

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 experiments 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 frigorific mixture, the distilled water readily sunk many degrees below  $32^{\circ}$ , still continuing fluid; and by repeating the experiment with care, I several times cooled it to  $24^{\circ}$ ,  $23^{\circ}\frac{1}{2}$ , and even almost to  $23^{\circ}$ . 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  $21^{\circ}$ . Subsequent experiments were attended

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 aerial 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 aerial 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 un-boiled distilled water; that is, at  $25^{\circ}$  or  $24^{\circ}$  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

middle of the water, was two or three degrees above  $32^{\circ}$ . 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 been to be cooled to  $24^{\circ}$  or  $25^{\circ}$ , 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  $32^{\circ}$ , 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\*.

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

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 its 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  $28^{\circ}$ , I cooled it to  $18^{\circ}\frac{1}{2}$  before it congealed. Another solution of the same salt, whose freezing point was  $16^{\circ}$ , bore to be cooled to  $9^{\circ}$ ; and a stronger solution, whose freezing point was  $13^{\circ}\frac{1}{2}$ , cooled to  $5^{\circ}$  before it shot. A solution of nitre, whose freezing point was  $27^{\circ}$ , cooled to  $16^{\circ}$ , that is, eleven degrees below its new freezing point; a solution of sal ammoniac, whose freezing point was  $12^{\circ}$ , cooled to  $3^{\circ}$ ; and one of Rochelle salt, freezing point  $27^{\circ}\frac{1}{2}$ , suffered the thermometer to sink in it to  $16^{\circ}$  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  $30^{\circ}$ , cooled below  $19^{\circ}$ : and, of salts with an

earthy basis, a solution of the common bitter purging salt, whose freezing point was at  $25^{\circ}\frac{1}{2}$ , bore to be cooled to  $19^{\circ}$ .

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  $18^{\circ}$  and  $19^{\circ}$ , sunk down to  $6^{\circ}$  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  $11^{\circ}$ , cooled down to  $1^{\circ}$ . A mixture of vitriolic acid and distilled water, whose freezing point was  $24^{\circ}\frac{1}{2}$ , cooled to  $14^{\circ}$ ; and one with the acid of salt, having its freezing point at  $25^{\circ}$ , sunk to  $16^{\circ}$  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  $25^{\circ}\frac{1}{2}$ , cooled to  $18^{\circ}$ ; and another, with the freezing point at  $15^{\circ}$ , sunk to  $8^{\circ}$ . A solution of crystallised soda, freezing point  $30^{\circ}$ , cooled to  $21^{\circ}$ ; and a solution of mild volatile alkali, freezing point  $19^{\circ}$ , to  $11^{\circ}$ . A mixture of rectified spirit of wine and water, whose freezing point was  $12^{\circ}$ , cooled to  $5^{\circ}$ ; and another, with the freezing point at  $8^{\circ}\frac{1}{2}$ , to  $2^{\circ}$ .

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

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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  $32^{\circ}$ ; 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 borne 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

cularly 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  $21^{\circ}$  before it froze. When this water was cooled to  $22^{\circ}$ , 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  $21^{\circ}$ . 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

\* 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 percussive motion 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.

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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  $20^{\circ}$ , 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 phenomenon, 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  $25^{\circ}$ , and that in the water at  $25^{\circ}\frac{1}{2}$ , 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 surface

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  
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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  $32^{\circ}$ . 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  
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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 phenomena, 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  $32^{\circ}$ , 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.

\* 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 phenomena 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  $20^{\circ}\frac{1}{3}$ , 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  $24^{\circ}$ , I tried the temperature of the air near its surface, and found it  $34^{\circ}$  or  $35^{\circ}$ , the experiment being performed in a room with a fire.

Another time I cooled some distilled water, covered with oil, below  $21^{\circ}$ , 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  $15^{\circ}$  \*. 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  $14^{\circ}$  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

\* 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<sup>c</sup> 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

\* 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.

