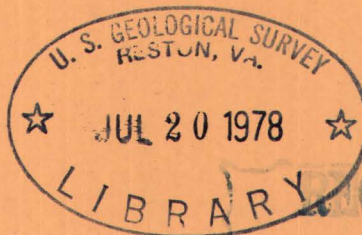


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Oxidation potential and state of some vanadium ores and the relation of woody material to their deposition

afred michael
By A. M. Pommer, 1916-



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UNITED STATES DEPARTMENT OF THE INTERIOR

✓ U.S. GEOLOGICAL SURVEY

OXIDATION POTENTIAL AND STATE OF SOME VANADIUM ORES AND
THE RELATION OF WOODY MATERIAL TO THEIR DEPOSITION*

By

Alfred Michael Pommer

February 1956

Trace Elements Investigations Report 586

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OXIDATION POTENTIAL AND STATE OF SOME VANADIUM ORES AND
THE RELATION OF WOODY MATERIAL TO THEIR DEPOSITION

By Alfred Michael Pommer

ABSTRACT

Oxidation potential studies with a multiple pH-potential recorder designed and constructed for this purpose demonstrated that some uranium-vanadium ores in the Colorado Plateau were in a reduced state when deposited. Any oxidation which took place occurred after deposition.

Experimental and theoretical reducing studies on fresh wood, wood degraded by burial for 450 years, and lignite, indicate that such ores may have been deposited by reduction of oxidized vanadium solutions by woody material.

A vanadium (III) mineral, $V_2O(OH)_4$, was prepared synthetically by reduction of a vanadium (V) solution with wood. This is the only reported synthesis of any reduced vanadium mineral by any method.

It was shown that the origin of almost all vanadium deposits currently of commercial importance involves life processes and products.

ACKNOWLEDGMENTS

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INTRODUCTION

Vanadium and uranium in the Colorado Plateau

The discovery of a practical means to utilize atomic energy has resulted in a very intensive search for uranium (1). The Colorado Plateau (fig. 1) remains the most important domestic source of uranium production (3). Four distinctive types of uranium ores have been recognized in the Colorado Plateau (4):

1. Uranium-vanadium ores
2. Uranium-copper ores
3. Uranium-hydrocarbon ores
4. Uranium ores in limestone

Currently the uranium-vanadium ores are the most prevalent. Sixty percent of all domestic uranium production is derived from vanadium-uranium ores of the Salt Wash member of the Morrison formation (fig. 2); the Shinarump conglomerate, which accounts for about one quarter of current uranium production, is vanadium bearing in Utah and Arizona (6,7).

Origin of the ores

As the most prevalent type of uranium ore in the most important domestic producing area contains very significant amounts of vanadium, a study

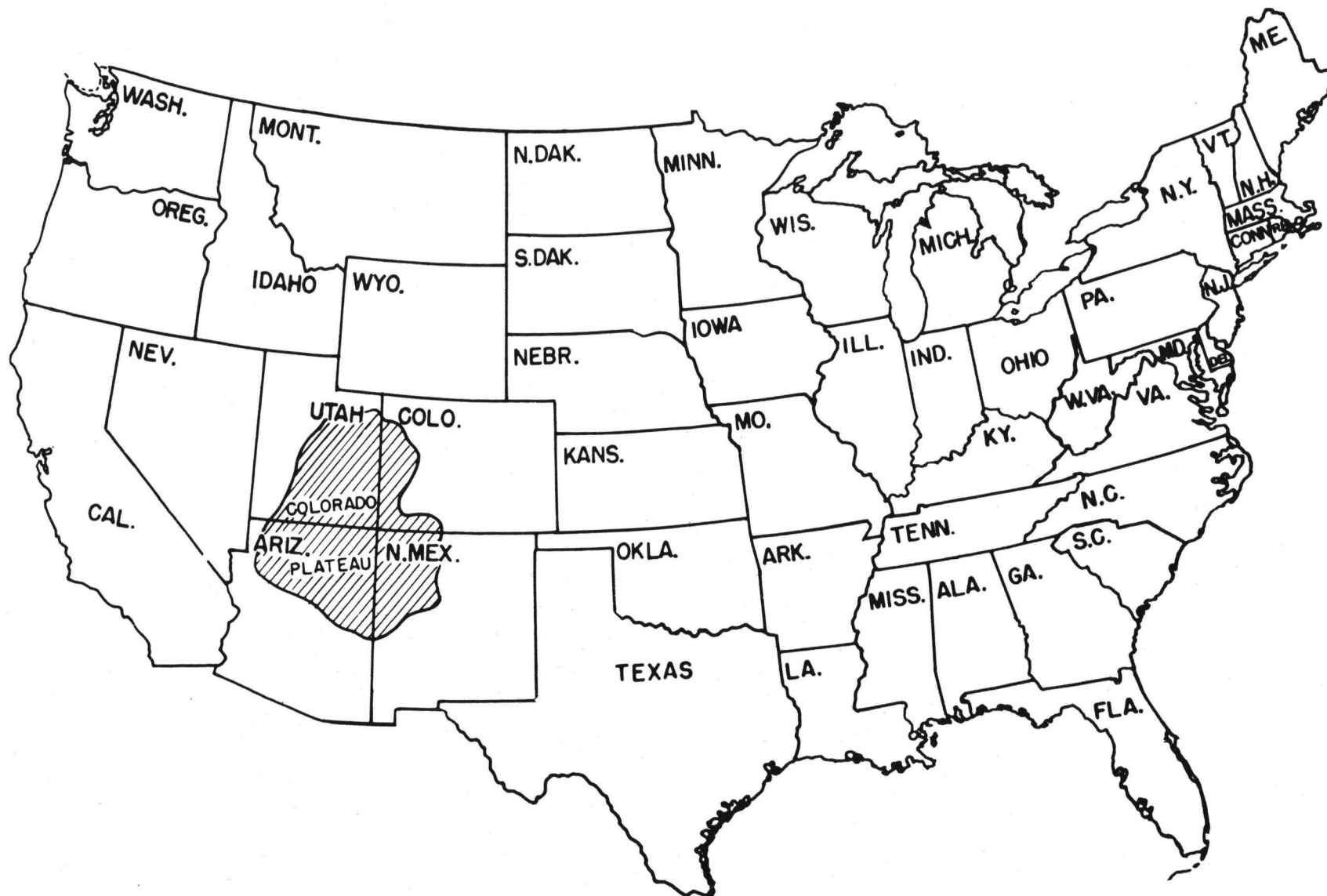


Figure 1.--Location map of the Colorado Plateau (2)

SYSTEM	FORMATION	SECTION	THICKNESS FEET	REMARKS	KNOWN URANIUM POTENTIAL CENTRAL PLATEAU
CENOZOIC	Eocene	WASATCH	3,000+	SHALE, SANDSTONE, LIMESTONE	POOR
			1,000±	SANDSTONE, SHALE, COAL	POOR
			2,000 TO 5,000	SHALE	VERY POOR
MESOZOIC	CRETACEOUS	MESA VERDE	50-200	SANDSTONE	POOR
			50-250	SANDSTONE, MUDSTONE	POOR
	CRETACEOUS	MANCOS	300-500	BRUSHY BASIN SHALE	POOR
			200-400	SALT WASH SANDSTONE	VERY GOOD
			50-400	SHALE, SANDSTONE	POOR
	CRETACEOUS	DAKOTA	0-250	SANDSTONE, SHALE, GYPSUM	POOR
			50-1,000	SANDSTONE	FAIR
			0-600	SHALE	VERY POOR
	JURASSIC	MORRISON	0-2,000	SANDSTONE	VERY POOR
		SUMMERVILLE	0-300	SANDSTONE	VERY POOR
		CURTIS	0-400	SANDSTONE	POOR
		ENTRADA	100-500	SHALE, SANDSTONE	VERY GOOD
		CARMEL	0-400	SANDSTONE	POOR
		NAVAJO	0-400	SANDSTONE	POOR
		KAYENTA	0-400	SANDSTONE	POOR
PALEOZOIC	PERMIAN	WINGATE	0-400	SANDSTONE	POOR
		CHINLE	0-400	CONGLOMERATIC SANDSTONE	VERY GOOD
		SHINARUMP	0-1,000	SHALE, SANDSTONE	FAIR
		MOENKOPI	0-6,000	SHALE, ARKOSE, LIMESTONE	FAIR
PALEOZOIC	PERMIAN	CUTLER AND RICO	0-400	CONGLOMERATIC SANDSTONE	VERY GOOD
			0-1,000	SHALE, SANDSTONE	FAIR

Figure 2.--Generalized stratigraphic column, central Plateau area on Colorado Plateau and outlying areas (5).

of the origin of vanadium in Colorado Plateau uranium ores may throw light on the origin of uranium in these ores and is of great importance.

The uranium content of vanadium ores in the Entrada sandstone (fig. 2) is generally too low to justify their exploitation for uranium (6) and these deposits will not be considered in this study. All other vanadium ores in the Colorado Plateau are also uranium ores and as such have elicited lively interest, especially recently. The voluminous and controversial literature dealing with the origin of uranium deposits on the Colorado Plateau has been reviewed by McKelvey, Everhart, and Garrels (8) who classify the main hypotheses as follows:

1. Placer concentration of the chief ore metals, followed by recrystallization and some redistribution (9); this mechanism has been suggested for one nonvanadiferous uranium deposit only.
2. Precipitation from surface or ground waters at the time the enclosing sediments were laid down or shortly thereafter (syngenetic deposition), followed by recrystallization and some redistribution (10,11,12,13).
3. Derivation from volcanic matter or sediments elsewhere in the stratigraphic column by ground water action (14,15,16,17,18).
4. Derivation from petroleum source beds (19).
5. Precipitation from hypogene solutions derived from igneous activity (20,21,22).

The lack of agreement between hypotheses and the persistence of controversy in this area indicate a lack of conclusive evidence necessary to solve the problem and demonstrate the desirability of collecting further data in this field. Although vanadium and uranium in the Colorado Plateau vanadium-uranium ores do not necessarily have the same origin, it may be expected that an investigation of vanadium chemistry as it pertains to the

deposition of these ores will be helpful.

The geologic setting

The ores consist of vanadium and uranium minerals in a sandstone or mudstone matrix containing some clays and nonvanadiferous minerals associated with the ore. The most important vanadium minerals found in the Colorado Plateau are listed in table 1. It can be noted from this table that uranium-vanadium minerals are found only in the oxidized state. Reduced vanadium-uranium ores consist of mixtures of minerals containing tervalent or quadrivalent vanadium such as montroseite or paramontroseite with minerals containing quadrivalent uranium, mostly uraninite (UO_2) and coffinite, a hydrated uranium silicate (25). Some reduced vanadium also is present in micaceous material (26).

It is possible to determine the age of uranium-bearing minerals by calculation from $\text{Pb}^{206}/\text{U}^{238}$, $\text{Pb}^{207}/\text{U}^{235}$, or $\text{Pb}^{207}/\text{Pb}^{206}$ ratios (27). A determination of the ages of a representative sample of uranium ores from the Colorado Plateau (28) shows that they were deposited in their present location about 60 million years ago. As the age of the Triassic and Jurassic sediments (cf. fig. 2) containing almost all of the uranium is about 185 to 130 million years (29), it appears that the uranium-vanadium ores may have been emplaced long after the sediments in which they are found were laid down. It is generally agreed (30) that most of the uranium and vanadium was introduced by solutions percolating through the more permeable layers of the sandstones and mudstones in the ore-bearing formations. In this connection it is of interest to note that the age of the ores indicates that they were emplaced at the time of the Laramide orogeny (31), the formation of the Rocky Mountains by folding of the Cordilleran

Table 1.--Some vanadium minerals found in the Colorado Plateau (23,24).

Vanadium (III) minerals

Tervalent oxides

Montroseite	VO(OH)
New vanadium mineral	$\text{V}_2\text{O(OH)}_4$

Vanadium (IV) minerals

Quadrivalent oxides

Paramontroseite	VO_2
Duttonite	VO(OH)_2

Vanadite

Simplotite	$\text{CaV}_4\text{O}_9 \cdot 5\text{H}_2\text{O}$
------------	--

Vanadium (IV) and vanadium (V) minerals

Mixed oxides

Corvusite	$\text{V}_2\text{O}_4 \cdot 6\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$
Corvusite-like mineral	$\text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5 \cdot 12\text{H}_2\text{O}$

Vanadium (V) minerals

Quinquevalent oxide

Navajoite	$\text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$
-----------	--

Vanadates

Hewettite	$\text{CaV}_6\text{O}_{16} \cdot 9\text{H}_2\text{O}$
Barnesite	$\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$
Pascoite	$\text{Ca}_3\text{V}_{10}\text{O}_{28} \cdot 16\text{H}_2\text{O}$
Hummerite	$\text{K}_2\text{Mg}_2\text{V}_{10}\text{O}_{28} \cdot 16\text{H}_2\text{O}$
Rossite	$\text{CaV}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$

Uranyl vanadates

Carnotite	$\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$
Tyuyamunite	$\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 5\frac{1}{2}\text{H}_2\text{O}$
Metatyuyamunite	$\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$

highlands. As this process involved considerable igneous activity, it is easy to see how mineralizing solutions could suddenly be introduced. These solutions, however, did not necessarily contain U or V at their point of origin.

The geochemical setting now can be summarized: there are minerals containing uranium and vanadium in different states of oxidation; these minerals were precipitated from solutions in a porous rock matrix.

The environment: Oxidizing and reducing agents

As the state of oxidation of vanadium and uranium in the ores appears to be a significant variable, it now becomes necessary to consider which oxidizing or reducing agents may be found in the environment of the minerals.

The only oxidizing agent of importance is free oxygen; it is present in the atmosphere and may be present as dissolved air in circulating ground waters; it has been shown that oxidation by moist air is a much more likely process than oxidation by ground waters, and that in the presence of pyrite (usually found in reduced vanadium-uranium ores) ferric sulfate solutions formed by pyrite weathering may act as intermediate oxidant (32).

The two possible reducing agents in a natural environment of the type under consideration are H_2S and organic matter. An examination of the literature discloses no evidence for or against the presence of H_2S at the time of deposition. Reduced uranium-vanadium ores are generally associated with pyrite (FeS_2) and marcasite (FeS_2), but a mineralogic investigation of the paragenesis of minerals of some typical ores indicates that some of the pyrite may have been present before the uranium-vanadium ore minerals were deposited (33).

The association of vanadium-uranium ores with organic matter is very striking. Hess (34) describes some typical occurrences:

"The carnotite commonly fills spaces in the sandstone, either filling breaks in the cementing material or coating joints in the rock and the sides of cracks in fossil wood... The carnotite also fills cavities in sandstone, petrified wood and carbonized rushes, and sometimes replaces wood with a comparatively solid mass... Where carnotite occurs in fossil wood the degree of decay seems to have largely governed the quantity of replacement... a length of more than 20 feet of a forked petrified tree was mined for ore, and in the tree the uranium was richest around the outer edge--the part which evidently was most decayed. Wood that shows its structure well carries little carnotite."

Wright (35) also comments on the association between the uranium ores of the Colorado Plateau and woody material, "...most of the deposits are associated with fossil organic matter, and this material appears to have acted as a precipitation agent. Pitchblende replacement of wood is common in some Shinarump deposits, and the association of pitchblende with fossil organic matter is almost universal."

The method: Oxidation potential studies

It is readily apparent that oxidation and reduction processes may be important in a system consisting of minerals containing V(III), V(IV), V(V), U(IV), U(VI), Fe(II) and Fe(III) (in the form of pyrite or marcasite and its oxidation products), associated with organic matter, and exposed to free oxygen. A powerful tool in the investigation of such processes may be found in oxidation potential studies. It now becomes necessary to consider the application of such studies to the problem at hand.

OXIDATION POTENTIAL STUDIES: SOME THEORETICAL CONSIDERATIONS

Conventions and definitions

The "Conventions concerning the signs of electromotive forces and electrode potentials" agreed on by the Commission on Physico-Chemical Symbols and Terminology and the Commission on Electrochemistry of the International Union of Pure and Applied Chemistry (36) is followed herein. Accordingly, an electrode potential is numerically equal to the electromotive force of a cell consisting of a standard hydrogen electrode on the left and the electrode in question on the right; this means that the half-cell potential of the standard hydrogen electrode is defined as zero. The electrode potential is given a positive sign if reduction occurs on the right electrode upon spontaneous discharge. Cell reactions are written as if reduction on the right electrode is always spontaneous; this means that electrons in the equation must always appear on the left side of the equality sign. The potential of an inert electrode in equilibrium with a reversible oxidation-reduction system then will be a measure of the tendency of the ions in equilibrium to pass from a higher to a lower state of oxidation; such a potential may be called an oxidation potential in accordance with Creighton's terminology (37). It then follows that an oxidation-reduction system with a high oxidation potential is strongly oxidizing, whereas a low oxidation potential indicates a reducing system. Under the conditions found in nature, most systems have a positive oxidation potential, but under highly reducing conditions negative oxidation potentials may be found.

If the cell reaction is known, it is possible to define a standard oxidation potential for the reaction. An oxidation potential will be

called a "standard oxidation potential" if all reactants and reaction products are at unit fugacity or unit activity.

The oxidation potential (E_h) is related to the standard oxidation potential (E°) by the Nerst equation. For the cell reaction



$$E_h = E^\circ + \frac{RT \ln 10}{nF} \log \frac{a_K^k a_M^m \dots}{a_Q^q a_S^s \dots} \quad (1)$$

where a_K , a_M , a_Q , and a_S mean the activities of the ions K, M, Q and S; k, m, q, s, and n are coefficients of the equation of the reaction; e^- is an electron; R (gas constant) is 1.987 cal./deg.mole; F (Faraday's constant) is 96480 absolute coulombs; and T the temperature in degrees Kelvin. At 25° C

$$\frac{RT \ln 10}{F} = 0.05916 \text{ cal/coul. mole.}$$

The oxidation potential is related to the Gibbs free energy, G, by the well-known equation

$$-\Delta G = nF E_h \quad (2)$$

where ΔG refers to the free energy of the final state minus the free energy of the initial state. By convention, the initial state is the state written on the left side of a cell reaction.

It is possible to calculate the E° of a cell reaction from equation (2), provided the ne^- term of the cell reaction is written on the left side. Many authors in the United States write the electrons on the right side (38), in accordance with a convention advocated by Lewis (39). Their free energy and "standard potential" values must be multiplied by (-1) to conform with the convention used here.

Equation (2) also may be written

$$-\Delta G = nFE \quad (2a)$$

where E is defined by the equation; it may be termed a "reaction potential." A reaction potential is an oxidation potential only if it meets the requirements of the definitions and conventions used. The reaction potential of a reversible oxidation-reduction system (the oxidation-reduction or redox potential) will be called an oxidation potential only if it can be determined by e.m.f. measurements with an inert electrode. Any convenient electrode may be used as reference, but if a standard hydrogen electrode is not used, the oxidation potential of the reference electrode must be added to the measured e.m.f. to obtain the E_h . Electrodes are the only solids to which the term oxidation potential can be applied. A solid phase in equilibrium with a solution in contact with an inert electrode can have a reaction potential but not an oxidation potential. An aqueous solution substantially free from reversible oxidation-reduction systems may be called a "redox-neutral electrolyte" (e.g. water or dilute sulfuric acid). We now define the oxidation potential of a solid phase as the oxidation potential of a redox-neutral electrolyte in equilibrium with the solid phase. Ions participating in a reversible oxidation-reduction equilibrium are called "redox-active" ions. Minerals yielding such ions upon solution are "redox-active" minerals.

As a solid phase has no direct effect on the measured e.m.f. used to define the oxidation potential, its activity should not be entered in equation (1), and the cell reaction should be written accordingly. It is often convenient to write the cell reaction as if solid phases participated. This can be done if the activity of such solid phases is defined as unity, because multiplying the numerator or denominator of the activity quotient in equation (1) by unity will not change the value of the E_h . Defining the activity of a solid phase as unity is equivalent to saying that a solid

is in its "standard state".

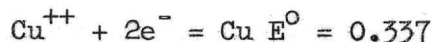
It is customary to define the activity of water as unity. Inasmuch as there are 55.5 moles in a liter of water, this is equivalent to saying that the activity coefficient of water in an aqueous solution is 0.018. This may appear strange but is a direct consequence of the conventional choice of expressing the concentration of a solute in moles per liter. In an aqueous solution this means expressing the concentration as moles of solute per 55.5 moles solvent. In a dilute solution the amount of water formed or consumed in a reaction is very small compared to the water present as solvent and may be disregarded.

If the concentration is expressed in moles of solute per mole of water, the practical activity coefficient of water is 1.

Since a reaction potential is related to the free energy by equation (2a), it is possible to predict from the E (or E_h) at which potential a reaction will proceed spontaneously. The example given here also illustrates the effect of the convention used.

Latimer (38) states: "For example, $\text{Cu} = \text{Cu}^{++} + 2\text{e}^-$ $E^\circ = -0.337$ will mean that the reaction $\text{Cu}^{++} + \text{H}_2 = \text{Cu} + 2\text{H}^+$ goes as written with a potential of 0.337 volt."

Using our convention we write the cell reaction as follows:



If the cell reaction is written in this fashion, the E° as written indicates the potential at which the reaction as written proceeds spontaneously. If we apply equation (2a), expressing F in cal/volt equivalents, we find

$$\Delta G = (2 \times 23060 \times 0.337) = -15530$$

Since the free energy change has a negative value, the cell reaction does proceed spontaneously.

Some pH-Eh relations

The oxidation potential of a vanadium ore as defined is a function of the activities of the redox-active ions (equation 1) dissolved in a redox-neutral electrolyte in equilibrium with the ore. The pH of the solvent may be expected to affect the solubility of the ore minerals. Since solvents of different pH may be used, we must consider the relations between Eh and pH.

It is obvious that a simple relationship between Eh and pH exists whenever hydrogen ions enter in the cell reaction. For the reaction



equation (1) may be written

$$Eh = E^0 + \frac{RT \ln 10}{nF} \log \frac{(H^+)^m a_{K\dots}^k}{a_{S\dots}^s}$$

but since $pH = -\log a_H$, we may write

$$Eh = E^0 + \frac{RT \ln 10}{nF} \log \frac{a_{K\dots}^k}{a_{S\dots}^s} - \frac{mRT \ln 10}{nF} pH$$

This equation yields on differentiation

$$\frac{dEh}{dpH} = - \frac{mRT \ln 10}{nF}$$

The pH also affects the Eh by its effect on the activity of an ionic species in a solution in equilibrium with a solid oxide or hydroxide. For example, if a solution containing ferrous and ferric ions is made alkaline, ferric and ferrous hydroxide will precipitate and remove some of the ions from solution. Unless equal amounts of each ionic species are removed, which is unlikely, the activity ratio and hence the Eh of the solution will change as the pH changes.

As the Eh very often is pH-dependent, it is necessary to measure the pH of a solution routinely whenever its Eh is determined. If the Eh of a

solution is calculated, the effect of pH on the cell reaction must be considered.

So-called pH potential diagrams are a convenient means to represent Eh-pH relations. Such diagrams were originated by W. M. Clark (40); they are treated in detail in the books of Pourbaix (41) and Charlot (42); and a brief description of the method of construction and application to chemical problems of such diagrams has been presented by Delahay, Pourbaix, and Van Rysselberghe (43). A pH-potential diagram is constructed by plotting an oxidation-reduction potential as a function of pH and delimiting the fields of stability of the ions and phases involved in terms of pH and oxidation-reduction potential. For example, $\text{Fe}(\text{OH})_2$ is stable only within a definite field; if the pH is too low, it dissolves to give Fe^{++} ; if the pH is too high, HFeO_2^- will be formed; if the oxidation-reduction potential is too low, it is reduced to metallic Fe, and if the oxidation-reduction potential is too high, it is oxidized to $\text{Fe}(\text{OH})_3$.

The oxidation potential of a vanadium ore

The pH of ground waters in contact with uranium-vanadium ores in the Colorado Plateau normally ranges from 4 to 8, but when sulfides are oxidized to sulfates under weathering conditions, values approaching the lower limit of the natural pH range (0-10) may be found (44). The natural pH environment of the ore ranges from strongly acid to slightly alkaline. The solubility of the redox-active minerals varies with pH from a minimum in the more or less neutral range to a maximum in the very acid range, as Fe, V, and U are cations, and to another maximum in the very alkaline range, as these species are easily oxidized at high pH and in their highest oxidation states are anions.

The redox-neutral electrolyte used in Eh studies on vanadium ores should be a solvent for all redox-active minerals, it should be acid because the natural environment is acid, and the acid should be the same as the acid in the natural environment. Many ores contain pyrite which upon oxidation yields sulfuric acid according to the reaction (45)



The negative value of E° indicates that the reaction proceeds spontaneously from right to left. Analyses of some spring and pore waters from the Colorado Plateau show the presence of considerable amounts of sulfate ions. A weak sulfuric acid solution should be satisfactory as redox-neutral electrolyte for vanadium ores. The acid concentration must not be too high or the solution will no longer be essentially aqueous. Of course it must be free from dissolved oxygen, or it will not be redox-neutral.

The "oxidation potential of a vanadium ore" will be used from now on to refer to the measured Eh of a dilute solution of H_2SO_4 of known pH in equilibrium with the ore, unless a different electrolyte is specified. Inasmuch as the measured oxidation-reduction system must be reversible, it is necessary for the solution to be at equilibrium, and sufficient time must be allowed before measurements are taken. As the measurement is made on the solution and not the original ore, the original ore does not need to be in a state of equilibrium for the measurement to be valid. The sulfuric acid dissolves some ore minerals and not others, and the ionic species in solution may react with each other; for this reason the oxidation-reduction equilibrium in the solution considered by itself has little meaning. There is no generally applicable method to make it significant but, as will be shown subsequently, the Eh of a given ore may in some cases be combined with other information concerning the particular ore to yield significant data. A discussion of

the equilibrium relations of some ores will be presented in a following section.

Instrumentation and method

Inasmuch as it appears necessary to make simultaneous measurements of pH and Eh under equilibrium conditions, it is desirable to have a way of determining whether equilibrium has been set up in a solution. The best way to determine whether enough time has elapsed is to repeat the determinations until the values remain constant. A convenient way to accomplish this is by use of recording instruments which can be run for long periods of time to assure constant readings. As ores may contain slowly soluble substances, it may become desirable to continue measurements for periods ranging from several hours to several days. It also is desirable to measure several samples simultaneously, as the length of individual runs may restrict the experimental output severely. Eh measurements must be taken in the absence of oxygen. The use of a controlled atmosphere requires constant attendance by an operator or the constant recording of measurements in order to detect leaks and reject spurious data. Accordingly, it was decided to construct a multiple pH-oxidation potential recorder which would meet the experimental requirements.

A MULTIPLE pH-OXIDATION-POTENTIAL RECORDER

Experimental method

The experimental technique for the determination of oxidation potentials and pH values is well known. Standard textbooks of physical chemistry, for instance Daniels et al., (46), and analytical chemistry, for instance

Kolthoff and Laitinen (47), present detailed discussions of techniques for measurement of pH and Eh and the application of such measurements to potentiometric titrations. If laboratory instruments can be used, it is possible to use a laboratory pH meter connected to a glass-calomel couple and a platinum electrode and to alternate between the glass and platinum electrodes with a single-pole double-throw switch for Eh and pH readings (48).

Available laboratory instruments could not be adapted to multiple recording and it became necessary to use industrial instruments. These are in essence direct-reading millivoltmeters of a potentiometric type which draw almost no current; this is important because the electrode potential changes if current is drawn. The operation of these instruments is very similar to that of direct-reading laboratory instruments except for the temperature compensation. Laboratory instruments as a rule have a control knob which is manually set to a reading corresponding to the temperature of the measured solution. Inasmuch as industrial instruments may be switched automatically between solutions of varying temperatures, it is not practical to adjust the temperature compensator by hand. Industrial pH meters, therefore, must provide for automatic temperature compensation; this involves mounting a temperature sensitive element alongside the electrodes. Resistance thermometers may be used for the purpose (49); as they change resistance with temperature, they modify the circuit characteristics of the pH meter to compensate for the effect of temperature change upon pH.

The apparatus

Figures 3-5 show the assembled apparatus. The following is a description of the individual components.

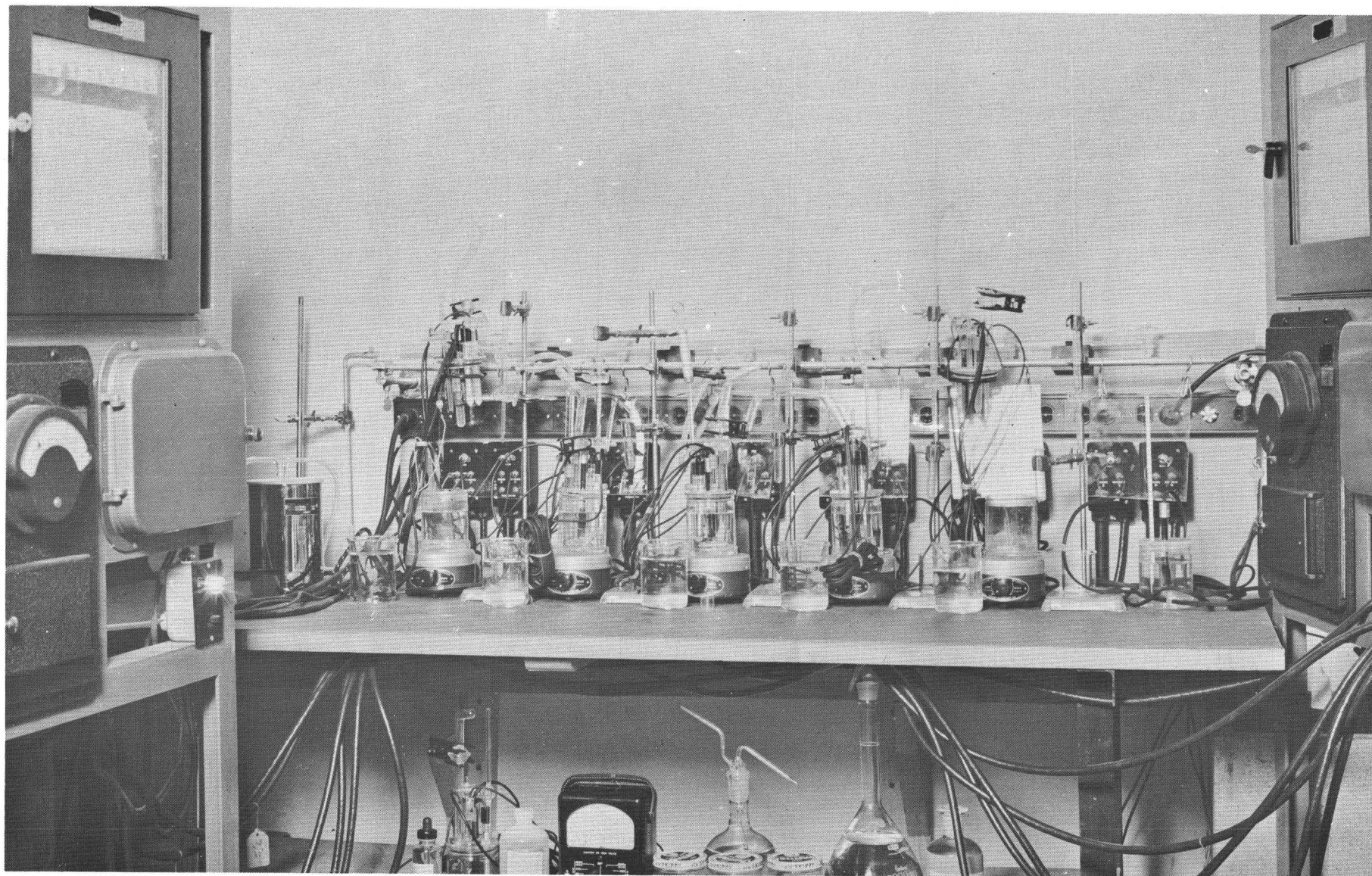


Figure 3.--Overall view of multiple pH-oxidation potential recorder assembly.

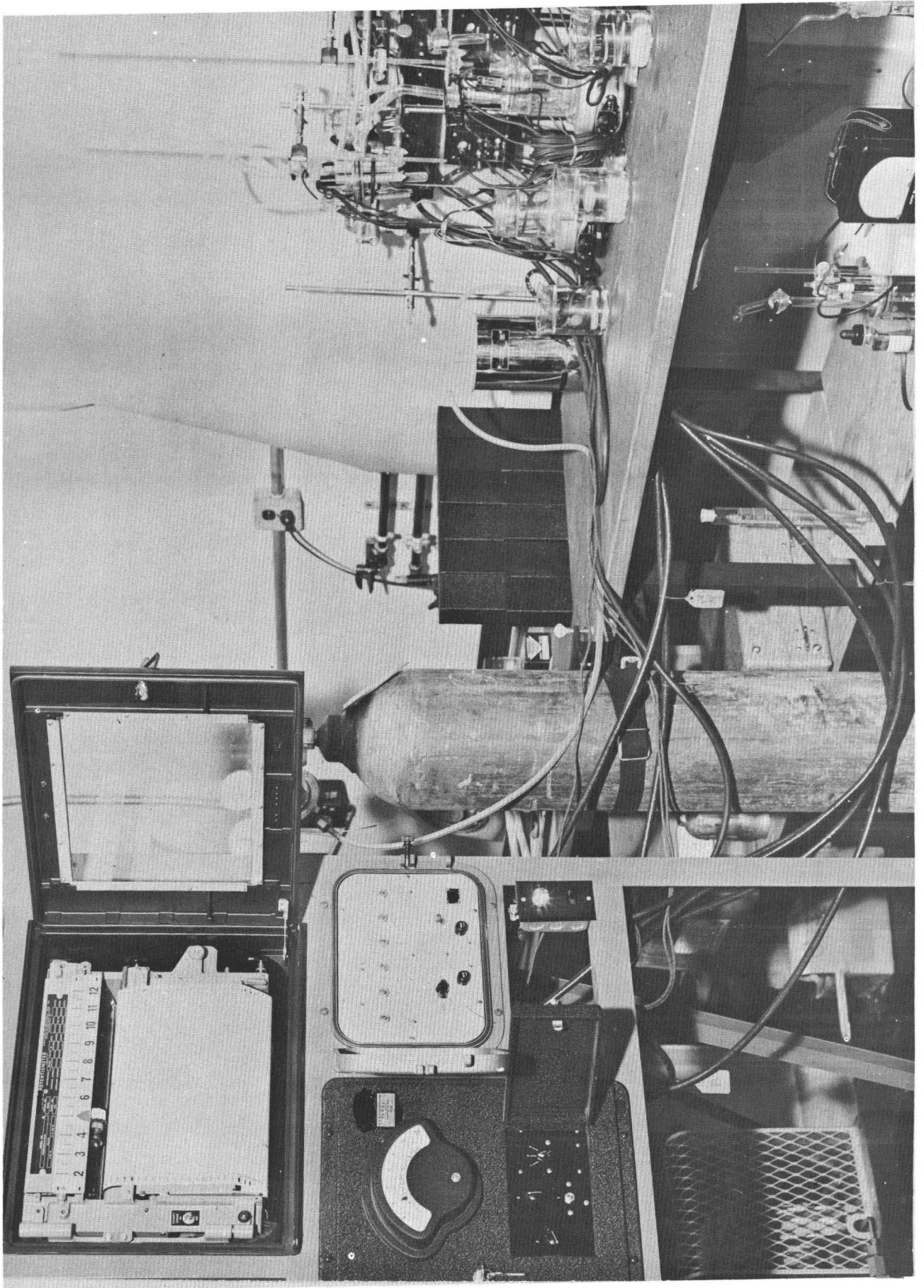
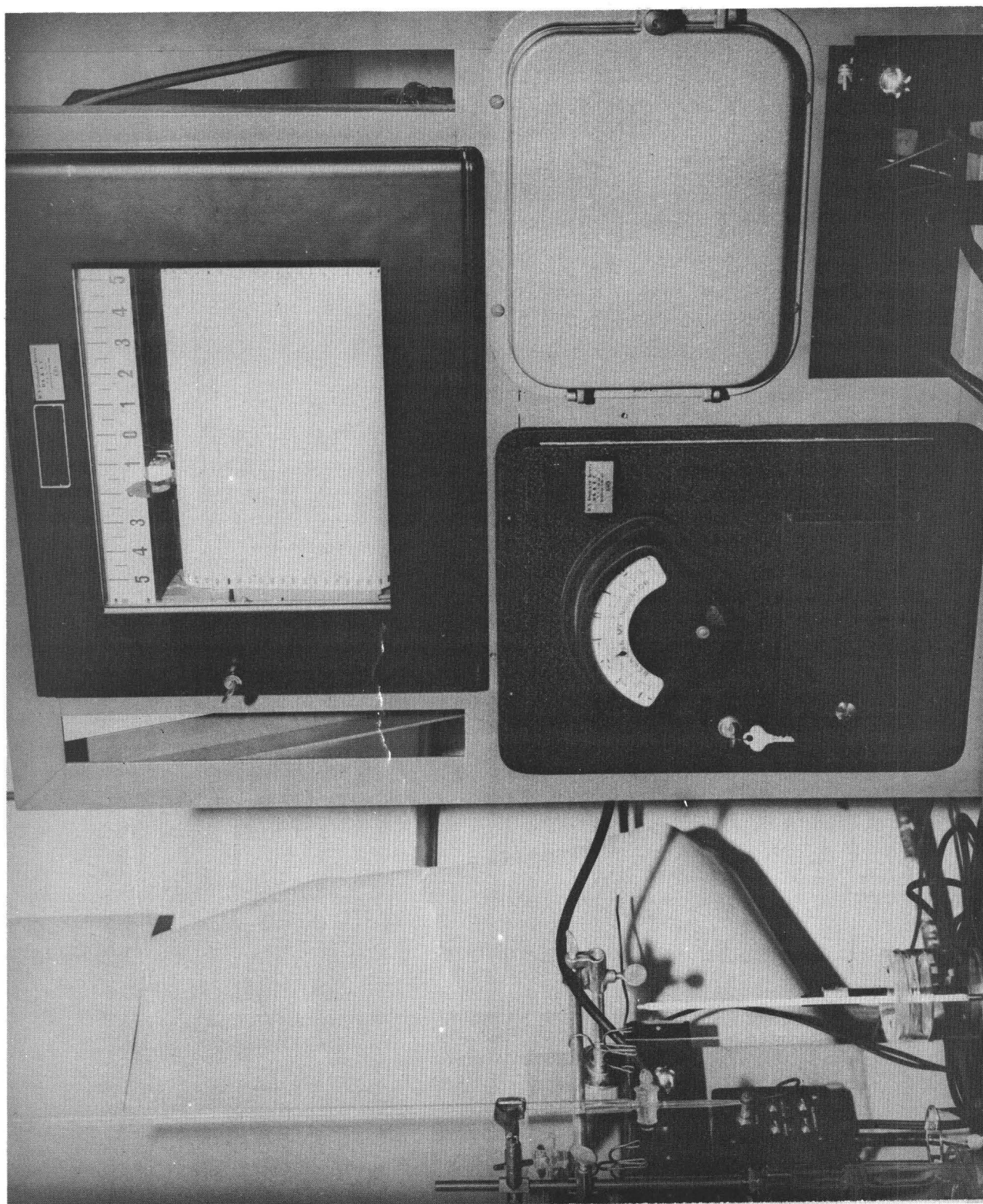


Figure 4.--pH instrument assembly.



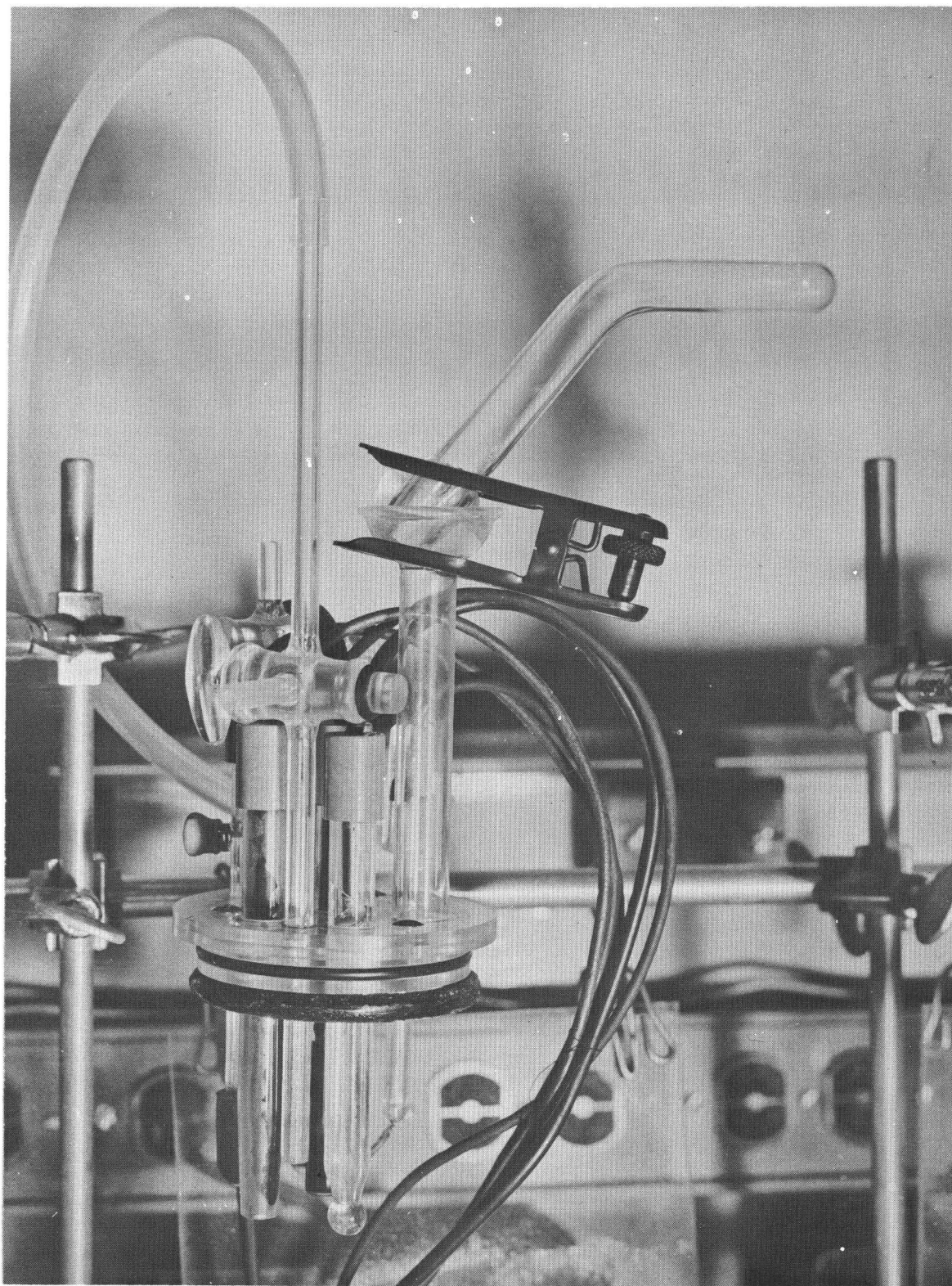
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Figure 5.--Millivolt instrument assembly

The reaction cell.--Commercial cylindrical jars, 10 cm high, with a diameter of about 8 cm and a capacity of 400 ml were used. Closures for the jars were designed by J. F. Abell, U. S. Geological Survey. Tops were made by fabricating a lucite disk, 8.6 cm diameter, 1.3 cm thick. A shoulder, 9.5 mm deep, with a diameter slightly less than the interior diameter of the jar was then machined and a 2.9-mm groove cut into the circumference of the shoulder approximately 9.5 mm from the bottom. A 7.25 cm by 2.9 mm rubber O-ring then was forced into the groove. Another lucite disk, 8.6 cm in diameter, 2.9 mm thick, was placed on top of the first disk as cover plate and secured with three metal bolts located on a 5.72 cm bolt circle. To accommodate electrodes or other devices inserted through the top, holes of the desired diameter were drilled through the top and the cover plate. The holes through the disk were counterbored 2.9 mm on top and a 2.9-mm thick rubber O-ring of suitable diameter placed thereon. The cover plate then was secured to the disk by means of the bolts, retaining the O-rings and squeezing them slightly; they now were reasonably airtight and could retain some excess pressure. The tops then were fitted with suitable electrodes. Beckman glass, platinum, and calomel reference electrodes were used. The solutions were grounded using a piece of platinum sealed in glass as solution ground. Resistance thermometers were used as temperature compensators in the pH measuring system. Glass tubes fitted with stopcocks served as gas inlets and outlets; the inlet tube had a side tube and a three-way stopcock. The outlet tube also was used as connection to a burette whenever liquids were added to the system. The inlet tube served as a device to withdraw liquid samples by means of a pipette filler. (See below.) A device for adding solids (see below) also was fitted onto the top. The jars were placed in Petri dishes to facilitate recovery of

accidentally spilled or leaked contents and then placed on magnetic stirrers. See figure 6 for illustration of top.

The cell service unit.--The reaction cells described above needed many service facilities. The glass electrode, two calomel electrodes, platinum electrode, resistance thermometer, and ground all had electrical leads requiring suitable connections. In addition, the magnetic stirrer had to be plugged in, a nitrogen stream had to be provided, the glass electrode kept wet at all times when not in use, and burettes available whenever necessary. As six reaction cells were run simultaneously, it became necessary to devise an arrangement permitting their servicing with a minimum of confusion and inconvenience. To achieve this, a cell service unit was constructed. It consisted of six individual stations. Each station contained two connector box and cable assemblies, one for the connection to the pH meter (glass and calomel electrode, ground, and resistance thermometer) the other for the connection to the millivolt meter (platinum and glass electrode). Attempts to use one calomel electrode with a split lead for both instruments or to connect the two calomel electrode outlets in both boxes with a jumper and use one calomel electrode only in the cell were unsuccessful. A power outlet was provided for the magnetic stirrers, with spare receptacles for future uses such as heaters, and a glass manifold provided a supply of nitrogen gas. Commercial "oxygen-free" nitrogen was satisfactory for this purpose. Tygon tubing was used as connection because some air diffused through the rubber tubing originally used. A ring stand was placed at every station, and all stands cross-connected by a horizontal rod, 1/2 in. in diameter, by means of Flexaframe connectors; 2 1/2 in. rings were connected to the rod in front of every station. These rings served as support for the cell tops whenever they were removed from the cells for



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Figure 6.--Top of reaction cell.

electrode cleaning, etc. Lucite plates were suspended from the rod by means of hose clamps and served as splash shields for the connector boxes. The ring stands were fitted with two clamps, one fitted with a burette, to be used for titrations, the other with a test tube containing distilled water. This clamp was placed underneath the glass electrode, and the test tube was raised in order to immerse the electrode and to prevent it from drying out during longer periods of storage. Of course, whenever the instrument was put away for very long periods, say a week or more, the glass electrode was permitted to dry out, and protective rubber caps were put on the calomel electrodes. It was convenient to place 100-ml beakers on the bases of the ring stands in order to catch small drips or to adjust the meniscus of the burettes during filling. A 400-ml beaker was placed in the vicinity of each cell. This beaker served to rinse the electrodes and glass tubes whenever the solutions were changed. Figures 7 and 8 illustrate the cell service unit with its stations.

The instrument assemblies.--Two instrument assemblies were used: the pH assembly and the millivolt assembly. The cables from the connector boxes were connected to two six-point automatic switches controlled by two six-point recording potentiometers, range -5 to +45 mv. One switch was in turn connected to an industrial direct-reading pH meter, which also was connected to the recorder controlling the switch. The other switch was connected to a millivolt indicator which also in turn was connected to the recorder controlling its switch. Each assembly also was provided with a main on-off switch and a pilot light. Figure 9 shows a block diagram of the circuit. An assembly using similar instrument components has been described (50).

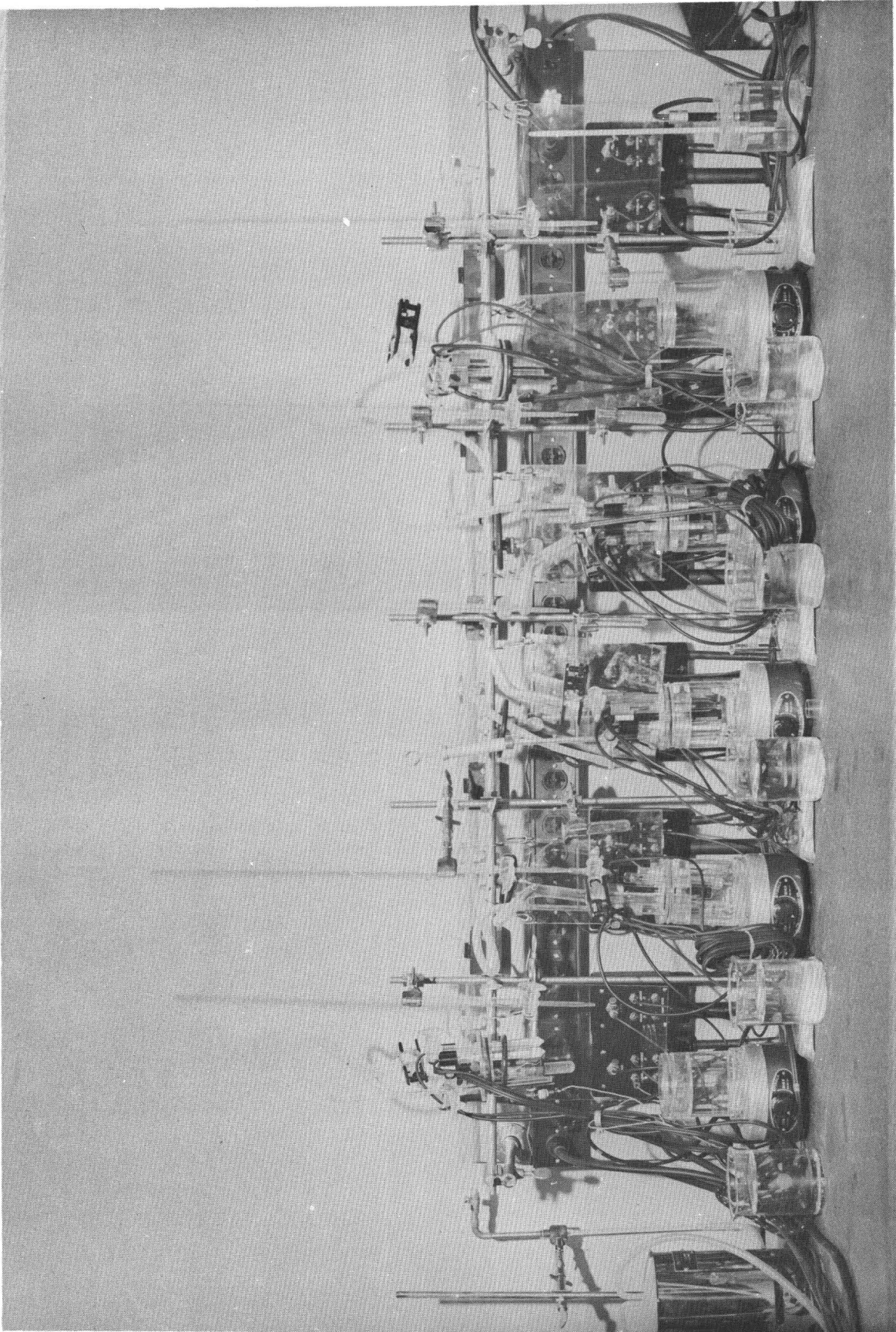
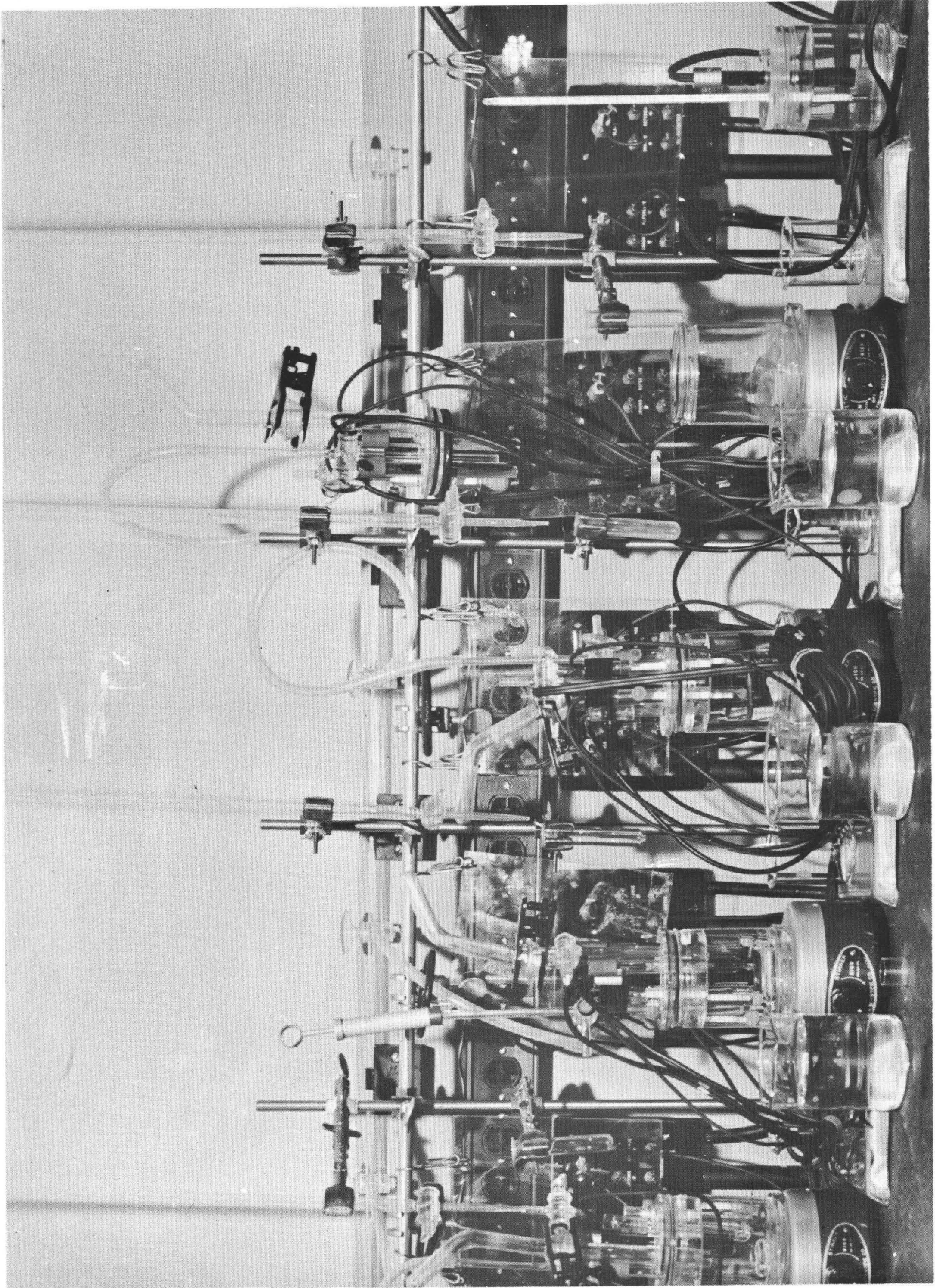


Figure 7.--Reaction cell service unit.

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Figure 8.--Close-up of reaction cell service unit.

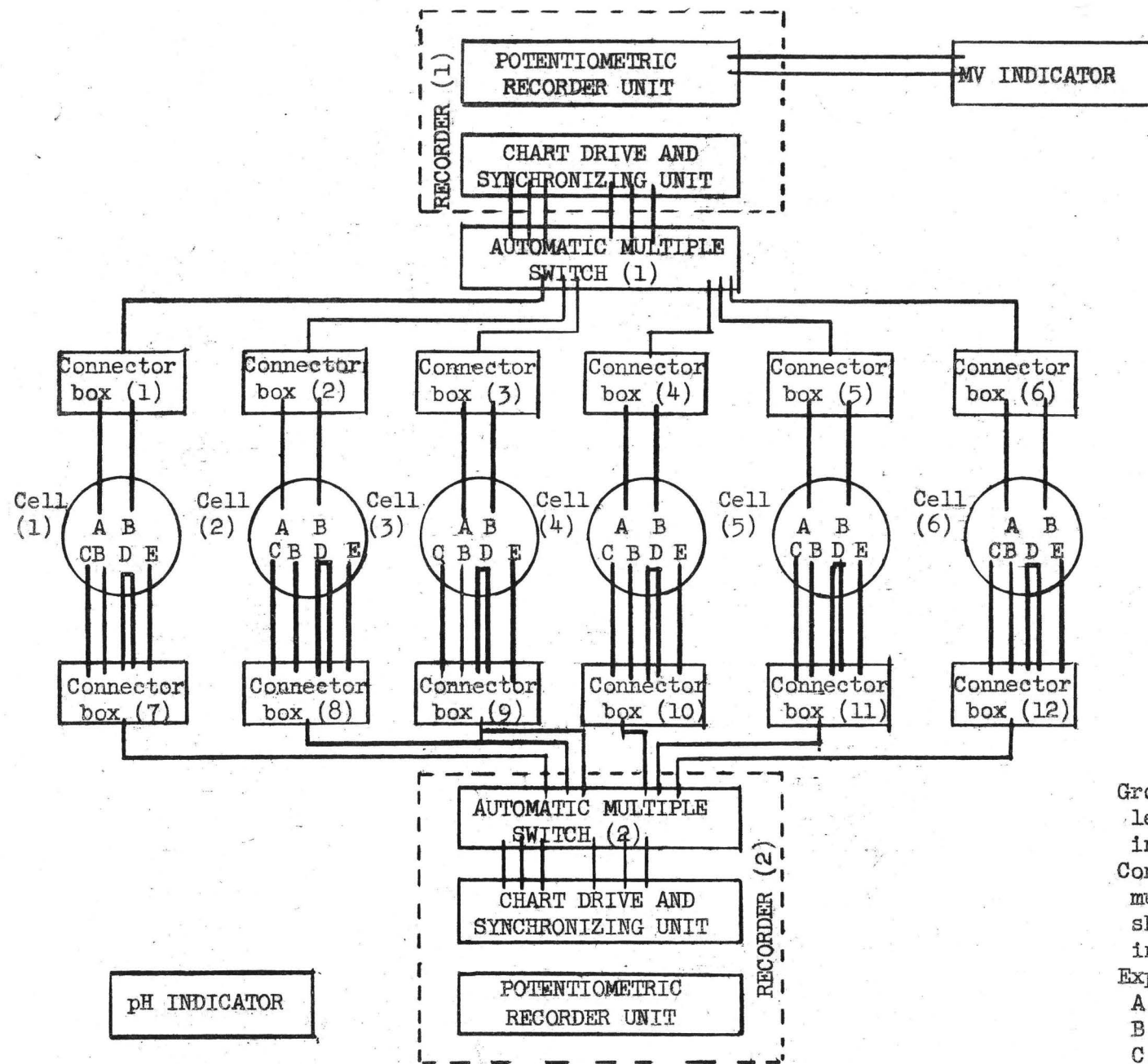


Figure 9.—Circuit diagram.

Ground connections and power leads are not shown. All instruments are grounded. Connection from automatic multiple switch to each shielded cable contains 5 internal leads.

Explanation of symbols

- A. Platinum electrodes
- B. Calomel reference electrodes
- C. Glass electrodes
- D. Resistance thermometers
- E. Platinum grounds

Experimental procedure

Placing the instrument in operation.--The instruments were prepared for operation in accordance with the manufacturer's instructions and strip charts installed in the recorders. A chart, range 2-12 pH, evenly graduated, was used for the pH assembly and a chart, range 5-0-5, evenly graduated, was used for the millivolt assembly. As the manufacturer's instructions (51,52) were difficult to follow and somewhat misleading, it is necessary to present here the sequence followed whenever the instruments were turned on:

1. Turn main on-off switch on both assemblies to ON.
2. Turn instrument power switches on both recorders to ON. Wait five minutes for amplifier tubes to warm up.
3. Turn chart drive switches on both instruments to ON.
4. Depress standardizing push button on each recorder. Repeat until pointer returns to the same position it had before button was depressed.
5. Turn chart drive switches OFF.
6. With selector switch of pH and mv indicator in no. 1 position and power switches OFF, adjust screws on face of meters until needle reads 3.0 on pH instrument and -4.0 on mv instrument.
7. Turn power switch of pH meter and millivolt meter ON. Wait about half a minute to permit indicator needle to stabilize. Adjust no. 1 controls (screw adjustments) until meters read 7.0 and 0.0, respectively.
8. Turn selector switches to position no. 2. Adjust no. 2 control knobs until recorders read 7.0 and 0.0, respectively.
9. Disconnect glass and reference electrode leads from side terminal panel of pH meter, and short circuit the glass and reference outlet of the instrument with a shielded connector and a short-circuit strap. (See fig. 10

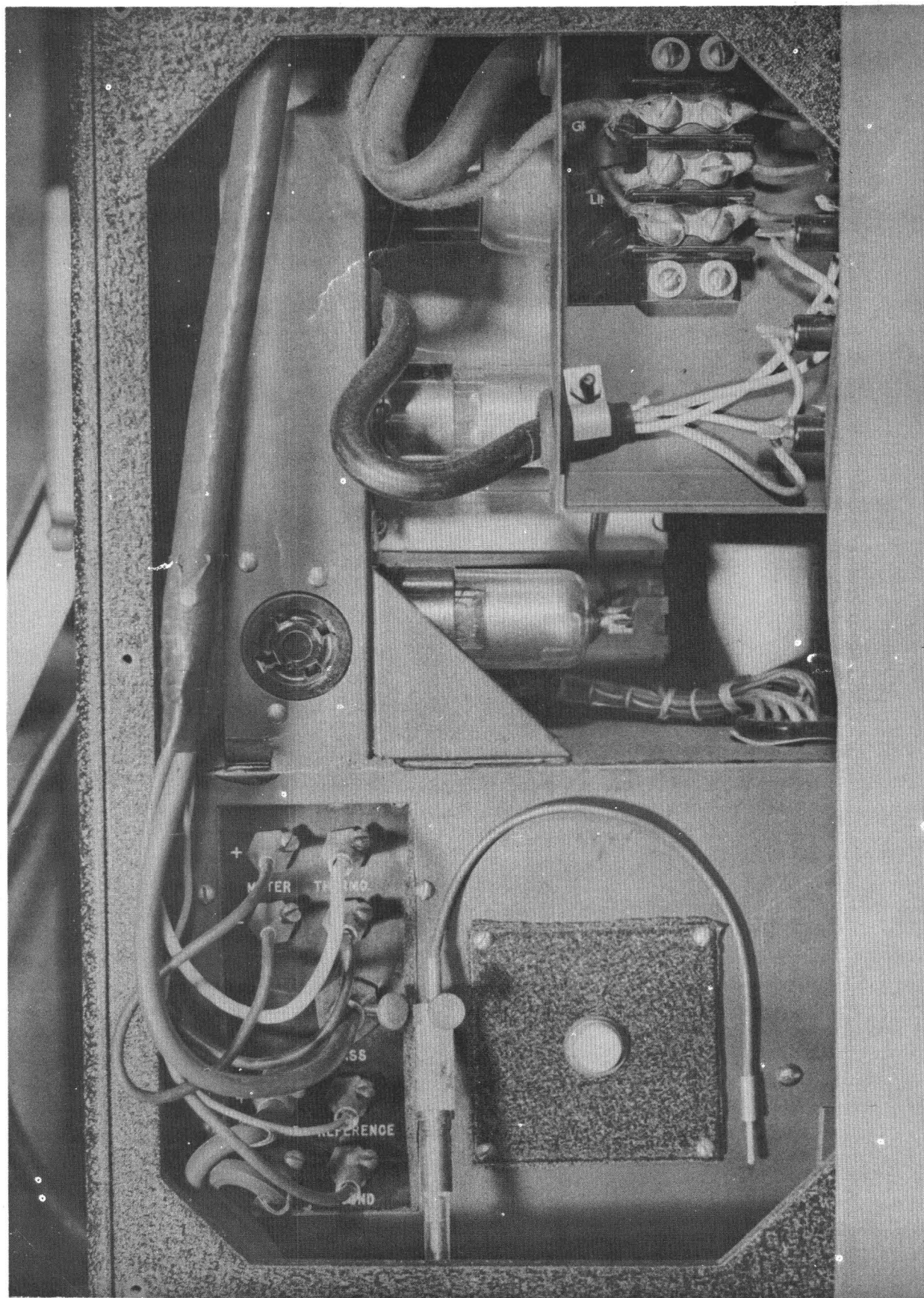


Figure 10.--Side panel of pH meter.

for view of side panel.) Connector and short-circuit strap are shown propped against lower right of panel.

10. Turn selector switch to position no. 3. Adjust no. 3 control knob until recorder reads 7.0. Turn selector switch back to position no. 2.

11. Remove connector and short-circuit strap from panel and reconnect the glass and reference leads. Steps 10 and 11 are taken for the pH meter only.

12. Turn power switch on both mechanical selector switches ON. Turn manual operating switches to their no. 1 position.

13. Fill no. 1 cell with buffer and place top on cell. Turn selector switch on pH meter to position 3, and adjust asymmetry potential screwdriver control no. 1 on mechanical switch until the recorder indicates the pH of the buffer. Return pH meter selector switch to no. 2 position. Advance manual operating switch to no. 2 position.

14. Repeat procedure 13 in no. 2 cell, advance manual operating switch to no. 3 position, and continue procedure through no. 5 cell.

15. Connect glass and reference electrode jacks of pH and mv connector box no. 6 by means of Model 700 connectors and short circuit straps. Place a resistance thermometer into a jar filled with distilled water and connect to pH connector box no. 6 jacks. Equip jar with a thermometer. Assuming that all cells in the room are at equal temperature, the temperature may then be read for all cells on cell no. 6. This cell also serves as a control during operation by continuing to print the instrument zero. With the manual operating switch of the automatic switch in the pH assembly in the no. 6 position, throw the selector switch of the pH meter in the no. 3 position, adjust the no. 6 asymmetry potential screwdriver control of the automatic switch until the recorder reads 7.0 and return the selector switch to the

no. 2 position.

16. Place the tops of cells 1-5 on the supporting ring, rinse the electrodes with distilled water, wipe with absorbent tissue. Immerse the glass electrodes in distilled water using the test tubes clamped to the ringstands for this purpose.

17. If desired, the platinum electrodes may be checked by immersing the platinum-calomel couple in a solution of known redox potential and observing the millivolt reading. ZoBell (53) recommends a solution M/300 in potassium ferrocyanide, M/300 in potassium ferricyanide, and M/10 in potassium chloride for this purpose. At 25° C this solution should give a reading of +185 mv. If the platinum electrodes are checked, step 16 must be repeated.

18. Follow the sequence given here for both instrument assemblies:

- a) Turn recorder chart drive switch ON.
- b) Permit printing mechanism to operate until the number one appears opposite the small red index on the print wheel carriage.
- c) Turn chart drive switch OFF. The manual operating switch of the selector switch should be in the no. 1 position.
- d) Turn manual operating switch to AUTO.
- e) Turn chart drive switch ON, record one cycle and turn instrument selector switches to position 3. The instrument assemblies are now ready for operation in all cells. In order to achieve stability of the circuit and to avoid drifting of the instrument, it is best to leave the instrument turned on at all times. In this case, only steps 3-5, 8, 13-14, and 16-18 must be repeated before every run.

If the instrument is run in one cell only, steps 3-5 and 8 are carried out as usual. The manual operating switches are placed in the position

corresponding to the number of the cell and steps 13, 16, and 17 are carried out for the one cell only, followed by step 18e.

Operating the instrument.--Generally speaking, the operation of the instrument presented no problem. pH and mv values were automatically recorded on the strip charts, and could be obtained therefrom whenever desired. There were, however, some operations which should be described in more detail.

a) Dissolving a solid in an oxygen-free atmosphere. The cells were charged with a solvent and the solid was put into the bent glass tube and a stream of nitrogen was passed through. The mv indicator was used to determine whether any dissolved oxygen likely to interfere with the run remained in solution. When the cell had been swept satisfactorily, the solid was added by tilting the glass tube and tapping until any material sticking to the glass had been dislodged.

b) Checking the glass electrode during a run. It is good practice to check glass electrodes against a buffer at regular intervals. As the glass electrodes could not be removed without interrupting the run and it was not practical to introduce buffer and rinsing facilities into a closed system, the following method was used:

- 1) Turn off stopcocks at gas inlet and outlet tubes, and disconnect gas supply.
- 2) Place pipette filler on inlet tube.
- 3) Open stopcock (side tube disconnected), aspirate solution above level of stopcock, and close stopcock.
- 4) Turn stopcock into position to connect upper tube with side tube (lower tube disconnected). The solution will run out through the side tube and may be collected in a 5-ml beaker. If an insufficient sample is obtained, repeat the operation.

5) Reconnect gas supply, open stopcocks on gas inlet and outlet tubes, and resume bubbling.

6) Check pH of withdrawn sample in pH meter with freshly standardized electrodes.

7) If necessary, adjust asymmetry potential screwdriver control on mechanical switch until pH recorder shows the reading obtained in step 6.

c) Shifting the range. The range of the instruments may be changed by adjusting the no. 1 and no. 2 controls of the pH and mv indicators to give a reading other than pH 7.0 and mv 0. If the pH meter is set to read 9.0 with the selector switch in the no. 2 position, every reading will be high by 2 pH units. The range of the instrument then is shifted from 2-12 to 0-10 pH units, and a correction of -2.0 must be applied to every reading. The reading of cell no. 6 will automatically record the zero to which the instrument is set, and it is easy to know at all times whether and what corrective factor to apply. It must be noted that this shift must apply to all cells in use at a given time.

d) Titrating during a run. It is easy to perform acid-base or redox titrations while recording. A burette is placed over the gas outlet tube and the liquid added against the gas stream. Deaerated titrants may be prepared but are not always necessary. By using two burettes, it should be possible to perform redox titrations at constant pH and acid-base titrations at constant Eh, though this is a very tedious procedure. If a titration is carried on very slowly, it is sometimes preferable to add the titrant from a pipette to avoid errors caused by the evaporation of the titrant in the burette. Some titrations were carried on drop by drop for several days. If this procedure is followed, the titrant must be standard-

ized by pipette using the same technique.

Collection of data

Any correction factors necessary owing to range shifting are applied first. The pH values then are ready for use. Mv values must be converted to Eh by adding the potential of the reference electrode at the temperature of the experiment to the mv reading; at 25° C the potential of the saturated calomel electrode was assumed to be 245 mv, the average of 244.3 (54) and 245.8 (55) mv.

A complete record of all actions and occurrences may be kept conveniently on the recording tape. For example, during a titration the amount of titrant added at any time is written on the tape. The tape moves at a preset rate, and the curves appearing on the tape are pH-time and mv-time curves. If the notations are written in proper position relative to the time axis, they can easily be related to the readings. At the end of a titration it is then possible to plot the equilibrium pH or mv reading (as determined by a value constant with time, after the curve stops drifting). As in any potentiometric titration the total amount of titrant added by the time the "break" appears corresponds to the equivalent amount.

The instrument may now be applied to the study of the origin of the vanadium ores. In this connection it appears that the first question which must be answered is: what is the significance of the Eh of a vanadium ore, and how can it be interpreted?

OXIDATION POTENTIAL STUDIES ON SOME VANADIUM ORES AND THE
RELATION OF THE STATE OF OXIDATION AT THE PRESENT
TIME TO THAT AT THE TIME OF DEPOSITION

Oxidation potential and state of oxidation

As the oxidation potential depends upon the ratio of oxidized to reduced ion activities, it is possible to use Eh data to study the state of oxidation of an ore. In this connection the following questions arise:

- a) The electrolyte used in Eh measurements on vanadium ores contains redox-active ions. Which ions are present and in what amounts?
- b) What is the state of oxidation of the redox-active elements in the ore? Are the redox-active minerals in thermodynamic equilibrium?
- c) What was the state of oxidation of the redox-active elements at the time of deposition of the ore?

It is now necessary to determine the requirements for the selection of actual ore samples for study. So-called channel samples appear most suitable for this purpose. A channel in a quarry is a cut along the line where rock or stone is to be split, and some geologists refer to a series of contiguous specimens cut from rock along a line as a channel sample. If an ore deposit is selected where the state of oxidation of the redox-active minerals varies along a spatial direction, a series of contiguous specimens may be selected which will yield information concerning the oxidation or reduction processes in the ore. If such processes occur, the remaining ore minerals in their present state constitute the products of the reaction. If in turn the reaction becomes known, the reactants may be identified. These reactants are the redox-active ore minerals in their original state. It then appears that a channel sample containing vanadium ores in different states of

oxidation should be a good source of material for Eh studies.

Channel sample from the Mineral Joe mine

The Mineral Joe is a vanadium-uranium mine in the Jo Dandy group of mines approximately 10 to 15 miles west of Naturita, Montrose County, Colorado. R. M. Garrels and H. T. Evans, Jr., U. S. Geological Survey, made a reconnaissance of a number of these mines and selected a channel sample from the Mineral Joe mine which consisted of 18 individual specimens labeled A-Q. The sample appeared suitable for detailed studies because it ranged from unmineralized sandstone (samples A-E) through a heavily mineralized zone (samples F-Q) which apparently contained ores in different oxidation states as evidenced by the color. Yellow and brown regions indicating a high state of oxidation (samples F-M, P-Q) and black colors indicating more reduced ores (samples N-O) were present. The samples represent an almost continuous strip of rock.

Sample preparation

The samples were wrapped in aluminum foil when collected but were left freely exposed to relatively dry air in the laboratory. Part of each sample was reserved for mineralogic and petrographic studies, and part was crushed to -40 mesh for chemical work, with special care taken to avoid contamination. About 1 percent of each sample was lost during crushing; the loss was mostly caused by the necessity to discard some of the material contaminated by the paint used in the original marking of the sample. For most of the chemical work 0.5-gram samples were obtained by careful hand splitting.

Equilibrium relations between the redox-active ions in solution

Semiquantitative spectrographic analysis (56) indicated that Fe, U, and V were the only redox-active elements present in amounts exceeding 0.05 percent in any sample (57), and it was necessary to consider the equilibrium relations of the redox-active species. Equations for the reversible oxidation-reduction equilibria involving ions of V, U, and Fe in aqueous solutions at $\text{pH} < 1.5$ are given in table 2.

If the activity ratio in these equations is expressed as percentage ratio, where % oxidized species + % reduced species = 100% for each equation, and if Eh^0 is defined as the Eh when $\text{pH} = 0$, then equations (3), (4), (5), and (6) may be plotted conveniently as functions of Eh^0 and percent of oxidized species (fig. 11) and it is possible to determine the activity ratios graphically. For equations (3), (4), and (5), $\text{Eh}^0 = \text{E}^0 + 0.12 \text{ pH}$, and for equation (6) $\text{Eh}^0 = \text{E}^0$.

Activity ratios of Fe, V, and U ions in acid extracts of ore samples may be determined as follows:

- 1) Determine the Eh and Ph of the sample.
- 2) Compute $\text{Eh} + 0.12 \text{ pH}$.
- 3) Find the intersection of Eh and line $\text{Fe}^{+++}/\text{Fe}^{++}$ on figure 11. The ordinate of this point is numerically equal to the activity ratio of ferric iron to total iron in solution.
- 4) Find the intersection of $(\text{Eh} + 0.12 \text{ pH})$ with the other lines on the graph and determine the vanadium and uranium activity ratios.

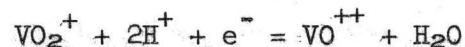
The activity ratios of the Mineral Joe ore sample in approximately 1 N H_2SO_4 were determined by this method and are presented in figure 12. The Eh values are plotted on the $\text{Fe}^{+++}/\text{Fe}^{++}$ line and $(\text{Eh} + 0.12 \text{ pH})$ values

Table 2.--Oxidation-reduction equations for Fe, V, and U ions in acid solutions (pH < 1.5).

Reaction	E°	Oxidation potential equation
$\text{VO}_2^+ + 2\text{H}^+ + \text{e}^- = \text{VO}^{++} + \text{H}_2\text{O}$	1.000 (58)	$\text{Eh} = 1.000 + 0.06 \log \frac{\text{VO}_2^+}{\text{VO}^{++}} - 0.12 \text{ pH}$ (3)
$\text{VO}^{++} + 2\text{H}^+ + \text{e}^- = \text{V}^{+++} + \text{H}_2\text{O}$	0.337 (59)	$\text{Eh} = 0.337 + 0.06 \log \frac{\text{VO}^{++}}{\text{V}^{+++}} - 0.12 \text{ pH}$ (4)
$\text{UO}_2^{++} + 4\text{H}^+ + 2\text{e}^- = \text{U}^{++++} + 2\text{H}_2\text{O}$	0.334 (60)	$\text{Eh} = 0.334 + 0.03 \log \frac{\text{UO}_2^{++}}{\text{U}^{++++}} - 0.12 \text{ pH}$ (5)
$\text{Fe}^{+++} + \text{e}^- = \text{Fe}^{++}$	0.771 (61)	$\text{Eh} = 0.771 + 0.06 \log \frac{\text{Fe}^{+++}}{\text{Fe}^{++}}$ (6)

Note: Oxidation potential equations are derived as illustrated below.

For the reaction



$$\text{Eh} = 1.000 + 0.06 \log \frac{\text{VO}_2^+(\text{H}^+)^2}{\text{VO}^{++}} = 1.000 + 0.06 \log \frac{\text{VO}_2^+}{\text{VO}^{++}} + 0.06 \log (\text{H}^+)^2$$

but

$$\log (\text{H}^+)^2 = 2 \log \text{H}^+$$

and

$$\text{Eh} = 1.000 + 0.06 \log \frac{\text{VO}_2^+}{\text{VO}^{++}} + 0.12 \log \text{H}^+$$

by definition

$$\text{pH} = -\log \text{H}^+$$

therefore

$$\text{Eh} = 1.000 + 0.06 \log \frac{\text{VO}_2^+}{\text{VO}^{++}} - 0.12 \text{ pH} \quad (3)$$

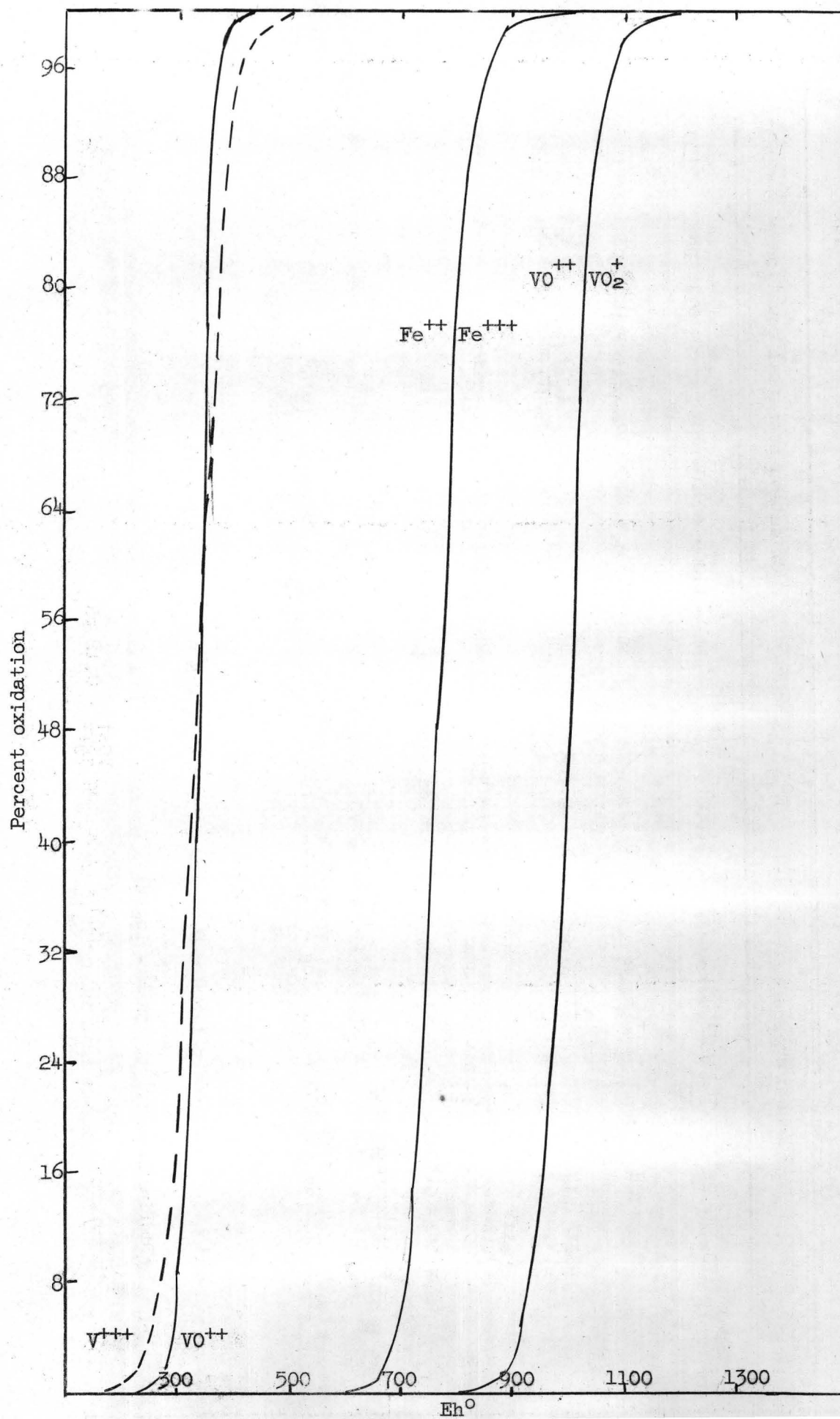
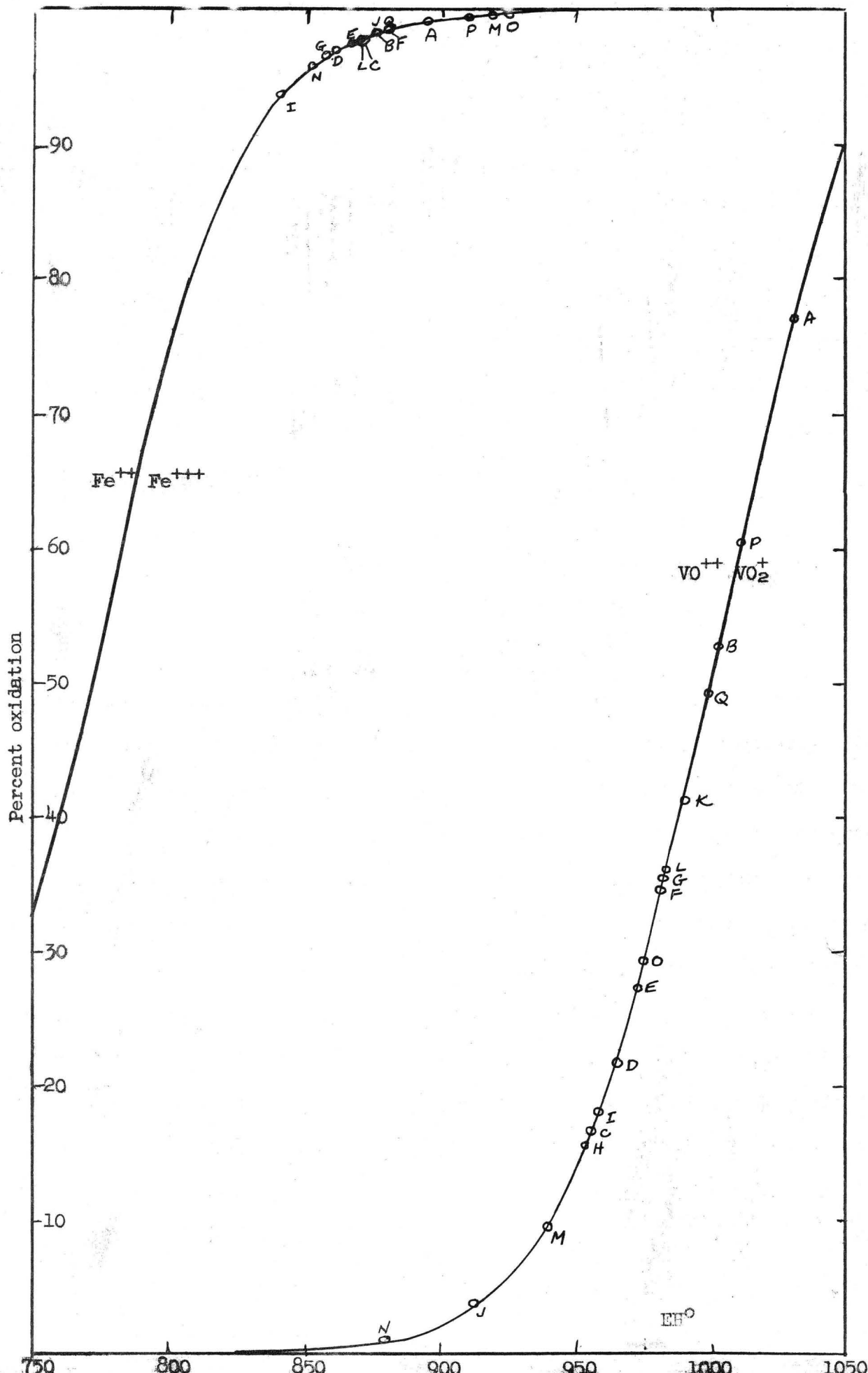


Figure 11. Eh° as function of "percent of oxidized species".

Figure 12.-- Eh° of Mineral Joe ore samples.

are plotted on the $\text{VO}_2^+/\text{VO}^{++}$ line.

As the necessary activity coefficients are not available, it is impossible to convert the activity ratios to concentration ratios. It is possible, however, to determine at any given Eh which concentrations are vanishingly small, as the activity of any ion in solution at extreme dilution is equal to its concentration. It is therefore possible to show the following from an inspection of figure 11: that in aqueous solutions at a pH of less than 1.5,

1. VO_2^+ and V^{+++} cannot coexist.
2. VO_2^+ and U^{++++} cannot coexist.
3. VO_2^+ and Fe^{++} cannot coexist.
4. Fe^{+++} and V^{+++} cannot coexist.
5. Fe^{+++} and U^{++++} cannot coexist.

It is possible to determine from these relations the concentration of all ionic species present in solution in appreciable amounts, provided that the total amount of Fe, V, and U, present is known, and that the reducing capacity of the solution is known. The reducing capacity (RC) of a sample refers to the amount of oxidant the sample can reduce. The term RC without qualification is used only if the oxidant used can oxidize each ionic species to its highest state of oxidation.

The reducing capacity may conveniently be expressed in milliequivalents per 100-gram sample. The reducing capacity expressed in this unit is given by the number of milliliters of a 1 N solution of oxidant reduced by a 100-g sample. As it is necessary to consider the reducing capacity of a sample in conjunction with its chemical composition, it is also convenient to express chemical composition in milliequivalents per 100-gram sample. If the equivalent weight of the oxidant is defined as the amount necessary to

oxidize one mole of any ion by removal of a single electron, a milliequivalent of any element is equal to one millimole of this element. For example, a specimen assaying 1 percent V_2O_5 or 0.56 percent V contains 0.56 g V or 11 millimoles V per 100 g; similarly, a specimen assaying 1 percent Fe_2O_3 contains 0.7 g Fe or 12 1/2 millimoles Fe per 100 g. The V or Fe content of an ore or solution in meq/100 g will be denoted by the symbols \underline{V} and \underline{Fe} .

A solution containing no redox-active elements other than U, V, and Fe has a reducing capacity of zero if all elements are in their most oxidized form. UO_2^{++} , Fe^{+++} , and VO_2^+ will be the only redox-active ions present.

If $0 < RC < \underline{V}$, VO^{++} is also present, but Fe^{++} , V^{+++} , or U^{++++} cannot coexist with VO_2^+ , as these ions do not appear in appreciable quantities if $RC < \underline{V}$. Under these conditions the reducing capacity results from the presence of VO^{++} only, and the Eh will be controlled by equation (3).

If $RC > \underline{V}$, VO_2^+ is substantially absent; Fe^{+++} may be expected to be present if $RC < (\underline{V} + \underline{Fe})$. But in the presence of Fe^{+++} , V^{+++} and U^{++++} cannot exist. The reducing capacity in this case results from the presence of VO^{++} and Fe^{++} and $(RC - \underline{V})$ results from the presence of Fe^{++} . The Eh now will be controlled by equation (4).

If $RC > (\underline{V} + \underline{Fe})$, neither VO_2^+ or Fe^{+++} can be present. Under these conditions the solution may contain any of the reduced ions, and the Eh is controlled by equations (5) and (6). In this connection it must be borne in mind that neither uraninite or coffinite, in the absence of air, will dissolve in dilute sulfuric acid to any appreciable extent and the presence of U^{++++} ions is unlikely. If U^{++++} ions can be excluded for this reason, any excess of RC over $(\underline{V} + \underline{Fe})$ results from the presence of V^{+++} ions. In this case, RC cannot exceed $(2\underline{V} + \underline{Fe})$, the limiting value for a totally reduced ore.

It is important to make allowance for the insolubility of pyrite in determining Fe; this usually entails a separate determination of acid soluble iron.

In any consideration of solubility relations it must be borne in mind that ferrous iron may be present in clays. Such clays may decompose only very slowly in dilute sulfuric acid, and their solution rate in strong sulfuric acid solutions is not too fast unless the solutions are heated.

Chemical studies on Mineral Joe ore samples

Table 3 summarizes the results of some analytical determinations on Mineral Joe ore samples.

It may be noted that the amount of acid insoluble uranium in any sample is vanishingly small compared to the total uranium present. This indicates that no U(IV) is present in the ores and is in line with what may be expected from a consideration of the Eh^0 values of the samples (fig. 12).

The redox-active ionic species present in the solutions of the samples are shown in table 4. Here it can be seen that sample N is the only sample yielding Fe^{++} ions in solution; and an inspection of table 3 reveals that it is the only sample containing a significant amount of acid insoluble iron. Both observations indicate the presence of pyrite in sample N only, and a mineralogical investigation (63) confirmed that only sample N contained a significant amount of pyrite.

Table 3.--Chemical analysis of Mineral Joe ore samples (62).

Sample no.	Acid sol. RC meq/100 g sample (a)	Total V ₂ O ₅ (percent)	Total Fe ₂ O ₃ (percent)	Acid soluble Fe ₂ O ₃ (a) (percent)	Total U (percent)	Acid insoluble U (b) (percent)
A	1.88	0.20	0.32	0.24	0.003	0.0005
B	1.88	0.24	0.17 (c)	0.18 (c)	0.003	0.0002
C	2.12	0.14	0.16	0.12	0.005	0.0004
D	1.79	0.18	0.14	0.12	0.003	0.0004
E	1.55	0.18	0.16 (c)	0.17 (c)	0.003	0.0006
F	19.39, 19.47	1.94	1.16	1.09	0.005	0.0005
G	29.00, 29.09	2.52	0.91 (c)	0.92 (c)	0.066	0.0010
H	17.74, 17.41	2.12	0.94	0.88	0.25	0.0014
I	20.04, 20.18	3.36	1.33	1.20	0.42, 0.47	0.0020
J	19.47, 20.37	3.68	1.41	1.38	0.36	0.0022
K	19.88, 20.37	2.96	0.79	0.72	1.22	0.0095
L	26.78, 25.80	3.60	1.70	1.68	0.85	0.0027
M	29.66, 29.50	5.60	2.26	2.22	1.26	0.0050
N	102.04	7.40	6.30	2.54	1.13	0.0112
O	59.42	8.60	0.97	0.94	1.88, 1.90	0.0113
P	30.07	3.12	1.19	1.16	1.74	0.0042
Q	7.71	0.84	0.54	0.50	0.009	0.0015

(a) Acid soluble refers to the fraction soluble in 33 1/3 percent H₂SO₄.

(b) Acid insoluble refers to the residue after 24 hour extraction with cold 1 N H₂SO₄.

(c) Discrepancy of 0.01 percent within permitted limit of accuracy.

Table 4.--Determination of ionic species in acid extracts of Mineral Joe ore samples.

Sample no.	<u>V</u> meq/100 g	Fe acid soluble meq/100 g	RC acid soluble (a) meq/100 g	RC > <u>V</u>
A	2.2	3.0	1.9	No (b)
B	2.6	2.2	1.9	No (b)
C	1.5	1.5	2.1	No (b)
D	2.0	1.5	1.8	No (b)
E	2.0	1.6	1.6	No (b)
F	21.4	14.5	19.5	No (b)
G	27.7	11.4	29.1	No (b)
H	23.5	11.0	17.6	No (b)
I	36.9	15.0	21.1	No (b)
J	40.4	17.6	19.9	No (b)
K	32.5	8.8	20.2	No (b)
L	39.5	21.2	26.3	No (b)
M	61.6	28.0	29.6	No (b)
N	81.4	33.8	102.0	Yes (c)
O	94.6	11.8	59.4	No (b)
P	34.3	14.5	30.1	No (b)
Q	9.2	6.7	15.4	No (b)

(a) Determined by titration with 0.1 N KMnO_4 (Analyst: L. B. Jenkins, U. S. Geological Survey).

(b) Ions present in electrolyte: V(V) V(IV) Fe(III), U(VI).

(c) Ions present in electrolyte: V(IV) Fe(III) Fe(II), U(VI).

Equilibrium relations between redox-active
minerals in ores

In nature many ores are in contact with water and may be expected to be at thermodynamic equilibrium. As the state of oxidation of elements in most minerals is known, because these minerals have been chemically characterized, it is possible to determine whether thermodynamic equilibrium between associated minerals exists, provided the equilibrium relations are known.

Garrels (64) calculated the thermodynamic equilibrium relations between the redox-active ore minerals of the Colorado Plateau. These resemble the relations of redox-active ions in solution discussed before with one important exception: V(IV) and Fe(III) may not coexist under equilibrium conditions, whereas V(V) and Fe(II) minerals may be in equilibrium with each other.

It now appeared that all Mineral Joe ore samples with the exception of N should contain V(V) minerals and Fe(II) minerals, but no Fe(III) minerals. Mineralogic investigations showed (63) that these specimens contained V(V) minerals and no Fe(III) minerals except for samples M and O, which were adjacent to sample N and where some reduced minerals could be found. Widely scattered dark spots of Fe(III) minerals could be found on some of the specimens, but the presence of Fe(II) minerals was not obvious on microscopic examination. As clays were present, it was likely that they contained Fe(II).

Inasmuch as it appeared that the ores contained V(V) minerals which were easily soluble and Fe(II)-bearing clays which could be expected to decompose only slowly, it became apparent that Eh measurements would confirm this relationship if it actually existed.

Eh-time curves: The "self-titration" of an ore

If an ore of the type discussed here is suspended in sulfuric acid and its Eh measured, the following may be expected: the vanadium (V) minerals dissolve immediately, and the Eh of the solution is considerably higher than 1000 mv, the E^0 of equation (3). The solution now contains VO_2^+ ions. The clays decompose slowly, releasing Fe^{++} ions which react with VO_2^+ to yield VO^{++} and Fe^{+++} ions. As the VO_2^+/VO^{++} ratio drops, the Eh drops slowly, until almost all of the VO_2^+ ions are reduced. The solution now contains VO^{++} and Fe^{+++} ions. As more Fe^{++} ions are released, they remain in solution, and change the Fe^{+++}/Fe^{++} ratio. The solution now is highly unpoised with respect to vanadium ions, but well poised with ferric/ferrous ions, and this equilibrium now controls the Eh. Under the circumstances a rather sharp drop in Eh may be expected whenever the VO_2^+ ions are reduced, and the Eh should finally stabilize in the vicinity of 771 mv, the E^0 of the Fe^{+++}/Fe^{++} couple. In other words, the ferrous ions reduce the vanadium (V) ions and the sample "titrates itself".

Four specimens of the Mineral Joe ore samples were selected for Eh-time studies. They were suspended in 33 1/3 percent sulfuric acid in a nitrogen atmosphere and their Eh taken daily. All samples showed a break after 4 to 6 weeks (fig. 13) and all Eh values were in the predicted range, indicating the presence of soluble V(V) minerals and difficultly soluble Fe(II).

The state of oxidation of the ore at the time of deposition

The ore in its original state at time of deposition is often referred to as primary ore. It is readily apparent that a study of the origin of an ore must take into account the condition of the primary ore.

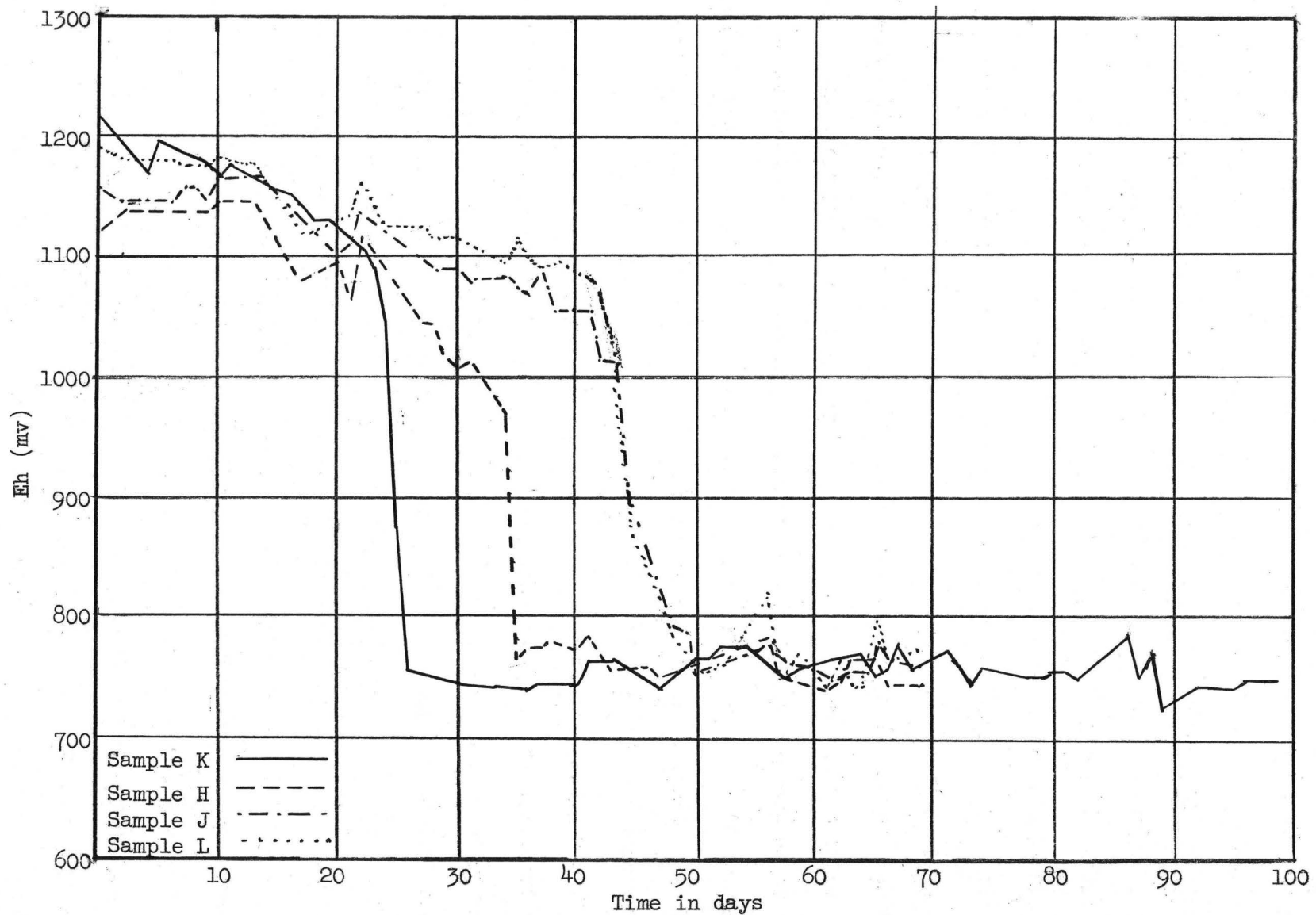


Figure 13.--Eh-time curves on some Mineral Joe channel samples.

The state of oxidation of the primary ore minerals must be different from the state of oxidation of the present minerals, for example, uraninite--the primary ore mineral--has been altered to carnotite. The present ores contain Fe (II) and vanadium (V) and were originally deposited from solutions; but these ions cannot coexist in acid solutions and Fe (II) is insoluble in alkaline solutions. Therefore, they must have been oxidized or reduced after they were deposited.

It is impossible to conceive of a reducing agent which can reduce ferric iron protected in a clay matrix and which would leave vanadium (V) in its oxidized state. We also know that the minerals after being deposited were exposed to air and subject to oxidation. For this reason it seems more logical to suggest that they were originally deposited in a reduced state and oxidized in place. The postulate that the clay matrix protected the Fe, while air oxidized the V, furnishes the only reasonable explanation of the experimental results.

The suggestion that the vanadium-uranium ores in the Colorado Plateau were deposited in their reduced form and later oxidized is not new. It had been proposed in general form previously by many authors, but Garrels (64) showed from thermodynamic considerations that it presented a consistent picture. Evans and Mrose (65) presented crystal chemical evidence that the vanadium (IV) mineral paramontroseite is metastable and may be formed only by oxidation of the vanadium (III) mineral montroseite. As considerable paramontroseite is present in sample N (63), it is mineralogical evidence that the vanadium originally was V(III).

If the ore of the Mineral Joe channel sample originally was in a reduced state and later oxidized in place, it may be expected that oxidation commences at the ore boundary and works toward the center. If an ore is examined during

an intermediate phase, after weathering has started but before it is completed, the ore should be more reduced in the center and more oxidized toward the edges. The Mineral Joe channel sample shows this pattern: sample N is most reduced and is surrounded by more oxidized ore.

The mechanism of ore deposition

As the evidence presented herein indicates that the vanadium ores were deposited in a reduced form by precipitation from a solution, it is now necessary to consider the mechanism of precipitation. The reduced ore minerals are largely oxides or hydrated oxides of V(III) and U(IV), and the questions which present themselves are:

- a) What was the composition of the solution from which the ore was precipitated?
- b) What was the mechanism of precipitation?

There are only two reasonable possibilities for the precipitation of reduced hydroxides: 1) Precipitation from reduced solution by increase in pH. 2) Precipitation from an oxidized solution by reduction.

The association of woody material, a reducing agent, with the ore which was originally precipitated in a reduced condition raises the following question: What are the possibilities of the ore having been deposited as a consequence of the reduction of an oxidized solution by woody material?

THE RELATION OF WOODY MATERIAL TO THE DEPOSITION OF VANADIUM ORES

The reducing capacity of woody material

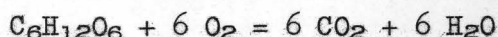
To determine whether woody material is a likely depositing agent for primary vanadium ores we must first know how much material is required to

precipitate a given amount of ore by reduction. This information is necessary to determine whether enough woody material could have been present in a given environment to account for all reduced ore minerals. There is no general way to calculate the reducing capacity of a carbon compound; for example, charcoal has no reducing capacity in aqueous systems, methane acts as reductant only under rather extreme conditions, cellulose may react or stay inert, and glucose is a good reducing agent under most conditions. It appears to be necessary to calculate the reducing capacity of woody material and to determine it experimentally under suitable conditions. No experimental or theoretical values of reducing capacities of woody material in solutions containing vanadium (V) could be found in the literature.

Some aspects of wood chemistry

Wood usually contains moisture ranging up to 10 percent and a fraction of a percent ash (66). The dry matter contains 40-50 percent cellulose, 10-30 percent hemicellulose, and 20-30 percent lignin. Cellulose and hemicellulose are polymers of glucose or its isomers. Some sugars of slightly different composition, such as xylose, are present, but they do not change the calculated results significantly and may be treated as glucose.

In the presence of a strong oxidizing agent glucose is decomposed according to the following reaction:

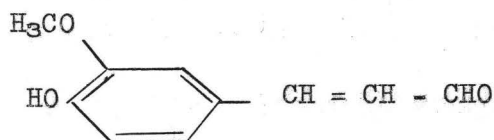


One mole (180 g) of glucose then requires 24 equivalents to oxidize it completely; it has an equivalent weight of 7.5.

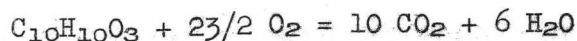
The cellulose monomer is $\text{C}_6\text{H}_{10}\text{O}_5$ with a molecular weight of 162. For complete oxidation: $\text{C}_6\text{H}_{10}\text{O}_5 + 6 \text{O}_2 = 6 \text{CO}_2 + 5 \text{H}_2\text{O}$. Thus, cellulose or its monomer, assuming complete oxidation to CO_2 and H_2O , also requires 24 equi-

valents and its equivalent weight is 6.75. In other words, 100 grams of cellulose has a theoretical reducing capacity of 14.8 equivalents, or 14,800 milliequivalents.

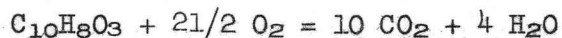
The oxidation of lignin is much more complicated. P. Klason (67) postulated lignin to be a polymer of coniferyl alcohol or coniferyl aldehyde



and this belief is currently accepted by many (68). Complete oxidation of the coniferyl aldehyde monomer to CO_2 and H_2O gives an equivalent weight of 4.05 and a reducing capacity of 24,700 milliequivalents per 100 g, more than twice that of cellulose, according to the reaction:



If a formula for lignin proposed by Russell (69) is used, the summary equation is:



The equivalent weight is 4.03 and the reducing capacity of 24,900 meq/100 g. These two examples illustrate that different proposed lignin structures do not differ greatly in reducing capacity.

We have no assurance, of course, that cellulose or lignin are completely oxidized.

Experimental determination of reducing capacities of some material

Experiments were carried out to determine the reducing capacity of wood. When wood is placed in an acidified solution of ammonium vanadate at room temperature and pressure, a green color is observed after a few days, indicat-

ing partial reduction of V(V) to V(IV). However, to simulate conditions in nature experiments were run at 150° C, a temperature representing a consensus of estimates of the maximum temperature of formation of the ores (70). Determinations of reducing capacity were carried out according to the following procedure: A 10 mg-sample together with 10 ml 0.1 N $(VO_2)_2SO_4$ solution containing an excess of free sulfuric acid and some Na_2SO_4 were placed in a Pyrex tube, sealed, and heated at 150° C at an estimated pressure of 70 lb/in² (ignoring the boiling point elevation of the solution by the added electrolytes) for three days; at the end of the run the reduced vanadium was titrated potentiometrically with the pH potential recorder. The Eh at the equivalence point always had a value similar to the E^0 of the V(IV)/V(V) couple, and there were no other breaks in the curve. This showed that only V(IV) was titrated. There were no breaks in the pH curve during the titration which indicated that no breaks were "masked" by a simultaneous pH change. It is conceivable that a simultaneous change in pH and activity ratio may take place at constant Eh [equation (3)]. Any remaining sample was recovered, washed, dried, and weighed. Results are shown in table 5. From the data two sets of reducing capacity values were obtained. The first set is the milliequivalents of vanadium reduced per 100 grams of original sample, the second set is the milliequivalents of vanadium reduced per 100 grams of wood or lignite decomposed (wood decomposed = original sample minus solid residue).

Since the experimental results were 58 percent of the calculated results, an attempt was made to obtain reducing capacities closer to the experimental value by extending the time of the run to 12 days. This attempt was not successful. Although it was possible to increase the reducing capacity of glucose under parallel conditions from 8900 meq/100 g to an apparent 10,000 meq/100 g by increasing the heating time from 3 to 12 days, the

Table 5.--Reducing capacity of wood and lignite.

	Wood (a) (meq/100 g)	Lignite (b)
Calculated reducing capacity (c)	15800	14600
Experimental reducing capacity (d)	10300 5100 9700	5600 6800 8200
Average experimental reducing capacity	8400	6900
Experimental reducing capacity corrected for insoluble constituents (e)	11300 7100	8600 8400
Average corrected reducing capacity (f)	9200	8500
Average corrected reducing capacity expressed as percentage of calculated reducing capacity	58%	58%

(a) Fresh spruce (Picea excelsa Lk) containing 58% cellulose and 29% lignin (71) (obtained from I. A. Breger).

(b) Lignite from the Beulah-Zap bed, Dakota Star mine, Miner County, N. Dak. containing 41.2% moisture and ash (72) (obtained from I. A. Breger).

(c) For details of calculation see text.

(d) All reducing capacities were determined by potentiometric titration of the product obtained by heating a 10-mg sample with 10 ml of a 0.1-formal vanadium(V) solution acidified to a pH of 0.7 in a sealed Pyrex tube for 3 days at 150° C. All values were corrected for a blank (0.15 ml).

(e) The undecomposed residue was isolated, washed, dried, and weighed, and the reducing capacity of the decomposed portion calculated. This was done on duplicate samples only owing to experimental difficulties on the triplicate run.

(f) This value was rounded off to 9000 in both samples for use in table 6.

reducing capacities of wood and lignite samples were of the same order of magnitude in the 3 day runs and the 12-13 day runs, with some of the long runs giving slightly lower reducing capacities. There are two possible explanations for this phenomenon, both probably contributing simultaneously: it was noted in the blank runs that the vanadate solution on heating gave a brown precipitate, which gave an X-ray pattern of $V_2O_5 \cdot H_2O$. If we consider that we have two competing reactions, one the precipitation of the vanadium (V) oxide which removes it from the reaction, and the other the reduction of the VO_2^+ ion by the slowly decomposing polymers of the woody material, it can be seen that relatively soon a point is reached where the concentration of vanadium (V) ions in the solution is so low that reduction becomes very slow and effectively ceases. The other effect is the formation of high-carbon polycyclic compounds by partial degradation of the wood which lose hydrogen and oxygen atoms during oxidation and results in reaction products becoming increasingly more resistant to attack. In the case of glucose this phenomenon does not take place.

The calculated reducing capacities used in table 5 were obtained as follows: the theoretical reducing capacity of a fresh spruce of the given composition is computed, assuming complete oxidation to CO_2 and H_2O and using the Russell formula for lignin. A 100-gram sample contains 58 g cellulose with a reducing capacity of (0.58×14800) 8600 milliequivalent per 100 g; it also contains 29 g lignin with a reducing capacity of (0.29×24800) 6700 milliequivalent per 100 g, giving a total reducing capacity of 15300 milliequivalent per 100 g. The experimental value at pH 0.7 corrected for undecomposed matter is 9200 milliequivalents per 100 g, or 58 percent of the theoretical maximum value.

The reducing capacity of the lignite used is substantially that of wood; this was an unexpected result. The chemistry of lignite is little known, but I. A. Breger (73) has presented evidence based on infrared spectra that the skeletal structures of humic acid and lignin are related and suggested that they may even be identical. Let us now assume that the reducing capacities of lignin and humic acid are the same. Let us next assume that lignite consists of moisture, ash, and humic acid only; while we know that this is not quite correct, this assumption would leave us with the same carbon content for lignite as for lignin. The carbon content of Russell lignin is 66 percent and its carbon-hydrogen ratio is 100:7.4; both of these values are not markedly different from typical lignite values and our assumption may not be far off. Since our lignite has a moisture and ash content of 41.2, it now is assumed to contain 58.8 percent humic acid (reducing capacity 24800 meq/100 g) and its reducing capacity assuming total oxidation is (0.588×24800) 14600 meq/100 g. The experimental value of 8500 meq/100 g then indicates either incomplete oxidation or the transition of some of the humic acid to fixed carbon, which is not too unlikely in a lignite. To investigate whether the oxidation of cellulose, lignin, wood, and lignite by vanadium (V) solutions proceeds to CO_2 and H_2O at least in part, or whether it does not proceed at all beyond some intermediate state, the reaction products of these substances with vanadium (V) solutions were examined by infrared spectroscopy; carbon dioxide was identified in all of them (74).

Amount of reducing agent required

If primary ore was deposited by the reduction of solutions carrying quinquevalent vanadium and sexivalent uranium ions, it may now be possible

to make rough estimates of the concentration of wood or lignite necessary for precipitation of a typical ore.

Therefore, it may be instructive to calculate the weight percent of fresh spruce or lignite necessary to precipitate each ore mineral from aqueous solution by reduction from a specified ion.

In this connection it must be noted that it is impossible to make a reasonable allowance for pyrite. In the first place, it is impossible to make a valid correction for the amount of pyrite present in sandstone prior to ore deposition, which must be deducted from the total pyrite in the ore. Also, no accurate correction can be made for other sulfides or sulfur compounds in the organic matter available for the reduction of possible ferric iron carried in a mineralizing solution. Finally, in the absence of sulfide made available by the woody material and free hydrogen sulfide fortuitously present in the system (which of course also would reduce vanadium and uranium ions) any pyrite sulfur must be produced by reduction of sulfate ions. Reduction of sulfate ions to sulfide or polysulfide in nature is known only in the presence of certain micro-organisms (e.g., Sporovibrio).

In table 6 there is presented a compilation of data which, it is hoped, will enable its user to compute the amount of woody material required to precipitate an ore containing a given amount of montroseite and pitchblende. He can then judge whether the amount of carbonaceous material expected in the formation under consideration is likely to be sufficient to make this process probable. Inasmuch as many sediments contain lignite concentrations of 2 percent or more, it can be seen from table 6 that woody material can easily be present in sufficient amounts to deposit typical ore concentrations from oxidized solutions by reduction, but of course this does not hold in every case.

Table 6.--Amount of reducing material required for the deposition of some reduced minerals from oxidized solutions.

Mineral species formed	Formula	Oxidized species in solution	Concentration of mineral species in sediment	Fresh spruce or lignite required					
				Theoretical			Experimental		
				Wt%	Lb/ton	%C	Wt%	Lb/ton	%C
Pitchblende	UO ₂	UO ₂ ⁺⁺	1 Wt% of mineral	0.048	0.96	0.022	0.082	1.6	0.037
			1 Lb/ton of mineral	0.002	0.048	0.001	0.004	0.082	0.002
			1 Wt% of U	0.055	1.10	0.025	0.092	1.8	0.040
			1 Lb/ton of U	0.002	0.055	0.001	0.005	0.092	0.002
Montroseite	VOOH	VO ₂ ⁺	1 Wt% of mineral	0.15	3.1	0.69	0.26	5.3	0.12
			1 Lb/ton of mineral	0.008	0.15	0.004	0.013	0.26	0.006
			1 Wt% of V	0.25	5.1	0.11	0.44	8.8	0.20
			1 Lb/ton of V	0.013	0.25	0.006	0.022	0.44	0.010

Notes for table 6

Values used in construction of table: "Theoretical" equivalent weight of wood or lignite: 6.5; this weight was obtained by averaging the equivalent weight for wood (6.3) and lignite (6.8) obtained from the calculated reducing capacities given in the text by the conversion formula; equivalent weight (in g) = 100000:: reducing capacity (in meq/100 g). The "experimental" value was obtained from the rounded off reducing capacity of 9000 meq/100 g. Both the wood and the lignite contained about 45 percent C (actual values: wood 46 percent, lignite 42 percent) (72).

Sample calculation: An ore contains 50 lb/ton montroseite, and 100 lb/ton pitchblende. What is the theoretical amount of lignite required for deposition?

Answer: $50 \times 0.15 + 100 \times 0.048 = 12.3$ lb/ton or about 0.6 wt % lignite.

Some typical reduction equations

It may be of interest to demonstrate some possible reducing reactions by writing down some speculative equations showing the reduction of uranyl and vanadate ions by cellulose (represented by $C_6H_{10}O_5$, its monomer). Of course, it is also possible to write similar reactions for lignin.

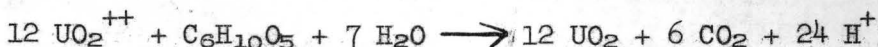
Reduction of vanadium (V) ion to montroseite



Reduction of vanadium (V) ion to duttonite



Reduction of uranyl ion to pitchblende



The reducing capacity of degraded woods

Lignite is a low-rank coal which derives its name from its obviously woody appearance. If all constituents of wood or lignite that do not substantially contribute to its reducing capacity are excluded from consideration, it may be seen from table 5 that the formation of lignite from wood may be described as the removal of cellulose from a cellulose-lignin mixture, followed by a change of lignin to "humic compounds". The metamorphosis of lignin probably does not affect its reducing capacity to any significant degree, but the removal of cellulose from wood may be expected to be important. For this reason it appeared desirable to study what effect was exercised by the degree of degradation of a wood upon its reducing capacity. It now became necessary to obtain some specimens of wood in various states of degradation.

I. A. Breger, U. S. Geological Survey, kindly furnished specimens of Norway spruce (Picea excelsa Lk.) suitable for this investigation. About 450 years ago a bridge was built in Rotterdam, called the Soetenbrug. After the bombing of Rotterdam by the German invaders in 1940, some of the bridge piling was removed for study. The surface of the wood had become quite degraded, while the interior retained the composition of fresh wood. A botanical description of this wood (sample SP-1) has been published (75) and the results of extensive chemical studies on this and similar ancient buried woods have been reported (71). In addition, I. A. Breger furnished a sample of spruce lignin prepared by him by the periodate method (76). The degraded wood was sliced into thin sections starting with the surface of the wood. Five 2-mm sections and three 4-mm sections were taken and the samples marked SP-1 (0-2), SP-1 (2-4), SP-1 (4-6), SP-1 (6-8), SP-1 (8-10), SP-1 (10-14), SP-1 (14-18) and SP-1 (18-22). Analytical results and calculated reducing capacities are presented in table 7, which also includes data on the fresh spruce and lignite samples discussed previously.

All experimental determinations were performed by the methods described previously, with the following modifications: an autoclave was substituted for the sealed glass tubes and operated at a temperature of 115-125° C for three days at a pressure of 10-20 lbs/in² above atmospheric pressure. This was done for two reasons:

- a) By performing measurements at two different temperatures, one an estimate of the maximum possible temperature and the other a conservative estimate, it was possible to show that the effect of temperature over the range was negligible.
- b) It was possible to make as many as 48 simultaneous runs in the autoclave. As only three sealed tubes could be heated simultaneously with

Table 7.--Reducing capacity of woody material calculated from analytical data.

Sample no.	Percent moisture	Percent ash	Percent lignin	Percent cellulose	Total	RC lignin	RC cellulose	RC calculated
SP-1 (0-2)	11.2 <u>1</u> /	1.2 <u>2</u> /	61.0 <u>3</u> /	27.2 <u>2</u> /	100.0	15100	4000	19100
SP-1 (2-4)	7.9 <u>1</u> /	1.3 <u>2</u> /	56.0 <u>3</u> /	40.2 <u>2</u> /	105.4	13900	6000	19900
SP-1 (4-6)	5.3 <u>1</u> /	0.9 <u>2</u> /	53.0 <u>3</u> /	42.1 <u>2</u> /	101.3	13200	6200	19400
SP-1 (6-8)	5.9 <u>1</u> /	1.0 <u>2</u> /	53.0 <u>3</u> /	38.9 <u>2</u> /	98.8	13200	5700	18900
SP-1 (8-10)	6.4 <u>1</u> /	0.4 <u>2</u> /	48.5 <u>3</u> /	49.6 <u>2</u> /	104.9	12000	7300	19300
SP-1 (10-14)	6.0 <u>1</u> /	0.3 <u>2</u> /	41.5 <u>3</u> /	49.0 <u>2</u> /	96.0	10300	7300	17600
SP-1 (14-18)	6.3 <u>1</u> /	0.3 <u>2</u> /	35.0 <u>3</u> /	51.2 <u>2</u> /	92.8	8700	7600	16300
SP-1 (18-22)	7.3 <u>1</u> /	0.3 <u>2</u> /	35.0 <u>3</u> /	48.0 <u>2</u> /	90.0	8700	7100	15800
Fresh spruce	9.6 <u>1</u> /	0.3 <u>2</u> /	29.0 <u>3</u> /	58.0 <u>3</u> /	96.9	6700	8000	14700
Lignite	35.6 <u>4</u> /	5.6 <u>4</u> /	58.8 <u>5,6</u> /		100.0	14600		14600
Lignin	8.6 <u>1</u> /		86.4	5.0 <u>5</u> /	100.0	21400	740	22200

- 1/ Analyst, J. C. Chandler, U. S. Geological Survey.
2/ Analyst, G. B. Magin, Jr., U. S. Geological Survey.
3/ Varossieau and Breger (71).
4/ Analyst, R. T. Moore, U. S. Geological Survey.
5/ Calculated by difference.
6/ "Humic material" considered as having the same RC as lignin.

existing facilities, this meant that the rate of completion of experiments was considerably accelerated.

Results of the determination of reducing capacities are presented in table 8 and the reducing capacities of the soluble fractions (RC^1) are shown in table 9. The method described in footnotes (d) and (e) of table 5 was used, except for the correction for reagent blank which was 0.2 ml in autoclave runs. All determinations were made in quadruplicate and the average (\overline{RC} and \overline{RC}^1) was computed. Standard deviations (S) are also shown. They indicate that the determination of the insoluble residue necessary for computation of RC^1 involves an additional source of errors, as the S values of RC are generally lower than those of RC^1 . Considering that 10-mg samples of wood were used and the method of preparation (slicing into parallel 2-mm sections) imposed rigid geometrical limitations making it impossible to allow for tree rings or anything except gross imperfections, it is surprising that the standard deviations were not higher.

Calculated and experimentally determined reducing capacities are compared in table 10, and again it appears that woody material shows a reducing capacity of about 60 percent of the calculated value after three days exposure to vanadium (V) solutions; under natural conditions, where exposure may persist much longer, it is likely that more complete reduction will take place. The degree of degradation of the wood does not appear to be very significant, except in wood totally metamorphosed to lignite. It appears likely that the polymers in the lignite have been rendered more susceptible to attack by the changes they underwent during the genesis of the lignite.

Table 8.--Reducing capacity (RC) of woody material determined experimentally.

Sample no.	RC ₁	RC ₂	RC ₃	RC ₄	RC	S
SP-1 (0-2)	11300	7300	9800	9300	9400	1400
SP-1 (2-4)	14200	6300	9700	9300	9900	1400
SP-1 (4-6)	10300	4000	9300	9000	8200	2400
SP-1 (6-8)	9800	8900	4700	9300	8000	2700
SP-1 (8-10)	11800	8300	6000	9900	9000	2700
SP-1 (10-14)	15300	7300	10300	9300	10600	2900
SP-1 (14-18)	10400	7300	10300	7800	9000	3500
SP-1 (18-22)	11400	4200	8800	8800	8300	2500
Fresh spruce	11300	5300	10700	9900	9300	2300
Lignite	8800	8300	8400	6800	8100	760
Lignin	8300	11300	11100	13900	11100	2000

Subscripts indicate replicate runs 1, 2, 3, and 4.

Table 9.--Reducing capacity of soluble fraction of woody material (RC¹) determined experimentally.

Sample no.	Insoluble residue weight (mg)				RC ₁ ¹	RC ₂ ¹	RC ₃ ¹	RC ₄ ¹	RC ¹	S
	RC ₁	RC ₂	RC ₃	RC ₄						
SP-1 (0-2)	0.0	0.5	0.0	1.9	11300	7700	9800	11500	10100	1500
SP-1 (2-4)	0.9	1.4	1.3	1.1	15600	7300	11100	10400	11100	3000
SP-1 (4-6)	1.1	1.1	1.8	1.5	11600	4500	11400	10600	9500	3900
SP-1 (6-8)	1.6	1.6	2.7	1.6	11700	10600	6400	11100	10000	2100
SP-1 (8-10)	2.0	2.1	0.7	4.7	14800	10500	6500	18600	12600	4700
SP-1 (10-14)	1.0	1.4	0.8	0.3	17000	8500	11200	9600	11600	3300
SP-1 (14-18)	1.3	1.5	0.2	1.0	12000	8600	10400	8700	9800	4800
SP-1 (18-22)	1.1	0.0	0.5	0.0	12800	4200	9300	8800	8800	3100
Fresh spruce	2.3	0.4	1.2	0.8	14700	5500	12100	10800	10800	3400
Lignite	3.7	4.4	1.6	4.1	14000	14800	10000	11500	12600	1900
Lignin	3.9	0.4	2.2	0.0	13600	11300	15800	13900	13600	1600

Table 10.--Efficiency of reduction of vanadium (V) solutions by woody material: experimentally determined reducing capacity of woody material expressed as percentage of calculated reducing capacity.

Sample no.	Average RC expressed as percent of calculated RC	Average RC of soluble fraction expressed as percent of calculated RC
SP-1 (0-2)	49.2	54.0
SP-1 (2-4)	49.8	55.8
SP-1 (4-6)	42.2	49.0
SP-1 (6-8)	42.3	53.0
SP-1 (8-10)	46.6	65.3
SP-1 (10-14)	60.2	65.8
SP-1 (14-18)	55.0	60.0
SP-1 (18-22)	52.5	55.7
Fresh spruce	63.2	73.5
Lignite	55.5	86.3
Lignin	50.0	61.2

The synthesis of a reduced vanadium mineral
by reduction with wood

As it had been demonstrated that the reducing capacity of woody material was sufficiently high to warrant its consideration, it became necessary to show that the reduction of a vanadium (V) solution by woody material actually could result in the formation of a reduced vanadium mineral. This was very important for an additional reason: an examination of the literature failed to disclose any successful attempt to produce any reduced vanadium mineral synthetically.

After a number of unsuccessful trials it was found that a vanadium mineral with the formula $V_2O(OH)_4$ (table 1) could be produced by the following method:

An 0.1 M ammonium metavanadate solution was adjusted to a pH of 2.04 with sulfuric acid, 100 mg Norway spruce shavings were added to 10 ml of this solution and the suspension was heated in a closed silver-lined bomb for 10 days at a temperature of $150^{\circ}C$. A black fine-grained precipitate was removed which upon X-ray examination showed the same pattern as a reduced vanadium mineral found in nature (77). This mineral, as yet unnamed, had been found near Carlile, Wyo., and in McKinley County, N. Mex. (78). Its crystal structure and chemical composition were subsequently determined by Evans and Mrose (79). It was found to have the formula $V_2O(OH)_4$ or $V_2O_3 \cdot 2H_2O$. This demonstrated that it was possible to produce a vanadium (III) mineral by reduction of a vanadium (V) solution with wood.

Reduction by wood as biochemical mechanism

Biochemistry may be defined as the branch of chemistry which deals with the processes and products of life. As wood is the product of plant life,

it may be said that vanadium minerals deposited by reduction with woody material were deposited by a biochemical mechanism. Such deposits may be called biogenous deposits. If it is possible that vanadium minerals in the Colorado Plateau are of biogenous origin, the question whether biochemical mechanisms in general are important in the formation of naturally occurring vanadium concentrations becomes significant and should be considered.

PROCESSES AND PRODUCTS OF LIFE AND THE DISTRIBUTION OF VANADIUM

The distribution of vanadium in nature

Vanadium is an element of considerable biochemical importance as it is one of the normal constituents of living matter. Its distribution in living organisms and inanimate matter has been the subject of intensive inquiry. It is surprising to note that Bertrand's monograph on the biogeochemistry of vanadium cites 237 references (80). Reference is made to this review for a discussion of the distribution of vanadium in plants, animals, and fossil material. It is, however, of interest at this time to consider the importance of biochemical processes upon the concentration of vanadium in ores of economic value.

Vanadium ore deposits

Sydney J. Johnstone (81) lists the following commercial sources of vanadium in order of present-day importance:

1. Carnotite and roscoelite from U. S. (Colorado Plateau).
2. Peruvian ores.
3. Lead vanadates from Northern Rhodesia, SW Africa, Mexico, Argentina, and western United States.

4. Vanadiferous iron ore from Sweden, France, Luxembourg, and Chile.
5. Vanadiferous phosphate rock from Wyoming and Idaho.

Let us next consider representative samples of each of these groups. The origin of vanadium in the Colorado Plateau is omitted from this consideration because it has been discussed.

Peruvian ores furnished the main supply of the world's vanadium (82) until V production from the Colorado Plateau became important during World War II. The main Peruvian vanadium mineral, patronite, is a vanadium sulfide with the probable composition $V_2S_5 + nS$ (83) and occurs associated with asphaltic hydrocarbons. It has been suggested that the deposits were formed from vanadiferous petroleum (84) which rose through fissures created during a period of igneous activity and underwent inspissation through evaporation of its more volatile components. The occurrence of vanadium in petroleum is discussed below.

Lead vanadates are an important source of vanadium, especially in Africa. The biggest and best known deposit is in Broken Hill, Northern Rhodesia. Here lead and zinc phosphates and vanadates form incrustations on the surface of lead and zinc sulfide ores. The body of these ores contain neither P or V. Schneiderhöhn (85) believes that P and V were deposited by the reaction of the lead and zinc sulfide with descending solutions carrying P and V, and that these elements were derived from organic sources within an ancient soil.

The next source described is vanadiferous iron ore. Here we can distinguish between two classes: vanadium-bearing titaniferous magnetites, as represented by Swedish ores of Taberg, which formed by differentiation during crystallization of a magma (86); and vanadium-bearing sedimentary iron ores of biogenous origin (Minette ores) found in France and Luxembourg.

Another source of economic interest is vanadium ash obtained from petroleum residues after burning and from petroleum flue dust (87). The existence of vanadium-porphyrin complexes in many petroleum was demonstrated by A. Treibs (88, 89), and Skinner (90) assigned a provisional formula to this complex bearing resemblance to that of hematin and chlorophyll. Vinogradov (91) postulated that vanadium-containing petroleum originated from vanadiferous marine organisms; this is in line with currently accepted beliefs that petroleum originates from organic matter (92).

Vanadium also is found in phosphate rocks in Idaho and recovered as byproduct in superphosphate manufacture. It is generally believed (93) that these rocks were formed by biochemical and physical reactions with phosphate-containing solutions or colloids on the bottom of an ancient sea.

A consideration of all commercial sources of vanadium of present-day importance other than the Colorado Plateau has indicated that, with the exception of Swedish iron ores, the processes or products of life were essential in the concentration and deposition of vanadium in nature. This is in line with the findings here presented showing that biological processes or products also might have been involved in the deposition of vanadium in the Colorado Plateau.

Suggestions for further work

It has been shown that the vanadium minerals of the Colorado Plateau were produced in their present state by air oxidation from reduced "primary" minerals, and evidence has been presented which indicates that these "primary" minerals were deposited by reduction by woody material from a solution. A solution of this type may be called an "ore-forming fluid."

The following approach to a further investigation of the origin of vanadium in the vanadium-uranium ores of the Colorado Plateau appears promising:

- a) Study as far as possible the composition the ore-forming fluid must have had.
- b) Study the path the ore-forming fluid must have taken and the location from which it originally came.
- c) Study whether the fluid contained vanadium originally or whether it extracted vanadium on its path from another source.
- d) Study the source of vanadium in the fluid.

As it appears that biochemical processes are important in the concentration of vanadium in nature, a biogenous origin for the source of the vanadium in the ore-forming fluid appears possible and should be considered in planning an investigation of the origin of vanadium. It may be of interest to show, as an example of such an approach, how a postulate of a biogenous origin of the source of vanadium may be considered in planning a study of the composition of an ore-forming fluid.

Erickson, Myers, and Horr (94) showed that the metal suite Co, Cr, Cu, Mo, Ni, Pb, V, and Zn is consistently present in the ash of crude oils produced in the western half of the United States, and that Ni and V consistently constituted the most abundant heavy metals in this suite. Analysis of the Mineral Joe channel ore specimens disclosed the presence of all of these elements with the exception of Ni, Co, and Zn (57). It now becomes of interest to see whether a fluid exists that cannot transport Ni, Co, and Zn, and that can transport the other elements named in the suite, in addition to U which is also present in the ore. If the composition of such a fluid is of a type which is not inconsistent with the restrictions placed on it by the

natural environment (pH and temperature range, solubility relations, thermodynamic stability, etc.), such fluids may be used in laboratory investigations. If, for example, it is possible to prepare a synthetic suite of ore minerals similar to that found in nature by the reduction of such a solution with woody material, it may be possible that the vanadium in the ore originally was extracted from petroliferous material by such a solution.

SUMMARY

The intense exploration for uranium in the Colorado Plateau has stimulated interest in the origin of the vanadium minerals in these ores. These minerals were introduced by deposition from a fluid in a sandstone matrix. They contain compounds of tervalent, quadrivalent, and quinquevalent vanadium. These compounds have been exposed to air oxidation and are associated with woody material, a possible reducing agent. It appears that oxidation potential studies may be useful in investigating the origin of these ores.

Theoretical considerations are reviewed which indicate that oxidation potential (Eh) measurements should be carried out in an inert atmosphere, that simultaneous pH determinations are often necessary to interpret Eh values, and that measurements must be continued for periods long enough to assure equilibrium. It can be shown that automatic recording is very desirable and that provisions for multiple recording of simultaneous measurements may be required to prevent undesirable delays in the production of data.

A versatile multiple pH-oxidation potential recorder is described, and details are given for its operation. Special techniques necessary for the application of the instrument to some problems are demonstrated. The instrument is very useful in the making of Eh-pH measurements and can be adopted

for potentiometric titrations even when equilibrium is very slowly attained.

It is predicted from thermodynamic and electrochemical theoretical considerations that the sulfuric acid extract of typical ore samples could contain V(IV) in the presence of Fe(III) ions and that in such solutions V(V) and Fe(II) ions could not coexist. On the other hand, in solid ores V(V) and Fe(II) ions can coexist and Fe(III) and V(IV) ions cannot occur in the presence of each other under equilibrium conditions. Experiments of a novel type were performed on several actual ore samples which showed this to be true. Eh-pH measurements performed on 17 specimens of vanadium ores in different states of oxidation yielded values within the range predicted by theoretical, analytical, and mineralogical considerations. Eh-pH and reducing capacity measurements were used to determine the state of oxidation of the redox-active minerals in the ore.

It is shown that the state of oxidation of Fe- and V-bearing minerals occurring together in the ores could be accounted for only if the minerals as now found had been formed by oxidation of originally reduced minerals. These findings are in accord with proposals previously made by other investigators based on geological and crystal chemical reasoning.

The reducing capacity of wood was calculated on the assumption that the main reactions involved were the oxidation of cellulose and lignin to CO_2 and H_2O . Fresh wood and degraded woods of different cellulose and lignin contents were exposed to vanadium (V) solutions at elevated temperatures and pressures, and it is shown that the actual reducing capacity of the woody material under the experimental conditions is about 60 percent of the calculated value.

The reducing capacity of lignite as determined under the same conditions is surprisingly high, and it is shown that this result may be explained by

assuming that lignite consisted of moisture, ash, and humic acid, and that humic acid could be expected to have a reducing capacity similar to that of lignin. Calculations are presented which showed that the reducing capacity of woody material as experimentally determined is high enough to make plausible the assumption that the reduced minerals may have been deposited from solutions by reduction with woody material.

A mineral containing tervalent vanadium was prepared synthetically from a vanadium (V) solution by reduction with fresh wood at elevated temperature and pressure. This is the first reported synthesis of any reduced vanadium mineral by any method. This synthesis demonstrated that reduction of vanadium solutions by woody material actually could produce reduced vanadium minerals.

Vanadium ores in the Colorado Plateau are at this time the most important commercial source of vanadium. As the results here presented indicate that biochemical processes were important in the formation of these deposits, the role of the processes and products of life in the origin of the six commercially most important types of vanadium deposits are reviewed, and it is shown that, with the exception of some Swedish vanadiferous iron ores, all vanadium deposits considered were probably concentrated by biological agents.

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