expressions

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

and

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

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_{exptl}/B_{theor} (or $e^{\gamma} = D_0^{exptl}/D_0^{theor}$) 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 $H\eta$ (*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

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

The E_{VD} here differs from our original $H\eta$ (*1, 2*) and is equal to:

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

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, 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:

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

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, $R = 1.9865$ cal(deg K)$^{-1}$ (g-atom)$^{-1}$].

For Na

$$\eta = 0.84 \times 10^{-6} T\, e^{-0.28} e^{+2500/RT}$$
$$D = 7.95 \times 10^{-4} T\, e^{+0.44} e^{-2500/RT}$$

and for Zn

$$\eta = 2.00 \times 10^{-6} T\, e^{-0.20} e^{+4800/RT}$$
$$D = 4.64 \times 10^{-4}\, e^{+0.42} e^{-4800/RT}$$

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 cm^3/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°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.

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Direct Readout of Sediment Analyses by Settling Tube for Computer Processing

Abstract. *Sediment fall-velocities measured by the Woods Hole Rapid Sediment Analyzer can now be obtained directly on punched paper tape in a form suitable for processing by a computer. This technique saves much time because it eliminates manual card punching, a step in which an operator transfers values from sediment analyses to punch cards in order to make the data acceptable to computers.*

One of the most useful measurements utilized by sedimentologists and engineers is the separation of a sediment sample into classes of grains according to their size. For many years the standard way of doing this has been to shake a weighed sample through screens of known sizes and to weigh the fractions collected on each screen. Another way to make the measurement has been to permit the sample to settle in a column of water and by one means or another to measure the spectrum of fall-velocities. Since fall-velocity is a function of grain-size, one can interpret the fall-velocities in terms of grain size. Although there are some difficulties associated with the interpretation of grain-size distribution from fall-velocity, such methods are widely used and for many problems are quite satisfactory.

A few years ago much of the tedium was removed from sedimentary analyses by fall-velocity techniques when an analyzer was built which recorded the frequency distribution of fall-velocities present in a sediment sample directly in the form of a linear graph *(1)*. Use of this instrument, the Woods Hole Rapid Sediment Analyzer, has been increasing. It has the advantage of being fast and providing highly reproducible results.

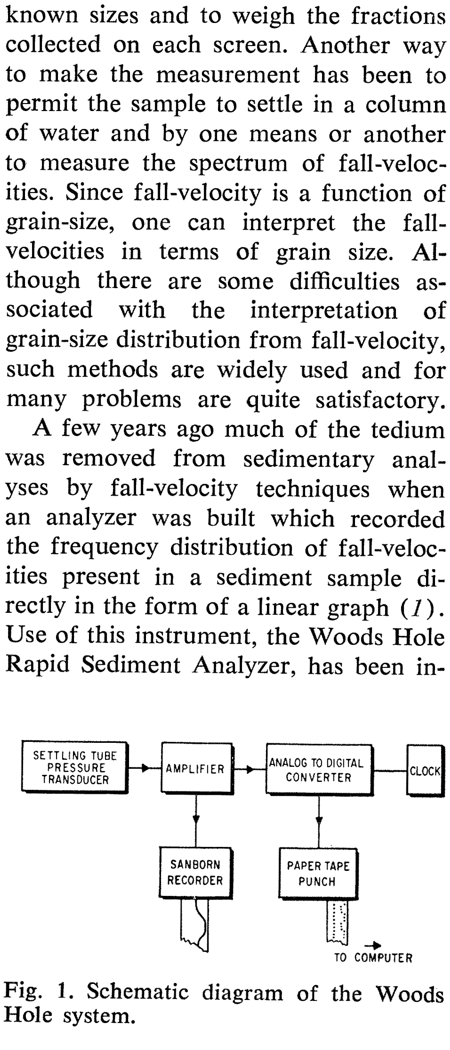

Fig. 1. Schematic diagram of the Woods Hole system.

We report here that the next logical step has been taken and that the output of this analyzer can now be obtained directly in a form acceptable to a high-speed computer. It is now possible to run as many samples as one wishes and get the resulting cumulative frequency distribution in the form of punched paper tape (Fig. 1). Since March 1964, a 1-meter settling tube with a Sanborn-270 pressure transducer and differential transformer has been used with the analyzer at Woods Hole. A Sanborn Carrier Pre-amplifier (Model 150-1100) with power supply (Model 150-400) excites the differential transformer and amplifies its signal which is fed into a Dynamic Systems Electronics analog-to-digital converter (Model ADC-1-B2PT) driving an eight-channel paper-tape punch at ten readings per second.

The punched tape is processed on a GE 225 information processing system which can be programmed to yield all the benefits of high speed computing.

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