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I.—*On some Compounds of Urea, and on a New Method for the Determination of Chloride of Sodium and of Urea in Urine.*

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In the number of the Annals of Chemistry and Pharmacy for October, 1851, I have mentioned a compound of urea with protoxide of mercury, which is obtained in the form of a white gelatinous precipitate when a solution of protochloride of mercury (corrosive sublimate) is poured into a solution of urea, previously made alkaline by potassa.

Werther had already previously observed, that urea forms with protochloride of mercury a compound, crystallizing in flat prisms of a pearly lustre, which yields, according to Piria, a white precipitate with potassa, resembling the amide of mercury, and exploding when heated.

I have obtained three compounds of urea with protoxide of mercury; one of which is formed in a direct manner, and was described by Dessaignes a few weeks after the publication of my notice quoted above; the other two are obtained by precipitating an alkaline solution of urea with corrosive sublimate or nitrate of protoxide of mercury.

* The substance of this paper was communicated to the Society on the 10th of January, 1852 (*See this Journal*, Vol. V, p. 30).

A. Urea and Protoxide of Mercury, $2 \text{ HgO} + \text{U}^*$.—On adding to a warm solution of urea protoxide of mercury suspended in water, the first portions are, as described by Dessaignes, completely dissolved in the liquor; an excess of protoxide of mercury is gradually changed into a white or yellowish-white powder. When dried *in vacuo*, the colour of this compound is slightly yellow; when heated in a tube, whilst dry, it is decomposed, without explosion; ammonia is given off, metallic mercury sublimes, and a yellow residue of mellon remains, which disappears only on ignition, when cyanogen gas is disengaged. In the moist state it decrepitates under the same circumstances; in the dark, sparks of a green light are observed.

By digesting protoxide of mercury in the water-bath with a solution of urea, I have in no instance succeeded in obtaining this compound entirely free from cyanate of protoxide or suboxide of mercury; a feeble, but very distinct disengagement of ammonia invariably takes place. The yellowish-white powder formed dissolves in this case, in hydrocyanic and hydrochloric acids, leaving a black residue of metallic mercury behind, and disengaging a small quantity of gas; the solution, when treated with milk of lime, gives off ammonia. This is the character of the cyanates. When digested in the water-bath for a longer period, the urea-compound loses its yellowish-white colour, and becomes lemon-coloured and granular. This latter compound exhibits the deportment of a basic cyanate of mercury.

2·000 grms., dissolved in hydrocyanic acid, gave on evaporation a dry residue of urea and cyanide of mercury weighing 2·394 grms., from which were obtained by precipitation with sulphuretted hydrogen 1·745 of sulphide of mercury, and by evaporation of the filtrate, 0·429 grm. of urea. This gives for

100 Urea and protoxide of mercury	Protoxide of mercury	81·09
	Urea	21·45
		<hr/>
		102·54

The increase in weight, amounting to upwards of $2\frac{1}{2}$ per cent, appears to confirm the formula of Dessaignes, according to which 1 equiv. of water separates by the entrance of protoxide of mercury into this compound. The urea obtained by me was not however perfectly dry; it remained somewhat pasty, and possessed, feebly, the

$^+$
* $\text{U} = 1$ equiv. of urea.

reactions of sulphocyanide of ammonium. I am therefore not quite sure about the fact of water separating from the urea, inasmuch as in the silver-compound which contains 3 equivs. of oxide of silver, a similar replacement of water by oxide of silver does not occur.

By the same process of digesting a solution containing about 10 per cent of urea with protoxide of mercury until the reddish-yellow colour of the oxide was completely converted into a yellowish-white, I have, in several instances, obtained a urea-compound containing 3 equivs. of protoxide, instead of 2, just as the compound to be described forthwith.

B. Urea and Protoxide of Mercury, 3 HgO + U.—On adding solution of potassa to a solution of urea, and mixing with it a solution of corrosive sublimate, the liquid being continually kept alkaline by renewed addition of solution of potassa, a thick, gelatinous, snow-white precipitate is obtained, which, when brought into boiling water whilst still moist, after being first completely washed, is converted into a sandy, granular powder of yellow or yellowish-white colour. The water is hereby rendered alkaline, and takes up a certain amount of urea.

When dried, the powder is reddish-yellow; on being heated in a narrow glass tube, it is decomposed with decrepitation, and when moist, frequently with explosion; in the dark, the substance becomes luminous during this decomposition, and beautiful green sparks are observed; water and carbonate of ammonia are hereby given off, and metallic mercury sublimes, mostly without any residue of mella; the compound dissolves in hydrocyanic and hydrochloric acids without effervescence; alkalies produce in the latter solution a yellowish-white precipitate.

The analysis of this compound from different preparations yielded the following results :

I. 4.606 grms. of substance, dried *in vacuo* over sulphuric acid, gave 4.152 of sulphide of mercury.

II. 2.685 grms. of substance, dried *in vacuo* over sulphuric acid, gave 2.436 of sulphide of mercury.

III. 2.1904 grms. of substance, dried *in vacuo* over sulphuric acid, gave 1.9605 of sulphide of mercury.

IV. 1.7578 grms. of substance, dried *in vacuo* over sulphuric acid, gave 1.5815 of sulphide of mercury.

V. 1.000 grms. of substance, by combustion with oxide of copper, gave 0.1144 of carbonic acid and 0.0594 of water.

VI. 2.094 grms. yielded by direct determination 0.350 grms. of urea.

Composition in 100 parts :

	Calculated.		I.	II.	III.	IV.	V.	VI.
Protoxide of mercury . .	324	84.37	84.1	84.3	83.91	84	—	—
Urea	60	15.63					15.6	16.6
	384	100.00						

C. Urea and Protoxide of Mercury, $4 \text{ HgO} + \text{U}^+$.—On precipitating a solution of nitrate of protoxide of mercury, instead of a solution of corrosive sublimate, with an alkaline solution of urea, a white, somewhat less gelatinous precipitate is obtained, which also loses this state in boiling water, and becomes a sandy powder. No distinct crystalline structure was observed under the microscope in either of these compounds.

The properties of this compound do not differ from those of the others previously described ; it contains, however, more protoxide of mercury. The substance from different preparations, dried over sulphuric acid, yielded by analysis the following results :

I. 0.987 grms. gave $0.932 = 94.4$ per cent. of sulphide of mercury.

II. 2.200 grms. gave $2.085 = 94.3$ per cent of sulphide of mercury and $0.279 = 12.7$ per cent of urea.

III. 3.000 grms. gave 2.860 of sulphide of mercury $= 95.3$ per cent and $0.329 = 10.96$ of urea.

IV. 2.000 grms. gave $1.880 = 94$ per cent of sulphide of mercury ; these numbers correspond to the following composition :

	Calculated.		Found.			
			I.	II.	III.	IV.
4 equivs. of protoxide of mercury . .	432	87.804	87.82	87.3	88.72	87.4
1 „ of urea	60	12.196	—	12.7	10.96	—
	492	100.000		100.0		

Urea and Protoxide of Silver.—When freshly precipitated oxide of silver in the moist state is put into a solution of urea, and the liquid left in a warm place of from 40° to 50° , the oxide of silver changes its colour after one or two hours, appears to swell up from one point, and becomes granular and of a lighter grey colour ; when the mass has assumed a uniform colour, and some of it is examined under the microscope, the powder is found to consist of transparent, pretty regular, scarcely coloured, prismatic crystals. The compound is readily soluble in nitric acid without disengagement of gas, but with

difficulty in ammonia; when touched at one point with an ignited body, it undergoes a tinderlike combustion, a large quantity of ammonia being disengaged, and is converted into a darker coloured coherent mass, which now effervesces with acids and evolves with nitric acid, besides carbonic acid, nitric oxide, or nitrous acid. On heating the burned mass in a tube, a strong smell of cyanic acid is perceived, and a white body sublimes possessing the properties of cyamelide. The urea-compound is converted by the first combustion into a mixture of metallic silver and cyanate of suboxide of silver. On being heated in a tube, a second incandescence takes place; the cyanate of suboxide of silver is decomposed; part of the cyanogen escapes in form of cyanic acid; and another portion remains with the silver; in fact, when the residue is boiled with dilute nitric acid, a mixture of white cyanide of silver and brown paracyanide of silver is left behind.

By analysing the compound, from different preparations, there was obtained:

I. From 2·0340 grms. of urea-oxide of silver, dried *in vacuo* over sulphuric acid, 0·2960 grms. of pure urea = 14·25 per cent.

II. From 1·052 of the compound 0·826 of metallic silver.

III.	„	1·585	„	„	1·248	„	„
IV.	„	1·547	„	„	1·222	„	„
V.	„	1·758	„	„	1·385	„	„
VI.	„	1·939	„	„	1·529	„	„
VII.	„	1·574	„	„	1·242	„	„

These results lead to the following composition:

	Calculated.		I.	II.	III.	IV.	V.	VI.	VII.
3 eqs. of oxide of silver	348	85·29	—	84·32	84·54	84·81	83·50	84·68	84·75
1 eq. of urea . . .	60	14·71	14·25	—	—	—	—	—	—
	408	100·00							

Nitrate of Urea and Protoxide of Mercury.—On adding a solution of nitrate of protoxide of mercury to a solution of urea, a snow-white, flocculent precipitate is immediately formed, containing urea, protoxide of mercury and nitric acid. According to the proportion in which the two solutions are mixed, or according to the amount of acid in the mercury-salt, three compounds or mixtures of them are formed, differing by their amount of protoxide of mercury.

These various compounds possess the following properties in common: they yield, when burned with oxide of copper, a mixture of gases containing nitrogen and carbonic acid, in the proportion of

3 to 2 volumes; this is the same proportion as that in nitrate of urea. On removing the protoxide of mercury by means of sulphuretted hydrogen, pure nitrate of urea remains in the liquor filtered off, which crystallizes to the last drop. These compounds differ, therefore, only by their unequal amount of protoxide of mercury; they dissolve in hydrocyanic and hot nitric acid without leaving a residue: potassa produces a white precipitate in the nitric solution. Heated for some time, when dry, in a current of warm air, decomposition ensues; they assume a yellowish colour, and their nitric solution yields now a yellowish precipitate with potassa.

A. $\text{NO}_5, \overset{+}{\text{U}} + 4 \text{HgO}$.—When the solution of urea is mixed with the mercurial solution in a *very dilute* and warm state, and the precipitate formed is digested with the liquor, it quickly aggregates to a heavy white powder, which presents under the microscope the form of roundish grains, consisting of very small, concentrically grouped needles. In the dry state this powder rolls on paper like fine sand. After being dried *in vacuo*, there was obtained by solution in hydrocyanic acid and precipitation with sulphuretted hydrogen from:

I. 1·990 grms. of the substance, 1·680 sulphide of mercury = 88·4 per cent.

II. 2·000 grms. of the substance, 1·700 sulphide of mercury = 85· per cent.

III. 2·000 gave, after the removal of the mercury, 0·410 of nitrate of urea, and after its saturation with carbonate of baryta 0·681 nitrate of baryta and urea. On treating this 0·681 grm. with alcohol, 0·462 of nitrate of baryta was left.

This compound accordingly consists of:

	Calculated.		I.	II.	III.
1 equiv. nitric acid. . . .	54	9·90	—	—	9·55
1 „ urea.	60	10·98	—	—	10·95
4 „ protoxide of mercury	432	79·12	78·58	79·14	—
	<hr/>	<hr/>			
	546	100·00			

B. $\text{NO}_5, \overset{+}{\text{U}} + 2 \text{HgO}$.—On adding a solution of crystallized nitrate of urea to a moderately dilute solution of nitrate of protoxide of mercury, mixed with some nitric acid, until a slight cloudiness ensues which does not disappear again, then filtering and allowing the mixture to stand quietly, solid hard crystalline crusts are deposited over night, consisting of an aggregate of small, rectangular, brilliant,

transparent tablets. By treatment with boiling water, these crystals are decomposed; they become dim and opaque, and are transformed into the compound just described, the water removing from them nitrate of urea. The analysis yielded the following results:

- I. 2·400 grms. gave 1·696 sulphide of mercury.
 II. 2·000 „ „ 1·414 „ „ „
 III. 2·000 „ „ 0·700 gm. nitrate of urea, from which were obtained 0·780 nitrate of baryta.

This compound therefore consists of:

	Calculated.		I.	II.	III.
1 equiv. nitric acid	54	16·37	—	—	16·1
1 „ urea	60	18·18	—	—	18·9
2 „ protoxide of mercury	216	65·45	65·6	65·7	—
	<hr/> 330	<hr/> 100·00			

C. $\text{NO}_5, \text{U} + 3 \text{HgO}$.—On adding a dilute solution of nitrate of protoxide of mercury to a solution of urea, as long as a precipitate is formed, and allowing the white mass to stand in a warm place of from 40° to 50° , the precipitate is converted into six-sided transparent tablets, amongst which are observed under the microscope, roundish grains of the first, and isolated square tablets of the second compound. In no instance have I succeeded in obtaining this compound quite pure and free from those admixtures; the microscope however plainly indicates that we have before us a compound totally different from the other two.

2·000 grms. gave 1·550 sulphide of mercury, 0·864 nitrate of baryta and urea, and from this 0·597 nitrate of baryta.

3·000 grms. gave 2·488 sulphide of mercury, 1·256 nitrate of baryta and urea, and 0·836 nitrate of baryta.

The first analysis yields for 100 substance, 77·5 sulphide of mercury; the second, 80·3. Assuming the compound to contain 3 equivs. of protoxide of mercury for 1 equiv. of nitrate of urea, 79·4 per cent of sulphide of mercury should be obtained from it, when in a pure state.

QUANTITATIVE DETERMINATION OF CHLORINE IN NEUTRAL LIQUIDS BY MEANS OF PROTOXIDE OF MERCURY.

Nitrate of protoxide of mercury added to a solution of urea, immediately produces a thick white precipitate; this precipitation does not take place with solution of corrosive sublimate.

On mixing a chlorine-compound of the alkali-metals with nitrate of

protoxide of mercury, a mutual transposition into sublimate and nitrate of the alkaline base takes place. A saturated solution of chloride of sodium, mixed with a concentrated solution of nitrate of protoxide of mercury, solidifies into a foliated mass of crystals of protochloride of mercury.

On mixing a solution of urea with chloride of sodium, and adding gradually, in small portions, a dilute solution of nitrate of protoxide of mercury, a white cloudiness ensues at the place where both liquids meet, disappearing, however, immediately on shaking, leaving the liquor as bright and transparent as before; without the chloride of sodium, it would have retained its cloudiness. This deportment lasts until the nitrate of protoxide of mercury added, exactly suffices to transform the chloride of sodium into corrosive sublimate; beyond this limit, a single drop of the mercurial salt produces a lasting white cloudiness.

From this deportment it is evident that, if we know the amount of mercury in the solution of nitrate of protoxide of mercury which has been added to a solution of urea, containing an unknown quantity of chloride of sodium, until a permanent precipitate is formed, we also know the amount of chlorine or of chloride of sodium in this solution; 1 equiv. of mercury in the mercurial solution used, corresponds exactly to 1 equiv. of chlorine (or chloride of sodium).

If, on the contrary, the amount of chloride of sodium in the solution of urea be known, and the amount of mercury in the mercurial solution be unknown, the latter amount may be calculated with facility.

This method of determining the amount of chloride of sodium is particularly applicable in the case of urine, inasmuch as no urea requires to be added; as a matter of course, it may also be used with advantage for the estimation of the chlorine in brine or sea-water, and, generally speaking, in every case when a large number of such determinations are to be made in the shortest possible time. In those cases in which the chloride of sodium is not to be estimated in urine, but in other neutral liquids, the method, now to be described, has to be modified in some points.

Preparation of the Nitrate of Protoxide of Mercury.—If chemically pure mercury be at our disposal, this preparation does not offer any difficulty. 5 parts of nitric acid of 1.425 spec. grav. are poured on 1 part of mercury in a beaker; this is then placed over a water-bath, and heated, with frequent additions of a few drops of nitric acid, until no more red vapours escape, and a drop of it mixed with solution of chloride of sodium ceases to produce a cloudi-

ness; the solution is then evaporated in the same vessel, and over the water-bath, to the consistence of a syrup. The mercury of commerce cannot be used for this purpose, because it always contains lead and bismuth, which render the determination of chlorine uncertain. The presence of lead or bismuth immediately produces a white cloudiness, or an opalescence, on mixing the mercurial solution with a solution of chloride of sodium containing urea, which renders it difficult to recognise clearly the limit—or the point when the urea-compound of the nitrate of protoxide of mercury is precipitated. It becomes, therefore, necessary first to obtain a crystallization of nitrate of suboxide of mercury by boiling dilute nitric acid with an excess of metallic mercury, concentrating and cooling. The crystals of this salt are then separated from the mother-liquor containing the other metals, washed first with some dilute nitric acid and then with water, whereby part of the salt may be transformed into a basic salt; they are next dissolved in nitric acid, and heated until no further escape of nitric acid takes place, and a drop of it tested by chloride of sodium is no longer precipitated. The solution of the salt of the protoxide is now evaporated in a water-bath, to the consistence of a syrup, and diluted with 10 times its bulk of water. Should there be, after 24 hours, a separation of basic salt of the protoxide from the mixture, it must be filtered off.

In order to employ this mercurial solution for the determination of chloride of sodium, it must be graduated—that is to say, reduced to a definite amount of protoxide. This may be effected in two ways: it is either graduated in a direct manner with a solution of pure chloride of sodium of a definite strength; or the amount of protoxide of mercury is estimated, and the solution then diluted with such a quantity of water, that a cubic centimeter of the dilute solution indicates exactly 10 milligrammes of chloride of sodium. Both methods require a solution of chloride of sodium of a definite strength.

When pure transparent rock-salt, in coarse pieces, is digested with water during twenty-four hours, at a temperature of from 12° to 24° , and the liquor frequently shaken during that time, an unvarying quantity of the salt is dissolved.

10 cub. cent. of the clear filtered solution contain a definite, invariable weight of chloride of sodium; a determination by the balance is hereby not required.

100 parts of water dissolve, according to the experiments of Fuchs, 36; according to the latest investigations of Fehling, 35.91; and

10 parts by weight of the solution contain 2·6423 of chloride of sodium. The spec. grav. of the solution is, according to Karsten, 1·2046; according to Anthon, 1·205; 10 cub. cent. of a saturated solution should consequently contain 3·183 grms. of chloride of sodium.

By evaporating 10 cub. cent. of saturated solution of chloride of sodium, I have obtained 3·185, 3·184, 3·195, 3·175, mean 3·184 grms. of chloride of sodium. This is the number obtained by Fuchs and Fehling.

If, therefore, 20 cub. cent. of solution of chloride of sodium, saturated at the ordinary temperature, be exactly measured by means of a pipette (the drop adhering to the end of the pipette not blown off), and mixed with 298·4 cub. cent. of water, we have:

298·4 cub. cent. of water	}	318·4 cub. cent.
20·0 „ „ solution of chloride of sodium		

of dilute solution of chloride of sodium containing 2×3184 milligrammes of this salt. 10 cub. cent. of this solution contain, therefore, 200 milligrammes of chloride of sodium.

Preparation of the test-liquor for the determination of Chloride of Sodium.—In a small pipette, holding exactly 10 cub. cent. of liquor when filled to a certain line in the narrow tube, 10 cub. cent. of the solution of chloride of sodium, just described, are measured off, and put into a small beaker; to this are added 3 cub. cent. of a solution of urea, containing in 100 cub. cent. 4 grms. or in 1 cub. cent. 40 milligrammes of urea.*

The dilute solution of mercury, to be graduated, is now put into a burette, the height of the liquor noted, and added drop by drop to the solution of chloride of sodium mixed with urea, whilst the liquor is kept in a rotatory motion. The test is finished as soon as a distinct precipitate is permanently formed in the liquor.†

If for 10 cub. cent. of solution of chloride of sodium 7·8 cub. cent. of the mercurial solution have been required to induce the precipitate, the latter is too concentrated to admit of an exact graduation;

* For the purpose of measuring this solution, a small measure is made of a narrow test-tube, in which 3 cub. cent. of liquor are measured off; the height of the liquor is marked by a scratch with a file; a few drops more or less are of no consequence.

† An opalescence of the liquor is not to be regarded; it is caused by a trace of foreign metals; it may immediately be recognised as not pertaining to the test, when, after its appearance, the cloudiness of the liquor is not increased by the addition of a few drops of the mercurial solution. This is not the case when the cloudiness has been caused by the urea-compound; every additional drop of the mercurial solution then produces a cloud, by which the liquor is rendered more opaque than it was before.

it has then to be diluted with its bulk of water, and the test to be made a second time. Suppose 15.5 cub. cent. of the mercurial solution have now been required to produce a cloudiness in 10 cub. cent. of the solution of chloride of sodium mixed with urea; then to 155 volumes of this mercurial solution, 45 volumes of water must be added, whereby 200 volumes of a solution are produced, of which 20 cub. cent. indicate exactly 200 milligrammes of chloride of sodium, or 1 cub. cent. 10 milligrammes.

If in the first trial 2.7 cub. cent. of mercurial solution be required for 10 cub. cent. of the solution of chloride of sodium, 5 or 6 times its bulk of water must be added before the first graduation is made. In short, the mercurial solution to be graduated should not be too far removed in concentration from the amount which it is ultimately to contain.

The correctness of the measurements is finally controlled by a special experiment; the degree of cloudiness, permanently obtained on mixing 20 cub. cent. of the test-liquor with 10 cub. cent. of the solution of common salt with urea, must be kept in view when making the real estimations. In these quantitative determinations of chloride of sodium, a source of error easily avoided, however, by a little practice, exists in using too much mercurial solution, whereby the cloudiness is increased, or too little, whereby it is diminished.

The test-liquor, the preparation of which I have just described, is calculated for those cases in which no other salts, besides chloride, and no excess of urea exist in the solution; it leads, however, to a slight error, when employed for determining the chloride of sodium in urine, inasmuch as it indicates a smaller amount in urine than really exists therein. This error is occasioned by the cloudiness, the index of the termination of the experiment, appearing somewhat earlier in the presence of much urea and other salts than without, inasmuch as the precipitate is less soluble in such liquids. A deposit of nitrate of urea and protoxide of mercury is, as a matter of course, not produced until the liquor is saturated with it; the mercurial solution always contains free nitric acid, which dissolves more of it than water, and this again more than a nitric solution of urea.

Since then urine generally contains more urea than has been added to the solution of chloride of sodium when graduating the mercurial solution, and this urea seizes part of the free nitric acid of the mercurial salt, forming nitrate of urea, the solvent power of the liquor for the precipitate is diminished, and the precipitate appears somewhat sooner—that is, somewhat less of the test-liquor is required to produce the cloudiness. This error is completely obviated by adding

5 cub. cent. of a cold saturated solution of sulphate of soda to the 10 cub. cent. of solution of chloride of sodium, mixed with 3 cub. cent. of solution of urea, and then graduating the test-liquor.

Nitrate of protoxide of mercury produces, with a solution of sulphate of soda, a yellow pulverulent precipitate of *turpethum minerale*. If the sulphate of soda contains chloride of sodium, the precipitate of turpethum, on addition of nitrate of protoxide of mercury, is not formed until the chloride of sodium is converted into sublimate; the addition of sulphate of soda alters, therefore, the experiment only in this manner, that the free acid of the mercurial salt combines with the sulphate of soda to form an acid salt, whereby the same effect is produced as by an excess of urea.

On adding urea and then nitrate of protoxide of mercury to a solution of sulphate of soda, free from chloride of sodium, the liquor coagulates, even when tolerably dilute, to a gelatinous mass of a snow-white compound, containing sulphuric acid, urea, and protoxide of mercury; it is somewhat less soluble in water and sulphuric acid than the corresponding nitrate.

The method of determining chlorine by means of a silver-salt is so exact that no more exact process could be said to exist; but the method of estimation with nitrate of protoxide of mercury, just described, is not inferior to that with nitrate of silver, as regards precision; it is applicable, however, only to neutral, or very slightly acid, or alkaline liquids, because an excess of acid prevents the precipitation of the urea-compound.

The following numbers enable us to make a comparison of both methods; they refer to very dilute solutions of chloride of sodium, presenting but very slight difference in the amount of chloride of sodium.

Amount in 10 cub. cent. of the solution.		Estimated by nitrate of protoxide of mercury.	
I.	81·5 milligrammes		81·6
II.	80·2 „		79·8
III.	82·7 „		82·3

We observe readily that these numbers do not differ from each other in a greater degree, than in the case of determinations made with standard solutions of nitrate of silver in the usual way.

The only advantage the nitrate of the protoxide of mercury has over the silver-salts consists, as I believe, in the circumstance, that the termination of the experiment is indicated by the commencement of the reaction. In using nitrate of silver the experiment is finished, when no farther precipitate is perceptible; in this case the cloudi-

ness of the liquor, the difficulty to render it clear in order to observe the end of the experiment, impedes the dispatch of the execution. In using the mercury-salt, some dozen analyses may be made in an hour; hence, this method is particularly applicable to technical purposes, for the estimation of chloride of sodium in Glauber's salt, and, after previous neutralization, in the soda of commerce.

In order to determine the chloride of sodium in urine, it is necessary to remove previously the phosphoric acid contained in it. I have found a mixture of 1 volume of a cold saturated solution of nitrate of baryta, and 2 volumes of cold saturated baryta-water, to answer this purpose very well. To 2 volumes of the urine to be examined, 1 volume of this mixture is added, and the precipitate formed filtered off; the liquor is alkaline from the excess of baryta; this alkaline reaction must be removed by means of nitric acid.

For the experiment, 15 cub. cent. of this liquor are taken, corresponding to 10 cub. cent. of urine; and for the measuring of it a small pipette is used, holding exactly this volume, when filled to the line, without subdivision. The liquor is put into a small beaker-glass (the last drop adhering to the pipette not blown or taken off), and mixed with the mercury-solution whilst it is continually being stirred. When cloudiness ensues, the quantity of test-liquor used is read off from the burette. Every cub. cent. used corresponds to 10 milligrammes of chloride of sodium.

By this method, I have made a large number of comparative experiments, with a solution of silver also graduated for 10 milligrammes of chloride of sodium in 1 cub. cent. of water; and the following numbers may furnish a specimen of the precision of the first, and of its close approximation to the ordinary method:

				By means of nitrate of:	
				silver.	protoxide of mercury.
				Milligrms.	Milligrms.
1.	10	cub. cent. of morning urine contained	. . .	115·4	115·0
2.	10	" " " " " of a child	. . .	110·	110·
3.	10	" " " " " of urine secreted after dinner	. . .	164·	164·
4.	10	" " " " " before dinner	. . .	189·	188·5
5.	10	" " " " " " " "	. . .	74·	74·
6.	10	" " " " " " " "	. . .	142·8	142·
7.	10	" " " " " after taking tea	. . .	127·5	127·5
8.	10	" " " " " " " beer.	. . .	27·7	27·7
9.	10	" " " " " { before bed-time, after taking beer	. . .	25·	25·
10.	10	" " " of the same urine	. . .	25·	25·
11.	10	" " " of urine (woman)	. . .	110·	110·
12.	10	" " " of the same urine	. . .	110·	110·

Chloride of sodium.

The correctness and accordance of these determinations depends chiefly upon this point, that, in neutralizing the urine mixed with the baryta and nitrate of baryta, no more nitric acid is added than is just required in order to produce a feebly acid reaction. For this reason it is preferable to acidulate with nitric acid the whole filtrate, of which a small portion is kept back, and not the 15 cub. cent. measured off for the test; one drop too much is of no consequence in 100 or more cub. cent. of liquor, whilst if added to the small portion for the test, it would interfere with the precision of the experiment.

In determining urea in urine, the amount of chloride of sodium in it causes an error, which, for very accurate analyses, is obviated by previously removing the chlorine; and in this case the determination of the chloride of sodium, by means of nitrate of mercury, serves to indicate the exact amount of silver-solution graduated for the same quantity of chloride of sodium, which is to be added to the urine without further experimenting.

DETERMINATION OF PROTOXIDE OF MERCURY IN A SOLUTION OF NITRATE OF MERCURY.

On mixing solutions of nitrate of protoxide of mercury and phosphate of soda, a white flocculent precipitate of phosphate of protoxide of mercury is immediately formed, which, on being left in the liquor, rapidly becomes crystalline.

Solution of corrosive sublimate, however, may be mixed with the alkaline phosphate without producing a precipitate.

On adding solution of chloride of sodium to the mixture of the two former salts, before the precipitate becomes crystalline, the phosphate of protoxide of mercury formed immediately decomposes with the chloride of sodium, into sublimate and phosphate of soda; the precipitate formed disappears, and the liquor becomes clear and bright.

On this deportment I have based a method of determining the amount of protoxide of mercury in its nitric solution with tolerable precision. 1 equiv. of phosphate of protoxide of mercury requires to redissolve it 1 equiv. of chloride of sodium; if, therefore, the amount of chloride of sodium added be known, the amount of mercury in the mercurial solution is also known.

Since the equivalent of chloride of sodium is almost one half of that of protoxide of mercury, this method is not so precise and accurate as the determination of chloride of sodium by means of the mercury-salt; inasmuch as a small error in the addition of the solution of chloride of sodium causes one which is twice as great in

the calculation of the mercury. For certain purposes, however, especially for those which I have in view, this method is sufficiently exact.

Preparation of the normal solution of Chloride of Sodium to be employed for determining the Mercury.—According to the equivalents of chloride of sodium and of the protoxide of mercury, 108 protoxide of mercury correspond to 58·6 chloride of sodium, or 200 of oxide correspond to 108·52 of the salt.

If, therefore, 20 c. c. of a saturated solution of chloride of sodium be mixed with 566·8 c. c. of water, we have 586·8 c. c. of a dilute solution of chloride of sodium, containing in the whole 6368 milligrammes of chloride of sodium (viz. the amount contained in 20 cub. cent. of the saturated solution); in 10 cub. cent. there are, therefore, 108·52 milligrammes of chloride of sodium, corresponding to 200 milligrammes of protoxide of mercury (1 cub. cent. of solution of chloride of sodium = 20 milligrammes of protoxide of mercury).

In order to determine with some accuracy the amount of oxide in a solution of nitrate of protoxide of mercury by means of this method, the solution should not be too concentrated, partly for the sake of measuring exactly, and partly on account of the limits of the reaction being more easily perceived in dilute liquors than in concentrated ones; it is desirable that the mercurial solution should not contain more than from 180 to 200 milligrammes of protoxide of mercury in 10 cub. cent.

In order to determine the concentration, the following preliminary experiment is made:—10 cub. cent. of the solution of chloride of sodium are mixed with 4 cub. cent. of a cold saturated solution of phosphate of soda (the officinal salt), and to this mixture the mercurial solution is poured from a burette, until, on shaking, the precipitate does not any longer disappear. Suppose 2·4 cub. cent. of mercurial solution had been used, they would then contain 200 milligrammes of oxide. This is too concentrated; 1 cub. cent. of it contains upwards of 80 milligrammes of oxide, but the exact determination requires that 1 cub. cent. should not contain more than 20 milligrammes. This solution should therefore be diluted with 3 volumes of water before the actual experiment is made.

Of this dilute solution of mercury, 10 cub. cent. are now put into a beaker, mixed with 4 cub. cent. of the above-mentioned solution of phosphate of soda, and the graduated solution of chloride of sodium added from the burette; the solution is kept in constant motion, and the test added very slowly towards the end, until the white precipitate formed is completely redissolved.

The addition of the solutions of phosphate of soda and of chloride of sodium must follow in rapid succession: if but a few minutes

elapse between the two additions, the phosphate of protoxide of mercury becomes crystalline, and does no longer dissolve, or at least with difficulty. Moreover, the solution of mercury must not contain too much free acid; it contains the proper amount, if, after the addition of the phosphate of soda, the mixture does not exhibit an acid reaction. If it has an acid reaction, it must previously be mixed with a few drops of carbonate of soda, until a basic salt is precipitated, which is redissolved by means of one or two drops of nitric acid.

It is a special character of this method that its errors depend chiefly on the circumstance of one or more drops of solution of chloride of sodium being added in excess, in order to redissolve the precipitate. The more chloride of sodium is used for a given volume of the solution of mercury to effect this end, the more oxide is supposed to be in this volume; the error in question increases, therefore, the amount of mercury found beyond the real amount. Since the phosphate of mercury is slightly soluble in the liquor, and since, finally, the solution of chloride of sodium is graduated with regard to this error, this discrepancy is generally very slight. If the method be reversed (*viz.*, if the solution of mercury be poured into a mixture of the solutions of chloride of sodium and phosphate of soda) a slight excess of solution of mercury is always added, to make the precipitate appear, because it does not become permanent until the liquor is saturated with it. According to this mode of proceeding, therefore, the amount of mercury obtained is too low.

The determinations become still more exact, if both methods are combined in the following manner:

(Method I).—10 cub. cent. of the solution of mercury are poured into a beaker, 3 to 4 cub. cent. of a solution of phosphate of soda added, and then immediately, without waiting till the precipitate has become crystalline, the solution of chloride of sodium is added from the burette, until the precipitate has disappeared. Suppose 12·5 cub. cent. of solution of chloride of sodium had been used for this purpose, 12·5 cub. cent. of the same solution are then measured off.

(Method II).—3 to 4 cub. cent. of phosphate of soda added, and the same solution of mercury poured into this mixture from the burette, until a precipitate appears. Suppose 10·25 cub. cent. of the solution of mercury have been used for this purpose, then the true amount is as follows:

There have been used for:

I.	10	c. c. of solution of mercury,	12·5	c. c. of solution of chloride of sodium.
II.	10·25	c. c. " " "	12·5	c. c. " " "
	20·25		25·0	

Now, since every cub. cent. of solution of chloride of sodium corresponds to 20 milligrammes of protoxide of mercury, the 25 cub. cent. used indicate $20 \times 25 = 500$ milligrammes of protoxide of mercury which are contained in 20.25 cub. cent. of the solution of mercury.

The following experiments may serve as a critical illustration of this method :

a. 7.480 grms. of pure mercury, and 24 grms. of nitric acid of 1.402 spec. grav., were put into a beaker, and evaporated in a water-bath to the consistence of a syrup, then mixed with water so as to bring the volume of the liquor to 400 cub. cent. 10 cub. cent. of this solution contained, therefore, 187 milligrammes of mercury.

When tested according to method I. it was found to contain 190.8 milligrms.

And according to method II. 184.8 "

Mean 187.8 " of mercury.

b. 6.993 of mercury dissolved in nitric acid in the same manner, and diluted to 400 cub. cent ; 10 cub. cent. contained 174.8 milligrammes of mercury :

Found according to the method I. . 177 milligrammes

" " " " II. . 172.4 "

Mean 174.7 " of mercury.

c. 8.321 of mercury dissolved in the same manner, and diluted to 500 cub. cent. ; 10 cub. cent. contained 166.4 milligrammes of mercury :

Found by the method I. . . 170.2 milligrammes

" " " II. . . 163.4 "

Mean 166.8 " of mercury.

d. From 10 cub. cent. of a solution of an unknown amount of oxide there was obtained by precipitation with potassa, 1.436 grms. of protoxide of mercury, and by the test-liquors in the mean, 1.446 grms.

e. 31.669 of mercury dissolved in nitric acid in the manner described above, and diluted with 443 cub. cent. of water ; 10 cub. cent. contained 772 milligrammes of oxide. 1 volume of this solution was mixed with 3 volumes of water ; 10 cub. cent. of this dilute liquor contained 193 milligrammes of oxide.

Found by the method I.	. .	192·5	milligrammes
„ „ „	II. . .	183·	„
Mean		187·9	„ of oxide.

Instead of phosphate of soda, pyrophosphate of soda, neutral chromate of potassa, and other salts which do not precipitate corrosive sublimate, may be used.

As a matter of course, this method is only applicable to nitric solutions of mercury, containing no metals that are precipitated by alkaline phosphates from their hydrochloric solution. A separation of the mercury from many other metals, may, however, be pretty readily effected by precipitating the solution of the mixed metals with phosphate of soda, then adding a solution of chloride of sodium in excess, and filtering; the mercury is dissolved under these circumstances, whilst the other metals remain undissolved in form of phosphates.

METHOD FOR THE DETERMINATION OF UREA IN URINE.

The methods just described for the determination of chloride of sodium and of mercury are mainly calculated for the determination of chloride of sodium and urea in urine, and are, perhaps, of particular value for this purpose only.

I will now proceed to describe a new method of determining urea in urine, which equals those now in use, in point of accuracy, but has this advantage, that it far excels them as regards rapidity of execution, and that its application does not require any particular skill, so that it is particularly applicable, as I think, for medical purposes, as a means of assisting the diagnosis of certain states of disease.

This method is based on the fact that urea is precipitated by nitrate of protoxide of mercury.

On gradually adding to a dilute solution of urea an equally dilute solution of nitrate of protoxide of mercury, and neutralizing the free acid of the mixture from time to time by baryta-water or dilute carbonate of soda, a flocculent, snow-white precipitate is obtained, which is insoluble in water. If the addition of the salt of mercury and of carbonate of soda, be continued alternately, as long as this precipitate is formed, a point is arrived at, when by the addition of the carbonate of soda, the mixture, or the spot with which the drop comes in contact, assumes a yellow colour of hydrated oxide of mer-

cury, or basic nitrate of protoxide of mercury. When filtered at this point, the liquor no longer contains any appreciable quantity of urea ; all the urea is precipitated. I have subjected to analysis this precipitate, which differs by its amorphous condition from the above-described compounds of urea and nitrate of protoxide of mercury, and I found it in every instance to contain 4 equivs. of protoxide of mercury for 1 equiv. of urea. By mixing a solution of urea with a solution of mercury, both of known strength, it can easily be demonstrated, that a precipitation of yellow oxide by the addition of carbonate of soda to the mixture, is not produced until a volume of the nitric solution of mercury is added, which contains 77 parts of protoxide of mercury, for 10 parts of urea in the solution of urea ; this, however, amounts to 4 equivs. of protoxide of mercury to 1 equiv. of urea.

On adding nitrate of protoxide of mercury to a solution of urea as long as a precipitate is formed, the mixture remains *white* on addition of carbonate of soda ; if, however, the original mixture be left quietly for some hours, the appearance of the precipitate is changed ; it becomes crystalline ; the six-sided tablets of the compound with 3 equivs. of protoxide of mercury are easily recognised in it, and the clear liquid, standing above the crystals, which was previously precipitated white, produces now a *yellow* precipitate with alkalis. The compound with 4 atoms of protoxide of mercury, is reduced in the acid liquor into a compound containing less oxide—that is to say, part of the oxide is redissolved.

In order to ascertain whether the exact quantity of the salt of mercury has been added, necessary for the formation of the urea-compound with 4 atoms of protoxide of mercury, it is requisite to neutralize the liquor with carbonate of soda, after the mercurial solution has been added. If the mixture—for instance, a drop of it on a watch-glass, mixed with a drop of solution of carbonate of soda—remain white, it may be assumed with certainty that free urea is still present in the liquor ; only when on mixing the two drops, a yellow skin appears on the surface, the limit is attained, or rather a little exceeded ; but a very slight excess of the mercurial solution is required to indicate that the requisite quantity for the precipitation of the urea has been added. From this it is evident that if the amount of mercury in the solution be known, the quantity of urea in a liquid containing it may be estimated by the amount of solution used, in the described manner, for the precipitation of the urea. Or if for the precipitation of a *known* quantity of urea—say 100 milligrammes—a certain volume of solution of mercury be necessary, an equal volume of it will indicate the same amount of

urea in a liquor, the amount of urea in which is unknown. From the volume of this solution, used for the precipitation, the quantity of urea present may be calculated; the consumption of half the volume indicates half as much; that of double the quantity, twice as much urea in the liquor.

On this point also my experiments have yielded perfectly concordant results, as the following numbers will show.

The first series indicates the amount of urea obtained from 10 cub. cent. of the solution by simple evaporation. The second series exhibits the amount of urea in the same volume of the same solution, as found by the determination with the graduated solution of nitrate of protoxide of mercury.

For 10 cub. cent. of solution of urea were obtained :

	I.	II.	III.	IV.	V.	
I. Urea by evaporation	371·5	412·	117·	98	512	milligrams.
II. „ by nitrate of mercury	372·5	412·	116·8	98	512·75	„

The methods for the determination of urea, up to the present time acknowledged as the best, are those of Ragski and Bunsen; both are based upon the same principle—viz., upon the transformation of the urea into carbonate of ammonia. Ragski determines the ammonia in the form of ammonio-chloride of platinum; Bunsen determines the carbonic acid in form of carbonate of baryta. Both methods give very trustworthy results, if in Ragski's method the potassio-chloride of platinum, precipitated simultaneously, be taken into account.

The following series of experiments, in which the amount of urea in urine of man was determined according to Ragski's method, and by means of nitrate of protoxide of mercury, may prove that the latter method is not inferior to the former.

20 cub. cent. of urine of different individuals contained of urea :

Determined by means of	I.	II.	III.	IV.*	
nitrate of mercury	450	360	450	508	milligrams.
Determined by Ragski's method	446	350	457	508	„

I have found on precipitating urine with a mixture of nitrate of baryta and baryta-water, filtering off the phosphate and sulphate of baryta, evaporating the liquid, extracting the residue with alcohol, evaporating the alcoholic extract to dryness, and again exhausting it with absolute alcohol, that this alcoholic solution contains tolerably

* These determinations have been made by my assistant, Dr. Mayer.

pure urea, crystallizing from it in colourless needles. This method may be used to prepare urea directly from the urine without precipitating with nitric acid; and this mode of proceeding may even be used for the quantitative determination, as the following experiments will show, for which the same urine was used as in the above determinations of urea.

	In 20 c. c. of urine.				In 10 c. c. of urine.*			
	I.	II.	III.	IV.	V.	VI.	VII.	
Urea by alcohol	428	326	439	503	223	219	198.5	milligrms.
„ by nitrate of protoxide of mercury	450	360	450	508	225	220	200	„

The solubility of chloride of sodium in alcohol is, however, somewhat increased by urea. According to an experiment made on this point, alcohol dissolved from a mixture of chloride of sodium and urea 1.0085 grms. consisting of 0.9785 urea, and 0.030 chloride of sodium. 100 parts of the dissolved substance contained accordingly 2.97 of chloride of sodium, and 9.703 of urea.

Finally I determined the urea by means of nitrate of protoxide of mercury in the urine of different persons, and then, in order to test the influence of the other constituents of urine, I mixed the same urine with weighed quantities of pure urea, and determined the latter again: the following results will show that these other constituents exert no influence in the determination.

10 cub. cent. of urine contained:

	I.	II.	III.	
Urea	272	212	170	} 195 milligrms. of urea.
After adding	100	250	25	
The second determination gave	373	464	196	„ „ „

In all the experiments with the test-liquor, the urine was previously precipitated with a mixture of baryta-water and nitrate of baryta, an operation which was omitted in the application of Ragski's method.

Preparation of the solution of Mercury, which serves for the precipitation of Urea in Urine.—4 grms. of pure urea are first dissolved in water, and diluted with water until the volume of the solution amounts to exactly 200 cub. cent. (by dissolving 4 grms. of urea in 200 cub. cent. of water, 201.75 cub. cent. of liquor would be obtained, an excess of 1.75 cub. cent.)

20 cub. cent. of the solution of nitrate of protoxide of mercury, to be used for the determination of urea in urine, should exactly suffice to indicate with precision the urea in 10 cub. cent. of the solution of

* These determinations were made by my assistant, Dr. Mayer.

urea just described, containing 200 milligrammes of urea: 1 cub. cent. of it should correspond to 10 milligrammes of urea. For this purpose the solution of mercury should contain a quantity of oxide sufficient to form with 100 milligrammes of urea, the nitrate with 4 equivs. of protoxide of mercury, besides a small excess of protoxide of mercury, for the purpose of indicating the complete precipitation of the urea; so that, on adding the last drop of the 10 cub. cent. of solution of mercury to the solution of urea, a distinct yellow colour is perceptible, when a few drops of the mixture are mixed with solution of carbonate of soda.

I have found by a series of experiments that for 100 milligrammes of urea, which require, according to calculation, 720 milligrammes of protoxide of mercury (in the form of nitrate), 10 cub. cent. of the solution of mercury should contain 772 milligrammes of protoxide of mercury, in order to produce a distinct reaction of protoxide of mercury in dilute liquids. Every cub. cent. of the liquor should, therefore, contain an excess of 5.2 milligrammes of protoxide of mercury. The test-liquor is best obtained by dissolving pure metallic mercury in pure nitric acid in a beaker; keeping the mixture heated, with frequent addition of some nitric acid, until no longer any trace of nitrous vapours escape; then evaporating to the consistence of a syrup in the same vessel, or a water-bath, and lastly diluting with water, until 100 cub. cent. of the dilute liquor contain exactly 7.140 grms. of mercury. This is the case when for 100 grms. of mercury (converted into nitrate of the protoxide), as much water is added as will bring the volume of the liquor to 1400 cub. cent.

When for the preparation of the nitrate of the protoxide, crystallized nitrate of suboxide of mercury is used, which may with greater facility be obtained in a state of purity and free from other metals than metallic mercury, and a concentrated solution of the salt of the protoxide of unknown strength is thus produced, the amount contained in it has to be determined, and the solution reduced by water to the proper degree. This is done by means of the method described, p. 14. Or a known volume of the concentrated solution is diluted with 10 times its bulk of water, and the amount of protoxide of mercury determined in 10 cub. cent. of it, by precipitation with potassa, or in the form of sulphide of mercury, by mixing the solution with a solution of sulphate of soda, and passing sulphuretted hydrogen through it, till the precipitated basic sulphate of protoxide of mercury is decomposed.

Previous to its application for determining the urea in urine, the dilute solution of mercury must be tested as to its correctness by

means of a solution of pure urea ; for this purpose we may use the solution of urea, mentioned above, containing in 10 cub. cent. 200 milligrammes of urea.

It is advisable, in diluting the concentrated solution of mercury not to reduce it, by the addition of water, at once to the calculated degree ; but to add rather less water at first, then test it with the solution of urea, and complete the process.

The best mode of proceeding is, to dilute 10 cub. cent. of the concentrated solution of mercury with 5 or 10 times its volume of water, according to concentration, and to determine approximately the amount of protoxide in 10 cub. cent. of this dilute solution, by means of phosphate of soda and the graduated solution of chloride of sodium.

Suppose, for 10 cub. cent. of the five times diluted solution of mercury, 18.5 cub. cent. of solution of chloride of sodium have been used ; the amount of water to be added may then easily be calculated.

For 10 cub. cent. of the concentrated solution should be used 38.5 cub. cent. of solution of chloride of sodium (corresponding to 772 milligrammes of protoxide of mercury) ; there have been actually used $5 \times 18.5 = 92.5$ cub. cent. of the solution of chloride of sodium. If then 92.5 cub. cent. solution of chloride of sodium be used for 10 cub. cent. of the concentrated solution of mercury, then exactly 4.16 cub. cent. of it are necessary for 38.5 of solution of chloride of sodium. If, therefore, 416 vols. of the concentrated solution of mercury be mixed with 584 vols. of water, 1000 vols. of a dilute solution are obtained, 10 cub. cent. of which correspond exactly to 38.5 cub. cent. of solution of chloride of sodium.

It is, as before stated, advisable, not to add the calculated quantity at once, but rather less. 10 cub. cent. of the normal solution of urea are now measured off, and then from a burette the approximatively diluted solution is added, until a few drops on a watch-glass produce a distinct yellow colour with carbonate of soda. Suppose 19.25 cub. cent. of the solution of mercury were used for this purpose ; then for 192.5 cub. cent. of the solution, 7.5 cub. cent. of water have to be added, and with this solution another trial experiment is made. When, after the addition of 20 cub. cent. the appearance of the yellow colour is distinct, the solution of mercury may then be used for determining the urea in urine.

Every possible care must be bestowed on the correctness of the test-liquor, inasmuch as it replaces a balance with which, when defective, the weighings made are the more incorrect, the smaller

the differences in the weights which have to be determined. In the case of an incorrect balance, the error may be met at each weighing; accurate weighings may be made with it; but in the case of a graduated liquid, the corrections must be made before it is used. The volume of the liquor does not add to the trouble, and it is therefore advisable to prepare as large quantities as possible at one time.

The slight excess of the protoxide of mercury in the test-liquor is like the index of the balance; the yellow colour is its deflection, the amount of which must be carefully noted.

The test-liquor is graduated with a solution of urea containing 2 per cent of this substance; 15 cub. cent. of this solution of urea require for the precipitation of the urea, and for indicating its termination, 30 cub. cent. of solution of mercury; 45 cub. cent. mixture are obtained, containing in the whole $30 \times 5.2 = 156$ milligrammes of free protoxide of mercury; every cub. cent. contains therefore 3.47 milligrammes of protoxide of mercury.

If the 15 cub. cent. of solution of urea contain 4 per cent of urea, and to 15 cub. cent. of it 60 cub. cent. of solution of mercury be added, a mixture of 75 cub. cent. is obtained, containing 312 milligrammes of protoxide of mercury; in every cub. cent. 4.16 milligrammes; there is, therefore, an excess of 0.69 milligramme of protoxide of mercury required to produce the original colour.

Careful experiments have proved that, in analyses of urine, when the amount of urea is increasing, an error is committed, tending to diminish the amount of urea; in the case just mentioned, only 59.37 cub. cent. instead of 60 cub. cent. of solution of mercury would be added to make the original colouring appear. In order to remove this error, an addition has to be made—for 15 cub. cent. of urine, and before the test is applied—of $\frac{1}{2}$ cub. cent. of water for every cub. cent. of solution of mercury which has been used over and above 30 cub. cent.; if, for instance 20 cub. cent. more than the 30 cub. cent. be required, we have to add 10 cub. cent. of water. It will always be found that, after the addition of the water, a few drops of the solution of mercury have to be added in order to produce the proper indication.

For the same reasons, when the quantity of urea in urine amounts to 1 per cent only, 15.3 cub. cent. and not 15 cub. cent. of the solution of mercury must be added to 15 cub. cent. of urine, in order to obtain the test; to remove this error, which increases the amount of urea, a deduction has to be made, in the more dilute urines, of 0.1 cub. cent. for every 5 cub. cent. of solution of mercury, used less than 30 cub. cent. If, therefore, 25 cub. cent. of solution

of mercury have been used for 15 cub. cent. of urine, the amount, 249 milligrammes, is expressed by 24.9 cub. cent. of solution of mercury, &c.

For the purpose of determining the urea in urine, a mixture of 2 vols. of baryta-water and 1 vol. of solution of nitrate of baryta, both saturated whilst cold, is first prepared, and 1 vol. of this alkaline liquor mixed with 2 vols. of urine. Here a small glass cylinder of optional capacity is conveniently used, which is first twice filled with urine to overflowing. The aperture of the cylinder is each time covered with a glass plate, causing the excess to flow off; the same cylinder is then filled once with the solution of baryta, and this added to the urine in a beaker. On mixing both liquors, a precipitate is formed, which is filtered off. 15 cub. cent. of the filtered liquor are measured off for each analysis, corresponding to 10 cub. cent. of urine.

To this volume of urine, without previously neutralizing, the graduated solution of the nitrate of protoxide of mercury is added from a burette, the liquor being constantly stirred, and the test applied when no further precipitate is observed, viz., no further thickening of the liquor. To this end, a few drops of the liquor with the precipitate are put into a watch-glass, and then a few drops of solution of carbonate of soda added, proceeding from the rim of the watch-glass; this is best done by means of a pipette of Indian-rubber.* If, after some minutes, the mixture retain its white colour, a further quantity of solution of mercury is to be added; and this process is continued till a fresh sample from the glass exhibits plainly the yellow colour after the addition of carbonate of soda.

The number of cub. cent. is then read off, and the figure obtained corrected, as described above, according to the contents of the urine.

Method of determining Urea in Urine containing Chloride of Sodium.—A series of experiments have proved that the amount of chloride of sodium in urine, when it reaches 1 to $1\frac{1}{2}$ per cent, exercises an influence on the determination of urea by means of nitrate of protoxide of mercury. When 20 cub. cent. of the graduated solution of mercury are added to 10 cub. cent. of the solution of pure urea, carbonate of soda produces in this mixture a distinct yellow colour of precipitated protoxide of mercury; if now 100 to 200 milligrammes of chloride of sodium be added to the mixture, and the test again applied, the yellow colour does not make its appearance

* See Mohr's *Lehrbuch d. Pharm. Tech.* 2 ed. 1853, p. 397.

on the addition of carbonate of soda; and in order to reproduce it, $1\frac{1}{2}$ to $2\frac{1}{2}$ cub. cent. of the solution of mercury have to be added. The determination shows, therefore, 15 to 25 milligrammes of urea too much.

Just the same occurs with urine. Of the many experiments which I have made on this point, I select the following, in order to show plainly this influence: In one portion of urine the amount of chloride of sodium was first determined; then, in an equal quantity, the urea by means of nitrate of protoxide of mercury. This determination was repeated with an equal volume of urine, after the chlorine had been removed by nitrate of silver; finally, the urea was determined according to Ragski's method in the same quantity of urine.

10 cub. cent. of urine contained milligrammes of urea:

	Chloride of sodium.	Before removing the chlorine.	After removing the chlorine.	According to Ragski's method.
I. . .	145	245	225	223
II. . .	155	210	180	175
III. . .	135	245	225	225.5

In Experiment I. the test indicated, before the chlorine was removed, 20; in II. 30; in III. 20 milligrammes of urea more than was actually contained in it. When the quantity of chloride of sodium amounts to more than 2 per cent., this error does not proportionally increase, but remains constant within certain limits.

It has been seen from the method of determining chloride of sodium by means of nitrate of protoxide of mercury, that a solution of urea containing chloride of sodium is not precipitated by nitrate of protoxide of mercury, until the chloride of sodium is completely transformed into corrosive sublimate. In a solution of 200 milligrammes of urea, and 10 milligrammes of chloride of sodium in 10 cub. cent. of water, to which have been added 20 cub. cent. of the solution of mercury, the excess of the salt of mercury (which would have produced the yellow colour on addition of carbonate of soda) is not contained in form of nitrate, but of corrosive sublimate, and it is evident that the change in the indication is effected by the formation and presence of the corrosive sublimate. Instead of 3.46 milligrammes of protoxide of mercury in the form of nitrate, the mixture contains the same amount of oxide in the form of corrosive sublimate.

On diluting a solution of corrosive sublimate with water, until it yields with carbonate of soda a distinct brownish-yellow precipitate of

oxychloride of mercury, then mixing the same solution of sublimate with a drop of nitric acid, and adding it to the carbonate of soda, the mixture of both remains clear; no precipitate is formed, or at most only a slight whitish cloudiness, from which, after long standing, single brownish-yellow tablets are deposited. In this condition, however, the excess of corrosive sublimate is contained in the mixture of the solutions of urea and of mercury; it contains the greater portion of the nitric acid of the latter in an uncombined state.

By this nitric acid, part of the carbonate of soda is converted into bicarbonate, which does not precipitate corrosive sublimate. When the mixture contains a larger amount of corrosive sublimate, in consequence of a larger amount of chloride of sodium in urine, the liberated carbonic acid is not sufficient to prevent the precipitation of all the protoxide of mercury; a brownish-yellow precipitate is now formed. This appears to me to be the cause why the indication of the complete precipitation of the urea is deferred, by the presence of a certain quantity of chloride of sodium, and why the limit of the reaction is not still further removed, when the amount of chloride of sodium is increased.

With urine containing 1 to $1\frac{1}{2}$ per cent of chloride of sodium, the correct number of milligrammes of urea in 10 cub. cent. of urine may be obtained at once by subtracting 2 cub. cent. from the number of cub. cent. used for the solution of mercury; and even when the amount of chloride of sodium in the urine of different individuals varies within certain limits, the differences obtained in the amount of urea are still correct, and comparable with each other; only in the absolute quantity there is an error which, uncorrected, amounts to 15 to 20 milligrammes for 10 cub. cent. of urine.

In determinations in which the absolute quantity of urea in urine is of importance, the chlorine in the urine must be removed, and the chloride of sodium converted into the nitrate; this is done by means of nitrate of silver. For this purpose a solution of silver is prepared from 11.601 grms. of fused nitrate of silver, which are dissolved in water and diluted until the volume of the solution amounts to 400 cub. cent. 1 cub. cent. contains 29.01 milligrammes of nitrate of silver corresponding to 10 milligrammes of chloride of sodium.

The solution of mercury, the preparation of which has been already described, pp. 8, 9, corresponds with this solution of silver; both indicate, when used in equal volumes, the same amount of chloride of sodium. If, therefore, 12.5 cub. cent. of the solution of mercury had to be added to 10 cub. cent. of urine until the appearance of

the cloudiness, the chlorine in the same volume of urine will be completely separated by 12.5 cub. cent. of silver-solution, whilst no silver remains dissolved.

Since the quantity of silver-solution to be added to the urine containing chloride of sodium, for the removal of the chlorine, may be ascertained in a few seconds by means of the solution of mercury, this operation loses all inconvenience, whilst otherwise it would be tedious, and require much time.

Suppose, for 15 cub. cent. of the urine precipitated by the solution of baryta (containing 10 cub. cent. of urine), 17.5 of solution of mercury had been used; then with the pipette, 30 cub. cent. of the same urine are measured off, and 35 cub. cent. of the solution of silver are added; the liquor is then at once filtered, and of the filtrate always one half of the sum of the mixed liquors taken for the test; in this instance, therefore, 32.5 cub. cent. contain 10 cub. cent. of urine. These are now mixed with the graduated solution of mercury, and the amount of urea ascertained in the manner described, taking into consideration the dilution in consequence of the solution of silver added.

The numerous experiments made by Professors Dr. Vogel and Dr. Bischoff, at whose instigation this method has been devised, leave no doubt as to its applicability and correctness. In describing such a proceeding, numerous difficulties present themselves, which in practice prove to be insignificant; indeed, the description is much more complicated than the execution.

The remarkable simplicity which this method of determining urea and chlorine has attained, is mainly owing to the deep interest which my two excellent friends have bestowed upon my experiments; it is the result of a whole series of methods, which one after the other were rejected, not so much for want of accuracy, but on account of the greater difficulty of execution; and on this occasion I have very plainly seen how important and requisite it is for the purpose in view, when the chemist is solving a physiological problem, does not work by himself alone, but in conjunction with a pathologist and a physiologist.

Chemists will observe that, by this determination of urea, mercury and chloride of sodium, another very interesting problem has been solved—viz. the determination by weight of chloride of sodium, mercury and urea, without having recourse to a balance. The paradox of a determination by weight without weighing, disappears by the consideration, that a solution of chloride of sodium, saturated at the ordinary temperature, contains a definite, unchanging weight

of chloride of sodium, and that in 10 cub. cent. exactly 3.184 grms. of chloride of sodium are obtained; by dilution with the proper quantity of water, a solution of chloride of sodium is obtained, containing in 1 cub. cent., 10 or 10.852 milligrammes of chloride of sodium. With these solutions, nitrate of protoxide of mercury may be graduated for the determination of chlorine, mercury and urea, without the necessity of using other instruments than a burette and a pipette.

ADDITIONAL REMARKS.

In order to prevent the rapid transformation of urea into carbonate of ammonia, it is requisite, when collecting the urine of animals kept in cages, to wash the bottom of the cage, if made of wood, from time to time, with some dilute nitric acid, and to put a few drops of nitric acid into the vessel in which the urine is collected.

With urine of man and of the dog, 1 vol. of solution of baryta to 2 vols. of urine is generally sufficient to remove all the phosphoric and sulphuric acids, and to leave some baryta in solution. If, however, the urine be alkaline from the presence of an alkaline carbonate, which may be under certain circumstances carbonate of ammonia derived from decomposed urea, 1 vol. of solution of baryta to 2 vols. of urine does not suffice; in such cases, to precipitate all the carbonic acid, more solution of baryta has then to be used.

When 3 vols. of solution of baryta are mixed with 4 vols. of urine, 17.5 cub. cent. of the liquor filtered off (corresponding to 10 cub. cent. of urine) must be taken for the determination of urea. Of a mixture of equal volumes of solution of baryta and of urine, 20 cub. cent. must be taken for the test, and so on.

I have investigated the influence of the putrefaction of urine on this method of determining the urea, and have frequently obtained the same results with putrid urine, provided the decomposition had not progressed too far, as with the same urine in the fresh state. If, after the addition of 19.5 cub. cent. to the fresh urine, the yellowish colour of the protoxide of mercury made its appearance, the same reaction ensued with urine which had stood for one or two days, after using the same portion of solution of mercury. This can, however, not be depended upon, as the following results will show.

For the precipitation of urine with nitrate of protoxide of mercury were used, for :

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10 cub. cent. of urine, whilst fresh . . .	27·	cub. cent. of solution of mercury.
10 „ „ of the same urine, after having stood for one day . . .	27·	„ „ „
10 „ „ of the same urine, after the third day	27·5	„ „ „
10 „ „ of the same urine, after the fourth day	28·	„ „ „

For another sample of dog's urine there were used, for :

10 cub. cent. whilst fresh . . .	36·5	cub. cent. of solution of mercury.
10 „ „ two days old . . .	41·	„ „ „ „
10 „ „ three days old . . .	42·	„ „ „ „
10 „ „ four days old . . .	42·	„ „ „ „

One equivalent of urea yields by its putrefaction 2 equivs. of ammonia; and if, by adding the solution of mercury, the compound described by C. G. Mitscherlich and Kane were formed, which contains 2 equivs. of mercury for 1 equiv. of ammonia or amidogen, just as much of the solution of mercury would be required for its precipitation as for the urea from which the ammonia has been formed. The experiments show, however, that somewhat more is required, which seems to indicate that, under these circumstances, ammoniacal compounds, with 3 and perhaps more equivs. of protoxide of mercury, are formed.

For exact determinations, no other resource is left than to determine the quantities of urea and of ammonia present, each separately, and to express the ammonia found, as urea. For this purpose, two portions of urine are taken; the first of which is used for the determination of the urea, the other for that of the ammonia.

In estimating the urea in this urine, it is not precipitated with the usual mixture, but only with baryta-water; of the liquor filtered off, a volume is taken, containing 10 cub. cent. of urine, and this is then heated in a water-bath, until no further escape of ammonia is perceptible. Since, after the treatment with baryta, the ammonia is in solution in form of caustic ammonia, its expulsion is readily effected; care is, of course, to be taken, that all the carbonate of ammonia is decomposed, and the addition of the baryta-water has to be regulated accordingly.

In the other portion of the urine, the ammonia is determined by means of one of the ordinary alkali-metrical methods. For this purpose it is best to use a dilute sulphuric acid, made with 16·333 grms. of pure hydrated sulphuric acid and so much water that the

mixture occupies 500 entire, or 1000 half cub. cent. $\frac{1}{2}$ cub. cent. of this sulphuric acid saturates exactly 5.66 milligrammes of ammonia; this is the quantity formed from 10 milligrammes of ammonia; 1 cub. cent. of this sulphuric acid used in saturating the ammonia in urine corresponds therefore to 20 milligrammes of urea.

These determinations are somewhat more precise when a measured volume (containing a known quantity of urine) of the urine, treated with baryta, is submitted to distillation, and the product collected in a receiver, containing a measured volume of the above dilute sulphuric acid, which must be larger than is requisite to neutralize the ammonia passing over; the quantity of free acid left is then determined by means of a dilute solution of ammonia, graduated for the dilute sulphuric acid. Thus, if 40 cub. cent. of the dilute sulphuric acid have been put into the receiver, and afterwards 15 cub. cent. of the graduated solution of ammonia were required to saturate the free acid left, a quantity of ammonia was obtained by the distillation corresponding to $40 - 15 = 25$ cub. cent. of the dilute sulphuric acid, or to 250 milligrammes of urea.