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**QUARTERLY PROGRESS REPORT No.7
ON THE MEASUREMENTS OF THE
PHYSICAL AND CHEMICAL PROPERTIES
OF THE SODIUM - POTASSIUM ALLOY**



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QUARTERLY PROGRESS REPORT No.7
ON THE MEASUREMENTS OF THE
PHYSICAL AND CHEMICAL PROPERTIES
OF THE SODIUM - POTASSIUM ALLOY

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May 24, 1948

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ABSTRACT

Physical and chemical properties of the sodium-potassium alloys are under study by this Laboratory and by contract with other laboratories. The status of active property measurements and all measured results obtained since the preceding Quarterly Report are presented. Included are final results for viscosity and density, together with preliminary reporting of surface tension and reaction studies with water. In the past, Mine Safety Appliances Company Reports have been bound with the Quarterly Reports; in the future all such reports will appear under separate binding with reference to same in the Quarterly Reports.

PROBLEM STATUS

This is an interim report on this problem; work is continuing.

AUTHORIZATION

This problem was initiated upon the request of the Bureau of Ships and was assigned NRL Problem Number COL-06 (BuShips P-149).

STATEMENT OF PROBLEM

To investigate the physical and chemical properties of liquid metals. The investigation to date has been concerned with the alkali metals.

PHYSICAL AND CHEMICAL PROPERTY MEASUREMENTS

VISCOSITY

REVIEW OF TECHNIQUES AND METHODS

This section of the report on viscosity will be presented in the form of a conclusive report on viscosity. In general, each division of the work has been covered in partial reports; however, changes in apparatus, adoption of more precise methods of calibration, addition to reported results, etc., necessitate that this report include a condensed, but overall, picture of each viscometer employed. The report will also correlate and analyze all viscosity results, presenting complete tabulations of experimental results and calibration data. Work will be presented for four viscometers of the capillary type. These four are listed below with reference to the partial report where the preliminary work may be found.

Viscometer I - A Fenske modification of the Ostwald viscometer of pyrex glass used to obtain measurements on two alloys up to about 200°C. (Quarterly Progress Report No. 3).

Viscometer II - A modification of the Ostwald viscometer of pyrex glass with extra large measuring and receiving bulbs used to obtain measurements on the pure metals and three alloys up to 200°C. Work on the pure metals was presented in Quarterly Progress Report No. 5.

Viscometer III - A modification of the Ostwald viscometer of nickel with a capillary tube of approximately 0.238 cms. and 570 cms.; inside diameter and length, respectively. Preliminary results for sodium and three alloys were presented in Quarterly Progress Report No. 2. In this report, more precise calibration methods have been employed and results for sodium and the three alloys are reported to 700°C. The preliminary measurements on 43.4 weight percent potassium alloy reported in Quarterly Progress Report No. 1 were in error and are not presented in this final section. In those measurements, it was tacitly assumed that the kinetic energy factor was negligible. It was later found that the high velocity of the liquids, notwithstanding the great length of the capillary, made the kinetic energy correction assume important proportions.

Viscometer IV - A modification of nickel viscometer III with a capillary tube of approximately 0.159 cms. and 640 cms., inside diameter and length, respectively. This viscometer has been used to obtain data on potassium up to 350°C.

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VISCOMETERS I & II (Glass Ostwald Types)

GENERAL REMARKS

Surface Tension and Effective Head - The import of the surface tension factor on measurements with the Ostwald viscometer has been covered extensively in preceding reports. It has been demonstrated that in order to obtain an accurate value of the mean effective head, it is necessary to resort to experiment. The mean effective head can be so determined by (1) noting the actual hydrostatic pressure, as registered by an attached manometer, corresponding to successive positions of the menisci between the upper and lower extremes, and (2) noting the times required for these positions to be reached when the liquid runs out under its own head. Now, from a plot of the experimental heads at successive positions of the falling menisci against the fraction of total time required to reach each position during the run, a mean hydrostatic head can be determined by graphical integration. The mean head, so obtained, differs from that calculated from the differences of level at mean time due to the surface effects. The use of this experimental method with the Fenske viscometer was applied successfully only to water, which is explained in the succeeding paragraphs.

An accurate value of the head at any position of the menisci between the two extremes, then, could normally be determined by noting the actual balanced hydrostatic pressure as registered by an attached manometer. With the metals, however, which have relatively high surface tensions, and peculiar wetting characteristics, changes in curvature of menisci as the moving menisci come to a stationary equilibrium can result in appreciable error. This was demonstrated in an attempt to measure alloy heads using the Fenske viscometer (NRL Report C-3105). With such a small measuring bulb (3cc volume) and receiving bulb (3 cm diameter), the head values as observed with the attached manometer were continually fluctuating. This was attributed to change in curvature of the menisci as equilibrium was reached, resulting in an increase in head, allowing the liquid to move down and repeat the cycle.

The mean effective heads for the alloy experiments with the Fenske viscometer were, therefore, determined by a method fashioned after that used by Kuenen and Visser.⁽¹⁾ The values of capillary effect for any given temperature at successive positions of the menisci between the upper and lower extremes were calculated from measurements of the diameters at those positions. The effective head at each position of the menisci was then obtained by applying the surface tension correction to the observed

(1) Kuenen and Visser, Comm. Univ., Leiden, 1913, 13, No. 136

difference in level. Then by plotting effective head against fractional time required to reach successive positions during runs at the same temperature, the mean effective head was, in like manner, determined by graphical integration. The determination of several values over the temperature range showed that the mean head over the entire range was constant within the experimental accuracy of the method.

The solution of the difficulties experienced in efforts with this viscometer lay in the use of a modified viscometer with a larger measuring bulb and a larger receiving bulb. Viscometer II had a 30 ml measuring bulb with a mean diameter of 5 cms and a receiving bulb with diameter of 7 to 4 cms. With the relatively large diameters the shape of the meniscus had little effect on the head value, and the heads were readily measured by the experimental method already described.

Calibration and Kinetic Energy - When relative measurements are to be made by a calibration of the viscometer with a fluid of known viscosity, the Poiseuille equation for absolute viscosity which includes the correction for any gain in kinetic energy reduces to:

$$\mu = A Pt - B d/t$$

$$\mu = \text{Absolute viscosity}$$

$$P = \text{Mean effective pressure}$$

$$d = \text{Density}$$

$$t = \text{Time}$$

A & B = Constants

To determine the viscometer constants A and B, the time of flow and the mean effective head for water were determined at several temperatures. Then, by plotting μ/Pt against d/Pt^2 , a straight line was obtained, the intercept and slope of which determined the values of A and B, respectively. The viscosities and densities for water were taken from the International Critical Tables. For the final results presented in this report, the best straight line for each set of water results was determined by the method of least squares. Having thus ascertained the values of the constants for a given viscometer, the absolute viscosity of the alloy at any temperature was then readily calculable from a knowledge of its density, the time of transpiration, and the mean effective pressure. The expansion factor in the pyrex capillary, though negligible, is reflected in the empirical constants.

DESCRIPTION OF APPARATUS AND OPERATIONS

Any change in either viscometer will be discussed under experimental results.

EXPERIMENTAL RESULTS

In order to effectively correlate all the viscosity data to be presented, it will be necessary to take the results of highest accuracy as a standard or basis of comparison. To this end, the viscosity results with pyrex viscometer II, which have a stated accuracy up to 200°C of better than ± 1 percent, have been chosen as this standard. It will be shown on ensuing pages that the adaptability of the results below 200°C to an equation of the type advanced by Andrade, and further the conformity to the appropriate mixture equation, justify a reliable extension of the experimental results to higher temperatures. Then, both the experimental values and the extended values will be used for comparison with all available data, which will further serve to establish the validity of the values.

Results - Viscometer II

The precautions adopted in the design of this viscometer avoid the possibility of appreciable error from either capillary or drainage effects. Any error due to varying retention of liquids on the surface of the measuring bulb is minimized due to the relatively small surface per unit volume. No adherence of the sodium or of the alloys to the walls of the measuring bulb was observed; however, a thin layer of potassium was noted to stick at the very top and at the very bottom of the bulb. This caused some difficulty in observation of the flow of liquid past the measuring marks, but the effect of volume change on viscosity results would be insignificant. The size of the measuring bulb also tends to lessen surface effects due to the relatively small ratio of circumference to surface area on the face of the meniscus. The procedure for experimentally determining a mean effective head which includes surface effects has been discussed. For any given temperature, the determination of approximately ten heads between the two extremes was found adequate to obtain an accurate value for the mean head. Figure I shows a typical head determination for one of the alloys. It is noted that the shape of the curve at the two extremes is not critical and does not appreciably affect the final integrated head value. The shape of the measuring bulb was such that the top meniscus was in the smaller diameters at the two extremes for only a very small fraction of the total time.

With the pure metals, variation of mean head in centimeters of metal with temperature was found experimentally to be practically negligible. Unfortunately, however, the rate of change of mean head was found to vary with the volume of metal introduced. The thickness of the glass in the receiving bulb resulted in a rapid decrease in diameter in the lower portion of the bulb (7 cms to 4 cms). As the volume of the alloy introduced in each case

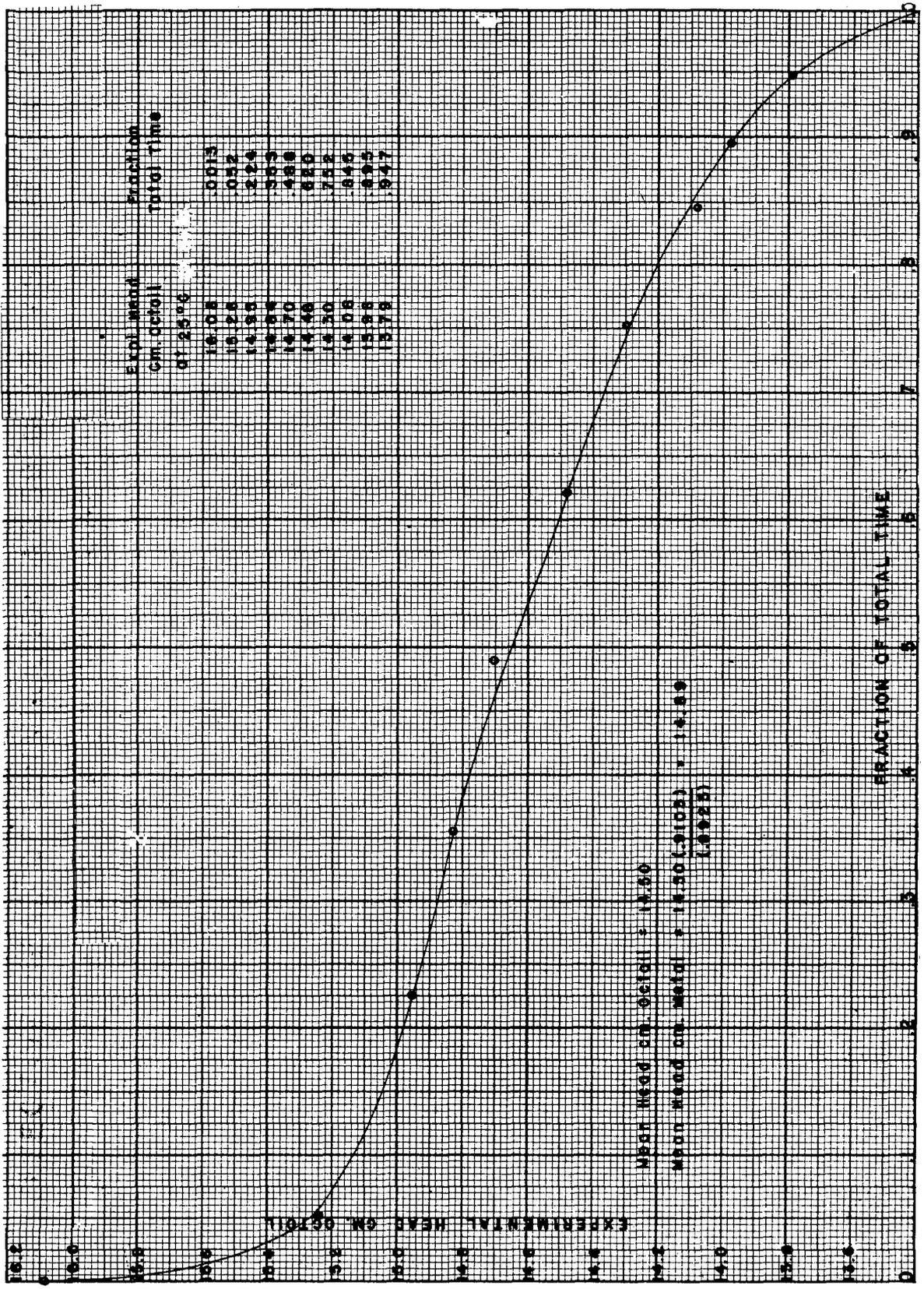


Fig. 1 Effective Head Determination at 58°C for Viscometer (49.0 Weight Percent Potassium)

was less than that for either of the pure metals, the rate of change of the head value for each alloy was greater than the corresponding change with the pure metals. This offered no particular disadvantage except for an increase in the number of head determinations required for each alloy - three to five. A typical set of mean head determinations over the temperature range for one of the alloys is presented in Figure II. The dotted line represents the rate of change of mean head as calculated from the volume change of the alloy and the appropriate diameters of the receiving bulb.

With the accuracy desired for Viscometer II, the temperature calibration of the five junction thermel below 100°C was of particular importance, as the accuracy of the final viscosity results would naturally be directly related to the water calibration. Since the previous calibration of the thermel (NRL Report C-3201), the same thermel was recalibrated with a platinum resistance thermometer up to 150°C. A discrepancy in the previous calibration was discovered; the thermel was found to have a slight dip in the EMF curve, relative to the standard curve between about 20° and 80°C, which went undetected in the previous calibration. This phenomena with iron-constantan apparently is not uncommon. The dip amounted to about 0.3°C, which by its effect on the water calibration, introduced an error of approximately 0.5% in the viscosity values for the pure metals previously reported. The final results presented in this report have been calculated on the basis of the new calibration which should be within $\pm 0.1^\circ\text{C}$ to 100°C and about $\pm 0.2^\circ\text{C}$ to 200°C.

The method for calibration of the viscometer by preliminary experiments with water has already been described and the complete data for the calibration is presented in Table I. The mean head for the water determinations was determined in the usual manner with the attached manometer, but it might be of interest to point out that the mean level was found to be within 0.3 percent of this value. The values of A and B, determined by the method of least squares, were 3.762×10^{-10} and 1.287×10^{-1} , respectively. These values supercede the graphical values (which included error from calibration of thermel) as previously reported; 3.792×10^{-10} and 1.35×10^{-1} , respectively. The accuracy of these constants and subsequently the accuracy of the viscosity values for the metals were necessarily dependent on the exactness of the water experiments. Therefore, two columns are included in Table I - one giving the value of the water viscosity as calculated from the derived constants and the other, the percent deviation of this value, so calculated, from the corresponding ICT value.

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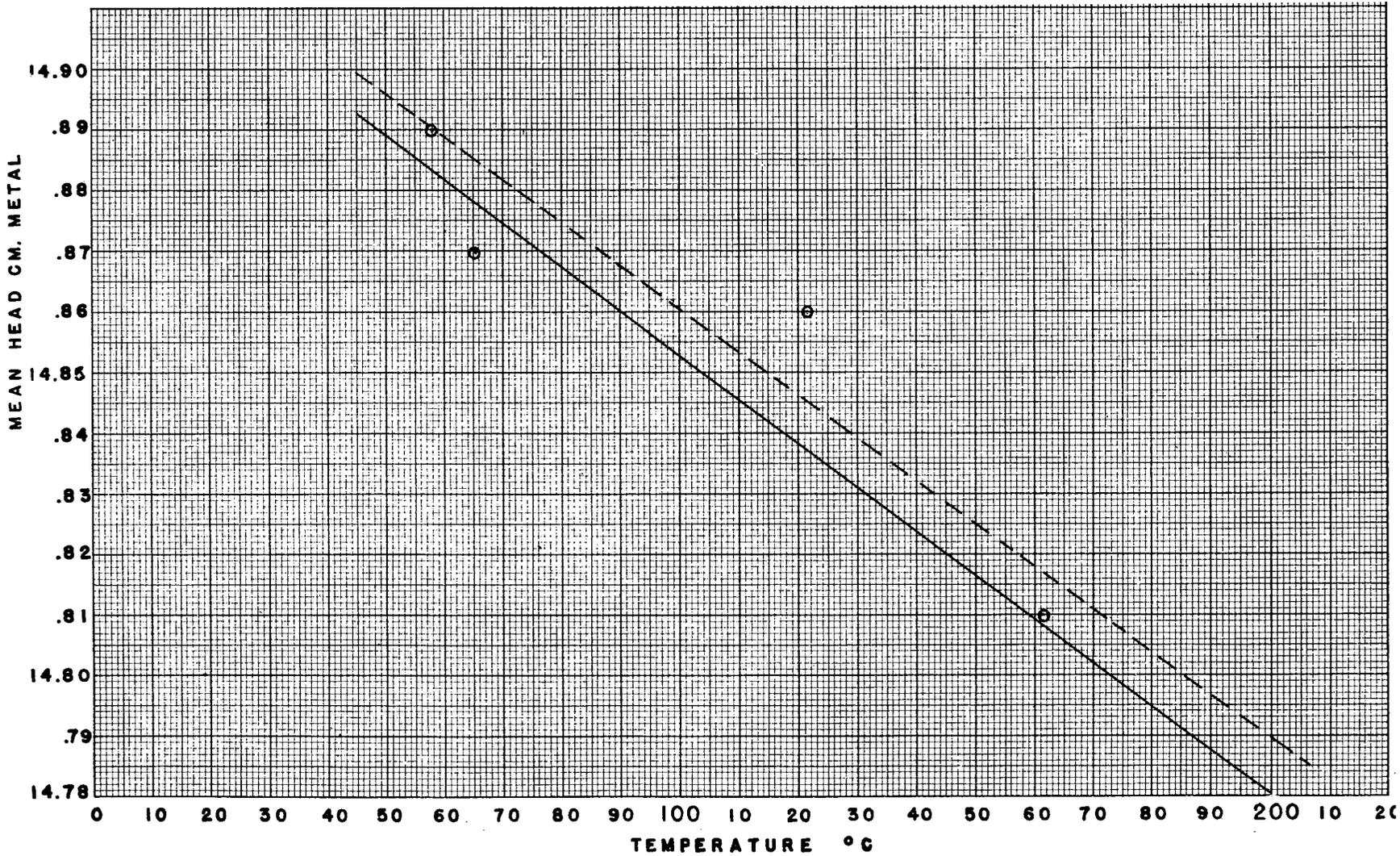


Fig. 2 Mean Effective Head vs Temperature Viscometer II
(49.0 Weight Percent Potassium)

TABLE I
PYREX VISCOMETER II
WATER CALIBRATION

$$A = 3.762 \times 10^{-10}$$

$$B = 1.287 \times 10^{-1}$$

Temp °C	Time sec	Head cm Water	Density gm/cc	ICT Viscosity poises	μ /Pt $\times 10^{-9}$	d/Pt ² $\times 10^{-9}$	Deter- mined Vis- cosity poises	Diff. Per- cent
38.65	1264.9	14.71	.9928	.00671	3.704	4.333	.006714	+0.06
38.65	1264.7	14.71	.9928	.00671	3.704	4.334	.006713	+0.05
48.2	1076.0	14.71	.9889	.00566	3.688	5.988	.005656	-0.07
48.2	1076.2	14.71	.9889	.00566	3.687	5.985	.005657	-0.05
58.4	925.0	14.71	.9840	.00481	3.663	8.102	.004803	-0.14
58.4	925.6	14.71	.9840	.00481	3.661	8.091	.004806	-0.08
69.6	801.0	14.71	.9780	.00409	3.619	10.804	.004094	+0.10
69.6	801.0	14.71	.9780	.00409	3.619	10.804	.004094	+0.10
38.75	1264.2	14.71	.9927	.00670	3.701	4.338	.006709	+0.15

Complete experimental results for the pure metals, partially reported in NRL Report No. C-3201, together with additional results for three alloys; 31.7, 49.0, and 78.6 percent by weight potassium, are presented in Tables III through VII. Each composition figure represents an analysis on the metal as removed from the viscometer at the conclusion of the measurements. As previously stated, it is believed that the metals used in these determinations were of highest purity. Each metal or alloy was distilled directly from the nickel still through a sintered glass filter into the viscometer, and no distillation was made unless the initial pressure was less than 0.1 micron. In the case of alloy, precautions were taken to assure intimate mixing before the start of the viscosity measurements. The overall accuracy of the reported viscosity results are believed to be better than ± 1 percent (relative to ICT values for water).

The temperature variation of viscosity for each of the five metals can be adequately expressed by the equation advanced by Andrade⁽²⁾:

$$\mu v^{1/3} = A e^{C/VT}$$

where: μ = Viscosity
 v = Specific Volume
 T = Absolute Temperature
A&C = Constants

(2) E.N. Andrade, DaCl, Phil. Mag., Ser. 7, 17, 698 (March 1934) Part II

By the method of least squares, the constants A and C for this equation were determined for each metal and alloy. A summary of these constants and a comparison with similar constants for the pure metals by Chiong⁽³⁾ are presented in Table II. In order to show the conformity of the experimental values to this viscosity-temperature equation, viscosities calculated from the Andrade constants are presented in each data table, along with percent deviations from corresponding experimental values. It is noted that the calculated values for all three alloys below about 100°C are definitely too low. In the future it may be possible to explain such by compounds, association, or like phenomena. Meanwhile, no attempt will be made to give the cause. The experimental values below 100°C for the alloys were not used in deriving the constants for the equations. Chiong, in fitting the equation to his experimental data for the pure metals, found a maximum deviation of only 0.59 percent for potassium and 0.72 percent for sodium. Eliminating two sodium values at 193°C, which were the first two runs with sodium and which are probably in error due to plugging of the capillary, it follows that our data for sodium and potassium fit an equation of the type advanced by Andrade equally well.

TABLE II
EMPIRICAL CONSTANTS FOR ANDRADE
FORMULAE
(by method least squares)

$$\mu V^{1/3} = Ae C/VT$$

Composition Weight Percent K	Constants NRL Data c.g.s.units		Constants Chiong's Data c.g.s.units	
	C	A	C	A
0.0	764.6	1.074x10 ⁻³	716.5	1.183x10 ⁻³
31.7	745.9	1.021x10 ⁻³		
49.0	728.9	1.012x10 ⁻³		
78.6	714.9	0.992x10 ⁻³		
100.0	735.8	0.929x10 ⁻³	600.0	1.293x10 ⁻³

(3) Y. S. Chiong, Proc. Roy. Soc. London, A157, 264 (1936)

TABLE III
VISCOMETER II
VISCOSITY SODIUM

Temp °C	Time sec	Head cm Metal	Density gm/cc	Viscosity centipoises		Differ- ence Percent
				Exptl.	Determined Andrade Equation	
103.7	1410.2	14.46	.9252	.6876	.6837	-0.57
103.7	1409.2	14.46	.9252	.6871	.6837	-0.50
121.6	1289.7	14.45	.9218	.6246	.6228	-0.29
121.6	1279.3	14.45	.9218	.6194	.6228	+0.55
121.6	1278.8	14.45	.9218	.6191	.6228	+0.60
147.0	1146.6	14.44	.9160	.5492	.5517	+0.46
147.0	1146.6	14.44	.9160	.5492	.5517	+0.46
167.6	1064.5	14.44	.9110	.5056	.5055	-0.02
167.6	1063.8	14.44	.9110	.5053	.5055	+0.04
192.7	983.5	14.43	.9052	.4621	.4587	-0.74
192.7	1010.0	14.43	.9052	.4752	.4587	-3.47
192.7	1008.7	14.43	.9052	.4746	.4587	-3.35

TABLE IV
VISCOMETER II
VISCOSITY SODIUM-POTASSIUM ALLOY
(31.7 Weight-Percent Potassium)
(21.5 Atom-Percent Potassium)

Temp °C	Time sec	Head cm Metal	Density gm/cc	Viscosity centipoises		Differ- ence Percent
				Exptl.	Determined Andrade Equation	
58.4	1610.0	14.74	.9094	.789 ⁰	.765 ²	-3.02
58.4	1610.2	14.74	.9094	.789 ¹	.765 ²	-3.03
58.4	1610.8	14.74	.9094	.789 ⁴	.765 ²	-3.07
69.5	1489.0	14.73	.9065	.725 ⁷	.710 ⁵	-2.09
69.5	1488.6	14.73	.9065	.725 ⁵	.710 ⁵	-2.07
103.8	1216.0	14.71	.8979	.583 ⁰	.582 ¹	-0.15
103.8	1215.0	14.71	.8979	.582 ⁵	.582 ¹	-0.07
103.8	1215.6	14.71	.8979	.582 ⁹	.582 ¹	-0.14
121.5	1118.4	14.70	.8935	.531 ⁶	.532 ²	+0.11
121.5	1118.3	14.70	.8935	.531 ⁶	.532 ²	+0.11
147.1	1004.2	14.69	.8871	.471 ⁴	.473 ⁶	+0.47
147.1	1007.0	14.69	.8871	.472 ⁸	.473 ⁶	+0.17
167.5	938.7	14.67	.8822	.436 ²	.435 ⁹	-0.04
167.5	939.1	14.67	.8822	.436 ²	.435 ⁹	-0.09
193.0	867.5	14.65	.8758	.397 ⁶	.396 ⁷	-0.23

TABLE V
 VISCOMETER II
 VISCOSITY SODIUM POTASSIUM ALLOY
 (49.0 Weight-Percent Potassium)
 (36.1 Atom-Percent Potassium)

Temp °C	Time sec	Head cm Metal	Density gm/cc	Viscosity centipoises		Differ- ence Percent
				Exptl.	Determined Andrade Equation	
58.3	1493.6	14.88	.8922	.723 ⁸	.692 ³	-4.35
58.3	1493.3	14.88	.8922	.723 ⁷	.692 ³	-4.34
65.2	1418.7	14.88	.8905	.685 ⁴	.662 ⁷	-3.31
69.7	1376.0	14.87	.8895	.663 ¹	.644 ⁴	-2.82
69.7	1375.6	14.87	.8895	.662 ⁹	.644 ⁴	-2.80
103.9	1127.2	14.85	.8810	.534 ⁰	.532 ³	-0.32
103.9	1127.3	14.85	.8810	.534 ⁰	.532 ³	-0.32
121.7	1037.5	14.84	.8765	.487 ⁰	.488 ¹	+0.23
121.7	1037.5	14.84	.8765	.487 ⁰	.488 ¹	+0.23
147.2	940.9	14.81	.8702	.435 ⁵	.436 ⁶	+0.25
147.2	941.5	14.81	.8702	.435 ⁷	.436 ⁶	+0.21
167.4	879.9	14.79	.8652	.402 ⁷	.403 ³	+0.15
167.4	880.2	14.79	.8652	.402 ⁸	.403 ³	+0.12
192.9	819.5	14.77	.8590	.370 ¹	.368 ⁵	-0.43

TABLE VI
 VISCOMETER II
 VISCOSITY SODIUM POTASSIUM ALLOY
 (78.6 Weight-Percent Potassium)
 (68.4 Atom-Percent Potassium)

Temp °C	Time sec	Head cm Metal	Density gm/cc	Viscosity centipoises		Differ- ence Percent
				Exptl.	Determined Andrade Equation	
58.3	1336.0	14.88	.8573	.620 ⁴	.598 ²	-3.58
58.3	1332.5	14.88	.8573	.618 ⁸	.598 ²	-3.33
69.6	1224.5	14.87	.8545	.565 ⁰	.558 ⁹	-1.08
69.6	1225.4	14.87	.8545	.565 ⁴	.558 ⁹	-1.15
103.7	1032.1	14.82	.8460	.466 ⁹	.466 ⁷	-0.04
103.7	1032.0	14.82	.8460	.466 ⁸	.466 ⁷	-0.02
121.4	958.7	14.80	.8417	.429 ³	.430 ¹	+0.19
120.8	964.4	14.80	.8420	.432 ²	.431 ³	-0.21
147.0	874.3	14.78	.8355	.386 ⁰	.386 ⁹	+0.23
147.0	874.2	14.78	.8355	.386 ⁰	.386 ⁹	+0.23
167.4	821.2	14.76	.8307	.358 ⁵	.358 ⁷	+0.06
167.4	822.2	14.76	.8307	.358 ⁹	.358 ⁷	-0.06
192.7	765.7	14.75	.8245	.329 ⁶	.329 ⁵	-0.03
192.7	765.7	14.75	.8245	.329 ⁶	.329 ⁵	-0.03

TABLE VII
VISCOMETER II
VISCOSITY POTASSIUM

Temp °C	Time sec	Head cm Metal	Density gm/cc	Viscosity centipoises		Differ- ence Percent
				Exptl.	Determined Andrade Equation	
69.6	1173	14.71	.8267	.5171	.5144	-0.52
69.6	1169	14.71	.8267	.5153	.5144	-0.17
69.6	1166	14.71	.8267	.5140	.5144	+0.08
103.7	997	14.70	.8187	.4321	.4298	-0.53
103.7	987	14.70	.8187	.4275	.4298	+0.54
121.5	918	14.70	.8150	.3943	.3966	+0.58
121.5	922	14.70	.8150	.3961	.3966	+0.13
147.0	840	14.69	.8087	.3558	.3566	+0.22
147.0	836	14.69	.8087	.3539	.3566	+0.76
167.4	790	14.69	.8040	.3312	.3309	-0.09
167.4	792	14.69	.8040	.3318	.3309	-0.27
192.7	739	14.68	.7984	.3056	.3042	-0.46
192.7	738	14.68	.7984	.3053	.3042	-0.36

The equation advanced by Andrade has been found to satisfactorily express the temperature variation of viscosity for numerous unassociated compounds and metals over wide temperature ranges. It will be shown that mixture equations for viscosity below 200°C and for density up to 700°C seem to exclude any appreciable compound formation or association in the liquid state, at least above 100°C. Therefore, viscosity values have been calculated for the pure metals and the alloys (using the derived temperature equations) up to 700°C. These values are presented in Table VIII and are plotted in Figure III. The curves represent experimental values between 100 and 200°C. The viscosity values for the pure metals by Chiong are plotted as dotted lines on Figure III for comparison. The values for sodium show excellent agreement with those reported by Chiong, while on the contrary, the NRL values for potassium would coincide with Chiong's data at 70°C, but diverge as the temperature is increased; the extended values differing by as much as 21 percent at 700°C. There is at present no explanation for this difference.

The mixture equation reported in NRL Report C-3105 does not accurately represent the variation of viscosity with composition for the alloys. The experimental viscosities for the two alloys reported in Report C-3105 were too high, and thus led to the erroneous use of mol fraction in the mixture equation. Since statistical data in the literature still leaves the question of the true-ideal-mixture equation quite undecided, one is at liberty to choose that equation which best fits the case at hand. The

TABLE VIII
VISCOMETER II
VISCOSITY OVER EXTENDED TEMPERATURE RANGE
BY ANDRADE FORMULA

Temp °C	Sodium		31.7 Wt. % K		49.0 Wt. % K		78.6 Wt. % K		Potassium	
	Density gm/cc	Viscos- ity Calc. Value								
103.7±.2	.925	.684	.898	.582	.881	.532	.846	.467	.819	.430
121.5±.2	.922	.623	.894	.532	.877	.488	.842	.430	.815	.397
147.0±.2	.916	.552	.887	.474	.870	.437	.836	.387	.809	.357
167.4±.2	.911	.506	.882	.436	.865	.403	.831	.359	.804	.331
192.9±.2	.905	.459	.876	.397	.859	.369	.825	.329	.798	.304
250	.893	.381	.862	.332	.844	.310	.811	.280	.783	.258
300	.879	.332	.850	.292	.832	.274	.798	.249	.771	.229
350	.866	.296	.838	.263	.820	.247	.787	.226	.759	.208
400	.854	.269	.826	.239	.808	.226	.775	.207	.747	.191
500	.829	.229	.802	.206	.785	.196	.751	.180	.723	.166
600	.805	.202	.779	.183	.759	.174	.727	.162	.698	.148
700	.780	.182	.754	.166	.736	.159	.704	.148	.674	.136

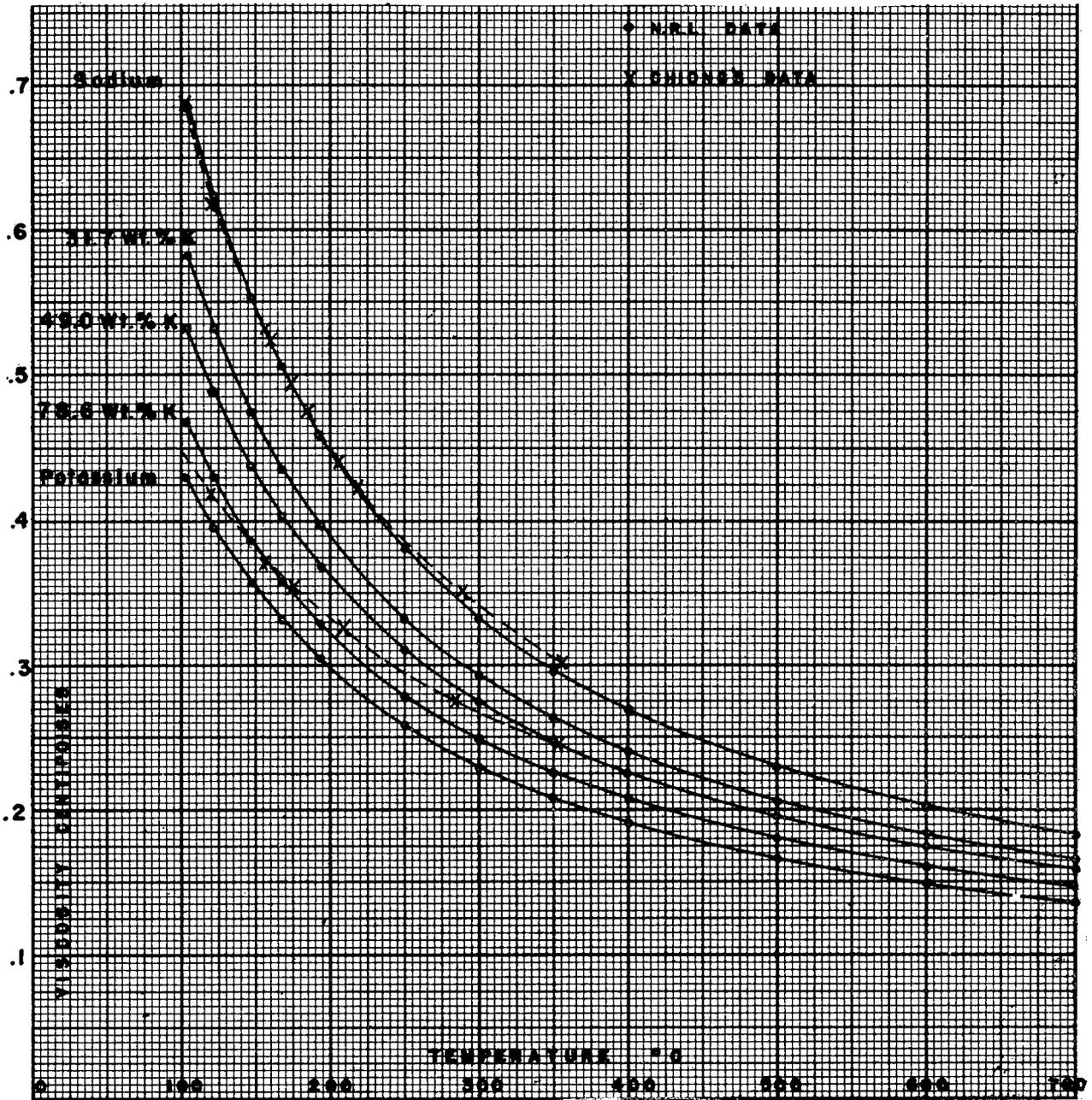


Fig. 3 Viscosity over Extended Temperature Range
 Andrade Formula
 (Viscometer II)

mixture equation found to accurately satisfy the variation of viscosity with composition was:

$$\phi = X_K \phi^{\circ}_K + X_{Na} \phi^{\circ}_{Na}$$

where: ϕ = Fluidity of Alloy
 X_K = Weight Fraction Potassium
 X_{Na} = Weight Fraction Sodium
 ϕ°_K = Fluidity Potassium
 ϕ°_{Na} = Fluidity Sodium

The applicability of the mixture equation to the experimental data for the pure metals below 200°C and to the extended data to 700°C is illustrated in Table IX. This table shows the values calculated by the mixture equation, and further, their deviation from the corresponding experimental or extended values. It is interesting to point out that assuming the extended values are of the same accuracy as the experimental values, then the mixture equation can be used to obtain values up to 700°C, which are in error by less than 1 percent in most cases and not more than 3.1 percent in any case.

TABLE IX
VISCOSITY BY MIXTURE EQUATION

Temp °C	Viscosity in Centipoises for Compositions in Weight Potassium										
	Sodium Table VIII Values	31.7 Percent			49.0 Percent			78.6 Percent			Potassium Table VIII Values
		Table Values	Calc. Values	Diff. Per- cent	Table Values	Calc. Values	Diff. Per- cent	Table Values	Calc. Values	Diff. Per- cent	
103.7 ± .2	.684	.582	.576	-1.0	.532	.530	-0.4	.467	.467	0.0	.430
121.5 ± .2	.623	.532	.527	-0.9	.488	.486	-0.4	.430	.430	0.0	.397
147.0 ± .2	.552	.474	.470	-0.8	.437	.436	-0.2	.387	.386	-0.3	.357
167.4 ± .2	.506	.436	.433	-0.7	.403	.402	-0.2	.359	.357	-0.6	.331
192.9 ± .2	.459	.397	.395	-0.5	.369	.367	-0.5	.329	.328	-0.3	.304
250	.381	.332	.331	-0.3	.310	.309	-0.3	.280	.277	-1.1	.258
300	.332	.292	.291	-0.3	.274	.272	-0.7	.249	.245	-1.6	.229
350	.296	.263	.261	-0.8	.247	.245	-0.8	.226	.222	-1.8	.208
400	.269	.239	.238	-0.4	.226	.224	-0.9	.207	.204	-1.4	.191
500	.229	.206	.204	-1.0	.196	.193	-1.5	.180	.176	-2.2	.166
600	.202	.183	.181	-1.1	.174	.171	-1.7	.162	.157	-3.1	.148
700	.182	.166	.164	-1.2	.159	.156	-1.9	.148	.144	-2.7	.136

Results - Viscometer I

This section presents corrected viscosity values with the Fenske glass viscometer on two alloys, 52.0 and 93.9 percent by weight potassium. It has been shown how the effective head values were obtained by a calculation of capillary effects in the viscometer. Admittedly, the literature values for surface tension, used in these calculations, were highly questionable. Relative to recent NRL measurements of surface tension, the literature values were several times too high. Therefore, the viscosity results reported in NRL Report C-3105 have been amended using NRL surface tension values.

The method for calibration of the viscometer by preliminary experiments with water has been described. Actually, two separate calibrations were used; both are presented (Tables X-XI). In calibration (A), the mean effective head was determined as with the alloy by calculating capillary effects. The second calibration (B) used head values as determined experimentally with the attached manometer. As in previous calibration tables, the viscosities for the water experiments as calculated from the empirical constants are compared with the ICT values. The calibration constants used in NRL Report C-3105 were obtained from calibration (A). The values of the constants, here reported for the same calibration, differ somewhat, due in part, to the use of the method of least squares and, in part, to the use of more precise viscosity-temperature curves for the ICT values.

The viscosity results for each alloy as calculated by both calibrations are presented in two Tables (XII-XIII). The values by the second calibration are presumed to be of higher accuracy. Thus, these values are used for comparison with corresponding values by Viscometer II - by mixture law. It will be noted that the values with Viscometer II differ in the case of the 93.9 percent alloy by a constant 4 percent, and in the case of the 52.0 alloy by a constant 8 percent. These discrepancies can readily be attributed to uncertainties existing in the estimation of the capillary effects. Now, surface effects for both alloys were figured on a non-wetting basis. Both alloys were distilled from glass, and the meniscus shape for the 93.9 percent alloy was definitely of a non-wetting type, whereas that with the other alloy indicated partial wetting; therefore, the results with the 52.0 percent alloy are admittedly probably too high.

The results with the Fenske viscometer offer no value in the final correlation of results. However, the values do serve to substantiate the general shape of the viscosity curves with Viscometer II. The principal error in results for the two alloys can be attributed to the magnitude of the effective head values which would have small effect on the relativity of the viscosity

values. It is particularly significant that the shape of the viscosity curve for the 93.9 weight percent alloy follows the same trend as the curve for pure potassium with Viscometer II, in that values for potassium by Chiong (see Figure III) diverge appreciably from the NRL values.

TABLE X
PYREX VISCOMETER I
WATER CALIBRATION A

$$A = 4.40 \times 10^{-9}$$

$$B = .00897$$

Temp °C	Time sec	Head cm Water	Density gm/cc	ICT Viscosity poises	μ /Pt $\times 10^{-9}$	d/Pt^2 $\times 10^{-9}$	Deter- mined Viscos- ity poises	Diff. Per- cent
32.0	223.2	8.05	.9950	.00767	4.375	2.543	.00767	0.00
32.0	223.2	8.05	.9950	.00767	4.375	2.543	.00767	0.00
35.3	208.5	8.05	.9940	.00716	4.376	2.914	.00716	0.00
35.4	207.7	8.05	.9939	.00715	4.387	2.936	.00713	-0.28
41.2	187.7	8.05	.9918	.00640	4.355	3.596	.00642	+0.31
41.9	185.4	8.05	.9914	.00632	4.356	3.685	.00634	+0.32
41.9	185.4	8.05	.9914	.00632	4.356	3.685	.00634	+0.32
49.0	163.9	8.05	.9885	.00558	4.363	4.715	.00557	-0.18
49.0	163.5	8.05	.9885	.00558	4.373	4.739	.00556	-0.36
61.2	136.7	8.05	.9826	.00462	4.357	6.779	.00460	-0.43
61.2	136.2	8.05	.9826	.00462	4.373	6.829	.00459	-0.65
70.7	120.8	8.05	.9774	.00403	4.324	8.681	.00403	0.00
70.9	120.6	8.05	.9773	.00402	4.321	8.710	.00402	0.00
79.2	109.4	8.05	.9723	.00361	4.299	10.584	.00361	0.00
79.6	109.0	8.05	.9721	.00359	4.292	10.661	.00360	+0.28

TABLE XI
PYREX VISCOMETER I
WATER CALIBRATION B

A = 4.460×10^{-9}

B = .00817

UNCLASSIFIED

Temp °C	Time sec	Head cm Water	Density gm/cc	ICT Viscosity poises	μ /Pt $\times 10^{-9}$	d/Pt ² $\times 10^{-9}$	Deter- mined Viscos- ity poises	Diff. Per- cent
39.9	186.7	8.17	.9923	.00655	4.413	.3581	.00658	+0.5
40.0	186.5	8.17	.9922	.00654	4.411	.3588	.00657	+0.5
41.6	181.0	8.17	.9916	.00635	4.416	.3809	.00637	+0.3
41.5	181.0	8.17	.9917	.00636	4.423	.3810	.00637	+0.2
50.8	155.2	8.17	.9877	.00542	4.413	.5182	.00543	+0.2
51.4	153.2	8.17	.9874	.00537	4.431	.5318	.00535	-0.4
51.4	153.2	8.17	.9874	.00537	4.431	.5318	.00535	-0.4
51.3	154.7	8.17	.9875	.00538	4.395	.5215	.00541	+0.6
62.0	131.3	8.17	.9822	.00456	4.413	.7240	.00455	-0.2
62.1	131.5	8.17	.9821	.00456	4.407	.7218	.00455	-0.2
62.3	131.2	8.17	.9820	.00454	4.398	.7251	.00454	0.0
66.3	124.4	8.17	.9799	.00429	4.392	.8065	.00429	0.0
74.3	112.4	8.17	.9753	.00384	4.372	.9879	.00385	+0.3
74.3	112.1	8.17	.9753	.00384	4.384	.9932	.00384	0.0
74.4	112.1	8.17	.9752	.00383	4.373	.9931	.00384	+0.3
36.8	196.5	8.17	.9934	.00695	4.444	.3232	.00693	-0.3
37.0	195.4	8.17	.9933	.00692	4.450	.3270	.00689	-0.4
37.0	195.5	8.17	.9933	.00692	4.448	.3266	.00690	-0.3

TABLE XII
 PYREX VISCOMETER I
 VISCOSITY SODIUM-POTASSIUM ALLOY

(52.0 Weight - Percent Potassium)
 (38.9 Atom-Percent Potassium)

Temp °C	Time sec	Head cm Metal	Density gm/cc	Viscosity Centipoises			Diff. Percent
				Exptl. A	Exptl. B	Exptl.*	
				Vis.I	Vis.I	Vis.II	
53.8	244.7	8.58	.889	.802	.813		
53.8	236.9	8.58	.889	.776	.787		
54.2	236.2	8.58	.889	.774	.785		
54.2	236.8	8.58	.889	.776	.787		
73.6	205.4	8.58	.885	.669	.679		
73.5	205.7	8.58	.885	.670	.680		
98.3	178.7	8.58	.878	.577	.585	.541	-7.5
98.3	179.1	8.58	.878	.578	.586	.541	-7.7
98.0	179.4	8.58	.878	.579	.587	.542	-7.7
127.0	157.5	8.58	.871	.503	.510	.471	-7.6
126.5	156.7	8.58	.871	.501	.508	.472	-7.1
126.3	157.1	8.58	.871	.502	.509	.472	-7.3
154.0	142.0	8.58	.865	.449	.456	.421	-7.7
170.5	134.3	8.58	.860	.422	.428	.395	-7.7
170.2	134.3	8.58	.860	.422	.428	.395	-7.5
201.0	122.4	8.58	.853	.380	.386	.356	-7.8
201.0	122.6	8.58	.853	.381	.387	.356	-8.0

* By Mixture Equation

TABLE XIII
PYREX VISCOMETER I
VISCOSITY SODIUM-POTASSIUM ALLOY

(93.9 Weight - Percent Potassium)
(89.9 Atom-Percent Potassium)

Temp °C	Time sec	Head cm Metal	Density gm/cc	Viscosity Centipoises			Diff. Per- cent
				Exptl. A	Exptl. B	Exptl.*	
				Vis.I	Vis.I	Vis.II	
40.5	211.7	8.36	.841	.639	.648		
42.5	210.2	8.36	.840	.633	.642		
43.4	209.1	8.36	.840	.630	.639		
43.4	209.1	8.36	.840	.630	.639		
42.7	211.0	8.36	.840	.636	.645		
43.1	211.4	8.36	.840	.637	.646		
45.9	206.3	8.36	.840	.621	.630		
46.7	204.7	8.36	.839	.616	.625		
46.5	204.5	8.36	.839	.615	.624		
54.8	194.0	8.36	.837	.582	.590		
55.1	193.8	8.36	.837	.581	.590		
59.8	187.9	8.36	.836	.563	.571		
60.2	187.1	8.36	.836	.560	.568		
61.0	186.7	8.36	.836	.559	.567		
70.5	176.9	8.36	.834	.528	.536		
70.6	176.1	8.36	.834	.526	.533		
94.3	156.4	8.36	.828	.462	.469		
94.5	158.0	8.36	.828	.467	.474		
94.5	158.0	8.36	.828	.467	.474		
114.0	146.3	8.36	.824	.430	.436	.421	-3.4
114.0	146.1	8.36	.824	.429	.436	.421	-3.4
136.2	136.0	8.36	.819	.396	.402	.384	-4.5
136.2	135.8	8.36	.819	.396	.402	.384	-4.5
142.4	131.2	8.36	.817	.381	.387	.373	-3.6
142.5	130.7	8.36	.817	.380	.385	.373	-3.1
161.0	124.9	8.36	.813	.361	.366	.349	-4.6
160.8	124.9	8.36	.813	.361	.366	.349	-4.6

*By Mixture Equation

VISCOMETER III
(NICKEL TYPE - 0.238 cm I.D. CAPILLARY)

GENERAL REMARKS

In the discussion of experimental results for sodium and three alloys presented in NRL Report P-3057, it was noted that there was some doubt as to the constancy of the kinetic energy factor into the higher temperature range. For the results presented at that time, the viscometer was calibrated with water in a manner similar to that used with the glass viscometers, where (A) and (B) in the viscosity equation are assumed to be constant over the experimental flow range. Since that time, further analysis of the data has shown that the supposed constants -- (A) and (B) -- change appreciably with the flow rate and also that the transition from streamline to turbulent flow begins at an approximate Reynold's number of 2200 for all the metals. It was further found that the water determinations made with the viscometer were more than adequate to provide a good calibration up to the turbulent region.

The nickel viscometer, with the non-standard length, size, and shape of capillary, advanced problems with no parallel in the literature. Therefore, two unusual calibration methods have been developed and applied to the solution of the results. Both of these methods, together with their application, will be discussed in detail below. Each method, in essence, corrects for any change in (A) and (B) in the viscosity equation. Method I, which corrects for (A) and (B) by a calibration with water over the flow range, has provided acceptable viscosity results for the metals up to 400 and 500°C. Method II, in which the changes in (A) and (B) are obtained from the experimental data on the metals without aid of water calibration data, has provided acceptable results for the metals over the entire experimental range up to 700°C.

Before discussing either method, it might be well to discuss the characteristics of the viscosity equation to be applied:

$$\mu = APt - Bd/t$$

where μ = Absolute Viscosity
P = Mean Effective Pressure
d = Density
t = Time Rate of Flow - sec/cc
A & B = Variables

It has been shown that each quantity in the equation must be considered as a variable in the measurements; however, (μ), (P),

and (d) have specified values for a given liquid and temperature. Both (P) and (d) are experimental values measured independently of the viscosity measurements, while (t) is the only variable determined directly from the flow measurements on the liquid. Now, any change in either (μ), (A) or (B) will be reflected in the experimental (t), and therefore in the experimental (Pt) and (d/t). Any change in either (A) or (B) must be reflected in both (Pt) and (d/t), and therefore, change in either or both will show up as effective changes in both.

Method I

Compared to the calibration of the glass viscometers, this method is merely a more exacting variation wherein the known and unknown are compared under the same flow characteristics such that the Reynold's number is the same; and, therefore, the (A) and (B) terms are the same. The values of (A) and (B), without doubt, must depend on the flow characteristics of the apparatus, and therefore, on the Reynold's number.

Now, the function (d/t μ) can be shown to be proportional to the Reynold's number for a given viscometer.

$$\text{Reynold's number} = \frac{VDd}{\mu} \quad (1)$$

where V = Velocity Rate of Flow
cm/sec
D = Diameter Capillary cm
d = Density gm/cc
 μ = Viscosity poises

Then, if (a) is the area of the capillary

$$\frac{d}{t\mu} = \frac{Vad}{\mu}$$

but $\frac{Vad}{\mu} \cdot (D/a) = \text{Reynold's number} = R$

$$\text{therefore } \frac{d}{t\mu} = kR \quad (2)$$

From this proportionality, it can be readily shown that when comparing two fluids in the same viscometer at the same Reynold's number, that certain equalities must exist.

In other words, if - - - - -

$$R_{H_2O} = R_{Metal}; \text{ then, } A_{H_2O} = A_{Metal} \text{ and } B_{H_2O} = B_{Metal}$$

it follows

$$(d/t\mu)_{H_2O} = (d/t\mu)_{Metal} \quad (3)$$

$$(Pt/\mu)_{H_2O} = (Pt/\mu)_{Metal} \quad (4)$$

$$\left(\frac{Pt^2}{d}\right)_{H_2O} = \left(\frac{Pt^2}{d}\right)_{Metal} \quad (5)$$

Now, obviously, one could compare experimental results for a metal with water under the same Reynold's number, and could obtain directly a correct value for the viscosity of the metal without an intermediate calculation of the effective values of (A) and (B). A convenient graphical method of solution is to, first, plot for water the experimental values of (Pt^2/d) against $(d/t\mu)$. Then, from the experimental value of (Pt^2/d) for the metal, one could read directly from the water figure the corresponding value of $(d/t\mu)$ for metal at the same Reynold's number. The viscosity of the metal being the only unknown, the solution is direct.

The method would naturally be limited by the flow range covered in the water experiments. The water data available was adequate to a value of $R = 2400$, which, as stated, provided viscosity values for sodium and the three metals to 400° and $500^\circ C$. A plot of the water experimental data, similar to that used for the solution of the results on the metals, is presented as Figure IV. It will be noted that an apparent break in the water curve appears at a point corresponding to $R = 2140$, which should correspond to the start of transition from streamline to turbulent flow.

A complicating factor in any mathematical analysis of this method is the difference in dimensions of the capillary with any difference of temperature. In the method, as described, the (A) and (B) terms include dimension factors. Now, when comparing water results with metal results, there exist differences in temperature and consequently differences in dimension factors. The inter-relationships involved for this change in dimension factor with corresponding changes in (A) and (B) and changes in Reynold's number cannot be predicted. However, the dimension factor effectively enters into the equation only to the third power and the maximum difference for any comparison of water with metal was only about 1 1/2 percent of the factor.

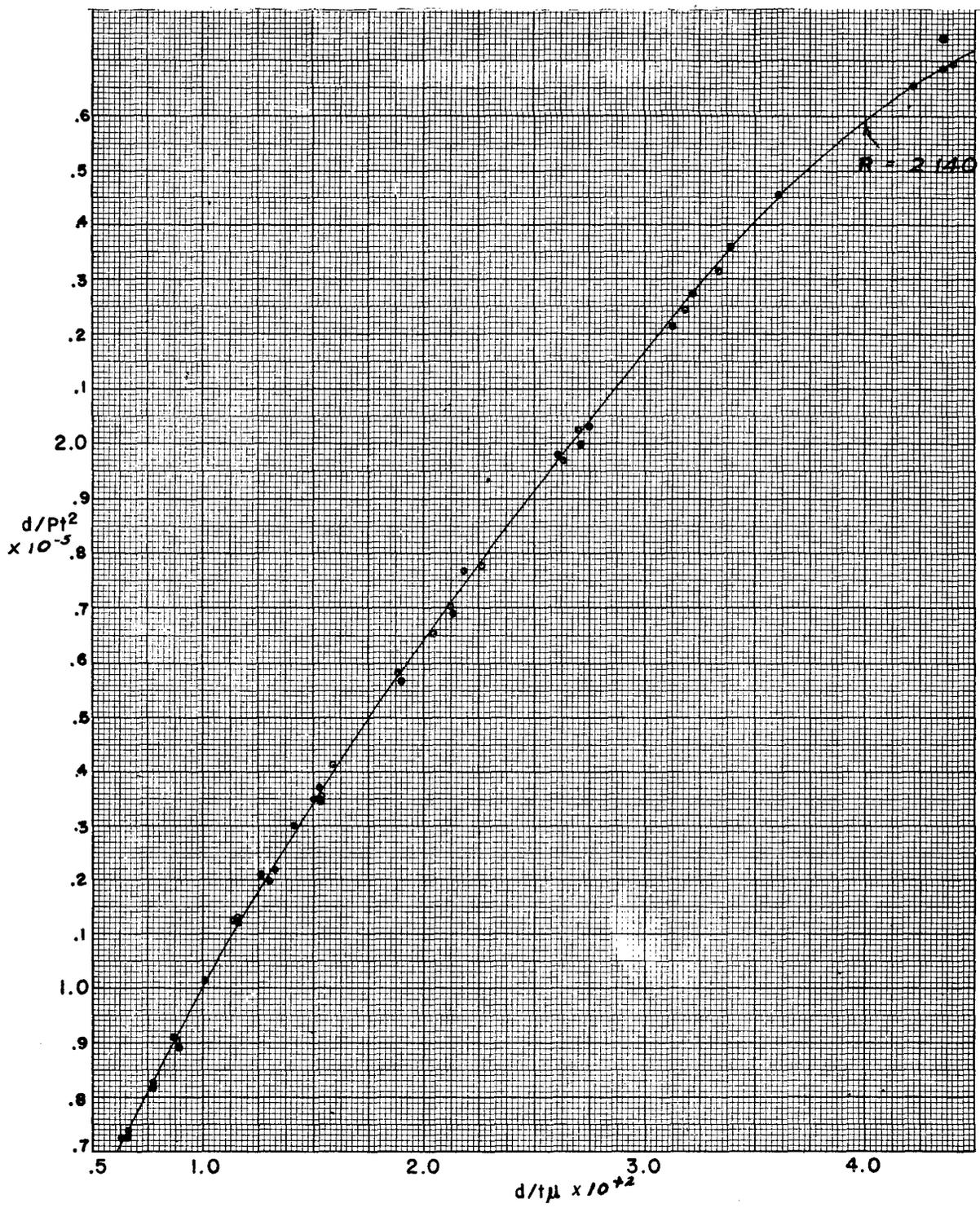


Fig. 4 Water Calibration
Nickel Viscometer III

Method II

Any acceptable method of calibration for the nickel viscometer must in some way compensate for the effective changes in the (A) and (B) factors of the Poiseuille equation. The advantage of Method II over the preceding method rests in the fact that the effective changes in (A) and (B) are evaluated directly from the experimental data with the metals, and, thus, would not be limited by the range of the water experiments. As might be expected, the principal assumption made in Method I must again persist; namely, that with no change in (Pt^2/d) , there should be no change in the value of (A) or (B). Now, if we specify an appropriate value of (Pt^2/d) as a base line and can obtain the effective changes in (A) and (B) over the flow range as related to this base line, the viscosity for the metal at an experimental point can be readily calculated, knowing the base line values of (A) and (B).

The principal step in the procedure is to obtain for each of the four metals that curve, which will be called an ideal curve, relating (Pt) and (d/t) with change in viscosity, but with no change in base line values of (A) or (B). It will be shown how such a curve for each metal enables one to correct for the effective changes in (A) and (B) over the flow range. Now, the so-called ideal relationship between (Pt) and (d/t) can be derived from an experimental plot of (Pt^2/d) vs (Pt) for any metal or for any pairing of metals. Such a plot combining the data for sodium and an alloy is illustrated on the next page, Figure V. Later it will be shown mathematically that the ideal relationships between (Pt) and (d/t) are independent of the metal pairing, but it will be necessary to refer to Figure V to clearly present the steps involved.

In Figure V, when proceeding horizontally from the sodium curve to the alloy curve at any fixed value of (Pt^2/d) , there must be a change in viscosity accompanied by no change in Reynold's number; and, therefore, there must be corresponding changes in (Pt) and (d/t) with a constancy of (A) and (B). Now, by a downward, stepwise procedure between the two curves, it is possible to obtain from the base line ideal changes in (Pt) and (d/t) over the flow range which should be valid for any metal and which should contain no reflected changes from (A) and (B). To justify this reasoning, we must then justify several points.

First, it must be shown that the ideal $\Delta(Pt)$ and $\Delta(d/t)$ on each step are essentially independent of the metal or metal pair. This can be shown mathematically in the following manner.

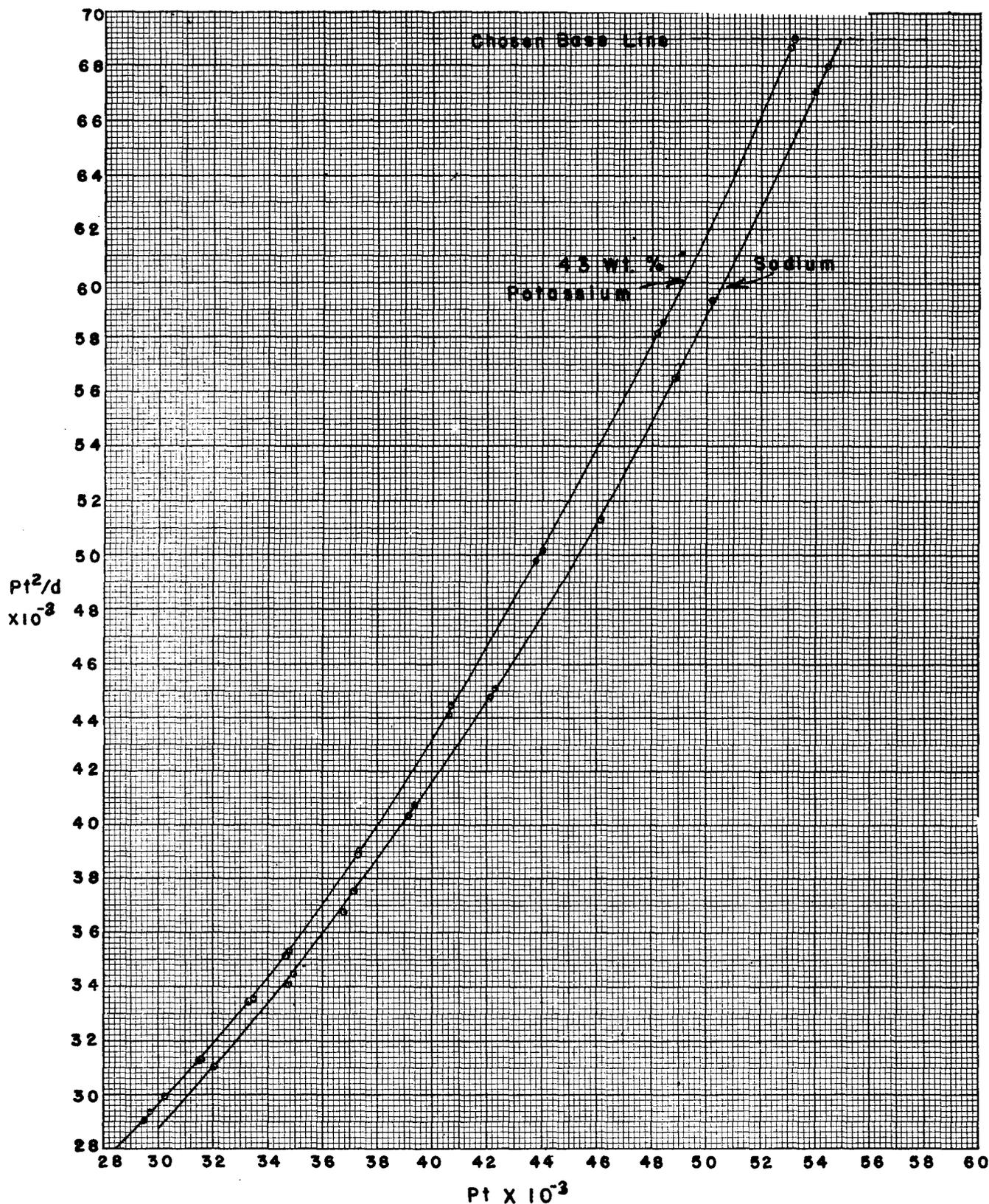


Fig. 5 Experimental Curves Pt/d vs Pt
Nickel Viscometer III

Labeling any two (Pt^2/d vs Pt) curves as 1 and 2, respectively;

Then from Method I (page 23)

If - - - - -

$$(R)_1 = (R)_2; \text{ then, } (A)_1 = (A)_2 \text{ and } (B)_1 = (B)_2$$

$$\text{and } (Pt^2/d)_1 = (Pt^2/d)_2; (Pt/\mu)_1 = (Pt/\mu)_2;$$

$$(d/t/\mu)_1 = (d/t/\mu)_2$$

and it follows - - - - -

$$(Pt)_2/(Pt)_1 = (d/t)_2/(d/t)_1 = (\mu)_2/(\mu)_1$$

$$\text{or } \frac{(Pt)_2 - (Pt)_1}{(Pt)_1} = \frac{(d/t)_2 - (d/t)_1}{(d/t)_1} = \frac{(\mu)_2 - (\mu)_1}{(\mu)_1}$$

Then -- across each step - - - - -

$$\Delta Pt/\Delta\mu = (Pt/\mu)_1 = (Pt/\mu)_2$$

$$\text{and } \Delta d/t/\Delta\mu = (d/t/\mu)_1 = (d/t/\mu)_2$$

$$\text{and } \Delta Pt/\Delta d/t = (Pt^2/d)_1 = (Pt^2/d)_2$$

These relationships will exist only when the values of (A) and (B) are constant and the following conclusions may be drawn. The magnitude of the $\Delta(Pt)$ and the $\Delta(d/t)$ across the same step will depend solely on the magnitude of the $\Delta\mu$. The ratio of $\Delta(Pt)/\Delta(d/t)$, on the other hand, will be constant for each step and equal to the value of (Pt^2/d) for the step; the ratio will, therefore, be independent of the metal or the metal pairing.

In the second place, it can be shown that the effective changes of (A) and (B) in proceeding from one step to the next will not be reflected in the values of $\Delta(Pt)$ and $\Delta(d/t)$. When proceeding from one step to the next, the effective values of (A) and (B) have changed, but these changes have been reflected in the values of (t) such that the changes in (Pt) and (d/t) for each metal have exactly compensated for the same changes in (A) and (B); therefore, the desired $\Delta(Pt)$ and $\Delta(d/t)$ on each step would necessarily be independent of any change in the value of (A) or (B). Now, the dimension change for the capillary from step to step is practically the same for each metal, and it can be reasoned, in like manner, that the $\Delta(Pt)$ and $\Delta(d/t)$ will be independent of any change in (A) and (B) due to dimension changes.

The stepwise procedure served as a convenient means of explaining the method, but such a procedure was too long and tedious for actual use; thus, an alternate procedure leading to the same final results was adopted. The first step in the new procedure was to obtain the ideal ratio of $\Delta(d/t) / \Delta(Pt)$ at consecutive values of (Pt^2/d) , beginning at the base line value and proceeding in equal increments over the experimental range. By obtaining mean values for this ideal ratio from the base line to each experimental value of (Pt^2/d) , the corresponding experimental changes of (Pt) would readily give ideal relations for $\Delta(Pt)$ and $\Delta(d/t)$. The ideal ratios were found to vary at a uniform rate over the range of (Pt^2/d) . Therefore, an adequate value for the mean-ideal-ratio from the base line to each value of (Pt^2/d) was obtained by a mathematical average of ratios up to each point. The values for the mean-ratios over the flow range are presented in Figure VI. This curve was derived independently of the metals by equating $\Delta(Pt) / \Delta(d/t)$ and (Pt^2/d) for consecutive values of (Pt^2/d) , and proceeding as described above. A curve similar to Figure VI can also be obtained from the experimental pairing of any two metals (Figure V) by reading ratios of $\Delta(d/t) / \Delta(Pt)$ between the two curves.

The ideal values of (Pt) and (d/t) for each metal were readily obtainable from the base line values of (Pt) and (d/t) , knowing the ideal changes in (Pt) and (d/t) as referred to the base line. The plot of ideal (Pt) vs (d/t) for each metal was the final graphical step. Final viscosity results were obtained directly from the experimental data and these ideal curves. A sample curve for sodium is shown as Figure VII. Along with the ideal curve for sodium, the experimental counterpart is included to illustrate how the changes in (A) and (B) are reflected in the experimental values. Now, for any experimental value of (Pt) , there will be an ideal value of (d/t) ; correspondingly, for each experimental (d/t) , there will be an ideal value of (Pt) . It follows that the ideal values for (Pt) and (d/t) , thus obtained, represent those values for a similar experimental run with no change in the base line values of (A) and (B). Then the viscosity at each experimental point could be obtained by a simple substitution of the corresponding ideal values in the viscosity equation, using the base line values of (A) and (B).

The base line values for (A) and (B) were obtained from water calibration data. Figure VIII gives a plot of (μ/Pt) vs (d/Pt^2) for the water experiments in the range of the base line. The abundance of the water experiments in this range gives high accuracy to this curve. The base line value of (Pt^2/d) was 69,000. Thus, the intercept and the slope for a tangent at the equivalent value of (d/Pt^2) determined the values of (A) and (B). The base line value for (A) was 1.250×10^{-7} and for (B) was 2.708×10^{-3} .

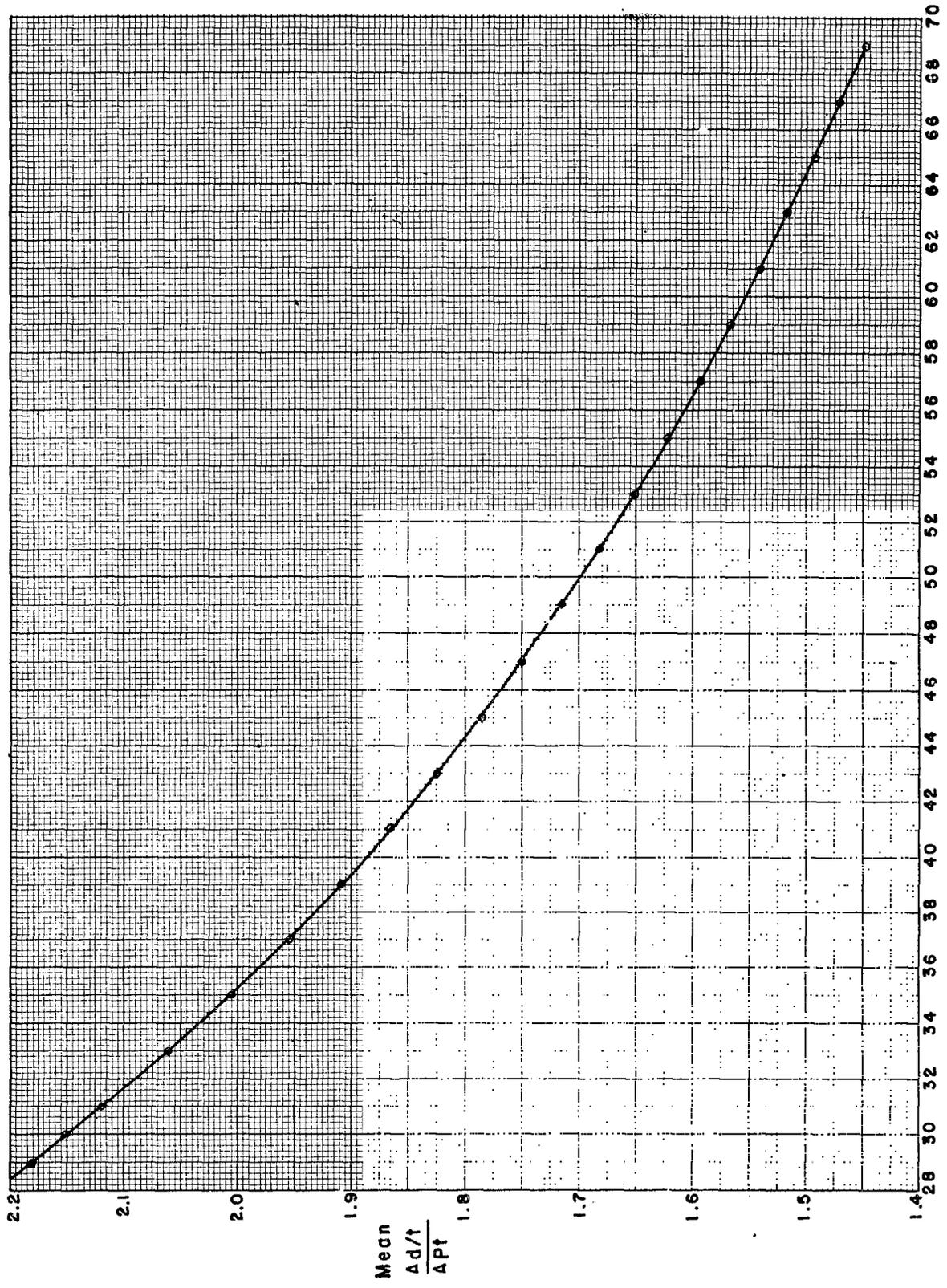


Fig. 6 Mean Ideal $\Delta d/t/\Delta Pt$ from Baseline to Values of Pt^2/d

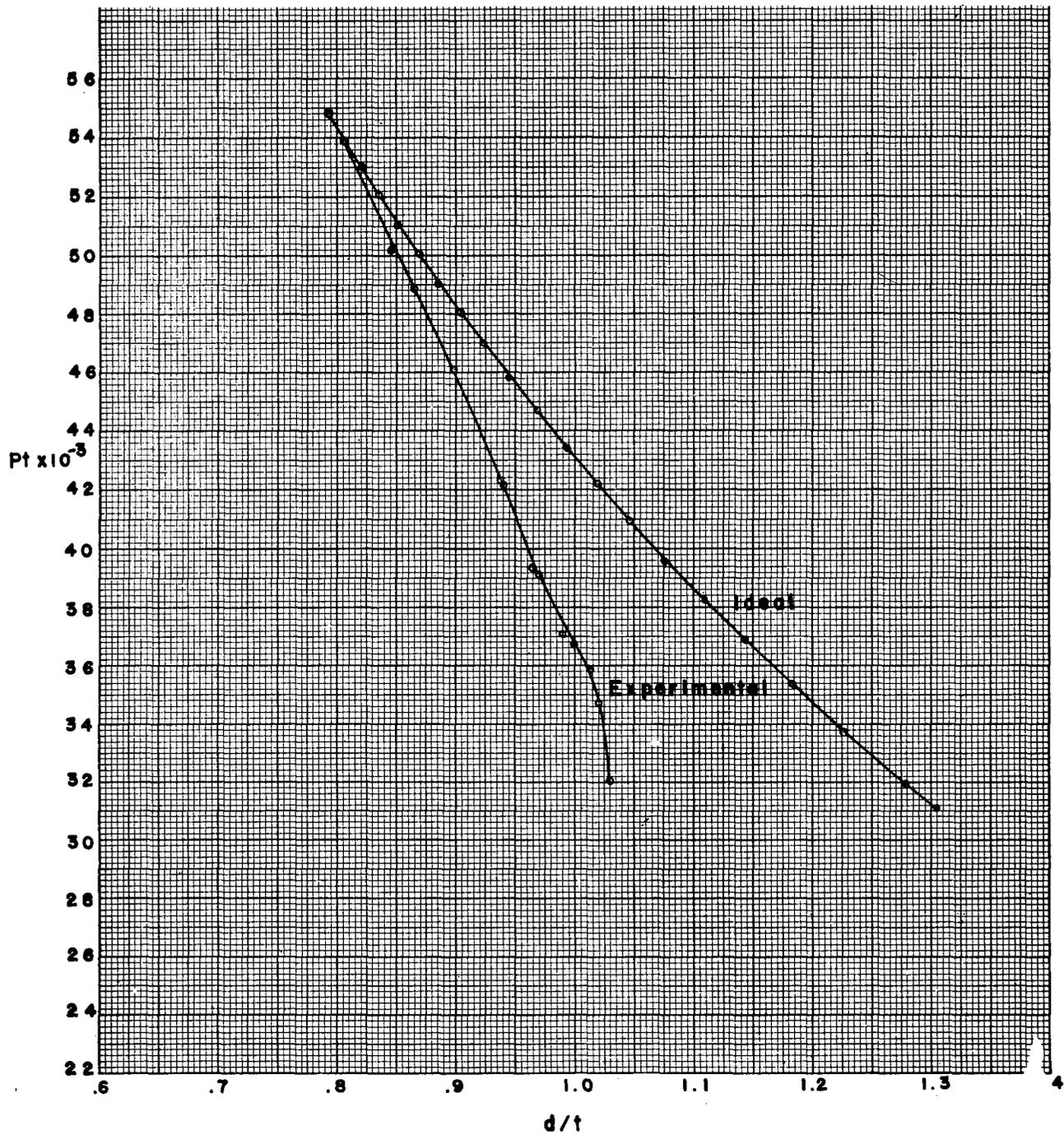


Fig. 7 Experimental and Ideal Curves
Pt vs d/t for Sodium Data
(Nickel Viscometer III)

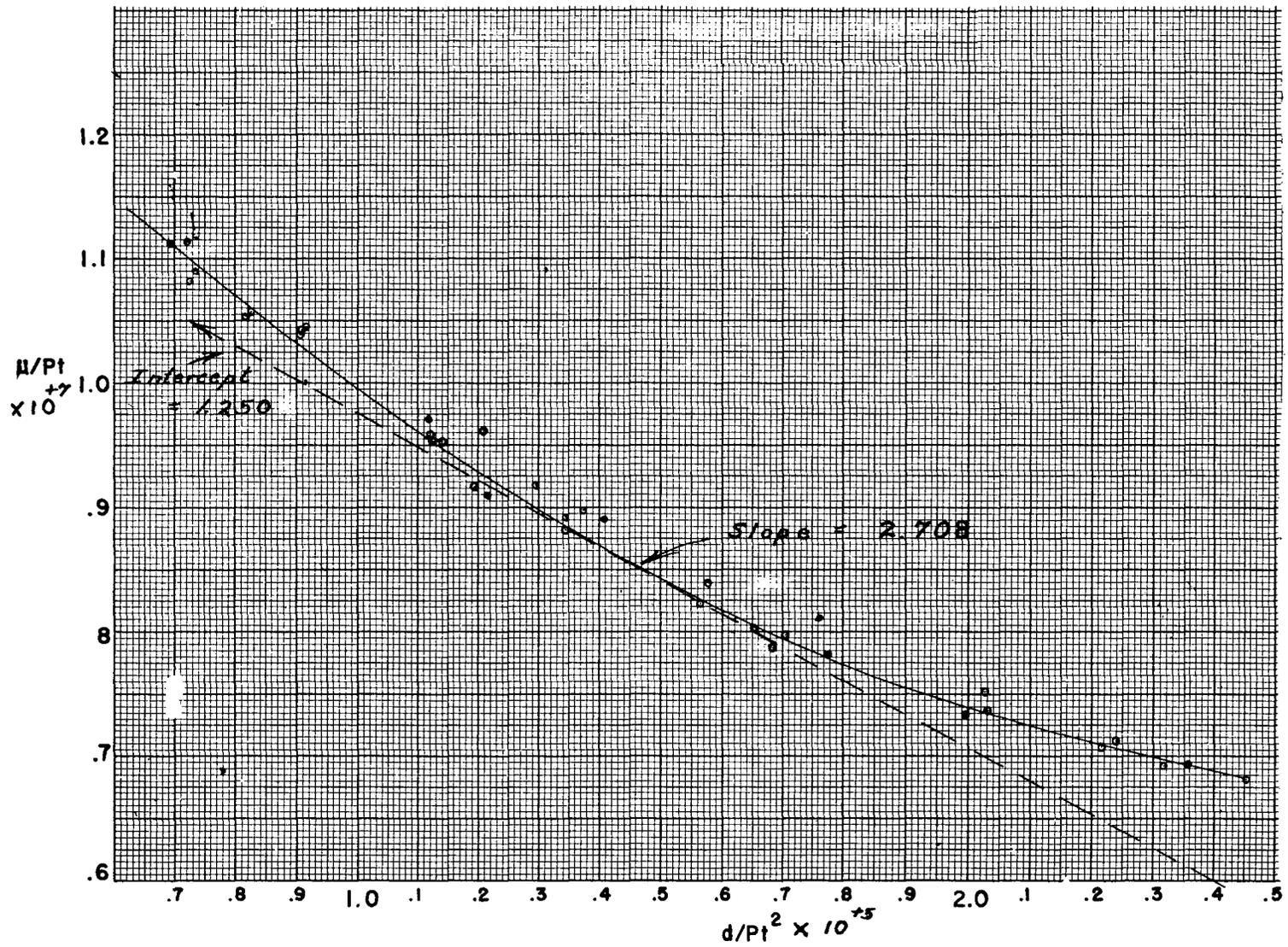


Fig. 8 Water Calibration Viscometer III

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DESCRIPTION OF APPARATUS AND OPERATIONS

Only a very brief description of the apparatus will be presented here. For a complete description refer to NRL Reports P-2931 and P-3057. Briefly, two horizontal nickel tanks were connected by a small nickel capillary (0.238 cms and 570 cms; inside diameter and length, respectively). The capillary was coiled such that it could be enclosed with the upper tank in an electrically heated furnace. The lower tank, wound with an electric heater, was placed directly on the platform of a sensitive pair of dial scales which was arranged to read the weight of the container continuously. To increase accuracy, an optical system was arranged for magnifying the scale readings. Though limited by the sensitivity of the scale and the flexibility of the arms connected to the lower tank, a reproducible accuracy of better than five grams was obtained over the entire scale range. The measurement of flow through the capillary was then made by noting weight change with time.

Temperature readings were noted with a thermocouple inside the top container and a Leeds and Northrup, type K, potentiometer. The thermocouple was roughly calibrated at several temperatures and for these measurements no correction factor from the standard EMF curve was required.

In the results previously reported, all flow measurements were made under gravity head. Though not mentioned at that time, a number of water calibration experiments were made with a constant applied head on either the upper or lower tank. These measurements have found importance, in that one of the new calibration methods requires water results over the flow range. The constant heads for these experiments were obtained with a mineral oil bubbler and were noted with an attached manometer.

EXPERIMENTAL RESULTS

This section will present the corrected results for viscosity measurements on metallic sodium and three alloys. The table below gives each alloy, along with two composition values, representing analyses on the alloy before and after the viscosity determinations. The slight composition change in each alloy can be attributed to some loss of the potassium-rich vapors at the higher temperatures.

Alloy	* * * *	
	Composition Weight Percent Potassium Before	Composition Weight Percent Potassium After
1	0.0 (Metallic Sodium)	0.0
2	28.3	28.3
3	43.5	43.1
4	67.0	66.8

It should be pointed out that the capillary and the tanks were disassembled once during the course of the measurements for cleaning purposes; however, a correlation of water results made before and after the cleaning operation has shown that the viscometer was not altered in any way. This simplified the calibration procedure, allowing a single calibration by each method for all four metals.

Another factor which has become worthy of consideration is the measurement of static heads. A static head for water or for metal at any temperature and at any position of the liquid relative to the top and bottom tank, was readily determined experimentally by noting the applied pressure on the bottom pot just necessary to start the liquid up and down, respectively. In practice, an average static head for a given temperature was determined between the positions of the liquid equivalent to those limits used in the flow experiments. Actually, only one experimental head was required; the corresponding values for the same liquid at any other temperature was then calculable from a knowledge of the density change and the dimensions of the apparatus. An alternate method which might be used to obtain the static heads for the metals would be to calculate the head values directly from the experimental water head. As the weight of metal or water introduced in each case corresponded to a volume of approximately 1000 cc., the static head for each metal was readily calculated from relative density values. A table comparing head values calculated in this manner with the corresponding experimental values is presented below.

* * * *

Average Static Head Values for Viscosity Experiments

Temp °C	Composition Weight Percent Potassium	Experimental Head	Experimental Head Calculated from Water Head
29	WATER	54.2	
150	0.0	56.1	54.2
125	28.3	54.2	54.2
125	43.5	55.1	54.5
100	67.0	55.2	54.6

* * * *

The results previously reported were based on experimental head values. The choice between the two sets of values seems of small import except in the case of sodium; for with the alloys, the difference between the two values is in the order of one percent or less. Now, it is believed that the experimental values for the metals may have been influenced by solid particles

of oxide, etc., particularly as the experimental value is in each case higher than the calculated value. The experimental water head is an average of numerous head determinations and we then feel justified in assuming that the calculated head values are of higher accuracy. Therefore, the calculated values have been used for the final results with the viscometer.

Both new calibration methods and their application to this viscometer have been discussed in detail. The water calibration experiments for Method I are presented in Table XIV. Method I, as stated, has been used to obtain results for the four metals up to 400° and 500°C, and Method II for results up to 700°C. The final viscosity values by both methods are presented in Tables XV-XVIII. Comparable values by both methods show exceptional agreement, differing in most cases by less than one percent. In each table, the average of the experimental values by both methods is compared with the corresponding value derived from the extension of the results in glass. The average deviation of the extended value from the experimental was approximately ± 5 percent.

The comparison between the experimental values in nickel and the estimated values from glass, was further extended with four curves relating the values (Figures IX-XII). Strangely enough, the experimental curve for each metal was found to have a definite break at around 350°C. No attempt will be made to interpret this break. It is interesting, however, that the break should occur at a temperature very near those reported for the wetting temperatures against nickel (which are now strongly suspected as being related to the reduction of nickel oxide). It seems doubtful that any change in physical properties of the metals would occur -- at 350°C; it would be more reasonable to attribute such a break to features of the calibration, such as wetting conditions in the capillary, etc.

TABLE XIV
VISCOMETER III
WATER CALIBRATION

Temp °C	Flow Rate gm/sec	Head cm H ₂ O	Density gm/cc	ICT Viscosity poises x 10 ⁺²	d/Pt ² x10 ⁺⁵	d/tμ ⁻² x10 ⁻²	Deter- mined Viscos- ity poises _{x 10} ⁺²	Per- cent Devi- ation
26.0	1.007	93.1	.9968	.875	1.118	1.151	.864	-1.3
26.6	1.010	93.2	.9967	.863	1.123	1.170	.863	0.0
26.0	1.320	132.5	.9968	.874	1.349	1.510	.874	0.0
26.1	1.331	132.4	.9968	.872	1.373	1.526	.859	-1.5
26.2	0.763	65.1	.9968	.870	0.917	0.877	.853	-1.9
26.2	0.761	65.4	.9968	.870	0.908	0.875	.860	-1.1
26.3	0.541	43.4	.9967	.869	0.693	0.623	.873	+0.5
27.2	0.553	43.4	.9965	.851	0.724	0.650	.844	-0.8
69.3	1.482	95.3	.9782	.411	2.456	3.606	.408	-0.7
68.3	1.815	130.8	.9787	.417	2.682	4.353	.422	+1.2
67.4	1.838	130.8	.9793	.422	2.747	4.355	.406	-3.8
67.1	1.145	68.7	.9794	.424	2.029	2.700	.423	-0.2
68.0	1.137	68.9	.9789	.418	1.998	2.720	.429	+2.6
74.7	1.196	69.2	.9751	.382	2.218	3.131	.385	+0.8
68.2	1.149	69.1	.9788	.417	2.034	2.755	.422	+1.2
65.5	1.380	90.2	.9803	.438	2.241	3.180	.438	+0.0
68.2	1.413	90.3	.9788	.417	2.354	3.388	.416	-0.2
65.5	1.836	134.6	.9803	.434	2.658	4.230	.434	0.0
54.0	1.721	134.0	.9862	.515	2.317	3.342	.519	+0.8
51.6	1.007	67.1	.9873	.535	1.581	1.882	.533	-0.4
49.8	0.693	41.4	.9882	.551	1.211	1.258	.533	-3.3
54.0	1.340	95.1	.9862	.515	1.980	2.602	.513	-0.4
50.9	0.858	54.4	.9877	.541	1.415	1.586	.530	-2.0
63.3	0.922	54.4	.9815	.448	1.654	2.058	.456	+1.8
27.5	0.661	54.4	.9964	.846	0.825	0.781	.847	+0.1
27.4	0.659	54.4	.9964	.848	0.820	0.777	.850	+0.2
30.3	0.693	54.4	.9956	.795	0.908	0.872	.788	-0.9
46.5	0.824	54.4	.9896	.582	1.300	1.416	.576	-1.0
64.9	0.952	54.4	.9806	.437	1.767	2.179	.431	-1.4
23.7	0.622	54.0	.9974	.923	0.736	0.674	.928	+0.5
23.8	0.618	54.0	.9973	.922	0.727	0.670	.936	+1.5
50.3	0.833	54.0	.9879	.547	1.345	1.523	.553	+1.1
50.4	0.835	54.0	.9879	.546	1.352	1.529	.551	+0.9
60.0	0.894	54.0	.9832	.470	1.564	1.902	.479	+1.9
56.1	0.858	54.0	.9852	.498	1.435	1.723	.520	+4.4
68.1	0.949	54.0	.9789	.418	1.778	2.270	.425	+1.7
65.7	0.925	54.0	.9802	.432	1.685	2.141	.448	+3.7
65.1	0.931	54.0	.9805	.436	1.706	2.135	.443	+1.6
23.5	1.085	107.7	.9974	.927	1.120	1.170	.927	0.0
23.5	1.082	107.7	.9974	.927	1.114	1.167	.933	+0.6
23.7	1.222	125.6	.9974	.923	1.219	1.324	.929	+0.7
23.5	1.213	125.7	.9974	.927	1.200	1.309	.948	+2.3
52.5	1.709	134.4	.9869	.528	2.275	3.236	.530	+0.4
66.5	1.853	135.3	.9795	.427	2.696	4.340	.426	-0.2
67.9	1.106	66.0	.9790	.419	1.972	2.640	.426	+1.7

TABLE XV
VISCOMETER III
VISCOSITY SODIUM

Temp °C	Flow Rate gm/sec	Head cm Metal	Density gm/cc	Viscosity Centipoises				Diff. Per- cent
				Exptl. Method I Vis. III	Exptl. Method II Vis. III	Exptl. Ave. Vis. III	Exptl.* Exten- ded Vis. II	
143	.710	54.2	.917	.604		.604	.563	-6.8
145	.724	54.2	.916	.582		.582	.558	-4.1
196	.800	54.3	.904	.468	.463	.465	.452	-2.8
198	.805	54.3	.903	.461	.457	.459	.449	-2.2
245	.845	54.3	.892	.409	.409	.409	.387	-5.4
250	.865	54.3	.891	.391	.388	.389	.381	-2.1
292	.898	54.4	.881	.353	.350	.351	.339	-3.4
368	.941	54.5	.862	.301	.300	.300	.286	-4.7
371	.937	54.5	.861	.303	.303	.303	.284	-6.3
447	.970	54.6	.842	.263	.263	.263	.249	-5.3
447	.965	54.6	.842	.266	.267	.267	.249	-6.7
506	.990	54.7	.828	.233	.237	.235	.227	-3.4
506	1.000	54.7	.828	.225	.228	.227	.227	0.0
571	1.014	54.8	.812		.207	.207	.209	+1.0
572	1.020	54.8	.812		.202	.202	.208	+3.0
686	1.031	54.9	.783		.174	.174	.185	+6.3

*Values obtained from Figure XIV

TABLE XVI
VISCOMETER III
VISCOSITY SODIUM - POTASSIUM ALLOY
(28.3 Weight - Percent Potassium)

Temp °C	Flow Rate gm/sec	Head cm Metal	Density gm/cc	Viscosity Centipoises				Diff. Per- cent
				Exptl. Method I Vis. III	Exptl. Method II Vis. III	Exptl. Ave. Vis. III	Exptl.* Exten- ded Vis. II	
144	.765	54.3	.890	.488	.482	.485	.488	+0.6
171	.800	54.4	.884	.441	.440	.440	.438	-0.5
176	.813	54.4	.883	.427	.426	.426	.429	+0.7
241	.868	54.5	.867	.360	.360	.360	.345	-4.2
252	.881	54.5	.865	.348	.347	.347	.335	-3.5
325	.923	54.6	.847	.297	.297	.297	.282	-5.0
332	.923	54.6	.846	.296	.297	.297	.277	-6.7
395	.965	54.7	.830	.254	.250	.252	.246	-2.4
395	.970	54.7	.830	.250	.246	.248	.245	-1.2
438	.989	54.7	.820	.225	.223	.224	.228	+1.8
447	.992	54.7	.818	.220	.220	.220	.225	+2.3
510	1.008	54.8	.803		.197	.197	.206	+4.6
516	1.009	54.8	.801		.195	.195	.204	+4.6
566	1.015	54.9	.789		.183	.183	.192	+4.9
570	1.021	54.9	.788		.178	.178	.191	+7.3
637	1.028	55.0	.772		.163	.163	.178	+9.2
702	1.032	55.1	.756		.150	.150	.167	+11.3
708	1.030	55.1	.755		.151	.151	.166	+9.7

TABLE XVII
 VISCOMETER III
 VISCOSITY SODIUM - POTASSIUM ALLOY
 (43.5 Weight - Percent Potassium)

Temp °C	Flow Rate gm/sec	Head cm Metal	Density gm/cc	Viscosity Centipoises				Diff. Per- cent
				Exptl. Method I Vis. III	Exptl. Method II Vis. III	Exptl. Ave. Vis. III	Exptl. Exten- ded Vis. II	
95	.689	54.5	.888	.586		.586	.574	-2.0
95	.687	54.5	.888	.590		.590	.574	-2.0
143	.771	54.5	.876	.460	.456	.458	.456	-0.4
146	.773	54.5	.876	.459	.454	.456	.450	-1.3
191	.829	54.6	.864	.390	.388	.389	.379	-2.6
192	.826	54.6	.864	.393	.391	.392	.378	-3.6
250	.878	54.6	.850	.333	.332	.332	.316	-4.8
256	.879	54.6	.848	.330	.330	.330	.311	-5.8
320	.915	54.7	.833	.289	.288	.288	.268	-7.0
327	.922	54.7	.831	.288	.283	.285	.264	-7.4
388	.959	54.8	.816	.243	.239	.241	.235	-2.5
392	.956	54.8	.815	.244	.242	.243	.233	-4.1
458	.987	54.9	.799	.204	.206	.205	.210	+2.4
464	.987	54.9	.798	.204	.205	.205	.209	+1.9
509	.997	54.9	.787		.191	.191	.197	+3.1
517	.997	55.0	.785		.190	.190	.195	+2.6
585	1.008	55.1	.768		.171	.171	.180	+5.3
588	1.007	55.1	.767		.170	.170	.179	+5.3
651	1.010	55.1	.752		.159	.159	.168	+5.7
681	1.010	55.1	.745		.155	.155	.164	+5.8
689	1.012	55.1	.743		.152	.152	.163	+7.2

TABLE XVIII
 VISCOSITY SODIUM - POTASSIUM ALLOY
 (67.0 Weight - Percent Potassium)

Temp °C	Flow Rate gm/sec	Head cm Metal	Density gm/cc	Viscosity Centipoises				Diff. Per- cent
				Exptl. Method I Vis. III	Exptl. Method II Vis. III	Exptl. Ave. Vis. III	Exptl. Exten- ded Vis. II	
74.4	.617	54.6	.867	.662		.662	.583	-11.9
76.6	.615	54.6	.867	.665		.665	.574	-13.7
82.0	.602	54.6	.868	.691		.691	.556	-19.5
142	.756	54.7	.851	.442	.440	.441	.412	- 6.6
146	.780	54.7	.850	.416	.413	.414	.406	- 1.9
188	.825	54.7	.840	.364	.361	.362	.348	- 3.9
195	.829	54.7	.838	.358	.356	.357	.340	- 4.8
203	.850	54.8	.836	.340	.335	.337	.331	- 1.8
211	.851	54.8	.835	.336	.333	.334	.323	- 3.3
221	.871	54.8	.832	.319	.313	.316	.314	- 6.3
232	.821	54.8	.830	.356	.360	.358	.304	-15.1
268	.878	54.8	.821	.300	.299	.299	.277	- 7.3
275	.886	54.8	.819	.293	.291	.292	.272	- 6.8
321	.924	54.9	.808	.259	.251	.255	.246	- 3.5
331	.910	54.9	.806	.264	.263	.263	.240	- 8.8
395	.951	55.0	.791	.220	.218	.219	.215	- 1.8
397	.948	55.0	.790	.223	.220	.221	.214	- 3.2
438	.958	55.0	.780		.195	.195	.202	+ 3.6
460	.976	55.1	.775		.188	.188	.195	+ 3.7
461	.957	55.1	.775	.200	.204	.202	.195	- 3.5
467	.968	55.1	.774		.194	.194	.194	0.0
479	.995	55.1	.770		.179	.179	.190	+ 6.2
490	.983	55.1	.768		.178	.178	.188	+ 5.6
511	.980	55.2	.763		.177	.177	.182	+ 2.8
560	.976	55.2	.751		.174	.174	.172	- 1.1
612	.983	55.3	.739		.161	.161	.163	+ 1.2
629	.983	55.3	.735		.158	.158	.160	+ 1.3
669	.991	55.4	.725		.146	.146	.155	+ 6.1
689	.990	55.4	.720		.143	.143	.153	+ 7.0

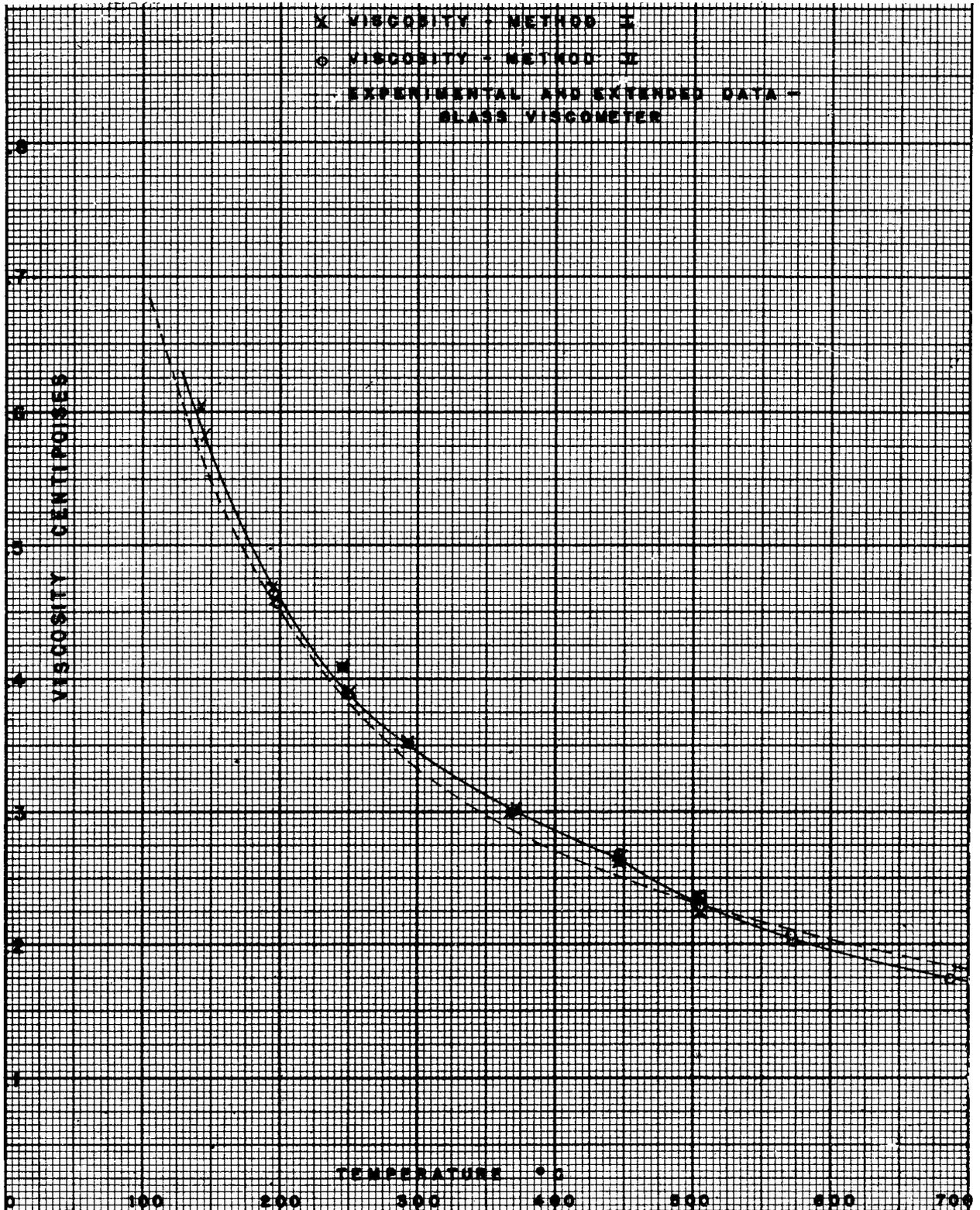


Fig. 9 Viscosity Sodium (Nickel Viscometer III)

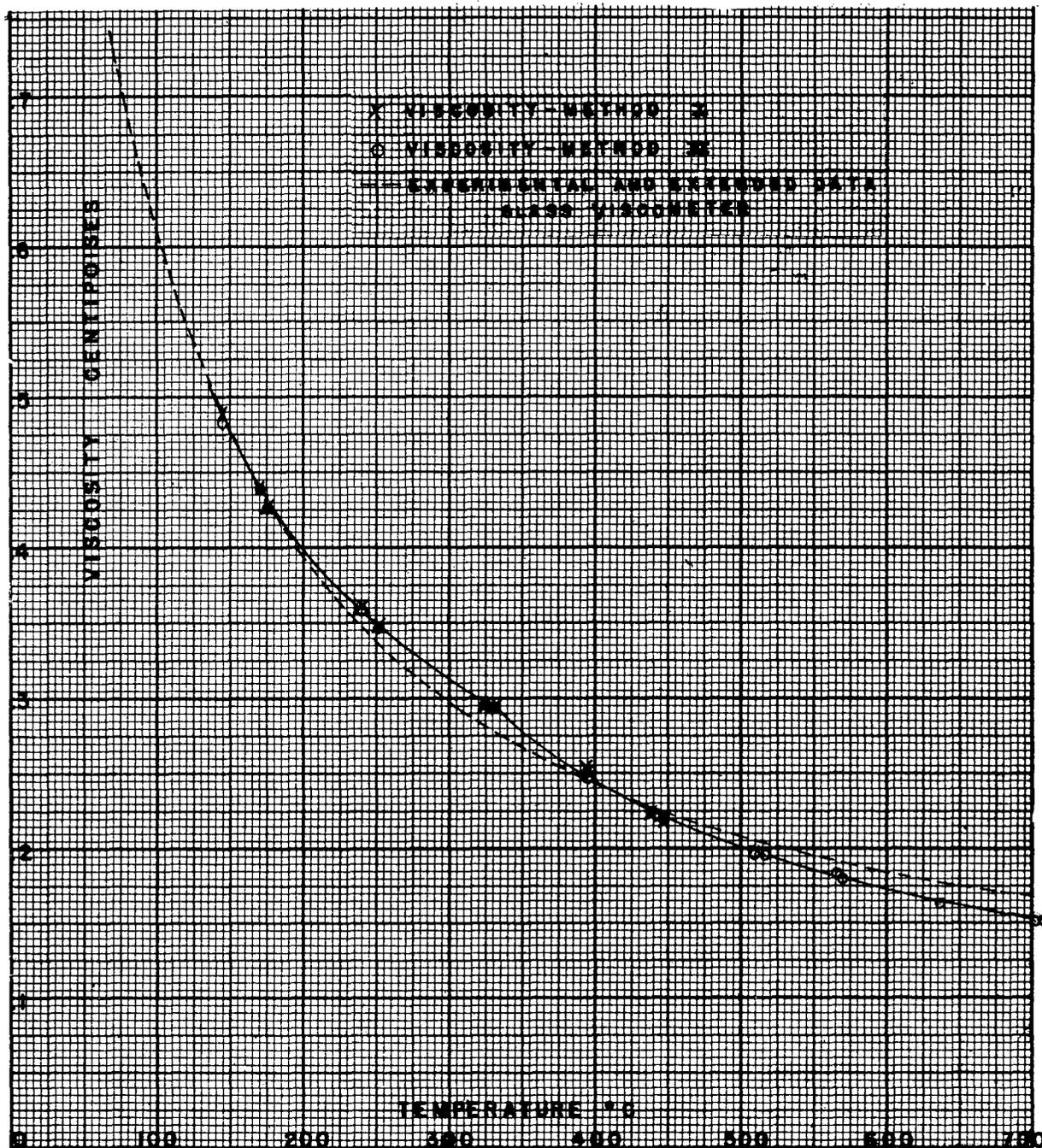


Fig. 10 Viscosity Sodium - Potassium Alloy
(28.3 Weight Percent Potassium)
Nickel Viscometer III

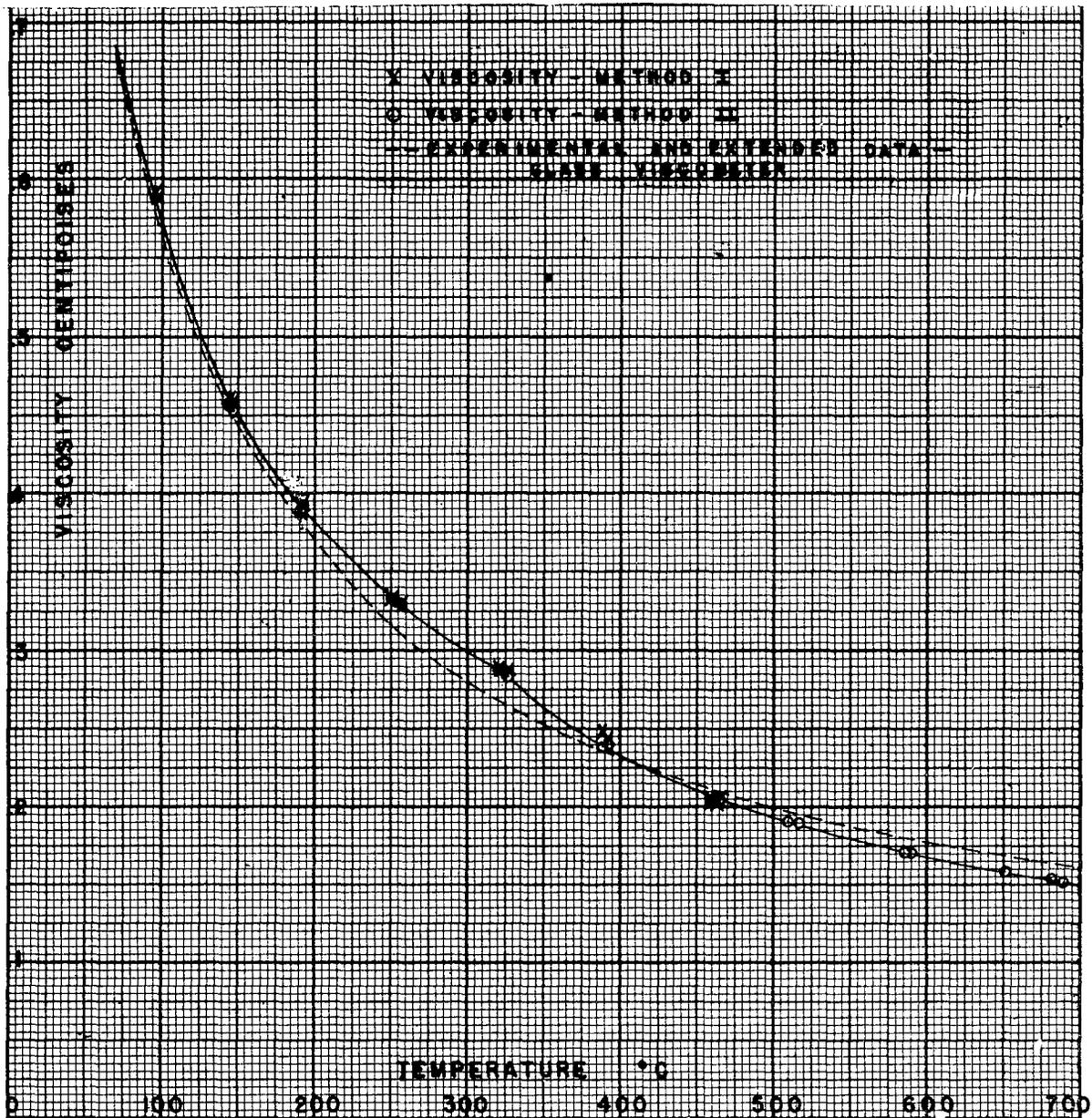


Fig. 11 Viscosity Sodium - Potassium Alloy
 (43.5 Weight Percent Potassium
 Nickel Viscometer III

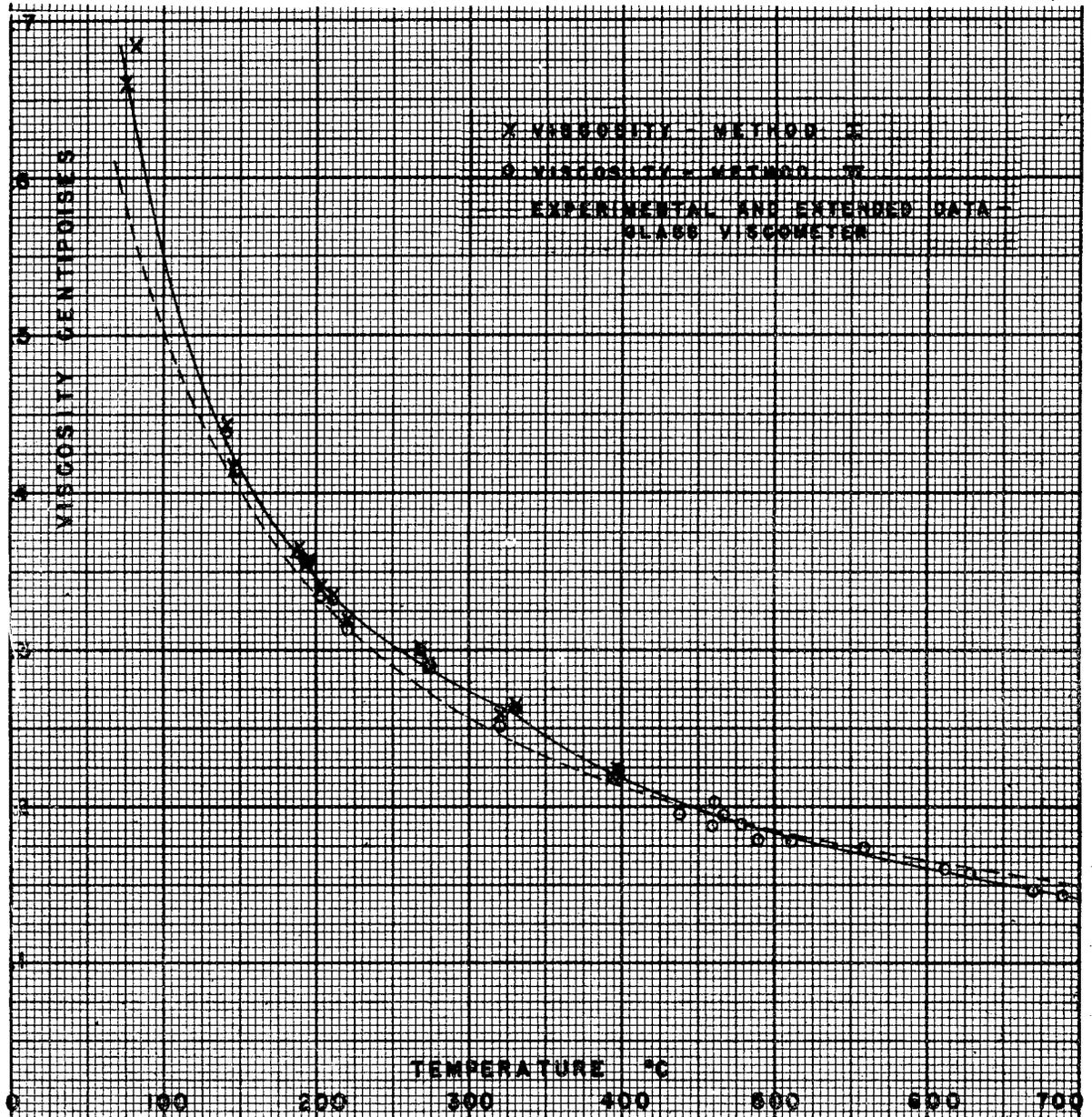


Fig. 12 Viscosity Sodium - Potassium Alloy
(67.0 Weight Percent Potassium)
Nickel Viscometer III

VISCOMETER IV
(NICKEL TYPE - 0.159 cm I.D. CAPILLARY)

GENERAL REMARKS

This viscometer, essentially, was identical with the other nickel model except for the smaller capillary which was installed to permit gravity flow experiments under smaller Reynold's numbers. The theory of capillary flow and the discussion of its application with the first nickel model, apply equally well for this viscometer. As would be expected, the viscometer terms -- (A) and (B) -- were found to change with the flow rate. Potassium was the only metal used in the viscometer, but both Method I and Method II were applicable for calibration. These methods, which have been described in detail, were used to calculate the final potassium results.

DESCRIPTION OF APPARATUS AND OPERATIONS

The description of Viscometer III and its operation, as finally reported, will in general, cover the modified model. No attempt will be made to repeat this discussion. There are, however, several features which were added and are worth mentioning. The smaller capillary installed was approximately .159 cms and 640 cms, inside diameter and length, respectively. All thermocouples were calibrated against Bureau of Standard thermocouples up to 600°C, particular care being exercised in the range below 100°C. A Rubicon potentiometer replaced the Leeds and Northrup type, mainly because the latter was no longer available. The capillary heater, which was manually controlled in the previous setup, was placed on a control circuit through a Brown recording potentiometer. In general, the apparatus was revamped in an effort to better the overall accuracy of the previous model.

EXPERIMENTAL RESULTS

The intention of the work with this viscometer was to obtain values for potassium up to 700°C, needed to round out the data with the previous nickel model. However, at about 400°C, a plug developed unexpectedly in the capillary and the measurements ended at that point. Actually, only about six experiments were obtained at three temperatures up to 350°C. The final results, as calculated by both methods, are presented in Table XX. Figure XIII also gives a plot of the experimental values from the nickel viscometer against the experimental and extended values from glass. An extrapolation of the water results was required for the solution of viscosities by Method I; and, thus, the values by Method II are believed to be of higher accuracy. In Table XX, therefore, the values by Method II have been used for comparison with the glass values. It will be noted that these measurements serve to verify the experimental and extended values for potassium in glass.

The water experiments with the viscometer are presented in Table XIX with the usual comparison of calculated with ICT values. It will be noted that the water experiments with this viscometer are of higher accuracy than those with the previous model. For Method I, an extrapolation curve was used to obtain the potassium results at 275° and 350°C. Such an extrapolation was thought to be justified in that the rate of change of the slope $d(Pt^2/d) / d(d/t\mu)$ in the streamline range was found to be of low magnitude and practically constant for the water experiments with this viscometer and with viscometer III.

It should also be mentioned that there is no relation between the water heads and metal heads as was the case with viscometer III. The height of the lower tank was varied after the water experiments. The head for potassium as listed in Table XX is an experimental head carefully determined as previously described.

TABLE XIX
WATER CALIBRATION
(VISCOMETER IV)

Temp °C	Flow Rate gm/sec	Head cm Water	Density gm/cc	ICT Viscosity poises $\times 10^{+2}$	d/Pt^2 $\times 10^{+6}$	$d/t\mu$ $\times 10^{-2}$	Deter- mined Viscos- ity poises $\times 10^{+2}$	Diff. Per- cent
41.3	.2080	58.8	.9917	.638	0.763	.3260	.630	-1.2
40.9	.2016	57.4	.9919	.643	0.734	.3135	.642	-0.2
38.4	.1996	58.8	.9928	.674	0.701	.2961	.672	-0.3
38.2	.1942	57.4	.9929	.677	0.680	.2869	.681	+0.6
56.7	.2430	58.8	.9849	.494	1.056	.4919	.493	-0.2
56.7	.2367	57.4	.9849	.494	1.026	.4791	.498	+0.8
54.0	.2369	58.8	.9862	.515	1.001	.4600	.514	-0.2
53.7	.2306	57.4	.9863	.518	0.971	.4452	.521	+0.6
69.4	.2714	58.8	.9781	.410	1.335	.6620	.406	-1.0
69.2	.2633	57.4	.9782	.412	1.287	.6391	.413	+0.2
67.7	.2660	58.8	.9791	.420	1.280	.6333	.420	0.0
67.9	.2607	57.4	.9790	.419	1.260	.6222	.420	+0.2
25.8	.1639	58.8	.9969	.878	0.469	.1867	.872	-0.7
25.6	.1589	57.4	.9969	.882	0.451	.1802	.883	+0.1
23.9	.1571	58.8	.9974	.918	0.430	.1711	.919	+0.1
23.8	.1519	57.4	.9974	.921	0.412	.1649	.932	+1.2
76.0	.2828	58.8	.9743	.376	1.461	.7521	.376	0.0
76.8	.2778	57.4	.9738	.372	1.446	.7468	.374	+0.5
77.6	.2861	58.8	.9733	.368	1.498	.7774	.368	0.0

TABLE XX
 VISCOSITY POTASSIUM
 (NICKEL VISCOMETER IV)

Temp °C	Flow Rate gm/sec	Head cm Metal	Density gm/cc	Viscosity Centipoises			Percent Difference (Vis. II Values from Vis. IV Values by Method II)
				Exptl. Method I Vis. IV	Exptl. Method II & Vis. IV	Exptl. Extended Vis. II	
197	.232	59.6	.796	.311	.310	.302	-2.6
197	.233	59.6	.796	.308	.308	.302	-1.9
272	.257	59.8	.778	.242	.253	.247	-2.4
273	.257	59.8	.778	.242	.253	.247	-2.4
350	.267	60.0	.759	.205	.226	.211	-6.6
350	.263	60.0	.759	.213	.233	.211	-9.4

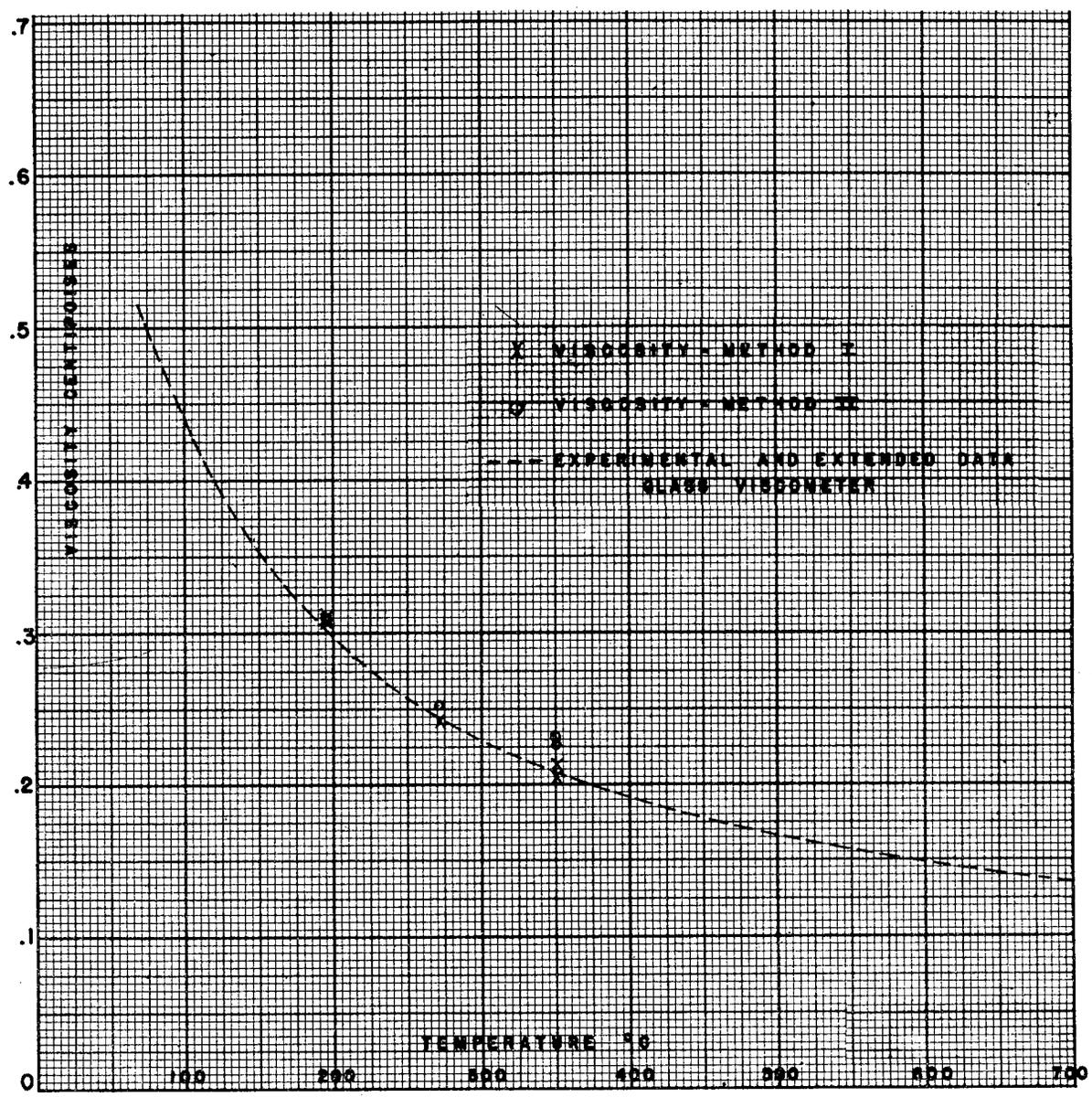


Fig. 13 Viscosity Potassium Nickel Viscometer IV

ANALYSIS OF ALL VISCOSITY RESULTS

The policy of basing all comparisons of the viscosity results on the experimental and extended values for glass viscometer II has been strictly followed in the discussion of results for each viscometer. In general, the following conclusions were drawn:

- (1) The results with glass viscometer I have served to check the general shape of the viscosity curves up to about 200°C.
- (2) The results with nickel viscometer III have served to verify the values up to 700°C within engineering accuracy, the purpose for which the values are intended. We feel adverse to attributing the breaks in the viscosity curves to the physical properties of the metals. If the future should shed light along this line, rectification can be made at that time.
- (3) The results with nickel viscometer IV have served to substantiate the values for potassium up to 350°C.

With this in mind, a composite curve was drawn up representing experimental viscosity data with viscometer II up to 200°C, and the extended data from 200° to 700°C (Figure XIV). The accuracy of values estimated from this curve should be better than $\pm 1\%$ below 200°C, and $\pm 8\%$ above 200°C.

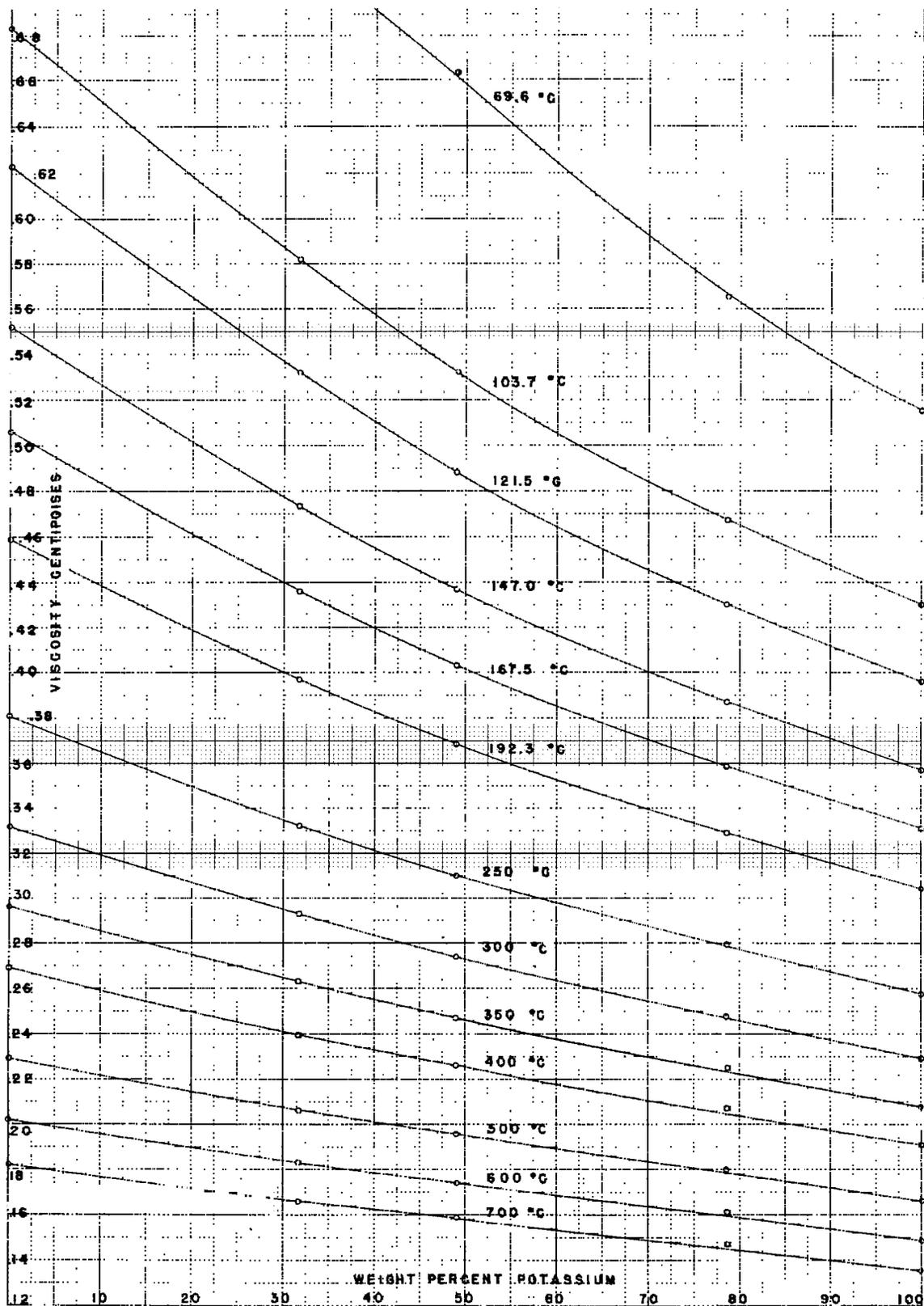


Fig. 14 Viscosity Sodium - Potassium System

DENSITY

REVIEW OF DENSITY DATA

Sundry density investigations for the NaK system have been completed at Mine Safety Appliances Company, at NRL, and elsewhere. In this report all available density values are correlated and presented in final form.

The investigation at MSA was limited in general to work with the seven master samples of NaK. Pyrex dilatometers were used to obtain values from the melting point up to about 200°C, and a buoyancy method for values from 300° to 700°C. This work in final form was included in NRL Report No. P-3010. Additional measurements of a preliminary nature were also reported in NRL Report No. C-3201.

Literature values to be considered are those from measurements on the pure metals reported by E. Rinck⁽⁴⁾ and by E. B. Hagen⁽⁵⁾.

The low temperature investigation at NRL was initiated in an effort to explain discrepancies in the dilatometric values at MSA. For this work, two quartz dilatometers, blown and calibrated at the Laboratory, were used.⁽⁶⁾ Density values for the pure metals and two high sodium alloys up to about 250°C were determined and reported in NRL Report No. C-3201. Since that time, in order to cover the composition range, measurements have been conducted on four additional alloys, using the same dilatometers, but varying the method somewhat. The results of this work and the methods employed are to be presented here.

NRL DILATOMETRIC MEASUREMENTS

DESCRIPTION OF APPARATUS AND OPERATIONS

Apparatus - As explained above, the quartz dilatometers were adapted for the present measurements. The bulb volume was 33 ml with stems having approximately 0.25 ml per cm of length. A liquid bath replaced the air furnace used previously. This bath, together with the temperature control assembly, was identical with that described for the viscosity measurements (NRL Report No. C-3201). Temperature readings were then noted with the five junction thermel and a Rubicon high-precision potentiometer, with which the temperature was, therefore, controlled and known to much better than the $\pm 0.5^\circ\text{C}$ which was quoted for the previous measurements.

(4) E. Rinck, Comptes Rendus, 189, 39-41 (1929)

(5) E. B. Hagen, Physik, 255, p 437 (1883)

(6) Dr. R. E. Leed assembled and calibrated the apparatus and made part of the measurements at NRL while on summer leave from VMI, Lexington, Virginia.

Operation - The operations involved were also similar to those previously described. The usual precautions having been taken to thoroughly clean the quartz surfaces (with a final preheat to approximately 300°C under vacuum), the alloy in each case was distilled from a nickel still directly into the dilatometer and the dilatometer fused off as a closed system under a slight negative pressure of nitrogen. Then, as before, to make a volume measurement (where $d = \frac{w}{v}$), it was necessary merely

to allow the bath to reach equilibrium at the desired temperature and to note with a cathetometer the height of the metal meniscus in the calibrated stem of the dilatometer. Again, the net weight of the metal had to be determined at the conclusion of the runs in order to eliminate an appreciable error arising from metal adhering to the walls of the tube extending from the capillary. Thus, the dilatometer was broken off in the capillary as near the calibrated zone as feasible, and the weight of the lower portion noted before and after removal of the metal. All weighings were carried out on a small beam balance, accurate to $\pm .05$ milligrams.

EXPERIMENTAL RESULTS

Dilatometric measurements at NRL have been made on the pure metals and six alloys. For completeness, the experimental results for all eight metals are presented in Tables XXI-XXVIII. The composition value at the head of each table represents an analysis on the metal as removed from the dilatometer at the conclusion of the measurements. Figure XV, applying these results, presents a plot of the density values for each metal against temperature. It is noted that density, in each case, is a straight line function of temperature.

The NRL dilatometric measurements have served to smooth out discrepancies in the low temperature work at MSA. Figure XVI effectively correlated low temperature values from both sources. At several temperatures, density values (derived from temperature-density figures) are plotted as a function of composition, and the best average curve drawn for each temperature. In many cases, the measurements at MSA were determined over very short temperature changes, and, therefore, the densities plotted in Figure XVI, in some cases, were derived by straight line extrapolations -- in no case, however, was the extrapolation greater than 50°C.

TABLE XXI
DENSITY OF SODIUM
(100.0 Percent Sodium)

Temperature °C	Density gm/cc	Temperature °C	Density gm/cc	Temperature °C	Density gm/cc
110.0	.9233	194.5	.9053	246.0	.8931
140.0	.9177	220.0	.8994	233.0	.8957
164.0	.9125	245.5	.8931	205.5	.9013
185.5	.9075	121.0	.9218	188.0	.9053
206.0	.9027	130.0	.9203	159.5	.9113
235.0	.8959	141.0	.9164	140.0	.9159
261.5	.8899	132.5	.9196	123.5	.9211
150.0	.9150	126.5	.9206	114.0	.9221
170.0	.9106	118.0	.9218	107.5	.9246

TABLE XXII
DENSITY OF SODIUM-POTASSIUM ALLOY
(4.8 Weight-Percent Potassium)
(2.9 Atom-Percent Potassium)

Temperature °C	Density gm/cc	Temperature °C	Density gm/cc	Temperature °C	Density gm/cc
149.0	.9120	137.0	.9150	263.0	.8848
175.5	.9053	160.5	.9095	274.5	.8824
197.5	.9012	184.5	.9039	288.0	.8788
208.0	.8982	219.0	.8966	243.5	.8888
124.0	.9170	235.5	.8909	206.0	.8976
		249.5	.8869		

TABLE XXIII
 DENSITY OF SODIUM - POTASSIUM ALLOY
 (21.5 Weight - Percent Potassium)
 (13.9 Atom - Percent Potassium)

Temperature °C	Density gm/cc	Temperature °C	Density gm/cc	Temperature °C	Density gm/cc
54.0	.9203	167.5	.8917	263.5	.8679
73.0	.9147	187.0	.8872	246.5	.8739
89.0	.9119	173.5	.8909	220.5	.8793
105.5	.9063	184.5	.8872	196.0	.8842
124.0	.9014	210.0	.8812	172.5	.8879
140.0	.8983	234.0	.8751	152.0	.8940
149.5	.8950	256.5	.8693	127.0	.9006
		281.5	.8648	102.5	.9058

TABLE XXIV
 DENSITY OF SODIUM-POTASSIUM ALLOY
 (41.3 Weight-Percent Potassium)
 (29.2 Atom - Percent Potassium)

Temperature °C	Density gm/cc
58.4	.9010
69.7	.8977
103.7	.8892
121.6	.8850
146.9	.8786
167.7	.8732
192.6	.8672

TABLE XXV
 DENSITY OF SODIUM - POTASSIUM ALLOY
 (63.9 Weight - Percent Potassium)
 (50.1 Atom - Percent Potassium)

Temperature °C	Density gm/cc
58.3	.8781
69.7	.8753
103.7	.8670
121.5	.8628
146.8	.8568
167.8	.8522
193.5	.8462
216.5	.8415

TABLE XXVI
 DENSITY OF SODIUM - POTASSIUM ALLOY
 (84.3 Weight - Percent Potassium)
 (75.9 Atom Percent Potassium)

Temperature °C	Density gm/cc
58.4	.8485
69.6	.8458
103.7	.8379
121.6	.8332
146.9	.8276
167.7	.8233
192.6	.8167
216.4	.8116

TABLE XXVII
 DENSITY OF SODIUM - POTASSIUM ALLOY
 (97.1 Weight-Percent Potassium)
 (95.1 Atom - Percent Potassium)

Temperature °C	Density gm/cc
64.4	.8304
103.7	.8212
121.6	.8172
146.9	.8111
167.8	.8058
192.6	.8006
216.4	.7956

TABLE XXVIII
 DENSITY OF POTASSIUM
 (100.0 Percent Potassium)

Temperature °C	Density gm/cc	Temperature °C	Density gm/cc	Temperature °C	Density gm/cc
90.5	.8204	144.5	.8089	214.0	.7937
105.0	.8182	164.5	.8044	228.0	.7908
128.0	.8133	188.0	.7997	241.5	.7869
		200.5	.7975	259.5	.7836

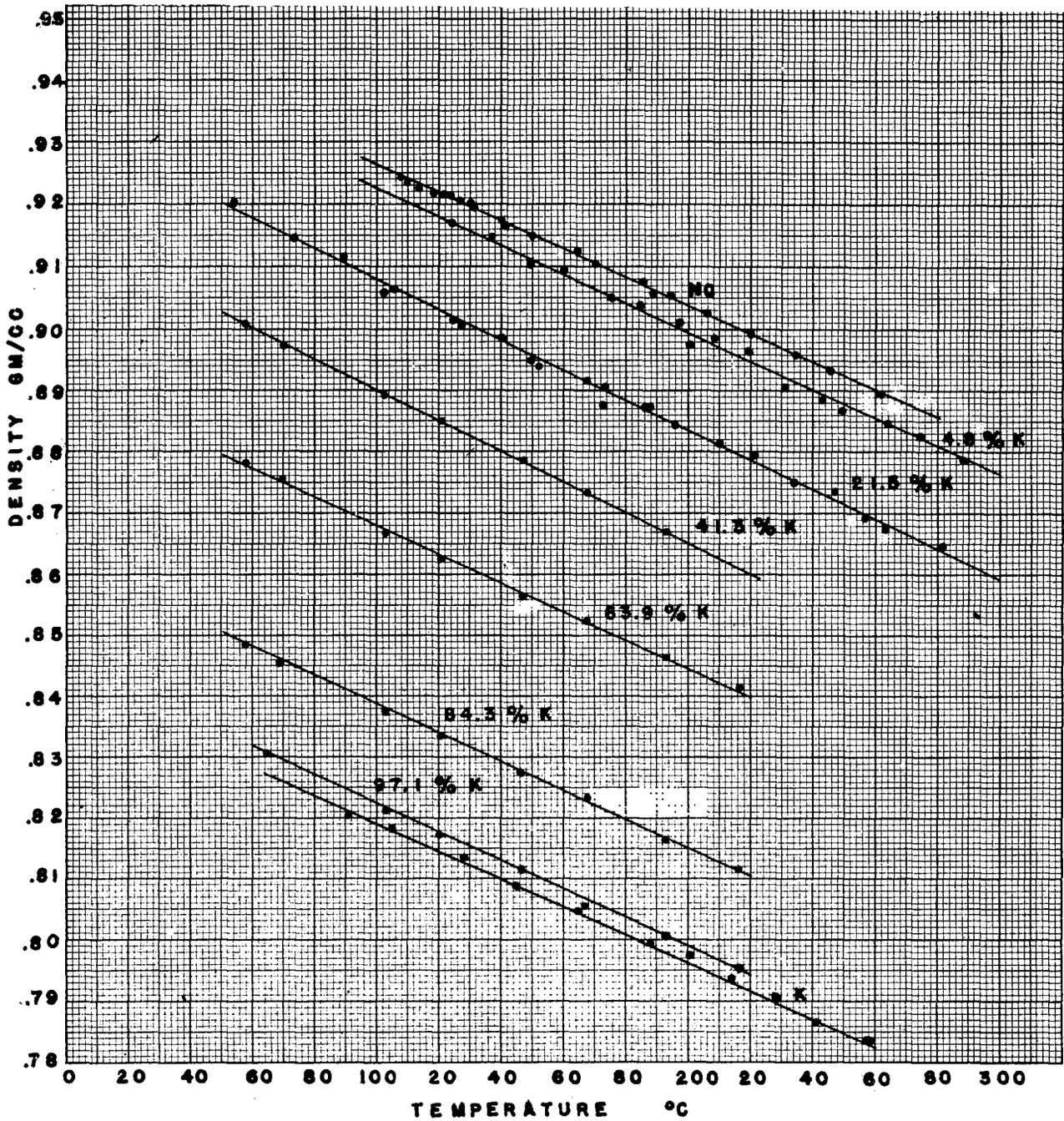


Fig. 15 Density Sodium - Potassium Alloy
N.R.L. Data - All Compositions (Weight Percent)

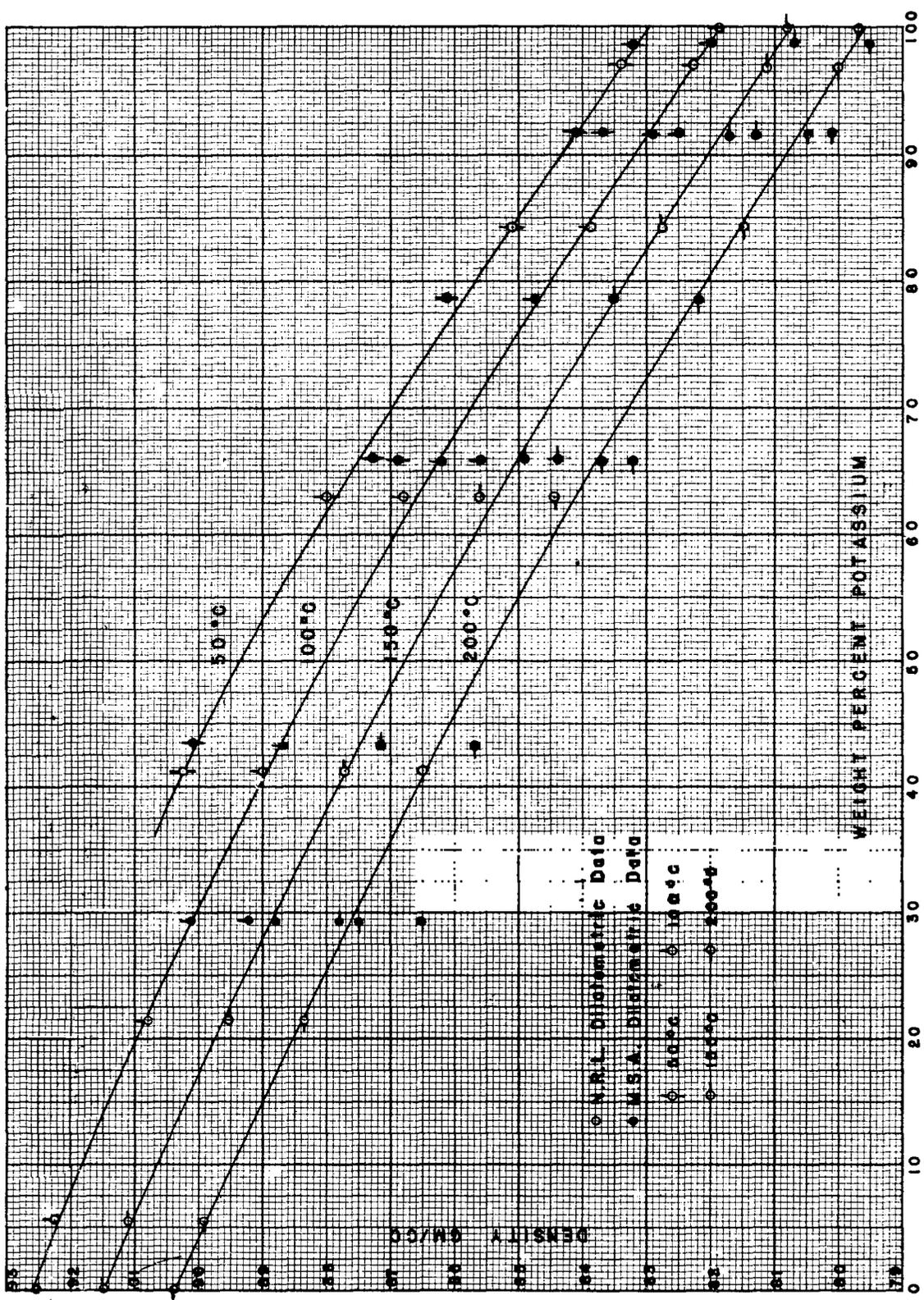


Fig. 16 Dilatometric Data
Density vs Weight Percent Potassium

ANALYSIS OF ALL DENSITY RESULTS

The purpose of this section is to correlate and analyze all existing density data, to obtain, thereby, the best density values for the temperature-composition range, and to present these values in readily available form for future reference. With this in view, it was found desirable, first, to obtain for each of the master samples (compositions used in MSA density work) the best density curve over the temperature range by combining available low temperature and high temperature values. Then, from the resulting family of curves, the composite curve for composition-temperature variation of density was readily drawn up.

The density-temperature figure for each master sample was derived by plotting the MSA buoyancy values with the corresponding low temperature values as determined from Figure XVI, and by ruling the best curve through all the values. The set of curves obtained in this manner are illustrated in Figures XVII-XXIV. In each case, a straight line was found to satisfactorily connect the dilatometric and buoyancy values, and thereby to represent the variation of density up to 700°C. The maximum variation from the straight line was noted to occur in buoyancy values for temperatures below 300 or 400°C, where the sensitivity of the balance was admittedly affected by surface tension and other phenomena. For each plot, the MSA dilatometric measurements for that master sample were added incidentally, for the dilatometric values from Figure XVI were given full weight in ruling the curve.

The density-temperature figures for 0.2 and 98.8 weight percent potassium alloys (Figures XVII and XXIV), which essentially are plots for the pure metals, also included the available literature values. Dilatometric measurements by E. B. Hagen and buoyancy measurements by E. Rinck for the pure metals are plotted along with the MSA and NRL data. The low temperature values by Hagen for both sodium and potassium are noted to coincide almost perfectly with the NRL and MSA values. The two melting point densities reported by Hackspill (7) would appear to be somewhat in error. The values reported by Rinck were obtained with a buoyancy method similar to that used by MSA, and the results seem to be of a reliable nature. Rinck's values were on the average about 0.5 percent higher than corresponding values by MSA. Some weight was given to the values by Rinck in drawing the density figures for the pure metals.

From the eight density figures discussed, the final composite curve of density-composition-temperature was drawn up and is included as Figure XXV. These composition-density iso-

(7) L. Hackspill -
Compt.rend., 152, 259-62

therms permit the evaluation of the density of any NaK alloy from melting point to 700°C with less than $\pm .8\%$ error. The density values below 400°C should contain less than $\pm .4\%$ error.

It was stated in a previous report that the density values as obtained at MSA by buoyancy measurements with a plated copper plunger would appear to be in error by the amount of the surface tension force acting on the support wire. It was also stated that this error could be as much as one percent based on literature values for surface tension. However, values of surface tension, as reported in this report, have shown that those gleaned from the literature were in all probability much too high. Assuming that the surfaces of the metal in the buoyancy work were such as to have surface tensions in the range of those reported (90 dynes/cm), this correction factor, at most, would amount to only 0.2 percent of the density value which would be negligible for these measurements. It is true that conditions at the surface can be such as to effectively provide higher surface tensions, perhaps approaching the high literature values. As there is no way of defining the surfaces in the buoyancy measurements, it shall be assumed that this correction is negligible. Assuming that the worst condition is a surface tension approaching 350 dynes/cm, this correction would amount to a maximum of 0.8 percent of the density at 700°C and would decrease nearly linearly to nil at 200°C.

The presentation of a mixture equation for density will offer no great advantage in estimating densities, as Figure XXV is adequate in itself; however, the mixture equation applicable will be presented for such use as desired. The equation found to satisfy the variation of density with composition was on the basis of specific volume and mol fraction:

$$V = M_K V_K + M_{Na} V_{Na}$$

where:

- V = Specific Volume Alloy
- V_K = Specific Volume Potassium
- V_{Na} = Specific Volume Sodium
- M_K = Mol Fraction Potassium
- M_{Na} = Mol Fraction Sodium

Admittedly, the equation is solely of an empirical nature. Actually, the ideal mixture equation for density would involve molal volume with mol fraction, or specific volume with weight fraction.

Table XXIX illustrates the accuracy to be expected for density values calculated with the mixture equation. Experimental values are compared with corresponding calculated values, and the maximum deviation of the calculated from the experimental value is shown to be about 0.7 percent. As the deviations are

all in the same direction and of approximately the same magnitude, a modification of the equation including a constant correction factor of about 0.3 percent of the density value would give calculated values over the range within ± 0.4 percent of the experimental value.

TABLE XXIX
 DENSITY BY MIXTURE EQUATION
 ($V = M_K V_K + M_{Na} V_{Na}$)

Temperature °C	Density Sodium gm/cc	Composition in Weight Percent Potassium												Density Potassium gm/cc			
		29.4%			43.4%			65.9%			78.6%				91.7%		
		Exptl	Calc	Per- cent Diff	Exptl	Calc	Per- cent Diff	Exptl	Calc	Per- cent Diff	Exptl	Calc	Per- cent Diff		Exptl	Calc	Per- cent Diff
100	.928	.901	.903	+0.2	.887	.890	+0.3	.862	.867	+0.6	.847	.850	+0.4	.830	.832	+0.2	.819
200	.903	.877	.880	+0.3	.862	.867	+0.6	.838	.842	+0.5	.823	.826	+0.4	.806	.808	+0.2	.795
300	.879	.853	.855	+0.2	.838	.842	+0.5	.814	.818	+0.5	.799	.802	+0.4	.782	.784	+0.3	.771
400	.854	.829	.831	+0.2	.814	.818	+0.5	.790	.793	+0.4	.775	.778	+0.4	.758	.759	+0.1	.747
500	.829	.805	.806	+0.1	.789	.793	+0.5	.766	.769	+0.5	.751	.754	+0.4	.734	.736	+0.3	.723
600	.805	.781	.782	+0.1	.765	.769	+0.5	.742	.746	+0.5	.727	.730	+0.4	.710	.713	+0.4	.701
700	.780	.758	.757	-0.1	.740	.745	+0.7	.718	.721	+0.4	.703	.706	+0.4	.686	.688	+0.3	.676

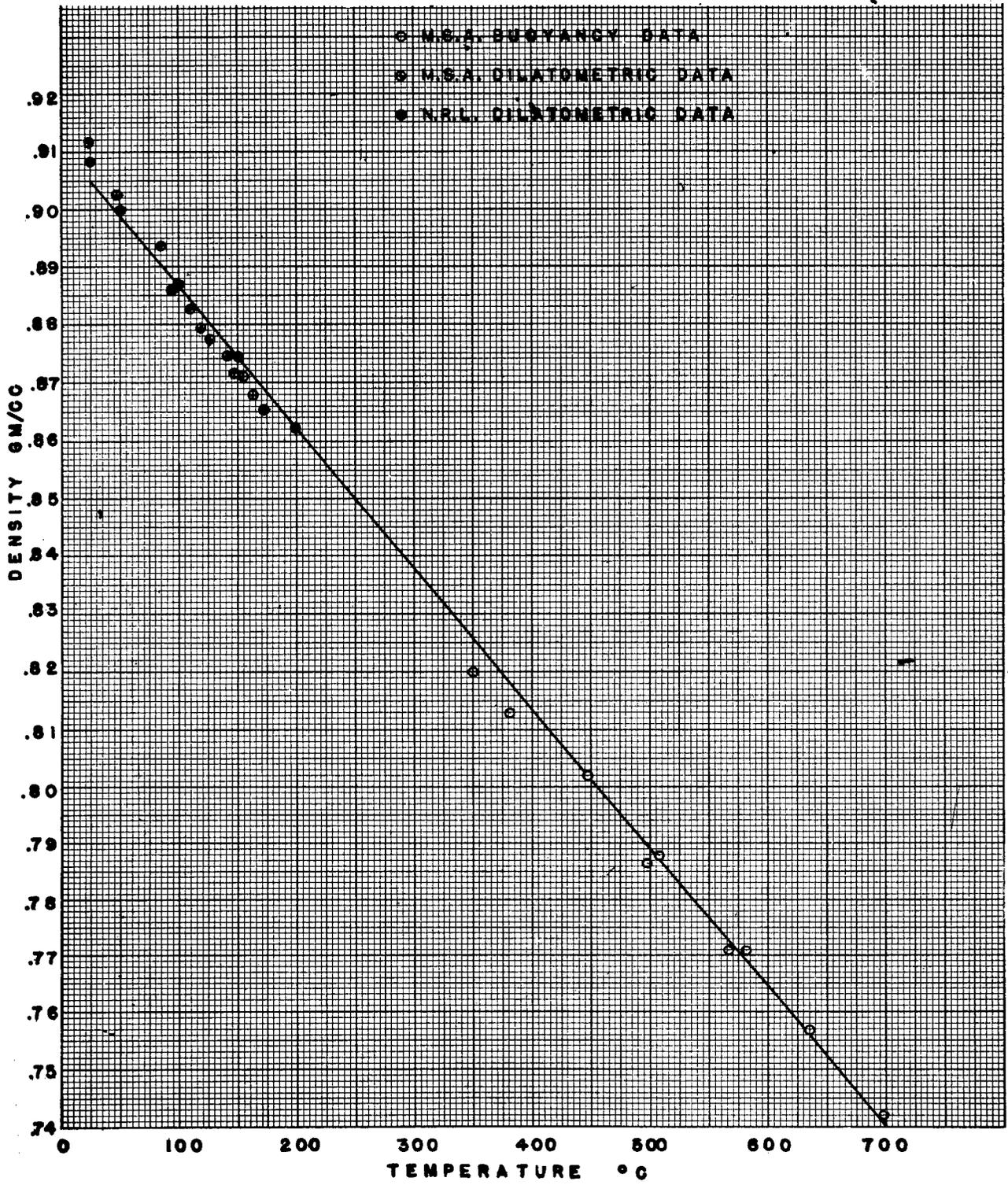


Fig. 17 Density Sodium
(0.2 Weight Percent Potassium)

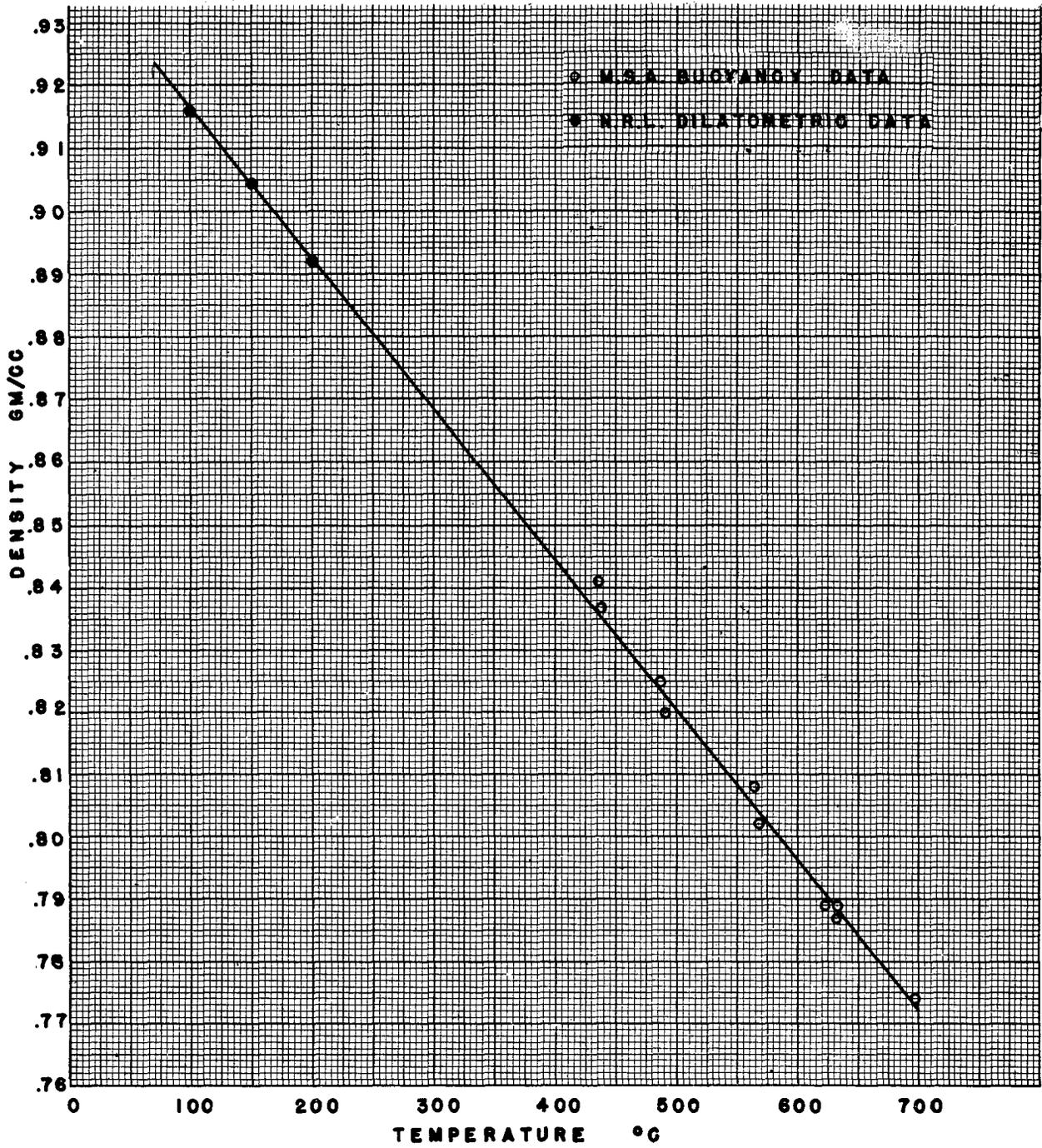


Fig. 18 Density Sodium - Potassium Alloy
(13.3 Weight Percent Potassium)

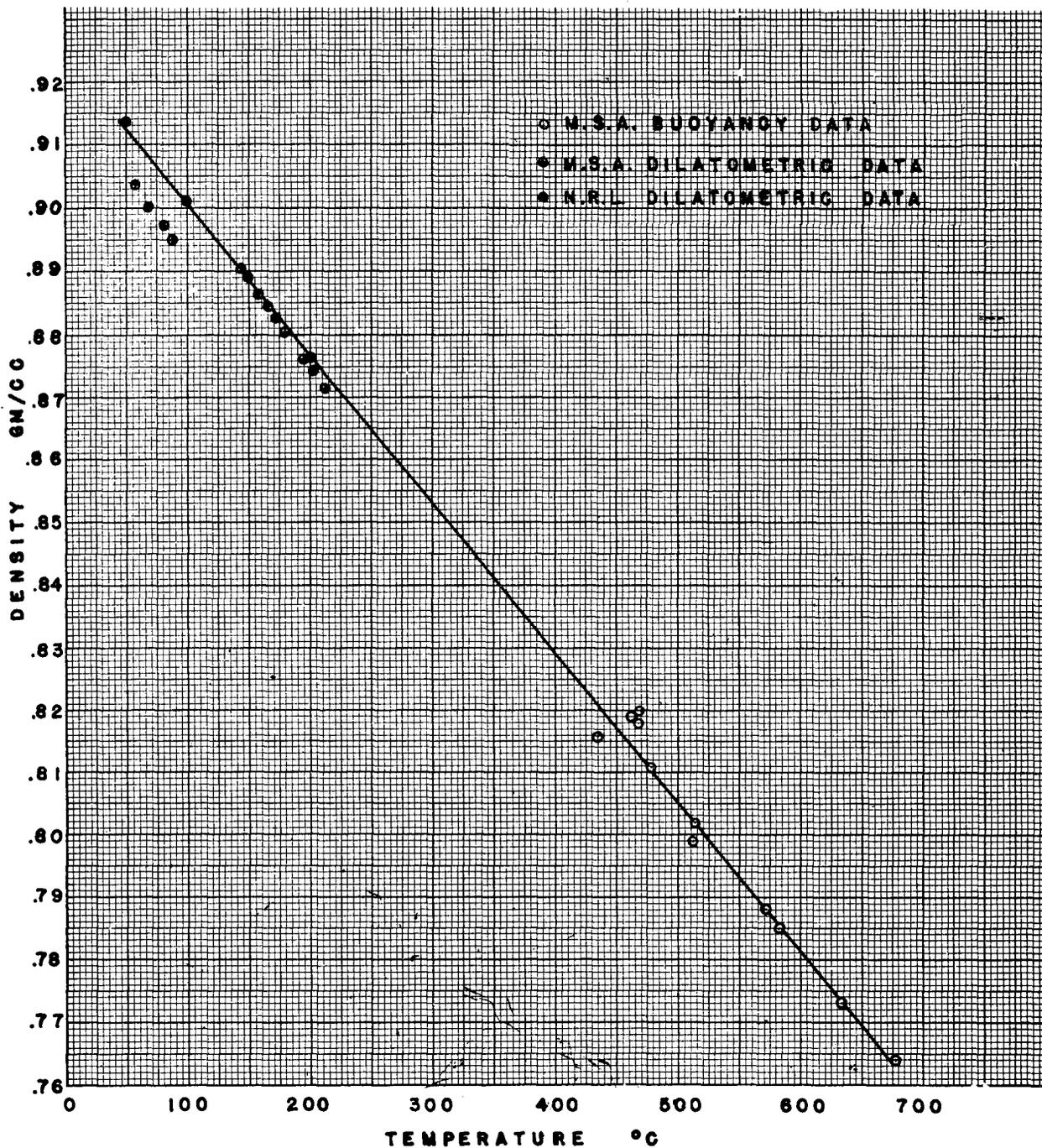


Fig. 19 Density Sodium - Potassium Alloy
(29.4 Weight Percent Potassium)

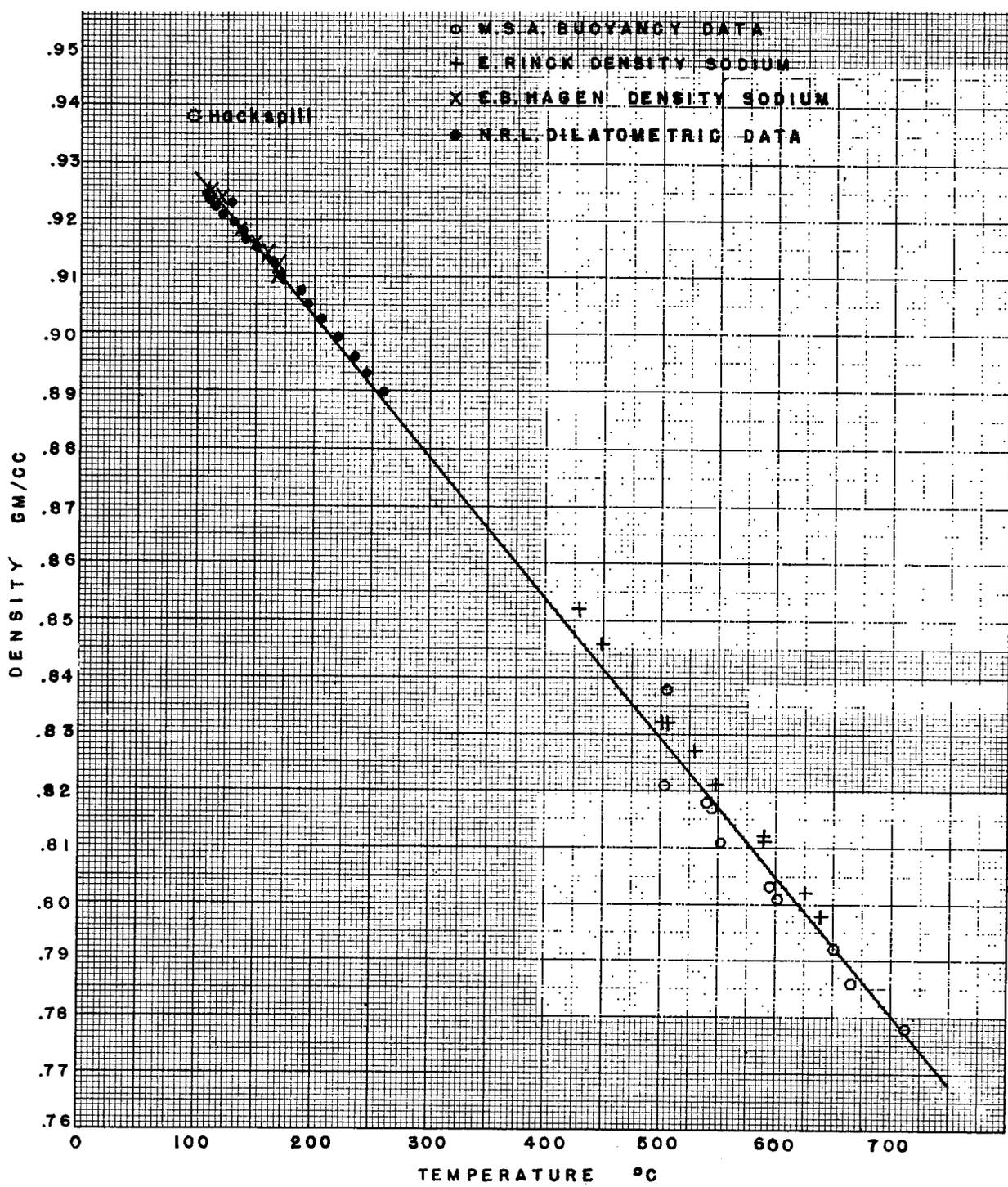


Fig. 20 Density Sodium - Potassium Alloy
(43.4 Weight Percent Potassium)

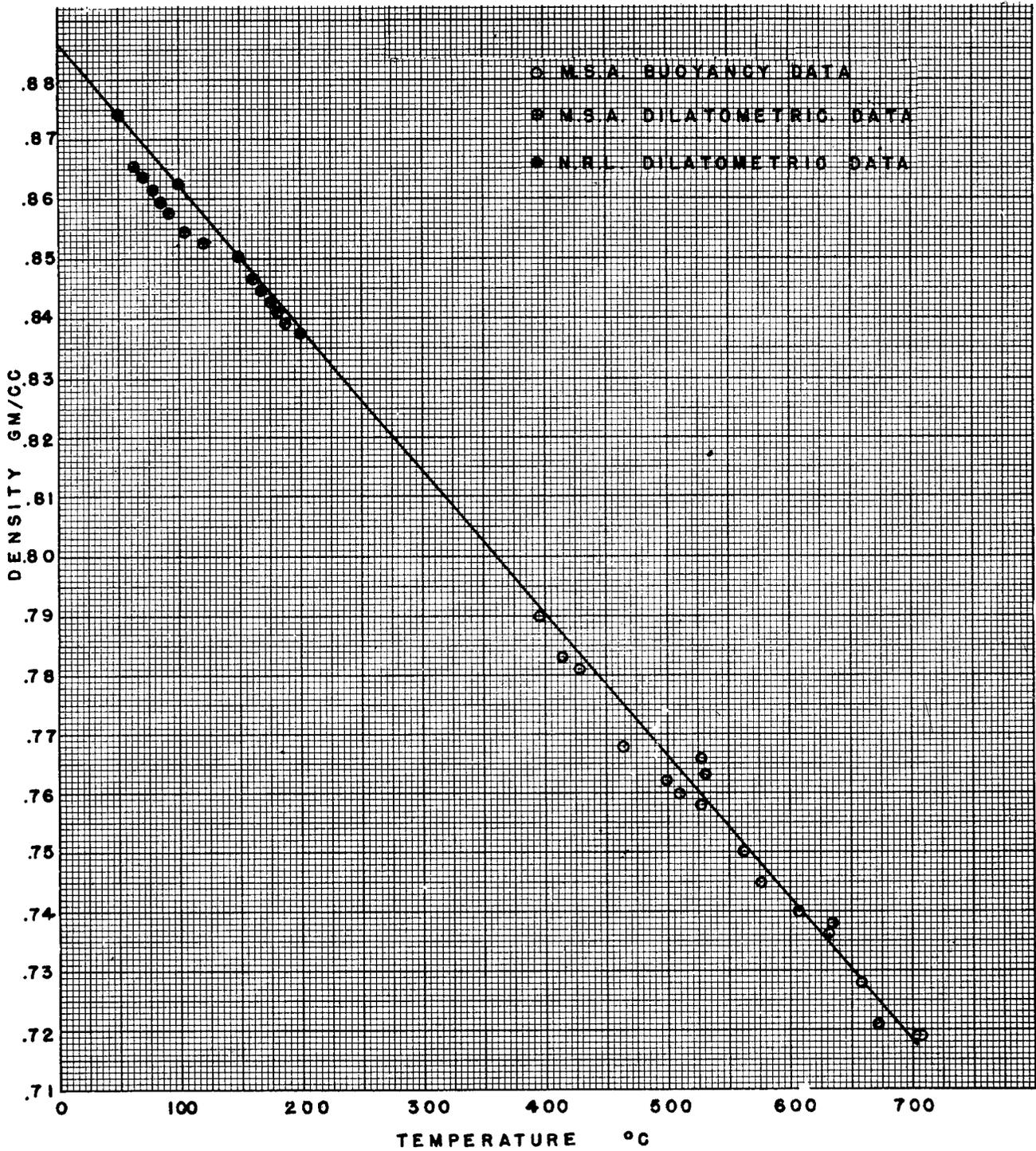


Fig. 21 Density Sodium - Potassium Alloy
(65.9 Weight Percent Sodium)

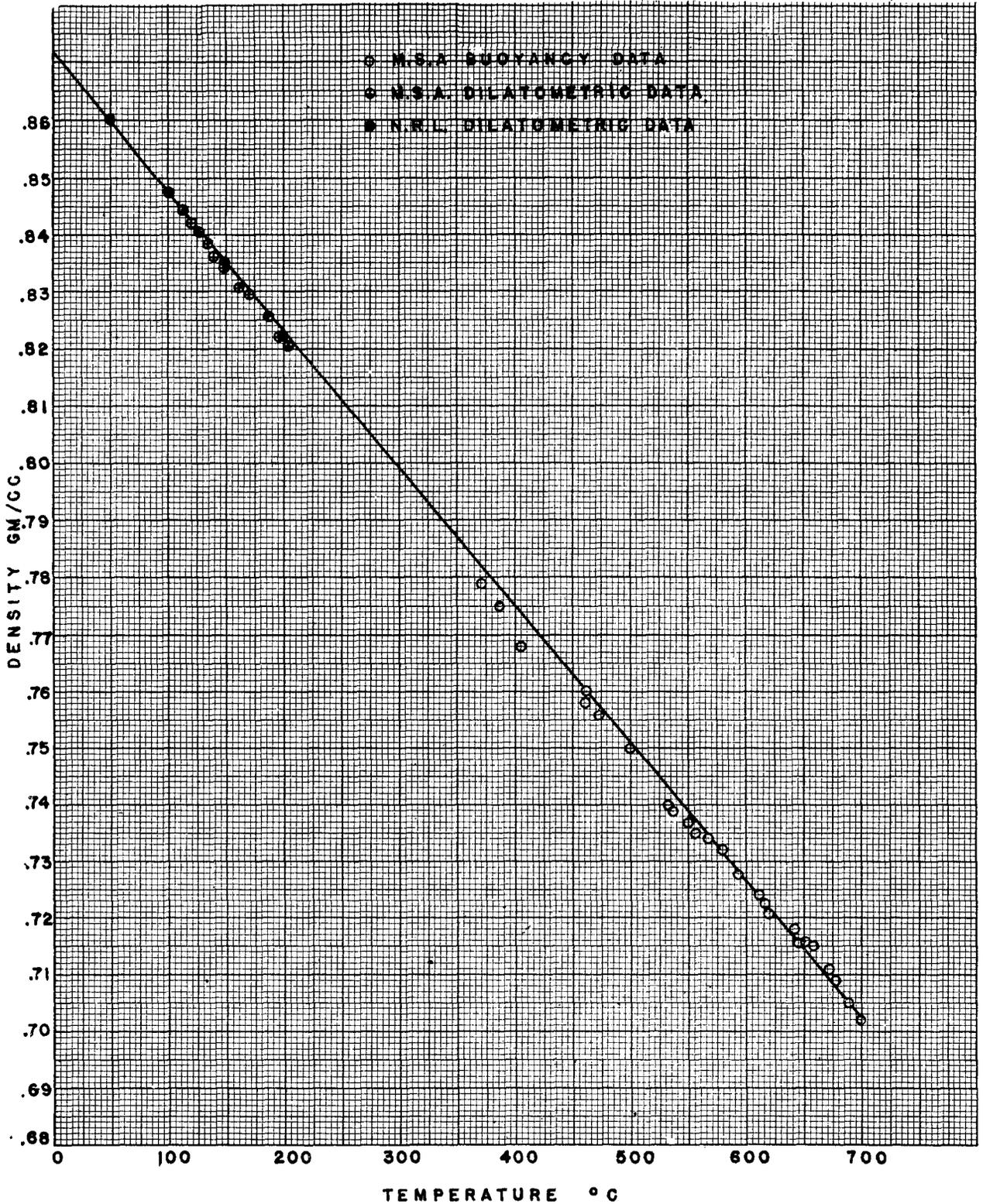


Fig. 22 Density Sodium - Potassium Alloy (78.6 Weight Percent Potassium)

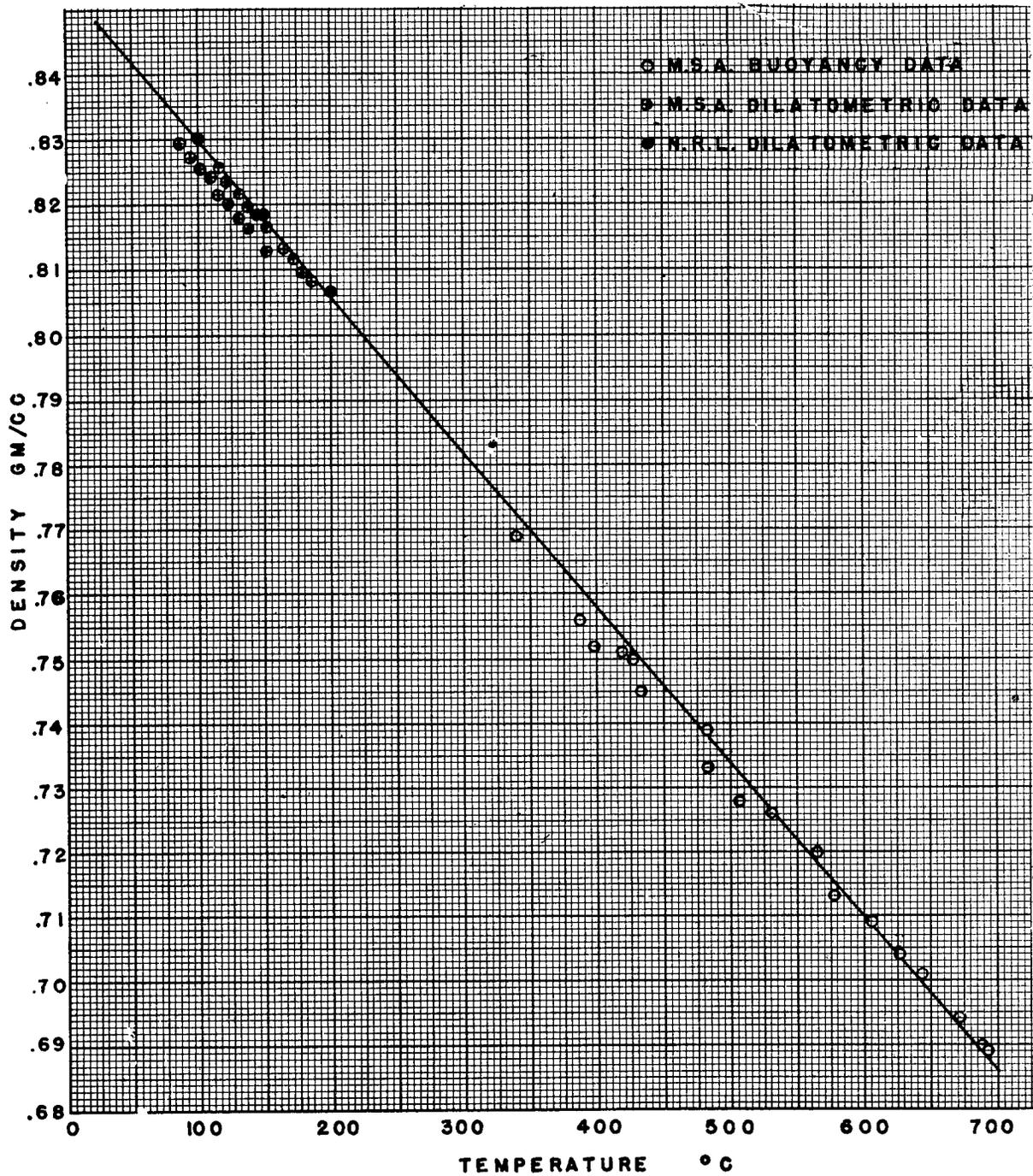


Fig. 23 Density Sodium - Potassium Alloy
(91.7 Weight Percent Potassium)

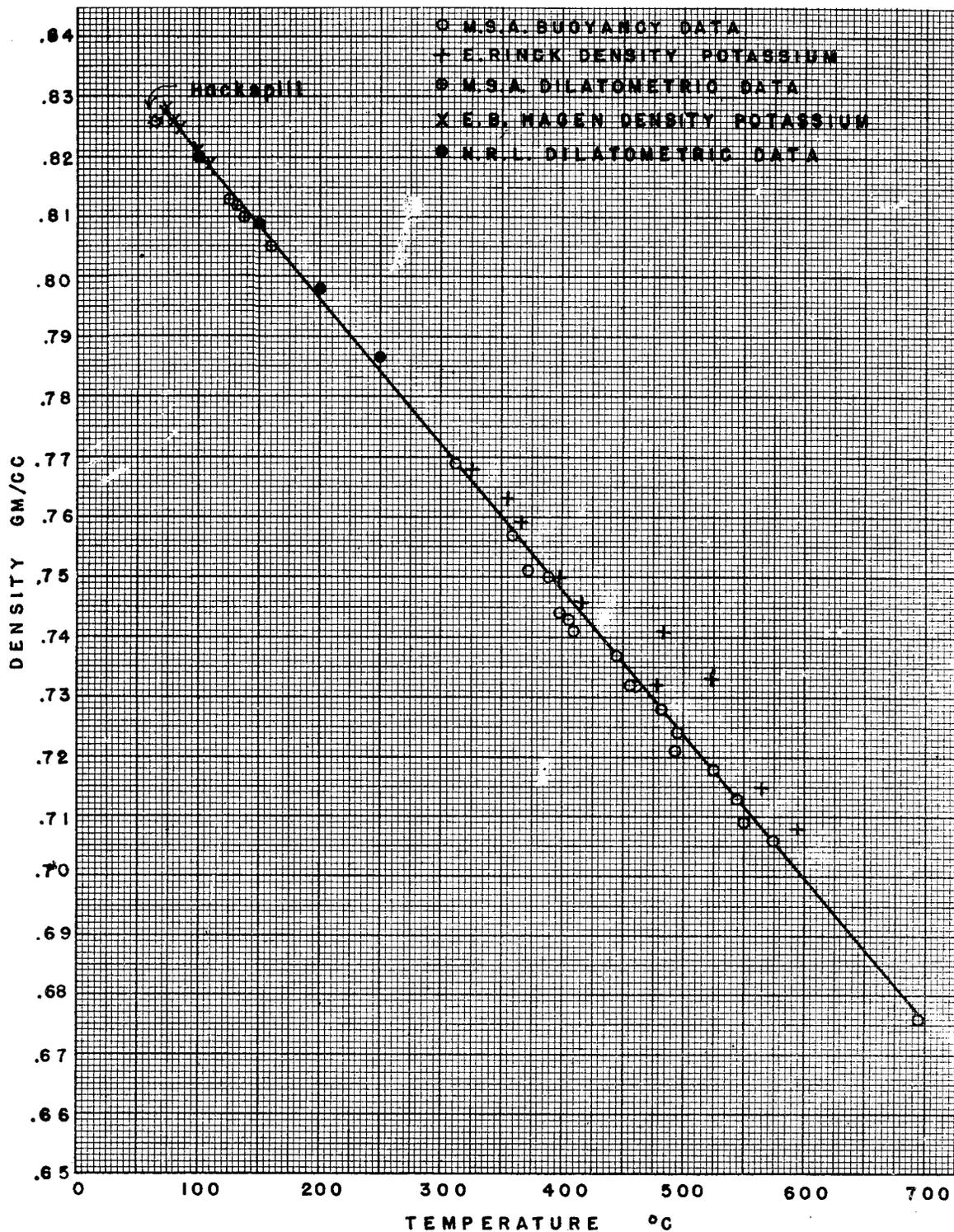


Fig. 24 Density Sodium - Potassium Alloy (98.8 Weight Percent Potassium)

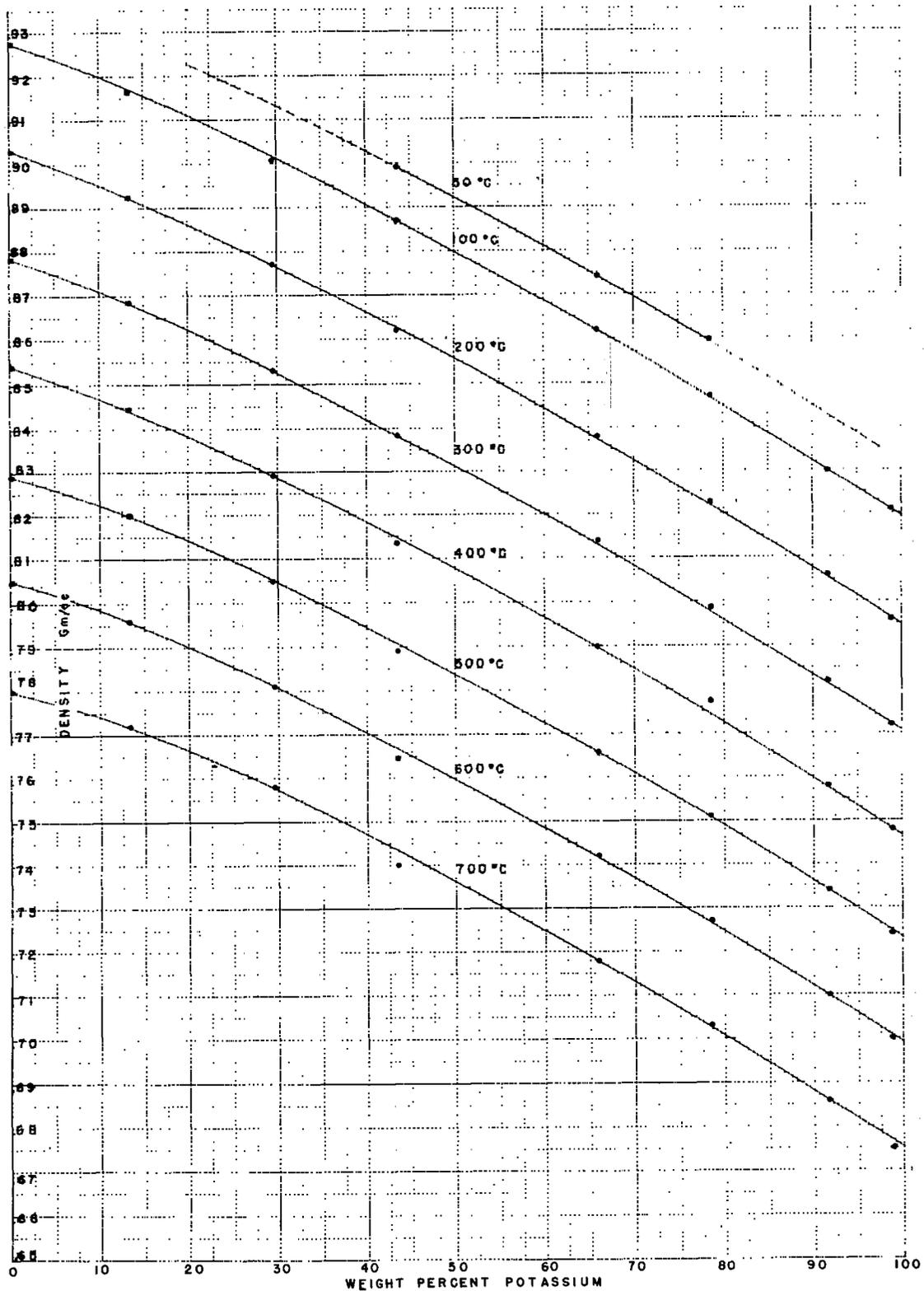


Fig. 25 Density Sodium - Potassium System

REACTIONS OF ALKALI METALS AND ALLOYS WITH WATER

UNCLASSIFIED

STATEMENT OF PROBLEM

The problem is to determine rates of reaction of sodium, potassium, and their alloys with water to fix the rate of hydrogen evolution and pressure increase in closed systems. This includes the study of the reaction rate under variable conditions of temperature, concentration, pH, and contact between the reactants.

METHODS OF MEASURING REACTION RATES

The reactions studied, being those of solids and liquids with water, are of the heterogeneous type on which little information is available in the literature. This absence of information is largely due to (1) non-availability of rapid means of quantitative measurement by which to follow the course of the reaction and (2) difficulty in controlling conditions and factors, such as active surface area, dispersion of gas bubbles, rupture of sample container, and mixing of reactants upon which the rate may depend.

Choice of a means of rate measurement is limited essentially by three inherent properties of the reaction and the reactants: (1) its extreme rapidity, completion being attained in some instances in a few milliseconds; (2) generation of gas during the reaction which fact eliminates the possibility of applying some of the optical and electronic methods; and (3) the low density of the solid reactant which obviates use of a continuous flow system. A consideration of methods showed that the generated gas had to be used as an index of the rate of the reaction; a commercially available composite of instruments were used to follow the pressure rise in a closed vessel. This apparatus and method are described in the following section.

DESCRIPTION OF APPARATUS AND METHOD

A schematic drawing of the apparatus is shown on Figure XXVIII. The pressure "pick-up" or transducer used in measuring pressure change is the Model 3700 Pressuregraph, manufactured by the Electro-Products Laboratories, Chicago, Illinois. It consists of a capacitance bridge, a 100 ks oscillator for a power source for the bridge, an amplifier for bridge-output, and a negative modulation suppressor and demodulator. To insure highest accuracy in actual operation, the demodulator and suppressor were never used. A brief description of the operation of this pressure "pick-up" is as follows: a source of pressure impinges on the steel diaphragm of a condenser in one arm of the bridge and changes its capacity, thereby, changing

the output of the bridge. This output is amplified and fed to the input terminals of a type 208B DuMont Oscilloscope on whose screen an increasing pressure is seen as a widening of the trace, which is photographically recorded by a General Radio strip camera. Figure XXIX reveals a portion of such a record. Figures XXVI and XXVII show the pressure bomb to which the pressure "pick-up" is attached. It consists of the bomb body which contains a chamber or well and the cap to which is attached the capsule breaking mechanism. The striker or plunger of this mechanism is actuated by a compressed spring and is released by rotating a cam through an external lever.

In making the determinations, all of which were at room temperature, the method of operating the equipment is as follows: The spring-driven plunger of the capsule-breaking mechanism is retracted and held by the lever-operated cam. A sample of the reactant sealed within a Pyrex capsule is placed beneath the plunger in a V-shaped groove and the bomb is assembled. Through an opening in the bomb cap a desired amount of distilled water is inserted, the bomb flushed-out with nitrogen to remove any residual air and the openings closed by means of the stopcocks provided. The camera focussed on the oscilloscope screen is started and when it is up to speed the reaction is started by releasing the plunger and allowing it to crush the capsule. Start of the reaction is indicated by a series of spark marks on the edge of the film which result from the depression of a switch at the time the plunger is released. In the on-position this switch permits the output of a General Radio "Strobotac" to energize the spark-coil of the camera at a predetermined frequency. The pressure rise within the bomb during a reaction could be evaluated from the trace width with the aid of a previous calibration of static pressure versus trace width.

APPARATUS, METHOD AND THEIR EVALUATION

In using an oscilloscope for recording purposes there was a small amount of 60 cycle pick-up from the laboratory wiring which showed on the scope screen and could not be avoided; contrary to being detrimental this pick-up was useful in serving as a check on the timing obtained on the film with the spark marks already described. When the capsule-breaking plunger was released, a foot-switch was tripped and this produced the first spark mark of a series of such marks on the film. This first mark was taken as the earliest possible moment of contact between the reactants. By a coordination of hand and foot movements, it was discovered that the spark mark coincided in a majority of runs with a ripple produced on the film by a disturbance set up in the bomb by the striking of the plunger. It is admitted that there is room for improvement in this method of indicating the breaking instant of the sample container, but as the value of data obtained from pressure measurements in a closed vessel is still somewhat questionable such an improvement was not considered worthwhile.

The response of the Model 3700 Pressuregraph to fast pressure transients appears to be good. The manufacturer has claimed response to pulses of less than 0.0001 second's duration, but this may be a little too optimistic as the carrier frequency is just 100 kc. Response of this pick-up as a function of position and diaphragm size is receiving further consideration. Runs made with CO₂ indicate no tendency for the "pick-up" to overshoot the equilibrium or final static pressure. In these studies, pulses of less than 0.0001 seconds duration were followed and it is felt that the curves obtained are a fair reproduction of the pressure change taking place in the bomb during the reactions. For faster reactions some means of damping or eliminating the ripples mentioned in the previous paragraph will have to be used as evaluation of pressure in the region where the ripple is present is impossible. Increasing the mass of the bomb may be beneficial since a greater energy input would be required to start it vibrating. The absence of a ripple when small samples were used agrees well with this idea.

Constant and uniform breakage of the sample capsule could not be assured and there is indication that this factor has limited substantially the rates as measured. The degree of subdivision of the glass capsule after each run is not proof that the glass was broken to that extent as the result of initial plunger crushing action. It was noted on two occasions that only a small break was initially produced, which, after an interval of time, was followed by a sudden reaction that shattered the glass. High speed movies taken of the reaction substantiated the progressive nature of this breakage and indicated the source of irregularities in the reaction rate curves. To achieve more uniform and instantaneous rupture of the glass, several variations in the capsule were tried; the wall-thickness was varied from one to one-half millimeters, criss-cross file notches were cut in the wall, and small bubbles, upon which the force of the striking-plunger would be concentrated, were blown in the wall. The last-mentioned appears to give the best performance; more high speed photography will give further information with respect to the breakage pattern and the time element involved.

The reaction bomb (Figure XXVI) had two openings of 0.063 inches in diameter interconnecting the bomb chamber with three threaded wells to which high pressure tubing was attached. The volume of the bomb proper was 89.9 ml at 25°C. The total volume of the attached tubes to the shut-off valves was 2.7 ml. When curves of reaction pressure versus time were obtained, a pressure peak, higher than the theoretical pressure obtainable from the reaction gas, was noticed. In accounting for this phenomenon, it was thought that the peak is a non-equilibrium pressure produced in part by the failure of the small openings to allow the gas in the 22.9 ml gas volume above the water to flow into the 2.7 ml volume as rapidly as it is produced. In one run, a shut-off

valve was accidentally left open and yet the pressure in the chamber was able to reach 65% of the value possible with the valve closed. This appeared to indicate that a non-equilibrium pressure exists between the two volumes when the pressure rise in the chamber is fast, but absence of a similar pressure peak in a run made by releasing gaseous CO₂ under pressure within the bomb is stronger evidence in favor of the peak being a function of the reaction. A further discussion is given under DATA in this section.

Of primary concern and importance in the measurements is the contact between water and the alkali metal. At no time could it be assured that the contact was continuous as the metal floats fairly rapidly to the surface if considerable turbulence is not present to prolong the immersion. Several instances occurred in which small bits of the metal were found clinging to the inner surface of the cap, probably tossed there by a sudden burst during the course of a reaction or carried there by a gas bubble escaping from the liquid surface. Complete filling of the chamber with water was found to offer possibility for continuous and complete immersion although such procedure limits the size of samples which can be taken.

Recording of solution temperature during the span of a reaction was not too successful, primarily, because of the non-availability of a fast and sensitive recorder. For future work a more suitable recorder will be used and somewhat more reliable data on the temperature change in the solution may be obtained. Because of its unreliability, no data on the temperature rise in solution has been presented in this report.

In most of the reactions, especially those in which large samples were used, highly damped ripples or waves (Figure XXIX) of less than one-sixtieth of a second's duration were recorded. To trace the cause of this ripple, capsules of compressed CO₂ gas were broken under water in the bomb and a record of the pressure rise was made. Exactly the same sort of ripples as in the reaction runs were obtained and this showed beyond doubt that the formation of ripples was due to the apparatus itself and not the reaction. Two possible sources for this disturbance exist; (1) the echo and re-echo of a pressure wave in the solution or in the water between the chamber-wall and diaphragm of the pressure "pick-up" and (2) vibration of the bomb or the "pick-up" diaphragm and fittings at a fundamental frequency, or a multiple thereof, as the result of rapid disturbance such as an explosion. Calculation of the time required by a sound wave to traverse the distance from the diaphragm to the wall and back again was less than the time for one cycle of the ripple by a factor of 100. On the other hand, the natural frequency of the bomb was in closer agreement and of the same order of magnitude. This analysis of the natural frequency was accomplished

by picking up the sound with a microphone when the bomb was put into vibration with a mallet blow, amplifying it and feeding the output of the amplifier to an oscilloscope or by an accelerometer attached to the bomb whose output was fed to an oscilloscope and comparing the resultant trace with that produced by a signal generator. Since the natural frequency is of the same order, it is believed that the ripple formation is associated with it; however, the cause of such phenomena is not too important just so long as it could be shown to be independent of the reaction rate and to be of considerably shorter duration than that of the reaction.

EXPERIMENTAL RESULTS

Data - It was not considered worthwhile to include the entire data in tabulated form. Instead, the following table is given to serve as an illustration of the type of data from which the curves in this report were obtained. In each reaction, 67 ml of distilled water was used unless otherwise specified on the curves.

TABLE XXX

Composition - 36.1 mol % K
Sample wt (gms) - 0.7190

Room Temperature - 22°C
Vol. of H₂O at room temp. - 67 ml

Time secs	Pressure PSI	Time secs	Pressure PSI	Time secs	Pressure PSI
0	0	2/3	206	1 5/6	200
1/15	60	11/15	222	2	206
2/15	88	4/5	240	2 1/3	196
1/5	106	13/15	240	2 2/3	196
4/15	128	14/15	230	3	193
1/3	160	1	227	3 1/3	191
2/5	181	1 1/6	220	3 2/3	191
7/15	188	1 1/3	214	4	191
8/15	193	1 1/2	212	5	191
3/5	196	1 2/3	203		

Discussion of Data - As may be seen from the curves of this report (Figures XXXI to XXXVI), the agreement between various reaction runs is relatively poor. Despite this lack of reproducibility, the data is of value in obtaining some idea as to the magnitude of the rates for the different alloys of sodium and potassium. By referring to a plot of the average reaction completion time versus the composition of the solid reactant (Figure XXX), a definite trend is noted even though an alloy having a maximum rate cannot be definitely identified. An alloy near the

eutectic, very possibly the eutectic, appears to have the maximum reaction rate. The time to complete a reaction was assumed to be the time at which the ultimate pressure peaks were obtained. Initial sample size was disregarded and the times to attain peak pressures were averaged to obtain values for Figure XXX. It should be noted at this point that sample size or the concentration of the alkali metal hydroxides in solution appeared to have no effect on the reaction rates; however, it may be that the data are too inaccurate to show it if such an effect is present.

Many of the pressure versus time curves are marked by sudden pressure rises which destroy the smoothness of the curves. Not until the capsule-breaking mechanism of the reaction bomb was placed in a glass walled container and the reaction photographed at a high film speed of one hundred feet in three seconds was their cause understood. The film revealed a number of near explosions taking place in the vicinity of the sample as well as some distance away from it. It is believed that such explosions were produced by the metal, which had become highly heated, combining extremely rapidly with water. It is unlikely that sufficient oxygen is present in the water to permit and sustain explosive combination with evolved hydrogen. As the explosions occurred, the glass envelope of the sample was fragmented a little more each time; this behavior was strong proof that an incompletely crushed sample container is of considerable hindrance to the reaction.

A feature, previously mentioned in this report, is the pressure peak present in each pressure versus time curve. This peak is approximately 25% higher than the static final pressure. As the theoretical pressures calculated for the reaction agreed with the observed final pressures, there is not much likelihood that such a peak pressure results from the absorption of hydrogen by the alkaline solution. As has been already stated, the peak is not due to the expansion of the gas at a finite rate through a small opening nor to the "pick-up" overshooting the true pressure. The remaining possibility is that it is produced by the energy of the reaction producing steam by local heating. Sometimes as much as ten degrees centigrade rise has been noted depending on the size of the sample taken, and the reaction soon reaches an equilibrium temperature. An intriguing postulate has been offered in an attempt to explain this peak phenomenon, it is that heat from the reaction is distributed unequally on the weight basis between the gas and the solution with a relatively larger part of the energy being in the gas until a sufficient time has elapsed to achieve an equilibrium distribution. Such a postulate is, however, mere conjecture in the absence of substantiating calorimetric data.

Because of the poor agreement of the data from run to run, no attempt has been made to convert bomb pressures to a basis

of fraction of the sample reacted or moles reacted at any instant. Had such a conversion been made a plot of the fraction reacted versus time would have yielded curves of essentially the same shape as presented in this report.

Calculations - A question has been raised as to what might happen if Na-K alloy and water in adjacent piping were permitted inter-access through a leak or rupture of the containers. A calculation of the time required to move a column of water a certain distance before the working pressure of the pipe is exceeded will show whether or not the time interval is of the same order of magnitude as the observed reaction rates for the alloy. For consideration, a 2 1/2" extra strong pipe (2.32" I.D.), 100 ft in length and a top working pressure of 1900 psi has been taken. A 10 gram sample of alloy (45 mol % K) is assumed to have been mixed with water to produce 3545 ml of gas (28 ml at 1900 psi).

$$\text{From } F = Ma = \frac{Mv}{t} = \frac{Ml(g)}{t^2} = M \frac{V}{St^2}$$

$$\text{Since } M = W/g; W = Sl(p)d \text{ and } F = (PS)1144$$

$$.1144 PS = F = \frac{Sl(p)d V}{g St^2}$$

$$\text{or } t = \sqrt{\frac{l(p)d V}{1144 PSg}}$$

- S = Cross sectional area of pipe in sq.ft. = 0.0294
- l(g) = Length of pipe which would contain 28 ml of gas
(1 x 10⁻⁴ ft³)
- d = Density of water in lbs/ft³ = 62.5
- l(p) = Length of pipe in feet = 100
- V = Volume of gas in ft³ = 1 x 10⁻⁴
- g = Acceleration of gravity in ft/sec² = 32.2
- P = Pressure in lbs/inch² = 1900
- t = Time in seconds for water column to move a distance equal to l(g)
- v = Velocity flow in ft/sec
- W = Weight
- M = Mass
- F = Force
- a = Acceleration

Substituting the values for the letters

$$t = \sqrt{\frac{100 \times 62.5 \times 10^{-4}}{1144 \times 1900 \times 0.0294 \times 32.2}} = 1.55 \times 10^{-3} \text{ secs.}$$

Reference to the curves in this report will show that a sample of 45 mol % alloy will have completely reacted in approximately one-half a second. Very possibly in the instance of alloy squirting into water through a leak in a pipe, the reaction time may be far less. To prevent dangerous pressure accumulation, the time which has been calculated should be considerably less than the reaction time of the alloy with water. In the case considered, the times are not very far off in their orders of magnitude.

ANALYSIS OF RESULTS

It is believed that the measured reaction times for potassium, sodium and their alloys are somewhat larger than those which would be obtained if the contact between the metal and water were unhampered by the walls of the glass capsule. The rates for alloys near the eutectic are the highest, 56 mol % potassium, samples up to one gram in weight, reacting completely in one-third to one-half seconds. What effect larger samples have on the rate is not known; the normal thing to expect would be a slowing.

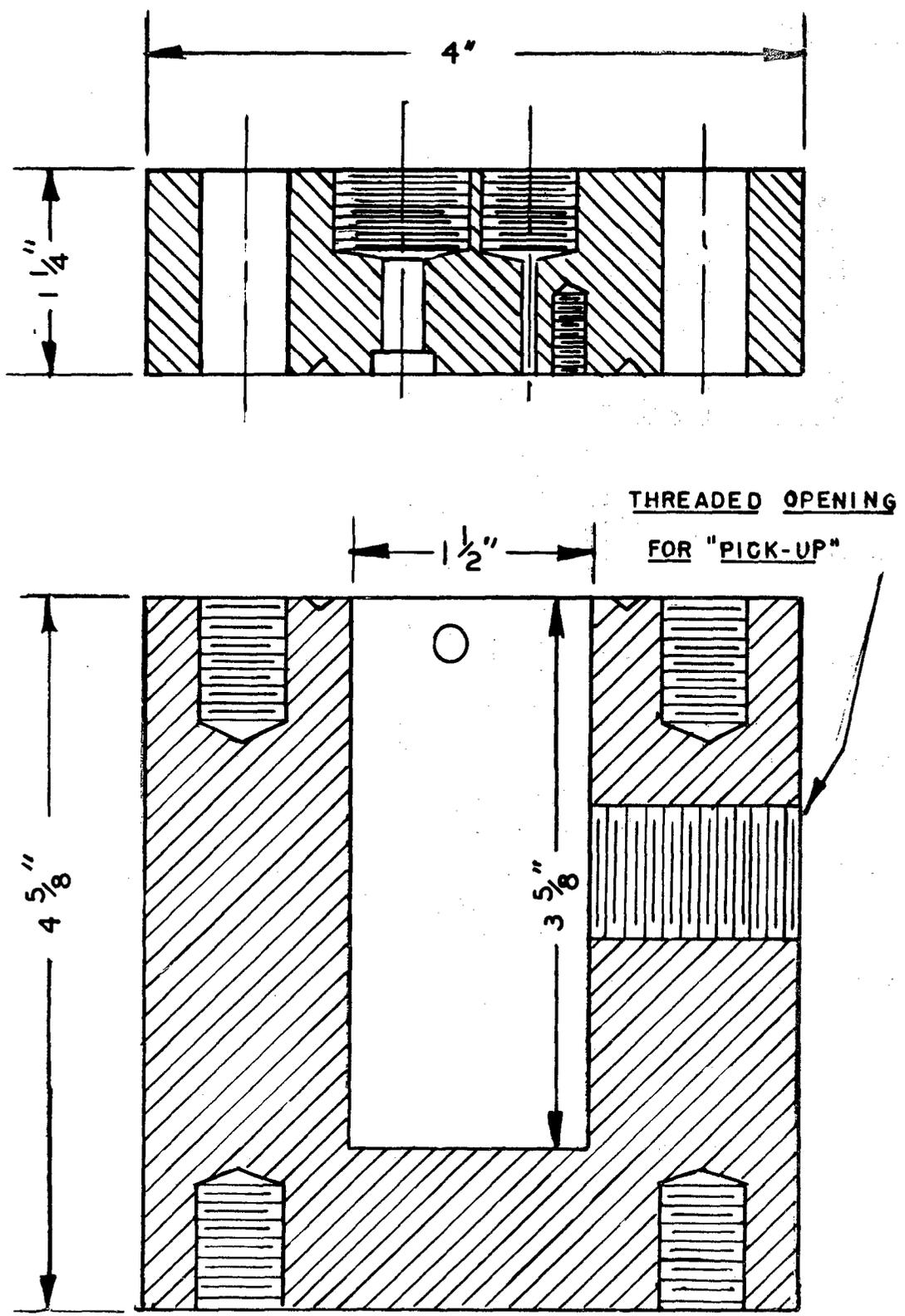


Fig. 26 Stainless Steel Bomb

BOMB TOP

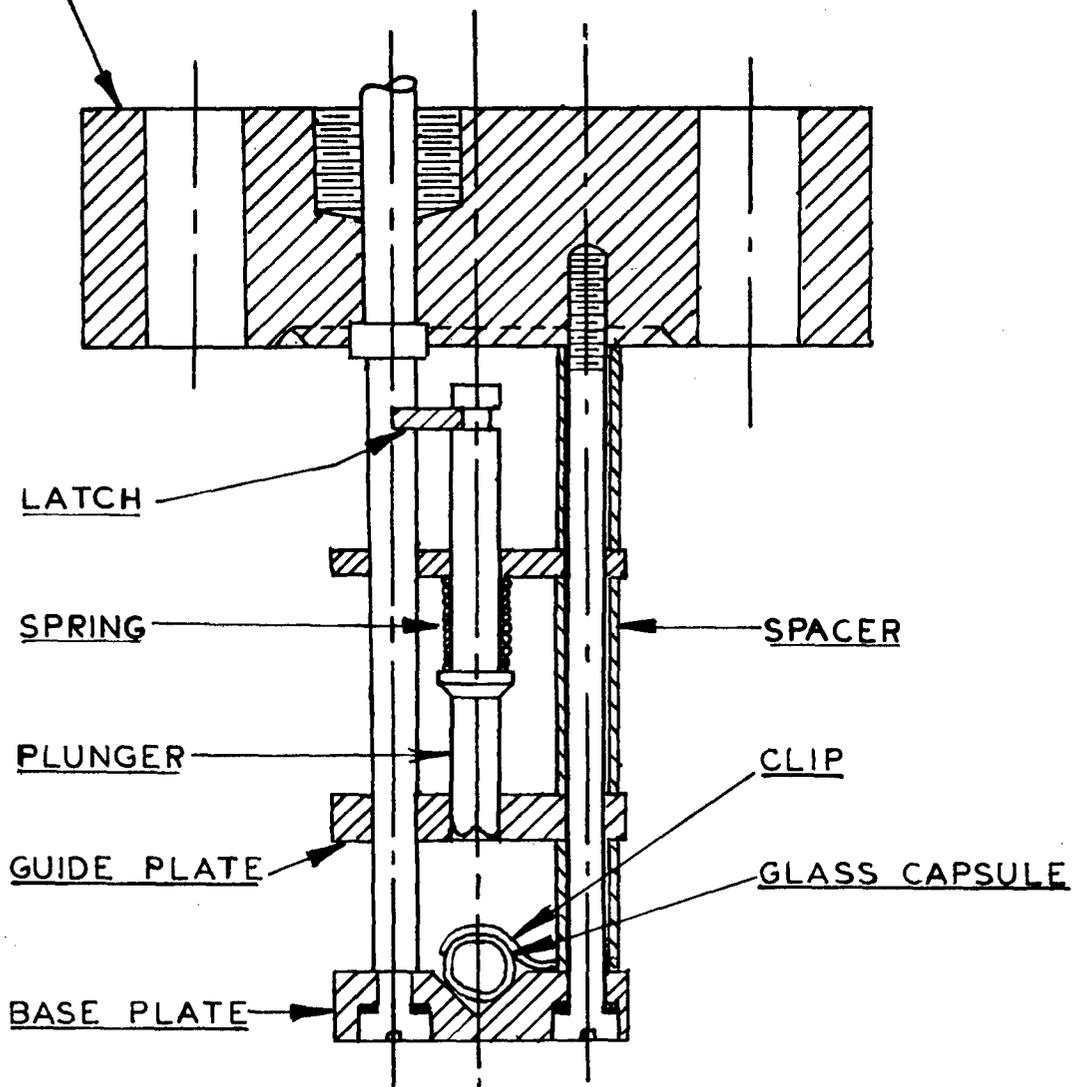


Fig. 27. Stainless Steel Capsule Crusher

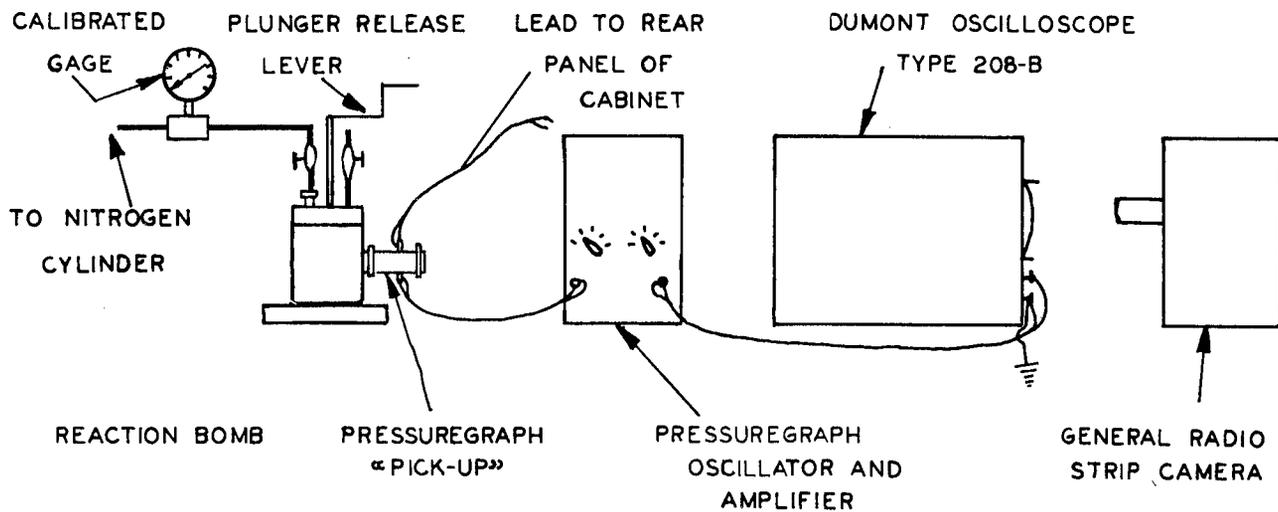


Fig. 28. Schematic Diagram of Apparatus

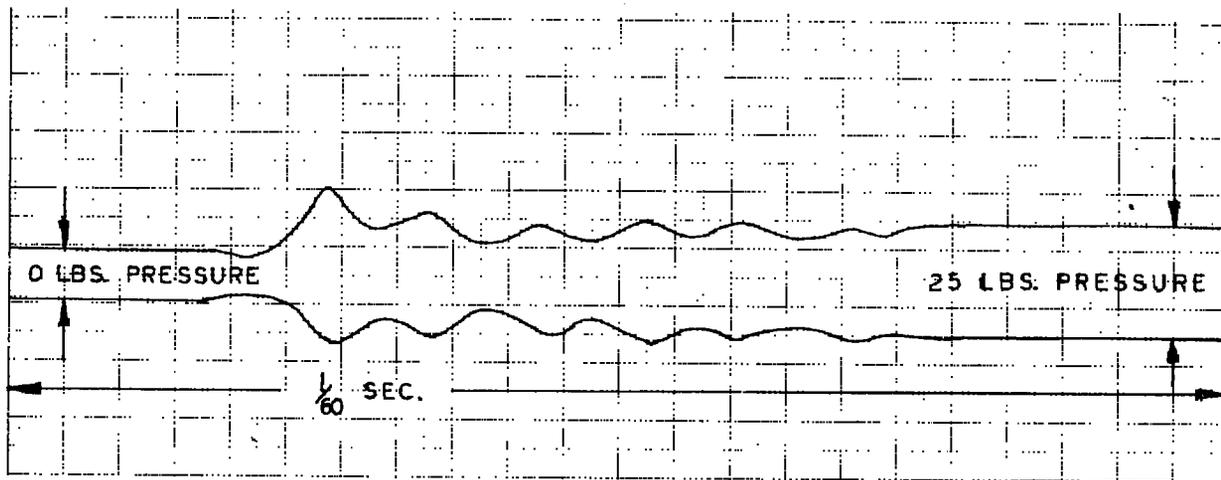


Figure 29

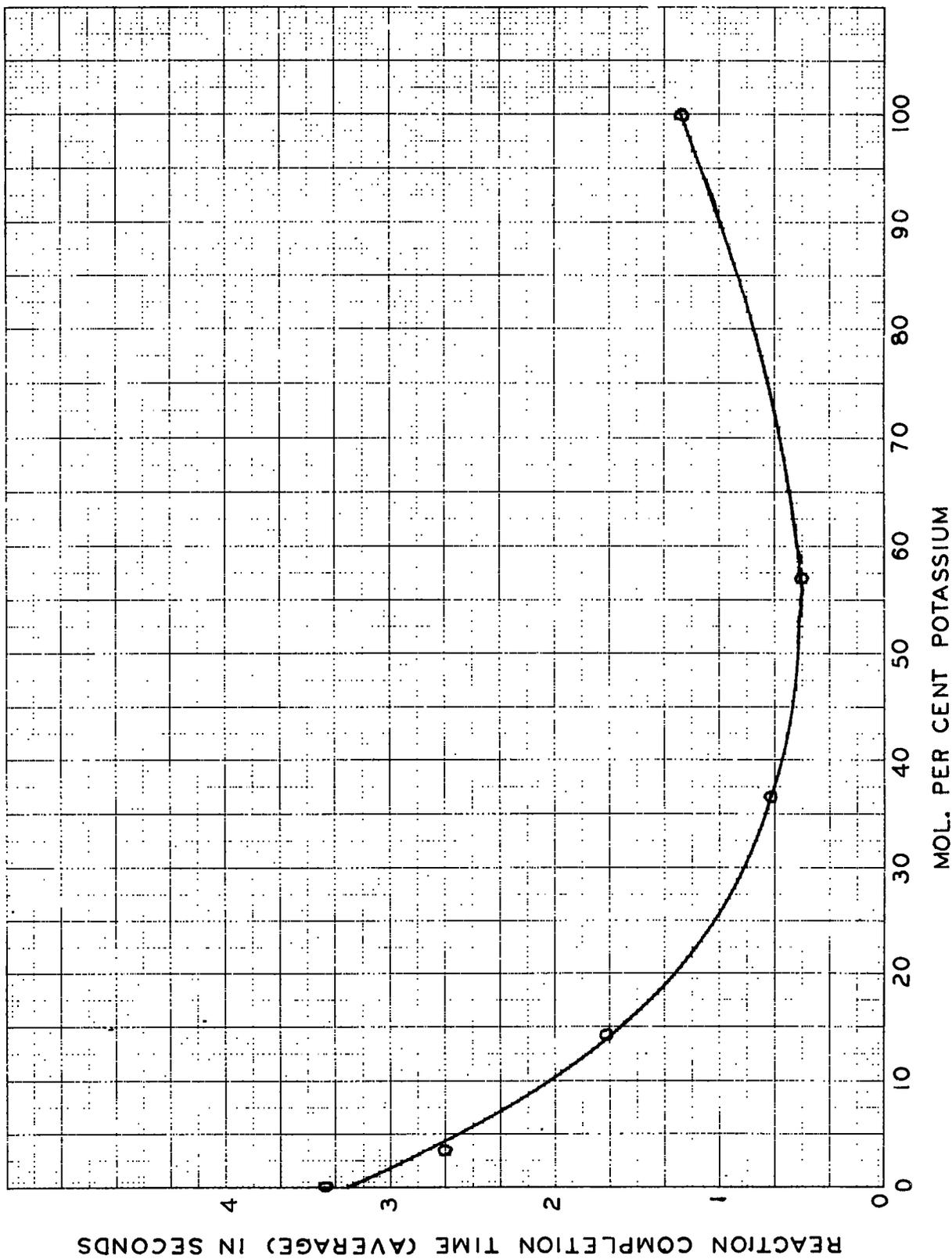


Fig. 30 Effect of Composition on Reaction Rate

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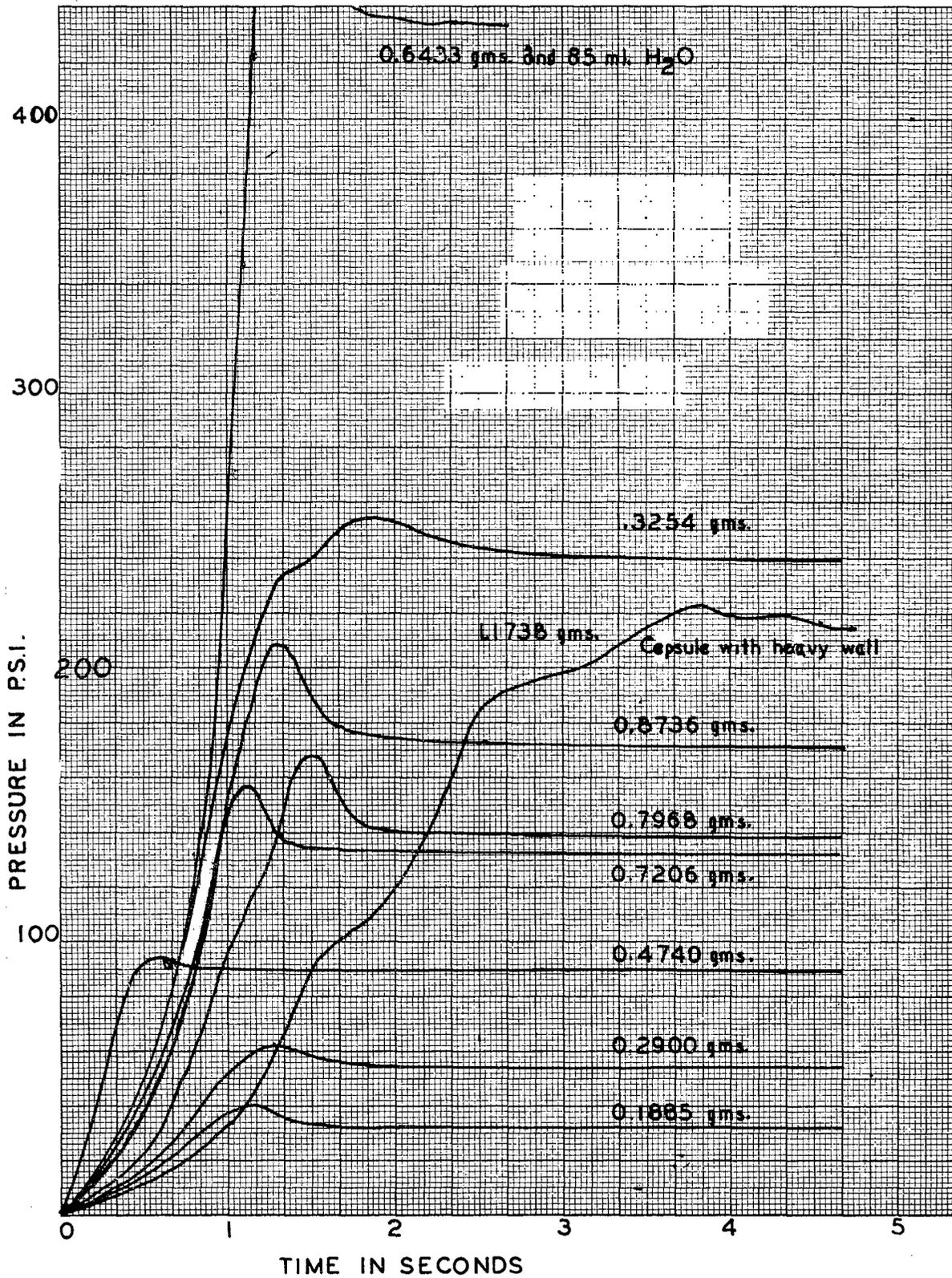


Figure 31

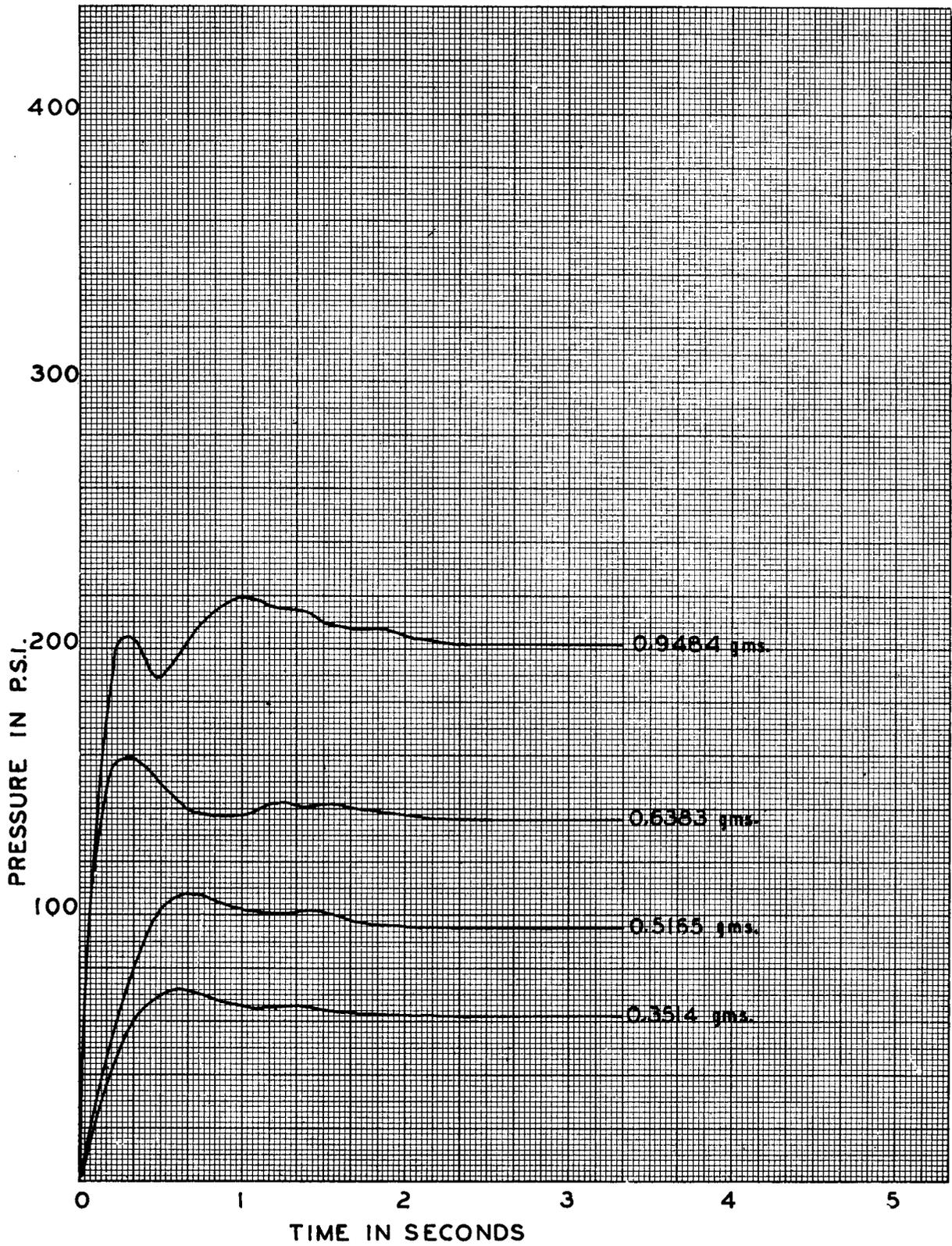


Figure 32

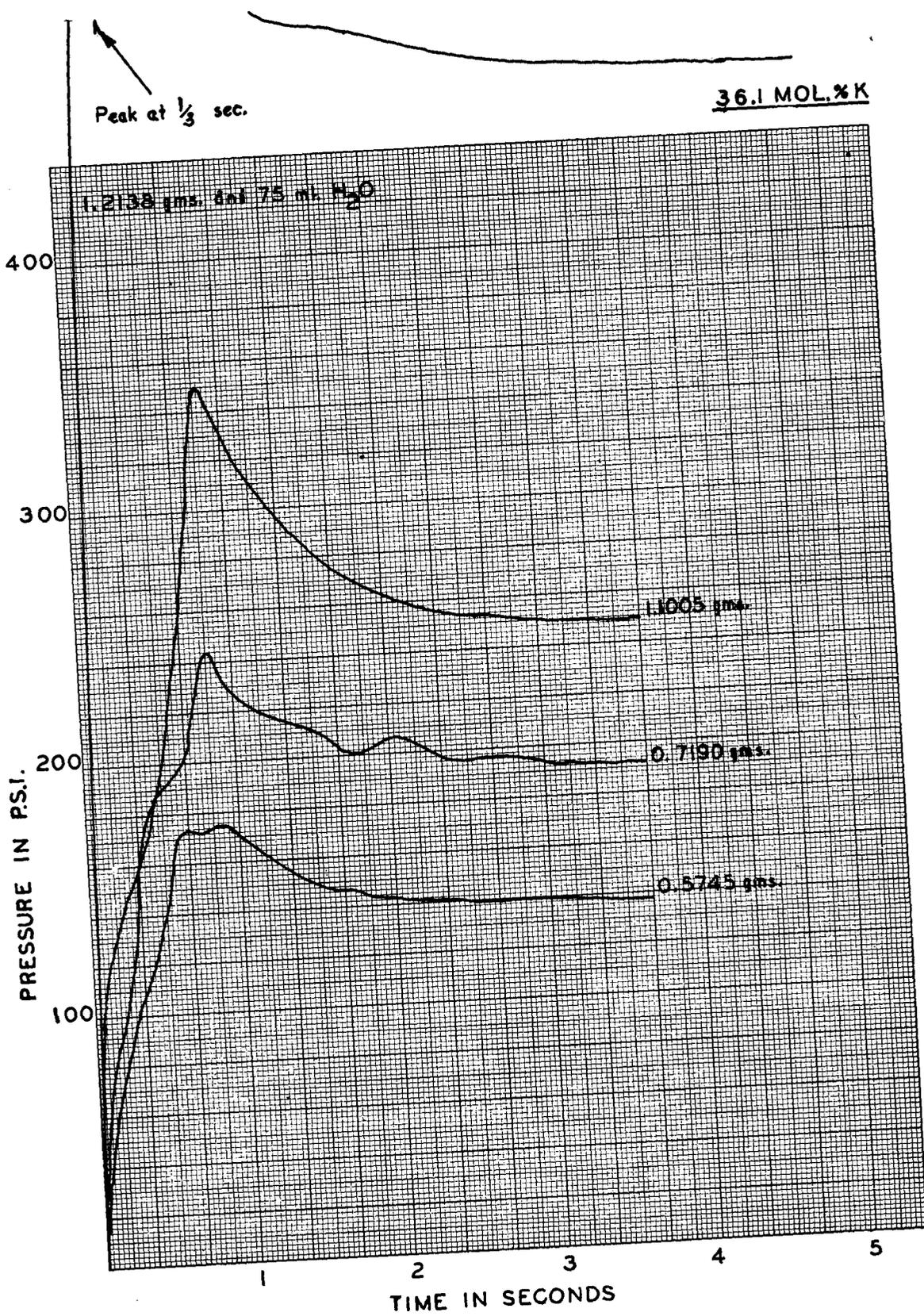


Figure 33

100
 200
 300
 400
 500
 600
 700
 800
 900
 1000

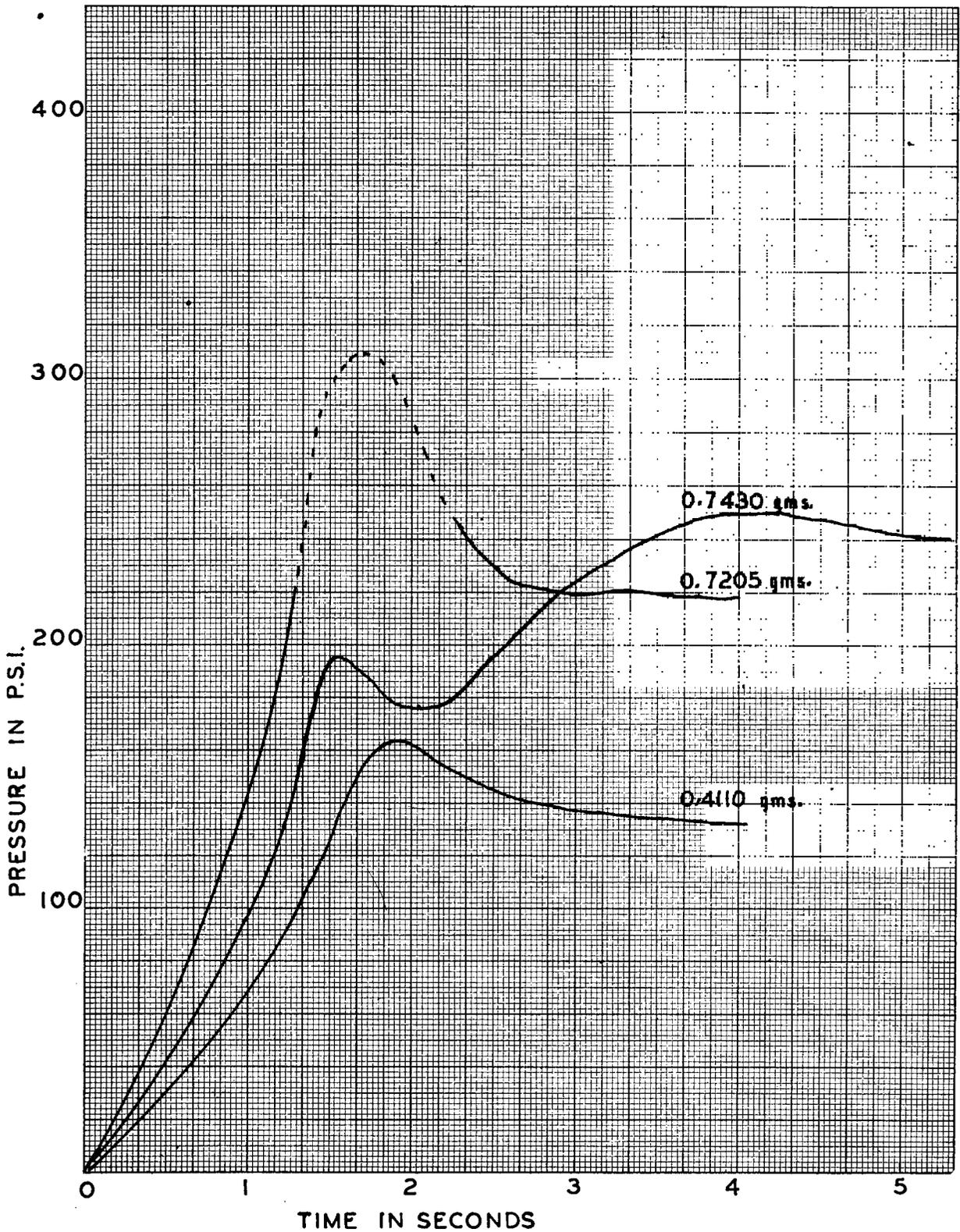


Figure 34

2.9 MOL. % K

UNCLASSIFIED

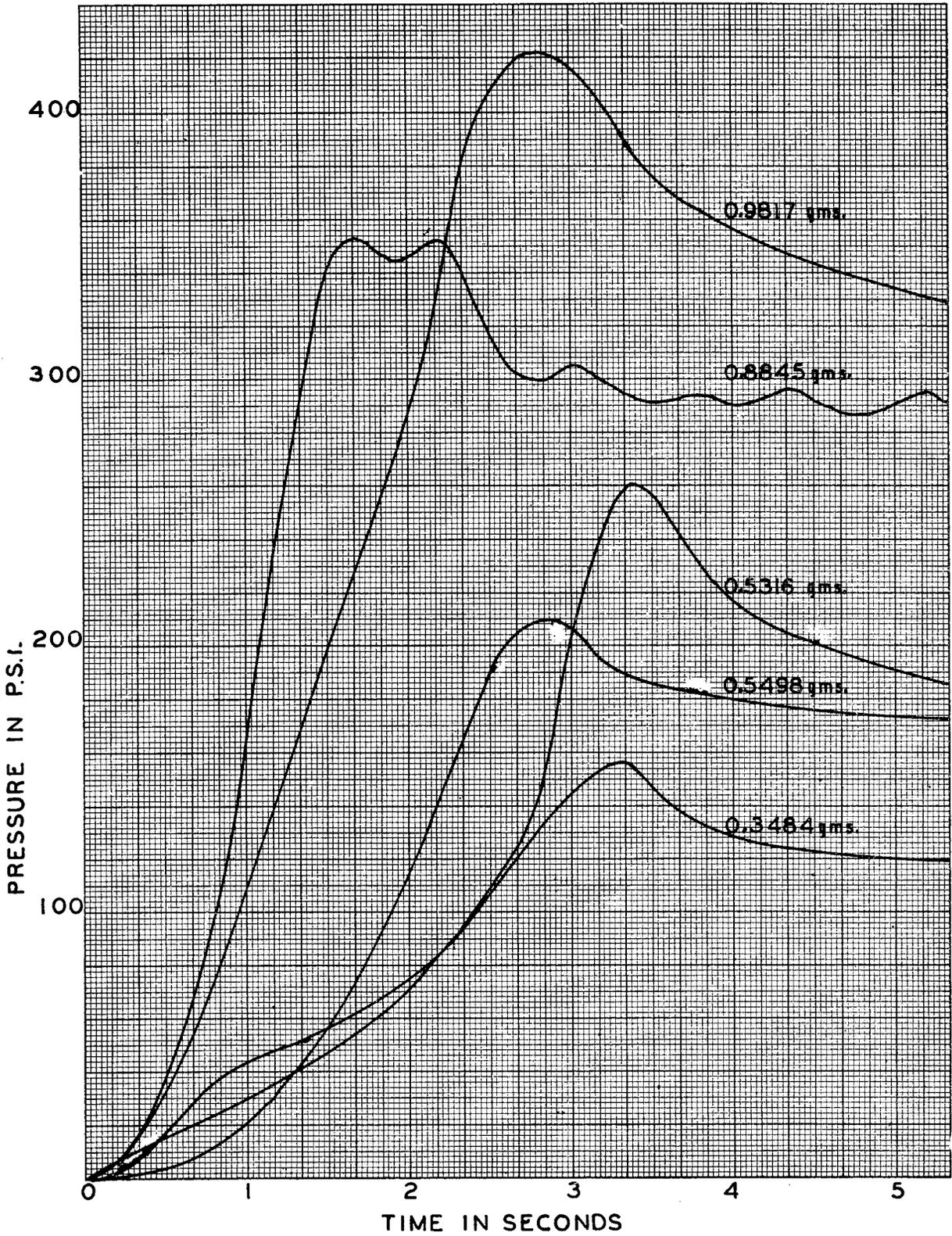


Figure 35

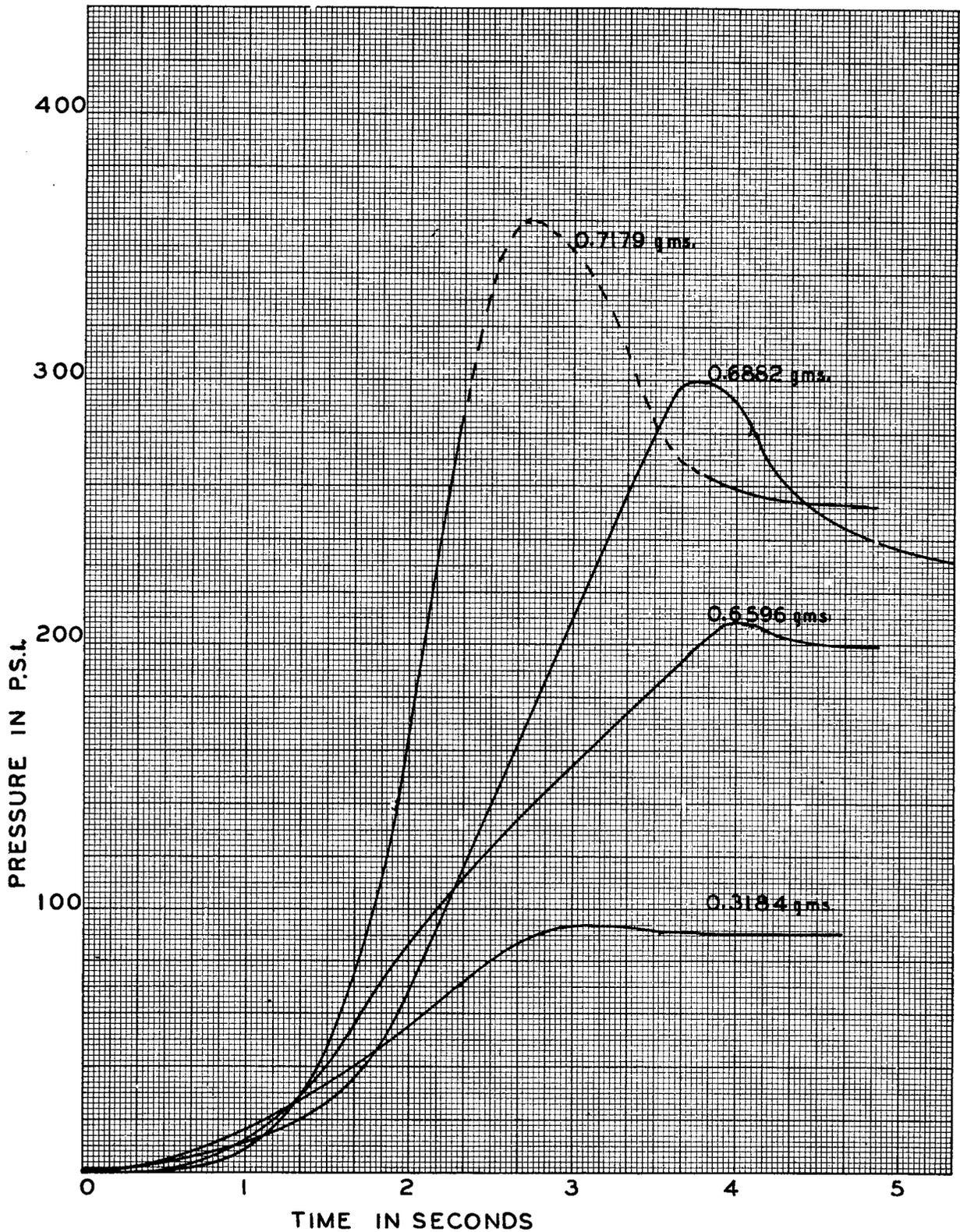


Figure 36

SURFACE TENSION

UNCLASSIFIED

GENERAL REMARKS

The surface tension study has been hampered in that the initial apparatus was designed to fit untrue conditions, partially imposed by high surface tension values which were gleaned from the literature. The capillary rise method, because of its simplicity and usual high accuracy, would have been desirable, but was dropped originally in favor of a modified method. (8) This method was similar to that devised by Ferguson and Dowson (8), where the liquid is forced up or down to the liquid level in a calibrated capillary immersed vertically in the liquid, and the pressure required to maintain the liquid at any position measured on a suitable differential manometer. The apparatus and procedure was explained in detail in NRL Report C-3152. With the apparatus as finally used, an expansion bulb replaced the mercury leveling bulb to provide a closed system.

The modified apparatus was found to give excellent results for water. Nevertheless, with the alloys several attempts to obtain results were unsuccessful. With each attempt, after a few rough measurements, the metal was found to stick in the small capillary. A check of cleaning procedures for the glass, and of techniques in general, failed to remedy this difficulty and the method was finally abandoned. For each experiment, the metal was distilled from the nickel still through a sintered glass filter into the surface tension apparatus. Even though no reportable results were obtained, the rough values served to indicate that the literature values were too high and also that wetting of glass capillaries could be expected. With this knowledge, an appropriate capillary rise apparatus, in its usual form, was assembled. This apparatus was used to obtain the results reported in this section.

If the angle of contact between the alloy and the glass is assumed to be zero, then in a narrow tube the radius of curvature of the meniscus is the same as the radius of the tube and the simple capillary rise formula may be used for the calculation of surface tension values:

$$\gamma = 1/2 \text{ hgdr}$$

where γ = Surface Tension
h = Column of Liquid
d = Density
r = Radius tube

(8) Ferguson, Dowson, Trans. Far.Soc.Vol.17,Part I, Dec. 1921

DESCRIPTION OF APPARATUS AND OPERATIONS

Apparatus - The pyrex apparatus is shown as Figure XXXVIII. It is of the usual capillary type, designed in this case for use as a closed system. Three capillaries varying in diameter from about 0.114 cms. to 0.054 cms., were positioned around the large bulb, such that the menisci of all three and that of the large bulb could be read conveniently with a cathetometer. Suitable lengths of capillary were obtained by checking both ends of numerous sections with a traveling microscope. Finding likely specimens, the diameter variation between the ends was checked by running a globule of mercury along the section. The large bulb was about 6 cms. inside diameter which should eliminate the effect of surface tension at the reference surface.

The bath with control assembly was identical with that used for the viscosity measurements (NRL Report No. C-3201).

Operation - Standard procedures were followed for cleaning and filling the apparatus, the glass being heated under vacuum immediately before introduction of the metal. The metal in each case was distilled from the nickel still through a sintered glass filter into the large bulb, and the apparatus sealed off. For each surface tension measurement, the metal was made to rise and fall in each capillary to its equilibrium height. When these two values checked, this height was used to calculate the surface tension at that temperature; thereby eliminating the factor of sticking. A thumping of the capillaries was necessary to make the columns reach apparent equilibrium.

EXPERIMENTAL RESULTS

Surface tension measurements were made on the pure metals and several alloys from room temperature or the melting point up to about 200°C. The variation of surface tension over the temperature range was well within the high experimental error. Therefore, only an average value over the temperature range for each metal is reported. The results of the measurements are presented in Table XXXI.

An interesting phenomenon was exhibited in the measurements. With some of the alloys, the surface tension values up to 190°C were of one magnitude, but after allowing the alloy to stand in the capillaries at the higher temperature, the surface tension values thereafter were higher over the same temperature range. The set of results for each metal in Table XXXI, marked A, represents values before standing at the higher temperatures, while the B set represents results afterwards. Where there is no B set of results, this phenomenon was not noticeable. The comparison is further extended to Figure XXXVII where both sets of values for each metal are plotted against composition in weight

percent potassium. There are indications that the change in surface tension values may be attributed to a change in contact angle resulting from, perhaps, a cleaning of the glass surfaces at the higher temperatures. This point is to be checked. If such should be true, the high values are probably more correct.

Two sets of capillaries were used in the course of the measurements. The first set, having measured diameters of 0.114 cms., 0.072 cms., and 0.054 cms., were used for samples 1 through 7. The second set, having diameters of 0.111 cms., 0.074 cms., and 0.054 cms., were used for the remaining samples. Each set of capillaries was tested with water before and after the measurements with the metals. The surface tension of water was checked in each case within about 5 percent.

The reported surface tensions are reproducible to about ± 10 percent. The absolute accuracy of the values is somewhat questionable and no set figure will be indicated for this report. In each case, the metals were found to wet the glass capillaries, and any estimation of the overall accuracy of the results would have to be based on an assumption of zero contact angle for the menisci in the capillaries. For a liquid to have zero angle of contact it is considered, with some authority, that a liquid film must cover the walls of the capillary tube above the meniscus. Such is not the case with the liquid metals.

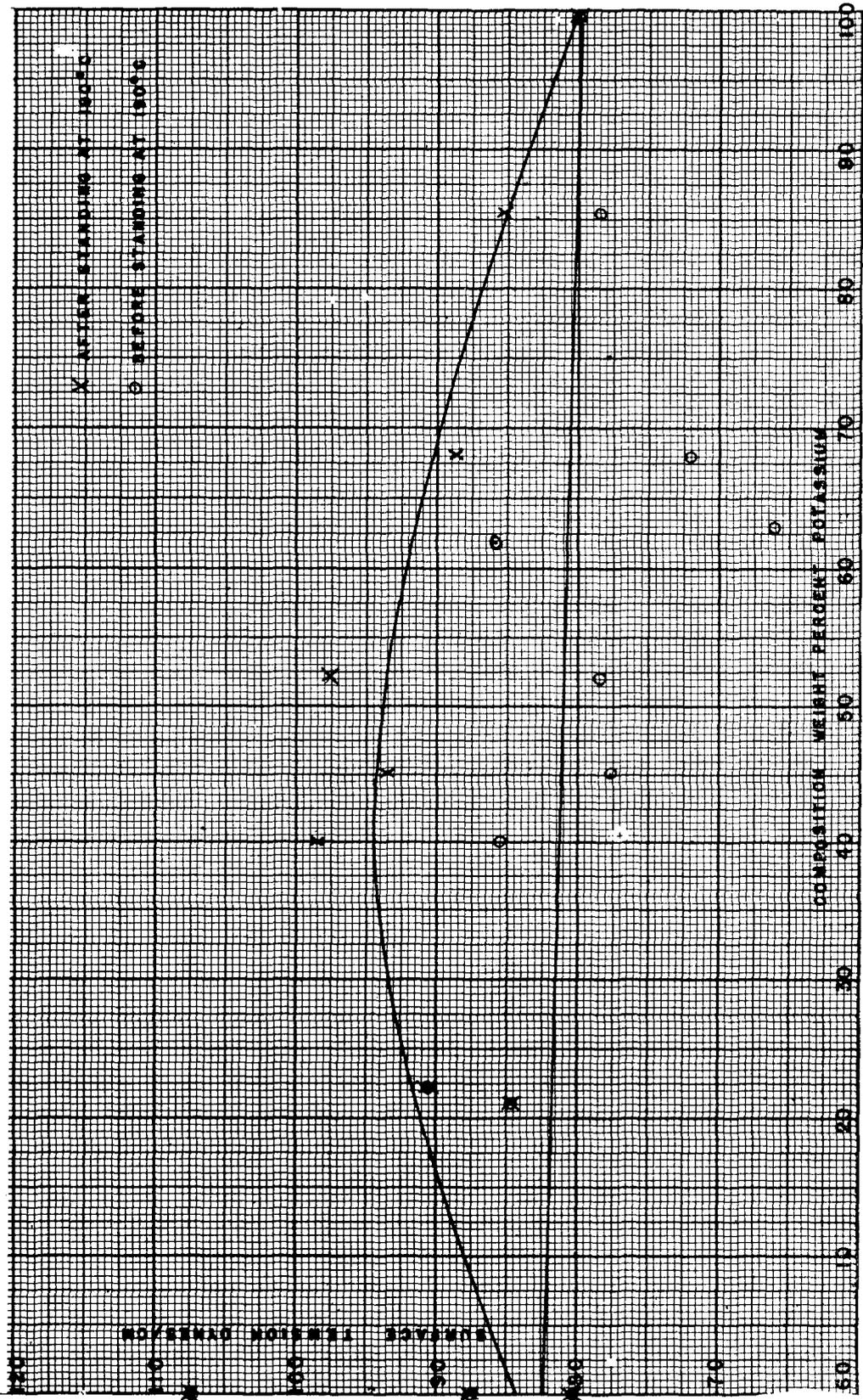


Figure 37

TABLE XXXI
SURFACE TENSIONS SODIUM - POTASSIUM

UNCLASSIFIED

Composition Sample Weight Per- cent Potas- sium	Average Surface Tension (mp-193°C) dynes/cm				
	Large Capillary	Medium Capillary	Small Capillary	Average Value	
62.9	A 1	64.3	69.2	64.8	66.1
0.0(Sodium)	A 2	72.8	82.0	85.4	80.1
99.6	A 3	80.6	82.6	86.9	80.0
45.2	A 4	69.5	86.4	77.3	77.7
	B	89.9	94.7	96.1	93.6
68.0	A 5	70.9	71.2	74.1	72.1
	B	80.2	95.7	90.3	88.8
85.4	A 6	93.3	77.2	64.9	78.5
	B	86.6	84.4	84.8	85.3
40	A 7	90.9	85.6	80.1	85.5
	B	94.6		102.6	98.6
21.0	A 8	84.7			84.7
0.0(Sodium)	A 9	97.9	99.8	124.5	107.4
0.0(Sodium)	A 10	78.0	86.7	98.2	87.6
22.2	A 11	87.7	91.3	92.9	90.6
52.2	A 12	78.6	78.0		78.3
	B	96.0	99.0		97.5
61.8	A 13	86.0	83.2	88.6	85.9

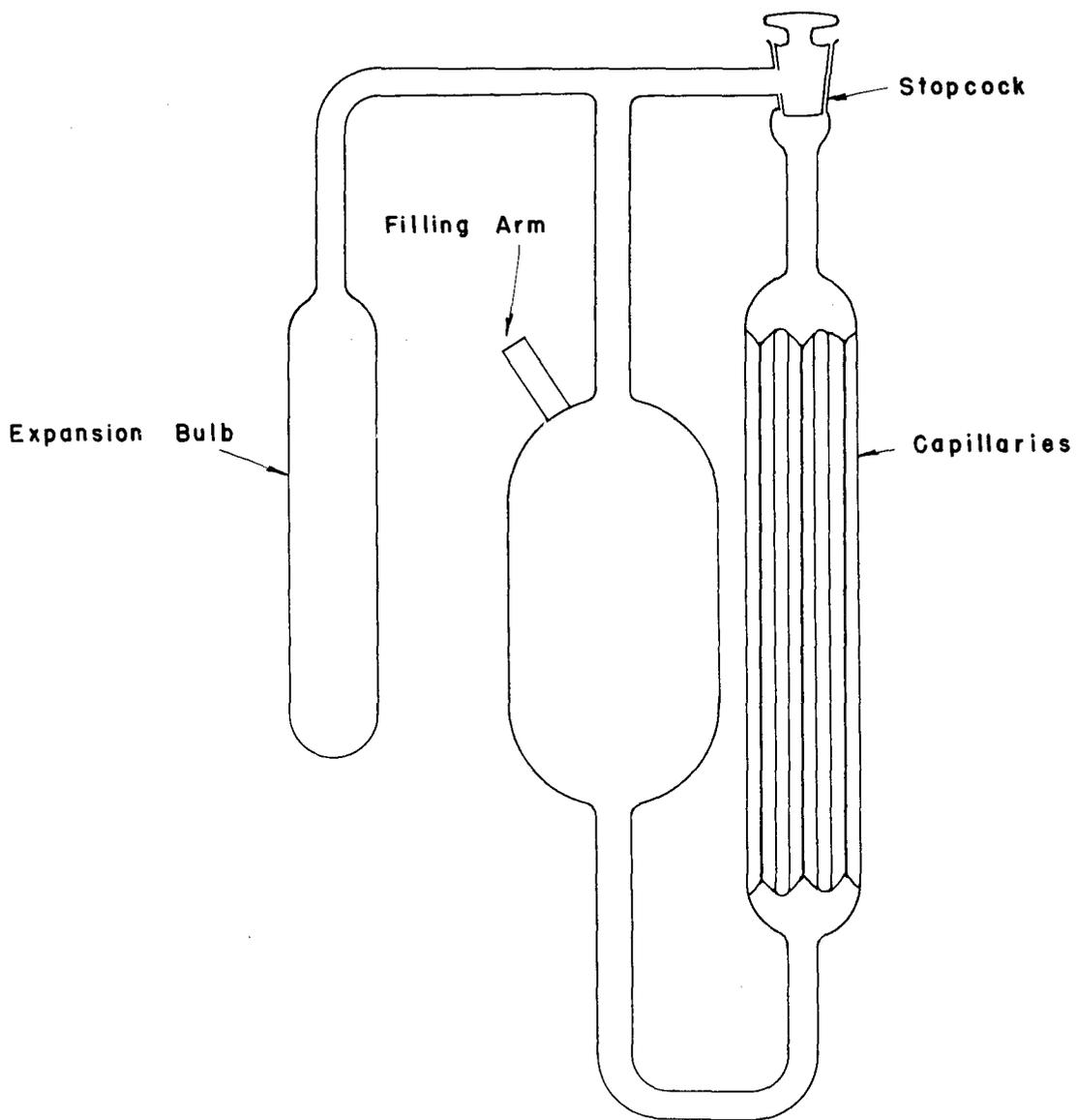


Fig. 38 Surface Tension Apparatus

CONCLUSIONS

A study of the properties of the sodium - potassium system is being continued. The measurements for viscosity and density are considered adequate, and no further work is anticipated for these properties. Work is either in progress or under consideration for specific heat, thermal conductivity, surface tension, and studies on contaminants, wetting and reaction rates.

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