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THERMOELECTRIC MATERIALS

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For the period: 1 January 1960 - 30 September 1961

Submitted by: T. S. Shevlin, Henry E. Wenden and S. R. Ali Zaidi
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FOREWORD

The final report covers the research period 1 January 1960 to 30 September 1961. This program was conducted under Contract NObs-78254 between Bureau of Ships, Department of the Navy, and The Ohio State University Research Foundation and the work has been assigned Index No. SR 10024-1BR. The research was conducted by S. R. Ali Zaidi under the immediate supervision of Thomas S. Shevlin and Henry E. Wenden.

THERMOELECTRIC MATERIALS

A. INTRODUCTION

Research under this contract has been directed toward the evaluation of molten vanadium oxysalts as thermoelectric materials.

The theoretical approach was based, in part, on the concept of thermally excitable electron transitions between states of nearly equal energy, thus affording a supply of electrons free to participate in thermoelectric flow. The vanadium atom with three 3d electrons and two 4s electrons at nearly equivalent energy levels displays ready transition between valence states and, hence, afford a high probability of such thermal transitions. It was proposed that these transitions might be further facilitated in an oxide melt in which the coordination of vanadium with oxygen depends on the valence state and in which no one of the possible coordination conditions is highly stable. In the solid state, change of coordination of the metal ion with respect to its coordinated oxygen ions is difficult and involves relatively large amounts of energy because of the requirement of long-range order in the crystal lattice. In comparison with such interchanges in the solid state between allotropic modifications, changes of coordination in the liquid state, in which order need only be maintained to the first or second coordination shell, should be relatively easy and hence should favor transitions capable of yielding thermal electrons. Further, electrical conductivity, generally low in well-ordered oxygen compounds, increases markedly in the liquid state, tending toward an improvement in figure of merit.

Prior experience on the part of one of us with sodium oxysalts of vanadium led to the choice of these materials rather than other compounds of the transition elements which might have appeared theoretically as favorable. Similar results might be expected with the sodium oxycompounds of manganese or perhaps of chromium. The materials were prepared by fusing together stoichiometric proportions of sodium carbonate and vanadium pentoxide. Two vanadates were prepared. These were sodium metavanadate, NaVO_3 , henceforth abbreviated NV, and sodium vanadyl vanadate, $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$, henceforth abbreviated NV_6 . It was found that NV_6 was more promising a material than NV. Hence, NV_6 was used throughout the studies reported herein.

A principal factor in the failure of many experiments was the difficulty of containing molten NV_6 , a highly corrosive fluid which attacks all substances, metallic and nonmetallic, tried as containers. High-alumina ceramic tubing of the densest and least permeable grade obtainable (Morganite, McDanel and Degussit) was quickly penetrated. Metals were quickly corroded, stainless steel forming an isolating layer of oxides. Platinum and silver were attacked, leading to recrystallization and mechanical failure. High-silica glass or fused quartz resists attack fairly well, and the only experiments in which container failure was not a principal factor are those carried out in such containers. Vanadate liquids show a strong tendency to migrate along the walls of the containing vessel, probably by a combination of capillary movement, sublimation and recrystallization and attack on the container. This phenomenon, hereafter alluded to as "creep," is also a principal source of experimental difficulty.

A number of different devices for the study of variation of thermoelectric potential with temperature, time, and atmosphere were designed and constructed. Initial experiments, using apparatus of very simple design, indicated sufficiently high potentials to warrant further work. Apparatus was then designed to permit control of the composition of the atmosphere over the hot junction. Repeated failure to obtain reproducible results as a consequence of attack on the container and creep led to the construction of a number of forms of the experimental vessel using metals, and ultimately to the use of the fused quartz U-tube. Forms assumed by the experimental device have included an open trough, a test-tube like vertical cell, concentric tubes, and a double armed U-tube. It seems likely that any of these forms would have yielded equally good results had not the factors of creep and container corrosion been present. It was the necessity for dealing with these factors, rather than any inherent advantage in the geometry of the device, that led to the construction of a number of forms of the apparatus. The essential features of a successful experimental vessel are (1) the materials of the device shall not be corroded by the molten thermoelement, (2) the form of the device must be such that creep does not result in a short useful life, (3) good electrical contact must be maintained to the fluid thermoelement at both hot and cold junctions, (4) no shunt paths must exist in the apparatus, loading or short-circuiting the thermoelements, (5) the atmosphere over both hot and cold junctions should be capable of being maintained at a chosen composition, and (6) the temperature of both hot and cold junctions should be measurable by convenient means. In a practical device the factors of cost, ease of manufacture, availability of materials, temperature range, life, and power capabilities

must be admitted to consideration as well. This study has not progressed to the design of a practical device.

Because the availability of oxygen is a factor in determining the coordination of oxygen ions about vanadium ions in the melt, and the coordination is thought to play a determining role in the provenance of electrons free to participate in thermoelectric flow, the atmosphere over the hot junction was varied. Oxygen, air, helium, and hydrogen were used to furnish successively lower oxygen activity and more reducing conditions, in the order named.

B. MATERIALS

The materials used were:

Sodium Carbonate (Reagent Grade)

Mallinckrodt Chemical Works, St. Louis, Mo.

Vanadium Pentoxide (Reagent Grade)

J. T. Baker Chemical Co.

Phillipsburg, New Jersey

C. PREPARATION

The two compounds used in these experiments, sodium metavanadate, NaVO_3 , and sodium vanadyl vanadate, $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$, were prepared by fusion of weighed molecular proportions of sodium carbonate and vanadium pentoxide in non-porous high alumina crucibles. Progress of the reaction was accompanied by evolution of CO_2 . Completion was assumed when gas was no longer evolved, but was not assured. The fusion was poured onto a steel plate to quench and cool. NV_5 evolved oxygen gas (O_2) during crystallization. The fused mass, which was visibly crystalline, was broken into small pieces for subsequent use.

X-ray diffractometer records of NV and NV₆ were taken, and indicated that each was a distinct crystalline phase, identical with material investigated in an earlier study dealing with oil-ash corrosion.

D. EQUIPMENT

The first exploratory experiments were carried out in 90 mm. alumina assay boats supported over the flames of three blast lamps using illuminating gas and compressed air. Platinum-platinum 10% rhodium thermocouples were used both for determination of junction temperatures and for electrical contact to the fluid thermoelement as well. The thermocouples were immersed in the fluid vanadate melt about one inch apart and the blast lamps adjusted by cut and try to yield a suitable temperature gradient between the two thermocouples, each of which was connected to a portable potentiometer. The potentiometers were electrically isolated, and thermoelectric potentials were measured by connecting a third potentiometer to either the two platinum or the two platinum-10% rhodium wires. This apparatus sufficed to reveal large potential differences roughly proportional to the temperature difference between the two immersed leads, and to demonstrate that the polarity of the potential difference reversed when hot and cold junctions were interchanged by movement of the blast lamps. In other respects, this form of apparatus was highly unsatisfactory. There was no possibility of independent control of atmosphere over the junctions, temperature was variable, fluctuating and could be measured only roughly, the alumina boat was quickly penetrated by the liquid vanadate and creep of the solid vanadate over the cooler portions of the boat quickly reduced the volume of useable melt and created unpredictable shunt paths that soon rendered the apparatus nonfunctional.

An improved form of apparatus using ceramic tubing was next constructed. This apparatus is shown in Fig. 1. A ceramic tube (a) contains the molten vanadate. Into the lower end of this tube another ceramic tube fits closely carrying platinum wire (p_1) which serves as a cold junction lead. The joint between tubes (a) and (c) is sealed with high temperature cement. An outer shield tube (b) acts as an auxiliary muffle to provide better heat distribution in the region between the hot and cold junctions (p_1) and (t_2). Thermocouple (t_1) measures cold junction temperature and is fixed to the outside of tube (a) with fine wire, so that the position of the junction is at the same level in the furnace as (p_1). Tubes (a), (b) and (c) are cemented together with wax, which is kept solid by a water-cooling coil (w). Tube (d) has four holes, two of which are used for the platinum-platinum 10% rhodium thermocouple which serves both as temperature measuring device for the hot junction and also as the hot junction electrical connection and lead. The other two holes are used for admission and exhaust of the gas used as the hot junction atmosphere. A hypodermic needle is connected to the main gas tank with an intermediate pressure-limiting mercury column (m) and is inserted through one hole of the four-hole tube (d) as a gas inlet, while another hypodermic needle is inserted into the other hole as a gas outlet, and is connected by gum tubing to an oil trap, through which the gas is vented to the atmosphere. The needles are sealed into tube (d) by means of wax. In operation, tube (d) is lowered until contact is made with the surface of the molten vanadate, then tube (d) is sealed in place with wax. Thermocouples (t_1) and (t_2) are connected to separate, isolated potentiometers for temperature measurement, and a third potentiometer is connected between (p_1) and the platinum lead of (t_2) for measurement of the thermoelectric e.m.f. Temperature gradient is controlled by varying the

Symbols For Fig. 1

Porcelain Tube

a - Main tube containing molten NV_6 .

b - Outer protection tube.

c - Protects platinum leads. It is cemented to tube a.

d - 4 hole tube contains thermocouple t_2 and needles n_1 and n_2 .

t_1 - Pt.-Pt.-10% Rh thermocouple for cold end.

t_2 - Pt.-Pt.-10% Rh thermocouple for hot end.

p_1 - Negative lead for e.m.f. in NV_6 .

p_2 - Positive lead for e.m.f. in NV_6 .

n_1 - Gas inlet needle.

n_2 - Gas outlet needle.

g_1 - Gas inlet hole in tube d.

g_2 - Gas outlet hole in tube d.

g_3 and g_4 - Holes in the tube d for the Pt.-Pt.-10% Rh thermocouple outlet t_2 .

v - Gas valve.

gt - Gas tank.

o - Oil trap.

m - Gas flow regulator; i.e., pressure limiting head of Hg.

r_1 - Rubber gum tubing.

r_2 - Rubber gum tubing.

f - Temperature gradient electrical resistance furnace.

w - Water cooling coil.

current in electrical resistance furnace (f) and by varying the vertical position of the entire assembly in the furnace muffle.

Failure of the apparatus shown in Fig. 1 came about as a result of penetration of, and corrosion of, tubes (a) and (c), corrosion and recrystallization of platinum elements (p_1) and (t_2) and creep of molten vanadate up the inner walls of tube (a) so that the position of the hot and cold junctions became indeterminate. Vanadate melt penetrated along the axis of tube (c), moving the cold junction downward to the position at which solid vanadate formed, while the nature of the junction at (t_2) became partly solid-solid and partly liquid-solid as a result of creep. This failure resulted with all materials tried, including Morganite, McDanel tubing and Degussit. These are extremely fine-grained, well-bonded and homogeneous high-alumina or pure alumina products specifically recommended by their manufacturers for gas-tight applications. Sections cut through tubes of these products after a few hours exposure to molten vanadate liquid revealed massive penetration by, and reaction with, the vanadate.

As a result of the failure of all types of ceramic products tested, an apparatus constructed of metal was designed and built. This apparatus is pictured in Fig. 2. An outer stainless steel tube (a) is separated from an inner stainless steel tube (b) by ceramic spacers (c) about 0.5-inch long, located along tube (a) at intervals of 1.5 inches. Chromel-alumel thermocouples (t_1) and (t_2) were soldered to the outside of tube (a) and the inside of tube (b), respectively. Water-cooling coils (w) were provided to keep the vanadate solid at the ends of the tube. The entire assembly was placed in a muffle furnace F and cooling air passed through the inner tube from (I) to (O)

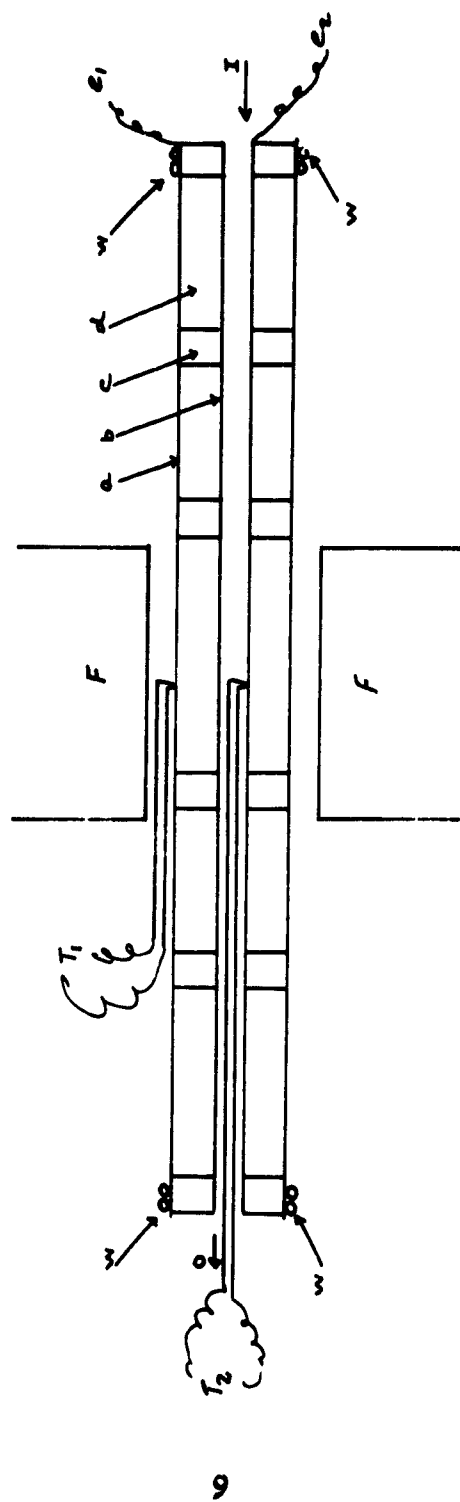


Figure 2

to maintain a temperature gradient. Stainless steel leads (e_1) and (e_2) were soldered to the outer and inner tubes, respectively. In operation, hot and cold junction temperatures were observed by means of potentiometers connected to (t_1) and (t_2), while thermoelectric effects were observed by means of a third potentiometer connected between (e_1) and (e_2). Molten vanadate was introduced by filling the spaces between spacers (c) with moistened powdered NV_6 . This was allowed to dry and then heated so that the space between tubes (a) and (b) was uniformly filled. In operation, the temperature of furnace (F) was maintained such that the cold junction temperature at (t_2) was above the melting point of NV_6 .

The apparatus shown in Fig. 2 failed to yield satisfactory experimental results. This is attributed to improper filling of the tube, so that no effective contact resulted, and to corrosion of the stainless steel by NV_6 , producing an oxide film in a very short time so that the molten vanadates were effectively isolated electrically from the steel tubes. The arrangement is inherently capable of useful application, as either the inner or the outer tube may be maintained at the higher temperature, and hence, permits application to situations in which energy is derived from a heated rod or pipe as well as those in which the thermoelement is immersed in the heated environment with cooling air passing axially through the thermoelement.

The same geometry of arrangement of the elements of the experimental device was retained in the next form tried, a short tubular element consisting of concentric stainless steel tubes sealed by means of ceramic spacers at the ends only. Except for the shorter length and simpler construction, the arrangement was that of Fig. 2. Large e.m.f. values were observed with this

latter form of the concentric tube element, and a third form was constructed, illustrated in Fig. 3. This form differed from its two predecessors in that the stainless steel tubes were closed at one end, forming a test-tube like device, in which the ceramic spacers, although still required, did not play so vital a role. Furthermore, provision could be made in this form of the device for variation in atmosphere at both junctions, and loading of the NV_6 was greatly simplified. However, only very low e.m.f. values were observed, and it is clear that devices using stainless steel in contact with molten vanadates are not likely to be satisfactory, as a result of formation of an isolating and insulating oxide film.

The last form of test apparatus attempted has the shape of a U-tube and is constructed of fused quartz, a substance which is little attacked by molten NV_6 . This device is shown in Fig. 4. Results with the quartz U-tube have been the most satisfactory and reproducible of any obtained during this study, and indicate fairly large potential differences at moderate temperature gradients. The difficulties attending design of a practical device using this costly, fragile and intractable material are formidable.

E. EXPERIMENTAL PROCEDURES

In the initial open trough type of experiment the alumina assay boat was heated by means of the blast lamps to red heat and fragments of NV and NV_6 dropped into the boat until an appreciable body of mobile fluid had formed. The two thermocouples, which were also used as electrodes for measurement of the thermoelectric effect, were attached to a ceramic bar and lowered simultaneously until both made contact with the pool of molten vanadate. The blast lamps were then adjusted by hand to produce a temperature

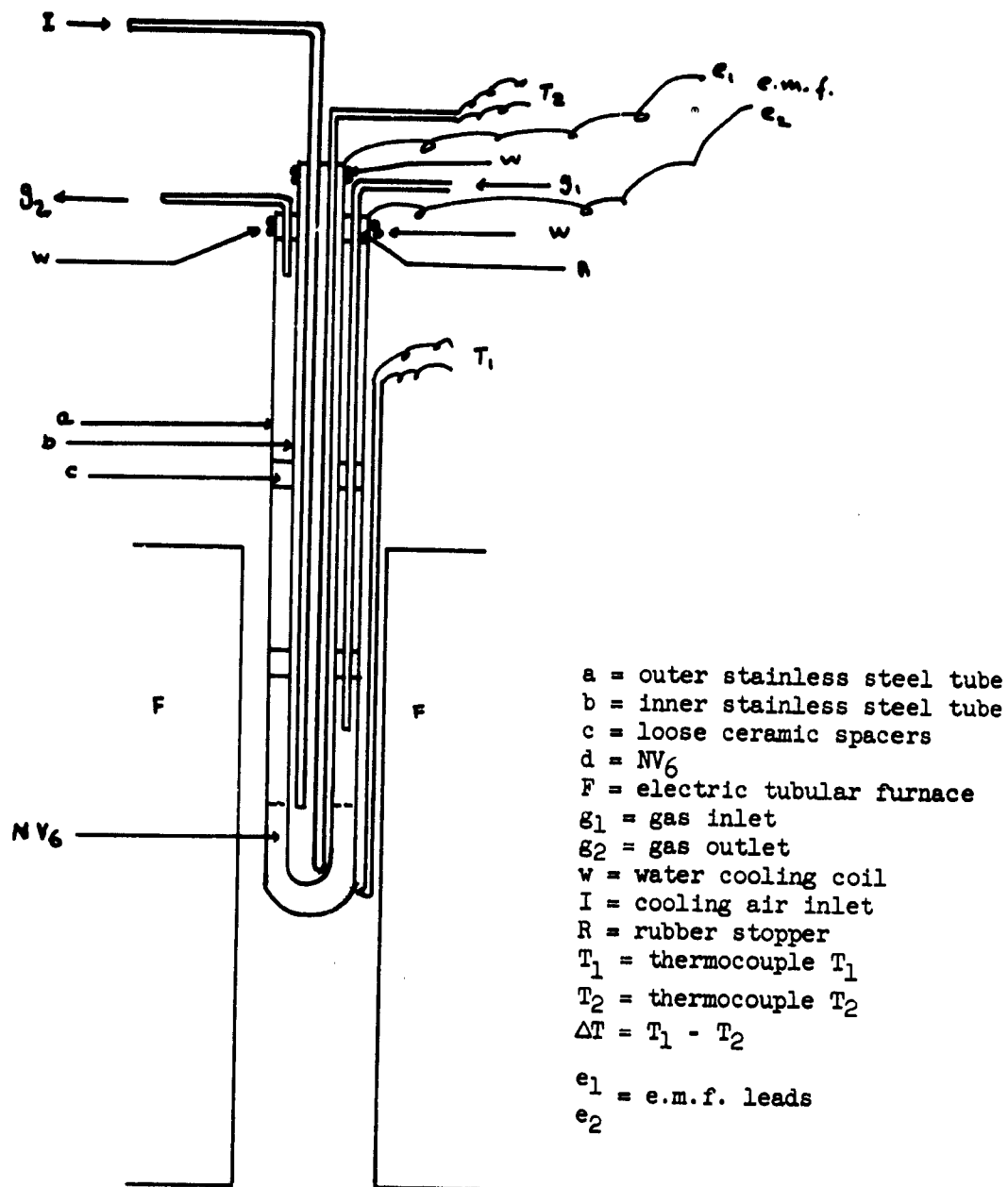
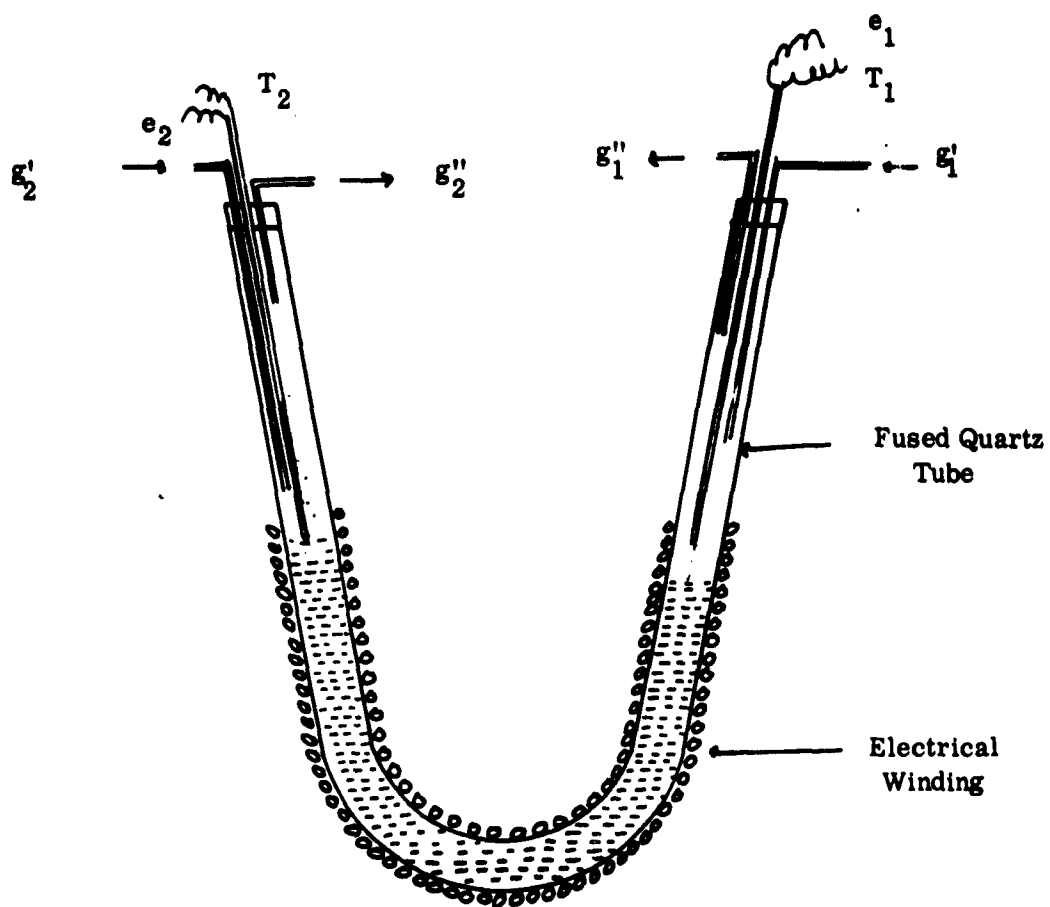


Figure 3



T_1 and T_2 = Pt-Pt 10% Rh. Thermocouples
 e_1 and e_2 = e.m.f. leads
 g_1' and g_2' = gas inlet
 g_1'' and g_2'' = gas outlet

FIGURE 4

difference of 20-70°C, as read by the portable potentiometers to which the two thermocouples were connected. The third potentiometer, which was connected between the platinum leads of the two thermocouples, was then read. The potential difference was then recorded, together with the simultaneous readings of the two temperature potentiometers. A new setting of the blast lamps was then obtained such that a different maximum temperature and a different difference between hot and cold junction temperatures resulted. After taking a number of readings in this way, establishing a rough proportionality between temperature difference between the hot and cold junctions and the e.m.f. measured between them, the blast lamps were readjusted so that the junction which had been the hotter became the cooler. No other factor was altered. The emf was observed to fall to zero and rise again with opposite polarity. This effect was taken as partial evidence that the e.m.f. observed was thermoelectric in origin, rather than electrochemical or of a fuel-cell nature. Operation of this simple device was very limited in time as a result of creep of NV_6 over the sides and bottom of the boat, and penetration of the body of the boat by the molten vanadate. The thermocouples also displayed some corrosion and discoloration as a result of contact with the melt.

The second form of apparatus was designed to permit maintenance of controlled atmosphere over the hot junction (although not over the cold), and better control of temperature and temperature gradient by use of an electrical resistance muffle furnace wound with platinum wire and supplied by a variable transformer. In operation, the tube apparatus is lowered into the muffle until the bottom of the inner tube is at red heat. Fragments of NV_6 are then dropped in until a molten mass covers the bottom of the tube. The

tube is then lowered a little and more NV_5 added. Alternate lowering of the tube and addition of reagent is continued until the tube is filled to the desired level. The upper tube assembly, carrying the upper thermocouple and gas inlet and outlet connections, is then lowered into the outer tube until contact is made between the upper thermocouple and the molten thermoelement. The inner tube is then sealed in place with wax and the flow of gas started until bubbling through the oil trap indicates flow through the furnace. Readings were taken on the isolated temperature measuring potentiometers and on the third potentiometer reading the thermal e.m.f. as gas was passed over the hot junction. After a period of time, the gas flow was shut off, the atmosphere sealed in, and observations continued under static conditions for a period of time.

Observations using the various forms of stainless steel apparatus were made in much the same way. The observations using the vitreous silica U-tube also follow the same general line of procedure: melting of the charge, establishing of the electrical circuit, reading of temperatures at both junctions and of the thermal e.m.f., circulation of different gases as atmosphere followed by measurements both in the dynamic (gas flowing) condition, and static (gas shut off and system sealed) condition. In all forms of the apparatus, maximum temperature was varied by adjustment of furnace temperature with the variable transformer, and temperature gradient was varied by lowering and raising the test assembly in the vertical muffle of the furnace. Good, although not very convenient, control of both parameters could be obtained in this way.

It is obvious that a gain in convenience and completeness of the record could be obtained by strip-chart recording of at least one of the parameters. A Leeds-Northrup Speedomax was obtained on loan and tried for recording of the thermal e.m.f. and many of the values recorded from the latter phases of this study were in fact obtained in this way. Further studies of this type should use recording.

F. EXPERIMENTAL RESULTS

The quantitative data gained in these experiments are presented in this section in tabular form in chronological order. The first table records some of the measurements taken using the simple open trough type of apparatus. The temperature of the hot junction is given as HIGHER TEMPERATURE in degrees Celsius, the difference in temperature between the hot and cold junctions is given as TEMPERATURE DIFFERENCE ΔT in degrees Celsius, and the potential difference read from the third potentiometer is given as e.m.f. in microvolts per degree. This format is used as standard throughout the tables, except that the e.m.f. is in some cases expressed only as a reading in millivolts, where the purpose of the table is comparison of different conditions.

TABLE I
Apparatus used: open trough
Atmosphere: air

Higher Temp., °C	Temp. Diff., °C	e.m.f., mv/°C
594	25	770
539	57	585
539	-23	-435

In Table II, including Tables IIa, IIb, IIc, and IId, the apparatus used was the test-tube device using ceramic tubing shown in Fig. 1. Table II shows dependence of the e.m.f. on time, using constant atmosphere at the hot junction. The results presented in Table IIa are shown in greater detail in Fig. 5, a graphical presentation of the complete results of the run during which the information in Table IIa was gathered. Tables IIb and IIc give the same information for runs in which the atmosphere over the hot junction was helium and hydrogen, respectively, and Figs. 6 and 7 give a graphical presentation of the results of these runs.

TABLE II. APPARATUS USED: VERTICAL CERAMIC TUBE FIGURE

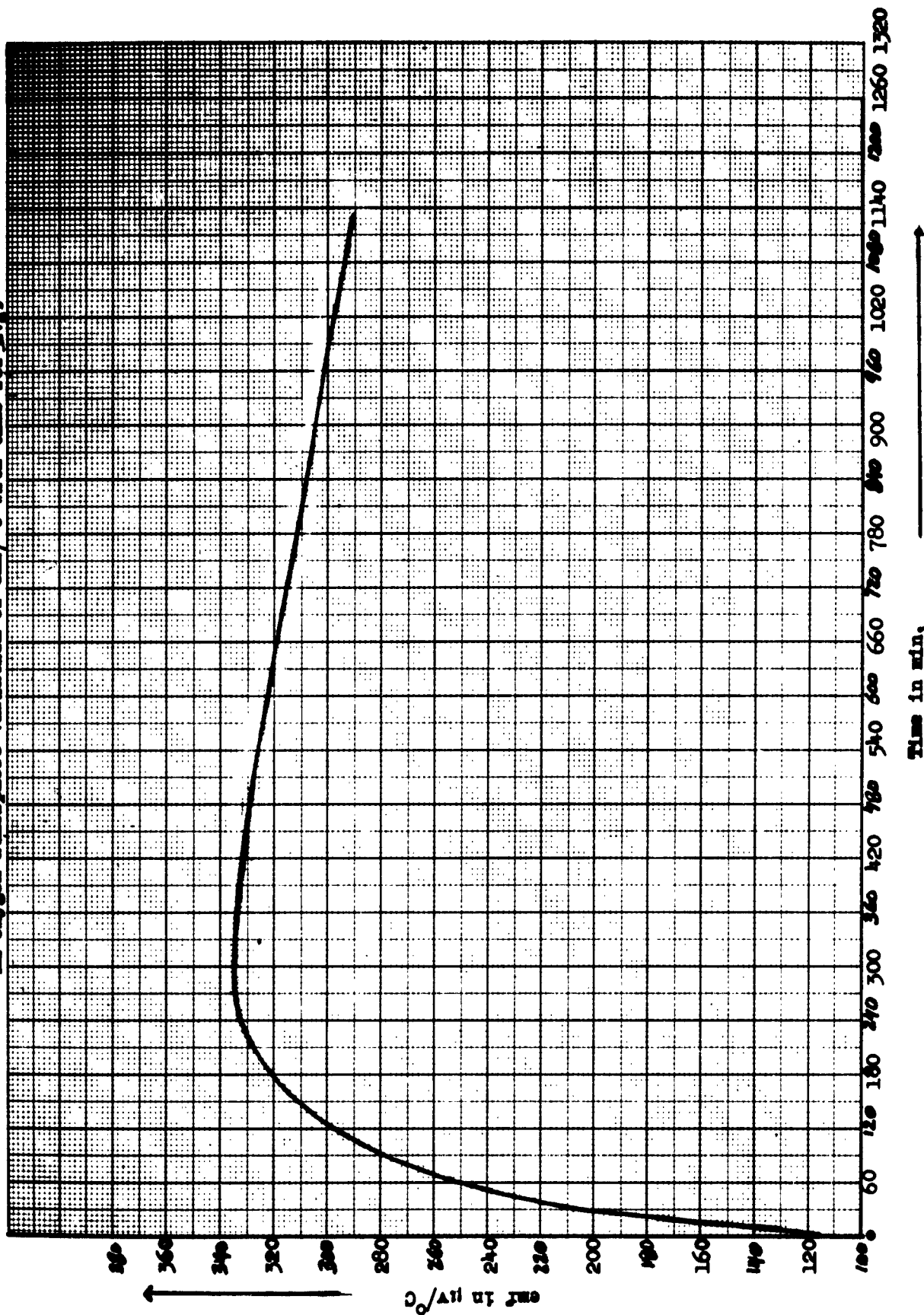
Table IIa. (Graph I) Oxygen Atmosphere at the Hot End

Higher Temp., T°C	Temp. Diff., ΔT	e.m.f. $\mu v/^{\circ}C$	Time, min.
1022	304	110	0
1024	310	330	240
1024	311	334	360
1002	306	291	1125

Table IIb. Helium Atmosphere at the Hot End

Higher Temp., T°C	Temp. Diff., ΔT	e.m.f. $\mu v/^{\circ}C$	Time, min.
865	140	560	0
880	140	120	85
872	140	181	350
862	138	270	1320
861	139	286	1710
			Stabilized

In oxygen atmosphere variation of emf/°C with time for Mg .



Time in min.
Figure 5

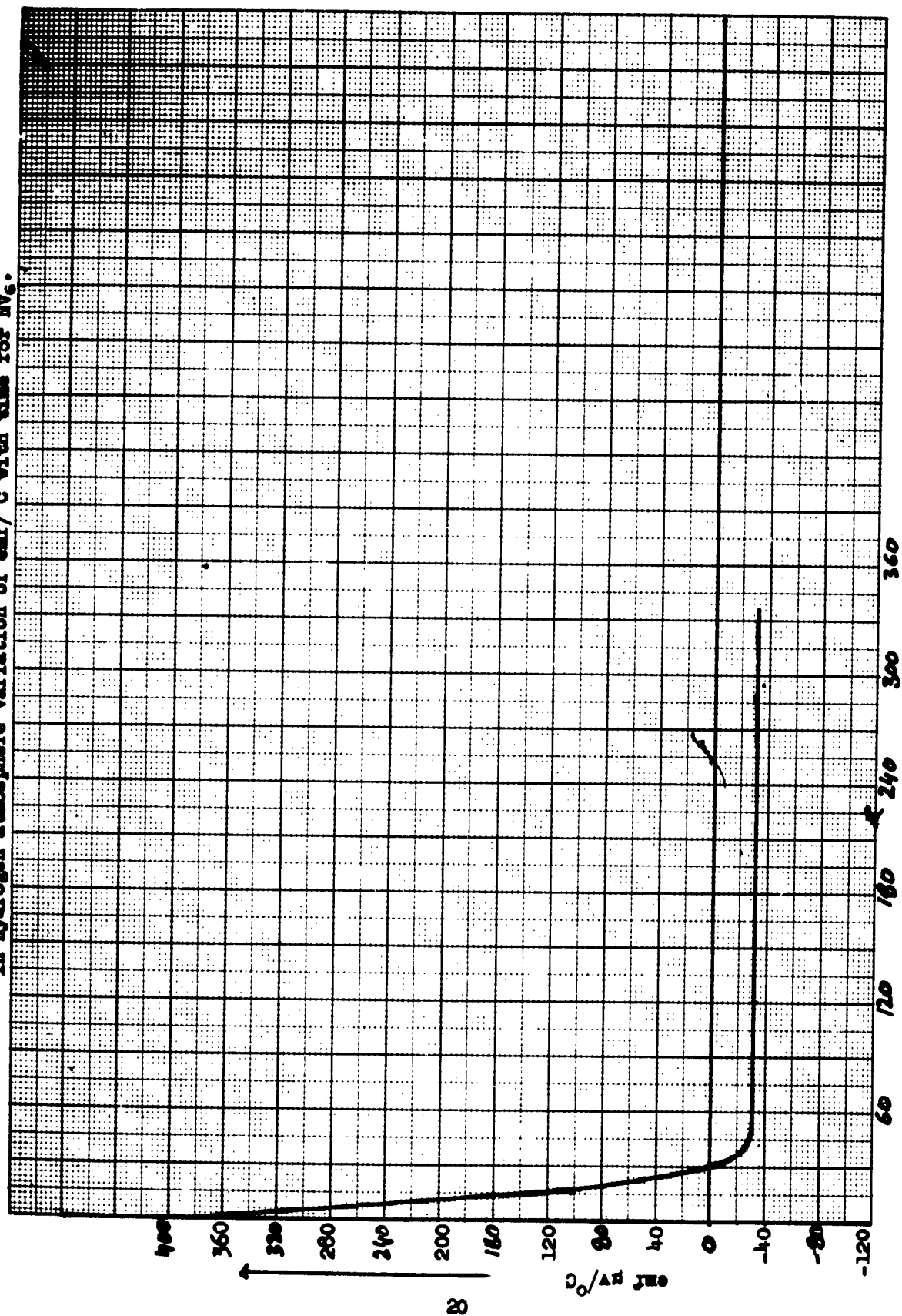
In helium atmosphere variation of emf/°C with time for IV₆.



Time in min. →

Figure 6

In hydrogen atmosphere variation of $\text{emf}/^{\circ}\text{C}$ with time for NiV_6 .



Time in min.

Figure 7

Table IIc. Hydrogen Atmosphere at the Hot End

Higher Temp., T °C	Temp. Diff., ΔT	e.m.f. $\mu v/^{\circ}C$	Time
996	245	381	0
1004	250	102	15
1004	251	000	30
1004	248	-38	40
996	236	-31	43
985	247	-32	120
981	182	-26	180
985	199	-31	240
994	204	-34	290

Table IIId. Air Atmosphere at the Hot End

Higher Temp., T °C	Temp. Diff., ΔT	e.m.f. $\mu v/^{\circ}C$
907	263	55
840	221	140
842	165	200
740	90	300
783	54	757

TABLE III. APPARATUS USED: CONCENTRIC STAINLESS STEEL TUBES

Table IIIa. NV_6 in Air Atmosphere

Higher Temp. $T^{\circ}C$	Temp. Diff., ΔT	e.m.f. mv
722	100	5.5
723	91	7.0
754	70	4.7
783	62	4.7

Table IIIb. NV_6 in He Atmosphere

Higher Temp. $T^{\circ}C$	Temp. Diff., ΔT	e.m.f. mv
≈ 600	≈ 100	4

Table IIIc. NV_6 in Oxygen Atmosphere

Higher Temp. $T^{\circ}C$	Temp. Diff., ΔT	e.m.f. mv
536	≈ 100	≈ 3
650	≈ 100	≈ 3

Table III, including Tables IIIa, IIIb, and IIIc, records the results of a series of experiments using apparatus made of concentric stainless steel tubing. Different gases were circulated, and the results for air are recorded in Table IIIa, helium in Table IIIb, and oxygen in Table IIIc. Results in this series were so poor and lacking in reproducibility that no effort has been made to present them graphically.

Table IV, including Tables IVa, IVb, IVc, IVd, IVe, IVf, and IVg, all record the results of runs made using the fused quartz U-tube. Different

combinations of sealed and open ends with different gases circulated over one or both ends account for the large number of experiments. Tables IVd, IVe, IVf, and IVg include the factor of time as well as atmosphere.

TABLE IV. APPARATUS USED: FUSED QUARTZ U-TUBE

Table IVa. Cold End Sealed - Hotter End in Air Atmosphere

Higher Temp., T°C	Temp. Diff., ΔT	e.m.f. $\mu v/^{\circ}C$
810	49	166
802	45	136
796	39	200

Table IVb. Cold End Sealed - Hotter End in O₂ Atmosphere

Higher Temp., T°C	Temp. Diff., ΔT	e.m.f. $\mu v/^{\circ}C$
742	37	2160
745	34	2420
750	33	2500
742	31	2600

Cold End Sealed with Air Atmosphere - Hotter End
in Oxygen Atmosphere

943	190	405
945	193	443
944	192	442

Table IVc. Cold and Hotter End Exposed to Air Atmosphere

Higher Temp., $^{\circ}\text{C}$	Temp. Diff., ΔT	e.m.f. $\mu\text{v}/^{\circ}\text{C}$
915	147	130
925	160	131
931	166	131
920	150	134
951	188	184

Table IVd. Cold and Hotter End Sealed with Air Atmosphere

Higher Temp., $^{\circ}\text{C}$	Temp. Diff., ΔT	e.m.f. $\mu\text{v}/^{\circ}\text{C}$	Time, min.
933	181	185	0
934	183	188	57
959	189	218	347
959	192	217	707
970	191	205	1357
964	194	203	1437

Table IVe. He Circulated on Cold End and Oxygen on Hotter End

Higher Temp., T°C	Temp. Diff., ΔT	e.m.f. $\mu v/^{\circ}C$	Time
943	191	447	0
943	191	221	1
943	190	270	8
939	190	293	37
939	190	220	50

He is Sealed at the Cold End and
Oxygen is Sealed at the Hotter End

939	190	394	
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Table IVf. Hydrogen Atmosphere Circulated at the Cold
End - Oxygen Sealed at the Hot End

Higher Temp., T°C	Temp. Diff., ΔT	e.m.f. $\mu v/^{\circ}C$	Time
939	190	402	0
939	180	255	1
939	180	204	9
929	173	231	13
929	180	229	21

Hydrogen and Oxygen Atmosphere Sealed in Completely

930	≈ 185	≈ 200	
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Table IVg. Oxygen Circulated at the Cold End - Oxygen Sealed in At the Hotter End

Higher Temp., T°C	Temp. Diff., ΔT	e.m.f. $\mu v/^{\circ}C$	Time, min.
954	197	157	0
954	197	-205	Instant
954	197	-(200 to 160)	9
Oxygen Sealed in Both End			
956	192	-40	

G. EVALUATION OF EXPERIMENTAL RESULTS

In general the precision and reproducibility of all results obtained were very low. Few replicate experiments were made, and at no time could any real assurance be had that conditions were actually the same as at the time of a previous run. Statistical arguments carry little weight in such a situation, and the data derived must be regarded as having a qualitative or only semiquantitative significance.

In attempting to estimate the magnitude and source of errors inherent in these experiments, a host of possibilities must be considered and even these can scarcely be exhaustive. During the course of a prolonged run (anything over a few minutes in duration) there is almost certainly an over all net change in composition of the entire molten mass as a result of expelling or taking up gas from the environment. This is borne out by the gradual change in observed e.m.f. that takes place after the flow of gas is shut off, eventually reaching some more or less stable static condition that is not closely like the dynamic condition (gas flowing). This indicates a constant interchange between melt and overlying gaseous phase during a run

that makes the composition of the melt uncertain and variable. Second, there is constant modification of the composition of the melt during a run by attack on and inclusion of the material of the container in the melt. During the runs made in ceramic tubes the final content of aluminum must have been appreciable. In the runs made in stainless steel tubing, the change in composition of the melt may have been less than when runs were made in alumina tubes, because of the formation of isolating layers of refractory and insoluble oxides preventing further attack on the steel.

In addition to changes in composition, the mass of melt undergoes changes in density and physical properties as a result of bubbling and marginal crystallization involved in the phenomenon of creep. Creep also diminishes the effective volume of melt and gives rise to shunt paths as well.

Shunt paths may have been a serious cause of error in some experiments as a film of conducting materials often developed on the outside of vessels and within ceramic elements supposed to serve as electrical insulators. An equally serious source of error was development by crystallization of the vanadate melt of solid-liquid contacts that placed high series resistance in the circuit, thus increasing the effective internal resistance of the thermoelement and yielding very poor regulation. Since the potentiometer was frequently used with a resistive voltage divider that actually loaded the thermoelectric cell, regulation was an important factor in determining the actual e.m.f. read. In no case could more than a very minute current be drawn from any thermoelement tested in this study without reducing the output voltage to an unmeasurably low level; that is, the power output of all cells tested was negligible.

The temperatures of the hot and cold junctions were generally obtainable only as an approximation, since only in the first and simplest experiment were both temperature measuring and sensing electrodes actually at the same point.

That the entire source of the e.m.f. observed is a Seebeck effect has not been unequivocally demonstrated by an experiment that has been performed. In the first and simplest experiment, the reversal of polarity of the potential difference when hot and cold junctions were interchanged tended to show that the effect was neither a fuel cell effect nor an electrochemical effect and, hence, by elimination that it was likely to be a Seebeck effect. On the other hand, in that as in all subsequent experiments, there were some sources of potential difference that were not wholly eliminated. Whenever there is mass transport involving ions, a potential difference may arise as a result of different rate of migration, or mobility, of the charge carriers. Since the mechanism by which charges are transported in vanadate melts is not known, such an electrochemical potential difference cannot be excluded. Simple battery effects arising out of interaction between container and melt can be quickly detected and eliminated by their irreversibility with change of temperature gradient.

In those experiments in which hydrogen was circulated over one junction, or in which there was a difference in partial pressure of oxygen over the two junctions, fuel cell behavior is not impossible and may have been a contributory source of e.m.f. Such an e.m.f. could even be reversible in polarity, if the partial pressures of oxygen were also varying as a result of emission or taking up of gas by reaction with melt, a phenomenon that actually takes place in NV_6 . However, in those runs in which helium was passed for

a long time over the junction or in which both junctions were sealed off, fuel cell behavior is impossible or at least very improbable.

To sum up, the e.m.f. observed may have been in whole or in part (1) a Seebeck effect, (2) an electrochemical effect arising out of reaction between melt and container or melt and electrode, (3) an e.m.f. arising out of differential mobility of ionic charge carriers in cases where mass transport is taking place, as in creep, (4) a fuel cell effect or, (5) the result of hitherto unknown effects. In those cases in which no reaction is possible that could give rise to fuel cell e.m.f. such as a sealed system or one sealed with a neutral atmosphere, (4) is excluded. In those cases in which simple reversal of the direction of the temperature gradient without other changes produced immediate and marked reversal of the e.m.f. polarity, (2) is excluded. Where creep, convection or other forms of mass transport were not a factor (3) could not be effective. No single experiment actually combined all of the necessary conditions, although experiments are recorded in the tables and figures that deal with each factor individually. Hence, although there is no single crucial experiment identifying this effect as a Seebeck effect, the balance of probability is strongly in favor of most of the e.m.f. values observed⁸ having arisen out of Seebeck effects.

H. CONCLUSIONS

Although no single crucial experiment unequivocally identifies the potentials observed as Seebeck potentials, the balance of probabilities seems to favor the interpretation of the observed effects as Seebeck effects.

Sodium vanadyl vanadate (NV_6) is a thermoelectric material in the liquid state yielding an observed potential difference of 2500 microvolts per degree

Celsius referred to platinum when oxygen is circulated over the hot junction and the cold junction is sealed. When air is circulated over the hot junction and the cold junction is sealed, a maximum potential difference of 700 microvolts per degree Celsius may be attained, as referred to platinum. (Table IV, above).

The observed potential difference varies markedly with magnitude of the difference in temperature between the hot and cold junctions. As the difference in temperature between hot and cold junctions decreases, the potential difference increases, rising to a maximum value at some temperature difference near 40°C. The behavior of the thermoelectric effect at smaller temperature differences has not been fully investigated. Figure 8 shows a graphical presentation of a large number of runs, showing this decline of observed e.m.f. with increasing temperature difference. Vertical height of the black bars is the temperature difference between hot and cold junctions, the horizontal coordinate is observed e.m.f. in microvolts per degree C, with values rising to the right. Note that, in general, the shortest bars lie farthest to the right.

The observed e.m.f. seems to vary little with temperature of the hot junction, as long as both junctions are at a temperature above the melting point of NV_6 . There seems to be a slight decline in potential difference as hot junction temperature is raised, all other factors being constant.

The effect of a reducing atmosphere over the hot junction is to reduce the thermal e.m.f., and, if made sufficiently reducing, to reverse the polarity of the e.m.f.; the effect of an oxidizing atmosphere is to raise the e.m.f., as compared with a neutral (helium) atmosphere. The effect of

In air atmosphere ΔT vs. $\text{enf } \eta/\text{°C}$ for M_0

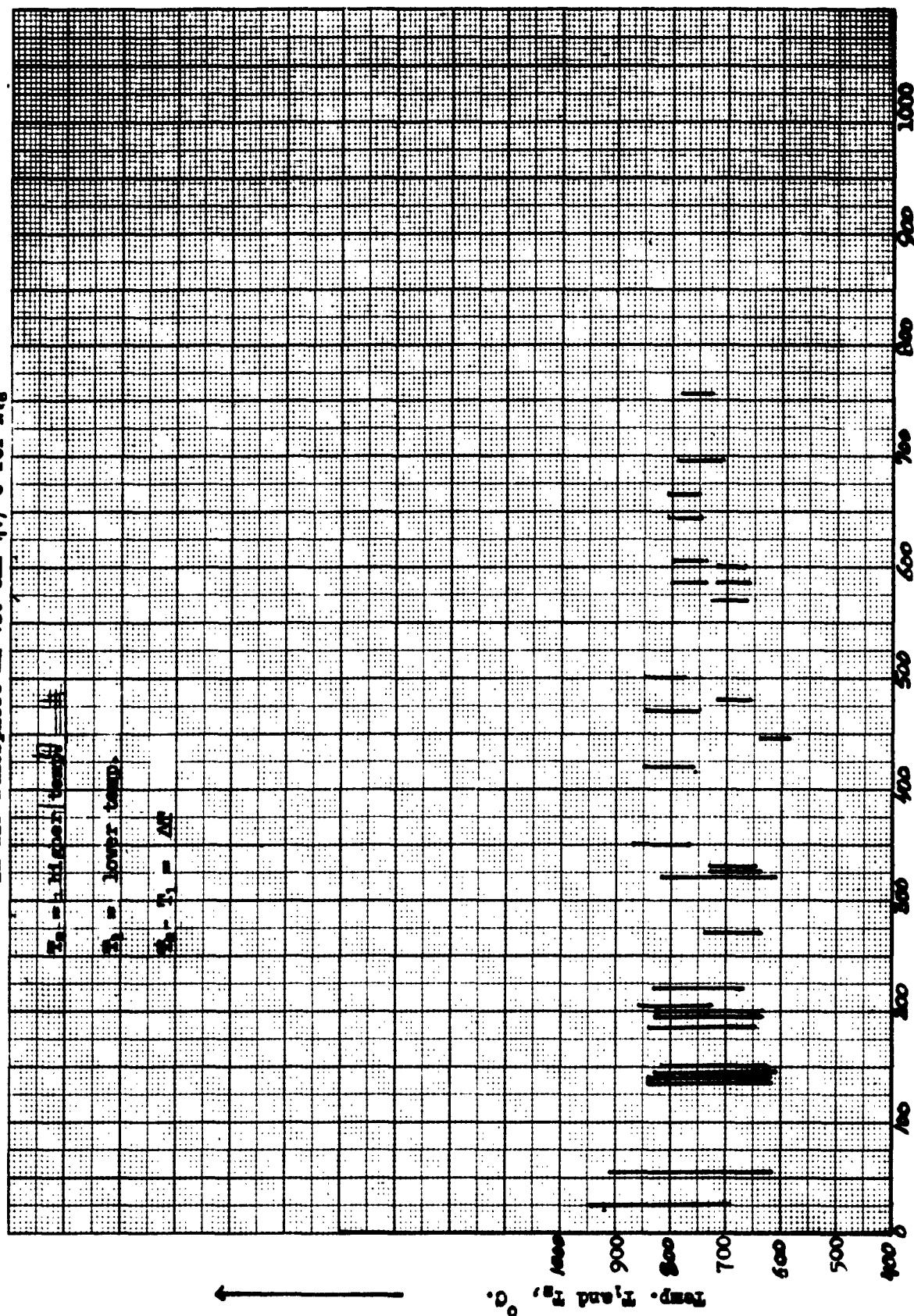


Figure 8

a reducing atmosphere over the cold junction is to raise the e.m.f., the effect of an oxidizing one to reduce it, and if, made sufficiently oxidizing, to reverse the polarity of the e.m.f.

The effect of oxygen concentration over the hot and cold junctions agrees well with the postulate, which may now be taken as a conclusion based on these findings, that the process by which the thermal e.m.f. is generated is intimately connected with the valence state and oxygen coordination of the vanadium ions, the lower valence ions being associated with the cold junction, which is electrically negative with respect to the positive hot junction with which the higher valence ions are associated. An oxidizing atmosphere at the hot junction tends to promote and stabilize this condition, as does a reducing environment at the cold junction, while reversal of these conditions tends to decrease the separation of charges thermally produced.

The high corrosive nature and tendency to surface migration (creep) of the NV_6 liquid makes it unsuitable for most practical applications. Only fused quartz has been found capable of containing the liquid for long periods of time. Formidable difficulties intervene between the apparently promising thermoelectric properties revealed by this study and a practical device.

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