J. Inorg. Nucl. Chem., 1961, Vol. 23, pp. 333 to 339. Pergamon Press Ltd. Printed in Northern Ireland

THE VISCOSITY OF LIQUID METALS AND AN EMPIRICAL RELATIONSHIP BETWEEN THEIR ACTIVATION ENERGY OF VISCOSITY AND THEIR MELTING POINTS[1]

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Abstract—It is shown that a simple empirical relationship exists between the activation energy of viscosity for liquid metals and their melting points. This relationship coupled with Da Andrade's expression for the viscosity of the liquid metal at the melting point ($T_{m.p.}$):

$$\eta_{m.p.}(\text{in poises}) = 5{\cdot}7 \times 10^{-4} \cdot \frac{\sqrt{(A \cdot T_{m.p.})}}{V_A^{2/3}}$$

(A = At. wt.; V_A = liq. at. volume at m.p.; °K)

permits us now to estimate the viscosity of *any metal having a closepacked crystal structure*, i.e., one for which the Andrade relationship holds, at any temperature.

All available experimental data on the viscosity of metals were used to establish the *empirical relationship shown in Fig.* 2.

THE metals, from Li, the lightest, to Lw (element 103), the heaviest, represent over 80 per cent of all known elements. It has been shown recently[2] that their liquid temperature range, i.e., the ranges from their respective melting points to their critical points, are greater by far than those of any other class of substances. As monatomic elementary [illegible] they are [illegible] amenable to theoretical treatment than more complex [illegible] the liquid viscosity of the latter shows a very great temperature dependence. In the case of the metals the change is much less dramatic.

All available data on the viscosity of metals are plotted in Fig. 1, the round points showing the experimental range. The experimental data for most metals were obtained from the *Liquid Metals Handbook*, Edition 1 and 2.[3] Additional data were taken for gallium[4] and tin.[5]

ANDRADE'S simple formula[6] expresses the relationship between the viscosity, η, and T, in °K., as follows:

$$\eta = a \cdot \exp(H_\eta/RT) \text{ or}$$

$$\log_{10} \eta = \frac{H_\eta}{2{\cdot}303 \cdot R} \cdot \frac{1}{T} + \log_{10} a,$$

(1) For additional details see report of A. V. GROSSE, "*The Liquid Range of Metals and Some of Their Physical Properties at High Temperatures*," The Research Institute of Temple University, September 5, 1960.
(2) A. V. GROSSE, *J. Inorg. Nucl. Chem.* **22**, 23 (1961).
(3) R. N. LYON, (Editor in Chief), *Liquid-Metals Handbook*, Sponsored by The Committee on the Basic Properties of Liquid Metals, Office of Naval Research, Department of the Navy, in Collaboration with The Atomic Energy Commission and The Bureau of Ships, Department of the Navy, Washington, D.C., June 1, 1950, NAVEXOS, P-733
R. N. LYON, (Editor-in-Chief), *Liquid-Metals Handbook*, Sponsored by The Committee on the Basic Properties of Liquid Metals, Office of Naval Research, Department of the Navy, in Collaboration with The Atomic Energy Commission and The Bureau of Ships, Department of the Navy, Washington, D.C., June 1952, *II edition of the above*, NAVEXOS P-733 (Rev.).
(4) K. E. SPELLS, *Proc. Phys. Soc.*, 48, 299–311 (1936); W. H. HOATHER, *ibid.* 699–707 (1936).
(5) A. J. LEWIS, *Proc. Phys. Soc.*, 47, 102–110 (1935).
(6) E. W. DA C. ANDRADE, *Phil. Mag.* 17, 698–732 (1934).

where a is a constant (in poises) and H_η the energy of activation for viscous flow, in cal/g at. The constants a and H_η for seventeen different metals have been calculated from all available data and are given in Table 1. As can be seen from Fig. 1, the experimental values of $\log_{10}\eta$ all fall on straight lines when plotted against $1/T$.

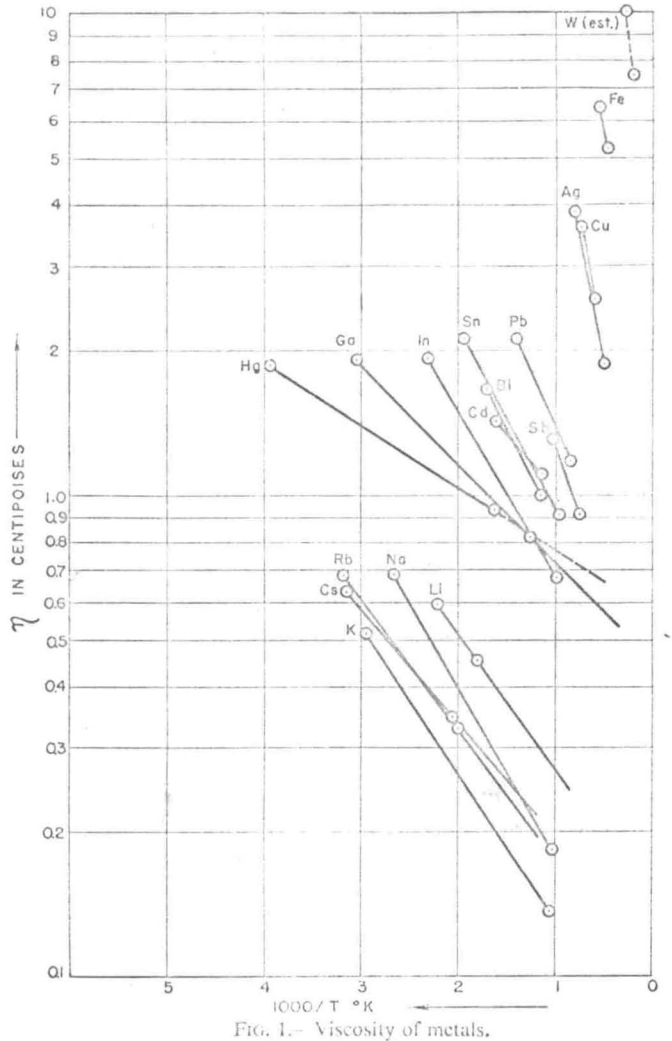

FIG. 1.—Viscosity of metals.

A more accurate viscosity formula takes cognizance of the change of density or specific volume with temperature and is also due to ANDRADE[6] (*loc, cit.* p. 704):

$$\eta \cdot v^{\frac{1}{3}} = a' \cdot \exp(c/vT),$$

where v is the specific volume at the temperature T.

From the theoretical standpoint it would be simpler to discuss the viscosity of metals *at constant volume*. Practically, over any reasonable temperature range, it would require very high pressures to keep the volume of the liquid metal constant and thus cannot be readily realized experimentally. We will therefore restrict ourselves to viscosity at constant pressure (i.e., 1 atm).

Furthermore, since the change in density or specific volume with temperature is comparatively small, i.e., of the order of a few per cent, we will use ANDRADE'S *first formula*, which is sufficiently accurate for our purposes.

TABLE 1.—VISCOSITY CONSTANTS, H_η AND a, OF ANDRADE'S VISCOSITY EQUATION, $\eta_T = a \exp(H_\eta/RT)$ (POISE) AND THE MELTING POINT OF METALS, T_M.

Metal	T_M (°K)	Constant a (poise)	H_η (cal/gm atom)
Hg	234	$5{\cdot}634 \cdot 10^{-3}$	600
Cs	301·7	$1{\cdot}135 \cdot 10^{-3}$	1060
Ga	303	$4{\cdot}359 \cdot 10^{-3}$	955
Rb	312·2	$0{\cdot}911 \cdot 10^{-3}$	1230
K	337	$0{\cdot}659 \cdot 10^{-3}$	1433
Na	371	$0{\cdot}787 \cdot 10^{-3}$	1625
In	430	$3{\cdot}020 \cdot 10^{-3}$	1590
Li	452	$1{\cdot}590 \cdot 10^{-3}$	1220
Sn	505	$3{\cdot}843 \cdot 10^{-3}$	1740
Bi	544	$3{\cdot}594 \cdot 10^{-3}$	1770
Cd	576	$4{\cdot}850 \cdot 10^{-3}$	2040
Pb	601	$4{\cdot}222 \cdot 10^{-3}$	2295
Zn	693	$4{\cdot}085 \cdot 10^{-3}$	2950
Sb	903	$2{\cdot}797 \cdot 10^{-3}$	2970
Ag	1234	$5{\cdot}750 \cdot 10^{-3}$	4690
Cu	1357	$8{\cdot}676 \cdot 10^{-3}$	3680
Fe	1812	$16{\cdot}060 \cdot 10^{-3}$	5070
W (est.)	3650	$36{\cdot}5 \cdot 10^{-3}$	≃7400

Empirical relationship between the activation energy of viscosity and the melting point of the metal

From the standpoint of inorganic chemistry we are interested in estimating, in a general way, the viscosity of any metal over a wide temperature range and finding any kind of relationship between viscosity and physical properties of the element.

The theory of the viscosity of liquids, using rate theory ideas, by EYRING.[7] EYRING'S viscosity theory is based on his theory of absolute reaction rates; his expression for η is:

$$\eta = \left(\frac{\delta}{d}\right)^2 . n . h . \exp(H_\eta/RT)$$

where δ is the distance between molecular layers and for simplicity is assumed to equal d, the distance between crystal lattice points, thus $\left(\frac{\delta}{d}\right)^2 \simeq 1$, n, the number of atoms/cm^3, h = Planck's constant and H_η is the free energy of activation for viscous flow, obtained from the slope of the logarithm of experimental viscosity data against $1/T$.

According to EYRING'S views H_η is proportional to the energy of vaporization, $\Delta U_{vap.} = \Delta H_{vap.} - RT$, since the processes are very similar. In many cases,[8] that is,

[7] H. EYRING, *J. Chem. Phys.* **4**, 283 (1936); see discussion of EYRING'S theory in book by J. O. HIRSCHFELDER, C. F. CURTISS and R. B. BIRD, *Molecular Theory of Gases and Liquids*, pp. 624–630. J. Wiley, New York (1954).

[8] J. F. KINCAID, H. EYRING and A. E. STEARN, *Chem. Rev.* **28**, 301 (1941).

for the "permanent" gases, hydrogen-bonded liquids and many ordinary compounds, H_η is found to equal $\Delta U_{\text{vap.}}/2{\cdot}45$.

The viewpoint *does not hold in the case of metals*,* however. A simple example of the two low melting metals, *mercury* and *gallium*, but boiling far apart, illustrates this point, as shown below:

	Melting point (°K)	H_η (Cal/g atom)	$\Delta U_{\text{vap.}}$ (Cal/g atom)	Normal b.p. (°K)
Mercury	234	600	12,884	630
Gallium	303	988	56,200	2510

H_η for mercury and gallium (taken from Table 1) and $\Delta U_{\text{vap.}}$ for these metals are compared in the table above. Whereas the H_η's show only a small difference, the corresponding values for $\Delta U_{\text{vap.}}$ are far apart; there is no simple relationship between H_η and $\Delta U_{\text{vap.}}$ for metals.

It was found, however, that *a simple relationship exists between* H_η and *the melting point of the metal*. This is shown graphically in Fig. 2. H_η increases as a monotonic function of the melting point of the metal. All known metals for which H_η data are available lie on or close to the smooth curve. Low melting metals, such as mercury, gallium or the alkali metals have low energies of activation H_η, while silver, copper and iron, melting above 1000°K, have high activation energies for viscous flow. The highest values are expected for the refractory metals, such as tantalum, rhenium and tungsten.

Use of this empirical relationship thus makes it possible to estimate the change of a metal's viscosity with temperature.

It should be understood that this empirical relationship represents a first approximation only. A more precise relationship will have to take into consideration the different changes in specific volume or density with temperature for various metals. Thus, for example, although the melting points of cesium and gallium are very close (see Table 1), their temperature coefficients dD/dt are quite different, since the critical temperatures[2] of cesium (2150°) and gallium (7620°K), are quite far apart. This empirical relationship can be expressed algebraically. However, it would be desirable to first obtain viscosity data on the high temperature branch of the curve, i.e., above the melting point of iron. It would be particularly interesting to get viscosity data for such high melting metals as molybdenum, tantalum and tungsten.

As has been shown also by ANDRADE[10], the viscosity of a liquid metal *at the melting point*, provided it has a close packed crystal structure, is given by the simple expression:

$$\eta_{\text{m.p.}}(\text{poise}) = \frac{5{\cdot}7 \times 10^{-4} \cdot \sqrt{(A \cdot T_{\text{m.p.}})}}{V_A^{2/3}},$$

* We are grateful to the reviewer for informing us that according to EYRING's latest development of the theory of significant liquid structures[9] the viscosity of metals involves the introduction of holes of *ionic size* rather than of atomic or molecular size, as in the case of *non-metallic* atoms or molecules. Thus a relationship similar to the one expressed in this article may be expected theoretically.

[9] H. EYRING and T. REE, *Proc. Nat. Acad.* 47, 562 (1961).

[10] E. N. DA C. ANDRADE, *Phil. Mag.* 17, 497-511 (1934).

where A is the atomic weight and V_A the liquid atomic volume at the melting point, $T_{m.p.}$.

Coupled with the first mentioned H_η vs. melting point relationship, i.e., Fig. 2, the viscosity of any metal with a closely packed crystal structure can be *estimated* without any experimental viscosity measurements by combining ANDRADE'S above formula with the new H_η vs. $T_{m.p.}$ relationship.

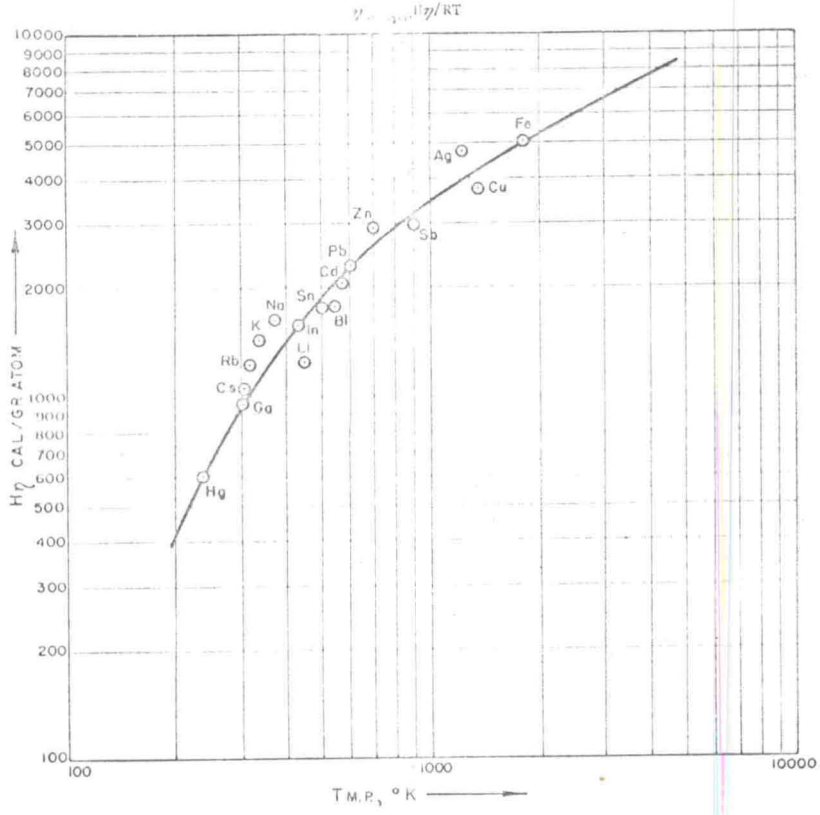

FIG. 2.—H_η, activation energy of viscosity vs. $T_{m.p.}$

The constant a in ANDRADE'S simple or first formula (see p. 333) can be expressed in terms of his above $\eta_{m.p.}$ formula.

The constant

$$a = \frac{5{\cdot}7 \times 10^{-4} \cdot \sqrt{(A \cdot T_{m.p.})}}{V_A^{2/3} \cdot \exp(H_\eta/RT_{m.p.})},$$

since at the melting point

$$\eta_{m.p.} = a \cdot \exp(H_\eta/R \cdot T_{m.p.}),$$

where the symbols have been defined previously.

To illustrate how these procedures can be used to arrive at an estimated viscosity value we take the specific example of liquid *uranium*, *plutonium* and *thorium*, since no experimental data are available on their viscosities.

γ-uranium, the stable modification of the element at high temperatures, is body-centred cubic with a space lattice constant = 3·48 Å at 785°C.[11] This corresponds to a density = 18·78 g/cm³ at 785°C. At the melting point of U, = 1133 ± 2°C or 1406°K,[11] the density of the solid = 18·39 g/cm³, based on a linear coefficient of thermal expansion = $1{\cdot}92 \times 10^{-5}$/°K. *Assuming*, as is true for a number of metals, a volume increase on fusion = 2·5 per cent, the density of *liquid* uranium, at the melting point, should equal: 17·92 g/cm³, or have $V_A = 13{\cdot}28$ cm³/g atom. ANDRADE'S formula for η at the melting point (see p. 333) applies to uranium, since it is body-centred cubic and leads to the value:

$$\eta_{\text{m.p.}} = \frac{5{\cdot}7 \times 10^{-4} \,.\, \sqrt{(238{\cdot}07 \,.\, 1406)}}{13{\cdot}28^{\frac{2}{3}}} = 5{\cdot}86 \times 10^{-2} \text{ poise}$$

$$= 5{\cdot}86 \text{ centipoise at } 1406^{\circ}\text{K}.$$

The *interpolated* activation energy, H_η for a metal melting at 1406°K., from Fig. 2, = 4300 cal/g atoms. Thus the viscosity of liquid uranium, η_u,

$$\eta_u = a \,.\, \exp(4300/RT).$$

At the melting point or 1406°K.

$$\eta_u = 5{\cdot}86 \times 10^{-2} = a \,.\, \exp(4300/1{\cdot}99 \,.\, 1406)$$

and thus the constant a for uranium,

$$a = 12{\cdot}62 \times 10^{-3} \text{ poise}.$$

The final Andrade equation becomes:

$$\eta_u = 12{\cdot}62 \times 10^{-3} \,.\, \exp(4300/RT) \text{ poises}.$$

ε-plutonium, the high temperature modification, at 500°C., is body-centred cubic.[14] The same is true[15] for thorium. Thus the ANDRADE relationship (see p. 336) applies to both metals.

TABLE 2.—PHYSICAL CONSTANTS OF LIQUID URANIUM, PLUTONIUM AND THORIUM[12]

	A	$T_{\text{m.p.}}$ (°K)	$D_{\text{Liq. at m.p.}}$ (g/cm³)	V_A (cm³/g atom)	H_η (cal/g atom), from Fig. 2.	η, (centipoise) at m.p.	at 2000°K.
U	238	1406	17·92 (est.)	13·28	4300	5·88	3·71
Pu	239	912·7	16·639[13]	14·36	3200	4·51	1·72
Th	232	2020	10·79 (est.)	21·55	5300	5·04	—

[11] J. KATZ and E. RABINOWITCH, *National Nuclear Energy Series, The Chemistry of Uranium*, Div. VIII, Vol. 5, pp. 133–152. McGraw-Hill, New York (1951).
[12] See J. J. KATZ and G. T. SEABORG, *The Chemistry of Actinide Elements*. J. Wiley, New York (1957).
[13] C. E. OLSEN, T. A. SANDERNAW and C. C. HERRICK, Report LA-2358 (1959); in contrast to most other metals plutonium contracts on melting.
[14] J. J. KATZ and G. T. SEABORG, *The Chemistry of Actinide Elements*, pp. 266–267. J. Wiley, New York (1957).
[15] J. J. KATZ and G. T. SEABORG, *The Chemistry of Actinide Elements*, pp. 28, 29 and 30. J. Wiley, New York (1957).

Using the same procedure as for uranium and from the data given in Table 2, the simple ANDRADE equation for plutonium is:

$$\eta_{Pu} = 7{\cdot}72 \times 10^{-3} \,.\, \exp(3200/RT) \text{ poise}$$

and for thorium:

$$\eta_{Th} = 13{\cdot}46 \times 10^{-3} \,.\, \exp(5300/RT) \text{ poise}$$

Thus it is expected that the viscosity of plutonium at 2000°K. = 1·72 centipoise (see Table 2) is slightly less than that of water at 0°C. (η = 1·79 centipoise.)