

XIX. *Experiments on the Congelation of Quickfilver in England.*
 By Mr. Richard Walker; in a Letter to Henry Cavendish,
 Esq. F. R. S.

Read May 28, 1789.

S I R,

I NOW beg leave to trouble you with the particulars of my experiments relative to the congelation of mercury; to which I shall add an account of a few experiments, relating to the production of artificial cold, made since my last Paper was written.

Exp. I. On December 28th last, a favourable opportunity offered of beginning some experiments on the congelation of mercury, which I was desirous of effecting completely; how far I have succeeded will appear in the sequel.

For this purpose I prepared a mixture of diluted vitriolic acid (reduced by water till its specific gravity was to that of water as 1,5596 to 1) and strong fuming nitrous acid, of each equal parts. I preferred this mixture of acid because it has been found by Mr. M^c NAB, in Hudson's Bay, to be capable of producing much greater cold, when the temperature of the materials at mixing is very low, than the nitrous acid alone; the former sinking a spirit thermometer to $-54^{\circ}\frac{1}{2}$, the latter never lower than -46° .

The glass tube of a mercurial thermometer, with its bulb half filled with mercury, was provided, this occurring to me

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as a convenient method of ascertaining when the mercury was congealed; for if, after being subjected to the cold of a frigorific mixture, the thermometer glass should be taken out and inverted, and the mercury found to remain completely suspended in that half of the bulb now uppermost, no doubt can remain of the success of the experiment; an hydrometer, with its lower bulb half an inch in diameter, and three-fourths full of mercury, was likewise provided, in case any accident should happen to the other.

It may be proper to premise here, that in all experiments of this kind I remove each vessel, when the liquor it contains is sufficiently cooled, out of the mixture in which it is immersed for that purpose, immediately previous to adding the snow or salts with intention to generate a still further increase of cold; and likewise prefer adding the snow or powdered salts to the liquor, instead of pouring the liquor upon these: it is necessary also to stir about the snow or salts, whilst cooling in a frigorific mixture, from time to time, otherwise it will freeze into a hard mass, and frustrate the experiment.

A half-pint glass tumbler, containing two ounces and a half of the above-mentioned diluted mixture of acids, being immersed in mixtures of nitrous acid and snow, until the liquor it contained was cooled to -30° , was removed out of the mixture and placed upon a table; snow, likewise previously cooled in a frigorific mixture to -15° , was added by degrees to the liquor in the tumbler, and the mixture kept stirring until a mercurial thermometer sunk to -60° , where it remained stationary; the hydrometer was then immersed in the mixture (the thermometer glass having been broken in the course of the experiment), and stirred about in it for a short time, and on taking the hydrometer out, and gently shaking it, I perceived

perceived the mercury had already acquired the consistence of an amalgam, and after immersing it again for a few minutes, and then taking out and inverting it, I was gratified for the first time with the sight of mercury in a state of perfect congelation. I applied my hand to the inverted glass bulb; this soon loosened the solid mercury, which, on shaking the hydrometer, was distinctly heard to knock with force against the glass; it was then immersed a second time, and when taken out was found adhering to the glass as before. I now inverted the glass again, and kept it in that situation until the whole of the mercury melted, and dropped down globule after globule into the stem of the hydrometer. The interval of time from taking the mercury out of the frigorific mixture in a solid state, the last time, to its perfect liquefaction, was not noticed; but, upon recollection immediately afterwards, was supposed to be not less than three or four minutes. In a succeeding experiment this circumstance was attended to, and the frozen mercury, weighing seven scruples, was not entirely melted under seven minutes, the temperature of the air $+30^{\circ}$.

The experiment which follows I consider the most extraordinary, because it proves beyond a doubt, that mercury may be frozen not only here in summer, but even in the hottest climate, at any season of the year, by a combination of frigorific mixtures, in the way described in the Philosophical Transactions, Vol. LXXVII. p. 285. in which attempt to freeze mercury, made April 20, 1787, the temperature of the air and materials being $+45^{\circ}$, I certainly reached (without the assistance of snow or ice) the point of mercurial congelation; but had then no satisfactory proof that any part of the mercury was absolutely congealed.

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Exp. 2. On December 30. three ounces of a mixture composed of strong fuming nitrous acid two parts, and strong vitriolic acid and water each one part, were cooled in a half pint tumbler immersed in a frigorific mixture, till the temperature of the diluted mixture of acids was reduced to -30° . The tumbler was then removed out of the mixture, and vitriolated natron (GLAUBER's salt) in very fine powder, previously cooled to -14° by a frigorific mixture, added by degrees to the liquor in the tumbler, stirring it together until the mercury in the thermometer sunk to -54° . The hydrometer used in the former experiment, with its lower bulb three-fourths full of mercury, was now immersed and stirred about in the mixture for a few minutes, when on taking it out, and inverting it, I had the satisfaction to find the same proof of the mercury being frozen as in the former instance. It was immediately shewn to the gentlemen present, who expressed likewise their entire satisfaction. Nearly four ounces of the powdered salt was added; but, I believe, some was added after the greatest effect was produced. I had no nitrated ammonia by me, otherwise I should have used upon this occasion, instead of vitriolated natron alone, a mixture of these two salts in powder, in the proportion of seven parts of the former to eight of the latter. The temperature of the room in which these experiments were made was $+30^{\circ}$ each time, and the mercury taken from a jar containing several pounds.

Exp. 3. By an experiment made purposely on January 10. last, at which Dr. BOURNE was present, I have found that mercury may be congealed tolerably hard, by adding fresh fallen snow, at the temperature of $+32^{\circ}$, to strong fuming nitrous acid, previously cooled to between -25° and -30° , which may be very easily and quickly effected by immersing

the vessel containing the acid in a mixture of snow and nitrous acid.

I use the *fuming* nitrous acid upon all occasions, because that does not require to be diluted, cold being immediately produced on the smallest addition of snow.

Exp. 4. On January 12, at Dr. THOMSON'S request, I repeated the experiment of freezing mercury, at the Anatomy School in Christ Church, in the presence of the honourable Mr. WENMAN, the rev. Dr. HOARE, Dr. SIBTHORP, junior, Dr. THOMPSON, the rev. Mr. JACKSON of Christ Church, and Mr. WOOD of this place, a gentleman well known for his ingenuity in mechanics.

For this purpose were provided a spirit thermometer graduated very low, and a mercurial thermometer graduated to -76° , two thermometer glasses, with bulbs very near, if not quite, an inch in diameter each, one filled with mercury nearly to the orifice of the tube, which was left open, the other with its bulb half filled, and an hydrometer with its lower bulb (considerably less than either of the others) likewise half filled with mercury; the temperature of the room at this time $+28^{\circ}$.

A pan, containing nine ounces of the mixture of acids prepared as in the first experiment, was placed in a larger pan, containing nitrous acid, and this, in a frigorific mixture of nitrous acid and snow, contained in another pan much larger. When the nitrous acid in the second pan was cooled by this mixture to -18° , and the mixed acids in the smallest pan nearly as much, snow at somewhat between $+20^{\circ}$ and $+25^{\circ}$, the temperature of the open air at that time, was added to the nitrous acid in the second pan, until the spirit thermometer sunk to near -43° ; then the thermometer, with its bulb half filled, was immersed a sufficient time, and when taken

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out, the mercury in it was found congealed, and adhering to the glafs. The pan containing the mixed acids, and which had been removed whilst the fnow was added to make the fecond mixture, was now replaced in it, in order to be cooled; and when the mixture of acids was reduced to the temperature of -34° , fnow previously cooled to -18° was added, keeping the mixture ftirred until the mercurial thermometer funk to -60° ; its temperature by the fpirit thermometer was then found to be -51° .

The three glaffes containing the mercury to be frozen were now immerfed in this mixture, and having been moved about in it for a confiderable time, during which the fpirit thermometer rofe fcarcely one degree, were then feverally taken out and examined.

As the examination of the frozen mercury was more immediately under the infpection of Dr. THOMSON, I fhall tranfcribe here that gentleman's account of the phænomena.

“ When the freezing mixture was fuppofed to have produced its effect, the bulb which was completely filled was taken out, and broken on a flat ftone by a moderate ftroke or two with an iron hammer. This bulb was eleven or twelve lines in diameter.

The folid mercury was feperated into feveral fharp and brilliant fragments, fome of which bore handling for a fhort time before they returned to a fluid form. One mafs, larger than the reft, confifting of nearly one-third of the whole ball, afforded the beautiful appearance of flat plates, converging towards a center. Each of thefe plates was about a line in breadth at the external furface of the ball, becoming narrower as it fhot inwards. Thefe facets lay in very different planes, as is common in the fracture of any cryftallized ball,
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whether of a brittle metal or of the earths, as in balls of calcareous stalactite. The solid brittle mercury in the present instance bore a very exact resemblance, both in colour and plated structure, to sulphurated antimony, and especially to the radiated specimens from Auvergne, before they are at all tarnished.

Instead of a solid center to this ball, it seemed as if there had been a central cavity, of about two lines in diameter, a considerable portion of which was evident in the fragment just described, at that part to which the radii converged. It is indeed possible, that this may have been merely the receptacle of some part of the mercury remaining fluid at the center. The hollow within was shining, but its edges were neither soft nor mouldering; on the contrary, they were sharp and well defined: nor was the brilliancy of the radii attributable to any exudation of mercury as from an amalgam.

In the two smaller bulbs, which were only half filled, the mercury preserved its usual lustre on the surface in contact with the glass, as well as on that surface which it had acquired in becoming solid. The latter was occupied by a conical depression, the gradations of which were marked by concentric lines.

One of these hemispheres was struck with a hammer, as in the former instance, but was rather flattened and crushed than broken. The other, on being divided with a sharp chisel, shewed a metallic splendour on its cut surface, but not equaling the polish of a globule of fluid mercury."

Thirteen ounces of snow in the whole were found to have been added to the mixed acids; but some was added to lower its temperature after the glasses containing the mercury were taken out, and the spirit thermometer had risen a few degrees.

This was a day remarkably favourable for such an experiment. My thermometer exposed to the open air stood, at three quarters past eight this morning, at $+6^{\circ}$, which is a very extraordinary degree of cold here; but this experiment was not begun till noon.

Exp. 5. On Jan. 14. I froze mercury at the Anatomy School again, in the presence of the rev. the Dean of Christ Church, the rev. Dr. HORNSBY, and Dr. THOMSON.

Four ounces now of the mixture of acids, prepared as in the first experiment, were cooled in a tumbler to -20° , which required somewhat more than an equal weight of snow, cooled nearly to the same temperature, to produce the greatest effect. This was somewhat less than in the last experiment, the spirit thermometer sinking no lower than -46° , owing chiefly to the weather having become much warmer, the temperature of the open air being now $+36^{\circ}$. The mercurial thermometer immersed in this mixture sunk to -55° , where it became stationary; then two thermometer glasses, one half filled with mercury, and the other filled to a considerable height up the tube, after being immersed some time, were examined. Upon breaking the shell of glass from the former of these, the mercury was found in a perfectly solid state; but its upper surface, which was highly polished, and of the colour of liquid mercury, instead of being only slightly depressed, as had been seen in every other instance which afforded an opportunity for inspection, now formed a perfectly inverted hollow cone. This great depression, as well as the concentric circles mentioned in a former instance, I suppose, might be owing to a rotatory motion accidentally given to it whilst congealing. The solid mercury was beaten out, but having been suffered to lie some time on the table for inspection, very quickly melted

melted into liquid globules. The flexibility of solid mercury was clearly to be observed in this beautiful specimen; for the external surface, particularly the upper thin rim of the concave part, was evidently bent by the first gentle stroke of the hammer. The globe of mercury in the other glass, which was very small, exhibited nearly the same phenomena, as in the instances before mentioned.

It happened in these experiments of mine, contrary to what has generally occurred to others, that the mercury never sunk lower than -60° , seldom so low, in the thermometer, and but little below the point of mercurial congelation in the tubes of the thermometer glasses filled nearly up to the orifice, with a view to shew the contraction of mercury in becoming solid by its great descent in the tube. On reflecting on this circumstance afterwards, it occurred to me, that the further descent of the mercury in these experiments was prevented not solely by the mercury freezing in the tube, the cause commonly assigned, but rather by the quick formation of a spherical shell of solid mercury within the bulb, by the sudden generation of cold.

Dr. BEDDOES expressing a desire to exhibit solid mercury at his Lecture before his Class, I undertook to freeze some at the Laboratory on March 12th last, and now resolved to satisfy myself respecting the cause which prevented the lower descent of the mercury in my former experiments. In this, as well as the former, the mercury in a thermometer graduated to -60° , and likewise in a thermometer glass, filled nearly to the orifice, which lengthened its scale to near -250° , sunk only a few degrees below the point of mercurial congelation, and then remained stationary. After waiting some time, I took the thermometer out of the mixture, and observed the bulb apparently full, and the short thread of mercury above unbroken.

I now embraced the lower part of the tube with my hand a few seconds, resting it upon the upper part of the bulb; and upon taking it away, I found that the whole of the mercury had subsided into the bulb, which it did not now quite fill, a small space at the top of the bulb remaining empty. I then took out the thermometer glass, and applied my hand to the tube; but the mercury remained stationary until I sunk my hand so as to communicate heat to that part of the bulb which is immediately connected with the tube, when the thread of mercury dropped entirely into the bulb. It was now immersed again for a short time, then taken out, and the shell of glass beaten off, which exposed a globe of solid mercury, nearly an inch in diameter. This bore several very smart strokes with a hammer before it began to liquify, but was not perfectly malleable.

In the course of these experiments, several fragments of the solid mercury were thrown into mercury in its ordinary liquid state, and were found to sink with considerable celerity.

In continuing my researches respecting the means of producing artificial cold, I have found that phosphorated natron produces rather more cold by solution in the diluted nitrous acid than the vitriolated natron.

At the temperature of $+50^{\circ}$, four parts of the diluted nitrous acid (prepared by mixing strong nitrous acid with half its weight of water) required eight parts of that neutral salt in fine powder to be added, in order to cause the thermometer to sink to -6° ; and again, by the addition of five parts of nitrated ammonia in fine powder, the thermometer sunk so low as -16° , in the whole sixty-six degrees.

A mixture of this kind made the thermometer sink from 80° (the temperature of the materials before mixing) to 0° .

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I was directed to the trial of this salt, by the like remarkable sensation of coldness without pungency, which, with its other similar properties to ice, first induced me, whilst pursuing the subject of cold, to try the effect of dissolving the vitriolated natron in the mineral acids.

Equal quantities, by weight, of phosphorated natron and vitriolated natron, were evaporated separately over a gentle fire, until each was reduced to a perfectly dry powder. I then weighed them, and found the residuum of the phosphorated natron somewhat lighter than that of the vitriolated natron; from whence it is probable the former contains the greatest quantity of water of crystallization.

I have found, that each of the neutral salts which produce any remarkable degree of cold by solution in the mineral acids, *viz.* phosphorated natron, vitriolated natron, and vitriolated magnesia, lose this property entirely, when deprived by any means of their water of crystallization.

A short time after I had first succeeded in freezing water in summer, by one mixture composed of three different salts in water (having been induced to try the effect of such a method, from the consideration that water, already saturated with one kind of salt, will dissolve a portion of another, and after that a third, or even more), I met with the account of an experiment made by M. HOMBERG, related in one of the earlier Volumes of the Philosophical Transactions, in which it is said he produced an extraordinary degree of cold, by pouring a pint and a half of distilled vinegar upon two pounds of a powder composed of equal parts of crude sal ammoniac and corrosive sublimate, and shaking them well together. I immediately (July 30, 1786) prepared a mixture of this kind in smaller quantity, but found it produced only thirty-two degrees of cold,

cold, the temperature of the air and materials before mixing being 63° ; which is no more than I have found may be effected by a solution in water of crude sal ammoniac alone, previously dried and powdered.

By a trial made with great accuracy, I find, that even the mixture composed of diluted vitriolic acid and vitriolated natron is adequate to any useful purpose that may be required in the hottest country; for, by adding eleven parts of the salt in fine powder to eight parts of the vitriolic acid diluted with an equal weight of water, the thermometer sunk from 80° , the mean temperature of the hottest climate, and to which these materials were purposely heated before mixing, to rather below 20° .

Vitriolated natron, added to the marine acid undiluted, produces very nearly as great a degree of cold as when mixed with the diluted nitrous acid. At the temperature of 50° , two parts of the acid, require three parts of the salt in fine powder, which will sink the thermometer to 0° ; and if three parts of a mixed powder, containing equal parts of muriated ammonia and nitrated kali, be added afterwards, the cold of the mixture will be increased a few degrees more.

The frigorific mixture above described, composed of phosphorated natron and nitrated ammonia dissolved in the diluted nitrous acid, being the most powerful, it will probably be found most convenient for freezing mercury, when snow is not to be procured. The materials for this purpose may be previously cooled in mixtures made of marine acid with vitriolated natron, muriated ammonia, and nitrated kali, in the proportions mentioned above, this being much cheaper than those made with diluted nitrous acid, and very nearly equal in effect.

In my last Paper I mentioned a freezing mixture, made by dissolving a powder composed of equal parts of muriated ammonia and nitrated kali in water, and therein directed six parts of the mixed powder to be added to eight parts of water; but I have found since, that the best proportions are, five parts of the former to eight of the latter, by which I have sunk the thermometer from 50° to 11° .

Having now prosecuted my subject relative to mixtures for generating artificial cold without the use of ice, from a possible method proposed by Dr. WATSON (Essays, Vol. III. p. 139.), for freezing water in summer in this climate, and carried it on to a certain method of freezing, not only water, but even mercury, in the hottest climate, I now intend to take my leave of it.

I have the honour to be, &c.

RICHARD WALKER.

