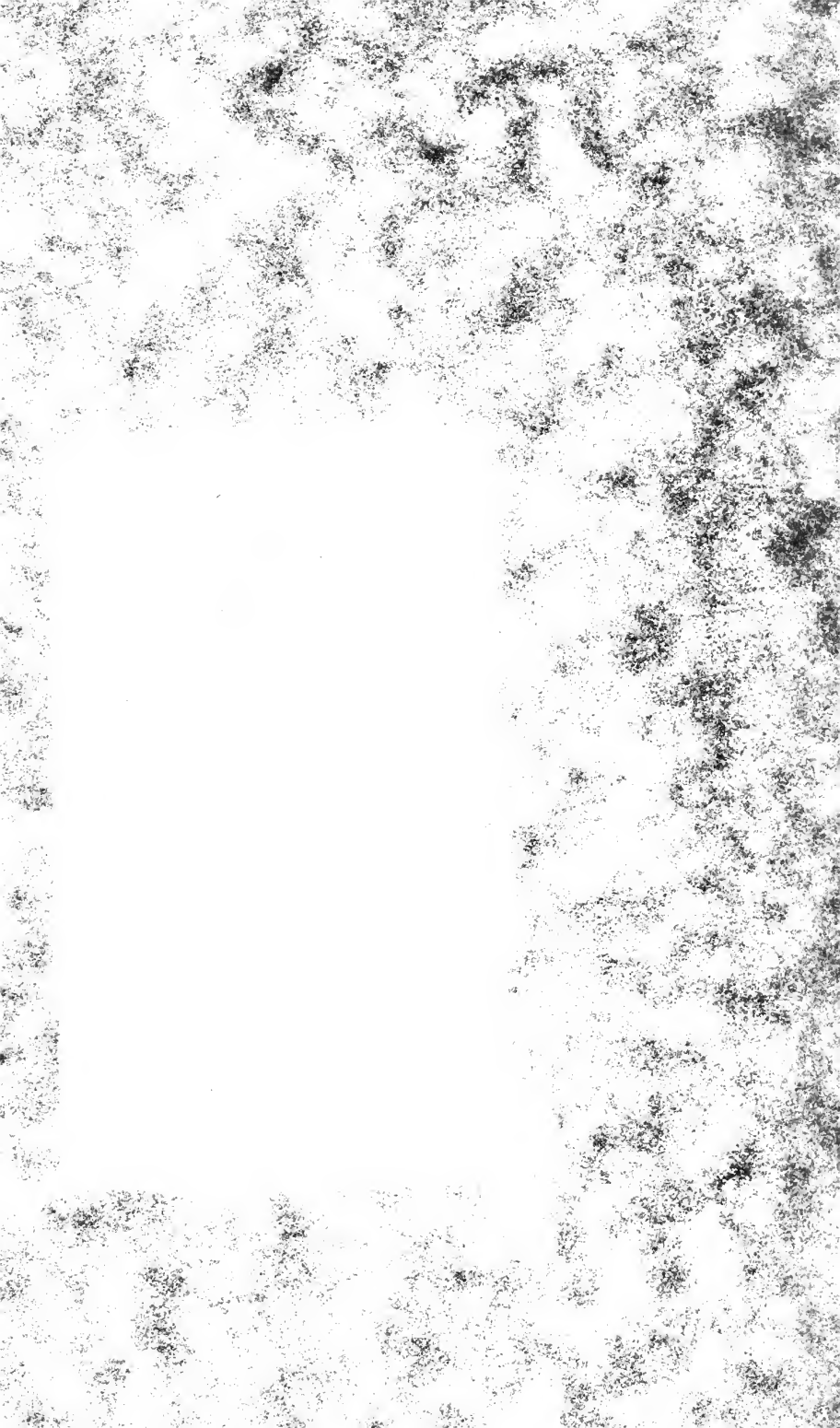


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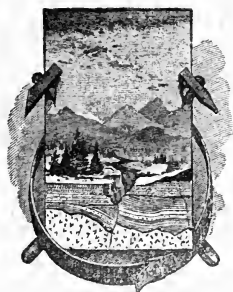
DEPARTMENT OF THE INTERIOR
UNITED STATES GEOLOGICAL SURVEY
J. W. POWELL DIRECTOR

IODINE

BY

DAVID T. DAY

ABSTRACT FROM "MINERAL RESOURCES OF THE UNITED STATES,
CALENDAR YEARS 1883 AND 1884"—ALBERT WILLIAMS, JR.,
CHIEF OF DIVISION OF MINING STATISTICS



WASHINGTON
GOVERNMENT PRINTING OFFICE
1885

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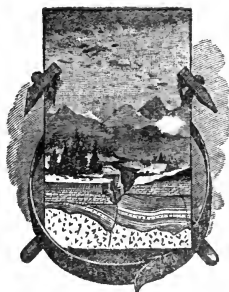
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I O D I N E .

BY DAVID T. DAY.

Domestic occurrences.—Traces of iodides have been found, together with chlorides and bromides, in the various salt wells, particularly those of the West Virginia and Ohio district. At Saratoga, New York, traces have been detected, but although the percentage of iodine in profitable sources is extremely small, the occurrences in the United States will, in all probability, remain entirely insignificant. Although iodine is not produced in the United States, its important influence upon the bromine industry, in which the United States holds first rank, makes a consideration of the peculiar features of the iodine industry advisable.

Sources and mode of manufacture.—Sea water and the South American nitrate deposits have served as the only sources of iodine. The minute trace of iodine in the former is concentrated by many varieties of algæ, so that these plants when perfectly dry contain from 0.0297 to 0.4535 per cent. of their weight in iodine, in the form of iodides of the alkali metals (Stanford). Before the discovery of iodine by Courtois, in 1811, these algæ were collected on the shores of Ireland, Scotland, and Normandy, and their ashes (“kelp,” “varec”) furnished a considerable part of the soda and potash of that time. According to the report of Mr. E. C. Stanford (*a*) the production of kelp, that is, the ashes of several varieties of seaweed, amounted to 20,000 tons from the western islands alone at the beginning of this century, and sold for £20 to £22 per ton. The importation of barilla then began, and this, together with the establishment of the Leblanc soda process, reduced the price of kelp to £10 per ton. Among the manufacturers of sodium salts from kelp was Courtois, in Paris. His discovery of iodine in the kelp was made at a time when theoretical discussions as to the elementary character of chlorine subjected the properties of that substance to careful study, and the analogous character of iodine led in an unusually short time to a general knowledge of this element and its possible uses. It was extracted from kelp during the preparation of soda; but small quantities fully satisfied the demand, so that its source was no more valuable than before iodine was discovered. In fact the price of kelp sank gradually to £2 per ton in 1831. Between 1841 and 1844, however, iodine was applied to the manufacture of aniline dyes. In 1845 the production of iodine began on a commercial scale, and kelp was again in demand.

The imports to the Clyde increased from 2,565 tons in 1841 to 6,000 tons in 1845. In the latter year there were four small works engaged in the manufacture of iodine; in 1846 this number increased to twenty. The kelp required was not the same; formerly that yielding most soda was needed, but this was poorest in iodides, which now became the important constituents. Moreover, it was found that kelp richest in iodine was also richest in potassium, which also was valuable; potassium chloride being worth £25 per ton. The following table gives the imports of kelp into the Clyde for thirty-five years, and also the price of iodine from the time of its industrial application up to the present. The earlier figures have been compiled by Mr. Stanford, of Glasgow, and the later prices of iodine have been furnished through the kindness of Messrs. Powers & Weightman, of Philadelphia.

Kelp imports into the Clyde, and price of iodine.

Years ending June 30—	Kelp im- ports.	Price of iodine.	Years ending June 30—	Kelp im- ports.	Price of iodine.
	<i>Long tons.</i>	<i>Per pound.</i>		<i>Long tons.</i>	<i>Per pound.</i>
1841	2,565	\$1.20	1865	13,741	\$1.84
1842	1,887	1.12	1866	8,858	2.40
1843	1,965	1.44	1867	8,174	2.88
1844	3,263	2.88	1868	8,116	3.04
1845	6,086	7.46	1869	8,978	3.12
1846	3,627	5.34	1870	9,257	3.04
1847	4,000	2.64	1871	9,384	3.44
1848	4,400	2.64	1872	10,049	8.16
1849	4,731	2.64	1873	9,449	5.12
1850	11,421	2.56	1874	10,923	{ a3.52
1851	7,320	2.08			{ b2.94
1852	5,418	3.64	1875	8,643	{ a2.44
1853	6,491	3.72			{ b2.25
1854	4,679	2.88	1876		{ a1.92
1855	5,826	3.20			{ b1.87
1856	6,349	3.28	1877		{ c3.28
1857	8,641	2.96	1878		{ e4.00
1858	8,123	2.52	1879		{ e4.48
1859	8,190	2.32	1880		{ d1.92
1860	7,754	2.04	1881		{ d2.00
1861	9,722	1.68	1882		{ d1.60
1862	9,414	1.36	1883		{ d1.28
1863	14,018	1.20	1884		{ d1.20
1864	11,349	2.00			{ e2.88

a Scotch. b Peruvian. c Combination. d Combination broken. e Recombination.

The extraordinary fluctuations in the price of iodine serve to indicate the complicated conditions of oversupply, extended production, combination of manufacturers, and open competition, to which an industry is occasionally subjected. During the early years of the manufacture the extended use of iodine, principally in the production of aniline dyes, caused sudden fluctuations in its price, while the price of the raw material remained practically unchanged. This involved many manufacturers in heavy losses, the profits under high prices usually falling to speculators, while the manufacturer was left to sustain the industry when prices were low. For this reason the number of manufacturers in Glasgow was reduced during 1873-1877 to about three, producing in all from 50 to 60 tons of iodine from about 10,000 tons of

kelp. The production in France at this time was somewhat less, amounting to 40 tons, derived from 16,000 tons of inferior "varec" or kelp.

As early as 1835 the presence of sodium iodate was noticed in the South American caliche (native sodium nitrate). The effort was made by Thiercelin to extract the iodine from the mother liquors from sodium nitrate by precipitating the iodine by means of acid sodium sulphite, or, better, sodium nitrite, prepared by fusing the domestic sodium nitrate with one-fifth its weight of charcoal. But the difficulty of drying the iodine thus obtained by spreading on porous plates, and the fact that frequently the greater part of the iodine existed as sodium iodide and escaped precipitation, prevented active competition with European iodine until Langbein's method was introduced in the province of Tarapaca, then belonging to Peru, but at present held by Chili. By this method the mother liquors were treated with an excess of sodium sulphite or acid sodium sulphite, converting the iodate into hydriodic acid, from which cuprous iodide was precipitated by copper sulphate and sodium sulphite. In 1874 South American iodine was offered upon the London market for $10\frac{1}{2}$ to 11 pence per ounce, against 13 pence for Scotch iodine. The result was an active competition, soon resolving into commercial warfare, which has exerted great influence upon the industry. All through 1874 Peruvian iodine was offered at prices about 20 per cent. below the Scotch product. At the beginning of 1875 both varieties sold for two-thirds the price of 1873, and the Peruvian iodine still led the way to lower prices, until at the close of 1876 the price had fallen to $5\frac{3}{4}$ pence per ounce, and both sides were ready to compromise or else give up the manufacture, which now yielded little profit to either. In order to keep up the competition the European method of producing iodine had undergone a revolution. Formerly the custom was to allow seaweed to collect during the winter months. It lay exposed upon the coasts until sometimes 90 per cent. of the iodine had been washed away from the partially decomposed weed, before it was burned and shipped to Glasgow. Further, the weed was burned in long kilns made of loose stone walls and turf; the burning seaweed here attained a very high temperature. This part of the work was done by women and children; the men then raked the ash with iron "clats" until it formed a molten slag. "During this laborious process," says Stanford, "more than 50 per cent. of the iodine is often wasted, and a large amount of potash; indeed, so intense is the heat that sufficient soda is volatilized to give an intense monochromatic flame. The high temperature also enables the carbon to deoxidize the alkaline sulphates to sulphides and other sulphur compounds; these become concentrated in the mother liquor, and entail a large expenditure of oil of vitriol, and give rise to great nuisance in the lixiviation." The first improvement, proposed in 1862, was to subject the kelp to destructive distillation in closed vessels, by which ammonia, acetic acid, naphtha, a considerable amount of illuminat-

ing gas, and finally a variety of charcoal better than others for decolorizing, etc., were obtained. From this charcoal twice as much iodine was obtained as from the kelp. This radical improvement was only used on the islands of Tyree and North Uist until the competition with Peru. The next improvement, proposed by Pellieux and Mazé-Launay, consists in drying the fresh seaweed for four or five days, then allowing it to ferment until decomposition begins. The object of the fermentation is to bring the seaweed into a condition in which no iodine will be lost in burning. The sulphur compounds in the algæ are converted into alkaline sulphides; these decompose the organic iodine compounds into alkaline iodides, which are not so easily volatilized. The water formed during the fermentation is carefully saved on account of its containing considerable iodine. The results of this process are very satisfactory. The lixiviation of iodine from the kelp is double. First, chlorides and iodides are extracted by cold water, then potassium sulphate by hot water. From the solution containing the iodides, iodine is precipitated by potassium chlorate, which separates it from small quantities of bromides. Before the end of the competition with Peru, it is said that vessels were sent out to collect seaweed for this purpose at times when the coast was bare. In March, 1877, a combination was effected between the European and South American producers, and the price set at 10½ pence per ounce. This combination was of especial value to the South American producers. It enabled them to erect new works and gave an impetus to the trade which continued even after the combination was broken in 1880. The price then fell to less than half, and with continued competition had reached by November, 1884, 3¾ pence per ounce, the same price which ruled in 1841, before iodine entered into chemical manufactures. It was predicted in November that a combination would be formed and the price then go to 9 pence per ounce. The prediction was fulfilled.

The yield from South American deposits has been estimated as follows:

Years.	Pounds.
1873	30,000
1874	100,000
1875	a100,000
1876	110,000
1877	200,000
1878	280,000
1879	350,000
1880	380,000
1881	200,000
1882	b80,000
	c32,000
1883	b124,544
	c30,000

a From 131 manufactories. b Chili. c Peru.

The processes have been markedly improved both in the methods and arrangement of the plant. The plant at Peruana, province of Tarapaca (formerly in Peru), erected in 1881, cost \$20,000, and yields

3,200 pounds of iodine each month. The sodium nitrate at this place contains sodium iodate, which according to the *Génie Civil*, 1884, may in extreme cases amount to 50 per cent. The average mother liquor contains:

	Per cent.
Sodium nitrate.....	28
Sodium chloride.....	11
Sodium sulphate.....	3
Magnesium sulphate.....	3
Sodium iodate.....	22
Water.....	33
	100

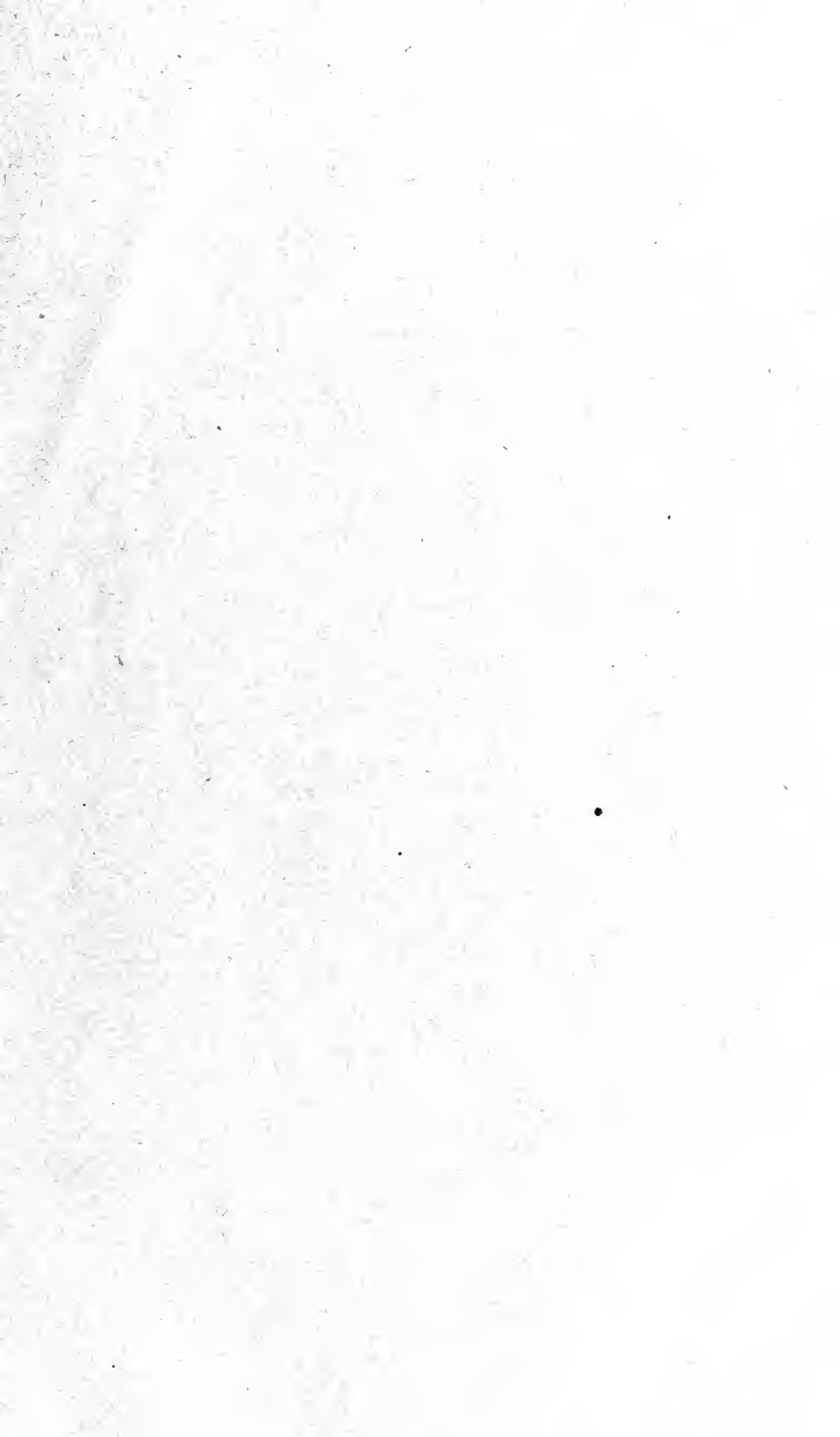
As the iodine is present largely as sodium iodate, it is precipitated by the old method of sodium acid sulphite. Very new and economical methods are used for preparing this substance, in regard to which full plans are given in Dingler's *Polytechnische Journal*, Vol. 255, page 299. In Chili much of the iodine occurs as sodium iodide, and is exported as cuprous iodide; 117,330 pounds of this substance were exported in 1883.

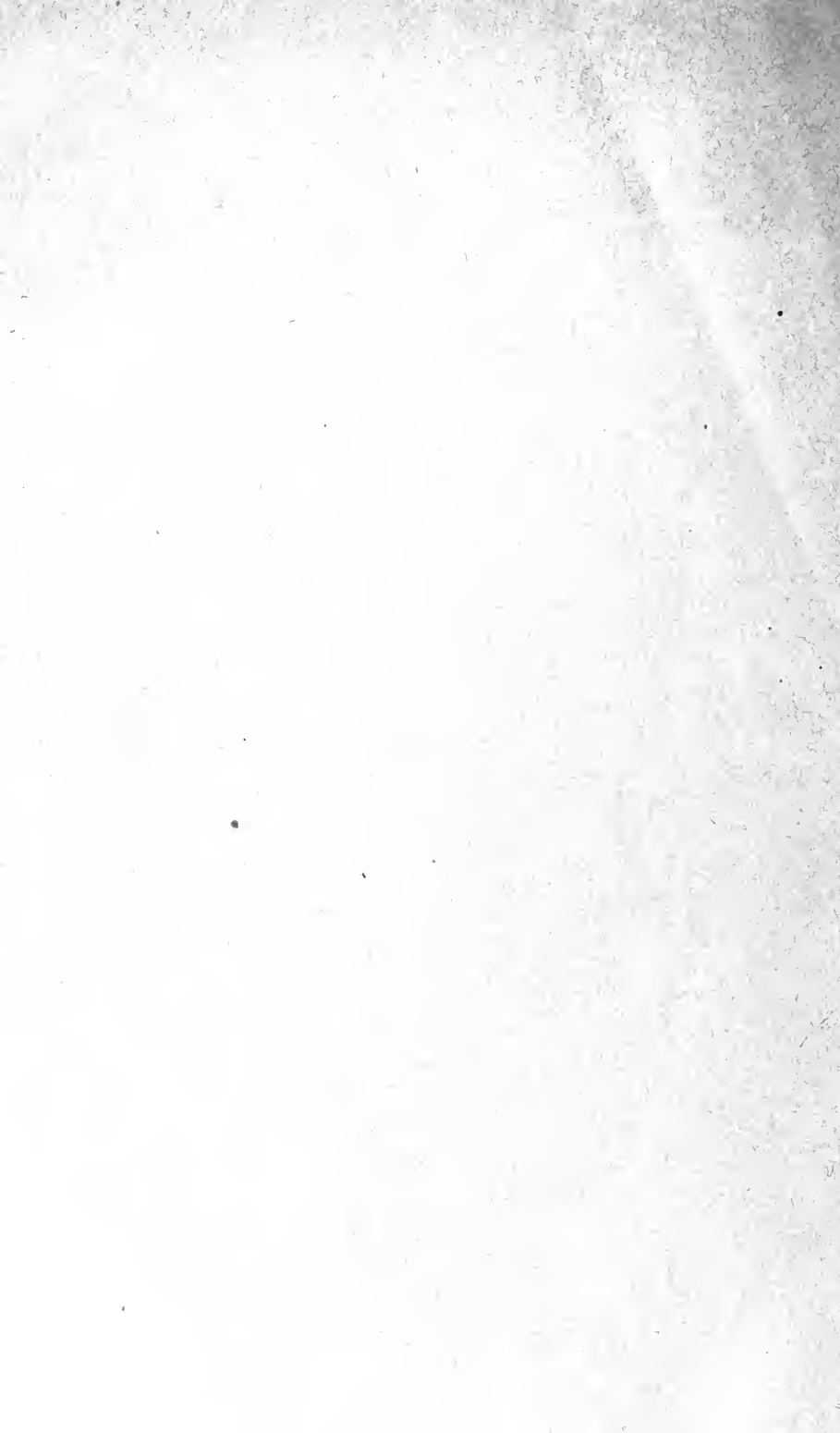
Imports.—The following table shows the imports of iodine into the United States from 1867 to 1884 inclusive. The principal use of iodine in this country is for making alcoholic tincture and iodine salts, principally potassium iodide.

Iodine imported and entered for consumption in the United States, 1867 to 1884 inclusive.

Fiscal years ending June 30—	Crude.		Resublimed.		Iodine salts.	Total.
	Quantity.	Value.	Quantity.	Value.		
	<i>Pounds.</i>		<i>Pounds.</i>			
1867.....	12,347	\$28,013	3,199	\$6,764	\$34,777
1868.....	18,994	55,869	5,527	16,178	72,047
1869.....	17,241	50,625	5,882	18,356	\$3,589	72,570
1870.....	27,825	70,777	2,233	6,251	77,028
1871.....	74,320	212,195	956	3,499	215,694
1872.....	81,437	292,998	258	2,166	41	295,205
1873.....	48,991	206,783	10	87	206,870
1874.....	23,861	89,305	2	16	89,321
1875.....	26,058	74,357	54	171	3	74,531
1876.....	24,913	55,443	55,443
1877.....	50,123	111,494	111,494
1878.....	73,687	230,041	12	230,053
1879.....	31,779	122,571	122,571
1880.....	104,703	501,957	2	12	501,969
1881.....	162,863	336,998	13	30	648	337,676
1882.....	119,952	213,311	15	28	1,266	214,605
1883.....	140,642	162,036	5	8	5,972	168,016
1884.....	153,550	173,251	336	493	(a)	173,744

(a) Not specified.









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