

In my paper before referred to it was suggested that, "considering the stability and mode of formation of these bases, it is not at all improbable that they may be produced by the simultaneous action of acetylene and its derivatives on hydrocyanic acid; thus as three molecules of acetylene condense and form benzol, so may two molecules of acetylene and one of hydrocyanic acid condense and produce pyridine."

A synthetical experiment of the kind suggested has been executed by Mr. Ramsay*, who finds that by transmitting a mixture of acetylene and hydrocyanic acid through a red-hot tube bases were unquestionably produced. Pyrrol, which may be so readily identified by means of its characteristic reaction with fir wood moistened with hydrochloric acid, may be formed synthetically by substituting ammonia for the hydrocyanic acid in the above experiment. The acetylene employed, however, contained a small quantity of bromide of vinyl, and it is possible the reaction may have taken place between that substance and ammonia. Only a small quantity of pyrrol is formed in this reaction, the principal substance formed being cyanide of ammonium; and the success of the experiment seems to depend on the maintenance of a carefully regulated temperature and a certain extent of porous surface. These and similar reactions are under investigation.

The theoretical bearings of this investigation have not been touched upon in the present paper, as an extensive research will be necessary before structural relations can be predicted with any certainty.

I am greatly indebted to Mr. W. F. Sell, B.A., and Mr. A. Scott, B.Sc., assistants in the Chemical Department, for aid in the course of the investigation.

Laboratory, Cambridge University.

III. "On the Density of Solid Mercury." By Prof. J. W. MALLETT, University of Virginia. Communicated by Prof. STOKES, Sec.R.S. Received February 22, 1877.

I have lately taken advantage of a heavy fall of very cold and finely pulverulent snow, well adapted to the preparation of freezing-mixtures, to redetermine, with accuracy I believe, the density of mercury in the solid state and at a definite temperature.

Such redetermination was not superfluous, as appeared from a collation of the statements to be found in various standard works. In the tables of specific gravities compiled by Prof. F. W. Clarke, and published by the Smithsonian Institution†, there are four authorities quoted, with the numbers given by these, as follows:—

* "On Picoline and its Derivatives," *Phil. Mag.* 1876, vol. ii. p. 269.

† "The Constants of Nature.—Part I." *Smithsonian Miscell. Coll.* 255, Washington 1873, p. 24.

	Sp. gr. of solid mercury.
Schulze	14·391
Biddle	14·485* at -60° C.
Kupffer and Cavallo	14 (approx.)
Joule	15·19

The last of these numbers, on reference to the original paper†, turns out to represent no actual experiment with mercury itself, but is the density *calculated* for this metal from the examination of a number of amalgams. Kupffer and Cavallo do not profess to give the exact density, but merely state it as about 14, the number apparently resting on no special experiment, though I have not been able to verify this by reference to their paper‡. The only other apparently independent statement I have met with occurs in the ‘*Annuaire du Bureau des Longitudes*’ for 1876 (p. 385), where the density 14·39 is given on the authority of Rivot; but I have not been able to find any reference to a paper by him bearing on this or any analogous point, and it seems probable that we have here only a reproduction of Schulze’s result. In different handbooks of chemistry and physics numbers between 14 and 15 are given as approximations, but with no other authority than some of the above. Some of the best and most recent works simply state that mercury undergoes considerable contraction in freezing. Hence our knowledge on this subject appears hitherto to have rested on the experiments of Schulze and Biddle, both of which date back to the early years of the present century. Schulze’s paper was published in ‘*Gehlen’s Journal*,’ vol. iv. p. 434, and therefore about 1807 or 1808, and Biddle’s§ belongs to the year 1805. I have had access to neither; but the character of the instrumental means (balances, thermometers, &c.) generally available at the time the experiments were made, and the then imperfect knowledge of the constants needed for corrections to be applied, make it unlikely that very exact results could have been obtained. Biddle alone seems to have noted the temperature of the frozen mercury, and Brande|| expresses doubt that this was determined with much accuracy. The temperature -60° C., if correctly quoted, is in itself somewhat improbable.

The method adopted in the experiments lately made in this laboratory was the following:—

(1) A specific-gravity flask was prepared from a large cylindrical pipette by closing in and smoothly rounding in the flame of the lamp one end of the cylinder, while the tube remaining attached to the other end was cut short and united by fusion to a second pipette of like shape but

* 14·465 as quoted by Brande in his ‘*Manual of Chemistry*.’

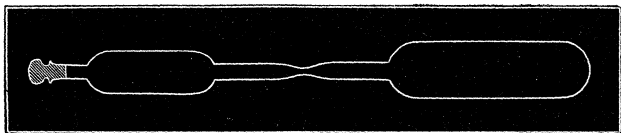
† Chem. Soc. Journ. [2] i. p. 387.

‡ Quoted at second hand from Playfair and Joule, “*On Atomic Volume and Specific Gravity*,” Chem. Soc. Mem. 2 (1845), p. 401, and 3 (1848), p. 57.

§ Nicholson’s Journal, vol. x. p. 253, and Tilloch’s Philos. Mag. vol. xxx. p. 134.

|| Manual of Chemistry, vol. i. p. 970.

smaller size, the upper and open end of the shortened tube of which was fitted with a small carefully ground glass stopper. The neck between the larger and smaller cylinders was drawn down to a small bore (about 2 millims.), and at this narrowed part a fine line marked round it with a diamond. The shape of the vessel is shown in the annexed sketch, on a linear scale of one half the real size. The principal cylinder held about 58 cubic centimetres, and the small reservoir above 25 cub. centims. The whole vessel weighed about 46 grammes.



It enabled the experiments to be carried out with more than half a kilogramme of frozen mercury.

(2) This vessel having been accurately weighed when empty and dry, its capacity up to the mark was ascertained by filling it to this point with pure water at exactly 4° C., keeping it immersed for some time in a large mass of water at this temperature before making the final adjustment to the mark, wiping the outside dry, allowing the whole to acquire the temperature of the balance-case, and carefully weighing. The result of this direct calibration, deducting the weight of the vessel, was 59.7323 grammes or cubic centimetres at 4° .

(3) It was checked by emptying and drying the vessel, filling it to the mark with pure mercury at 0° C., the temperature being secured by keeping the whole surrounded by melting ice long enough to obtain perfect steadiness of position of the mercury, and weighing after the temperature of the balance-case had been regained. The mercury weighed 811.9997 grammes.

(4) The vessel was now surrounded by steam, and the mercury again brought to the mark, the temperature actually attained being $99^{\circ}5$ C. (corrected for pressure). Allowed to cool down to the temperature of the balance-case, and again weighed, the mercury was found = 799.7032 grammes. From the last two weighings the coefficient of cubical expansion for 1° C. of the glass used was, by the usual formula (taking absolute expansion of mercury from 0° to $100 = 0.18153$, as determined by Regnault), found = 0.00027346.

(5) If now the density of mercury at 0° as referred to water at 4° be taken at 13.596 (Regnault), the weighing obtained in (3) gives the capacity of the vessel up to the mark at $0^{\circ} = 59.7234$ cub. centims., or, applying the above coefficient of expansion of glass, 59.7300 cub. centims. at 4° . The mean of this value and that obtained in (2), =
$$\frac{59.7300 + 59.7323}{2}$$
 = 59.7311 cub. centims., was taken to represent the true capacity of the vessel at 4° .

(6) The freezing-mixtures used were prepared by cooling commercial hydrochloric acid (sp. gr. = 1140) in the snow out of doors, the temperature of which, as well as of the air, was on the first day about -9° C., but on subsequent days rose to about -5° , mixing equal weights of this cooled acid and of snow, using separate portions of this first mixture to cool more acid and snow, and finally bringing together these last.

It soon appeared that little advantage was gained by trying to cool the snow, on account of its very low conducting-power in such a loose porous condition; and in the later experiments the temperature of the acid alone was lowered before the final mixture with snow. The glass vessels containing the mixtures were large enough to maintain the cold required for a long time, and steadiness of temperature was secured by surrounding them on all sides with a layer of cotton wadding, kept in place by stiff brown paper, and by conducting all the operations out of doors in the unusually cold atmosphere prevailing at the time.

(7) In determining the temperature of the freezing-mixtures an alcohol thermometer was used, graduated to single degrees, and admitting of half a degree being read; but the scale being found by no means accurate, its absolute readings were altogether discarded. By comparison with a good mercurial thermometer at three or four points between -10° and $+40^{\circ}$ C., and calculation from *Is. Pierre's* coefficients, the real length of a degree on the part of the stem corresponding to -40° was determined; and the temperature of fusion of the mercury being accurately noted and assumed = $-38^{\circ}85$ C., as determined by Balfour Stewart*, the addition or subtraction of four or five degrees, as above obtained, gave all the other temperatures observed.

(8) The above weighings and all others to be mentioned were made with an excellent balance by Becker, carefully adjusted and tested at the outset. With a load of a kilogramme in each pan a difference of weight of $\frac{1}{10}$ milligramme can be detected, and $\frac{1}{5}$ milligramme may be fully relied upon. All weighings were reduced by calculation to the corresponding results *in vacuo*, the temperature and pressure of the atmosphere being noted on each occasion; and the results quoted are those thus corrected.

(9) The specific-gravity flask was now filled with alcohol (at one time absolute, but which, by long keeping in the laboratory and occasional opening of the bottle, had absorbed some moisture, and was really about 95 or 96 per cent.), and three weighings were obtained after the liquid had been carefully adjusted to the mark at temperatures close to the freezing-point of mercury†.

* With an air-thermometer (*Proc. Roy. Soc.* 1863, vol. xii. p. 674).

† The alcohol, as afterwards mercury, was brought to near the required temperature before introduction into the final freezing-mixture, and a separate small portion in a tube was similarly cooled, to be used in filling up to the mark if necessary. The stopper was carefully inserted as soon as the adjustment of the liquid was secured, so as to avoid any loss by evaporation.

Applying the correction for capacity of vessel at the respective temperatures, the three results were :—

cub. centims.	grms.
59·6625 of alcohol at -37° C.	$=50\cdot7010$
59·6600 " " -40°	$=50\cdot8316^{*}$
59·6576 " " $-42^{\circ}\cdot5$	$=50\cdot9092$

or, reducing to one common weight,

cub. centims.	grms.
117·6752 of alcohol at -37°	$=100$
117·3679 " " -40°	$=100$
117·1843 " " $-42^{\circ}\cdot5$	$=100$

(10) Taking the difference between (a) the first and second, (b) the second and third, and (c) the first and third of these numbers, and dividing each difference by the number of degrees in the interval of temperature, we get as the change of volume of 100 grammes of alcohol for 1° C. :—

	cub. centim.
From (a)	$\cdot1024$
(b)	$\cdot0734$
(c)	$\cdot0893$

and the mean of these ($\cdot0884$) may be taken to represent the coefficient for 1° C. within a range of a few degrees either side of the freezing-point of mercury. Using this coefficient to reduce the three weighings to their corresponding values for the same temperature, say -39° C., we have

grms.	cub. centims.
100 of the alcohol in question at -39°	$=117\cdot4984$
" " " " " "	$=117\cdot4563$
" " " " " "	$=117\cdot4937$

the mean of which is $117\cdot4828$ cub. centims.

(11) The specific-gravity flask having been emptied and dried, $558\cdot9353$ grammes of mercury was introduced, the metal having just previously been purified by careful treatment with dilute nitric acid, washing with water, and quiet distillation from a glass retort. Filling up with the same alcohol as that used in the above experiments, and which had been kept in a well-stoppered bottle, the flask was gradually cooled, and finally, in the last freezing-mixture, the mercury frozen, and the alcohol brought exactly to the mark, taking care that it became and remained quite stationary, while during the freezing of the mercury the change of volume was very rapid and easily observable. The temperature having been noted when the final adjustment was made, the little flask was set aside, stoppered, until it could be washed off and dried, and was then allowed

* This weighing was not quite so satisfactory as the remainder; the temperature a little doubtful.

to acquire the temperature of the balance-case, and weighed. Three such experiments gave, aside from the weight of the flask itself,

A.	Mercury + alcohol at -39° C.	^{grms.} = 576·2029
B.	„ „ „ $-41^{\circ}5$	= 576·2522
C.	„ „ „ -42°	= 576·2639

Deducting the mercury, the quantity of which remained constant throughout, it appears that the flask contained of alcohol :—

		^{grms.}
A.	at -39° 17·2676
B.	„ $-41^{\circ}5$ 17·3169
C.	„ -42° 17·3286

From the data in (10) these weights represented at the respective temperatures the following volumes :—

	^{cub. centims.}
A 20·2865
B 20·3061
C 20·3122

From the data in (4) and (5) we get the capacity of the flask up to the mark at the same temperatures :—

	^{cub. centims.}
At -39° 59·6609
„ $-41^{\circ}5$ 59·6568
„ -42° 59·6560

Subtracting the volume of alcohol in each case, that of mercury was,

	^{cub. centims.}
In A 39·3744
„ B 39·3507
„ C 39·3438

Hence the specific gravity as obtained

In A 14·1954 at -39°
„ B 14·2034 „ $-41^{\circ}5$
„ C 14·2064 „ -42°

(12) By comparing these numbers in pairs, we have as the difference apparently due to a difference of temperature of 1° C.* :—

From A and B ·0032
„ B and C ·0060
„ A and C ·0037

of which the mean is ·0043.

Reducing, by using this coefficient, the above results to a single tem-

* Of course really including errors in determination of weights and temperatures.

perature, and adopting that of the fusing-point of the metal as determined by Balfour Stewart, we get

From A	14·1948	at	—38°·85	C.
„ B	14·1920	„	„	
„ C	14·1929	„	„	

and, as a final mean of these three, 14·1932 as the number representing the density of solid mercury at its fusing-point as referred to water at 4°C. taken as unity. I think this result (which, it will be seen, differs considerably from the figures hitherto quoted) may be fairly accepted with confidence.

In these experiments most of the weighings were made by Adjunct Professor Dunnington, and the freezing-mixtures were managed, at no small cost of personal discomfort, by Messrs. Bryan and Memminger, students in this Laboratory. To these gentlemen my thanks are due.

IV. “The Automatic Action of the Sphincter Ani.” By W. R. GOWERS, M.D., Assistant Physician to University College Hospital. Communicated by J. S. BURDON SANDERSON, M.D., F.R.S., Jodrell Professor of Human Physiology in University College, London. Received February 24, 1877.

The observations described in the following paper had for their object the determination of the form of the reflex or automatic action of the sphincter ani of man when voluntary power over it is lost. This reflex action is believed, from the researches of Masius*, to depend on an “ano-spinal centre,” situated in the lumbar enlargement of the spinal cord, controlled in health by higher (encephalic) centres. It appears, however, to be very uniform in its character in various conditions, the most conspicuous common character of which is the entire loss of voluntary power.

The larger number of observations were made on a man who, by a violent fall on the sacrum, had apparently injured the posterior roots of all the sacral nerves and both roots of the lowest sacral nerves. A depression existed over the lower part of the sacrum. Sensibility to touch and pain was lost in all parts supplied by branches from the sacral plexus, the limitation being exact. There was no muscular paralysis or loss of nutrition except in the levator ani, the sphincter ani, and the sphincter vesicæ, all of which were paralyzed to the will. The anus and the mucous membrane of the rectum were quite insensitive. There was no evidence of any injury to the spinal cord; with this, indeed, the symptoms were incompatible. It would thus appear that the only lesion was a division of the direct communication between the sphincter

* Bull. de l'Académie Royale de Belgique, 1867, t. xxiv. p. 312, and Journal de l'Anatomie et Physiologie, 1868, p. 197.

