

XX. *Observations on Mr. Hutchins's Experiments for determining the Degree of Cold at which Quickfilver freezes.* By Henry Cavendish, Esq. F. R. S.

Read May 1, 1783.

THE design of the following paper is to explain some particulars in the apparatus sent by me to Mr. HUTCHINS, the intention of which does not readily appear; and also to endeavour to shew the cause of some phenomena which occurred in his experiments; and point out the consequences to be drawn from them.

This apparatus was intended to determine the precise degree of cold at which quickfilver freezes: it consisted of a small mercurial thermometer, the bulb of which reached about  $2\frac{1}{2}$  inches below the scale, and was inclosed in a glass cylinder swelled at bottom into a ball, which, when used, was filled with quickfilver, so that the bulb of the thermometer was entirely surrounded with it. If this cylinder is immersed in a freezing mixture till great part of the quickfilver in it is frozen, it is evident, that the degree shewn at that time by the inclosed thermometer is the precise point at which mercury freezes; for as in this case the ball of the thermometer must be surrounded for some time with quickfilver, part of which is actually frozen, it seems impossible, that the thermometer should be sensibly above that point; and while any of the quickfilver in the cylinder remains fluid, it is impossible that it should sink sensibly

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below it. The ball of the thermometer was kept constantly in the middle of the swelled part of the cylinder, without danger of ever touching the sides, by means of some worsted wound round the tube. This worsted also served to prevent the access of the air to the quicksilver in the cylinder, which, if not prevented, would have made it more difficult to have communicated a sufficient degree of cold. The diameter of the bulb of the thermometer was rather less than one-fourth of an inch, that of the swelled part of the cylinder was two-thirds, so that there was no where a much less thickness of quicksilver between the ball and cylinder than one-sixth of an inch. The bulb of the thermometer was purposely made as small as it conveniently could, in order to leave a sufficient space between it and the cylinder, without making the swelled part thereof larger than necessary, which would have caused more difficulty in freezing the quicksilver in it. Two of these instruments were sent for fear of accidents.

One of the most striking circumstances in the experiments which have been made for freezing mercury, is the excessively low degree to which the thermometers sunk, and which, if it had proceeded, as was commonly supposed from the freezing mixture having actually produced such a degree of cold, would have been really astonishing. The experiments, however, made at Petersburg afforded the utmost reason to suppose, and Mr. HURCHINS's last experiments have put beyond a possibility of doubt, that quicksilver contracts in the act of freezing, or in other words, that it takes up less room in a solid than in a fluid state; and that the very low degree to which the thermometers sunk was owing to this contraction, and not to the intensity of the cold produced: for example, in one of Mr. HURCHINS's experiments a mercurial thermometer, placed in  
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the freezing mixture, sunk to  $450^{\circ}$  below nothing, though the cold of the mixture was never more than  $-46$ ; so that the quicksilver was contracted not less than  $404^{\circ}$  by the action of freezing.

If a glass of water, with a thermometer in it, is exposed to the cold, the thermometer will remain perfectly stationary from the time the water begins to freeze till it is intirely congealed, and will then begin to sink again. In like manner, if a thermometer is dipped into melted tin or lead, it will remain perfectly stationary, as I know by experience, from the time the metal begins to harden round the edges of the pot till it is all become solid, when it will again begin to descend; and there was no reason to doubt that the same thing would obtain in quicksilver.

From what has been just said it was concluded, that if this apparatus was put into a freezing mixture of a sufficient coldness, the thermometer would immediately sink till the quicksilver in the cylinder began to freeze, and would then continue stationary, supposing the mixture still to keep cold enough, till it was intirely congealed. This stationary height of the thermometer is the point at which mercury freezes, though in order to make the experiment convincing, it was necessary to continue the process till so much of the quicksilver in the cylinder was frozen as to put the fact out of doubt.

If the experiment had been tried with no further precautions, I apprehended that considerable difficulties would have occurred, from want of knowing whether the cold of the mixture was sufficiently great, and when a sufficient quantity of the quicksilver was frozen; for, in the first place, there would be no judging when a sufficient quantity was frozen without taking out the apparatus now and then to examine it, which could not

be done without a loss of cold; and what is still worse, if before the experiment was completed the cold of the mixture was so much abated as to become less than that of congealing mercury, the frozen quicksilver would begin to melt, and the operator would have no way of detecting it, but by finding that great part of his labour was undone. For this reason two other mercurial thermometers were sent called A and B by Mr. HUTCHINS, the scales of which were of wood, for which reason I shall call them, for shortness, the wooden thermometers, as I shall call the two others the ivory ones, their scales being of that material; they were graduated to about  $600^{\circ}$  below nothing, and their balls were nearly equal in diameter to the swelled part of the cylinders, in order that the quicksilver in both should cool equally fast; and it was recommended to Mr. HUTCHINS to put one of these into the freezing mixture along with the apparatus: for then, if the cold of the mixture was sufficient, both thermometers would sink fast till the quicksilver in the cylinder began to freeze, when the ivory thermometer would become stationary, but the wooden one would still continue to sink, on account of the contraction of the quicksilver in its ball by freezing; but if this last thermometer, after having continued to sink for some time after the ivory one had become stationary, ceased at last to descend, it would shew, that the mixture was no longer cold enough to freeze mercury; for as long as that was the case, the wooden thermometer would continue to descend by the freezing of fresh portions of quicksilver in its ball, but would cease to do so as soon as the cold was at all less than that. As I was afraid, however, that the quicksilver might possibly freeze and stick tight in the tube of this thermometer, and prevent its sinking, which would make the cold of the mixture appear too small  
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when in reality it was not, one of these thermometers instead of having a vacuum above the quicksilver as usual, was made with a bulb at top filled with air, in order that the pressure might serve to force down the quicksilver.

If the degree of cold at which mercury freezes had been known, a spirit thermometer would have answered better; but that was the point to be determined.

Another advantage which I expected from the wooden thermometer was, that it would afford a guess when a sufficient quantity of the quicksilver in the cylinder was frozen; for if the cold was continued long enough to make that thermometer sink to near  $400^{\circ}$  below nothing, I supposed, a very visible portion of the quicksilver would be frozen.

It must be observed, however, that in Mr. HUTCHINS's experiments the natural cold approached so near to the point of mercurial congelation, and in consequence the freezing mixture retained its cold so long as to make these precautions of not so much use as they would otherwise have been.

As it appeared, from Mr. HUTCHINS's table of comparison, that these thermometers did not agree well together, they were all examined after they came back, except the ivory thermometer F, which was broke before it arrived. This loss, however, is of little consequence, as it appeared from the above-mentioned table, that F and G agreed well together. The boiling and freezing points were first examined in the presence of Sir JOSEPH BANKS, Dr. BLAGDEN, Mr. HUTCHINS, Mr. NAIRNE, and myself, when the divisions on the scale answering thereto were found to be as follows:

		Boiling point.		Freezing point.
A	-	220,3	-	29,9
B	-	218,8	-	30,9
G	-	215,3	-	32

The boiling point was tried in the manner recommended in the report of the Committee of the Royal Society, printed in the Philosophical Transactions for the year 1777, and allowance made, as there directed, for the height of the barometer at that time. In fixing the freezing point also allowance was made for the temperature of the room in which it was tried.

The great difference in the position of the boiling point on these thermometers seems owing only to care not having been taken to keep the quicksilver in the tube of the same heat as that in the ball, which is a circumstance that was very little attended to when they were made; and I am afraid is not so much observed at present as it ought to be, and which in A and B, whose tubes contained upwards of 900° of quicksilver, caused an excessively great error, and much more than it did in G, which contained fewer degrees in its tube.

In order to see whether the inequalities of the bore of the tube were properly allowed for, a column of quicksilver, about 100° long, was separated from the rest; and it was examined, whether its length comprehended the same number of degrees on the scale in different parts of the tube; when no sensible error could be found in this respect in G, and none worth regarding in B. The thermometer A, by reason of its being constructed with a bulb filled with air at top, could not be examined in this manner; but there is no reason to think, that it was faulty in this respect.

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From what has been said it appears, that  $183^{\circ},3$  on the scale of G are equal to only  $180^{\circ}$  on a thermometer adjusted as recommended by the Committee, and therefore  $72^{\circ}$  are equal to  $70^{\circ}\frac{2}{3}$ ; so that the point of  $-40^{\circ}$  answers really to  $-38^{\circ}\frac{2}{3}$ ; that is, the cold shewn by this thermometer at the temperature of about  $-40^{\circ}$  is  $1^{\circ}\frac{1}{3}$  too great. In like manner it appears, that the cold shewn at that temperature by B is  $4^{\circ}\frac{1}{3}$ , and by A  $6^{\circ}\frac{1}{3}$ , too great.

On the whole, these thermometers seem to have been carefully made, their disagreement being owing only to a faulty manner of adjusting the boiling point, and to not allowing for the temper of the air in settling the degree of freezing; and as these points were examined after they came back, the experiments made with them are just as much to be depended on as if they had been truly adjusted at first.

These instruments were made in the year 1776, and were intended to have been sent to Mr. HUTCHINS that year, through the hands of the late Dr. MATY, who promised to recommend the experiment to him; but, by not being got ready time enough to be sent that year, and a mistaken supposition that Mr. HUTCHINS was to come back the next summer, they were prevented from being sent till 1781; when Sir JOSEPH BANKS was informed by Mr. WEGG, that there was a gentleman at Hudson's Bay who was willing to undertake any experiments of that kind; and that the Hudson's Bay Company would be at the expence of any instruments necessary for the purpose. Then, as Sir JOSEPH thought the abovementioned apparatus well adapted to the purpose, I gladly embraced the opportunity of sending it. It appears, however, from the letter inserted by Mr. HUTCHINS, that Dr. BLACK, without being acquainted with

with what I had done, recommended nearly the same method of determining the degree of cold at which mercury freezes.

Besides the abovementioned instruments, there were sent to Mr. HUTCHINS two spirit thermometers and a thermometer marked C, made at the expence of the Hudson's Bay Company. The two spirit thermometers were made at the recommendation, and under the inspection of Dr. BLAGDEN, and were of great use, as they serve to ascertain several circumstances relating to the experiments, which could not otherwise have been determined. The intention of the thermometer C will be mentioned in the course of this paper.

Before I enter into the examination of Mr. HUTCHINS's experiments, it will be proper to take notice of a phenomenon which occurs in the freezing of water, and is now found to take place in that of quicksilver, and which occasioned many remarkable appearances in these experiments.

It is well known, that if a vessel of water, with a thermometer in it, is exposed to the cold, the thermometer will sink several degrees below the freezing point, especially if the water is covered up so as to be defended from the wind, and care is taken not to agitate it; and then, on dropping in a bit of ice, or on mere agitation, spiculæ of ice shoot suddenly through the water, and the inclosed thermometer rises quickly to the freezing point where it remains stationary\*.

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\* Though I here say conformably to the common opinion, that mere agitation may set the water a freezing, yet some experiments, lately made by Dr. BLAGDEN, seem to shew, that it has not much, if any, effect of that kind, otherwise than by bringing the water in contact with some substance colder than itself. Though in general also the ice shoots rapidly, and the inclosed thermometer rises very quick; yet I once observed it to rise very slowly, as, to the best of my remembrance, it took up not less than half a minute before it rose to the freezing point;



This shews, that water is capable of being cooled considerably below the freezing point, without any congelation taking place; and that, as soon as by any means a small part of it is made to freeze, the ice spreads rapidly through the remainder of the water. The cause of the rise of the thermometer, when the water begins to freeze, is the circumstance now pretty well known to philosophers, that all, or almost all, bodies by changing from a fluid to a solid state, or from the state of an elastic to that of an unelastic fluid, generate heat; and that cold is produced by the contrary process. This explains all the circumstances of the phenomenon perfectly well; for as soon as any part of the water freezes, heat will be generated thereby in consequence of the abovementioned law, so that the new formed ice and remaining water will be warmed, and must continue to receive heat by the freezing of fresh portions of water, till it is heated exactly to the freezing point, unless the water could become quite solid before a sufficient quantity of heat was generated to raise it to that point, which is not the case; and it is evident, that it cannot be heated above the freezing point, for as soon as it comes thereto, no more water will freeze, and consequently no more heat will be generated.

The reason why the ice spreads all over the water, instead of forming a solid lump in one part, is, that as soon as any small portion of ice is formed, the water in contact with it will be so much warmed as to be prevented from freezing; but the water at a little distance from it will still be below the freezing point, and will consequently begin to freeze.

point; but in this experiment the water was cooled not more than one or two degrees below freezing; and it should seem, that the more the water is cooled below that point, the more rapidly the ice shoots, and the inclosed thermometer rises.

If it was not for this generation of heat by the act of freezing, whenever a vessel of water, exposed to the cold, was arrived at the freezing point, and began to freeze, the whole would instantly be turned into solid ice; for as the new formed ice is not sensibly colder than water beginning to freeze, it follows, that as soon as all the water in the vessel was cooled to that point, the least addition of cold would convert the whole into ice; whereas it is well known, that though the whole vessel of water is cooled to, or even below, the freezing point, there is a long interval of time between its beginning to freeze and being intirely frozen, during all which time it does not grow at all colder.

In like manner, it is the cold generated by the melting of ice which is the cause of the long time required to thaw ice or snow. It is this also which is the cause of the cold produced by freezing mixtures; for no cold is produced by mixing snow with any substance, unless part of the snow is dissolved.

I formerly found, by adding snow to warm water, and stirring it about till all was melted, that the water was as much cooled as it would have been by the addition of the same quantity of water, rather more than  $150^{\circ}$  colder than the snow; or, in other words, somewhat more than  $150^{\circ}$  of cold are generated by the thawing of snow; and there is great reason to think, that just as much heat is produced by the freezing of water. The cold generated was exactly the same whether I used ice or snow\*.

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\* I am informed, that Dr.-BLACK explains the abovementioned phenomena in the same manner; only, instead of using the expression, heat is generated or produced, he says, latent heat is evolved or set free; but as this expression relates to an hypothesis depending on the supposition, that the heat of bodies is owing to their  
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I have formerly kept a thermometer in melted tin and lead till they became solid; the thermometer remained perfectly stationary from the time the metal began to harden round the sides of the pot till it was intirely solid; but I could not perceive it to sink at all below that point, and rise up to it when the metal began to harden. It is not unlikely, however, that the great difference of heat between the air and melted metal might prevent this effect from taking place; so that though I did not perceive it in those experiments, it is not unlikely that those metals, as well as water and quicksilver, may bear being cooled a little below the freezing or hardening point (for the hardening of melted metals and freezing of water seems exactly the same process) without beginning to lose their fluidity.

Mr. HUTCHINS's five first experiments were made with the apparatus, and in the manner above described. In the first experiment the ivory thermometer, inclosed in the cylinder, sunk to  $-40^{\circ}$ , where it remained stationary for about half an hour, though the wooden thermometer, placed in the same mixture, kept sinking almost all the while. At the end of that time the apparatus was taken out of the mixture to be examined, and the quicksilver in the cylinder was found frozen. It seems evident, therefore, that the true point at which mercury freezes is  $40^{\circ}$  below nothing on the thermometer F, which was that made use of in the experiment. It cannot be lower than that,

their containing more or less of a substance called the matter of heat; and as I think Sir ISAAC NEWTON's opinion, that heat consists in the internal motion of the particles of bodies, much the most probable, I chose to use the expression, heat is generated. Mr. WILKE also, in the Transactions of the Stockholm Academy of Sciences, explains the phenomena in the same way, and makes use of an hypothesis nearly similar to that of Dr. BLACK. Dr. BLACK, as I have been informed, makes the cold produced by the thawing of snow  $140^{\circ}$ ; Mr. WILKE,  $130^{\circ}$ .

for if it was, the thermometer could not have remained so long stationary at that point, while surrounded with freezing quicksilver; and it cannot be higher, as the thermometer could not sink below the freezing point, while much of the quicksilver, with which it was surrounded, remained unfrozen.

To those who have attended to the former part of this paper it is needless saying, that the reason why the wooden thermometer continued sinking so long after the ivory thermometer became stationary is, that as the former was placed in the freezing mixture, the quicksilver in its ball froze, and therefore it continued descending during the greatest part of that half hour, by the continual freezing of fresh portions of quicksilver in its ball, and the contraction occasioned thereby; whereas the latter, which was placed only in freezing quicksilver, did not freeze.

There is a circumstance, however, in this experiment, the reason of which does not so readily appear; namely, on putting back the apparatus into the freezing mixture, after it was taken out to be examined, the thermometer sunk to  $-42^{\circ}$ ; but in about four or five minutes returned back to  $-40^{\circ}$ . The like happened on removing the apparatus into a fresh freezing mixture, and it then remained about ten minutes before it returned to  $-40^{\circ}$ . It seems probable from this, that the quicksilver in the cylinder became intirely frozen about the time that it was first taken out to be examined, and that it then grew  $2^{\circ}$  colder than the freezing point; and that this degree of cold was not sufficient to make the quicksilver in the inclosed thermometer freeze, since mercury, as was before said, will bear being cooled a little below its freezing point without freezing. What confirms this explanation is, that the spirit thermometers shew that the cold of the mixture was actually much the same as that shewn by the ivory thermometer.

In the second experiment, tried with the same apparatus, the ivory thermometer quickly sunk to  $-43^{\circ}$ ; but, in about half a minute, rose to  $-40^{\circ}$ , where it remained stationary for upwards of 17'. It appears, therefore, that in this experiment the quicksilver was cooled  $3^{\circ}$  below the freezing point, without losing its fluidity; it then began to freeze, and the inclosed thermometer immediately rose to  $-40^{\circ}$ : so that this experiment, besides confirming the former, shews, that quicksilver is capable of being cooled a little below the freezing point without freezing; and that it suddenly rises up to it as soon as it begins to lose its fluidity.

In this experiment the cold was carried far enough to freeze the quicksilver in the ivory thermometer, which was not the case in the former: for after it had remained 17' stationary at  $-40^{\circ}$ , it began to sink again, and in about a minute sunk to  $-44^{\circ}\frac{1}{2}$ ; it then sunk instantaneously to  $-92^{\circ}$ , and soon after remained fixed for an hour and a quarter at  $95^{\circ}$ ; being then left without examination for three-quarters of an hour, the mercury was found to have sunk into the ball, the spirit thermometer shewing at that time that the mixture was rather above the point of freezing, whereas before it had been below it. It appears, therefore, that the quicksilver in the thermometer, after having descended to  $-44^{\circ}\frac{1}{2}$ , froze in the tube, and stuck there; but, being by some means loosened, sunk instantly to  $-92^{\circ}$ , and again stuck tight at  $-95^{\circ}$ , till at last the mixture rising above the freezing point, the quicksilver in the tube melted, and sunk into the ball, to supply the vacuum formed there by the frozen quicksilver. A similar accident of the quicksilver freezing in the tube of the thermometer, and sticking there, and then melting and sinking into the ball as the weather grew warmer, has been found by Dr. BLAGDEN to have

have happened to several gentlemen whose thermometers froze by the natural cold of the atmosphere, and with reason caused much perplexity to some of them.

In this experiment the apparatus was not taken out to be examined till the ivory thermometer had sunk to  $-95^{\circ}$ ; it was then found to be frozen solid.

The third experiment was tried while the former was carrying on, and was made by putting the other apparatus, namely, that with the thermometers G and B, into the first mixture made for the former experiment, and which may consequently be supposed to have lost great part of its cold. The ivory thermometer quickly sunk to  $-43^{\circ}$ , where it remained stationary for near 12'. The apparatus being then taken out to be examined, the quicksilver in the cylinder was found fluid, but thick and in grains, like crumbs of bread. The apparatus was then put back into the mixture; and, on observing the thermometer, it was found to have risen to  $-40^{\circ}$ , where it remained stationary about 40'; being then examined, the quicksilver was found solid.

It appears, therefore, that the cold of the mixture was sufficient to cool the quicksilver in the cylinder about  $3^{\circ}$  below the point of freezing, but did not make it freeze till, on taking out the apparatus, the agitation suddenly set it a freezing, and produced the appearance described by Mr. HUTCHINS. This immediately made the inclosed thermometer rise; so that when it was replaced in the mixture and observed, it stood exactly at the freezing point. It appeared, by the spirit thermometer, that the cold of the mixture, at the time the apparatus was first taken out to be examined, was only  $2^{\circ}$  below the point of freezing, which agrees very well with this explanation.

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This experiment, therefore, affords a fresh confirmation that the point of mercurial congelation is  $-40^{\circ}$  on these thermometers; and that quicksilver will bear being cooled a little below that point without freezing.

As in these two experiments the quicksilver in the cylinder and ivory thermometer bore being cooled a few degrees below the freezing point without freezing, it is natural to conclude, that the same fluid in the wooden thermometer should do so too; and it may, perhaps, be supposed that, in consequence of it, this thermometer, after having sunk a little below the point of freezing, ought suddenly to have risen up to it, which was not observed. But there is great reason to think, that though the quicksilver in it did bear cooling in this manner, it would not have occasioned any such appearance: for suppose that it is cooled below the freezing point, and then suddenly freezes, its bulk will be increased, on account of the heat generated thereby; but then it will be diminished on account of the contraction in freezing; so that, unless the expansion by the heat generated exceeds the contraction by freezing it will cause no rise in the thermometer. I do not, indeed, know how much the heat generated by freezing in quicksilver is, but in water it is about  $150^{\circ}$ , and the contraction by freezing is at least as much as its expansion by  $400^{\circ}$ ; so that, unless the heat generated by freezing is two or three times as great in quicksilver as in water, the thermometer ought not to rise on this account.

In the fourth, fifth, sixth, and seventh experiments a new phenomenon occurred, namely, the ivory thermometer sunk a great deal below the freezing point without ever becoming stationary at  $-40^{\circ}$ . In the fifth experiment, tried with the apparatus G, it quickly sunk to  $-42^{\circ}$ , and then, without remaining stationary at any point, sunk in half a minute to

$-72^{\circ}$ , and soon after remained fixed at  $-79^{\circ}$ . While it was at  $-79^{\circ}$ , the apparatus was twice examined, and the quicksilver found fluid; but being again examined after having been removed into a fresh mixture, it was found solid.

It seems likely from hence, that the quicksilver, in the cylinder was quickly cooled so much below the freezing point as to make that in the inclosed thermometer freeze, though it did not freeze itself. If so, it accounts for the appearances perfectly well; nor does there seem any thing improbable in the explanation, except that it is contrary to what happened in the three first experiments; but the degree to which fluids will bear being cooled below the freezing point without freezing seems to depend on such minute circumstances, that, I think, this forms no objection. It must be observed, that the cold of the mixture appeared by the spirit thermometer to be five or six degrees below the freezing point; so that if the quicksilver in the cylinder was as cold as the mixture, and I have no reason to think it was not, it is not at all extraordinary that the thermometer should have froze; the only thing extraordinary is, that the quicksilver in the cylinder should have borne that cold without freezing.

The same phenomenon occurred in the sixth and seventh experiments, on putting the same apparatus into the freezing mixture.

In the fourth experiment the ivory thermometer sunk quickly to  $-42^{\circ}$ ; but soon after rose half a degree, probably from the cold of the mixture diminishing; it then, after having remained six or seven minutes at those two points, sunk very quick to  $-77^{\circ}$ . It does not appear, at what time the quicksilver in the cylinder began to freeze, as it was not examined till long after the thermometer had sunk to  $-77^{\circ}$ , when it was found



found solid; but from the resemblance of this to the three former experiments, I think it much most likely, that it did not begin to freeze till after the thermometer had sunk to  $-77^{\circ}$ .

In the fifth experiment the wooden thermometer was partly frozen before it was put into the freezing mixture, and the ivory one was at  $-40^{\circ}$ . On putting them into the mixture, they both rose; the latter, half a degree; the former, many degrees; which shews that the part of the mixture in which they were placed was rather warmer than the freezing point, though that in which the spirit thermometer was placed was colder; but as there seems nothing to be learnt from this, it is not worth while entering into a detail of the circumstances.

Though these experiments do not serve to shew what the freezing point of quicksilver is, yet they do not at all contradict the conclusion drawn from the three former.

If these experiments only had been made, I should have been inclined to suppose, that quicksilver froze with a less degree of cold in vacuo than in the open air, as the quicksilver in the ivory thermometer was in vacuo, and that in the cylinder was not; but, as in the three former experiments, the event was different, the quicksilver in the cylinder there freezing first, I have no reason to think that this is the case.

Though in the sixth experiment the thermometer in the apparatus G froze without the quicksilver with which it was surrounded freezing, yet in trying the apparatus F in the same mixture, this did not happen; but, on the contrary, it afforded as striking a proof that the point of freezing quicksilver answers to about  $-40^{\circ}$  on this thermometer as any of Mr. HUTCHINS's experiments; for, on taking out the apparatus after it had been two minutes in the mixture, the quicksilver in the cylinder was found frozen solid, the inclosed ther-

mercury standing at  $40^{\circ}$  or  $41^{\circ}$  below nothing. After having been exposed for near an hour to the air, which was then very little above the point of freezing quicksilver, only a small quantity of the surface was become fluid; the rest formed a frozen globe round the ball of the thermometer, resembling polished silver, and in 17' after this only a segment of a globe of frozen quicksilver, with a concavity on the inside, formed by the ball of the thermometer, was observed, the thermometer all this while continuing the same as before, namely, at  $40^{\circ}$  or  $41^{\circ}$  below nothing; so that in this experiment the ball of the thermometer was surrounded for more than an hour with quicksilver, which was visibly frozen and slowly melting, and during all which time it continued stationary at  $40^{\circ}$  or  $41^{\circ}$  below nothing.

It must be observed, however, that in the first and second experiments, which were both tried with this apparatus, the freezing point came out exactly  $-40^{\circ}$ , whereas in this it seemed about half a degree lower; the reason of which, in all probability, is, that the tube of this thermometer was not so well fitted to its scale but that it had a little play, which would make the freezing point appear near half a degree higher or lower, according as the tube was pushed up or down.

Though the foregoing experiments leave no reasonable room to doubt, that this is the true point at which quicksilver freezes, yet Mr. HUTCHINS has, if possible, made this still more evident by his two last experiments; as, in the first of them, he froze some quicksilver in a gally-pot immersed in a freezing mixture, so that the quicksilver was in contact with, and covered by, the snow and spirit of nitre; and in the latter in the open air, by the natural cold of the weather, and then dipping the ball of the thermometer into the unfrozen part, observed

what degree it stood at. These experiments agree with the former in shewing the freezing point to be  $-40^{\circ}$  on the two mercurial thermometers; and also shew what degree on the spirit thermometers answers thereto, namely,  $29^{\circ}\frac{3}{4}$  or  $28^{\circ}\frac{1}{2}$  on D, and  $30^{\circ}$  on E; for in these two experiments the spirit thermometers also were dipped into the frozen quicksilver.

In all the experiments, therefore, tried with the thermometer G, the freezing point came out  $-40^{\circ}$ . In those tried with F, it came out either  $-40^{\circ}$ , or about  $-40^{\circ}\frac{1}{2}$ ; so that as it appears, from Mr. HUTCHINS's table of comparison, that F stood at a medium a quarter of a degree lower than G, the experiments made with that thermometer also shew the freezing point to be  $-40^{\circ}$  on G; and as it appeared from the examination of this thermometer after it came home, that  $-40^{\circ}$  thereon answers to  $-38^{\circ}\frac{2}{3}$ , on a thermometer adjusted in the manner recommended by the Committee of the Royal Society, it follows, that all the experiments agree in shewing that the true point at which quicksilver freezes is  $38^{\circ}\frac{2}{3}$ , or in whole numbers  $39^{\circ}$  below nothing.

From what has been said it appears, that the point at which quicksilver freezes has been determined by Mr. HUTCHINS in different ways, all perfectly satisfactory, and all agreeing in the same result. In the three first experiments the thermometer was surrounded by quicksilver, which continued freezing till it became solid. In the sixth experiment the quicksilver with which it was surrounded continued slowly melting till the whole was dissolved; and in both cases the thermometer remained stationary all the while at what we have just said to be the freezing point. In the ninth and tenth experiments, the ball of the thermometer was dipped into quicksilver, previously frozen and beginning to melt, as usually practised in settling the

freezing point on thermometers, and agreed in the same result, the quicksilver in the last experiment being frozen by the natural cold of the atmosphere; and in the former, by being immersed in, and in contact with, a freezing mixture; so that this point appears to be determined in as satisfactory a manner as can be desired; and the more so, as it seems impossible that experiments should be made with more care and attention, or more faithfully and circumstantially related than these have been. The second and third experiments also shew, that quicksilver, as well as water, can bear being cooled a little below the freezing point without freezing, and is suddenly heated to that point as soon as it begins to congeal.

*On the contraction of quicksilver in freezing.*

All these experiments prove, that quicksilver contracts or diminishes in bulk by freezing; and that the very low degrees to which the thermometers have been made to sink, is owing to this contraction, and not to the cold having been in any degree equal to that shewn by the thermometer. In the fourth experiment the thermometer A sunk to  $-45^{\circ}$ , though it appeared by the spirit thermometers that the cold of the mixture was not more than  $5^{\circ}$  or  $6^{\circ}$  below the point of freezing quicksilver. In the first experiment also, it sunk to  $-44.8^{\circ}$ , at a time when the cold of the mixture was only  $2^{\circ}\frac{1}{2}$  below that point; so that it appears, that the contraction of quicksilver, by freezing, must be at least equal to its expansion by  $404^{\circ}$  of heat\*. This, how-

\* The numbers here given are those shewn by the thermometer without any correction; but if a proper allowance is made for the error of that instrument it will appear, that the true contraction was  $25^{\circ}$  less than here set down, and from the manner in which thermometers have been usually adjusted, it is likely, that in the following experiment of Mr. HUTCHINS, as well as those of Professor BRAUN, the true contraction might equally fall short of that shewn by observation.

ever, is not the whole contraction which it suffers ; for it appears, by an extract which Mr. HUTCHINS was so good as to give me from a meteorological journal, kept by him at Albany Fort, that his thermometer once sunk to  $490^{\circ}$  below nothing, though it appeared, by a spirit thermometer, that the cold scarcely exceeded the point of freezing quicksilver. There are two experiments also of Professor BRAUN, in which the thermometer sunk to  $544^{\circ}$  and  $556^{\circ}$  below nothing, which is the greatest descent he ever observed without the ball being cracked. It is not indeed known how cold his mixtures were ; but from Mr. HUTCHINS's, there is great reason to think that they could not be many degrees below  $-40^{\circ}$ . If so, the contraction which quicksilver suffers in freezing is sometimes not much less than its expansion by  $500^{\circ}$  or  $510^{\circ}$  of heat, that is almost  $\frac{1}{2}$  of its whole bulk, and in all probability is never much more than that.

It is very likely, however, that the contraction which quicksilver suffers in freezing is no very determinate quantity ; for a considerable difference may frequently be observed in the specific gravity of the same piece of metal, cast different times over, and almost all cast metals become heavier by hammering ; and it is likely that the same thing may obtain in quicksilver, which is only a metal which melts with a much less degree of heat than the rest. I do not know, indeed, how much this variation can amount to ; but, on casting the same piece of tin three times over, I found its density to vary from 7,252 to 7,294, though I have great reason to think that no hollows were left in it, and that only a small part of this difference could proceed from the error of the experiment. This variation of density is as much as is produced in quicksilver by an alteration of  $66^{\circ}$  of heat ; and it is not unlikely, that the descent of a thermometer, on account of the contraction of the quicksilver in its ball by freezing, may

may vary as much in different trials, though the whole mass of quicksilver is frozen and without any vacuities.

The thermometer marked C was intended for trying how much the contraction of quicksilver is; but the experiments made with it were not attended with success, as in the first experiment it did not sink so low as A had done, owing, most likely, to the great cold of the weather which froze the quicksilver in the tube; and in the second experiment the ball broke.

*On the cold of the freezing mixtures.*

The cold produced by mixing spirit of nitre with snow is owing, as was before said, to the melting of the snow. Now, in all probability, there is a certain degree of cold in which the spirit of nitre, so far from dissolving snow, will yield out part of its own water, and suffer that to freeze, as is the case with solutions of common salt; so that if the cold of the materials before mixing is equal to this, no additional cold can be produced. If the cold of the materials is less, some increase of cold will be produced; but the total cold will be less than in the former case, since the additional cold cannot be generated without some of the snow being dissolved, and thereby weakening the acid, and making it less able to dissolve more snow; but yet the less the cold of the materials is, the greater will be the additional cold produced. This is conformable to Mr. HUTCHINS's experiments; for in the fifth experiment, in which the cold of the materials was  $-40^{\circ}$ , the additional cold produced was only  $5^{\circ}$ . In the first experiment, in which the cold of the materials was only  $-25^{\circ}$ , an addition of at least  $19^{\circ}$  of cold was obtained; and by mixing some of the same spirit of nitre with snow in this climate, when the heat of the materials

materials was  $+26^{\circ}$ , I have sunk the thermometer to  $-29^{\circ}$ ; so that an addition of  $55^{\circ}$  of cold was produced.

It is remarkable, that in none of Mr. HUTCHINS's experiments the cold of the mixture was more than  $6^{\circ}$  of the spirit thermometer below the point of freezing quicksilver, which is so little that it might incline one to think, that the spirit of nitre used by him was weak. This, however, was not the case, as its specific gravity at  $58^{\circ}$  of heat was 1,4923. It was able to dissolve  $\frac{1}{1,42}$  its weight of marble, and contained very little mixture of the vitriolic or marine acid: as well as I could judge from what experience I have of spirit of nitre, it was as little phlogisticated as acid of that strength usually is.

But, however extraordinary it may at first appear, there is the utmost reason to think, that a rather greater degree of cold would have been obtained if the spirit of nitre had been weaker; for I found, by adding snow gradually to some of this acid, that the addition of a small quantity produced heat instead of cold; and it was not until so much was added as to increase the heat from  $28^{\circ}$  to  $51^{\circ}$ , that the addition of more snow began to produce cold; the quantity of snow required for this purpose being pretty exactly one-quarter of the weight of the spirit of nitre, and the heat of the snow and air of the room, as well as of the acid, being  $28^{\circ}$ . The reason of this is, that a great deal of heat is produced by mixing water with spirit of nitre, and the stronger the spirit is, the greater is the heat produced. Now it appears from this experiment, that before the acid was diluted, the heat produced by its union with the water formed from the melted snow was greater than the cold produced by the melting of the snow; and it was not till it was diluted by the addition of one-quarter of its weight of that

that substance, that the cold generated by the latter cause began to exceed the heat generated by the former. From what has been said it is evident, that the cold of a freezing mixture, made with the undiluted acid, cannot be quite so great as that of one made with the same acid, diluted with a quarter of its weight of water, supposing the acid and snow to be both at  $28^{\circ}$  of heat, and there is no reason to think, that the event will be different if they are colder; for the undiluted acid will not begin to generate cold until so much snow is dissolved as to increase its heat from  $28^{\circ}$  to  $51^{\circ}$ , so that no greater cold will be produced than would be obtained by mixing the diluted acid heated to  $51^{\circ}$  with snow of the heat of  $28^{\circ}$ . This method of adding snow gradually to an acid is much the best way I know of finding what strength it ought to be of, in order to produce the greatest effect possible.

By means of this acid, diluted in the above-mentioned proportion, I froze the quicksilver in the thermometer called G by Mr. HUTCHINS, on the 26th of last February. I did not, indeed, break the thermometer to examine the state of the quicksilver therein; for as it sunk to  $-110^{\circ}$  it must certainly have been in part frozen; but immediately took it out, and put the spirit thermometer in its room, in order to find the cold of the mixture. It sunk only to  $-30^{\circ}$ ; but, by making allowance for the spirit in the tube being not so cold as that in the ball, it appears, that if it had not been for this cause it would have sunk to  $-35^{\circ}$ \*, which is  $5^{\circ}$  below the point of freezing, and  
is

\* As the surface of the freezing mixture answered to  $-185^{\circ}$  on the tube, there were  $155^{\circ}$  of spirit in the tube which could hardly be cooled much below the temper of the air, and which must, therefore, be warmer than that in the ball by about  $55^{\circ}$  of this thermometer, as the heat of the spirit in the ball was before



is as great a degree of cold, within  $1^{\circ}$ , as was produced in any of Mr. HUTCHINS's experiments.

In this experiment the thermometer G sunk very rapidly, and, as far as I could perceive, without stopping at any intermediate point, till it came to the above-mentioned degree of  $-110^{\circ}$ , where it stuck. The materials used in making the mixture were previously cooled, by means of salt and snow, to near nothing; the temper of the air was between  $20^{\circ}$  and  $25^{\circ}$ ; the quantity of acid used was  $4\frac{1}{4}$  oz.; and the glass in which the mixture was made was surrounded with wool, and placed in a wooden box, to prevent its losing its cold so fast as it would otherwise have done.

Some weeks before this, I made a freezing mixture with some spirit of nitre, much stronger than that used in the foregoing experiment, though not quite so strong as the undiluted acid, in which the cold was less intense by  $4^{\circ}\frac{1}{2}$ , as the thermometer G sunk to  $-40^{\circ}\frac{1}{2}$ . It is true, that the temper of the air was much less cold, namely,  $35^{\circ}$ ; but the spirit of nitre was at least as cold, and the snow not much less so. The experiment was tried in the same vessel and with the same precautions as the former.

The cold produced by mixing oil of vitriol, properly diluted with snow, is not so great as that procured by spirit of nitre, though it seems not to differ from it by so much as  $8^{\circ}$ ; for a freezing mixture, prepared with diluted oil of vitriol, whose

said to be  $-35^{\circ}$ , and the temper of the air above  $+20$ . Therefore, the correction must be equal to the expansion of a column of spirits  $155^{\circ}$  long, by an alteration of heat equal to  $55^{\circ}$  on this thermometer, which, if  $1^{\circ}$  on the scale answers to  $\frac{1}{1700}$ th of the bulk of the spirit, is equal to  $\frac{55 \times 155}{1700}$  or  $5^{\circ}$ .

specific gravity, at  $60^{\circ}$  of heat, was 1,5642, sunk the thermometer G to  $-37^{\circ}$ , the experiment being tried at the same time, and with the same precautions, as the foregoing. It was previously found, by adding snow gradually to some of this acid, as was done by the spirit of nitre, that it was a little, but not much stronger than it ought to be, in order to produce the greatest effect.

