H. J. H

J. Inorg. Nucl. Chem., 1965, Vol. 27, pp. 979 to 987. Pergamon Press Ltd. Printed in Northern Ireland

(1)

(2) THE REDUCED DYNAMIC (ABSOLUTE) AND KINEMATIC VISCOSITIES OF THE METALS—MERCURY, SODIUM AND POTASSIUM—OVER THEIR ENTIRE 3 LIQUID 4 RANGE, i.e., 5 FROM THE MELTING POINT TO THE CRITICAL POINT, AND A COMPARISON WITH VAN DER WAALS' SUBSTANCES*

melting (6)

A. V. GROSSE
Research Institute of Temple University, Philadelphia, Pa.

(*Received* 26 *October* 1964)

Abstract—Recently it has been possible to estimate both the dynamic (absolute) and kinematic viscosities of three metals—mercury, potassium and sodium—over their entire liquid temperature range from experimental data and the use of da C. ANDRADE's II equation and the law of hyperbolic diameter. The reduced viscosities of the three metals, both dynamic and kinematic, v. T_{red}. are derived and compared with the same functions for van der Waals's substances. It is demonstrated that the three liquid metals (and presumably other metals) behave quite differently from van der Waals substances. It is also shown that the behaviour of mercury, as described in the literature, is contrary to present day factual knowledge.

WE have recently been able, as part of our high temperature research program, to estimate the viscosities of the three metals—mercury,(1) sodium and potassium,(2) both dynamic and kinematic,(3) over their *entire liquid temperature range*—from the melting point to the critical point. In connection with our high temperature containment of liquids,(4,5) we are particularly interested in the porperties of liquid metals *and* their vapours *along the saturation line* all the way from the melting point to the critical point. Thus, in the references (1), (2) and (3), the viscosities of the *saturated vapours* of the three metals are included.

In order to apply the new knowledge gained with these three metals to other metals, it is advisable to apply to them the law of corresponding states and express these properties in terms of reduced variables, i.e., the reduced dynamic viscosity, $\eta_{\text{red.}}$,

$$\eta_{\text{red.}} = \eta/\eta_{\text{crit.}},$$

reduced kinematic viscosity, $\nu_{\text{red.}}$,

$$\nu_{\text{red.}} = \nu/\nu_{\text{crit.}}$$

---

* This work was supported by the U.S. Atomic Energy Commission under Contract No. AT(30-1)-2082.

(1) A. V. GROSSE, *J. Phys. Chem.* **68**, 3419 (1964).

(2) A. V. GROSSE, *Science*, March (1965).

(3) A. V. GROSSE, *J. Phys. Chem.*, Submitted for publication, Oct. (1964).

(4) A. V. GROSSE, *The Liquid Range of Metals and Some of Their Physical Properties at High Temperatures*, Research Institute of Temple University, Philadelphia, Pa., Report of September 5, 1960.

(5) A. V. GROSSE, *Science*, **140**, 781–89 (1963).

and reduced temperature, $T_{\text{red.}}$ ($= T/T_{\text{crit.}}$). It is also useful to compare graphs of these reduced variables of metals with various other substances for which similar information is available.

In the well-known book of HOUGEN and WATSON on *Chemical Process Principles*, WATSON presents,(6) as part of his extremely useful correlation of many properties of substances in terms of reduced variables, also the reduced viscosity(6) vs. reduced temperature (see Fig. 175, *loc. cit.*, p. 871); he states, "This relationship is based on consideration of all available data on the variation of viscosity with temperature and pressure in both the liquid and gaseous states. It is approximately the same for all substances."

In recent years CODEGONE(7) developed Watson's concepts further and extended them to other properties such as thermal conductivity. He specifically uses liquid mercury as an example of a metal which conforms to the Watson viscosity relationship.

We have seen, however, that metals do not always fit, in view of the very nature of the metallic bond, correlations which do fit many other substances. Thus, for example, the critical temperatures of metals(5,8) are 2·5–4 times higher than their N.B.P., whereas for all van der Waals liquids(9)

$$T_{\text{crit.}} \simeq 1{\cdot}75 \cdot T_{\text{N.B.P.}} \, .$$

Therefore, pertinent investigations should be made whether metals, as a class, *do* or *do not* follow a particular relationship. A large volume of experimental information is available over the whole liquid range—from the melting point to the critical point—for many properties of homopolar compounds, such as hydrocarbons (and recently fluorocarbons), CCl_4, CO_2 SO_2, the nonmetallic elements—H_2, O_2, N_2, Cl_2—and the ideal liquids, such as the noble gases—all of them, either as molecules or atoms (in the case of the noble gases), being held together in the liquid by comparatively weak *van der Waals* forces.

We shall show presently that our three liquid metals (and presumably other typical metals) differ substantially from van der Waals substances (a comparison with a third type of compounds—*ionic salts* in the liquid state, such as NaCl—will have to be postponed to the future until more data on their entire liquid range becomes available(10)).

The experimental data on the viscosities and densities (or specific volumes) of the three metals and the procedures used and estimates made of the same properties, all the way up to the critical point, have been given in references (1) and (2). The reduced viscosities, both dynamic (absolute) and kinematic, of the three metals have been calculated from the above data and are presented, as a function of reduced temperature, in Table 1a and 1b for mercury, Table 2a and 2b for potassium and Table 3a and 3b for sodium. The absolute values of the critical viscosities and critical temperatures used in these calculations are correlated in Table 6.

(6) O. A. HOUGEN and K. M. WATSON, *Chemical Process Principles*, p. 870, Vol. 3, J. Wiley, New York City (1944).

(7) C. CODEGONE, *Allgemeine Waermetechnik*, **8**, 49–53 (1957).

(8) A. V. GROSSE, *J. Inorg. Nucl. Chem.* **22**, 23–31 (1961).

(9) A. V. GROSSE, *Inorg. Chem.* **1**, 436–7 (1962).

(10) See A. D. KIRSHENBAUM, J. A. CAHILL, P. J. MCGONIGAL and A. V. GROSSE, *J. Inorg. Nucl. Chem.* **24**, 1287–1296 (1962).

TABLE 1a.—REDUCED DYNAMIC (ABSOLUTE), $\eta_{red.}$, AND KINEMATIC, $\nu_{red.}$, VISCOSITY OF *liquid* MERCURY

$T_{red.}$	$\eta_{red.}$	$\nu_{red.}$	
0·135 = m.p.	4·94	1·85$_9$	↑ Experimental Range ↓
0·215	2·91$_8$	1·12$_5$	
0·273	2·47$_6$	0·97$_2$	
0·331	2·18$_8$	0·87$_5$	
0·388	1·95$_0$	0·79$_8$	
0·445	1·82$_3$	0·75$_9$	
0·503	1·73$_8$	0·74$_0$	
0·561	1·64$_4$	0·709	↑ Extrapolated Range ↓
0·619	1·568		
0·677	1·50$_8$	0·701	
0·735	1·45$_4$		
0·792	1·39$_9$	0·709	
0·850	1·34$_2$		
0·907	1·28$_8$	0·755	
0·965	1·17$_6$		
1·000 = c.p.	1·000	1·000	

TABLE 1b.—REDUCED DYNAMIC (ABSOLUTE), $\eta_{red.}$, AND KINEMATIC, $\nu_{red.}$, VISCOSITY OF THE *saturated vapour* OF *mercury*

$T_{red.}$	$\eta_{red.}$	$\nu_{red.}$
0·331	0·095$_2$	343
0·445	0·207$_8$	41·9
0·561	0·317	12·3
0·677	0·439	6·16
0·792	0·561	3·48
0·850	0·629	2·72
0·907	0·683	2·01
0·965	0·776	1·37$_5$
1·000	1·000	1·000

TABLE 2a.—REDUCED DYNAMIC (ABSOLUTE), $\eta_{red.}$, AND KINEMATIC, $\nu_{red.}$, VISCOSITY OF *liquid* POTASSIUM

$T_{red.}$	$\eta_{red.}$	$\nu_{red.}$	
0·1375 = m.p.	10·77	2·208	↑ Experimental Range ↓
0·204	5·31	1·14$_3$	
0·286	3·56	0·8169	
0·367	2·83	0·694$_7$	
0·449	2·32$_7$	0·615$_2$	
0·490	2·17$_3$	0·597$_3$	
0·531	2·03$_8$	0·583$_5$	
0·571	1·92$_3$	0·574$_0$	
0·653	1·77$_3$	0·585$_1$	↑ Extrapolated Range ↓
0·735	1·61$_2$	0·595$_6$	
0·816	1·48$_7$	0·631$_9$	
0·898	1·36$_2$	0·680$_6$	
0·980	1·18$_8$	0·792$_4$	
1·000 = c.p.	1·000	1·000	

TABLE 2b.—REDUCED DYNAMIC (ABSOLUTE), $\eta_{red.}$, AND KINEMATIC, $\nu_{red.}$, VISCOSITY OF THE *saturated vapour* OF POTASSIUM

$T_{red.}$	$\eta_{red.}$	$\nu_{red.}$
0·653	0·635	10·21
0·816	0·764	4·85$_0$
0·898	0·818	3·21$_6$
0·980	0·873	1·44$_1$
1·000 = c.p.	1·000	1·000

TABLE 3a.—REDUCED DYNAMIC (ABSOLUTE), $\eta_{red.}$, AND KINEMATIC, $\nu_{red.}$, VISCOSITY OF *liquid* SODIUM

$T_{red.}$	$\eta_{red.}$	$\nu_{red.}$	
0·1325 = m.p.	10·00	1·88$_8$	Experimental Range
0·169	6·52	1·26$_3$	
0·205	4·93	0·97$_9$	
0·240	4·03	0·82$_3$	
0·276	3·46	0·728	
0·312	3·07	0·665	
0·348	2·80	0·624	
0·383	2·59	0·597	
0·419	2·42	0·576	
0·430	2·38	0·571	
0·500	2·13	0·548	Extrapolated Range
0·571	1·94	0·540	
0·643	1·78	0·540	
0·714	1·67	0·554	
0·786	1·54	0·572	
0·857	1·43$_5$	0·608	
0·929	1·32	0·669	
0·964	1·25	0·720	
1·000	1·000	1·000	

TABLE 3b.—REDUCED DYNAMIC (ABSOLUTE), $\eta_{red.}$, AND KINEMATIC, $\nu_{red.}$, VISCOSITY OF *saturated vapour* OF SODIUM

$T_{red.}$	$\eta_{red.}$	$\nu_{red.}$
0·714	0·696	—
0·857	0·754	4·12
0·893	0·771	3·18
0·929	0·828	2·50
0·964	0·884	1·70
1·000	1·000	1·000

We choose argon and water as representatives of van der Waals liquids and their vapours; *argon* (and the other noble gases) because it is an *ideal liquid* from a physicochemical standpoint, and *water* because it is a "slightly polar" homopolar compound and because most homopolar substances (such as hydrocarbons, i.e., C_2H_6, CO_2) will lie between the curves of these two substances, when their reduced viscosities are plotted against their reduced temperatures.

Although CODEGONE(7) gives the reduced properties of argon and water in his curves, the actual values used in his plots are lost because of the small scale of reproduction; furthermore, the sources of his experimental data are not given.

Therefore, and because argon and water are also *standard substances* useful for many comparisons, experimental data have been collected, evaluated and the reduced viscosities calculated. In the case of these two substances, *all* their properties have been determined *experimentally up to the critical temperature*.

The viscosities of *argon* were calculated from the η and D data presented by HOLLIS HALLET.(11) The data for *water* were obtained from the most comprehensive and complete compilation of the properties of H_2O, namely, the "water volume" of the *Gmelin Handbook*,(12) i.e., section (Lieferung) 5 of the oxygen volumes (System No. 3) (η and ν—pp. 1451–1465, particularly p. 1457; * for D—pp. 1317–1331, particularly 1324).

The critical viscosity of water, 1·27 ms, is based on the Gmelin data of 0·413 mp for $\eta_{\text{crit.}}$ and $D_{\text{crit.}} = 0{\cdot}3250$ g/cm.³ The most recent and excellent review of THEISS and THODOS(13) on the viscosity properities of water gives $0{\cdot}430_0$ mp for $\eta_{\text{crit.}}$, which is in good agreement with the above GMELIN value.

The reduced dynamic and kinematic viscosities of argon, both for the liquid and saturated vapour, are presented in Table 4a and 4b; the corresponding data for water and saturated steam are given in Table 5a and 5b, respectively. Again the absolute values of $\eta_{\text{crit.}}$, $\nu_{\text{crit.}}$ and $T_{\text{crit.}}$ for Ar and H_2O are presented in Table 6.

It is not our purpose here to re-evaluate critically the reduced data on many homopolar substances used by WATSON(6) and CODEGONE(7); this has been adequately done by these two authors. CODEGONE(7) has specifically considered the η of liquid H_2, O_2, N_2, He, Ne, Ar, CO, CO_2, H_2O, NH_3, SO_2, CCl_2F_2, CH_3Cl, C_2H_4, benzene, the paraffin hydrocarbons from CH_4 to C_8F_{18} and *mercury*. WATSON's and CODEGONE's data fit the points of argon and water of our Fig. 1, the only exception being the metal *mercury*, as we shall discuss later.

The combined data of our ten tables are graphed in Fig. 1 and Fig. 2; the reduced dynamic viscosities are plotted in Fig. 1 and the reduced kinematic viscosities in Fig. 2.

A perusal of the *upper* half of Fig. 1, showing the curves of the *liquids*, immediately demonstrates that liquid metals form a set of curves *far apart* from the van der Waals liquids, where $\eta_{\text{red.}}$ rise steeply with decreasing reduced temperatures; all of these three metals have *much smaller* $\eta_{\text{red.}}$ at the same $T_{\text{red.}}$ than the van der Waals liquids.

---

* There is an error in the decimal power factor (p. 1457) *loc. cit.*; actually the η's, as given, are in 10^{-2} centipoises and ν in centistokes!

(11) A. C. HOLLIS HALLET: Argon, Helium and the Rare Gases I. (Ed. by G. A. COOK), Chap. IX, pp. 313–385. Interscience, New York (1961).

(12) *Gmelin Handbook of Inorganic Chemistry*, (8th Ed.), 1963, Verlag Chemie, Weinheim, Germany (1963).

(13) R. V. THEISS and G. THODOS, *Chem. Engng. Data* **8**, 390–5 (1963).

TABLE 4a.—REDUCED DYNAMIC (ABSOLUTE) VISCOSITY OF ARGON

$T_{\text{red.}}$	$\eta^{\text{red.}}_{\text{liq.}}$	$\eta^{\text{red.}}_{\text{sat. vap.}}$
0·556	7·15	$0{\cdot}27_0$
0·597	5·80	$0{\cdot}30_0$
0·664	4·25	$0{\cdot}31_8$
0·730	3·50	$0{\cdot}35_0$
0·796	2·85	$0{\cdot}40_0$
0·863	2·25	$0{\cdot}48_0$
0·929	$1{\cdot}72_5$	$0{\cdot}60_0$
0·982	$1{\cdot}32_5$	$0{\cdot}75_0$
1·000	1·000	1·000

TABLE 4b.—REDUCED KINEMATIC VISCOSITY OF ARGON

$T_{\text{red.}}$	$\nu^{\text{red.}}_{\text{liq.}}$	$\nu^{\text{red.}}_{\text{sat. vap.}}$
0·556	2·70	—
0·597	2·24	19·92
0·664	1·73	9·39
0·730	1·50	5·67
0·796	1·31	3·67
0·863	1·12	2·43
0·929	0·97	1·78
0·982	0·91	1·35
1·000	1·000	

TABLE 5a.—REDUCED DYNAMIC (ABSOLUTE) VISCOSITY OF WATER, $\eta^{\text{red.}}_{\text{liq.}}$, AND SATURATED STEAM, $\eta^{\text{red.}}_{\text{sat. vap.}}$

t (°C)	$T_{\text{red.}}$	$\eta^{\text{red.}}_{\text{liq.}}$	$\eta^{\text{red.}}_{\text{sat. vap.}}$
−9·30	$0{\cdot}407_7$	61·71	
0 = m.p.	$0{\cdot}422_1$	43·39	
20	$0{\cdot}453_0$	24·26	
80	$0{\cdot}545_6$	$8{\cdot}61_5$	
100	$0{\cdot}576_5$	$6{\cdot}85_2$	
150	$0{\cdot}653_8$	$4{\cdot}57_6$	$0{\cdot}370_5$
200	$0{\cdot}731_0$	$3{\cdot}41_4$	$0{\cdot}428_6$
250	$0{\cdot}808_3$	$2{\cdot}71_1$	$0{\cdot}491_5$
300	$0{\cdot}885_5$	$2{\cdot}25_2$	$0{\cdot}569_0$
320	$0{\cdot}916_4$	$2{\cdot}10_7$	$0{\cdot}605_3$
340	$0{\cdot}947_3$	$1{\cdot}91_3$	$0{\cdot}658_6$
360	$0{\cdot}978_2$	$1{\cdot}64_6$	$0{\cdot}736_1$
370	$0{\cdot}993_7$	$1{\cdot}40_4$	$0{\cdot}808_7$
374·15 = c.p.	1·0000	1·000	1·0000

Here it should be noted that CODEGONE$^{(7)}$ shows, in complete disagreement with this work, mercury to follow closely the van der Waals liquids (see *loc. cit.*,$^{(7)}$ p. 50 his Fig. 1); he shows $(\mathrm{Hg})_{\mathrm{liq.}}$ (identified as ┌─○) to have at $T_{\mathrm{red.}} \simeq 0{\cdot}36$ a $\eta_{\mathrm{red.}} \simeq 27$. Our Table 1a and Fig. 1 show that $\eta_{\mathrm{red.}} = 2{\cdot}05$ at $T_{\mathrm{red.}} = 0{\cdot}36$, i.e., is 13x smaller than CODEGONE'S value. Similarly, in his Fig. 4 (*loc. cit.*, p. 50) he shows $\nu_{\mathrm{red.}}$ of liquid mercury to equal 10 at $T_{\mathrm{red.}} \simeq 0{\cdot}40$, not far from the curve of van der Waals liquids, whereas in our Fig. 2, $\nu_{\mathrm{red.}} = 0{\cdot}58$ @ $T_{\mathrm{red.}} = 0{\cdot}40$, i.e., has a 17× smaller value!

TABLE 5b.—REDUCED KINEMATIC VISCOSITY OF WATER, $\nu^{\mathrm{red.}}_{\mathrm{liq.}}$, AND SATURATED STEAM, $\nu^{\mathrm{red.}}_{\mathrm{sat.\,vap.}}$

t (°C)	$T_{\mathrm{red.}}$	$\nu^{\mathrm{red.}}_{\mathrm{liq.}}$	$\nu^{\mathrm{red.}}_{\mathrm{sat.\,vap.}}$
−9·30	$0{\cdot}407_7$	20·110	
0 = m.p.	$0{\cdot}422_1$	14·110	
20	$0{\cdot}453_0$	7·904	
40	$0{\cdot}483_8$	5·183	
60	$0{\cdot}514_7$	3·747	
80	$0{\cdot}545_6$	2·883	
100	0·5765	2·325	
150	0·6538	1·5906	46·378
200	0·7310	1·2598	17·402
250	0·8083	$1{\cdot}078_7$	$7{\cdot}850_4$
300	0·8855	$1{\cdot}007_9$	$3{\cdot}929_1$
320	$0{\cdot}916_4$	$1{\cdot}007_9$	$2{\cdot}984_3$
340	$0{\cdot}947_3$	1·0000	2·2520
360	$0{\cdot}978_2$	1·0000	1·6380
370	0·9937	1·0000	1·2913
374·15 = c.p.	1·000	1·0000	1·0000

TABLE 6.—ABSOLUTE VALUES OF CRITICAL VISCOSITIES AND CRITICAL TEMPERATURES

		Hg	Na	K	Ar	H_2O
$T_{\mathrm{crit.}}$	°C	1460°	2530°	2180°	−122·46°	374·15°
	°K	1733°	2800°	2450°	150·69°	647·31°
$\eta_{\mathrm{crit.}}$ (mP)		4·25	0·69	0·52	0·40	0·413
$\nu_{\mathrm{crit.}}$ (mS)		0·841	3·94	3·06	0·753	1·270

More drastic are the differences in *reduced kinematic viscosities* as can be seen in Fig. 2; the $\nu_{\mathrm{red.}}$ of *all three metallic liquids* decrease *below* the critical viscosity for most of the liquid range and only rise above the critical viscosity in the vicinity of the melting points. In contrast, the liquid argon curves *dips* for only a few degrees below the critical temperature and then rises abruptly like the curve for liquid water.

A few words regarding *fluidity*, ϕ, may be in order; it is defined as $\phi = 1/\eta$ (and measured in reciprocal poises or rhes) and reduced fluidity, $\phi_{\mathrm{red.}}$, $= 1/\eta_{\mathrm{red.}}$. A plot of $\phi_{\mathrm{red.}}$ v. $T_{\mathrm{red.}}$ on a logarithmic plot is a *mirror image* reflected by a plane through the $\eta_{\mathrm{crit.}}$ line of the curve of $\eta_{\mathrm{red.}}$ v. $T_{\mathrm{red.}}$ (since $\log \phi = -\log \eta$) and does *not disclose* any new relationships not disclosed in Fig. 1.

The *saturated vapours* of metals, as Fig. 2 shows, have $\nu_{\mathrm{red.}}$, very close to the ν_{red}

of vapours of the van der Waals substances. This is to be expected from theory since the characteristic metallic properties disappear completely in the gas phase; thus, the atoms of mercury or argon in a gas behave as described by simple kinetic theory.

The $\eta_{red.}$ however, as Fig. 1 shows, demonstrates a varied behaviour. $\eta_{red.}$ of mercury is close to the curve of steam and argon (which, as saturated vapours, differ among themselves much more than when they are liquids-see upper or combined liquid curve in Fig. 1)! $\eta_{red.}$ of both sodium and potassium, which lie close together, deviate substantially from mercury. It should be remembered that these latter data are not experimental, but are calculated based on simple kinetic theory; direct experimental measurements are highly desirable here.

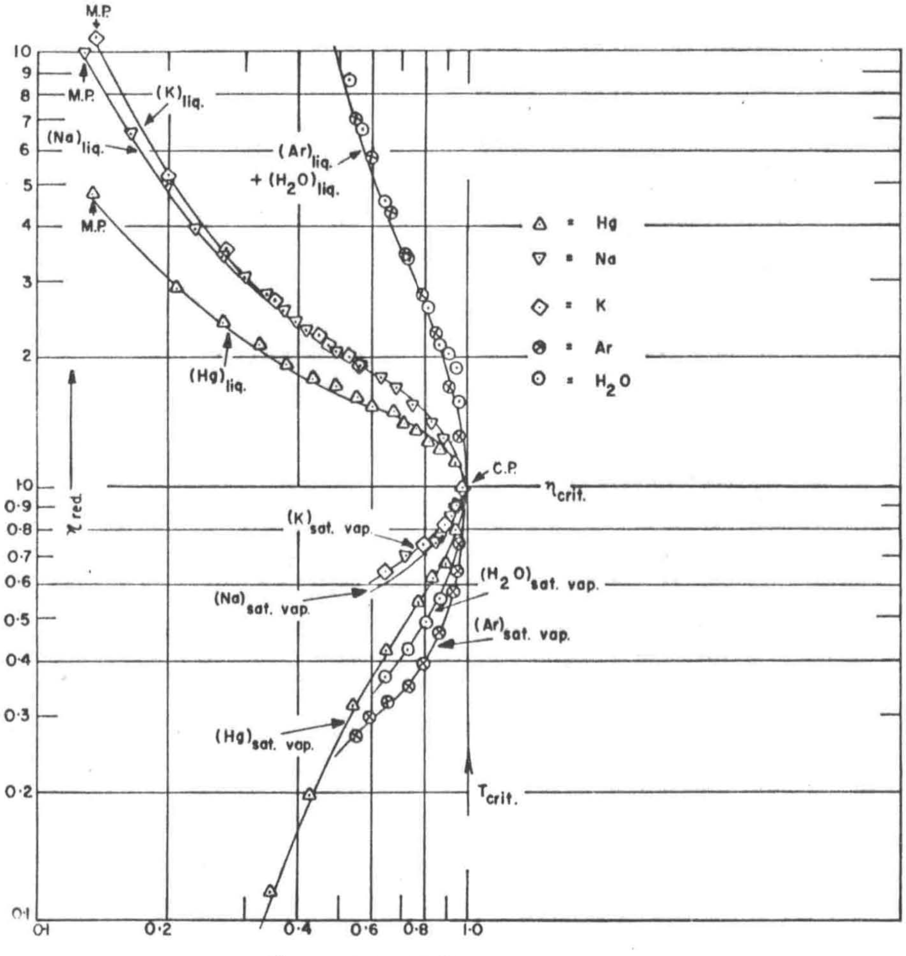

FIG. 1.—$\eta_{red.}$ or reduced dynamic (or absolute) viscosity of Hg, Na and K vs. $T_{red.}$.

The *characteristic dips or minima* in the $\nu_{red.}$ v. $T_{red.}$ curves are subject to *experimental verification* in the *near future* since they are within the range of present day experimentation methods.

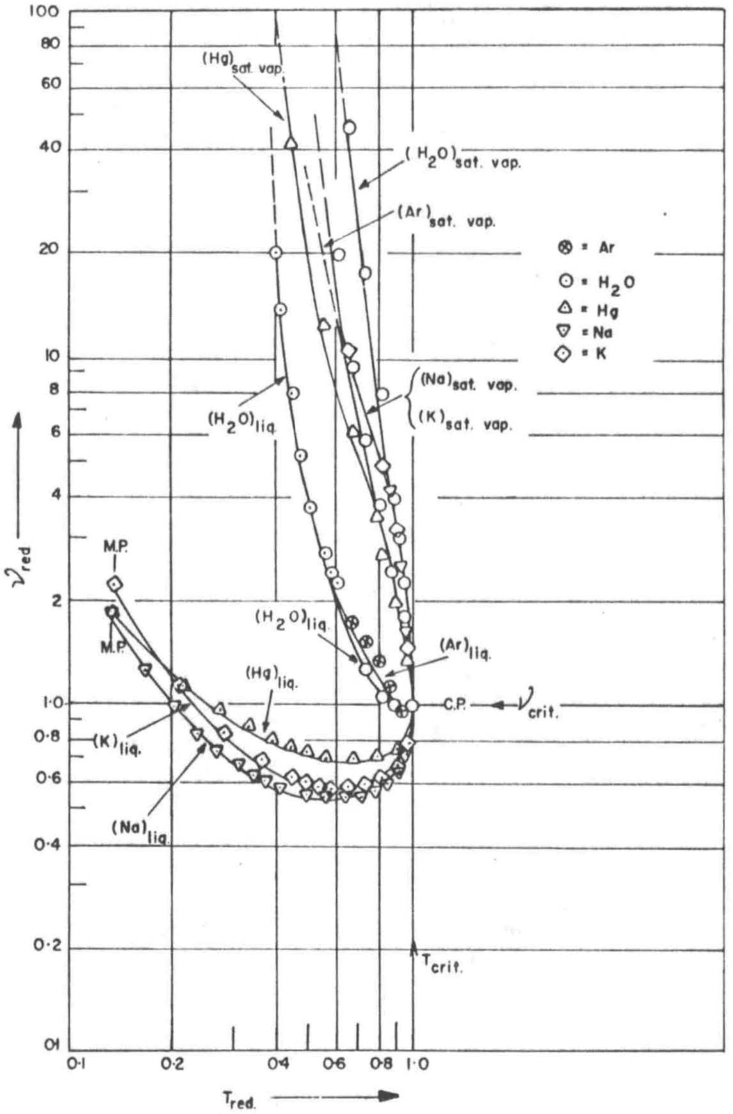

FIG. 2.—$\nu_{red.}$, or reduced kinematic viscosity vs. $T_{red.}$.

It is obviously desirable to extend viscosity measurements to additional metals and to proceed to higher temperatures, preferably up to 2500°K. Estimates up to the critical point can be made based (1–3) on da C. ANDRADE's II equation and density measurements.

In view of the different viscosity behaviour of metals, it is also obvious that CODEGONE's(7) similar relationship (see reference (7), Fig. 2) for the reduced *thermal conductivity* of liquids would have to be changed as far as its application to *liquid metals* is concerned.