UNITED STATES DEPARTMENT OF THE INTERIOR
J. A. Krug, Secretary
GEOLOGICAL SURVEY
W. E. Wrather, Director

Bulletin 950

CONTRIBUTIONS TO GEOCHEMISTRY

1942-45

SHORT PAPERS BY
R. C. WELLS AND OTHERS

UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON : 1946

For sale by the Superintendent of Documents, U. S. Government Printing Office, Washington, D. C.
Price, 40 cents

E57677

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FOREWORD

By Roger C. Wells

Beginning shortly after the founding of the Geological Survey in 1879, many of the results of research work of the Chemical Laboratory were published in a series of bulletins entitled "Report of work done in the Division of Chemistry and Physics." The last of this series was published in 1893. In 1900, Bulletin 167, "Contributions to chemistry and mineralogy from the laboratory of the United States Geological Survey," and in 1905, Bulletin 262, "Contributions to mineralogy from the United States Geological Survey," were issued. Later, a new series, "Mineralogical notes," was issued, series 1 in 1911 as Bulletin 490; series 2 in 1912 as Bulletin 509; and series 3 in 1916 as Bulletin 610. Since 1905, the Geological Survey has not published any similar group of papers embodying the results of research by several members of the staff of the Chemical Laboratory. Such results have appeared as individual reports and shorter papers, published either by the Geological Survey or by scientific societies both in this country and abroad.

With the advent of the second World War every effort was directed by the Geological Survey to the search for strategic and critical minerals. Many useful chemical elements are contained as minor constituents in other ores that may be either rare or abundant. As the search for these elements became more intensive the required tests and chemical analyses of the ores became more complicated and difficult; hence, in addition to making many analyses of ores by recognized methods it has been necessary for the Survey chemists to develop new methods for the solution of many of the problems presented to them. Increased use has been made of colorimetric, spectrographic, and X-ray methods.

It was suggested by Dr. Margaret D. Foster, Geochemist of the Chemical Laboratory, that the contributions by the members of the Laboratory, resulting from this work, from 1942 to 1945, be published as the first bulletin in a new series similar to the one that terminated in 1893. This series will contain miscellaneous contributions to chemistry, physics, mineralogy, and related subjects, under the general term "Contributions to Geochemistry" followed by the year or years covered by the investigations.

The present bulletin contains a series of papers on some of the methods developed and the results obtained during these investigations. There is no attempt here to report all the miscellaneous analyses made, as most of them are published in connection with the geologic studies to which they relate; however, owing to the constant demand from chemists throughout the country and from other Government bureaus for information on improved methods of analysis developed by the Survey's chemists, it appears advisable to publish this collection of papers as a Survey bulletin. This bulletin also contains short notes on useful apparatus, as well as papers relating to the end-member formulas of micas, the gelatinization of silicate minerals, the gamma-ray activity of potassium salts, and a theoretical discussion of the arrangement of atoms in aluminosilicates.

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ANALYSES OF PETROLEUM-COKE ASHES

By Roger C. Wells

In a note published some years ago[1] the writer briefly summarized some preliminary observations on minor constituents found in the ashes of petroleum cokes, but did not give analytical data. Some of the ashes showed traces of vanadium. In view of the present interest in all possible sources of this rare metal, it seems advisable to report those and other analyses in full, and to list the fields from which the different oils were obtained, so far as they are definitely known. The study of the petroleum cokes was initiated by K. C. Heald, formerly of the Federal Geological Survey, who assisted in collecting samples from a number of fields.

In the table below, sample 16 contained 0.01 percent of CuO. No significant quantity of uranium was found in any of the cokes. The absence of chlorides in many of the samples does not necessarily mean that chlorides were absent in the crude oils, as it seems probable that sulfuric acid, which may have been produced during the ashing, may have displaced any hydrochloric acid present. Sulfates of calcium, magnesium, and sodium seem to be the chief constituents of the ash, aside from silica and iron oxide.

Longobardi[2] cites a petroleum ash of 0.037 percent that contained 11.93 percent of V_2O_5, as well as traces of some 21 other elements, including nickel, arsenic, silver, gold, lead, tin, barium, strontium, and lithium.

Vanadium has been found in a number of natural petroleum residues. A tar in breccia from Terlingua, Tex., submitted by J. R. Balsley, of the Geological Survey, was found to contain 0.22 percent of V_2O_5. Asphalt from Baboso well 1, Bermudez Lake, Venezuela, submitted by R. H. Richards, contained 0.043 percent of vanadium, equivalent to 61 percent of the ash—that is, the ash was mainly vanadium oxide. Another asphalt from Guanoca, State of Monogas, Venezuela, showed a vanadium content of 0.016 percent, or 30 percent of the ash. Grahamite from near Page, Okla., yielded ash containing 12.2 percent of V_2O_5, and asphalt from Nevada yielded ash that contained 45 percent. These products probably represent a very slowly formed undisturbed concentration of the nonvolatile components of petroleum, whereas in oil drawn from wells under pressure there is such great turbulence that some solutions with their dissolved mineral matter became mixed with the oil, as indicated in the analyses of the petroleum cokes. These cokes were intentionally selected from stills treating crude oil, as far as possible. The asphalts, unfortunately, although having a higher content of vanadium, do not occur in sufficient quantity to make the vanadium a profitable byproduct, whereas

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[1] Wells, R. C., Observations on the minor constituents of petroleum: Econ. Geology, vol. 20, pp. 286–288, 1925.

[2] Longobardi, E., The minera constituents of petrolleum: Jour. Inst. Petroleum Technology, vol. 21, p. 132, 1935.

the ashes of petroleum and flue dust, are collected in a few places especially for their vanadium content.

Analyses

	1	2	3	4	5	6	7	8
Ash in coke....percent	12.4	6.88	4.8	0.30	1.09	0.75	0.24	63.9
Ash insoluble in water:								
SiO_2	1.7	32.0	77.9	6.1	2.7	5.1	48.4	
$(Al, Fe)_2O_3$	[1] .9	63.0	1.6	20.4	3.5	6.9	[1] 27.9	
CaO		1.0	.5	7.7	4.0	3.7	4.1	
MgO		[2] .4	[3] .3	2.8	2.4	2.9	3.3	
NiO		Tr.	.01					
V_2O_5	[4] Tr.	None	2.6	[4] Tr.	None	[4] None	[4] None	[4] Tr.
Undetermined					12.7	2.4	3.2	[5] 94.40
Ash soluble in water:								
Cl	42.4		None	None		None		.78
SO_4	20.8	[6] 2.0	[7] 12.5	[6] 63.0	[6] 74.7	[6] 79.0	13.1	2.95
Ca	6.4							.24
Mg	1.4							.02
Na	25.1							[8] 1.61
K	.5							
V_2O_5			3.6		None			
	99.2	98.4	99.0	100.0	100.0	100.0	100.0	100.00

	9	10	11	12	13	14	15	16
Ash in coke....percent	0.69	0.25	0.21	0.81	0.43	0.21	3.89	[9] 1.36
Ash insoluble in water:								
SiO_2				5.7	8.8	18.3	2.2	4.4
$(Al, Fe)_2O_3$				7.4	36.2	73.4	4.1	1.4
CaO				1.0	3.7			[10] 10.6
MgO				1.2	2.9			
NiO				Tr.	Tr.	Tr.	.004	.38
V_2O_5	[4] 8.1	[4] None	[4] None	[4] 5.9	[4] 1.2	[4] None	[4] .65	[4] 11.4
Undetermined	18.0	[11] 56.5	[11] 85.6	5.8		2.7	8.7	(12)
Ash soluble in water:								
Cl	[13] 6.4				None		29.2	29.0
SO_4	54.7	[14] 43.5	[14] 14.4	[6] 73.0	[6] 47.3	[6] 5.7	24.5	15.1
Ca	11.9						3.8	2.2
Mg	[15] 6.3				Tr.		Tr.	1.4
Na	[8] 12.6						[8] 26.4	20.9
K								[16] 3.2
	100.0	100.0	100.0	100.0	100.1	100.0	99.6	100.0

	17	18	19	20	21	22	23	24
Ash in coke____percent	0.54	18.1	0.85	10.20	24.0	3.28	1.05	0.33
Ash insoluble in water:								
SiO_2	43.8	--------	3.7	0.36	0.16	6.1	2.7	3.0
$(Al, Fe)_2O_3$	5.8	--------	6.9	3.66	96.00	[17] 88.3	Tr.	90.9
CaO	--------	--------	7.0	--------	--------	.8	--------	--------
MgO	--------	--------	--------	--------	--------	1.3	--------	--------
NiO	None	Tr.	.8	.004	None	.15	.3	Tr.
V_2O_5	[4] 1.9	[4] .007	--------	[4] Tr.	[4] .03	[4] .9	[4] 5.8	None
Undetermined	10.5	97.4	10.0	14.74	--------	(18)	7.5	--------
Ash soluble in water:								
Cl	None	--------	--------	--------	--------	--------	--------	--------
SO_4	[6] 38.0	[6] 2.6	47.8	55.67	3.24	2.1	56.9	4.7
Ca	--------	--------	2.4	23.95	.04	.8	5.0	1.4
Mg	--------	--------	2.2	[19] .17	.02	--------	1.2	.3
Na	--------	--------	[8] 16.8	--------	1.28	.2	20.2	--------
K	--------	--------	--------	--------	--------	--------	.3	--------
V_2O_5	--------	--------	[4] 2.4	--------	--------	--------	--------	--------
	100.0	100.0	100.0	98.55	100.77	100.7	100.0	100.3

[1] P and Cr absent.
[2] MnO=0.05; CuO=0.005.
[3] Trace of MnO.
[4] Total V_2O_5.
[5] By difference.
[6] Na_2SO_4 and Ca SO_4.
[7] $CaSO_4$ and $MgSO_4$.
[8] Calculated.
[9] Percent of asphalt.
[10] Includes some undetermined.
[11] Total insoluble.
[12] SrO, 0.03; Ti, Ba, Zr, none; CuO, 0.01.
[13] SiO_2.
[14] Total soluble.
[15] Undetermined.
[16] SiO_2 and undetermined.
[17] Includes 4.9 percent Al_2O_3.
[18] P, Li, U, none.
[19] Includes 0.03 percent Mn.

1. Coke from stills running Osage, Okla., crude oil. Cosden Oil Co.
2. Coke from cut of crude oil, Marland Oil Co.
3. Coke at least in part from original crude oil. Cosden & Co. through E. T. Dumble.
4. Coke, Mid-Continent crude oil, National Refining Co., Coffeyville, Kans.
5. Coke from oil of 33.8 gravity from Bartlesville, Okla., and Florence, Kans., crude oil. National Refining Co., Coffeyville, Kans.
6. Similar to sample 5 except that "slops" were present in the oil.
7. Coke from Midwest Refining Co., Casper, Wyo.
8. Coke from Kans-Tex Refining Co., Arkansas City, Ark.
9. Coke from Standard Oil Co. of Kansas, Neodesha, Kans.
10 and 11. Similar to sample 9.
12. Coke from Roxana Petroleum Corp., Arkansas City, Kans.
13. Coke from Vickers Oil Co., Wichita, Kans.
14. Coke from Moore Refining Co., Arkansas City, Kans.
15. Hard coke from mixture of Kansas and Oklahoma crude oils. Sinclair Refining Co., Coffeyville, Kans.
16. Liquid asphalt, Murray County, Okla.; depth, 1,232 feet. Sample sent by Wm. J. Scott. See Eng. & Min. Jour.-Press, vol. 117, no. 20, p. 799, 1924.
17. Coke from Dubbs cracking unit, Roxana Petroleum Corp. Other bottom heavy-oil fractions contained detectable traces of vanadium.
18. Coke dust from Jenkins cracking still, Grant Oil Co., Augusta, Kans. Slaked lime added in process.
19. Petroleum coke, Standard Oil Co. of Illinois, Wood River, Ill.
20. Coke from Skelly Oil Co., Eldorado, Kans.
21. Coke from White Eagle Oil and Refining Co., Kansas City, Mo.
22. Coke from oil from Meyer sand, 4,336–4,667 feet, Sant Fe Springs, Calif. Altitude of well, 125 feet above sea level.
23. Coke from Roxana Petroleum Corp. Oklahoma crude oil from Tonkawa, Burbank, Healdton, Hewitt, Cushing, Yale, and other pools is tapped to a fuel oil of 25° American Petroleum Institute. The fuel oil is further handled in a Dubbs cracking unit from which treatment the coke resulted.
24. Coke from Kendall Refining Co., Bradford, Pa.

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STUDIES ON THE PEROXIDE METHOD FOR DETERMINING VANADIUM IN MINERALS AND ORES

By Margaret D. Foster

ABSTRACT

Electrophotometric studies on peroxidized solutions containing 4.0 milligrams of V_2O_5 in 50 milliliters show that the kind of mineral acid used is of little effect and that it may be chosen with reference to the material under examination. Solutions containing from 10 to 15 percent of sulfuric acid and from 10 to 20 percent of nitric acid, with 5 drops to 5 milliliters of hydrogen peroxide, give the same reading.

With hydrochloric acid and 5 drops of hydrogen peroxide there is no difference in the color for acidities ranging from 15 to 25 percent, but when 5 milliliters of hydrogen peroxide is used the intensity of the color increases with increase in acid concentration.

Time effects are very small for most solutions but slight decreases in the color occur after several hours in the more concentrated hydrochloric acid solutions containing too little hydrogen peroxide.

The close conformity of peroxidized vanadium solutions to Beer's law makes it possible to use a factor to convert readings obtained in the electrophotometer on unknown solutions to percentages of vanadium.

Titanium and iron interfere seriously and should be removed at the start by a sodium peroxide or carbonate fusion of the sample, followed by water extraction. The sodium salts thus introduced into the solution do not interfere in the vanadium determination; nor does aluminum or silica, most of which will be found in the water leach. Both molybdenum and chromium in excess of 1 milligram as MoO_3 or Cr_2O_3 interfere; if feasible, therefore, the concentration of the interfering elements should be known and unknown vanadium solutions should be referred to standards containing similar concentrations of the interfering elements. If chromium is the interfering element small amounts can be removed from the solution by extraction with ethyl acetate. Tungsten in excess of 10 milligrams of WO_3 in 50 milliliters should be removed.

INTRODUCTION

In the course of determinations of vanadium made in connection with an investigation of vanadium ores by the Geological Survey, it was found advisable to reexamine the peroxide colorimetric method for the effect both of acid and peroxide concentration and of other elements on the color produced.

This well-known method for determining vanadium is based on the red-brown color that is developed when hydrogen peroxide is added to an acid solution containing vanadium. Hillebrand[3] recommended the use of nitric acid, whereas Maillard[4] used hydrochloric acid. Visual comparisons indicate that the color is intensified by increase in acidity and bleached by an excess of hydrogen peroxied. Meyer and Pawletta[5] reported that an excess of hydrogen peroxide gives a yellow instead of a red-brown color, and that when too much acid is present hydrogen peroxide causes reduction to a vanadyl salt. They recommended using 15 to 20 percent sulfuric acid

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[3] Hillebrand, W. F., The analysis of silicate and carbonate rocks: U. S. Geol. Survey Bull. 700, p. 187, 1919.

[4] Maillard, L., Colorimetric estimation of vanadium: Chem. News, vol. 82, p. 19. 1900.

[5] Meyer, J. and Pawletta, A., Uber den Nachweis der Vanadinsaure mit Wasserstoffperoxyd Zeitschr. anal. Chemie, Band 69, p. 15, 1926.

and a ratio of V to H_2O_2 of about 1 to 1. Wright and Mellon[6] recommend a lower acid concentration—between 0.6 and 6.0 N; that is, 1.7 to 17 percent—in sulfuric, nitric, or hydrochloric acid, and a peroxide concentration containing between 0.2 and 3.0 milliliters of 3 percent hydrogen peroxide per 100 milliliters. They also found that an excess of hydrogen peroxide decreases the color but that consistent use of more hydrogen peroxide (up to 10 milliliters) is permissible. It was hoped that a systematic study might decide between these various and somewhat inconsistent recommendations.

EFFECT OF ACID AND HYDROGEN PEROXIDE CONCENTRATION

Electrophotometric readings, over a period of 7 hours, on solutions containing 4.0 milligrams of V_2O_5 in 50 milliliters with several concentrations of sulfuric, nitric, and hydrochloric acids are given in the accompanying tables, which include comparative readings for two concentrations of 3 percent hydrogen peroxide—5 drops and 5 milliliters. These readings and all others here recorded were made on the logarithmic scale of a Fisher electrophotometer, using a filter transmitting an approximate spectral band of 425 millimicrons.

Electrophotometric readings showing the effect of sulfuric acid and hydrogen peroxide concentration on color produced by 4.0 milligrams of V_2O_5 in 50 milliliters

Time (hours)	Acid concentration (percent) and quantity of hydrogen peroxide added (in drops and ml.)									
	5 percent		10 percent		15 percent		20 percent		25 percent	
	5 drops	5 ml.	5 drops	5 ml.	5 drops	5 ml.	5 drops	5 ml.	5 drops	5 ml.
At once	43.0	43.3	43.7	43.7	43.8	43.7	41.9	43.3	41.0	43.0
1	43.4	43.1	43.7	43.6	43.9	43.6	41.5	43.0	39.3	42.9
2	43.6	43.1	43.8	43.9	44.2	44.1	41.2	43.0	38.6	43.0
3	43.6	43.4	44.0	44.0	44.3	44.3	41.0	43.5	38.1	43.6
4	43.7	43.7	44.4	44.1	44.8	44.4	40.8	43.4	37.4	43.3
5	43.7	44.2	44.7	44.4	44.6	44.3	40.9	43.9	36.8	43.2
6	43.6	43.9	44.4	44.5	44.6	44.6	40.4	43.4	36.3	43.0
7	43.4	44.0	44.4	44.2	44.4	44.4	39.7	43.7	35.7	42.9

Electrophotometric readings showing the effect of nitric acid and hydrogen peroxide concentration on color produced by 4.0 milligrams of V_2O_5 in 50 milliliters

Time (hours)	Acid concentration (percent) and quantity of hydrogen peroxide added (in drops and ml.)									
	5 percent		10 percent		15 percent		20 percent		25 percent	
	5 drops	5 ml.	5 drops	5 ml.	5 drops	5 ml.	5 drops	5 ml.	5 drops	5 ml.
At once	42.3	40.2	43.5	43.3	43.5	43.3	43.5	43.6	45.1	44.1
1	42.3	40.9	43.3	43.3	43.4	43.4	43.9	44.1	44.7	43.9
2	42.2	41.2	43.6	43.6	43.5	43.5	43.6	44.4	44.1	43.9
3	42.1	41.4	43.7	43.6	43.7	43.5	43.6	43.9	43.6	43.6
4	41.9	41.6	43.2	43.8	43.4	43.2	43.3	43.8	43.4	43.5
5	41.9	41.8	43.0	44.2	43.4	43.2	43.0	43.7	43.4	43.6
6	41.9	42.2	43.1	43.9	43.4	43.3	43.0	43.7	43.4	43.6
7	42.0	42.0	43.2	43.3	43.0	43.1	43.0	43.6	42.7	43.6

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[6] Wright, E. R., and Mellon, M. G., The peroxide method for vanadium: Ind. and Eng. Chem. Anal Edition, vol. 9, p. 375, 1937.

Electrophotometric readings showing the effect of hydrochloric acid and hydrogen peroxide concentration on color produced by 4.0 milligrams of V_5O_5 in 50 milliliters

Time (hours)	Acid concentration (percent) and quantity of hydrogen peroxide added (in drops and ml.)									
	5 percent		10 percent		15 percent		20 percent		25 percent	
	5 drops	5 ml.	5 drops	5 ml.	5 drops	5 ml.	5 drops	5 ml.	5 drops	5 ml.
At once	42.0	35.3	43.0	40.8	44.2	42.0	44.2	43.3	44.1	44.0
1	42.6	36.4	42.9	41.4	43.8	43.0	43.8	43.3	43.8	44.0
2	42.6	37.4	43.3	42.1	43.9	43.1	44.3	43.7	44.1	44.4
3	42.9	37.4	43.5	42.2	44.1	43.6	44.1	43.6	44.0	44.0
4	43.0	37.5	43.2	42.2	44.1	43.3	44.2	43.3	44.1	43.9
5	42.3	37.6	43.1	42.1	44.1	43.1	43.8	43.3	43.6	43.8
6	42.1	37.8	43.2	42.4	44.2	43.1	43.7	43.4	43.2	43.9
7	42.0	37.7	43.0	42.3	43.5	42.6	43.0	43.0	42.7	43.9

The readings indicate that for both sulfuric and nitric acids there is a range of acid concentration within which either a change in the acid concentration or an increase in the quantity of hydrogen peroxide added, from 5 drops to 5 milliliters, causes no difference in the intensity of the color. For sulfuric acid this range is from 10 to 15 percent, for nitric acid it is from 10 to 20 percent. At those concentrations the intensity of the color produced in sulfuric acid is essentially identical with that in nitric acid. Decreasing the sulfuric acid concentration from 10 to 5 percent or increasing it from 15 to 20 percent had very slight effect on the intensity of the color when 5 milliliters of hydrogen peroxide was used, but somewhat more when only 5 drops of hydrogen peroxide was used. Decreasing the nitric-acid concentration from 10 to 5 percent decreased the color more when 5 milliliters of hydrogen peroxide was used than when 5 drops of hydrogen peroxide was used. Increasing the nitric-acid concentration from 20 to 25 percent increased the color somewhat more when 5 drops of hydrogen peroxide was used than when 5 milliliters was used.

For hydrochloric acid through the range from 15 to 25 percent, there was no change in the intensity of the color when 5 drops of hydrogen peroxide was used. When 5 milliliters of hydrogen peroxide was used, however, increase in the acid concentration caused a progressive increase in the color and there was no range of acid concentration within which the color remained exactly constant. In all concentrations of hydrochloric acid up to and including 20 percent the color with 5 drops of hydrogen peroxide was somewhat greater than with 5 milliliters of hydrogen peroxide. In 25 percent hydrochloric acid, however, there was no difference with the two concentrations of hydrogen peroxide.

In general, the color in sulfuric and nitric acids increased slightly during the period of the test, except in the higher acid concentrations when 5 drops of hydrogen peroxide was used. In hydrochloric acid the color remained stable or increased slightly in the lower acid concentrations but decreased slightly in the higher acid concentrations.

The tests indicate that the kind of mineral acid used may be chosen with reference to convenience in dissolving the material under examination. Suitable conditions are 10 percent of sulfuric or nitric acid or 20 percent of hydrochloric acid and 0.5 milliliter of hydrogen peroxide per 50 milliliters of solution.

COLOR FORMATION AND BEER'S LAW

To determine whether peroxidized vanadium solutions follow Beer's law, which requires that the absorbing power of the constituent be independent of the degree of dilution, electrophotometric readings were made on 3 series of solutions in which the V_2O_5 content ranged from 1.0 to 6.0 milligrams. The three series contained, respectively, 10 percent of sulfuric acid, 10 percent of nitric acid and 20 percent of hydrochloric acid. The readings, which were made immediately after development of the color, indicate that the color intensity conforms closely to Beer's law over the range investigated.

Electrophotometric readings on solutions of 10 percent H_2SO_4, 10 percent HNO_3, and 20 percent HCl

[Conditions: 0.5 ml. of H_2O_2 in 50 ml.]

V_2O_5 (mg.)	H_2SO_4 (10 percent)	HNO_3 (10 percent)	HCl (20 percent)
1	10.8	10.6	10.1
2	22.1	21.9	21.5
4	43.7	43.5	43.0
6	65.5	65.4	64.6
8	85.0	----------	----------

EFFECT OF OTHER CONSTITUENTS

Iron and titanium, very commonly found in ore and rock materials, may interfere with the accuracy of the vanadium determination unless an appropriate method is used to prepare the test solution. As little as 0.05 milligram of titanium causes a 2-percent increase in color.[7] The yellow color of iron in acid solution is very much less intense, but the quantities of iron commonly present in ore materials are so large as to cause a significant error in the vanadium determination. Phosphoric acid decolorizes iron but does not bleach the titanium color formed with hydrogen peroxide. Hydrofluoric acid decolorizes both iron and titanium, but in the acid solutions used in the vanadium determination hydrofluoric acid attacks glass containers rapidly, producing a turbidity that interferes seriously in reading the color. It is much more satisfactory, therefore, to eliminate iron and titanium at the start by making a sodium carbonate or peroxide fusion of the sample, followed by extraction with water. These fusions have the added advantage of removing many other elements from the solution prepared for the determination of vanadium. If an acid attack of the rock material is made, iron and titanium should be removed by precipitation with sodium hydroxide before proceeding with the determination of vanadium.

The sodium salts introduced into the solution by such a procedure have no effect on the vanadium color, as indicated in the table (column 3). Alumina and silica (columns 6 and 9), the greater proportion of which are found in the water extract of a sodium peroxide or carbonate fusion, are also without effect.

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[7] Wright, E. R., and Mellon, M. G., op. cit.

Electrophotometric readings showing the effect of different elements on the light transmitted by peroxidized vanadium solutions

[Conditions: 5 ml. H_2SO_4 (sp. gr. 1.84), 0.5 ml. H_2O_2 (3.0 percent) in 50 ml.]

V_2O_5 mg	No salts added	Na_2SO_4 6 gm	1 ml. H_3PO_4 =1.04 gm. P_2O_5	2 gm. Na_2HPO_4 =1.00 gm. P_2O_5
1.0	10.5	10.6	10.4	10.6
2.0	22.1	22.1	22.2	22.0
4.0	43.7	43.7	43.7	43.9
6.0	65.1	64.9	65.0	65.0

V_2O_5 mg.	$Al_2(SO_4)_3$ =0.40 gm. Al_2O_3	$MnSO_4$ =0.40 gm. Mn	Na_2WO_4 =10 mg. WO_3	6 gm Na_2SO_4 +0.4 gm. SiO_2
1.0	10.7	10.8	11.5	10.4
2.0	22.1	22.5	22.8	22.1
4.0	43.7	44.2	44.5	43.7
6.0	65.5	65.8	66.5	65.0

Among elements not removed by a sodium peroxide or carbonate fusion are some that may interfere in the vanadium determination because (1) they give colored compounds in acid solutions on the addition of hydrogen peroxide, (2) their colored compounds do not change on addition of hydrogen peroxide, and (3) their colored compounds change color on addition of hydrogen peroxide.

The only elements beside vanadium and titanium that give colored compounds with hydrogen peroxide are molybdenum, bromine, and iodine. Of these only molybdenum is likely to interfere with the determination of vanadium in ores.

The yellow color that molybdenum gives with hydrogen peroxide, by formation of a yellow peroxy acid, is much less intense than the titanium color, but it causes more trouble in the determination of vanadium because molybdenum is not removed by fusion with sodium peroxide or carbonate or by precipitation with sodium hydroxide. Neither can it be decolorized by hydrofluoride or phosphoric acids. Willard and Diehl[8] state that if the solution is acidified with oxalic acid, the interference of molybdenum is eliminated. Tests in this laboratory, however, show that oxalic, as well as citric and tartaric acids, intensify rather than diminish the color of molybdenum with hydrogen peroxide. When molybdenum is present in a solution in which vanadium is to be determined, the yellow color developed by the molybdenum increases the color of the solution as a whole by an amount related to the amount of molybdenum present, as shown in the table below. Consequently, if the molybdenum content and the intensification of color due to that amount of molybdenum is known, readings on unknown vanadium solutions can be corrected or the same amount of molybdenum may be added to reference solutions. If such a correction is not applied, the presence of molybdenum causes a positive error in the vanadium determination.

In visual comparisons 1 to 3 milligrams of MoO_3 in 50 milliliters volume does not affect the hue of a peroxidized vanadium solution sufficiently to cause much difficulty, but there is an apparent lightening of the color which would lead to a negative error in the amount of vanadium reported. The writer found that 11 milligrams of MoO_3 changes the hue from red-

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[8] Willard, H. H. and Diehl, H. C., Advanced quantitative analysis, p. 107, Brumfield and Brumfield, Ann Arbor, Michigan, 1939.

brown to yellow and makes visual comparison impossible, particularly if the vanadium content is low, unless a similar amount of MoO_3 is added to the reference solutions.

Electrophotometric readings showing the effect of molybdenum on the color of vanadium solutions

[Conditions: 5.0 ml. H_2SO_4, 0.5 ml. H_2O_2 in 50 ml.]

V_2O_5 Mg.	No MoO_3 added	1.1 mg. MoO_3 added		3.3 mg. MoO_3 added	
		Reading	Difference	Reading	Difference
1.0	10.8	11.6	0.8	13.3	2.2
2.0	22.1	22.9	.8	24.3	2.2
4.0	44.0	44.8	.8	46.4	2.4
6.0	65.1	66.0	.9	67.6	2.5

V_2O_5 Mg.	11.0 mg. MoO_3 added		33.0 mg. MoO_3 added	
	Reading	Difference	Reading	Difference
1.0	15.9	5.1	20.8	10.0
2.0	27.6	5.5	32.5	10.4
4.0	49.4	5.4	54.6	10.6
6.0	70.5	5.1	75.8	10.7

Besides iron, elements whose colored compounds do not change color on addition of hydrogen peroxide include copper, nickel, cobalt, ruthenium, rhodium, palladium, osmium, iridium, uranium, and gold. Many of them are seldom encountered in ore analysis, or, if encountered, are found in very small quantities, and most of them would not be present in a water extract of a sodium peroxide or carbonate fusion.

Chromium is the only element whose colored compounds change color on addition of hydrogen peroxide that is likely to interfere in the determination of vanadium. On addition of hydrogen peroxide the orange dichromate color changes to the blue of perchromate, which is then quickly reduced to a green chromic salt. In visual comparison even 1 milligram of Cr_2O_3 in 50 milliliters alters the hue of a peroxidized vanadium solution and makes comparison with a standard vanadium solution difficult; much more than 1 milligram of Cr_2O_3 makes comparison impossible.

Electrophotometric readings showing the effect of Cr_2O_3 in peroxidized vanadium solutions

[Conditions: 5.0 ml. H_2SO_4, 0.5 ml. H_2O_2 in 50 ml.]

V_2O_5 (mg)	No Cr_2O_3 added	1 mg. Cr_2O_3 added		3 mg. Cr_2O_3 added	
		Reading	Percent difference	Reading	Percent difference
1.0	10.5	10.7	+ 1.9	11.8	+ 12.4
2.0	22.0	22.0	± 0.0	22.6	+ 2.7
4.0	43.9	42.0	− 4.4	42.1	− 4.0
6.0	66.5	62.6	3.6	61.9	− 6.9

In electrophotometric comparisons 1 milligram of Cr_2O_3 in 50 milliliters has little or no effect on the intensity of the light transmitted by solutions containing 2 milligrams or less of V_2O_5, but it decreases by about 4 percent the readings on solutions containing more than 2 milligrams of V_2O_5. As much as 3 milligrams of Cr_2O_3 increases the readings on solutions containing 2 milligrams or less of V_2O_5, but it decreases the readings on solutions containing more than 2 milligrams of V_2O_5.

If the Cr_2O_3 content of the solution is known, the interfering effect of the Cr_2O_3 can be obviated by adding the same amount of Cr_2O_3 to the standards used for comparison. Another method is to remove small amounts of Cr_2O_3 from the solution by extraction with ethyl acetate. (See pp. 15–18.)

At the acidity used in the determination of vanadium with hydrogen peroxide, WO_3 in excess of 10 milligrams per 50 milliliters precipitates. The slight increase in the readings for peroxidized vanadium solutions containing 10 milligrams of WO_3, as shown in the table, may be due to incipient precipitation. Therefore, if tungsten is believed to be present it should be removed at the start by acid treatment of the sample.

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THE SEPARATION OF SMALL AMOUNTS OF CHROMIUM FROM VANADIUM WITH ETHYL ACETATE

By Margaret D. Foster

ABSTRACT

The solubility of blue perchromic acid in ethyl acetate offers a means of separating chromium from vanadium. The blue perchromic acid, formed on the addition of hydrogen peroxide to an acid solution of a chromate, increases in stability with decrease in the acidity of the solution. If a slightly acid solution containing chromate and vanadate ions is mixed with ethyl acetate in a separatory funnel, hydrogen peroxide added, and the mixture shaken vigorously, all the perchromic acid dissolves in the ethyl acetate without loss from reduction. Vanadium remains in the water layer and may be drawn off and determined. The perchromic acid in the ethyl acetate layer may be reconverted to chromate by the addition of a 10 percent potassium hydroxide solution. On vigorous shaking the chromate dissolves in the aqueous solution and may be drawn off and determined.

INTRODUCTION

Chromium is rarely if ever a prominent constituent of the types of rocks in which vanadium has been reported. While examining certain samples for vanadium, however, the chemists of the Geological Survey experienced considerable difficulty in determining small amounts of vanadium colorimetrically because of the chromium content of the samples. When hydrogen peroxide is added to an acid aqueous solution containing a chromate, blue perchromic acid forms but rapidly decomposes to give a chromic salt. The green color of this chromic salt alters the hue of the peroxidized vanadium solution and causes difficulty in the determination of vanadium.

The formation of perchromic acid with hydrogen peroxide, first described by Barreswil[9] in 1847, has long been used as a sensitive test for chromium. The reaction has not been used in a quantitative way, however, because of the instability of perchromic acid in mineral-acid solutions. In general, acids decompose perchromic acid into chromic salt and oxygen.[10] Perchromic acid is therefore much more stable in a solution of low acidity than in one of high acidity. If the acidity of the solution is very low, perchromic acid is sufficiently stable to permit its solubility in ethyl acetate to be used as a means of removing chromium from an aqueous solution without loss from the formation of a chromic salt.

Barreswil also observed that if an alkali is added to an ether solution of perchromic acid, oxygen is evolved and alkali chromate is formed. This reaction also takes place in ethyl acetate solution. The alkali chromate thus formed is insoluble in ether or ethyl acetate and can be recovered in aqueous solution by the addition of water.

When an alkali is added to an ethyl acetate solution of blue perchromic

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[9] Barreswil, L. C. A., Memoire sur un nouveau composé oxygènée du chrome: Annales de chimie et de physique, ser. 3, tome 20, p. 364, 1847.

[10] Martinon, M., Action de l'eau oxygènée sur les oxides de chrome: Soc. chim. France, Bull., ser. 2, tome 45, p. 862, 1886.

acid and the mixture shaken, the blue solution becomes first brown violet and then yellow. It is inferred from this that the alkali salts of perchromic acid are violet or brown violet,[11] but that, being unstable, they soon decompose with evolution of oxygen to form chromates.

SOLUTION OF THE SAMPLE

For most rock materials in which small percentages of vanadium are to be determined the following procedure has been found satisfactory: Mix 0.4 gram of 80-mesh rock powder with 2 grams of sodium peroxide in an iron crucible, cover the charge with 1 gram of sodium peroxide, and fuse. Extract the cooled melt with water containing a drop of alcohol to reduce manganate, digest on a steam bath for 30 minutes, filter and wash. Neutralize the filtrate with sulfuric acid (1:1) and add 2 drops in excess. Evaporate the solution to about 40 milliliters and cool to room temperature. It is advisable to limit the volume of the acid aqueous solution as much as is compatible with its salt content because of the solubility of ethyl acetate in water (8 milliliters in 100 milliliters at 20° C.).

Other methods may be used to get the rock powder into solution but, whatever method is used, it is essential that the solution—as prepared for the separation of chromium from vanadium—be free from iron, titanium, and manganese, and be very low in acidity.

SEPARATION AND DETERMINATION OF CHROMIUM AND VANADIUM

Transfer the slightly acid solution to a 250 milliliter separatory funnel, and add 80 to 150 milliliters of ethyl acetate, the quantity depending on the chromate content of the solution as estimated from the color of the filtrate from the fusion. Add 0.5 milliliter of 3 percent hydrogen peroxide and shake the funnel vigorously for a few seconds. If the ethyl acetate does not acquire a blue color it may be assumed that the solution extracted contains less than 0.014 milligram of chromium for each 10 milliliters of ethyl acetate used. Transfer the lower or water layer to a second funnel and make a second extraction, using about 15 milliliters of ethyl acetate. Transfer the water layer to a 100-milliliter beaker (beaker A). Add the ethyl acetate in the second funnel to that in the first funnel and rinse the second funnel into the first with two 10-milliliter portions of distilled water. Shake the ethyl acetate and rinse water together and draw off the water into beaker A. Set beaker A aside for the determination of vanadium. If the Cr_2O_3 content of the solution before separation is much greater than 3.0 milligrams it may be necessary to use more than 15 milliliters of ethyl acetate in the second extraction and even to make a third extraction in order to remove chromium completely.

The solubility of perchromic acid in ethyl acetate (and in the various other organic solvents) is relatively low—15 milliters of ethyl acetate takes into solution only about 1 milligram of Cr_2O_3 as perchromic acid. Because of the volume of ethyl acetate required the method is therefore practicable for the removal of only small amounts of chromium.

To the blue ethyl-acetate solution in the separatory funnel add 1 milliliter of 10 percent potassium hydroxide and shake until the color has changed from blue to pure yellow. Add about 10 milliliters of distilled

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[11] Mellor, J. W., A comprehensive treatise on inorganic and theoretical chemistry, vol. 11, p. 353, Longmans, Green and Co., London, 1931.

water, shake again and, after the ethyl acetate and water layers have separated, draw off the water solution into a 100-milliliter beaker (beaker B). Repeat the treatment with potassium hydroxide and water, drawing off the water solution into beaker B, and then wash the ethyl acetate with 10-milliliter portions of distilled water until the washings are colorless. After each treatment add the water solution to the chromate solution in beaker B. Usually one or two such washings are sufficient. Set this beaker aside for the determination of chromium.

As the vanadium solution in beaker A already contains hydrogen peroxide, it is necessary only to increase the acidity and adjust the volume in order to determine vanadium colorimetrically. Add 5 milliliters of concentrated sulfuric acid, adjust the volume to 50 milliliters and compare with standards having the same acid concentration.

The alkaline solution in beaker B is ready, after adjustment of volume, for the colorimetric determination of chromium.

DETERMINATIONS ON KNOWN MIXTURES

Definite quantities of potassium chromate and ammonium vanadate solutions of known titer were carefully measured into 100-milliliter beakers. The volumes of the mixtures were adjusted to 40 milliliters and the solutions were made slightly acid by adding 3 drops of 1:1 sulfuric acid; 5 grams of sodium sulfate, approximately the amount of sodium salts that would be found in a solution of a rock powder after fusion with sodium peroxide, also were added. The chromium in the mixtures was then separated from the vanadium by the procedure outlined above and each metal was determined colorimetrically.

An electrophotometer was used for the colorimetric determinations. The red-brown color of pervanadic acid follows Beer's law closely, making it possible in routine work to use a factor to convert photometric readings to quantities of vanadium. But the yellow chromate color deviates so markedly from Beer's law that it is necessary to refer the photometric readings to a curve based on readings for solutions of known chromate content. In these determinations, however, all the readings on the test solutions were compared with readings on known solutions of chromium and vanadium made up at the same time. The vanadium standards had approximately the same salt content as the test samples. The results obtained (table 1) show that the extraction method using ethyl acetate effectively separates chromium from vanadium, and that the separation is complete.

TABLE 1.—*Determinations of chromium and vanadium in known mixtures.*

Test No.	Taken		Found	
	Cr_2O_3 (mg.)	V_2O_5 (mg.)	Cr_2O_3 (mg.)	V_2O_5 (mg.)
1	0. 50	7. 28	0. 50	7. 30
2	1. 00	6. 06	1. 00	6. 11
3	2. 00	4. 85	1. 94	4. 86
4	3. 00	3. 64	2. 96	3. 64
5	4. 00	2. 43	4. 00	2. 45
6	5. 00	1. 21	5. 04	1. 24

In a second series of tests, definite amounts of chromium and vanadium (as potassium chromate and ammonium vanadate solutions) were added to 0.4-gram samples of powdered feldspar, which was by analysis free from chromium and vanadium. The samples were dried and then fused with sodium peroxide in iron crucibles. The leaching of the melt, subsequent digestion and filtration, and the separation of chromium from vanadium were carried out according to the procedure herein described. The results obtained are given in table 2.

TABLE 2.—*Determinations of chromium and vanadium that had been added to feldspar.*

Test No.	Taken		Found	
	Cr_2O_3 (mg.)	V_2O_5 (mg.)	Cr_2O_3 (mg.)	V_2O_5 (mg.)
1	0.50	7.28	0.46	7.32
2	1.00	6.06	.93	6.08
3	2.00	4.85	1.89	4.95
4	3.00	3.64	2.90	3.65
5	4.00	2.43	3.95	2.46
6	5.00	1.21	4.90	1.29

COMPARISON OF METHODS OF DETERMINATION

Table 3 gives determinations of Cr_2O_3 and V_2O_5 by the method herein described on six samples of phosphate rock from western Wyoming. Also given, for comparison, are determinations of V_2O_5 only, made by Victor North, of the Geological Survey, who fused the samples with sodium peroxide and determined vanadium by titration with ferrous sulfate, after selective oxidation of vanadium with permanganate, and by treatment with sodium nitrite and urea, according to the method of Walden, Hammett, and Edmonds.[12] The close agreement in the data obtained for V_2O_5 confirms the reliability of the separation of chromium and vanadium by ethyl acetate and indicates that the phosphate in the samples had no interfering effect on the separation of chromium and vanadium.

TABLE 3.—*Comparative determinations on phosphate rock.*

Sample No.	Colorimetric determination after separation		Reductive volumetric determination of vanadium
	Cr_2O_3 (percent)	V_2O_5 (percent)	V_2O_5 (percent)
1	0.13	0.73	0.72
2	.14	.87	.86
3	.14	.81	.79
4	.12	.81	.79
5	.14	.69	.67
6	.12	.68	.67

INTERFERENCE

Peroxidized molybdenum, like peroxidized vanadium is not soluble in ethyl acetate; it remains in the water solution and may introduce an error in the vanadium determination. Molybdenum decreases the intensity of the light transmitted by a peroxidized vanadium solution, the amount of decrease being proportional to the molybdenum content. If the molybdenum content is less than 1 milligram in 50 milliliters the error in the vanadium determination is negligible, but if the molybdenum content is greater than 1 milligram in 50 milliliters correction should be made for the molybdenum present.

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[12] Walden, G. H., Hammett, L. P., and Edmonds, S. M., Phenanthroline-ferrous ion. II. Oxidation potentials at high acidities and the determination of vanadium: Am. Chem. Soc. Jour., vol. 56, p. 57, 1934.

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A FIELD TEST FOR VANADIUM

By Joseph M. Axelrod

During their investigation of the vanadium-bearing phosphate and shale beds of the Phosphoria formation in Wyoming and Utah, the geologists of the Geological Survey, United States Department of the Interior, had need of a simple, rapid, and dependable field test for vanadium, preferably one that at least would be roughly quantitative.

Members of the Geological Survey had learned[13] that vanadium would color a cooled potassium pyrosulfate melt yellow. The intensity of the color was found to be more than twenty times as great as that of the color given by any other element and the field test developed is based on this fact. For accurate results the tests have to be made under standardized conditions; the quantities of sample, standard, and flux must be measured, and the heating must be controlled.

REAGENTS AND APPARATUS

Small scoops for measuring the rock samples were made from metal rods by drilling a hole in the end or in the side at the end of each rod. The scoops made held 0.19 milliliter, 0.046 milliliter, 0.015 milliliter, 0.01 milliliter, 0.006 milliliter, and 0.004 milliliter. For measuring the flux, scoops were made by attaching handles to short pieces of brass tubing closed at one end—cork borers and blunt pencil-point protectors were satisfactory. The scoop used in the laboratory held 3 milliliters, about 4 grams, and the tests were made in ½- by 5-inch pyrex test tubes. The flux consisted of a sized mixture, 6 to 20 mesh, of five parts of potassium pyrosulfate to one part of potassium nitrate. It was sized in order to minimize segregation of the components and to facilitate the escape of gases formed during the fusion. The potassium nitrate was added only to eliminate the interference of organic matter found in the Phosphoria beds. A Meker burner with an inserted tube for compressed air was used for heating, and ordinarily from 1 to 2 minutes was required to bring the charge to a bright red heat—about 750°C. For some samples the melt foamed considerably so that more gradual heating was necessary, but heating was always continued to a bright red heat.

In the field, the tests were run on a smaller scale. The scoop for measuring the flux held about 0.5 milliliter, the test tubes were 10 millimeters by about 75 millimeters, and the melt was heated by a gasoline blowtorch or acetylene burner. The size of the sample scoop to be used will depend on the vanadium content of the sample; a 0.01-milliliter scoop was used for samples from the Phosphoria formation.

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[13] The test was suggested to E. B. Eckel of the Geological Survey by the late R. J. Leonard. It also is mentioned in Fansett, G. R., Field tests for the common metals: Univ. Arizona Bull. 121, Ariz. Bureau of Mines, 1926.

PROCEDURE

To make a test, take a sample by pressing a scoop several times into the finely powdered rock, wipe off the outside of the scoop and level it, tap out into a pyrex test tube, add a level scoopful of flux, and heat the charge in a hot flame to a bright red heat. Cool the melt and compare its color with the colors of standard melts that have been heated to about the same temperature and that contain either analyzed samples or known quantities of some vanadium compound. In the field test, a 0.01 milliliter sample containing 0.25 percent of vanadium trioxide yields a melt about the color of solid potassium chromate in the absence of interferences and 0.02 percent is detectable. Iron colors the molten or hot melt yellow to brown, but on cooling this color disappears.

INTERFERENCES

Before developing the method for field use, laboratory tests were necessary to determine the behavior of vanadium in the presence of other elements. Most of the elements were tested for interference with the vanadium color by including various quantities of a compound of each in four gram melts containing two tenths of a milligram of vanadium trioxide. They were also tested in melts containing no vanadium compound to see if they would themselves give a color to a cooled melt. Of the compounds of those elements that gave no color of their own to a melt, $Li_2SO_4.H_2O$, Na_2SO_4, $SnCl_2.2H_2O$, $ZnSO_4.7H_2O$, $CdSO_4.\frac{8}{3}H_2O$, Tl, $Al_2(SO_4)_3.18H_2O$, $Ti_2(SO_4)_3$, Na_2SiO_3, $Na_2B_4O_7.10H_2O$, SeO_2, $La(NO_3)_3.6H_2O$, $(NH_4)_2SO_4$, S, or sodium or potassium salts of various anions of nitrogen, carbon, sulfur, chlorine, bromine, and iodine did not interfere when a 0.19 milliliter scoopful (the largest quantity tested) was added to a four gram melt. No appreciable effect was caused by 0.046 milliliter of MgO, $CaCO_3$, $Ca_3(PO_4)_2$, $PbCl_2$, HgO, BeO, As_2O_3, NaF, $Th(NO_3)_4.4H_2O$, $NaBiO_3$, WO_3, or ZrO_2; 0.030 milliliter of $Fe_2(SO_4)_3$; 0.015 milliliter of $Sr(NO_3)_2$, Cb_2O_5, MoO_3, or $BaCl_2.2H_2O+CaCO_3$ (each); 0.004 milliliter of $BaCl_2.2H_2O$ or 0.0002 gram of Sb_2O_5, but a larger quantity interfered by partly or completely bleaching the vanadium color.

Other elements gave their own colors to the melts and more or less obscured the vanadium color. The quantity, measured in scoops, necessary to give in the absence of vanadium a color roughly equal in strength

Colors given by chromatic elements

Compound	Quantity[1]		Cooled melt
	(ml.)	(grams)	
$UO_2(NO_3)_2.6H_2O$	0.38	(0.30)	Lemon yellow, greener than vanadium color.
$NiSO_4.6H_2O$	.046	(.058)	Yellow, matches vanadium color.
$Ce_2(C_2O_4)_3$	.030	(.018)	Yellow, browner than vanadium color.
$Nd(NH_4)_2(NO_3)_5.4H_2O$	.19	(.18)	Lavender, strength about 1/5 that of color given by 0.2 mg. of V_2O_3.
$Co(NO_3)_2.6H_2O$	.015	(.014)	Magenta.
$CuSO_4.5H_2O$	.030	(.042)	Blue.
$K_2Cr_2O_7$	.015	(.023)	Green.
$MnSO_4$	.030	(.039)	Gray with a little lavender.
$(NH_4)_2PtCl_6$	.015	(.016)	Gray.
Ag_2SO_4	Insoluble in the melt but coats the glass tube brown; 0.015 ml. is not perceptible, 0.046 ml. (0.10 gm.) gives a color about 1/5 the strength of the color given by 0.2 mg. of V_2O_3.		

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[1] Quantities were measured in scoops and, later, scoopfuls similarly packed were weighed.

to the color given by 0.2 milligram of vanadium trioxide is shown in the table page 20. The color of such a vanadium melt is about that of solid potassium chromate.

Because a false positive test was obtained in the field with a manganiferous sample, tests were made with mixtures of iron and manganese sulfates. A few other mixtures suspected of interfering also were tested. The data obtained are given in the table below.

Colors given by mixtures

Mixture	Quantity of each (ml.)	Color	Strength[1]
$Fe_2(SO_4)_3$-$MnSO_4$	0.015	Brown	Equal
$NaBiO_3$-$MnSO_4$	.015	Purple brown	Equal
$(NH_4)_2PtCl_6$-$MnSO_4$	.015	Gray	
$Fe_2(SO_4)_3$-$NaBiO_3$	.046	White	
$Fe_2(SO_4)_3$-$(NH_4)_2PtCl_6$	.015	Gray and yellow	Yellow=about 1/10
$NaBiO_3$-$(NH_4)_2PtCl_6$	.015	Gray	
$Fe_2(SO_4)_3$-$MnSO_4$	.001 gm.	Light gray	Less than 1/10

[1] Strength of color compared with color given by 0.2 mg. of V_2O_3.

In the presence of a blue, green, magenta, or gray of the same intensity, the yellow color caused by vanadium may be detected, but not always with certainty, and it is impossible to distinguish it from a yellow or brown color caused by some other element. One-tenth of a percent of vanadium may be detected, however, and reported with a fair degree of confidence in the presence of 1 percent of cobalt, 2 percent of copper, chromium, manganese, nickel, or cerium, 5 percent of platinum, 20 percent of silver or uranium, or 50 percent of neodymium.

DECOMPOSITION OF MINERALS BY THE FLUX

Various powdered minerals were heated strongly with potassium pyrosulfate to see which ones would be attacked. This treatment completely dissolved the spinel group, ilmenite, columbite, carnotite, vanadinite, descloizite, and the mineral sulfides, carbonates, sulfates, and tungstates; it decomposed topaz, stilbite, chloritoid, micas (including roscoelite), prehnite, an amphibole, garnierite, and chrysocolla; it merely leached iron from red zircon; and it did not visibly affect jasper, cassiterite, the feldspars, a pyroxene, olivine, tourmaline, or spessartite garnet. Most of the resistant silicates could be satisfactorily tested for vanadium in the laboratory by grinding, treating with hydrofluoric and sulfuric acids, bringing to fumes and then transferring to a pyrex test tube for the fusion, but such a procedure is inconvenient for a field test. Any vanadium in resistant minerals will not be detected by the fusion test.

RESULTS IN THE LABORATORY

Two series of samples from the Phosphoria formation previously analyzed for vanadium were tested by the field test. In one series the vanadium-trioxide contents ranged from 0.01 percent to 0.25 percent and the strengths of the color obtained varied in order with the vanadium contents; in the other series of six the samples highest and lowest in vanadium were used as standards and the intermediate values estimated from the colors of the melts.

Results of laboratory tests on phosphate rocks

Percent V_2O_3 by chemical analysis[1]	Percent V_2O_3 by field test
0.30	0.30 (Standard)
.36	.40
.77	.60
.85	.65
.97	.85
1.05	1.05 (Standard)

[1] Analyses by F. S. Grimaldi, of the Geological Survey laboratory.

The agreement is within the limits of error of sampling and color estimation.

RESULTS IN THE FIELD

Several hundred samples were tested in the field by W. W. Rubey, of the Geological Survey, and his associates, and some of the samples were later analyzed by a standard chemical procedure by Victor North, of the Survey laboratory. The chemical results agreed well with the results of the field test for most samples and in order of magnitude for all samples. Two analyzed samples containing 0.97 percent and 0.37 percent of vanadium trioxide were used as standards from which the vanadium contents were estimated.

Field tests on samples from the Phosphoria formation and bordering beds

Sample No.	Percent V_2O_3 by field test	Percent V_2O_3 by chemical analysis
208	1.0	0.80
243	.7	.35
340	.05	.12
341	.2	.34
342a	.35	.22
342b	.2	.14
342c	.2	.13
342d	.42	.45
343	.3	.2
490a	Negative	.09
490b	Negative	.11
490c	.25	.23
491	.15	.17
492	.4	.37
495	.5	.65
495a	.8	.78
495b	1.0	1.2
G-12	.6	.42
I-8	.8	.55
I-9	.9	.61
I-10	1.2	1.5
J-10	.5	.20
K-43	.7	1.2
K-44	Weak	.20
K-45	.15	.19
K-71	.7	.27

TESTS ON OTHER ROCK TYPES

To study the method on rock types other than phosphate, a number of rocks that had been analyzed for vanadium were selected from the files of the laboratory and tested. For the few vanadium ores and vanadium-bearing basalts available, the average deviation of the results of the field test from those of chemical analyses was about 25 percent of the vanadium content. For a series of 18 granular magnetite samples, it was necessary first to heat the melts very hot in order to dissolve the sample, and then, after cooling, to add several drops of sulfuric acid and reheat to a dull red heat, because the initial strong heating weakened the vanadium color. If the melt was not again brought to a red heat, the vanadium color was weak or did not develop at all. With these precautions the results were consistently about 25 percent low when comparisons were made with melts containing only flux and known quantities of a vanadium compound. Using 0.006 milliliter of sample (about 13 milligrams), 3 milliliters of flux, and a correction factor of 1.33, the average deviation of the results from those of chemical analyses was 8 percent—less than the uncertainty of matching. The small size of sample necessarily used to keep down the iron concentration did not permit estimation of vanadium trioxide contents of less than 1/10 of a percent. A tungsten-cobalt-chromium-vanadium-molybdenum tool-bit steel (Carpenter, Rex 95) gave a good test for vanadium when a very small sample was used; a file steel gave a negative test.

CONCLUSIONS

Laboratory tests under standardized conditions on one rock type give results that are as accurate as the accuracy of matching colors. When directions are followed in the field, tests run under approximately standard conditions or on different rock types show at least whether vanadium is present in negligible, small, or large quantity. In samples with only small percentages of interfering elements, 1/100 of a percent of vanadium trioxide can be detected, but in ores of chromatic elements, such as manganese ores, only large quantities of vanadium can be recognized. Nickel, manganese, certain rare earths, uranium, and perhaps silver may be mistaken for vanadium, but the tests show that only in the presence of much unsuspected antimony or in barium minerals not recognized as such, will more than 1/10 of a percent of vanadium be overlooked.

Contributions to geochemistry, 1942–45
Geological Survey Bulletin 950

THE SIGNIFICANCE OF INTERNAL STRUCTURE IN GELATINIZING SILICATE MINERALS

By K. J. Murata

ABSTRACT

Silicate minerals that dissolve in hydrochloric or nitric acid to give gelatinous silica fall into two classes, based on their internal atomic structure:

1. Minerals containing silicate radicals of small molecular weight, namely orthosilicates, pyrosilicates, possibly silicates with the ring structure of three silicon atoms, and possibly silicates with the ring structure of six silicon atoms.
2. Minerals with large continuous silicon-oxygen frameworks that will disintegrate into units of low molecular weight under acid attack. (a) Disilicates, sheet structures, containing large amounts of ferric iron in the silicon-oxygen sheets. (b) Minerals with three-dimensional structures that contain aluminum in the ratio of at least two aluminum atoms to three silicon atoms.

Minerals that separate insoluble silica, instead of gelatinizing, upon being treated with acid are characterized by silicon-oxygen structures of large dimensions that do not disintegrate into small units under acid attack. These structures are SiO_3 chains, Si_4O_{11} double chains, Si_2O_5 sheets not containing large amounts of ferric iron replacing silicon, and three-dimensional frameworks having an aluminum content less than the ratio of two aluminum atoms to three silicon atoms.

These relationships may be interpreted through the qualitative hypothesis that small silicon-oxygen units or radicals dissolve in acid to yield gelatinous silica, whereas large units will yield insoluble separated silica. The maximum size of the soluble units is as yet undetermined.

INTRODUCTION

At the time when silicate minerals were looked upon as compounds of various hypothetical silicic acids, attempts were made, notably by Tschermak,[14] to demonstrate the existence of these silicic acids by studying the hydrated silica obtained from the different silicates on treating them with acids. This and other indirect methods of deducing the constitution of crystalline silicate minerals led to inconclusive results. They have now been replaced by X-ray methods of crystal analysis, which in recent years have so successfully established the internal atomic structures of the crystalline silicates.

The situation today is just the reverse of what it was in Tschermak's time. It has become possible to consider the nature of the different kinds of hydrated silica liberated from silicate minerals on the basis of the known constitution of those minerals.

Silicate minerals that are decomposed by hydrochloric or nitric acid fall into two groups depending on their behavior when attacked by an acid. (1) About 80 minerals whose silica does not dissolve in acid but is left behind as residual separated silica when the mineral undergoes decomposition and (2) 135 minerals that dissolve completely in acid to

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[14] Tschermak, G., Metasilikate und Trisilikate: K. Akad. Wiss. Wien, Math.-naturwiss. Kl., Sitzungsber. Band 115, Abt. 1, pp. 217–240, 1906.

yield a clear, filterable solution, which sets to a firm silicic acid gel. The distinction between these groups is precise enough to form the basis of one of the most successful determinative schemes for minerals, that of Brush and Penfield.[15] About 200 silicate minerals are unattacked or only slightly attacked by acid, and they can therefore offer no information as to the behavior of various types of internal structure under effective acid attack.

An interesting physical difference between dried silica gel and dried separated silica is given in Brunauer's recent book[16] on physical adsorption. The surface area of silica gel is around 600 square meters per gram, whereas that for the silica separated from glauconite, a mineral with a micalike sheet structure, is around 80 square meters per gram.

In a recent paper[17] the writer discussed the correlations between the gelatinizing behavior of the minerals of group 2 and their internal structure and gave a review of the evidence for the correlations. The present paper treats entirely of the chemical implications of certain rules arising from the correlations and ignores the few apparent exceptions to each of those rules.

Grateful acknowledgment is made of helpful discussions and criticisms by S. B. Hendricks, of the Bureau of Plant Industry, Soils, and Agricultural Engineering, United States Department of Agriculture, and J. M. Axelrod, of the Geological Survey, in the preparation of this paper.

The different types of internal structure that have been found for the silicate minerals are shown in figures 1 to 4, taken from Berman's paper on the classification of silicates.[18] His numbering of the figures has been followed.

Owing to the large size of the oxygen atoms bonded to the silicon atoms, these silicon-oxygen structures dominate the internal make-up of silicate minerals and largely determine their physical and chemical properties. Aluminum freely substitutes for silicon, giving one, two, and three-dimensional structures made up not only of SiO_4 tetrahedra but also of SiO_4 and AlO_4 tetrahedra linked together. Other bases, such as calcium, magnesium, sodium, and potassium, are distributed variously and neutralize the excess negative charges of the silicon- and aluminum-oxygen structures.

STRUCTURES OF GELATINIZING MINERALS

When the gelatinizing minerals are classified according to their silicon-oxygen structures, it becomes immediately apparent that they are restricted to the following structural types:

Orthosilicate (fig. 4a).
Pyrosilicate (fig. 4b).
Possibly the ring structure containing three silicon atoms (fig. 4c).
Possibly the ring structure containing six silicon atoms (fig. 4e).
Sheet structure (fig. 2) that contains large amounts of ferric iron substituting for silicon.
Three-dimensional structure (fig. 1) that contains sufficient aluminum substituting for silicon to give an aluminum to silicon ratio of at least two aluminum atoms to three silicon atoms.

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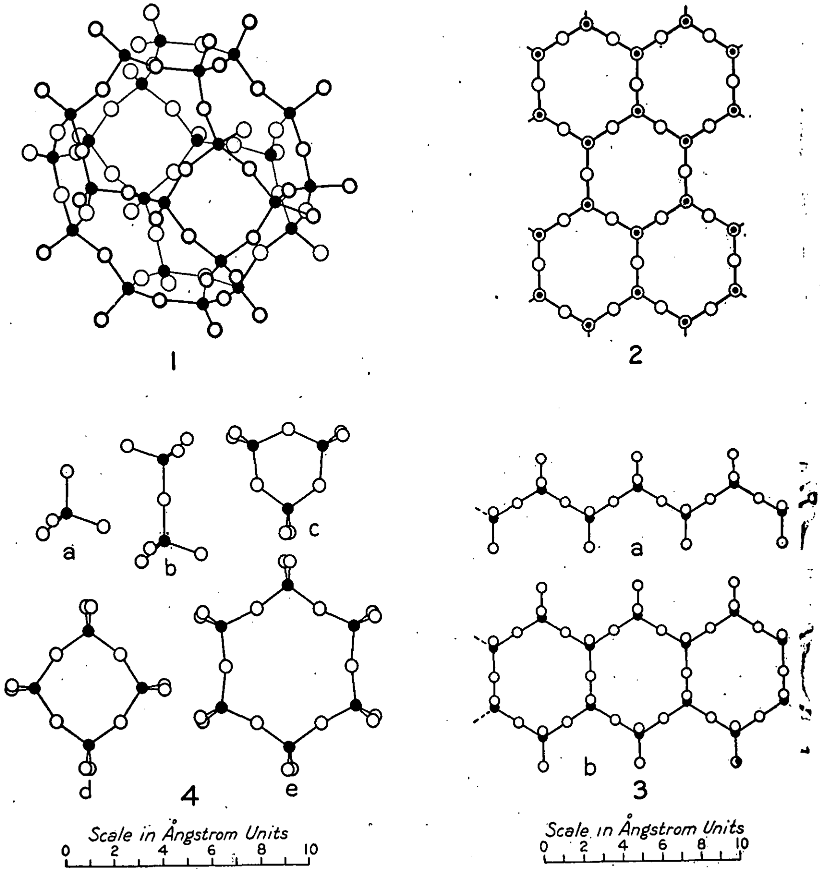
[15] Brush, G. J. and Penfield, S. L., Manual of determinative mineralogy, 16th ed., John Wiley & Sons, 1898.

[16] Brunauer, S., The adsorption of gases and vapors, vol. 1, physical adsorption, p. 298, Princeton Univ. Press, 1943.

[17] Murata, K. J., Internal structure of silicate minerals that gelatinize with acid: Am. Mineralogist, vol. 28, pp. 545–562, 1943.

[18] Berman, Harry, Constitution and classification of the natural silicates: Am. Mineralogist, vol. 22, pp. 342–408, 1937.



FIGURES 1–4.—Linkages of silicon-oxygen tetrahedra. Black indicates silicon, with or without aluminum; white indicates oxygen. After Bragg, through Berman.

1. Silica type, SiO_2; three-dimensional linkage.
2. Disilicate type, Si_2O_5; two-dimensional linkage.
3. Metasilicate type: a, SiO_3, single-chain linkage; b, Si_4O_{11}, double-chain linkage.
4. a, Orthosilicate type, SiO_4, independent tetrahedra; b, pyrosilicate type, Si_2O_7, paired tetrahedra; c, ring linkage, Si_3O_9; d, ring linkage, Si_4O_{12}; e, ring linkage, Si_6O_{18}.

The gelatinizing minerals have silicon- and aluminum-oxygen linkages as follows: In figure 1, only those with the amount of aluminum that replaces silicon equal to or exceeding the ratio of two aluminum atoms to three silicon atoms; in figure 2, only those with a large amount of ferric iron replacing silicon; all those in figures 4a, 4b, and possibly 4c and 4e.

Minerals that separate insoluble silica instead of gelatinizing have the linkages shown in figures 1 and 2 (except for the particular compositions noted above), 3a and 3b.

The data on the behavior of the ring linkages 4c, 4d, and 4e are meager.

In the sections that follow, the hypothesis is developed that in order for a mineral to gelatinize, its siliceous structure must be of such a nature that, when attacked by an acid, it will break down into soluble units of small molecular weight not containing more than some maximum number of silicon atoms.

ORTHOSILICATE AND PYROSILICATE TYPES

The gelatinization of the orthosilicate minerals is not surprising in view of the extensive literature[19] on the formation of silicic acid gel from the orthosilicate ion. Altogether, 49 minerals of this type gelatinize.

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[19] Hurd, C. B., Theories for the mechanism of the setting of silicic acid gels: Chem. Rev., vol. 22, pp. 403–406, 1938. Carman, P. C., Constitution of colloidal silica: Faraday Soc. Trans., vol. 36, p. 964, 1940.

The ready gelatinization of 16 pyrosilicate minerals securely establishes the interesting fact that a silicon-oxygen unit containing two silicon atoms also will form a silicic acid gel. With this pyrosilicate unit and all other condensed silicate structures, which arise from mutual sharing of oxygen among adjacent silicon atoms, the reasonable assumption is made that the silicon-oxygen bond, -Si-O-Si-, among these adjacent silicons is strong enough to withstand attack by acids.

The integrity of the condensed silicon-oxygen structures is seen in a most striking way in the various forms of residual silica that are obtained from minerals that separate insoluble silica. Coherent plates of hydrated silica are obtained from biotite and gillespite[20], and coherent fibers from chrysotile. Current theories on the formation of silicic-acid gels in acid and neutral solutions postulate simple silicate molecules polymerizing by forming silicon-oxygen linkages of the type found in silicate structures and thereby require that these be stable in such solutions.

In addition to the basic assumption that the silicon-oxygen bond withstands acid attack, one other assumption is required, namely, that all elements external to the silicon-oxygen framework, like potassium, calcium, magnesium, zirconium, and fluorine, have negligible influence in determining whether a mineral gelatinizes or separates insoluble silica. This assumption is justified by the fact that no correlation is apparent between the presence of these elements and the behavior of a mineral towards acids. On the other hand, elements like aluminum and iron, which occur within the silicon-oxygen frameworks as substitutes for silicon, directly affect the behavior of these frameworks under acid attack

STRUCTURES CONTAINING THREE TO SIX SILICON ATOMS

Data on the behavior of the Si_3O_9 ring are meager because only two minerals, benitoite,[21] ($BaTiSi_3O_9$) and catapleiite[22] ($(Na_2,Ca) ZrSi_3O_9.2H_2O$) have been shown through X-ray structure analysis to contain this three-membered ring, although a number of other minerals with analogous composition and crystallographic character have had this structure tentatively assigned to them by Berman. An X-ray study by Barnick[23] indicates that parawollastonite (monoclinic) is also made up of Si_3O_9 rings, but this mineral is classified by Berman among those having the single-chain linkage. As benitoite is unattacked by acid, catapleiite is the only mineral available for a study of the behavior of Si_3O_9 rings.

There are conflicting reports in the literature as to whether catapleiite gelatinizes or separates insoluble silica. In the original description,[24] the mineral from Brevik, Norway, when powdered, is said to be decomposed in a short time by hydrochloric acid without gelatinization. Flink[25] describes natron-catapleiite from Greenland as being decomposed by warm hydrochloric acid with separation of pulverulent silicic acid. On the other

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[20] Schaller, W. T., The properties and associated minerals of gillespite: Am. Mineralogist, vol. 14, pp. 319–322, 1929. Pabst, A., Crystal structure of gillespite, $BaFeSi_4O_{10}$: Am. Mineralogist, vol. 28, pp. 388–390, 1943.

[21] Zachariasen, W. H., The crystal structure of benitoite: Zeitschr. Kristallographie, Band 74, p. 139, 1930.

[22] Brunowsky, B. K., Die Struktur des Katapleits: Acta Physicochimica U. R. S. S., vol. 5, pp. 863–892, 1936.

[23] Barnick, M., Strukturuntersuchung des natürlichen Wollastonits: Die Naturwissenschaften, Band 23, pp. 770–771, 1935.

[24] Weibye, P. H., et al., Neue Mineralien aus Norwegen: Annalen der Physik u. Chemie (Poggendorff), Band 19, p. 300, 1850.

[25] Flink, G., Om några mineral från Grönland: Geol. fören. Stockholm Förh., Band 15, p. 206, 1893.

hand, catapleiite from Bearpaw Mountains, Mont. is said by Pecora[26] to gelatinize. The writer has tested two Norwegian specimens, obtained from the United States National Museum through the courtesy of E. P. Henderson. These specimens were No. R6989 from Eikaholmen and No. 49025 from Brevik. Both samples gelatinized.

Further systematic study of this interesting mineral is desirable. The peculiar inversions that it undergoes at moderate temperatures, noted by Flink[27] and by Gordon,[28] add an element of uncertainty to the interpretation of its behavior towards acids. It would be especially interesting to determine whether the material X-rayed by Brunowsky gelatinizes. Those samples that definitely gelatinize point to the possibility that the Si_3O_9 ring undergoes gelatinization.

A very unusual type of silicon-oxygen condensed structure has been proposed for zunyite,[29] $Al_{13}Si_5O_{20}(OH,F)_{18}Cl$. The silicon-oxygen tetrahedra are linked together into clusters of five, made up of one central tetrahedron with a tetrahedron attached to each of its four corners. Unfortunately for our purpose, the mineral is unattacked by acids, but it is mentioned here on account of its remarkable structure.

In a recent paper, Belov[30] concludes from X-ray structure analysis that the gelatinizing mineral dioptase, $Cu_6Si_6O_{18}.6H_2O$, contains independent Si_6O_{18} rings of the type shown in figure 4e. If this interpretation is correct, the mineral would offer an example of a silicon-oxygen unit of such a size and configuration gelatinizing. An earlier X-ray study[31] had indicated that dioptase is an orthosilicate, H_2CuSiO_4, with a structure like that of phenakite.

SHEET STRUCTURES

The behavior of the minerals considered up to this point emphasizes the fact that silicate units of small molecular weight are involved in gelatinization. When the gelatinizing minerals with large, continuous structures are examined, it is seen that they are so constituted that they become thoroughly disintegrated during acid attack and as a consequence also liberate small silicon-oxygen units.

For example, the chlorite mineral cronstedtite, which has the continuous sheet structure of figure 2, has every other silicon atom replaced by ferric iron[32]. Each iron atom may be thought of as a point of weakness against acid attack, and thus the silicon-oxygen units that are liberated as the sheet falls apart are orthosilicate radicals. Other sheet-structure minerals that are decomposed by acid, like biotite and glauconite, do not have this unusual and extensive substitution of ferric iron for silicon, and they do not gelatinize but give residual sheets of hydrated silica that retain the shape of the original mineral grains.

The brittle micas, margarite, seybertite, and xanthophyllite, have very large amounts of aluminum substituting for silicon in the silicon-oxygen

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[26] Pecora, W. T., Nepheline syenite pegmatites, Rocky Boy stock, Bearpaw Mountains, Mont.: Am. Mineralogist, vol. 27, p. 418, 1942.

[27] Flink, G., Undersøgelser af Mineraler fra Julianehaab: Meddelelser om Grönland, vol. 24, pp. 93–103, 1901.

[28] Gordon, S. G., Minerals obtained in Greenland on the second Academy-Vaux expedition, 1923: Acad. Nat. Sci. Philadelphia Proc., vol. 76, pp. 258–260, 1924.

[29] Pauling, Linus, The crystal structure of zunyite: Zeitschr. Kristallographie, Band 84, p. 442, 1933,

[30] Belov, N. V., New silicate structures: Acad. Sci. U. R. S. S. Comptes rendus (Doklady), vol. 37. pp. 139–140, 1942.

[31] Gottfried, C., Über die Struktur der Phenakit-Dioptasgruppe: Neues Jahrb., Beilage-Band 55A, p. 393, 1927.

[32] Hendricks, S. B., Random structures of layer minerals as illustrated by cronstedtite: Am. Mineralogist, vol. 24, pp. 529–539, 1939.

sheet. It would be of interest to find out if these minerals react towards acids in the same way as does cronstedtite. They are usually described as being only slightly attacked by acids, so presumably the effect of acid on their aluminum-rich silicon-oxygen sheets cannot be determined. However, as some samples of margarite and seybertite are decomposed to a considerable extent, these minerals seem worthy of further study. The interpretation of the results of such a study will be complicated by the fact that the mode of distribution of the aluminum atoms, either ordered or random, in the sheets has not been fixed by X-ray analysis, as has been the mode of distribution of ferric iron in cronstedtite. This point is considered further in the section on three-dimensional structures, and is discussed in detail in the paper by W. G. Schlecht. (See p. 35.)

STRUCTURES WITH THREE-DIMENSIONAL LINKAGE

The gelatinizing minerals with three-dimensional structures are characterized by large amounts of aluminum substituting for silicon. The aluminum atoms are points of weakness in these structures. This is directly indicated by the fact that the residual silica obtained from the nongelatinizing minerals of this group is free of aluminum, as illustrated by Rinne's experiments[33] on heulandite. In figure 5 are plotted the aluminum to silicon ratios of 44 minerals of the three-dimensional type which are attacked by acids. Those that gelatinize are designated with black circles and those that separate insoluble silica, with open circles. In plotting, the mineral davyne was lumped with microsommite, and faroelite with thomsonite so the total number of gelatinizing minerals is two less than given in an earlier paper.

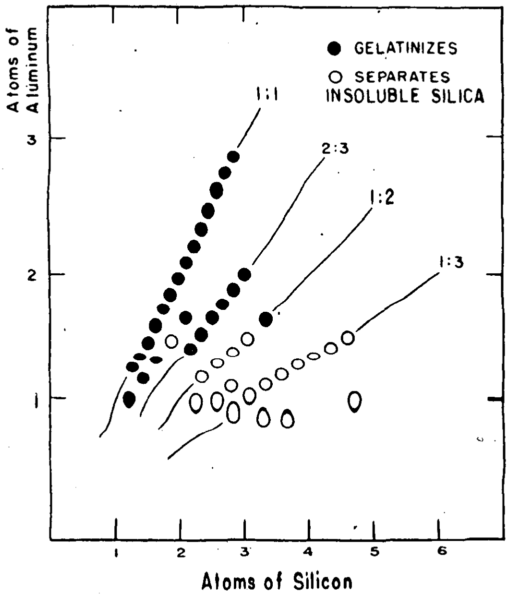

FIGURE 5.—Ratio of aluminum to silicon in three-dimensional silicates and the behavior of these silicates on acid attack.

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[33] Rinne, F., Uber die physikalisch-chemische Einwirkung von Schwefelsäure and Salzsäure auf Heulandit: Neues Jahrb., 1896, Band 1, pp. 139–148.

From the data shown in figure 5 the rule is derived that silicates having a three-dimensional structure with a ratio of at least two aluminum atoms to three silicon atoms will gelatinize; those that are less aluminous, or conversely more siliceous, separate insoluble silica. The two apparent exceptions to the rule (laumontite and wellsite) cannot be explained with the information at hand.[34]

The physical interpretation of this rule in terms of a limiting size of the the silicon-oxygen unit that will undergo gelatinization is blocked by the fact that X-ray methods fail to reveal the mode of distribution of the aluminum atoms in these structures. For example, in discussing the structure of sodalite (Al:Si=1:1), Bragg[35] states, "***it is not possible to say whether Al and Si have this [ordered] arrangement, or replace each other at random." In picturing these three-dimensional structures breaking up at points where the aluminum atoms are located, it is highly important to know the way in which these aluminum atoms are distributed throughout the structures in order to arrive at the sizes of the resulting silicon-oxygen fragments.

W. G. Schlecht, of the Geological Survey, has made a preliminary study of the problem, and his analysis is given on pages 35 to 82. Assuming a perfect random distribution of aluminum and silicon atoms, he has calculated, for different aluminum to silicon ratios, the fractional part of the total number of silicon atoms that would be included in clusters of various sizes when continuous structures like the hexagonal sheet and the three-dimensional ultramarine framework disintegrate. His curves for the distribution of cluster sizes are given in figures 11 and 15, and typical random groupings are illustrated in figures 16, 18, and 20. The data clearly show that, in the composition range in which gelatinization occurs (Al:Si=1:1 to 2:3), a random arrangement places a very large proportion of the silicon atoms in clusters of considerable size. With the gelatinizing composition of two aluminum to three silicon atoms, illustrated in the hexagonal sheet of figure 20, the silicon clusters are so large as to suggest that an appreciable part of the framework would hold together if the aluminum atoms were dissolved out. A similar condition is indicated for the ultramarine framework by Schlecht's preliminary calculations.

This cannot be reconciled with the observed fact that gelatinizing minerals dissolve completely in acid to give a clear, filterable solution, and it is not in harmony with the working hypothesis that gelatinization depends on small silicon-oxygen clusters. Furthermore, the way in which the aluminum-silicon ratio controls the gelatinization of minerals of the three-dimensional structural type seems inexplicable in terms of slight differences in the proportions of very large clusters that are indicated for compositions near the 2:3 boundary ratio.

The presumption is that the aluminum atoms are not distributed at random in such minerals but have some degree of order in their arrangement that produces smaller silicon-oxygen clusters. If the arrangement were of the highest type of symmetry for the 1:1 ratio of aluminum to silicon, every other atom in a framework would be an aluminum atom so that the silicon-oxygen fragments that are released would be orthosilicate

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[34] A third exception, given by the writer in a previous paper (Murata, K. J., Internal structure of silicate minerals that gelatinize with acid: Am. Mineralogist, vol. 28, pp. 545–562, 1943) was arduinite, which separates insoluble silica. On calculating the aluminum-to-silicon ratio on the only published analysis of this mineral (Dana's System of Mineralogy, 6th ed., 3d appendix; Barth, T. F. W. and Berman, Harry, Neue optische Daten wenig bekannter Minerale: Chemie der Erde, Band 5, p. 42, 1930) it was found that the ratio was 1 : 2.88 rather than 2 : 3 as given in Berman's classification. For this reason, the mineral is no longer considered as an exception.

[35] Bragg, W. L., Atomic structure of minerals, p. 268, Cornell Univ. Press, 1937.

radicals. Schlecht's analysis clearly shows how ordered and partly ordered arrangements place large proportions of the silicon atoms into small clusters. The maximum size of the silicon-oxygen clusters that undergo gelatinization, however, has not yet been deduced.

The question of the mode of distribution of the aluminum atoms has become critical in interpreting the atomic structures of the feldspars. Sanidine, microcline, and orthoclase[36] are believed to differ only in the way the aluminum atoms are arranged in the basic framework that all three have in common.

X-ray studies[37] of the plagioclase feldspars have disclosed a more complicated condition than the old concept of a single isomorphous series in which (Ca+Al) replaced (Na+Si) at random. Surprising differences in the size of the unit cells in the *c* direction have been found in different parts of the series, particularly in the more aluminous compositions represented by labradorite, bytownite, and anorthite. The explanation for the differences must wait until the internal structure of the plagioclases has been completely determined.

The plagioclase series and the scapolite series of minerals are of special interest in the present study because their composition (Al:Si = 1:3 to 1:1) extends across the 2:3 boundary ratio for the gelatinization of minerals of the three-dimensional type. Future work on the internal structures of these minerals may, therefore, furnish a detailed picture of how the aluminum atoms are arranged in three-dimensional structures on both sides of the 2:3 ratio boundary and what kind of silicon-oxygen clusters occur in the gelatinizing and nongelatinizing ranges of composition.

Some new observations by Gordon and Wichers[38] on the decomposition of the plagioclase feldspars by acid have recently been published. In the course of extensive experiments in which they successfully decomposed many refractory minerals and artificial compounds by treating them with acids in sealed tubes at elevated temperatures, these investigators tested several members of the plagioclase series and found remarkable differences in their resistance toward hydrochloric acid. When treated for 48 hours at 300°C., three samples with compositions between no percent and 37 percent anorthite were virtually unattacked, whereas four samples with compositions between 40 percent and 100 percent anorthite were completely decomposed.

The critical composition at which the abrupt change in the resistance toward acid occurs was determined within narrow limits (37–40 percent anorthite) through a fortunate choice of samples. This composition corresponds to an aluminum-silicon ratio of 1:1.9, which, as may be seen from figure 5, lies near the lower limiting ratio for minerals that separate insoluble silica. No observations were made on whether the four samples that were decomposed gelatinized or separated insoluble silica, so the results do not establish an exact boundary ratio between the two types of behavior. The discovery of an abrupt break in the decomposition curve for this series of isomorphous minerals, however, is of great interest in connection with the interpretations given for similar breaks or "resistance

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[36] Chao, S. H., Hargreaves, A., and Taylor, W. H., The structure of orthoclase: Mineralog. Mag., vol. 25, p. 511, 1940. Barth, T. F. W., Polymorphic phenomena and crystal structure: Am. Jour. Sci., 5th ser., vol. 27, pp. 280–282, 1934.

[37] Chao, S. H., and Taylor, W. H., Isomorphous replacement and superlattice structures in the plagioclase feldspars: Royal Soc. London Proc., ser. A, vol. 176, pp. 76–87, 1940.

[38] Wichers, Edward, Schlecht, W. G., and Gordon, C. L., Preparing refractory oxides, silicates, and ceramic materials for analysis, by heating with acids in sealed tubes at elevated temperatures: U. S. Nat. Bur. Standards Jour. Research, vol. 33, pp. 451–456, 1944.

limits" in other isomorphous series like AgCl-NaCl and the gold-copper alloys.

When aged mixed crystals of AgCl-NaCl are leached with water all the sodium chloride is dissolved out from crystals containing less than 0.6 mole fraction of AgCl, but if the crystals contain more than 0.8 mole fraction of AgCl none of the sodium chloride is leached out.[39] Tammann's interpretation is that in aged crystals, there is an ordered arrangement of the silver and sodium atoms with respect to each other so that the NaCl groups are too completely surrounded by insoluble AgCl to be dissolved by the water. Likewise, gold-copper alloys, whose atomic structure has been ordered by annealing, are not attacked by nitric acid if they contain more than 0.5 atomic fraction of gold; if they contain more than half copper, all the copper is dissolved by the acid.[40]

The AgCl-NaCl series and the gold-copper alloys are discussed in greater detail by W. G. Schlecht on pages 59 to 60. There is considerable modern physico-chemical data and information based on X-ray analysis that fully confirm Tammann's early interpretations. It seems highly probable that the break in the decomposition curve for the plagioclases is likewise due to an ordered arrangement of the constituent atoms, particularly aluminum and silicon. The question of decomposition of the plagioclases, therefore, leads to the same conclusion as that reached in explaining the gelatinization of numerous other aluminosilicate minerals of the three-dimensional structural type that are decomposed by acid.

Because X-ray methods in the past could not distinguish the aluminum tetrahedra from the silicon tetrahedra in the several silicate networks, aluminum and silicon atoms have ordinarily been considered, as a first approximation, to be identical. In the present study, however, the marked chemical difference between aluminum and silicon has become emphasized, and the position of the aluminum atoms in aluminosilicate networks has become a matter of primary concern.

SUMMARY

The behavior of silicate minerals, representing a wide variety of internal structures, indicates that small silicon-oxygen units, whose maxiumum size is as yet undetermined, will dissolve in acid to yield gelatinous silica whereas large units are insoluble and yield separated silica. In explaining the behavior of minerals with three-dimensional structures, the conclusion was reached, with the aid of calculations by W. G. Schlecht, that the aluminum atoms in the gelatinizing minerals of this type are not distributed at random but have some degree of order in their arrangement. The results of this preliminary survey seem to be of sufficient interest to call for further systematic studies on minerals and artificial compounds with known internal structure.

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[39] Schmidt, K. W., Dissertation, Göttingen, 1917, described in Tammann, G., Über dem atomistischen Aufbau nicht metallischer Mischkristalle: K. Gesell. Wiss. Göttingen, Math.-physikal. Kl., Nachr., 1918, pp. 298–299.

[40] Tammann, G., Über die Resistenzgrenzen von Mischkristallen und die Molekularverteilung in Raumgittern: K. Gesell. Wiss. Göttingen, Math.-physikal. Kl., Nachr., 1916, pp. 199–265.

Contributions to geochemistry, 1942–45
Geological Survey Bulletin 950

SYMMETRICAL ARRANGEMENT OF ATOMS IN ALUMINOSILICATES AND RANDOM ARRANGEMENT OF TWO KINDS OF OBJECTS IN A REGULAR ARRAY[40a]

By William G. Schlecht

ABSTRACT

In aluminosilicate minerals the exact location of aluminum and silicon atoms in the structure with respect to each other cannot ordinarily be distinguished by X-ray diffraction measurements, because the atoms of both elements have practically the same scattering power toward the X-rays. Some other way must be used to determine if the relative arrangement of the two kinds of atoms is haphazard or symmetrical.

It is shown that random arrangement of two kinds of objects, such as silicon and aluminum atoms, in a regular array results in a smaller number of small clusters than does symmetrical arrangement of the same objects in the array. The method of calculating the distribution of small clusters in an array is described. No systematic way has been found of expressing the chance that a given atom is part of a cluster of a given size in terms of the chance that it is part of a smaller cluster. Therefore it must be found by enumeration of cases. Distribution equations and their curves are given for small clusters on plane hexagonal, plane tetragonal (apophyllite-type), square, cubic, and tetrakaidecahedral (ultramarine-type) arrays. Typical random arrangements on a plane hexagonal array are shown.

In mixtures with compositions like those of aluminosilicate minerals, the number of small clusters becomes negligible as complete randomness of arrangement is approached, and it is concluded on the small-cluster hypothesis of gelatinization of silicate minerals that the arrangement of aluminum and silicon atoms must be very symmetrical with respect to each other; otherwise clusters too large to gelatinize would be formed when the minerals are decomposed. It is shown, however, that a limited degree of randomness not only may be present, but must necessarily be possible in crystals forming continuous isomorphous replacement series; it is the type of arrangement already known in metal alloys, in which random arrangements of atoms are not restricted by the types of interatomic forces found in less metallic crystals. The occurrence of such arrangements is called the "order-disorder" phenomenon by physicists. A simplified hypothetical example, the plane hexagonal array, is adopted to illustrate the results of random arrangement, superlattice, and partly disordered states in more complex but similar arrays of actual crystals.

INTRODUCTION

In studying the relation between the gelatinization of silicate minerals and the atomic structures of their crystals, K. J. Murata, of the Geological Survey, found it necessary to consider the problem of how aluminum and similar atoms are arranged among the silicon atoms in the crystals. (See p. 25.) X-ray analysis shows that in aluminosilicate minerals at least some of the aluminum atoms occupy the same type of positions as silicon

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[40a] The term *array* is here used as a general name for any arrangement of points, because some of the arrays of points treated in this paper are not considered to be lattices or nets as defined in the standard terminology recommended by the Nomenclature Committee of the American Society for X-ray and Electron Diffraction, at the Gibson Island Conference in 1944. The Committee proposed that the use of the terms *row*, *net*, and *lattice* be restricted to those regular arrays of points that are derivable from groups of translation operations in space of one, two, and three dimensions, respectively. The Committee further urged that, in referring to the actual array of atoms constituting the structure of crystals, the term *crystal structure* be used, not "crystal lattice." The term *lattice* will then be available for use in the more restricted sense as recommended by the Committee, and there will be no need of resorting to such a term as "translation lattice" for describing this special kind of array.

atoms, but does not show how the two kinds of atoms are arranged with respect to each other. The symmetrical arrangement of positions of the atoms is shown, but it is not found how the two kinds of atoms are distributed among these positions.

The behavior of silicate minerals when treated with acids depends on the sizes of oxygen-silicon units released when the aluminum or other soluble atoms among the silicon units are dissolved away. The relation found by Murata between gelatinization and composition is strikingly shown in figure 5 of ratios of aluminum to silicon in minerals that gelatinize and those that separate insoluble silica when treated with acid. If the composition is such that small clusters of silicon-oxygen units are released when the aluminum is dissolved, the mineral will gelatinize, otherwise insoluble silica will be separated. The sharp distinction in behavior between minerals with aluminum-silicon ratios above and below two to three shows that there must be a difference in the sizes of clusters released from the different compositions.

If the pattern of relative arrangement of silicon and aluminum atoms in gelatinizing minerals is symmetrical, the clusters will be very small, as is shown by examples. Simple arithmetical calculations show that there could be very few small clusters if the arrangement were haphazard. Both findings indicate that the arrangement is symmetrical.

This conclusion is supported theoretically by the known nature of valence forces or chemical bonds between atoms. Unsymmetrical arrangements of atoms are usually less stable than symmetrical arrangements; they have higher potential energies and so whenever possible change spontaneously to the more symmetrical forms having lower energies.

Experimental evidence on both metallic and nonmetallic crystals also supports this conclusion. In the gelatinizing mineral cronstedtite, the iron atoms replacing silicon atoms are symmetrically arranged. In both metallic and nonmetallic crystals containing two kinds of atoms that are able freely to replace one another in the structure, experimenters have found that the crystal structures with unsymmetrical distributions of atoms will change to ordered arrangements whenever possible.

There are limits to the degree of symmetry possible in the arrangement of atoms in some crystals. In substances whose compositions are not very simple ratios, and in pairs of substances that form miscible crystals in all ratios, there are some ratios that cannot form simple symmetrical patterns of atomic arrangement. There is abundant experimental evidence that such substances are not completely random in atomic arrangement, but have a limited degree of randomness. Simple calculations show that if the randomness in atomic arrangement is limited the atoms still may form small clusters.

ACKNOWLEDGMENTS

I thank Dr. W. Edwards Deming, of the Bureau of the Budget; Dr. F. G. Brickwedde, Mr. Harold W. Wooley, and Mr. Donald D. Wagman, of the National Bureau of Standards; Dr. George Tunell, of the Geophysical Laboratory, Carnegie Institution of Washington; Professor J. D. H. Donnay, of the Johns Hopkins University; and Dr. Sterling B. Hendricks, of the Bureau of Plant Industry, Soils, and Agricultural Engineering, U. S. Department of Agriculture, for advice and encouragement; and Ruth Wester Schlecht for calculating a table of random sampling numbers for binominal distributions, for making a model of the ultramarine type skeleton, and for drawing most of the illustrations.

MECHANISM OF GELATINIZATION

According to the hypothesis adopted to explain gelatinization, the behavior of silicate minerals when treated with acids depends on the sizes of clusters of neighboring silicon-oxygen tetrahedral units remaining when the skeletons such as those shown in figures 1, 2 and 3 are broken up by removing only the atoms that are not silicon. Any group of silicon-oxygen tetrahedra that is separated from others in the skeleton by atoms that will dissolve in the acid is thought to survive the acid treatment as a cluster. If the clusters left when the framework is destroyed are small enough to dissolve in the solution, they may polymerize to form a gel; if they are too large, they are not soluble enough to do this and separate as insoluble silica.

By a cluster is meant a group of silicon atoms connected to each other without any other kind of atoms between them, except the oxygen atoms that bind them together. A cluster may be unbranched, so that it forms a simple isolated open or closed chain, or it may be branched; in a branched cluster at least one of the silicon atoms is connected by single oxygen bonds to at least three other silicon atoms. If a single silicon atom is isolated from the rest of the silicon atoms by having other kinds of atoms for all of its nearest neighbors, it is called a cluster of one.

To study the arrangement of the silicon atoms in clusters we may neglect the oxygen atoms, which bind the other atoms together to form the skeleton, and draw a simplified diagram in which all the oxygen atoms are omitted. The diagram shows only the sites occupied by silicon atoms and those atoms replacing silicon in the mineral. It is understood that there is an oxygen atom connecting any two nearest neighbors on the diagram. On the simplified framework the number of nearest neighbors to an atom is fixed by the type of skeleton of the mineral. For example, an atom on either a plane hexagonal arrangement (fig. 11), or a plane tetragonal arrangement of the apophyllite-type (fig. 12), has three nearest neighbors; an atom on either a square arrangement (fig. 13), or a tetrakaidecahedral arrangement of the ultramarine type (fig. 15), has four nearest neighbors; and an atom on a cubic arrangement (fig. 14), has six nearest neighbors.

The frameworks discussed here are not the arrangements of the complete atomic structures of crystals, but simplified frameworks containing only the sites of the silicon atoms and atoms replacing silicon. The symmetries of the simplified skeletons are not necessarily the same as the symmetries of the complete crystal structures. Care should therefore be taken to avoid confusing the simplified skeletons described here with the actual complete structures of the crystals.

As far as calculating the number of kinds of clusters and the ways in which they may be formed are concerned, the symmetry of a particular kind of arrangement sets certain limits. The type of array fixes the number of branches at a point on the array and the ways the branches are connected. In terms of the atoms in the skeleton these properties of symmetry determine the number of nearest neighbors to an atom in the skeleton and the possible ways of forming closed chains. Therefore, the cluster size distribution calculated for a given simplified skeleton is not affected in any way by puckering of the skeleton, or in fact by distortion of the most extreme kind. As long as the distortion is not so great as actually to destroy the skeleton, the same cluster-size equations apply.

When the relative positions of the two kinds of atoms, silicon and silicon-replacing atoms are marked on the simplified framework, the silicon clusters are shown separated from each other by the other kinds of atoms. These positions are generally found from X-ray diffraction measurements,[41] but cannot be found for aluminosilicates because aluminum atoms have practically the same scattering power for X-rays as silicon atoms; all that can be found by X-ray measurements is that certain sites on the skeleton are occupied by either aluminum or silicon atoms. For this reason it has not been possible for crystallographers to say whether the relative arrangement of the silicon and the aluminum atoms is in a simple symmetrical pattern or a haphazard one on the points of the skeleton. If the two kinds of atoms are so nearly alike that they can be substituted for each other without changing the shape of the skeleton very much, many other properties of the crystal besides its X-ray diffraction pattern may also be expected to be the same no matter what the relative arrangement is. If, however, the two kinds of atoms differ in the least amount in some of their properties, the behavior of the crystal will be at least a little different in some respects; even two kinds of atoms of the same element that differ only in their masses have a slight difference in their chemical behavior, called the "isotope separation factor."

If the gelatinizing property depends on the sizes and shapes of clusters of silicon separated by the aluminum atoms, it must be particularly sensitive to differences in the mode of arrangement between the two kinds of atoms in the framework. By simply comparing some typical arrangements in symmetrical patterns (figs. 19 and 22) and in random distribution (figs. 18 and 20) it can be seen that, in the range of composition corresponding to aluminosilicate minerals that gelatinize, a symmetrical arrangement results in small clusters but a totally haphazard arrangement reduces greatly the number of small clusters. It is therefore concluded that the relative arrangement of aluminum and silicon atoms must be very symmetrical with respect to each other in the gelatinizing minerals, otherwise the clusters would be too large to dissolve and would not form gels when the mineral is treated with acid.

Aluminum is so different from silicon that is is not surprising that some properties of the aluminosilicate minerals are affected by the relative arrangement of the atoms. The electric charges of the atoms differ by a ratio of three to four. If large clusters of one kind of atoms are formed, the difference in charge of the two kinds of atoms makes a more uneven distribution of electrical charge and one less stable than a symmetrical arrangement, so the symmetrical arrangement is also somewhat favored by the nature of the chemical forces between the atoms.

THEORETICAL EVIDENCE FOR SYMMETRICAL ATOMIC ARRANGEMENT

RANDOM-CLUSTER FORMATION

CALCULATION OF DISTRIBUTION

If two kinds of atoms are randomly mixed with one another in the skeleton, the kinds of clusters formed in a mixture of given composition cannot be described as simply as they could in a symmetrically arranged mixture, in which only one kind or at most very few kinds of clusters make up the whole array. If the atoms are randomly distributed there

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[41] Simple diagrams explaining the diffraction of X-rays by sets of parallel planes of atoms in crystals are given by Bain, Edgar C., Studies of crystal structure with X-rays: Chem. Met. Eng., vol. 25, pp. 657–664, 1921.

is no practical limit to the number of possible kinds of clusters, so the mixture is conveniently described in terms of a distribution of atoms among clusters, such that a certain fraction of the atoms are present in clusters of each possible kind. The process used gives the same result as sorting the clusters into piles, and comparing the sizes of the different piles.

The distribution of very small clusters may be calculated from simple considerations of chance. In a group of so enormous a number of atoms as is contained in a crystal, the actual fraction of atoms in clusters of a given kind may be considered equal to the chance that a given atom is part of such a cluster. For simplicity and generality the silicon and aluminum atoms are replaced in the following calculations by black and white balls in the ratio of p to (1—p), distributed at random in the array; in the illustrations the clusters of silica are represented by clusters of black balls.

In a mixture of equal numbers of black and white balls the chance that a given ball is black is the same as the fraction of black balls, $p = \frac{1}{2}$, and equal to the chance $(1-p) = \frac{1}{2}$ that it is white. Similarly for any mixture, the fraction p of black balls in the mixture is equal to the chance that a given ball on the lattice is black, and the remaining fraction $(1-p)$ of white balls in the mixture is equal to the chance that the given ball is white.

The fraction or relative number of white balls in the array is thus equal to the chance that a given ball is white, which we have already defined as $(1-p)$; white balls are of course not members of any cluster of black balls, so we might call it the chance that a given ball is a member of a cluster of zero black balls, $P_c' = P_0' = 1-p$, where P_c' is the fraction of black balls in clusters of size c, as explained below. As $c = 0$, and the fraction P_0' thus refers to white balls only, it is of no interest in a count of the clusters of black balls.

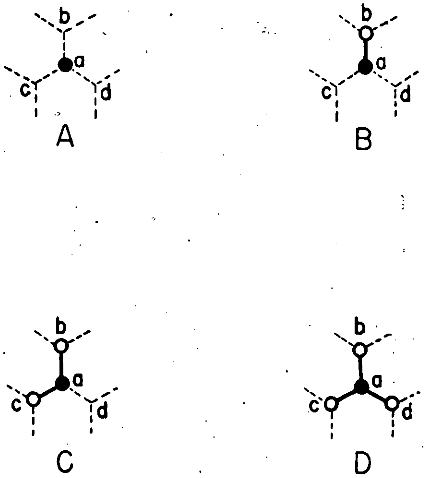


FIGURE 6.—Formation of clusters of one in a plane hexagonal array. If a mixture of $\frac{1}{6}$ black balls and $\frac{5}{6}$ white balls is arranged at random in a plane hexagonal array $\frac{5}{6} \times \frac{5}{6} \times \frac{5}{6} \times \frac{1}{6} = \frac{1}{6} \times (\frac{5}{6})^3$ of the balls will be isolated black balls—clusters of one.

A, $\frac{1}{6}$ of all points on the network are occupied by black balls.

B, $\frac{5}{6}$ of all the black balls also have a white neighbor in position b; so $\frac{5}{6} \times \frac{1}{6}$ of all points in the array are occupied by black balls with this arrangement.

C, $\frac{5}{6}$ of all the black balls with arrangement B also have white neighbors in position c; so $\frac{5}{6} \times \frac{5}{6} \times \frac{1}{6}$ of all points in the array are occupied by black balls with this arrangement.

D, $\frac{5}{6}$ of all the black balls with arrangement C also have white neighbors in position d, so $\frac{5}{6} \times \frac{5}{6} \times \frac{5}{6} \times \frac{1}{6}$ of all points in the array are occupied by black balls with this arrangement.

All the rest of the balls are black and so they are by definition members of clusters; since the fraction of black balls is p, the chance that a given ball is part of a cluster of black balls is the same as the chance that it is black, $1-P_0'=p$; we may call this expression the fraction of balls that are not in clusters of zero black balls. These are the balls whose distribution into clusters we wish to know; the fraction of balls that are contained in clusters of size c we shall call P_c'; then P_c' is equal to the chance that a given ball is part of a cluster of c black balls. For the cluster to consist of c black balls, the chance P_c' is the product of the chances that each of the c balls is black, and the chances that each of the balls immediately surrounding the cluster is white.

Suppose for example that one-sixth of the balls are black and the other five-sixths are white. The only way that a given ball can be a member of a cluster of one is for it to be black and all its nearest neighbors white. One-sixth of all the balls in the array are black; the number of those that are isolated black balls—clusters of one—depends on the kind of array. To form a cluster of one in a plane hexagonal array, a black ball at the position *a* in figure 6, A, must be surrounded by white balls in positions *b*, *c*, and *d*. Now of all the $\frac{1}{6}$ black balls on the lattice, $\frac{5}{6}$ will have as neighbors white balls in position *b* (fig. 6, B) because $\frac{5}{6}$ of all the balls are white, so $\frac{5}{6}\times\frac{1}{6}$ of all the balls in the array are in this arrangement. Of all these $\frac{5}{6}\times\frac{1}{6}$ pairs $\frac{5}{6}$ will also have white balls in position *c* (fig. 6, C) for the same reason, so $\frac{5}{6}\times\frac{5}{6}\times\frac{1}{6}$ of all the balls in the array will have this arrangement. But $\frac{5}{6}$ of these will by the same reasoning also have white balls in position *d* (fig. 6, D); these are the black balls completely isolated from all other black balls by white balls, so $\frac{5}{6}\times\frac{5}{6}\times\frac{5}{6}\times\frac{1}{6}=\frac{1}{6}\times(\frac{5}{6})^3$ is the fraction of balls that are contained in clusters of one.

If instead of a mixture of $\frac{1}{6}$ black balls and $\frac{5}{6}$ white balls we had taken any mixture whatever whose fractions of black and white balls were p and $(1-p)$, respectively, we should have found by the same reasoning that the fraction of balls in clusters of one in a plane hexagonal array is

$$P_1'=p(1-p)^3.$$

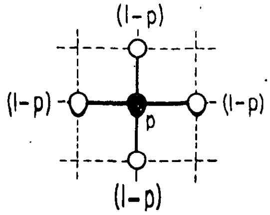


FIGURE 7.—Formation of clusters of one in a square array. The chance that a point on a square array is occupied by an isolated black ball is $p(1-p)^4$.

In a square array, the only way that a ball can be an isolated black ball is for it to have four white nearest neighbors (fig. 7) so the fraction of balls in clusters of one,

$$P_1'=p(1-p)^4$$

is arrived at by the same reasoning.

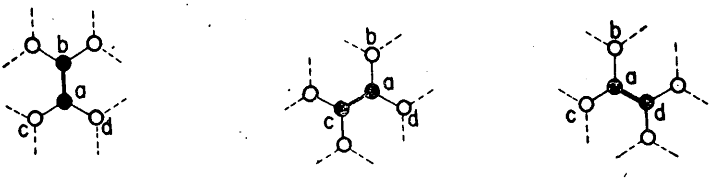


FIGURE 8.—Formation of clusters of two in a plane hexagonal array. The three ways in which a ball in a plane hexagonal array can be a member of a cluster of two black balls.

A black ball can be a member of a cluster of two in more than one way. On a plane hexagonal framework there are three ways in which it can be a member of a cluster of two. On this framework one of its three nearest neighbors must be black and four balls immediately surrounding the black pair must be white. By the method described we can find that $p^2(1-p)^4$ of all the balls are members of each of the three kinds of clusters of two (fig. 8) so the total fraction

$$P_2'=3p^2(1-p)^4.$$

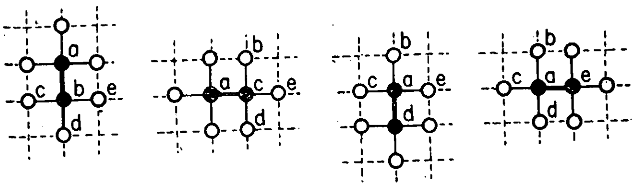


FIGURE 9.—Formation of clusters of two in a square array. There are four ways in which an atom *a* in a square array can be a member of a cluster of two black balls.

In a square array (fig. 9) there are four ways in which a ball can be a member of a cluster of two black balls; calculating as before we find that each of the four arrangements contains $p^2(1-p)^6$ of all the balls in the array, so the relative abundance of clusters of two is

$$P_2'=4p^2(1-p)^6.$$

Two more examples of calculation of cluster-size distribution are shown in plate 1 and figure 10; the fraction of balls in clusters of size *c* is calculated as before for each possible way that the cluster can be formed, and all the fractions are added together. Plate 1, B shows that some clusters of three or more need fewer white balls to isolate them than do others, because of the way in which they are bent or branched; those joined in rings also need fewer than do open chains. This complicates the expressions for P_c by making two or more terms in the equations, so that there is no simple formula for P_c in terms of *c* as well as *p*; the equations are found by the tedious method of drawing diagrams of all possible arrangements, calculating their chances, and adding these individual chances together. The labor becomes practically prohibitive for clusters greater than about six, because of the complexities introduced by the increasing branching of clusters.

The fractions P_c' give a census of the clusters in the array, expressed as parts of the total number of balls, both black and white. The cluster-size count can conveniently be expressed in terms more directly related to experimental results by eliminating the fraction of white balls from

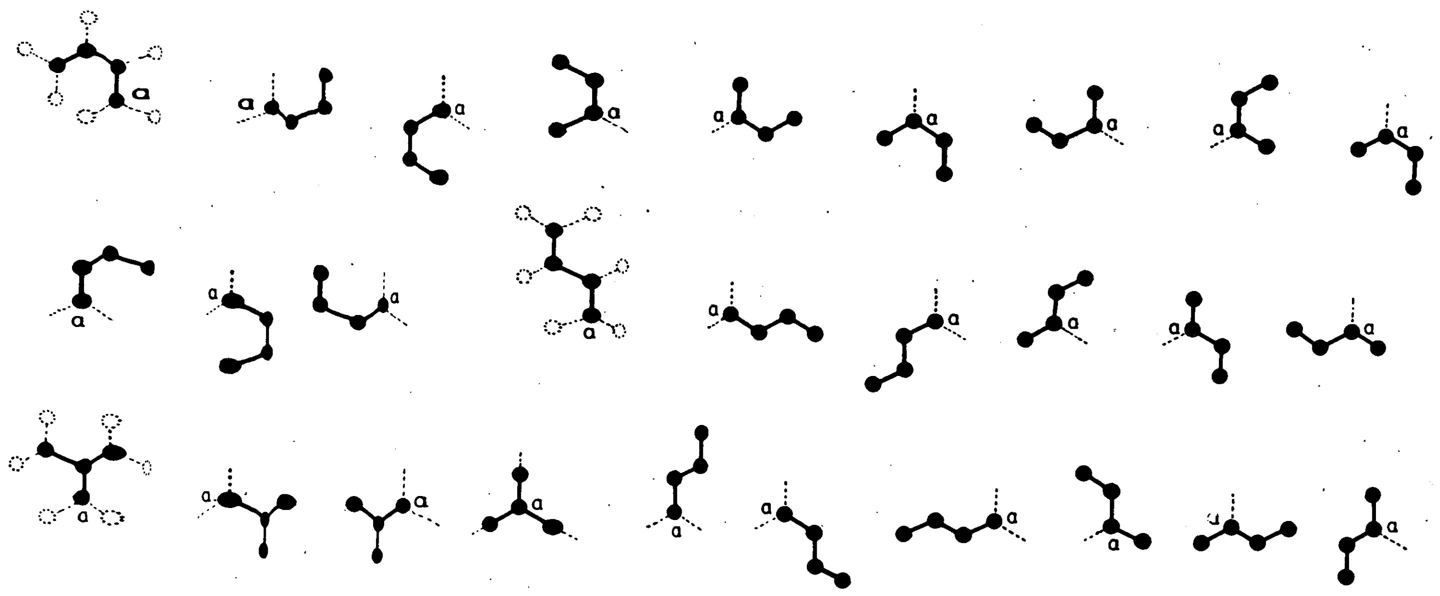
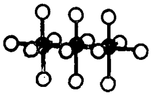
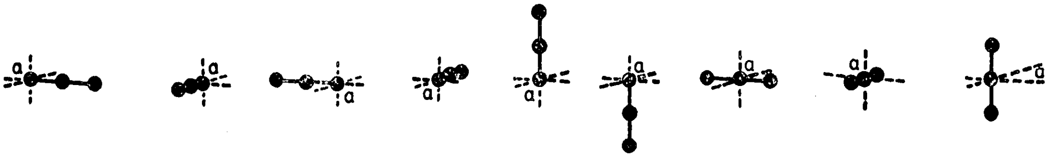


FIGURE 10.—Clusters of 4 black balls in a plane hexagonal array. There are 28 ways that a black ball can be a member of a cluster of 4 in this array. Three particular balls connected with it must be black, and 6 other particular balls around them must be white. If the chance that a ball is black is p, and the chance that it is white is $1-p$, then the chance that the given black ball is arranged in one of the ways that make it a cluster of 4 is $p^3(1-p)^6$. Since it can be a member of a cluster of 4 in 28 different ways, the total chance that it is a member of a cluster of 4 black balls is $P_4=28p^3(1-p)^6$.

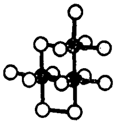


A straight cluster of 3 black balls on a cubic lattice requires 14 white balls to isolate it from other black balls. The chance that a given black ball is connected with 2 other black balls is p^2. The chance that the necessary 14 balls surrounding the cluster are white is $(1-p)^{14}$. Therefore the chance that a given black ball is a member of some cluster of 3 black balls is $p^2(1-p)^{14}$

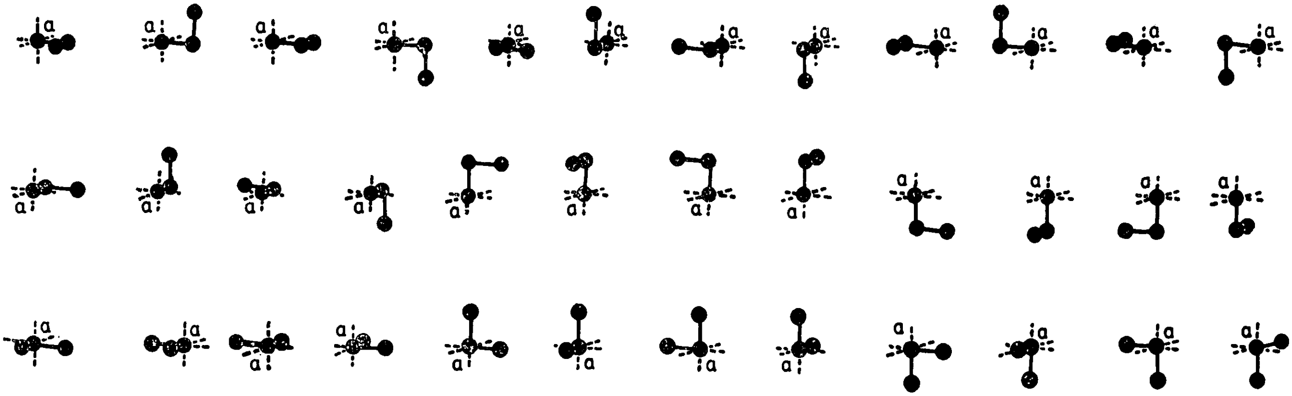


There are 9 ways that a given black ball *a* may be a member of a straight cluster of 3, so the total chance that a given black ball is a member of a straight cluster of 3 is $9p^2(1-p)^{14}$.

A



A bent cluster of 3 black balls on the cubic lattice requires only 13 white balls to isolate it from other black balls, so the chance that the given black ball is a member of a bent cluster of 3 is $p^2(1-p)^{13}$.



There are 36 ways that a given black ball *a* may be a member of a bent cluster of 3 black balls, so the total chance that a given black ball is a member of a bent cluster of 3 is $36p^2(1-p)^{13}$.

B

CLUSTERS OF 3 BLACK BALLS ON A CUBIC LATTICE

The total chance that a black ball is a member of a cluster of 3 black balls on this lattice is the sum of the chances of all the different ways that it can be a member of a cluster of 3,

$$P_3 = 9p^2(1-p)^{14} + 36p^2(1-p)^{13}$$

the results and converting the distribution into fractions of the total number of black balls only by dividing them by p, the fraction of black balls in the mixture. The reasoning is as follows:

The number of black balls in clusters of c is equal to Pc' times the total number of balls in the array.

Dividing by the total number of *black* balls, the fraction

$$\frac{\text{number of balls in clusters of } c}{\text{number of black balls}}=\frac{Pc' \times \text{total number of balls}}{\text{number of black balls}},$$

but, $\frac{\text{total number of balls}}{\text{number of black balls}}=\frac{1}{p}$, because p is the fraction of black balls in the mixture.

Calling this fraction P_c,

$$P_c=\frac{\text{number of balls in clusters of } c}{\text{number of black balls}}=P_c'\times\frac{1}{p},$$

the fraction of *black* balls in clusters of size c. The new fraction,

$$P_c=\frac{P_c'}{p},$$

gives the chance that a given *black* ball is part of a cluster of size c, so it is equal to the fraction of *black* balls that are contained in clusters of c. This is equal to the fraction of the silicon atoms in a mineral that are in clusters of c, so if the various kinds of clusters can be roughly separated by any actual process, such as filtration or sedimentation, and the silicon content of each fraction found, the weights of silicon can be compared with the calculated values of P_c.

Thus, for a silicate mineral $P_c=\frac{P_c'}{p}$ is the number of atoms in clusters of size c per atom of silicon, which is also equal to the number of grams, for example, of silicon in clusters of c, per gram of silicon in the mineral.

CLUSTER-DISTRIBUTION EQUATIONS FOR RANDOM ARRANGEMENT

The fractions of black balls distributed among the smallest-sized clusters are given in the accompanying tables for completely random distribution in some common types of array.

Random distribution of two kinds of objects in clusters in regular arrays

[p =fraction of the first kind of objects in the array (represented by black balls in the examples); $1-p$= fraction of the second kind of objects in the array (represented by white balls in the examples). Either p or $1-p$ completely expresses the composition of the mixture. P_c =the fraction of the first kind of objects in clusters of size c]

1. Plane hexagonal array

c	P_c
1	$(1-p)^3$
2	$3p(1-p)^4$
3	$9p^2(1-p)^5$
4	$28p^3(1-p)^6$
5	$15p^4(1-p)^6+75p^4(1-p)^7$
6	$3p^5(1-p)^6+90p^5(1-p)^7+189p^5(1-p)^8$

2. Plane tetragonal array of octagons and squares (corresponding to Si and Al sites on array of the apophyllite type)

c	P_c
1	$(1-p)^3$
2	$3p(1-p)^4$
3	$3p^2(1-p)^4+6p^2(1-p)^5$
4	$p^3(1-p)^4+12p^3(1-p)^5+12p^3(1-p)^6$

3. Square array

   c P_c
   1....$(1-p)^4$
   2....$4p(1-p)^6$
   3....$12p^2(1-p)^7+6p^2(1-p)^8$
   4....$36p^3(1-p)^8+32p^3(1-p)^9+8p^3(1-p)^{10}$
   5....$5p^4(1-p)^8+100p^4(1-p)^9+140p^4(1-p)^{10}+60p^4(1-p)^{11}+10p^4(1-p)^{12}$

4. Tetrakaidecahedral array (corresponding to Si and Al sites in the ultramarine type of array)

   c P_c
   1....$(1-p)^4$
   2....$4p(1-p)^6$
   3....$6p^2(1-p)^7+12p^2(1-p)^8$
   4....$2p^3(1-p)^8+48p^3(1-p)^9+32p^3(1-p)^{10}$

5. Simple cubic array

   c P_c
   1....$(1-p)^6$
   2....$6p(1-p)^{10}$
   3....$36p^2(1-p)^{13}+9p^2(1-p)^{14}$
   4....$32p^3(1-p)^{15}+100p^3(1-p)^{16}+192p^3(1-p)^{17}+12p^3(1-p)^{18}$

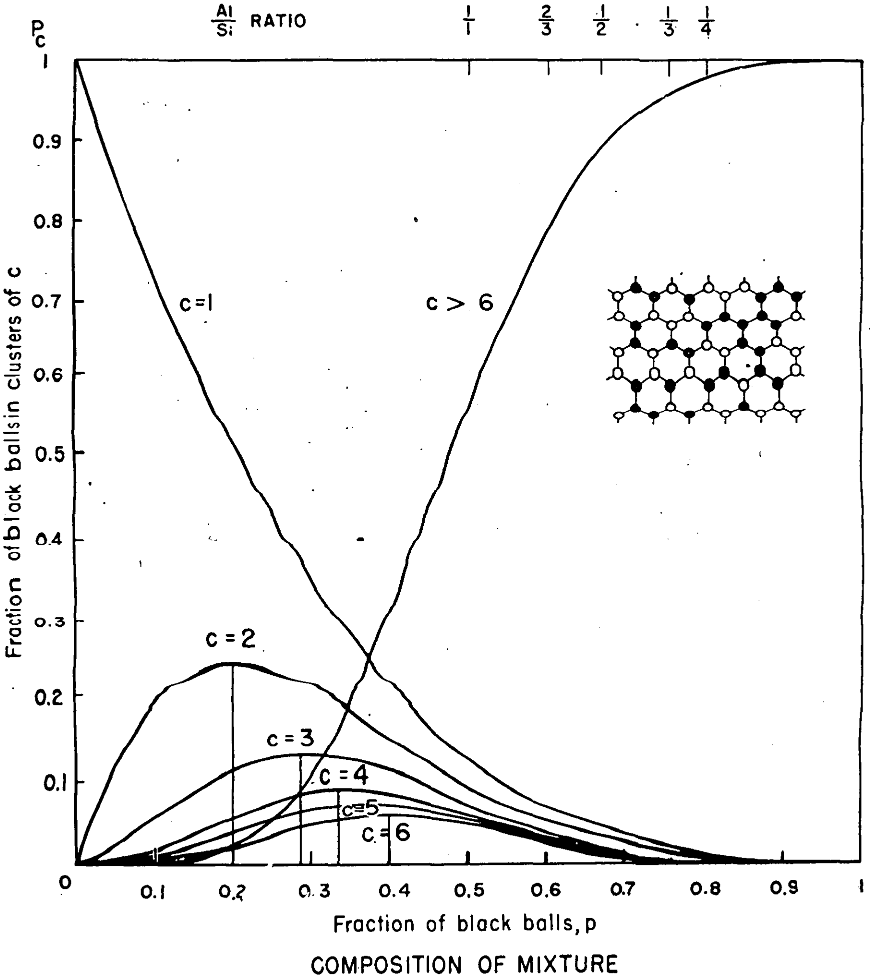


FIGURE 11.—Random cluster distribution of a mixture of black and white balls in a plane hexagonal array. Fraction of black balls in clusters of size c in a mixture containing $100p$ percent black balls.

The curves of these equations (figs. 11 to 15) show that in the range of composition corresponding to silicate minerals with three-dimensional structures, which contain at least as much silicon as aluminum (Al:Si ratio 1:1 or less), the fraction of small clusters of silicon would be negligible if the relative arrangement of aluminum and silicon atoms were completely random. None of the minerals with three-dimensional structures studied by Murata could be expected to gelatinize if they had such a distribution. This is vividly illustrated for the plane hexagonal array by figures 16 and 17, 18 and 19, and 20 and 21, respectively, of some typical random samples compared with regular arrangements in which 1/6, 1/2, and 2/3, of the balls are black.

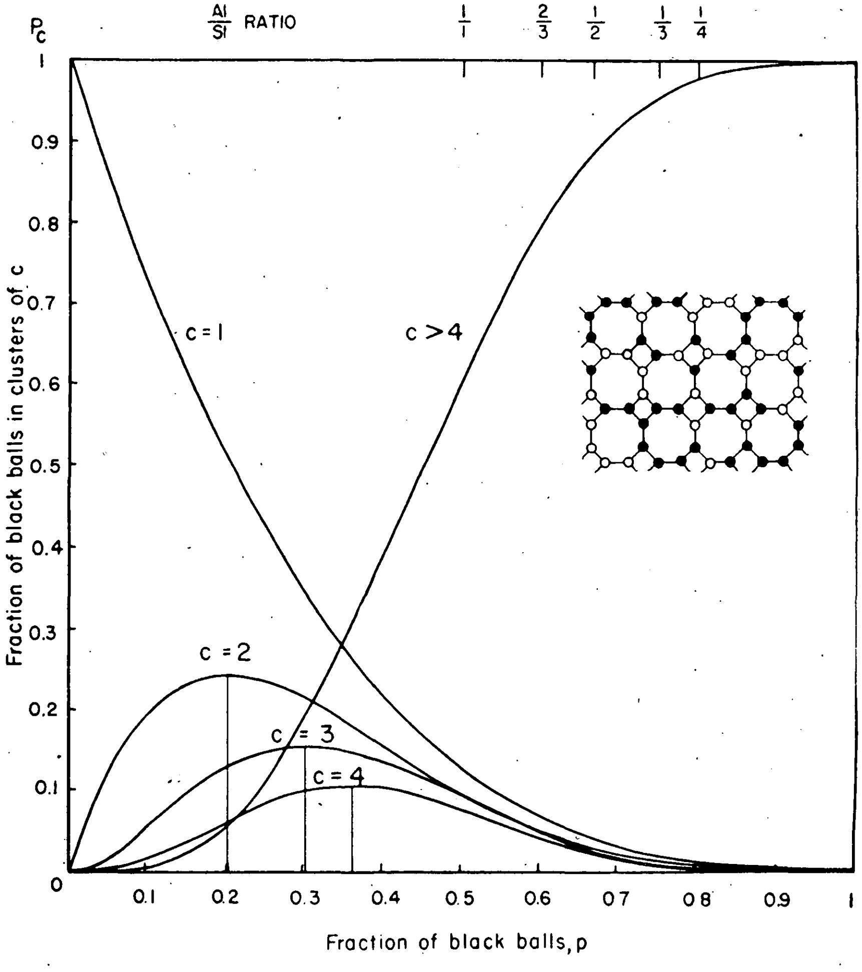


FIGURE 12.—Random cluster distribution of a mixture of black and white balls in a plane tetragonal array Fraction of black balls in clusters of size c in a mixture containing $100p$ percent black balls.

Figure 13 gives curves for the fraction of black balls in clusters up to six in a plane hexagonal array. This is the simplified model used to indicate the effects of randomness on cluster-size distribution; it is not yet known whether it can be taken to represent the condition in silicate minerals with the hexagonal sheet structure. The curve marked $c > 6$ is found by subtracting from unity, the sum of all those for clusters smaller than $c = 7$; so it gives the fraction of black balls in clusters larger than six in the mixture in the array.

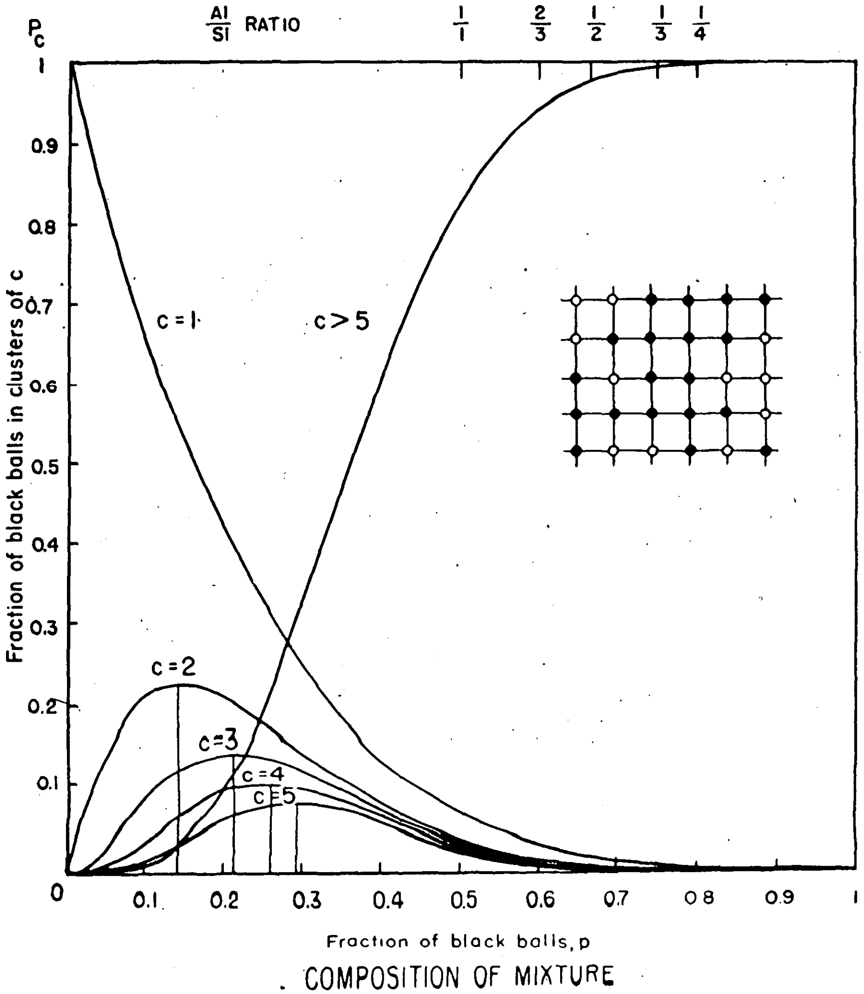


FIGURE 13.—Random cluster distribution of a mixture black and white balls in a square array. Fraction of black balls in clusters of size c.

The tetragonal array shown in the inset of figure 12 is an idealized combination of squares and octagons which gives the same cluster-size distribution as a distorted form of the same arrangement found in apophyllite. In this mineral there is no aluminum in the sheet structure, so the curves do not apply to it.

The square array (fig. 13) has a more complex distribution of cluster sizes than the hexagonal and tetragonal ones shown, respectively, in figures 11 and 12 because a ball in the square array has four nearest neighbors instead of three; and so more complicated branched clusters are possible.

The cubic array (fig. 14) on which a ball has six nearest neighbors, is the most complicated one shown. The possible branched clusters are far more complex than for the other arrays. The similarity of its curves, as well as those for the square array, to the curves for simpler arrays shows that the increased complexity does not greatly change the distribution of small-sized clusters.

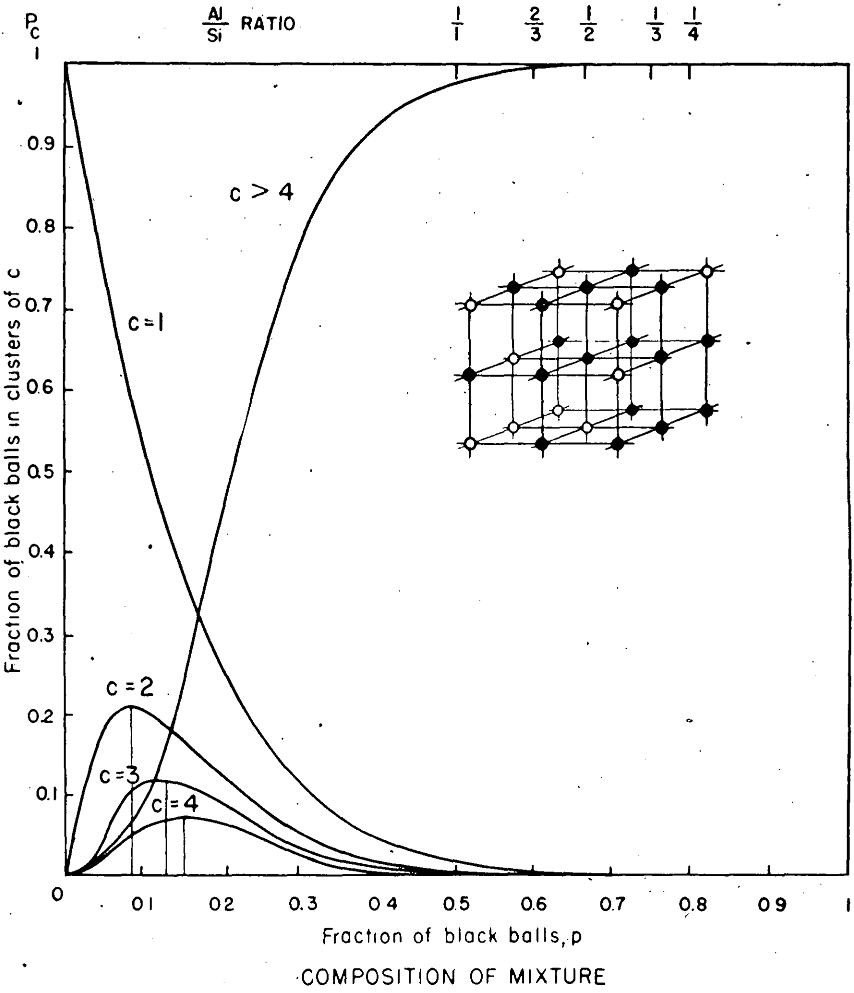


Figure 14.—Random cluster distribution of a mixture of black and white balls in a cubic array. Fraction of black balls in clusters of size c.

The tetrakaidecahedral array (fig. 15) has its points at the corners of an equilibrium form of the cube and octahedron, which is a space-filling tetrakaidecahedron. This lattice corresponds to the simplified skeleton of minerals like sodalite; it is called the ultramarine structure. These are the only curves shown that correspond to an actual known aluminosilicate imneral that gelatinizes; however, there is one ferrisilicate mineral with

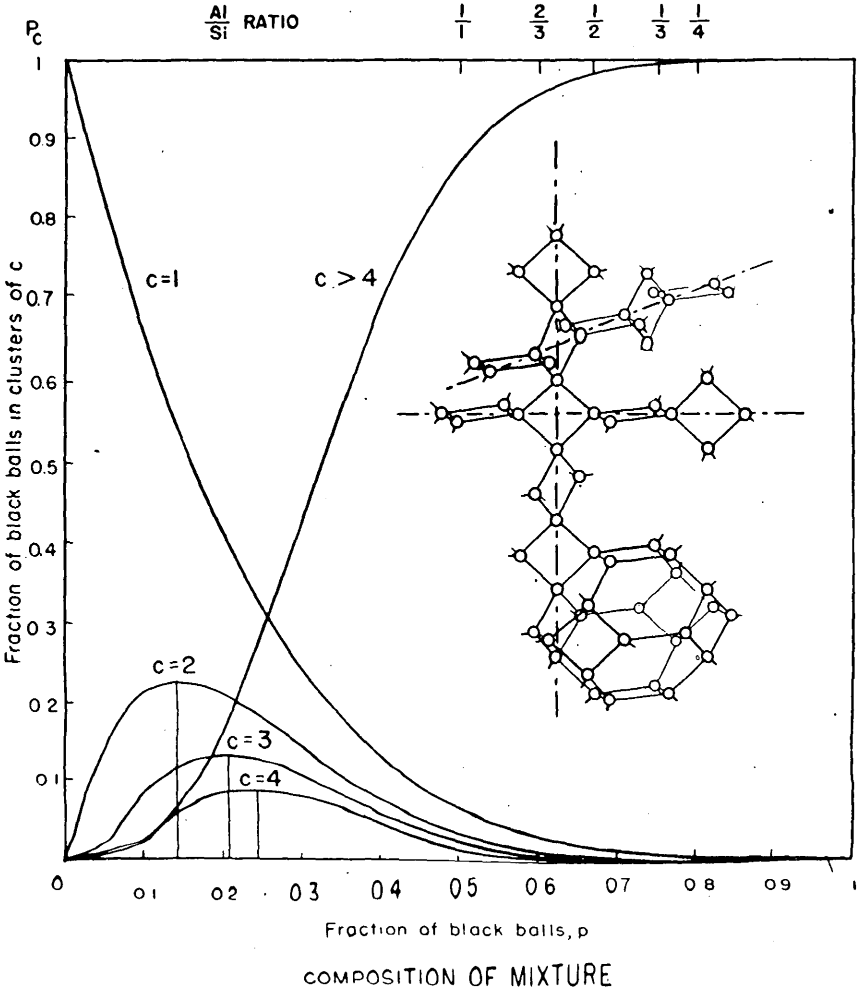


FIGURE 15.—Random cluster distribution of a mixture of black and white balls on a tetrakaidecahedral array. Fraction of black balls in clusters of size c.

the hexagonal-sheet structure that is known to gelatinize—the mineral cronstedtite, discussed in the section on symmetrical patterns. (See p. 52.) The distribution curves for the ultramarine structure do not differ greatly from those for the plane hexagonal array used in the examples.

The equations for cluster frequencies on the tetrakaidecahedral array were found by counting the numbers of possible arrangements of objects on the corners of a space model, made by joining appropriate lengths of toothpicks with Duco cement.

SIMPLIFIED ILLUSTRATIONS OF RANDOM AND SYMMETRICAL ARRANGEMENTS

The plane hexagonal array is used for the illustrations of symmetrical and random distributions, because it is the simplest one. The distribution curves show that in this array the effect of composition on distribution of small clusters is about the same as in the other arrays.

The examples of completely random distribution were made by counting the circles across the diagrams in successive rows from the tops of the diagrams downward. Whether a given circle was to be black or white was determined by simultaneously taking successive numbers from Tippett's table of random sampling numbers,[42] and inspecting the numbers for a property which is possessed by the desired fraction of all numbers. Tippett's tables have been thoroughly tested and are accepted by statisticians as satisfactorily random in their distribution. The remainder when a number is divided by the denominator of the composition fraction p serves for this purpose; for example, one-sixth of all numbers have the remainder zero when divided by six; one-sixth have the remainder one, and so forth; the six possible remainders are the numbers 0, 1, 2, 3, 4, 5. If the series of numbers is truly random, one-sixth of the numbers will have each of the possible remainders in the long run, but the remainders will occur in entirely haphazard order. To make the diagram for $p = 1/6$ a circle was made black whenever its corresponding random sampling number had the remainder zero when divided by six, otherwise it was made white. Any other one of the six possible remainders would have done as well. To make a series for which $p = 2/5$ the remainders are found for the random sampling numbers when divided by five; any two of the five possible remainders 0, 1, 2, 3, 4 are chosen to determine that the ball shall be labeled black; otherwise it shall be white. In the same way distributions can be found for any value of p from the random sampling numbers.

The first and third examples also will obviously yield typical random samples of mixtures in which $5/6$ and $1/3$, respectively, of the balls in the mixture are black, by simply interchanging the colors of the balls.

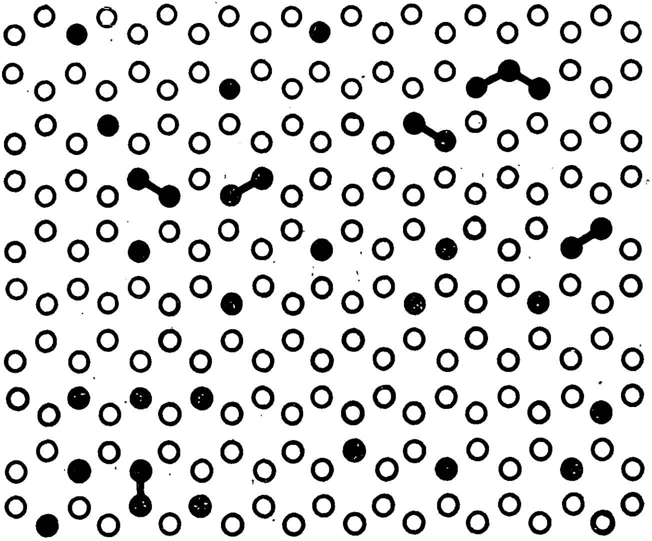


FIGURE 16.—Typical random distribution of a binary mixture containing $1/6$ black balls and $5/6$ white balls in a plane hexagonal array.

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[42] Tippett, L. H. C., Random sampling numbers: Univ. London, Univ. Coll., Tracts for computers, no. 15, London, Cambridge University Press, 1927.

The examples given are areas taken from larger arrays of 820 circles, so that the numbers of black balls in clusters on the edges might be known as nearly as practicable. The larger samples were marked by using a table of the remainders from dividing the first thousand numbers in Tippett's table by each of the integers from two to ten. The numbers of additional balls in clusters extending beyond the figures are marked alongside them. In figure 20, $p = 2/3$, some of the clusters extended even to the edges of the larger diagram, so only a lower limit can be set for their sizes. The resulting numbers of clusters of each size in the figures agree very satisfactorily with those calculated from the equations represented by the curves, so the examples are considered typical of the actual distributions to be expected.

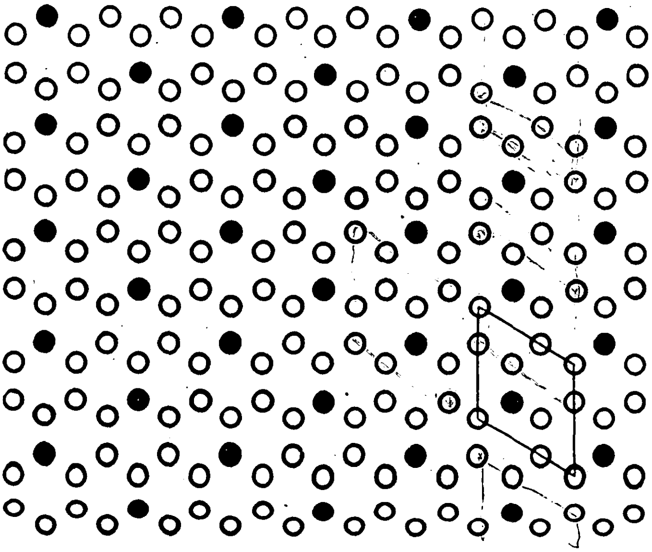

FIGURE 17.—Symmetrical arrangement of a binary mixture containing $1/6$ black balls and $5/6$ white balls in a plane hexagonal array. This regular pattern can be represented by its "unit cell," or unit of repetition; the pattern is reproduced by fitting unit cells together so as to repeat them in all directions. The unit cell of this pattern contains six balls, one black and five white.

The difference in numbers of small clusters for $p = 1/6$ (figs. 16 and 17) is not great. In the symmetrical pattern (fig. 17) all black balls are in clusters of one, so $P_1 = 1$; and in the random arrangement (fig. 16) there is some chance of formation of clusters of two, a smaller chance for clusters of three, and so on; the calculated fraction of black balls in clusters of one is $P_1 = 0.5787$. Although the black balls in the random arrangement do not form a pattern they become more widely separated as the fraction p is decreased; they approach the same state as a regular arrangement in that an area of a given size will usually contain the same number of black balls in either arrangement. This has no particular interest for small fractions of black balls, representing silicon fractions that do not occur in minerals; but it also applies to the aluminum atoms in minerals containing very high fractions of silicon. In crystals containing very small fractions of aluminum the aluminum atoms will not form clusters large enough to appreciably weaken the structure toward acid attack.

In the extremely silicon-rich aluminosilicate minerals containing say five or more times as much silicon as aluminum, it will make no difference in their behavior towards acids whether the relative arrangement of their silicon and aluminum atoms is random or symmetrical.

SYMMETRICAL PATTERNS

UNIT CELLS

The idea of a unit cell is illustrated by the cell drawn in figure 17. For the composition fraction $p = 1/6$ it is a rather large section of the structure. The unit cell is the unit of repetition of a pattern; the design may be extended by repeating the unit cell in all directions, fitting adjacent sides of the unit cells together.[43] As shown here, each unit cell wall cuts a white ball into halves; each of these white balls is shared with the adjoining cell. The four white balls cut by the sides thus contribute two white balls to each unit cell. In a more complicated way the four white balls at the corners are shared so as to contribute one white ball to each unit cell. Thus each unit cell contains a total of five white balls and one black ball. Larger unit cells may be taken. Any section of the arrangement which produces the pattern by repetition will serve as a unit cell.

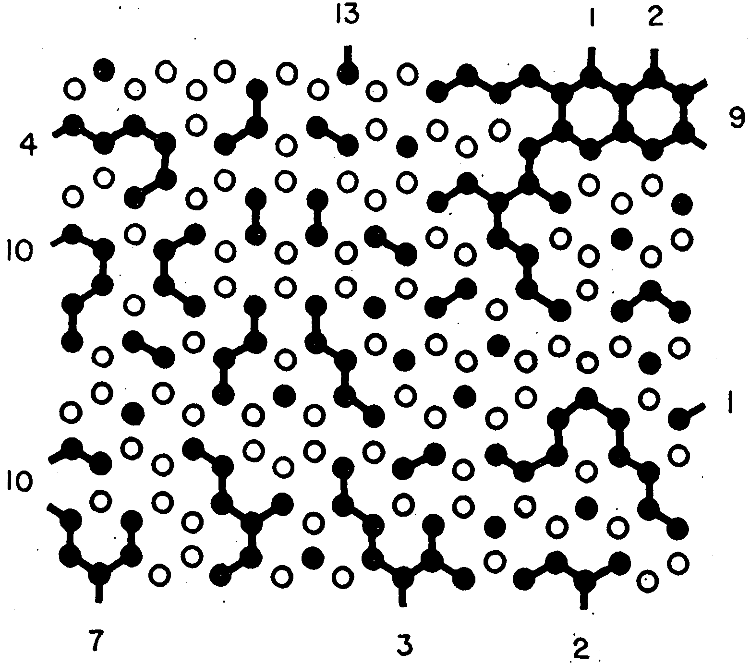

FIGURE 18.—Typical random distribution of a binary mixture containing ½ black balls and ½ white balls in a plane hexagonal array.

The smallest possible unit cell is smallest for the simplest composition fractions, and as the denominator of the composition fraction increases the minimum-sized unit cell also generally increases. If the number of black balls in a unit cell is compared with the number in a cell of the

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[43] Bragg, W. L., in Bragg, W. H. and Bragg, W. L., The crystalline state, vol. 1, pp. 1–5, Macmillan Co., New York, 1934; Atomic structure of minerals, pp. 4–6, Cornell University Press, Ithaca, N. Y., 1937.

same size on a random arrangement, they become more nearly alike as the fraction of black balls is made smaller. The only difference in the limiting state is that the positions of the black balls within the cells are not always the same and also their number varies slightly from cell to cell in the random arrangement.

In an equal mixture of black and white balls, the fraction of small clusters is very small for $p = \frac{1}{2}$ in a random arrangement (fig. 18) and all the clusters are single black balls in the symmetrical arrangement (fig. 19).

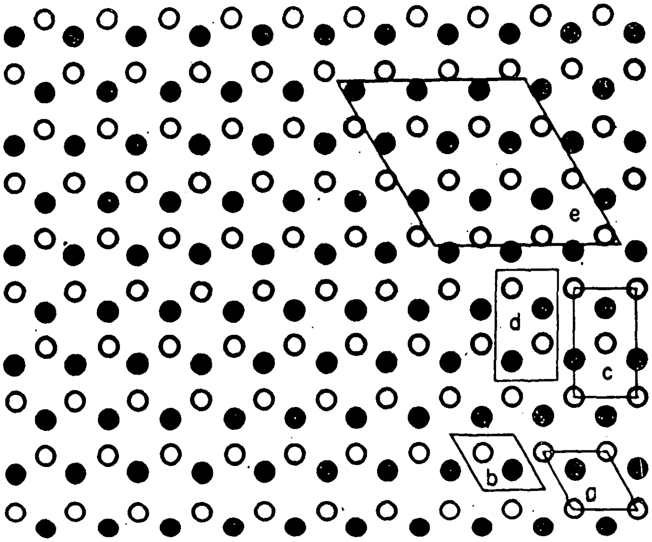


FIGURE 19.—Symmetrical arrangement of an equal binary mixture of black and white balls ($p = \frac{1}{2}$) in a plane hexagonal array. Unit cells containing 2 (*a*), 4 (*c*), and 18 (*e*) balls.

Several forms of unit cell are shown on the $p = \frac{1}{2}$ symmetrical arrangement in figure 19. The simplest unit cell, *a*, contains one black and one white ball; a doubled unit cell is shown by *c*, and one containing 18 balls by *e*. These unit cells intersect balls along their sides and at their corners, thus sharing the balls with neighboring unit cells. For convenience in counting balls and clusters, equivalent unit cells may be drawn by slightly shifting the outlines so as to completely enclose an equivalent number of balls, as in *b* and *d*.

In the mineral cronstedtite the iron and the silicon atoms are known from X-ray analysis to be arranged in sheets having the hexagonal structure shown in figure 19, with the silicon and iron atoms in the respective positions shown by black and white balls; in the actual sheet structure they are of course connected by oxygen atoms. The mineral gelatinizes when treated with acid, as is to be expected of a symmetrical arrangement that forms clusters of one silicon atom.

The random distribution of a mixture with $p = \frac{2}{3}$ black balls (fig. 20) shows that as the fraction of silicon increases beyond $p = \frac{1}{2}$, the number of small clusters becomes negligible; if the white balls are removed, practically only very large clusters remain. In the more silicon rich mixtures,

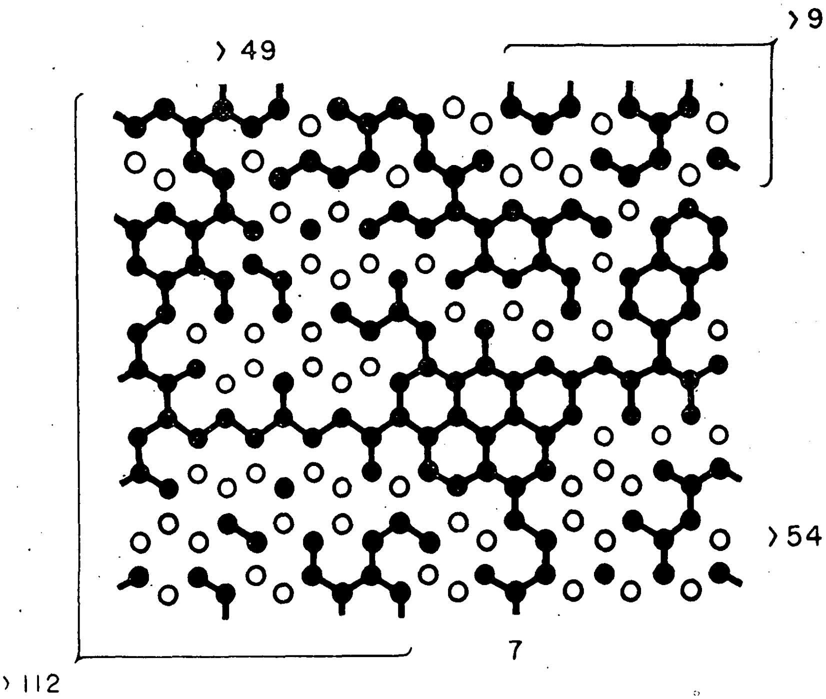


FIGURE 20.—Typical random distribution of a binary mixture containing ⅔ black balls and ⅓ white balls in a plane hexagonal array.

the aluminum atoms are so surrounded by silicon atoms that attack by acid may be hindered. Even in the symmetrical arrangement for $p = \frac{2}{3}$ (fig. 21) there are no clusters of one black ball; as can be seen by compari-

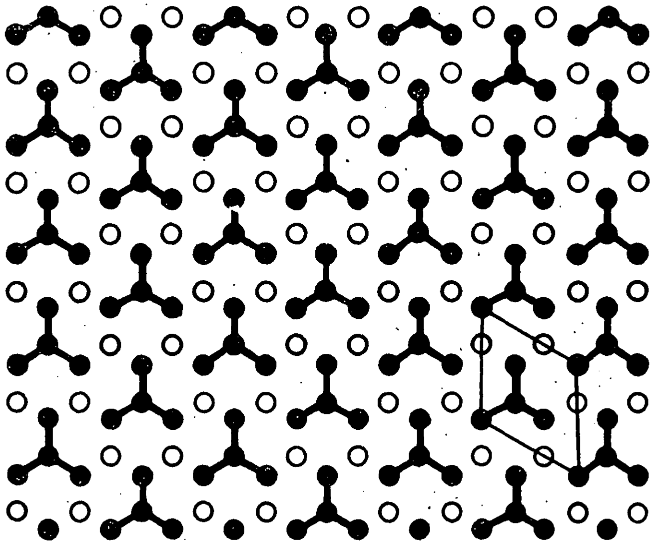


FIGURE 21.—Symmetrical arrangement of a mixture of ⅔ black balls and ⅓ white balls in a plane hexagonal array. The smallest possible unit cell contains six balls, four white and two black. It can be made into a unit cell with a symmetrical pattern for $p = \frac{1}{3}$ black balls by simply interchanging the colors of the balls.

son of the two arrangements the introduction of randomness allows the formation of a few clusters of one and two.

The manner of clustering in the random mixtures containing more than half black balls shows that in the range of composition representing the aluminosilicate minerals with three-dimensional structures, there could be no gelatinization if the distribution were completely random.

EFFECT OF COMPOSITION ON SYMMETRY OF ARRANGEMENT

The simplest unit cells shown in the illustrations of symmetrical distribution, figures 17, 19, and 21, are not extremely large. If the composition fraction is simple, that is if its denominator is a small number when the fraction is reduced to lowest terms, the mixture can be arranged in a symmetrical pattern whose unit cell is fairly small, except for fractions not simply related to the symmetry of the array; for example, $p=1/5$ or $p=1/7$ mixtures will not form simple symmetrical patterns in the plane hexagonal array. As the fractions are made more complex, the simplest possible symmetrical patterns will have larger unit cells.

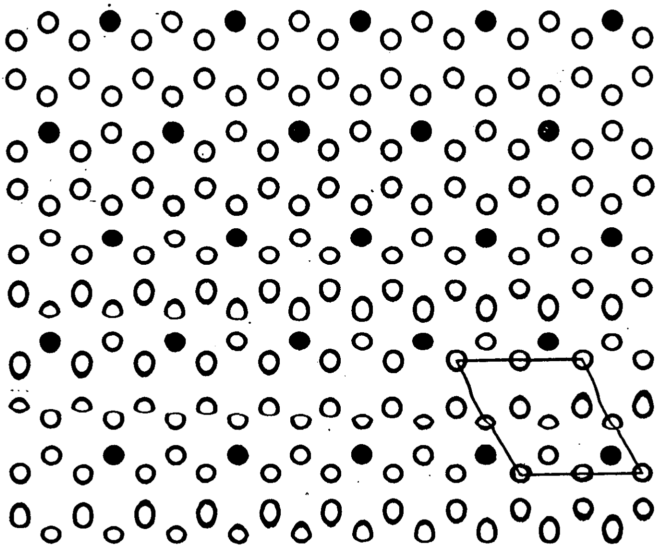


FIGURE 22.—Symmetrical arrangement of a mixture of $1/8$ black balls and $7/8$ white balls on a plane hexagonal array. The simplest unit cell contains eight balls, one black and seven white.

In a mixture of $p=1/8$ black balls and $(1-p)=7/8$ white balls (fig. 22) the unit cell shown contains 8 balls. Now if the figure showing the pattern of black balls in this arrangement is superposed on the figure showing the pattern of $p=1/2$ black balls (fig. 19), and if the remaining balls are white, the new pattern will be a symmetrical arrangement with $p=5/8$ black balls (fig. 23). Both symmetrical arrangements, for $p=1/8$ and $p=5/8$, have a larger unit cell than those for $p=1/2$ and $p=2/3$.

Again, figure 24 shows a symmetrical arrangement containing $1/12$ black and $11/12$ white balls; its simplest unit cell contains 12 balls.

The relation of increasing complexity of unit cell to the complexity of the composition fraction of a symmetrically arranged mixture is shown in figure 20. The unit cell for $p=1/2$ contains only 2 balls; those for $p=1/6$

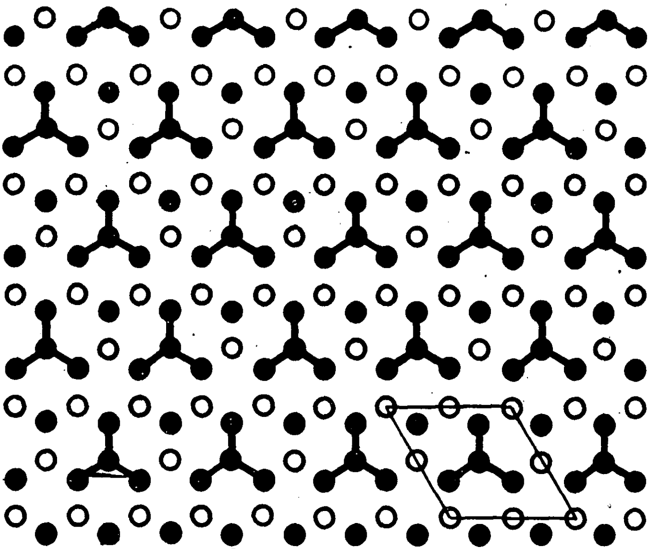


FIGURE 23.—Symmetrical arrangement of a mixture of ⅝ black balls and ⅜ white balls in a plane hexagonal array. Three of the eight balls in the unit cell are white; the other five are a cluster of one black ball and a cluster of four black balls. Note that this pattern of black clusters can be made by superposing the symmetrical arrangement of $p=1/8$ black balls (fig. 22) upon that of $p=1/2$ black balls (fig. 19) and making the remaining ⅜ of the balls white.

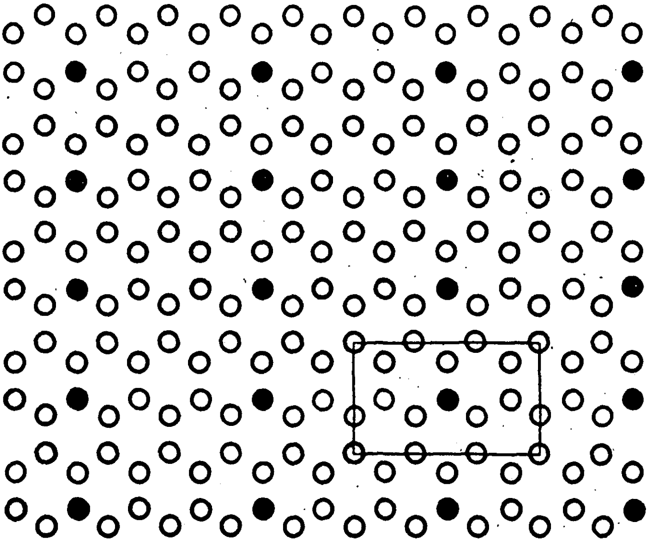
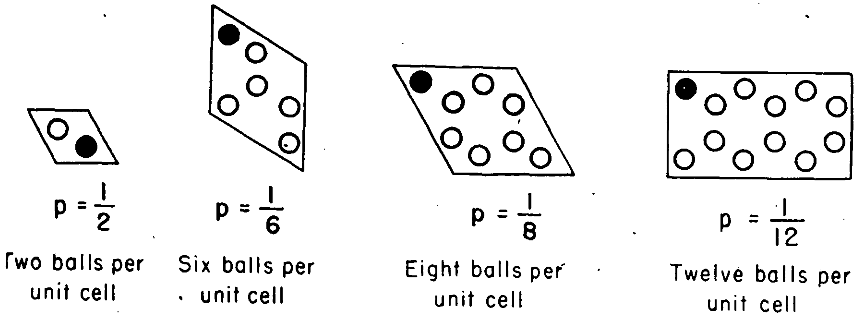


FIGURE 24.—Symmetrical arrangement of a mixture of $1/12$ black balls and $11/12$ white balls. The unit cell contains 1 black ball and 11 white balls.

and $p=1/3$ contain 6 balls; those for $p=1/8$ and $p=1/4$ contain 8 balls, and that for $p=1/12$, 12 balls.



Two balls per unit cell

Six balls per unit cell

Eight balls per unit cell

Twelve balls per unit cell

FIGURE 25.—Unit cells for symmetrical arrangements in the plane hexagonal array. The simpler the composition fraction of a mixture the smaller the unit cell that may be taken to describe its simplest symmetrical patterns. The nature of the array also restricts the smallness of the unit cell; in the plane hexagonal array the unit cell for $p = \frac{1}{3}$ as well as that for $p = \frac{1}{6}$ must contain at least six balls; and that for p ¼ must contain at least eight balls, the same as for $p \times \frac{1}{8}$.

SYMMETRICAL FORCES IN CRYSTALS

The main type of force that holds together the atoms in silicate crystal structures is ionic or electrostatic binding; the silicon and aluminum atoms have lost their outer electrons, leaving them positively charged ions. Each silicon or aluminum ion is surrounded by four oppositely charged oxygen ions, forming a tetrahedral unit from which the crystal structures are mainly built up. The ionic or polar bonds give the ionic type of crystals great strength and rigidity compared with metal crystals whose atoms are electrically neutral.

The aluminum-oxygen tetrahedral groups, and other such units, must be much like the silicon-oxygen groups in order to replace silicon-oxygen units in the crystal structures at all freely; but they have at least small differences in size, which might slightly affect the electrostatic fields surrounding them, and the bonds in silicate crystals are not completely ionic, as in the simplest crystals, such as the alkali halides. If there is some slight degree of nonpolar character in them, there may be small differences in the directional properties of the electrical fields surrounding the two kinds of groups in the silicate structures, and such differences might at least weakly influence their arrangement and properties.

So far as other natural limitations do not prevent, the electric fields of valence force surrounding the groups will produce the most symmetrically arranged patterns possible. Simple patterns are more stable than complex ones because these chemical forces are very feeble beyond near neighbors. If the only possible symmetrical arrangement of a group of atoms is a very complex pattern, the units of the pattern are large compared with the distance between nearest neighbors, and a given atom in the unit is not strongly affected by another atom several atoms away from it. It is not strongly prevented from deviating slightly from its place in the perfect pattern. For the same reason, if the fraction of one of the kinds of atoms is very small, they will be distributed too far apart to be held very exactly in a regular pattern.

It has already been mentioned that the greater the difference in two kinds of atoms substituted interchangeably in a crystal skeleton, the more likely they are to be arranged symmetrically with respect to each other. In aluminosilicates the less highly charged aluminum atoms are equalized to a degree more comparable to the silicon atoms by the attachment of other metal ions to the framework, but the presence of these extra atoms prevents the charge distribution from being a perfect compromise. There is still a lack of uniformity of charge distribution that would result in neighboring regions greatly differing in charge, if the atoms could be forced into clusters as large as those shown for completely random distributions. The atoms in a large cluster would repel each other very strongly and would be strongly attracted by atoms of the other kind outside the cluster, so the crystal would be very unstable compared with one in which the distribution was more symmetrical.

Inside the crystal structure the atoms of one kind are surrounded by atoms of the other kind in such a way that the forces around them are equalized as much as possible in all directions. Within the screening effect of such a uniform environment, the net result is as though the unlike atoms attract each other more strongly than like atoms,[44] and the simplest compromise is the most symmetrical arrangement possible. The manner of arrangement of atoms in complex structures has been summarized by Pauling[45] in a set of five empirical rules, by which the most likely structures can be predicted.

The random examples, therefore, are not considered to represent the state of distribution of atoms in the aluminosilicate skeletons, except possibly those containing very little aluminum. They are instructive, however, in showing the extreme state towards which any lack of symmetry will change the arrangement.

EXPERIMENTAL EVIDENCE FOR SYMMETRICAL ATOMIC ARRANGEMENT

ORDER-DISORDER PHENOMENA IN METAL ALLOYS

A type of crystal exists in which the limiting forms shown by the examples may actually be present; this is the metallic type. Atoms in the metallic state are neutral. They attract each other only because electrons may very easily be detached from them. These mobile electrons circulate freely in the crystals, behaving somewhat as though communally shared by all the atoms in the crystal. The resulting fields of valence force around the metal atoms have no directional properties as do those of atoms in the nonmetallic state. Their electric fields are very uniform in all directions, so the atoms cling together in simple arrangements like piles of spheres. They are not so strongly bound together as in nonmetallic crystals, so the crystals have less mechanical strength; this accounts for the relatively great ductility and softness of metals. The atoms, being more loosely held together, diffuse rather freely among one another. Because the atoms are so nearly alike they may be randomly distributed without causing segregation of electric charges.

In some alloys of similar metals the extreme condition of completely random distribution is actually found. These are the pairs of metals that form continuous series of miscible crystals in all ratios. However, the description of symmetrical arrangements formed by even small differences in properties applies to them also. If such an alloy is carefully annealed the different kinds of atoms segregate at least partly into a more or less symmetrical pattern that may be regarded as the formation of

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[44] Bain, Edgar C., The nature of solid solutions: Chem. Met. Eng., vol. 28, p. 24, 1923.

[45] Pauling, Linus, The principles determining the structures of complex ionic crystals: Am. Chem. Soc. Jour., vol. 51, pp. 1010–1026, 1929; The nature of the chemical bond: Cornell University Press, Ithaca, N. Y., 2nd ed., pp. 378–400, 1940. Evans, R. C., An introduction to crystal chemistry, Cambridge, Cambridge University Press, pp. 218–220, 1939.

interpenetrating skeletons of crystals of the two metals. The atoms of each metal are farther apart than in an ordinary crystal of the pure metal, and the superposed lattices of the two metals generally have different properties than either of the component metals. The new arrangement is called a superlattice.

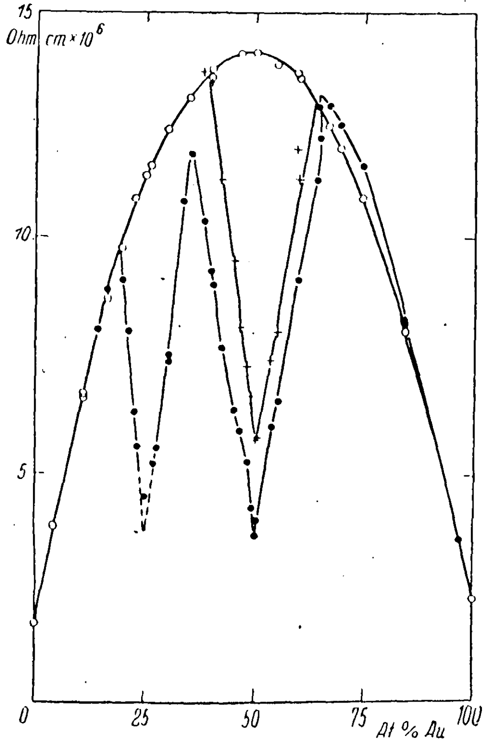

FIGURE 26.—Electrical resistivities of ordered and disordered alloys. Quenched (°) and annealed (•) gold-copper alloys. From Johanssen & Linde: Ann. Physik., vol. 25, p. 36, fig. 10, 1936.

Simple symmetrical patterns can be formed only if the two kinds of atoms are present in ratios of small whole numbers, e.g., the pattern for a ratio of 1:1 shown in figure 13. Minerals whose aluminum-silicon ratios are such simple fractions may thus have simple symmetrical patterns of silicon and aluminum atoms in their arrays. Most of the minerals represented in figure 5 (p. 30) have simple aluminum-silicon ratios, but some of them may have variable ratios. If two substances form miscible crystals in all ratios only a few of the possible mixtures will have simple enough ratios to form symmetrical patterns in the networks. Those mixtures whose ratios are between two of the simplest ratios must have either very complex patterns, whose units of repetition (unit cells) are very large, or at least some degree of randomness in arrangement. If the most symmetrical patterns possible are very large they will not be particularly stable and random variations from the patterns may result. This is strikingly shown by studies of properties that are sensitive to the degree of clustering produced by random arrangement.

Besides gelatinization in silicate minerals, some of the properties of crystals that are sensitive to degree of randomness or disorder are: electrical resistivity,[46] heat capacity,[47] magnetic properties,[48] and susceptibility to attack by chemical reagents.[49] Buerger[50] has suggested that since the vibrational heat energy of a substance is partitioned among clusters so that unsymmetrical clusters have more vibrational energy than symmetrical ones, the degree of clustering of atoms in a crystal might measurably affect its infrared and Raman spectra.

Figure 26 shows the effect of annealing gold-copper alloys of different composition. If an alloy is heated, the increased thermal agitation of its atoms may be made vigorous enough to overcome the chemical valence forces that hold the atoms in the ordered pattern. If the alloy is then suddenly quenched to a temperature that freezes the atoms in place, the disordered arrangement of atoms gives the crystal a higher resistivity than one with an ordered arrangement. The resistivities of such quenched alloys are shown by the upper curve in the figure. If instead of being suddenly quenched the alloy is slowly cooled the ordering forces are effective as soon as the thermal agitation has decreased to a critical temperature, below which the agitation is not vigorous enough completely to oppose the valence forces. As the alloy cools below the critical ordering temperature the ordered arrangement is gradually formed. If the composition ratio is a simple enough fraction the atoms may become completely ordered into simple symmetrical patterns. Alloys with this ordered distribution into symmetrical small clusters have a much lower resistivity than the disordered ones, as shown at the composition ratios ¼ and ½ on the lower curve in the figure.

If the composition ratio of the mixed crystal is not a very simple fraction, its atomic arrangement can have only a limited symmetry, and so the resistivity of such an alloy is higher than that of a completely ordered one. The lower curve in the figure shows that for composition ratios departing farthest from simple fractions it is impossible to form an arrangement whose resistivity is much different from that of the completely disordered form shown by the upper curve. Such alloys have randomly arranged atoms like the distribution shown in the examples of figures 16, 18, and 20, but on three-dimensional arrays instead of on a plane.

A similar effect of great change in a property when the composition changes slightly is shown when ordered copper-gold alloys are treated with nitric acid. If more than half the atoms in the ordered alloy are copper, the alloy completely dissolves in nitric acid; if more than half of the atoms are gold, the alloy is not attacked at all by the acid. Such

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[46] Kurnakow, N., Zemczuzny, S., and Zasedatelev, M., The transformations in alloys of gold with copper: Jour. Inst. Metals, vol. 15, pp. 305–331, 1916. Johansson, C. H., and Linde, J. O., Röntgenographische und elektrische Untersuchungen des CuAu-Systems: Annalen Physik, Band 25, pp. 1–48, 1936.

[47] Nix, F. C., and Shockley, W., Order-disorder transformations in alloys: Rev. modern physics, vol. 10, pp. 59–61, 1938. This article is a comprehensive review of the subject.

[48] Tammann, G., Über die Resistenzgrenzen von Mischkristallen und die Molekularverteilung in Raumgittern: K. Gesell. Wiss. Göttingen, Math-phys. Kl., Nachr. 1916, pp. 199–265.

[49] Tammann, G., Die Goldgehalte, bis zu denen die Kupfer-Gold- und Silber-Gold Mischkristalle bei Einwirkung chemischer Agentien sich verändern: K. Gesell. Wiss. Göttingen, Math.-phys. Kl., Nachr., 1917, pp. 385–425; Über den atomistischen Aufbau nichtmetallischer Mischkristalle. K. Gesell. Wiss. Göttingen, Math.-phys. Kl., Nachr., 1918, pp. 296–318. A detailed review of Tammann's work on mixed-crystal series may be found in Tammann, G., Die chemischen und galvanischen Eigenschaften von Mischkristallreihen und ihre Atomverteilung, Zeitschrift anorg. Chemie, Band 107, pp. 1–239, 1919. His work and views on metal alloys are summarized in his Text book of metallography, the third edition of which has been translated into English by Reginald Scott Dean and Leslie Gerald Swenson, New York, Chemical Catalog Co., 1925.

[50] Buerger, M. J., The kinetic basis of crystal polymorphism: Nat. Acad. Sci. Proc., vol. 22, pp. 682-685, 1936.

behavior is not restricted to metal alloys: Tammann's student Schmidt[51] found that annealed miscible crystals of silver chloride and sodium chloride give the same effect when leached with water. If the miscible crystals contain less than 5/8 mol fraction silver chloride, all of the sodium chloride can be dissolved out from them by water; if they contain more than 3/4 mol fraction silver chloride no sodium chloride is dissolved.

The simplest explanation of such experiments on susceptibility to attack is that if there are enough atoms of the insoluble substance in the crystal the soluble atoms are completely surrounded by them and cannot be attacked by the reagent. In random arrangement the number of soluble atoms protected from attack by reagents increases gradually with increasing fraction of insoluble atoms, but in regular arrangements either all the soluble atoms are exposed or all are protected.

If the X-ray scattering powers of the two kinds of atoms in an alloy are appreciably different, ordering may be detected by X-ray measurements. When the alloy is disordered it diffracts X-rays into the same kinds of patterns as do either of the pure metals forming the alloys, because for all reflecting planes formed by atoms in either of the pure metals there are corresponding planes of atoms in the alloy. Because of the randomness of arrangement of the two kinds of atoms on the points making a given plane, the diffraction of X-rays by any set of parallel planes is an average for the two kinds of atoms. When, however, an alloy such as copper-gold is ordered, certain planes may have higher concentrations of gold than other planes parallel to them. The intensities of reflection by these planes will not now be equal, and the relative intensities of diffraction lines from them will be different. In directions along which previously the reflections from two such planes interfered completely, there will now be weak reflections that were not present in the pattern of the pure compound. The ordered arrangement may be considered as being made up of two superimposed ordered structures which interpenetrate to form superlattice structure, and the extra X-ray diffraction lines are called superlattice lines. Abundant evidence of order-disorder phenomena and the formation of superlattice structures in metal alloys has been obtained by investigators working with X-rays.[52]

The superlattice symmetry is more complex than that of either of the component lattices, and so its unit cell is larger than those of the pure substances. As described above, the simplest possible symmetrical arrangements are those of mixtures whose composition ratios are expressed by small whole numbers; and the less simple the ratio, the larger the pattern unit or unit cell must be to describe the symmetry completely. In some metal alloys whose atoms are not too different in their properties the superlattice unit cells can apparently be rather large.[53] In miscible crystals whose atoms are not so alike as those of a metal alloy very large superlattices will be less stable; it is not so likely that such miscible crystals

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[51] Schmidt, K. W., Dissertation, Göttingen, 1917, described by Tammann, G., Über den atomistischen Aufbau nichtmetallischer Mischkristalle: K. Gesell. Wiss. Göttingen, Nachr., 1918, pp. 296–318. Schmidt's results have been independently confirmed by electrochemical measurements by Wachter, A., Thermodynamic properties of solid solutions of silver chloride and sodium chloride, Am. Chem. Soc. Jour., vol. 54, pp. 919–928, 1932.

[52] Surveys of the order-disorder phenomena and the formation of superlattice structure in alloys may be found in the following publications: Bain, Edgar C., Cored crystals and metallic compounds: Chem. Met. Eng., vol. 28, pp. 65–69, 1923. Barrett, Charles S., A correlated abstract on superlattices: Metals and Alloys, vol. 8, pp. 251–256, 260, 1937; Structure of Metals, pp. 230–250. New York, McGraw-Hill Book Co., 1943. Nix, Foster C., Superstructures in alloy systems: Jour. Applied Physics, vol. 8, pp. 783–794, 1937. Slater, J. C., Introduction to chemical physics, pp. 291–304. New York, McGraw-Hill Book Co., 1939. Seitz, Frederick, The modern theory of solids, pp. 35–42, and pp. 502–511. New York, McGraw-Hill Book Co., 1940.

[53] Barrett, Charles S., op. cit., p. 233, shows a superlattice unit cell ten times the size of the primitive unit cell in the alloy AuCu.

can form very large superlattices. On the other hand, as has been shown, completely random arrangement is impossible in such crystals.

With the aid of the simple superlattice idea one can easily explain the formation of miscible crystals with simple integral ratios of the two components; but in many cases of miscible-crystal formation a pair of isomorphous substances can form a continuous series of solid solutions. There is a narrow limit to the number of mixtures that can form simple, perfectly ordered arrangements; between these compositions are mixtures that if ordered would be unstable because of their extremely large superlattices and if disordered would be unstable because of the inhomogeneity of the electric-charge distribution caused by the clustering of like atoms. A possible compromise between these two extreme conditions is a limited degree of randomness in the arrangement of the two kinds of atoms.

These considerations show that any pair of substances that forms a series of solid solutions whose ordinary properties vary gradually with change in composition will nevertheless show sudden changes in some properties with slight changes in composition. The properties behaving in this abruptly changing manner are those sensitive to the mode of distribution of clusters of the two kinds of substances. X-ray diffraction is governed by the relative arrangement of the two kinds of units in the structural pattern, if they scatter the X-rays differently enough.

PARTIAL RANDOMNESS IN SILICATES

The relative positions of aluminum and silicon in aluminosilicates are not shown by X-ray diffraction measurements because their X-ray scattering powers are so nearly alike. Chao and Taylor,[54] however, have by very careful work succeeded in detecting a slight effect from the difference in size of the groups containing the respective two kinds of atoms in feldspars. This work reveals another example of sharp changes in an isomorphous series usually thought continuous. Evidence had already been found by Taylor, Derbyshire, and Strunz[55] that the length along the c-axis of the unit cell of anorthite and labradorite is double that of albite, and Chao and Taylor's very accurate X-ray measurements confirm this. With respect to detailed internal structure albite and anorthite do *not* form a single isomorphous series. Miscible crystals have the albite structure from pure albite up to somewhere between 22 and 57 percent anorthite; they apparently have the doubled unit cell from pure anorthite to somewhere between 20 and 33 percent albite. Moreover, the structure of miscible crystals in the intermediate range is different still, and much more complicated than near the end members. Chao and Taylor suggest that the results for the intermediate plagioclases may be accounted for by an alternating layered structure of the superlattice type, of sheets with albite and with anorthite structure.

For two of their samples they propose true unit cells with the alternating layer structure having lengths along the *c*-axis of 5 and 7 times that of albite, respectively. As already mentioned, an alternative explanation to the idea of very large superlattice structures is that of limited randomness in the arrangement.

The conclusion that the aluminum and silicon atoms in aluminosilicate

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[54] Chao, S. H. and Taylor, W. H., Isomorphous replacement and superlattice structures in the plagioclase felspars: Roy. Soc. London Proc., ser. A, vol. 176, pp. 76–87, 1940.

[55] Taylor, W. H., Derbyshire, J. A., and Strunz, H., An X-ray investigation of the felspars: Zeitschr Kristallographie, Band 87, pp. 464–498, 1934.

minerals have ordered arrangements has received striking experimental confirmation by Gordon and Wichers,[56] who have made what is probably the first determination of a resistance limit for a natural mineral series. By heating members of the albite-anorthite series with hydrochloric acid in sealed tubes at 300°C., they find a curve for degree of attack entirely similar to that of Schmidt for ordered silver chloride-sodium chloride crystals. The resistance limit occurs at the aluminum: silicon ratio 1:2, in complete agreement with the figure found by Murata by the less direct method of comparing the behavior towards acids of different individual minerals having various aluminum-silicon ratios.

Pure substances as well as miscible crystals may have limited randomness in the relative arrangement of structurally equivalent atoms. The X-ray measurements of sanidine by Taylor[57] and of orthoclase by Chao, Hargreaves, and Taylor[58] show structural complexities that are not consistent with completely ordered arrangements of atoms. A completely ordered arrangement of the aluminum atoms in the unit cell of sanidine would give a structure that conflicts with the observed crystal symmetry, and such an arrangement in orthoclase would give a higher symmetry than that observed. Further indications of complicated behavior in the structure of feldspars are given by the thermal studies of orthoclase and microcline by Rosenholtz and Smith.[59] When the temperatures of these minerals are varied between 0° and 1000°C., their volumes do not change gradually with temperature, but undergo a large number of abrupt changes in the rates of expansion or contraction.

Taylor and his coworkers suggest that the difference in the two minerals is caused by a difference in the distribution of the 12 silicon atoms and the 4 aluminum atoms in each unit cell. They further suggest that there is a limited randomness in the relative arrangement of these atoms within the unit cells, and that the difference in the two minerals is a result of of differing degrees of symmetry in the arrangements within the cells.

This proposed partly random distribution of some of the atoms within a unit cell, with the provision that every unit cell in the crystal contains the same number of the respective kinds of atoms, is the kind of stable arrangement mentioned above as the alternative to the two extreme arrangements—a very large unstable superlattice structure and an unstable completely random arrangement.

The idea of variation in positions of atoms within a unit cell requires a change in the idea of the unit cell itself. If the arrangement of every atom in the unit cell is not the same in every unit cell of a crystal, it of course no longer represents the unit of repetition of a symmetrical pattern of atoms; the complete arrangement of atoms in the crystal cannot be formed by repeating a cell, no matter how large a cell be taken. Such a cell does not correspond to the definition of a true unit cell.

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[56] Wichers, Edward, Schlecht, W. G., and Gordon, C. L., Preparing refractory oxides, silicates, and ceramic materials for analysis, by heating with acids in sealed tubes at elevated temperatures: Nat. Bur. Standards Jour. Research, vol. 33, pp. 451–456, 1944.

[57] Taylor, W. H., The structure of sanidine and other felspars: Zeitschr. Kristallographie, Band 85, pp. 425–442, 1933.

[58] Chao, S. H., Hargreaves, A., and Taylor, W. H., The structure of orthoclase: Mineralog. Mag., vol. 25, pp. 498–512, 1940.

[59] Rosenholtz, J. L., and Smith, D. T., Linear thermal expansion of adularia: Am. Mineralogist, vol. 26, pp. 391–394, 1941; Thermal studies of orthoclase and microcline: Am. Mineralogist, vol. 27, pp. 344–349, 1942.

VARIATE ATOM EQUIPOINTS

Barth and Posnjak[60] first discovered such partly random arrangements of atoms, in certain substances of the spinel type. They proposed that the idea of a unit cell be extended to include such structures. By adopting a unit cell of the same size, as though the relative arrangement of the atoms were alike in every cell throughout the crystal, the structure can be represented in every detail except for the actual positions of those particular atoms that have the random arrangement. Such a unit cell represents the symmetrical pattern of points, the array in which the atoms are arranged, but it does not represent the structural arrangements of atoms in the crystal.

This unit cell with partly random distributions was named by Barth and Posnjak the unit cell with variate atom equipoints. In several substances with the spinel structure they found unit cells with variate atom equipoints,[61] and Barth[62] also showed that still other substances have this type of atomic arrangement. Barth[63] later showed that the variate-atom-equipoint structure accounts for the behavior of the albite-anorthite series and for the polymorphism of potash feldspar, including the behavior of orthoclase and sanidine studied by Taylor, as well as their relation to microcline. This type of partly random structure also solves the problem of atomic arrangement in minerals of the sodalite family and other substances with the ultramarine-type structure.[64]

DEFECT STRUCTURES

Experimental studies indicate that the variate-atom-equipoint structure in crystals is by no means rare. Besides the type in which two kinds of atoms may occupy the same kind of positions in a crystal structure, there are substances in which some of the variate positions are unoccupied. Strock[65] has proposed that the name "defect lattices" be given to structures in which either each set of equivalent positions is occupied by more than one kind of atom—"complete lattices"—or some of the positions are vacant—"incomplete lattices."

Solid solutions of those pairs of alkali halides that form miscible crystals apparently have the two kinds of alkali atoms or halogen atoms distributed at random with respect to each other. None of the workers[66] studying these crystals have been able to detect such extra X-ray lines as would be expected in the diffraction patterns of the crystals if the arrangement were ordered.

Complete defect structures have been detected by X-ray measurements

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[60] Barth, T. F. W., and Posnjak, E., The spinel structure: an example of variate atom equipoints: Wash. Acad. Sci. Jour., vol. 21, pp. 255–258, 1931. Posnjak, E., and Barth, T. F. W., A new type of crystal fine-structure: lithium ferrite ($Li_2O \cdot Fe_2O_3$): Phys. Rev., vol. 38, pp. 2234–2239, 1931.

[61] Barth, Tom. F. W., and Posnjak, E., Spinel structures: with and without variate atom equipoints: Zeitschr. Kristallographie Abt. A, Band 82, pp. 325–341, 1932.

[62] Barth, Tom. F. W., Strukturen mit ungleichwertigen Atomen in Gleichwertigen Punktlagen: Fortschr. Mineralogie, Band 17, pp. 25–27, 1932.

[63] Barth, Tom. F. W., Polymorphic phenomena and crystal structure: Am. Jour. Sci., 5th ser., vol. 27, pp. 273–286, 1934. A review of the evidence for random arrangement of atoms in alloys and other crystals is given by Evans, An introduction to crystal chemistry, Chaps. 5 and 7, Cambridge, Cambridge Univ. Press, 1939.

[64] Barth, Tom. F. W., The structure of the minerals of the sodalite family: Zeitschr. Kristallographie, Abt. (A), Band 83, pp. 405–414, 1932.

[65] Strock, L. W., A classification of crystal structures with defect lattices: Zeitschr. Kristallographie, Band 93, pp. 285–311, 1936. Evans, An introduction to crystal chemistry, Cambridge, Cambridge Univ. Press, pp. 203–214, 1939.

[66] Vegard, L., Die Konstitution der Mischkristalle und die Raumfüllung der Atome: Zeitschr. Physik, Band 5, pp. 17–26, 1921. Vegard, L. and Schjeldrup, H., Die Konstitution der Mischkristalle: Physik. Zeitschr., Band 18, pp. 93–96, 1917. Havighurst, R. J., Mack, E., Jr., and Blake, F. C., Solid solutions of the alkali and ammonium halides: Am. Chem. Soc. Jour., vol. 47, pp. 29–43, 1925.

of ammonium oxyfluomolybdate,[67] potassium cyanate,[68] complex cobalt ammines,[69] and parabromochlorobenzene[70]; by entropy measurements of solid carbon monoxide,[71] and by X-ray studies of cadmium bromide[72] and nickel bromide.[73]

The existence of incomplete defect structures is a confirmation of the strong ordering tendency of the atoms in cyrstals. In crystals of this type the structure is formed in spite of the fact that there are not enough atoms to occupy all the positions in the structure; the vacant positions are randomly distributed. Pyrrhotite,[74] for example, contains more sulfur than is accounted for by the formula FeS, yet its structure is not that of a solid solution of sulfur in ferrous sulfide. The actual structure is that of FeS with some of the Fe positions vacant. Other substances having incomplete defect structures are the sodium-tungsten bronzes,[75] the gamma modification of alumina,[76] and the alpha, high-temperature, modification of silver iodide.[77] The complex salt, silver mercuric iodide,[78] has both the complete and the incomplete defect characters in its structure; the silver and mercury atoms are randomly arranged with respect to each other, and leave one-fourth of the equivalent positions vacant, the unoccupied positions being randomly distributed.

SIMPLIFIED ILLUSTRATIONS OF PARTLY RANDOM DISTRIBUTIONS

The results of partly random distribution may be illustrated with some simplified hypothetical examples by using the plane hexagonal skeleton. Two kinds of partial randomness will be illustrated. One (case 1) corresponds to the unit cell with variate atom equipoints, in which each unit cell has the same composition but a limited number of atoms randomly distributed, the others being fixed. It is found that the number of small clusters in such an arrangement may be appreciably larger than in a completely random arrangement. In the other kind of partial randomness (case 2) a simple fraction of the atoms is arranged in a symmetri-

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[67] Pauling, Linus, The crystal structures of ammonium fluoferrate, fluoaluminate and oxyfluomolybdate: Am. Chem. Soc. Jour., vol. 46, pp. 2738–2751, 1924.

[68] Hendricks, Sterling B. and Pauling, Linus, The crystal structure of sodium and potassium trinitrides and potassium cyanate and the nature of the trinitride group: Am. Chem. Soc. Jour., vol. 47, pp. 2904–2920, 1925.

[69] Hassel, O., Über die Existenz einer streng strukturtheoretisch nicht erlaubten isomorphie höhersymmetrischer Kristalle von Hexammin-, Pentamminaquo- und Tetrammindiaquo-Komplexen: Norsk. geol. Tidskr. Band 10, pp. 33–38, 1928.

[70] Hendricks, Sterling B., Para-bromochlorobenzene and its congeners: variate equivalent points in molecular lattices: Zeitschr. Kristallographie, Band 84, pp. 85–96, 1932.

[71] Clayton, J. O., and Giauque, W. F., The heat capacity and entropy of carbon monoxide: Am. Chem. Soc. Jour., vol. 54, pp. 2610–2626, 1932.

[72] Bijvoet, J. M., and Nieuwenkamp, W., Die "Wechselstruktur" von $CdBr_2$: Zeitschr. Kristallographie, Band 86, pp. 466–470, 1933.

[73] Ketelaar, J. A. A., Die kristallstruktur des Nickelbromide und -jodids: Zeitschr. Kristallographie, Band 88, pp. 26–34, 1934.

[74] Laves, Fritz, Die Bau-Zusammenhänge innerhalb der Kristallstrukturen. 2te Teil.: Zeitschr. Kristallographie, Band 73, pp. 306–307, 1930. Hägg, Gunnar, Vacant positions in the iron lattice of pyrrhotite: Nature, vol. 131, pp. 167–168, 1933. Hägg, Gunnar, and Sucksdorff, Ingrid, Der Kristallstruktur von Troilit und Magnetkies: Zeitschr. physikal. Chemie, Band B22, pp. 444–452, 1933.

[75] Hägg, Gunnar, The spinels and the cubic sodium-tungsten bronzes as new examples of structures with vacant lattice points: Nature, vol. 135, p. 874, 1935. Zur Kenntnis der kubischen Natrium—Wolfram-Bronzen: Zeitschr. physikal. Chemie, Band B29, pp. 192–204, 1935.

[76] Hägg, Gunnar, and Soderholm, G., Die Kristallstruktur von Mg-Al Spinellen mit Al_2O_3-Überschuss und von γ-Al_2O_3: Zeitschr. physikal. Chemie, Band B29, pp. 88–94, 1935. Verwey, E. J. W., The crystal structure of γ-Fe_2O_3 and γ-Al_2O_3: Zeitschr. Krist., Band 91, pp. 65–69 (1935). Kordes Ernst, Kristallchemische Untersuchungen über Aluminiumverbindungen mit spinellartigem Gitterbau und über γ-Fe_2O_3: Zeitschr. Krist., Band 91, pp. 193–228, 1935.

[77] Strock, L. W., Kristallstruktur des Hochtemperatur-Jodsilbers α-AgJ: Zeitschr. physikal. Chemie, Band B25, pp. 441–459, 1934. Ergänzung und Berichtigung zu: Kristallstruktur des Hochtemperatur-Jodsilbers α-AgJ: Zeitschr. physikal. Chemie, Band B31, pp. 132–136, 1935.

[78] Ketelaar, J. A. A., Die Kristallstruktur des Hochtemperaturmodifikationen von Ag_2HgJ_4 und Cu_2HgJ_4: Z. Krist., Band 87, pp. 436–445, 1934. Das elektrische Leitvermögen des Ag_2HgJ_4. Ein Beitrag zur Frage nach dem Leitungsmechanismus in den gutleitenden festen Stoffen: Zeitschr. physikal. Chemie, Band B26, pp. 327–334, 1934. Die spezifische Wärme von Ag_2HgJ_4 in Zusammenhang mit der Kristallstruktur: Zeitschr. physikal. Chemie, Band B30, pp. 53–60, 1935.

cal pattern on the skeleton, the rest being distributed entirely at random throughout the remainder of the skeleton. In the latter arrangement the composition of the group of atoms may vary between certain fixed limits within every region enclosed by a cell whose size is the same as a unit cell of symmetrical arrangement with the same composition. It is found that for compositions whose ratios are not simple fractions this arrangement may form an even largern umber of small clusters than a symmetrical arrangement does.

Further details of the calculation of the fraction of small clusters in partly random arrangements are given in the Appendix. (See pp. 73 to 82.)

CASE 1. MIXTURES WITH SIMPLE COMPOSITION FRACTIONS

The mixture of equal numbers of black balls and white balls illustrated by figure 27 may be allowed to vary in relative arrangement in such a way that each unit cell still contains an equal number of black and of white balls. The cell is then a unit cell with variate equipoints.

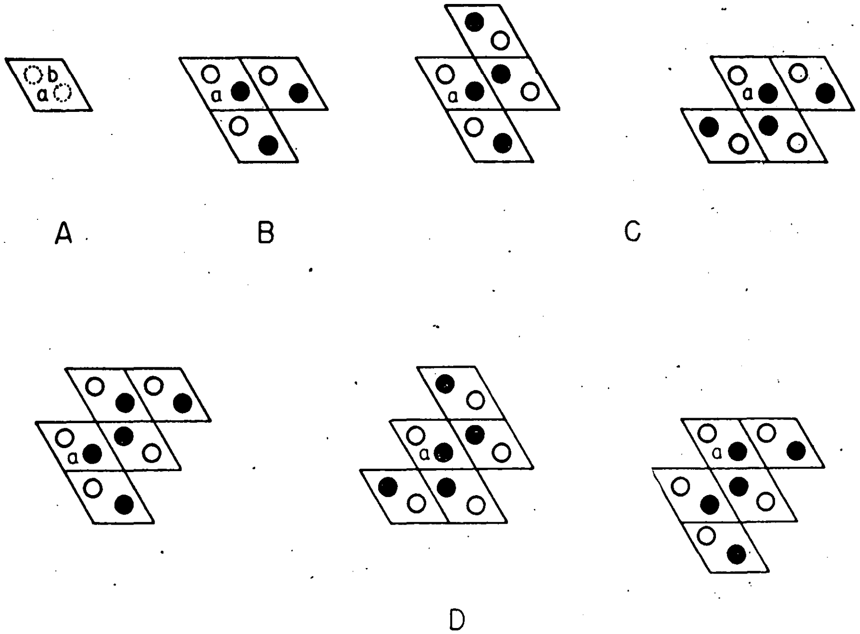

FIGURE 27.—Limited randomness, case 1-A1, $p = \frac{1}{2}$.

A, Unit cell with two variate equipoints in the plane hexagonal array. Either of the variate points *a* and *b* may be occupied by a black ball, and the other by a white ball.

B, There is only one way in which a given black ball *a* can be a cluster of one black ball. The chance of this arrangement is $\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = (\frac{1}{2})^3$.

C, There are two ways in which a black ball *a* can be part of a cluster of two. The chance of each arrangement is $\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = (\frac{1}{2})^4$, so the total chance that a black ball is part of a cluster of two is $2 \times (\frac{1}{2})^4 = (\frac{1}{2})^3 = \frac{1}{8}$.

D, There are three ways in which a black ball *a* can be part of a cluster of three, and the chance of each arrangement is $\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = (\frac{1}{2})^5$; so the total chance that it is part of a cluster of three is $3 \times (\frac{1}{2})^5 = \frac{3}{32}$.

Case 1–A1.—If the smallest possible unit cell be taken for the arrangement, cell b in figure 19, all the positions on the skeleton must be variate equipoints. The balls may be arranged in a unit cell in two ways: black, *a*, and white, *b* (fig. 27, A), and the reverse arrangement. The composition of each cell is restricted to an equal number of black and of white balls. In this arrangement there is only one way in which a given atom *a* (fig. 27, B) may be a single isolated black ball, or cluster of one, on the skeleton. The black ball *a* must be in the position shown and the two neighboring cells must have the arrangement shown; balls in all other neighboring cells are then separated from ball *a* by white balls. The chance that *a* is black is $\frac{1}{2}$ and the chance that each of the two neighboring cells have the arrangement shown is $\frac{1}{2}$, so the chance that a ball is a cluster of one is $\frac{1}{2}\times\frac{1}{2}\times\frac{1}{2}$; that is, the fraction of balls in clusters of one is

$$P_1'=(\tfrac{1}{2})^3=\tfrac{1}{8}.$$

Dividing by the fraction of black balls in the mixture, we have the fraction of *black* balls in clusters of one,

$$P_1=\frac{(\frac{1}{2})^3}{\frac{1}{2}}=(\tfrac{1}{2})^2=\tfrac{1}{4}.$$

If the ball in position *b* were black the network of unit cells could be so shifted that this black ball would be in the position shown for *a* in figure 27, B and the result would be the same; there is only one way in which a black ball could be a cluster of one.

There are two arrangements by which a black ball can be in a cluster of two, as shown in figure 27, C. The fraction of black balls in each arrangement is $\frac{(\frac{1}{2})^4}{\frac{1}{2}}=(\tfrac{1}{2})^3$.

$$P_2=(\tfrac{1}{2})^3+(\tfrac{1}{2})^3=(\tfrac{1}{2})^2=\tfrac{1}{4}.$$

Similarly (fig. 27, D) there are three ways in which a black ball can be

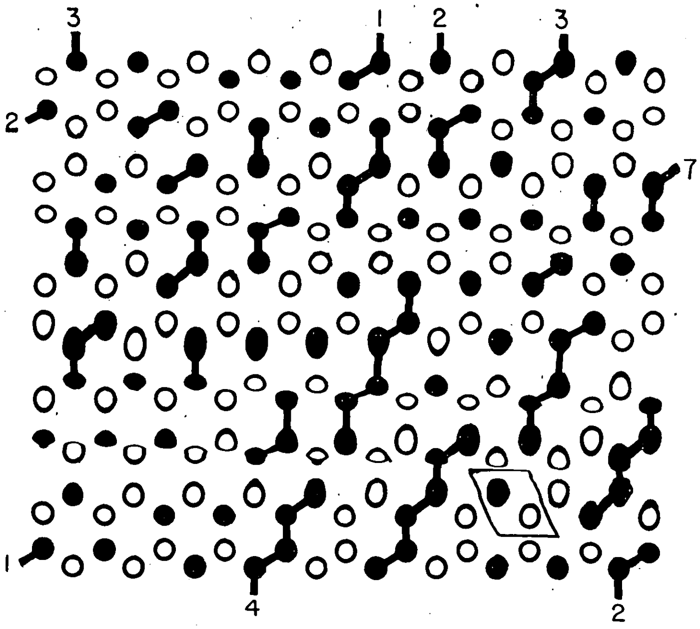

FIGURE 28.—Partly random distribution in a binary mixture, case *1-A1*. Typical arrangement of an equal mixture of black and white balls in a plane hexagonal array, with the limited randomness described in case 1–A1. Every unit cell of the size shown in the inset must contain one black and one white ball, but their positions on the two sites within the cells are a matter of chance.

in a cluster of three and the fraction of black balls in each arrangement is $\frac{(\frac{1}{2})^5}{\frac{1}{2}}=(\frac{1}{2})^4$.

$$P_3=3\times(\tfrac{1}{2})^4=\tfrac{3}{16}.$$

A typical sample of an equal mixture of black and of white balls distributed on a plane-hexagonal skeleton in the partly random manner of case 1—A1 is shown in figure 28. It was made by using Tippett's random sampling numbers.

Case 1–A2.—Suppose that a unit cell is taken twice as large (that is, containing twice as many balls) as in case 1–A, corresponding to the unit cell in figure 19, d, with the same fifty-fifty mixture of black and white balls. If all four positions in the cell are variate the labor of counting the number of possible ways of forming clusters is great. The fraction of black balls in clusters of one is $\frac{1}{6}$; details of the calculation are given in the Appendix, case 1–A2.

When the degree of randomness within a unit cell is not restricted beyond the requirement of a definite composition, it is increased, of course, by an increase in the size of the unit cell. From this standpoint it may be considered that the completely random distribution is the extreme or limiting condition approached as the size of the unit cell is increased without limit. The arrangement of case 1–A2 thus gives a fraction of small clusters intermediate between that of case 1–A1 (fig. 28) and that of the extreme limiting case of a completely random distribution (fig. 18).

Figure 29 shows a typical sample of the case 1–A2 arrangement of an equal mixture of black and white balls made by using Tippett's random sampling numbers.

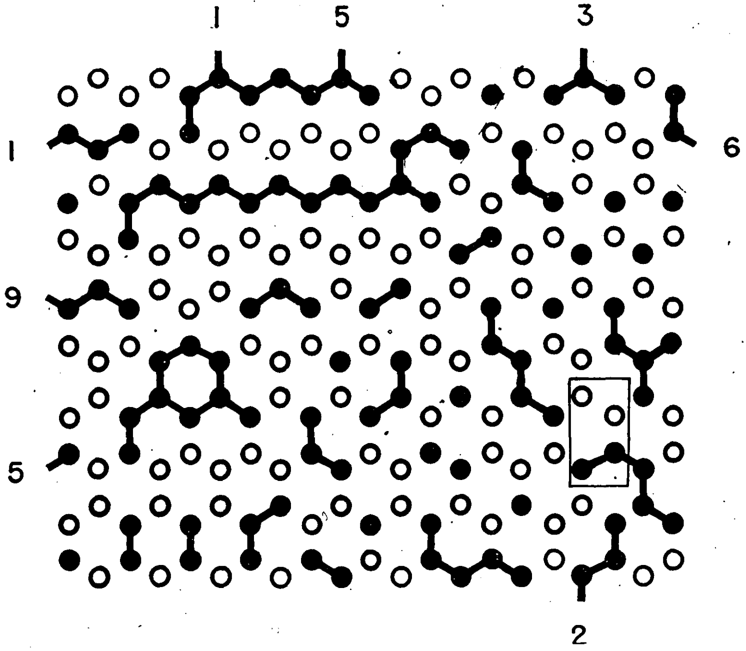

FIGURE 29.—Partly random distribution in a binary mixture, case 1–A2. Typical arrangement of an equal mixture of black and white balls in a plane hexagonal array with the limited randomness described in case 1–A2. Every unit cell of the size shown in the inset must contain two black and two white balls, but their positions on the four sites are random.

Case 1–A3.—If a still larger variate-atom unit cell is taken, containing six variate balls (see Appendix, case 1—A3) the fraction of black balls in clusters of one is $3/20$. This is still nearer to P_1 for the completely random distribution with $p = 1/2$ in the plane-hexagonal array. The table illustrates the approach toward completely random distribution as the size of the unit cell is increased when all points in the array are variate equipoints.

Summary of Case 1–A.—The three arrangements considered under case 1–A have unit cells in which all points are variate equipoints; that is, all cells in a given arrangement have the same composition.

Effect of increasing size of unit cells on fraction of small clusters
$p = 1/2$, plane hexagonal array

Arrangement	Number of variate points per unit cell	Fraction of black balls in clusters of one, P_1
Completely symmetrical, (fig. 19)	0	1
Variate-equipoint unit cell:		
Case 1-A1, (fig. 27)	2	.25
Case 1-A2, (fig. 29)	4	.1667
Case 1-A3, (fig. 31)	6	.15
Completely random, (fig. 18)	No limit	.125

Case 1–B.—Instead of allowing the two black and two white balls in the doubled unit cell to be distributed entirely by random, suppose that their arrangement be partly restricted. If only two of the four positions in the cell (fig. 30) be variate the other two balls are fixed—one black and one white. The dotted circles 1 and 2 represent positions in which either ball is black and the other white; these are the variate equivalent positions.

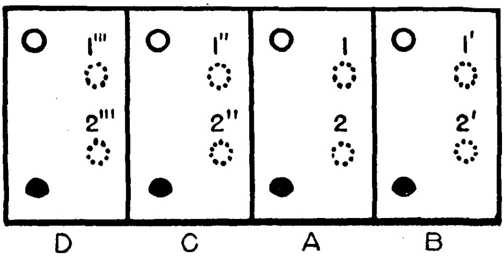

FIGURE 30.—Limited randomness, (case 1–B). A doubled unit cell A with three neighboring unit cells B, C, and D whose arrangements affect the sizes of black clusters in cell A. The two atoms per unit cell which are fixed in case 1–B are here shown as solid circles on the left sides of the cells; the other two atoms, one being black and the other white, which may occupy two sites interchangeably, are shown as dotted circles.

The fraction of black balls in clusters of 1, 2, and 3 balls may be calculated by labeling the variate points in a unit cell and those in each neighboring cell affecting the size of clusters reaching into the first cell, and counting the arrangements that will make each size of cluster. There are 2 possible arrangements in each unit cell, so there are $2 \times 2 \times 2 \times 2 = 16$ possible arrangements of the set of 4 unit cells shown in the figure. In each of these 16 possible arrangements cell A contains 2 black balls, a total of $2 \times 16 = 32$ black balls.

The 4 arrangements of cell A with black balls in positions 1, 1′, 1″ and 1, 2′, 1″ each contains 2 clusters of 1, totaling 8 clusters of 1; the 4 arrangements with black balls in positions 1, 1′, 2″ and 1, 2′, 2″ each contain one cluster of 1, totaling 4 clusters of 1, making altogether $8+4=12$ clusters of 1 out of 32 black balls. None of the other arrangements form clusters of 1 in cell *A*, so the fraction of black balls in clusters of 1 is

$$P_1 = {}^{12}\!/_{32} = {}^{3}\!/_{8}.$$

None of the 16 arrangements contain clusters of 2 black balls, so

$$P_2 = 0.$$

The 2 arrangements with black balls in positions 2, 1′, 1″ each have 2 black balls in cell A arranged as members of a cluster of 3, totaling $2\times2=4$ black balls in clusters of 3. The 2 arrangements with black balls in positions 1, 1′, 2″, 1‴ and 1, 2′, 2″, 1‴ each have 1 of the black balls in cell A as members of a cluster of 3, totaling $2\times1=2$ black balls in clusters of 3; these are the only 2 arrangements in cell A which are affected by the arrangement in cell D. This makes altogether $4+2=6$ black balls in clusters of 3, out of the 32 black balls in the 16 arrangements of cell A. The fraction of black balls in clusters of 3, therefore, is

$$P_3 = {}^{6}\!/_{32} = {}^{3}\!/_{16}.$$

This kind of arrangement gives a larger number of clusters of one black ball than does arrangement 1–A. If the distribution of black balls in clusters larger than three is wanted, a larger number of neighboring cells must be counted. It may be seen, however, that it is impossible with this particular arrangement of the variate equipoints to form clusters containing an even number of black balls, so $P_2 = P_4 = P_6 = \ldots P_{2x} = 0.$

A typical sample of an equal mixture of black and white balls distributed according to arrangement 1–B is shown in figure 31. It was made by using Tippett's random sampling numbers.

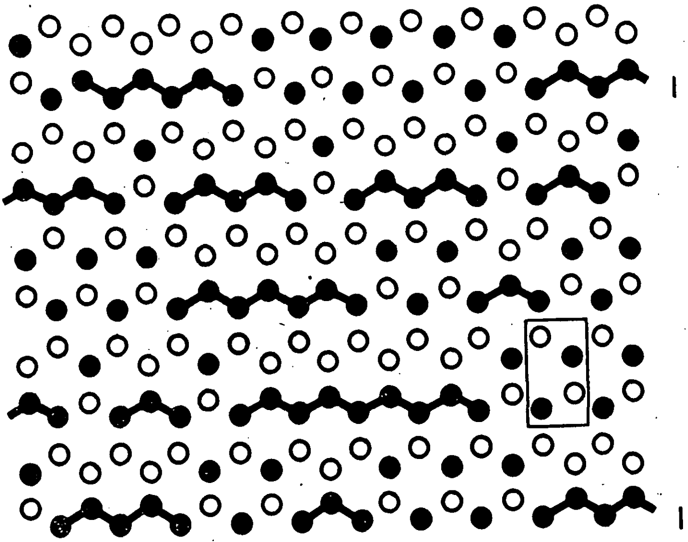

FIGURE 31.—Partly random distribution in a binary mixture, case 1–B. Typical arrangement of an equal mixture of black and white balls in a plane hexagonal array, with the limited randomness described in case 1-B. Every unit cell of the size shown in the inset must contain two black and two white balls; one of each is in the position shown, but the other two may have either of the possible positions at random.

Case 1–C.—In the cases of partial randomness so far illustrated there is no limit to the sizes of clusters that may form. If the randomness of an arrangement is restricted enough, there may be an upper limit to the possible sizes of clusters.

In a very large unit cell the nonvariate positions may be so fixed that none of the black balls are members of clusters extending into neighboring cells. For example, a unit cell containing 18 balls may be so formed that 6 of its balls occupy variate positions in a ring at the center of the cell (See page 78 case 1–C); the other balls are so arranged that no cluster can form containing more than 5 black balls. The fraction of black balls in clusters of 1 is $^{11}/_{20}$.

The number of small clusters formed by the arrangement of case 1–A is still larger than that formed in case 1–B because the arrangement is more symmetrical; that is, the randomness is more limited. The restriction of randomness to centers far enough apart to prevent the formation of clusters of more than five black balls makes it possible to calculate the complete distribution of cluster sizes. In cases 1–A and 1–B there is no limit to the size of clusters that may be formed.

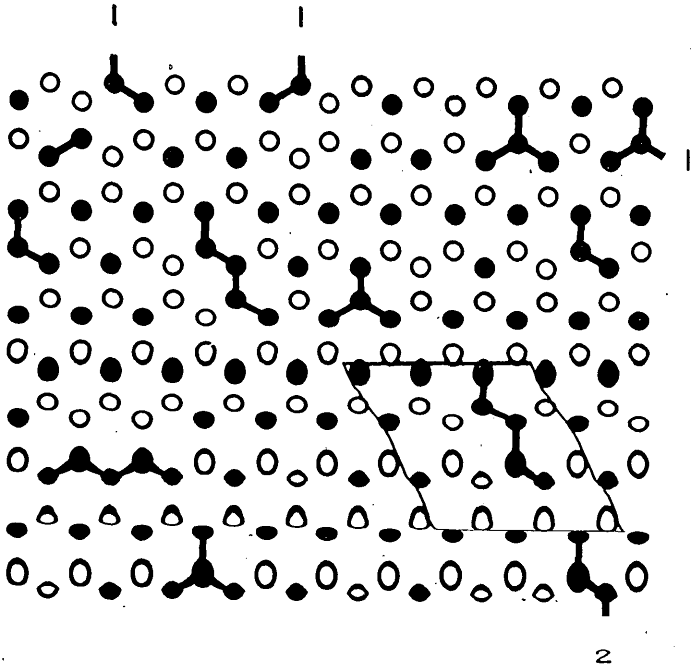

FIGURE 32.—Partly random distribution in a binary mixture, case 1–C. Typical arrangement of an equal mixture of black and white balls in a plane hexagonal array with the limited randomness described in case 1–C. The only randomness in arrangement is in the rings of six balls within the cells that are completely separated from each other by white balls, so there can be no clusters larger than five black balls.

Figure 32 shows a typical random distribution arranged in the manner of case 1–C (fig. 35), made with the use of Tippett's random sampling numbers.

Summary of case 1.—The fractions of clusters of sizes 1 to 3 formed in cases 1–A, 1–B, and 1–C are compared with those in the two extreme cases of completely random and completely symmetrical arrangement in the accompanying table.

Comparison of cluster-size fractions in distributions having different degrees of randomness. Equal mixture of black and white balls on plane hexagonal skeleton

	Fraction of black balls in clusters of size c, Pc		
	P_1	P_2	P_3
Completely random (fig. 18)	0.125	0.0938	0.0703
Partly random:			
All points variate (case 1–A1; fig. 28)	.25	.25	.1875
Half of points variate (case 1–B; fig. 31)	.375	0	.1875
One-third of points variate (case 1–C; fig. 32)	.55	.10	.20
Completely symmetrical (fig. 19)	1	0	0

The fractions of black balls in small clusters clearly show the effect of increasing the symmetry of arrangement by increasing the restrictions on randomness. Successively restricting the randomness within the cell in cases 1–A1, 1–B, and 1–C increases the symmetry and therefore increases the number of small clusters.

These distributions of a mixture with composition $p = 1/2$ give a rough idea of the behavior to be expected in simple compounds and in mixed crystals with composition ratios that are simple fractions. If the restriction of uniform composition of all the unit cells is partly relaxed, the distributions may indicate the behavior of mixed crystals with compositions intermediate between the simplest fractional ratios, as well as that of more complex pure compounds.

CASE 2. MIXTURES WITH INTERMEDIATE COMPOSITION FRACTIONS

If the composition fraction of a mixture is complex—that is, if it lies between the simplest ratios—it is not possible to arrange the mixture in a pattern with a high degree of symmetry. At best, the most symmetrical arrangement possible for such complex fractions as, for example, $7/13$, or $71/129$, would have an enormous unit cell, and its formation in a crystal structure would require extremely long-range forces between atoms to insure against slight variations in arrangement from cell to cell. The smallest possible unit cell must contain at least as many atoms as the denominator of the composition fraction and generally contains some whole multiple of this number of atoms. The unit cell with variate atom equipoints described so far does not remedy the difficulty of accounting for the chemical stability of a large unit cell, so long as each cell is required to have exactly the same composition.

If the cell may vary slightly in composition as well as in arrangement, it need not be so large as if each cell contained exactly the same number of black balls and white balls. A simple approach to the problem is to treat the pattern as if it were made by superposing a random distribution of a few black balls on a fixed symmetrical pattern whose composition is the simplest possible fraction; for example, the simplest possible symmetrical pattern of two kinds of objects is that formed by the mixture having the simplest possible composition fraction, $p = 1/2$. This simple approach is illustrated in cases 2–A2, 2–B2, and 2–C2 (see Appendix) for three mixtures containing successively larger fractions of black balls. The fractions of clusters of one black ball in mixtures having this arrangement are contrasted with the fractions of clusters of one in the same mixtures having the randomness restricted to unit cells of constant composition. (See cases 2–A1, 2–B1, and 2–C1 in the Appendix, pp. 79 to 82.)

The table below shows the increasing fraction of clusters of one formed in intermediate mixtures by the introduction of limited randomness of two different degrees, compared with the symmetrical arrangement and with completely random distribution. The completely random arrangement forms only a negligible fraction of clusters of one.

The first type of partly random arrangement is the variate atom unit cell with constant composition, in which half the balls are fixed in the most symmetrical arrangement—that for $p=1/2$.

The second type of partly random arrangement is the distribution in which half the balls are still fixed in the symmetrical arrangement but the rest are not restricted in their distribution by any cell size.

Effect of partial randomness on cluster size in intermediate mixtures; fraction of black balls in clusters of one black ball, P_1

Arrangement	Fraction of black balls in mixture, p		
	$7/12$ (case 2–B)	$5/8$ (case 2–A)	$2/3$ (case 2–C)
Completely symmetrical	0.429	0.2	0
Partly random:			
Type 1	.464	.284	.185
Type 2	.496	.338	.222
Completely random	.072	.053	.038

These partly random examples indicate how the arrangement of atoms in a crystal may be regular enough to account for its ordinary properties and yet have enough variation from regularity in their arrangement to permit such behavior as mixed-crystal formation and gelatinization.

If mixed crystals form in *all* proportions, the most symmetrical distributions of their atoms for very complex ratios will have such large unit cells that they may be considered unstable; it is naturally to be expected that every region of the size of such a large cell will not have exactly the same arrangement of atoms within it. If it is assumed that most of the atoms are symmetrically arranged as in a mixture of simple proportions, the remaining atoms will be too far apart to force one another into exactly symmetrical positions.

In silicates containing too little aluminum to form very small clusters a limited degree of randomness in their arrangement may permit the formation of an appreciable amount of small clusters. For example, the one exceptional mineral with the Al:Si ratio of 1:2 plotted on Murata's diagram (fig. 5, p. 30) is reported to gelatinize. If this proves to be correct, the behavior may possibly have some such explanation.

SUMMARY

A study of the ways of arranging two kinds of objects in an array shows by analogy that if the arrangement of aluminum and silicon atoms in minerals were completely random, there would be so few small clusters of silicon atoms formed that the mineral would not gelatinize on treatment with acid. It is therefore concluded that the arrangement of atoms in gelatinizing minerals is not completely random, and this conclusion is supported by consideration of the nature of valence forces. Experimental evidence from the study of both metallic and nonmetallic crystals confirms this conclusion.

Calculation of cluster-size distributions for a simplified hypothetical example, the plane hexagonal array, indicates that in mixtures whose symmetrical arrangement does not give very many small clusters, and in mixtures that cannot be arranged very symmetrically because their composition cannot be expressed by small whole numbers, a fairly large fraction of small clusters may be formed if there is a restricted randomness in the arrangement of their atoms. The randomness may be restricted to regions of limited size in the crystal or to certain of the atoms.

APPENDIX

FRACTION OF SMALL CLUSTERS IN PARTLY RANDOM ARRANGEMENTS

It is not practicable to use any one particular method for finding the fraction of small clusters in the case of limited randomness. The artifices of calculation that will make a given calculation as simple as possible depend on the individual case; enough cases are given here to indicate the general method of approach in handling such problems.

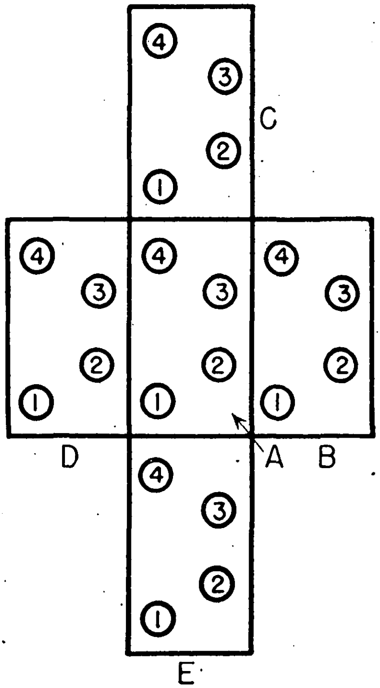

FIGURE 33.—Limited randomness, case 1–A2, $p = \frac{1}{2}$. Unit cell with four variate equipoints in the plane hexagonal array. Any two of the four variate points 1, 2, 3, 4 may be occupied by black balls and the other two by white balls. Cell A is shown surrounded by the four other cells whose arrangement affects the size of clusters included in A.

Case 1–A2.—The formation of clusters of one black ball in cell A (see fig. 33) is affected by the arrangement of balls in the four neighboring unit cells B, C, D and E. There are six ways in which two black and two white balls can be arranged on the variate points 1, 2, 3, and 4 in each unit cell. A simple way of describing the arrangement of balls in a cell is to list the numbers of the two variate points occupied by the two black balls and the letter showing the location of the cell. Thus the symbol 13A means that there are black balls in positions 1 and 3 in cell A, and so on.

The balls in each of the five cells may be arranged in six different ways, so there are $6\times6\times6\times6\times6=6^5$ different arrangements affecting the clusters in cell A. Each of these has two black balls in cell A, so the total number of black balls to be counted is 2×6^5. There are three different arrangements within a cell in which the two black balls are separated from each other by a white ball; they are positions 13A, 14A and 24A. Position 24A is the mirror image of position 13A, so its arrangements need not be counted separately, their number being the same as for 13A.

In arrangement 13A both the black balls are clusters of one if cell B has its black balls in any of the three positions 12B, 13B and 23B; cell C has any of its six possible arrangements; cell D has any of the three arrangements 13D, 14D and 34D; and cell E has any of the three arrangements 12E, 13E and 23E. Thus there are three ways in which cells A and B can be so arranged that balls 1 and 3 in cell A are not connected with black balls in cell B. With each of the three arrangements cell C can be arranged in six ways without disturbing the isolation of black balls 1 and 3 in cell A, so there are 3×6 ways of arranging cells A, B, and C to form two clusters of one black ball in A. Each of the 3×6 arrangements may have cell D arranged in three different ways, making $3\times6\times3$ combinations of cells A, B, C and D; and each of these $3\times6\times3$ arrangements can have cell E arranged in three ways, making $3\times6\times3\times3$ combinations of cells A, B, C, D and E that have two clusters of one black ball in cell A.

Conditions for two clusters of one black ball in arrangement 13A

Cell	A	B	C	D	E
Positions of black balls in the cell	13	12, 13, 23	All	13, 14, 34	12, 13, 23
Number of positions	1	3	6	3	3

The total number of arrangements in which cell A can have two clusters of one black ball in arrangement 13A is $1\times3\times6\times3\times3=2\times3^4$. Each of these A cells contains two clusters of one, so the total number of black balls in clusters of one in arrangement 13A, both 1 and 3 being clusters of one, is $2\times2\times3^4=2^2\times3^4$.

Now for every arrangement 24A there is a corresponding arrangement 13A which is its mirror image, so the total number of black balls in clusters of one, both 2 and 4 being clusters of one, is the same as that for 13A, which is $2^2\times3^4$.

The only other arrangement in which the two black balls in a cell are separated by white balls is that in which the black balls are in positions 1 and 4. Cell A may have two clusters of one black ball in positions 1 and 4 under the following conditions: 14A (1); all B (6); 23C, 24C, 34C (3); 14D (1); 12E, 13E, 23E (3); thus $1\times6\times3\times1\times3=2\times3^3$ arrangements. Each has two black balls in clusters of one in cell A, so the number of black balls in clusters of one is $2\times2\times3^3=2^2\times3^3$.

The other arrangements to be counted are those in which one of the black balls in cell A is a cluster of one, but the other is not because one or more of its nearest neighbors in adjacent cells are black. The following arrangements will give a single cluster of one black ball in cell A, having black balls in the position 13A.

13A (1); 12B, 13B, 23B (3); all C (6); 12D, 23D, 24D (3); all E (6) or $1\times3\times6\times3\times6=2^2\times3^4$ arrangements.

13A (1); 12B, 13B, 23B (3); all C (6); 13D, 14D, 34D (3); 14E, 24E, 34E (3) or $1\times3\times6\times3\times3=2\times3^4$ arrangements.

13A (1); 14B, 24B, 34B (3); all C (6); 13D, 14D, 34D (3); 12E, 13E, 23E (3) or $1\times3\times6\times3\times3=2\times3^4$ arrangements.

Adding the numbers of arrangements, we have

$$2^2\times3^4+2\times3^4+2\times3^4=(2+1+1)\times2\times3^4=2^3\times3^4 \text{ arrangements}$$

with black balls in position 13A, only one of the two black balls being a cluster of one.

Now each of these arrangements having black balls in position 13A is a mirror image of an arrangement of 24A, so the total number of clusters of one black ball in arrangement 24A with single clusters of one in cell A is the same as that for 13A, which is $2^3\times3^4$.

The only other arrangements giving clusters of one black ball in cell A are those with two black balls in position 14A, only one of which is a cluster of one black ball. This occurs under the following conditions.

14A (1); all B (6); 12C, 13C, 14C (3); 13D, 14D, 34D (3); 12E, 13E, 23E (3) or $1\times6\times3\times3\times3=2\times3^4$ arrangements.

14A (1); all B (6); 23C, 24C, 34C (3); 13D, 34D (2); 12E, 13E, 23E (3) or $1\times6\times3\times2\times3=2^2\times3^3$ arrangements.

14A (1); all B (6); 23C, 24C, 34C (3); 12D, 24D (2); all E (6) or $1\times6\times3\times2\times6=2^3\times3^3$ arrangements.

14A (1); all B (6); 23C, 24C, 34C (3); 14D (1); 14E, 24E, 34E (3) or $1\times6\times3\times1\times3=2\times3^3$ arrangements.

Adding the numbers of arrangements gives

$$2\times3^4+2^2\times3^3+2^3\times3^3+2\times3^3=(3+2+4+1)2\times3^3=2^2\times3^3\times5$$

arrangements with black balls in position 14A, only one of the two black balls being a cluster of one.

Adding all the black balls in clusters of one from the different arrangements, we have for cell A,

Two clusters of one		One cluster of one	
Position of black balls	Number of black balls	Position of black balls	Number of black balls
13	$2^2\times3^4$	13	$2^3\times3^4$
24	$2^2\times3^4$	24	$2^3\times3^4$
14	$2^2\times3^3$	14	$5\times2^2\times3^3$

Total number of black balls in a cluster of one. . . . . 2^5 x 3^4

Dividing the total number of black balls in clusters of one by the total number of black balls in the A cells of all the different possible arrangements, we have

$$P_1=\frac{2^5\times3^4}{2^6\times3^5}=\frac{1}{2\times3}=1/6,$$

the fraction of black balls in clusters of one.

Case 1–A3.—A still larger unit cell may be taken in the plane hexagonal array by enclosing six variate equipoints in a hexagonal cell. (See fig. 34.) If $p=1/2$ and each cell contains three black balls and three white balls, arranged at random within the cell, the number of different arrangements of this variate atom unit cell is given by the formula

$$C_n^m=\frac{m!}{(m-n)!n!}$$

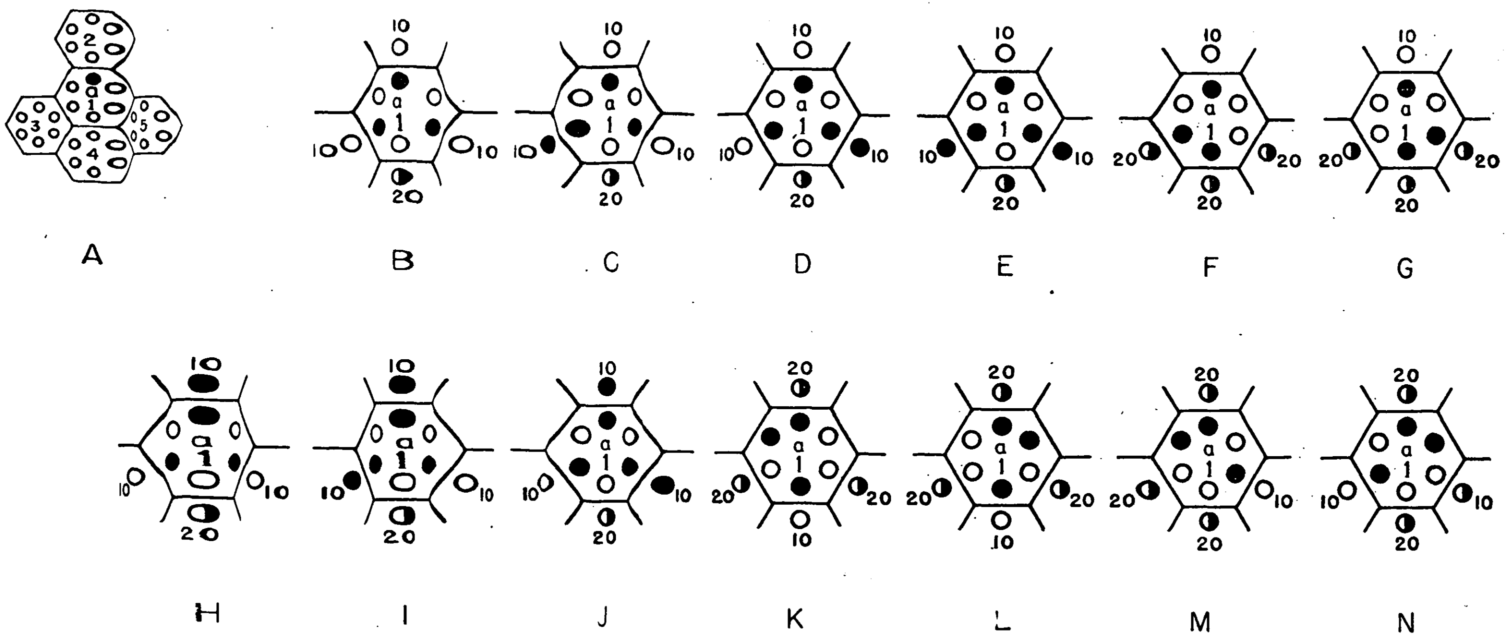

FIGURE 34.—Limited randomness, case 1-A3. A unit cell containing three black balls and three white balls, all six of whose positions are equivariate. The formation of clusters in cell 1 is affected by the arrangements in the surrounding cells 2, 3, 4, and 5; the diagrams show the number of ways that each neighboring cell can be arranged without disturbing the arrangement of clusters of one shown in cell 1. A circle that is half white and half black means that the ball in the neighboring cell so marked may be either white or black, so that the arrangement of that particular cell does not affect the arrangement in cell 1. The number of ways in which a given arrangement in cell 1 can be formed is the product of the number of ways in which the four neighboring cells can be arranged in the case shown; for example, the arrangement B in cell 1 can be formed in 10×10×20×10 different ways.

where the binomial coefficient[79] C_n^m is the number of different combinations of m things taken n at a time. The exclamation point after a number, for example, x!, is used to represent the product of all integers from 1 to x, inclusive; this notation is read "factorial x." For the three black and three white balls arranged on the six variate points labeled 1, 2, 3, 4, 5, and 6, there are

$$C_3^6 = \frac{6!}{(6-3)! \times 3!} = \frac{6!}{3! \times 3!} = \frac{6 \times 5 \times 4 \times 3 \times 2 \times 1}{(3 \times 2 \times 1) \times (3 \times 2 \times 1)} = 5 \times 4 = 20$$

different arrangements in the unit cell.

If the position of a given black ball *a* is fixed in cell 1 the other 2 black and 3 white balls in the cell can be arranged in

$$C_2^5 = C_3^5 = \frac{5!}{(5-2)!2!} = \frac{5!}{3!2!} = \frac{5 \times 4 \times 3 \times 2 \times 1}{3 \times 2 \times 1 \times 2 \times 1} = 10$$

different ways. Figure 34 shows that only 7 of these 10 arrangements have at least 1 black ball with a white ball on both sides of it in the cell; the number of clusters of 1 in each of the 7 arrangements depends partly on the color of one particular ball in each of some neighboring cells.

If black ball *a* is to be a cluster of 1, its nearest neighbor in cell 2 must be white; there are 10 ways that this can be arranged. If the 2 nearest neighbors of ball *a* within cell 1 are white the nearest neighbor in cell 2 must be black, if *a* is not to be a cluster of 1; there are 10 ways that this can happen.

The number of ways in which each arrangement in cell 1 can be formed is the product of the numbers of ways in which each of the four neighboring cells can be arranged to give that arrangement.

The total number of arrangements to be counted in which ball *a* in cell 1 is black is $10 \times 20 \times 20 \times 20 \times 20 = 2^9 \times 5^5$; each has three black balls in cell 1, so the total number of black balls to be counted is $2^9 \times 3 \times 5^5$.

There is one arrangement that has three clusters of one black ball in cell 1 (fig. 34, *B*); it can be formed in $10 \times 10 \times 20 \times 10 = 2^5 \times 5^4$ ways. Each arrangement has three black balls in clusters of one, so the total number of black balls in cell 1 in this arrangement is $2^5 \times 3 \times 5^4$.

There are three arrangements, C, D, and H, that have two clusters of one black ball in cell 1. Each can be formed in $10 \times 10 \times 20 \times 10$ ways, and each has two clusters of one black ball in cell 1, so the total number of black balls to be counted in these arrangements is

$$3 \times 10 \times 10 \times 20 \times 10 \times 2 = 2^6 \times 3 \times 5^4.$$

The other nine arrangements in cell 1 each form one cluster of one black ball. The three E, I, and J can each be formed in $10 \times 10 \times 20 \times 10 = 2^5 \times 5^4$ ways, making $2^5 \times 3 \times 5^4$ clusters of one black ball for the three; and the other six arrangements, F, G, K, L, M and N can each be formed in $10 \times 20 \times 20 \times 20 = 2^7 \times 5^4$ ways, making $2^8 \times 3 \times 5^4$ clusters of one black ball for the six.

Adding all the clusters of one black ball,

$$2^5 \times 3 \times 5^4 + 2^6 \times 3 \times 5^4 + 2^5 \times 3 \times 5^4 + 2^8 \times 3 \times 5^4$$
$$= (1+2+1+2) \times 2^5 \times 3 \times 5^4 = 2^7 \times 3 \times 5^4.$$

Dividing by the total number of black balls in cell 1 in all possible arrangements,

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[79] Fry, Thornton C., Probability and its engineering uses, pp. 25–31, D. Van Nostrand Co., New York, 1928. A table of binomial coefficients up to C_{50}^{100} is given in appendix 3, pp. 439–452.

$$P_1=\frac{2^7\times3\times5^4}{2^9\times3\times5^5}=\frac{3}{4\times5}=\frac{3}{20},$$

the fraction of black balls in clusters of one.

Case 1–C.—It has been mentioned that a variate-equipoint unit cell may be imagined such that none of its black balls can be members of clusters extending into neighboring cells; for example, the unit cell shown in figure 35 contains 18 balls, 9 of them black and the other 9 white. Six variate positions of 3 black and 3 white balls are arranged in a ring at the center of the cell; the other 12 balls are arranged around the central pattern as shown, 6 black balls and 6 white balls. In this example, there can be no clusters larger than 5 black balls.

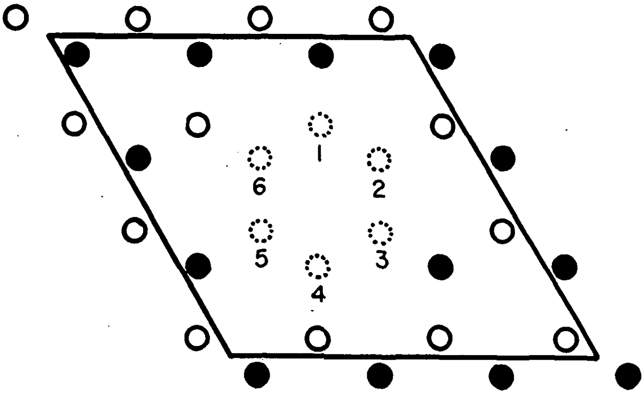

FIGURE 35.—Limited randomness, case 1–C. Tripled unit cell of 18 balls with 6 white and 6 black balls in fixed positions and 3 black and 3 white balls randomly arranged in a ring in the center of the cell.

The formula given above in case 1–A3 shows that the number of different arrangements of this variate atom unit cell is $C^6{}_3=20$. The number of clusters of each size c in the unit cell is listed for each of these 20 combinations and counted. The total number of back blalls in each size of cluster is divided by the total number, $20\times9=180$, of black balls in the 20 different unit cells, to find the fraction P_c of black balls in clusters of size c, as shown in the accompanying table.

Distribution of clusters in variate-equipoint unit cell, case 1–C (see fig. 36)

Cluster size (c) and position of black balls on variate equipoints	Number of arrangements (Z)	Number of clusters of size c formed per unit cell (n)	Number of black balls in clusters of size c per unit cell (nc)	Total number of black balls in clusters of size c (Znc)	Fraction of black balls in clusters of size c $\left(P_c=\frac{Znc}{180}\right)$
When $c=1$:					
123, 125, 134, 136, 145, 156, 235, 345, 356.	9	4	4	36	0.55
124, 146, 236, 245, 256, 346	6	6	6	36	
126, 234, 456	3	5	5	15 } 99	
135	1	3	3	3	
246	1	9	9	9	
When $c=2$:					
125, 134, 136, 145, 235, 356	6	1	2	12 } 18	.10
135	1	3	6	6	
When $c=3$:					
124, 125, 134, 136, 145, 146, 235, 236, 245, 256, 346, 356	12	1	3	36	.20
When $c=4$:					
126, 234, 456	3	1	4	12	.0667
When $c=5$:					
123, 156, 345	3	1	5	15	.0833
				180	1.0000

Case 2–A.—The symmetrical arrangement shown in figure 24 for $p=5/8$ black balls contains equal numbers of clusters of one and four black balls, so one out of every five black balls is a cluster of one, and four out of five are members of clusters of four. The complete cluster size distribution is $P_1=1/5$, $P_2=4/5$, and $P_c=0$ when c is any number other than 1 or 2. This pattern can be considered a superposition of the symmetrical patterns for $p=1/2$ and $p=1/8$, and a simple way of introducing randomness into the $p=5/8$ arrangement is to keep the black balls fixed in the positions corresponding to the $p=1/2$ pattern, and to distribute the remaining black balls randomly instead of in the positions they have in the $p=1/8$ symmetrical pattern.

Case 2–A1.—If five black balls and three white balls are confined in each unit cell so that each cell has the same composition (as was true in case 1), with four black atoms fixed in the symmetrical $p=1/2$ positions, there are four variate equipoints left in the $p=5/8$ unit cell. (See fig. 36.) Three white balls and one black ball are variate within the unit cell, so the chance that the variate black ball will be in a given position is $1/4$; the chance that it will be in either one of two given positions is $1/4+1/4=1/2$, and the chance that it will be in any one of three given positions is $1/4+1/4+1/4=3/4$. Since the remaining sites are occupied by white balls, the chance that a ball in a given position is white is equal to the chance that the other three are black, or $3/4$; the chance that any two given balls are white is equal to the chance that neither of them are black, which is $1/2$; and the chance that any three given balls are white is equal to the chance that the remaining one is black, or $1/4$.

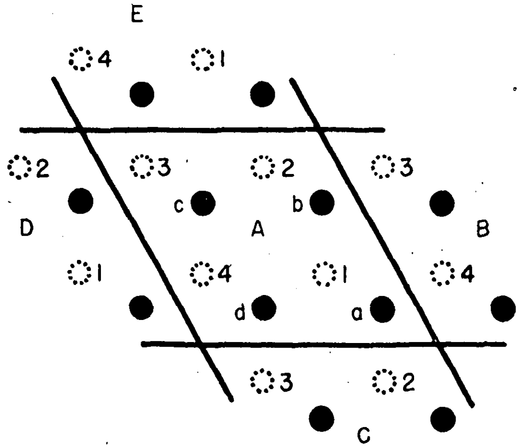

FIGURE 36.—Limited randomness, case 2–A1. A unit cell containing four fixed black balls in the symmetrical pattern for $p=1/2$ in the plane hexagonal array. The other four points in the unit cell are are variate equipoints. The four neighboring cells containing nearest neighbors to balls in cell A are indicated.

Thus, by inspection of the unit cell A and its neighboring balls in figure 36, one can calculate the chance that a given ball is a cluster of one black ball. There is, however, no position in which the variate black ball can be a cluster of one, so the chance of this happening is zero. The nearest neighboring balls in cells D and E are fixed black balls; hence there is no need to consider the arrangement of the variate balls in these two neighboring cells.

Ball *a* will be a cluster of one if ball 1 in cell A, ball 4 in cell B, and ball

2 in cell C are white, and not otherwise. The chance that one particular ball in a cell is white is $\frac{3}{4}$, so the chance that a ball in each of the three different cells is white is the product of the chance of each, or

$$P_1(a) = \tfrac{3}{4} \times \tfrac{3}{4} \times \tfrac{3}{4} = \tfrac{27}{64}.$$

Ball *b* will be a cluster of one if both balls 1 and 2 in cell A are white and ball 3 in cell B is white. The chance that two given balls in a cell are white is $\frac{1}{2}$ and the chance that any one is white is $\frac{3}{4}$; so the chance that both cells A and B have the necessary arrangement is

$$P_1(b) = \tfrac{1}{2} \times \tfrac{3}{4} = \tfrac{3}{8}.$$

Ball *c* will be a cluster of one if balls 2, 3, and 4 in cell A are white; the chance of this arrangement is $\frac{1}{4}$, so $P_1(c) = \frac{1}{4}$.

Ball *d* will be a cluster of one if balls 1 and 4 in cell A and ball 3 in cell C are white; the respective chances of these arrangements are $\frac{1}{2}$ and $\frac{3}{4}$, so $P_1(d) = \frac{1}{2} \times \frac{3}{4} = \frac{3}{8}$.

The total of the chances that cell A contains a cluster of one black ball is therefore

$$P_1(\mathrm{A}) = P_1(a) + P_1(b) + P_1(c) + P_1(d) = \tfrac{27}{64} + \tfrac{3}{8} + \tfrac{1}{4} + \tfrac{3}{8} = \tfrac{91}{64}.$$

But the chance that a black ball is in a given position *a*, *b*, *c*, or *d*, in the cell is $\frac{1}{5}$, because $\frac{1}{5}$ of the black balls are in each position. The chance, therefore, that a given ball is a cluster of one is

$$P_1 = \tfrac{1}{5} \times \tfrac{91}{64} = \tfrac{91}{320} = 0.2844,$$

so this variate-equipoint unit-cell arrangement forms more clusters of one than does the symmetrical arrangement.

Case 2–A2.—If instead of restricting the composition of the unit cell to a single value, we distribute the $\frac{1}{8}$ variate black balls at random over the whole set of remaining positions, the fraction of clusters of one black ball formed may be calculated from inspection of figure 37. A cell of

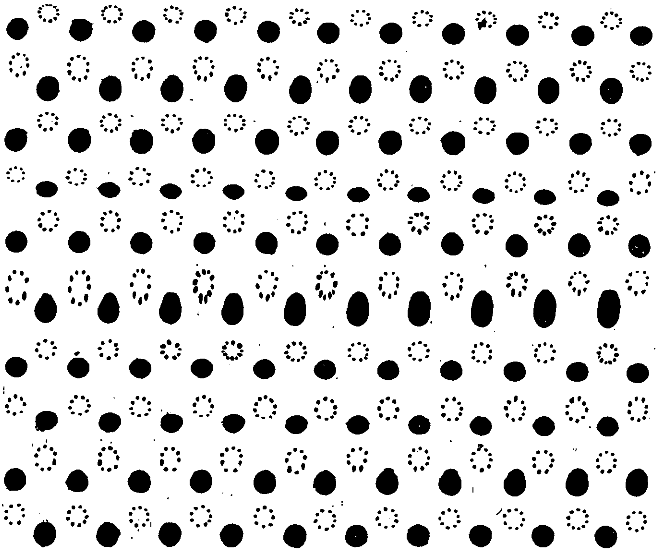

FIGURE 37.—Limited randomness, case 2–2. Half the sites in the arrangement are occupied by black balls fixed in the symmetrical pattern for $p = \frac{1}{2}$, the rest of the points are variate equipoints. In case 2–A2, the other half of the sites are variate equipoints among which the remaining $\frac{1}{8}$ black balls and $\frac{3}{8}$ white balls are distributed at random. In case 2–B2, $p = \frac{7}{12}$, and $\frac{1}{6}$ of the variate equipoints are occupied by black balls; the other $\frac{5}{6}$ of the variate balls are white. In case 2–C2, $p = \frac{2}{3}$; one-third of the variate balls are black and two-thirds of them white.

the size taken in case 2–A1 could now contain from four to eight black balls. As in case 2–A1, half the black balls are fixed in the symmetrical arrangement, but the rest may occupy any $\frac{1}{4}$ of the remaining $\frac{1}{2}$ of the sites.

As before, a variate black ball cannot be a member of a cluster of one because there is no site that it can occupy without having other black balls for nearest neighbors. The other $\frac{4}{5}$ of the black balls occupy the fixed sites, so the chance that a given black ball is not randomly placed is $\frac{4}{5}$. In order that it may be a cluster of one, all three of its variate nearest neighbors must be white; but the chance that a given variate ball is white is $\frac{3}{4}$, because $\frac{3}{4}$ of the variate balls are white and $\frac{1}{4}$ are black. The chance, therefore, that a given black ball is a cluster of one is

$$P_1 = \frac{4}{5} \times \frac{3}{4} \times \frac{3}{4} \times \frac{3}{4} = \frac{27}{80} = 0.3375,$$

a still larger fraction of black balls in clusters of one than in type 2–A1.

Case 2–B1.—An example with a larger unit cell may be made by superposing the regular pattern for $p = \frac{1}{12}$ (fig. 24) on the regular $p = \frac{1}{2}$ pattern; this unit cell will contain 12 balls—7 black and 5 white. Of the 7 black balls 4 will be in a cluster of 4, and the other 3 will be clusters of 1; the distribution of black balls in clusters is then $P_1 = \frac{3}{7} = 0.4286$, $P_4 = \frac{4}{7}$, and $P^c = 0$ for any other value of c. If instead of arranging the extra ball in the $p = \frac{1}{12}$ site, we fix the 6 black balls in the $p = \frac{1}{2}$ pattern and let the extra one occupy any of the other 6 sites in the cell the variate unit cell will have the form shown in figure 38. By calculations similar to those made for case 2–A1, it is found that the fraction of black balls in clusters of one is $P_1 = \frac{701}{1512} = 0.4636$, slightly larger than in the symmetrical arrangement. The slight randomness allows some of the balls to form clusters larger than 4, leaving a larger number of others isolated than before.

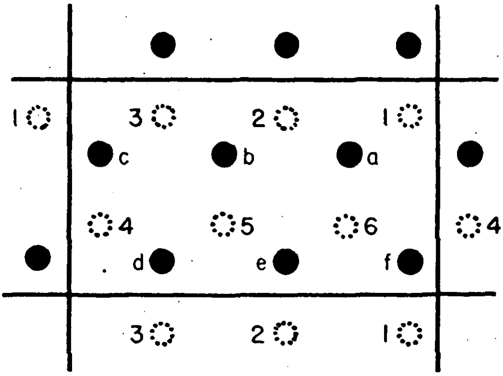

FIGURE 38.—Limited randomness, case 2–B1, $p = \frac{7}{12}$. A variate-equipoint unit cell containing 12 balls, 7 of them black and 5 white. Six of the black balls are fixed in the positions *a*, *b*, *c*, *d*, *e*, and *f* of the symmetrical arrangement for $p = \frac{1}{2}$; the other black ball and the 5 white balls are variate on the other 6 positions in the cell. The chance that n particular variate balls in a cell are white is $\frac{6-n}{6}$, because there are $6-n$ possible sites left for the one black ball. The chance that either ball *a* or ball *b* is a cluster of one black ball is then the chance that its 3 nearest neighbors are white, or $\frac{3}{6} = \frac{108}{216}$; the chance that any one of the 3 balls *c*, *d*, and *e* are clusters of one is $\frac{4}{6} \times \frac{5}{6} = \frac{120}{216}$; and the chance that ball *d* is a cluster of one is $\frac{5}{6} \times \frac{5}{6} \times \frac{5}{6} = \frac{125}{216}$. The variate black ball cannot be a cluster of one. Therefore, the sum of the respective chances that each of the 7 balls in the cell is a cluster of one black ball is $\frac{108+108+120+120+120+125}{216} = \frac{701}{216}$. Since the cell contains 7 black balls, the chance that a given black ball is a cluster of one black ball is $P_1 = \frac{1}{7} \times \frac{701}{216} = \frac{701}{1512} = 0.4636$.

Case 2–B2.—If the extra $\frac{1}{7}$ of the black balls are randomly distributed over all the sites not occupied by the $6/7$ of the black balls fixed in the symmetrical $p=1/2$ pattern (fig. 37) the variate balls will be $1/6$ black and $5/6$ white. Only $6/7$ of the black balls can be clusters of one, so the chance that a given black ball is one of these is $6/7$; and the chance that its three nearest neighbors are white is $(5/6)^3$. Therefore the chance that a given black ball is a cluster of one is $P_1=6/7\times(5/6)^3=125/252=0.4960$, a still larger fraction of clusters of one black ball than in the variate equipoint unit cell arrangement of case 2–B1.

Case 2–C.—In the symmetrical pattern for $p=2/3$ (fig. 21) there are no clusters smaller than four black balls; in the random arrangement (fig. 20) there are very few. If, however, the randomness is limited to those balls in excess of the fraction ($1/2$) that will form the simplest symmetrical arrangement, the fraction of clusters of one is rather large.

Case 2–C1.—If the randomness is confined within a unit cell containing six balls, with three of the black balls fixed in the symmetrical pattern for $p=1/2$, the other one black ball and three white balls are variate. (See fig. 39.) By the method already described, the fraction of clusters of one black ball is calculated to be $P_1=5/27=0.1852$.

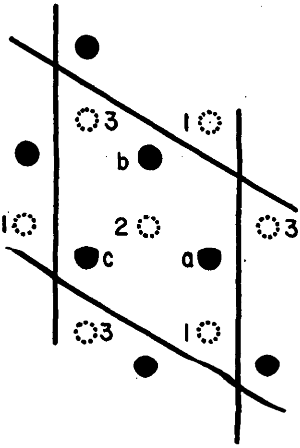

FIGURE 39.—Limited randomness, case 2–C1, $p=2/3$. A variate-equipoint unit cell containing six balls—four black and two white. Three of the black balls are fixed in the symmetrical positions *a*, *b*, and *c* of the pattern for $p=1/2$; the other black ball and the two white balls are variate on the other three positions in the cell. The chance that any one variate ball in the cell is white is $2/3$, and the chance that any two are white is $1/3$. Therefore, the chance that black ball *a* is a cluster of one is $1/3\times2/3=6/27$; the chance that *b* is a cluster of one is also $1/3\times2/3=6/27$; and the chance that *c* is a cluster of one is $2/3\times2/3\times2/3=8/27$. All possible positions of the variate black ball have black nearest neighbors, so its chance of being a cluster of one is zero. Adding these chances, the chance that a cell contains a cluster of one black ball is $\frac{6+6+8}{27}=\frac{20}{27}$. But, since the cell contains four black balls, the chance that a given black ball is in a fixed position in the cell is $1/4$, so the chance that a given black ball is a cluster of one is $P_1=1/4\times20/27=5/27=0.1852$.

Case 2–C2.—If the limitation of a unit cell of constant composition is removed, but the restriction of half the balls to the symmetrical pattern is kept, $3/4$ of the black balls are in the fixed positions of the patterns of figure 37. The other $1/4$ of the black balls are randomly distributed over all the equipoints; of the balls so distributed $1/3$ are black and $2/3$ are white. The chance that a given black ball is in a fixed position, where it can be a cluster of one, is $3/4$, and the chance that it is surrounded by three white balls is $(2/3)^3$; so the chance that a given black ball is a cluster of one is $P_1=3/4\times(2/3)^3=2/9=0.222$, a fraction of clusters of one large enough to account for at least partial gelatinization in an aluminosilicate.

Contributions to geochemistry, 1942–45
Geological Survey Bulletin 950

A STUDY OF METHODS FOR THE DETERMINATION OF VANADIUM

By Victor North

In the course of investigations conducted by the Geological Survey of the vanadium deposits in the Phosphoria formation some difficulty was encountered in making a proper appraisal of the grade and extent of workable deposits. Inconsistent results for vanadium were obtained by different methods of chemical analysis. Investigations have therefore been carried out in the Chemical Laboratory of the Geological Survey to ascertain

1. The true vanadium content of certain samples;
2. Methods that will give the true content with a minimum expenditure of time and materials; and
3. Causes of discrepancies in the different methods.

Two methods have been found that give reproducible results, which, from supplementary work, seem to be the correct results.

SAMPLES

The material used in this investigation was collected by James Noble of the Wyodak Coal and Manufacturing Co., an agent of Metals Reserve Co., from trenches located by W. W. Rubey of the Geological Survey.

Two samples from each of three canyons in Sublette Ridge, Wyo., were used. These particular samples were selected for use in this investigation because they were ground and reduced from 25 pound samples, this providing a better basis for evaluation of the trench. Splits from these samples were sent to reputable laboratories for vanadium determinations. By using these samples any results obtained would be easily compared with methods used by different investigators. Results from six laboratories reporting 8 determinations of vanadium gave averages for the six samples ranging from 0.71 to 0.96 per cent V_2O_5. The results and methods used by other laboratories were collected by Mr. Noble.

METHODS

Methods used for vanadium determinations may be classed as colorimetric and volumetric.

Colorimetric methods as ordinarily carried out are always subject to a personal error. The vanadium content is determined by matching the pervanadic acid color developed in the unknown sample with a standard solution similarly treated. The accuracy of the determination depends on the ability of the analyst to determine when an exact color match is obtained. A method was developed in the field for determining vanadium in this manner by using readily available chemicals. The method consisted of fusing the sample with an oxidizing alkaline flux of potassium nitrate and sodium hydroxide, extracting vanadium from the sample with water, and developing the vanadium color with hydrogen peroxide in a solution of nitric acid. Sodium peroxide, which also can be used as the fusion agent, possesses the advantage of being ready to use without preliminary mixing. An average of the six samples analyzed after using the sodium hydroxide-potassium nitrate fusion method showed a vanadium content of 0.77 percent V_2O_5. The Homestake Mining Company, after using a sodium peroxide fusion obtained an average of 0.79 percent for the six samples.

The volumetric methods may be further divided, depending on the valence change of the vanadium, into oxidative and reductive titrations.

Oxidative titrations involve measuring the amount of standard reagent required to raise vanadium from a lower valence state to a higher one. The change from V^{+4} to V^{+5} is usually measured. The oxidizing reagent usually employed is potassium permanganate. Objections have been raised to this method of titration because of the slowness of the reaction at room temperature. This factor renders the endpoint rather difficult to determine. The speed of the reaction can be increased by raising the temperature, but this procedure introduces a possible error through oxidation of any chromium present in the sample.

The United States Vanadium Corporation used a method similar to that proposed by Hamner,[80] consisting of an acid attack on the sample and subsequent reduction of the vanadium with ferrous sulfate. The excess reductant was destroyed with ammonium persulfate and the resulting solution was titrated with standard permanganate solution. Findings by the Vanadium Corporation gave an average of 0.71 percent V_2O_5 for the six samples.

Ledoux & Co. and Union Assay office used a modification of a method first proposed by Campagne[81] and later improved by Smoot.[82] This method involves the use of hydrochloric acid as a reducing agent in the presence of excess ferric iron. The reduced vanadium is titrated with standard permanganate. Ledoux reported an average of 0.91 percent on the samples while Union Assay reported an average of 0.96 percent which was later changed on subsequent checking to 0.84 percent.

A method proposed by Gibbs[83] was tried by the Wyodak Coal and Manufacturing Co. The method involves separation of vanadium from the bulk of the sample by alkali fusion with subsequent water extraction. The vanadium in the extract is reduced with hydrogen sulfide or sulfur dioxide and subsequently titrated with permanganate. This titration was conducted in a hot solution, rendering the results questionable, as chromium also would be present. In the experimental section (see p. 87) it will be shown that traces of iron might easily contaminate the solution and introduce a positive error by being titrated along with the vanadium. Using this method the Homestake Mining Co. reported an average of 0.91 percent.

The other type of volumetric determination, reductive titration, requires the use of an accessory reagent to indicate the endpoint of the reaction. Vanadium is usually reduced from V^{+5} to V^{+4} by the use of a standardized reducing agent. Diphenylamine has been used as an internal indicator in vanadium determinations,[84] but it is not ideal for this deter-

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[80] Hamner, H. L., Determination of vanadium in steel: Met. Chem. Eng., vol. 17, p. 206, 1917.

[81] Campagne, E., Ueber eine neue Methode zur Bestimmung des Vanadins und der Anwendung auf metallurgische Produkten: Ber. Band 36, p. 3164, 1903.

[82] Smoot, A. M., in Scott's Standard Methods of Chemical Analysis, 5th ed., p. 1046, D. Van Nostrand Co., Inc., 1939.

[83] Gibbs, W., Researches on the complex inorganic acids: Am. Chem. Jour., vol. 5, p. 372, 1883.

[84] Someya, K., Selective Bestimmung von Vanadin in Gegenwort von Eisen und Chrom. I. Bestimmung von Vanadin in Gegenwort von Eisen: Zeitschr. anorg. Chemie, Band 139, p. 237, 1924.

mination. It has been noted that a correction must be made for the amount of indicator added; furthermore, the endpoint is not sharp, and results vary with the concentration of acid in the test solution.[85] Diphenylamine sulfonic acid has been suggested as an internal indicator for this titration by Sarver and Kolthoff,[86] but a rather large blank correction must be taken into account when this reagent is used. By the use of a partly oxidized indicator under standardized conditions the blank correction may be diminished. Willard and Young[87] have reported the magnitude of this correction and have given some results using the oxidized indicator.

The Bureau of Mines used a method first proposed by Lang and Kurtz.[88] After an acid attack on the sample, chromium and vanadium are reduced to the trivalent and quadrivalent states, respectively. The vanadium then is selectively oxidized to the pentavalent state by treatment with permanganate in the cold. The excess permanganate is destroyed with nitrous acid which in turn is destroyed with urea. This solution is titrated with standard ferrous sulfate solution using diphenylamine as an internal indicator. An average of 0.74 percent was reported by the use of this method. Wyodak Coal and Manufacturing Co. used this method following a peroxide-fusion attack on the sample. They obtained an average of 0.81 percent for the suite of samples.

International Minerals and Chemical Corporation reported that they used the method of Marvin,[89] which consists of peroxide fusion followed by acid solution. The resultant solution was oxidized with permanganate, and then titrated with standard ferrous sulfate solution, potassium ferricyanide being used as an outside indicator. This method is subject to a positive error if chromium is present, as it would be changed to the hexavalent state in the preliminary treatment and would be titrated along with the vanadium. The International Minerals and Chemical Corporation did not work with the above-mentioned samples, but a comparison can be made on one sample, analyzed by the hydroxide colorimetric method which indicated a V_2O_5 content of 1.0 percent, whereas the corporation reported 1.75 percent.

EXPERIMENTAL

As most of the procedures mentioned above were carried out in the presence of nearly all the original constituents of the sample, it seemed desirable to obtain results in which the vanadium of the sample was selectively concentrated and purified before being subjected to quantitative measurement. Concentration methods necessarily require more time for their completion, but the results obtained can be evaluated with greater certainty, as the composition of the final titrated solution is known.

An alkaline-oxidizing fusion seemed to be required for this particular type of sample. Through its use the sample can be readily cleaned of any organic matter. The usual acid attack leaves most of the organic matter

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[85] Willard, H. H., and Young, P., Vanadium in chromium vanadium tungsten steels. Volumetric determination: Ind. and Eng. Chemistry, vol. 20, p. 767, 1928.

[86] Sarver, L. A., and Kolthoff, I. M., Indicator corrections for diphenylamine, diphenylbenzidine, and diphenylamine sulfonic acid: Jour. Am. Chem. Soc., vol. 53, pp. 2906–2909, 1931.

[87] Willard, H. H., and Young, P., Indicators for determining chromium and vanadium in alloy steels: Ind. and Eng. Chemistry, Anal. Edition, vol. 5, p. 154, 1933.

[88] Lang, R., and Kurtz, F., Neue Ferrosolzmethoden zur Bestimmung von Chrom, Vanadin und Mangan, nebeneinander unter Berüchsichtigen der Analyse von Stohl: Zeitschr. anal. Chemie., Band 86, p. 288, 1931.

[89] Marvin, T., in Scott's Standard Methods of Chemical Analysis, 4th ed., D. Van Nostrand Co., Inc., 1938.

unchanged; thus drastic treatment with oxidizing acids must be employed. For this reason all the samples were subjected to the fusion treatment before being brought into solution.

The concentration procedure of Hillebrand[90] with but slight modification, method A, was applied to some of the samples. The method consisted of a carbonate-niter fusion with subsequent water leach. The vanadium in the aqueous solution was concentrated by precipitation as mercurous vanadâte. Mercury was then driven off by heat. The residue of oxides was brought into solution by water leach following a carbonate fusion. Filtration of this solution removed any traces of basic metals that may have escaped previous filtrations—arsenic and molybdenum, if present, could be precipitated as sulfides, and the resulting solution should contain only chromium and vanadium. After treatment by sulfur dioxide the vanadium was titrated with permanganate solution. Chromium interference was reduced to a minimum by titration at room temperatures. A peroxide fusion was substituted in this procedure for the carbonate-niter fusion with no appreciable change in the results. Values obtained for vanadium are given in the table below.

Determination of vanadium (percent V_2O_5) in samples from the Phosphoria formation, Sublette Ridge, Wyo.

	1	2	3	4	5	6	Aver.
Carbonate-nitrate fusion Hg^+ separation (Hillebrand method A)	0.73	0.89	--------	--------	--------	--------	--------
Peroxide fusion Hg^+ extraction (method A)	--------	.86	0.82	0.79	--------	--------	--------
Acid solution hydroxide separation (method B)	[1] 1.20 [2] .70	[1] 1.00 [2] .78	--------	--------	--------	--------	--------
Lead separation (method C)	[1] .92	[1] 1.14	--------	--------	--------	--------	--------
Gibbs' method (method D)	[1] .96 [2] .71	[1] 1.05 [2] .77	--------	--------	--------	--------	--------
Oxidative titration (method E)	.71	.85	.81	.77	0.65	0.61	0.75
Oxidative titration HCl reduction (method F)	.84 .88 .91	1.02 .95 --------	.83	.89	.85	.83	.88
Reductive titration (method G)	.72	.86	.79	.79	.67	.67	.75
Visual colorimetric (method H)	.76	.84	.85	.80	.69	.67	.77
Photoelectric colorimetric (method I)[3]	.73	.87	.81	.81	.69	.68	.77

[1] Iron present; estimated 2 to 4 milligrams Fe_2O_3.

[2] Vanadium obtained after iron removal.

[3] Percentages obtained by M. D. Foster.

1. Coal Canyon.
2. Coal Canyon.
3. Petereit Canyon.
4. Petereit Canyon.
5. Evans Canyon.
6. Evans Canyon.

Three other concentration methods were tried with unsatisfactory results. One, which might be called an acid-solution method, method B, involved the following treatment: Solution of the sample with peroxide fusion followed by acid treatment, removal of silica with hydrofluoric acid, removal of basic metals by double precipitation in concentrated sodium hydroxide solution containing hydrogen peroxide, concentration of vanadium from the filtrate by precipitation as lead vanadate, decomposition of lead vanadate with sulfuric acid, and finally reduction and titration of the liberated vanadium. Results are given in the table above. However, traces of iron which would introduce a positive error were found in the final test solution.

Another attempted method involved the use of peroxide fusion and water extraction, method C. Vanadium was precipitated by the addition of lead acetate to the filtrate neutralized with nitric acid. The lead

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[90] Hillebrand, W. F., The analysis of silicate and carbonate rocks; U. S. Geol. Survey Bull. 700, p. 185, 1919.

vanadate was treated as in the preceding method. Iron was found in the final solution.

The removal of most of the basic metals by the previously described Gibbs' method, method D, also was attempted. Traces of iron were found in the final solution although a double filtration through Whatman No. 40 paper was employed in the preliminary treatment.

The traces of iron were removed from the titrated solutions obtained by the acid-solution method and Gibbs' method by collection of iron and vanadium with zinc oxide followed by carbonate fusion. The filtrate from the water leach of this fusion was found to be iron free. Results from titration of these solutions are given in the table on page 86. The results obtained from these two methods are lower than values obtained by the other methods. A possible explanation for this fact is the loss of vanadium in the purification process attempted.

The oxidative titration method of Hamner, previously described, was employed on the suite of samples from Sublette Ridge with the results noted under method E.

The method of Campagne-Smoot involving the use of hydrochloric acid also was used on this group of samples after removal of silica with hydrofluoric acid—method F. The table shows that results by this method deviate appreciably from the grouping of the other methods. Work has been conducted in the laboratory of the Geological Survey to attempt to account for this difference. A study was made to determine the effect of polyvalent elements and of elements that might have a complexing effect on the titration of vanadium, but at the present time no experimental evidence is available to account for the discrepancies noted.

A reductive method of titration also was used to determine the vanadium content of the Phosphoria formation samples. However, instead of diphenylamine, an internal indicator suggested by Walden and his coworkers[91] was used. These workers studied the variation of electrode potentials of quadrivalent and pentavalent vanadium, the orthophenanthroline ferrous complex, and divalent and trivalent iron in solutions of varying acidities. It was shown theoretically that orthophenanthroline should be a highly satisfactory indicator for the determination of vanadium by the reductive titration of pentavalent vanadium with ferrous sulfate if the acid concentration of the solution was about five molar with respect to sulfuric acid. Experimental evidence presented seemed to indicate that very good results could be obtained using this indicator. An advantage that it possesses is the sharp color change at the endpoint. The Walden modification of the method of Lang and Kurtz was used for the determination of the vanadium in the Sublette samples. The procedure outlined below was used in making the determination.

REDUCTIVE TITRATION METHOD

Two grams of sample was fused with 8 grams of sodium peroxide in an iron crucible, which was then placed in a beaker and about 50 milliliters of water was added. After the melt had been decomposed about 15 milliliters of 5.0-molar sulfuric acid was added. The crucible was washed and removed, and any crucible scale was filtered from the solution. To the cool solution, ferrous-sulfate solution was added in slight excess—ferricyanide spot test. This insured the reduction of any chromium that might be

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[91] Walden, Jr., G. H., Hammett, L. P., and Edmonds, S. M., Phenanthroline-ferrous ion. II. Oxidation potentials at high acidities and the determination of vanadium: Am. Chem. Soc. Jour., vol. 56, p. 57, 1934.

present. Then 0.1-molar permangate solution was added until a pink color persisted for 2 minutes; 0.5-molar sodium nitrite solution was then added dropwise until the pink color disappeared; 5 grams of urea was immediately added followed by 100 milliliters of 10-molar sulfuric acid. After dilution to about 200 milliliters and cooling, one drop of 0.025 molar phenanthroline ferrous indicator oxidized to its end-point color was added and the solution titrated with about 0.02 molar ferrous sulfate. Results obtained are shown in the table—method G.

A check of the orthophenanthroline method was undertaken. Two samples were prepared in duplicate, and 5 milliliters of vanadium solution —each representing 0.05 percent V_2O_5—were added to one of each of the duplicates, and the determinations were carried out on the four samples. The results are given in the table below.

Reductive titrations using orthophenanthroline indicator

Sample No.	Percent V_2O_5
1	0.72
2	.86
1V[1]	.99
2V[2]	1.13

[1] Sample 1 plus 5 milliliters of vanadium solution.
[2] Sample 2 plus 5 milliliters of vanadium solution.

Samples 1V and 2V show the same increment in vanadium content over samples 1 and 2, namely, 0.27 percent, which is a very satisfactory agreement.

Results obtained by North in the field, using the hydroxide nitrate colorimetric method, are given in the first table under method H.

EXTRACTION METHOD OF SEPARATING VANADIUM FROM CHROMIUM

Miss M. D. Foster, of the chemical laboratory of the Geological Survey, has investigated the use of the photoelectric colorimeter for the determination of vanadium by method I and has studied the effect of all the ions that might possibly be in the final test solution. A paper giving the results of her investigations is being prepared. She also has developed a new method of separating vanadium and chromium that has proved helpful in arriving at correct results, though possibly not always required. When desired, both vanadium and chromium may be determined on the same sample. A brief description of method I as developed by Miss Foster, is here outlined.

A fusion of a 0.4-gram sample mixed with 2 grams sodium peroxide and covered with 1 gram peroxide was made in an iron crucible. The cooled melt was placed in a beaker and nearly covered with water. Two drops of ethyl alcohol were added, and the contents of the beaker were allowed to digest for one-half hour on the steam bath. The solution was filtered through No. 40 Whatman filter paper and washed five times with water. The alkaline filtrate was neutralized with 1:1 sulfuric acid and two drops excess acid added. The volume was then reduced to about 40 milliliters and the cooled solution placed in a separatory funnel. An amount of ethyl acetate ranging from 75 to 150 milliliters would be added depending upon the amount of chromium color visible in the solution; about 75 milliliters was used with the Sublette Ridge samples. To this mixture 0.5 milliliter of 3 percent hydrogen peroxide solution was added and the separatory funnel shaken. After two layers separated, the lower aqueous layer was drawn off and transferred to a second separatory funnel. Fifteen to thirty milliliters additional ethyl acetate was added to the solution which was again shaken. The aqueous layer resulting from this separation was drawn off into a beaker. The ethyl acetate solutions were combined in the first funnel and shaken with 10 milliliters wash solution from the second funnel. The water layer was added to the main vanadium solution. This aqueous solution contained the vanadium free from chromium.

Vanadium was determined by adding 5 milliliters of concentrated sulfuric acid to the water solution and adjusting the volume to 50 milliliters. This solution was placed in a photoelectric colorimeter and a reading of the transmitted light taken. A Fisher electrophotometer with a blue filter transmitting a spectral band of approximately 425 millimicrons was used. From a comparison of the reading with a calibration curve prepared from known vanadium solutions containing the same salt concentrations a value for vanadium in the sample was obtained.

The vanadium determination by the colorimetric method could be made more rapidly by omitting the chromium-removal procedure, but, according to Foster, a little accuracy would be sacrificed by this modification. If a standard curve were made with an amount of chromium equal to that present in the samples the error would be minimized. The chromium content of the Sublette Ridge samples ranged from 0.12 to 0.14 percent Cr_2O_3.

CONCLUSIONS

The agreement of the results obtained by at least three different methods and by two investigators increases the probability that the percentages obtained are correct. This is further substantiated by results obtained from adding additional vanadium to duplicate samples and obtaining the same increment of vanadium percentage.

An attempt also has been made to locate any possible source of error in other reported methods, but this has not been entirely successful.

The reductive titration method using orthophenanthroline as an internal indicator and the colorimetric method using a photoelectric colorimeter with removal or correction for chromium can be recommended for giving reproducible information quickly.

Contributions to geochemistry, 1942–45
Geological Survey Bulletin 950

DETERMINATION OF BERYLLIUM IN ORES[92]

By Rollin E. Stevens and Maxwell K. Carron

ABSTRACT

Aluminum and beryllium can be separated from each other by a sodium carbonate fusion of their phosphates and leaching with water. The separation is accurate and dependable if the beryllia residue is allowed to settle overnight.

The three methods studied for the removal of iron were the cupferron, the sodium hydroxide, and the 8-hydroxyquinoline. Of these the cupferron method is preferable, as little or no loss of beryllium occurs, and such interfering elements as titanium and zirconium are completely removed with the iron. The sodium hydroxide method gives good results if tin has been previously removed, although slight contamination of the BeO with zirconia and titania is shown spectrographically. The 8-hydroxyquinoline method seems to show small losses of beryllium. All three methods require further treatment to determine or remove residual aluminum and iron.

After the removal of iron, sodium carbonate fusion of the phosphates and water leaching eliminates aluminum as soluble sodium aluminate, beryllia remaining quantitatively in the residue. The still impure beryllia is dissolved in hydrochloric acid and precipitated with ammonia at pH 8, while residual iron is kept in solution as ferrous o-phenanthroline complex.

Results of the determinations are given both for standard solutions of the elements and for beryl-latite rock mixtures. In many of the experiments, spectrographic studies of the separated BeO were made to show the quantity and kind of contaminants wherever present.

INTRODUCTION

The need for a more dependable method for the determination of beryllium was evidenced by the experiences of members of the laboratory of the Geological Survey and by the data obtained from other reputable laboratories on low-grade ores, the beryllia content of which had been estimated spectrographically. In the accompanying table the data obtained by these laboratories are compared with those obtained spectrographically. Spectrographic results are essentially in agreement, whereas those obtained chemically differ widely. The analyses were made by modifications of the 8-hydroxyquinoline method, which has become the standard procedure in most laboratories.

The 8-hydroxyquinoline method was first proposed by Kolthoff and Sandell[93] and later studied by Knowles.[94] The results given by Kolthoff and Sandell show a maximum error of +0.0019 gram probably due to incomplete precipitation of aluminum, although the quantity of alumina taken in most of the experiments, 0.11 gram or less, was not as much as is frequently present in a gram sample of ore. They assume that a larger excess of the acetic acid solution of 8-hydroxyquinoline would remove aluminum more completely. That alumina is incompletely precipitated in the 8-hydroxyquinoline method and must be corrected for is generally recognized, as shown by details of the procedures of other laboratories made available to us.

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[92] Presented before the Division of Analytical and Micro Chemistry at the 106th Meeting of the American Chemical Society, Pittsburgh, Pa., Sept. 9, 1943.

[93] Kolthoff, I. M. and Sandell, E. B., Rapid method for the separation of aluminum and beryllium: Am. Chem. Jour., vol. 50, p. 1900, 1928.

[94] Knowles, H. B., Use of 8-hydroxyquinoline in the determination of aluminum, beryllium, and magnesium: Nat. Bur. Standards Jour. Research, vol. 15, p. 87, 1935.

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Spectrographic and chemical determinations of beryllium (percent BeO) by several laboratories

[Beryllium ores from Iron mountain, N. Mex., beryllium present as helvite. Submitted by Bureau of Mines]

	1	2	3	4	5	6	7	8[1]
Quantitative spectrographic:								
Laboratory A	0.01	0.01	0.26	0.21	1.28	0.21	0.45	0.53
Laboratory B	.01	.01	.51	.30	1.60	.23	.39	.50
Laboratory C	.02	.01	.25	.11	.97	.25	.28	.47
Chemical:								
Laboratory D	<1.00	<1.00	<1.00	<1.00	1.60	<1.00	<1.00	<1.00
Laboratory E	.66	.30	.63	.87	1.26	1.12	.81	.13
Laboratory F	.01	Tr.	.03	.33	.02	.38	.38	-------

[1] Duplicate of 7.

A complete review of the extensive literature on the determination of beryllium does not seem necessary. The earlier methods are adequately reviewed by Kolthoff and Sandell[95] and H. T. S. Britton.[96] Among the earlier methods of separating aluminum and beryllium are: (1) the sodium hydroxide method of Gmelin[97] and Schaffgotsch,[98] with later studies by others[99] [1]; (2) the sodium bicarbonate method of Parsons and Barnes[2]; (3) the carbonate fusion and water extraction of the oxides proposed by Wunder and Wenger[3]; and (4) Havens'[4] ether-hydrochloric acid method. In general, these older methods are deficient in accuracy or are too difficult and lengthy for routine purposes. Somewhat similar to the 8-hydroxyquinoline method is the method of Moser and Niessner,[5] in which aluminum alone is precipitated by a saturated solution of ammonium acetate containing 3 percent of tannin.

A good separation of beryllium from aluminum, iron, and other elements is shown by the results of Jílek and Kotă,[6] who precipitate beryllium with guanadine carbonate while keeping iron, aluminum, and the like in solution as complex tartrate ions. However, the maximum quantity of other oxides separated from the beryllia was 0.1 gram, making further study of the method advisable before applying it to ores. Similarly Miller[7] precipitated beryllium hydroxide with ammonia while keeping other elements in solution as tartrates.

Nichols and Schempf[8] made further studies of the separation of beryllium from aluminum by means of tannin. Precipitation of beryllium as

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[95] Kolthoff, I. M., and Sandell, E. B., Rapid method for the separation of aluminum and beryllium: Am. Chem. Jour., vol. 50, p. 1900, 1928.

[96] Britton, H. T. S., The separation of aluminum from beryllium: Analyst, vol. 46, pp. 359, 437, 1921; The separation of aluminum from beryllium: Analyst, vol. 47, p. 50, 1922.

[97] Gmelin, L., Neue Methode die Beryllerde von Thonerde zutrennen: Annalen der Physik (Poggendorff), Band 50, pp. 175–181, 1840.

[98] Schaffgotsch, F., Beitrage zur Kenntniss der Beryllerde: Annalen der Physik (Poggendorff), Band 50, pp. 183–188, 1840.

[99] Penfield, S. L., and Harper, D. N., Chemical composition of herderite and beryl, with a note on the precipitation of aluminum and separation of beryllium and aluminum: Am. Jour. Sci., 3d ser., vol. 32, p. 107, 1886.

[1] Zimmermann, Adolf, Zur Trennung der Thonerde und der Beryllerde: Zeitschr. anal. chemie, Band 27, p. 61, 1888.

[2] Parsons, C. L., and Barnes, S. K., Separation and estimation of beryllium: Am. Chem. Jour., vol. 28, p. 1589, 1906.

[3] Wunder, M. and Wenger, P., Über ein neues Verfahren zur Trennung von Beryllerde und Tonerde: Zeitschr. anal. chemie, Band 51, p. 470, 1912.

[4] Havens, F. S., Separation of aluminum and beryllium by the action of hydrochloric acid: Am. Jour. Sci., 4th ser., vol. 4, p. 111, 1897.

[5] Moser, Ludwig, and Niessner, Moritz, Die quantitative Trennung des Berylliums vom Aluminium: Monatsh, Chemie, Band 48, p. 113, 1927.

[6] Jílek, Ant., and Kotă, Jan, Über die gewichtsanalytische Bestimmung des Berylliums und seine Trennung von Aluminium durch Guanidincarbonat: Zeitschr. anal. Chemie, Band 87, p. 422, 1931.

[7] Miller, H. S., Determination of beryllium in the presence of complex tartrates: Ind. and Eng. Chemistry, anal. ed., vol. 9, p. 221, 1937.

[8] Nichols, M. L. and Schempf, J. M., Separation and determination of aluminum and beryllium with tannin: Ind. and Eng. Chemistry, anal. ed., vol. 11, pp. 278–80, 1939.

hydroxide while aluminum and iron are kept in solution as fluorides has been suggested by Tananaev and Talipov.[9]

Dyes that form lakes with beryllia are frequently used to measure the beryllia after it has been separated from other amphoteric oxides. Chief among these dyes are quinalizarin[10] and morin.[11]

The method here described is based upon the separation of aluminum and beryllium by sodium carbonate fusion of their phosphates and extraction with water, after most other elements have been removed by suitable methods. Sodium carbonate fusion of the oxides and leaching with water, as proposed by Wunder and Wenger,[12] requires extensive fusions and retreatments,[13] with consequent losses of beryllia. The phosphates, on the other hand, decompose readily upon fusion with sodium carbonate, and on disintegration of the product with water and standing overnight the beryllia remains quantitatively in the residue, while P_2O_5, Al_2O_3, SiO_2, and other oxides remain in solution as soluble sodium salts. This method was studied in connection with preliminary removal of iron by the cupferron,[14] sodium hydroxide, and 8-hydroxyquinoline methods. Of these, cupferron is preferred as the sodium hydroxide method is more subject to interference by other elements, and the 8-hydroxyquinoline method gives slight losses of beryllia. Other methods of removing iron, which may be found more suitable in some analyses, are ether extraction as first proposed by Rothe,[15] electrolysis with a mercury cathode according to Cain,[16] and Fairchild's[17] separation of iron as basic sulfate.

MINERALOGICAL CONTENT OF BERYLLIUM ORES

A knowledge of the mineralogical content of beryllium ores is desirable in order to know the kind and amount of other elements that need to be separated in the analysis. The common ores of beryllium are those containing beryl ($Be_3Al_2Si_6O_{18}$), found for the most part in pegmatites. As pegmatites are the loci for the accumulation of many rare elements and minerals, methods of analyzing pegmatites should provide for separation of the rare elements. Furthermore, as beryl contains nearly 20 percent of Al_2O_3, separation of at least this percentage needs to be considered in selecting a method.

Recently helvite [$(Mn,Fe,Zn)_4Be_3Si_3O_{12}S$], discovered by Strock[18] at Iron Mountain, New Mex., has become known as a potential source of beryllium. The helvite occurs in rocks containing major proportions of magnetite, garnet, and manganese minerals, together with such minor constituents as zinc, and the method selected for this ore should provide separation of large quantities of iron and moderate quantities of manga-

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[9] Tananaev, Iv. and Talipov, Sh., Use of fluorine compounds in chemical analysis: Bull. acad. sci. U.R.S.S., classe sci. math. nat., ser. chim., pp. 547–53, 1938.

[10] Fischer, Hellmut, Der Nachweis und die Bestimmung geringer Mengen Beryllium mit Hilfe von Chinalizarin: Zeitschr. anal. Chemie, Band 73, pp. 54–64, 1928.

[11] Sandell, E. B., Determination of small amounts of beryllium in silicates: Ind. and Eng. Chemistry, anal. ed., vol. 12, pp. 674–5, 1940.

[12] Wunder, M. and Wenger, P., Über ein neues Verfahren zur Trennung von Beryllerde und Tonerde: Zeitschr. anal. chemie, Band 51, p. 470, 1912.

[13] Wenger, P., and Wuhrmann, J., Separation du fer, de l'aluminium, du chrome, du glucinium, du titane et du zirconium par la methode au carbonate de sodium: Annales de chimie anal. et de chimie appl., Tome 1, pp. 337–9, 1919.

[14] Baudisch, Oskar, Quantitative Trennung mit "Cupferron": Chem.-Zeitung, Band 33, p. 1298, 1909.

[15] Rothe, J. W., Trennung des Eisens von anderen Elementen nach einem neuen Verfahren: Stahl und Eisen, Band 12, p. 1052, 1892.

[16] Cain, J. R., Determination of vanadium in vanadium and chrome-vanadium steels: Ind. and Eng. Chemistry, vol. 3, p. 476, 1911.

[17] Fairchild, J. G., Basic sulfates of iron and aluminum in analytical separations: Ind. and Eng. Chemistry, anal. ed., vol. 13, p. 83, 1941.

[18] Strock, L. W., A new helvite locality—a possible beryllium deposit: Econ. Geology, vol. 36, p. 748, 1941.

nese and zinc. The method here proposed seems to fulfill these requirements.

Other minerals containing beryllium that have as yet no importance as ores are phenakite (Be_2SiO_4), chrysoberyl ($BeAl_2O_4$), idocrase (vesuvianite), the borate hambergite, and rare silicates and phosphates.

PROCEDURE IN DETERMINATION OF BERYLLIUM

Fuse a 1-gram sample of ore, ground to pass a 200-mesh sieve, with 5 grams of sodium carbonate for half an hour in a platinum crucible. Decompose the resulting cake in an excess of dilute hydrochloric acid and evaporate to dryness. To the dry mass add 10 milliliters of concentrated hydrochloric acid and 100 milliliters of water and place on the steam bath until soluble salts are dissolved. Filter off the silica, washing with hot 1 percent hydrochloric acid, and ignite in a platinum crucible. Volatilize the silica with hydrofluoric acid and a little sulfuric acid, evaporate, and heat the resulting residue, covered, until SO_3 fumes cease. Fuse the residue with a little fused sodium bisulfate. In most samples complete decomposition is obtained, but if any residue fails to dissolve in the red-hot bisulfate, undecomposed beryl is indicated, and retreatment of the residue by fusions with sodium carbonate and bisulfate are needed. Further removal of silica is not necessary. Combine the clear water solution of the bisulfate fusion with the filtrate from the silica. The solution then contains all the beryllium in the sample with most of the silica removed.

Remove calcium, magnesium, manganese, and zinc by double precipitation of the hydroxides of Be, Al, Fe, and the like, with ammonia at pH 8—the distinct red color of phenol red. Dissolve the hydroxides in dilute hydrochloric acid and proceed to the removal of iron by one of the following methods:

Cupferron method.—As given by Hillebrand and Lundell,[19] procedure *a*, pages 110 and 111. Destroy cupferron as directed. Filter to remove any silica separated in the process.

Sodium hydroxide method.—Add to the solution, having a volume of about 200 milliliters and containing 10 milliliters concentrated hydrochloric acid, about 1 gram of ammonium phosphate, bring just to boiling, and add a 50-percent solution of sodium hydroxide until phenolphthalein turns red, or, if iron is present in large quantity, until the solution begins to turn brown from decomposition of the iron phosphate to hydroxide. Immediately add 20 milliliters of 50 percent sodium hydroxide solution and boil gently about a minute. Digest on the steam bath until the iron hydroxide is well coagulated. Filter and wash with hot 5 percent sodium hydroxide solution. Repeat. Essentially all the beryllium is in the filtrates after two precipitations of the ferric hydroxide.

8-hydroxyquinoline method.—As given by Hillebrand and Lundell,[20] procedure *a*. The excess reagent need not be destroyed. Phosphates should be absent.

After the removal of iron add to the solution about 2 grams of ammonium phosphate, if not previously added in using the sodium hydroxide method, and precipitate the phosphates of beryllium and aluminum at steam-bath temperature by adding ammonia until the yellow end point

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[19] Hillebrand, W. F., and Lundell, G. E. F., Applied inorganic analysis, pp. 110–111, New York, John Wiley and Sons, 1929.

[20] Hillebrand, W. F., and Lundell, G. E. F., op. cit., p. 116.

of methyl red pH 6.2, is reached. Digest on the steam bath until the precipitated phosphates have settled in the beaker. Filter, police the beaker with a piece of damp filter paper on the end of the finger, and wash six times with a hot solution of 1 percent NH_4Cl that contains ammonia added to the red color of phenol red. Ignite the phosphate precipitate in a platinum crucible but not necessarily to a dead white. Add to the cooled crucible 5 grams of anhydrous sodium carbonate, stir with a platinum rod until most of the phosphates have risen to the top, keeping particles away from the sides of the crucible. Cover and start the fusion with a low flame, gradually increasing the heating until effervescence begins. When the effervescence has ceased, increase the flame to its full intensity. If 8-hydroxyquinoline has been used to remove iron, fuse the phosphates for 10 minutes; for the other methods fuse 20 minutes. Care should be taken that any phosphate particles adhering to the sides of the crucible are acted upon by the hot sodium carbonate. Before cooling, swirl the melt to facilitate the leaching with water. Transfer the fusion product to a beaker containing a pulped Fisher filtration accelerator, policing the wet crucible to assure complete transfer.

Dilute to 150 milliliters and set on the steam bath until the cake disintegrates. Allow to stand overnight at room temperature. Filter through a 9-centimeter, fine filter paper (Whatman No. 42) and wash a dozen times with hot 0.5 percent sodium carbonate solution, carefully preventing creeping of the fine residue by adding wash solution below the edge of the paper only. Place the beryllia residue and filter paper in the beaker, pulp the paper in 10 milliliters of concentrated hydrochloric acid, dilute with an equal amount of water and set on the steam bath for 5 minutes. Dilute to 150 milliliters and precipitate the beryllium hydroxide at steam-bath temperature in the following way: add an excess of sulfurous acid to reduce residual iron, a few drops of phenol-red indicator solution, and ammonium hydroxide, dropwise, until the indicator changes from pink to yellow. Then add ortho-phenanthroline monohydrate in excess of the ferrous iron in the solution. The solution becomes strawberry red from the ferrous ortho-phenanthroline complex formed. Continue to add ammonium hydroxide until a drop of solution on the end of the stirring rod becomes distinctly red on addition of phenol-red indicator and the solution smells distinctly of ammonia. Digest on the steam bath until the beryllium hydroxide is thoroughly coagulated. Filter through fine paper (Whatman No. 42), again taking care to avoid creeping of beryllia residue that may have escaped decomposition by the acid. Police beaker and stirring rod with damp filter paper on the end of the finger. Wash 8 times with 1 percent NH_4Cl solution made alkaline to phenol red with ammonia. Ignite, and heat the BeO to constant weight in the blast lamp. Subtract a blank determination made on 10 grams of sodium carbonate fused in a platinum crucible and treated just for the removal of Al and residual Fe. Also subtract 0.5 percent of the weighed BeO as Al_2O_3 if iron was removed with cupferron or sodium hydroxide.

ANALYTICAL STUDIES

PREPARATION OF BERYLLIUM STANDARD

In preparing the beryllium standard solution used in the studies, Eimer and Amend C. P. beryllium nitrate was converted to sulfate and twice recrystallized. The purity of the standard was established by a spectrogram, made by K. J. Murata, of the Geological Survey, of the BeO obtained by evaporating and igniting a portion of the standard solution.

PRECIPITATION OF BERYLLIUM AS HYDROXIDE AND AS PHOSPHATE

Precipitation of beryllium hydroxide is not complete at the pH commonly used for precipitating aluminum hydroxide, pH 6.2, a further addition of ammonia being needed. Cottin[21] found the minimum pH for this precipitation to be 7.2.

The table below shows the effect of pH on the precipitation of beryllium hydroxide from hydrochloric acid solutions of the element.

Effect of pH on precipitation of beryllium hydroxide (in grams) at 90–100° C.

Experiment No.	1	2	3	4
BeO taken[1]	0.0879	0.0879	0.1544	0.1544
BeO recovered at pH 6.2	0.0710	0.0610		
Additional BeO recovered[2]	.0167	.0271		
BeO recovered at pH 8			0.1545	0.1543
Total BeO recovered	0.0877	0.0881	0.1545	0.1543

[1] Determined by direct ignition of $BeSO_4$.
[2] 1 milliliter excess NH_4OH added.

At pH 6.2 it can be noted that considerable beryllia was not recovered, requiring the addition of more ammonia to precipitate the beryllium hydroxide completely. Experiments 3 and 4 show complete recovery at pH 8.

Precipitation of beryllium phosphate, according to Čupr,[22] is complete at pH 4.2. Experiments in this laboratory showed that beryllium is quantitatively removed from solution as phosphate at pH 6.2, although a lower pH may suffice. The precipitate forms rapidly and is quickly complete even for small concentrations of beryllium.

SEPARATION OF BERYLLIUM AND ALUMINUM

The separation of beryllium and aluminum by sodium carbonate fusion of the phosphates and water extraction is essentially quantitative as shown by the results in the accompanying table.

Separation of aluminum and beryllium (in grams) by Na_2CO_3 fusion of phosphates and leaching with water

[Results corrected for blank of 0.0005 gram]

Experiment No.	5	6	7	8	9	10	11
BeO taken	None	0.0006	0.0012	0.0031	0.0093	0.0154	0.1237
Al_2O_3 taken	.1944	.1944	.1944	.1944	.1944	.1944	.1944
BeO found	None	.0008	.0012	.0030	.0092	.0155	.1244
Error	None	+.0002	None	−.0001	−.0001	+.0001	+.0007

Experiment No.	12	13	14	15	16	17
BeO taken	0.1237	0.1237	0.1237	0.1237	0.1237	0.1544
Al_2O_3 taken	.1944	.1944	.1944	.1944	.1944	None
BeO found	.1242	.1244	.1242	.1240	.1243	.1544
Error	+.0005	+.0007	+.0005	+.0003	+.0006	None

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[21] Cottin, G., Etude de L'hydrolyse des systèmes glucinium, aluminium, fer, sodium, potassium: Ing. chim., tome 23, pp. 39–61, 1939.

[22] Cupr, V., Über die Bestimmung des Berylliums als pyrophosphat und wasserfreies sulfat: Zeitschr. anal. Chemie, Band 76, pp. 173–91, 1929.

Determination of beryllium (in grams) in various solutions

[Results corrected for blank of 0.0005 gram]

Experiment No.	Iron removed by	BeO taken	Al_2O_3 taken	Fe_2O_3 taken	TiO_2 taken	SnO_2 taken	ZrO_2 taken	BeO found	Error	Spectrographic examination[1] of BeO		
										±1 mg.	0.1–0.6 mg.	<0.1 mg.
18	Cupferron, excess destroyed	None	0.1944	0.2292	0.010	0.010	0.010	None	None			
19		0.0006	.1944	.2292	.010	.010	.010	0.0003	−0.0003		Al_2O_3	Mg, Ti, Fe, Ca, Sn, Ba.
20		.0155	.1944	.2292	.010	.010	.010	.0155	None		Al_2O_3	Mg, Ti, Fe, Ca, Sn, Zr.
21		.0618	.1944	.2292	.010	.010	.010	.0619	+ .0001		Al_2O_3, Sn	Mg, Fe, Ca.
22		.1544	.1944	.2292	.010	.010	.010	.1550	+ .0006	Al_2O_3		Mg, Ti, Fe, Ca, Sn.
23	Cupferron, excess not destroyed	None	.1944	.2292	.010	.010	.010	None	None			
24		.0006	.1944	.2292	.010	.010	.010	.0003	− .0003			
25		.0155	.1944	.2292	.010	.010	.010	.0153	− .0002			
26		.0618	.1944	.2292	.010	.010	.010	.0616	− .0002		Al_2O_3	Mg, Ti, Fe, Ca.
27		.1544	.1944	.2292	.010	.010	.010	.1554	+ .0010	Al_2O_3		Mg, Ti, Fe, Ca.
28	NaOH	None	.0778	.4584	.012			None	− .0002			
29		.0006	.0778	.4584	.012			.0004	− .0002			
30		.0155	.0778	.4584	.012			.0151	− .0004			
31		.0618	.0778	.4584	.012			.0614	− .0004			
32		.1544	.0778	.4584	.012			.1544	None			
33	8-hydroxyquinoline	None	.0778	.4584	.009			None	− .0001			
34		.0006	.1944	.2292				None	− .0006			
35		.0062	.1944	.2292				.0057	− .0005			
36		.0124	.0778	.4584	.009			.0115	− .0009			
37		.0309	.0778	.4584	.009			.0305	− .0004			
38		.0618	.1944	.2292				.0616	− .0002			
39		.1237	.1944	.2292				.1231	− .0006			
40		.1544	.0778	.4584	.009			.1535	− .0009			

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[1] Determinations by K. J. Murata.

When small or moderate quantities of beryllia are taken (exper. 5 to 10, inclusive) the determinations are within the accuracy of the weighings. With larger quantities of beryllia together with much alumina (exper. 11 to 16, inclusive), retained alumina, about 0.5 percent of the BeO weighed, becomes a weighable quantity. After correcting the experiments for this retention of Al_2O_3 the maximum error in the results is 0.0003 gram (exper. 15). Experiment 17 with no alumina gave no loss of beryllia.

COMPARISON OF RESULTS FOR BeO WITH DIFFERENT METHODS OF REMOVING IRON

Results of determinations of BeO in various solutions in which the three alternate methods of removing iron were tried are shown in the table below. The results are corrected for a blank of 0.0005 gram, determined by four experiments yielding 0.0005, 0.0004, 0.0005, and 0.0005 gram. The results are not corrected for retained Al_2O_3, but if such correction is made in the experiments with cupferron the results are improved.

The results with cupferron, with excess destroyed (exper. 18 to 22, inclusive), seem to be the best although errors resulting from other methods of removing iron also are small. In experiments where the excess cupferron was not destroyed (exper. 23 to 27, inclusive) difficulty was encountered in filtering the phosphates, which were of a slimy nature. Cupferron had best be destroyed. The sodium hydroxide method (exper. 28 to 32, inclusive) seems to show a slight loss of beryllia, although the quantity of iron and alumina taken is more than is normally present in a gram of ore. The 8-hydroxyquinoline method (exper. 33 to 40, inclusive) seems to result consistently in small losses of beryllia. Knowles[23] reports complete recovery of beryllia after reprecipitation of the quinolates. Our results, however, indicate that a second precipitation would not improve the recovery of beryllia because losses of beryllia are equally large when only small quantities are taken (exper. 34, 35, and 36). Coprecipitation of beryllium phosphate with the quinolates may account for slight losses of beryllia, but the use of chemically pure reagents throughout the experiments seems to preclude any appreciable loss from this cause.

RESULTS OF TESTS ON ROCK-BERYL MIXTURES

The table below lists data obtained with mixtures of beryl and latite rock, this rock being selected because of the presence of a large number of possible interfering elements and because its mixture with beryl makes a representative ore composition. The percentage of BeO in the beryl was found to be 12.40 by five determinations using cupferron, the individual results being 12.47, 12.40, 12.32, 12.48, and 12.35 percent. The latite rock, as analyzed by R. C. Wells, contains the following percentages: SiO_2, 61.85; Al_2O_3, 16.22; Fe_2O_3, 5.07; FeO, 0.69; MgO, 1.50; CaO, 3.60; Na_2O, 3.87; K_2O, 4.14; H_2O-, 0.66; H_2O+, 0.78; TiO_2, 0.68; WO_2, 0.02; CO_2, 0.03; P_2O_5, 0.15; S, 0.21; MnO, 0.08; BaO, 0.09; SrO, 0.04; Li_2O, None; Total 99.68.

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[23] Knowles, H. B., Use of 8-hydroxyquinoline in the determination of aluminum, beryllium, and magnesium: Nat. Bur. Standards Jour. Research, vol. 15, p. 87, 1935.

Determination of BeO in beryl-latite mixtures

[Results corrected for blank of 0.0005 gram]

Experiment No.	Iron removed by	Beryl taken (gram)	Latite taken (gram)	SnO_2 taken (gram)	Zircon taken (gram)	BeO taken (percent)	BeO found (percent)	Difference	Spectrographic examination[1] of BeO		
									±1 mg.	0.1–0.6 mg.	<0.1 mg.
41	Cupferron, excess destroyed	None	1.0000	0.0100	0.0100	None	None	None	------	------	------
42		0.0100	.9900	.0100	.0100	0.12	0.13	+0.01	------	------	------
43		.0500	.9500	.0100	.0100	.61	.58	− .03	------	------	------
44		.1000	.9000	.0100	.0100	1.22	1.20	− .02	------	Al_2O_3, Sn	Mg, Ti, Fe, Ca, Zr, rare earths.
45		.5000	.5000	.0100	.0100	6.08	6.11	+ .03	------	Al_2O_3, Sn	Mg, Ti, Fe, Ca, Zr, rare earths.
46	NaOH	None	1.0000	------	------	None	.05	+ .05	------	------	------
47		.0100	.9900	------	------	.12	.19	+ .07	------	TiO_2	Al, Mg, Fe, Zr, Sn.
48		.0500	.9500	------	------	.62	.59	− .03	TiO_2	ZrO_2	Al, Mg, Fe, Ca, Sn.
49		.1000	.9000	------	------	1.24	1.25	+ .01	TiO_2	Al_2O_3, ZrO_2	Mg, Fe, Ca, Sn.
50		.5000	.5000	------	------	6.20	6.32	+ .11	Al_2O_3	Sn	Mg, Ti, Fe, Ca, Zr.
51	8-hydroxyquinoline	None	1.0000	------	------	None	.01	+ .01	------	------	------
52		.0100	.9900	------	------	.12	.03	− .09	------	------	------
53		.0500	.9500	------	------	.62	.54	− .08	------	TiO_2, Sn	Al, Mg, Fe, Ca, Zr, rare earths.
54		.1000	.9000	------	------	1.24	1.13	− .11	------	TiO_2	Al, Mg, Fe, Ca, Zr, Sn, rare earths.

[1] Determinations by K. J. Murata.

The results using cupferron are essentially quantitative whereas those with sodium hydroxide indicate slight retention of other elements. If the sodium hydroxide procedure is used, most of the tin in the sample probably will be weighed as BeO.

Again, as in the experiments with standard solutions, the results using 8-hydroxyquinoline show small losses of beryllia even when small quantities are present, indicating that reprecipitation of the quinolates would not be beneficial. The results also would be improved by correction for included Al_2O_3, where such correction is justified.

SPECTROGRAPHIC EXAMINATION OF SEPARATED BERYLLIA

In many of the experiments represented in the tables on pages 97 and 99, estimates of the quantities of elements included in the separated BeO were made spectrographically by K. J. Murata. This spectrographic examination was very useful in choosing the best of the three methods of removing iron, in confirming the extent of correction for alumina in the BeO, and in showing that the figures obtained were essentially free from compensating errors. In examining the spectrographic results, a few tenths of a milligram of Al_2O_3 should be subtracted, as it is included in the blank of 0.0005 gram, which consisted largely of silica and alumina with a little soda. The elements listed as being less than 0.1 milligram are present in unweighable quantity and are to some extent accounted for in the blank. Rare earths seem to be completely removed by sodium hydroxide and not by cupferron or 8-hydroxyquinoline.

It will be noted in the experiments on beryl-latite rock mixtures that the sodium hydroxide failed to remove titania and zirconia completely, and this method also would be subject to even greater error in the presence of appreciable tin. In the spectrographic data tin seems to be somewhat erratic, appearing in barely weighable quantities in the determinations with cupferron and 8-hydroxyquinoline but to a lesser extent with sodium hydroxide.

The accompanying plate (pl. 2) is a part of a spectrographic series including the iron spectrum, the beryllium spectrum, that of BeO containing 0.1 percent Al_2O_3, that of BeO containing 1 percent Al_2O_3, and spectra of the BeO from experiments 45, 44, 43, and 42, using cupferron. It shows that the included Al_2O_3 is consistently about 1 percent of the BeO. This is accounted for by the alumina retention shown by experiments 11 to 16, inclusive, together with the alumina in the blank.

A further test of the method as applied to low-grade beryl ores was obtained from the chemical and spectrographic data shown in the table below, indicating satisfactory agreement.

Chemical and spectrographic determinations of beryllium in low-grade ores.

Sample No.	Percent BeO (chemical)	Percent BeO (spectrographic)[1]
1	0.03	0.03
2	.07	.03
3	.04	.03
4	.03	.08
5	.10	.08
6	.04	.04
7	.10	.07
8	.04	.06
9	.07	.06
10	.11	.09
11	.09	.08
12	.03	.05

[1] Determinations by K. J. Murata

Contributions to geochemistry, 1942–45
Geological Survey Bulletin 950

A SYSTEM FOR CALCULATING ANALYSES OF MICAS AND RELATED MINERALS TO END MEMBERS

By Rollin E. Stevens

ABSTRACT

A table is given by which the formulas of all end members of alkali micas, alkaline-earth micas, hydromicas, vermiculites, talcs and pyrophyllites, chloritoids, kaolinites, chlorites, and serpentines may easily be derived according to present knowledge of the atomic structures of these minerals. Use of the table is illustrated by derivation of end-member formulas of potassium fluormicas and hydroxymicas. A method of calculating analyses of minerals having the mica type of structure to percentages of end members also is described, with examples of such calculations for alurgite, lepidolite, margarite, xanthophyllite, seybertite, and biotite.

INTRODUCTION

The pioneering work of investigators, such as Mauguin,[24] Pauling,[25] Hendricks[26] and others, has well explained the arrangement of atoms in micas, and the structural relationships found have led to definite requirements in chemical composition. The limits of composition thus established by X-ray and chemical studies now make possible a systematic treatment of the formulas of micas. Complex compositions can be given in percentages of relatively simple end-member formulas, and all such simple formulas that satisfy the chemical and structural requirements of a mica can now be devised. Some of these end-member formulas express compositions of known micas, others may be considered as referring to micas existing only in solid solution with other micas, and many of the formulas express compositions not yet found, many of which may remain hypothetical.

With such a set of end-member formulas a chemical analysis of a mica may easily be calculated to percentages of the end members. These percentages may be found useful in correlating optical and physical properties. The system of end members also may serve as a basis for classifying members of the mica group.

The system of end members here presented for micas was planned to include all possible compositions and to show relationships in other structurally related groups. A system of nomenclature for the end members is given by which each is named according to its composition. A simple method of calculating a chemical analysis to end members is described and illustrated by examples.

The present study was made in preparation for proposed work with W. T. Schaller, Michael Fleischer, and J. J. Fahey in which all analyses of micas in the literature are to be calculated to atomic ratios. It is hoped that the system of end members will find useful application in that

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[24] Mauguin, Charles, Study of the micas (not containing fluorine) by means of X-rays: Compt. Rend., Tome 186, pp. 879–881, 1928.

[25] Pauling, Linus, Structure of micas and related minerals: Nat. Acad. Sci. Proc., vol. 16, pp. 123–129, 1930.

[26] Hendricks, S. B., Polymorphism of the micas: Am. Mineralogist, vol. 24, pp. 729–771, 1939.

study. Discussion with R. C. Wells and W. T. Schaller led to many improvements and expansions of the general concepts involved in the study.

IONIC GROUPS IN THE STRUCTURE OF MICAS

The mica structure is composed of sheets of ionic thickness and of indefinite extent. In the silicon-aluminum sheets the cations are arranged in a pattern of hexagons in which each aluminum or silicon ion is in tetrahedral coordination, i. e., surrounded by four oxygen atoms. These silicon-aluminum sheets are held together alternately by sheets of large cations and by sheets of cations in octahedral coordination, i. e., cations surrounded by six anions. The large cation is usually potassium, but it may be sodium, calcium, barium, rubidium, or cesium. The large cation is in twelvefold coordination and the basal cleavage of micas occurs along the large-cation layer. Cations occurring in octahedral coordination may include Al, Fe^{++}, Fe^{+++}, Mg, Mn, Zn, Li, Sn, Cr, Cb, V, Zr, and Ti.

The position that each cation takes in the structure is due to its size and not to its valence and chemical characteristics. Larger metal ions are surrounded by more anions; thus aluminum and silicon with ionic radii of less than 0.6 angstrom unit are in tetrahedral coordination, ions up to 0.9 angstrom unit in radius are in octahedral coordination, and the larger ions in the mica structure, those from about 1.0 to 1.65 angstrom units, are in twelvefold coordination.

The unit cell of a mineral is the smallest possible unit of structure that repeats indefinitely in all directions. As shown by Hendricks,[27] the unit cells of micas may range in size from a cell containing only 1 layer of ions in octahedral coordination to an arrangement requiring 24 such layers to a unit cell, and the arrangement of layers causes the micas to conform to different crystal systems.

The formulation of micas is simplified, however, by viewing the unit cell as composed of simpler structural units, at least as far as composition is concerned. Thus the chemical formula of biotite may be written $K.(Mg,Fe^{++})_3.AlSi_3O_{10}(OH,F)_2$, although the unit cell of biotite may contain two to six such units.

Other examples of similar formulas are those of muscovite, $K.Al_2.AlSi_3O_{10}(OH)_2$; polylithionite, $K.Li_2Al.Si_4O_{10}F_2$; and margarite, $Ca.Al_2.Al_2Si_2O_{10}(OH)_2$. As usually written, the large cation is given first, then the ions in octahedral coordination, next the ions in tetrahedral coordination, and finally the oxygen, fluorine, and hydroxyl groups. The division into the respective groups examined here is indicated by the periods in the formulas. In this paper the groups may be termed for convenience the large cation group, the octahedral group, the tetrahedral group and the hydroxyl, fluorine, or oxygen group. The octahedral group may vary from two to three ions, but the tetrahedral group always contains four ions.

DIOCTAHEDRAL AND TRIOCTAHEDRAL FORMULAS

Winchell[28] classifies micas into two types: Heptaphyllite micas containing 7 positive to 12 negative ions, and octophyllite micas having 8 positive to 12 negative ones. This classification is expressed in the general formula of micas, $X.Y_{2-3}.Z_4O_{10}(OH,F)_2$, in which $Y = 2$ for the heptaphyllite micas and $Y = 3$ for the octaphyllite micas; that is, for the heptaphyllite micas there is one vacant position in octahedral coordination.

A classification that seems to be of more general application is to

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[27] Hendricks, S. B., Polymorphism of the micas: Am. Mineralogist, vol. 24, pp. 729–771, 1939.

[28] Winchell, A. N., Studies of the mica group (abstract): Am. Mineralogist, vol. 10, p. 53, 1925.

designate formulas as dioctahedral or trioctahedral; this classification will be adopted in the present study. Thus, the formulas of biotite ($K.R^{++}_3.AlSi_3O_{10}(OH)_2$) and of talc ($Mg_3.Si_4O_{10}(OH)_2$) are trioctahedral, whereas those of muscovite ($K.Al_2.AlSi_3O_{10}(OH)_2$) and pyrophyllite ($Al_2.Si_4O_{10}(OH)_2$) are dioctahedral, having one vacant octahedral position in the formula. In Winchell's system biotite is an octaphyllite, talc a heptaphyllite, although all three octahedral positions are filled. Accordingly, pyrophyllite would be a hexaphyllite. Classification of the formulas as dioctahedral and trioctahedral seems simpler and of more general application..

STRUCTURAL SIGNIFICANCE OF END-MEMBER PERCENTAGES

An expression of an analysis as percentages of end-member formulas means that the various end-member compositions either may be present as discrete particles in an impure sample or they may form a solid solution in a pure mineral. The purity of the sample must be considered and this has been done in most mineral analyses, so that the end-member compositions may be thought to be in solid solution. In a solid solution the end members lose their identity as separate minerals, their ions being in random arrangement in the structure in positions with proper coordination for the ion considered.

FORMULATION OF END-MEMBER MICAS

END-MEMBER REQUIREMENTS

The two requirements that should be satisfied in an end-member formula are: (1) The formula represents the maximum substitution of one element for another—maximum tenor of one element in the combination; and (2) as a consequence of requirement 1, the end-member formula cannot be expressed as a combination of two or more simpler formulas. These requirements have been adopted for the present compilation.

End-member formulas expressing the compositions of lepidolites have been given by the writer.[29] The end members suggested meet the above requirements for end-member formulas and are: muscovite ($K.Al_2.AlSi_3O_{10}(OH)_2$), polylithionite ($K.Li_2Al.Si_4O_{10}F_2$), lithium muscovite ($K_2.Li_3Al_3.Al_2Si_6O_{20}F_4$),[30] and biotite ($K.R^{++}_3.AlSi_3O_{10}F_2$). Winchell[31] accepts the first three of these end members, although he believes muscovite to be present as submicroscopic intergrowth and not in solid solution. In place of biotite Winchell suggests the formula $K_2.LiFe^{++}_4Al.Al_2Si_6O_{20}F_4$, which he calls protolithionite. Winchell's protolithionite, however, does not satisfy the above requirements for an end member, as it does not express a maximum tenor for any element in the octahedral group and its composition can be expressed as a combination of one lithium muscovite ($K_2.Li_3Al_3.Al_2Si_6O_{20}F_4$) and four biotite ($K.R^{++}_3.AlSi_3O_{10}F_2$).

EQUIVALENTS IN THE IONIC GROUPS

In the table below are given all possible groups or combination of ions that may make up end-member formulas of micas, considering most

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[29] Stevens, R. E., New analyses of lepidolites and their interpretation: Am. Mineralogist, vol. 23, p. 607–628, 1938.

[30] Holzner uses this formula to express the ideal composition of lepidolite. See Holzner, Julius, Über den "anomalen" Kristallbau der Biotite: Zeitschr. Krist., Band 95, p. 440, 1936.

[31] Winchell, A. N., Further studies of the lepidolite system: Am. Mineralogist, vol. 27, pp. 114–130, 1942.

Ionic groups in the end-member formulas of micas and related minerals

Cations								Anions	Equivalents
Large cation	Equivalents	In octahedral coordination				In tetrahedral coordination	Equivalents		
		Dioctahedral	Intermediate	Trioctahedral	Equivalents				
Micas:		$R^{++}_{2}, LiR^{+++}, \frac{1}{3}(Li_4Ti_2)$		$Li_2R^{++}, \frac{1}{2}(Li_5R^{+++}), \frac{1}{3}(Li_8Ti)$	4	Tetrasilicic (Si_4)	16	Fluormicas or hyroxy-micas: $O_{10}(F,OH)_2$	22
Alkali (K, Na, Rb, Cs)	1	$R^{++}R^{+++}, \frac{1}{2}(R^{++}_{3}Ti), \frac{1}{2}(LiR^{+++}_{3}), LiTi$	$\frac{1}{2}R^{++}_{5}$	$LiR^{++}_{2}, Li_2R^{+++}, \frac{1}{3}(Li_7Ti_2)$	5				
Alkaline earth (Ca, Ba)	2	$R^{+++}_{2}, R^{++}Ti, \frac{1}{3}(Li_2Ti_4)$		$R^{++}_{3}, \frac{1}{2}(Li_3R^{+++}_{3}), Li_2Ti$	6	Trisilicic ($AlSi_3$)	15	Oxymicas: O_{12}	24
Hydromicas: $2H_2O+R^{+}_{0.5}$	.5	$R^{++}Ti, \frac{1}{3}(LiTi_5), \frac{1}{2}(R^{++}Ti_3)$	$\frac{1}{3}R^{+++}_{7}$	$LiR^{+++}_{2}, R^{++}_{2}R^{+++}, \frac{1}{3}(Li_5Ti_4), \frac{1}{2}(R^{++}_{5}Ti)$	7	Disilicic (Al_2Si_2)	14	Chloritoids: $O_{10}(OH)_4$	24
Vermiculites: $4H_2O$	0	Ti_2	$\frac{1}{3}R^{+++}_{8}$	$\frac{1}{3}(Li_4Ti_5), R^{++}_{2}Ti, \frac{1}{2}(LiR^{+++}_{5}), R^{++}R^{+++}_{2}$	8	Monosilicic (Al_3Si)	13		
Talc-pyrophyllite: None	0		$\frac{1}{4}Ti_9$	$R^{+++}_{3}, LiTi_2, \frac{1}{2}(R^{++}_{3}Ti_3)$	9				
Chloritoids, kaolinites, chlorites, and serpentine (?):			$\frac{1}{2}Ti_5$	$\frac{1}{3}(Li_2Ti_7), R^{++}Ti_2, R^{+++}_{2}Ti$	10	Silicon-free (Al_4)	12	Kaolinites, chlorites, and serpentine (?):	
Octahedral repeat in large-cation position →			$\frac{1}{4}Ti_{11}$	$\frac{1}{3}(LiTi_8), \frac{1}{2}(R^{++}Ti_5), R^{+++}Ti_2$	11			$O_{10}(OH)_8$	28
				Ti_3	12				

isomorphous replacements that may take place. The total equivalents for each element or combination of elements in a group follow at the right, an equivalent being that quantity of an ion carrying a valence charge of one. The alkali ion, for example, in the large-cation position is univalent and represents one equivalent. Calcium, on the other hand, is bivalent and a calcium ion would represent two equivalents.

Among groups of ions in octahedral coordination shown in the table all the usual elements found in this group in micas are considered, although pentavalent columbium found in small quantity in polylithionite by the writer[32] is not considered in this paper. Tetravalent zirconium and tin may be substituted for titanium. The bivalent ions, Mg, Fe^{++}, Mn, Zn, are represented by R^{++} and the trivalent ions, Al, Fe^{+++}, V, Cr, by R^{+++}. In micas with a large cation the equivalents for the octahedral groups vary from 4 as in the hypothetical calcium mica $Ca.Mg_2.Si_4O_{10}(OH)_2$ to 11 as in the hypothetical silicon-free oxymica $K.AlTi_2.Al_4O_{12}$. Six-coordinated Ti_3 can be reached only in the absence of a large cation as in the oxytalc type of formula, $Ti_3.Al_4O_{12}$.

As an example of the method of deriving the end-member octahedral groups the series having six octahedral equivalents, as in muscovite, may be considered. The six equivalents could be represented by two trivalent ions R^{+++}_2, making a dioctahedral mica. These trivalent ions may be partly replaced by lithium to make the trioctahedral group $\frac{1}{2}(Li_3R^{+++}_3)$, or completely replaced by bivalent ions to form R^{++}_3. No substitution of R^{+++}_2 by titanium alone is shown because this substitution could not take place without reducing the filled octahedral positions to less than two out of a possible three, which never occurs, so far as is known. Bivalent ions in the trioctahedral group R^{++}_3 may be replaced by trivalent ions to form dioctahedral R^{+++}_2 or by titanium to form dioctahedral $R^{++}Ti$. In addition, lithium and titanium can combine in the dioctahedral $\frac{1}{3}(Li_2Ti_4)$ and in the trioctahedral Li_2Ti groups. These, then, are all the combinations of two elements in six-equivalent octahedral groups, and it completes the formulation of that series, as all three- or four-element octahedral groups can be resolved into various proportions of these one- and two-element groups.

The tetrahedral groups actually range from a group consisting entirely of silicon ions, Si_4, to a group consisting of one atom of silicon to three atoms of aluminum, Al_3Si; theoretically a silicon-free group, Al_4, may be postulated. The replacement of silicon by aluminum may be considered to take place atom by atom and the groups designated as tetrasilicic, Si_4; trisilicic, $AlSi_3$; disilicic, Al_2Si_2; monosilicic, Al_3Si; and silicon-free, Al_4.

The anions in micas are commonly $O_{10}(F,OH)_2$ and, as oxygen is bivalent and fluorine and hydroxyl univalent, 22 anion equivalents are thus represented. Many analyses of micas show an excess of combined water for $(OH)_2$, but this seems to be due to incomplete removal of uncombined water at 110° C. A few analyses show insufficient water plus fluorine to constitute $(F,OH)_2$ in the formula, and this may be due either to analytical error or to substitution of oxygen for hydroxyl or fluorine to make O_{12} in the formula.

END-MEMBER FORMULAS FOR POTASSIUM HYDROXYMICAS OR FLUORMICAS

The derivation of end-member formulas from the data in the table

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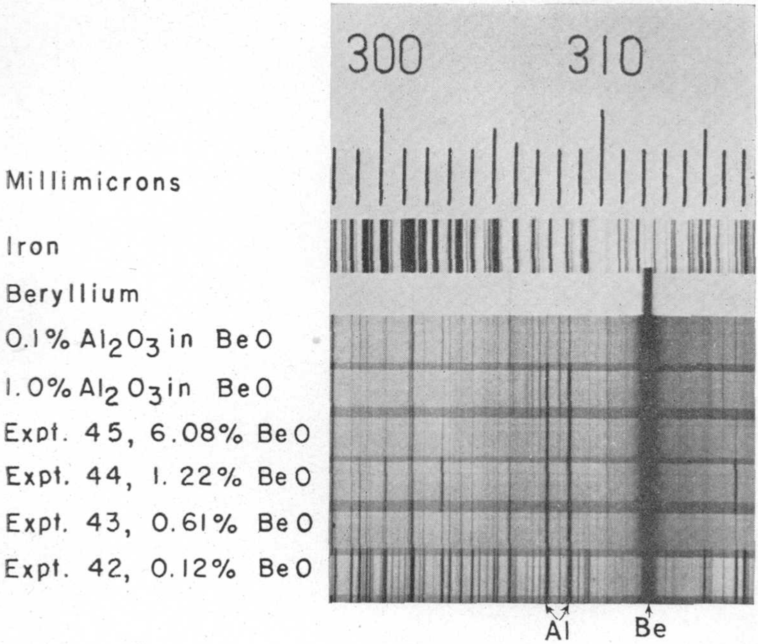
[32] Stevens, R. E., New analyses of lepidolite and their interpretation: Am. Mineralogist, vol. 23, pp. 607–628, 1938.

is a routine matter and will be illustrated only by the derivation of formulas of the potassium hydroxymica or fluormica end members. Other series may be derived quickly from the table. The hydroxymicas or fluormicas all contain 22 anion equivalents which are balanced by 22 cation equivalents. For the tetrasilicic (Si_4) series 16 equivalents are silicon and 1 equivalent is alkali ion, leaving 5 equivalents for the group of ions in octahedral coordination. The groups of ions in octahedral coordination constituting 5 equivalents, are then taken from the table to make the 8 end members in the series. The trisilicic, disilicic, monosilicic, and silicon-free series are similarly derived.

The potassium hydroxymica or fluormica end members are given in the table below. A system of nomenclature for the formulas is used that is descriptive of the compositions. In the naming of the formulas the large cation is given first; the group of ions in octahedral coordination follows, specified as dioctahedral or trioctahedral with its composition; then the tetrahedral group; finally the formula is specified as that of a fluormica, hydroxymica or oxymica. The words dioctahedral or trioctahedral are omitted when an intermediate composition is specified. Other formulas based on the first table may be similarly named. This system of nomenclature makes possible the writing of a formula when the name alone is given.

Alkali hydroxymica or fluormica end members

Tetrasilicic series:		
1.	$K.MgAl.Si_4O_{10}(OH)_2$	Potassium dioctahedral magnesium-aluminum tetrasilicic hydroxymica (alurgite).
2.	$K_2.Mg_3Ti.Si_8O_{20}F_4$	Potassium dioctahedral magnesium-titanium tetrasilicic fluormica.
3.	$K_2.LiAl_3.Si_8O_{20}F_4$	Potassium dioctahedral lithium-aluminum tetrasilicic fluormica.
4.	$K.LiTi.Si_4O_{10}F_2$	Potassium dioctahedral lithium-titanium tetrasilicic fluormica.
5.	$K_2.Mg_5.Si_8O_{20}F_4$	Potassium magnesium tetrasilicic fluormica.
6.	$K.LiMg_2.Si_4O_{10}F_2$	Potassium trioctahedral lithium-magnesium tetrasilicic fluormica (taeniolite).
7.	$K.Li_2Al.Si_4O_{10}F_2$	Potassium trioctahedral lithium-aluminum tetrasilicic fluormica (polylithionite).
8.	$K_3.Li_7Ti_2.Si_{12}O_{30}F_6$	Potassium trioctahedral lithium-titanium tetrasilicic fluormica.
Trisilicic series:		
9.	$K.Al_2.AlSi_3O_{10}(OH)_2$	Potassium dioctahedral aluminum trisilicic hydroxymica (muscovite).
10.	$K.MgTi.AlSi_3O_{10}(OH)_2$	Potassium dioctahedral magnesium-titanium trisilicic hydroxymica.
11.	$K_3.Li_2Ti_4.Al_3Si_9O_{30}(OH)_6$	Potassium dioctahedral lithium-titanium trisilicic hydroxymica.
12.	$K.Mg_3.AlSi_3O_{10}(OH)_2$	Potassium trioctahedral magnesium trisilicic hydroxymica (phlogopite).
13.	$K_2.Li_3Al_3.Al_2Si_6O_{20}F_4$	Potassium trioctahedral lithium-aluminum trisilicic fluormica (lithium muscovite).
14.	$K.Li_2Ti.AlSi_3O_{10}(OH)_2$	Potassium trioctahedral lithium-titanium trisilicic hydroxymica.
Disilicic series:		
15.	$K.AlTi.Al_2Si_2O_{10}(OH)_2$	Potassium dioctahedral aluminum-titanium disilicic hydroxymica.
16.	$K_3.LiTi_5.Al_6Si_6O_{30}(OH)_6$	Potassium dioctahedral lithium-titanium disilicic hydroxymica.
17.	$K_2.MgTi_3.Al_4Si_4O_{20}(OH)_4$	Potassium dioctahedral magnesium-titanium disilicic hydroxymica.
18.	$K_3.Al_7.Al_6Si_6O_{30}(OH)_6$	Potassium aluminum disilicic hydroxymica



CONSTANCY IN PERCENTAGE OF ALUMINA CONTAMINATION IN SEPARATED BeO.

19. $K.LiAl_2.Al_2Si_2O_{10}(OH)_2$ ......Potassium trioctahedral lithium-aluminum disilicic hydroxymica.
20. $K.Mg_2Al.Al_2Si_2O_{10}(OH)_2$ .....Potassium trioctahedral magnesium-aluminum disilicic hydroxymica.
21. $K_3.Li_5Ti_4.Al_6Si_6O_{30}(OH)_6$ .....Potassium trioctahedral lithium-titanium disilicic hydroxymica.
22. $K_2.Mg_5Ti.Al_4Si_4O_{20}(OH)_4$ ....Potassium trioctahedral magnesium-titanium disilicic hydroxymica.

Monosilicic series:

23. $K.Ti_2.Al_3SiO_{10}(OH)_2$ ....Potassium dioctahedral titanium monosilicic hydroxymica.
24. $K_3.Al_8.Al_9Si_3O_{30}(OH)_6$ ....Potassium aluminum monosilicic hydroxymica.
25. $K_3.Li_4Ti_5.Al_9Si_3O_{30}(OH)_6$ .....Potassium trioctahedral lithium-titanium monosilicic hydroxymica.
26. $K.Mg_2Ti.Al_3SiO_{10}(OH)_2$ ......Potassium trioctahedral magnesium-titanium monosilicic hydroxymica.
27. $K_2.LiAl_5.Al_6Si_2O_{20}(OH)_4$ .....Potassium trioctahedral lithium-aluminum monosilicic hydroxymica.
28. $K.MgAl_2.Al_3SiO_{10}(OH)_2$ ......Potassium trioctahedral magnesium-aluminum monosilicic hydroxymica.

Silicon-free series:

29. $K_4.Ti_9.Al_{16}O_{40}(OH)_8$ ....Potassium titanium silicon-free hydroxymica.
30. $K.Al_3.Al_4O_{10}(OH)_2$ ....Potassium trioctahedral aluminum silicon-free hydroxymica.
31. $K.LiTi_2.Al_4O_{10}(OH)_2$ ....Potassium trioctahedral lithium-titanium silicon-free hydroxymica.
32. $K_2.Mg_3Ti_3.Al_8O_{20}(OH)_4$ ......Potassium trioctahedral magnesium-titanium silicon-free hydroxymica.

FORMULATION OF END MEMBERS OF MINERALS RELATED STRUCTURALLY TO MICAS

Other minerals represented in the first table are the alkaline earth micas—margarite and xanthophyllite—hydromicas, vermiculites, talc, pyrophyllite, chloritoids, kaolinites, chlorites, and serpentine. Their end-member formulas may be written from the table simply by selecting the proper cation groups to make cation equivalents equal anion equivalents. They differ in composition from the alkali micas in several ways.

The alkaline earth micas[33] have micalike structures generally containing calcium as the large cation; they are formulated like the alkali micas but have two equivalents to the large cation.

In the talc-pyrophyllite structure[34] the large-cation position is vacant, and in the vermiculites[35] that position in the formula is taken by four molecules of water. These minerals are formulated like the other micas, but no equivalents are assigned to the large-cation position in the formula.

Hydromicas, according to Gruner, are composed of interstratified mica layers and vermiculite layers. Their end members may be formulated by taking equal quantities of mica and of vermiculite end members.

Formulas corresponding in type to chloritoid,[36] chlorites,[37] kaolinite,[38] and serpentine are similarly formulated, but an additional group of ions in octahedral coordination is used in place of the large cation, thus increasing the cation and anion requirements. The structure of serpentine is still in question, but its composition seems to fit the formulation of kaolinite and the chlorites. The formula of serpentine may be interpreted as being that of kaolinite with 6 Mg in place of 4 Al.

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[33] Pauling, Linus, Structure of micas and related minerals: Nat. Acad. Sci. Proc., vol. 16, pp. 123–129, 1930.

[34] Gruner, J. W., The crystal structure of talc and pyrophyllite: Zeitschr. Kristallographie, Band 89, pp. 412–419, 1934.

[35] Gruner, J. W., The structures of vermiculites and their collapse by dehydration: Am. Mineralogist, vol. 19, pp. 557–575, 1934.

[36] Machatschki, F., and Mussgnug, F., Crystal structure of chloritoid: Naturwissenschaften, Band 30, p. 106, 1942; Mineral. Abstracts, vol. 8, p. 291, 1942.

[37] Pauling, Linus, The structure of the chlorites: Nat. Acad. Sci. Proc., vol. 16, pp. 578–582, 1930.

[38] Idem.

The inclusion of talc, pyrophyllite, serpentine, and kaolinite in the first table seems to imply variations that have not been and may not be found. The compositions of the minerals that have been studied closely approximate $Mg_3.Si_4O_{10}(OH)_2$ for talc, $Al_2.Si_4O_{10}(OH)_2$ for pyrophyllite, $Mg_6.Si_4O_{10}(OH)_8$ for serpentine, and $Al_4.Si_4O_{10}(OH)_8$ for kaolinite.

Glauconite and celadonite[39] may be formulated in the same way as the micas, but a component in which the large-cation position is vacant—talc or pyrophyllite—must be added to account for the deficiency of alkalies.

The montmorillonite clays[40] are also related structurally to the minerals considered above, but their formulation is not included for practical reasons. They may be considered solid solutions of a component with a mica formula and a vermiculitelike component having a variable water content. This last component would remain hypothetical with undeterminable physical properties; thus, formulation of montmorillonites in terms of end members in this way would only be an expression of composition and would seem to serve no useful purpose.

PRACTICAL CONSIDERATIONS

End members are represented in the first table as composed of a few simple ionic groups, and 32 potassium hydroxymicas or fluormicas are formulated in the second table. However, when all substituting ions are expressed in end members, for example, considering each element represented by R^{+++} and by R^{++}, the number of end members becomes very large. The number of end members for the potassium hydroxymicas alone is 115, and for all fluormicas or hydroxymicas there are 920 end members, not including micas containing Zr, Zn, Sn, Cb.

Some of the compounds represented by formulas may be impossible because of the structural limitations of isomorphism, and others may require unusual conditions for their formation. The end-member formulas represented in micas formed under the geochemical environments usually existing would probably be far less than the number of possible formulas.

Under a usual geochemical environment the maximum tenor of one element replacing another may not be attainable, and it may be found practical to correlate properties with formulas representing only partial substitution.

In formulating an analysis of a mica to end members a choice may usually be made between several groups of end members that express the composition; for example, lepidolites have been expressed as solid solutions of muscovite, biotite, lithium muscovite, and polylithionite. In place of biotite to express the bivalent ion content, taeniolite ($K.LiR^{++}_2.Si_4O_{10}F_2$) or alurgite ($K.R^{++}Al.Si_4O_{10}F_2$) may be substituted. The end members may be chosen in such a way as to agree with mineralogical series.

CALCULATION OF SOME ANALYSES OF MICAS TO END MEMBERS

METHOD OF CALCULATION

The number of anions in the formula of a mica may be considered to be 12, usually $O_{10}+(OH,F)_2$. The number of cations, however, may

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[39] Hendricks, S. B., and Ross, C. S., Chemical composition and genesis of glauconite and celadonite: Am. Mineralogist, vol. 26, pp. 683–708, 1941.

[40] Ross, C. S., and Hendricks, S. B., Clay minerals of the montmorillonite group: their mineral and chemical relationships and the factors controlling base exchange: Soil Sci. Soc. of America Proc., vol. 6, pp. 58–62, 1941.

range from 7 in a dioctahedral mica to 8 in a trioctahedral mica and is 6 in pyrophyllite; but, as the cation chemical equivalents, the hydrogen equivalents, must balance the anion equivalents, it seems best first to calculate the analytical percentages to equivalents, then to adjust the cation equivalents to equal the total number of anion equivalents in the formula, and finally to convert the equivalents thus found to numbers of atoms in the formula by dividing by the respective valences. Below is given a compilation of equivalent weights used in the calculations.

Equivalent weights of constituents of micas arranged alphabetically

[Based on international atomic weights, 1941–42]

Aluminum oxide, Al_2O_3	16.99
Barium oxide, BaO	76.99
Calcium oxide, CaO	28.04
Cesium oxide, Cs_2O	140.86
Chlorine, Cl	35.46
Chromic oxide, Cr_2O_3	25.34
Columbium oxide, Cb_2O_5	26.58
Ferric oxide, Fe_2O_3	26.62
Ferrous oxide, FeO	35.93
Fluorine, F	19.00
Lithium oxide, Li_2O	14.94
Magnesium oxide, MgO	20.16
Manganic oxide, Mn_2O_3	26.31
Manganous oxide, MnO	35.47
Potassium oxide, K_2O	47.10
Rubidium oxide, Rb_2O	93.48
Silicon oxide, SiO_2	15.01
Sodium oxide, Na_2O	31.00
Titanium oxide, TiO_2	19.98
Vanadium oxide, V_2O_3	24.98
Water, H_2O	9.01
Zinc oxide, ZnO	40.69
Zirconium oxide, ZrO_2	30.80

Each constituent in the analysis is first divided by its equivalent weight to find the equivalents, column e, in the examples below. The hydroxymicas or fluormicas contain 22 anion equivalents, $O_{10}+(OH,F)_2$, and the same number of cation equivalents. To make the total of the cation equivalents equal 22 it is necessary to multiply the values in column e by a factor f—where $f=\frac{22}{\Sigma e_m}$—in which Σe_m is the sum of the metal-cation equivalents derived from the analytical percentages (omitting H_2O and F). The figures thus obtained are shown under e′. The atoms per formula are finally obtained by simply dividing the equivalents per formula, e′, by the valences of the respective elements.

In solid solutions of oxymicas with hydroxymicas or fluormicas, if the equivalents of OH and F are added to the sum of the cation equivalents ($\Sigma e'_m$), the sum is 24 equivalents; this may be used as a basis for calculating the atomic ratios. Then $f=\frac{24}{\Sigma e}$, where Σe is the sum of equivalents of cations plus OH and F. This method of calculating atomic ratios is not recommended where there is sufficient OH and F to correspond to $(OH,F)_2$, because in many analyses uncombined water has not been determined and not all uncombined water is necessarily lost at 110° C.; thus, the apparent figure for (OH,F) may exceed 2. Only when there is insufficient hydroxyl and fluorine to make $(OH,F)_2$ must the figure for combined water be assumed correct and $\Sigma e'$ taken to be 24; but then the accuracy of the figures for H_2O and F are questionable.

Sufficient aluminum atoms are then assigned to the tetrahedral group to make the total of silicon and aluminum atoms in that group 4.00, and the remainder of the aluminum is assigned to the octahedral group. In a good analysis of an alkali or alkaline-earth mica the sum of octahedral atoms should not be less than 2 or more than 3, and the sum of the large cations should approximate 1. Usually the OH+F totals a little over 2 because of failure to remove all uncombined water at 110° C., but if oxygen replaces fluorine or hydroxyl OH+F will be less than 2. The sum of the large cation group may be less than 1 if alkali-free mica-type structures, like talc, are present.

The percentages of monosilicates, disilicates, trisilicates, and tetrasilicates are then calculated from the number of aluminum atoms in tetrahedral coordination, the lower silicate being represented by the fractional part of the aluminum atoms in tetrahedral coordination; for example, 0.50 tetrahedral Al represents 50 percent trisilicate, 1.50 tetrahedral Al represents 50 percent disilicate, and so on.

The percentages of dioctahedral and trioctahedral members are next determined. The trioctahedral members will be represented by the sum of the octahedral positions filled minus 2, the remainder being dioctahedral members; for example, a total of 2.25 atoms in octahedral coordination represents 25 percent trioctahedral and 75 percent dioctahedral members.

The large-cation group is then examined to obtain the percentages of alkali and alkaline-earth formulas. Their percentages may be read directly from the atomic ratios; for example, 0.10 Ca represents 10 percent of calcium mica.

All end-member formulas containing the ions listed in the octahedral groups in the analysis and corresponding to the above three criteria are then derived from the table on page 104. A selection is then made of the smallest number of these end-member formulas to account for all ions present in the analyses and percentages of them are taken to satisfy atomic ratios and the above three criteria. The end-member solution is simplest if the ions present in smallest percentage are first accounted for as end members. As examples, the end-member selections and calculations of alurgite and lepidolite will be given in detail below.

The solutions in the examples given in the following pages do not include all end-member combinations that satisfy the analyses, as usually a choice of several combinations of end members may be made. One selection of several may best satisfy mineralogical requirements. The solutions given illustrate the manner of calculating analyses to end members and may or may not be the best selection of end members.

ALURGITE

An analysis that is simple in its end-member calculation is that of alurgite by Penfield, given in table 1. (See p. 112.) The atomic ratios show that it contains only alkali trisilicic and tetrasilicic hydroxyl end members and that is entirely dioctahedral with only bivalent and trivalent ions in octahedral coordination. Equivalents in the octahedral group are 6 for alkali trisilicic hydroxyl end members and 5 for alkali tetrasilicic hydroxyl end members, and in the first table the only two dioctahedral groups having these requirements in equivalents and containing only bivalent and trivalent ions are R^{+++}_2 and $R^{++}R^{+++}$, which may be written in the end-member formulas as $K.Al_2.AlSi_3O_{10}(OH)_2$ and

$K.MgAl.Si_4O_{10}(OH)_2$. No other end-member solution of the analysis seems possible.

Below the formula percentages of end members are the number of atoms of elements in the percentages of the formulas stated. The totals of the different atoms agree well with the atomic ratios calculated from the analysis.

Schaller[41] has shown that alurgite and mariposite are essentially the same mineral and that the name alurgite is preferable as it was given prior to the name mariposite.

LEPIDOLITE

The calculation of an analysis of lepidolite to end members is given in table 2 (p. 113). The analysis satisfies the requirements for the composition of a mica in regard to the summation of ions in octahedral coordination, large cation, and OH+F.

In the tetrahedral group, 0.42 Al in tetrahedral coordination shows that 42 formula percent of a trisilicic member is present in the sample, which leaves 58 formula percent of a tetrasilicic member. The summation of ions in octahedral coordination, 2.75, indicates 75 percent of trioctahedral and 25 of dioctahedral formulas.

Tetrasilicic and trisilicic formulas that satisfy the ionic content of the octahedral group are $K.R^{++}Al.Si_4O_{10}(OH)_2$; $K_2.LiAl_3.Si_8O_{20}F_4$; $K_2R^{++}{}_5.Si_8O_{20}(OH)_4$;$K.LiR^{++}{}_2.Si_4O_{10}F_2$;$K.Li_2Al.Si_4O_{10}F_2$;$K.Al_2.AlSi_3O_{10}(OH)_2$; $K.R^{++}{}_3.AlSi_3O_{10}(OH)_2$; and $K_2.Li_3Al_3.Al_2Si_6O_{20}F_4$.

An examination of these formulas shows four containing bivalent ions, R^{++}, so that four different solutions are possible to account for the small quantity of bivalent ions. The remaining ions in octahedral coordination, Li and Al, represent percentages of $K.Li_2Al.Si_4O_{10}F_2$, $K.Al_2.AlSi_3O_{10}(OH)_2$, and $K_2.Li_3Al_3.Al_2Si_6O_{10}F_4$. The formula $K_2.LiAl_3.Si_8O_{20}F_4$ is not used to account for lithium and aluminum in octahedral coordination because it does not seem to give a proper balance of lithium to aluminum for the remaining end members.

In the first end-member solution of lepidolite all the bivalent ions are taken to represent biotite. The percentage of biotite is $\frac{R^{++}\times 100}{3}$, where R^{++} represents the bivalent atoms given under atomic ratios. The 25 percent of dioctahedral mica is all taken as muscovite, and this with biotite leaves 15 percent of trisilicate which must be trioctahedral $K_2.Li_3Al_3.Al_2Si_6O_{20}F_4$. All of the tetrasilicate is represented by trioctahedral $K.Li_2Al.Si_4O_{10}F_2$ (polylithionite).

Two end-member combinations are calculated that satisfy the analysis equally well, one in which bivalent ions are calculated as biotite and one in which they are calculated as taeniolite. If the bivalent ions are taken as representing alurgite ($K.R^{++}Al.Si_4O_{10}(OH)_2$) or are considered as $K_2.R^{++}{}_5.Si_8O_{20}(OH)_4$, two additional end-member solutions are possible. If the last of these formulas is used for bivalent ions, only half of its percentage is subtracted from the dioctahedral percentage.

If desirable, the different alkalies, bivalent ions, hydroxyl, and fluorine found in the analysis may each be represented in an individual formula.

MARGARITE

The analysis of margarite given in table 3 (p. 115) was made by Genth in 1873. The sum of the atoms in the different groups indicates a satis-

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[41] Schaller, W. T., Mineralogic notes, ser. 3: U. S. Geol. Survey Bull. 610, p. 139, 1916.

factory analysis. Two solutions are given, one of four end members, and one of three end members ignoring 3 percent of monosilicate indicated by the analysis. Use of the end member $Na_3.Al_7.Al_6Si_6O_{30}(OH)_6$, intermediate between a dioctahedral and a trioctahedral mica, seems necessary to account for the dioctahedral content.

XANTHOPHYLLITE

The analysis of xanthophyllite by Meitzendorf in 1843 was calculated to end members with the results shown in table 4. Some error in the analysis or impurity in the sample is indicated by the sum of the octahedral ions exceeding 3. The atomic ratios show the formula of xantho-

TABLE 1.—*Calculation of an analysis of alurgite to end members*

[Alurgite from Piedmont, Italy. Penfield,[a] analyst]

	Percent	Relative equivalents		Atomic ratios	
		e	$e' = 4.052e$ [b]		
				Tetrahedral:	
SiO_2	53.22	3.547	14.37	Si	3.59
Al_2O_3	21.19	1.247	5.06	Al[c]	.41
				Σ	4.00
				Octahedral:	
				Al[c]	1.27
Fe_2O_3	1.22	.046	.19	Fe^{+++}	.06
Mn_2O_3	.87	.033	.14	Mn^{+++}	.05
MnO	.18	.005	.02	Mn^{++}	.01
MgO	6.02	.299	1.21	Mg	.61
				Σ	2.00
				Large cation:	
CaO	-----	-----	-----		
Na_2O	.34	.011	.04	Na	0.04
K_2O	11.20	.238	.96	K	.96
		Σe_m 5.426	$\Sigma e'_m$ 21.99	Σ	1.00
H_2O+	5.75	0.639	2.59	OH	2.59

PERCENTAGE OF END-MEMBER TYPES

Tetrasilicic	59
Trisilicic	41
	100
Dioctahedral	100

FORMULA PERCENTAGES OF END MEMBERS

Alurgite, $K.MgAl.Si_4O_{10}(OH)_2$	60
Muscovite, $K.Al_2.AlSi_3O_{10}(OH)_2$	40
	100

CHECK ON ATOMIC RATIOS

	Si	R^{+++}	R^{++}
$0.60[K.MgAl.Si_4O_{10}(OH)_2]$	2.40	0.60	0.60
$.40[K.Al_2.AlSi_3O_{10}(OH)_2]$	1.20	1.20	-----------
	3.60	1.80	0.60

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[a] Penfield, S. L., Am. Jour. Sci., 3d ser., vol. 46, p. 288, 1893. Cited by Schaller, W. T., Mineralogic notes, 3d ser.: U. S. Geol. Survey Bull. 610, p. 139, 1916.

[b] $f = \frac{22}{\Sigma e_m} = \frac{22}{5.426} = 4.052.$

[c] Atomic ratio of total aluminum is 1.68; sufficient is taken to make Σ tetrahedral 4.00, the remainder taken in octahedral coordination.

phyllite to be essentially $Ca.Mg_2Al.Al_3SiO_{10}(OH)_2$, a monosilicate, together with some of the disilicates, $Na.Mg_2Al.Al_2Si_2O_{10}(OH)_2$, and $Ca.Mg_3.Al_2Si_2O_{10}(OH)_2$.

SEYBERTITE

An analysis of seybertite by Sipöcz, 1854, is formulated in table 5. (See p. 117.) The calculations give 65 percent xanthophyllite, 34 percent $Ca.Mg_3.Al_2Si_2O_{10}(OH)_2$, and 1 percent margarite.

BIOTITE

In table 6 (see p. 118) the calculation of an analysis of biotite to end members illustrates the method of calculation of analyses in which oxymica is indicated by insufficient water and fluorine to make $(OH,F)_2$ in the formula. Analyses showing a deficiency of water and fluorine for $(OH,F)_2$ are not uncommon. Some of the excellent analyses of lepidolite by Berggren[42] show this deficiency, as do also many other dependable analyses of micas. In many analyses, however, the percentages of water and fluorine may be incorrect, and in many fluorine was not determined.

In calculating an analysis showing oxymicas in solid solution with fluormicas and hydroxymicas the equivalents calculated from the analysis are simply adjusted to 24 equivalents of cations plus hydroxyl and fluorine ($\Sigma e' = 24.00$).

As calculation of the analysis shows 12 percent of both disilicic and calcium mica, margarite ($Ca.Al_2.Al_2Si_2O_{10}(OH)_2$) seems a logical end-member selection. An atomic ratio of 0.06 Ti and the presence of 6 formula percent of oxymica suggest the combination of these two requirements in the oxymica formula $K.R^{++}_2Ti.AlSi_3O_{12}$. Biotite, muscovite, and lithium muscovite are then needed to account for the remaining constituents.

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[42] Berggren, Thelma, Minerals of the Varuträsk pegmatite, XV, Analyses of mica minerals and their interpretation: Geol. Fören, Förh., Band 62, p. 182, 1940; XXV, some new analyses of lithium-bearing mica minerals: Geol. Fören. Förh., Band 63, p. 262, 1941.

TABLE 2.—*Calculation of an analysis of lepidolite to end members*

[Lepidolite from Pala, Calif., collected by W. T. Schaller. Stevens,[a] analyst]

	Percent	Relative equivalents		Atomic ratios	
		e	$e'+4.019e$[b]		
				Tetrahedral:	
SiO_2	53.45	3.561	14.31	Si	3.58
Al_2O_3	22.15	1.304	5.24	Al[c]	.42
				Σ	4.00
				Octahedral:	
				Al[c]	1.33
FeO	.16	.005	.02	Fe^{++}	.01
MgO	.14	.007	.03	Mg	.02
MnO	.52	.015	.06	Mn	.03
Li_2O	5.04	.338	1.36	Li	1.36
				Σ	2.75
				Large cation:	
Na_2O	.74	.024	.10	Na	0.10
K_2O	9.58	.203	.82	K	.82
Rb_2O	1.56	.017	.07	Rb	.07
Cs_2O	.48	.003	.01	Cs	.01
		Σe_m 5.477	$\Sigma e'_m$ 22.02	Σ	1.00
H_2O+	1.28	0.142	0.57	OH	0.57
F	7.22	.380	1.53	F	1.53
				Σ	2.10

TABLE 2.—*Calculations of an analysis of lepidolite to end members*—Continued

PERCENTAGE OF END-MEMBER TYPES

Tetrasilicic	58
Trisilicic	42
	100
Trioctahedral	75
Dioctahedral	25
	100

FORMULA PERCENTAGES OF END MEMBERS

Muscovite, $K.Al_2.AlSi_3O_{10}(OH)_2$	25
Biotite, $K.R^{++}_3.AlSi_3O_{10}F_2$	2
Lithium muscovite, $\frac{1}{2}[K_2.Li_3Al_3.Al_2Si_6O_{20}F_4]$	15
Polylithionite, $K.Li_2Al.Si_4O_{10}F_2$	58
	100

CHECK ON ATOMIC RATIOS

	Si	Al	R^{++}	Li
$0.25[K.Al_2.AlSi_3O_{10}(OH)_2]$	0.75	0.75		
$.02[K.R^{++}_3.AlSi_3O_{10}F_2]$	.06	.02	0.06	
$.15[\frac{1}{2}[K_2.Li_3Al_3.Al_2Si_6O_{20}F_4]]$	.45	.38		0.22
$.58[K.Li_2Al.Si_4O_{10}F_2]$	2.32	.58		1.16
	3.58	1.73	0.06	1.38

ALTERNATE FORMULATION OF PERCENTAGES OF END MEMBERS

Muscovite, $K.Al_2.AlSi_3O_{10}(OH)_2$	25
Lithium muscovite, $\frac{1}{2}[K_2.Li_3Al_3.Al_2Si_6O_{20}F_4]$	17
Taeniolite, $K.LiR^{++}_2.Si_4O_{10}F_2$	3
Polylithionite, $K.Li_2Al.Si_4O_{10}F_2$	55
	100

ALTERNATE CHECK ON ATOMIC RATIOS

	Si	Al	R^{++}	Li
$0.25[K.Al_2.AlSi_3O_{10}(OH)_2]$	0.75	0.75		
$.17[\frac{1}{2}[K_2.Li_3Al_3.Al_2Si_6O_{20}F_4]]$	.51	.43		0.25
$.03[K.LiR^{++}_2.Si_4O_{10}F_2]$	.12		0.06	.03
$.55[K.Li_2Al.Si_4O_{10}F_2]$	2.20	.55		1.10
	3.58	1.73	0.06	1.38

[a] Analysis 6, Stevens, R. E., Am. Mineralogist, vol. 23, p. 615, 1938.

[b] $f=\frac{22}{\Sigma e_m}=\frac{22}{5.477}=4.019.$

[c] Atomic ratio of total aluminum is 1.75; sufficient is taken to make Σ tetrahedral 4.00, the remainder being taken in octahedral coordination.

TABLE 3.—*Calculation of an analysis of margarite to end members*

[Margarite from Cullakenee Mountain, N. C.[a] Genth, analyst]

	Percent	Relative equivalents		Atomic ratios	
		e	e′ = 3.991e[b]		
				Tetrahedral:	
SiO_2	29.63	1.975	7.88	Si	1.97
Al_2O_3	51.19	3.012	12.03	Al[c]	2.03
				Σ	4.00
				Octahedral:	
				Al[c]	1.98
Fe_2O_3	.59	.022	.09	Fe^{+++}	.03
Cr_2O_3	.13	.005	.02	Cr	.01
MgO	1.09	.054	.22	Mg	.11
				Σ	2.13
				Large cation:	
CaO	11.28	.402	1.60	Ca	0.80
Na_2O	1.22	.039	.16	Na	.16
K_2O	.20	.004	.02	K	.02
		Σe_m 5.513	$\Sigma e'_m$ 22.02	Σ	.98
H_2O+	4.73	0.526	2.10	OH	2.10

PERCENTAGE OF END-MEMBER TYPES

Disilicic	97
Monosilicic	3
	100
Trioctahedral	13
Dioctahedral	87
	100
Alkali mica	18
Calcium mica	82
	100

FORMULA PERCENTAGES OF END MEMBERS

Xanthophyllite, $Ca.Mg_2Al.Al_3SiO_{10}(OH)_2$	3
Margarite, $Ca.Al_2.Al_2Si_2O_{10}(OH)_2$	77
$Na.Mg_2Al.Al_2Si_2O_{10}(OH)_2$	2.5
$\frac{1}{8}[Na_3.Al_7.Al_6Si_6O_{30}(OH)_6]$	17.5
	100.0

CHECK ON ATOMIC RATIOS

	Si	R^{+++}	Mg	Ca	Na, K
$0.03[Ca.Mg_2Al.Al_3SiO_{10}(OH)_2]$	0.03	0.12	0.06	0.03	
$.77[Ca.Al_2.Al_2Si_2O_{10}(OH)_2]$	1.54	3.08		.77	
$.025[Na.Mg_2Al.Al_2Si_2O_{10}(OH)_2]$	.05	.08	.05		0.025
$.175[\frac{1}{8}[Na_3.Al_7.Al_6Si_6O_{30}(OH)_6]]$	.35	.76			.175
	1.97	4.04	0.11	0.80	0.200

ALTERNATE FORMULATION OF PERCENTAGES OF END MEMBERS[d]

Margarite, $Ca.Al_2.Al_2Si_2O_{10}(OH)_2$	77
$Ca.Mg_3.Al_2Si_2O_{10}(OH)_2$	3
$\frac{1}{8}[Na_3.Al_7.Al_6Si_6O_{30}(OH)_6]$	20
	100

TABLE 3.—*Calculation of an analysis of margarite to end members*—Continued

ALTERNATE CHECK ON ATOMIC RATIOS

	Si	R^{+++}	Mg	Ca	Na, K
0.77[$Ca.Al_2.Al_2Si_2O_{10}(OH)_2$]	1.54	3.08		0.77	
.03[$Ca.Mg_3.Al_2Si_2O_{10}(OH)_2$]	.06	.06	0.09	.03	
.20[⅓[$Na_3.Al_7.Al_6Si_6O_{30}(OH)_6$]]	.40	.87			0.20
	2.00	4.01	0.09	0.80	0.20

[a] Analysis 10, Dana, p. 637, 1920.

[b] $f=\frac{22}{\Sigma e_m}=\frac{22}{5.513}=3.991.$

[c] Atomic ratio of total aluminum is 4.01; sufficient is taken to make Σ tetrahedral 4.00, the remainder being taken in octahedral coordination.

[d] Ignoring 3 percent monosilicate.

TABLE 4.—*Calculation of an analysis of xanthophyllite to end members*

[Xanthophyllite from Shiskimskaya Mountains, Russia.[a] Meitzendorf, analyst]

	Percent	Relative equivalents		Atomic ratios	
		e	e′=4.220e [b]		
				Tetrahedral:	
SiO_2	16.20	1.079	4.55	Si	1.14
Al_2O_3	44.96	2.648	11.16	Al [c]	2.86
				Σ	4.00
				Octahedral:	
				Al [c]	0.86
FeO	2.73	.076	.32	Fe^{++}	.16
MgO	19.43	.964	4.07	Mg	2.04
				Σ	3.06
				Large cation:	
CaO	12.15	.433	1.83	Ca	0.92
Na_2O	.55	.018	.08	Na	.08
		Σe_m 5.218	$\Sigma e'_m$ 22.01	Σ	1.00
H_2O+	4.33	.481	2.03	OH	2.03

PERCENTAGE OF END-MEMBER TYPES

Disilicic	14
Monosilicic	86
	100
Trioctahedral	100
Sodium micas	8
Calcium micas	92
	100

FORMULA PERCENTAGES OF END MEMBERS

Xanthophyllite, $Ca.Mg_2Al.Al_3SiO_{10}(OH)_2$	86
$Na.Mg_2Al.Al_2Si_2O_{10}(OH)_2$	8
$Ca.Mg_3.Al_2Si_2O_{10}(OH)_2$	6
	100

TABLE 4.—*Calculation of an analysis of xanthophyllite to end members*—Continued

CHECK ON ATOMIC RATIOS

	Si	Al	R^{++}_{oct}	Ca	Na
0.86[$Ca.Mg_2Al.Al_3SiO_{10}(OH)_2$]	0.86	3.43	1.72	0.86	
.08[$Na.Mg_2Al.Al_2Si_2O_{10}(OH)_2$]	.16	.24	.16		0.08
.06[$Ca.Mg_3.Al_2Si_2O_{10}(OH)_2$]	.12	.12	.18	.06	
	1.14	3.79	2.06	0.92	0.08

[a] Analysis 3, Dana, p. 640, 1920.

[b] $f=\frac{22}{\Sigma e_m}=\frac{22}{5.218}=4.220.$

[c] Atomic ratio of total aluminum is 3.72; sufficient is taken to make Σ tetrahedral 4.00, the remainder being taken in octahedral coordination.

TABLE 5.—*Calculation of an analysis of seybertite to end members*

[Seybertite from Amity, N. Y.[a] Sipöcz, analyst]

	Percent	Relative equivalents		Atomic ratios	
		e	$e'=4.224e$[b]		
				Tetrahedral:	
SiO_2	19.19	1.278	5.40	Si	1.35
Al_2O_3	39.73	2.340	9.88	Al[c]	2.65
				Σ	4.00
				Octahedral:	
				Al[c]	0.64
Fe_2O_3	.61	.023	.10	Fe^{+++}	.03
FeO	1.88	.052	.22	Fe^{++}	.11
MgO	21.09	1.046	4.42	Mg	2.21
				Σ	2.99
				Large cation:	
CaO	13.11	.468	1.98	Ca	0.99
		Σe_m 5.207	$\Sigma e'_m$ 22.00		
H_2O+	4.85	0.538	2.28	OH	2.28
F	1.26	.106	.45	F	.45
				Σ	2.73

PERCENTAGE OF END-MEMBER TYPES

Disilicic	35
Monosilicic	65
	100
Trioctahedral	99
Dioctahedral	1
	100

FORMULA PERCENTAGES OF END MEMBERS

Xanthophyllite, $Ca.Mg_2Al.Al_3SiO_{10}(OH)_2$	65
Margarite, $Ca.Al_2.Al_2Si_2O_{10}(OH)_2$	1
$Ca.Mg_3.Al_2Si_2O_{10}(OH)_2$	34
	100

TABLE 5.—*Calculation of an analysis of seybertite to end members*—Continued

CHECK ON ATOMIC RATIOS

	Si	R^{+++}	R^{++}_{oct}	Ca
0.65[$Ca.Mg_2Al.Al_3SiO_{10}(OH)_2$]	0.65	2.60	1.30	0.65
.01[$Ca.Al_2.Al_2Si_2O_{10}(OH)_2$]	.02	.04	------	.01
.34[$Ca.Mg_3.Al_2Si_2O_{10}(OH)_2$]	.68	.68	1.02	.34
	1.35	3.32	2.32	1.00

[a] Analysis 3, Dana, p. 638, 1920.

[b] $f=\frac{22}{\Sigma e_m}=\frac{22}{5.207}=4.224.$

[c] Atomic ratio of total aluminum is 3.29; sufficient is taken to make Σ tetrahedral 4.00, the remainder being taken in octahedral coordination.

TABLE 6.—*Calculation of an analysis of biotite (pegmatitic) to end members*

[Biotite from Ridgway, Va., collected by W. T. Schaller. Stevens, analyst]

	Percent	Relative equivalents		Atomic ratios	
		e	$e'=4.351e$[a]		
				Tetrahedral:	
SiO_2	39.70	2.645	11.52	Si	2.88
Al_2O_3	15.92	.937	4.08	Al[b]	1.12
				Σ	4.00
				Octahedral:	
				Al[b]	0.24
Fe_2O_3	3.31	.124	.54	Fe^{+++}	.18
Cr_2O_3	.08	.003	.01	------	------
FeO	8.96	.249	1.08	Fe^{++}	.54
MgO	16.15	.802	3.49	Mg	1.74
MnO	.24	.007	.03	Mn	.02
TiO_2	1.11	.056	.24	Ti	.06
Li_2O	.11	.007	.03	Li	.03
				Σ	2.81
				Large cation:	
CaO	1.60	.057	.25	Ca	0.12
Na_2O	.86	.028	.12	Na	.12
K_2O	8.08	.172	.75	K	.75
				Σ	0.99
H_2O+	3.21	.357	1.55	OH	1.55
F	1.40	.074	.32	F	.32
		Σe 5.518	Σe′ 24.00	Σ	1.87

PERCENTAGE OF END-MEMBER TYPES

Trisilicic	88
Disilicic	12
	100
Trioctahedral	81
Dioctrahedral	19
	100
Alkali mica	88
Calcium mica	12
	100
Hydroxyfluormica	94
Oxymica	6
	100

TABLE 6.—*Calculation of an analysis of biotite (pegmatitic) to end members*—Continued

FORMULA PERCENTAGES OF END MEMBERS

Margarite, $Ca.Al_2.Al_2Si_2O_{10}(OH)_2$	12
$K.R^{++}_2Ti.AlSi_3O_{12}$	6
Lithium muscovite, $\frac{1}{2}[K_2.Li_3Al_3.Al_2Si_6O_{20}(OH)_4]$	2
Biotite, $K.R^{++}_3.AlSi_3O_{10}(OH)_2$	73
Muscovite, $K.R^{+++}_2.AlSi_3O_{10}(OH)_2$	7
	100

CHECK ON ATOMIC RATIOS

	Si	R^{+++}	Ti	R^{++}_{oct}	Li	Ca	R^{+}
$0.12[Ca.Al_2.Al_2Si_2O_{10}(OH)_2]$	0. 24	0. 48				0. 12	
$.06[K.R^{++}_2Ti.AlSi_3O_{12}]$	.18	.06	0. 06	0. 12			0. 06
$.02[\frac{1}{2}[K_2.Li_3Al_3.Al_2Si_6O_{20}(OH)_4]]$	.06	.05			0. 03		.02
$.73[K.R^{++}_3.AlSi_3O_{10}(OH)_2]$	2. 19	.73		2. 19			.73
$.07[K.R^{+++}_2.AlSi_3O_{10}(OH)_2]$	.21	.21					.07
	2. 88	1. 53	0. 06	2. 31	0. 03	0. 12	0. 88

[a] $f=\frac{24}{\Sigma e}=\frac{24}{5.518}=4.351.$

[b] Atomic ratio of total aluminum is 1.36; sufficient is taken to make Σ tetrahedral 4.00, the remainder being taken in octahedral coordination.

Contributions to geochemistry, 1942–45
Geological Survey Bulletin 950

THE COMPOSITION OF ROSCOELITE

By Roger C. Wells and W. Wallace Brannock

ABSTRACT

One revised and several older analyses of roscoelite have been studied for the purpose of showing that they represent either mixtures or solid solutions of a relatively few end members. The dominant end member, which we call roscoelite, has the formula $K.V^{+++}_2.AlSi_3O_{10}(OH)_2$, which is the formula of muscovite with vanadium replacing the aluminum in octahedral coordination. Two known roscoelites contain 70 molecular percent of this end member, the others less. The principal other end members are formulated as muscovite, alurgite, and pyrophyllite. A review of the older analyses by Genth and Hillebrand suggests that some of them may have contained extraneous silica.

INTRODUCTION

Analyses of different samples of roscoelite show considerable variation. Although this mineral has been considered to be closely related to muscovite, with aluminum more or less replaced by vanadium (V^{+++}), careful examination of available analyses shows certain other variations.

In an analysis made several years ago by Wells[43] silica present as quartz was not determined separately. This has now been done by the method originally used by Genth,[44] and the corrected analysis is shown under 1 in the table of analyses on page 123.

The principal advance in understanding the composition of roscoelite is based on the newer knowledge of the structure of minerals, as revealed by X-rays, and on Stevens' interpretations of end members in the mica group. (See p. 101.) X-ray-powder photographs made by Joseph M. Axelrod, of the Geological Survey, show that our sample of roscoelite belongs to the mica group, with lines very close to those of muscovite, paragonite, and biotite. The layer spacing is slightly larger than that of muscovite and paragonite and smaller than that of biotite. The indices of refraction, as determined by Marie L. Lindberg, of the Geological Survey, were: $\alpha = 1.59$, $\beta = 1.63+$, $\gamma = 1.64+$ which compare with $\alpha = 1.610$, $\beta = 1.685$, $\gamma = 1.704$ found by Wright[45] for roscoelite from the Stockslager mine, Placerville, Calif. These values are consistent with the percentages of vanadium in the two samples.

PREVIOUS FORMULAS OF ROSCOELITE

It may be of interest to cite the formulas proposed for roscoelite in the past. Roscoe[46] himself writes:

> The following formula approximately represents the composition of this mineral, a portion of the alumina being replaced by sesquioxides of iron and manganese, and a portion of the potassium oxide by lime, magnesia and soda:
>
> $$2(Al_2O_3.V_2O_5)+2K_2O.9SiO_2+H_2O,$$
>
> or $$4AlVO_4+KSi_9O_{20}+H_2O.$$

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[43] Wells, R. C., Analyses of rocks and minerals from the laboratory of the United States Geological Survey 1914–1936; U. S. Geol. Survey Bull. 878, p. 110, 1937.

[44] Genth, F. A., On some American vanadium minerals: Am. Jour. Sci., 3d ser., vol. 12, p. 32, 1876.

[45] Wright, F. E., Optical properties of roscoelite: Am. Jour. Sci., 4th ser., vol. 38, p. 305, 1914.

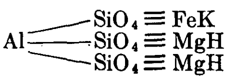
[46] Roscoe, H. E., Roy. Soc. London Proc., vol. 25, p. 109, 1876.

The main objections to the above conclusions are that the vanadium, iron, and manganese are presumably present in their lower valences and that, structurally, magnesium cannot replace potassium.

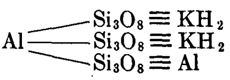
The next formula proposed was that of Genth,[47] namely $K_2(MgFe)Al_4V_4Si_{12}O_{32}+4H_2O$. This formula, as it stands, does not seem to correspond to the analysis, and a nearer approximation would be $K_3(Mg,Fe)Al_4V_5Si_{12}O_{39}+4H_2O$, which has a resemblance to modern formulas but is not as illuminating as the interpretation given later.

Many years later, Clarke[48] attempted to interpret roscoelite as a molecular mixture of the three compounds

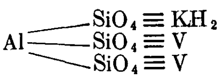
1



2



3



in the ratio of 21:22:159, or nearly 1:1:8.

Of these component molecules the first represents the normal phlogopite type, the second is a trisilicic biotite type, and the third, which forms 74.5 percent of the whole mass, is a muscovite in which two-thirds of the aluminum have been replaced by vanadium, in short, a vandium muscovite.

Clarke thus interprets roscoelite as a mixture or solid solution of certain "compounds." This explanation and the formulas proposed by Clarke take account of a variation in the relative proportions of silicon, aluminum, and oxygen in minerals of this type. The silicon:oxygen ratios, for example, ranging from Si_9O_{24} to Si_3O_{12}, or Si_9O_{36}, provide for considerable variation. The interpretation is mathematically correct, and the formulas are in accordance with the requirements of valence and equivalents, but unfortunately they imply a variation in the number of oxygen atoms with more or less fixed aluminum, whereas the number of oxygen atoms is fixed and the variation is in the metallic ions. Clarke's formulas fail to recognize the essential feature that aluminum atoms may occupy the role of silicon atoms and also miss other significant features. Present ideas of structure therefore make the formulas of Clarke of historical interest only.

ANALYSES OF ROSCOELITE

Contrary to a statement in Dana, but agreeing with Genth and Hillebrand, roscoelite is slowly but almost completely decomposed by acids. In our analysis only 0.39 percent of V_2O_3 remained in the unattacked residue. The vanadium in the analyses, where orginally denoted other than V_2O_3, was recalculated to V_2O_3. Genth found it to be at least $2V_2O_3.V_2O_5$ and Hillebrand at least nine-tenths V_2O_3, and both assumed that in fresh samples it would be entirely V_2O_3. Altogether, 10 analyses of roscoelite are available, as shown in the table below.

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[47] Genth, F. A., On some tellurium and vanadium minerals: Am. Philos. Soc. Proc., vol. 17, p. 119, 1877.

[48] Hillebrand, W. F., Turner, H. W., and Clarke, F. W., Am. Jour. Sci., 4th ser., vol. 7, p. 451, 1899.

Analyses

	1	2	3	4	5	6	7	8	9	10
SiO_2	42.87	41.25	47.69	47.82	48.60	46.81	46.09	56.74	45.17	46.06
Al_2O_3	21.90	14.14	14.10	12.60	11.76	15.78	17.46	91.62	11.54	22.55
FeO	1.74	[1] 1.13	1.67	3.30	2.27	1.58	1.95	3.84	1.60	[1] .73
MgO	1.06	2.01	2.00	2.43	1.95	2.31	2.18	2.63	1.64	.92
V_2O_3	17.42	23.59	20.56	19.94	21.40	18.82	16.38	7.78	24.01	12.84
CaO	.07	.61	Tr.	Tr.	.23	Tr.	-------	-------	-------	.44
Na_2O	.27	.82	.19	.33	.34	.60	.18	.94	.06	.22
K_2O	9.91	8.56	7.59	8.03	5.98	8.89	8.66	8.11	10.37	8.84
H_2O+	4.76	3.35	4.96	5.13	5.95	3.87	6.37	undet.	4.29	4.07
H_2O-	-------								.40	1.98
Mn_2O_3	-------	1.15	-------	-------	-------	-------	-------	-------	-------	-------
TiO_2	-------	-------	-------	-------	-------	-------	-------	-------	.78	-------
BaO	-------	-------	-------	-------	-------	-------	-------	-------	-------	1.35
	100.00	96.61	98.76	99.58	98.48	98.66	99.27	99.66	99.86	100.00

[1] Fe_2O_3.

1. Wells and Brannock. Sample of material collected by F. L. Hess in Paradox Valley, Colo. The earlier analysis by Wells has been corrected by calculating Fe_2O_3 to FeO, determining SiO_2 present as quartz by the method of Genth and Hillebrand, omitting quartz, pyrite, and TiO_2 and calculating the balance to 100 percent.

2. Mean of two analyses by H. E. Roscoe of material from the Stockslager mine, Placerville, Calif. Royal Soc. London Proc., vol. 25, p. 109, 1876.

3–6. Several samples of material from the same locality as samples for analysis 2. Analyzed by F. A. Genth and described in Am. Jour. Sci., 3d ser., vol. 12, p. 31, 1876.

7. A mineral resembling dark green chlorite from the same locality as sample 2.

8. Roscoelite from the Magnolia district, Boulder County, Colo. Analyzed by Genth and described in Am. Philos. Soc. Proc., vol. 17, p. 119, 1877.

9. Material from the Stockslager mine. Analyzed by W. F. Hillebrand and described by W. F. Hillebrand, H. W. Turner, and F. W. Clarke in Am. Jour. Sci., 4th ser., vol. 7, p. 451, 1899.

10. Green coloring matter in sandstone, Placerville, Colo., described by W. F. Hillebrand and F. L. Ransome in Am. Jour. Sci., 4th ser., vol. 10, p. 120, 1900.

CALCULATION OF END MEMBERS

In the table below is shown in detail the calculation of analysis 1 to end members, according to Stevens' procedure. (See p. 103.) The percentages in the second column are divided by the equivalent weights—the molecular weights reduced to a univalent basis—giving e, in the third column. The fourth column, e′, is obtained by multiplying e by the factor 4.2603, derived as shown, on the assumption that the formula of roscoelite is that of a mica having 22 equivalents of cations, 10 atoms of oxygen, and 2 hydroxyl groups. Dividing the figures in the fourth column

Calculation of analysis 1 to end members[a]

	Percent	Relative equivalents		Atomic ratios	
		e	e′=4.2603e[b]		
				Tetrahedral:	
SiO_2	42.87	2.856	12.17	Si	3.05
Al_2O_3	21.90	1.289	5.49	Al[c]	.95
				Σ	4.00
				Octahedral:	
				Al[c]	0.88
FeO	1.74	.048	.20	Fe^{++}	.10
MgO	1.06	.053	.23	Mg	.11
V_2O_3	17.42	.697	2.97	V^{+++}	.99
				Σ	2.08
				Large cation:	
CaO	.07	.002	.01	Ca	0.01
Na_2O	.27	.009	.04	Na	.04
K_2O	9.91	.210	.89	K	.89
		Σe_m 5.164	$\Sigma e'_m$ 22.00	Σ	0.94
H_2O+	4.76	0.528	2.25	OH	2.25

Calculation of analysis 1 to end members—Continued

PERCENTAGE OF END-MEMBER TYPES

Tetrasilicic	5
Trisilicic	95
	100
Trioctahedral	8
Dioctahedral	92
	100

FORMULA PERCENTAGES OF END MEMBERS

Roscoelite, $K.V_2.AlSi_3O_{10}(OH)_2$	49
Muscovite, $K.Al_2.AlSi_3O_{10}(OH)_2$	44
Biotite, $K.R^{++}_3.AlSi_3O_{10}(OH)_2$	2
Talc, $R^{++}_3.Si_4O_{10}(OH)_2$	5
	100

CHECK ON ATOMIC RATIOS

	Si	Al	V	R^{++}	R^+
$0.49[K.V_2.AlSi_3O_{10}(OH)_2]$	1.47	0.49	0.98		0.49
$.44[K.Al_2.AlSi_3O_{10}(OH)_2]$	1.32	1.32			.44
$.02[K.R^{++}_3.AlSi_3O_{10}(OH)_2]$	.06	.02		0.06	.02
$.05[R^{++}_3.Si_4O_{10}(OH)_2]$	.20			.15	
	3.05	1.83	0.98	0.21	0.95

[a] See table on page 123.

[b] $f=\frac{22}{e_m}=\frac{22}{5.164}=4.2603.$

[c] Atomic ratio of total aluminum is 1.83; sufficient is taken to make tetrahedral 4.00, the remainder taken in octahedral coordination.

by the respective valences gives the atomic ratios in the fifth column. Enough Al is allotted to the tetrahedral group to make a total of 4, and the balance is allotted to the octahedral group. The ratio of aluminum to silicon in the tetrahedral group, the total of the octahedral group, and the total for the large cation agree fairly well with the requirements of a dioctahedral trisilicic mica. The large cation group is only slightly deficient and the excess of water over that required for $(OH)_2$ is probably hygroscopic water that was not completely removed at 105° C.

The selection of end members is somewhat arbitrary and subject to the necessary uncertainties of sampling, purification, and analysis. The major end member, roscoelite, is simply $K.V_2.AlSi_3O_{10}(OH)_2$, completely analogous to muscovite, $K.Al_2.AlSi_3O_{10}(OH)_2$, which is the other chief end member. Thus the analysis works out to 49 percent of roscoelite, 44 percent of muscovite, 2 percent of biotite and 5 percent of talc. The talc end member may very well be a hydrous material of the vermiculite type; if so, it will account for part of the excess H_2O+.

The terms dioctahedral and trioctahedral are those proposed by Stevens to denote end members that have respectively two or three ions in octahedral coordination.

In the table below are summarized the atomic ratios calculated for the ten analyses recorded above.

Atomic ratios of roscoelites

	1	2	3	4	5	6	7	8	9	10
Tetrahedral:										
Si	3.05	3.08	3.40	3.42	3.50	3.32	3.31	3.66	3.31	3.24
Al	.95	.92	.60	.58	.50	.68	.69	.34	.69	.76
	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Octahedral:										
Al	0.88	0.32	0.58	0.48	0.50	0.64	0.79	1.15	0.31	1.11
Fe++	.10	.06	.10	.20	.14	.10	.12	.21	.10	.04
Mg	.11	.22	.21	.26	.21	.23	.23	.25	.18	.10
Mn++		.06								
V+++	.99	1.41	1.17	1.14	1.23	1.07	.94	.40	1.41	.72
	2.08	2.07	2.06	2.08	2.08	2.04	2.08	2.01	2.00	1.97
Large cation:										
Ca	0.01	0.05			0.02					0.04
Ba										.04
Na	.04	.12	0.03	0.05	.05	0.08	0.03	0.12		.03
K	.89	.81	.69	.73	.55	.81	.79	.67	0.97	.79
	0.94	0.98	0.72	0.78	0.62	0.89	0.82	0.79	0.97	0.90
OH	2.25	1.68[1]	2.36[1]	2.45[1]	2.85[1]	1.83[1]	3.05[1]		2.10	1.91

[1] Total water by ignition.

Several features appear in all the tabulations of atomic ratios. The Si exceeds 3 and consequently less than 1 Al is required to make a total of 4 atoms. The excess of Si over 3 indicates the amount of a tetrasilicic end member or members present. The totals of the octahedral ions are generally only slightly above 2, which indicates only a small amount of a trioctahedral end member or members. The totals of the large cation group are uniformly below 1, which indicates the presence of an end member or members having the mica structure but without a large cation. These end members have been interpreted as talc and pyrophyllite. The figure for OH in most formulations is above 2, probably on account of failure to remove all hygroscopic water in the analyses in which H_2O+ was determined; in the other formulations it may be attributed to H_2O- which is included in the figures for total water. That V^{+++} should not be used to replace Si^{++++} seems to be indicated by its relatively large ionic radius, 0.75,[49] compared with 0.55 for Al^{+++} and 0.40 for Si^{++++}. The iron and magnesium ratios are generally low, calcium is very low, and barium and manganese are each reported in only one analysis.

The results of calculating the atomic ratios to end members are shown in the next table. End members are not shown for analysis 10, however, because it does not yield a satisfactory formulation. The selection of the end members was made from the table of end members of the mica group listed by Stevens (p. 106), to whom we are greatly indebted for suggesting appropriate end members and for checking the calculations.

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[49] Wyckoff, R. W. G., The structure of crystals, Am. Chem. Soc. Mon. 19, p. 192, 1931.

Formula percentages of end members of roscoelite

	1	2	3	4	5	6	7	8	9
Roscoelite, $K.V_2.AlSi_3O_{10}(OH)_2$	49	70	58	57	50	53	47	20	70
Muscovite, $K.Al_2.AlSi_3O_{10}(OH)_2$	44	11	2	------	------	15	22	14	------
Alurgite, $K.R^{++}Al.Si_4O_{10}(OH)_2$	------	6	12	20	11	21	14	45	28
Talc, $R^{++}{}_3.Si_4O_{10}(OH)_2$	5	2	6	9	8	4	7	------	------
Pyrophyllite:									
$Al_2.Si_4O_{10}(OH)_2$	------	------	22	14	19	7	10	21	2
$V_2.Si_4O_{10}(OH)_2$	------	------	------	------	12	------	------	------	------
Biotite:									
$K.R^{++}{}_3.AlSi_3O_{10}(OH)_2$	2	6	------	------	------	------	------	------	------
$Ca.R^{++}Al.AlSi_3O_{10}(OH)_2$	------	5	------	------	------	------	------	------	------

It is clear from the table of end members that roscoelite, the high-vanadium end member, predominates over any other end member, except in column 8. Muscovite, alurgite, and pyrophyllite appear in nearly every formulation of the end members, and small amounts of talc are shown in most of them.

Close inspection of the tabulation of end members suggested that extraneous silica might be present in several of the analyses. We found that by reducing the silica percentages up to a certain limit for all but two analyses a reasonable formulation was also obtained. Beyond that limit it was impossible to make a satisfactory formulation.

Any reduction of the silica for analyses 1 and 2 gave a poor end-member formulation. For analyses 3 to 8, by Genth, the limits of possible extraneous silica ranged from 5 to 16 percent. Genth reported that it was necessary to remove quartz from the samples before making the analyses; it is possible that his efforts to remove the quartz were not entirely successful. His samples also may have contained opaline silica, which was not separated from the roscoelite before the analyses were made. In analysis 1 (see p. 123), a test for opaline silica was made, but only a small amount, 0.18 percent, was found, which is in harmony with the fairly simple formulation for that analysis. The table below shows the permissible limits of silica reduction and the formulation of end members at that limit.

Adjusted formula percentages of end members of roscoelite

	1	2	3	4	5	6	7	8	9
Roscoelite, $K.V_2.AlSi_3O_{10}(OH)_2$	49	70	64	64	67	60	52	25	73
Muscovite, $K.Al_2.AlSi_3O_{10}(OH)_2$	44	11	11	17	------	22	26	40	1
Alurgite, $K.R^{++}Al.Si_4O_{10}(OH)_2$	------	6	------	3	------	8	------	19	25
Talc, $R^{++}{}_3.Si_4O_{10}(OH)_2$	5	2	11	16	12	------	------	------	------
Pyrophyllite, $Al_2.Si_4O_{10}(OH)_2$	------	------	14	------	21	------	9	4	------
Biotite:									
$K.R^{++}{}_3.AlSi_3O_{10}(OH)_2$	2	6	------	------	------	10	13	12	1
$Ca.R^{++}Al.AlSi_3O_{10}(OH)_2$	------	5	------	------	------	------	------	------	------
Silica adjustment, in percent	0	0	−5	−8	−6	−8	−7	−16	−2

The formulations are not changed greatly by making the silica reductions; the formula percentages of roscoelite are slightly higher, those of muscovite are relatively more prominent, and those of alurgite and pyrophyllite are lower. If material were available it would be interesting to study the nature of the silica present in the samples analyzed by Genth and Hillebrand.

As shown in both tables of end members, the deficiency of alkalies in all the analyses necessitates the formulation of talc and pyrophyllite. These two end members, however, may represent end members of the vermiculite type.

An end member of the kaolin type could not be considered because of the low water content of the samples, although further information on the role of water would be desirable. The higher content of ions in octahedral coordination in kaolin also suggests the absence of such an end member.

CONCLUSIONS

The tables of end members show that roscoelite is dominantly a dioctahedral trisilicic mica. The high-vanadium end member predominates over any other end member except in column 8.

The possibility that vanadium may occupy the octahedral positions of any of the dioctahedral end members cannot be dismissed, but nevertheless most of the vanadium must be represented by the roscoelite end member.

A FIELD TEST FOR THE DETECTION AND ESTIMATION OF TUNGSTEN

By Victor North and F. S. Grimaldi

The Feigl-Krumholz[50] reaction has been developed to serve as a simple field test for tungsten. Tungsten minerals that do not fluoresce under ultraviolet light can be readily detected by this method.

By using a standardized procedure and a set of synthetic standards the test can be used to furnish a semiquantitative estimate of the grade of ore, especially low-grade ores.

MATERIALS

Peroxide-measuring scoop: A measuring cup with a capacity of about 0.20 milliliter.
Sample-measuring scoop: A scoop made from metal rod having a depression in one end that will hold about 50 milligrams of sample. The capacity of the one used in the tests here described was 0.038 milliliter.
Sodium Peroxide; Granular.
Potassium thiocyanate solution: Dissolve 25 grams of KCNS in 100 milliliters of water.
Stannous chloride solution: Dissolve 20 grams of stannous chloride dihydrate in 500 milliliters of concentrated hydrochloric acid and dilute with 100 milliliters of water.
Pyrex test tubes: 18 by 150 millimeters.
Porcelain crucibles: No. 000, used to roast ores containing arsenic.

PROCEDURE

Place a 50-milligram sample in a dry tube and add a peroxide scoopful of sodium peroxide. Heat over a flame until the mixture has melted and resolidified, generally after about half a minute. Allow to cool and add 10 milliliters of water. After the melt has disintegrated add 15 milliliters of thiocyanate reagent and 15 milliliters of stannous chloride reagent. If tungsten is present in amounts above 1 percent a yellow color will develop after 3 or 4 minutes. This color will develop more slowly if smaller amounts are present. Tungstic-oxide concentrations of less than 1 percent can be estimated by comparison with a set of standards after the color has been developing for an hour and a quarter. By using double amounts of sample and peroxide, 0.02 percent of WO_3 can be detected.

PREPARATION OF ARTIFICIAL STANDARDS

Prepare a ferric-chloride solution in hydrochloric acid (1+4) containing one milligram of iron per milliliter. On adding this solution to hydrochloric acid (1+4) a yellow color very similar to the tungsten color will be produced.

A set of standards can be made by adding the iron solution from a burette to 10-milliliter portions of hydrochloric acid (1+4) in the proportions indicated below. The resulting solutions will have approximately

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[50] See Grimaldi, F. S., and North, Victor, Determination of tungsten in low-grade tungsten ores: Ind. and Eng. Chemistry, anal. ed., vol. 15, p. 652, 1943.

the same colors as equivalent volumes of tungsten test solutions when a 50-milligram sample is used for each test.

Tungsten concentration

[Iron solution added from a burrette to 10-milliliter portions of HCl (1+4)]

WO_3 (percent)	Iron solution (milliliters)
0.2	0.4
.4	.7
.6	1.15
.8	1.65
1.0	3.3

These standards may be sealed into test tubes of the same size as used in the field tests for permanent color standards.

Elements that produce colored ions under the conditions of the test should preferably be absent, but if a 50-milligram sample is taken the following percentages of metals may be present without interference: nickel 6, cobalt 2, chromium 0.6, and vanadium 0.4.

Molybdenum may be detected by the formation of a transitory amber coloration when the acid stannous chloride solution is first added. This color quickly fades to a pale yellow color and is noninterfering if the molybdenum oxide concentration is less than 4 percent. This concentration of molybdenum oxide will produce a color equivalent to a tungsten concentration of 0.1 percent. Larger amounts of molybdenum will produce a corresponding increase in apparent tungsten content.

Arsenic should preferably be absent, as the brownish colloidal metallic arsenic formed by reaction with the test reagents makes tungsten difficult to detect. Arsenic interference can be minimized by preliminary roasting of the rock with an equal amount of lampblack in a porcelain crucible prior to fusion with peroxide.

Titanium when present in amounts larger than about 15 percent produces a yellow coloration that renders the tungsten test doubtful.

Most minerals are completely attacked by a peroxide fusion and subsequent acid attack. Some of the more refractory oxide minerals such as rutile and magnetite were tested by this procedure. Magnetite did not enter into complete solution when acid was first added but dissolved slowly and produced a clear solution after half an hour. Rutile produced a cloudy yellow solution which would mask any tungsten color if it were present. Pyrolusite and hematite were completely attacked and produced a clear solution. Occasionally a cloud of silica will be formed when silicate rocks are tested, but this translucent cloud settles rather quickly and does not interfere with the test.

EXPERIMENTAL

The use of a small cup for measuring the size of the sample is not entirely satisfactory from a theoretical standpoint because of density variations among different samples. This is, however, the most practical method for readily securing nearly comparable amounts of test material in the field. The variation in weight of tungsten ores measured by the sample scoop ranged from 49 to 66 milligrams.

Pyrex test tubes used for the tests are attacked by the peroxide fusion, but they may be used repeatedly until failure occurs. The ordinary test tubes do not fail until after three or four fusions, and thicker walled tubes would probably remain usable for a longer period.

Most common elements present in tungsten-bearing rocks do not interfere with the test. Experiments made by the writers have indicated that most elements present in tungsten ores are noninterfering. Iron, manganese, calcium, magnesium, aluminum, antimony, copper, lead sodium, phosphorus, and silicon do not have an adverse effect on the test.

Results of field test compared with analysis of tungsten ores

Locality	WO_3 present	Field-test estimate
California	0.21	0.2
	.01	None
	.16	.1
	.01	None
	.34	.5
	.46	.9
	.68	.9
Nevada	.04	< .1
	.14	.1
	.26	.3
	.51	.6
Alaska	.11	[1] .2
	.19	[1] .3
	.75	.9
	.48	.8
	1.1	1.0
	4.3	> 1.0
	3.9	> 1.0
	6.7	> 1.0
	2.5	> 1.0
Idaho	.01	< .1
	1.0	1.0

[1] Contained arsenic.

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AN EASILY CLEANED MEASURE FOR POWDERS USED IN SPECTROGRAPHY

By Cyrus Feldman

The chief disadvantage in the use of a scoop for powders used in spectrochemistry has been the difficulty of cleaning particles out of the inside corners of small cavities. The measure here described has no inside corners. It is a flat sheet of high-carbon steel, 0.7 millimeter thick, tempered in oil and with a hole at one end. The walls of the hole define a frustrum of a 60° cone; the lower opening, which is 1.5 millimeters in diameter, permits efficient emptying and cleaning.

The measure used by the writer, as here illustrated (fig. 40, *A*), is 1 by 16 centimeters, with a hole at each end. At one end it is 0.7 millimeter thick, and at the other the thickness is stepped up to 2.5 millimeters to provide for a second hole, not shown in the illustration, which will accommodate a larger charge with no increase in the diameter of the lower opening.

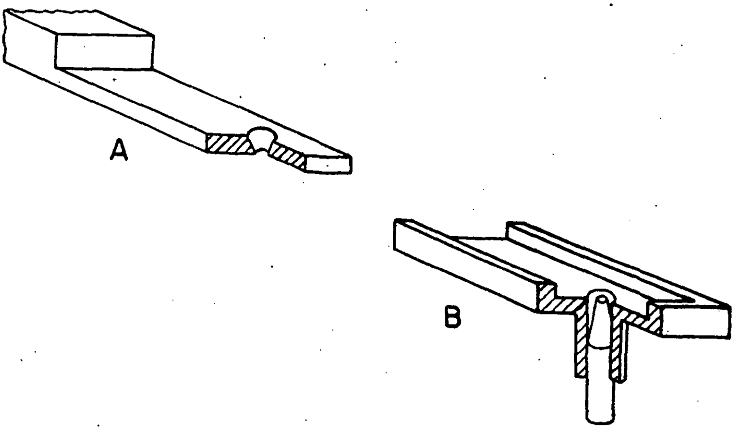

Figure 40.—Measure for powders used in spectrography. *A*, The measure, showing the location of hole; *B*, centering guide.

To be filled, the measure is placed on a flat surface, and the powder is tamped in gently and leveled off with a straightedge. If difficulty is experienced with cohesion, the powder may be dampened, provided the water is driven off with a Bunsen flame before the arc is struck.

When ground to 270 mesh or finer, rock powders or mixtures of quartz and artificial oxides with as much as 70 percent of quartz are retained by the measure. To insure this retention, the hole in the bottom of the measure should not exceed 1.5 millimeters in diameter.

The charge is transferred to the electrode by inserting the measure in the centering guide (fig. 40, *B*), shown in place on the electrode, and pushing the powder down with a small brush. The electrodes used in the chemical laboratory of the Geological Survey are turned from spectrographic carbon rods ¼ inch in diameter. The cavities are 35½° cones, drilled to provide openings with a diameter of 1.8 or 2.5 millimeters and beveled as illustrated.

The measure may easily be cleaned by drawing a pipe cleaner through the hole.

The writer wishes to express his thanks to Mr. A. H. Frazier and Mr. A. C. Wolf, of the Geological Survey, for their valuable suggestions and to Mr. Wolf for making the measure.

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THE GRAVIMETRIC DETERMINATION OF TUNGSTEN WITH BRUCINE

By F. S. Grimaldi and Norman Davidson[51]

INTRODUCTION

In the gravimetric procedure for the determination of tungsten, cinchonine has commonly been used to assist in the complete precipitation of tungstic acid. During the second World War, the unavailability of cinchonine for this purpose, because of its medicinal use by the armed forces, led to the study of possible substitutes for analytical purposes. Beta-naphthoquinoline,[52] rhodamine B,[53] tannic acid-antipyrine,[54] anti-1,5-di-(p-methoxyphenyl)-1-hydroxylamino-3-oximino-4-pentene,[55] are some of the reagents that have been proposed. The writers have found that brucine is a satisfactory reagent for the determination of tungsten.

Many reagents that precipitate tungsten, such as quinoline, 8-hydroxyquinoline, beta-naphthoquinoline, quinaldic acid, cinchonine, brucine, strychnine, and cacotheline, contain a quinoline nucleus. This suggests that the quinoline nucleus is the active group. The reactions of brucine are almost identical with those of cinchonine, the similarity being confirmed by a number of check experiments. The use of brucine for the gravimetric determination of tungsten therefore involves no significant changes in established procedures.

REAGENTS

Brucine solution: Dissolve 20 grams of brucine in 200 milliliters of hydrochloric acid (1+3).

Brucine wash solution: 10 milliliters of above brucine solution and 10 milliliters of concentrated hydrochloric acid diluted to 1 liter with water.

Ammonia wash solution: 1 liter of solution contains 100 milliliters of concentrated NH_4OH and 10 milliliters of concentrated hydrochloric acid.

Hydrochloric acid wash solution: hydrochloric acid solution (1+9).

EXPERIMENTAL TESTS

Experiments were made to determine the optimum conditions for complete precipitation of tungsten, and the behavior of various cations and anions under these conditions was studied. All tests were made in a final total volume of 50 milliliters.

Two milliliters of brucine solution was added to 48 milliliters of the test solution containing hydrochloric acid and a soluble salt of the element under study. The solution was digested on the steam bath for 30 minutes and then allowed to cool at room temperature for at least 3 hours. The precipitate, if any, was then filtered off, washed with brucine wash solution and determined.

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[51] Presented before the Division of Analytical and Microchemistry at the 107th meeting of the American Chemical Society, Cleveland, Ohio, April 1944.

[52] Platunov, B. A., and Kirillova, N. M., Uchenye Zapiski Leningrad, Gosudarst. Univ., Ser. Khim. Nauk 1940, no. 5 (no. 54), pp. 269–275; and Khim. Referat. Zhur. 4, no. 4, p. 73, 1941.

[53] Oats, J. T., Eng. Min. Jour. 144, no. 4, pp. 72–73, 1943.

[54] Peterson, H. E., and Anderson, W. L., U. S. Bureau of Mines, R.I. 3709, 1943.

[55] Yoe, J. H., and Jones, A. L., Ind. Eng. Chem. Anal. 16th ed., pp. 45–48, 1944.

Under these conditions 5 milligrams of WO_3 were quantitatively recovered even when the acidity was as high as 1+6 HCl, the highest used. Two milligrams of tungstic oxide also gave complete recovery in these acidities when the test solution was allowed to stand overnight. One milligram of WO_3 was recovered quantitatively with acidities up to 1+14 HCl. The acidity of 1+19 HCl—5 percent by volume HCl—was considered optimum, as it gave complete precipitation of tungsten and was high enough to minimize the hydrolysis of elements that form basic insoluble salts. This acidity was therefore used in all the other tests.

The action of brucine on various elements present alone in a final volume of 50 milliliters of 1+19 HCl is summarized below. Unless otherwise indicated the quantity of the element used is 0.4 gram calculated as the element.

Lead, silver, and mercurous mercury precipitated out as chlorides. Brucine gave no reaction if experiments were conducted in nitric-acid solutions. Alkali metals, Be, 0.1 gram; Mg, Ca, Ba, Ce^{+++}, 0.05 gram; Ti, 0.2 gram; Zr, Th, 0.1 gram; V^{+4}, 0.2 gram; Cr^{+3}, U^{+6}, 0.2 gram; Mn, Fe^{++}, 1.0 gram; Fe^{+++}, 1.0 gram; Co, Ni, Cu, Zn, Al, As^{+3}, As^{+5} gave no reaction. One milligram of WO_3 was precipitated quantitatively from a solution containing 1 gram of ferric iron.

Strong oxidizing agents, such as bromine water (10 milliliters of saturated solution), Ce^{+4} (10 milligrams Ce), NO_3^- (0.5 gram $NaNO_3$), V^{+5} (0.2 gram V), $Cr_2O_7^-$ (0.2 gram Cr), and MnO_4^- (10 milliliters of n. $KMnO_4$), gave a characteristic amber-to-red color to the brucine solution.

One milligram of WO_3 was easily recovered in the presence of those oxidizing agents which were not already destroyed by the hydrochloric acid in the solution.

Complete recovery of 1 milligram of WO_3 was obtained in the presence of agents that form with tungsten complexes such as silicate, borate, arsenate, and phosphate. Phosphate is probably carried down as phosphotungstic acid with a mol ratio of 24 WO_3 to 1 P_2O_5.[56] Tungsten, however, was precipitated very incompletely in the presence of oxalate, citrate, and fluoride. Large concentrations of alkali and ammonium salts did not particularly interfere with the precipitation of tungsten as 1 milligram was recovered from solutions containing 5 grams of NH_4Cl and 5 grams of NaCl.

More than 10 milligrams of Sb^{+3} or Sb^{+5}, 0.1 gram Sn^{+2} or Sn^{+4} was partly hydrolyzed from the 50 milliliters acid solution, but these quantities did not react with brucine. The platinum metals,[57] Bi^{+++}, Hg^{++}, Au^{+++} gave very characteristic precipitates with brucine. The bismuth precipitate is soluble, and the precipitates of the other elements are to some extent soluble in the brucine wash solution. The occlusion of bismuth with tungsten in the general procedure for ores should prove very slight. Mercury is volatile at the ignition temperature of tungstic oxide. It is rare that the platinum metals are found in sufficient quantities in tungsten ores to cause serious interference.

One-tenth gram of molybdenum oxide when present alone in the 50-milliliter volume gave no precipitate with brucine, but larger quantities are precipitated incompletely. Thus, for 0.2 gram of MoO_3 the brucine precipitate amounted to a few milligrams of MoO_3. Molybdenum is more

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[56] Simpson, S. G., Schumb, W. C., and Siemenski, M. A., Effect of phosphate on the determination of tungsten: Ind. and Eng. Chemistry, anal. ed., vol. 10, p. 243, 1938.

[57] Ogburn, S. C., Jr., Some new analytical reactions of the platinum metals: Am. Chem. Soc. Jour., vol. 48, p. 2498, 1926.

soluble at higher acidities and less soluble at lower acidities than 5 percent by volume of hydrochloric acid. Cadmium tends to precipitate from solutions more concentrated than 1 milligram Cd per milliliter. Occlusion of cadmium with tungsten, however, should be very slight as the cadmium precipitate is soluble in the brucine wash solution.

PROCEDURE

The procedure for the gravimetric determination of tungsten in ores is essentially the same as that outlined in Scott.[58] The important difference is that tungsten precipitations are made in solutions containing a minimum of nitric acid. In this manner the occlusion of molybdenum oxide with tungstic oxide is considerably diminished.

To 0.4 to 4 grams of finely ground ore in a 400-milliliter beaker add 100 to 200 milliliters of concentrated hydrochloric acid. Cover the beaker with a watch glass and digest on the steam bath for at least 2 hours, stirring occasionally. Remove the cover glass and evaporate to a volume of about 40 milliliters. Add 5 milliliters of nitric acid—more if undecomposed sulfides remain—and evaporate to dryness. Take up with 70 milliliters of 1+4 HCl, digest 20 minutes on the bath, and then dilute to 300 milliliters with water. Add 5 milliliters of brucine solution and digest on the steam bath for about 30 minutes. Remove from the bath and let stand at least 4 hours or preferably overnight at room temperature. The succeeding operations of filtering, extraction of the residue with ammonia, and washing are the same as those used by Scott, except that brucine wash solution is substituted for the cinchonine wash solution.

Evaporate the ammonia extract to a small volume to remove excess ammonia. Add 20 milliliters of concentrated nitric acid and take to dryness on the steam bath. Take up in 35 milliliters of 1+4 HCl, digest a few minutes on the bath, and then dilute to 200 milliliters with water. Add 10 milliliters of brucine solution and digest on the bath for about 30 minutes. Remove from the bath and cool at room temperature for about 4 hours. The next operations of filtering, ignition of the precipitate, volatilization of silica, and correction for impurities are the same as those used by Scott. The correction for molybdenum may be made conveniently a method previously described by Grimaldi and Wells.[59]

COMPARATIVE RESULTS WITH TUNGSTEN ORES

Determinations, using brucine, of tungsten in various ores were found to agree well with similar determinations using cinchonine, as shown in the table below.

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[58] Scott, W. W., Standard methods of chemical analysis, 5th ed., vol. 1, p. 1005, New York, D. Van Nostrand Co., 1939.

[59] Grimaldi, F. S. and Wells, R. C., Determination of small amounts of molybdenum in tungsten and molybdenum ores: Ind. and Eng. Chemistry, anal. ed., vol. 15, p. 315, 1943.

Comparison of determinations of tungsten in ores using brucine and cinchonine

[Analyses of samples 4 and 5 by Victor North and K. J. Murata]

Sample No.	Location	Tungsten mineral in ore	Sample taken (grams)	Percent WO_3 with cinchonine	Percent WO_3 with brucine	Impurities in final tungsten precipitate with brucine (percent of original sample)
1	Cuba	Ferberite	0.4	76.30	76.15	0.10 R_2O_3
2	North Carolina	Wolframite	.4	71.04	70.86	.05 R_2O_3
3	Alaska	Scheelite	1.0	10.22	10.20	.07 R_2O_3
4	California	Scheelite	2.0	4.61	4.41	.02 R_2O_3 .03 MoO_3
5	Nevada	Scheelite	4.0	1.02	1.01	.03 R_2O_3
6	Idaho	Powellite	3.0	.97	.98	.01 R_2O_3 .05 MoO_3
7	Alaska	Scheelite	4.0	.69	.70	.02 R_2O_3
8	California	Scheelite	4.0	.49	.51	.02 R_2O_3
9	California	Scheelite	4.0	.42	.46	.03 R_2O_3
10	Wyoming	Scheelite	4.0	.18	.16	.01 R_2O_3

Sample 1 contained 21.35 percent FeO, 1.79 percent MnO.

Sample 4 contained 1.0 percent MoO_3. The cinchonine procedure gave 0.11 percent MoO_3 as impurity in the final tungsten precipitate.

Sample 5 contained much pyrite.

Sample 6 contained 2.87 percent MoO_3 and 9.95 percent Cu.

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A VOLUMETRIC METHOD FOR THE DETERMINATION OF CARBON DIOXIDE

By Joseph J. Fahey

The quantitative determination of carbon dioxide in rocks and minerals, made by measuring the volume of the gas evolved upon treatment with acid, is very old. Some form of gas-measuring burette is essential. Atmospheric pressure has heretofore been approximated within the gas burette by adjusting the height of the mercury column by means of a leveling bulb. A modification of this procedure, herein described, affords a quick and accurate means of quantitatively determining carbon dioxide in inorganic materials that are decomposed by hydrochloric acid.

The accuracy of the method depends on the following precautions:

1. Complete decomposition of the sample by an acid.
2. Freedom from material other than carbonate that evolves gas when treated with acid.
3. A reaction chamber of minimum size containing a minimum quantity of solution that is a poor solvent for carbon dioxide.
4. Accurate readings of the temperature and barometric pressure.
5. Accurate means of making the pressure within the apparatus equal to that of the atmosphere.

APPARATUS

The apparatus shown in figure 41 consists of a reaction chamber *A* connected to the 50-milliliter burette *D* by the condenser *B* and rubber tubing *C*. The burette, open at the lower end, is held immovable, by a clamp, to the iron stand. The tube *E*, closed at the lower end is a sleeve that can be moved vertically. It contains the burette *D* and is filled with mercury to within about 10 centimeters of the top. *F* is a glass capsule 4 centimeters long with an inside diameter of 7 millimeters. It is the container for the hydrochloric acid.

The reaction chamber *A* is a pyrex test tube, 12 centimeters long with an inside diameter of 12 millimeters. The condenser *B* is a glass tube 40 centimeters long with an inside diameter of 5 millimeters. A 45° bend is made at the midpoint and a 135° bend at the upper end. *C* is a tightly fitting piece of rubber tubing about 5 centimeters long, which acts as a hinge when the reaction chamber *A* is tilted at a 45° angle to the horizontal. *D* is a 50-milliliter burette, the stopcock of which has been cut off. *E* is about 55 centimeters long, with an inside diameter of 2 centimeters. It is filled with mercury to the level marked by *G*. The two stoppers are one-hole rubber stoppers. The component parts are supported by clamps

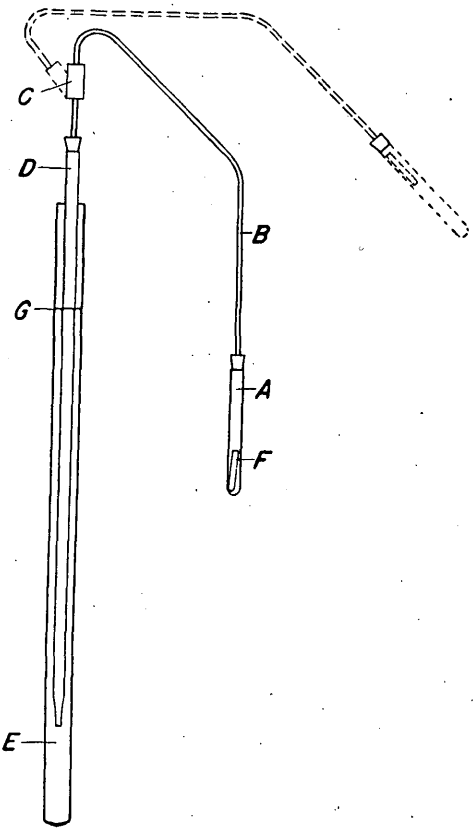

FIGURE 41.—Apparatus for determining carbon dioxide.

and rings attached to an iron stand having a vertical rod about 120 centimeters long.

REAGENTS

1. Saturated solution of sodium chloride.
2. Concentrated hydrochloric acid.
3. Distilled water.

PROCEDURE

A sample, ground to pass a 100-mesh sieve, is weighed and placed in the reaction chamber *A*. The size of the sample should be such that it will yield not more than 70 milligrams of carbon dioxide—35.4 milliliters under standard conditions. If the sample is known to be predominantly a carbonate the weight taken should not exceed 0.1500 gram. If the carbonate content is very low a 1.000-gram sample may be used. To the reaction chamber, in which has been placed a glass rod 4 centimeters long and 1 millimeter in diameter to prevent bumping, is added 2 milliliters of a saturated solution of sodium chloride and 2 milliliters of distilled water. The test tube is slowly heated until gentle boiling takes place, in order to expel any air entrapped in the sample. A rubber stopper is inserted in the test tube, which is then cooled in running tap water to about room temperature and placed in a beaker of water, which is at room temperature, for about 20 minutes. The sleeve *E* is raised until the level of the mercury in the burette *D* is near the zero mark. The rubber stopper is removed, and the glass capsule containing 1 milliliter of concentrated hydrochloric acid is carefully inserted just beyond the opening of the test tube held at an angle of about 45°. The moisture on the inside of the test tube will keep the capsule from sliding down the tube into the salt solution. The test tube is then connected to the condenser *B* by means of a one-hole rubber stopper and held in the 45° position by a support attached to the iron stand. This position is shown by the dotted line in the figure. The pressure inside the burette is now made equal to that in the room by raising or lowering the sleeve *E* until the level of the mercury inside the burette is equal to that in the sleeve. The initial reading is now recorded.

The test tube and condenser are now swung through 45°, the former attaining a vertical position, causing the capsule containing the acid to drop down and into the salt solution. The acid mixes with the salt solution and attacks the carbonate of the sample. Heat from a burner is gently applied, care being taken to prevent a too violent evolution of carbon dioxide, until the reaction ceases. The solution is then gently boiled for about one minute to drive out the dissolved carbon dioxide. During the heating the sleeve *E* is gradually lowered to prevent overflow of the mercury. The test tube and contents are cooled with cold water in a beaker held around the test tube for 2 or 3 minutes. The beaker is then replaced with one containing water at room temperature, which is allowed to remain for 20 minutes. The mercury levels are again adjusted for the final reading. The volume of carbon dioxide evolved is the difference between the final and initial readings. This is reduced to standard conditions of temperature and pressure and the factor 0.001977, which is the weight in grams of 1 milliliter of carbon dioxide at standard conditions, applied to give the weight of carbon dioxide in the sample.

Results with dolomite and calcite

Quantity of sample taken (Grams)	Theoretical CO_2 (Grams)	CO_2 found (Grams)	Error (Grams)
Dolomite:			
0.1000	0.0479	0.0470	−0.0009
.1000	.0479	.0471	− .0008
.1000	.0479	.0470	− .0009
.1000	.0479	.0471	− .0008
.0500	.0240	.0238	− .0002
.0500	.0240	.0238	− .0002
.0100	.0048	.0046	− .0002
Calcite: .1000	.0440	.0438	− .0002

The dolomite used in the tests recorded above contained a visible quantity of clay, which contributed to the minus error in the determinations.

The method here described has been found to be especially suitable for rocks containing less than 10 percent of carbon dioxide.

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GAMMA-RAY STUDIES OF POTASSIUM SALTS AND ASSOCIATED GEOLOGIC FORMATIONS

By H. Cecil Spicer

ABSTRACT

Experimental studies have been made of radioactivity of potassium salts and geological formations associated with the saline deposits of southeastern New Mexico, based on their gamma-ray activity as measured by means of an improved counting-rate meter that gives a rapid and accurate count of the penetrating gamma radiation emitted by the K^{40} isotope of potassium. These studies show that the method may be used to determine potassium with an accuracy that is a function of the time and the quantity of material used. Determinations of potassium were compared with those of uranium and found to agree with the generally accepted ratio of activities within the limits of experimental error. The results also were expressed in terms of the radium equivalent in grams of radium per gram of sample.

INTRODUCTION

The Geiger-Müller tube counter has recently been improved by certain constructional features, with correspondingly more varied adaptions in the measurement of weak radiation, such as radioactivity logs of wells and the radioactive emanations from rocks and minerals. Greatly improved reliability has been achieved by the development of electrical circuits using electronic tubes to assist in the control of the counter tube. Hunt[60] described an audio-frequency meter that could be easily adapted to the counting of randomly spaced pulses, and Gingrich, Evans, and Edgerton[61] adapted a tank circuit and meter, with some other modifications, to this frequency meter for the measurement of random pulses from radioactive emanations. An improved design of the counting-rate meter has been described by Evans and Adler,[62] and a description of a complete new design has been given by Kip and Evans.[63]

The writer is pleased to acknowledge the use of a description and circuit diagram of the counting-rate meter, supplied by Dr. Kip and Dr. Evans as a basis for the apparatus used in this work. Dr. L. F. Curtiss, of the Bureau of Standards, generously constructed the first counter tubes used in the development of the apparatus, and R. K. Bailey, of the Geological Survey, made chemical determinations of potassium for the correlation of many results. The support of all who have contributed in some way to the project is gratefully acknowledged.

It is well known that many rocks and certain minerals contain, in different amounts, one or more of the radioactive elements, uranium, thorium, and potassium. Radioactive substances all possess the common property of emanating optically invisible rays, designated as alpha, beta

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[60] Hunt, F. W., A direct reading frequency meter suitable for high speed recording: Rev. Sci. Inst., vol. 6, pp. 43–46, 1935.

[61] Gingrich, N. S., Evans, R. D., and Edgerton, H. E., A direct reading counting rate meter for random pulses: Rev. Sci. Inst., vol. 7, pp. 450–456, 1936.

[62] Evans R. D., and Adler, R. L., Improved counting rate meter: Rev. Sci. Inst., vol. 10, pp. 332–336, 1939.

[63] Kip. A. F., and Evans, R. D., Improved counting rate meter for radioactivity detection (abstract): Phys. Rev., vol. 59, p. 920, 1941.

and gamma rays. Two of the three are really particles instead of rays; the alpha rays are positively charged helium nuclei and the beta rays negatively charged high-speed electrons. Gamma rays are uncharged electromagnetic radiation intermediate in wave length between cosmic radiation and X-rays and similar in many respects to X-rays. Each radioactive material is only partly recognized by its emanation, and other means are required for complete identification.

The gamma-rays are of primary importance for the present study, and some of their related properties will be briefly emphasized; for more complete information the reader is referred to standard treatises.[64] Electrical and magnetic fields have no effect on the gamma rays. The wave length ranges from 10^{-8} to about 10^{-11} centimeters; the shorter the wave length the more penetrating the radiation and the greater its so-called hardness. The absorption coefficient μ for gamma rays is usually very small and the half-value thickness of penetration $\left(\frac{0.693}{\mu}\right)$ is much larger than for the other radiations. For example, the hardest beta rays are reduced to half their initial value by 0.5 millimeter of aluminum and all are absorbed by 3 millimeters, whereas 30 times as much lead, 1.5 centimeter, is required to reduce the hardest gamma rays to half their initial number; in fact, one foot of iron is penetrated by the hardest rays. In the light of present knowledge, only cosmic rays exceed the gamma-rays in power of penetration. The gamma rays do not ionize the material penetrated directly, but in colliding with molecules they remove electrons, and as beta rays the electrons produce ionization.

Among the common elements known to be radioactive is potassium. Primarily, it gives off beta emanation, but compared to uranium only in the ratio 1:500. Two kinds of beta rays are given off, the softer having a hardness of about 400×10^3 electron volts and the harder 700×10^3 electron volts, with absorption coefficients (μ) for aluminum of 75 and 29, respectively. This indicates a half-value penetration thickness of 0.09 millimeter and 0.24 millimeter, respectively. The hardness of the gamma radiation, however, is 2×10^6 electron volts, comparable to that of the hardest gamma radiation from radium C. The intensity is, as expected, extremely low, being $1/1 \times 10^{10}$. Only three gamma radiations are emitted as 100 potassium atoms disintegrate. Smythe and Hemmendinger[65] have shown that of the potassium isotopes K^{39}, K^{40}, K^{41} only K^{40} is radioactive and thus responsible for the emanations. The abundance ratio of K^{40}/K is given as 1/9000 by Bramley and Brewer.[66] Determinations by Bramley and Brewer[67] for the other radioactive constants of potassium are: $\lambda = (1.56 \pm 0.6) \times 10^{-17}$ second^{-1}; $\theta = 20.3 \times 10^8$ years; $T = (14.2 \pm 3.0) \times 10^8$ years, where λ = disintegration constant, θ = average life, and T = half life period. The isotope ${}_{19}K^{40}$ has a very long life and probably was formed in preterrestrial time by the capture of a neutron ${}_0n^1$ represented by one or both of the following reactions:

$${}_{19}K^{39} + {}_0n^1 = {}_{19}K^{40} \text{ (Simple capture)}$$

$${}_{20}Ca^{40} + {}_0n^1 = {}_{19}K^{40} + {}_1H^1 \text{ (Transmutation with proton emission)}$$

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[64] Rutherford, E., Chadwick, J., and Ellis, C. D., Radiations from radioactive substances, Cambridge Univ. Press, 1930. Hevesy, G. and Paneth, F. A., A manual of radioactivity, Oxford Univ. Press, 1938. Meyer, S. and Schweidler, E., Radio-aktivität, B. G. Teubner, Berlin, 1927.

[65] Smythe, W. R., and Hemmendinger, A., The radioactive isotope of potassium: Phys. Rev., vol. 51, pp. 178–182, 1938.

[66] Bramley, A., and Brewer, A. K., Radioactivity of potassium: Phys. Revs., vol. 53, pp. 502–505, 1938.

[67] Bramley, A., and Brewer, A. K., op. cit.

As the radioactive ${}_{19}K^{40}$ isotope disintegrates into ${}_{20}Ca^{40}$ or into ${}_{18}A^{40}$, electrons, positrons, beta and gamma rays are ejected. Recently Marshak[68] has suggested that K^{40} probably decays by orbital electron capture as well as negatron beta-ray emission.

DESCRIPTION OF COUNTING-RATE METER

The apparatus here described was developed primarily for studying the radioactivity of rocks in general. Its application to potassium salts arose in consequence of the extended investigation of potassium by the Geological Survey and the obvious possibility of using the procedure as an analytical method. While the investigation was in progress a paper on this subject was published by Barnes and Salley.[69] Their method, in which solutions are employed, is discussed in this paper. (See p. 160.) The studies by the writer were made entirely on solid salts and solid samples of various associated substances.

As the Kip-Evans counting-rate meter contained a number of specially designed units not commercially available, it seems appropriate to describe the circuit and some of the changes made, and to give photographs of the completed instrument.

The electrical circuit of the counting-rate meter is composed of the following sections: Counter tube and preamplifier; amplifier; pulse equalizer; integrator; speaker output; visual and recording milliammeter; high-voltage direct-current supply and stabilization; and low-voltage direct-current plate supply and stabilization.

A voltage pulse, produced by the penetration of an ionizing ray through the counter tube, is fed to the 6J7 preamplifier tube, which is connected in the circuit as in the Neher-Pickering[70] design, except that all batteries have been eliminated and the screen-grid voltage supplied by a series-dropping resistor on the high voltage. The preamplifier assists in extinguishing the discharge set up in the counter tube, enabling it to recover faster and be ready for another ionizing ray. It also delivers an amplified negative pulse to the 6SJ7 amplifier tube. The pulse is raised in voltage in the amplifier tube to a level adequate to insure that a minimum pulse size from the counter tube will be sufficient to operate the next stage, a pulse equalizer. The pulse from the amplifier is sharpened down to the resolving time of the equalizer stage, about 10^{-5} second, so that at no time will a single pulse from the counter give more than one pulse through the equalizer. Two 6SJ7's connected as a bias-controlled multivibrator compose the pulse equalizer stage. Oscillation is manually controlled by adjusting the bias.

Leakage losses, with attendant spurious counts, were eliminated between the amplifier-preamplifier stages by a modified version of the coupling condenser used by Kip, the moulded variety being unobtainable. Two circular pieces 14 millimeters in diameter were cut from a 0.005-inch brass sheet, leaving an extruding lug at one point for connection. These discs were separated by a suitable thickness of select mica $\frac{7}{8}$ inch square and the assembly with lugs on opposite sides cemented between two polystyrene pieces 1 by 1 by $\frac{1}{8}$ inch with Amphenol 912B and kept under pressure and slightly raised temperature until completely dry. Capacity

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[68] Marshak, R. E., Forbidden transitions in β-decay and orbital electron capture: Phys. Rev., vol. 61, pp. 431–449, 1942.

[69] Barnes, R. B., and Salley, D. J., Analysis of potassium by its natural radioactivity: Ind. and Eng. Chemistry, anal. ed., vol. 15, pp. 4–7, 1943.

[70] Neher, H. V. and Pickering, W. H., A modified high speed counter circuit: Phys. Rev., vol. 53, p. 316, 1938.

of the resulting condenser is approximately 50$\mu\mu$f and its resistance extremely high under all atmospheric conditions.

The leveled pulses from the equalizer are coupled by condensers to the audio output circuit and to the integrating circuit. The former circuit operates a 6K6G power output having a variable volume control and a small speaker. The latter provides constant voltage pulses to the grid of a 6SJ7, and the output from this tube is of proper sign to energize the condenser-resistance tank circuit. The energy transferred to the tank circuit is controlled by the screen-grid voltage. Voltage on the tank condenser is read by a degenerative vacuum-tube voltmeter, thus giving the average counting rate.[71]

A tank condenser with a polystyrene dielectric was unobtainable, and a dykanol-filled high-voltage, high-resistance unit was substituted. Hysteresis losses are perhaps slightly more in the substitute condenser, but highly satisfactory performance has been maintained over a long period of operation.

Tank-circuit sensitivity is controlled by variation of the screen-grid potential of the 6SJ7 and by changing the resistance or time-constant of the CR tank. These two controls are ganged together so that, in changing ranges, appropriate time constants are introduced with screen voltage. The sensitivity, or counting rate, for full-scale deflection of the indicating meter is calibrated in eight controllable ranges to read from 100 to 20,000 counts per minute.

A 6AC7 tube connected as a triode is used as a degenerative vacuum-tube voltmeter. Output readings are linear to a high degree as a result of the inverse feed back. Full-scale output is 5 milliamperes; this operates a panel meter and a recording meter, which may be removed from the circuit. Compensation for removal of the recorder from the circuit is made automatically by introducing a resistor in its place by means of a plug-and-jack switching arrangement.

The recorder, which is a model AW Esterline-Angus 5-milliampere graphic meter in a wall case, is driven by a synchronous motor. It is automatically turned on and off by the main instrument switch. Five paper speeds are provided, but the 3-inch- and 6-inch-per-hour speeds have been found most useful.

Calibration of the counting-rate meter ranges is accomplished by a pulse generator. It is a bias-controlled multivibrator fed by low-voltage 60-cycle alternating current and is arranged to give constant frequencies of uniformly sharp pulses in eight ranges. The pulse generator is calibrated by delivering the pulses to the deflecting plates of an oscilloscope and adjusting the variable resistance in each range until the proper wave form is indicated on the screen.

Direct current for the plate supply is obtained by full-wave rectification of 350 volts by a 6X5 and smoothed by a choke-input, resistor, high-capacity electrolytic condenser filter, and the filter-output voltage is stabilized by two VR105/30 tubes in series and operated near midcurrent range. For the reference voltage required by the 6C6 to control the high-voltage regulator, the output from the VR105/30 tubes is further stabilized by two ¼-watt resistorless neon lamps having sufficient resistance in series to glow with their cathodes entirely active.

The high-voltage direct current required for the operation of the counter tube is obtained by half-wave rectification of the output from a

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[71] Schiff, L. I., and Evans, R. D., Statistical analysis of the counting rate meter: Rev. Sci. Inst., vol. 7, pp. 456–462, 1936.

television transformer by the 2X2 tube, and is smoothed by a condenser-input-resistance filter and stabilized by a degenerative feedback amplifier. A 0.3-megohm, 1-watt resistor in the cathode circuit of the 2X2 is required to drop the voltage to the value for which the filter was designed. Taps are provided and input and output resistances ganged so that voltages from 400 to 2000 may be obtained. A linear potentiometer controlling the screen-grid voltage of the 6C6 in the filter adjusts the between-range high voltage. Additional stabilization for the entire counting-rate meter is provided by a saturated core-type line-voltage regulator which keeps the line voltage constant to ± 2 percent.

A front view of the complete instrument is shown in plate 3. The preamplifier unit is in the cabinet at the top left and the pulse generator is below it. The other parts of the counting-rate meter are in the large cabinet, and the graphic meter is at the right. A rear view of the instruments with the cabinets removed is in plate 4. In this view, the preamplifier is at the right on the large panel, and the pulse generator is at the left. A third view (pl. 5) shows the components inside the chassis.

All range controls, range switches, high-voltage control, bias and volume adjustments, and vacuum-tube voltmeter controls are mounted on the panels. Pin-jacks are brought out for testing voltages and connecting a signal into the amplifier.

The greatest care was exercised in shielding and insulation to avoid spurious counts from leakage. All wires carrying a pulse were shielded and isolated, and high-voltage wires were placed in varnished cambric tubing. All wiring was done with radio-frequency insulated wire.

As essentially the same technique for adjustment of the counting-rate meter was described by Kip and Evans[72] it will not be discussed here.

TECHNIQUE OF MEASUREMENT

Among the methods of measurement tried, only one gave consistently reproducible quantitative results and left the sample available for further study. Flat trays or other containers, placed near the counter tube, made it possible to determine whether a pulverized sample contained any radioactive material. Large pieces placed in close proximity to the counter tube also gave qualitative indications. The shape of the samples in the above methods made quantitative determinations of radioactivity very nearly impossible. The technique described by Evans and Mugele[73] of casting a measured quantity of the powdered sample in a plaster-of-paris mold was used with little success. A good mixture of the sample and plaster was hard to obtain, and after being cast the sample was no longer readily available for further study.

Coaxial cylindrical containers were constructed to hold the pulverized sample in the space between cylinders, and the inner cylinder made to fit snugly over the sensitive area of the counter tube. The outer cylinder was lead-free brass tubing, 1¾ inch in outer diameter, with a wall thickness of 1/32 inch; the inner cylinder was 0.005 inch brass shim stock, ⅞ inch inside diameter, which is sufficiently thick to absorb all beta rays. One end was closed, and a tightly fitting cap placed over the other to enclose the sample. The volume available for the sample was approximately 150 milliliters. This apparatus was developed independently of that described by Pontecorvo.[74]

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[72] Kip, A. F., and Evans, R. D., Improved counting rate meter for radio-activity detection (abstract): Phys. Rev., vol. 59, p. 920, 1941.

[73] Evans, R. D., and Mugele, R. A., Increased gamma-ray sensitivity of tube counters: Rev. Sci. Inst., vol. 7, pp. 441–449, 1936.

[74] Pontecorvo, B, Radioactivity analyses of oil-well samples: Geophysics, vol. 7, pp. 90–94, 1942.

A number of materials were tested for use as a blank for making the background test and as a mixing material to use with intense radioactive

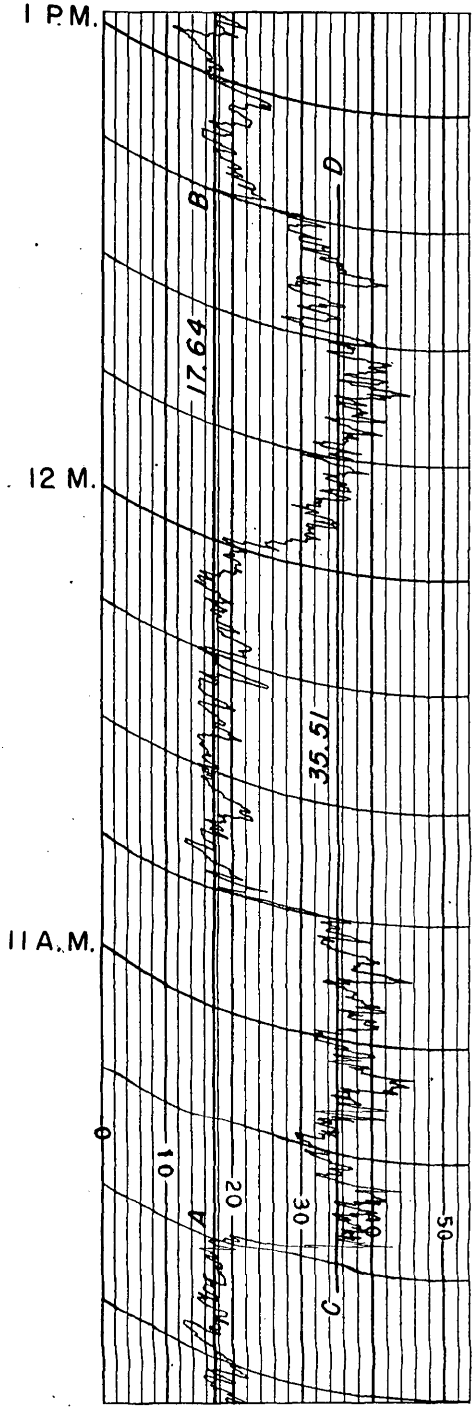

Figure 42.—Record of a counting test with potassium bicarbonate.

substances. When anhydrous sodium sulfate, chemically pure, which has a specific gravity near that of average rock, was tested for radioactivity, it caused no measurable increase in background. It was therefore adopted for use as the blank material.

In order to reduce the background count, a lead cylinder was cast to enclose the sample container and counter tube. In this way 5 centimeters of lead completely surrounds the active counter area, and the background was reduced in this manner to about 40 percent of the unshielded background count. It can be shown by statistical theory that a considerable increase in the accuracy of measurement is gained by background reduction.

The samples, on which gamma-ray measurements were to be made, were pulverized to pass a 60-mesh sieve. A container was filled with the powder and the sample weight determined. The sample and blank containers were then alternately placed over the counter tube for equal intervals, usually 15 to 45 minutes, and the measurements extended until the desired accuracy was obtained. Weakly radioactive materials require longer runs for a cêrtain accuracy than do strongly radioactive ones. This results from the demonstration in statistical theory that a definite number of gamma-ray counts above background are required to give a certain degree of accuracy.

Part of a chart from a test run on a sample of radioactive material alternated with the background is shown on the accompanying record of a test with potassium bicarbonate. (See fig. 42.) The chart speed was 3 inches an hour with each section representing a 15-minute interval. The full counting-rate scale is 100, and each line shows 2 counts. The

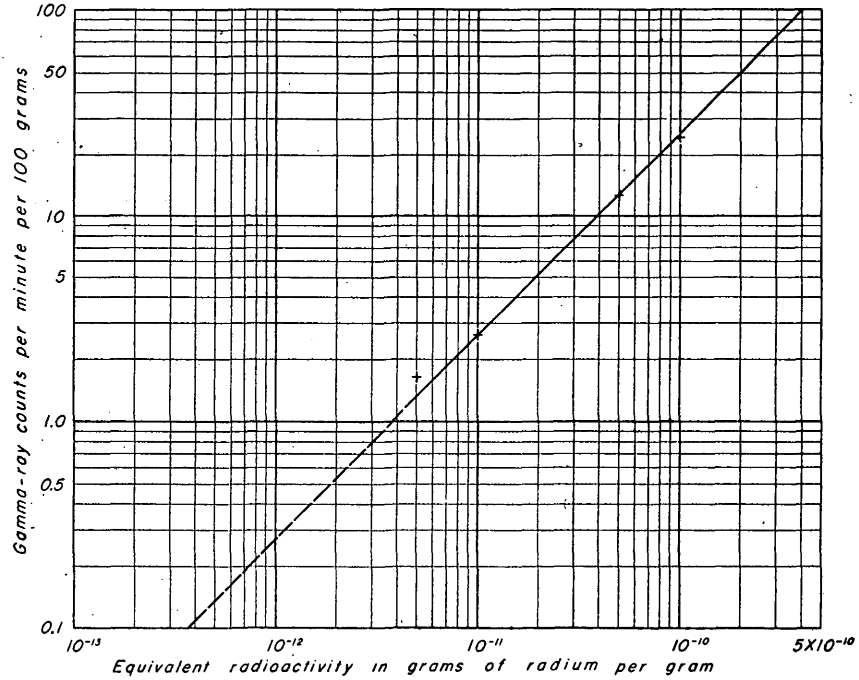

FIGURE 43.—Gamma-ray counts per minute in terms of grams of radium per gram of sample.

line *A–B* drawn through the background shows the average background rate per minute measured for the entire period covered by the test, and the line *C–D* shows the average rate of gamma rays per minute for potassium bicarbonate—17.64 and 35.51 counts per minute, respectively.

The chart of the test is analyzed by measuring the areas under sections of the trace with a planimeter and computing the average counting rate for each period and a composite result for background rate and sample rate for the entire run. Two minutes are removed from the beginning of each period on the record during which the counting-rate meter normalizes itself to the new counting rate. The statistical values of standard deviation and probable error are next computed for each rate. Formulas are given in the section on statistics.

The difference between the average sample and average background rates is the effect of the radioactivity present in gamma-ray counts per minute. This procedure was adopted to convert the value to gamma-ray counts per minute per 100 grams of sample, but any other arbitrary unit would be equally satisfactory. Figure 43 is a chart prepared from determinations of the gamma-ray activity of radioactive standards and gives the equivalent radioactivity in grams of radium for each gram of sample in terms of gamma-ray counts per minute.

Standards of low radioactive content were prepared by adding calculated amounts of carnotite of known uranium content to sodium sulfate. The mixtures were then compared by the counting-rate meter with radium standards supplied by the Bureau of Standards as prepared under the direction of L. F. Curtiss.

USE OF STATISTICAL THEORY

A statistical analysis of the radiation measured by the Geiger-Müller counter connected as an output meter, or counting-rate meter, was given by Schiff and Evans.[75] If pulses, in this instance produced by gamma-rays, are randomly generated from a source of constant strength and are distributed according to Poisson's law, they will build up a charge on the counting-rate meter tank condenser, each pulse adding a small amount of charge. The resistance across the condenser, however, causes a decay of the condenser charge at a definite rate; thus the reading of the output meter is proportional to the charge remaining on the condenser and is a measure of the counting rate.

The expected fractional standard deviation of a single reading is $\sigma=(2xRC)^{1/2}$, and the expected value of *n* readings is the same as for a single reading. Fractional standard deviation is the standard deviation divided by the charge expected per unit of time caused by an expected constant number of pulses. By observing the output meter continuously for a period of time *T*, the expected fractional standard deviation becomes

$$(T)=\frac{(1+2T/RC)^{1/2}}{(1+T/RC)}\sigma_1 \tag{1}$$

with a fractional probable error

$$p(T)=0.6745\sigma(T) \tag{2}$$

In the above equations

σ = fractional standard deviation,

σ_1 = fractional standard deviation of a single observation,

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[75] Schiff, L. I., and Evans, R. D., Statistical analysis of the counting rate meter: Rev. Sci. Inst., vol. 7, pp. 456–462, 1936.

T = time interval in minutes,
RC = electrical time constant—1 minute unless otherwise noted for results given.

The observational limit of counting x particles per unit of time against a background of y particles per unit of time has the statistical limit as shown by Evans[76]

$$x = 0.6745\ (y)^{1/2} \qquad (3)$$

Thus it is evident that lowering the background reduces the time necessary to obtain a reading having a probable error of equal amount.

Care should be taken to see that the counting-rate meter has been operated long enough to reach temperature equilibrium. Also, in changing rates time should be allowed for equilibrium to be reached; it may be computed from

$$t_0 = RC(1n\ 2x\ RC/2 + 0.394) \qquad (4)$$

For counting rates up to about 1,500 per minute, 2 minutes suffices for equilibrium time.

GAMMA-RAY ACTIVITY OF FORMATIONS IN THE CARLSBAD, N. MEX. AREA

Recent measurements of radioactivity in drill holes suggested that some quantitative study of the radioactivity of the formations associated with the potash deposits would be of value. Such a study was started in the fall of 1941, but it was not completed until recently because of other assignments.

Samples of the potassium ores and refined products were obtained for the tests by H. I. Smith, of the Geological Survey, through the courtesy of the United States Potash Co., the Potash Co. of America, and the Union Potash Co., all of Carlsbad, N. Mex. Most of the formation samples were collected by R. H. King upon request by the writer.

The samples tested for gamma-ray activity are listed in the table below, with description and location and the collector's name. As no drill cuttings had been saved from the formations above the salt, it was necessary to collect samples of the formations desired from known outcrops close by or from recent drill cores.

All samples were measured for their gamma-ray activity by the method previously described. The period of testing, with few exceptions, was extended sufficiently to obtain a fractional probable error of less than ±0.01. Because the statistical treatment adopted for all similar materials was the same, intercomparisons are possible.

The results of gamma-ray counting with the counting-rate meter will now be presented. In the table below columns 5 and 6 give the expected counts per minute and the radium equivalent, computed from the best determination in each group, and the variation from the expected quantities tabulated in columns 7 and 8. The accuracy of the results may be judged from the ratios in columns 9 to 12. Counts per minute/percent *K* corresponds to the reciprocal slope of the linear relation of the gamma emanation from potassium. Determination of its experimental value will be explained in a following section (p. 159); for a comparative figure, counts per minute/percent K = 0.2425. The closeness of similarity of the three remaining ratios is also an indication of accuracy of the over-all measurements. Percentage differences between the three ratios are noted to be small. For those preferring interpretation and comparison by

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[76] Evans, R. D. and Mugele, R. A., Increased gamma-ray sensitivity of tube counters: Rev. Sci. Inst., vol. 7, pp. 441–449, 1936.

Samples tested

Collectors: R. K. Bailey (B); R. H. King (K); R. H. King and W. E. Hale (K-H); W. B. Lang (L); R. D. Reeder (R); H. I. Smith (S)]

Sample	Location (sec., T., R.)	Description	Thickness (feet)	Collector
Pierce Canyon redbeds:				
Red shale	5, 21 S., 30 E	Contains bands of gray sandstone, locally cross-bedded on small scale; blotches of gray sandstone, streaks of maroon sandstone; some gray waxy shale; color is more or less mottled.	6–8	K
Red-brown sandstone	5, 21 S., 30 E	Massive, thick-bedded, cross-bedded; weathers to rounded hummocks; forms bench and scarp.	30	K
Brownish-red sandstone, bed 17	5–16, 21 S., 30 E	Soft, shaly, friable, laminated; abundant gray reduction spots; harder zones form benches or prominent ledges.	105	K
Orange-brown sandstone, bed 19	5–16, 21 S., 30 E	Thin to medium-bedded; gray reduction spots; exhibits peculiar structure resembling septarian concretions.	5	K
Rustler formation:				
Green shale	2, 23 S., 28 E	Greenish to yellowish, seemingly transitional.	1/2–1	K
Maroon shale	2, 23 S., 28 E	Very waxy, upper part greenish-gray; contact very irregular.	3–5	K-H
Dolomite	2, 23 S., 28 E	Tan and buff, thin-bedded; some cavities; bands of small nodules of dolomite crystals; small geodes lined with dolomite crystals. Numerous *joints filled with Gatuna sand.*	20–30	K-H
Gypsum	2, 23 S., 28 E	Massive to sugary, white to light gray, some pink; very fine-banded.	3	K-H
Anhydrite	18, 21 S., 30 E	Contains some polyhalite core from 951 ft.	----	R
Halite	18, 21 S., 30 E	Various impurities in small amounts. Core from 970 ft.	----	R
Blue halite	--------	Large pieces obtained from Potash Co.	----	S
White polyhalite	18, 21 S., 30 E	Contains some halite and anhydrite; core from 930 ft.	----	R
Salado formation:				
Crude sylvite	--------	Mine ore from Potash Co. of America.	----	S
Crude sylvite	--------	Mine ore from U. S. Potash Co.	----	S
Crude langbeinite	--------	Mine ore from Union Potash Co.	----	S
Carnallite	--------	From Union Potash Co.	----	S
Miscellaneous and refined products:				
Coarse concentrate	--------	From Potash Co. of America.	----	S
Fine concentrate	--------	do	----	S
Tails	--------	do	----	S
Granular muriate	--------	From U. S. Potash Co.	----	S
Refined muriate	--------	do	----	S
50 percent muriate	--------	From Union Potash Co.	----	S
60 percent muriate	--------	do	----	S
Sulfate of potash 50–60 percent	--------	do	----	S
Carnallite	--------	From Thompson, Utah.	----	S
Calcite	--------	Stalactite from Carlsbad Cavern.	----	L

Results of tests on potassium ores

Sample	Potassium as K (percent)	Gamma-ray counts per minute per 100 grams	Radium in 10^{-11} grams/gram	Gamma-ray counts per minute expected	Radium expected	Variation of gamma-ray counts per minute per 100 grams	Variation of radio-activity equivalent	Ratio of gamma-ray counts per minute to percent K	K percent	Radium equivalent	Gamma-ray counts per minute
				Based on percent K in coarse concentrate					Ratio of sample to coarse concentrate		
Potash Co. of America:											
Crude sylvite	21.95	5.17	1.97	5.29	2.00	−0.12	−0.03	0.2355	0.4276	0.4095	0.4176
Coarse concentrate	51.33	12.38	4.81	12.38	4.81	.00	.00	.2412	1.0000	1.0000	1.0000
Fine concentrate	50.52	12.09	4.71	12.18	4.75	− .09	− .04	.2393	.9842	.9792	.9766
Tails	.60	.06	[1]< .04	.14	----------	− .08	----------	.1000	.0117	----------	.0050
				Based on percent K in refined muriate					Ratio of sample to refined muriate		
United States Potash Co.:											
Crude sylvite	18.21	4.20	1.60	4.43	1.68	−0.23	−0.08	0.2306	0.3526	0.3343	0.3245
Granular muriate	41.77	10.36	4.02	10.16	3.93	+ .20	+ .09	.2531	.8087	.8154	.8248
Refined muriate	51.65	12.56	4.93	12.56	4.93	.00	.00	.2432	1.0000	1.0000	1.0000
				Based on percent K in 60 percent muriate					Ratio of sample to 60 percent muriate		
Union Potash Co.:											
Crude langbeinite	18.30	4.31	1.64	4.44	1.70	−0.13	−0.06	0.2355	0.3597	0.3410	0.3487
50 percent muriate	42.19	10.41	4.07	10.25	4.00	+ .16	+ .07	.2467	.8294	.8462	.8422
60 percent muriate	[2] 50.87	12.36	4.81	12.36	4.81	.00	.00	.2430	1.0000	1.0000	1.0000
Sulfate of potash, 50–60 percent	37.73	8.90	3.42	9.17	3.55	− .27	− .07	.2359	.7417	.7110	.7201

[1] In 10^{-12} grams/gram radium equivalent.

[2] Potassium content redetermined by R. K. Bailey.

Results of gamma-ray measurement of material from various formations

[P.C.A., Potash Co. of America; U.P.C., Union Potash Co.; U.S.P.C., United States Potash Co.]

Sample (N)	Background (B) only			Sample and background (N+B)			Gamma-ray counts per minute per 100 grams	Relative sensitivity $\frac{N-B}{\sqrt{N+B}}$	Radium equivalent in 10^{-12} grams/gram
	Gamma-ray counts per minute	Statistical constants (fractional)		Gamma-ray counts per minute	Statistical constants (fractional)				
		Standard deviation	Probable error		Standard deviation	Probable error			
Pierce Canyon redbeds:									
Red shale	17.24	±0.015	±0.010	18.38	±0.007	±0.005	0.87	0.191	3.29
Red-brown sandstone	18.93	± .008	± .005	22.26	± .006	± .004	1.76	.519	6.65
Brownish-red sandstone (bed 17)	19.39	± .008	± .006	20.61	± .008	± .006	.69	.193	2.59
Orange-brown sandstone (bed 19)	10.29	± .014	± .010	12.17	± .013	± .009	.96	.397	3.62
Rustler formation:									
Green shale	12.52	± .011	± .007	14.13	± .010	± .007	.93	.312	3.50
Maroon shale	12.87	± .012	± .008	14.07	± .011	± .007	.64	.519	2.40
Dolomite	12.44	± .014	± .009	13.36	± .012	± .008	.55	.181	2.07
Gypsum	11.33	± .011	± .008	11.56	± .011	± .008	.13	.048	.48
Anhydrite	10.64	± .014	± .010	11.26	± .014	± .009	.26	.132	.59
Halite	11.53	± .012	± .008	11.72	± .011	± .008	.11		.40
Blue halite	41.78			41.86			.08		<.40
White polyhalite (in gypsum)	10.96	± .013	± .008	11.35	± .012	± .008	.18	.083	.67
Salado formation:									
Crude sylvite	33.79	± .006	± .004	43.09	± .005	± .003	5.17	1.061	19.70
Crude sylvite	18.41	± .009	± .006	25.85	± .004	± .003	4.20	1.118	16.00
Crude langbeinite[3]	34.74	± .007	± .004	44.58	± .005	± .003	4.31	1.105	16.40
Carnallite[3]	18.43	± .009	± .006	22.17	± .008	± .005	2.91	.587	11.10
Miscellaneous and refined products:									
Coarse concentrate[1]	34.34	± .007	± .005	57.08	± .005	± .004	12.38	2.378	48.10
Fine concentrate[1]	34.37	± .007	± .005	55.70	± .005	± .004	12.09	2.248	47.10
Tails[1]	14.84	± .011	± .008	14.90	± .011	± .007	.06	.011	<.40
Granular muriate[2]	18.36	± .009	± .006	36.40	± .006	± .004	10.36	2.438	40.20
Refined muriate[2]	34.94	± .007	± .005	57.59	± .006	± .004	12.56	2.355	49.30
50 percent muriate[3]	34.39	± .006	± .004	51.93	± .005	± .004	10.41	1.888	40.70
60 percent muriate[3]	34.24	± .007	± .005	55.41	± .005	± .004	12.36	2.236	48.10
Sulfate of potash 50-60 percent[3]	34.37	± .007	± .005	52.32	± .006	± .004	8.90	1.928	34.20
Carnallite[4]	18.20	± .009	± .006	20.65	± .008	± .006	1.73	.393	6.55
Calcite[5]	10.17	± .010	± .007	10.99	± .013	± .009	.37	.178	1.38

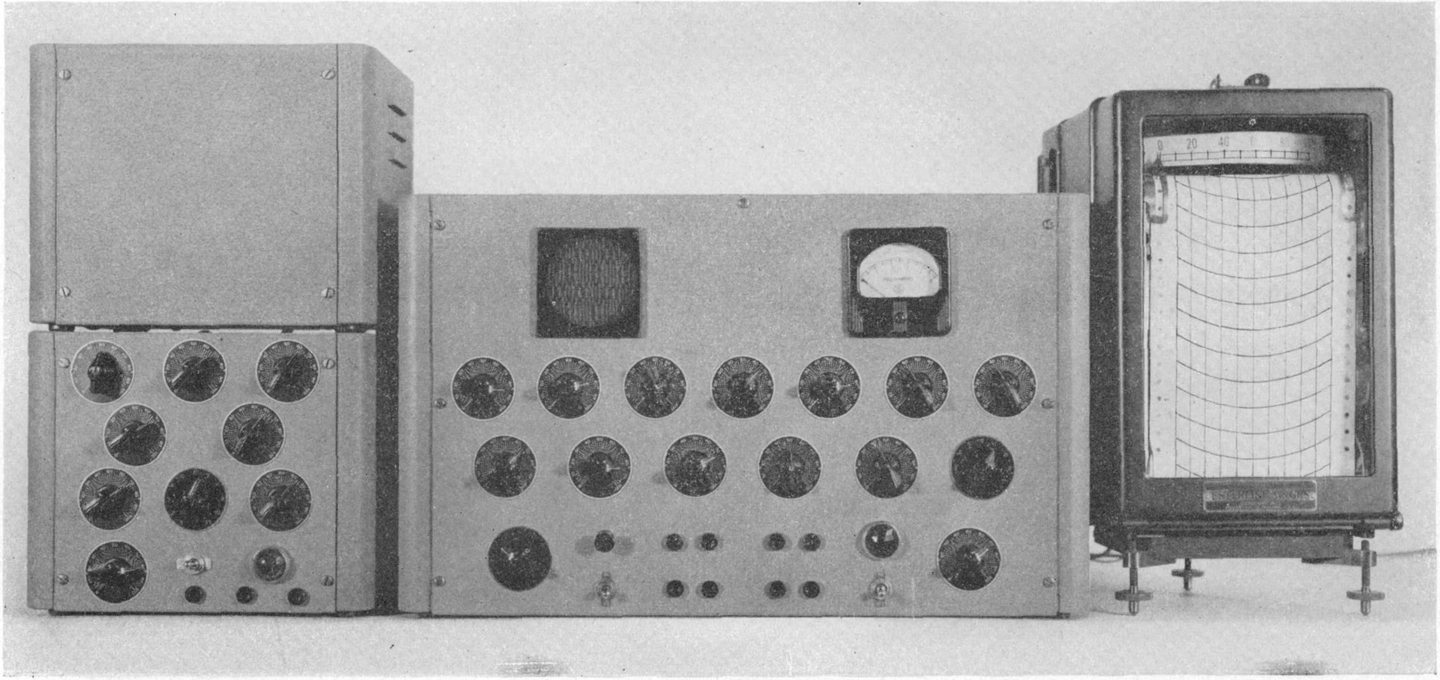
[1] Potash Company of America.

[2] United States Potash Company.

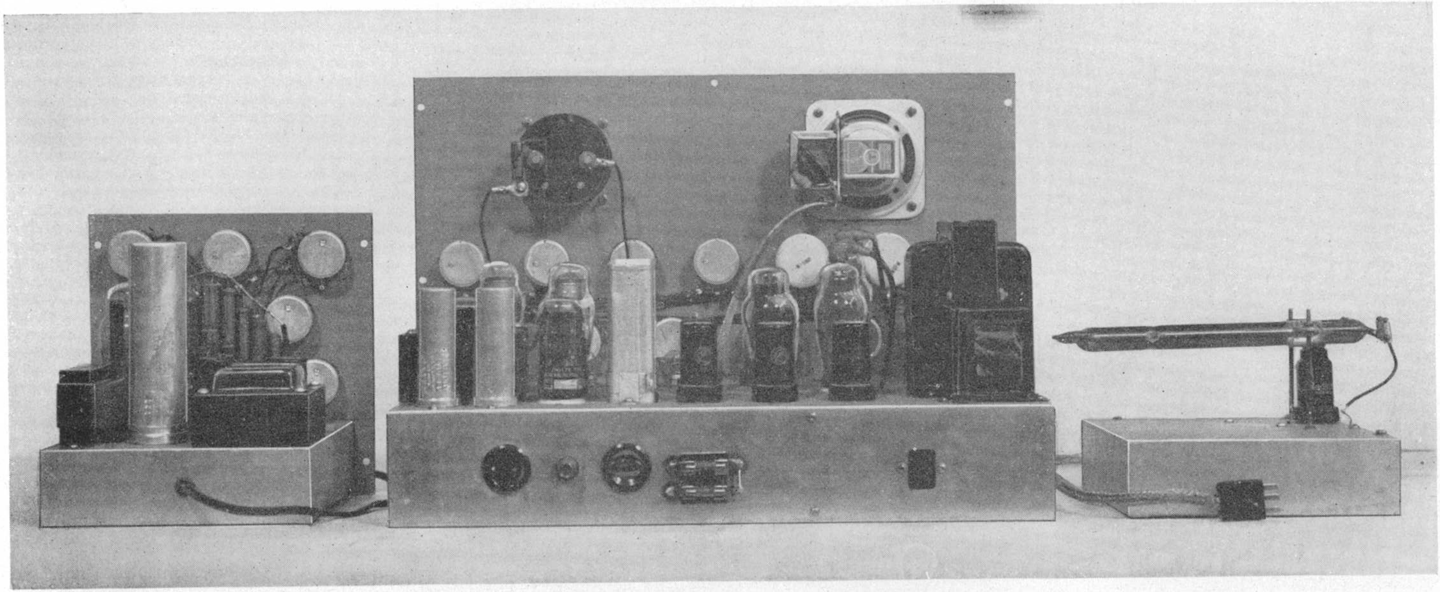
[3] Union Potash Company.

[4] Carnallite from Thompson, Utah.

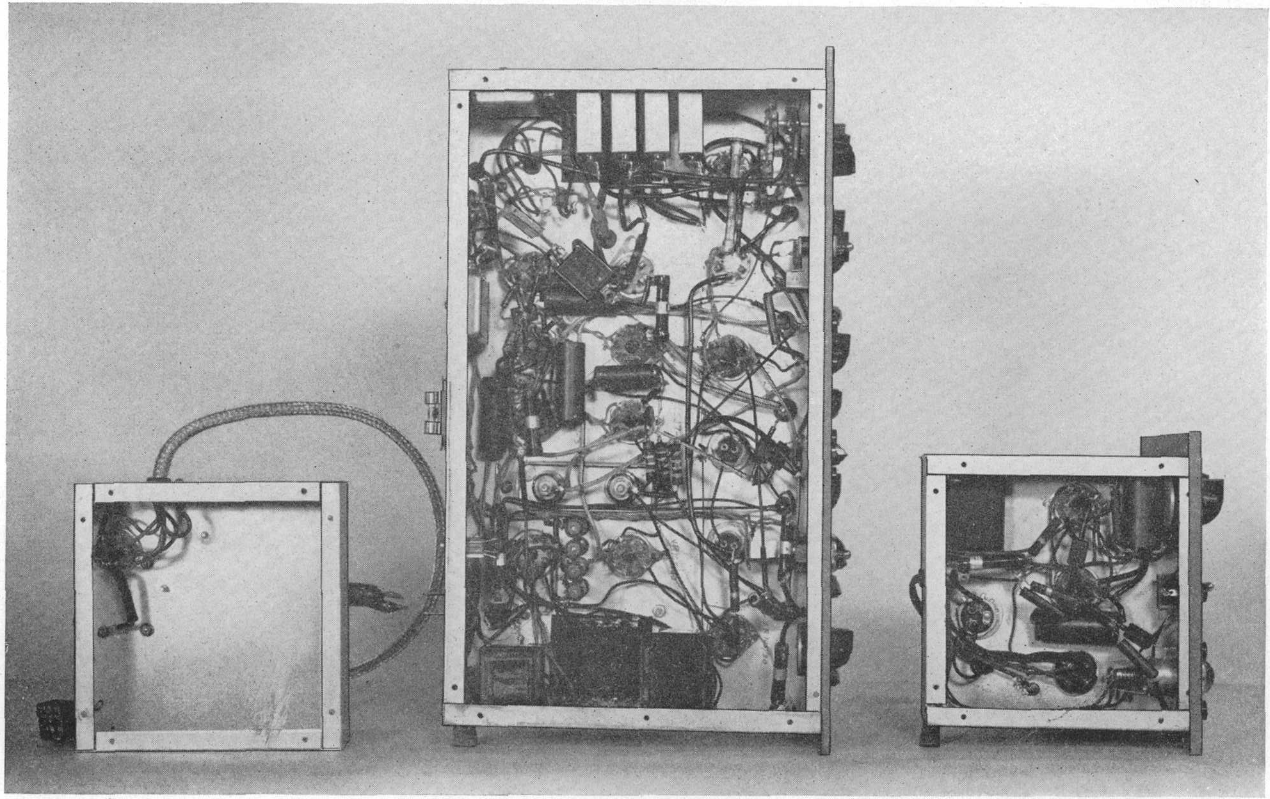
[5] Stalactite from Carlsbad Cavern.



FRONT VIEW OF COUNTING-RATE METER.



REAR VIEW OF COUNTING-RATE METER.



INSIDE VIEW OF COUNTING-RATE METER.

charts the results are expressed by companies in bar graphs in later figures, except that the ratio of counts per minute/percent K is omitted.

Gamma-ray measurements with the counting-rate meter have been made on some of the formations associated with the salt deposits, as described in the table below.

The results for the potassium-bearing substances tested are included for comparison. Two substances of interest, but indirectly related, also are added—a stalactite from Carlsbad Cavern, and carnallite from southeastern Utah.

In the table, column 9 shows the relative sensitivity of the counter, according to Evans.[77] This is a statistical quantity and forms a part of the fractional probable error; thus, the precision of a measurement depends linearly upon it.

A bar graph showing the radium equivalent in grams/gram obtained for the formations is presented in figure 44. Bar graphs of results of tests on ores and concentrates from the several potash companies are presented in figures 45, 46, and 47. The numerical values are in the tables on pages 153 and 154.

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[77] Evans, R. D., and Mugele, R. A., op. cit.

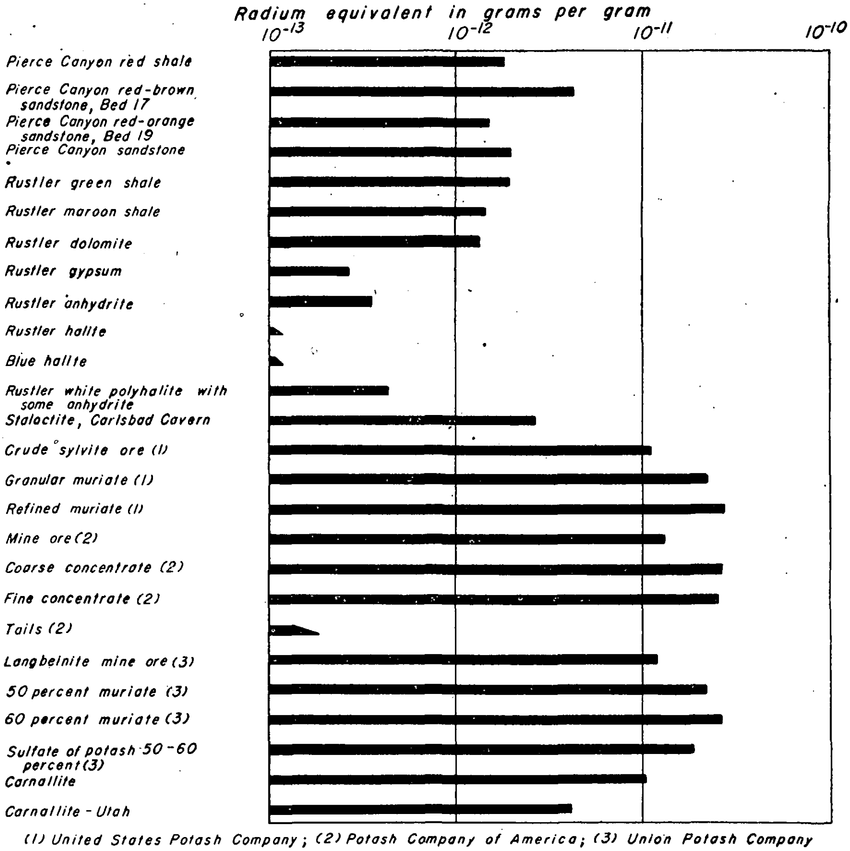

FIGURE 44.—Radium equivalent of formations tested.

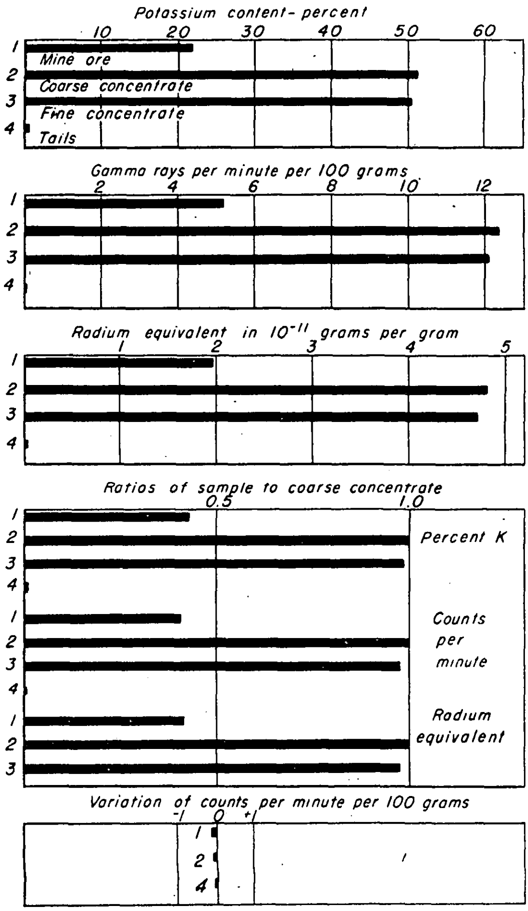

FIGURE 45.—Measurements on ores and concentrates, Potash Company of America.

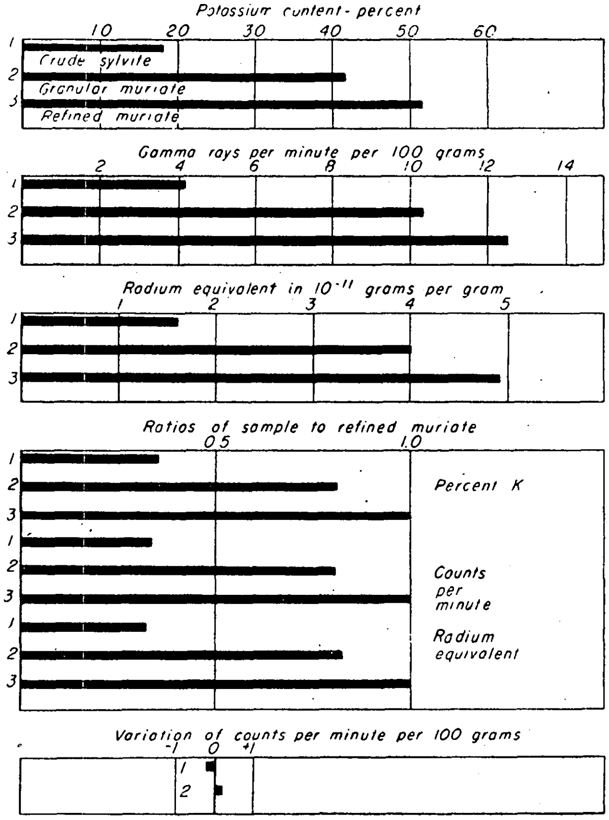

FIGURE 46.—Measurements on ores and concentrates, United States Potash Co.

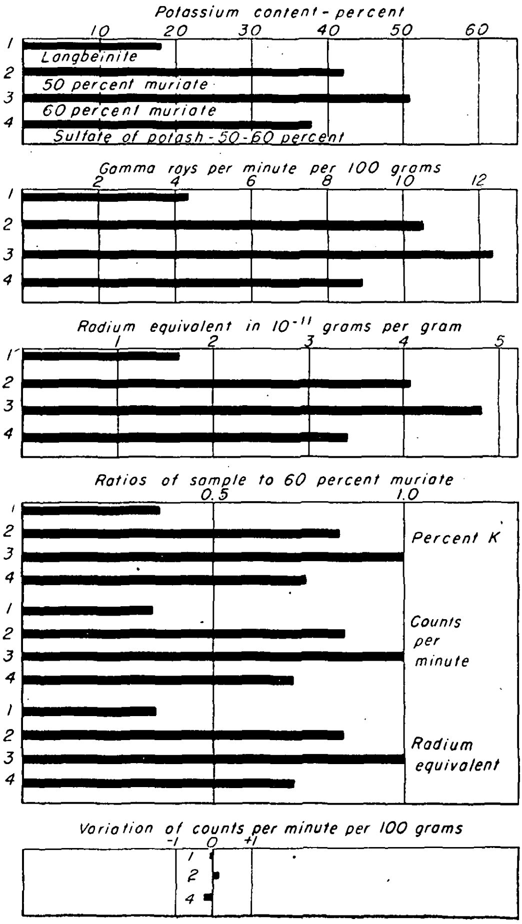

FIGURE 47.—Measurements on ores and concentrates, Union Potash Co.

EXPERIMENTAL DETERMINATION OF THE SLOPE OF THE LINEAR RELATION OF THE GAMMA EMANATION FROM POTASSIUM

That the radioactivity of potassium is proportional to the potassium content is stated by Hevesy and Paneth[78]. To test the results obtained by the counting-rate meter on the potassium samples, counts per minute per 100 grams of sample were plotted as abscissas, and potassium contents in percent as ordinates in figure 48.

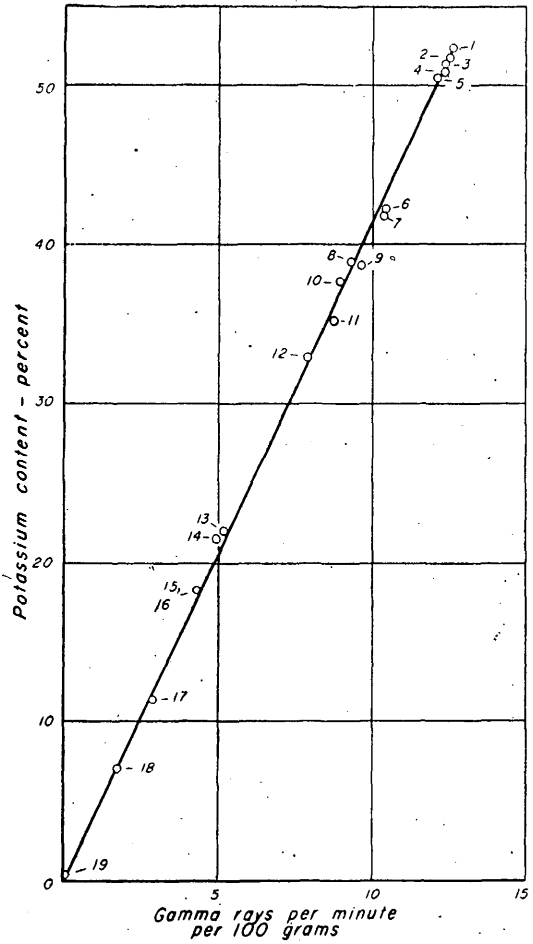

FIGURE 48.—Relation between gamma rays per minute and potassium content.

The table below gives the complete numerical results of the tests on potassium samples from which figure 48 was prepared. The numbered order of the samples corresponds to the numbers on figure 48. The last two columns show the probable errors of the sample and of the sample minus background.

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[78] Hevesy, G., and Paneth, F. A., Radioactivity, 2d ed., p. 236, Oxford Univ. Press, London, 1938.

Gamma-ray counts per minute on various potassium samples

Sample	Percent K	Gamma-ray counts per minute per 100 grams	Standard deviation of sample (N)	pT of sample (N)	pT of N−B
1 KCl (Am. Chem. Soc.)	52.44	12.62	±0.42	±0.28	±0.31
2 Refined muriate (U.S.P.C.)	51.65	12.56	± .33	± .22	± .26
3 Coarse concentrate (P.C.A.)	51.33	12.38	± .31	± .21	± .26
4 60 percent muriate (U.P.C.)	50.87	12.36	± .29	± .29	± .26
5 Fine concentrate (P.C.A.)	50.52	12.09	± .29	± .20	± .26
6 50 percent muriate (U.P.C.)	42.19	10.41	± .27	± .19	± .24
7 Granular muriate (U.S.P.C.)	41.77	10.36	± .29	± .20	± .26
8 Potassium bicarbonate	39.06	9.30	± .27	± .18	± .23
9 Potassium nitrate	38.69	9.62	± .42	± .28	± .34
10 50–60 percent K_2SO_4 (U.P.C.)	37.73	8.90	± .29	± .20	± .24
11 Potassium bisulfite	35.17	8.77	± .40	± .27	± .33
12 Potassium bromide	32.85	7.83	± .36	± .24	± .28
13 Mine ore (P.C.A.)	21.95	5.17	± .22	± .15	± .21
14 Potassium iodide	21.66	4.93	± .35	± .24	± .31
15 Langbeinite (U.P.C.)	18.30	4.31	± .23	± .15	± .21
16 Crude ore (U.S.P.C.)	18.21	4.20	± .10	± .07	± .13
17 Carnallite (U.S.P.C.)	11.37	2.91	± .17	± .11	± .13
18 Carnallite (Utah)	6.81	1.73	± .17	± .11	± .16
19 Tails (P.C.A.)	.60	.06	----------	----------	------

Measurements on the crude and refined ore materials were augmented by tests with the counting-rate meter on six potassium salts; the potassium chloride was pure according to standards of the American Chemical Society. The results of these tests served to fill in the ranges between the mined salts. The potassium iodide selected for test was of United States Pharmacopeia grade and the results, when plotted, varied far beyond the probable error expected for the salt, indicating by its position that the potassium content was low. A quantitative test by R. K. Bailey verified the determination by the counting-rate meter, and a qualitative test gave a strong indication of sodium.

The slope of the line in figure 48 represents the linear relation of the gamma counts to the potassium content. Its value is $m=4.124$ in the equation of a straight line $y=mx+b$; because the intercept $b=0$ it reduces to $y=mx$. The reciprocal slope $1/m=0.2425$. As this value of the slope of the linear relation existing between the gamma counts per minute per 100 grams and the potassium content has been determined, it is very convenient and accurate to use the counting-rate meter as a method for the quantitative determination of potassium in any dry powdered or granular substance. Counts per minute per 100 grams multiplied by the slope gives the potassium content in percent.

For the length of time the sample was tested and the small amount of sample used, about 175 grams, the average accuracy of a determination is within ±1 percent. The accuracy may be improved by longer tests and more material in each sample. By applying the probable error to each test the range of error can be statistically determined.

Recently a method was described by Barnes and Salley[79] for determining the potassium content of solutions by means of a specially designed counter tube in which a mixture of beta and gamma rays are counted to give a quantitative determination of potassium. Because the beta emanations are easily absorbed and a variation in density causes an inverse effect upon the number of rays absorbed, a correction factor for solution density has to be appled in this method.

The absorption constants μ for the beta emanation of potassium are 75 and 29 in aluminum, and for the gamma rays, 0.59 in lead. The hard-

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[79] Barnes, R. B., and Salley, D. C., Analysis of potassium by its natural radioactivity: Ind. and Eng. Chemistry, anal. ed., vol. 15, pp. 4–7, 1943.

ness of the gamma radiation from potassium is similar to that from RaC, and, assuming the value of μ/density to be a constant, the value of μ in aluminum for gamma radiation is 0.14. For both types of emanation, the intensity of a beam, I, after penetrating d centimeters of absorbing material is

$$I=I_0e^{-\mu d} \tag{5}$$

in which e is the base of natural logarithms and I_0 is the original beam intensity. Expressed logarithmically,

$$\log_e I=\log_e I_0-\mu d \tag{6}$$

From equation (6), the correction for absorption of gamma or beta emanations may be computed. It is very small for gamma rays and for short tests is well below the fractional probable error of measurement. The use of a thicker layer of sample in a larger cylinder will make an absorption correction necessary, however.

TEST OF MEASUREMENTS

The ratio of the strength of potassium to that of uranium in terms of the beta-ray activity of UX_1 is given by Hevesy and Paneth as 1:500, the measurements having been made with the Geiger-Müller counter. It has been demonstrated by theory and measurement that one gamma ray is emitted along with each beta ray in these two materials. To test the accuracy of the present results, a uranium standard was prepared from uranium oxide and sodium sulfate with a concentration of 0.005965 gram of uranium per gram. A test on the uranium standard with the counting-rate meter gave 119 gamma-ray counts per minute per gram of uranium. Using the same methods of measurement, one gram of K, consisting of K^{39}, K^{40}, and K^{41}, gave 0.24 gamma counts per minute. The resulting ratio was 1/496, which agrees within the limits of experimental probable error.

Computations from the results of the tests to obtain a value for the disintegration constant λ favor the value of Muhlhoff[80] of 23 betas emitted per second per gram of potassium.

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[80] Mühlhoff, W., Aktivität von Kalium und Rubidium gemessen mit dem Elektronenzählrohr: Annalen der Physik, Band 7, pp. 205-224, 1930.

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