

phosphors are listed in approximate order of decreasing sensitivity in Table II.

TABLE II

ACTIVATORS WHICH GIVE INFRARED SENSITIVE PHOSPHORS WITH $\text{La}_2\text{O}_2\text{S}$

Activators	Color for phosphorescent and stimulated light
Pb In	Green
Pb Eu	Orange
Bi Eu	Orange
Sm Eu	Orange
Gd Eu	Orange
In Eu	Orange
Bi In	Green

Indium and lead were tested using concentrations varying from 50 to 500 parts per million of lead and 50 to 2000 parts per million of indium. The most sensitive were those containing about 200 parts per million of lead to about 400 parts per million of indium. None of the phosphors was as sensitive as strontium sulfide activated with samarium and europium.

The lanthanum oxysulfide phosphors differ from those of the alkaline earth sulfides and selenides in that they do not appear to be affected adversely by grinding. On the

other hand, no suitable flux was found for these phosphors. Several phosphates, fluorides, borates and sulfates were used but only to the detriment of the infrared sensitivity.

Summary

The preparation of a new compound, lanthanum oxysulfide, $\text{La}_2\text{O}_2\text{S}$, is described. It is apparently formed by the reduction of the oxysulfate, $\text{La}_2\text{O}_2\text{SO}_4$, which is produced by the thermal decomposition of $\text{La}_2(\text{SO}_4)_3$ above 700° . Lanthanum oxysulfide when activated with several pairs of elements is shown to give a phosphor which can be stimulated with infrared. The most outstanding activators found were lead-indium and lead-europium. The phosphors are excited by ultraviolet radiation.

Somewhat analogous reactions occur with lanthanum selenite but the decomposition tends to proceed to give lanthanum oxide.

Lattice spacings corresponding to the three most intense X-ray reflections are given for $\text{La}_2(\text{SO}_4)_3$, $\text{La}_2\text{O}_2\text{SO}_4$, $\text{La}_2\text{O}_2\text{S}$ and $\text{La}_2\text{O}_2\text{SeO}_3$.

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[CONTRIBUTION FROM THE CHEMICAL AND PHYSICAL LABORATORIES OF HARVARD COLLEGE]

A Comparison of the Abundance Ratios of the Isotopes of Terrestrial and of Meteoritic Iron¹

BY GEORGE E. VALLEY AND HERBERT H. ANDERSON

The identity of elements occurring in meteorites with the same elements from terrestrial sources has been the subject of numerous investigations during the past thirty years.² Only with carbon have even slight differences been detected, but in this case the percentage difference between the masses of the isotopes is favorable for isotopic separation by physical means as well as by isotopic exchange. Even if it is assumed that the genesis of the elements in the solar system was the same throughout and if, as is generally supposed, most meteorites are of solar origin, it is an open question whether some may have arrived on the earth's surface from more distant sources, and consequently the component elements may be of

different isotopic composition. Such a difference with elements of greater isotopic masses might well be due to differences in the conditions of genesis rather than to isotopic separation after formation.

Because iron occurs abundantly both on the earth and in meteorites, in this investigation we have compared the abundance ratios of the isotopes of iron from various terrestrial and meteoritic sources. Within the limit of accuracy of the method no differences were detected among the various specimens of material.

The known isotopes of iron have the mass numbers 54, 56, 57 and 58. The mass spectroscopy used for the determination of abundance ratios was capable of detecting an ion present to the extent of about $1/10000$; hence it was necessary that the specimens of iron examined should be essentially free from every element which contains isotopes of these mass numbers or any multiple of them. Since nickel accompanies iron in meteorites the most important isotope from this standpoint is Ni^{58} which constitutes about 66.4% of nickel. The isotope Cr^{54} (2.3 per cent.) is obviously to be avoided, while Mn^{55} which falls between the two lower iron isotopes is objectionable.

Doubly charged ions of Cd^{108} , Cd^{112} , Cd^{114} and Cd^{116} , Sn^{114} and Sn^{116} and Pd^{108} all fall in close

(1) This work was initiated and supervised by the Committee on Meteorites of Harvard University: G. P. Baxter (Chairman), K. T. Bainbridge, H. Berman (deceased), Francis Birch, A. B. Greninger, F. G. Watson. Financial aid was received from the Associates of Physical Science of Harvard University. The following results have already been reported briefly: Valley and Anderson, *Phys. Rev.*, **59**, 113 (1941).

(2) Below are references to the most recent results: Baxter and Hoover, *ibid.*, **34**, 1657 (1912); nickel: Baxter and Ishimaru, *ibid.*, **51**, 1729 (1929); cobalt: Baxter and Dorcas, *ibid.*, **46**, 357 (1924); chlorine: Harkins and Stone, *ibid.*, **48**, 938 (1926); silicon: Jaeger and Dijkstra, *Koninkl. Verslag. Akad. Wetenschappen Amsterdam*, **27**, 393 (1924); oxygen: Manian, Urey and Bleakney, *THIS JOURNAL*, **56**, 2601 (1934); carbon: Murphey and Nier, *Phys. Rev.*, **59**, 771 (1941); uranium: Schumb, Evans and Hastings, *THIS JOURNAL*, **61**, 3451 (1939); potassium: Schumb, Evans and Leaders, *ibid.*, **63**, 1203 (1941).

proximity to the iron isotopes and therefore must be removed.

Although distillation of ferric chloride and crystallization of ferric nitrate were found to be effective methods of purifying iron, the method finally adopted was the conventional hydrochloric acid-ether method (*cf.* Mellor, "Comp. Treatise," XIV, 87). Precipitation of ferric hydroxide with excess of ammonia is notoriously ineffective for removal of nickel and cobalt. The chlorides of chromium, manganese, cobalt and cadmium are very slightly soluble in ether. Stannic chloride is appreciably soluble but even in this case three repetitions of the extraction process described below with 1 g. of stannic chloride showed only a trace of tin in the ether extract.

The removal of nickel by this process was examined with especial care. When 100 ml. of a hydrochloric acid solution containing 0.2 g. of nickel was extracted with 100 ml. of ether, only 0.2 mg. of nickel was found in the ether extract. For a single extraction the distribution ratio is therefore not far from 10^{-3} and for the three extractions always employed the original Ni/Fe ratio should be reduced to 10^{-9} times its original value. If the original Ni/Fe ratio is taken as 7×10^{-2} , the final proportion of nickel in the purified iron becomes less than 10^{-10} , whereas a single extraction probably would suffice. This conclusion is supported by an experiment in which a solution containing 1 g. of iron and 0.1 mg. of nickel was extracted with ether. The nickel remaining in the aqueous layer was found to be essentially that originally taken.

The minerals or meteorites were dissolved in 6 *N* hydrochloric acid, with the addition of nitric acid in the case of the metallic meteorites. After filtration the volume of the solution was adjusted to 100 ml. with the hydrochloric acid concentration 6 *N* and the nitric acid concentration 1 *N* to prevent reduction of the ferric salt. The solution, at 15°, was then extracted in a separatory funnel with successive portions of 100, 50, 25 and 25 ml. of ether. The ethereal solution was then extracted four times with distilled water, and the aqueous solution was evaporated to small volume. The whole extraction process was repeated a second and third time and the resulting ferric chloride was converted to ferric sulfate by evaporation with sulfuric acid.

As a source of vapor in the mass spectrograph platinum wire of 0.32 mm. diameter was electroplated with iron to a diameter of approximately 0.70 mm. The electrolyte was prepared by adding the ferric sulfate solution to ammonium oxalate and was maintained nearly neutral during electrolysis by adding oxalic acid.

All reagents were purified by distillation or recrystallization of initially pure materials.

Iron from the following specimens was subjected to examination.

A. TERRESTRIAL IRON MINERALS, ARRANGED IN THE ORDER OF DECREASING TEMPERATURE OF FORMATION

1. Native iron in basalt from Disco Island, Greenland (85957 H.C.),* presumably derived from a magmatic source, the iron being formed through reduction by incorporated carbonaceous material.

2. Magnetite, from Kiruna, Sweden, formed by direct segregation from a highly ferrous magma.

3. Magnetite, Port Henry, N. Y. (88994 H. C.),* formed probably in the same way as no. 2, above, or as a contact metamorphic product of iron minerals previously deposited in sediments.

4. Magnetite from Townsend Quarry, Mass., crystals from a coarse pegmatitic phase in a granite, probably formed at a somewhat lower temperature than the specimens enumerated above, and certainly under a different geologic environment.

5. Siderite, Ivigtut, Greenland (90982 H. C.),* formed at a temperature probably near that of the magnetite of no. 4 above, but in a considerably different environment. The main mineral of the Ivigtut deposit is cryolite.

6. Magnetite, Chester, Vermont, small crystals embedded in a chlorite schist and undoubtedly formed by metamorphism of the sedimentary rock, and probably at a lower temperature than the samples enumerated above.

7. Pyrite, Chester, Vermont, found in the same rock as specimen no. 6.

B. METEORITIC SPECIMENS

1. Cumpas, Sonora, Mexico, medium octahedrite.

2. Pavlodar, Siberia, pallasite.

3. Charlotte, Tenn., fine octahedrite.

4. Estherville, Iowa, two pebbles, stony iron.

5. Holbrook, Ariz., stone.

6. Homestead, Iowa, stone.

7. Cosby's Creek, Tenn., coarse octahedrite.

8. Britstown, Cape Colony, fine octahedrite.

9. Finmarken, Arctic Norway, stony iron pallasite.

10. Canyon Diablo, Ariz., octahedrite.

11. Kokomo, Indiana, nickel-rich ataxite.

The composition of these specimens as found by analysis by others is given in Table I.

The mass spectrometer was of the type commonly used for isotope abundance measurements.³ In this design, a beam of monoenergetic ions is formed by means of a precisely constructed source. This beam is then magnetically analyzed into a momentum spectrum. All ions having the same charge, energy and momentum, have identical masses.

We have made some changes in the details of the ion source which make it worthwhile to exhibit

* This represents the designation in the Harvard mineralogical collection.

(3) Sampson and Bleakney, *Phys. Rev.*, **50**, 732 (1936); Nier, *ibid.*, **53**, 282 (1938).

TABLE I
CHEMICAL ANALYSES IN PER CENT.

	Metallic Material									
	Fe	Vi	Co	Cu	S	P	C	FeO	FeCl ₂	
Cumpas	93.8	6.00	0.093	0.010	0.014	0.148				
Pavlodar	86.6	8.0	.6		.01		0.19		Tr	Traces of Si, Ca, Mg
Charlotte	91.15	8.01	.72	.06		Tr				
Estherville	92.0	7.10	.69	Tr		.11				
Cosby's Creek	91.5	6.4	.72	.02	.81	.40	.20			Schreibersite 2.63%, triolite 2.22%
Britstown	No analysis									
Finmarken	No analysis of metal									
Canyon Diablo	89.17	7.34	.51	.15	.009	.261	.113	2.52	0.10	Trace of Si
Kokomo	83.2	15.8	1.07	.01	Tr	.08				

	Silicate Material															
	O	Si	Al	Fe	Ca	Na	Mg	Mn	Ni	Co	Cu	S	P	Cr	K	
Pavlodar	42.3	18.6	0.14	12.7			26.4									Olivine ^a
Estherville	43.5	21.9	.02	13.5		0.06	21.2							Tr		
Holbrook	36.4	17.1	1.98	24.1	1.50	Tr	15.5	0.17	0.69	0.05	0.01	2.75	0.17			Triolite 7.56% Metal 4.85%
Homestead	35.6	18.4	1.11	23.3	1.27	.68	15.0	.06	1.19	.09		2.28	.11	0.22	0.11	Triolite 6.25% Metal 10.99%
Finmarken	44.3	18.3		20.7			26.6									Olivine

^a Computed on the assumption of one half bronzite, one half olivine; their proportion varies through the material.

its construction here. Figure 1 shows that its chief components are the flat circular plates A, B, C and D. These are held together by four glass-insulated studs and are spaced by Pyrex glass collars. These studs are screwed into holes equally spaced near the periphery of plate D and pass through radial slots in plates A, B and C. This construction allows thermal expansion of the ensemble to take place without warping and cracking the insulators.

The specimen f consists of a hot wire of the metal to be studied. It is surrounded by shield g. A beam of vapor from f issues through the wide slits S₁ and S₂ into the region between B and C. A beam of electrons from the tungsten filament e is accelerated by a potential applied be-

tween e and the shield h and is collected by the box j. Ions formed at the intersection of vapor and electron beams are assisted to pass through slit S₃ by a small potential applied between B and C. The main accelerating potential of several hundred volts is applied between C and D. The ions pass through the slit S₄ into the electric field-free region of the magnetic analyzer and emerge through a fifth slit S₅ at the other end where they impinge on a plate connected to a d.c. amplifier. S₄ and S₅ lie on the diameter of a circle of radius 12.5 cm. To allow for the cycloidal path of the ions in the region between S₃ and S₄ it is a satisfactory approximation to place the center of the slit S₃ on the same circle. The filament f consisted of a platinum wire 0.32 mm. in diameter on which

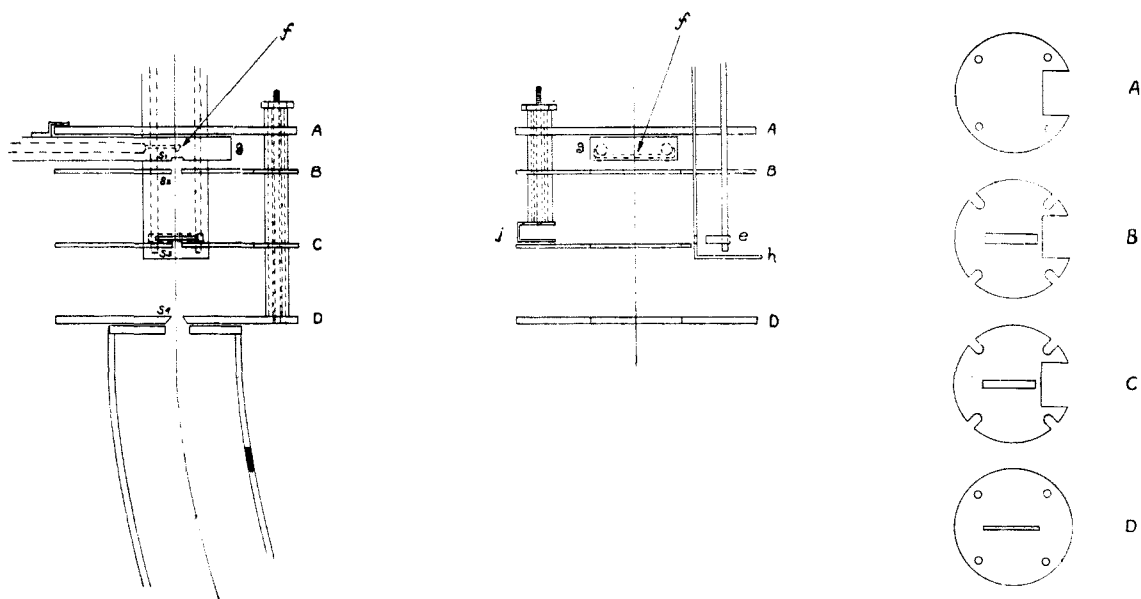


Fig. 1.

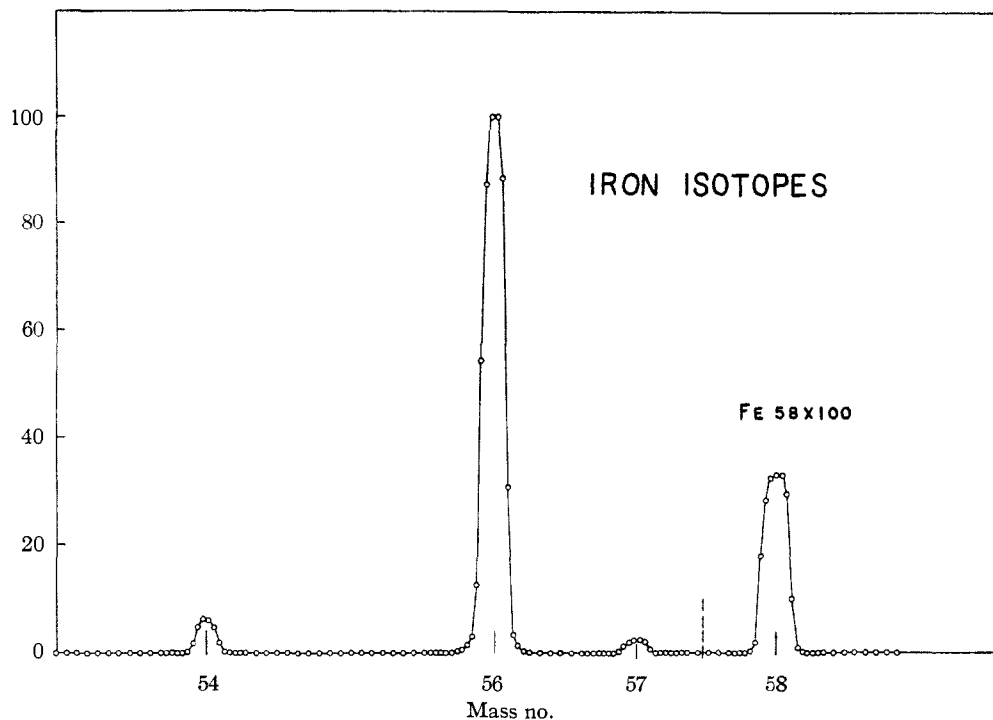


Fig. 2.

the iron was electroplated to a diameter of 0.70 mm. It was U-shaped and about 1 cm. long on each of the three sides. When heated by about 10 amp. such a filament would emit iron vapor at a satisfactory rate for from two to four hours. It was found that this current when obtained from a 100 ampere-hour storage battery dropped off at a rate sufficient to compensate for the increase in temperature which would otherwise occur due to the thinning of the filament as it evaporated. The advantage of using the iron in this form was that the instrument did not have to be cleaned after each specimen.

All the voltages and currents needed were supplied by batteries. The d.c. amplifier employed a W. E. D 96475 tube in a Barth circuit.⁴ It was

TABLE II
ISOTOPIC COMPOSITION OF IRON

Isotope	Terrestrial							
	First series				Second series			
	54	56	57	58	54	56	57	58
Disco Island	6.43	100	2.43	0.38	6.27	100	2.41	0.33
Townsend Quarry	6.37	100	2.46	.36	6.40	100	2.34	.34
Chester Pyrites	6.35	100	2.45	.37	6.35	100	2.35	.32
Chester Magnetite	6.39	100	2.31	.30	6.32	100	2.30	.31
Port Henry Magnetite	6.47	100	2.45	.38	6.29	100	2.39	.33
Ivigtut Siderite	6.47	100	2.36	.36	6.49	100	2.31	.31
Kiruna Magnetite	6.40	100	2.34	.34	6.31	100	2.28	.32
Averages	6.41	100	2.40	.36	6.32	100	2.33	.32
Average deviation	0.04		0.05	.02	0.06		0.03	.01
ad/\sqrt{n}	.015		.02	.007	.02		.01	.003
Mean mass number	55.9111				55.9110			

(4) D. B. Penick, *Rev. Sci. Instruments*, **6**, 115 (1935).

Isotope	Meteoritic			
	54	56	57	58
Cumpas	6.35	100	2.34	0.32
Pavlodar metal	6.32	100	2.34	.32
Pavlodar stone	6.30	100	2.32	.32
Charlotte	6.32	100	2.27	.32
Estherville	6.31	100	2.32	.31
Holbrook	6.43	100	2.38	.35
Homestead	6.29	100	2.32	.32
Cosby's Creek	6.35	100	2.34	.32
Britstown	6.30	100	2.32	.32
Finmarken	6.25	100	2.34	.32
Canyon Diablo	6.30	100	2.29	.32
Kokomo	6.27	100	2.33	.32
Average	6.32	100	2.33	.32
Average deviation	0.03		0.02	.006
Ad/\sqrt{n}	.01		.005	.002
Mean mass number	55.9113			

Average of terrestrial (second series) and meteoritic values

Isotope	54	56	57	58
	6.33	100	2.34	0.32
Mean mass number	55.9112			

operated at a sensitivity of about 50,000 mm./volt.

The mass spectroscopic results are given in Table II. Figure 2 represents a typical spectrum, in which ion current ($Fe^{56} = 100$) is plotted against isotopic weight.

The second series of results with terrestrial and that with meteoric material were made with a different magnetic analyzer tube from that used in the first series of experiments with terrestrial samples. Furthermore, in this first series with terrestrial samples experience was being gained

with the experimental technique. In all probability, therefore, the second series of experimental results with terrestrial samples is more directly comparable with the meteoritic results than the first. From the isotopic proportions found, one can only conclude that the terrestrial and meteoritic materials are identical within the experimental error.

Summary

The isotopic composition of samples of purified terrestrial and meteoritic iron has been measured with a mass spectrograph. There were no certain differences in composition either among the different samples of each of the two varieties of material or between the two varieties themselves.

The following ratios and percentages of the four iron isotopes were found.

	Ratios	Percentages	
		This paper	Nier
Fe ⁵⁴	6.33	5.81	6.04
Fe ⁵⁶	100.00	91.75	91.57
Fe ⁵⁷	2.34	2.15	2.11
Fe ⁵⁸	0.32	0.29	0.28

These give a mean mass number of 55.911 for iron. The atomic weight calculated with the packing fraction -7.15×10^{-4} and the conversion factor 1.000275 is 55.856. Nier's⁵ isotopic percentages given above yield the atomic weight 55.851. The International atomic weight, 55.85, depends on the analyses of ferric oxide,⁶ 55.847, of ferric chloride,⁷ 55.853, and of ferrous bromide,⁸ 55.850.

(5) Nier, *Phys. Rev.*, **55**, 1143 (1939).

(6) Baxter and Hoover, *THIS JOURNAL*, **34**, 1657 (1912).

(7) Hönigschmid, Birkenbach and Zeiss, *Ber.*, **56B**, 1473 (1923).

(8) Hönigschmid and Liang, *Z. anorg. Chem.*, **241**, 361 (1939).

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A Phase Study of Sodium Palmitate-Alkaline Electrolyte-Water Systems

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During the past twenty-five years numerous publications on the phase behavior of aqueous soap systems have appeared.¹ Considerable information has also become available on the effects of sodium or potassium chloride on these systems.^{2,3,4} Very little is apparently known at present, however, of the effects of other electrolytes, although alkaline salts such as the silicates and phosphates are industrially important as soap builders. A review of the available literature is given in a separate paper which reports a study of the phase behavior of ten commercial mixed sodium soap-water-electrolyte systems.⁵ The salts used were sodium chloride, carbonate, tetraborate, trisodium phosphate, tetrasodium pyrophosphate, Calgon ("sodium hexametaphosphate"), sodium metasilicate, sodium silicates of SiO₂/Na₂O ratios by weight of 2.46 and 3.93, and a potassium silicate of SiO₂/K₂O ratio by weight of 2.04. This paper reports a similar study on aqueous sodium

palmitate systems with trisodium phosphate, tetrasodium pyrophosphate, sodium metasilicate, and sodium silicates of SiO₂/Na₂O ratios by weight of 2.46 and 3.92. Data are given outlining the regions of existence of isotropic solutions up to 160° and showing the influence of these electrolytes on the transition from hydrated crystalline to liquid crystalline soap.

Work on the sodium palmitate-water system has recently been summarized by McBain and Lee.^{1a} The ternary system with sodium chloride has been studied by McBain, Lazarus and Pitter,⁶ and more completely at 90° by Vold and Ferguson.³

Experimental

Materials.—The sodium palmitate was made by neutralizing to phenolphthalein a hot alcoholic solution of Eastman Kodak Co. best quality palmitic acid, with an alcoholic solution of sodium ethylate and subsequent crystallization of the soap. It was dried to constant weight at 105° before use. The acid recovered from the soap in a yield 99.6% of theoretical melted over the range 61.5–62.0° and had a molecular weight by titration of 260 (calcd. 256). The amounts of impurities present are too small to affect significantly the results on the systems containing less than 50% soap studied in this paper. The impurities are higher and lower molecular weight fatty acids whose effects on solubility tend to counter balance each other.

The phosphates were C. P. chemicals. Analyses of the silicates are given in a separate paper.⁵ The most silicious silicate was further purified. In addition to the metasilicate pentahydrate, an anhydrous metasilicate containing about 3% sodium carbonate was used. Both gave essentially the same results.

Method.—All data were obtained by the standard synthetic method. Systems of known composition in sealed

(1) See, e. g., (a) J. W. McBain and W. W. Lee, *Oil & Soap*, **20**, 17 (1943); (b) J. W. McBain, R. D. Vold and M. J. Vold, *THIS JOURNAL*, **60**, 1866 (1938); (c) J. W. McBain in Alexander, "Colloid Chemistry," Vol. I, Chemical Catalog Co., New York, 1926, p. 132; (d) R. H. Ferguson, F. B. Rosevear and R. C. Stillman, *Ind. Eng. Chem.*, **35**, 1005 (1943); (e) M. J. Buerger, L. B. Smith, F. V. Ryer and J. E. Spike, *Proc. Natl. Acad. Sci.*, **31**, 226 (1945).

(2) See, e. g., (a) J. W. McBain, R. D. Vold and K. W. Gardiner, *Oil & Soap*, **20**, 221 (1943); (b) J. W. McBain, W. J. Elford and R. D. Vold, *J. Soc. Chem. Ind.*, **59**, 243 (1940); (c) J. W. McBain, K. W. Gardiner and R. D. Vold, *Ind. Eng. Chem.*, **36**, 808 (1944); (d) J. W. McBain, R. C. Thorburn and C. G. McGee, *Oil & Soap*, **21**, 227 (1944).

(3) R. D. Vold and R. H. Ferguson, *THIS JOURNAL*, **60**, 2066 (1938).

(4) R. H. Ferguson and A. S. Richardson, *Ind. Eng. Chem.*, **24**, 1329 (1932).

(5) R. C. Merrill, *ibid.*, **39**, 158 (1947).

(6) J. W. McBain, L. H. Lazarus and A. V. Pitter, *Z. physik Chem.*, **A147**, 87 (1930).