X. *Experiments on the cooling of Water below its freezing Point.* *By* Charles Blagden, *M. D. Sec. R. S. and F. A. S.*

Read January 31, 1788.

WHEN the experiments for determining the degree of cold at which quickſilver becomes ſolid, related in the Philoſophical Tranſactions for 1783, were under conſideration, no difficulty occurred in explaining the phænomena that had been obſerved, except in the few inſtances where the mercury in the thermometer congealed, whilſt it was ſurrounded with ſome of the ſame metal in a fluid ſtate. The well-known property of water, that under different circumſtances it will bear to be cooled ſeveral degrees below its freezing point without congealing, afforded from analogy the moſt probable ſolution of this difficulty; but as neither the cauſe of that property had been inveſtigated, nor the circumſtances by which it is modified had been aſcertained, I was led to attempt ſome expements on the ſubject; not only in hopes of elucidating the above-mentioned phænomenon of the quickſilver, but alſo becauſe this very quality in water was itſelf a curious ſubject of reſearch.

I began with endeavouring to determine, whether this property belongs to it as pure water, or depends upon extraneous admixtures. For that purpoſe I poured ſome clean diſtilled water into a common tumbler glaſs, till it reached two or three inches above the bottom, and then ſet the glaſs in a

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frigorific mixture, made with ſnow and common ſalt. This was the method I uſed in moſt of the following experiments, ſometimes employing ice inſtead of ſnow, ſubſtituting a glaſs jar or cylinder inſtead of a tumbler, and filling the veſſel to a greater or leſs height above the bottom. I found that, in the frigoric mixture, the diſtilled water readily ſunk many degrees below 32°, ſtill continuing fluid; and by repeating the experiment with care, I ſeveral times cooled it to 24°, 23°½, and even almoſt to 23°. The temperature was aſcertained by means of a ſmall thermometer with a ſliding ſcale; and though the water was not of the ſame degree of cold throughout, yet the difference, when the experiment had been well conducted, was not conſiderable; and I was particularly careful that the thermometer ſhould not touch the ſides or bottom of the glaſs, ſo as to be affected immediately by the cold of the mixture. From theſe experiments therefore it ſeemed evident, that the property of being cooled below the freezing point did not depend on extraneous admixture, eſpecially as I found, by comparative trials, that common pump-water would ſcarcely ever bear to be cooled ſo much. An ambiguity, however, ſtill remained, on account of the air which is always mixed with water that has lain expoſed to the atmoſphere. In order to determine what might be aſcribed to this circumſtance, I put ſome of the ſame diſtilled water over the fire to boil, in a clean ſilver veſſel, and kept it in violent ebullition for a conſiderable time. In a few minutes after it had been taken off the fire, and before it was nearly cold, I ſet it in the frigorific mixture after the uſual manner; when, inſtead of freezing more readily, it bore to be cooled two degrees lower than I had ever been able to reduce the unboiled water, not congealing till the thermometer in it had ſunk to 21°. Subſequent experiments were attended with a ſimilar reſult, and have ſufficiently convinced me, that, other things equal, boiled water may be cooled a greater number of degrees below the freezing point, without congealing, than water which, not having undergone that operation, retains the air it naturally imbibes.

As a further proof that the preſence of an aërial fluid in water rather leſſens than increaſes its quality of being cooled below the freezing point, I found that diſtilled water, which had been for that purpoſe impregnated with fixed air, generally ſhot into ice at a leſs degree of cold than the ſame water in its ordinary ſtate. I ſuſpect, however, that it is uſually by the admixture of other aërial ſubſtances, ſuch as dephlogiſticated air, phlogiſticated air, or perhaps both, and not of fixed air, that water is inclined to congeal ſoon after it has paſſed the freezing point; for, as will be ſeen hereafter, *acids* rather improve than diminiſh the quality in water of reſiſting congelation.

To determine the effect of other extraneous ſubſtances, I took ſome very hard pump-water, ſuch as is found in the northern parts of London, and ſet it in the frigorific mixture. In general it congealed ſooner by one or two degrees than unboiled diſtilled water; that is, at 25° or 24° of the thermometer; and as there was ſome variation in this reſpect, I was led to remark, that the greateſt cooling uſually took place when the water was moſt clear and tranſparent. With a view to this circumſtance I took ſome New-River water, which happened at that time to be conſiderably turbid, and tried it in the frigorific mixture; when I found, very unexpectedly, that it was not in my power to cool any of it below the freezing point; a cruſt of ice always forming round the ſides and at the bottom of the veſſel, whilſt the thermometer, ſuſpended about the middle of the water, was two or three degrees above 32°. To try how far this depended on the foulneſs of the water, I collected ſome of the muddy ſediment which had been depoſited from the New-River water, and added it to the pump-water, which had before born to be cooled to 24° or 25°, ſo as to render it turbid; when it congealed, in the ſame manner as the New-River water had done, before the thermometer in the middle of it came to the freezing point. It muſt not however be imagined, that water thus made turbid is incapable of being cooled below 32°, without freezing: I have ſince repeated the experiments, with more caution in conducting them, and reduced it two or three degrees below the point of congelation. But ſtill they have all confirmed the general fact, that ſubſtances which leſſen the tranſparency of water, render it at the ſame time much more difficult to be cooled below the freezing point, and diſpoſe it to ſhoot into ice more readily, after it has paſſed that point, than pure water would do. It ſeems to be of little conſequence what the ſubſtance is that renders the water turbid: ſmall particles of any kind floating through it, I believe, have this effect, which does not take place, or at leaſt to the ſame degree, when the extraneous ſubſtance has ſubſided to the bottom.

It is this circumſtance, I ſuppoſe, which gave riſe to the opinion, that boiled water freezes ſooner than unboiled: for if the water contain calcareous earth, held in ſolution by means of fixed air, as is the caſe with moſt kinds of ſpring-water, this will be precipitated by the boiling, and will ſenſibly trouble the tranſparency of the water; which, if expoſed to the cold in that ſtate, will be liable to freeze ſooner than the ſame kind of water unboiled and tranſparent *.

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* See Philoſophical Tranſactions, Vol. LXV. p. 124.

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The effect of this want of tranſparency was very different from that of chemical mixture, as appeared by ſubſequent experiments.

Though the property of being cooled below the freezing point appeared to belong eſſentially to water in it's pure ſtate, it was probable that it would be in ſome meaſure altered or modified by the various ſubſtances which are capable of being diſſolved in, or chemically combining with, the water. But here a further circumſtance came to be conſidered. It is well known, that ſuch ſubſtances, uniting with water, have a power of lowering its point of congelation a greater or leſs number of degrees, according to the nature and quantity of the ſubſtance employed. The firſt object, therefore, was to determine in what manner the property of bearing to be cooled would be affected with regard to that new point of congelation. For this purpoſe I made many experiments with ſeveral different ſubſtances, which it would be too long to relate in detail, but the principal were as follows.

Having diſſolved in diſtilled water as much common ſalt as lowered its freezing point to 28°, I cooled it to 18°½ before it congealed. Another ſolution of the ſame ſalt, whoſe freezing point was 16°, bore to be cooled to 9°; and a ſtronger ſolution, whoſe freezing point was 13°½, cooled to 5° before it ſhot. A ſolution of nitre, whoſe freezing point was 27°, cooled to 16°, that is, eleven degrees below its new freezing point; a ſolution of ſal ammoniac, whoſe freezing point was 12°, cooled to 3°; and one of Rochelle ſalt, freezing point 27°½, ſuffered the thermometer to ſink in it to 16° before it froze; a cooling equal to the greateſt I ever obtained with the pureſt diſtilled water boiled. A ſolution of green vitriol, whoſe freezing point was near 30°, cooled below 19°: and, of ſalts with an earthy baſis, a ſolution of the common bitter purging ſalt, whoſe freezing point was at 25°½, bore to be cooled to 19°.

Acids, as I have already had occaſion to remark, rather augment this quality of being cooled below the freezing point. A combination of nitrous acid with diſtilled water, in ſuch proportions that the new freezing point was between 18° and 19°, ſunk down to 6° before it congealed; which being fully 12 degrees of cooling, is greater than I have been able to produce with pure water. Another mixture of the ſame kind, ſo ſtrong as to have its freezing point about 11°, cooled down to 1°. A mixture of vitriolic acid and diſtilled water, whoſe freezing point was 24°½, cooled to 14°; and one with the acid of ſalt, having its freezing point at 25°, ſunk to 16° before it froze. It is here to be obſerved, that theſe acid mixtures were rather remarkable for the ſteadineſs with which they bore to be cooled, and the little tendency they ſhewed to ſhoot before they were ſunk much below the freezing point, than for exceeding the number of degrees which pure water might be cooled. Of the alkalies, a ſolution of tartar, whoſe freezing point was 25°½, cooled to 18°; and another, with the freezing point at 15°, ſunk to 8°. A ſolution of cryſtalliſed ſoda, freezing point 30°, cooled to 21°; and a ſolution of mild volatile alkali, freezing point 19°, to 11°. A mixture of rectified ſpirit of wine and water, whoſe freezing point was 12°, cooled to 5°; and another, with the freezing point at 8°½, to 2°.

All theſe facts, with many others of the ſame nature which I obſerved, ſufficiently ſhew, that foreign ſubſtances, chemically combined with or diſſolved in water, do not take away its property of being cooled below its point of congelation; though, by depreſſing that point, they alter the degree of cold at at which the property commences. The experiments ſhew, that in ſome caſes the mixed water bore to be cooled as much below its new freezing point, as pure water below 32°; and with regard to the others, I think the variation was no greater than uſually takes place with different portions of common water. Scarcely any, perhaps none, of the above-mentioned points, were abſolutely the loweſt to which the ſolutions or mixtures could have been reduced, if the experiment had been conducted ſtill more ſlowly and cautiouſly. But however much they might all poſſibly have born to be cooled, a great difference occurred among them in the eaſe with which the operation ſucceeded. For inſtance, the ſolutions of nitre, and of Rochelle ſalt, would hardly ever ſhoot till they were cooled many degrees below their reſpective freezing points, however negligently the operation was conducted; whereas thoſe of common ſalt, ſalt of tartar, and ſome others, required conſtant attention to keep them from freezing, as ſoon as they were got four or five degrees below the point of congelation. Their difference in this reſpect may depend in part upon ſomething unknown in the nature of each particular ſalt; but there was one circumſtance to be diſtinctly traced, correſponding to what had been obſerved with pure water; namely, that the moſt tranſparent, moſt limpid ſolutions, were thoſe which admitted of being cooled with the greateſt eaſe and certainty. The ſame obſervation holds good with regard to the mixtures: thus the rectified ſpirit I employed aſſumed ſomething of an opaline tinge upon being mixed with the water (from the ſeparation of an oil it contained) and the compoſition bore to be cooled but ill, though a film of oil, regularly ſpread on its ſurface, would rather have retarded the freezing; and the acid mixtures, which cooled ſo remarkably well, ſtruck the eye particularly on account of their very perfect and uniform tranſparency. In this laſt caſe, perhaps, another circumſtance might contribute to the eaſy cooling, that the acids, by combining with the water, ſeemed to expel the air it contained more perfectly than moſt other ſubſtances, as appeared from the innumerable ſmall bubbles that were almoſt immediately formed.

Want of tranſparency, however, is only one among ſeveral cauſes which impair the property water naturally poſſeſſes, of bearing to be cooled many degrees below its freezing point. M. MAIRAN, in his elaborate Treatiſe upon Ice, having occaſion to examine this ſubject, was led by his experiments to conclude, that the cooling of water below its freezing point depends upon reſt, and that agitation is the general cauſe by which it is brought to ſhoot into ice. In this opinion he has been almoſt implicitly followed by all the writers I have ſeen, excepting only Profeſſor WILCKE, of Stockholm *. To bring it to the teſt of experiment, I ſet in the frigorific mixture ſome diſtilled water, which by boiling had been rendered capable of ſuſtaining a cold of 21° before it froze. When this water was cooled to 22°, I agitated it, by moving the tumbler, by ſhaking a quill in it, and by blowing on it ſo as to ruffle the ſurface; but it ſupported all theſe trials without congealing, and did not ſhoot till a minute or two afterwards, when by continuance in the frigorific mixture it was cooled down to 21°. In other experiments, however, all the above-mentioned kinds of agitation made ſimilar water inſtantly congeal, even when not cooled ſo low by ſeveral degrees. The congelation, therefore, muſt in theſe caſes have depended on ſome further circumſtance than the mere want of reſt. One that I ſuſpected is a ſort of tremulation, rather agitating ſmall portions of the

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* Kongl. Vetenſk. Acad. Handlingar, Vol. XXX. p. 103. 105.

water ſeparately, than moving the whole together. I have found, that ſtriking the bottom of the tumbler againſt a board would produce inſtant congelation, when ſtirring the water, or ſhaking the tumbler in the hand, would have no effect. In like manner, when in ſtirring the cooled water the quill, or ſtick of glaſs, employed for that purpoſe, ſtrikes againſt the ſide or bottom of the tumbler, the water, which had reſiſted the general ſtirring, is often by this percuſſion made to freeze. The ſame effect is produced, and with leſs uncertainty, if the quill, or ſtick of glaſs, be rubbed, and as it were ground, againſt the ſide of the tumbler. But of all ſuch methods of bringing on the congelation, that which I have found to fail the ſeldomeſt, is to rub a bit of wax againſt the ſide of the tumbler under the water; a particular roughneſs in the motion is felt, with ſome ſound, approaching to a muſical tremulation, and a cruſt of ice is immediately perceived under the wax upon the glaſs. This effect of the wax I take to be mechanical, depending on its particular ſtate of conſiſtence. Wood acts in the ſame manner, though with leſs certainty; ſo does a quill, and likewiſe glaſs; but the latter, being very hard, produces the effect with leaſt certainty. It is a mechanical action upon the water in contact with the rubbing ſubſtance and the glaſs: for if the outſide of the tumbler, or any part of the inſide above the water, be rubbed, even if it be wet ſo as to communicate a ſimilar feeling of tremulation, yet ſtill the congelation is not produced.

All theſe modes of bringing on the congelation ſucceed beſt, as might be expected, in proportion as the water is more cooled below the freezing point. Unleſs the cooling amount to four or five degrees, the friction with wax is often in vain.

From the above-mentioned facts it appears, that M. MAIRAN's poſition, though not deſtitute of foundation, was enounced by him too generally, and without ſufficient preciſion. It is the natural property of water to bear to be cooled a certain number of degrees without freezing; reſt favours this property negatively, by giving it no interruption; but moſt kinds of agitation interfere with its operation to a greater or leſs degree, and ſome perhaps would prevent it altogether; whilſt others affect it ſo little, as not to ſuperinduce the congelation, even when the cooling is brought within one degree of the greateſt that the water will bear.

Whatever be the effect of agitation, there is another cauſe which much more powerfully haſtens the congelation of water. It has been long known, that when water is cooled below its freezing point, the contact of the leaſt particle of ice will inſtantly make it congeal, the glacial cryſtals ſhooting all through the liquor, from the ſpot where the ice touches it, till the whole comes up to the freezing point. Few experiments of the minute kind afford a more ſtriking ſpectacle than this, eſpecially when the water has been cooled nearly as much as poſſible below the freezing point; both from the beautiful manner in which the cryſtals ſhoot through it, and the rapidity with which the mercury in the thermometer immerſed in it runs up through a ſpace of 10 or 11 degrees, ſtopping and fixing always at 32 in pure water. If from any circumſtance, however, as a leſs cooling, or the addition of a ſalt, the ſhooting of the ice proceed more ſlowly, the thermometer will often remain below the freezing point even after there is much ice in the liquor; and does not riſe rapidly, or to its due height, till ſome of the ice is formed cloſe to its bulb; which exemplifies the evolution of the latent heat from the very particles that congeal.

Many of the circumſtances attending the greater or leſs cooling of water below its freezing point depend upon this principle. In a calm day, when the temperature of the air was about 20°, I expoſed two veſſels with diſtilled water to the cold; one of them was ſlightly covered with paper, the other was left open: the former bore to be cooled many degrees below the freezing point, whilſt a cruſt of ice always formed on the ſurface of the other before the thermometer immerſed in the middle of it came to the freezing point. This phænomenon, which other obſervers have remarked without being able to account for it, appears to me clearly owing to frozen particles, which in froſty weather are almoſt always floating about in the air, often perceptibly to the ſenſes. They come moſt commonly either from clouds paſſing over head, or from ſnow or hoar-froſt lying upon the earth; and when they touch the cooled ſurface of the water, inſtantly make it freeze. That the effect does not depend ſimply on the contact of cold air, is plain from the following experiment. I expoſed to the cold a glaſs jar, with ſome diſtilled water, and placed in it two thermometers; one immerſed in the water, the other ſuſpended a little above its ſurface, in the empty part of the jar. The latter ſunk faſter than the former; but after a certain time, the thermometer above the ſurface was at 25°, and that in the water at 25°½, yet the water continued unfrozen. I perceive too by M. WILCKE's experiments, that in much more intenſe cold than we uſually experience in this country, veſſels of water ſtanding within doors in a laboratory are often cooled ſo far below the freezing point as to become almoſt full of ice upon being made to ſhoot, though the

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ſurface of the water be in no wiſe defended from the cold air of the laboratory. Oil ſpread over the ſurface of water has been found to prevent it from freezing, when other water ſimilarly expoſed has had a cruſt of ice formed upon it. This I aſcribe entirely to the prevention of frozen particles from coming in contact with the water: for in experiments with frigorific mixtures, in a room of moderate temperature, I do not find that oil on the ſurface has any ſenſible effect in enabling water to ſupport more cold, unleſs, indeed, where the operation is otherwiſe too much precipitated. Alſo a crack in the tumbler containing the water prevents it from cooling below the point of congelation, a thin film of ice inſinuating itſelf through the crack into contact with the water. And often, in experiments with frigorific mixtures, the congelation is brought on by raiſing the immerſed thermometer a little out of the water, and lowering it down again; ſome of the adhering water having frozen upon its ſtem.

Several other circumſtances, though not ſo diſtinctly aſcertained as the preceding, appear to facilitate the congelation of cooled water. For inſtance, in experiments with frigorific mixtures, if the cold be very intenſe, the water freezes almoſt immediately round the ſides of the veſſel, as if ſomething depended on too ſudden a change of temperature. Accordingly, the only way of inſuring the greateſt degree of cold in water without freezing, is to cool it in a very gradual manner, keeping the cold of the frigorific mixture regularly only two or three degrees below that of the water. Sudden cooling, therefore, may be conſidered as one of the cauſes which haſten congelation. No doubt this will ſometimes depend on ſuch a cold as water cannot reſiſt without freezing, being propagated through the glaſs to the neareſt part of the water, quicker than it can be be diſtributed to the reſt of the water; but, I think, the above-mentioned effect takes place when no part of the fluid can be ſuppoſed to be many degrees below the freezing point.

It has been alledged, that metal in contact, either with the outſide of the veſſel containing the water, or with the water itſelf, diſpoſes it to freeze ſooner after it is cooled below 32°. Though upon repeating this experiment I have found it poſſible to cool water in a metal veſſel many degrees below its freezing point, and even to touch it, when ſo cooled, with metal equally cold, without producing congelation; yet the metal certainly tends to haſten the freezing, and, I believe, on the above-mentioned principle of too quick a change of temperature, occaſioned by its quality as a good conductor of heat. For the ſame reaſon it is more difficult to cool water much below the freezing point in thin veſſels than in thoſe whoſe bottom and ſides are of conſiderable thickneſs; the latter tranſmitting the heat more ſlowly, and allowing it thereby to be diffuſed more equably.

In cooling water below its freezing point by frigorific mixtures, it is of conſequence to keep the mixture ſome way below the upper edge of the water within the tumbler, otherwiſe the congelation quickly begins at that place. This very likely depends on the principle laſt mentioned, that the thin edge of water riſing up againſt the ſide of the glaſs, being more in contact with air than with the general maſs of water, does not ſo eaſily diſtribute its cold, and therefore ſuffers a more rapid change of temperature by the action of the mixture. Hence one of the moſt eſſential precautions for cooling water to the utmoſt without congelation, is to perform the experiment in a warm room, that the air in contact with the edges and ſurface of the water may prevent their ſudden cooling. And one of the moſt convenient veſſels for the purpoſe is a round body terminating in a neck, the body to be ſurrounded with the frigorific mixture, whilſt the water in the neck is kept above the freezing point.

Theſe are the principal facts with which my experiments have furniſhed me relative to the cooling of water below its point of congelation. I ſee no general circumſtance that applies to them all. At one time I thought that much depended on reducing the water into thin plates; an idea which was principally ſuggeſted by the more ready congelation of the edges of the water where it riſes up as a thin film on the ſides, and by the effect of extraneous ſubſtances floating in the water to haſten its freezing, which might be ſuppoſed frequently in their motions to intercept ſmall portions of the fluid, and form it into thin plates. Agitation likewiſe might act by reducing the water in ſome part or another into ſimilar plates. And as water impregnated with air appeared leſs capable of being cooled than the ſame water deprived of its air, it ſeemed not impoſſible that the air might act likewiſe by producing thin plates in different parts of the fluid. With a view to this hypotheſis I made ſeveral experiments. Into a tumbler with diſtilled water I put a quantity of ſand, which ſettled looſely to the bottom, and left the water above as tranſparent as before. This tumbler being placed in the frigorific mixture, the water bore to be cooled as well as it had done without this addition. Laying thin bits of glaſs upon one another at the bottom of the tumbler, in place of the ſand, I found no difference in the effect. By this latter experiment it was moreover proved, that points in the water do not perceptibly facilitate its cryſtalliſation into ice. Now the thin plates or wedges of of water, which muſt be intercepted by the bits of ſand or glaſs, ſeem very analogous to ſuch as may be produced by floating particles of extraneous matter; and therefore the effect of the latter is probably to be aſcribed to ſome other cauſe, ſuch as haſtening the cooling, or rendering it leſs uniform, or, perhaps, communicating motion to the fluid.

In the preceding inſtances, however, the water may be conſidered as conſtituting, by its adheſion, a ſort of continued body with the ſubſtance it touches; and it might be ſuppoſed that, if one or both ſurfaces of the thin plate were in contact with air only, the congelation would take place. I therefore put down ſome air, retained by a ſmall diſh of wax, into the water to be cooled, and let it ſtay there till the whole was reduced many degrees below the freezing point; but no congelation enſued: I then contrived to turn up the diſh of wax in the water, ſo that the air it had carried down, eſcaping from under it, aſcended as a bubble to the top of the water, and there burſt: ſtill the water retained its fluidity, notwithſtanding the contact of a looſe bubble of ſuch cold air, and the motion produced by its exploſion on the ſurface. In other experiments, I have indeed ſeen the burſting of a bubble on the ſurface apparently bring on the congelation; but ſeemingly from the agitation it occaſioned. And though a wetted ſurface, or a ſmall thin portion of water, freeze in general more readily than a larger maſs, yet I have ſeen inſtances of a jar cooled many degrees below the freezing point, and the water and air in it equally cold, which had, notwithſtanding, upon its inſide, from the ſurface of the water to an inch or more above it, an evident dew that remained quite fluid, and rendered the ſurface of the glaſs wet. Under the ſame circumſtances alſo, I have raiſed the thermometer out of the cooled water, without occaſioning any congelation in the adhering thin film of that fluid. Theſe facts, though they do not ſhew but that a film of water, in contact on both ſides with air below its freezing point, would at once congeal, yet, I think, are ſufficient to prove, that its formation into thin plates is not a general cauſe of its early freezing.

From a conſideration of the above-mentioned cauſes of freezing, and their various exceptions, I am led to think, that the matter in queſtion depends upon ſome circumſtance of the more intimate nature or compoſition of the water; for inſtance, the arrangement, attractions, and perhaps ſhape, of its particles. If we ſuppoſe the particles of water to poſſeſs a kind of polarity, that is, to have particular attracting points or ſurfaces, properly arranged, not only its cryſtalliſation in regular angles, but likewiſe moſt of the above-mentioned phænomena, admit of ſome kind of explanation. For latent heat, be it a matter or motion, may be conſidered as a cauſe either leſſening the power or impeding the operation of this polarity; the effect of which is gradually diminiſhed by external cold, till at length the polarity entirely overcomes the reſiſtance it occaſions, and the attracting points or ſurfaces ruſh together. Whatever tends, therefore, to bring theſe particles into a ſtate more advantageous for their junction, as by preſenting their attracting ſurfaces more directly to one another, forcing them nearer together, or removing attractions of a contrary tendency, and allowing the particles free ſcope to follow the impulſe of their polarity, muſt tend to haſten the congelation. When particles of water, already frozen, are preſented to other fluid water of a proper degree of coldneſs, not only the attracting ſurfaces will be in the moſt favourable poſition from the arrangement they have taken in the freezing, but very poſſibly their power may be ſtronger from their union with one another; and hence ſuch water is inſtantly brought to freeze. Indeed it is this circumſtance which conſtitutes the freezing point; for that point is evidently nothing elſe but the degree of cold which renders the particles of any fluid incapable of reſiſting the attractive power of other particles of the ſame fluid, already reduced into a ſolid form: and the fact, that the cold of the freezing point is leſs than the fluid will otherwiſe bear, ſeems a proof that when the particles have acquired this arrangement of ſolidity, their attractive powers are the ſtrongeſt; ſo that the difference between the freezing point, and the greateſt cold the fluid will bear, may be conſidered as the meaſure of this additional attractive force.

Agitation may be eaſily conceived, by the various motions impreſſed upon the particles, to occaſion ſome of them to apply their polar points in a more advantageous poſition, or even to force them nearer together; and theſe effects are more likely to be produced by an intimate agitation, than by a general motion of the whole maſs. The want of tranſparency, in certain caſes, as in ſome ſolutions of ſalts, ſeems not owing to the preſence of foreign matters, but rather to depend upon a particular arrangement of the combined particles, which may diſpoſe thoſe of the water to join more readily, and detach thoſe of the ſalt. Extraneous ſubſtances, beſides their indirect effect, may, by various chances attending their floating in the water, throw the particles into favourable ſituations; and if thin plates are more diſpoſed to freeze, it may be, that the particles of water in ſuch are more free from counteracting attractions.

Sudden cooling may promote congelation ſimply by occaſioning the water at the bottom and ſides of the veſſel to acquire a greater degree of cold than the reſt. But perhaps it may have alſo another effect, admitting of a particular explanation.

nation. Water in freezing undergoes a conſiderable expanſion. This may be aſcribed to ſuch a form of its particles, and poſition of their poles, as ſhall make them, when touching and adhering by thoſe poles alone, intercept very large interſtices, which may be conſidered as the *pores* of the ice. Various poſitions of the poles and figures of the particles may be conceived, which ſhould cauſe them to occupy more ſpace, when touching in certain points only, than they filled when lying near without any contact. But in whatever way the expanſion is produced, experiment hath ſhewn that it begins ſome time before congelation; ſo that when water is cooled down to 32°, it is already ſenſibly expanded; and if the congelation does not take place here, this expanſion augments, in proportion as the water is further cooled *. The expanſion, therefore, being ſo evidently an approach to freezing, may be conſidered as an indication that the polarity already prevails ſo far as to draw the particles ſomewhat out of the ſituation they naturally aſſume in the higher temperatures. And it is conceivable, that if this operation go on very quick, and the conſequent change of poſition in the particles be made with ſome degree of velocity, they may acquire a ſmall momentum of motion, enabling them to overcome a reſiſtance which would otherwiſe prevent their junction.

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* In experiments where the water has cooled much below its freezing point, I have ſeen the expanſion ſo great as to bear a conſiderable proportion to the whole expanſion produced by freezing, which laſt, I believe, is more than one-ſeventh of the volume of the water. It ſeemed to me as if the expanſion proceeded in an increaſing ratio, being much greater upon the laſt degrees of cooling than it was upon the firſt. The difficulty of procuring a proper apparatus for theſe experiments has hitherto prevented me from aſcertaining the quantities with preciſion.

As chemical combinations all depend upon attractions between the ſubſtances which unite, it is not difficult to conceive, that a particle of ſalt, an acid, or the like, may attract a particle of water in ſuch a manner as ſhall oppoſe or diminiſh its attraction for the other particles of water. Hence the polarity may be ſo much weakened, as not to bear the ſame proportion to the reſiſting power of the latent heat, till this alſo is diminiſhed by a greater degree of cold, which conſtitutes the new freezing point. But when, by increaſing the cold, all the powers are reduced to a ſimilar ſtate of equilibrium, exactly the ſame phænomena take place as belong to the natural freezing point of the water.

To aſſiſt the conception, I have here reaſoned upon the particles of water as ſolid, and of a determinate ſhape. But it ſeems moſt probable, that the particles of matter in general are nothing more than centres to certain attractive and repulſive powers; on which hypotheſis it may be underſtood, that if two or more of theſe central points are brought much within the limits of their reſpective attractions and repulſions, theſe powers will no longer be equal at equal diſtances from their common centre. Now ſuch a combination of central points may be conſidered as one particle of any particular matter; and the unequal diſtances from the common centre at which the attractions and repulſions are equal will define what may be called the ſhape of that particle. And if, at equal diſtances, the attraction or repulſion is much greater at one point than at another, that will conſtitute a polarity.

The greateſt cold I have been able to make water acquire without freezing, is near 12 degrees of FAHRENHEIT's ſcale below its common freezing point. Some diſtilled water was boiled about a quarter of an hour in a tin cup, and placed in the ſame veſſel, whilſt ſtill warm, in the frigorific mixture. The mixture was made to act very ſlowly, ſo that the operation continued more than an hour. When the immerſed thermometer had ſunk to 20°⅓, the water was ſtill fluid: I then ſhook it conſiderably, but no ice formed. After waiting ſome time, and finding the thermometer would ſink no lower, becauſe by the length of the proceſs the ſnow of the mixture was almoſt conſumed, I added ſome freſh materials, which could not be done without ſhaking the tin cup. Still, however, the water did not freeze inſtantly, though it ſhot as ſoon after as it can be ſuppoſed to have felt the influence of the new frigorific mixture. When this water was cooled to 24°, I tried the temperature of the air near its ſurface, and found it 34° or 35°, the experiment being performed in a room with a fire.

Another time I cooled ſome diſtilled water, covered with oil, below 21°, by ſimilar precautions.

This, however, is by no means the greateſt cooling of which water is ſuſceptible. In FAHRENHEIT's experiment, with an exhauſted globe half full of boiled rain water, it ſeems to have been cooled to 15°*. M. DE LUC likewiſe informs us, † that having filled a thermometer with ſome water he had purged of air by the means deſcribed in his great work upon the atmoſphere, he expoſed it to a cold which ſunk a mercurial thermometer to 14° of FAHRENHEIT's ſcale. The water in the thermometer continued tranſparent, and upon breaking the ball was found to be liquid, but froze that inſtant. In ſome of my experiments too with mixtures of nitrous acid and water, the liquor bore to be cooled as much as 13 degrees

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* Philoſophical Tranſactions, Vol. XXXIII. p. 81.

† Idées ſur la Météorologie, Tom, II. p. 105.

below its new freezing point; and it has been already obſerved, that the addition of an acid always expelled much air from the water. It is not improbable, therefore, that if water could be thoroughly purged of air, it would readily bear to be cooled 18 degrees, or more, below its freezing point, without congelation; though the deprivation of air, obtained by boiling it, is ſuch only as will barely enable it to admit a cooling of 12 degrees.

Other fluids may bear to be cooled much more below their proper point of conſolidation. This is evidently the caſe in what Mr. CAVENDISH calls * the ſpirituous congelation of acids. Mr. M^c^ NAB's nitrous acid bore to be cooled from 30 to near 40 degrees below its freezing point †; and Mr. KEIR's vitriolic acid at the ſtrength of eaſieſt freezing continued fluid at 29°, though its heat became 46°½ when it began to congeal ‡. How low quickſilver may be cooled has not yet been aſcertained, but probably many degrees below −40°.

So many of the above-mentioned facts were obſerved in the year 1783, that I then ventured to remark, that "independently of theſe circumſtances, neither ſtirring, agitation, a current of freſh air on the ſurface, nor the contact of any extraneous body not colder, would [neceſſarily] cauſe the water to ſhoot into ice, notwithſtanding the repeated aſſertions of authors to the contrary **." Similar experiments, made in the courſe of the ſucceeding winters, have confirmed in general the former reſults, and furniſhed the materials of the preceding ſheets. I am very ſenſible, that the

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* Philoſophical Tranſactions, Vol. LXXVI. p. 261.

† Ibid. p. 252.

‡ Ibid. Vol. LXXVII. p. 279.

** Ibid. Vol. LXXIII. p. 358.

ſubject ſtill remains involved in great obſcurity; nor ſhould I have troubled the Society with an account of experiments which leave ſo much uncertainty, had I not thought that they tended to elucidate a few points, and to correct ſome erroneous opinions. I hope that perſons inhabiting a climate more advantageous for the purpoſe, will be induced to undertake ſuch experiments in another, and probably a more ſucceſsful way, by expoſure to *natural* cold.