carefully performed with Liebig's proportions, the lixiviate always contains undecomposed cyanid of potassium, it occurred to me to try the effect of a more thorough oxydation, and the result proved very favorable. The following was the course adopted.

Of roasted ferrocyanid of potassium 850 grammes are mixed with 318 grammes of thoroughly dried carbonate of potash in grains, and fused in an iron vessel. When decomposition is complete, the vessel is a little cooled and 1900 grammes of red lead are to be added, not all at once, but 300 to 400 grammes at a time, with intervals of 10 minutes, stirring and keeping up heat enough to retain the whole in a state of fusion.

After the last addition of red lead the mixture is suffered to remain half an hour on the fire to complete the reaction. Heat is applied in all for about four hours. In this way the cyanid of potassium becomes thoroughly oxydized. The process is concluded in the usual manner, and 500 grammes of urea are obtained. No particular precaution is necessary during the fusion, or even the lixiviation with cold water, but in evaporating the solutions the greatest care must be taken to carry off the vapors.*

Philadelphia, April, 1861.

ART. XX.—*Contributions to the History of Picric Acid;* by M. CAREY LEA, Philadelphia.

Solubility in Sulphuric Acid.

IT is stated in the text-books that picric acid is insoluble in sulphuric acid. It is however soluble to a small degree in strong sulphuric acid; in a more dilute acid it is apparently wholly insoluble, until the dilution reaches a certain point when it increases again. If picric acid be left in contact with oil of vitriol, and the latter be decanted, and mixed with two or three times its volume of water, the picric acid is deposited on cooling in what appear to be very minute square or nearly square scales.

Picric acid crystallizes in the rhombic system, and if we suppose these scales to be formed by predominating $\infty \bar{P} \infty$ planes bounded at the edges by octahedral planes, they should be rhombs approaching very nearly to squares, having their axes as ·9374 : 1·0000.

If cold saturated aqueous solution of picric acid be mixed with sulphuric acid diluted with an equal volume of water, the following results are obtained:

1 vol. solution of picrate, 4 vols. dilute sulphuric acid. (1 vol. acid, 2 vols. water.)	No precipitate, solution remaining as colorless as water.

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* For continuation of Mr. Lea's "Contributions," see p. 210.

1 vol. sol. picric acid, 2 dilute sulphuric acid, same dilution.	No precipitate, solution very nearly colorless, faintest tinge of yellow only visible.
2 vols. solution picric acid, 1 vol. sulphuric acid, same dilution.	Nearly the whole of the picric acid was precipitated.

The amount remaining in solution continued in further trials to diminish as the sulphuric acid became more dilute, until a maximum was reached with

3 vols. solution picric acid, 1 vol. dilute sulphuric acid, same dilution.

It thus appears that mixtures of sulphuric acid and water reach their minimum of solvent power for picric acid when the mixture consists of about 1 vol. acid to 11 vols. water. The proportion of water may be still further increased without materially increasing the solvent power for picric acid. If a cold saturated solution of picric acid be mixed with even but $\frac{1}{17}$ of its volume of sulphuric acid, almost the whole is thrown down.

The fact that the characteristic color of picric acid, which it maintains so persistently through all its combinations, and which is so powerful that, as I have found by actual experiment, a milligramm will distinctly tinge a kilogramm of water, or in other words, that water is colored by one millionth of its weight of picric acid—the fact that this color is totally destroyed by sulphuric acid of a certain strength, without in any way decomposing the acid, is very remarkable. Four volumes of sulphuric acid diluted with five volumes of water exhibit this property, and picric acid dissolves in such a mixture to a colorless solution. This peculiar property has no doubt led to the supposition of the insolubility of picric acid in sulphuric acid above referred to.

Water containing $\frac{1}{10.000}$ of picric acid exhibits a bright yellow color. With $\frac{1}{300.000}$ the color is still distinct, even in a stratum of not over an inch in thickness. But in large quantities a millionth gives a distinct color as above mentioned.

Tests for Picric Acid.

The best tests for picric acid are

Ammoniacal solution of sulphate of copper, which gives a greenish crystalline precipitate.

Alkaline sulphid with excess of alkali, which with heat gives a deep red liquid.

Alkaline cyanid with ammonia, which when heated gives also a red liquid.

The following table will exhibit the relative sensibility of these reagents:

Strength of aqueous solution of picric acid.	Ammonio sulphate of copper.	Potash liver of sulphur (heat.)	Cyanid of potassium.
$\frac{1}{1000}$	Immediate precipitate.	Solution becomes sherry wine red.	Pale sherry red, with heat becoming deep red.
$\frac{1}{4000}$	No precipitate at first, but by standing a few minutes a distinct one.	Deep yellow with a tinge of sherry color.	Deep yellow, tinge of sherry color, deepened by heating.
$\frac{1}{5000}$	Distinct precip. by standing.		
$\frac{1}{10000}$	No precipitate.	The yellow color was slightly deepened, the cyanid test is the more delicate of the two.	

Purification of Picric Acid.

Since my former observations on the purification of picric acid,* I have had occasion to prepare considerable quantities of the acid for my examinations and find that all purifications by converting into potash salt are inapplicable except for very small quantities. The picrate of potash crystallizes out by so small a fall of temperature that the filters, even when kept heated by a double funnel become immediately clogged, and the operation becomes to the last degree tedious and troublesome. As the picrate of lime is very soluble, it seemed probable that it might afford a convenient means of solution; it has indeed been already recommended for that purpose.† But I find it wholly inadmissible. A basic salt is formed which falls to the bottom with the excess of hydrate of lime, and great waste ensues. The insolubility of alkaline picrates in cold alkaline solutions which I have described in a previous number of this Journal, furnished me with an excellent process. The crude acid is saturated with carbonate of soda, an excess of which is to be avoided as it tends to dissolve resinous matter. The hot solution is then easily filtered, and into the filtrate a few clear crystals of carbonate of soda are placed. On cooling, the picrate of soda crystallizes out almost as completely as the potash salt would have done, and all the wearisome delay in filtration is avoided. From the mother water more picric acid may be recovered by the addition of a little carbonate of potash. In decomposing alkaline picrates to separate the acid sulphuric, (and not as usually recommended, chlorhydric) acid should be used, because a moderate excess of sulphuric acid throws down a great portion of the acid which would otherwise

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* This Journal, Nov., 1858.

† See Gmelin, Eng. Ed., vol. xi, p. 214.

remain in the mother water. A moderate but decided excess of acid is absolutely necessary, because otherwise a portion of alcaline picrate escapes decomposition. Even then, it is advisable to recrystallize the acid from alcohol. If picric acid be dissolved by the aid of heat in a solution of sulphate, nitrate, or almost any salt of potash, more or less picrate of potash will crystallize out on cooling. I have thought this process not devoid of interest, because picric must become more extensively known in the laboratory and in the arts than hitherto.

Effect of Reducing Agents.

The effects of reducing agents when alkali is not present, or not present in excess, (in presence of excess of alkali, picramic acid is formed), are very variable, depending upon slight differences which it is very difficult to seize. I subjoin some of the best marked results obtained.

A mixture of picric acid, alcohol, iron filings, and acetic acid, were digested for an hour at a heat a little below 212°. The filtrate was intensely blue, by standing for half an hour or less, became brown and muddy, depositing a blackish powder, in small quantity, and without trace of crystallization. This filtrate was not changed in color by acids, or apparently affected by them. Alkalies decolorized it. Its shade of blue varied considerably in different experiments, sometimes full blue, sometimes violet, sometimes greenish.

Other experiments were made by acting on picric acid by zinc and dilute sulphuric acid. After an action of some hours, the solution was mixed with alcohol and filtered. The filtrate heated with bicarbonate of potash in successive portions, gave a fine violet liquid, which with further addition of alkali became deep blue with a tinge of violet. According as acid or alkali were present in excess there was more of the violet or blue shade. The colors were always very fugitive, and changed to dirty brown by standing, with deposit of an amorphous blackish powder, (very small in quantity compared with the picric acid used,) which was soluble in acids, and insoluble in alcalies.

These experiments although many times repeated did not lead to the isolation of any substance of interest. There is a certain amount of resemblance between these reactions, and those of some of the decomposition products of phenylamine: the latter contains the radical $C_{12}H_5$ which exists in a substituted form in picric acid.

Philadelphia, April, 1861.