A Course of Lectures ON URINE, URINARY DEPOSITS, AND CALCULI.

DELIVERED AT THE PATHOLOGICAL LABORATORY,
DURING THE SESSION 1857-58.

BY

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LECTURE III.

Healthy Urine. III. INORGANIC CONSTITUENTS. *On the Salts generally; Changes effected in the Composition of the Salts by Incineration: Proportion of the Saline Matter in Urine: Phosphates; Common Phosphate of Soda; Alkaline Phosphate of Soda; Acid Phosphate of Soda; Phosphate of Soda and Ammonia; Phosphate of Magnesia; Phosphate of Ammonia and Magnesia; Phosphate of Lime; Estimation of the Alkaline and Earthy Phosphates; Quantity: Sulphates; Quantity; Estimation: Carbonates: Chloride of Sodium; Quantity; Detection; Circumstances affecting the Excretion of Chloride of Sodium: Bases in Urine: Soda and Potash: Lime: Magnesia: Iron: Silica: Alumina: Systematic Quantitative and Qualitative Examination of the Saline Matter of Healthy Urine.*

III.—INORGANIC CONSTITUENTS OF HEALTHY URINE.

THE saline or inorganic constituents of healthy urine are composed of those substances which remain after the solid matter has been exposed to a red heat, and the carbon burnt off so as to leave a pure white ash. If a little of the solid matter be placed in a platinum capsule, or upon a piece of platinum foil, which should be very large in proportion to the quantity of solid matter operated on, and exposed to the red heat of a spirit or gas lamp, it will melt and boil, giving rise to the evolution of offensive gases, which result from the decomposition of the organic constituents of the urine. When this has ceased, a charred mass, consisting of carbon and the indestructible saline matters of the urine, remains. After this black spongy mass has been kept in the open capsule, at a dull red heat, for a few hours, the carbon will gradually disappear, in consequence of the action of the oxygen of the air, which at this temperature combines with it, and forms carbonic acid. A pure white ash, which has an alkaline reaction, alone remains; and this consists entirely of saline or inorganic material, which is indestructible at a red heat.

Changes effected in the Composition of the Salts by Incineration. Now, it must not be concluded that the salts which we find in the ash existed in precisely the same state in the urine previous to incineration; for we know that many of these salts, when heated together, undergo mutual decomposition. Some of them may even be volatilised, if kept for a considerable time at a red heat. A mixture of carbonate of soda and chloride of ammonium becomes decomposed at a red heat. Chloride of sodium remains behind, while carbonate of ammonia is evolved. Any lactates, oxalates, and salts, of other organic acids present in the urine, will be found in the ash, in the form of carbonate, although no carbonate existed in the urine originally. The ammoniaco-magnesian or triple phosphate will be found in the ash as phosphate of magnesia; the phosphate of soda and ammonia, as phosphate of soda. Other phosphates also become completely changed by the process of incineration, and by the action of other salts present in the ash upon them. During the incineration, a considerable loss of chlorine also takes place.

Again, unoxidised substances, such as sulphur and phosphorus, and partially oxidised compounds, in combination with organic materials, will become oxidised in the process of decarbonisation; and will, therefore, be found in the ash in the form of sulphuric and phosphoric acid. These will react upon some of the bases present, and sulphates and phosphates will be formed.

Professor Rose of Berlin, in a beautiful series of experiments, has proved that the mineral constituents exist in very different states in various organic substances. From the *carbonaceous* ash of some organic matters, the greater proportion

of the salts can be extracted with water or acids; while, in other cases, but little saline matter can be separated, unless the mass be exposed to the oxidising action of the air for some time. This shows that the substances must have originally existed in an unoxidised or in a partially oxidised state, probably in combination with some organic material. In certain substances, then, the greater quantity of the mineral material is perfectly oxidised (*teleoxidic*); in others, it exists partly in an oxidised and partly in an unoxidised state (*meroxidic*). Professor Rose was not able to discover any substance in which it occurred completely unoxidised (*anoxidic*). In blood, milk, yolk of egg, and flesh, a considerable portion of the mineral constituents are *meroxidic*; while, in urine and bile, they are almost entirely *teleoxidic*; which is exactly what we should expect, when we consider the different nature and offices of these fluids.

Proportion of Saline Matter in Urine. About one-fourth of the solid matter of healthy urine consists of saline constituents which are not destroyed by a red heat.

One thousand grains of healthy urine, containing from forty to sixty grains of solid matter, will give from ten to fifteen grains of fixed salts. Of the salts, more than nine-tenths are soluble in water (alkaline salts); while the remainder can only be obtained in solution by adding an acid (earthy salts). A mere trace remains behind, which is insoluble in water, acids, and alkalies. This consists of silica, with perhaps a little carbon which has resisted oxidation. These numbers are, of course, only approximative, as the amount of salts is liable to great variation.

The saline constituents soluble in water are composed of the following acids and bases.

Sulphuric acid	Potash
Phosphoric acid	Soda (and sodium).
Hydrochloric acid (chlorine)	

The salts may be readily obtained in a crystalline state by dissolving the residue in hot water, and evaporating a few drops of the solution on a glass slide. The crystals are represented in the *Illustrations of Urine*, Pl. I, Fig. 2.

The mineral constituents insoluble in water are composed of the following acids and bases.

Phosphoric acid	Lime
Carbonic acid (occasionally)	Magnesia
Silicic acid or silica	Alumina (sometimes).

In disease, the mineral constituents have been found to vary in quantity quite as much as the organic substances; and other salts are not unfrequently found, which will come under our notice at a future time: while occasionally one or more of the saline compounds mentioned in the above list are altogether absent.

The organic constituents of the urine have hitherto received a greater share of attention than has been given to the inorganic salts; but, from recent investigations, it seems probable that, before long, the physician will regard a departure from the healthy standard in the saline constituents with as much attention as he has been accustomed to observe an increase or diminution in the quantity of the urea, uric acid, or other organic ingredients.

Phosphates. The phosphates are a very important class of salts, which exist in greater or less quantity in all the tissues of the body, in the secretions, and in considerable proportion in the blood. The salts of phosphoric acid which are carried off from the organism in the urine, may be divided into two classes.

1. The *alkaline phosphates* are soluble in water, and are not precipitated from their solutions by ammonia or other alkalies. When ammonia is added to healthy urine, the *alkaline* phosphates are not thrown down. Some of the most important alkaline phosphates are, *phosphate of soda, acid phosphate of soda, and phosphate of soda and ammonia.*

2. The *earthy phosphates* are insoluble in water, but are dissolved by the mineral acids. Most are soluble in organic acids, although they dissolve very slowly if the acids are dilute. They are held in solution even by carbonic acid. Most albuminous substances have the power of dissolving earthy phosphates; and casein holds in solution a considerable quantity of phosphate of lime. The earthy phosphates, as phosphate of lime and phosphate of magnesia, are always precipitated when ammonia is added to healthy urine.

Of the phosphoric acid eliminated in the urine in the form of phosphates, the greater proportion is doubtless taken in the food; but a certain amount is formed in the organism by the oxidation of the phosphorus of albuminous tissues, which takes place during their disintegration. Much of the phos-

phoric acid formed in the organism is doubtless produced in the nervous tissue.

In these lectures, I have purposely avoided the use of chemical formulæ, partly because, in many instances, I should have had to enter too far into the province of chemistry to explain them, and partly because I felt that all that was necessary for the clinical examination of the urine might be explained without their use. It is, however, impossible to allude to the composition of the phosphates without giving their chemical formulæ; and I therefore propose to make an exception in the case of this class of salts.

Phosphoric acid is one of those acids which exist in three forms—the monobasic, bibasic, and tribasic acids, which combine respectively with one, two, or three equivalents of base, to form three different classes of salts.

Tribasic phosphates . . .	$3 \text{ Na O, PO}^5 + 24 \text{ Aq.}$
	$2 \text{ Na O, HO, PO}^5 + 24 \text{ Aq.}$
	$\text{Na O, 2 HO, PO}^5 + 2 \text{ Aq.}$
Bibasic or pyrophosphates	$\text{Na O, HO, NH}^4 \text{ O, PO}^5 + 8 \text{ Aq.}$
Monobasic or metaphosphates	$2 \text{ Na O, PO}^5 + 10 \text{ Aq.}$
	Na O, PO^5

Now, the phosphates found in the organism are all *tribasic phosphates*, and consist of three equivalents of base, combined with one equivalent of phosphoric acid, with different proportions of water of crystallisation. The elements of the base of a tribasic phosphate may be various. Thus, they may consist of three equivalents of soda or other base, or two equivalents of soda and one of water acting the part of a base, or one equivalent of soda and one of ammonia and one of water acting the part of a base, combined with one equivalent of phosphoric acid.

The chemical composition of the phosphates occurring in urine is represented in the following table.

Common or rhombic phosphate of soda, having an alkaline reaction . . .	$2 \text{ Na O, HO, PO}^5 + 24 \text{ Aq.}$
Acid phosphate of soda, having an acid reaction . . .	$2 \text{ HO, Na O, PO}^5 + 2 \text{ Aq.}$
Alkaline phosphate of soda, having a highly alkaline reaction . . .	$3 \text{ Na O, PO}^5 + 24 \text{ Aq.}$
Phosphate of potash* . . .	3 KO, PO^5
Phosphate of ammonia and magnesia, ammoniaco-magnesian or triple phosphate . . .	$2 \text{ Mg O, NH}^4 \text{ O, PO}^5 + 12 \text{ Aq.}$
Acid phosphate of lime . . .	$2 \text{ Ca O, HO, PO}^5 + 3 \text{ Aq.}$
Phosphate of lime (bone-phosphate) . . .	3 Ca O, PO^5

Alkaline Phosphates.

Common Phosphate of Soda— $2 \text{ Na O, HO, PO}^5 + 24 \text{ Aq.}$ This salt exists in healthy urine in the proportion of about two grains in one thousand. The fixed salts contain perhaps from 20 to 30 per cent. of ordinary phosphate of soda. Its presence in healthy urine may be proved by adding absolute alcohol to the syrupy fluid obtained by evaporating the urine over a water bath. This concentrated fluid is poured off from the salts which have crystallised, and placed in a small glass vessel. The alcohol is added; and, after the mixture has stood for some time, the crystals are deposited upon the sides of the glass. This method is given by Robin and Verdeil (*Traité de Chimie Anat. et Physiol.*, par Ch. Robin et F. Verdeil.)

Acid Phosphate of Soda— $\text{Na O, 2 HO, PO}^5 + 12 \text{ Aq.}$ This salt has only been found in the urine; and to it, at least in many cases, the acid reaction of the urine is due. This acid phosphate of soda may be formed from the common phosphate (which has an alkaline reaction), by the addition of uric acid, which removes from the common phosphate one equivalent of soda, forming *urate of soda*; and the reaction of the mixture becomes acid, in consequence of the formation of the *acid phosphate*.

The acid phosphate of soda may be obtained from the concentrated urine treated with absolute alcohol, after the separation of the common phosphate. The acid salt, which is much more soluble, becomes deposited in the course of a few days; but its separation may be expedited by the addition of ether. This phosphate has been separated from the urine by MM.

* It is doubtful if phosphate of potash usually exists in urine, as chloride of sodium and phosphate of potash decompose each other, forming chloride of potassium and phosphate of soda. It is not improbable that it may exist in urine in which the chloride of sodium is present in very small quantity, or altogether absent, as in pneumonia and some other acute diseases.

Robin and Verdeil, who attribute the acid reaction of urine to its presence (*Comptes Rendus. Mém. de la Soc. de Biologie*, Paris, 1850, p. 25; also *Traité de Chimie Anat. et Physiol.*, 1853). The crystals of this salt are figured in Robin and Verdeil's *Atlas*, Pl. ix, Fig. 2.

Alkaline or Basic Phosphate of Soda— $3 \text{ Na O, PO}^5 + 24 \text{ Aq.}$ This phosphate is considered by some to be present in urine; but it is so readily altered by other salts present, that it is impossible to obtain it from the animal fluids in a state of purity. In the presence of carbonic acid, it is decomposed: one equivalent of soda unites with the carbonic acid to form carbonate of soda, and common phosphate of soda is formed, both which salts have an alkaline reaction— $3 \text{ Na O, PO}^5 + \text{CO}^2 + \text{HO} = 2 \text{ Na O, HO, PO}^5 + \text{Na O, CO}^2$.

Liebig has shown that it is not present in healthy urine, as was stated by Heller; and Messrs. Robin and Verdeil do not enumerate this phosphate as one of the constituents of urine: indeed, if this phosphate were formed, it would, in all probability, be at once resolved into salts of a more stable nature.

Phosphate of Soda and Ammonia— $\text{Na O, NH}^4 \text{ O, HO, PO}^5 + 8 \text{ Aq.}$ This salt, although probably not present in perfectly fresh urine, is usually enumerated as one of the phosphates found in the secretion. The crystals of phosphate of soda and ammonia, or microcosmic salt, are beautiful transparent four-sided prisms.

Phosphate of Potash— 3 KO, PO^5 —is probably not present in healthy human urine; but it has been detected by Boussingault in the urine of the pig, in the proportion of 1.02 per 1000.

Many vegetable tissues contain a large quantity of phosphate of potash; and it is met with in the juice of muscle in considerable quantity.

The proportion of alkaline phosphates in the organism varies according to the nature of the food. Generally, the proportion is smaller in herbivorous than in carnivorous animals. Muscular fibre contains a large amount of phosphates. Wheat, and the seeds of the cerealia generally, contain a considerable quantity of alkaline phosphates. Robin and Verdeil found in the ash of the blood of a dog fed upon flesh as much as 12 per cent. of phosphoric acid, combined with soda and potash; while the ash of the blood of the ox did not contain more than 3 per cent. When the dog was fed upon potatoes, the proportion fell to 9 per cent. The ash of the blood of man contained about 10 per cent. of phosphoric acid. In urine, Berzelius found 2.94 per 1000; and Simon, from 1.25 in slightly acid urine, to 2.75 in very acid urine.

Breed and Winter estimate the quantity of phosphoric acid removed from the organism in the urine, in the course of twenty-four hours, at from 59.48 to 79.97 grains. The proportion increased considerably after taking food. This quantity corresponds to from 120 to 160 grains of phosphatic salts.

The quantity of phosphoric acid increases for some hours after a meal. Vogel, Winter, and others, have made numerous experiments on this point; and their researches show that the hourly variation in the excretion of phosphate is regular. The morning urine contains the smallest quantity. In some of Dr. Bence Jones's analyses, however, the quantity of alkaline phosphates is even greater in the urine passed before than in that excreted after a meal (*Animal Chemistry*, p. 81).

The proportion of phosphates in the urine depends much upon the nature of the food. The quantity is increased if phosphorus is taken, proving that this substance does become oxidised in the organism. That the greater proportion of the alkaline phosphates present in the urine are derived from the food is rendered evident by referring to the amount introduced into the organism in this manner. A man taking about fourteen ounces of bread and twelve ounces of meat, with half a pound of potatoes and half a pint of milk, would take about 130 grains of alkaline phosphates.* As we have seen, he would eliminate, in his urine, about the same quantity. It is true that these numbers are only to be regarded as rough approximations to the truth; but I think, at present, it must be admitted that the quantity of phosphate excreted in the urine, but found in the organism, is so small in comparison to that which is derived from the food, the amount of which is liable to great variation, that, in the present state of animal chemistry, it is quite impossible to form an estimate of the amount

* 14 oz. of bread contain 53.2 grs. of phosphates.

12 oz. of beef " 40.7 " "

1 lb. of potatoes " 11.0 " "

1 pint of milk " 32.0 " "

136.9 grs. of mixed phosphates.

arising from the former source, or to separate this from the phosphates taken in the ingesta.

Still it is certain that some of the phosphoric acid is formed within the organism, by the oxidation of the phosphorus of the albuminous tissues; but this must bear but a small proportion to the whole amount of phosphate removed in the urine, as the above data conclusively show.

The fluid which surrounds the elementary fibres of muscle has an acid reaction, depending probably upon the presence of acid phosphate of soda, produced by the action of lactic or some other organic acid upon phosphate of soda. Du Bois Raymond has, however, shown that this acid reaction is not met with when the muscles are at rest. The ashes of most tissues contain phosphates in large proportion; and Schmidt has shown that a considerable quantity of phosphate is always present in young tissues. The quantity of alkaline phosphate required by the organism is considerable; for, besides the large proportion which is excreted in the urine, the ash of the solid excrements contains as much as 20 per cent. alone. The phosphoric acid required is, no doubt, supplied principally by the food, partly in the form of phosphatic salts, partly as phosphorus which is oxidised in the organism. We shall recur to this subject when we have to consider the elimination of the phosphates in disease.

[To be continued.]

Reviews and Notices.

A MANUAL OF OBSTETRICS, THEORETICAL AND PRACTICAL. By W. TYLER SMITH, M.D., Member of the Royal College of Physicians; Physician-Accoucheur to, and Lecturer on Midwifery at, St. Mary's Hospital. Pp. 628. London: John Churchill. 1858.

THE present unpretending-looking volume is one of Mr. Churchill's very valuable series of Manuals, and assuredly not the least important and valuable of them. As the author says in his preface, it consists of the substance of a course of lectures which appeared in the *Lancet* in the year 1856. Now, a *manual* is generally understood to be merely a compilation or epitome of certain doctrines and opinions held by the profession as established. Dr. TYLER SMITH's book goes much further than this; for while he freely lays before the reader such doctrines and theories as have been accepted as fixed, and gives with strict impartiality the views and opinions of others on points which are *adhuc sub judice*, he, with bold originality, gives his own doctrines and opinions; in the former case, often turning quite aside from the beaten track; in the latter, endeavouring to throw the light of his own independent views and experience on the subjects discussed; in both cases—

"Nullius addictus jurare in verba magistri."

We have not space to comment on all the subjects discussed in this manual. In the first chapter—that on Generation—we find the philosophy of the subject clearly laid down, including many curious points, which, though not bearing exactly on obstetrics practically considered, are yet of considerable scientific interest: such, for example, as the strange phenomenon in reproduction to which the term "parthenogenesis" has been given. The anatomical and physiological descriptions are given with the brevity demanded by the occasion, but nevertheless with sufficient clearness. In the chapter on the Signs of Pregnancy, we find the opinion once prevalent on the subject of the uterine *souffle*—that that sound was caused by the placental function, being thence denominated *bruit placentaire*—effectually disposed of. "It has been heard in cases where putrid foetuses have been born", and where there was other proof that there could be no circulation going on in the placenta: therefore, "the uterine *souffle* is no proof of the life of the foetus".

Speaking of the *decidua vera*, we find our author adhering to the opinion that it is identical with the uterine mucous membrane, and that it is entirely thrown off after parturition, in the

form of the lochial discharge, in the same way as, he says, the mucous membrane is removed with every menstruation. That this is "a startling doctrine", our author admits; but, nevertheless, certain facts adduced by himself, and by others before him, would seem to confirm it. We think, however, that Dr. Matthews Duncan, and some others, have published somewhere other facts, which equally strongly contradict it. The subject is one of but little practical value; and, therefore, we leave it.

The subject of the Duration of Pregnancy is highly important, and we have a very elaborate chapter upon it. Dr. Smith considers that the duration of pregnancy is a multiple of the catamenial period; "labour coming on at what would have been a catamenial period, had the woman remained unimpregnated". On this principle, he says, he constructed his well known PERIODOSCOPE, "upon the data that conception generally occurs a few days after the completion of a catamenial period, and that labour may be expected on some day of what would have been the tenth period, had pregnancy not intervened." Dr. Smith, however, with perfect impartiality, favours his readers with the views of those who differ from him on this point—of those, namely, who maintain that the time of labour is determined somewhat arbitrarily by the maturity of the foetus. As "the last hypothesis respecting the variable duration of pregnancy", he mentions "that advanced by Dr. Clay of Manchester, who argues that the younger the parent, the shorter is the term of gestation". We must say on this point that, having carefully read Dr. Clay's paper on the subject, we think that the facts adduced by him confirm his theory very strongly; while, if the theory be true, it must upset the catamenial or ovarian doctrine.

On the question of the mechanism of parturition—a somewhat vexed one—we find our author follows Nägele, with too implicit acquiescence, we are inclined to think; but we are bound to say that, in so doing, he has the majority with him.

We recollect that, on the occasion of "a consultation at Norwich", in the year 1851, Dr. Murphy was much reflected upon for maintaining that it was possible for a portion of retained placenta to undergo hydatid degeneration. Our own opinion certainly was, that such a doctrine was preposterous. Dr. Smith, in the work before us, seems to hold with Dr. Murphy. He says that "Drs. Montgomery and Ramsbotham believe that small portions of placenta retained *in utero*, after parturition at the full term, may become the nucleus of hydatigenous formations; but Dr. Barnes combats this view, from the general history of hydatigenous formations, and the destruction of the foetal vessels of the placenta which occurs at the time of birth." He adds, that the question—a very interesting one—must be considered, to some extent, as still unsolved. Dr. Smith, while on this subject, does not allude to the famous Murphy controversy of 1851. We could have wished that he had done so, as the opinion of a physician of such eminence as Dr. Murphy, put forward so prominently as it was, is of great importance; and the question itself is clearly one which ought to be settled, if possible; for, on the occasion referred to, the reputation of a most respectable man was seriously assailed.

The danger to the life of the fetus in the administration of ergot of rye to the mother during parturition, is a vexed question which it is desirable should be settled. Dr. Hannotte Vernon, of the Great Northern Hospital, in a paper published a few years ago, argues for a poisonous influence of the drug, producing, as a perceptible effect, a gradual slowing of the fetal pulse. He maintains that the child is sure to be still-born, if the foetal pulsations become reduced below a specified rate. Dr. Smith, in the work before us, on the contrary, attributes the danger, if any, to "the spastic contraction of the uterus, caused by this medicine, which interferes with the utero-placental circulation;" adding, that "the state of the child should be watched